UNIT-1

Crystal Structure: Space Lattice, Index System ,Atomic Packing

Structure of the Unit

References and Suggested Readings

1.0 Objectives

The objective of this unit is to make familiar the readers with the basics of solid state. The basic constituents of the materials in the view of solid state will be discussed. The arrangement of the basic constituents at the atomic or molecular level will be discussed. The different types of solid state structures of the materials and the arrangement of the atoms or molecules in the crystals are to be explained. The different tools to study the arrangement of the atoms or molecules in the structures will be explained.

1.1 Introduction

The unit deals with the study of the basics of solid state physics. In this unit different types of solids, the basic unit of the crystal and various types of crystal structures are explained. The arrangement of atoms or molecules in the basic unit of the solid structure and packing of these in the basic unit are explained. The arrangement of these atoms or molecules in various sets of parallel planes and the directions of these planes are discussed with examples. At last ,the size of the basic unit of the crystal is related to the size of the atom in terms of atomic radius.

1.2 Introduction to Crystal Structure

The solid state materials can be grouped into two broad categories:(1) Crystalline and (2) Non-crystalline or amorphous materials. These materials cannot be distinguished at macroscopic level but can only be distinguished at microscopic level. They are distinguished from each other by the degree of arrangements of fundamental particles of their composition. The particles of their composition may be atoms, molecules or ions. These particles are called as their building blocks.

1.2.1 Crystalline Solids

The solids in which the atoms or molecules or ions are arranged in a regular or periodic manner in the three dimensional space are called as crystalline solids. In such solids the whole crystal can be obtained by repetition of a well defined pattern unit. The crystalline solid can further be classified as: Single crystals and Polycrystals. In the single crystals ,the regularity of the pattern unit is observed throughout the whole crystal of the solid. In case of polycrystalline solids ,the regularity of the pattern unit is observed over a small region of the solid. In such solids there are numbers of small crystalline regions of various shapes and sizes separated by grain boundaries. In such solids, there is breakdown of the regularity at the interface of two crystalline regions called as grain boundaries. In the grain boundaries ,there is an irregular arrangement of the building blocks of the solids.

Most of the solids in nature are polycrystalline. The single crystals materials are synthesized for special purpose. Most of the materials used in semiconductor industry are single crystalline. The examples of crystalline materials are metals, ceramics, salts, etc.

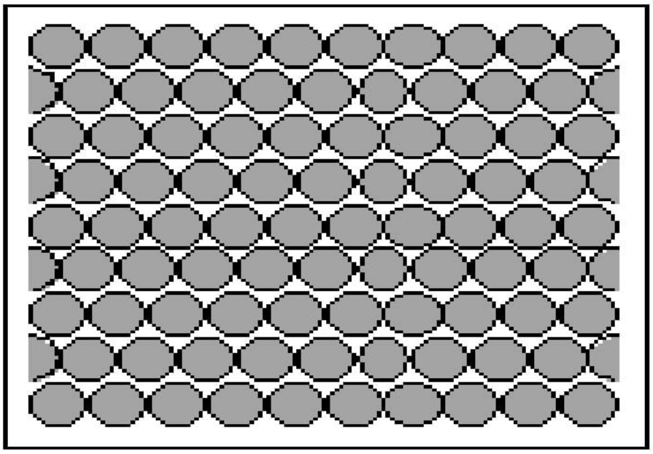


Figure1.1: Single crystal

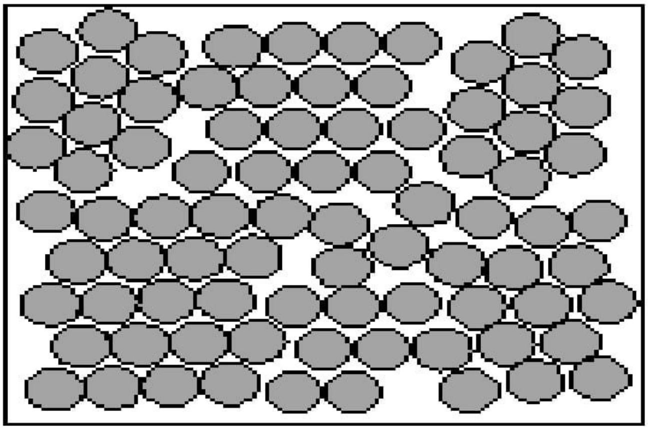


Figure1.2 : Polycrystals

1.2.2 Non-crystalline Solids (Amorphous Solids)

When the atoms, molecules or ions are not arranged periodically in the solids ,then such solids are called as non-crystalline or amorphous solids. In other words if the ordering extends up to the size of the pattern unit,then the nature of the solid is of amorphous type. Most of the solids in nature prefer to be crystalline, because it lowers the energy of the solid. However if the atoms in the solid are not allowed to arrange themselves properly ,then they result in non-crystalline structure.

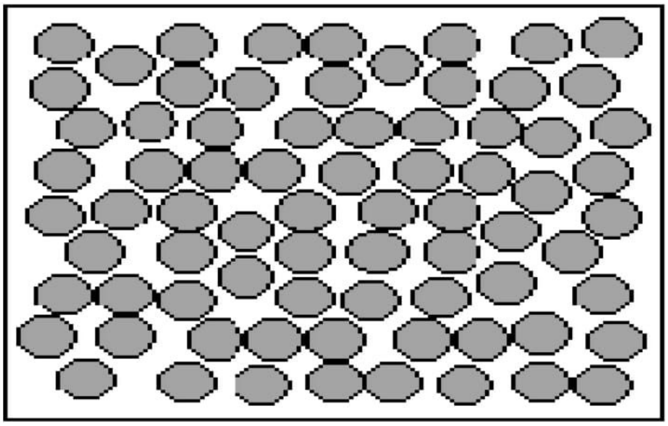


Figure1.3: Amorphous solids

1.3 Lattice and Basis

A lattice is a regular or periodic arrangement of points in space. The arrangement about any point remains same throughout. The points in the lattice are connected by a vector defined by

$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

The lattice can be generated by the translation vector $\vec{T}$ i.e. if we consider one lattice point and use the translation vector having different values of n_1, n_2 and n_3 ,then we get the whole lattice. Here n_1 , n_2 and n_3 are integers and $\vec{a}, \vec{b}, \vec{c}$ are called as fundamental lattice vectors.

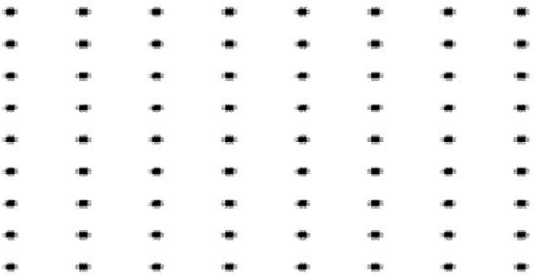


Figure 1.4: Lattice points

Any point in the lattice can be represented by following position vector

$$\vec{r}_2 = \vec{r}_1 + \vec{T}$$

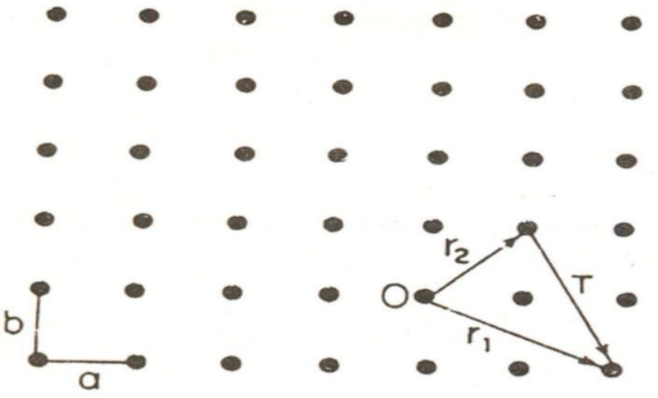


Figure 1.5: Translation operation in lattice and translational vector

The group of atoms or molecules that forms the macroscopic crystal by infinite repetition is called basis. The basis is placed at a set of mathematical/abstract points that form the lattice (also called Bravais lattice). So, a crystal is a combination of a basis and a lattice. Although the basis usually consists of only few atoms, it can also contain complex organic or inorganic molecules (for example, proteins) of hundreds and even thousands of atoms.

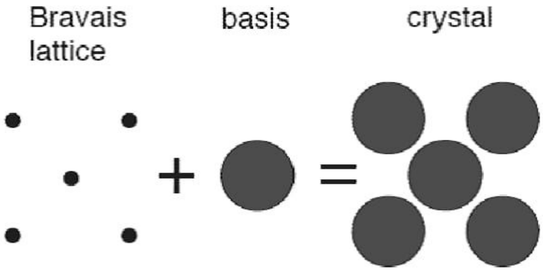


Figure 1.6: Atomic type basis

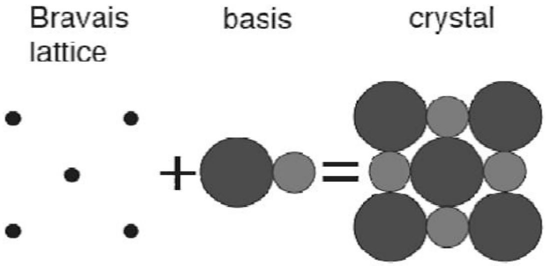


Figure 1.7: Molecular type basis

1.4 Unit Cell

The smallest part of a crystal is called as unit cell. It is formed by combination of atoms and molecules. The whole crystal structure can be formed by the repetition of these unit cells. The unit cell may be primitive or non-primitive.

1.4.1 Primitive Unit Cell

The unit cell of smallest volume is called as primitive unit cell. A unit cell having volume less than the primitive unit cell is not possible. The more accurate definition of the primitive unit cell is "The unit cell having lattice point density equal to unity is called as primitive unit cell".

1.4.2 Non-primitive Unit Cell

The volume of the crystal which on repetition gives the whole crystal structure, but the lattice point density of that cell is greater than unity is called as non-primitive unit cell. On repetition of such a unit cell no lattice point or not any space of the crystal is left.

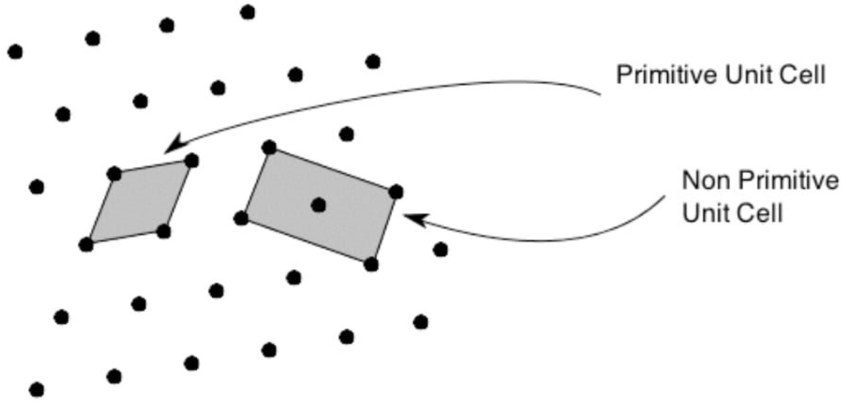


Figure 1.8: 2D Primitive and Non-primitive unit Cell

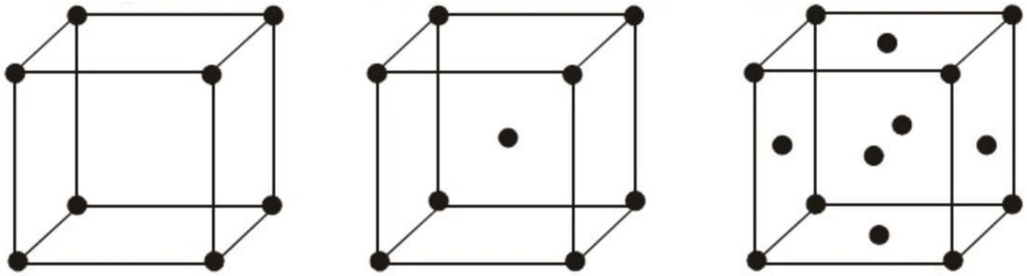


Figure 1.9: 3D Primitive and Non-primitive unit Cell

1.4.3 Wigner-Seitz Unit Cell

Another way of choosing the primitive unit cell is the choice of Wigner-Seitz unit cell. The cell is constructed by connecting a lattice point with its nearest neighbours. Now the lines connecting these points are bisected. The cell within the bisected region about the point is called as Wigner-Seitz unit cell.

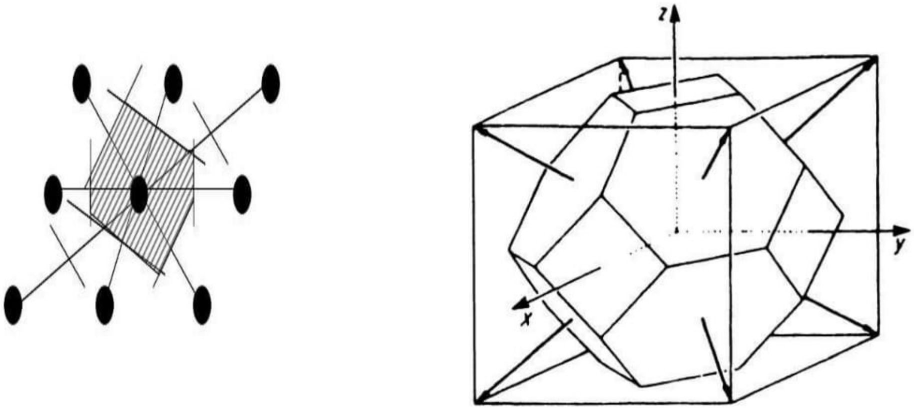


Figure 1.10 Wigner-Seitz Unit Cell of 2D and 3D

1.5 Classification of Lattices

Crystal lattices can be carried into themselves by lattice translation operation and by various other symmetry operations. The class of other operations include rotation about an axis passing through a lattice point, reflection about a plane passing through a lattice point, inversion about a lattice point, rotation-inversion, rotation-reflection, etc.

1.5.1 Two Dimensional Lattices

Although there is no restriction on the selection of length of the lattice translation vectors and the angle between them, but due to the restriction imposed by various symmetry operations there are only five types of Bravais lattices in two dimensions. Theses lattices are as

1. Oblique lattice
2. Square lattice
3. Hexagonal lattice
4. Rectangular lattice
5. Centered rectangular lattice

The length of the translation vectors and the angle between them are given in the table below.

Lattice type	Length of axes a_1, a_2	Angle between the axes γ
1.Oblique	$a_1 \neq a_2$	$\gamma \neq 90^\circ, 120^\circ$
2.Square	$a_1 = a_2$	$\gamma = 90^\circ$
3.Hexagonal	$a_1 = a_2$	$\gamma = 120^\circ$
4.Rectangular	$a_1 \neq a_2$	$\gamma = 90^\circ$
5.Centred rectangular	$a_1 \neq a_2$	$\gamma = 90^\circ$

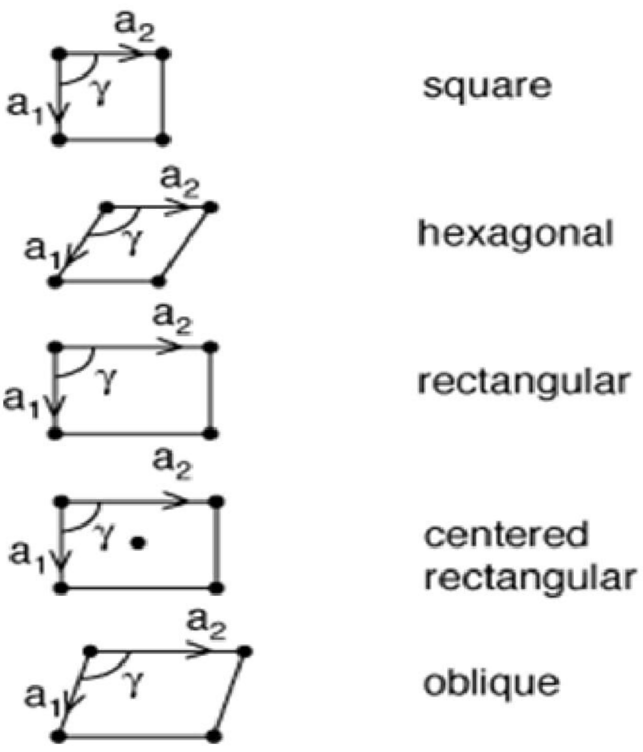


Figure: 1.11 Two Dimensional lattices Types

1.5.2 Three Dimensional Lattices

The point symmetry groups in three dimensions require 14 types of different lattices. The general lattice is triclinic and 13 types of special lattices. The 14 types of lattices are grouped into seven systems depending upon the choice of cell. The seven systems and 14 types of three dimensional lattices are listed in the table below.

System	Conventional cell axes length	Angles between the axes	No. of lattices
1.Triclinic	$a_1 \neq a_2 \neq a_3$	$\alpha \neq \beta \neq \gamma$	1
2.Monoclinic	$a_1 \neq a_2 \neq a_3$	$\alpha = \gamma = 90^o \neq \beta$	2
3.Orthorhombic	$a_1 \neq a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^o$	4
4.Tetragonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^o$	2
5.Cubic	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma = 90^o$	3
6.Trigonal	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma \neq 90^o, < 120^o$	1
7.Hexagonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = 90^o, \gamma = 120^o$	1

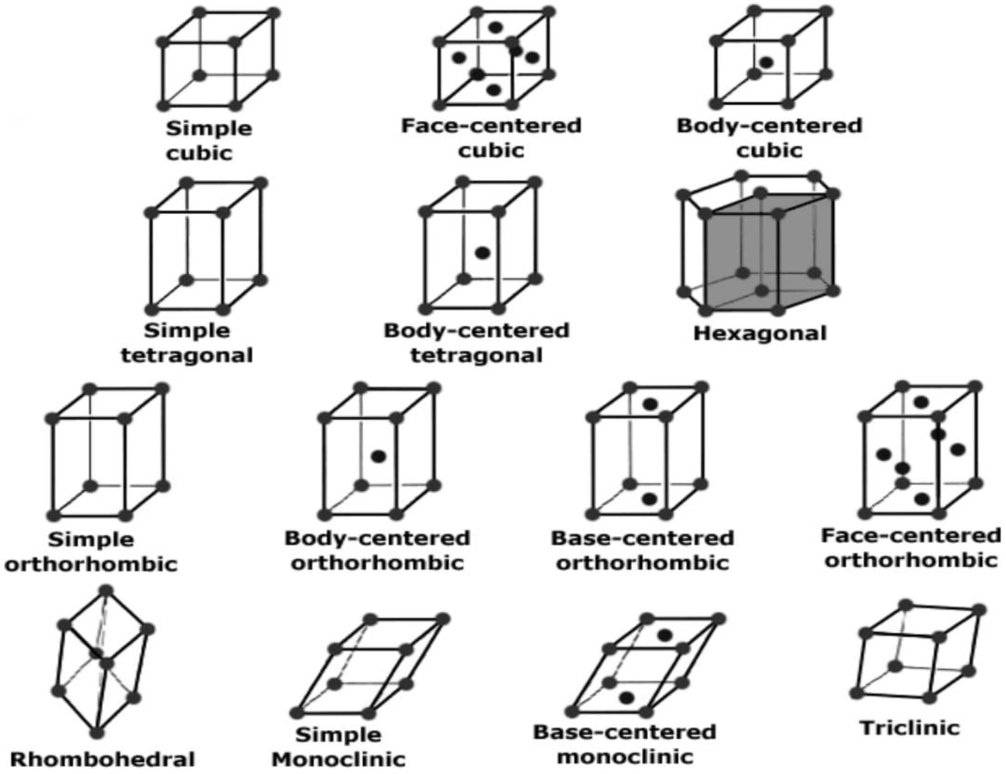


Figure 1.12: Three Dimensional Lattices types

1.6 Index System For Crystal Planes

In the lattice the lattice points are arranged in space periodically. These lattice points are supposed to be arranged in various sets of parallel planes. Each set of parallel planes has unique direction which is determined by a set of three numbers called as Miller Indices. The Miller indices of a set of parallel plane can be determined as follows:

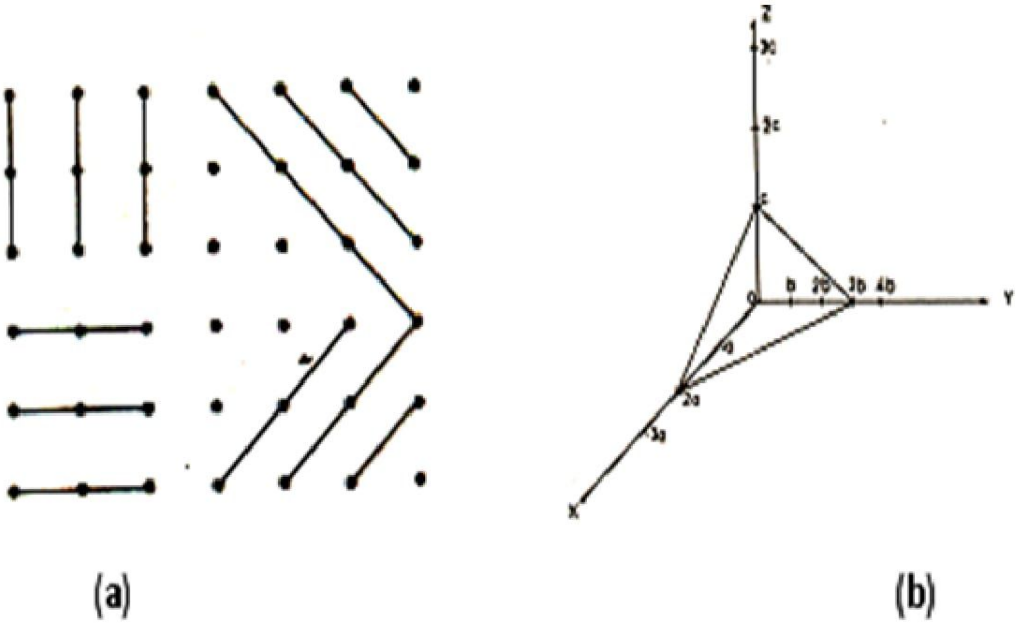
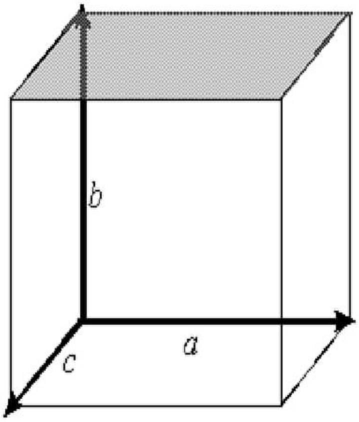


Figure 1.13: Sets of Parallel Planes and Crystallographic axes.

1. Take any lattice point as origin in the lattice and select the co-ordinates axes which may be primitive or non-primitive.
2. Select one plane of a set of parallel planes and determine its intersects on the co-ordinates axes in terms of primitive lattice constants ‘a’, ‘b’ and ‘c’ i.e. convert the intercepts in terms of product of ‘a’, ‘b’ and ‘c’. Let the intercepts are along the three axes are pa, qb and rc respectively.
3. Take the reciprocals of the coefficients of ‘a’, ‘b’ and ‘c’ of intercepts i.e. $\frac{1}{p},\frac{1}{q},\frac{1}{r}\ \frac{1}{p},\frac{1}{q},\frac{1}{r}$.
4. Convert these reciprocals into smallest set of integers.
5. The set of integers are the Miller Indices of that set of parallel plane and

represented by (hkl).

6. If a plane intersects any axis on negative side then the Miller Index of that axis is represented by a bar on the value of index. For example if a plane makes intercept of 1/2, -1/3 and 1, respectively, then the reciprocals are 2, -3 and 1. So the Miller Indices of the plane are $(2\bar{3}1)$.
7. If any plane is parallel to any axis then its intercept is taken as infinity, so the Miller Index of that axis is zero. For example the intercepts of a plane are $\infty, 1b, 2c$, then the Miller Indices are (021).



- Intercepts are ∞,1,∞
- Miller indices of the plane are:

$$\left(\frac{1}{\infty}\frac{1}{1}\frac{1}{\infty}\right) = (010)$$

Figure 1.13: Miller Indices of Parallel Plane

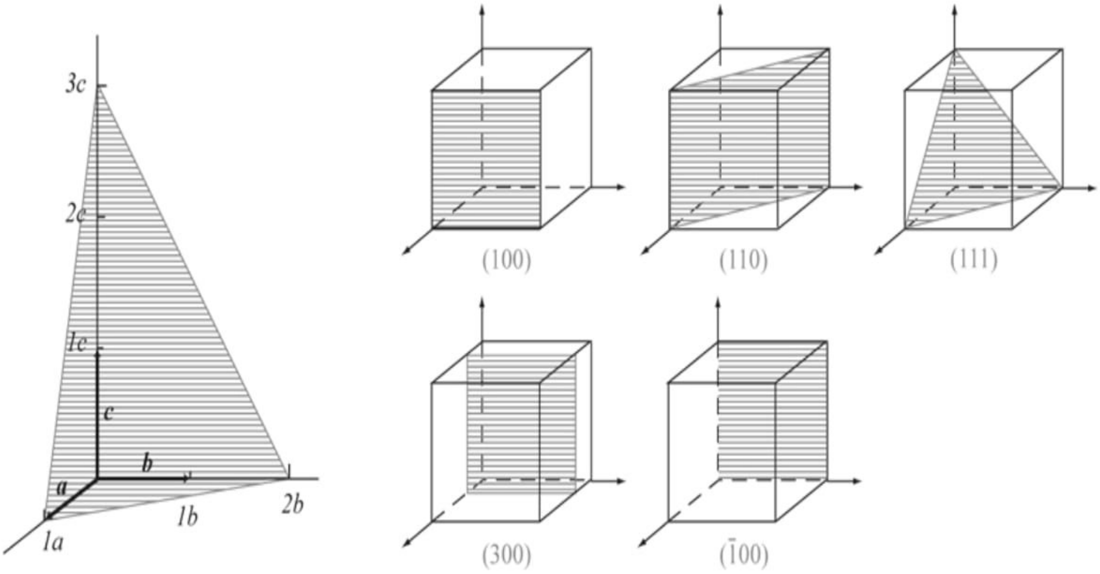


Figure 1.14: Representation of Different Planes with different Miller Indices in Unit Cell

Let us explain the Miller Indices by an example

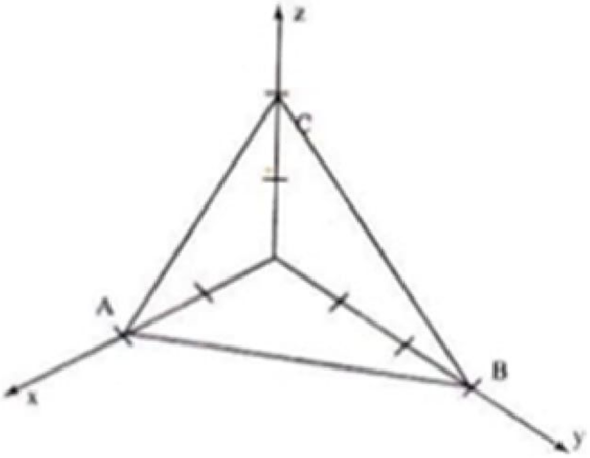


Figure 1.13: Intercepts of a Plane on different axes

The intercept of the plane along x axis = 2a

The intercept of the plane along x axis = 3b

The intercept of the plane along x axis = 2c

The coefficients of a, b and c are 2, 3 and 2 respectively. So the Miller indices are as

$$(\frac{1}{2}\frac{1}{3}\frac{1}{2}) \rightarrow (323) \qquad (\frac{1}{2}\ \frac{1}{3}\ \frac{1}{2}) \rightarrow (3\ 2\ 3)$$

So the Miller indices of the plane are (323).

1.7 The Cubic Crystal and Number of Atoms per Unit Cell

In cubic system there are three types of lattices permitted by symmetry operations. These lattices are given as

Simple Cubic or Primitive Lattice (SC)

Body Centered Cubic Lattice (BCC)

Face Centered Cubic Lattice (FCC).

Simple Cubic or Primitive Lattice (SC): In SC lattice all the atoms lies at the corners of the unit cell. If ‘a’ is the lattice constant then the volume of the unit cell or primitive unit cell is a^3. The co-ordination number or nearest neighbors are 6.

The nearest neighbor distance is 'a'. At each corner eight unit cells intersect so each atom of the corner is shared by eight unit cells. The contribution of each atom to a unit cell is 1/8. So the number of atoms in a unit cell is one.

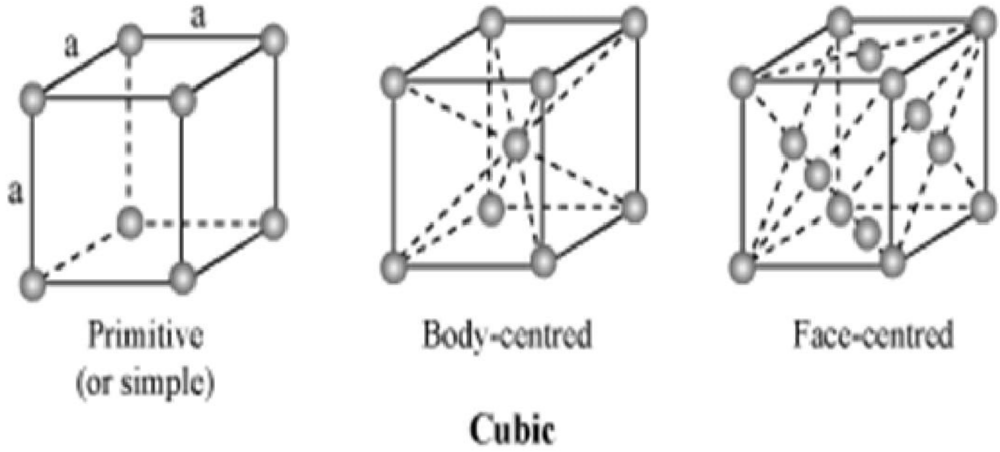


Figure 1.14: Atomic Arrangement in SC, BCC and FCC

Body Centered Cubic Lattice (BCC):

In BCC lattice there are eight atoms that lie at the corners of the unit cell. There is an additional atom at the center of the unit cell. If 'a' is the lattice constant ,then the volume of the unit cell is a^3. The co-ordination number or nearest neighbors are 8. The nearest neighbor distance is '$a\sqrt{3}/2$'. At each corner, eight unit cells intersect, so each atom of the corner is shared by eight unit cells. The contribution of each atom to the unit cell is 1/8, while the center atom totally belongs to unit cell. So the number of atoms in the unit cell is two. The volume of the primitive unit cell is $a^3/2$.

Face Centered Cubic Lattice (FCC):

In FCC lattice there are eight atoms that lie at the corners of the unit cell. There are additional atoms at the center of each face of the unit cell. If 'a' is the lattice constant ,then the volume of the unit cell is a^3. The co-ordination number or nearest neighbors are 12. The nearest neighbor distance is '$a\sqrt{2}/2$'. At each corner eight unit cells intersect, so each atom of the corner is shared by eight unit cells. The contribution of each atom to a unit cell is 1/8, while the face center atom has contribution 1/2 to unit cell. So the number of atoms in a unit cell is four. The volume of the primitive unit cell is $a^3/4$.

1.8 Atomic Packing and Atomic Radius

Atomic packing factor is defined as the ratio of volume occupied by the atoms to the volume of the unit cell. For the calculation we treat the atoms as hard spheres and the sphere touch each other. For cubic system the co-ordination number is 6, 8 and 12 for SC, BCC and FCC lattices respectively. The number of lattice points in the unit cell of SC, BCC and FCC are 1, 2 and 4 respectively.

1. SC Lattice: Let us consider the lattice constant of SC lattice is 'a' and 'R' is the atomic radius. The atoms are at the corners and touch each other so the lattice constant and atomic radius is related to each other as shown in Fig. 1.15

$a = 2R$

So the atomic packing factor is defined as

$$APF = \frac{4}{3} APF = \frac{Volume\ occupied\ by\ the\ atoms}{Volume\ of\ the\ unit\ cell}$$

The volume of an atom = $4/3\pi R^3$

Volume of unit cell $=a^3$

$$APF = \frac{4}{3}\frac{\pi R^3}{a^3} = \frac{4}{3}\frac{\pi R^3}{(2R^3)} = \frac{\pi}{6} = 0.524$$

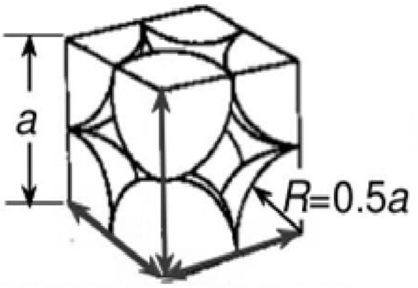


Figure 1.15: Atomic Packing in SC

2. BCC Lattice: Let us consider the lattice constant of BCC lattice is 'a' and 'R' is the atomic radius. The atoms are at the corners and there is one atom at the center of unit cell. The number of lattice points in the unit cell is 2. The diagonal corner atoms touch the center atom so the lattice constant and atomic radius is related to each other as shown in Fig. 1.16

$a\sqrt{3}=4R$

So the atomic packing factor is defined as

$$APF = \frac{Volume\ occupied\ by\ the\ atoms}{Volume\ of\ the\ unit\ cell}$$

The volume of an atom=$(4/3)\pi R^3$
Volume of unit cell =a^3

$$APF = 2 \times \frac{4}{3} \frac{\pi R^3}{(\frac{4}{\sqrt{3}} R)^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

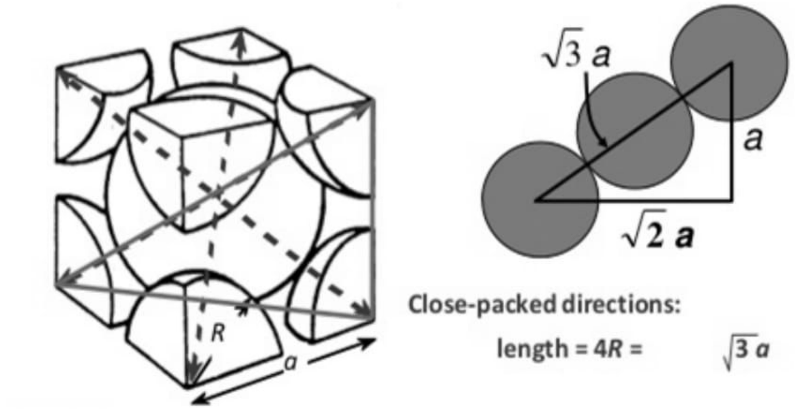


Figure 1.16: Atomic Packing in BCC

3. FCC Lattice: Let us consider the lattice constant of FCC lattice be ‘a’ and ‘R’ be the atomic radius. The atoms are at the corners and there is one atom at the center of each face of the unit cell. The number of lattice points in the unit cell is 4. The diagonal corner atoms of a face touch each other ,so the lattice constant and atomic radius is related to each other as shown in Fig. 1.17

$$a\sqrt{2} = 4R$$

So the atomic packing factor is defined as

$$APF = \frac{Volume\ occupied\ by\ the\ atoms}{Volume\ of\ the\ unit\ cell}$$

The volume of an atom=$(4/3)\pi R^3$
Volume of unit cell= a^3

$$APF = 4 \times \frac{4}{3} \frac{\pi R^3}{a^3} = 4 \times \frac{4}{3} \frac{\pi R^3}{(\frac{4}{\sqrt{2}} R)^3}$$

$$= \frac{\sqrt{2}\pi}{6} = 0.74$$

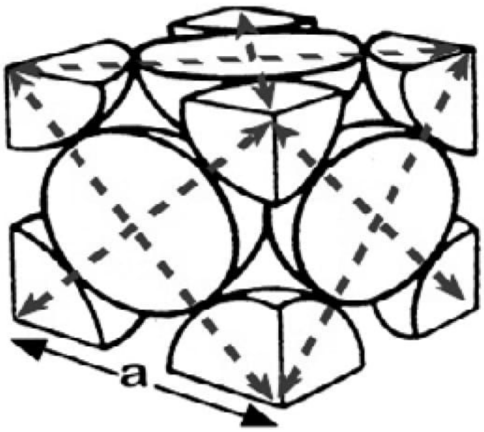


Figure 1.17: Atomic Packing in FCC

1.9 Self Learning Exercise

Q.1 What are crystalline materials? Explain with examples.

Q.2 Discuss the various types of crystalline materials.

Q.3 Name the various symmetry operations permitting the possibility of various types of lattices in 3D.

Q.4 Find the Miller Indices of a crystal plane that makes intercepts 3a, -3b and 3/2c on x, y and z axes respectively.

Q.5 Explain the concepts of lattice, basis and crystal.

Q.6 Explain the translational vector.

Q.7 Explain the symmetry operations. Write the various symmetry operations.

Q.8 Classify the two dimensional lattices. Draw their unit cells.

Q.9 Draw the various lattices of cubic system.

Q.10 Name the various systems of lattices of 3D. Write the number of different lattices in each system.

Q.11 Write a short note on the Miller Indices.

Q.12 Find the Miller Indices of a plane whose intersects on the three axes as 2a, -3b, 1c respectively.

Q.13 Represent the following planes of given Miller Indices in Cubic unit cell (100), (010), (001), (111), (121), (132).

Q.14 Write the numbers of atoms in the unit cell, co-ordination number and volume of primitive unit cells of the SC, BCC and FCC.

Q.15 Write the atomic radius in terms of lattice constants for SC, BCC and FCC.

1.10 Summary

This unit deals with the basics of the solid state physics. The solids are classified as crystalline and amorphous solids. In the crystalline solid materials, there is a regular or periodic arrangement of atoms or molecules or ions ,while in case of amorphous solid there is no regular or periodic arrangement. In the basic concepts of lattice, basis, translational; vector, unit cell, etc. are discussed. Different types of unit cell and the differences among them are also discussed. The various types of 2D and 3D lattice systems and the different lattices in system are discussed at the end of the chapter. The unit cells of various 2D and 3D lattices are also represented pictorially. The table is also given regarding the lengths of axes and the angle between the axes of 2D and 3D lattices systems. The arrangement of lattice points in different planes has been discussed in terms of Miller Indices. The cubic crystals are discussed in detail. Finally the atomic packing and atomic radius of the cubic crystals are discussed.

1.11 Glossary

Building blocks : Making units

Synthesized : Prepared

Periodic : Repeating after a fixed scale

Amorphous : Non-crystalline

Symmetry : Similar pattern

Symmetry operation : Act of getting similar pattern.

Bravais : Used for different lattices in a system.

Translation: Linear displacement in space.

Point operation: Operation taken about a lattice point.

Inversion: Changing the direction by 180^0.

Rotation-reflection: Rotation and followed by reflection.

1.12 Answers to Self Learning Exercise

Ans.1: The materials in which the atoms or molecules or ions are arranged in a well defined or periodic manner in space are called as crystalline materials. All metals, alloys, salts, metal oxides etc. have crystalline structure.

Ans.3: The fundamental symmetry operation is the translation operation. The other symmetry operation includes rotations, inversion, reflection, and their combined operations like rotation-inversions, rotation-reflection, etc.

Ans.4: The intercepts are written as

$pa = 3a$

$qb = -3b$

$rc = 3/2c$

So the Miller Indices are

$$(\frac{1}{3}\frac{1}{-3}\frac{2}{3}) \rightarrow (1\,\bar{1}2)$$

1.13 Exercise

Q.1 Explain the types of various materials.

Q.2 Classify the three dimensional lattices.

Q.3 Explain the unit cell. Discuss the various types of unit cells.

Q.4 Explain poly-crystals.

Q.5 What are primitive and centered unit cell?

Q.6 Why a pentagon can't be a unit cell in 3D lattice.

Q.7 Write primitive vectors for lattices of cubic system.

Q.8 Explain the Miller Indices of a plane or set of parallel plane.

Q.9 How the Miller Indices of a set of parallel plane can be determined?

Q.10 Find the Miller Indices of a plane that is parallel to x- axis and intercepts along y and z-axes are 4b and 2c.

Q.11 Draw the various lattices of the orthorhombic system.

Q.12 Write the packing fraction in SC, BCC and FCC and find the atomic radius.

1.14 Answers to Exercise

Ans.4: The crystalline materials in the ordering of atoms or molecules or ions extend over a small region. There are numbers of such ordered regions in materials separated by disordered regions called as grain boundaries. In the grain boundaries there is random arrangement of atoms or molecules or ions.

Ans.5: The unit cell in the number of lattice points is equal to unity is called as primitive unit cell. The primitive unit cell has the smallest volume. The other unit cell is called as centered unit cell or non-primitive unit cell. In these unit cells the lattice points are greater than one. In these unit cells there are additional atoms at body centered or face centered or base centered positions in addition to corner atoms in the unit cell.

Ans.6: When the unit cell in the form of pentagon is selected and it reaped in space then repetition of the cell leaves uncovered space in the lattice i.e. a volume of the space is left on repeating the pentagon see figure 1.18. There is violation of translation symmetry.

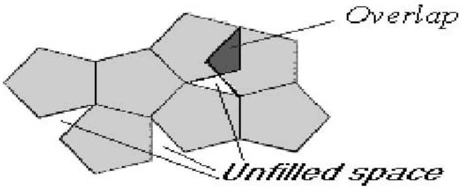


Figure 1.18: Pentagon as unit cell

Ans.7: A cubic system has three types of Bravais lattices e.g. simple cubic, body centered and face centered lattice. In the simple lattice all the atoms are at the corners of cube. The primitive lattice vectors are

$$\vec{a}_1 = a\hat{i}$$

$$\vec{a}_2 = a\hat{j}$$

$$\vec{a}_3 = a\hat{k}$$

The primitive unit cell is a cube of length ‘a’ and angle between the edges is 90^o.In case of body centered cubic lattice the primitive lattice vectors are as

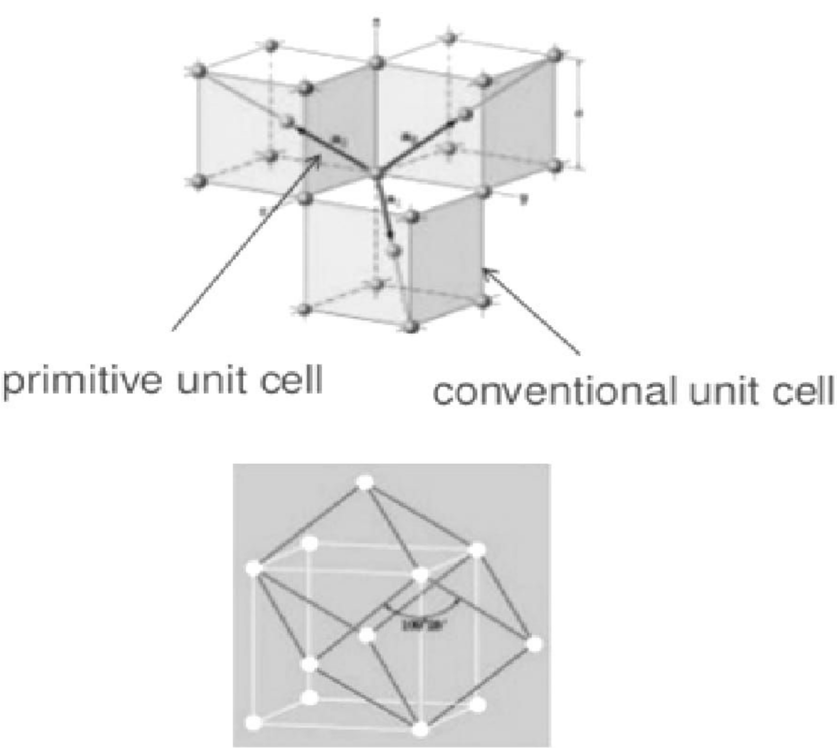


Figure 1.19 Primitive unit cell of bcc

$$\vec{a}_1 = \frac{a}{2}(\hat{i} + \hat{j} - \hat{k})$$

$$\vec{a}_2 = \frac{a}{2}(-\hat{i} + \hat{j} + \hat{k})$$

$$\vec{a}_3 = \frac{a}{2}(\hat{i} - \hat{j} + \hat{k})$$

The primitive unit cell is a rhombohedron of edge $\frac{1}{2}\sqrt{3}a$. The angle between the edges is $109^{\circ}28'$.

The primitive lattice vectors of face centered lattice are as

$$\vec{a}_1 = \frac{a}{2}(\hat{i} + \hat{j})$$

$$\vec{a}_2 = \frac{a}{2}(\hat{j} + \hat{k})$$

$$\vec{a}_3 = \frac{a}{2}(\hat{i} + \hat{k})$$

The primitive unit cell of fcc is a rhombohedron of edge $\frac{1}{2}\sqrt{2}a$. The angle between the edges is 60^{o}.

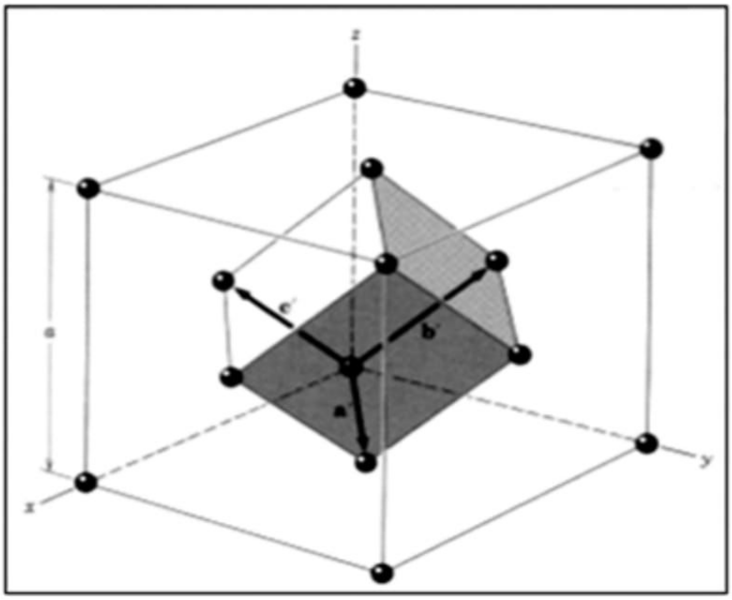


Figure 1.20 Primitive unit cell of fcc

Ans.8: In the crystal the lattice points lie on the planes. There can be number of sets of parallel planes possible having different directions of each set. The direction of a plane or a set of parallel plane is represented by set of three numbers called as miller indices of the plane or a set of parallel plane.

Ans.10: The intercepts are written as

$pa = \infty$

$qb = 4b$

$rc = 2c$

So the Miller Indices are $(\frac{1}{\infty}\frac{1}{4}\frac{1}{2}) \rightarrow (012)$

References and Suggested Readings

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UNIT-2

Crystal Symmetry and Simple Crystal Structures

Structure of the Unit

2.0 Objectives

This unit is aiming to make familiar with the symmetry found in crystals. The various symmetry operations possible in the crystal will be explained. The crystal structure of some popular materials with arrangements of atoms or molecules in the basic unit and their packing will be explained.

2.1 Introduction

The classification of various crystal structures and various lattices is based on the symmetry operations found in crystals. The various types of symmetry elements found in crystals are classified and explained in detail. The crystal structure of some crystals like NaCl, hcp, diamond, Zinc blend, perovskites, etc. are discussed in detail.

2.2 Introduction to Symmetry Elements

An operation that takes the crystal into itself is called as symmetry operation. If any operation is performed on the crystal then change is observed in the surrounding of the crystal. The symmetry operations may be grouped into three classes

1. Translation Symmetry Operation
2. Point Symmetry Operations
3. Hybrid Symmetry Operations.

2.2.1 Translation Symmetry Operations

A translation operation is defined as the displacement of a crystal parallel to itself by a crystal translation vector. The translation operation is permitted in every fundamental space lattice of the crystal when a lattice point is moved through a displacement vector defined by equation (1). The final point of the displacement is also a lattice point around which the arrangement of lattice points is identical as before the operation. The fundamental space lattice of a crystal is commonly known as Bravais lattice.

$$\vec{r}_1 = \vec{r}_2 + \vec{T} \qquad (1)$$

where $\vec{T}$ is the translation vector which is given by

$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \qquad (2)$$

Here n_1, n_2 and n_3 are integers and $\vec{a}, \vec{b}, \vec{c}$ are called as fundamental lattice vectors.

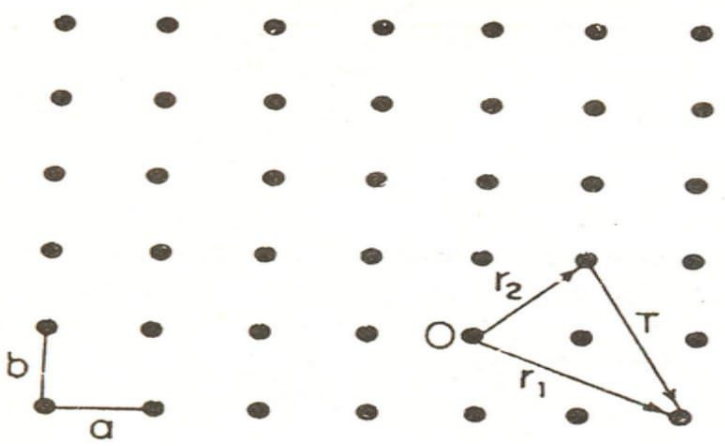


Figure 1.Translation operation in lattice and translational vector

2.2.2 Point Symmetry Operation

Point operations are performed at a point within a Bravais lattice. The point symmetry operations include the following operations.

The Mirror Reflections Symmetry Operation:

In this operation the reflection of a structure at a mirror plane "m" passing through a lattice point leaves the crystal unchanged. The mirror plane is composed of atoms lying on the concerned imaginary plane.

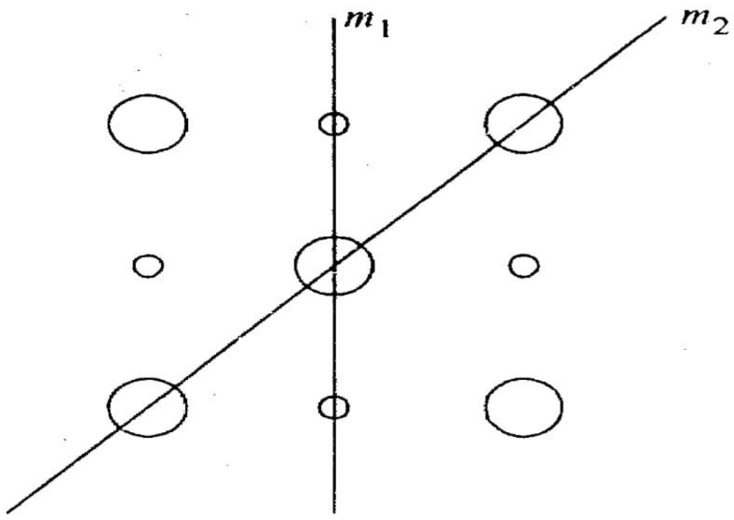


Figure 2: Mirror planes in two dimensional crystal

The Inversion Symmetry Operation:

Let us consider a lattice point represented by a position vector $\vec{r}$, considering any lattice point O as origin.

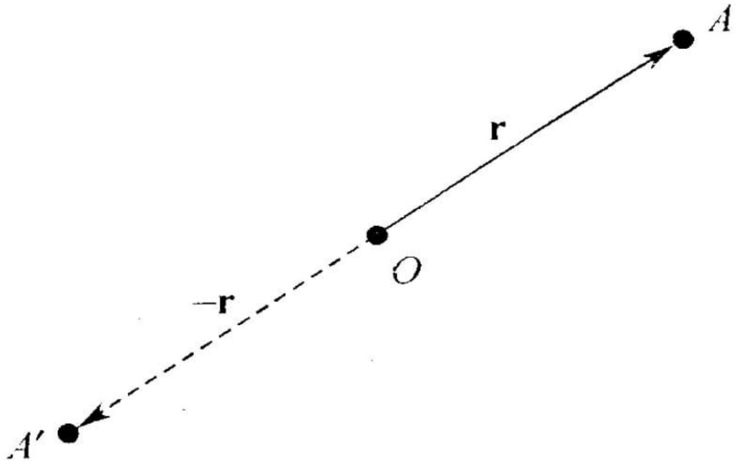


Figure 3: Inversion Symmetry Operation

If there exists a lattice point in the crystal represented by a position vector $-\vec{r}$, then we can say that the crystal inversion symmetry. The origin is called as centre of inversion and represented by symbol "i". The inversion operation shows that the inversion of a lattice point at centre of inversion leaves the crystal unchanged.

Rotation Symmetry Operation:

The crystal can be repeated by rotation of it about an axis passing through the crystal. By rotating the crystal through certain angle gives the unchanged picture of the crystal. The axis of rotation is called as symmetry axis.

If the crystal is rotated by an angle θ such that the environment appears to be unchanged ,then the axis of rotation is termed as n-fold axis where the angle of rotation is given by

$$\theta = \frac{2\pi}{n}, n = 1, 2, 3, ...$$

Every crystal has 1-fold axis of rotation. The symmetry axes commonly observed in crystals are 1-fold, 2-fold, 3-fold, 4-fold and 6-fold. The 5-fold symmetry axis is not observed in the crystals.

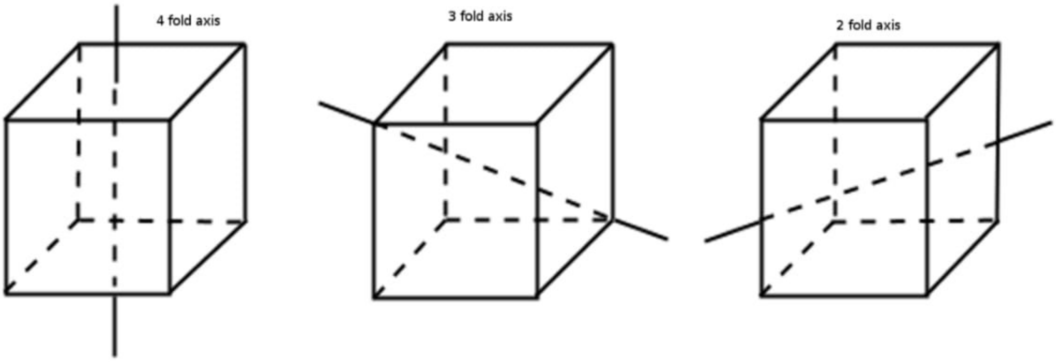


Figure 4: **Symmetry axes of rotation in cubic crystal**

2.2.3 Hybrid Symmetry Operations

In the proper rotation the right handed object repeated as right handed and left handed as left handed. But in improper rotation the right handed object is repeated as left handed. The improper rotation when followed by some other operation like reflection or translation leads to congruence. Similarly, a reflection operation may combine with a translation operation to produce congruence. The combined symmetry operations are called as hybrid symmetry operations.

The Rotoreflection:

It is the combination of an n-fold rotation and a reflection at a plane perpendicular to the axis of rotation. It is represented by n/m having n=1, 2, 3, 4, 6. The Rotoreflection 2/m is equivalent to inversion operations.

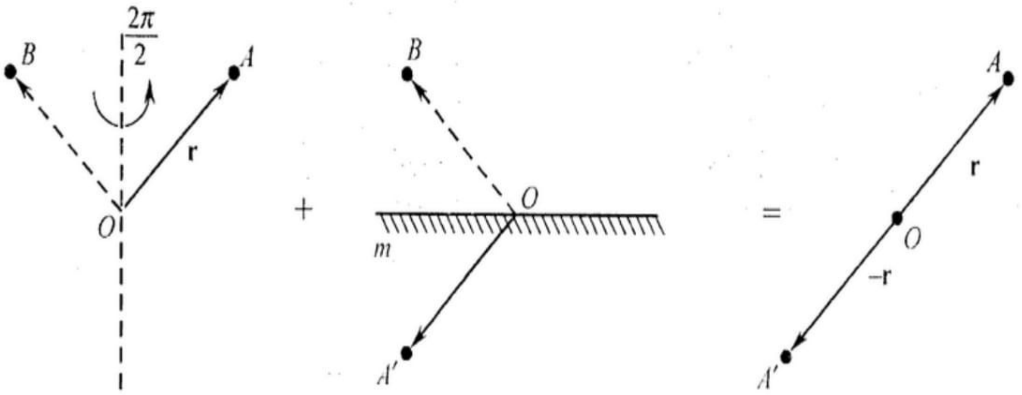


Figure 5: Rotoreflection Symmetry

The Rotoinversion:

This operation includes an n-fold rotation followed by an inversion. It is represented as $\overline{n}$.

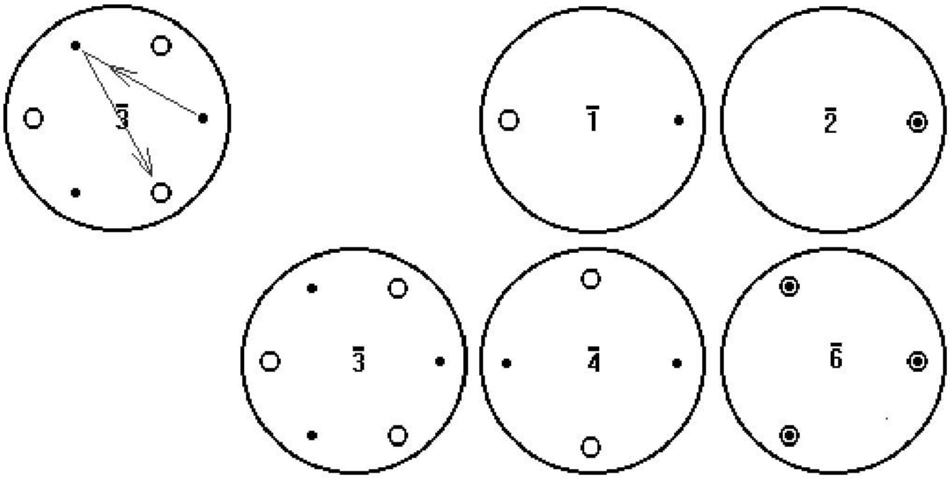


Figure 6: Rotoinversion Symmetry

The Screw Translation:

The n-fold rotation combined with a translation parallel to rotation axis is called as screw rotation.

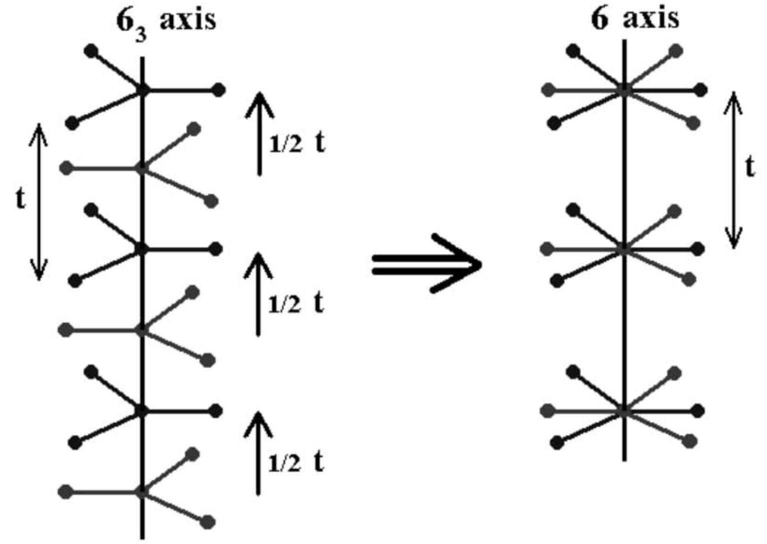


Figure 7: Screw Translation Symmetry

The Glide reflection:

When the reflection is combined with a translation parallel to plane of reflection the combined operation is called as glide reflection.

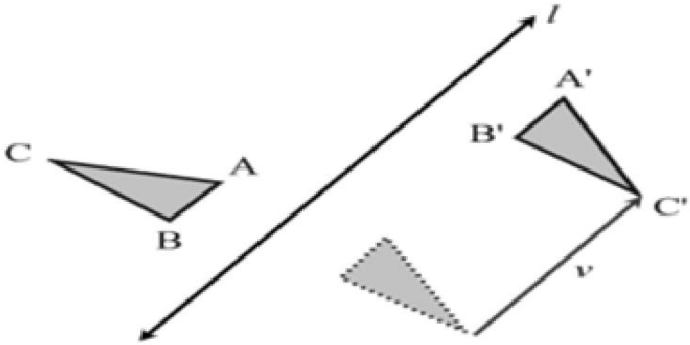


Figure 8: Glide Reflection Symmetry

2.3 The Crystal Structure of NaCl

The space lattice of NaCl crystal is FCC. The arrangement of Na and Cl atoms in the lattice is shown in the Figure 9. No sodium atom is located at any corner point, but one of them is at the centre and others are at mid points of 12 edges of the cube. An atom on the edge contribute ¼th of the atom. So there are 3 atoms contributed by edges atoms and one by the centre atom. So there are 4 sodium atoms in the unit cell. Similarly there are 4 atoms of chlorine in the unit cell. A single unit cell accommodates four formula unit cells of NaCl. The position of Na and Cl atoms in the unit cell are as

$$Na:\left\{\frac{1}{2},\frac{1}{2},\frac{1}{2}\right\},\left\{0,0,\frac{1}{2}\right\},\left\{0,\frac{1}{2},0\right\},\left\{\frac{1}{2},0,0\right\}$$

$$Cl:\left\{0,0,0\right\},\left\{\frac{1}{2},\frac{1}{2},0\right\},\left\{\frac{1}{2},0,\frac{1}{2}\right\},\left\{0,\frac{1}{2},\frac{1}{2}\right\}$$

The basis is composed of two atoms which are separated by a distance $\frac{\sqrt{3}a}{2}$, where *a* is the length of cube edge. The lattice parameter of NaCl is 5.63 A^0.

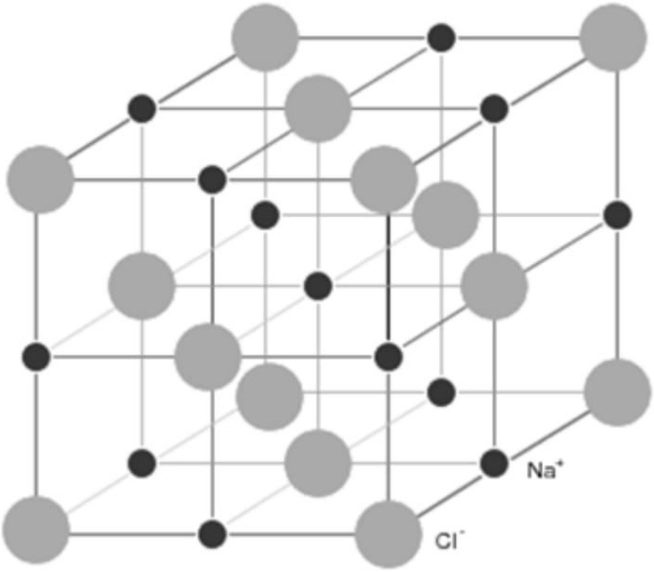


Figure 9: Crystal Structure of NaCl

2.4 The Crystal Structure of CsCl

The space lattice of CsCl is simple cubic. The basis has one Cs^+ ion at {0,0,0} and Cl^- ion at {1/2,1/2,1/2}. The atom at the centre of the cube is opposite to the ions on the corners of the cube. The lattice points of CsCl are two interpenetrating simple cubic lattices, the corners of one sublattice is the body centre of the other. One sublattice is occupied by Cs^+ and other by Cl^- ions. The lattice parameter of CsCl is $4.11A^0$.

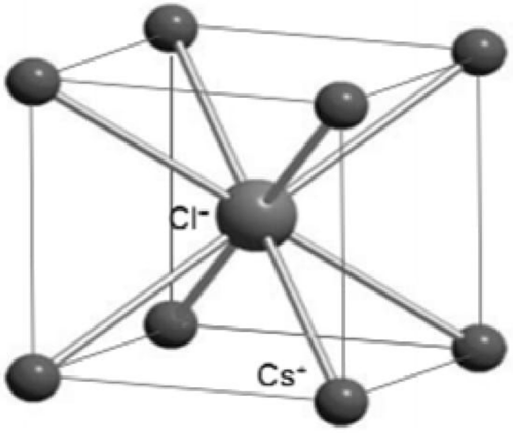


Figure 10: Crystal Structure of CsCl

2.5 The Hexagonal Close Pack Structure (hcp)

The unit cell of hexagonal structure contains an atom at each corner, one atom at the centres of hexagonal faces and three more atoms within the body of the cell. Each atom touches three atoms in the layer below its plane, six atoms in its plane and three atoms in the layer above. So the coordination number of this structure is 12. The top layer contains seven atoms. Each corner atom is shared by six surrounding hexagon cells and the centre atom is shared by two surrounding cells. Three atoms within the body of the cell are fully contributing to the cell. So there are 6 atoms in an unit cell.

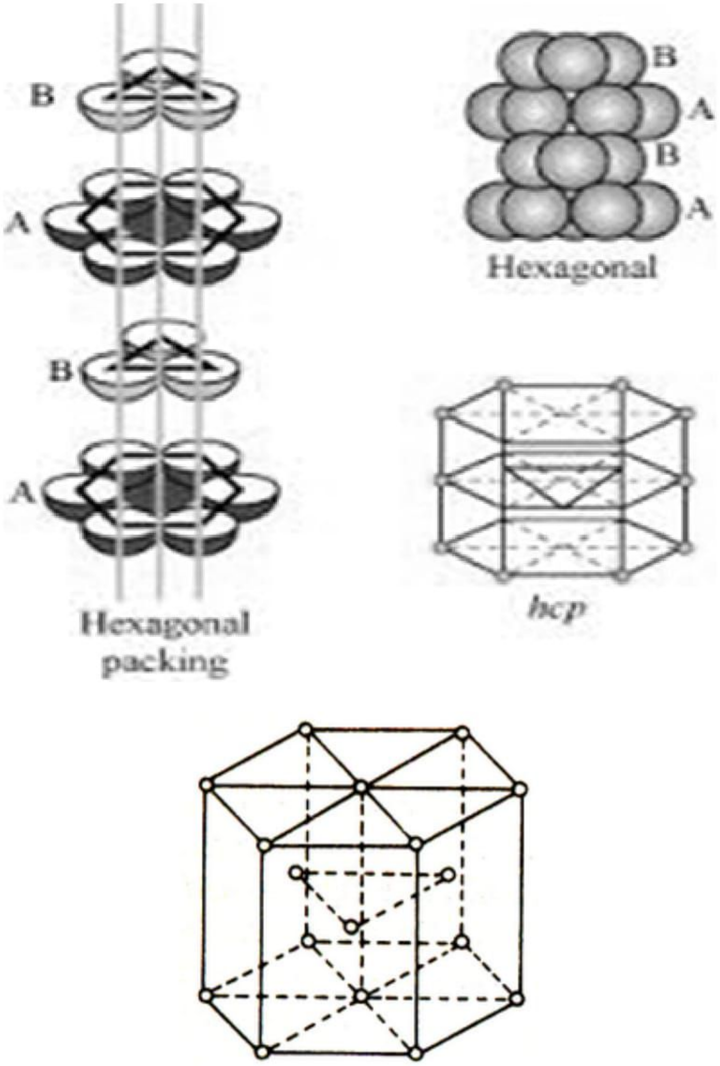


Figure 11: Hexagonal Close Pack Structure

Let “c” is the height of unit cell and “a” be the length of the edge.

For given figure below ,let the edge of hexagonal base =a

The height of hexagon = h

Radius of sphere = r

The centre sphere of the first layer lies exactly over the void of 2nd layer B.

The centre sphere and the spheres of 2nd layer B are in touch .

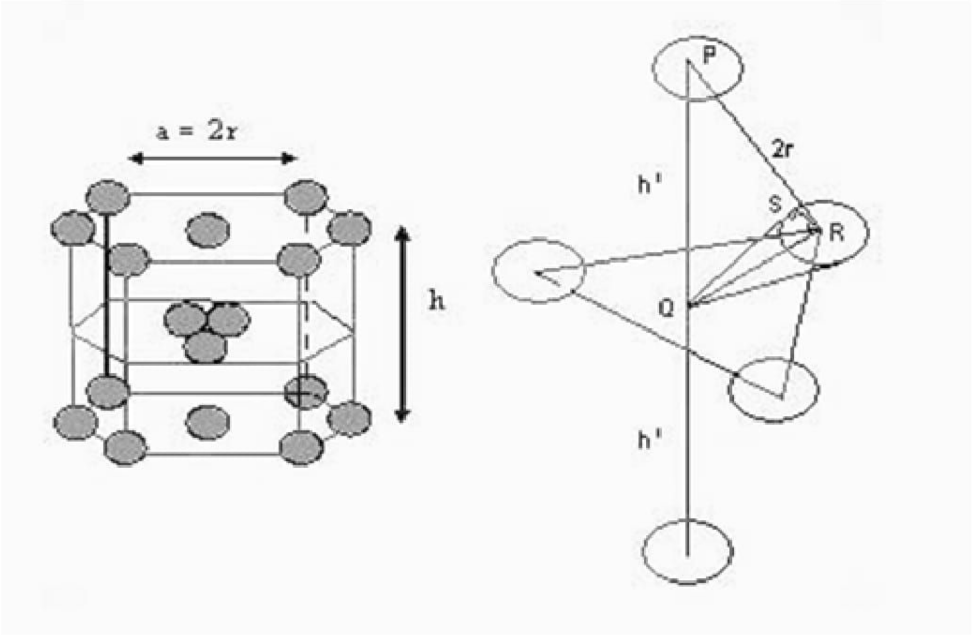
So, In Δ PQR (an equilateral triangle)

PR = 2r, draw QS tangent at points

In Δ QRS $\angle QRS = 30°$, SR = r

$$\text{Cos}30° = \frac{SR}{QR}$$

$$QR = \frac{r}{\sqrt{3}/2} = \frac{2r}{\sqrt{3}}$$



PQ = $\sqrt{PR^2 - QR^2}$

$$= \sqrt{4r^2 - \frac{4r^2}{3}}$$

h^1 = $\sqrt{\frac{8r^2}{3}} = 2\sqrt{\frac{2}{3}}r$

h = 2h^1 = $4\sqrt{\frac{2}{3}}r$

Now, volume of hexagon = (area of base) x (height)

Volume = $\frac{6\sqrt{3}a^2}{4} \times h$

$$= \frac{6\sqrt{3}}{4}(2r)^2 \times 4\sqrt{\frac{2}{3}}r$$

$$= 24\sqrt{2}r^3$$

Area of hexagonal can be divided into six equilateral triangles with side 2r.

No. of spheres in hcp = $12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 = 6$

Volume of spheres = $6 \times \frac{4}{3}\pi r^3$

Percentage of space occupied by sphere = $\frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}r^3} \times 100\%$

$$= \frac{\pi}{3\sqrt{2}} \times 100 = 74\%$$

2.6 The Diamond Structure

The diamond lattice is supposed to be formed by interpenetrating two fcc lattices along the body diagonal by ¼ th cube edge. One sublattice has its origin at the point (0,0,0) and at a point quarter of the way along the body diagonal at a point (a/4,a/4,a/4).

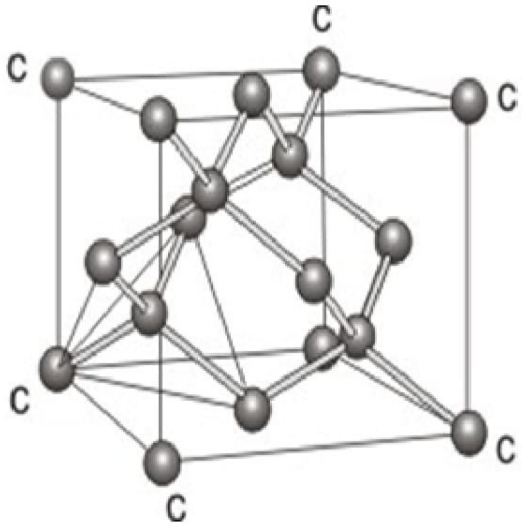


Figure 12: Diamond Structure

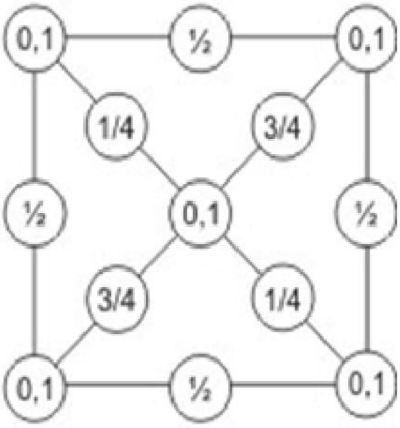


Figure 13: Top view of Diamond Structure

The packing factor of this structure is 34%. Carbon, Silicon and Germanium crystallize in this structure.

2.7 The Zinc Blende Structure

The Zinc Blende structure is almost identical to diamond structure except that the two interpenetrating fcc sublattices are of different atoms and displaced from each other by one-quarter of the body diagonal.

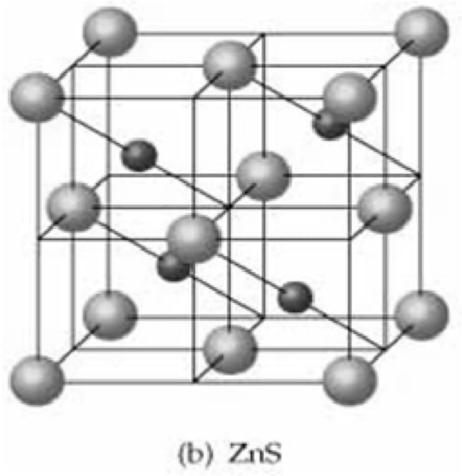


Figure 14: Zinc Blende Structure.

The cubic Zinc Sulphide structure results when Zinc atoms are placed at fcc lattice and S atoms on the other fcc lattice. There are four atoms per unit cell. The examples of the compounds which have Zinc Blende structure are CuCl, ZnS, InSb, CdS, etc.

2.8 Perovskite Structure

The structural family of perovskites is a large family of compounds having crystal structures related to the mineral perovskite $CaTiO_3$. In the ideal form the crystal structure of cubic ABX_3 perovskite can be described as consisting of corner sharing BX_6 octahedra with the A cation occupying the 12-fold coordination site formed in the middle of the cube of eight such octahedra. The ideal cubic perovskite structure is not very common and also the mineral perovskite itself is slightly distorted. The perovskite family of oxides is probably the best studied family of oxides. The interest in compounds belonging to this family of crystal structures arise in the large and ever surprising variety of properties exhibited and the flexibility to accommodate almost all of the elements in the periodic system.

Distorted perovskites have reduced symmetry, which is important for their magnetic and electric properties. Due to these properties, perovskites have great industrial importance, especially the ferroelectric tetragonal form of $BaTiO_3$ (Figure 15), $SrTiO_3$ (Figure 16).

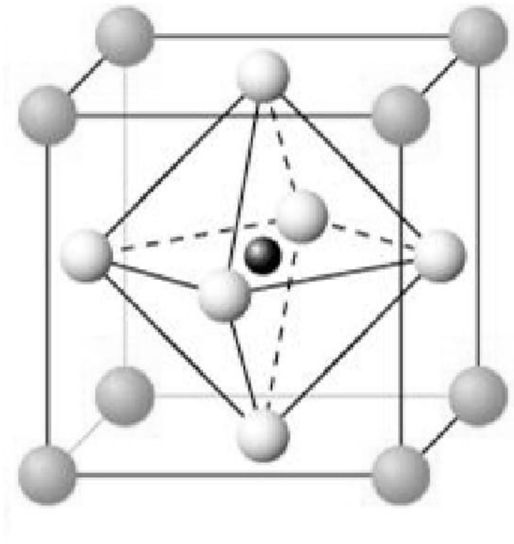


Figure 15: Crystal Structure of $BaTiO_3$

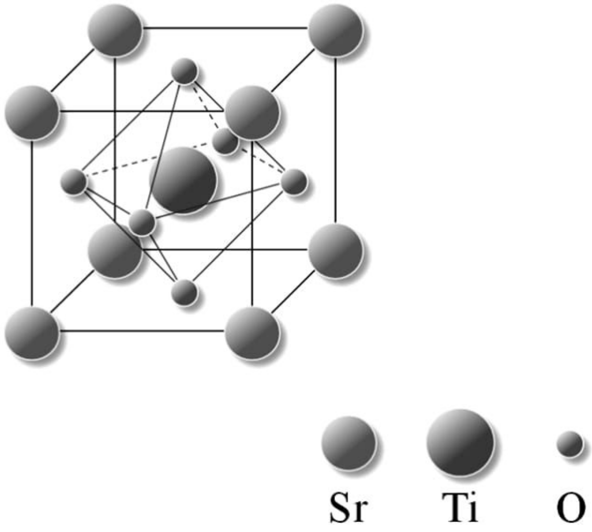


Figure 16: Crystal Structure of $SrTiO_3$

If the large oxide ion is combined with a metal ion having a small radius the resulting crystal structure can be looked upon as close packed oxygen ions with metal ions in the interstitials. This is observed for many compounds with oxygen ions and transition metals of valence +2, *e.g.* NiO, CoO and MnO. In these crystal structures the oxygen ions form a cubic close packed lattice with the metal ion in octahedral interstitials (*i.e.* the rock salt structure). Replacing one fourth of the oxygen with a cation of approximately the same radius as oxygen (*e.g.* alkali, alkali earth or rare earth element) reduces the number of octahedral voids, occupied by a small cation, to one fourth. The chemical formula can be written as ABX_3 and the crystal structure is called perovskite. X is often oxygen but also other large ions such as F^- and Cl^- are possible.

The ideal cubic structure is realized, in $CaRbF_3$ and $SrTiO_3$. The latter can be described as Sr^{2+} and O^{2-} ions forming a cubic close packed lattice with Ti^{4+} ions occupying the octahedral holes created by the oxygen. The perovskite structure has a three dimensional net of corner sharing TiO_6 octahedral with Sr^{2+} ions in the twelve fold cavities in between the polyhedral.

2.9 Self Learning Exercise

Q.1 Discuss the various symmetry operations in detail.

Q.2 Explain the hybrid symmetry operation with suitable diagrams.

Q.3 Explain the Zinc Blende and Diamond structure of crystals.

Q.4 Explain the point symmetry operations.

2.10 Summary

This unit deals with the symmetries found in the crystals. The crystal symmetry operations are then classified into three categories. These symmetry operations are translational, point and hybrid symmetry operations. The three symmetry operations are then discussed and their further classifications are also explained with diagrams. After this some crystal structures are discussed with diagrams of unit cell. The positions of different atoms in the unit cell are explained. The lattice parameters and packing fractions of some crystal structures are discussed. The unit cells of NaCl, CsCl, HCP, Diamond structure, Zinc Blende structure and perovskite structure are explained with diagrams.

2.11 Glossary

Symmetry : Similar pattern

Symmetry operation : Act of getting similar pattern.

Lattice : Arrangement of lattice points in space.

Translation : Linear displacement in space.

Point operation : Operation taken about a lattice point.

Hybrid : Combined or mixed.

Congruent : Similar

Inversion: Changing the direction by 180^0.

Rotoreflection : Rotation and followed by reflection.

Accommodate : Occupy.

Interpenetrating : Getting one into other.

Co-ordination number : Number of nearest neighbours.

Perovskite : A kind of crystal structure (named since its origin in history)

2.12 Exercise

Q.1 Explain the concept of symmetry operation.

Q.2 Write a short note on the translation and rotation symmetry operations.

Q.3 Discuss the rotational symmetry operation in a cubic unit cell.

Q.4 Describe the crystal structure of NaCl and CsCl.

Q.5 Explain the crystal structure of hexagonal close packing and find its packing fraction.

Q.6 Explain the perovskite structure and write the examples of this structure.

References and Suggested Readings

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UNIT-3

Reciprocal Lattice

Structure of the Unit

3.0 Objectives

The aim of the unit is to explain the principles of x-ray diffraction and to derive related equations. After going through this unit you will be able to explain the principles of x-ray diffraction, the diffraction conditions and the concept of reciprocal lattice and Brillouin zones.

3.1 Introduction of Reciprocal Lattice

X-rays from part of the electromagnetic spectrum and the energy (E) of an x-ray photon is related to the wavelength by Planck's relation

$E = h\nu = hc/\lambda$

where h is Planck's constant and c is the speed of light. Thus the energy of the x-ray photon of wavelength 1 A^0 is of the order of 10 keV.

X-rays are produced when high speed electrons strike some target material. Metals of high melting point are used as target material and they should have high atomic weight for abundant production of x-rays. Metals like tungsten, copper and molybdenum are used as target materials. When electrons accelerated to very high speeds strike the target they give up their kinetic energy and thereby produce both characteristic and continuous x-rays.

The discovery of the diffraction of x-rays by crystals in 1912 is one of the most important discoveries in Physics. Since x-rays can usually penetrate solids non-destructively, the diffraction of these rays by crystals provides information about the internal structure of the crystal. Experiments had indicated that wavelength of x-rays is of the order of 1A^0,which is about the same as the interatomic spacing in a solid. It occurred to Van Laue in 1912,that if the atoms in a crystal were arranged in a regular way, the crystal might serve as a three dimensional crystal grating.

Techniques using x-ray diffraction immediately provided powerful tool for determining virtually the structures of any material. X-ray diffraction has great value, since in a crystal it represents wave propagation in a periodic structure.

3.2 Bragg's Law

Consider a set of atomic planes called Bragg planes as shown in Fig. (3.1). A parallel beam of X-ray is incident on these planes making a glancing angle θ with

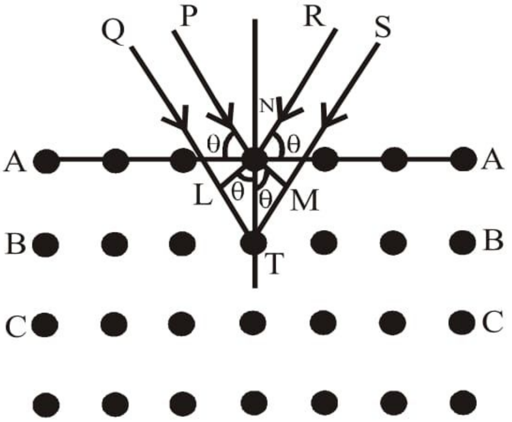

Fig. 3.1: Geometry of Bragg's reflection

the planes as shown. All wavelets scattered from one plane combine constructively only in one direction which makes the same angle with the plane under consideration as the incident ray. In all other directions they combine destructively. This is the condition of normal optical reflection. Because of this aspect, the actual scattering process is termed as reflection. When scattering from different parallel planes is considered, the reflected rays obey the conditions of constructive and destructive interference.

Consider two parallel rays incident on a set of parallel planes. These rays suffer Bragg reflections by atoms N and T in two successive planes. T is vertically below N and the lattice separation is d. From N drop perpendiculars NL and NM on the incident and reflected ray respectively at T ,the glancing angle is θ.

Comparing the path of rays reflected at N and at T, the additional path travelled by the ray reflected at T is (LT + TM) i.e. the path difference in the rays reflected from the two planes is

$$\Delta = LT + TM$$

If distance between the two planes NT = d then from the triangle ΔLNT and ΔMNT

$$\frac{LT}{NT} = \sin\theta \text{ and } \frac{MT}{NT} \sin\theta$$

$$\therefore \quad LT = d \sin \theta \text{ and } MT = d \sin \theta$$

The path difference is $\Delta = 2 \text{ d} \sin \theta$

According to the necessary condition for constructive interference path difference is

$$\Delta = n\lambda$$

where λ is the wavelength of X-rays and n is an integer.

$$\therefore 2d \sin \theta = n\lambda.$$

This equation is called Bragg equation. This equation represents the relation between inter spacing distance d, reinforce angle θ and wavelength λ of X-ray .

From the Bragg's equation it is clear that for the wavelength of X-rays, the minimum value is d.

$$d = \frac{n\lambda}{2\sin\theta}$$

It is possible the value of d is minimum when

$$(\sin\theta)_{\max} = 1$$

$$\therefore\ d_{min} = \frac{n\lambda}{2}$$

for n = 1 $\quad d_{min} = \frac{\lambda}{2}$

Thus we see that when the diffraction pattern is obtained from the crystal, the distance between the lattice planes is $\frac{\lambda}{2}$ or more.

3.3 Fourier Analysis for Scattered Wave Amplitude

The Bragg derivation of the diffraction condition gives a neat statement of the condition for the constructive interference of waves scattered from the lattice points. We need a deeper analysis to determine the scattering intensity from the basis of atoms, which means from the spatial distribution of electrons within each cell.

Fourier Analysis

We have seen that a crystal is invariant under any translation of the form $T = u_1\, \mathbf{a_1} + u_2\, \mathbf{a_2} + u_3\, \mathbf{a_3}$, where u_1, u_2, u_3 are integers and $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$ are the crystal axes. Any local physical property of the crystal, such as the charge concentration electron number density, or magnetic moment density is invariant under T. What is most important to us here is that the electron number density n (r) is a periodic function of r, with period's a_1, a_2, a_3 in the directions of the three crystal axes, respectively. Thus

$$n\,(\mathbf{r} + \mathbf{T}) = n\,(\mathbf{r}). \qquad (1)$$

Such periodicity creates an ideal situation for Fourier analysis. The most interesting properties of crystals are directly related to the Fourier components of the electron density.

We consider first a function n (x) in one dimension with period *a* in the x direction.

We expand n(x) in a Fourier series of sines and cosine:

$$n(x) = n_0 + \sum_{p>0} \left[C_p \cos\left(2\pi px/a\right) + S_p \sin\left(2\pi px/a\right) \right] \tag{2}$$

Where the p is positive integers and C_p, S_p are real constants, called the Fourier coefficients of the expansion. The factor 2π/a in the arguments ensures that n(x) has the period *a*:

$$n(x+a) = n_a + \sum \left[C_p \cos\left(2\pi px/a + 2\pi p\right) + S_p \sin\left(2\pi px/a + 2\pi p\right) \right]$$

$$= n_a + \sum \left[C_p \cos\left(2\pi px/a\right) + S_p \sin\left(2\pi px/a\right) \right] = n(x) \tag{3}$$

We say that 2πp/a is a point in the reciprocal lattice or Fourier space of the crystal. In one dimension these points lie on a line. The reciprocal lattice points tell us the allowed terms in the Fourier series eq.(3) or (4). A term is allowed if it is consistent with the periodicity of the crystal, as in Fig. 3.2; other point in the reciprocal space are not allowed in the Fourier expansion of a periodic function.

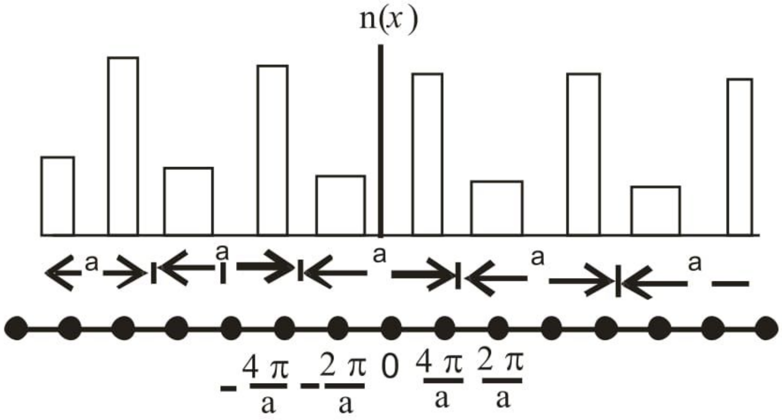

Fig. 3.2: ***A periodic function n (x) of period a, and the terms 2πp/a that may appear in the Fourier transform***

It is convenient to write the series (3) in the compact form

$$n(x) = \sum_p n_p \exp\left(i2\pi px/a\right) \tag{4}$$

where the sum is over all integers p : positive, negative, and zero. The coefficients n_p now are complex numbers. To ensure that n (x) is a real function, we require.

$$n^*_{-p} = n_p, \tag{5}$$

For then the sum of the terms in p and -p is real. The asterisk on n^*_{-p} denotes the complex conjugate of n_{-p}.

With $\varphi = 2\pi px/a$, the sum of the terms in p and -p in (4) is real if (5) is satisfied. The sum is

$$n_p(\cos\varphi + i\sin\varphi) + n_{-p}(\cos\varphi - i\sin\varphi)$$

$$= (n_p - n_{-p})\cos\varphi + i(n_p - n_{-p})\sin\varphi \qquad (6)$$

which in turn is equal to the real function

$$2\,\mathrm{Re}\,(n_p)\cos\varphi - 2\mathrm{Im}\,(n_p)\sin\varphi \qquad (7)$$

If (5) is satisfied. Here $\mathrm{Re}[n_p]$ and $\mathrm{Im}[n_p]$ are real and denote the real and imaginary parts of n_p. Thus the number density n (x) is a real function desired.

The extension of the Fourier analysis to periodic functions n(r) in three dimensions is straightforward. We must find a set of vectors G such that

$$n(\vec{r}) = \sum_G n_G \exp(i\vec{G}.\vec{r}) \qquad (8)$$

is invariant under all crystal translations T, that leaves the crystal invariant . It will be shown below that the set of Fourier coefficients n_G determines the x-ray scattering amplitude.

Inversion of Fourier series:

We now show that the Fourier coefficient n_p in the series (4) is given by

$$n_p = a^{-1}\int_0^a n(x)\exp(-i2\pi px/a)dx \qquad (9)$$

Substitute (4) in (9) to obtain

$$n_p = a^{-1}\sum_p n_p \int_o^a \exp[i2\pi(p'-p)x/a]dx \qquad (10)$$

If p' ≠ p the value of the integral is

$$\frac{a}{i2\pi(p'-p)}\left(e^{i2\pi('p'-p)} - 1\right) = 0$$

Because (p' – p) is an integer and exp [i2π (integer)] =1. For the term p' = p, the integrand is exp (i0) = 1, and the value of the integral is a, so that $n_p = a^{-1} n_p a = np$, which is an identity, so that (9) is an identity.

As in (9), the inversion of (8) gives

$$n_G = V_c^{-1} \int_{cell} n(\vec{r}) \exp(-i\vec{G}.\vec{r}) dV. \qquad (11)$$

Here V_C is the volume of a cell of the crystal.

3.4 Self Learning Exercise - I

Section A: Very Short Answer Type Questions

Q.1 Write the formula of Bragg Equation.

Q.2 The first order spectrum is viewed at a grazing angle of 8^0 through a Bragg spectrometer. Calculate the wavelength of x-rays if spacing between successive planes is 2.82 A^0. [Sin $8^0 = 0.1392$]

Q.3 What is the wavelength of x-ray photon?

Section B : Short Answer Type Questions

Q.4 X-rays of wave-length $1.3A^0$ are diffracted in a Bragg spectrometer at an angle of 25^0. Find the spacing between the atomic planes of the crystals.

Q.5 The solid crystal is in the form of bcc crystal. The Bragg angle corresponding to the first order diffraction (200) planer in a crystal is $16^0 6'$ when x-rays of wave length 1.54 A^0 is used ,then find the lattice constant of unit Cell.

Q.6 The Bragg angle corresponding to the first order diffraction from (111) planes in a crystal is 30^0 when x-rays of wave length $1.75A^0$ are used. Calculate the lattice constant of crystal.

3.5 Reciprocal Lattice Vector

The diffraction of X-rays by a crystal may be thought as reflection by sets of parallel planes in the crystal. When the planes of several slopes are considered in the same problem, difficulty arises in visualizing the several relative slopes of these two dimensional surfaces. Crystallographers have long struggled with the problem of representing adequately crystallographic planes of several slopes. The slope of the plane is fixed by the geometry of the plane or the geometry of the normal to the plane. The normal has one less dimension than the plane and thus provides an easier means of thinking of the slope of a plane. A device for tabulating both the slopes and the inter planer spacing's of the places of a crystal lattice is provided by a concept known as the reciprocal lattice. The concept or reciprocal lattice is as follows:

(i) Each point in the reciprocal lattice preserves the characteristics of the set of planes which it represents.

(ii) Its direction with respect to the origin represents the orientation of the planes and

(iii) Its distance from the origin represents the inter planer spacing of the planes.

In a crystal, there exists many sets of planes with different orientations and spacing. These planes can cause diffraction. If we draw normal to all sets of planes, from a common origin, the length of normal being proportional to the reciprocal of the inter planar spacing of the corresponding set, then the end points of normal from a lattice which is called as 'reciprocal lattice'.

The general procedure for locating the reciprocal lattice points corresponding to these planes is as allows:

(i) A lattice point is taken as common origin.

(ii) From the common origin, draw a normal to each plane.

(iii) Place a point on the normal to each plane (h, k l) at a distance from the origin equal to $\frac{1}{d_{hkl}}$.

(iv) Such points from a periodic array called reciprocal lattice.

Vector Development of the Reciprocal Lattice

First of all, a relationship between the normal to a plane and the crystallographic axes a, b and c will be developed. This can be done by considering a primitive unit cell as shown in Fig. 3.3. When the height of this cell d_{100} is multiplied by the area of the parallelogram given the volume V of this primitive cell.

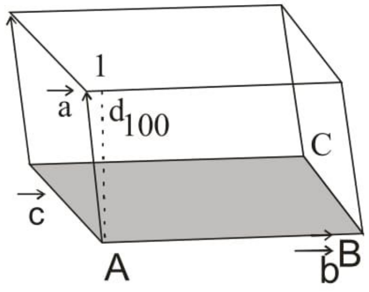

Fig. 3.3: Primitive cell and their axes

∴ Volume of the primitive cell

V = area × d_{100}

$$\therefore \quad \frac{1}{d_{100}} = \frac{area}{Volume} \tag{1}$$

In vector notation, the normal to a plane is represented by the unit vector $\hat{n}$ hence the equation can be written as

$$\vec{\sigma}_{100} = \frac{1}{d_{100}}\hat{n} = \frac{area}{Volume} = \frac{A}{V} \tag{2}$$

If any plane is represented by integers (h, k, l) then

$$\vec{\sigma}_{hkl} = \frac{1}{d_{hkl}}\hat{n} = \frac{A}{V}$$

Area of the parallelogram from by the vector $\vec{b}$ and $\vec{c}$

$$= \vec{b} \times \vec{c}$$

$$\therefore \vec{\sigma}_{100} = \frac{1}{d_{100}}\hat{n} = \frac{\vec{b} \times \vec{c}}{V}$$

We know that volume of the primitive cell formed by the vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$

$$V = \vec{a} \,.\, \overline{\vec{b} \times \vec{c}} = \vec{b} \,.\, \overline{\vec{c} \times \vec{a}} = \vec{c} \,.\, \overline{\vec{a} \times \vec{b}} \tag{3}$$

$$\therefore \quad \vec{\sigma}_{100} = \frac{1}{d_{100}}\hat{n} = \frac{\vec{b} \times \vec{c}}{\vec{a} \,.\, \overline{\vec{b} \times \vec{c}}} \tag{4a}$$

Similarly expression can be written for $\vec{\sigma}_{010}$ and $\vec{\sigma}_{001}$.

$$\vec{\sigma}_{010} = \frac{1}{d_{010}}\hat{n} = \frac{\vec{c} \times \vec{a}}{\vec{a} \,.\, \overline{\vec{b} \times \vec{c}}} \tag{4b}$$

$$\vec{\sigma}_{001} = \frac{1}{d_{001}}\hat{n} = \frac{\vec{a} \times \vec{b}}{\vec{a} \,.\, \overline{\vec{b} \times \vec{c}}} \tag{4c}$$

These three vectors are chosen as the three reciprocal axes for defining three dimensional reciprocal lattices.

$$\vec{a}\,^* = \vec{\sigma}_{100} = \frac{\overline{\vec{b} \times \vec{c}}}{\vec{a} \,.\, \overline{\vec{b} \times \vec{c}}} \tag{5a}$$

$$\vec{b}\,^* = \vec{\sigma}_{010} = \frac{\overline{\vec{c} \times \vec{a}}}{\vec{a} \,.\, \overline{\vec{b} \times \vec{c}}} \tag{5b}$$

$$\vec{c}\,* = \vec{\sigma}_{001} = \frac{\overrightarrow{\mathrm{a}} \times \vec{b}}{\vec{a}\,.\,\overrightarrow{b} \times \vec{c}} \tag{5c}$$

This reciprocal lattice vectors axes bear simple relationship to the crystal axes, from the vector notation for equation (6).

$$\vec{a}\,* = 2\pi = \frac{\overrightarrow{\mathrm{b}} \times \vec{c}}{\vec{a}\,.\,\overrightarrow{b} \times \vec{c}} \tag{6a}$$

$$\vec{b}\,* = 2\pi = \frac{\overrightarrow{\mathrm{c}} \times \vec{a}}{\vec{a}\,.\,\overrightarrow{b} \times \vec{c}} \tag{6b}$$

$$\vec{c}\,* = 2\pi = \frac{\overrightarrow{\mathrm{a}} \times \vec{b}}{\vec{a}\,.\,\overrightarrow{b} \times \vec{c}} \tag{6c}$$

Form equation (5a)

Vector $\vec{a}\,*$ is normal to $\vec{b}$ and $\overrightarrow{c}$

Hence $\vec{a}*\,.\,\overrightarrow{\mathrm{b}} = 0$

$\vec{a}*\,.\,\overrightarrow{\mathrm{c}} = 0$

Similarly from equation (5b)

Vector $\vec{b}*$ is normal to $\vec{c}$ and $\vec{a}$

$\therefore \vec{b}*\,.\,\overrightarrow{\mathrm{c}} = 0$

and $\vec{b}*\,.\,\overrightarrow{\mathrm{a}} = 0$

Vector $\vec{c}*$ is normal to $\vec{a}$ and $\vec{b}$

$\therefore$ $\vec{c}*\,.\,\overrightarrow{\mathrm{a}} = 0$

and $\vec{c}*\,.\,\overrightarrow{\mathrm{b}} = 0$

From scalar product of reciprocal vectors to direct vector for equation (5)

$$\left.\begin{array}{l} \vec{a}*.\vec{a} = \dfrac{\vec{a}\,.\,\vec{b} \times \vec{c}}{\vec{a}\,.\,\vec{b} \times \vec{c}} = 1 \\ \vec{b}*.\vec{b} = \dfrac{\vec{b}\,.\,\vec{c} \times \vec{a}}{\vec{b}\,.\,\vec{c} \times \vec{a}} = 1 \\ \vec{c}*.\vec{c} = \dfrac{\vec{c}\,.\,\vec{a} \times \vec{b}}{\vec{c}\,.\,\vec{a} \times \vec{b}} = 1 \end{array}\right] \tag{7}$$

Using these reciprocal lattice vectors, a lattice can be constructed. The successive points in the* direction represent successive sub multiples h of the spacing of (100), and in the b* direction successive sub multiples k of the spacing of (010) and similarly in c* direction, successive sub multiples *l* of the spacing of (001).

3.6 Laue Equations of X- Rays Diffraction

Laue Treatment Illustrates effectively the way in which X-rays scattered from different atoms can combine for the formation of diffracted beam. It also provides the validity of Bragg's picture. Let us consider the radiation scattered by two identical scattering centers P_1 and P_2 separated by a distance $\vec{r}$. Suppose $\hat{i}$ is the unit vector in the direction of the incident beam and $\hat{s}$ the unit vector in an arbitrary scattering direction as shown in Fig. (3.4). The incident radiation is assumed to be a parallel beam and the scattered beam is assumed to be detected at a long distance away. If P_2A and P_1B are the projection of **r** on the incident and scattered way directions respectively, the path difference between the radiation scattered at P_2 and that scattered at P_1 then

$$P_2A - P_1B = \hat{i} \cdot \vec{r} - \hat{s} \cdot \vec{r} = \left(\hat{i} - \hat{s}\right) \cdot \vec{r}$$

$$= \vec{S} \cdot \vec{r}$$

where $\vec{s} = \hat{i} - \hat{s}$ is the direction of the normal to a plane that reflects the incident direction into the scattered direction as shown in Fig. (3.4)

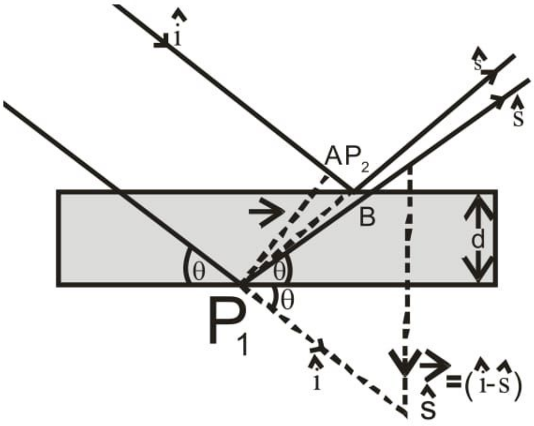

Fig. 3.4: Geometry of Laue Equation

From $\left|\vec{s}\right| = 2\sin\theta$ [$\because$ $\hat{i}$ and $\hat{s}$ are unit vector]

∴ Phase difference between the radiations scattered at the two points is

$$\phi = \frac{2\pi}{\lambda} \text{(Path difference)} = \frac{2\pi}{\lambda}\left(\vec{s}\ .\ \vec{r}\right) \tag{1}$$

The condition that there will be a diffraction maxima in the direction $\hat{s}$ is that the scattering contribution from point be an integral multiple of 2π.

If $\vec{a}$, $\vec{b}$ and $\vec{c}$ are the primitive lattice vectors for lattice point P_1 with respect to P_2 ,then from equation (1)

$$\left.\begin{aligned} \phi_a &= \frac{2\pi}{\lambda}\left(\vec{s}\ .\ \vec{a}\right) = 2\pi h' \\ \phi_b &= \frac{2\pi}{\lambda}\left(\vec{s}\ .\ \vec{b}\right) = 2\pi k' \\ \phi_c &= \frac{2\pi}{\lambda}\left(\vec{s}\ .\ \vec{c}\right) = 2\pi l' \end{aligned}\right\} \tag{2}$$

Where h', k' and l' are integers and ϕ_a, ϕ_b and ϕ_c are the phase difference of scattering ray.

If α, β and γ are the angle between the scattering normal $\vec{s}$ and the $\vec{a}$, $\vec{b}$ and $\vec{c}$ primitive lattice vectors respectively, then

$$\vec{s}\ .\ \vec{a} = |\vec{a}|\ |\vec{s}| \cos\ \alpha = 2a\ \sin\theta\ \cos\alpha$$

$$\vec{s}\ .\ \vec{b} = |\vec{b}|\ |\vec{s}| \cos\ \beta = 2b\ \sin\theta\ \cos\beta$$

$$\vec{s}\ .\ \vec{c} = |\vec{c}|\ |\vec{s}| \cos\ \gamma = 2c\ \sin\theta\ \cos\gamma$$

From equation (2)

$$\left.\begin{aligned} 2a\ \sin\theta\ \cos\alpha &= h'\lambda \\ 2b\ \sin\theta\ \cos\beta &= k'\lambda \\ 2c\ \sin\theta\ \cos\gamma &= l'\lambda \end{aligned}\right\} \tag{3}$$

For above equation (3), are called Laue's equations for X-ray diffraction. This is the second form of Bragg equation 2d sinθ = nλ which can be calculated by the Laue equations.

Calculated Bragg Equation by the Laue's Equation

From equation (3),we have

$$\left.\begin{aligned} \cos\alpha &= \frac{\lambda}{2a\sin\theta}h' \\ \cos\beta &= \frac{\lambda}{2b\sin\theta}k' \\ \cos\gamma &= \frac{\lambda}{2c\sin\theta}l' \end{aligned}\right\} \qquad (4)$$

Hence these direction of cosines are in the ratio of h', k' and l' respectively ,but the directional cosines are normal to the plane of the miller indices (hkl) are in the ratio of h, k, l respectively. Therefore these integers are mutually equal in ratio.

$$h', k', l' = h : k : l$$

∴ $h' = nh$, $k' = nk$ and $l' = nl$

Substituting these integers from equation (4)

$$\cos\alpha = \frac{n\lambda}{2a\sin\theta}h$$

$$\cos\beta = \frac{n\lambda}{2b\sin\theta}k$$

$$\cos\gamma = \frac{n\lambda}{2c\sin\theta}l$$

From the property of directional cosine

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

or $$\left(\frac{n\lambda}{2\sin\theta}\right)^2\left[\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right] = 1$$

or $$\frac{n\lambda}{2\sin\theta}\left[\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right]^{-1/2}$$

But the distance between the planes of the miller indices (h, k, l)

$$d = \left[\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right]^{-1/2}$$

Hence $$\frac{n\lambda}{2\sin\theta} = d$$

or $$\boxed{2d\sin\theta = n\lambda}$$

This equation is called Bragg condition or equation.

3.7 Ewald Construction- Bragg's Law in Terms of Reciprocal Lattice Vectors

The Bragg condition which was earlier derived by considering reflections from lattice planes can be seen as expressing a relation between the vectors in the reciprocal lattice.

P. P. Ewald was responsible for interpreting Laue's results in terms of reciprocal lattices. He devised a simple geometric construction that demonstrates the relationship in quite elegant.

Bragg's Law: The Bragg equation has a more elegant form in the reciprocal lattice. All the vectors are magnified by a constant scale factor of 2π and are related as shown. The vector G is 2π times the vector, OB shown in Ewald construction.

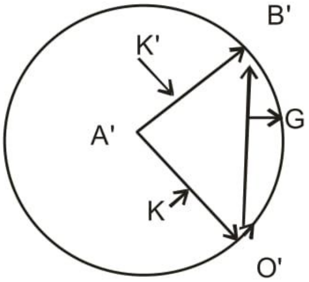

Fig. 3.5: Vector disposition in Ewald construction

Similarly the vectors K and K' are 2π times the vectors AO and AB. The disposition of the vectors, however, is of the same type. Therefore for diffraction it is necessary that the magnitude of A' B' (K' = K + G) must be equal to the magnitude of A' O' (K)

Thus Bragg condition imply that $(K + G)^2 = K^2$

or $(K+G) . (K+G) = K^2$

or $K^2 + 2KG + K^2 = K^2$

or $2K.G + G^2 = 0$

This is the Bragg law in terms of reciprocal lattice vectors.

3.8 Brillouin Zones

Through Ewald construction, we have seen the physical significance of Bragg reflection condition- whether or not a K-value is reflected depends upon Ewald sphere's intersecting a point of reciprocal lattice of the crystal under consideration. We now wish to construct in the reciprocal lattice the locus of all these K-values that can be Bragg reflected.

Let us consider a simple square lattice. Its primitive translation vectors are represented by

$$\mathbf{a} = a\hat{i}, \mathbf{b} = a\hat{j}$$

Where a is its side and ***i*** and ***j*** are the unit vectors. The corresponding reciprocal lattice translation vectors are,

$$\mathbf{a}^* = (1/a)\ \hat{i} \text{ and } \mathbf{b}^* = (1/a)\ \hat{j}$$

So that the G- type reciprocal lattice vector

$$\mathbf{G} = (2\pi/a)\ (h\hat{i} + k\hat{j}),$$

where h and k are integers.

Suppose that the wave vector for an x-ray is $K = iK_x + jk_y$, if it is measured from the origin of the reciprocal lattice.

The Bragg condition now requires, $2\mathbf{K}.\mathbf{G}. + \mathbf{G}^2 = 0$.

Substituting the values of **K** and **G** this becomes,

$$h\ K_x + k\ K_y = (-\pi/a)\ (h^2 + k^2)$$

By taking all possible combinations of h and k, we can get the value of k which will be Bragg reflected.

If $h = \pm 1$, and $k = 0$; $k_x = \pm \pi/a$ and K_y is arbitrary

If $h = 0$ and $k = \pm 1$; $K_y = \pm \pi/a$ and K_x is arbitrary.

These four lines are plotted in the figure3.6. All K vectors originating at the origin and terminating on these lines will produce Bragg reflection. Beside this set of lines, some other sets of lines as, for example $\pm K_x \pm K_y = 2\pi/a$ are also possible (for $h = \pm 1$ and $k = \pm 1$).

The regions included in such lines are called Brillouin zones or Weigner-Seitz cells. In particular, the square bounded by $K_x = \pm \pi/a$ and $K_y = \pm \pi/a$ is the first Brillouin zone. The first Brillouin zone is the smallest volume entirely enclosed by planes that are perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.

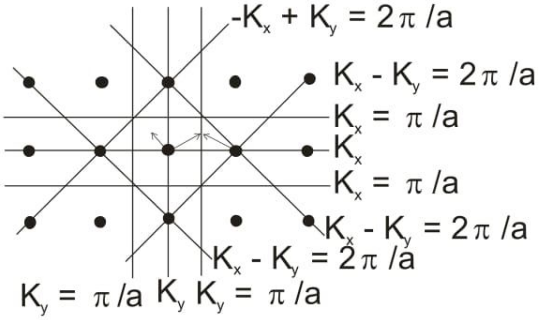

Fig. 3.6: Schematic representation of Brillouin zones

The additional area included by $\pm K_x \pm K_y = 2\pi/a$ is the second Brillouin zone, and so on. The Brillouin zone boundary thus represents the locus of K-values that are Bragg reflected; as such, it may be considered as the reflecting plane-the boundaries of the first zone as the reflecting plane for the first order reflections, the boundaries of the second zone as the reflecting plane for the second order reflections etc. It may be added that within a Brillouin zone no K-vectors can give Bragg reflection.

The form of the Brillouin zones in three dimensions can be easily evaluated by using the generalized equation.

$$hK_x + kK_y + lK_z = -\pi/a\ (h^2 + k^2 + l^2)$$

The first zone is clearly a cube intersecting the K_x, K_y and K_z axes at the points (π/a) and thus having its sides ($2\pi/a$). The second zone is made up of pyramids added to each face of the first zone cube in the manner in which the triangles are added to the first zone square in two dimensions. Higher zones are constructed similarly.

3.9 Properties of the Reciprocal Lattice

(i) Reciprocal Lattice to Simple Cubic Lattice

The basis vectors of a simple cubic lattice may be written as

$$\vec{a} = \hat{i}\ a$$
$$\vec{b} = \hat{j}\ a$$
$$\vec{c} = \hat{k}\ a$$

∴ Volume of the primitive cell

$$V = \vec{a}\ .\ \vec{b}\times\vec{c}$$

$$= a^3\left[\hat{i}\ .\ \left(\hat{j}\times\hat{k}\right)\right] = a^3$$

Components of the reciprocal vector

$$\vec{a}* = \frac{\vec{b}\times\vec{c}}{\vec{a}\ .\left(\vec{b}\times\vec{c}\right)} = \frac{a^2\left(\hat{j}\times\hat{k}\right)}{a^3} = \frac{1}{a}\hat{i}$$

Similarly $$\vec{b}* = \frac{\vec{c}\times\vec{a}}{\vec{a}\ .\left(\vec{b}\times\vec{c}\right)} = \frac{a^2\left(\hat{k}\times\hat{i}\right)}{a^3} = \frac{1}{a}\hat{j}$$

$$\vec{c}* = \frac{\vec{a}\times\vec{b}}{\vec{a}\ .\left(\vec{b}\times\vec{c}\right)} = \frac{a^2\left(\hat{i}\times\hat{j}\right)}{a^3} = \frac{1}{a}\hat{k}$$

Hence simple cubic is a reciprocal lattice of simple cubic lattice but with lattice constant equal to 1/a.

(ii) Reciprocal Lattice to Body Centered Cubic Lattice

The basis vectors of the bcc lattice are as follows:

$$\vec{a} = \frac{a}{2}\left(-\hat{i}+\hat{j}+\hat{k}\right)$$

$$\vec{b} = \frac{a}{2}\left(\hat{i}-\hat{j}+\hat{k}\right)$$

$$\vec{c} = \frac{a}{2}\left(\hat{i}+\hat{j}-\hat{k}\right)$$

∴ Volume of the primitive cell

$$V = \vec{a}\ .\ \left(\vec{b}\times\vec{c}\right)$$

$$= \frac{a^3}{8}\left[\left(-\hat{i}+\hat{j}+\hat{k}\right).\left(\hat{i}-\hat{j}+\hat{k}\right)\times\left(\hat{i}+\hat{j}-\hat{k}\right)\right] = \frac{a^3}{2}$$

Vector components of Reciprocal lattice

$$\vec{a}* = \frac{\vec{b}\times\vec{c}}{\vec{a}.\left(\vec{b}\times\vec{c}\right)}$$

$$= \frac{1}{2a}\left[\left(\hat{i} - \hat{j} + \hat{k}\right) \times \left(\hat{i} + \hat{j} - \hat{k}\right)\right]$$

$$= \frac{1}{2a}\left[+\hat{k} + \hat{j} + \hat{k} + \hat{i} + \hat{j} - \hat{i}\right]$$

or $$= \frac{1}{a}\left(\hat{j} + \hat{k}\right)$$

Similarly $$\vec{b}^* = \frac{1}{a}\left(\hat{i} + \hat{k}\right)$$

and $$\vec{c}^* = \frac{1}{a}\left(\hat{i} + \hat{j}\right)$$

Vector $\vec{a}^*, \vec{b}^*, \vec{c}^*$ are the basis vector of the face centered cubic lattice. Thus face centered cubic lattice is the reciprocal lattice of the body centered cubic lattice.

(iii) Reciprocal Lattice to Face Centered Cubic Lattice

The basis vectors of a fcc lattice are as follows:

$$\vec{a} = \frac{a}{2}\left(\hat{i} + \hat{j}\right)$$

$$\vec{b} = \frac{a}{2}\left(\hat{j} + \hat{k}\right)$$

$$\vec{c} = \frac{a}{2}\left(\hat{k} + \hat{i}\right)$$

∴ Volume of primitive cell

$$V = \vec{a} \,.\, \left(\vec{b} \times \vec{c}\right)$$

$$= \frac{a^3}{8}\left[\left(\hat{i} + \hat{j}\right).\left(\hat{j} + \hat{k}\right) \times \left(\hat{k} + \hat{i}\right)\right]$$

$$= \frac{a^3}{8}\left[1 + 1\right] = \frac{a^3}{4}$$

Vector component of reciprocal lattice

$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{\vec{a}.\left(\vec{b} \times \vec{c}\right)}$$

$$= \frac{1}{a}\left[\left(\hat{j} + \hat{k}\right) \times \left(\hat{k} + \hat{i}\right)\right]$$

$$= \frac{1}{a}\left(\hat{i} - \hat{k} + \hat{j}\right)$$

or $\quad \vec{a}^* = \frac{1}{a}\left(\hat{i} + \hat{j} - \hat{k}\right)$

Similarly $\quad \vec{b}^* = \frac{1}{a}\left(-\hat{i} + \hat{j} + \hat{k}\right)$

or $\quad \vec{c}^* = \frac{1}{a}\left(\hat{i} - \hat{j} + \hat{k}\right)$

There are the basis vectors of the body centered cubic lattice. Thus body centered cubic lattice is the reciprocal lattice of the face centered cubic lattice.

3.10 Self Learning Exercise - II

Section A : Very Short Answer Type Questions

Q.1 What do you mean by lattice?

Q.2 Define Brillouin Zone.

Q.3 What is the volume of the first Brillouin zone of a simple cubic lattice of lattice constant *a*?

Section B : Short Answer Type Questions

Q.4 A two dimensional lattice has the basis vectors $\vec{a} = 2i, \vec{b} = \hat{i} + 2\hat{j}$. Find the basis vectors of the reciprocal lattice.

Q.5 The basis vector of the lattice are $\vec{a} = \frac{a}{2}\left(\hat{i} + \sqrt{3}\hat{j}\right), \vec{b} = \frac{a}{2}\left(-\hat{i} + \sqrt{3}j\right)$ and $\vec{c} = c\hat{k}$. Find the basis vectors of the reciprocal lattice.

Q.6 What is the reciprocal lattice to simple cubic lattice?

3.11 Summary

X-ray diffraction is understood in terms of Bragg's and Laue equation. Any function invariant under a lattice translation T may be expanded in a Fourier series of the form $n(\mathrm{r}) = \sum_G n_G \exp(i\vec{G}.\vec{r})$. Reciprocal lattice is a geometrical projection of a normal Bravais lattice and is used to make various crystallographic and diffraction calculations. Bragg's law is also understood in terms of the reciprocal lattice using Ewald construction. The locus of all the wave vector values that are

Bragg reflected is the Brillouin zone.

3.12 Glossary

Lattice: Regular periodic arrangement of ions or molecules in a crystalline solid.

Bravais : Non-Primitive unit cells have to be chosen in order to make the symmetry of the unit cell compatible with the symmetry of the entire lattice.

Reciprocal : Collection of nodal points, derived mathematically from the real lattice using a reciprocal relationship.

3.13 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: $2d \sin\theta = n\lambda$

Ans.2: $\lambda = 0.84\ A^0$

Ans.3: $\lambda = 1A^0$

Ans.4: $d = 3A^0$

Ans.5: $d_{200} = 2.8\ A^0$, $a=5.6A^0$

Ans.6: $3.03\ A^0$

Answer to Self Learning Exercise-II

Ans.1: A regular, Periodic configuration of particles in a crystalline solid.

Ans.2: A Brillouin zone is define as a Wigner- Setiz cell in the reciprocal lattice-

Ans.3: $(2\pi / a)^3$

Ans.4: $\vec{a}* = \frac{1}{4}\left(-\hat{j} + 2\hat{i}\right), \vec{b}* = \frac{1}{2}\hat{j}$

Ans.5: $\vec{a}* = \frac{1}{a}\left(\hat{i} + \frac{\widehat{j}}{\sqrt{3}}\right), \vec{b}* = \frac{1}{a}\left(\frac{\widehat{j}}{\sqrt{3}} - i\right), \vec{c}* = \frac{1}{C}\hat{k}$

Ans.6: $\vec{a}* = \frac{1}{a}\hat{i}, \vec{b}* = \frac{1}{a}\hat{j}, \vec{c}* = \frac{1}{a}\hat{k}$

3.14 Exercise

Section-A : Very Short Answer Type Questions

Q.1 What are Laue's equations.

Q.2 What is a Laue's diagram?

Q.3 Why crystal is more suitable for the study of x-ray diffraction?

Q.4. Explain the Bragg's law of x-ray diffractions.

Q.5. Write the condition of Bragg's Reflection.

Section- B : Short Answer Type Questions

Q.6 State Bragg's law.

Q.7 If $\vec{a}, \vec{b}, \vec{c}$ are the basis vector of the direct lattice then write the vector of reciprocal lattice?

Q.8 Show that the reciprocal lattice of fcc is Bcc.

Q.9 Write Bragg's law in terms of reciprocal lattice vector.

Q.10 What is the reciprocal lattice?

Section C : Long Answer Type Questions

Q.11 Explain Bragg's law for x-ray diffraction. What information can be obtained using Bragg's law?

Q.12 Arrive at the Laue equations for x-ray diffractions for a crystalline solid. Show that these equations are equivalent to Bragg's law.

Q.13 What is Ewald Construction? How does it help in the interpretation of x-ray diffraction photographs?

Q.14 Explain the concept of reciprocal lattice. Discuss its properties. Show that the reciprocal lattice of a bcc bravais lattice is an Fcc lattice.

Q.15 Prove that fcc lattice is the reciprocal lattice of the bcc lattice and bcc lattice is a reciprocal lattice of fcc lattice.

References and Suggested Readings

1. M.A. Omar, Elementary Solid State Physics, Addison Wesley, 1993.
2. Charles Kittle, Introduction to solid state Physics Wiley (New York), 2004.
3. Neil W. Ashcroft and N. David Mermin, Solid State Physics, Harcourt, 1976.
4. Steven H. Simon, The oxford solid state Basis, Oxford University Press, 2013.

UNIT-4

Fourier Analysis of the Basis and Structure Factor

Structure of the Unit

4.0 Objectives

The main objective of the unit is to familiarize the readers with the concept of structure factor and atomic form factor. Structure factor and atomic form factors are important in the study of crystal structures, hence an understanding of these concepts are fundamental to the study of solid state physics. The unit discusses the Fourier analysis of the basis and introduces the readers to the calculation of structure factor of simple cubic, base centered, body centered and face centered cubic lattices.

4.1 Introduction

In study of X-ray crystallography the structure factor plays a central role in investigating and solving the problem of crystal structure determination. During the study of crystal structures X-ray diffraction method is used in which the scattered or diffracted beams combine to form an image. In a microscope the recombination of rays is done physically by the lenses but in crystallography the recombination of diffracted beams is done by mathematical methods. The formation of image by recombination of diffracted rays depends on the direction, amplitude and phase of each ray. The intensities of the diffracted beams are observed separately as blackness of spots on X-ray film or by diffractometer. The division of the diffracted beam is specified by identifying the Miller indices (hkl) of the crystal plane causing diffraction.

The structure factor represents the resultant amplitude and phase of scattering due to electron concentration in a unit cell. The superposition of waves from each atom in the unit cell is taken for calculation of the resultant. The amplitude of each wave depends on the number of electrons in the atom. The phase of each wave depends on the position of the atom in the unit cell. Thus superposition of these waves conveys information about amplitudes and phases in a combined manner. The resultant scattering is actually calculated for one unit cell but since whole structure consists of a large number of unit cells ,scattering in phase with each other, the structure factor represents the resultant X-ray scattering power for whole crystal structure. Thus structure factor tells about the constructive interference occurring at a given point of the reciprocal lattice due to atoms in a unit cell. The interference effects from different electrons within an atom are described through atomic form factor.

4.2 Fourier Analysis of the Basis

For study of the crystal structure, diffraction pattern of the crystal is examined, which represents the reciprocal lattice of the crystal. The reciprocal lattice is in Fourier space of the crystal and the dimensions of the vectors in reciprocal lattice are of $\left[\frac{1}{length}\right]$.

The possible X-ray reflections from a crystal are determined with the help of the reciprocal lattice vector **G**, where

$$\vec{G}=h\vec{a}^*+k\vec{b}^*+l\vec{c}^* \tag{1}$$

where h,k,l are integers and $\vec{a}^*,\vec{b}^*,\vec{c}^*$ are primitive vectors of the reciprocal lattice.

Let us consider a crystal sample on which a beam $e^{i\vec{k}.\vec{r}}$ is incident and the outgoing beam is $e^{i\vec{k}'.\vec{r}}$ where $\vec{k}$ and $\vec{k}'$ are the wave vectors for incident and outgoing beams as shown in Fig-1. Consider two volume elements separated by distance r where one element is at origin O. The beam scattered from the volume elements have phase factor difference as exp $\left[i\left(\vec{k}-\vec{k}'\right).\vec{r}\right]$ or exp $\left[-i\Delta\vec{k}.\vec{r}\right]$

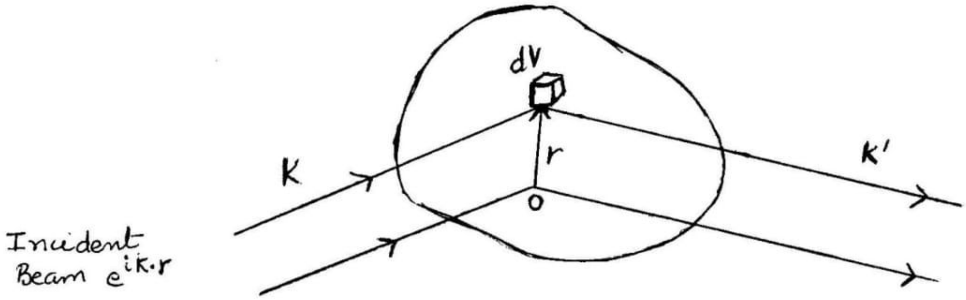

Fig.1: *Volume element at distance r from origin and the incident and outgoing beams.*

The scattering amplitude for the wave scattered in the direction of $\vec{k}'$ is given by

$$F = \int n(\vec{r})\exp(-i\Delta\vec{k}.\vec{r})dV \tag{2}$$

Here $\Delta\vec{k}$ is known as scattering vector, dV is the volume element at distance r from origin, $n(\vec{r})$ is the local electron concentration.

The scattering amplitude F is negligibly small if the value of the scattering vector $\Delta\vec{k}$ significantly different from reciprocal lattice vector. The diffraction condition states that Bragg reflections occur when the change in wave vector $\vec{k}$ is a vector of the reciprocal lattice. Thus for $\Delta\vec{k} = \vec{G}$

The expression of scattering amplitude for a crystal of N cells becomes

$$F = N \int_{cell} dV\ n(\vec{r}) \exp(-i\vec{G}.\vec{r})$$

$$\text{or } F = N\ S_G \tag{3}$$

Here S_G is known as structure factor. The structure factor tells about the interference between atoms in a unit cell. It gives information about the constructive interference occurring at a given point of the reciprocal lattice. Considering a basis of m atoms and atoms are taken as $i = 1\ to\ m$ of the basis. The electron concentration $n(\vec{r})$ can be expressed as superposition of electron concentration functions $n_i(\vec{r} - \vec{r}_i)$ where $\vec{r}_i$ shows the atomic locations of the i^{th} atom. Thus the total electron concentration may be written as

$$n(\vec{r}) = \sum_{i=1}^{m} n_i\ (\vec{r} - \vec{r}_i) \tag{4}$$

which gives the sum over all m atoms of the cell. Thus the scattering amplitude may be written as –

$$F = N \sum_i \int dV\ n_i(\vec{r} - \vec{r}_i) \exp(-i\ \vec{G}.\vec{r}) \tag{5}$$

and structure factor may be written as

$$S_G = \sum_i \int dV\ n_i(\vec{r} - \vec{r}_i) \exp(-i\vec{G}.\vec{r})$$

$$= \sum_i \exp(-i\,\vec{G}.\vec{r}_i) \int dV n_i(\vec{r} - \vec{r}_i) \exp\{-i\vec{G}.(\vec{r} - \vec{r}_i)\} \tag{6}$$

The expression

$$f_i = \int dV\ n_i(\vec{r} - \vec{r}_i) \exp\{-i\vec{G}.(\vec{r} - \vec{r}_i)\} \tag{7}$$

It is known as atomic form factor.

Thus structure factor becomes

$$S_G = \sum_i f_i \exp(-i\,\vec{G}.\vec{r}_i) \tag{8}$$

The location of $i^{th}\,atom$ with respect to real lattice is given by (9)

$$\vec{r}_i = x_i\vec{a} + y_i\vec{b} + z_i\vec{c}$$

Therefore we have

$$\vec{G}.\vec{r}_i = 2\pi\left(hx_i + ky_i + lz_i\right) \tag{10}$$

and $$S_G = \sum_i f_i \exp\left[-2\pi i\left(hx_i + ky_i + lz_i\right)\right] \tag{11}$$

This is the expression for structure factor which may not necessarily be real. The diffraction intensity involves $|S|^2$ which is real.

4.3 Structure Factor for Simple Cubic

The expression for structure factor is

$$S = \sum_i f_i \exp\left[-2\pi i\left(hx_i + ky_i + lz_i\right)\right]$$

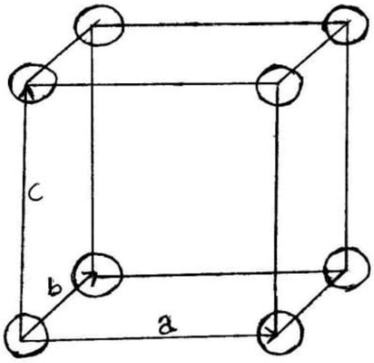

Fig.2: *Schematic of simple cubic unit cell*

For one atom basis $(0,0,0)$

$$S = f\left\{\exp\left[-2\pi i\left(0.h + 0.k + 0.l\right)\right]\right\}$$
$$= f\left\{\exp\left[-2\pi i(0)\right]\right\}$$
$$= f\left\{\exp\left[(0)\right]\right\}$$
$$= f$$

Thus for a simple cubic structure the intensity is at every reciprocal point. Reflections are present for any value of h,k,l no reflections are absent.

4.4 Structure Factor for Base Centered Cubic Unit Cell

A base centered unit cell schematic is shown in Fig.3. For this unit cell two atoms of the same type are situated at $(0,0,0)$ and $\left(\frac{1}{2},\frac{1}{2},0\right)$.

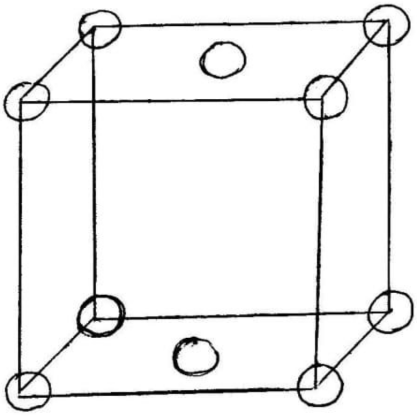

Fig.3: *Schematic of base centered unit cell*

The structure factor for base centered unit cell is calculated as

$$S=\sum_i f_i \exp\left[-2\pi i\left(hx_i+ky_i+lz_i\right)\right]$$

$$=f\exp\left[-2\pi i(0)\right]+f\exp\left[-2\pi i\left(h/2+k/2\right)\right]$$

$$=f\;+\;f\exp\left[-\pi i\left(h+k\right)\right]$$

$$=f\left\{1+\exp\left[-\pi i\left(h+k\right)\right]\right\}$$

Thus S depends on the combination of *h* and *k*. If both *h* and *k* are even or both odd, in that case $h+k$ is even and therefore

$$\exp\left[-\pi i\left(h+k\right)\right]=+1 \text{ if } h+k= \text{ even integer ,then } S=2f$$

If one of from h and k is even and other one odd then h+k becomes odd and therefore

$\exp\left[-\pi i\left(h+k\right)\right]=-1$ if $h+k$ =odd integer, then S=0.

The value of *l* index does not show any effect on the structure factor and therefore 111, 112, 113 etc. have the same value of structure factor S.

4.5 Structure Factor For Body-Centered Cubic Unit Cell

The body centered unit cell has been shown in fig.4. Here two atoms of same type are located at $(0,0,0)$ and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$.

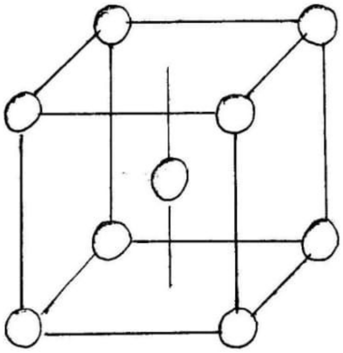

Fig. 4: *Schematic of body centered unit cell*

The structure factor for body centered unit cell is calculated as

$$S = f\left\{\exp\left[-2\pi i\left(0.h+0.h+0.l\right)\right]+\exp\left[-2\pi i\left(\frac{1}{2}.h+\frac{1}{2}.k+\frac{1}{2}.l\right)\right]\right\}$$

$$= f\left\{1+\exp\left[-\pi i\left(h+k+l\right)\right]\right\}$$

Thus the structure factor depends on the combination of h,k,l .

$$\exp\left[-\pi i\left(h+k+l\right)\right]=+1 \text{ if } h+k+l= \text{ even integer}$$

$$\exp\left[-\pi i\left(h+k+l\right)\right]=-1 \text{ if } h+k+l=\text{odd integer}$$

Therefore $S=2f$ if $h+k+l=$ even integer

$S=0$ if $h+k+l=$ odd integer

4.6 Structure Factor For Face-Centered Cubic (Fcc) Unit

The basis of the fcc structure consist of four atoms of the same kind located at $(0,0,0)$, $\left(\frac{1}{2},\frac{1}{2},0\right)$ $\left(0,\frac{1}{2},\frac{1}{2}\right)$ $\left(\frac{1}{2},0,\frac{1}{2}\right)$

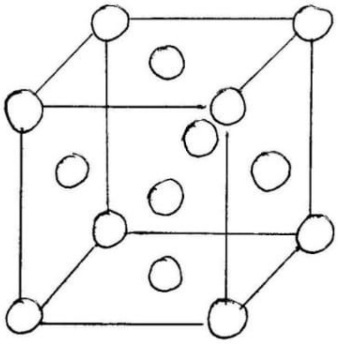

Fig. 5: *Schematic of face centered unit cell*

Thus the structure factor is calculated as

$$S = f\left\{\exp\left[-2\pi i\left(0.h+0.k+0.l\right)\right]+\exp\left[-2\pi i\left(\frac{1}{2}.h+\frac{1}{2}.k+0.l\right)\right]\right.$$
$$\left.+\exp\left[-2\pi i\left(0.h+\frac{1}{2}.k+\frac{1}{2}.l\right)\right]+\exp\left[-2\pi i\left(\frac{1}{2}.h+0.k+\frac{1}{2}.l\right)\right]\right\}$$

$$S = f\left\{1+\exp\left[-\pi i\left(h+k\right)\right]+\exp\left[-\pi i\left(k+l\right)\right]+\exp\left[-\pi i\left(h+l\right)\right]\right\}$$

If h,k and l are unmixed i.e. all are even or odd then the sum $(h+k),(k+l),(h+l)$ will be even integers and in that case each term in the above equation becomes 1.

If h,k and l are mixed even or odd then the sum of the exponentials becomes -1 and so S will vanish.

Therefore,

$S = 4f$ for all indices even or odd integers

$S = 0$ for mixed even odd indices

Thus for fcc structure reflections may occur for planes such as (111), (200) and (220) but not for planes $(100),(110),(210),(112)$ etc. i.e. there cannot be any reflections in fcc structure when the indices are partly even or partly odd.

4.7 Illustrative Examples

Example 1 Calculate the Structure factor for NaCl.

Sol. Each unit cell of NaCl consists of 4Na and 4Cl atoms in a cubic lattice. The atoms are located at

$$\text{Na};(0,0,0)\left(\frac{1}{2},\frac{1}{2},0\right)\left(\frac{1}{2},0,\frac{1}{2}\right)\left(0,\frac{1}{2},\frac{1}{2}\right), \quad \text{Cl};\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)\left(\frac{1}{2},0,0\right)\left(0,\frac{1}{2},0\right)\left(0,0,\frac{1}{2}\right)$$

The structure factor is given as

$$S = f_{Na}\exp\left[-2\pi i(0)\right]+f_{Na}\exp\left[-2\pi i\left(\frac{h}{2}+\frac{k}{2}\right)\right]$$
$$+f_{Na}\exp\left[-2\pi i\left(\frac{h}{2}+\frac{l}{2}\right)\right]+f_{Na}\exp\left[-2\pi\left(\frac{k}{2}+\frac{l}{2}\right)\right]$$

$$+f_{Cl}\exp\left[-2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)\right]+f_{Cl}\exp\left[-2\pi i\left(\frac{h}{2}\right)\right]$$

$$+f_{Cl}\exp\left[-2\pi i\left(\frac{k}{2}\right)\right]+f_{Cl}\exp\left[-2\pi i\left(\frac{l}{2}\right)\right]$$

$$S = f_{Na}\left\{1+\exp\left[-\pi i(h+k)\right]+\exp\left[-\pi i(h+l)\right]+\exp\left[-\pi i(k+l)\right]\right\}$$

$$+f_{Cl}\left\{\exp\left[-\pi i(h+k+l)\right]+\exp\left[-\pi ih\right]+\exp\left[-\pi ik\right]+\exp\left[-\pi il\right]\right\}$$

It can be rewritten as

$$S = f_{Na}\left\{1+\exp\left[-\pi i(h+k)\right]+\exp\left[-\pi i(h+l)\right]+\exp\left[-\pi i(k+l)\right]\right\}$$

$$+f_{Cl}\exp\left[-\pi i(h+k+l)\right]\left\{1+\exp\left[\pi i(k+l)\right]+\exp\left[\pi i(h+l)\right]+\exp\left[\pi i(h+k)\right]\right\}$$

As $e^{n\pi i}=e^{-n\pi i}$ so changing signs in second term

$$S = f_{na}\left\{1+\exp\left[-\pi i(h+k)\right]+\exp\left[-\pi i(h+l)\right]+\exp\left[-\pi i(k+l)\right]\right\}$$

$$+f_{Cl}\exp\left[-\pi i(h+k+l)\right]\left\{1+\exp\left[-\pi i(k+l)\right]+\exp\left[-\pi i(h+l)\right]+\exp\left[-\pi i(h+k)\right]\right\}$$

$$S=\left[f_{Na}+f_{Cl}\exp\left\{-\pi i(h+k+l)\right\}\right][1+\exp\left\{-\pi i(h+k)\right\}+\exp\left\{-\pi i(h+l)\right\}$$

$$+\exp\left\{-\pi i(k+l)\right\}]$$

The first factor contains the terms corresponding to the face centered translations. The second factor contains the terms that describe the basis of the unit cell i.e. Na atom at (0,0,0) and the Cl atom at $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$. The first term has a total value of zero for mixed indices and value 4 for unmixed indices. This shows clearly that NaCl has a face centered lattice.

Example 2. Find the expression for structure factor of CsCl. It is given that Cs atom is located at $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ and Cl atom at (0,0,0).

Sol. By eq. (11) of section 4.3 we have.

$$S_a=\sum_i f_i\exp\left[-2\pi i\left(hx_i+ky_i+lz_i\right)\right]$$

For $C_s\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ $C_l(0,0,0)$

$$S=f_{Cl}\exp\left[-2\pi i\left(h.0+k.0+l.0\right)\right]+f_{Cs}\exp\left[-2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)\right]$$

This $S=f_{Cl}+f_{Cs}\exp\left[-\pi i\left(h+k+l\right)\right]$

It is the expression for structure factor for $CsCl$.

Example 3 Find the expression for structure factor of AB_2 crystal. The atomic coordinates are given by

$$A;\left(0,0,0\right),B;\left(\frac{1}{2},\frac{1}{2},0\right)\left(\frac{1}{2},0,\frac{1}{2}\right)\left(0,\frac{1}{2},\frac{1}{2}\right)$$

Sol. The structure factor is given by

$$S_G=\sum_i f_i\exp\left[-2\pi i\left(hx_i+ky_i+lz_i\right)\right]$$

Considering the atomic coordinates as given

$$S=f_A\exp\left[-2\pi i\left(h.0+k.0+l.0\right)\right]+f_B\left\{\exp\left[-2\pi i\left(h.\frac{1}{2}+k.\frac{1}{2}+l.0\right)\right]\right.$$
$$\left.+\exp\left[-2\pi i\left(h.\frac{1}{2}+k.0+l.\frac{1}{2}\right)\right]+\exp\left[-2\pi i\left(h.0+k.\frac{1}{2}+l.\frac{1}{2}\right)\right]\right.$$

Thus

$$S=f_A\exp\left[-2\pi i\left(0\right)\right]+f_B\left\{\exp\left[-\pi i\left(h+k\right)\right]+\exp\left[-\pi i\left(h+l\right)\right]+\exp\left[-\pi i\left(k+l\right)\right]\right\}$$

or $S=f_A+f_B\left\{\exp\left[-\pi i\left(h+k\right)\right]+\exp\left[-\pi i\left(h+k\right)\right]+\exp\left[-\pi i\left(k+l\right)\right]\right\}$ is the desired expression.

4.8 Self Learning Exercise -I

Very Short Answer Type Questions

Q.1 When is structure factor non-zero for base centered cubic unit cell?

Q.2 Structure factor is non-zero for which condition for bcc structure?

Q.3 Does reflection occur for (112) plane for fcc structure?

Short Answer Type Questions

Q.4 What is diffraction condition?

Q.5 What information does structure factor convey ?

4.9 Atomic Form Factor

The expression for structure factor given by eq.(11) of section 4.3 contains a quantity f_i known as atomic form factor. Atomic form factor f_i represents the scattering power of the i^{th} atom in the unit cell. The value of f is dependent on the

- number and distribution of atomic electrons i.e. arrangement
- wavelength and scattering angle of radiation.

Structure factor conveys information about the radiation scattered by a unit cell whereas atomic form factor conveys information about the radiation scattered by a single atom. Atomic form factor takes into account the interference effects within the atom.

As defined earlier the atomic form factor may be given by

$$f_i = \int dV\, n_i\left(\vec{R}\right)\exp\left(-i\vec{G}.\vec{R}\right) \quad \text{where } \vec{R} = \vec{r} - \vec{r}_i$$

Here integral is over the election concentration of single atom. Considering an electron distribution which is spherically symmetric about the origin and the angle between $\vec{R}$ and $\vec{G}$ to be α the expression for form factor becomes

$$f_i = 2\pi \int dR\, R^2 d\left(\cos\alpha\right) n_i\left(R\right)\exp\left(-i\; GR\; \cos\alpha\right)$$

$$= 2\pi \int dR\, r^2\; n_i\left(R\right).\frac{e^{iGR} - e^{-iGR}}{i\; GR}$$

Here integration has been done over $d\left(\cos\alpha\right)$ between the limits -1 and $+1$.

Therefore the form factor is given by.

$$f_i = 4\pi \int dR\; n_i\left(R\right) R^2\; \frac{\sin GR}{GR}$$

If the total election density is concentrated at R=0 then in that case only $Gr = 0$ would contribute and hence $\frac{\sin GR}{GR} = 1$. For this case the atomic form factor is

$$f_i = 4\pi \int dR\, n_i\left(R\right) R^2 = Z$$

i.e. atomic form factor is equal to the number of atomic electrons. Thus atomic form factor can be defined as the ratio of the amplitude of the radiation scattered by an atom to the amplitude of the radiation scattered by one election localized at a point. For any atom scattering in the forward direction f is equal to its atomic number Z. As α increases, the radiation scattered by individual electrons become out of phase resulting in decrease of f. The atomic scattering factor also depends on the wavelength of incident beam; for shorter wavelength f will be smaller as path differences will be larger relative to the wavelength leading to greater interferences between the scattered beams.

The name atomic form factor is given because it depends on the way the elections are distributed around nucleus in an atom.

4.10 X-Ray Diffraction

(i) X-rays

X-rays diffraction is one of the most useful and important technique for characterization of crystalline material and for determination of their crystal structures.

X-rays also called as Roentgen rays and these are electromagnetic radiation of wavelength $\sim 1\dot{A}$ i.e. $\sim 10^{-10} m$. In the electromagnetic spectrum these occur between $\gamma -$rays and ultraviolet. X-rays are produced when cathode rays consisting of fast moving electrons accelerated by about 30000 V strike on a metal target. The frequency of the wavelength of X-rays produced depends on the target material. When accelerated electrons strike the target, some of the electrons in inner shells of the target atoms are knocked off. The vacancies are then filled with the higher orbital electrons. K-series X-rays are produced when electrons from n = 2 orbital or above jump into the orbital n = 1. If electrons from orbitals $n=3$ or above jump into orbital n = 2 then L-series X-rays are produced. X-rays produced have a wavelength range. The lower wavelength limit corresponds to X-rays of highest energy. The lower wavelength limit can be calculated from

$\lambda_{\min}\left(\dot{A}\right)=\frac{12400}{V}$ where V is accelerating voltage fig.6 shows the curve for X-ray intensity as a function of wavelength (λ). For K$-$radiation three peaks β, α_1 and α_2 are seen are shown in Fig. 6. K_α transition is result of transition $2p \rightarrow 1s$ and

K_β is result of 3p→ls transition for copper. K_α transition is more frequent and more intense, and actually it is a doublet K_{α_1} and K_{α_2}.

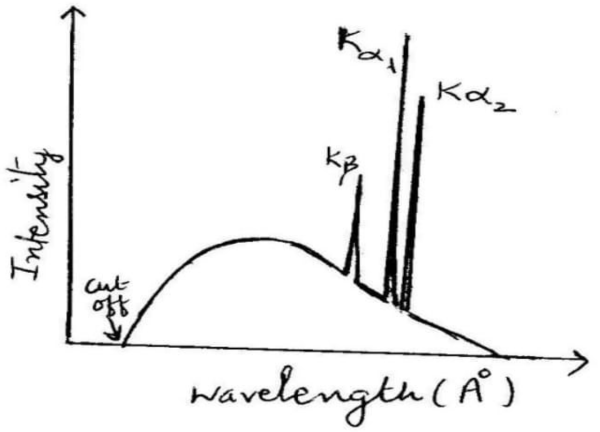

Fig. 6: *X-ray emission spectra of a metal showing three peaks.*

The doublet is due to slightly different energy for the two possible spin states of the 2p electron. The characteristic wavelength of the X-rays depends on metal and is given by Moseley's law $f^{\frac{1}{2}} = \left(\frac{c}{\lambda}\right)^{\frac{1}{2}} \alpha Z$

(ii) X-ray diffraction

As X-rays have wavelength of the order of $\sim 1\,\mathring{A}$. These are capable of study of crystal structures which have interatomic separation $\sim 1\,\mathring{A}$ through crystal diffraction studies. Three types of radiation i.e. X-rays , electron beam and neutron beam are used for the crystal diffraction studies. The fundamental equation used in the crystal studies is the Bragg's law

$$n\lambda = 2d\sin\theta$$

Here n is the order of reflection

λ is the wavelength of incident X-rays

d is the perpendicular distance between the adjacent hkl planes

θ is the glancing angle (Bragg angle).

The reflected beams are in phase when Bragg's law is satisfied and constructive interference takes place in this case. Angles at which Braggs condition is satisfied, the reflected beams are in phase and interfere constructively.

For crystal diffraction studies through X-rays, the required experimental setup consists of an X-ray source, the sample under investigation and a detector to pick up the diffracted X-rays.

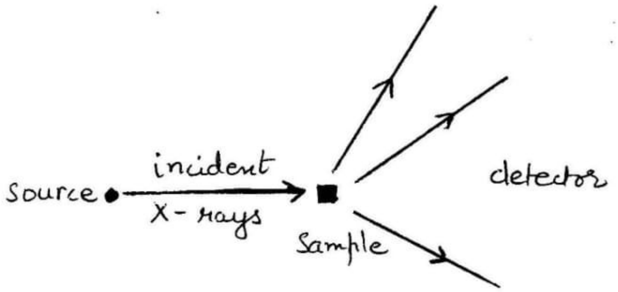

Fig. 7: *Schematic diagram of X-ray diffraction experimental setup.*

There are three X-rays techniques based on three variables-

- Radiation-monochromatic or variable wavelength (λ)
- Sample – single crystal powder or a solid piece
- Detector – photographic film or radiation counter.

These techniques can be classified as

Table 1. Classification of different X-ray diffraction techniques

Wavelength	Sample	Detector	Method
Fixed	Powder	Counter	Diffractometer
		Film	Debye-Scherrer
			Guinier (focusing)
	Single crystal	Film	Rotation (Oscillation)
			Weissenberg Precession (Buerger)
		Counter	Automatic Diffractometer
Variable	Solid piece	Film	Laue

(Reference- Solid State Chemistry and its applications-Anthony R. West)

4.11 Debye-Scherrer Method (Powder Method)

The powder method of X-ray diffraction consists of a finely powdered sample which has crystals randomly arranged in every possible orientation. In a powdered sample the various lattice planes are also present in every possible orientation. When X-rays are incident on a powdered sample, some of the crystals satisfy the condition of beam incidence at Bragg angle, thus diffraction occurs for these crystals and planes which can be studied (Fig.8).

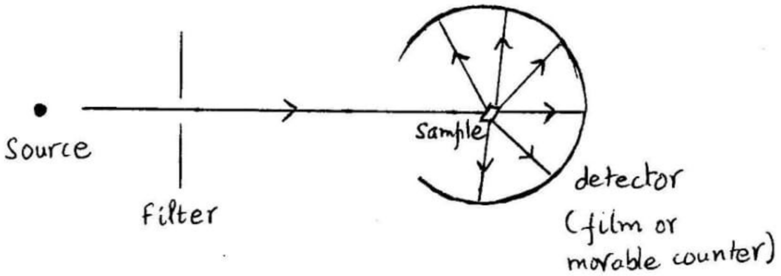

Fig. 8 : *Schematic diagram of X-ray diffraction experimental setup of powder method*

For detection of the diffracted beam either the sample is surrounded by a strip of photographic film as in Debye-Scherrer and Guinier focusing method or a moving detector is used such as Geiger counter connected to a chart recorder (diffractometer). The original powder method is Debye-Scherrer method, though nowadays modern methods are mainly used. Here we shall discuss the Debye Scherrer method.

For study of the powder diffraction pattern the sample in powdered form is filled in a thin capillary glass tube which is sealed and mounted. A narrow beam of monochromatic X-rays is made to fall on the sample. As the crystals in powdered sample are randomly oriented, some of them satisfy the diffraction conditions. The diffracted beams that are produced appear to be emitted from the sample as cones of radiation as shown in Fig. 9.

If θ is the Bragg angle then the angle between diffracted and undiffracted beams is given by 2θ , and the angle of the cone is 4θ . Each cone is actually a collection of large number of closely spaced diffracted beams. Each set of planes produces their own cone which is detected by strip of film around the sample. The cone leaves impression on the film in form of two short arcs.

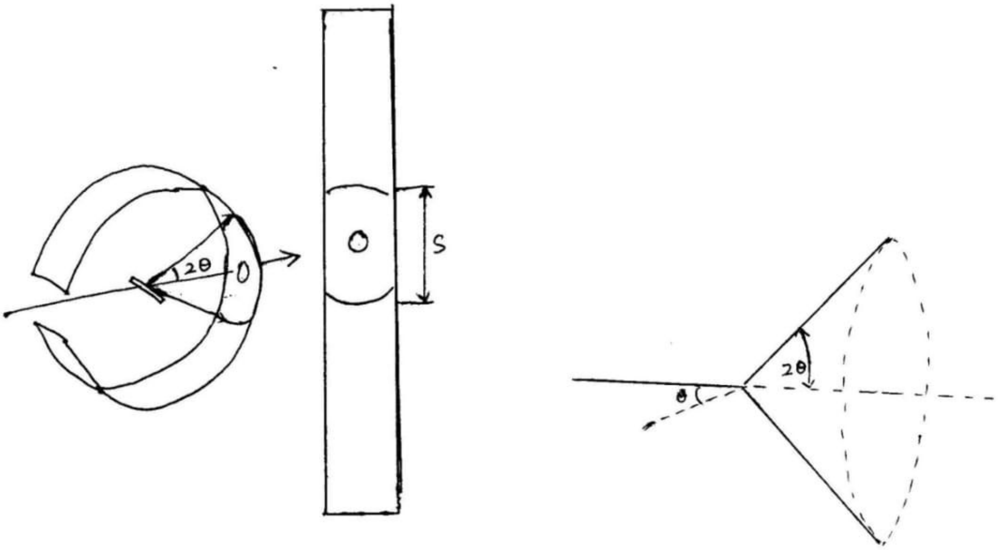

Fig. 9. *Formation of cones on film in Debye-Scherrer method*

A schematic of typical X-ray powder pattern has been shown in Fig.10

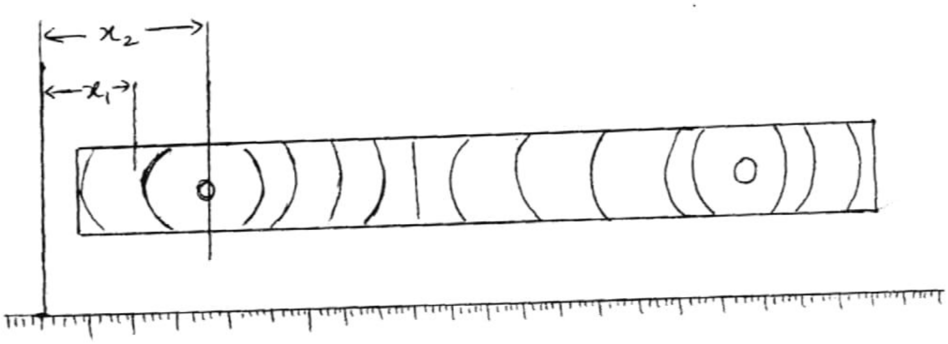

Fig. 10. *Schematic of an X-ray powder pattern*

In order to calculate the d-spacing, the separation S between the pairs of corresponding areas on the Debye – Scherrer film need to be measured. The distance S is given by $x_2 - x_1$ mm as shown in fig. If R is the radius of camera (film) then

$$4\theta = \frac{S}{R}\, radians$$

or $\frac{4\theta}{360}=\frac{S}{2\pi R}$ degrees

Therefore $\theta=\left[\frac{180}{\pi}.\frac{1}{4R}\right]S$ degrees and $d=\frac{\lambda}{2\sin\theta}$

As $\frac{180}{\pi}=57.3$ so if $R=57.3$ mm ,then the glancing angle can be directly obtained in terms of S. This is the reason why commercial camera usually have a radius 57.3 or 114.6 mm. Debye – Scherrer method can be used to confirm the formation of material by comparing the observed d value with the reported (standard) ASTM (American Society for Testing of Material) data. The disadvantages of this method are long exposure times (6 to 24 hours), low resolution of closely spaced areas, and losing of weak lines due to background radiation. Modern methods for powder samples are Guinier focusing and diffractometer techniques.

The most important use of powder method is the qualitative identification of crystalline compounds or phases. It does not give direct information about the chemical constitution.

4.12 Illustrative Examples

Example 4

The diffraction peaks for an element are obtained for 2θ angles(in degrees): 40, 58, 73 ……… The wavelength of X-ray is 0.154mm. Determine whether the structure is BCC or FCC and find lattice constant *a*.

Sol. We know $d=\frac{a}{\sqrt{h^2+k^2+l^2}}$ and $2d\sin\theta=\lambda$

$$\therefore \quad \sin^2\theta=\frac{\lambda^2}{4a^2}\left(h^2+k^2+l^2\right)$$

Here in question $2\theta=40,58,73....$

Taking first two $2\theta_A=40$ $2\theta_B=58$

$\theta_A=40$ $\theta_B=29$

$\sin\theta_A=0.3420$ $\sin\theta_B=0.4848$

$\sin^2\theta_A=0.1170$ $\sin^2\theta_B=0.2350$

Taking ratio $\frac{\sin^2\theta_A}{\sin^2\theta_B}=\frac{0.1170}{0.2350}=0.5$

This implies it is a BCC structure because BCC structure has this ratio for $(110),(200)$ as 0.5 whereas for FCC $(111),(200)$ the ratio is 0.75.

Lattice constant $a=\frac{\lambda}{2}\frac{\sqrt{h^2+k^2+l^2}}{\sin\theta}=\frac{0.154}{2}\times\frac{\sqrt{2}}{0.342}$

$$a=0.318nm$$

4.13 Self-Learning Exercise-II

Very Short Answer Type Questions

Q.1 If the total electron density is concentrated at R = 0, what is atomic form factor equal to ?

Q.2 What is the order of wavelength of X-rays ?

Q.3 What type of X-rays are used in powder method of X-ray diffraction ?

Short Answer Type Questions

Q.4 What is the effect on form factor if angle between **R** and **G** increases ?

Q.5 What does the name atomic form factor implie ?

Q.6 What is the basic equation used in crystal diffraction studies ?

4.14 Summary

This chapter presented the Fourier analysis of basis and defined structure factor. Structure factor for various unit cells such as simple cubic, base centered, body centered and face centered cubic cells have been calculated. Atomic form factor and X-ray diffraction are introduced. Debye Scherrer technique of powder X-ray diffraction method has been explained.

- **Structure Factor**-The structure factor tells about the interference between atoms in a unit cell. It gives information about the constructive interference occurring at a given point of the reciprocal lattice.
- **Structure factor for simple cubic**- $S=f$
- **Structure factor for base centered unit cell**

  $S=f\left\{1+\exp\left[-\pi i\left(h+k\right)\right]\right\}$

- **Structure factor for body centered unit cell**

  $S = f\{1+\exp[-\pi i(h+k+l)]\}$

- **Structure factor for face centered unit cell**

  $S = f\{1+\exp[-\pi i(h+k)]+\exp[-\pi i(k+l)]+\exp[-\pi i(h+l)]\}$

- **Atomic form factor**- The atomic form factor conveys information about the radiation scattered by a single atom. Atomic form factor takes into account the interference effects within the atom.

- **X-ray diffraction**-X-rays are capable of study of crystal structures which have interatomic separation $\sim 1\overset{\circ}{A}$. The fundamental equation used in the crystal studies is the Bragg's law.

- **Debye-Scherrer method of X-ray diffraction-** For detection of the diffracted beam in this method the sample is surrounded by a strip of photographic film.

4.15 Glossary

X Ray : Electromagnetic wave of the order of $1A^0$

FCC : Face centered Cubic

BCC : Body centered Cubic

4.16 Answers to Self-Learning Exercises

Answers to Self-Learning Exercise-I

Ans.1: h and k both even or both odd

Ans.2: $h+k+l=$ even integer

Ans.3: No

Ans.4: $\Delta k = G$

Ans.5: Interference between atoms in a unit cell

Answers to Self-Learning Exercise-II

Ans.1: Z, number of electrons

Ans.2: $1A^0$

Ans.3: Narrow beam of monochromatic rays

Ans.4: Atomic form factor decreases.

Ans.5: It gives the distribution of electrons around nucleus in an atom.

Ans.6: Bragg equation $2d\sin\theta = n\lambda$

4.17 Exercise

Very Short Answer Type Questions

Q.1 If $h+k$ = even integer for base centered cubic unit cell then what is the value of structure factor?

Q.2 When is structure factor zero for body centered cubic unit cell?

Q.3 Will reflection occur for (220) plane for FCC structure?

Q.4 Which index does not affect reflection condition for base centered cubic unit cell?

Q.5 What is the angle of cone in Debye Scherrer method?

Short Answer Type Questions

Q.6 Define structure factor.

Q.7 Define atomic form factor.

Q.8 Give expression for lower wavelength limit of X-rays.

Q.9 How are X-rays produced?

Q.10 How is distance between two areas S calculated in Debye Scherrer method?

Long Answer Type Questions

Q.11 Derive the expression for structure factor through Fourier analysis of basis.

Q.12 Show that structure factor is zero for mixed indices for FCC structure.

Q.13 Describe the Debye Scherrer technique for X-ray diffraction by crystals. What are its advantages and disadvantages of this technique?

Q.14 Describe the concept of atomic form factor.

Q.15 Show that by using diffraction studies the values of $\frac{\sin^2\theta_A}{\sin^2\theta_B}$ for first two sets of diffraction planes for FCC and BCC are respectively 0.75 and 0.5.

References and Suggested Readings

1. Introduction to Solid State Physics, Charles Kittel, Wiley-India, 2007.
2. Solid State Physics, Ashcroft and Mermin, Thomson- Brooks/Cole, 2007.
3. Principles of the Solid State, H.V. Keer, New Age International Publishers, 2009.
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UNIT-5

Point Defects & Dislocations

Structure of the Unit

References and Suggested Readings

5.0 Objectives

In this unit we are going to study the difference between a perfect or ideal crystal and real crystal. Further we study how the defects present in the real crystals are classified into different categories.Then we study point defects in detail and obtain expressions for the equilibrium concentration of point defects both in metals and ionic crystals. Then we study about the color centers and their models. The student will be able to understand the difference between edge and screw dislocation and their characteristics. Finally they can differentiate between edge and screw dislocation by constructing the Burger's circuit around the dislocation line.

5.1 Introduction

A crystal is defined as a perfect periodic structure. The crystal possesses a periodic ordering of atoms at the lattice sites confirming to a specified space group. However, crystals in practice show deviations from perfect ordering of atoms. All deviations from the specified three dimensional periodicity are called lattice defects or imperfections. A crystal without defects is an ideal case. Real crystals are never perfect and they contain a considerable density of defects/imperfections that effect their physical, chemical, mechanical and electrical properties. The existence of defects also plays an important role in various technological processes such as annealing, precipitation, diffusion, sintering, oxidation and others.

It should be noted that defects do not necessarily have adverse effects on the properties of materials. There are many situations in which a judicious control of the type and amount of imperfections can bring about specific characteristics desired in a system. This can be achieved by proper processing techniques. In fact, defect engineering is emerging as an important activity. In fact some of the properties like diffusion, ionic conductivity owe their existence to the presence of defects.

If the presence of the deviations does not affect the long-range order in crystals, the deviations are called the defects of first order. Lattice vibrations, structural imperfections, chemical imperfections belong to the above category. If the solid structure deviates due to the presence of deviations, such lattice defects are called the imperfections of the second kind. Hence, the long range ordering is disturbed.

This type of disorder is applied to polycrystalline and amorphous solids. We can also add here macroscopic or bulk defects such as pores, cracks and foreign inclusions that are introduced during production and processing of the solid state.

5.2 Classification of Imperfection

Structural imperfections refer to all deviations from perfect arrangement of the crystal atoms. Based on the spatial dimensions, these deviations occupy, they can be classified as point defects, line defects, planar defects and volume defects.

1.Point Defects

A lattice defect which spreads out very little in all the three dimensions is called a point defect. These are zero dimensional defects. A point defect produces strain in a very small volume of the crystal surrounding the defect, but does not affect the perfection of more distant parts of the crystal. The important point defects are: vacancies, interstitials and impurity atoms.

(a) Vacancies: Vacancies are sites which are usually occupied by an atom but which are unoccupied. The atoms from these lattice sites have migrated on to the surface thereby leaving vacancies. These vacancies are also known as Schottky defects. In case of ionic crystals a Schottky defect is one anion vacancy together with a cation vacancy. This is required to maintain charge neutrality in the interior of the crystal.

(b) Interstitials:- Interstitials are atoms which occupy a site in the crystal structure at which there is usually not an atom. Lattice particle or atoms can move to an interstitial site leaving a vacancy in the original positions. The combination of a vacancy and interstitial is called Frenkel defects. However, even interstitial atoms can also exist without getting paired to a vacancy. These defects are usually referred to as intrinsic defects and the associated vacancies as intrinsic vacancies. These defects preserve the stoichiometry of crystal, that is the ions even in the defective crystal are present in exactly the numbers required by the chemical formula. Besides the intrinsic vacancies, there are also extrinsic vacancies introduced so as to compensate the excess charge of an external substitutional Impurity with wrong valency. However these vacancies do not preserve the stoichiometry of the crystal.

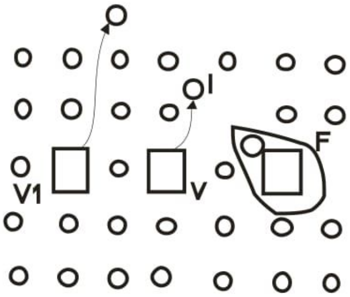


Fig. 5.1 ***Point Defects present in metallic crystal V1- Schottky defect ,V-Vacancy to give interstitial, I F-Frenkel defect***

In case of metals we have both Frenkel and Schottky defects. Further in ionic crystals we have either cationic Frenkel defects or anionic Frenkel defects.

(c) Impurities : The most obvious point defect in the presence of an impurity atom in an otherwise perfect crystal. It may fit into the structure in two ways. (i) It may occupy a position normally occupied by the crystal atom (host atom) in which case it will be called as substitutional impurity (ii) It may occupy the normally unfilled volume, termed as the interstices between the atoms of the host crystal and is called as interstitial impurity.

If the impurity atom has roughly the same size and valency as the host atoms, then the substitutional impurity is created. On the other hand if the host crystal has relatively large interstices then the interstitial impurity is accommodated in the crystal. Obviously, the interstitial impurity can exist only in ionic and covalent crystals and not in closed packed crystals, where as the reverse may be the case with the substitutional impurity.

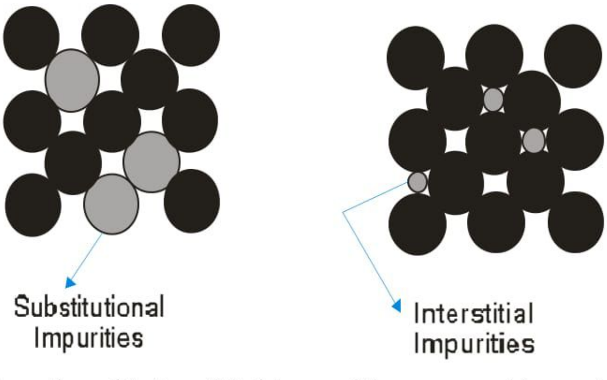


Fig. 5.2 ***Substitutional and interstitial impurities present in metallic crystals***

2. Line Defects

They are defects along closed or open lines, which end on the surfaces of crystals. Around such line defects, the atoms get displaced from their normal positions and cause strains that spread over a volume. However, the defect is of one atomic separation. They are called dislocations. They are classified geometrically as edge dislocations & screw dislocations. They are different from point defects even if the point defects get arranged in an array. A vector called Burger's vector is associated with each dislocation. It is a lattice vector. It is perpendicular to edge dislocation and parallel to screw dislocation.

3. Planar Defects

Two dimensional lattice defects belong to this category. Two types of planar defects exist. They are, (a) grain boundaries - The orientation of the crystal on one side is different that of the other surface. It is a series of dislocations (b) Stocking faults- Two lattice planes are mutually shifted by a vector which is not a lattice vector. All close packed structures exhibit stocking faults. They are the result of irregular sequences of layers of atoms in a crystalline structure.

4. Volume Defects

Three dimensional defects belong to this category. Voids, impurity precipitates, cracks, pores, other phases and air bubbles are examples of volume defects.

5.3 Schottky Defects in Metals

Schottky defects are simply the vacancies (the missing atoms) at the lattice sites of the crystal. The reason for the existence of vacancies at all temperatures arises from the thermodynamical considerations, that the free energy should be minimum at a particular temperature during the crystal formation. The concentration of vacancies in any crystal depends on the energy of formation in that crystal. At any specified temperature, the concentration of vacancies is fixed.

Let us compute an expression for the equilibrium concentration of vacancies in a crystal. Consider that the crystal consists of N identical atoms at a temperature T. The free energy of this unstable crystal is denoted by $F_{perfect}(T)$. Suppose we create n vacant lattice sites by transferring n atoms from the regular lattice sites on to the surface. Let the energy of formation of Schottky defect (vacancy) is E_v and E_v is independent of temperature. It is the energy necessary to remove a lattice atom from a regular lattice site onto the surface. We shall also assume that E_v is independent of n, which is justified as long as n<<N. Due to the creation of, n vacancies the energy of the imperfect crystal increases by nE_v relative to that of the perfect crystal. Also S_{cf} is the configurational entropy associated with the imperfect crystal. Further, let ΔS_{th} be the increase in thermal entropy per vacancy. We then write the expression for free energy of the perfect crystal as

$F_{perfect} = U_p - T\,S_p = U_p - T\,(S_{th} + S_{cf}) = U_p - TS_{th}$. Since $S_{cf} = 0$ for a perfect crystal.

The free energyexpression for an actual crystal containing n vacancies is written as

$$F_a\,(n, T) = U_p + nE_v - T\,(S_{th} + n\Delta S_{th}) - kT \log W_{cf} \tag{1}$$

$$= U_p - TS_{th} + nE_v - nT\Delta Sth - kT\log\left[\frac{N!}{(N-n)!n!}\right]$$

$$= F_p + nE_v - nT\,\Delta\,Sth - kT\log\left[\frac{N!}{(N-n)!n!}\right]$$

Employing Sterling's formula in the form

$$Logx! = x\log x \;\; for\, x >> 1$$

$$F\,(n, T) = F_p + nE_v - nT\Delta S_{th} - kT\,[N \log N - (N-n) \log (N-n) - n \log n\,] \tag{2}$$

In order to find equilibrium value of n, we make use of the fact that in equilibrium,

$$\left(\frac{\partial F_a}{\partial n}\right)_T = 0 \tag{3}$$

Then differentiating the equation (2) partially w.r.t, n and equating to 0, we get

$$\left(\frac{\partial F_a}{\partial n}\right)_T = E_v - T\Delta S_{th} - kT\,[\log (N- n) - \log n] = 0,$$

dividing through out by KT and taking exponentials we get

$$\frac{n}{N-n} = e^{\frac{\Delta S_{th}}{k}} \; e^{-\frac{E_v}{kT}}$$

If N >> n, $\quad \dfrac{n}{N} = A\, e^{-\frac{E_v}{kT}}$ (4)

where A is the pre exponential factor.

This is the expression for the equilibrium concentration of point defects in a metal at a temperature, T. The number of vacancies is exponentially growing function of temperature thus apart from a constant determined by ΔS_{th}, the probability for a given lattice to be unoccupied is given by a Boltzmann factor containing the energy of formation of a vacancy.

5.4 Frenkel Defects in Metals

In metals, when atoms which initially occupy normal lattice positions migrate into interstitial positions gives rise to Frenkel defects. A Frenkel defect is a combination of a vacancy and the atom in the interstitial sites. Let a metallic crystal at a temperature T contain a total of N atoms, N_i interstitial positions. Suppose, n Frenkel defects i.e., n vacancies and n interstitial atoms are created in its interior. Let E_f be the energy required to create a Frenkel defect. Let us assume that E_f is independent of n and T. Then the free energy expression for the crystal containing n Frenkel defects at a temperature T can be written as -

$$F_a(n, T) = U_p + nE_f - T(S_{th} + n\Delta S_{th}) - kT \log W_c \qquad (1)$$

$$= U_p - TS_{th} + nE_f - nT\Delta S_{th} - kT \log \left[\frac{N!}{(N-n)!n!} + \frac{N_i!}{(N_i-n)!n!} \right]$$

The term in the square bracket indicates the number of ways in which, n Frenkel defects can be produced. Using Sterling's approximation, we get

$$F_a(n, T) = F_p + nE_f - nT\Delta S_{th} - kT\,(N \log N - (N-n)\log(N-n) - n\log n + N_i \log N_i - (N_i-n)\log(N_i-n) - n\log n] \qquad (2)$$

At equilibrium, $\left(\frac{\partial F_a}{\partial n}\right)_T = 0$

Then differentiating the equation (2) partially w.r.t., n and equating to 0, we get

$$\left(\frac{\partial F_a}{\partial n}\right) = E_f - T\,\Delta S_{th} - kT\,[\log (N-n)(N_i-n) - \log n^2] = 0$$

dividing throughout by kT and taking exponentials we get

$$\frac{n^2}{(N-n)(N_i-n)} = e^{\frac{\Delta S_{th}}{k}} \; e^{-\frac{E_f}{kT}}$$

If N >> n and Ni >>n, $\frac{n^2}{NN_i} = Ae^{E_f/kT}$

Or N = $\sqrt{NN_i}\,Ae^{-E_f/2kT}$ (3)

This is the expression for the equilibrium concentration of Frenkel defects in metals.

5.5 Schottky Deffects in Ionic Crystals

An ionic bond is formed when metallic atoms like alkali or alkaline- earth metals, or transition element metals, etc., loose electrons and give them to halogens atoms, or oxygen, Sulphur, etc. By doing so, both the atoms go into ionic state possessing inert gas configuration. The ionic crystals consist of positive and negative ions. Let us see how the point defects exist in these crystals. There are two types of vacancies in ionic crystals. (1) the cation (positive ion) vacancies,(2) the anion (negative ion) vacancies.

A Cation vacancy is formed when a positive ion from the interior of the crystal moves out of the crystal to the surface as shown in Fig. 5.3 and similarly an anion vacancy is created when a negative ion moves out of the crystal on to the surface.

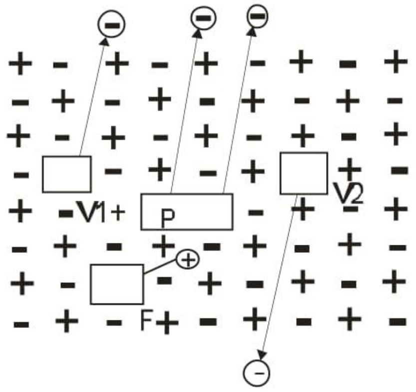


Fig. 5.3 ***Formation of defects in ionic crystal:*****V1 - Negative ion Vacancy , V2 - Positive ionic vacancy, P- a vacancy pair, F- Cationic Frenkel defect**

Suppose a cation vacancy is produced in a crystal. A cation vacancy possesses an effective negative charge. To maintain charge neutrality inside the crystal, a negative ion moves out from the interior on to the surface to form a negative ion vacancy V2. The effective charge of this vacancy is positive .Thus, vacancies in ionic crystal are formed in pairs in order to maintain charge neutrality both on the surface and the interior. It is to be noted that even if the energy required to produce a single cation vacancy were appreciably different from the energy required to produce a single negative ion vacancy, they would occur in approximately equal numbers.

Therefore, the Schottky defect in an ionic crystal is an anion- cation vacancy pair. We have considered the case of a crystal like NaCl. Each vacancy of sodium ion tends to result in the formation of one chloride ion vacancy. A positive ion vacancy and a negative ion vacancy on adjacent sites (P) can form a neutral defect.

Suppose an ionic crystal contains a total of N cations and N anions and n Schottky defects. The n Schottky defects are formed by removing n cations and n anions from the interior of the crystal. Let E_v be the energy required to create a Schottky defect. Let us assume that E_v is independent of n and T ,then the free energy expression for the crystal containing n Schottky defects at a temperature T can be written as

$$F_a(n, T) = U_p + nE_v - T(S_{th} + n\Delta S_{th}) - kT \log W_{cf}$$

$$= U_p - TS_{th} + nE_v - nT\Delta S_{th} - kT \log \left[\frac{N!}{(N-n)!n!}\right]^2 \qquad (1)$$

The term in the square brackets represents the number of ways in which (N-n) positive ions and n positive ion vacancies may be distributed over a total of N cation sites. The same holds for the negative ion sites, hence the square.

Using the Sterling's approximation

$$F_a(n, T) = U_p - TS_{th} + n E_v - nT\Delta S_{th} - 2kT [N \log N - (N-n) \log (N-n) - n \log n] \qquad (2)$$

At equilibrium $\left(\frac{\partial F_a}{\partial n}\right)_T = 0$

Then differentiating the equation (2) partially w.r.t. n and equating to 0, we get

$$\left(\frac{\partial F_a}{\partial n}\right)_T = E_v - T\Delta S_{th} - 2kT\left[\log\frac{(N-n)}{n}\right]=0$$

Dividing throughout by kT and taking exponentials we get

$$\frac{n}{(N-n)} = e^{\frac{\Delta S th}{k}} \; e^{-\frac{E_v}{kT}}$$

If N>> n, $\frac{n}{N_\delta} = Ae^{-E_v/2KT}$ (3)

where A is the pre-exponential factor.

The energy needed to form a pair of vacancies in NaCl is of the order of 2eV. The number of ions, per unit volume are of the order of 10^{22}. Then, the concentration of the Schottky defects is of the order of 10^{6} which is far less than the total number of ions in the Crystal.

5.6 Frenkel Defects in Ionic Crystals

A Frenkel defect is formed when a positive ion or a negative ion leaves from its normal site and occupies an interstitial position. Depending on the type of the ion involved, it can be called as cationic Frenkel defect or anionic Frenkel defect. A Frenkel defect is shown in Fig. 5.3. Unlike in case of Schottky defects, in ionic crystal it is not necessary to have equal number of positive and negative Frenkel defects, because their formation does not require the setting up of space charges over macroscopic distances. Generally depending on the energy required for their formation either the cationic or anionic Frenkel defects will be predominant. They may also occur in combination with Schottky defects. Following the lines as given for metals, the expression for the concentration of Frenkel defects in ionic crystals (either cationic or anionic) is given as

$$n=\sqrt{NN_i}\,Ae^{-E_f/2KT}$$

Where E_f is the formation energy for a Frenkel defect.

Even though both Schottky and Frenkel types of defects can be formed in crystals, but only one type of defect would predominate over the other. From the experimental studies it is observed that in alkali halides like NaCl, KCl, KBr, NaBr etc. Schottky vacancies are more common. Anions are larger in size than the cations in alkali halides and hence a positive ion vacancy is a dominant defect. In silver halides, Frenkel defects are most common.

Due to the introduction of Schottky defects the volume of the crystal is increased without any change in mass and consequently, production of these defects lowers the density of the crystal. On the other hand, the production of Frenkel defects does not change the volume of the crystal so that the density of the crystal remains constant.

5.7 Self Learning Exercise-I

Section A: Very Short Answer Type Questions

Q.1 Write the expression for the equilibrium concentration of Schottky defects in metals.

Q.2 Write the expression for the equilibrium concentration of Frenkel defects in metals.

Q.3 Write the expression for the concentration of Frenkel defects in ionic crystals.

Section B : Short Answer Type Questions

Q.4 What are point defects?

Q.5 What are line defects.

Q.6 Define edge dislocation.

5.8 Steady State Diffusion - Fick's First Law

Consider the diffusion of atoms along x-direction between two parallel atomic planes parallel to the page separated by a distance x shown in Fig. 5.4.

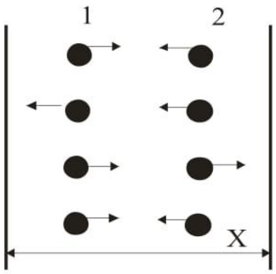


Fig. 5.4 Steady state diffusion of atoms in a concentration gradient

Let the concentration of atoms at plane 1 be C_1 and that at plane 2 be C_2. There is no change of concentration at the planes C_1 and C_2 with time. Such diffusion condition is called the steady state condition. Such diffusion is possible in cases where the atoms that are diffusing don't interact with the host atoms. No chemical reaction takes place inside the solid. Because of the concentration difference, diffusion takes place from higher concentration to the lower concentration. The flux or flow of atoms in this case is represented by the equation

$$J = -D\frac{dC}{dx} \tag{1}$$

where J is the flux or net flow of atoms. D is the diffusion coefficient or diffusivity. $\frac{dC}{dx}$ is the concentration gradient.

The negative sign indicates that the diffusion is from a higher to a lower concentration. The above equation is called Fick's first law of diffusion. According to it, the net flow of atoms by atomic diffusion is equal to the diffusivity D times the concentration gradient. The units of diffusivity are m^2/sec. The values of diffusivity depend on several variables. Some of them are

1. The type of diffusion mechanism in principle, the diffusion can take place only in real crystals. The defects like Schottky or Frenkel defects get involved in the diffusion process. The mass transport through such defects is called self-diffusion. In these cases, only the lattice atoms are involved. Impurity atoms also can diffuse through a crystal.

2. The temperature at which diffusion takes place- the diffusion process is a thermally activated process. The diffusivity is more efficient at higher temperatures.

3. The type of the crystal structure of the solvent lattice- the best example is the diffusion of carbon in BCC iron carbon diffuses very efficiently (D~10-12 m^2/sec at 5000C) in BCC iron compared to its diffusion in FCC iron (D~10-15 m^2/sec). The diffusion depends on the atomic packing factor.

4. The nature of imperfections present in the crystal- the steady state diffusion is dependent on the type of imperfection. Open structures allow more higher rates of diffusion of atoms. Grain boundaries are examples for this.

5. The flux density of diffusing species.

5.9 Non Steady State Diffusion- Fick's Second Law

Normally the steady state diffusion is not possible in many materials. In real cases, we encounter with non-steady state conditions. In such cases, the concentration of diffusing atoms at any point in the crystal changes with time. When atoms like carbon diffuse into steel the surface settles well and carbon produces hardening of steel. However, the carbon concentration at any point below a few atomic layers of the surface, the diffusion continuously takes place. In such cases a continuity equation is set up. It is given as

$$DivJ + \frac{\partial C}{\partial t} = 0 \tag{1}$$

$$\frac{\partial C}{\partial t} = \text{div (D gradC)} \tag{2}$$

C(x,y,z) is the particle or atomic density. J is the flux density. Diffusivity D is a second rank tensor. We can consider D as a scalar quantity that depends on the temperature and the crystal but is independent of the density of migrating atoms. The relation (2) can rewritten as

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{3}$$

The expression given in equation (2) is called Fick's second law. This law states that the rate of compositional change is equal to the diffusivity times the rate of change of the concentration gradient. We can write the equation (2) as

$$\frac{dC_x}{dt} = \frac{d}{dx}\left(d\frac{dC_x}{dx}\right) \tag{4}$$

When we consider the diffusion to take place along x-direction.

5.10 Color Centers

Ionic crystals have a band gap of about 6eV which corresponds to about $2000A^0$, that is in ultraviolet. From the dielectric properties, it is known that the ionic polarizability, resonates at wavelength of 60 microns, in the far infrared and due to this vibrational transitions occur at 60 microns. Due to this a perfect ionic crystal should not absorb visible light and so it should be perfectly transparent throughout the visible region. Because of their excellent transparency, crystals of NaCl, K*Cl*, LiF and other alkali halides are made into prisms and lenses for use in optical spectrometers. But there are several circumstances under which absorption bands can occur in the visible, near ultraviolet or near infrared in these crystals thereby giving characteristic colours to crystals. When crystals get coloured, it is said to have color centers. In fact it is the presence of certain lattice defects in these crystals that is responsible for the color centers. A color centre is a lattice defect that absorbs visible light.

Production of color centers

It is possible to color crystals in a number of different ways. The colour centers in general can be produced in the following ways.

1. **By addition of chemical impurities:** By the addition of chemical impurities like transition element ions (Ti, V, Cr, Mn, Cu, and Zn) with excited energy levels color centers can be produced. The salts added are normally coloured.

2. **Additive colouring :** When an alkali halide crystal like NaCl is heated to a high temperature in the vapour of excess of one of their components, the colour centers are produced. This is called as additive coloration. Atoms from the gas diffuse into the crystal and become ions. In the process, electrons are given off to the crystal. These excess electrons get bound to the vacancies present in the crystal. Thus the colour centers are produced. Even if the alkali halide crystal is heated in the vapours of divalent atoms like calcium, the colour centers like F-centre are produced. The colouration would be stronger in such a case. Divalent ions produce additional vacancies so that the concentration of vacancies increases. The colors produced depend on the nature of the crystal.

3.**Electrolytic Colouring :** Suppose a crystal sample like NaCl is inserted in a furnace. The upper surface of the crystal is attached to a pointed electrode the forms a cathode. The lower surface is attached to a flat electrode that is maintained at positive potential. Then the temperature of the crystal is increased by heating it and then a high potential is applied. The electrons are injected into the crystals filling the vacancies. The applied voltages is switched before the electrons reach the flat electrode. In this process all electrons get trapped. The colouration produced is very deep.

4. **Irradiation with High energy radiation :** Radiation like x-rays, γ-rays, accelerated electrons or protons possess high energies. When a thin sample of alkali halide is subjected to this radiation, the photons, electrons or protons ionize

the crystal components. In the process electrons or holes are released. These electrons or holes get trapped in the respective vacancies to produce the coloration. The concentration and the type of the colour centers produced depend on the temperature at which the colouration is done. The colour is also strongly dependent on the type and the concentration of the impurities present in the crystal.

The ionic crystals contain point defects like vacancies .Similarly excess vacancies can be created by incorporating metallic atom into the lattice. The metal atom enters into the lattice and gives an electron. The metal ion may occupy the cation vacancy sites. An electron is left which moves in the field of positive ions and moves into the missing negative ion site. It forms a defect center. There can be a metal ion in the lattice with a hole on it. The hole is positively charged and moves in the field of the negative cation vacancy. This forms a defect center. These defect centers give rise to what are called colour centers. They are very strong centers and the energy needed to separate such centers is of the order leV and less the point defects in ionic crystal which by virtue of their effective charge, bind electrons or holes are called color centers.

Let us consider only the case of alkali halides. The most important defect centers that are found in alkali halides like NaCl, KCl, KBr etc. are:

(1) F-Centers (2) F-Centers (3) M-Centers (4) V-Centers

1. F- Centers

Its name comes from the German word Fabre which means colour. F centers are generally produced by heating a crystal in an excess of an alkali vapour or by irradiating the crystal by x-rays. An excess electron trapped at a negative ion vacancy is called an F-centre. This model was first suggested by De-Boer and was further developed by Mott and Gurney.

The physical characteristics of the F-center are determined by the interactions of the electron with the ions in the crystal. The electron is treated as trapped one at an anion vacancy. It possesses a number of eigen values. Its transition from ground state to the first excited state gives F-center absorption band.

The position of the peak of the absorption band follows Mollow relation given as $E_f d^2$ = constant where d is the inter atomic distance. The above relation is well suited for crystals with NaCl structure. The following are some of the experimental observations in crystals containing F-centers:

These crystals can absorb a band of wavelengths from the visible spectrum and this band is called F-band.The band optical absorption is characteristic of the crystal and not of the alkali metal used in the vapour for additive coloration. F-Band is not symmetrical about the central wavelength value, but has a tail on the short wavelength side. The name K band has been proposed for this tail.The width of the band increases and the position of the peak shifts to lower energies when the temperature increases. Coloration produced by x-rays can be removed or bleached by heating or illuminating with light which lies in the F-band of wavelengths and whereas coloration due to excess metal, cannot be bleached. Colored crystals show electronic photoconductivity when illuminated by F-band light. F-colored crystals are less dense than uncolored crystals.

2. F'- Centers

When crystal samples containing F-centers are irradiated with a light of F-band frequencies, the F-band decreases in height and a new band at longer wavelength starts growing as shown in Fig. 5.5. This new band is called as F band.

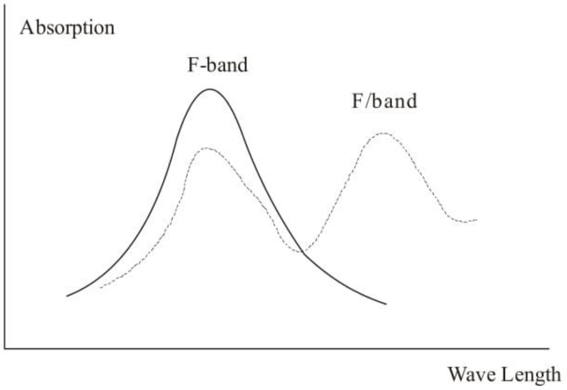


Fig. 5.5 ***Suppression of F-bands and appearance of F-band peaks due to F-light bleaching***

In fact, during this bleaching process of F-centers, photoconductivity is observed F centre is a defect centre with two electrons trapped at anion vacancy as shown in the Fig. 5.5. Normally, F-centers are produced only when the crystal is bleached with F-light. The F centers are stable only at rather low temperatures, because the electrons causing F absorption are more loosely bound than those in the F-centers. Thus at high temperatures F centers dissociate thermally and form F centers again. Two F centers must disappear for the creation of one F center. Because the anion vacancy is equivalent to a single positive charge, the two electrons are only weakly bound. Since the second electron is loosely bound, it can be detached by lower energy photons. This explains the appearance of F-band and its longer wavelength.

3. Coagulation of F-centers

Suppose a crystal sample that contains F-centers is irradiated with F-light at room temperature, the F-absorption peak decreases in height but a few absorption peaks appear in the longer wave length region of the spectrum. Such bands are due to coagulated centers of F-Centre. They are the result of the coagulation of F-centers and vacancies as shown in Fig. 5. These coagulated centers can also be produced by slowly colouring the crystal to lower temperature from the temperature at which colouration is done. Some of the coagulated centers are: (a) R1- two neighboring vacancies in the anionic lattice with one electron (b) R2 - two neighboring vacancies in the anionic lattice both two electrons (c) M-centre- The M-centre is a coagulated center. It consists of two anion vacancies and a cation vacancy trapping an electron. Its absorption lies in longer wavelengths of the visible spectrum.

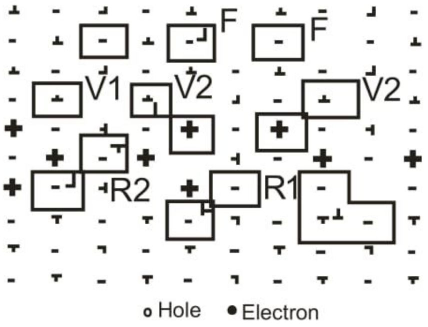


Fig. 5.6 Color Centers Models

4. V-Centers

The alkali halides can be coloured by heating the samples in the vapour of excess halogen atoms. These atoms when they are into the lattice, the hole gets trapped. The hole-binding centers are called V-centers. They can also be produced by electrolytic coloration method. The V2 centre consists of two cation vacancies trapping two holes. V3 centre has one hole trapped by two colour vacancies. The V1 centre, an analogous center to the F-centre, is formed by a cation vacancy trapping a hole. These centers are not stable at high temperatures as the F-centers and disappear at room temperature.

5. Z - Centers

These are also called as impurity centers, as they arise due to the presence of divalent impurities like Ca^{2+}, Ba^{2+} in alkali halides. Z centre is understood to be a perturbed F-centre. The perturbation is due to the presence of divalent impurities adjacent to the F-centre. Sometimes at reasonably high concentration of impurities, impurity-vacancy dipoles are formed and they also perturb the F-centers.

5.11 Dislocations

Large crystals are built up from three - dimensional array of atoms producing a perfect crystal. A crystal structure is nothing but a stacking of atoms in sequence just like arrangement of oranges in layers by a fruit vendor. However faults can occur in the sequences of arrangements of atoms. Similarly there can be additional atom layers in the periodic structure of atomic layers or distorted atomic layers. These distortions cause linear defects or dislocations in the crystal structure. Dislocations in crystal structure can arise as a result of growth in crystal structure and growth faults or due to the stress centers in the crystals.

When a shear stress is applied on a plane of a crystal, atoms are displaced from their original position or the perfect planes of atoms are sheared over one another. The stress must overcome the attraction between each atom in one plane and its nearest neighbours. The critical stress to do this is $G/2\pi$, where G is the shear modulus. This is of the order $1\text{-}2\times10^6$ psi, for metallic crystals. However the experimental values are much lower, usually around $10^1\text{-}10^3$ psi for FCC crystals. This anomalous behaviour is attributed to the movement of certain line imperfections in the crystals under the action of a deforming force. These imperfections are commonly known as dislocations. Metallic crystals undergo plastic deformation. The plastic deformation is a non-recoverable deformation. This deformation can only be explained on the basis of existence and movement of dislocations in the crystals. All crystals, except those grown under special conditions, usually contain a high concentration of dislocations. A general dislocation may follow any curved route through the crystal.

There are two major dislocation types. They are (1) Edge dislocations and (2) Screw dislocations. We shall study the nature of these dislocations.

5.12 Edge Dislocation

An edge dislocation is defined as a dislocation for which the Burgers vector is perpendicular to the dislocation line. An edge dislocation is characterized by the presence of an extra half plane of atoms in the crystal. The edge of this extra half plane of atoms which is a line is called as edge dislocation. Its formation may be visualized in terms of slip process. Let us first consider the geometry of edge dislocations. Consider a simple cubic crystal. The atoms are bound to each other by chemical bonds. Suppose the crystal is cut across the area ABEF (Fig. 5.7 (a)) such that across this area the upper and lower parts are disconnected. The upper half of the crystal is then pushed sideways such that the line A'B' which initially coincided with AB is shifted by an amount b as shown in figure. If in this position the two halves were glued together, we would have produced an edge dislocation. Under these conditions the upper half of the block will clearly be under compression, and the lower half under tension. A square network of lines drawn on the front face BCD before the operation and after the operation look as shown in Figures 5.7 (b) and (c). The strained pattern in figure (c) suggests an alternate method for the production of edge dislocation.

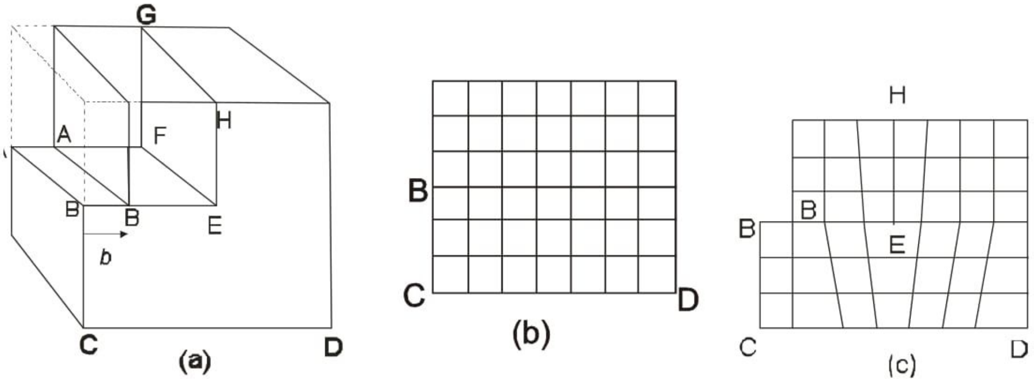
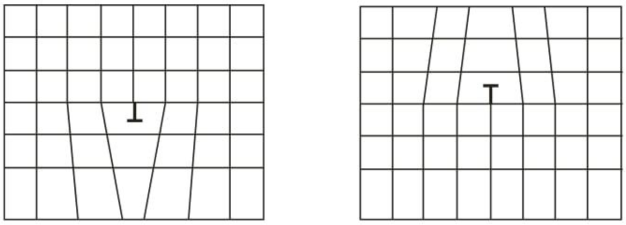


Fig. 5.7 ***(a) Represents an edge dislocation line EF (b) A square network of lines drawn on the front face BCD before the operation (c) Represents the stain pattern***

Consider the intersections of the network of line of figure 5.7 (c) as representing rows of atoms perpendicular to the plane of the paper. The edge dislocation may then be obtained by cutting the block along the plane EFGH, and putting the half plane of atoms initially above AB, inside the cut. This gives rise to the 'extra half plane' of atoms corresponding to HE (figure 5.7 (c)), which is typical of an edge dislocation. The plane on which the extra half plane lies is called the slip plane. An edge dislocation can move on this plane by glide motion. If the extra half plane HE were displaced to right, slip process would progress and when HE has finally reached the right hand side of the block. The upper block has completed slip by an amount, b, called the Burger's vector. It is to be noted that, only if the slip process terminates within the crystal it gives rise to a dislocation. On the other hand if the slip proceeds to the end of the crystal, the dislocation moves out of the crystal and cannot be observed.

1. Positive and Negative edge dislocations

Edge dislocations for which the extra half plane lies in the upper half these above the slip plane are called positive edge dislocations and are denoted by '⊥' fig 5.8 (a)



(a) (b)

Fig. 5.8 (a) Positive edge dislocation (b) Negative edge dislocation

If the extra plane is in the lower half of the crystal, that is below the slip plane, the dislocation is called a negative edge dislocation and is indicated as 'T'. This is shown in Fig. 5.8 (b).

2. Characteristics of edge dislocations

The edge dislocation does not necessarily be straight. In fact, any curved line will do as long as it is perpendicular to the Burger's vector. An edge dislocation may therefore contain jogs as indicated in figure 5.9. If an atom such as J diffuses into the lattice interstitial atom may be produced or vacancies annihilated at the expense of the extra half plane. Similarly if an atom occupying a normal lattice position were to move into the position directly on the left of J, the extra half plane would grow and a vacancy would be produced or an interstitial annihilated in the lattice itself. Thus edge dislocations may act as sources or sinks for vacancies and interstitials.

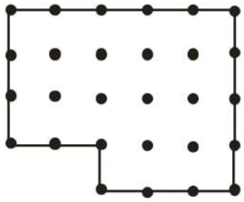


Fig. 5.9. Extra half plane of atoms which jogs at J

The presence of an extra half plane of atoms in an edge dislocation restricts the motion of an edge dislocation mainly to the slip plane. The reason is that any motion perpendicular to the slip plane requires either a growth or a reduction of the half plane. Thus the easy direction of motion of an edge dislocation is in the slip plane since the number of atoms in the extra half is conserved in this case. Any motion of an edge dislocation perpendicular to the slip plane performed non conservative, because it involves either rejecting or accepting extra atoms. N conservative motion is, of course not excluded, but its occurrence depends on whether the diffusion of atoms is rapid enough to sustain it.

3. Burger's Vector and Burger's Circuit

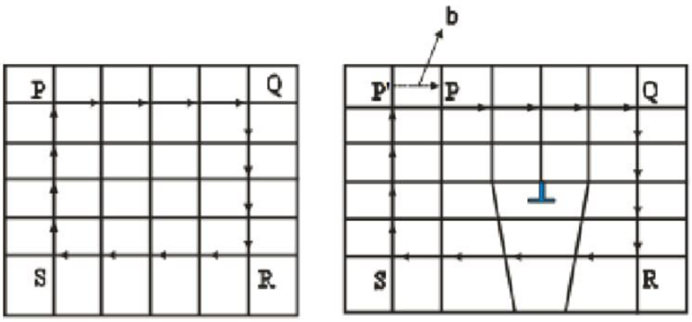
A Burgers circuit is a clockwise trace around the core of a dislocation, going from lattice point to lattice point.

- must go an equal number of steps left and right
- must go an equal number of steps up and down

If the crystal does not contain any dislocation, the circuit will be closed (fig 5.10 (a)). However if the crystal contains an edge dislocation, the extra half-plane of atoms will always cause the circuit to be open rather than closed (Fig. 5.10 (b)) The vector that points from the end of the Burgers circuit to its beginning is called the Burgers vector, **b**

- **b** always points from one lattice point to another
- **b** always has the same length and direction for a given dislocation, regardless where the circuit starts.
- For an edge dislocation (shown above), **b** is always perpendicular to it.The strength of a dislocation is indicated by a parameter called Burger's vector.
- The loop around the dislocation is P→Q→R→S→P'→P. It is an atom by atom circuit around the dislocation. It fails to close the circuit by a distance PP', as

compared to a closed loop in a perfect circle. The gap PP' in a crystal containing the edge dislocation is the Burger's vector. In a regular crystal the closer failure of the atom to atom movement must be between two atom sites and is a lattice vector.



(a) (b)

Fig. 5.10. (a) Burgers circuit in a perfect crystal (b) Burgers circuit in a crystal containing an edge dislocation

- The Burger's vector in any crystal normally would be the shortest distance between the atoms in that crystal. For example FCC crystal has its shortest distance between the atoms along [110] directions. Then the Burger's vector of an edge dislocation would be $\frac{a}{\sqrt{2}}=[110]\cdot$ The length of the vector is $\sqrt{\frac{a^2}{4}+\frac{a^2}{4}+0}=\frac{a}{\sqrt{2}}$. The Dislocation tries to move only in closed packed planes in a crystal.

5.13 Screw Dislocation

A screw dislocation is produced by displacing a part of the crystal on one side of ABCD (Fig. 5.11) relative to the other side in the direction AB. Figure 5.11 represents the atomic configuration in the vicinity of a screw dislocation piercing the surface of a simple cubic lattice. This configuration may be obtained by cutting the block across the area LGHM and then pushing the upper part backward in the direction of the Burger's vector **b** as indicated. The dislocation line LM is parallel to **b**. The screw dislocation line is necessarily straight, in contrast with an edge dislocation line. As one moves around the dislocation line along the circuit ABCDEF, one advances in the direction of BM by an amount equal to **b** for every turn and hence the term screw dislocation.

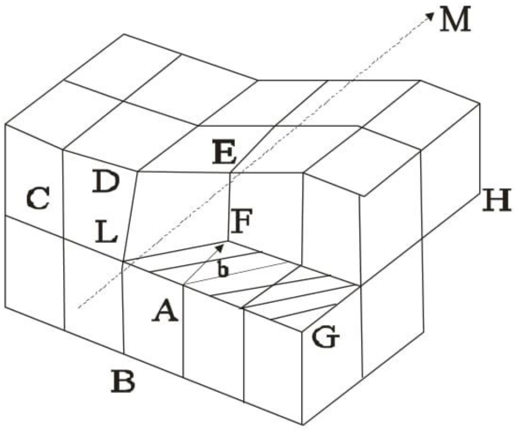


Fig. 5.11 ***Screw dislocation in a cubic lattice. The dislocation line LM is parallel to the Burger's vector b***

Since no extra half plane is involved in a screw dislocation, one cannot speak in this case of non conservative motion. Thus the motion of a screw dislocation is less restricted than that for an edge; the screw dislocation can infact move along any cylindrical surface with the Burgers as its axis. In the figure 5.11, the dislocation line moves to the left, slip proceeds; thus screw dislocations, like edge can produce plastic flow.The examination of the atomic layers around the line DC shows that the atoms are displaced in a spiral staircase fashion. Imagine the line DC as a screw, suppose you rotate the screw in an anticlockwise direction, the screw moves one atomic spacing for every 3600 rotation.

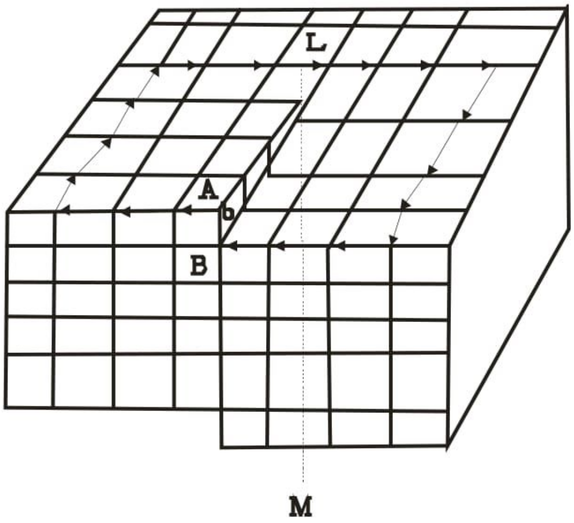


Fig. 5.12 ***Burger's circuit around a screw dislocation line, LM. It fails to close the circuit by the gap AB, the Burger's vector, b***

The Burger's circuit is drawn around the dislocation as shown in Fig. 5.12. The Burger's vector is parallel to the dislocation line.

5.14 Energy of Dislocation

The presence of a dislocation in the crystal always increases the energy of the crystal. There exists an elastic distortion around the dislocation. As atoms are displaced from the original positions, a strain is introduced in the crystal. A stress field is introduced around the dislocation.

(1) Elastic Energy of Screw Dislocation

The elastic distortion around the dislocation is represented in terms of deformation of cylindrical ring of isotropic material as shown in Fig. 5.13

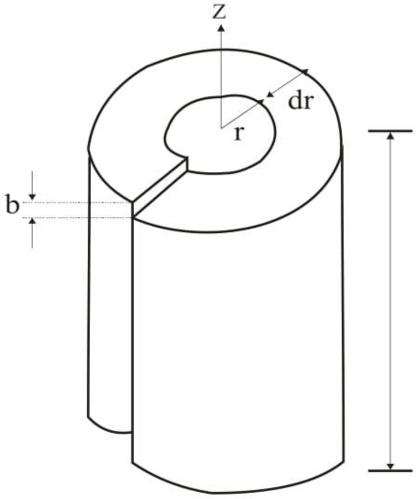


Fig. 5.13 ***Shell of elastically distorted crystal surrounding Screw dislocation with burgers vector b***

Let the cylinder be of length *l*. Let the screw dislocation possess Burger's vector **'b'** along the axis of cylindrical ring. The ring is deformed to produce a distortion same as the screw dislocation. A radial slit PQRS is cut in the ring parallel to the z-axis (i. e. the axis of the ring i.e. along the dislocation direction) and the free surfaces are displaced rigidly with respect to each other by the distance b. A uniform elastic strain $\in_{\theta z}$ is produced throughout the ring. This strain is given by

$$\in_{\theta z} = \frac{b}{2\pi r} \tag{1}$$

The corresponding stress is

$$\tau_{\theta z} = \frac{Gb}{2\pi r} \tag{2}$$

Where G is the shear modulus. As the displacement of the ring is produced by a shear along Z-direction, we do not find displacements in the x - and y- direction. The stress field around the dislocation consists of two pure shears, $\tau_{\theta z}$ in radial planes to the Z-direction and $\tau_{\theta z}$ in planes normal to the Z-axis perpendicular to the radius.

The presence of the stress field around a dislocation indicates that the dislocation is associated with elastic strain energy. This is equal to work done in forming the dislocation of unit length. The elastic energy, $E_{el}(S)$ is given as

$$E_{el}(S) = \frac{1}{2}\int \tau_{\theta z}\, b dr \tag{3}$$

$$= \frac{1}{2}\int \frac{Gb^2}{2\pi r} br \tag{4}$$

The limits of integration are r_0 and R. The value of r_0 can not be zero or R cannot be infinite. Hooke's law is not valid for $r_0 = 0$. r cannot be large as strain field approaches zero

$$E_{el}(S) = \frac{1}{2}\int_{r_o}^{R} \frac{Gb^2}{2\pi}\frac{dr}{r} = \frac{Gb^2}{4\pi} ln \frac{R}{r_o} \tag{5}$$

If the dislocation has the length '*l*', then the elastic energy of a screw dislocation is

$$E / el(S) = \frac{Gb^2 l}{4\pi} In \frac{R}{r_o} \tag{6}$$

When R >> r, *ln* (R/r) → 4π, then, $E'_{el}(S) = lGb^2$ (7)

The energy is proportional to the square of Burger's vector and the length of the dislocation in the crystal.

2. Energy of an edge Dislocation

Consider an edge dislocation. Consider a ring around the dislocation (Fig. 5.13).

A strain field is produced in the ring. The strain in the z-direction is zero. The stress components are

$$\sigma_r = \sigma_\theta = -\frac{b}{2\pi r}\frac{G\sin\theta}{(1-v)}$$

$$\tau_\theta = \tau_{r\theta} = \frac{b}{2\pi r}\frac{G\cos\theta}{(1-v)} \tag{8}$$

$$\sigma_z = v\left(\sigma_r + \sigma_\theta\right) \tag{9}$$

The stress fields have two components. One corresponds to dilation component and the other is shear component. The strain energy for the edge dislocation is given as

$$E_{el}(e) = \frac{1}{2}\int \tau_{r\theta}\, dr \tag{10}$$

Once again, the limits of the integration are r_o and R.

$$E_{el}(e) = \frac{1}{2}\int_{r_o}^{R} \frac{Gb^2}{2\pi(1-v)}\frac{Cos\theta dr}{r} \tag{11}$$

To make it simple, let the displacement in along the slip plane, then cos θ = 1

$$E_{el}(e) = \frac{1}{2}\int_{r_o}^{R} \frac{Gb^2}{2\pi(1-v)}\frac{dr}{r}$$

$$= \frac{G b^2}{4\pi(1-v)} ln\left(\frac{R}{r_o}\right) \tag{12}$$

Thus, the elastic energy of an edge dislocation is more than that of screw dislocation of the same length. If the length of the dislocation is taken into consideration, the energy becomes

$$E_{el}(e) = \frac{Gb^2 l}{4\pi(1-v)} ln\left(\frac{R}{r_o}\right) \tag{13}$$

The energy of core of the dislocation is calculated to be around 0.5-1.5 eV for each atom plane threaded by the dislocation. However the total energy of the dislocation is much higher than this. For example, for copper crystal, the energy of an edge dislocation is about 8 eV for each atom plane threaded by the dislocation.

5.15 Mixed Dislocation

In the above discussion it has been assumed that dislocations are straight. However dislocations move under slight stresses. They can not remain straight. A part from it, a straight dislocation requires a lot of energy to remain in the crystal. However, it can go to low energy configuration, if it is bent. These dislocations are generally bent and irregular, especially after the crystal suffers from external stress (like plastically deformed crystal). The dislocation possesses a shape as shown in Fig. 5.14. The dislocation AB is a mixed dislocation.

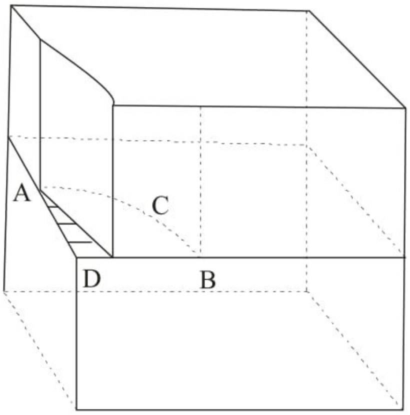


Fig. 5.14 ***Mixed dislocation - At B it has a pure edge character, at A pure screw and at C mixed character***

The boundary between the slipped and un-slipped regions of the crystal is curved. i.e. the dislocation is curved. But the Burger's vector is the same all along the dislocation length. At point B the dislocation is normal . The dislocation has pure edge character. The dislocation is parallel to the vector 'b' …………………… is a pure screw dislocation between A and B, the dislocation is bent as shown in figure. At any point C, it has both screw character as well as an edge character.

5.16 Observation of Dislocation

Many methods are available to observe dislocations. Three main methods are

1. Surface methods
2. Transmission electron microscopy.
3. X-ray diffraction methods.

The other more complicated method is field ion microscopy.

(i) Surface methods

The dislocations end on the surface of the crystal. If the crystal surface is subjected to environment that removes atoms from the surface, the dislocation sites loose more number of atoms than the free surface. The removal of atoms at the dislocation sites is more because of (a) the lattice distortion and subsequent strain field at the dislocation site (b) the geometrical planes would be in the form of spiral steps.

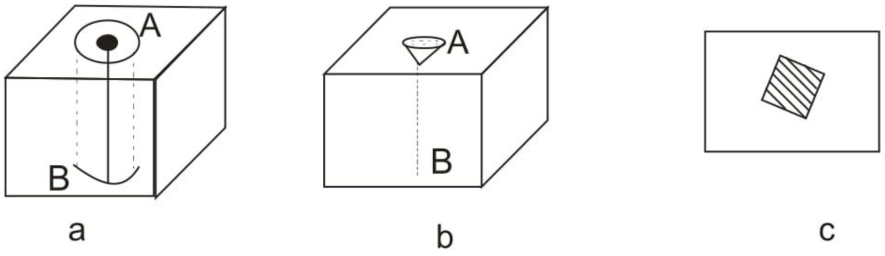


Fig. 5.15 (a) AB is the dislocation (b) Dislocation at A is more (c) An etch pit

As the rate of removal of the atoms at the dislocation sites is more, a pit is formed at the site of the dislocation when subjected to a chemical environment. The chemical etching method is most commonly used. The number of pits per unit area on the surface would directly give the number of dislocations in the crystals. The only problem is to find the suitable 'etchants' for different crystals. The removal of atoms can also be found by evaporating the crystal surface at higher temperatures, at temperatures less than the melting point of the crystal. This process is known as thermal etching. However, thermal etching is not employed usually to find the dislocation densities because of the complications involved in controlling the evaporation of the surface.

(2) Electron Microscopy

This is a widely used method to understand the dislocation interactions, dislocation networks, stacking faults, grain boundary structures. Here electrons have a wavelength is the order of 1A°. When electrons fall on a crystal, they get diffracted. There would be intensities differences in the diffracted beams coming from the dislocation sites and dislocation free sites. At the dislocation sites incoherent scattering of electrons takes place,the principle involves the observation of more fringes in optics. The resolution of the electron microscope is about 4A°. This limit does not allow the atoms to be revealed around the dislocations.

Dislocations and stacking faults can be revealed by a technique which examines the interference between transmitted and diffracted beams resulting from a beam of electrons incident on a very thin foil of a crystal, usually about 1000-5000 A^o thick. A contrast in the image is produced as the planes near the dislocations are slightly bent as compared to the dislocation free regions. The transmitted electron beam would show less intensity at the dislocation sites. The dislocation would appear as dark lines.

(3) X-ray diffraction method- Topography

This method is similar to electron diffraction. However the resolution is far less in the case of x-ray diffraction. The method is useful only for the crystal containing low dislocation densities like 10^6 cm^{-2}. However x-rays penetrate much deeper as compared to electrons, so that thicker samples can be used. The image contrast is produced on a film. The dislocations can be recorded as a dark line.

A monochromatic x-ray beam is passed through a crystal slice set at particular Bragg angle with respect to the x-ray beam. The transmitted x-ray beams are collected on a photographic plate. The crystal is moved along its axis in the direction set for a Bragg angle. The x-ray beam scans a number of atoms the crystal. The x-ray diffraction pattern reveals the topography showing the dislocation as dark lines. The method gives a direct way of observing dislocation.

5.17 Grain Boundaries

Any crystalline solid consists of a large number of grains that are randomly oriented with respect to each other. Each grain is separated from the other grain by grain boundaries. Each grain has its own crystallographic orientation and contains both point defects as well as the dislocations. In the polycrystalline solid, the grains are separated by large angle grain boundaries and the orientation of the crystalline grain would be differing from that of the other grain by an angle more than 10^o. In a single crystal even though it is expected to be single crystallographic orientation, would consist of missorientation of a region of a crystal from the neighboring region by an angle sometimes a few minutes of an arc to a few degrees. These regions are separated by the boundaries called small angle grain boundaries. These grain boundaries consists of an array of dislocations either edge or screw dislocations. Two simple dislocation boundaries are (1) Tilt boundaries and (2) Twist boundaries.

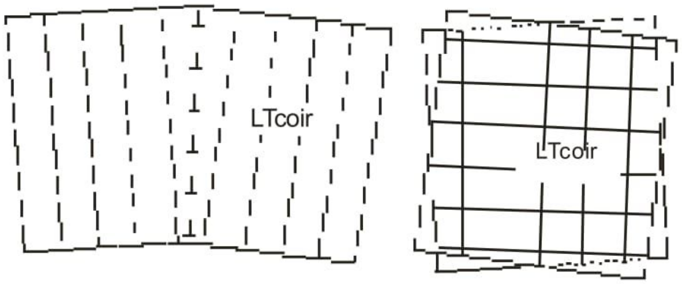


Fig. 5.16 Shows low angle tilt and twist boundaries

(1)Tilt boundaries

The simplest boundary is the symmetrical tilt boundary. It consists of an array of edge dislocations spaced one above the other as shown in the Figure 5.16. Such an array results a tilt between the grains on opposite sides of the boundary.

If we consider a simple cubic lattice with edge dislocation b = a [010], the boundary consists of a sheet of equally spaced dislocations lying parallel to the x-axis. The symmetry plane that is the plane of the sheet will be y =0 i.e. [010]. The crystals on either side of the boundary differ in orientation by an angle θ. Suppose the dislocations are separated by a distance 'h', then $\frac{b}{h} = 2\sin\theta/2$, where b is the Burger's vector of the dislocation. For small values of θ (in radians) $\frac{b}{h} \approx \theta$

Consider that q $\approx 1^o$ and $b = 2.5 \times 10^{-8}$ cm the spacing between dislocations is around 140 A^o. Such tilt boundaries are observed in single crystals of metals or oxides or alkali halides A boundary represents a stable configuration. A grain boundary can move if the dislocations in it move by climb process. For the climb process to take place, a good amount of thermal energy has to be provided. This thermal energy results in the creation of vacancies and when the vacancy concentration reaches sufficiently high, dislocation climb becomes possible as vacancies diffuse into the boundary. Only short range diffusion is required for the processes to take place.

(2) Twist Boundary

A simple boundary formed from a cross grid of pure screw dislocations is a twist boundary. A single set of screw dislocations (shown in fig. 5.16) possesses a long range stress field and is therefore unstable. But the second set of screw dislocations possessing equal long range stress field cancels the stress field due to the first one. The two sets of equally spaced .Parallel dislocation lie in the boundary that lies in the plane of the diagram shown in fig. 5.16. The two sets produce a rotation about an axis normal to the boundary of one half of the crystal with respect to the other. The spacing between the dislocations in each set is $\frac{b}{\theta} \approx h$.

The boundary is symmetrical twist boundary. The boundary can move by the application of stress to the crystal or by creating vacancies in the crystal. A pure twist boundary can move by glide motion of the dislocation. In general case, both edge and screw components are required in a boundary and a given boundary will have a mixed tilt and twist character.

5.18 Self Learning Exercise -II

Section A : Very Short Answer Type Questions

Q.1 What is F- Centers ?

Q.2 Write the formula of the elastic energy of screw dislocation ?

Q.3 Write the formula of the energy of an edge dislocation ?

Section A : Short Answer Type Questions

Q.4 State Fick's second Law.

Q.5 How many methods are available to observe dislocations?

Q.6 What are positive and negative dislocations.

5.19 Summary

All real crystals do contain defects. Based on the spatial dimensions, these defects occupy, they can be classified as Point defects, line defects, planar defects and volume defects do not necessarily have adverse effects on the properties of materials. There are many situations in which a judicious control of the type and amount of imperfections can bring about specific characteristics desired in a system. Color centers in ionic crystals are produce due to the presence of defects.

One-dimensional defects are called dislocations. There are two types of dislocation called edge and screw dislocations. Grain boundaries, both tilt and twist, are examples of two-dimensional defects. Dislocations can be observed directly using etching, electron microscopy and X-ray topography methods.

5.20 Glossary

Dislocation: a displacement of part of a crystal lattice structure.

Defects: A short coming, imperfection, or Lack.

Diffusion: The intermingling of substances by the natural movement of their particles.

5.21 Answer to Self Learning Exercises

Answer to Self Learning Exercise-I

Ans.1: $\frac{n}{N}=Ae^{-Ev/KT}$

Ans.2: $n=\sqrt{NN_i}\,Ae^{-E_f/2KT}$

Ans.3: $n=\sqrt{NN_i}\,Ae^{-E_f/2KT}$

Answer to Self Learning Exercise-II

Ans.1: An excess electron trapped at a negative ion vacancy is called F-centre.

Ans.2: $E_{el}(s)=\frac{Gb^2 l}{4\pi}\ln\frac{R}{r_o}$

Ans.3: $E_{el}(s)=\frac{eb^2}{4\pi(1-v)}l\ln\frac{R}{r_o}$

5.22 Exercise

Section A : Very Short Answer Type Questions

Q.1 What are zero dimensional defects ? Give examples.

Q.2 Distinguish between Schottky and Frenkel defects.

Q.3 On what factor does the vacancy concentration in a crystal depend ?

Q.4 What are V-centers ? How are they produced ?

Q.5 Why should there be dislocations in crystals ?

Section-B: Short Answer Type Questions

Q.6 Distinguish between F and F' centers ?

Q.7 Give the method of producing F' - Centers.

Q.9 What are the important applications of color centers ?

Q.10 Explain the effect of divalent impurity on the Schottky defect in NaCl crystal.

Q.11 State and explain the first Fick's law of diffusion.

Q.12 How second Fick's Law explains non steady state diffusions ?

Q.13 Distinguish between the edge and screw dislocations.

Sections C: Long Answer Type Questions

Q.14 What are imperfections ? How are they classified ? Explain the various point defects present in the crystals.

Q.15 What are Schottky defects? Obtain an expression for the equilibrium concentration of Schottky defects in ionic crystals.

Q.16 Explain the difference between Schottky and Frenkel defects in metals. Calculate the density of Frenkel defects in a copper crystal.

Q.17 What are intrinsic and extrinsic Vacancies ? How are extrinsic vacancies created in ionic crystals. Explain the effect of Schottky and Frenkel defects on the density of an ionic solid.

Q.18 Obtain an expression for the equilibrium concentration of vacancies in a metallic crystal. How does this expression change for an ionic crystal.

References and Suggested Readings

1. Introduction to Solid State Physics, 7e, Charles Kittel, Willey India Pvt. Ltd.
2. Solid State Physics, S. L. Gupta & V. Kumar, K. Nath & Co.
3. Solid State Physics, S. O. Pillai, New age International (P) Limited.

UNIT-6

Elastic Constants

Structure of the Unit

6.0 Objectives

The crystalline materials are supposed to exhibits elastic properties. This chapter is aimed to acquaint the readers with the basics of elastic properties, elastic constants, relation among various elastic constants, variation of elastic properties along the different direction of crystals and propagation of elastic waves in crystals.

6.1 Introduction

In solid state we study the properties of solids which are supposed to be rigid, but in practice they are not absolutely rigid. The shapes and sizes of the solid can be changed by application of some external force on them. Within the range of small changes if the external force is removed then the solids returns to their original shapes and sizes. This property of solids is called as elasticity. We will here study the elastic properties of single crystal and find their elastic constants. In the study we will consider the crystal as a homogeneous continuous medium rather than a periodic array of atoms.

6.2 Analysis of Stress

Let us consider the uniform deformation of a crystal in the form of a cubical shape. When an external force is applied on the crystal then an internal force is developed within the crystal as a reaction force. This internal force acting on the unit area of the crystal is called as stress. We here consider that the applied force is within elastic limit i.e. the Hook's law is applicable. The stress acting on six faces of the crystal is expressed as σ_{xx}, σ_{xy}, σ_{xz}, σ_{yx}, σ_{yy}, σ_{yz}, σ_{zx}, σ_{zy}, σ_{zz}. The first subscript denotes the direction of the applied force and the second subscript denotes the direction of the normal to the face on which the force is applied. So the stress is tensor of rank two and it is expressed in the matrix form.

$$[\sigma_{\mu\upsilon}] = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

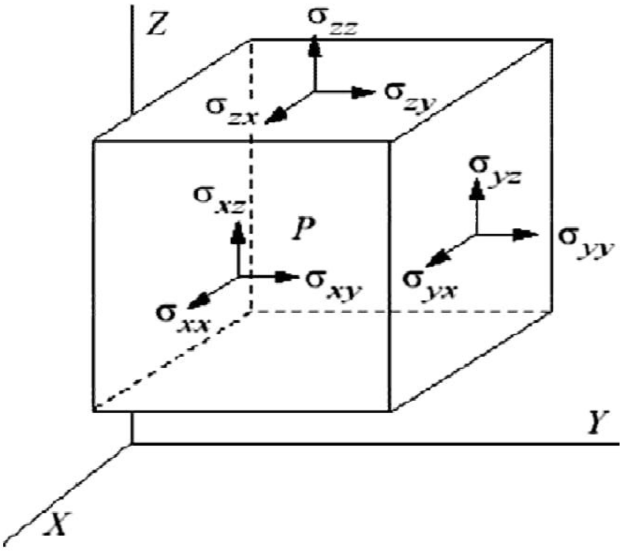


Figure 1. Stress Components

Here $\mu,\upsilon = x, y, z$.

The components σ_{xx}, σ_{yy} and σ_{zz} denote the normal stress components acting on the yz, zx and xy faces. The remaining six components represent the tangential components of stress on each pair of faces. If the cube is in static equilibrium and it does not rotate under the influence of tangential stress components i.e. $\sigma_{\mu\upsilon}$ and $\sigma_{\upsilon\mu}$ produces the equal and opposites rotations. Hence, $\sigma_{\upsilon\mu} = \sigma_{\mu\upsilon}$ so the nine stress components reduced to six independent components.

6.3 Analysis of Strain

Let us consider three orthogonal unit vectors $\hat{i}, \hat{j}, \hat{k}$ in a crystal which is unstrained. Suppose on straining the crystal by a deforming force these unit vectors transforms to non-orthogonal vectors say $\vec{l}, \vec{m}, \vec{n}$ respectively. The magnitudes of these vectors are different to unity. The new coordinate axis are expressed as

$$\vec{l} = (1+\varepsilon_{xx})\hat{i} + \varepsilon_{xy}\hat{j} + \varepsilon_{xz}\hat{k}$$

$$\vec{m} = \varepsilon_{yx}\hat{i} + (1+\varepsilon_{yy})\hat{j} + \varepsilon_{yz}\hat{k}$$

$$\vec{n} = \varepsilon_{zx}\hat{i} + \varepsilon_{zy}\hat{j} + (1+\varepsilon_{zz})\hat{k}$$

where coefficients $\varepsilon_{\alpha\beta}$ define the deformations and are dimensionless and very small i.e. $\varepsilon_{\alpha\beta} << 1$. By taking the dot products $\vec{l}.\vec{l}$, $\vec{m}.\vec{m}$, $\vec{n}.\vec{n}$ we can easily show that the magnitude of each new vector is different from unity and the dot products $\vec{l}.\vec{m}$, $\vec{m}.\vec{n}$, $\vec{n}.\vec{l}$ do not vanish indicating that $\vec{l}$, $\vec{m}$, $\vec{n}$ are not orthogonal vectors. The strain components $e_{\alpha\beta}$ in terms of $\varepsilon_{\alpha\beta}$ are as

$$e_{xx} = \varepsilon_{xx}, e_{yy} = \varepsilon_{yy}, e_{zz} = \varepsilon_{zz} \tag{1}$$

and $$e_{xy} = \vec{l}.\vec{m} = \varepsilon_{yx} + \varepsilon_{xy} \tag{2}$$

$$e_{yz} = \vec{m}.\vec{n} = \varepsilon_{zy} + \varepsilon_{yz} \tag{3}$$

$$e_{zx} = \vec{n}.\vec{l} = \varepsilon_{xz} + \varepsilon_{zx} \tag{4}$$

In the above equations the terms of the order ε^2 are neglected since $\varepsilon_{\alpha\beta} << 1$. The strain components here are defined in terms of the changes in angles between the axes. Therefore, for a rigid rotation in which angles do not change, we have

$$e_{xy} = e_{yz} = e_{zx}, \varepsilon_{xy} = -\varepsilon_{yx}; \varepsilon_{yz} = -\varepsilon_{zy}; \varepsilon_{zx} = -\varepsilon_{xz}$$

If we do not consider pure rotation since they are not deformation we may always take

$$\varepsilon_{xy} = \varepsilon_{yx}; \varepsilon_{yz} = \varepsilon_{zy}; \varepsilon_{zx} = \varepsilon_{xz}$$

So,

$$\varepsilon_{xy} = \varepsilon_{yx} = \frac{1}{2} e_{xy}$$

$$\varepsilon_{yz} = \varepsilon_{zy} = \frac{1}{2} e_{yz}$$

$$\varepsilon_{zx} = \varepsilon_{xz} = \frac{1}{2} e_{zx}$$

Let us now consider an atom in the unstrained crystal whose position vector is given by

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

The position vector of the same atom in the strained crystal is

$$\vec{r}' = x\vec{l} + y\vec{m} + z\vec{n}$$

The displacement of the atom under the action of deforming force is

$$\Delta\vec{r} = \vec{r}' - \vec{r}$$

$$\Delta\vec{r} = \{xe_{xx} + \frac{1}{2}ye_{yx} + \frac{1}{2}ze_{zx}\}\hat{i} + \{\frac{1}{2}xe_{xy} + ye_{yy} + \frac{1}{2}ze_{zy}\}\hat{j} + \{\frac{1}{2}xe_{xz} + \frac{1}{2}ye_{yz} + ze_{zz}\}\hat{k}$$

Let us now write

$$\Delta\vec{r} = u\hat{i} + v\hat{j} + w\hat{k}$$

Where

$$u = xe_{xx} + \frac{1}{2}ye_{yx} + \frac{1}{2}ze_{zx}$$

$$v = \frac{1}{2}xe_{xy} + ye_{yy} + \frac{1}{2}ze_{zy}$$

$$w = \frac{1}{2} x e_{xz} + \frac{1}{2} y e_{yz} + z e_{zz}$$

u, v, and w are the components of displacement along the coordinate axes. The strain components in terms of u, v and w are as

$$e_{xx} = \frac{\delta u}{\delta x}; e_{yy} = \frac{\delta v}{\delta y}; e_{zz} = \frac{\delta w}{\delta z};$$

$$e_{xy} = \frac{\delta v}{\delta x} + \frac{\delta u}{\delta y}$$

$$e_{yz} = \frac{\delta w}{\delta y} + \frac{\delta v}{\delta z}$$

$$e_{zx} = \frac{\delta u}{\delta z} + \frac{\delta w}{\delta x}$$

So, the strain can also be written in terms of tensor of rank two as below.

$$[e_{\alpha\beta}] = \begin{pmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{pmatrix}$$

6.4 Dilation

The fractional increase in volume due to deformation is called as dilation. The volume of a unit cube after deformation is

$$V' = \vec{l}.(\vec{m} \times \vec{n}) \tag{1}$$

As

$$\vec{l} = (1+\varepsilon_{xx})\hat{i} + \varepsilon_{xy}\hat{j} + \varepsilon_{xz}\hat{k} \tag{a}$$

$$\vec{m} = \varepsilon_{yx}\hat{i} + (1+\varepsilon_{yy})\hat{j} + \varepsilon_{yz}\hat{k} \tag{b}$$

$$\vec{n} = \varepsilon_{zx}\hat{i} + \varepsilon_{zy}\hat{j} + (1+\varepsilon_{zz})\hat{k} \tag{c}$$

Substituting the values from equation (a), (b) and (c) in equation (1) and neglecting the product of two strain components we get

$$V' = \{(1+\varepsilon_{xx})\hat{i} + \varepsilon_{xy}\hat{j} + \varepsilon_{xz}\hat{k}\}.[\{\varepsilon_{yx}\hat{i} + (1+\varepsilon_{yy})\hat{j} + \varepsilon_{yz}\hat{k}\} \times \{\varepsilon_{zx}\hat{i} + \varepsilon_{zy}\hat{j} + (1+\varepsilon_{zz})\hat{k}\}]$$

$$V' = 1 + e_{xx} + e_{yy} + e_{zz}$$

Therefore the dilation δ can be expressed as

$$\delta = \frac{V' - V}{V} = e_{xx} + e_{yy} + e_{zz}$$

Here V=1 was considered for unstrained cube.

6.5 Elastic Compliance and Stiffness Constants

According to Hooke's law, the strain is directly proportional to the stress for small deformation. Therefore ,for small elastic deformation of a crystal the stress tensor components and strain tensor components are linearly related as

$$\begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{bmatrix}$$

Conversely, the strain components can be expressed as the linear function of the stress components as

$$\begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46} \\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56} \\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66} \end{bmatrix} \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix}$$

The coefficients C_{ij} are called as elastic stiffness constants and represent the moduli of elasticity. The coefficients S_{ij} are called as elastic compliance constants.

6.6 Elastic Energy Density

In analogy with the energy of a stretched string, the elastic energy density Φ is a quadratic function of strains in the approximation of Hooke's law

$$\Phi = \frac{1}{2}\sum_{\mu=1}^{6}\sum_{\upsilon=1}^{6} \bar{C}_{\mu\upsilon} e_{\mu} e_{\upsilon}$$

$$\Phi = \frac{1}{2}\sum_{\mu=1}^{6}[\bar{C}_{\mu 1}e_{\mu}e_1 + \bar{C}_{\mu 2}e_{\mu}e_2 + \bar{C}_{\mu 3}e_{\mu}e_3 + \bar{C}_{\mu 4}e_{\mu}e_4 + \bar{C}_{\mu 5}e_{\mu}e_5 + \bar{C}_{\mu 6}e_{\mu}e_6]$$

$$\begin{aligned}\Phi = \frac{1}{2}\{&(\bar{C}_{11}e_1e_1 + \bar{C}_{12}e_1e_2 + \bar{C}_{13}e_1e_3 + \bar{C}_{14}e_1e_4 + \bar{C}_{15}e_1e_5 + \bar{C}_{16}e_1e_6)\\ &+(\bar{C}_{21}e_2e_1 + \bar{C}_{22}e_2e_2 + \bar{C}_{23}e_2e_3 + \bar{C}_{24}e_2e_4 + \bar{C}_{25}e_2e_5 + \bar{C}_{26}e_2e_6)\\ &+(\bar{C}_{31}e_3e_1 + \bar{C}_{32}e_3e_2 + \bar{C}_{33}e_3e_3 + \bar{C}_{34}e_3e_4 + \bar{C}_{35}e_3e_5 + \bar{C}_{36}e_3e_6)\\ &+(\bar{C}_{41}e_4e_1 + \bar{C}_{42}e_4e_2 + \bar{C}_{43}e_4e_3 + \bar{C}_{44}e_4e_4 + \bar{C}_{45}e_4e_5 + \bar{C}_{46}e_4e_6)\\ &+(\bar{C}_{51}e_5e_1 + \bar{C}_{52}e_5e_2 + \bar{C}_{53}e_5e_3 + \bar{C}_{54}e_5e_4 + \bar{C}_{55}e_5e_5 + \bar{C}_{56}e_5e_6)\\ &+(\bar{C}_{61}e_6e_1 + \bar{C}_{62}e_6e_2 + \bar{C}_{63}e_6e_3 + \bar{C}_{64}e_6e_4 + \bar{C}_{65}e_6e_5 + \bar{C}_{66}e_6e_6)\}\end{aligned}$$

In the above equation there are 36 terms. Six terms are of type $C_{ii}e_ie_i$, where (i = 1,2,3…6) and 30 other terms. Out of these 30 terms 15 pair are possible of the terms $C_{ij}e_ie_j$ and $C_{ji}e_je_i$. So there will be total 21 terms effectively in the above equationthat will be obvious from following discussion.

So the above equation now becomes

$$\begin{aligned}\Phi = \frac{1}{2}\{&(\bar{C}_{11}e_1^{\,2} + \bar{C}_{22}e_2^{\,2} + \bar{C}_{33}e_3^{\,2} + \bar{C}_{44}e_4^{\,2} + \bar{C}_{55}e_5^{\,2} + \bar{C}_{66}e_6^{\,2})\\ &+(\bar{C}_{12}e_1e_2 + \bar{C}_{21}e_2e_1) + (\bar{C}_{13}e_1e_3 + \bar{C}_{31}e_3e_1) + (\bar{C}_{14}e_1e_4 + \bar{C}_{41}e_4e_1)\\ &(\bar{C}_{15}e_1e_5 + \bar{C}_{51}e_5e_1) + (\bar{C}_{16}e_1e_6 + \bar{C}_{61}e_6e_1) + (\bar{C}_{23}e_2e_3 + \bar{C}_{32}e_3e_2)\\ &+(\bar{C}_{24}e_2e_4 + \bar{C}_{42}e_4e_2) + (\bar{C}_{25}e_2e_5 + \bar{C}_{52}e_5e_2) + (\bar{C}_{26}e_2e_6 + \bar{C}_{62}e_6e_2)\\ &+(\bar{C}_{34}e_3e_4 + \bar{C}_{43}e_4e_3) + (\bar{C}_{35}e_3e_5 + \bar{C}_{53}e_5e_3) + (\bar{C}_{36}e_3e_6 + \bar{C}_{63}e_6e_3)\\ &+(\bar{C}_{45}e_4e_5 + \bar{C}_{54}e_5e_4) + (\bar{C}_{46}e_4e_6 + \bar{C}_{64}e_6e_4) + (\bar{C}_{56}e_5e_6 + \bar{C}_{65}e_6e_5)\}\end{aligned}$$

Also $C_{ij}e_ie_j = C_{ji}e_je_i$, so

$$\begin{aligned}\Phi = \frac{1}{2}\{&(\bar{C}_{11}e_1^{\,2} + \bar{C}_{22}e_2^{\,2} + \bar{C}_{33}e_3^{\,2} + \bar{C}_{44}e_4^{\,2} + \bar{C}_{55}e_5^{\,2} + \bar{C}_{66}e_6^{\,2}) \\ &+(2\bar{C}_{12}e_1e_2 + 2\bar{C}_{13}e_1e_3 + 2\bar{C}_{14}e_1e_4 + 2\bar{C}_{15}e_1e_5 + 2\bar{C}_{16}e_1e_6 + 2\bar{C}_{23}e_2e_3) \\ &+(2\bar{C}_{24}e_2e_4 + 2\bar{C}_{25}e_2e_5 + 2\bar{C}_{26}e_2e_6 + 2\bar{C}_{34}e_3e_4 + 2\bar{C}_{35}e_3e_5) \\ &+(2\bar{C}_{36}e_3e_6 + 2\bar{C}_{45}e_4e_5 + 2\bar{C}_{46}e_4e_6 + 2\bar{C}_{56}e_5e_6)\}\end{aligned}$$

Or

$$\begin{aligned}\Phi = &\frac{1}{2}\bar{C}_{11}e_1^{\,2} + \frac{1}{2}\bar{C}_{22}e_2^{\,2} + \frac{1}{2}\bar{C}_{33}e_3^{\,2} + \frac{1}{2}\bar{C}_{44}e_4^{\,2} + \frac{1}{2}\bar{C}_{55}e_5^{\,2} + \frac{1}{2}\bar{C}_{66}e_6^{\,2} \\ &+(\bar{C}_{12}e_1e_2 + \bar{C}_{13}e_1e_3 + \bar{C}_{14}e_1e_4 + \bar{C}_{15}e_1e_5 + \bar{C}_{16}e_1e_6 + \bar{C}_{23}e_2e_3) \\ &+(\bar{C}_{24}e_2e_4 + \bar{C}_{25}e_2e_5 + \bar{C}_{26}e_2e_6 + \bar{C}_{34}e_3e_4 + \bar{C}_{35}e_3e_5) \\ &+(\bar{C}_{36}e_3e_6 + \bar{C}_{45}e_4e_5 + \bar{C}_{46}e_4e_6 + \bar{C}_{56}e_5e_6)\end{aligned}$$

Let us define the indices 1 to 6 as

$$1 \equiv xx; 2 \equiv yy; 3 \equiv zz;$$

$$4 \equiv yz; 5 \equiv zx; 6 \equiv xy$$

The stress components are found from the derivatives of Φ or U i.e. potential energy with respect to the associated strain components. This result follows from the definition of potential energy. Let us consider the stress applied to one face of the cube while keeping the opposite face fixed. The stress is given by

$$X_x = \frac{\delta U}{\delta e_{xx}} \equiv \frac{\delta U}{\delta e_1} = \bar{C}_{11}e_1 + \bar{C}_{12}e_2 + \bar{C}_{13}e_3 + \bar{C}_{14}e_4 + \bar{C}_{15}e_5 + \bar{C}_{16}e_6$$

$$Y_y = \frac{\delta U}{\delta e_{yy}} \equiv \frac{\delta U}{\delta e_2} = \bar{C}_{12}e_1 + \bar{C}_{22}e_2 + \bar{C}_{23}e_3 + \bar{C}_{24}e_4 + \bar{C}_{25}e_5 + \bar{C}_{26}e_6$$

$$Z_z = \frac{\delta U}{\delta e_{zz}} \equiv \frac{\delta U}{\delta e_3} = \bar{C}_{13}e_1 + \bar{C}_{23}e_2 + \bar{C}_{33}e_3 + \bar{C}_{34}e_4 + \bar{C}_{35}e_5 + \bar{C}_{36}e_6$$

$$Y_z = \frac{\delta U}{\delta e_{yz}} \equiv \frac{\delta U}{\delta e_4} = \bar{C}_{14}e_1 + \bar{C}_{24}e_2 + \bar{C}_{34}e_3 + \bar{C}_{44}e_4 + \bar{C}_{45}e_5 + \bar{C}_{46}e_6$$

$$Z_x = \frac{\delta U}{\delta e_{zx}} \equiv \frac{\delta U}{\delta e_5} = \bar{C}_{15}e_1 + \bar{C}_{25}e_2 + \bar{C}_{35}e_3 + \bar{C}_{45}e_4 + \bar{C}_{55}e_5 + \bar{C}_{56}e_6$$

$$X_y = \frac{\delta U}{\delta e_{xy}} \equiv \frac{\delta U}{\delta e_6} = \bar{C}_{16}e_1 + \bar{C}_{26}e_2 + \bar{C}_{36}e_3 + \bar{C}_{46}e_4 + \bar{C}_{56}e_5 + \bar{C}_{66}e_6$$

6.7 Elastic Stiffness Constants of Cubic Crystals

The number of independent elastic constants is further reduced by the symmetry elements possessed by the crystal. In cubic crystal X_x is the stress along x direction .From the symmetry and isotropy of the crystals we observe $C_{12} = C_{13}$. Similarly as Y_y is the stress along y direction ,so we observe $C_{21} = C_{23}$ and for stress Z_z along z direction we observe $C_{31} = C_{32}$. Also from symmetry and isotropy of the cubic crystals crystal we have

$$C_{11} = C_{22} = C_{33}$$

$$C_{12} = C_{13} = C_{21} = C_{23} = C_{31} = C_{32}$$

$$C_{44} = C_{55} = C_{66}$$

The other coefficients are zero as

$$C_{14} = C_{15} = C_{16} = C_{24} = C_{25} = C_{26} = C_{34} = C_{35} = C_{36} = C_{45} = C_{46} = C_{56} = 0$$

So the potential energy is given by

$$\Phi = \frac{1}{2}\bar{C}_{11}e_1^{\,2} + \frac{1}{2}\bar{C}_{22}e_2^{\,2} + \frac{1}{2}\bar{C}_{33}e_3^{\,2} + \frac{1}{2}\bar{C}_{44}e_4^{\,2} + \frac{1}{2}\bar{C}_{55}e_5^{\,2} + \frac{1}{2}\bar{C}_{66}e_6^{\,2}$$

$$+(\bar{C}_{12}e_1e_2 + \bar{C}_{13}e_1e_3 + 0 + 0 + 0)\ +(\bar{C}_{23}e_2e_3 + 0 + 0 + 0)$$

$$+(0+0+0)\ +(0+0)\ +0$$

$$\Phi = \frac{1}{2}\bar{C}_{11}(e_1^{\,2} + e_2^{\,2} + e_3^{\,2}) + \frac{1}{2}\bar{C}_{44}(e_4^{\,2} + e_5^{\,2} + e_6^{\,2}) + \bar{C}_{12}(e_1e_2 + e_1e_3 + e_2e_3)$$

$$\Rightarrow \Phi = \frac{1}{2}\bar{C}_{11}(e_{xx}^{\,2} + e_{yy}^{\,2} + e_{zz}^{\,2}) + \frac{1}{2}\bar{C}_{44}(e_{yz}^{\,2} + e_{zx}^{\,2} + e_{xy}^{\,2}) + \bar{C}_{12}(e_{xx}e_{yy} + e_{xx}e_{zz} + e_{yy}e_{zz}) \quad (1)$$

So in cubic crystal there are only three independent stiffness constants. There exists no other quadratic term like as given below do not occur

$$(e_{xx}e_{xy} + ...);(e_{yz}e_{zx} + ...);(e_{xx}e_{yz} + ...) \qquad (2)$$

The minimum symmetry requirement for a cubic structure is the existence of four three-fold rotation axes. The axes are in [111] and equivalent directions, the effect of a rotation of 2π/3 about these four is to interchange the x, y, z axes according to below schemes

$$x \rightarrow y \rightarrow z \rightarrow x; \qquad -x \rightarrow z \rightarrow -y \rightarrow -x \qquad (3a)$$

$$x \rightarrow z \rightarrow -y \rightarrow x \qquad\qquad -x \rightarrow y \rightarrow z \rightarrow -x \qquad (3b)$$

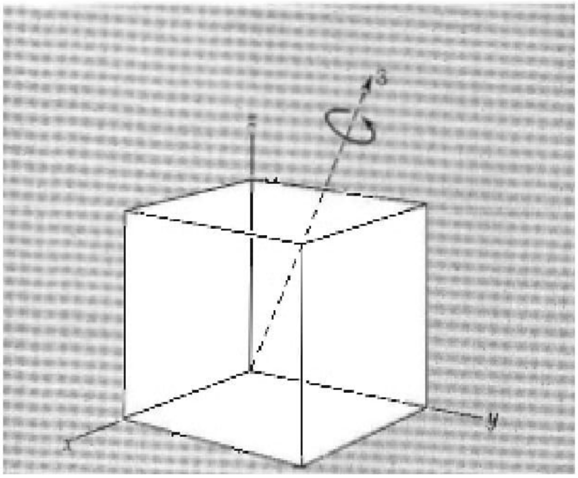


Figure 2.Rotation by 2π/3 about the axis shown

Under the first of these schemes, for example,

$$e_{xx}^2 + e_{yy}^2 + e_{zz}^2 \rightarrow e_{yy}^2 + e_{zz}^2 + e_{xx}^2$$

and for the others terms also, the above equation (1) is invariant under the operation considered. But each term of the equation is odd in one or more indices. A rotation in the set of equations (3a, 3b) can be found which will change the sign of the term, because $e_{xx} = -e_{x(-y)}$. Now we have

We now replace here $\bar{C} = C$

$$\frac{\delta\Phi}{\delta e_{xx}} = X_x = C_{11}e_{xx} + C_{12}e_{yy} + C_{12}e_{zz}$$

$$\frac{\delta\Phi}{\delta e_{yy}} = Y_y = C_{12}e_{xx} + C_{11}e_{yy} + C_{12}e_{zz}$$

$$\frac{\delta\Phi}{\delta e_{zz}} = Z_z = C_{12}e_{xx} + C_{12}e_{yy} + C_{11}e_{zz}$$

Also $\quad C_{12} = C_{13}\,, \quad C_{14} = C_{15} = C_{16} = 0$

$$C_{61} = C_{62} = C_{63} = C_{64} = C_{65} = 0$$

and $\quad C_{66} = C_{44}$

Further, $\quad \dfrac{\delta\Phi}{\delta e_{yz}} = Y_z = C_{44}e_{yz}$

$$\frac{\delta\Phi}{\delta e_{zx}} = Z_x = C_{44}e_{zx}$$

$$\frac{\delta\Phi}{\delta e_{xy}} = X_y = C_{44}e_{xy}$$

All the above equations can be written as

$$\frac{\delta\Phi}{\delta e_{xx}} = X_x = C_{11}e_1 + C_{12}e_2 + C_{12}e_3$$

$$\frac{\delta\Phi}{\delta e_{yy}} = Y_y = C_{12}e_1 + C_{11}e_2 + C_{12}e_3$$

$$\frac{\delta\Phi}{\delta e_{zz}} = Z_z = C_{12}e_1 + C_{12}e_2 + C_{11}e_3$$

$$\frac{\delta\Phi}{\delta e_{yz}} = Y_z = C_{44}e_4$$

$$\frac{\delta\Phi}{\delta e_{zx}} = Z_x = C_{44}e_5$$

$$\frac{\delta\Phi}{\delta e_{xy}} = X_y = C_{44}e_6$$

Thus from the equations the values of the elastic stiffness constants is reduced for the cubic crystal to matrix form as below

$$\begin{pmatrix} X_x \\ Y_y \\ Z_z \\ Y_z \\ Z_x \\ X_y \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{pmatrix}$$

Or

$$\begin{pmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}^{-1} \begin{pmatrix} X_x \\ Y_y \\ Z_z \\ Y_z \\ Z_x \\ X_y \end{pmatrix}$$

For cubic crystals the stiffness and compliance constants are related by

$$C_{44}=\frac{1}{S_{44}};C_{11}-C_{12}=\frac{1}{S_{11}-S_{12}};C_{11}+2C_{12}=\frac{1}{S_{11}+2S_{12}}$$

$$\begin{pmatrix}X_x\\Y_y\\Z_z\end{pmatrix}=\begin{pmatrix}C_{11}&C_{12}&C_{12}\\C_{12}&C_{11}&C_{12}\\C_{12}&C_{12}&C_{11}\end{pmatrix}\begin{pmatrix}e_1\\e_2\\e_3\end{pmatrix}$$

Or

$$\begin{pmatrix}e_1\\e_2\\e_3\end{pmatrix}=\begin{pmatrix}C_{11}&C_{12}&C_{12}\\C_{12}&C_{11}&C_{12}\\C_{12}&C_{12}&C_{11}\end{pmatrix}^{-1}\begin{pmatrix}X_x\\Y_y\\Z_z\end{pmatrix}\qquad \text{or}$$

$$\begin{pmatrix}e_1\\e_2\\e_3\end{pmatrix}=\begin{pmatrix}S_{11}&S_{12}&S_{12}\\S_{12}&S_{11}&S_{12}\\S_{12}&S_{12}&S_{11}\end{pmatrix}\begin{pmatrix}X_x\\Y_y\\Z_z\end{pmatrix}$$

So we $S=C^{-1}$ or $SC=I$

$$\begin{pmatrix}S_{11}&S_{12}&S_{12}\\S_{12}&S_{11}&S_{12}\\S_{12}&S_{12}&S_{11}\end{pmatrix}\begin{pmatrix}C_{11}&C_{12}&C_{12}\\C_{12}&C_{11}&C_{12}\\C_{12}&C_{12}&C_{11}\end{pmatrix}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

6.8 Bulk Modulus and Compressibility

Let us consider a strained crystal which is uniformly dilated. This require the condition as

$$e_{xx}=e_{yy}=e_{zz}=\frac{1}{3}\delta$$

So the energy density of the cubic crystal is given by

$$\Phi=\frac{1}{6}(C_{11}+2C_{12})\delta^2 \qquad (1)$$

The energy density in terms of bulk modulus B is given by

$$\Phi=\frac{1}{2}B\delta^2 \qquad (2)$$

Comparing equation (1) and (2)

$$B = \frac{1}{3}(C_{11} + 2C_{12})$$

The inverse of the bulk modulus is the measure of compressibility K

$$K = \frac{1}{B} = \frac{3}{C_{11} + 2C_{12}}$$

6.9 Elastic Waves in Cubic Crystals

Consider an elementary cube of sides $\Delta x = \Delta y = \Delta z$ within the volume of a cubic crystal. The edges of the cube are along x, y and z axis. The x component of force on an elementary cube of volume $\Delta V = \Delta x.\Delta y.\Delta z$ of the crystal is given by

$$F_x = (\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z})\Delta x.\Delta y.\Delta z$$

where $X_{x,}$ $X_{y,}$ and X_z are the stresses on x, y, z faces of the cube. If ρ is the density of the crystal the mass of the elementary cube is $\rho\,\Delta x.\Delta y.\Delta z$. The equation of motion along x direction

$$\rho\frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 X_x}{\partial x^2} + \frac{\partial^2 X_y}{\partial y^2} + \frac{\partial^2 X_z}{\partial z^2}$$

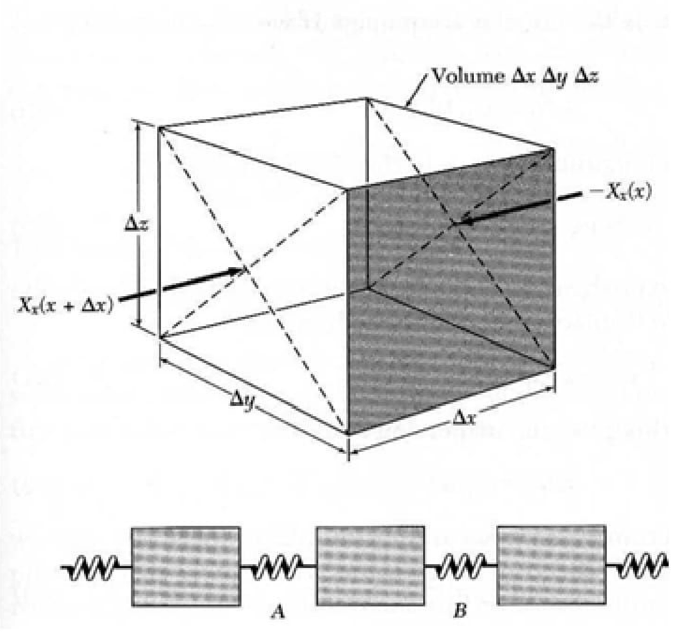


Figure 6.3 Stress in a cubic crystal and waves in the crystals

Here u is the displacement in x direction. The equations are similar in y and z directions. In terms of elastic stiffness constants the above equation can be written as

$$\rho\frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial e_{xx}}{\partial x} + C_{12}(\frac{\partial e_{yy}}{\partial x} + \frac{\partial e_{zz}}{\partial x}) + C_{44}(\frac{\partial e_{xy}}{\partial y} + \frac{\partial e_{zx}}{\partial z})$$

From the definition of strain components

$$\rho\frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial^2 u}{\partial x^2} + C_{44}(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}) + (C_{12} + C_{44})(\frac{\partial^2 v}{\partial x\partial y} + \frac{\partial^2 w}{\partial x\partial z}) \qquad (1)$$

Here u, v and w are components of displacements along three axes. Similar to above the equation of motion along y and z directions are

$$\rho\frac{\partial^2 v}{\partial t^2} = C_{11}\frac{\partial^2 v}{\partial y^2} + C_{44}(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2}) + (C_{12} + C_{44})(\frac{\partial^2 u}{\partial x\partial y} + \frac{\partial^2 w}{\partial y\partial z}) \qquad (2)$$

And

$$\rho\frac{\partial^2 w}{\partial t^2} = C_{11}\frac{\partial^2 w}{\partial z^2} + C_{44}(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2}) + (C_{12} + C_{44})(\frac{\partial^2 u}{\partial x\partial z} + \frac{\partial^2 v}{\partial y\partial z}) \qquad (3)$$

Now let us the solutions of these equations for some special cases.

Waves in the [100] direction:

Let the solution of the equation (1) is

$$u = u_0 \exp[i(Kx - \omega t)]$$

On substituting in the equation (1) we get

$$\omega^2\rho = C_{11}K^2$$

So the velocity of longitudinal wave along [100] direction

$$\vartheta = \upsilon.\lambda = \omega / K = (C_{11} / \rho)^{\frac{1}{2}}$$

Similarly the solution of equation (2)

$$v = v_0 \exp[i(Kx - wt)]$$

$$\omega^2\rho = C_{44}K^2$$

So the velocity of transverse waves in the [100] direction

$$\vartheta = \upsilon.\lambda = \omega / K = (C_{44} / \rho)^{\frac{1}{2}}$$

Similar velocity is obtained for displacement along z direction.

Waves in the [110] direction:

Let us consider a shear wave propagating in x-y plane with particles displacement w in the z direction

$$w = w_0 \exp[i(K_x x + K_y y - wt)]$$

So from equation (3) we get

$$\omega^2 \rho = C_{44}(K_x^{\ 2} + K_y^2) = C_{44} K^2 \tag{4}$$

Consider other waves that propagate in the x-y plane with particle motion in x-y plane

$$u = u_0 \exp[i(K_x x + K_y y - wt)]$$

And

$$v = v_0 \exp[i(K_x x + K_y y - wt)]$$

Substituting in equations (1) and (2) we get

$$\omega^2 \rho u = (C_{11} K_x^{\ 2} + C_{44} K_y^2) u + (C_{12} + C_{44}) K_x K_y v \tag{5}$$

$$\omega^2 \rho v = (C_{11} K_y^{\ 2} + C_{44} K_x^2) v - (C_{12} + C_{44}) K_x K_y u \tag{6}$$

The equations (5) and (6) in the direction [110] for which $\mathrm{K_x} = \mathrm{K_y} = \mathrm{K} / \sqrt{2}$. The condition for the solution to exists that the determinant of coefficients of u and v should be equal to zero.

$$\begin{pmatrix} -\omega^2 \rho + \frac{1}{2}(C_{11} + C_{44}) K^2 & \frac{1}{2}(C_{12} + C_{44}) K^2 \\ \frac{1}{2}(C_{12} + C_{44}) K^2 & -\omega^2 \rho + \frac{1}{2}(C_{11} + C_{44}) K^2 \end{pmatrix} = 0$$

This equation has the roots as

$$\omega^2 \rho = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}) K^2 \text{ and } \quad \omega^2 \rho = \frac{1}{2}(C_{11} - C_{12}) K^2$$

The first root describes a longitudinal wave and the second describes a shear wave.

The direction of particle displacement can be determined by substituting the first root in equation (5) as

$$\frac{1}{2}(C_{11}+C_{12}+2C_{44})K^2u=\frac{1}{2}(C_{11}+C_{44})K^2u+\frac{1}{2}(C_{12}+C_{44})K^2v$$

The displacement components satisfy u = v. So the particle displacement is along [110] and parallel to the K vector. The second root when substituted in equation (6) then it gives

$$\frac{1}{2}(C_{11}-C_{12})K^2u=\frac{1}{2}(C_{11}+C_{44})K^2u+\frac{1}{2}(C_{12}+C_{44})K^2v$$

Which shows u = -v. The particle velocity is along $[1\bar{1}0]$ and perpendicular to the K vector.

6.10 Self Learning Exercise

Q.1 Explain the concept of elastic properties of crystals.

Q.2 Explain the strain tensor.

Q.3 Explain the dilation in crystals.

Q.4 Explain the elastic energy density

Q.5 Derive the expression for velocity in cubic crystal in [110] direction.

6.11 Summary

This unit deals with the elastic properties of the solid material like stress and strain. The crystal is considered as homogeneous medium. The unit starts with discussion on stress analysis and stress tensor. After the stress analysis the strain analysis and strain tensor is discussed. The increase in volume due to deformation i.e. dilation, elastic compliance coefficients and elastic stiffness coefficients are derived. The elastic energy density, stiffness constant for cubic crystal and bulk modulus and compressibility is discussed. At the end the equation for elastic waves in the cubic crystal are derived and solution of the wave is discussed. The velocity of the waves in the cubic crystal particularly in [110] and [110] direction are calculated.

6.12 Glossary

Rigid: Difficult to change inter-particle distance

Homogeneous: Same throughout

Array: Arrangement of atoms in space.

Deformation: Change in shape or size by external force.

Orthogonal: Perpendicular.

Unstrained: Without any change in shape or size

Invariant: Remain unchanged.

6.13 Exercise

Q.1 Explain the stress tensor.

Q.2 Explain the elastic compliance and stiffness constants

Q.3 Derive the expression for bulk modulus and compressibility

Q.4 Derive the differential equation of wave in cubic crystals.

Q.5 Derive the expression for velocity in cubic crystal in [100] direction.

References and Suggested Readings

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UNIT-7

Vibrations of Crystals

Structure of the Unit

7.0 Objectives

The aim of this unit to study lattice vibrations of crystals and propagation of elastic waves in one dimensional monoatomic and diatomic lattices. Then we will study concept of phonon through quantization of elastic waves and phonon momentum. In the last we will study inelastic scattering by phonons.

7.1 Introduction

In nature, a solid is composed of atoms or molecules which are closely packed and their arrangement is ordered. A lattice may be regarded as a regular arrangement of atoms (molecules) which are joined together by elastic springs. Atoms in solid execute complex thermal vibrations about their equilibrium positions. The motion of any single atom is, therefore, shared by all the atoms ,i.e. the motion of the atom is coupled. The motion of atoms is due to thermal energy of solid. The interatomic interaction, however, causes the atoms to vibrate about their mean position. As these atoms are present at the lattice points, these vibrations are known as Lattice Vibrations. These vibrations yield information about the thermal properties of solids, such as specific heat and thermal conductivity. In order to investigate the characteristics of elastic vibrational motion of a crystal lattice, we have to consider a one dimensional lattice, i.e. a lattice consisting of linear chains of atoms.

7.2 Vibrations of One Dimensional Monoatomic Basis

In order to study the vibration of one dimensional monoatomic lattice, consider a one-dimensional linear chain of identical atoms, having mass m and spaced at a distance *a* (i.e. lattice constant), connected by massless ideal springs. Practically this is possible in the case of elastic vibrations of a crystal with one atom in the primitive cell. When a wave propagate in cubic crystal along the directions [1,0,0], [1,1,0], [1,1,1], then all the planes of atoms move in phase with displacement either perpendicular or parallel to the direction of wave vector $(\vec{K})$. In such a case the displacement of a plane can be described by only one coordinate, so displacement of wave becomes one dimensional. The interaction between atoms in lattice is identical to elastic forces and obeys Hooke's Law $(F \propto -x)$.

Let us consider the equilibrium state the atoms, when atoms are at rest. The coordinate of n^{th} atom is represented by $x_n = na$. Thus at equilibrium position, the atoms are situated at equally spaced sites represented by .... (n–3), (n–2), (n–1) n, (n+1), (n+2), (n+3) ...... with x coordinates as (n–3)*a*, (n–2)*a*, (n+1)*a*, n*a*, (n+1)*a*, (n+2)*a*, (n+3)*a*...... and so on as shown in figure 7.1.

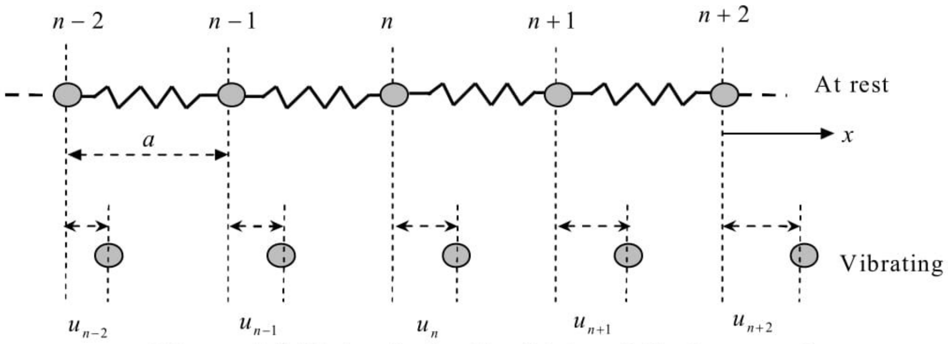


Figure 7.1 State of vibration(state of displacement)

As the atoms in the crystal start vibrational motion along the x-axis, the atoms will execute periodic motion about their equilibrium position and produces elastic waves which propagate through the medium. Let at any instant of time u_n denotes the displacement of n^{th} atom from mean position. Similarly u_{n-1}, u_{n+1}, u_{n-2}, u_{n+2}……denote the displacement of (n–1), (n+1), (n–2) and $(n+2)^{th}$ atom respectively. The vibrational motion of each atom is simple harmonic. This type of one dimensional monoatomic lattice is shown in figure (7.1). Since springs are ideally elastic, so according to Hooke's law ,the force between any two atoms must be linear and in opposite direction i.e. the force required to produce an atomic displacement is proportional to the displacement itself $(F \propto -x)$. Since the force experienced by any atom be mainly due to its nearest neighbour's and the force due to another atoms can be taken as negligible. Therefore the force experienced by n^{th} atom will be only due to $(n+1)^{th}$ and $(n-1)^{th}$ atoms. The elastic force on the n^{th} atom due to $(n+1)^{th}$ atom will be $\beta(u_{n+1} - u_n)$ and due to $(n-1)^{th}$ atom will be $-\beta(u_n - u_{n-1})$,where β is interatomic force constant. So the net elastic force acting on n^{th} atom due to its nearest neighboring atoms $(n+1)^{th}$ and $(n-1)^{th}$ is given by

$$F_n = \beta(u_{n+1} - u_n) - \beta(u_n - u_{n-1})$$

$$\therefore F_n = \beta(u_{n+1} + u_{n-1} - 2u_n) \tag{7.1}$$

According to Newton's second law motion, the equation of motion of n^{th} atom is given by

$$m\frac{d^2u_n}{dt^2} = \beta(u_{n+1} + u_{n-1} - 2u_n) \tag{7.2}$$

where $\frac{d^2u_n}{dt^2}$ denotes the acceleration of n^{th} atom and m is mass of the atom. Since the propagation of disturbance in crystal is in the form of elastic wave. Equation (7.2) is a differential equations in displacement and has a periodic travelling wave solution as:

$$u_n = Ae^{i(\omega t\text{-}Kx_n)} \tag{7.3}$$

$$u_n = A\ e^{i(\omega t\text{-}Kna)} \tag{7.4}$$

where x_n=na, represents the x- coordinate of n^{th} atom in equilibrium state. ω and K are constants, ω being the angular frequency and $K = \frac{2\pi}{\lambda}$ is wave vector or propagation vector. Since a is the spacing between the two nearest atoms of linear chain.

Differentiating equation (7.4) we get

$$\frac{du_n}{dt} = A\, i\omega e^{i(\omega t - Kna)} \tag{7.5}$$

Again differentiating eq.(7.5) we get

$$\frac{d^2u_n}{dt^2} = -A\, \omega^2 e^{i(\omega t - Kna)} \tag{7.6}$$

On the basis of equation (7.4) we can write

$$u_{n+1} = A\ e^{i[\omega t - K(n+1)a]} \tag{7.7}$$

$$u_{n-1} = A\, e^{i[\omega t - K(n-1)a]} \tag{7.8}$$

Now substituting the values from equations (7.4), (7.6), (7.7) and (7.8) in equation (7.2) we get-

$$-A\,\omega^2\, m\, e^{i\,(\omega t - Kna)} = \beta\left[A\, e^{i\,[(\omega t - K\,(n+1)a]} + A\, e^{i\,[\omega t - K(n\text{-}1)a]} - 2A\, e^{i[\omega t\text{-}Kna]}\right]$$

$$= \beta\ A\ e^{i(\omega t - Kna)}[e^{-i\ Ka} +\ e^{i\,ka} - 2]$$

$$-\omega^2 m = \beta[e^{-iKa} + e^{iKa} - 2]$$

$$= \beta\,[2\cos \mathrm{Ka} - 2]$$

$$= 2\beta\,[\cos \mathrm{Ka} - 1]$$

$$-\omega^2 m = 2\beta\left[-2\ \sin^2\frac{Ka}{2}\right]$$

$$\therefore\ \omega^2 = \frac{4\beta}{m}\sin^2\frac{Ka}{2}$$

$$\text{or} \qquad \omega = \sqrt{\frac{4\beta}{m}}\sin\frac{Ka}{2} \tag{7.9}$$

We have taken only + ve sign because angular frequency is always positive. Since the maximum value of $\sin\frac{\mathrm{Ka}}{2}$ is one ,therefore

$$\omega_{\max} = \sqrt{\frac{4\beta}{m}} \tag{7.10}$$

$$\omega = \omega_{\max}\sin\frac{Ka}{2} \tag{7.11}$$

Since equation (7.11) gives relation between ω and K. So this relation is known as dispersion relation(ω on y axis and K on x axis) and is plotted in figure (7.2)

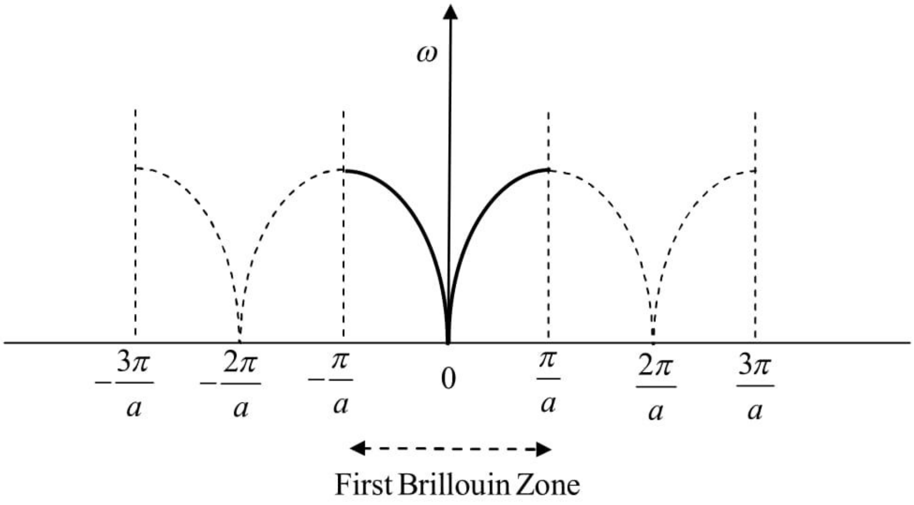


Figure 7.2 : Dispersion curve for a one dimensional monoatomic lattice

The following important results are obtained from equation (7.11):

(I) At low frequency : when $K \to 0$, i.e. when wave length is very large in comparison to a (interatomic distance) ,then this is known as long wavelength limit. In this case $K \to 0$,$\sin\frac{Ka}{2} \approx \frac{Ka}{2}$

or $$\omega = \sqrt{\frac{4\beta}{m}}\frac{Ka}{2} = Ka\sqrt{\frac{\beta}{m}} \tag{7.12}$$

$$\therefore \text{ Phase velocity } V_p = \frac{\omega}{K} = a\sqrt{\frac{\beta}{m}} = V_0 \tag{7.13}$$

$$\text{and group velocity } V_g = \frac{d\omega}{dK} = a\sqrt{\frac{\beta}{m}} = V_0 \tag{7.14}$$

where V_0 is velocity of sound in crystal lattice and *a* is lattice constant. The relation $V_0 = \frac{\omega}{K}$ is the same as that for a homogeneous continuous line. Thus for long wavelength limit ,phase velocity and group velocity do not depend upon frequency. In this state medium is nondispersive and behaves as homogeneous continuum.

(II) At high frequency: When the value of K is large, then graph between ω and K is not linear, because dispersion takes place. In this state lattice behaves as discontinuous medium.

Phase velocity $$V_p = \frac{\omega}{K} = a\sqrt{\frac{\beta}{m}}\left(\frac{\sin\frac{Ka}{2}}{\frac{Ka}{2}}\right) = V_0\left(\frac{\sin\frac{Ka}{2}}{\frac{Ka}{2}}\right) \qquad (7.15)$$

and group velocity $$V_g = \frac{d\omega}{dK} = a\sqrt{\frac{\beta}{m}}\left(\cos\frac{Ka}{2}\right)$$

$$= \mathrm{V}_0\left(\cos\frac{\mathrm{Ka}}{2}\right) \qquad (7.16)$$

From equation (7.15) and (7.16) it is clear that both velocities are function of frequency. In optics ,when light passes through a medium, the refractive index depends upon frequency, so phenomenon of dispersion of light takes place.Thus present medium is also dispersive in similar manner to optical case.

(III) At frequency $\omega = \sqrt{\frac{4\beta}{m}}$ (maximum value) : The maximum frequency of elastic waves which can propagate through the lattice can be obtained from equation (7.10) i.e.

$$\omega_{\max} = \sqrt{\frac{4\beta}{m}} = 2\sqrt{\frac{\beta}{m}} = 2\pi\upsilon_{\max}$$

Also for $\omega_{\max} = \sqrt{\frac{4\beta}{m}}$, from equation (7.11) $\sin\frac{\mathrm{Ka}}{2} = 1 = \sin\frac{\pi}{2}$

$$\therefore \mathrm{K}_{\max}\frac{\mathrm{a}}{2} = \pm\frac{\pi}{2}$$

or $$\frac{2\pi}{\lambda_{\min}}\frac{\mathrm{a}}{2} = \frac{\pi}{2}$$

$$\therefore \lambda_{\min} = \pm 2\mathrm{a}$$

or $$\upsilon_{\max} = \frac{1}{\pi}\sqrt{\frac{\beta}{m}} = \frac{V_0}{\lambda_{\min}} = \frac{V_0}{2a} \qquad (7.17)$$

Since $\mathrm{K} = \frac{\pi}{\mathrm{a}}$ and $\frac{\mathrm{Ka}}{2} = \frac{\pi}{2}$

$\therefore$ Phase velocity $$\mathrm{V}_\mathrm{p} = \frac{2}{\frac{\pi a}{a}}V_0 \sin\frac{\pi}{2} = \frac{2}{\pi}V_0 \qquad (7.18)$$

Now substituting $\mathrm{K} = \frac{\pi}{\mathrm{a}}$ and $\frac{\mathrm{K}a}{2} = \frac{\pi}{2}$ in equation (7.16), we get

$$V_g = V_0 \cos\frac{\pi}{2} = 0 \tag{7.19}$$

So $V_g=0$ and V_p is finite. Since V_g represents the velocity of energy transmission in the medium. So no signal or energy is propagated at $K = \pm\frac{\pi}{a}$ and the wave is a standing wave.

Therefore, it is interesting to note that only frequencies $\omega \le \sqrt{\frac{4\beta}{m}}$ will propagate in a linear lattice. Thus a monoatomic lattice acts as a low-pass filter, which transmits only the frequencies in the range between zero and $\sqrt{\frac{4\beta}{m}}$.

For most of the solids $V_0 = 10^3\,\mathrm{m/sec}$ and $\lambda_{\mathrm{minimum}} = a = 10^{-10}$ m. Therefore Highest frequency limit is approximately given by $\upsilon_{\mathrm{maximum}} \approx \frac{V_0}{\lambda_{\min}} \approx \frac{10^3}{10^{-10}} \approx 10^{13}\,\mathrm{Hz}$. So the cutoff frequency of one dimensional monoatomic lattice is obtained in infrared region.

Brillouin Zones : Since the ratio of the displacements of two successive planes is given by equation (7.4) and (7.7)

$$\frac{u_n}{u_{n+1}} = \frac{A\,e^{i(\omega t - Kna)}}{A\,e^{i\{\omega t - K(n+1)a\}}} \approx e^{i\,Ka} \tag{7.20}$$

Equation (7.20) show that all independent values of e^{iKa} are covered by a range of 2π for Ka. Since the wave can propagate to both right or left, so we can take both +ive and –ive values of K. Therefore, the range of independent values of K is given by

$$-\pi \le Ka \le \pi$$

$$-\pi/a \le K \le +\pi/a \tag{7.21}$$

This range of values of K is called the first Brillouin Zone and is shown in figure (7.2) and is of utmost importance in dealing with periodic structures. The region for which $\frac{-2\pi}{a} < K < -\frac{\pi}{a}$ and $\frac{\pi}{a} < K < \frac{2\pi}{a}$ is the second Brillouin zone. The third zone corresponds to the region $\frac{-3\pi}{a} < K < \frac{-2\pi}{a}$ and $\frac{2\pi}{a} < K < \frac{3\pi}{a}$ and so on.

Since for long wavelength limit, phase and group velocities are equal. This is due to the fact that waves of long wavelength are not sensitive to the discreteness of the structure i.e. a large number of atoms participate in all displacements as on a homogeneous line. The dispersion effects are negligible and hence the medium acts as elastic, continuous and homogeneous. Since at the edge of first Brillouin zone i.e. at $K = \pm \pi/a$, V_g=0. So no energy is propagated at $K = \pm \pi/a$ and the wave is standing wave.

7.3 Vibrations of One Dimensional Diatomic Basis (Linear Lattice)

In order to study the vibrations of one dimensional diatomic lattice, let us consider a one dimensional diatomic lattice of infinite length, such as NaCl in which there are two atoms per unit primitive cell{One sodium (Na) atom and another chlorine (Cl) atom}. Let mass of one atom be m and that of the other M (m<M) and the distance between nearest neighbors be '*a*'. So the distance betweeb of same kind of atoms is 2a. The atoms are numbered in this manner that atoms of mass m are at even numbered points and those of mass M at odd numbered points. One dimensional diatomic lattice is shown in figure (7.3)

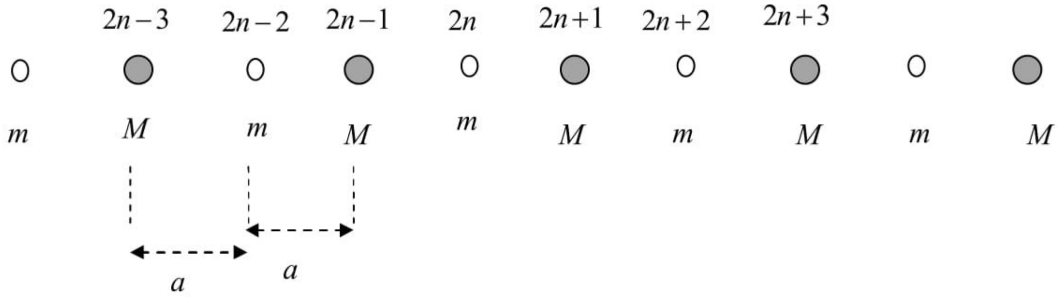


Figure 7.3: One dimensional diatomic lattice

As the atoms in the crystal start vibrating motion along the x-axis, the atoms will execute periodic motion about their equilibrium position. Let u_{2n} be the displacement of an atom corresponding to the $2n^{th}$ site at any time during vibratory motion of atoms and similarly u_{2n-1} be the displacement of another atom corresponding to the $(2n-1)^{th}$ site at the same time. Now using the similar assumptions as we have used in monoatomic case, we will obtain two different equations of motion, one for the lighter atoms of mass m and another for heavier atom of mass M. If the mutual interaction force between nearest neighboring atoms is only effective, then equations of motion will be:

$$\frac{md^2u_{2n}}{dt^2} = \beta(u_{2n+1} + u_{2n-1} - 2u_{2n}) \quad (7.22)$$

For atoms of mass M placed at odd point

$$\frac{Md^2u_{2n+1}}{dt^2} = \beta[u_{2n+2} + u_{2n} - 2u_{2n+1}] \quad (7.23)$$

Since the masses of atoms is different so their amplitude of vibrations will be different. Let A is amplitude of vibration for atom of mass m and B is amplitude of vibration for atom of mass M.

The solutions of equations (7.22) and (7.23) in the form of travelling wave with different amplitudes A and B are given by

$$u_{2n} = A\, e^{i\,(\omega t - 2\,nKa)} \quad (7.24)$$

$$u_{2n+1} = B\, e^{i\,[\omega t - (2\,n+1)Ka]} \quad (7.25)$$

Similarly we can write

$$u_{2n+2} = A\, e^{i\,[\omega t - (2\,n+2)Ka]} \quad (7.26)$$

$$u_{2n-1} = B\, e^{i\,[\omega t - (2\,n-1)Ka]} \quad (7.27)$$

where K is the wave vector of a particular mode of vibration. Since both types of atoms participate in the same wave motion, so the vibrational frequency of both types of atoms is taken to be same. Now differentiating equations (7.24) and (7.25) two times w.r. to t we get

$$\frac{d^2u_{2n}}{dt^2} = -A\omega^2\, e^{i\,(\omega t - 2nKa)}$$

Hence $$m\frac{d^2u_{2n}}{dt^2} = -Am\omega^2 e^{i\,(\omega t - 2nKa)}$$

or $$-Am\omega^2 e^{i\,(\omega t - 2nKa)} = \beta\,[Be^{i[\omega t-(2n+1)Ka]} + Be^{i[\omega t-(2n-1)Ka]} - 2A\, e^{i\,(\omega t - 2nKa)}]$$

or $$-m\omega^2\, A = \beta B(e^{iKa} + e^{-iKa}) - 2\beta A \quad (7.28)$$

Similarly $$M\frac{d^2u_{2n+1}}{dt^2} = -BM\omega^2 e^{i[\omega t-(2n+1)Ka]}$$

from equation (7.23), (7.25), and (7.26)

$$\therefore -BM\omega^2\, e^{i[\omega t-(2n+1)Ka]} = \beta\{A\, e^{i[\omega t-(2n+2)\,Ka]} + A\, e^{i(\omega t-2nKa)} - 2B\, e^{i[\omega t-(2n+1)Ka]}\}$$

or $$-M\omega^2 B = \beta A(e^{iKa} + e^{-iKa}) - 2\beta B$$

Since $\quad e^{iKa} + e^{iKa} = 2\cos \mathrm{Ka}$

$$-M\omega^2 B = \beta A 2 \cos \mathrm{Ka} – 2\beta \mathrm{B}$$

$$\therefore (2\beta - M\omega^2)B = 2\beta A \cos Ka \ldots$$

or $\quad -2\beta \text{ A } \cos\mathrm{Ka} + (2\beta - M\omega^2)B = 0 \qquad (7.29)$

From equation (7.28)

$$(2\beta - m\omega^2)A - 2\beta B \cos Ka = 0 \qquad (7.30)$$

From equation (7.29) and (7.30) nonvanishing solutions for A and B can possible only if the determinant of the coefficients of A and B is zero.

$$\begin{vmatrix} (2\text{ B}–\mathrm{M}\omega^2) & -2\beta\cos Ka \\ -2\beta \cos Ka & 2\beta - M\omega^2 \end{vmatrix} = 0$$

or $\quad (2\beta – \mathrm{m}\omega^2)\ (2\beta - m\omega^2) - 4\beta^2 \cos^2 Ka = 0$

$$4\beta^2 - 2\beta m\omega^2 - 2\beta M\omega^2 + mM\omega^4 - 4\beta^2 \cos^2 Ka = 0$$

$$mM\omega^4 - 2\beta\omega^2(m + M) + 4\beta^2(1 - \cos^2 Ka) = 0$$

or $\quad \omega^4 - 2\beta\left(\dfrac{m+M}{mM}\right)\omega^2 + \dfrac{4\beta^2}{mM}\sin^2 Ka = 0 \qquad (7.31)$

Equation (7.31) is a quadratic equation in ω^2 and its solution will be

$$\omega^2 = \beta\left[\frac{1}{m} + \frac{1}{M}\right] \pm \beta\sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - 4\frac{\sin^2 Ka}{mM}} \qquad (7.32)$$

Equation (7.32) represents dispersion relation for linear diatomic lattice. From equation (7.11) the corresponding dispersion relation for monoatomic lattice is

$$\omega^2 = \frac{4\beta}{m}\sin^2 Ka$$

We know that ω should always be positive. We find that in monoatomic case there is only one value of ω for a single value of K ,whereas in diatomic lattice case there are two values of ω for single value of K. These two values of ω can be represented as ω_+ and ω_- .

$$\therefore \omega_+^2 = \beta\left[\frac{1}{m} + \frac{1}{M}\right] + \beta\sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - 4\frac{\sin^2 Ka}{mM}} \qquad (7.33)$$

and $\quad \omega_-^2 = \beta\left[\dfrac{1}{m} + \dfrac{1}{M}\right] - \beta\sqrt{\left(\dfrac{1}{m} + \dfrac{1}{M}\right)^2 - 4\dfrac{\sin^2 Ka}{mM}} \qquad (7.34)$

Various branches of the dispersion relation curve: Since the graph between ω and K leads to two different branches: one branch corresponding to ω_+ is known as optical branch, while another branch corresponding to ω_- is known as acoustical branch as shown in figure (7.4).

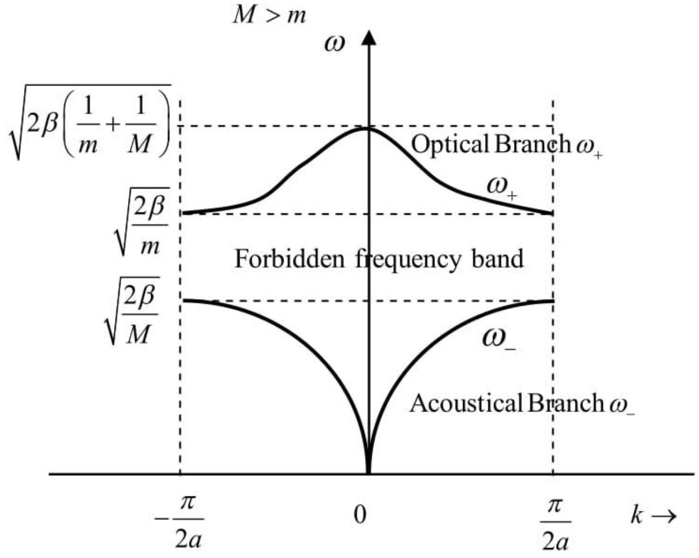


Figure 7.4: Dispersion Curve For One Dimensional Diatomic Lattice

(1) Optical mode (branch): Now we take case of ω_+, for $K \rightarrow 0$ we know that $\sin Ka \rightarrow 0$, so from equation (7.33) we get

$$\omega_+^2 = 2\beta\left(\frac{1}{m}+\frac{1}{M}\right) \quad \therefore\ \omega_+ = \sqrt{2\beta\left(\frac{1}{m}+\frac{1}{M}\right)} \tag{7.35}$$

Now for $K \rightarrow \frac{\pi}{2a}$, $\sin Ka = \sin\frac{\pi}{2a}a = \sin\pi/2 = 1$,so from equation (7.33)

$$\omega_+^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) + \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4}{mM}} = \beta\left(\frac{1}{m}+\frac{1}{M}\right) + \beta\left(\frac{1}{m}-\frac{1}{M}\right) = \frac{2\beta}{m}$$

$$\therefore \omega_+ = \sqrt{\frac{2\beta}{m}} \tag{7.36}$$

(2) Acoustical mode (branch) : Now we take case of ω_-, for $K \rightarrow 0$ we can write $\sin Ka = Ka$ .We cannot take $\sin Ka = 0$,because if we take $\sin Ka = 0$, then value of ω_- comes out to be zero, that is not acceptable. So from equation (7.34) we get

$$\therefore \omega_-^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) - \beta\left(\frac{1}{m}+\frac{1}{M}\right)\sqrt{1 - \frac{4K^2a^2}{mM}\left(\frac{mM}{m+M}\right)^2}$$

or $$=\beta\left(\frac{1}{m}+\frac{1}{M}\right)\left[1-\left\{1-\frac{4K^2a^2}{mM}\left(\frac{mM}{m+M}\right)^2\right\}^{1/2}\right]$$

Now applying binomial theorem and neglecting higher power

or $$\omega_-^2=\beta\left(\frac{1}{m}+\frac{1}{M}\right)\left[1-1+\frac{mM\,2K^2a^2}{(m+M)^2}+....\right]$$

or $$\omega_-^2=\left(\frac{2\beta}{m+M}\right)K^2a^2$$

or $$\omega_-=Ka\sqrt{\frac{2\beta}{m+M}} \tag{7.37}$$

Now for $K=\frac{\pi}{2a}$, then $\sin Ka=\sin\frac{\pi}{2a}a=\sin\pi/2=1$ .So from equation (7.34)

$$\omega_-^2=\beta\left[\frac{1}{m}+\frac{1}{M}\right]-\beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2-\frac{4}{mM}}$$

$$=\beta\left[\frac{1}{m}+\frac{1}{M}\right]-\beta\sqrt{\left(\frac{1}{m}-\frac{1}{M}\right)^2}=\beta\left[\frac{1}{m}+\frac{1}{M}\right]-\beta\left[\frac{1}{m}-\frac{1}{M}\right]$$

$$\therefore\omega_-^2=\frac{2\beta}{M}\quad\text{or}\quad\therefore\omega_-=\sqrt{\frac{2\beta}{M}} \tag{7.38}$$

The whole curves for ω_+ and ω_- against K are shown in figure (7.4). In order to understand the physical importance of existing vibrations in the both branches i.e. acoustic and optical. We determine the value of $\frac{A}{B}$.

In optical branch when $K\to 0$, then $\cos Ka\to 1$ and from equation (7.30)

$$(2\beta-m\omega^2)A-2\beta B=0$$

or $$\frac{\omega^2}{2\beta}=-\left(\frac{A-B}{mA}\right) \tag{7.39}$$

Similarly from equation (7.29)

$$-2\beta A+(2\beta-M\omega^2)B=0$$

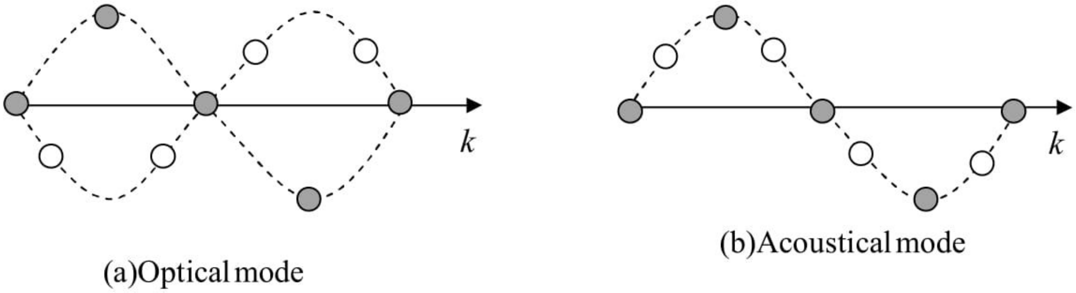
or $$\frac{\omega^2}{2\beta}=-\left(\frac{A-B}{M\,B}\right) \tag{7.40}$$

Comparing equation (7.39) and (7.40) we shall get

$$\mathrm{m\,A = -M\,B}$$

or $$\frac{\mathrm{A}}{\mathrm{B}} = -\left(\frac{\mathrm{M}}{\mathrm{m}}\right) \tag{7.41}$$

This shows that in optical branch the atoms vibrate in opposite direction and their amplitudes are inversely in the ratio of their masses in such a way that their centre of mass (of unit cell) remains at rest during the period of motion. Such type of mode of vibration is shown in figure. (7.5) (a)



(a)Optical mode

(b)Acoustical mode

Figure 7.5: Types of modes of vibrations

When $\mathrm{m = M}$, $\frac{\mathrm{A}}{\mathrm{B}} = -1$

So, eventhough their masses are equal, atoms always move in opposite directions.

Now in acoustical branch as $\mathrm{K} \to 0$, then $\cos \mathrm{Ka} = 1 - \frac{\mathrm{K^2a^2}}{2} + \ldots..$

In this case, we cannot neglect second term because it is significant. So from equation (7.30) we get

$$(2\beta - m\omega^2)A \;\; -2\beta B\left(1 - \frac{K^2a^2}{2}\right) = 0$$

$$-m\omega^2 A = 2\beta B\left(1 - \frac{K^2a^2}{2}\right) - 2\beta A \tag{7.42}$$

Similarly from equation (7.29) we get

$$-2\beta A\left(1 - \frac{K^2a^2}{2}\right) + (2\beta - M\omega^2)B = 0$$

or $$-M\omega^2 B = 2\beta A\left(1 - \frac{K^2a^2}{2}\right) - 2\beta B \tag{7.43}$$

Now adding equations (7.42) and (7.43), we get

$$-\omega^2\left(mA + MB\right) = -K^2a^2\beta(A + B)$$

from equation (7.37) $\omega = Ka\sqrt{\frac{2\beta}{m+M}}$

or $$\omega^2 = K^2a^2\left(\frac{2\beta}{m+M}\right)$$

$$-K^2a^2\left(\frac{2\beta}{m+M}\right)(mA + MB) = -K^2a^2\beta(A+B)$$

or $$2(mA + MB) = (m+M)(A+B)$$

or $$m\,A + M\,B = M\,A + m\,B$$

$$(m - M)\,A = (m - M)\,B$$

$$\therefore \frac{A}{B} = +1 \tag{7.44}$$

Thus in the acoustical branch ,the two atoms of different masses i.e. lighter (m) and heavier (M) move in the same direction with the same amplitudes as shown in figure (7.5) (b). In acoustic branch ,there is movement of centers of masses as well.

The acoustical branch can be excited by same kind of force, that forces all the atoms in the crystal to go in the same direction such as sound waves. This is the reason that it is called as acoustic branch. Such type of vibrations exist in monoatomic crystals, while the optical branch vibrations can be excited by a force that produces opposite effect on the two atoms. This type of motion can be excited by means of electric field of the light waves which tends to move the ions in opposite directions. The term optical branch is used for this case as these wave interact with light waves ,example is of diamond.

Forbidden Frequency Band:

We know that in optical branch (ω_+ branch), the value of ω_+ is maximum for K=0 and minimum for $K = \pm\frac{\pi}{2a}$.

$$\omega_{+(\max)} = \sqrt{2\beta\frac{(m+M)}{mM}}$$

and $$\omega_{+(\min)} = \left[\beta\left(\frac{m+M}{mM}\right) + \beta\left\{\left(\frac{m+M}{mM}\right)^2 - \frac{4}{mM}\right\}^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

$$= \left[\beta \left(\frac{m+M}{mM} \right) + \beta \frac{(M-m)}{mM} \right]^{\frac{1}{2}} = \sqrt{\frac{2\beta}{m}} \tag{7.45}$$

Similarly in acoustic branch (ω_- branch), the value of ω is minimum (zero) for K=0 and maximum for $K = \pm \frac{\pi}{2a}$.

$$\text{So } \omega_{-(\min)} = 0 \text{ and } \omega_{-(\max)} = \sqrt{\frac{2\beta}{M}}$$

From figure (7.4) it is clear that in frequency band $\sqrt{\frac{2\beta}{m}} < \omega > \sqrt{\frac{2\beta}{M}}$ wave like solutions do not exist. In other words there is a band of frequencies between the two branches that cannot propagate in one dimensional diatomic lattice. This frequency interval is known as forbidden frequency band (gap). This is shown in figure (7.4) by dotted portion. The width of this forbidden band depends on the difference of the masses i.e. (M–m). The larger the mass ratio $\left(\frac{M}{m}\right)$ the frequency gap between two branches is wider. If M=m ,the acoustical and optical frequency coincide at $K = \pm \frac{\pi}{2a}$ and forbidden band tends to zero . In this manner one dimensional diatomic lattice behaves as a mechanical band stop filter. The first Brillouin zone in the case of one dimensional diatomic lattice lies between the following values of K, $\left(\frac{-\pi}{2a}\right) \le K \le \left(\frac{+\pi}{2a}\right)$ .Hence we can say that the smallest possible wavelength of this first zone is 4a which corresponds to $K = \pm \frac{\pi}{2a}$ at the zone boundary.

Some important facts pertaining to one dimensional diatomic lattice are following:

(1) If the masses m and M are equal, the frequency range in both monoatomic and diatomic lattice is same. There forbidden frequency band does not exist.

(2) At Brillouin zone boundary $\left(K = \pm \frac{\pi}{2a}\right)$ only one of the sublattices vibrate, the lighter atom (m) vibrates in the optical branch, whereas the heavier atom (M) vibrates in acoustical branch .

(3) If the heavier mass M tends to infinity, then acoustical branch disappears and the optical branch becomes flat such that all K values have same frequency.

(4) The optical branch disappears, if the lighter mass m tends to zero and the acoustical branch remains as it is.

(5) Only those frequencies which lie in discrete bands corresponding to the optical and acoustical branches can propagate through lattice.

(6) Since the optical mode is actually the natural frequency of the lighter atoms m, which is perturbed by the heavier sublattice. At $K = \frac{\pi}{2a}$ the heavy atom is stationary and the natural frequency of the vibrating lighter atoms is $\sqrt{\frac{2\beta}{m}}$.

7.4 Quantization of Elastic Waves : Concept of Phonon

We know that solid is composed of atoms, which are closely packed by fixed forces or bonds. These bonds work as coupling between two neighboring atoms. So when any atom acquires the state of vibration, then all the atoms start vibrating, because these bonds transmit these vibrations successively. These vibrations in atoms, construct elastic waves in solid. Since these atoms are present at the lattice point, so these vibrations are also known as lattice vibrations.

As we have studied that the energy of an electromagnetic wave is quantized and the quantum of energy is known as photon. In the similar manner the energy of lattice vibrations or an elastic waves is also quantized and the quantum of this energy is known as phonon. All Kinds of lattice vibrations are composed of phonons or elastic waves in crystal are made up of phonons. Thermal vibrations in crystal are thermally excited phonons like the thermally excited photons of black body electromagnetic radiations in a cavity. Sound waves are acoustic phonons and the excitation of the optical branch results in optical phonons . All the concepts like wave-particle duality which apply to photons also apply to phonons. A phonon wave travels in a medium with the velocity v of sound. The energy of a phonon is given by $h\nu = \hbar\omega$. Where ω is angular frequency of a mode of vibration. According to quantum theory the energy of an elastic mode of angular frequency ω is

$$\in = \left(n + \frac{1}{2}\right)\hbar\omega \qquad (7.46)$$

i.e. the mode is excited to quantum number n. The term $\frac{1}{2}\hbar\omega$ is the zero point energy of the mode. It occurs for both phonons and photons as a consequence of their equivalence to a quantum harmonic oscillators of frequency ω, for which the energy eigen values are also $\left(n+\frac{1}{2}\right)\hbar\omega$. Hence the energy of a quantum of elastic wave of lattice vibration i.e. phonon is therefore quantized. The experimental evidence that the energy of an elastic wave or phonon is quantized is provided by the fact that the lattice contribution to the heat capacity of solids always tends to zero as the temperature approaches zero. This can be explained only if the lattice vibrations are quantized. Another experimental evidence for phonons is found in inelastic scattering of x-rays and scattering of neutrons by crystals in which momentum and energy changes corresponding to the creation or absorption of one or more phonons. Similarly by measuring the recoil of scattered x-rays or neutrons, we can determine the properties of the individual phonon. The frequency range of phonon wave may vary from 10^4–10^{12} Hz. The lower frequency lies in the acoustic region and consists of sound waves in a crystal lattice, while the higher frequency lies in the infrared region and is due to thermal vibrations in a crystal. Since phonons like photons have finite spin quantum number. So phonons obey Bose-Einstein statistics and B.E. distribution law.

7.5 Phonon Momentum

A phonon on a lattice does not carry momentum. While a phonon of wave vector K interacts with other particles and behaves as if its momentum were $\hbar$K. This momentum $\left(\hbar K=\frac{\hbar}{2\pi}\times\frac{2\pi}{\lambda}=\frac{h}{\lambda}\right)$ is also known as crystal momentum. In crystals there exist selection rules for wave vector (K) for allowed transitions between quantum states. The physical significance of $\hbar$K is provided by the momentum conservation laws in crystals. We have seen that the elastic scattering of x-ray photon by a crystal i.e. Braggs diffraction is governed by the wavevector selection rule or wavevector conservation law:

$$\vec{K}'=\vec{K}+\vec{G} \tag{7.47}$$

where $\vec{K}'$ is the wavevector of scattered photon, $\vec{K}$ is wavevector of incident photon and $\vec{G}$ is the reciprocal lattice vector of crystal. In this case the crystal as a whole will recoil with momentum $-\hbar\vec{G}$. In this process the frequency remains unchanged and is called normal process.

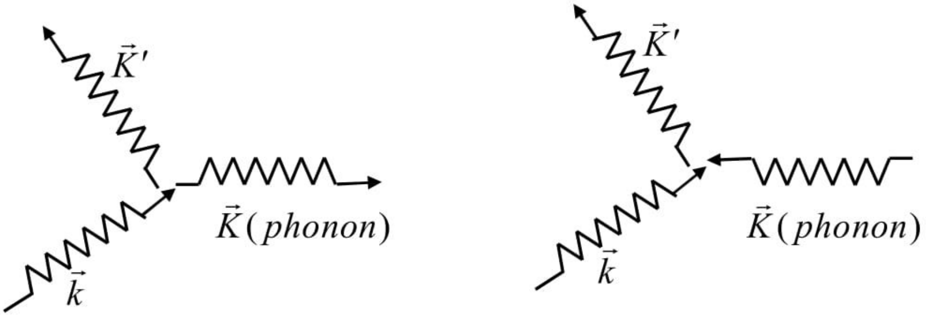
Hence equation (7.47) is an example of the rule that the total wavevector of interacting waves is conserved in a periodic lattice, with the possible addition of a reciprocal lattice vector ($\vec{G}$). So the true momentum of the whole system always is rigorously conserved.

If the scattering of the photon by crystal is inelastic, the frequency of the incident photon changes and a phonon is created (emitted) or absorbed in the process.

(I) If a phonon of wavevector $\vec{K}$ is created (emitted) during the scattering then applying wavevector conservation law we get:

$$\underset{\text{(scattered)}}{\vec{K}'} + \vec{K} = \underset{\text{(incident)}}{\vec{k}} + \vec{G} \tag{7.48}$$

where $\vec{K}$ is the wave vector of created phonon as shown is figure (7.6a)



Emission of Phonon Absorption of Phonon

Figure 7.6(a),(b) Emission and absorption of phonon in an inelastic scattering of photon

(II) If a phonon of wave vector $\vec{K}$ is absorbed during the scattering ,then applying wave vector conservation law we get:

$$\underset{\text{(scattered)}}{\vec{K}'} = \underset{\text{(incident)}}{\vec{k}} + \vec{K} + \vec{G}$$

This is shown in figure 7.6 (b). Hence the process in which frequency of incident photon changes is called an UmKlapp process and in this process the momentum is transferred to the crystal as whole.

7.6 Inelastic Scattering by Phonons

(a) Now we study the inelastic scatting of photons by phonons . We know that a crystal can be considered to be a continuum of refractive index μ . When a photon of frequency $\upsilon = \dfrac{\omega}{2\pi}$ is propagating in a crystal ,then wavevector of photon is given by

$$K=\frac{\omega\mu}{C} \text{ or } \quad \omega=\frac{CK}{\mu} \qquad \text{Or} \qquad \lambda\upsilon=v_s=\frac{C}{\mu} \tag{7.49}$$

where c is velocity of light. Now the photon interacts with a phonon beam i.e. with a sound wave in the crystal and this photon is scattered by sound wave, because refractive index of the crystal changes due to change in concentration of atoms brought about by the elastic strain field of the sound waves. Therefore sound wave can also change optical properties of the medium. On the other hand, the reverse is also true, i.e. the electric field of light wave sets up mechanical vibrations in the medium and thereby changing the elastic properties of the medium.

We know that in an inelastic scattering of photon by the crystal, phonon can be either created (emitted) or absorbed. In this process of scattering ,let the ω wave vector of the photon changes from $\vec{K}$ to $\vec{K}'$ and its frequency changes from ω to ω'. A phonon of wave vector $\vec{k}$ and frequency Ω be created (emitted) during the inelastic scattering as shown in figure 7.7 (a).

Then according to the law of conservation of energy, we have

$$\hbar\omega=\hbar\omega'+\hbar\Omega \tag{7.50}$$

and according to the law of conservation of momentum, we have

$$\hbar\vec{K}=\hbar\vec{K}'+\hbar\vec{k} \tag{7.51}$$

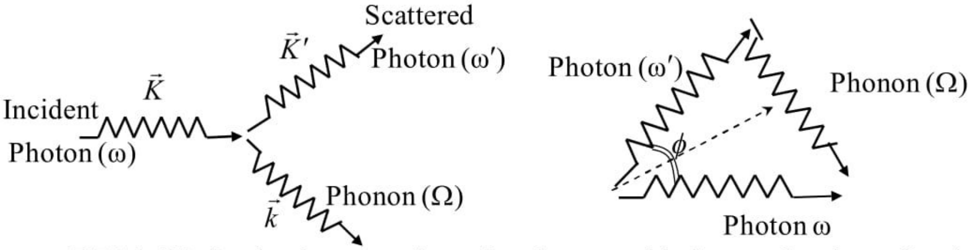


Figure 7.7(a),(b) (Inelastic scattering of a photon with the production of a phonon)

Now if V_s velocity of sound is constant, then the angular frequency (Ω) of created phonon having wavevector k is given by

$$V_s=\lambda\upsilon=\lambda\frac{\Omega}{2\pi}$$

$$\text{or} \qquad \Omega=V_s\frac{2\pi}{\lambda}=V_s\,k \tag{7.52}$$

Since the emitted phonon can carry only a fraction of the energy of the incident photon. We know that velocity of sound $V_s \ll c$. If k is comparable in magnitude with K, we have $V_S k << cK$. Also $\omega = cK$ and $\Omega = V_S k$, therefore $\omega >> \Omega$. So from equation (7.50) ,we have $\omega' \approx \omega$ and therefore, $K' \approx K$. So the process as shown above in figure 7.7(a), can be represented by the momentum balance diagram in figure 7.7(b). If $K' = K$, then the triangle becomes isosceles. The base of the triangle is given by

$$\mathrm{k} = 2\mathrm{K} \sin \phi / 2 \tag{7.53}$$

Putting the value of $K = \mu \dfrac{\omega}{c}$ from equation (7.49) in equation (7.52) and using equation (7.53), we get

$$\mathrm{V_s k} = \frac{2\mathrm{V_s}\omega\mu}{\mathrm{C}} \sin\frac{\phi}{2}$$

or

$$\Omega = \frac{2\mathrm{V_s}\omega\mu}{\mathrm{C}} \sin\frac{\phi}{2} \tag{7.54}$$

This gives the frequency of created (emitted) phonon, when photons are scattered inelastically at an angle ϕ from the incident direction. Now if the calculated and experimental values of Ω are very close, then we have very strong evidence in favor of phonon's existence and their behavior

(b) In the similar manner neutron inelastic scattering by phonons is the most common method for the experimental determination of phonon dispersion relations. It is also possible to obtain phonon lifetime from the angular width of the scattered neutron beam. A neutron sees the crystal lattice mainly by interaction with the nuclei of the atoms. The kinematics of the inelastic scattering of a neutron beam by the crystal lattice are described by the general wavevector selection rule:

$$\vec{K} + \vec{G} = \vec{K}' \pm \vec{k} \tag{7.55}$$

Here $\vec{k}$ is the wave vector of the phonon emitted (+) or absorbed $(-)$ in the process and $\vec{G}$ is reciprocal lattice vector. We choose $\vec{G}$ such that k lies in the first Brillouin zone, as it must for a phonon. $\vec{K}$ is wavevector of incident neutron and $\vec{K}'$ is wave vector of scattered neutron.

According to law of conservation of energy:

$$\frac{\hbar^2 K^2}{2M_n} = \frac{\hbar^2 K'^2}{2M_n} \pm \hbar\omega \tag{7.56}$$

where M_n is mass of neutron and $\hbar\omega$ is the energy of phonon created (+) or absorbed (−) in the process. The dispersion relation can be obtained from equations (7.55) and (7.56). It is necessary in the experiment to find energy gain or loss of the scattered neutrons as a function of the scattering direction $\vec{K} - \vec{K}'$.

7.7 Self Learning Exercise

Q.1 What do you mean by lattice?

Q.2 What is UmKlapp process?

Q.3 Explain forbidden energy gap in one dimensional diatomic lattice, in which wave cannot transmit.

7.8 Summary

In this unit we have studied about vibration of one dimensional monoatomic lattice and diatomic lattice. We find that in monoatomic lattice there is only one value of ω for a single value of K ,whereas in diatomic lattice there are two values ω for single value of K. These two values of ω can be represented by ω_+ and ω_-. The branch corresponding to ω_+ is the optical branch, while the branch corresponding to ω_- is acoustical branch. There is a forbidden energy gap between these two branches. The width of this forbidden band depends on the difference of masses. If masses of two atoms in diatomic lattice are equal i.e. M=m, then frequency range in both monoatomic and diatomic lattices is the same and there is no forbidden region. The quantum unit of a lattice vibration is a phonon. If the angular frequency is ω, then the energy of phonon is $\hbar\omega$. When a phonon of wavevector K is created by inelastic scattering of a photon or neutron from crystal then wavevector changes from $\vec{K}$ to $\vec{K}'$. The wavevector selection rule that governs the scattering process is $\vec{K} = \vec{K}' + \vec{k} + \vec{G}$, where $\vec{G}$ is a reciprocal lattice vector. All lattice waves can be described by wave vectors that lie within the first Brillouin zone in reciprocal space.

7.9 Glossary

Phase Velocity: $v_p = \dfrac{\omega}{k}$

Group Velocity: $v_g = \frac{d\omega}{dk}$

7.10 Answers to Self Learning Exercise

Ans.1: A lattice consisting of linear chains or lines of atoms.

Ans.2: If in an inelastic scattering of a photon by a crystal, the frequency of the photon changes is known as UmKlapp process.

7.11 Exercise

Section-A :Very short Answer Type Questions

Q.1 What is lattice vibrations.

Q.2 What do you mean by diatomic lattice?

Q.3 What is phonon?

Section-B : Short Answer Type Questions

Q.4 Deduce vibrational modes of a finite one-dimensional monoatomic lattice.

Q.5 Differentiate between optical and acoustical branches of diatomic linear lattice.

Q.6 What are normal and UmKlapp process ? Explain it with the help of vector diagram?

Q.7 Explain briefly quantization of lattice vibrations.

Section-C: Long Answer Type Questions

Q.7 Show that the dispersion relation for the lattice waves in an one dimensional monoatomic lattice of mass m, spacing *a* and nearest neighbor interaction β is $\omega = \sqrt{\frac{4\beta}{m}} \sin\left| 1/2\vec{K}a \right|$ where ω is the angular frequency and $\vec{K}$ the wave vector.

Q.9 Derive the vibrational modes of a diatomic linear lattice. Name the different branches of the dispersion relation curve. Show that the group velocity vanishes at the zone boundary. Give the physical interpretation of the result.

Q.10 What is phonon? What is phonon momentum? What are the experimental evidences that the energy of an elastic wave is quantized.

Q.11 Discuss the inelastic scattering of photon by phonons and obtain the expression for the frequency of phonon emitted in the process.

Q.12 Calculate the maximum phonon frequency generated by scattering of visible light of wave length 5000A^0. Given velocity of sound V_s=5×10^{5}cm/sec and refractive index $\mu = 1.5$ .Also calculate the wave vector of the phonon.

7.12 Answers to Exercise

Ans.1: The interatomic interaction, however, causes the atoms or molecules present at the lattice point to vibrate about their mean position. These vibrations are known as lattice vibration.

Ans.2: If there are two atoms per unit primitive cell, then this type of lattice formed by these atoms is known as diatomic lattice.

Ans.3: A quantum of elastic wave of lattice vibration is known as phonon.

Ans.12: (I) Maximum phonon frequency$= \Omega = 1.89 \times 10^{11}$ / Sec

(II) Wavevector of phonon $\vec{K} = 3.77 \times 10^5 / \text{cm}$

References and Suggested Readings

1. Introduction to solid state Physics by C. Kittel
2. Elementary Solid state Physics by Rama Swami
3. Solid State Physics by A.J. Dekker
4. Fundamentals of Solid State Physics by Saxena, Gupta and Saxena
5. Solid State Physics By S. O. Pillai

UNIT-8

Thermal Properties of Solids

Structure of the Unit

8.0 Objectives

The aim of this unit to know about thermal properties of solid, such as specific heat or heat capacity, thermal conductivity and thermal expansion. We will discuss the Einstein and Debye approximation to the phonon heat capacity associated with the lattice vibrations of crystals. The features of more exact calculations are shown.

Then we consider effects of anharmonic lattice interaction including thermal expansion and the thermal conductivity of lattice. In the last we will discuss Umklapp process.

8.1 Introduction

In unit (7) we studied the dynamical properties of lattice. In this unit, we want to study the thermal properties of lattice. For this, we must know an expression for the internal energy “U” of the lattice. In case of solids (crystal) the model of a vibrating lattice that we have developed in unit (7) will provide the information we need .We know that heat capacity per unit of mass of a substance is known as specific heat. Specific heat is really a measure of degrees of freedom of a system. Since degree of freedom imply freedom to absorb potential or kinetic energy. Here System is the oscillating lattice. Atoms vibrate about their mean equilibrium lattice points in a solid. These vibrations occur at any temperature, even near absolute Zero. They are almost entirely responsible for the thermal properties , heat capacity, thermal expansion and thermal conductivity etc. of insulators and contribute the greater part of heat capacity of metals. The conduction electrons contribute only a small part of heat capacity to metals but are almost entirely responsible for the thermal conductivity of metals.

8.2 Phonon Heat Capacity

As we have studied that energy of a lattice vibration or an elastic wave is also quantized and a quantum of this energy is known as phonon. All types of lattice vibrations in crystals comprise phonons. Thermal vibrations are thermally excited phonons, sound waves are acoustical phonons and excitations of the optical branch generate optical phonons. So phonon is associated with lattice vibrations. Hence phonon heat capacity is also known as lattice heat capacity.

An ideal solid may be considered as consisting of a space lattice of independent atoms vibrating about their mean position, however, the atoms are assumed to be non-interacting with each other and their vibrations is considered strictly harmonic. Whenever heat energy is imparted to solids, then their temperature and internal energy increase. In solids, the increase in internal energy takes place in two ways:

(i) The atoms, which ordinarily vibrate freely about their equilibrium positions, are set into rigorous vibrations. This is manifested by a rise in temperature.

(ii) The free electrons in case of semiconductors and metals get thermally excitation to higher energy states.

If we denote the energy contribution due to atomic vibrations in crystal lattice as U_{lattice} and thermal excitation of electrons as U_{electron}, then

Internal energy of Solid $U = U_{\text{lattice}} + U_{\text{electron}}$ (8.1)

So specific heat of solid at constant volume

$$C_V = \left(\frac{dU}{dT}\right)_V$$

$$\therefore C_v = \left(\frac{dU}{dT}\right)_V = \frac{dU_{lattice}}{dT} + \frac{dU_{electron}}{dT}$$

$$\therefore C_V = C_{V\,lattice} + C_{V\,electron} \tag{8.2}$$

The quantity C_V is known as lattice specific heat or lattice heat capacity i.e. phonon heat capacity. In discussing the specific heat of solids like crystal, we assume that no free electrons are present and the entire specific heat of a crystal is due to the excitations of thermal vibrations of the lattice.

Therefore, for our discussion,

$$(C_V)_{\text{solid}} = C_{V\,lattice} \tag{8.3}$$

By heat capacity, we shall usually mean the heat capacity at constant volume, which is more fundamental than the heat capacity at constant pressure, that is what the experiments determine. In the case of solids, the two specific heats donot differ very much, specially at low temperature. This is due to the fact that the volume expansion of solids is small and work done in expansion is generally negligible. There is a small difference (about 2%) in C_p and C_v at ordinary temperature (at 300K). The heat capacity at constant volume is defined as

$$C_V = T\Sigma\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{8.4}$$

where S is the entropy, U the internal energy and T the temperature.

8.3 Planck's Distribution

Planck had given theory in 1900 for the explanation of Black body spectrum, known as quantum theory. According to Planck, a harmonic oscillator does not have continuous energy spectrum, as considered in the classical theory. But it can have only energy values equal to an integer time $h\upsilon$, where h is Planck's constant and υ is frequency. Thus the possible energy levels of an oscillator may be represented as:

$$\varepsilon_n = nh\upsilon \quad ,\text{where n} = 0,1,2,3,\ldots \tag{8.5}$$

Average energy is given by

$$\langle\varepsilon\rangle = \frac{\int_0^\infty (nh\upsilon)e^{-\frac{nhv}{kT}}d\upsilon}{\int_0^\infty e^{-\frac{nhv}{kT}}d\upsilon} \tag{8.6}$$

As the energy values are not continuous but discrete. So that integration is replaced by summations, we have for average energy;

$$\langle\varepsilon\rangle = \frac{\sum_{n=0}^{\infty}(nh\upsilon)e^{-\frac{nh\upsilon}{kT}}}{\sum_{n=0}^{\infty}e^{-\frac{nh\upsilon}{kT}}} \tag{8.7}$$

To evaluate this equation (8.7) first consider the denominator

$$\sum_{n=0}^{\infty}e^{-\frac{nh\upsilon}{kT}} = 1 + e^{-\frac{h\upsilon}{kT}} + e^{-\frac{2h\upsilon}{kT}} + e^{-\frac{3h\upsilon}{kT}} + \ldots\ldots\ldots\ldots = \left[1 - e^{-\frac{h\upsilon}{kT}}\right]^{-1} \tag{8.8}$$

Differentiating equation (8.8) w.r.to T, One obtains

$$\sum_{n=0}^{\infty}\left(-\frac{nh\upsilon}{k}\right)e^{-\frac{nh\upsilon}{kT}}\left(\frac{-1}{T^2}\right) = -1\left[1 - e^{-\frac{h\upsilon}{kT}}\right]^{-2}\left[\frac{h\upsilon}{k}e^{-\frac{h\upsilon}{kT}}\right]\left[-\frac{1}{T^2}\right]$$

or $$\sum nh\upsilon e^{-\frac{nh\upsilon}{kT}} = \frac{h\upsilon e^{-\frac{h\upsilon}{kT}}}{\left[1 - e^{-\frac{h\upsilon}{kT}}\right]^2} \tag{8.9}$$

Now substituting the values from (8.9) and (8.8) into equation (8.7) we get

Energy of each oscillator $$\langle\varepsilon\rangle = \frac{h\upsilon e^{-\frac{h\upsilon}{kT}}}{1 - e^{-\frac{h\upsilon}{kT}}} = \frac{h\upsilon}{\left(e^{\frac{h\upsilon}{kT}} - 1\right)} \tag{8.10}$$

Equation (8.10) represents Planck's distribution formula.

The normal modes of vibration of a lattice are independent if Hooke's law is applicable. Thus the energy of a lattice mode depends only on its frequency ν, and phonon occupancy n, and is independent of the occupancy of the other lattice modes. In thermal equilibrium at temperature T ,the occupancy of a phonon mode is given by the plank's distribution law

$$\langle n \rangle = \left(\frac{1}{e^{\frac{hv}{kT}} - 1} \right) \tag{8.11}$$

where < > denotes the average in thermal equilibrium and k is the Boltzmann's constant.

8.4 Normal Mode Enumeration

The energy in thermal equilibrium of a collection of oscillators of different frequencies v_K is

$$U = \sum_k n_K h v_K \tag{8.12}$$

where each n is related to v_K by the Planck distribution law. It is often convenient to replace the summation by an integral. Suppose that the crystal has $Z(v)dv$ modes of vibrations in the frequency range v to $v + dv$. Then the energy is

$$U = \int dv\, Z(v) n(v,T) hv \tag{8.13}$$

The heat capacity is found from this by differentiation of $n(v,T)$ with respect to temperature .The general problem is to find $Z(v)$, the number of modes per unit frequency range. This function is also called the density of modes. The best practical way to obtain the density of modes is to measure the dispersion relation in selected crystal direction by inelastic scattering of neutrons.

8.5 Density of States in One Dimension

Consider a one-dimensional continuous string of a length L to be vibrating with its fixed ends. Let $u(x,t)$ represents the displacement of the string at any point x at any instant . Then the wave equation will be

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v_s^2} \frac{\partial^2 u}{\partial t^2} \tag{8.14}$$

where $v_s = \sqrt{\frac{Y}{\rho}}$ represents the velocity of propagation of the wave along the one dimensional equation. Since the end points of the string are fixed , the solution of equation (8.14) should corresponds to standing waves.

$$u(x,t) = A\sin\left(\frac{n\pi x}{L}\right)\cos 2\pi \upsilon_n t \tag{8.15}$$

where n is a positive integer ≥ 1. The wavelengths and frequencies of the possible vibrations represented by equation (8.15) are given by

$$\lambda_n = \frac{2L}{n} \quad \text{and} \quad \upsilon_n = \frac{v_s}{\lambda_n} = \frac{nv_s}{2L} \tag{8.16}$$

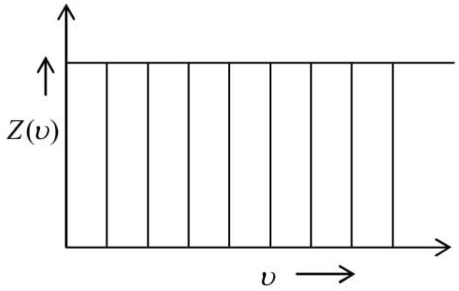


Figure (8.1) [Frequency spectrum of a continuous string]

From equation (8.16), it is clear that frequency of the string has discrete values only. The frequency spectrum is discrete ,one frequency corresponding to each integer value n. Note that for one dimensional string the frequency spectrum corresponds to an infinite number of equidistant lines as illustrated in Figure (8.1). From equation (8.16), we have

$$n = \frac{2L}{v_s}\upsilon_n \tag{8.17}$$

The number of possible modes of vibrations in a frequency interval $d\upsilon$ is obtained by differentiating equation (8.17) we shall get

$$dn = \left(\frac{2L}{v_s}\right)d\upsilon \tag{8.18}$$

i.e. equation (8.18) gives the number of possible modes of vibrations in frequency interval $d\upsilon$ in one dimensions i.e. density of states in one dimensions.

8.6 Density of States in Three Dimensions

In three-dimensional case, the wave equation leads

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{v_s^2}\frac{\partial^2 u}{\partial t^2} \tag{8.19}$$

Assuming a continuous medium in the shape of a cube of edge L , whose faces are fixed .The possible standing wave solution of equation (8.19) in analogy with (8.15) is given by

$$u(x,y,z,t) = A\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{L}\right)\sin\left(\frac{n_z \pi z}{L}\right)\cos 2\pi \upsilon t \tag{8.20}$$

where n_x ,n_y, n_z, are positive integers ≥ 1

Differentiating equation (8.20) twice with respect to x, we get

$$\frac{\partial^2 u}{\partial x^2} = -\left(\frac{n_x \pi}{L}\right)^2 A\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{L}\right)\sin\left(\frac{n_z \pi z}{L}\right)\cos 2\pi \upsilon t$$

$$\frac{\partial^2 u}{\partial x^2} = -\left(\frac{n_x \pi}{L}\right)^2 u(x,y,z,t) \tag{8.21}$$

Similarly differentiating equation (8.20) with respect to y, z and t respectively , we get

$$\frac{\partial^2 u}{\partial y^2} = -\left(\frac{n_y \pi}{L}\right)^2 u(x,y,z,t) \tag{8.22}$$

$$\frac{\partial^2 u}{\partial z^2} = -\left(\frac{n_z \pi}{L}\right)^2 u(x,y,z,t) \tag{8.23}$$

$$\frac{\partial^2 u}{\partial t^2} = -(2\pi\upsilon)^2 u(x,y,z,t) \tag{8.24}$$

Substituting these values from (8.21) , (8.22) (8.23) and (8.24) into (8.19) we get

$$\left(\frac{n_x \pi}{L}\right)^2 + \left(\frac{n_y \pi}{L}\right)^2 + \left(\frac{n_z \pi}{L}\right)^2 = \frac{1}{v_s^2}(2\pi\upsilon)^2$$

or $$\left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right) = \frac{1}{v_s^2}(2\pi\upsilon)^2 = \frac{4\pi^2}{\lambda^2} \tag{8.25}$$

In this case the wavelength and frequencies of possible vibrations are given by three integers. Let us now find out the number of possible modes of vibration $Z(\upsilon)d\upsilon$ in the frequency range υ and $\upsilon + d\upsilon$. For this ,let us consider a network of points in which each point being determined by three cartesian positive integer coordinates n_x, n_y, and n_z . Thus the radius vector (R) from the origin to any point is given by

$$R^2 = n_x^2 + n_y^2 + n_z^2 \tag{8.26}$$

Equation (8.26) represents equation of sphere in integer space. Now comparing equation (8.26) with equation (8.25) we shall get –

$$R^2 = \frac{4L^2\upsilon^2}{v_s^2} \quad \Rightarrow R = \frac{2L\upsilon}{v_s}$$

or $$dR = \frac{2Ld\upsilon}{v_s} \tag{8.27}$$

We know that each point occupies on an average a unit volume in the space of integers , the number of points present in the volume dV of spherical shell, between radii R and (R+dR) is numerically equal to

$$dn = 4\pi R^2 dR$$

Since a mode of vibration is always determined by the positive values of n_x, n_y, and n_z only , we must consider the number of points lying in the octant defined by these positive integers only.

Volume of octant of spherical shell $= dV = \frac{1}{8}4\pi R^2 dR$ Therefore the number of possible modes of vibrations between frequency range υ and $\upsilon + d\upsilon$ are given by

$$Z(\upsilon)d\upsilon = \frac{1}{8}4\pi R^2 dR \tag{8.28}$$

Now substituting the value of R^2 and dR from equation (8.27) in equation (8.28) , we shall get .

$$Z(\upsilon)d\upsilon = \frac{1}{8}4\pi\left(\frac{2L\upsilon}{v_s}\right)^2 \frac{2Ld\upsilon}{v_s} = \frac{4\pi L^3}{v_s^3}\upsilon^2 d\upsilon$$

Or $$Z(\upsilon)d\upsilon = \frac{4\pi\upsilon^2 d\upsilon}{v_s^3}V \tag{8.29}$$

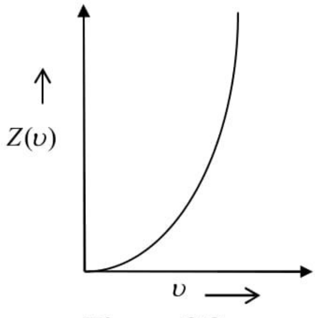


Figure 8.2

where V = L^3 , the volume of the cube of solid. For a perfect continuum , the possible frequencies may vary between 0 and ∞, the number of such possible vibrations increasing with the square of frequencies as shown in figure (8.2). This situation holds , for example in case of electromagnetic waves in a box of volume V. Eq.(8.29) is therefore basic expression in the theory of black body radiation. In the case of elastic waves (in solids), we may distinguish between transverse and longitudinal waves. In general the velocity of propagation say C_t and C_l respectively, will not be equal . To set up an expression for $Z(\upsilon)d\upsilon$, in this case one should keep in mind that for each frequency or wavelength, there are two transverse mode and one Longitudinal mode i.e. in the longitudinal mode the deflection is along the direction of propagation, while in transverse mode the deflection is perpendicular to the direction of propagation, which gives two independent components. Hence, the total number of modes of vibrations between υ and $\upsilon + d\upsilon$ for elastic waves is given by

$$Z(\upsilon)d\upsilon = \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) 4\pi V \upsilon^2 d\upsilon \tag{8.30}$$

Equation (8.30) will be used for the determination of specific heat of Solids.

8.7 Einstein Model of Specific Heat

The Classical theory of specific heat i.e. Dulong Petit law could not explain the variation of specific heat for many solids with temperature, particularly at low temperature. This discrepancy was removed by Einstein on the basis of Planck's quantum theory. The following assumptions were made by Einstein to explain specific heat of Solids.

1. All the atoms of solids are identical and independent ,simple harmonic oscillators.
2. All atomic oscillators vibrate in identical environment and have the same frequency.
3. The energy spectrum of atomic oscillator is not continuous as assumed in classical theory but has discrete values as given by quantum theory. According to quantum theory an oscillator of frequency υ has only discrete values of energy given by $E_n = nh\upsilon$ where n= 0,1,2… etc, called quantum number and *h* is Planck's constant.
4. The vibrational mode of each atom is composed of all vibrating oscillators in x, y,z directions.So a solid containing N atoms is considered to be equivalent to 3N

harmonic oscillators.

5. The oscillators form an assembly of system which are distinguishable due to their location at separate and distinct lattice sites in the crystal. These, therefore obey Maxwell Boltzmann's (M.B.) statistics and have M.B. distribution of energy.

In accordance to the above assumptions the probability that the atomic oscillator has the energy $E_n = nh\upsilon$ at temperature T is governed by Boltzmann's distribution function of $e^{-\frac{nh\upsilon}{kT}}$. Now we will calculate the average energy of oscillator in the following way.

Let N_0, N_1, N_2………… be the number of atomic oscillators having energy $0, h\upsilon, 2h\upsilon....$ respectively . According to Maxwell – Boltzmann's distribution

$N_1 = N_0 e^{-\frac{h\upsilon}{kT}}, N_2 = N_0 e^{-\frac{2h\upsilon}{kT}}, N_3 = N_0 e^{-\frac{3h\upsilon}{kT}}$,….where k is Boltzmann's constant.

∴ Total Number of oscillators = N= $N_o + N_1 + N_2 + N_3 +$…………,

$$N = N_0 + N_0 e^{-\frac{h\upsilon}{kT}} + N_0 e^{-\frac{2h\upsilon}{kT}} + N_0 e^{-\frac{3h\upsilon}{kT}} + ...$$

$$N = N_0\left(1 + e^{-\frac{h\upsilon}{kT}} + e^{-\frac{2h\upsilon}{kT}} + e^{-\frac{3h\upsilon}{kT}} + ...\right) = N_0\left(1 - e^{-\frac{h\upsilon}{kT}}\right)^{-1}$$

$$N = \frac{N_0}{\left(1 - e^{-\frac{h\upsilon}{kT}}\right)} \tag{8.31}$$

Now total energy of oscillators

$$\mathrm{E} = \mathrm{N}_0 \times 0 + \mathrm{N}_1 \times \mathrm{h}\upsilon + \mathrm{N}_2 \times 2\mathrm{h}\upsilon + \mathrm{N}_3 \times 3\mathrm{h}\upsilon + ...$$

$$E = N_0 e^{-\frac{h\upsilon}{kT}} h\upsilon + N_0 e^{-\frac{2h\upsilon}{kT}} 2h\upsilon + N_0 e^{-\frac{3h\upsilon}{kT}} 3h\upsilon + ...$$

$$E = N_0 e^{-\frac{h\upsilon}{kT}} h\upsilon\left(1 + 2e^{-\frac{2h\upsilon}{kT}} + 3e^{-\frac{3h\upsilon}{kT}} + ...\right)$$

$$E = N_0 h\upsilon \frac{e^{-\frac{h\upsilon}{kT}}}{\left(1 - e^{-\frac{h\upsilon}{kT}}\right)^2} \tag{8.32}$$

∴ Average energy of atomic oscillator is given by

$$\langle E \rangle = \frac{\text{Total energy E}}{\text{Total number of oscillators N}}$$

From equation (8.31)& (8.32)

$$\langle E \rangle = \frac{N_0 h\upsilon \dfrac{e^{-\frac{h\upsilon}{kT}}}{\left(1-e^{-\frac{h\upsilon}{kT}}\right)^2}}{\dfrac{N_0}{\left(1-e^{-\frac{h\upsilon}{kT}}\right)}}$$

$$\therefore \langle E \rangle = \frac{h\upsilon}{\left(e^{\frac{h\upsilon}{kT}}-1\right)} \tag{8.33}$$

According to Quantum mechanics the possible energy levels of a harmonic oscillator are given by

$$E_n = \left(n+\frac{1}{2}\right)h\upsilon \tag{8.34}$$

This has the effect of shifting all energy levels by constant amount of $\frac{1}{2}h\upsilon$ and instead of (8.33) we will get

$$\langle E \rangle = \frac{1}{2}h\upsilon + \frac{h\upsilon}{\left(e^{\frac{h\upsilon}{kT}}-1\right)} \tag{8.35}$$

This first term is called the zero point energy of the atomic oscillator because $\langle E \rangle = \frac{1}{2}h\upsilon$ for T=0K, Thus according to quantum mechanics the atoms have vibrational energy even at the absolute zero ,but this term does not make any contribution to lattice heat capacity because it does not contain temperature factor.

In Einstein model the vibrational energy of a solid element containing N atoms is equal to energy provided by 3N oscillators.

The internal energy of the solid can be obtained by multiplying the average energy per oscillator by the 3N oscillators.

$$U = 3N\langle E\rangle = \frac{3}{2}Nh\upsilon + \frac{3Nh\upsilon}{\left(e^{\frac{h\upsilon}{kT}} - 1\right)} \tag{8.36}$$

∴ The first term of equation (8.36) is temperature independent zero point energy.

Hence, lattice specific heat $C_V = \left(\frac{dU}{dT}\right)_V = 3Nk\left(\frac{h\upsilon}{kT}\right)^2 \frac{e^{\frac{h\upsilon}{kT}}}{\left(e^{\frac{h\upsilon}{kT}} - 1\right)^2}$

Put $\frac{h\upsilon}{k} = \theta_E = \text{Einstein Temperature}$ (8.37)

$$\therefore C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2} = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2} \tag{8.38}$$

where Nk=R, We now discuss the following Cases

(1) At high temperature : At high temperature, $\left(\frac{\theta_E}{T}\right)$ approaches very small value, so $e^{\frac{\theta_E}{T}} = 1 + \frac{\theta_E}{T} + \ldots$

$$\therefore C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{\left(1 + \frac{\theta_E}{T} + \ldots\right)}{\left(1 + \frac{\theta_E}{T} + \ldots\ldots - 1\right)^2} = \frac{3R\left(\frac{\theta_E}{T}\right)^2\left(1 + \frac{\theta_E}{T}\right)}{\left(\frac{\theta_E}{T}\right)^2} \approx 3R\left(1 + \frac{\theta_E}{T}\right)$$

$$\therefore C_V \approx 3R \text{ as } T \to \infty,\ \frac{\theta_E}{T} \to 0$$

So at high temperatures, the lattice heat capacity approaches the classical value 3R which agrees with experimental results. Obviously, this is the same value as obtained by the Dulong - Petit's law.

(2)At low temperature : At very low temperature $\left(\frac{\theta_E}{T}\right)$ will be sufficiently very high, so we can neglect number 1 in comparison to $\left(\frac{\theta_E}{T}\right)$.

So $e^{\frac{\theta_E}{T}} >> 1$ and $e^{\frac{\theta_E}{T}} - 1 \approx e^{\frac{\theta_E}{T}}$ .Therefore equation (8.38) becomes

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}}\right)^2} = 3R\left(\frac{\theta_E}{T}\right)^2 e^{\frac{-\theta_E}{T}} \tag{8.39}$$

Thus for T<< θ_E, the lattice heat capacity is proportional to $e^{-\left(\frac{\theta_E}{T}\right)}$, which is the dominating factor. At low temperature, the lattice heat capacity falls exponentially with decrease in temperature. As the value of T decreases to absolute zero, then the value of C_V also decreases towards zero i.e. T $\to 0, C_V \to 0,$ But this is not in agreement with experimental observations, since it has been observed experimentally that for most of the solids ,the lattice heat capacity at very low temperatures varies as T^3 i.e. $C_V \propto T^3$. As shown in figure (8.3), which is drawn according to equation (8.38).

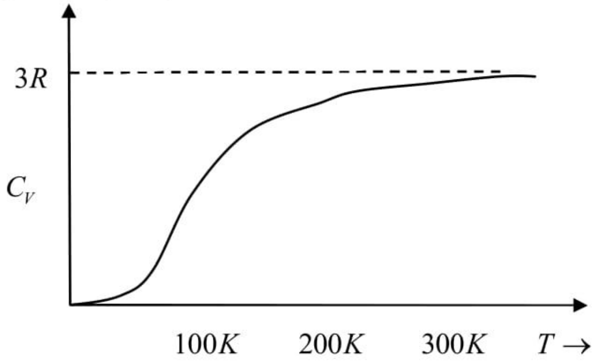


Figure 8.3

Thus, we can conclude that the Einstein's Theory qualitatively agrees with experimental facts. But the value of C_V obtained theoretically from equation (8.38) does not agree with the experimental value. In case of copper and aluminum, it is observed that the atomic heat capacity at low temperature decreases more slowly than predicted by this theory. So this theory suffers from a serious drawback.

Shortcomings of Einstein Theory

(1) It explains the specific heat curve up to a certain point, but fails completely at extremely low temperature, where T^3 law holds good.

(2) υ and θ_E are obtained empirically and cannot be verified from any independent physical data.

(3) According to hypotheses of Einstein, atoms in the solid are independent oscillators and all vibrate with the same frequency. In fact these atoms are bound with each other under the influence of elastic force. Therefore, the atoms would behave collectively as system of coupled oscillators, which cannot vibrate independently. Thus while examining the vibrations in a crystal, it would be better if instead of a single frequency, a spectrum of frequencies to be considered, so this fact is taken into account in the Debye's model, which will be discussed now.

8.8 Debye Model of Specific Heat

Debye proposed in 1912 ,a more realistic model for the frequency spectrum of the solid. He retained the essential feature introduced by Einstein, the quantization of oscillator energies. Debye assumed the solid as a system of coupled oscillators. Thus while examining the vibrations in a crystal, it would be better if instead of a single frequency, a spectrum of frequencies is considered. The Debye model is based on the following assumptions.

(1) A solid can be assumed as an isotropic elastic continuum.

(2) Each atom of the solid worked as coupled oscillator with another atom. The vibrations of this coupled system can be described in terms of normal modes.

(3) There are 3N normal modes in a solid having N atoms. 3N frequencies can have values from zero to cut off frequency υ_D . The cut off frequency υ_D is also known as Debye characteristic frequency. The restriction to the maximum frequency υ_D applies because the waves for which half of the wavelength is less than the inter-atomic distance a (i.e. $\frac{\lambda}{2} < a$) , cannot propagate through the crystal.

(4) According to Debye model ,the internal energy of a solid is present in the elastic standing waves originated from the vibrations of individual atoms.

(5) The value of Debye cut off frequency υ_D is same for transverse and longitudinal modes.

Debye Approximation: According to Debye if the wavelength of the moving elastic wave is large compared with interatomic distance a ,the crystal medium can be assumed as continuum . In such type of medium the total number of vibrational modes is taken to be 3N, where N is the total number of atoms in the crystal. The frequency of these vibrational mode is limited from 0 to υ_D . The υ_D frequency is known as Debye cut off frequency . It is common to transverse and longitudinal modes of vibrations. Thus the frequency spectrum related to perfect continuum has cut off limit at Debye frequency υ_D , so as to comply with a total of 3N modes as shown in figure (8.4).

Thus Debye frequency can be determined by equating the total number of possible vibrations to 3N.

So $\int_0^{\upsilon_D} Z(\upsilon)d\upsilon = 3N$,but from equation (8.30) we have –

$$Z(\upsilon)d\upsilon = 4\pi V\left(\frac{2}{C_t^3}+\frac{1}{C_l^3}\right)\upsilon^2 d\upsilon \tag{8.40}$$

$$\therefore \int_0^{\upsilon_D} 4\pi V\left(\frac{2}{C_t^3}+\frac{1}{C_l^3}\right)\upsilon^2 d\upsilon = 3N$$

or

$$4\pi V\left(\frac{2}{C_t^3}+\frac{1}{C_l^3}\right)\frac{\upsilon_D^3}{3} = 3N$$

or

$$\upsilon_D^3 = \frac{9N}{4\pi V}\left(\frac{2}{C_t^3}+\frac{1}{C_l^3}\right)^{-1} \tag{8.41}$$

Now putting the value of $\left(\frac{2}{C_t^3}+\frac{1}{C_l^3}\right)$ from (8.41) into equation (8.40)

$$Z(\upsilon)d\upsilon = \frac{9N\upsilon^2}{\upsilon_D^3}d\upsilon \tag{8.42}$$

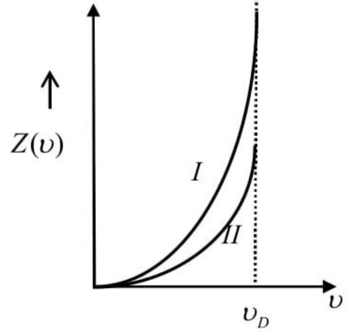


Figure 8.4

In Debye model it was assumed that phonon gas behaves like a photon gas . So average energy <E> per mode at a temperature T is given by Planck's distribution law as follows

$$\langle E\rangle=\frac{\sum_{n=0}^{n=\infty}E_n e^{\frac{-E_n}{kT}}}{\sum_{n=0}^{n=\infty}e^{\frac{-E_n}{kT}}}=\frac{h\upsilon}{\left(e^{\frac{h\upsilon}{kT}}-1\right)} \tag{8.43}$$

Since a quantum harmonic oscillator is associated with each vibrational mode of the same frequency. So the vibrational energy of the crystal is given by

$$U=\int_O^{\upsilon_D}<E>Z(\upsilon)d\upsilon \tag{8.44}$$

Now putting values from (8.42) and (8.43) in equation (8.44) we will get

$$U=\int_0^{\upsilon_D}\frac{h\upsilon}{e^{\frac{h\upsilon}{kT}}-1}.\frac{9N\upsilon^2 d\upsilon}{\upsilon_D^3}=\frac{9N}{\upsilon_D^3}\int_0^{\upsilon_D}\frac{h\upsilon^3}{e^{\frac{h\upsilon}{kT}}-1}d\upsilon \tag{8.45}$$

Now put $\frac{h\upsilon}{kT}=x$ and $\frac{h\upsilon_D}{kT}=x_m$ or $\upsilon=\frac{xkT}{h}$ and $d\upsilon=\frac{kT}{h}dx$

Hence equation (8.45) will take the from as follows

$$U=\frac{9Nh}{\upsilon_D^3}\left(\frac{KT}{h}\right)^4\int_0^{x_m}\frac{x^3}{e^x-1}dx=9N\left(\frac{kT}{h\upsilon_D}\right)^3 kT\int_0^{x_m}\frac{x^3dx}{e^x-1} \tag{8.46}$$

Let us introduce a characteristic temperature θ_D, known as Debye temperature defined as $\theta_D=\frac{h\upsilon_D}{k}$, so $x_m=\frac{\theta_D}{T}$ .So equation (8.46) becomes

$$U=9NkT\left(\frac{T}{\theta_D}\right)^3\int_0^{\left(\frac{\theta_D}{T}\right)}\frac{x^3}{e^x-1}dx$$ where N is Avogadro's number

$$U=9RT\left(\frac{T}{\theta_D}\right)^3\int_0^{\left(\frac{\theta_D}{T}\right)}\frac{x^3}{e^x-1}dx \tag{8.47}$$

Hence lattice specific heat $C_V=\left(\frac{dU}{dT}\right)_V=9R\left(\frac{T}{\theta_D}\right)^3\int_0^{\left(\frac{\theta_D}{T}\right)}\frac{x^4e^x}{(e^x-1)^2}dx$ (8.48)

(1) At high temperature: At high temperature, Debye temperature is very small i.e. T>> θ_D then $x = \frac{h\upsilon}{kT}$ has very small value i.e. $x << 1$,so that $e^x = 1 + x$ and

$$\frac{x^3}{e^x - 1} = x^2 \text{ and } \int_0^{\theta_D/T} x^2 dx = \left[\frac{x^3}{3}\right]_0^{\frac{\theta_D}{T}} = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

So putting these values in equation (8.48)

$$C_V = 9R\left(\frac{T}{\theta_D}\right)^3 \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3 = 3R \tag{8.49}$$

This is Dulong and Petit law . Thus at high temperature Debye's theory agrees with classical theory i.e. Dulong Petit law .

(2) At low temperature : At low temperature, Debye temperature θ_D is very large , so that limit of integration $\left(\frac{\theta_D}{T}\right)$ can be taken as infinity . As T<< θ_D

So $x_m = \frac{\theta_D}{T} \to \infty$,therefore from equation (8.48)

$$C_V = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^\infty \frac{e^x x^4}{\left(e^x - 1\right)^2} dx$$

The value of integration comes out to $\frac{4\pi^2}{15}$

$$\therefore C_V = \frac{12}{5}\pi^4 R \; \frac{T^3}{{\theta_D}^3} \tag{8.50}$$

In this way according to Debye's model, at very low temperatures, the molar specific heat is proportional to T^3(i.e. cube of temperature) .This law is known as Debye T^3 law and this is more closely in agreement with experimental results for Ag and Al.

Shortcomings of Debye Model:

(1) Debye does not consider the crystal structure of solids in his model.

(2) Debye's model neglects completely the inter-atomic interaction and electronic contribution to lattice specific heat.

(3) In Debye's theory, Debye's temperature θ_D is taken as a constant, while through experiment it was observed that θ_D depends upon temperature.

(4) In Debye's model the cutoff frequency υ_D is taken same for longitudinal and transverse waves, while $C_t \neq C_l$, so there should be two different values of υ_D for longitudinal and transverse waves .

8.9 Thermal Expansion

As we know that thermal expansion of a solid is a result of displacement of ions of the material due to the change in temperature .As the thermal expansion of a solid is characterized by linear thermal expansion coefficient $\alpha = \frac{1}{l}\left(\frac{dl}{dT}\right)$.

Many properties of the crystalline solids are well explained on the basis of harmonic approximation. In the theory of lattice vibrations as discussed above we limited ourselves in the potential energy to terms quadratic in the interatomic displacements, as in the harmonic theory. However, the harmonic approximation is incapable of accounting for the existence of thermal expansion , temperature dependence of elastic constants, inequality between specific heat at constant pressure and constant volume and so many other properties. In case of an ionic lattice the atoms are held together by Coulomb forces . The electron clouds of the atoms can interpenetrate only to certain extent to give rise to repulsive forces .The repulsive energy increases rapidly when the ions approach one another during vibrations (r<r_o) compared to the attractive forces, but it is close to zero when the ions deviate from one another. This behaviour makes the resultant force generally nonlinear or anharmonic. Another reason for anharmonicity according to Born, may also be due to the lack of proportional displacements of both the nucleus and the electrical charges. Anharmonicity in a lattice is thus a normal property and this alone explain the existence of thermal expansion in the crystal.

Expression for coefficient of thermal expansion: A necessary preliminary relation which one requires while computing the coefficient of thermal expansion is the realtion between interatomic distance and temperature. The origin of thermal expansion can be understood by considering a classical oscillator with taking the effect of anharmonic terms in the potential energy at a temperature T. The potential energy of an atom at $0^o K$ and at a displacement x from its equilibrium position r_o. For small values of $x = r - r_o$. We can set the U(x) as

$$U(x) = cx^2 - gx^3 - fx^4 + ... \tag{8.51}$$

where c, g, and f are all positive. Here the term in x^3 represents the asymmetry of the mutual repulsion of the atoms and the term in x^4 represents the softening of the vibrations at large amplitudes. The average displacement can be calculated by using the Boltzmann's distribution function and it gives the possible values of x. According to their thermodynamical probability:

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x e^{\frac{-U(x)}{kT}} dx}{\int_{-\infty}^{\infty} e^{\frac{-U(x)}{kT}} dx} \qquad (8.52)$$

Now putting the value of U(x) from (8.51) in equation (8.52) we shall get:

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x e^{\frac{-(cx^2-gx^3-fx^4)}{kT}} dx}{\int_{-\infty}^{\infty} e^{\frac{-(cx^2-gx^3-fx^4)}{kT}} dx} \qquad (8.53)$$

For small displacements, the anharmonic terms in the energy are small in comparison to kT, we may expand the integrands as:

Numerator of (8.53) $\int_{-\infty}^{\infty} x e^{\frac{-(cx^2-gx^3-fx^4)}{kT}} dx = \int_{-\infty}^{\infty} x e^{\frac{-(cx^2)}{kT}} e^{\frac{(gx^3+fx^4)}{kT}} dx$

$$= \int_{-\infty}^{\infty} x e^{\frac{-(cx^2)}{kT}} \left[1 + \frac{g}{kT}x^3 + \frac{f}{kT}x^4\right] dx$$

$$= \int_{-\infty}^{\infty} x e^{\frac{-cx^2}{kT}} dx + \int_{-\infty}^{\infty} \frac{g}{kT} x^4 e^{\frac{-cx^2}{kT}} dx + \int_{-\infty}^{\infty} \frac{f}{kT} x^5 e^{\frac{-cx^2}{kT}} dx$$

$$= 0 + \int_{-\infty}^{\infty} \frac{g}{kT} x^4 e^{\frac{-cx^2}{kT}} dx + 0$$

$$\therefore Numerator = \frac{g}{kT}\frac{3}{4}\sqrt{\frac{\pi}{\left(\frac{c}{kT}\right)^5}} \qquad (8.54)$$

Denominator $= \sqrt{\frac{\pi}{\left(\frac{c}{kT}\right)}} + \frac{f}{kT}\frac{3}{4}\sqrt{\frac{\pi}{\left(\frac{c}{kT}\right)^5}}$ (8.55)

$$\therefore \bar{x} = \frac{\dfrac{g}{kT}\dfrac{3}{4}\sqrt{\dfrac{\pi}{\left(\dfrac{c}{kT}\right)^5}}}{\sqrt{\dfrac{\pi}{\left(\dfrac{c}{kT}\right)}} + \dfrac{f}{kT}\dfrac{3}{4}\sqrt{\dfrac{\pi}{\left(\dfrac{c}{kT}\right)^5}}} = \frac{\dfrac{3}{4}\dfrac{g}{c^2}kT}{\left(1+\dfrac{3f}{4c^2}kT\right)}$$

Now here 1>> $\left(\frac{3f}{4c^2}kT\right)$, So we can expand it as

$$\bar{x} = \frac{3g}{4c^2}(kT)\left[1-\frac{3f}{4c^2}kT\right] \tag{8.56}$$

We can write this relation in a more general form by replacing the classical value of energy of the atomic oscillator kT by its corresponding quantum mechanical value E, as

$$\bar{x} = \frac{3g}{4c^2}E - \frac{9gf}{16c^4}E^2 \tag{8.57}$$

Expression for the coefficient of thermal expansion can now be written in the following form

$$\alpha = \frac{1}{r_o}\frac{d\bar{x}}{dT} = \frac{3g}{4c^2}\left[1-\frac{3fE}{2c^2}\right]\frac{C_V}{r_o} \tag{8.58}$$

The Second term of equation (8.58) is usually small but this alone represents the temperature dependence of α. The temperature independent value of α, i.e. α_o is obtained by deleting the second term of equation (8.58) and is given by

$$\alpha_o = \frac{3g}{4c^2}\frac{C_V}{r_o} \tag{8.59}$$

This equation agrees well with the experimental results of thermal expansion. The thermal expansion coefficient vanishes as $T \to 0$, as required by the third law of thermodynamics which by the way also requires that $C_V \to 0$ as $T \to 0$. So α also tends to zero. In lowest order the thermal expansion does not involve the symmetric terms $f\,x^4$ in U(x), but only the antisymmetric term gx^3 exists.

8.10 Thermal Conductivity

We know that the thermal conduction is the process of heat transfer in solid. Heat flows through vibrational motion of atoms. Atoms of the hot end of rod vibrate with more amplitude and transfer heat energy to neighbouring atom. In this manner heat transfers from one place to another. In crystals heat transfer takes place through phonons, photons, free electrons, free holes or free hole electron pairs. In metals, heat transfer takes place through free electron or electron gas, while in non-metals heat transfer takes place through phonon. Since transfer of lattice vibrations i.e. phonons takes place with velocity of sound. So we can suppose the transfer of heat with velocity sound. If the coefficient of thermal conductivity of heat transfer through free electrons is represented by K_{el} and K_{lat} is the coefficient of thermal conductivity of heat transfer through phonon. Then in general the coefficient of thermal conductivity of solid.

$$K = K_{el} + K_{lat} \tag{8.60}$$

The coefficient of thermal conductivity K of a solid is most easily defined with respect to the steady state flow of heat down a long rod with a temperature gradient $\frac{dT}{dx}$:

$$Q = -K\left(\frac{dT}{dx}\right) \tag{8.61}$$

where Q is the amount of heat flowing per unit area per second and K is coefficient of thermal conductivity and Q is also known as heat current density. Equation (8.61) shows that the process is random i.e. the heat energy diffuses through the specimen, suffering frequent collision, besides entering one end and proceed directly in the straight path to the other end. Without diffusion or in steady state, the expression will depend only upon the difference of temperature between the ends of specimen and not upon the temperature gradient regardless of the length of specimen. From kinetic theory of gases and transport phenomenon, we find the following

$$K = \frac{1}{3} C_V \lambda \bar{c} \tag{8.62}$$

where C_V is the heat capacity per unit volume, λ is the mean free path of a particle between collisions and $\bar{c}$ is the average particle velocity. This result was applied first by Debye to describe thermal conductivity in dielectric solids, with C_V as the heat capacity of the phonons, $\bar{c}$ the phonon average velocity and λ the phonon mean free path, because in dielectric solids ,heat is conducted by phonons, which give rise to lattice thermal conductivity.

The thermal conductivity of solids can be most easily understood by regarding the crystal as a container enclosing a " gas of phonon" .This is found to behave like an ideal monoatomic gas. Now from transport phenomena in conduction ,the transport of energy takes place from one layer to another layer, when there exits temperature gradient between different layers. Suppose we are having three layers at temperature $\left(T-\lambda\frac{dT}{dx}\right)$, T and $\left(T+\lambda\frac{dT}{dx}\right)$. Then net amount of heat energy passing per sec per unit area of the layer is given as

$$Q=\frac{1}{3}\lambda\bar{c}C_V\frac{dT}{dx} \tag{8.63}$$

From theory of thermal conductivity ,the amount of heat passing per sec per unit area of the layer is equal to

$$Q=K\frac{dT}{dx} \tag{8.64}$$

Comparing equation (8.63) and (8.64) we get $K=\frac{1}{3}\lambda\bar{c}\,C_V$ (8.65)

8.11 Umklapp Process

In an inelastic scattering of the photon by a crystal, the frequency of incident photon undergoes a change and a phonon is created (emitted) or absorbed. If a phonon of wavevector ***k*** is emitted or created during the scattering, then according to wavevector conservation law-

$$\vec{K}'(scattered)+\vec{k}=\vec{K}(incident)+\vec{G} \tag{8.66}$$

where $\vec{G}$ is reciprocal lattice vector. This has been shown graphically in figure 8.5(a). If a phonon of wave vector ***k*** is absorbed during the scattering then according to wavevector conservation law:

$$\vec{K}'(scattered)=\vec{K}(incident)+\vec{k}+\vec{G} \tag{8.67}$$

This has been shown graphically in figure [8.5(b)]

where **G** is the reciprocal lattice vector of the crystal.

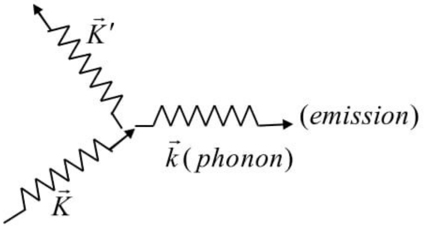


Figure (8.5a):Phonon Emission

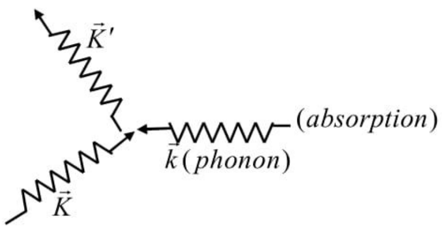


Figure (8.5b):Phonon Absorption

Such a process in which the frequency of incident phonon changes is called an Umklapp process or U- process. This process can be considered as a creation or absorption of a phonon with simultaneously a Bragg's reflection. In this process the momentum is obviously transferred to the crystal as a whole.

Examples of Umklapp process are as follows :

(1) Interactions of three lattice waves due to anharmonic lattice forces, which produce intrinsic thermal resistance in non-metals.

(2) Scattering of electrons by lattice waves, causing electrical and thermal resistance in metals.

(3) Bragg refection, which can be regarded as an Umklapp process involving only two waves.

8.12 Self Learning Exercise

Q.1 What is lattice specific heat?

Q.2 What is Umklapp- process?

Q.3 Derive an expression for density of state in three dimensions.

Q.4 What are the assumptions made in Einstein's theory of specific heat?

8.13 Summary

In this unit we have studied phonon heat capacity i.e. lattice heat capacity as lattice vibrations and we derived Planck's distribution formula. We have calculated number of modes of vibrations in one and three dimensions in crystal . Then we discussed Einstein and Debye model of specific heat for solids. The introduction of anharmonic term in the potential energy expression, successfully explains the thermal expansions. Then we discussed thermal conductivity of crystals by lattice waves or phonons. Treating the phonons as a gas and using results of kinetic Theory, we derived the formula $K = \frac{1}{3} C_V \bar{c} \lambda$, where λ is mean free path of phonon. In the last, we discussed Umklapp process, through an inelastic scattering of the photon by a crystal, the frequency of incident photon undergoes a change and a phonon is created (emitted) or absorbed .

8.14 Glossary

Phonon : quanta of lattice vibration

Longitudinal Mode: The deflection is along the direction of propagation.

Transverse Mode: deflection in perpendicular to the direction of propagation.

8.15 Answers to Self Learning Exercise

Ans.1: It is due to rigorous vibrations of the atoms in crystal lattice.

Ans.2: Such a process in which the frequency of incident phonon changes is called Umklapp or U-process, In this process a phonon is created or absorbed in addition to the Bragg refection and the momentum is transferred to the crystal as a whole.

8.16 Exercise

Section A: Very Short Answer Type Questions

Q.1 What is Einstein Temperature?

Q.2 What do you mean by density of modes?

Q.3 What is Debye- T^3 law?

Section B : Short Answer Type Questions

Q.4 What are the refinements of Debye's theory over Einstein theory?

Q.5 Explain Planck's distribution law?

Q.6 Discuss briefly the importance of UmKlapp process in explaining an inelastic scattering of a x- ray photon by a crystal.

Section C :Long Answer Type Questions

Q.7 Derive an expression for the specific heat of solid on the basis of Einstein's theory. Discuss the variation of specific heat with temperature.

Q.8 Discuss the Debye model of specific heat of solids, Show how far it agrees with the experimental values.

Q.9 What is anharmonicity? The anharmonic potential as a function of atomic displacement x in a solid is given by $U(x) = ax^2 - gx^3 - fx^4$, where a, g, and f are constants. Prove that the temperature independent part of the thermal expansion is $\alpha_0 = \frac{3g}{4c^2}\frac{C_V}{r_o}$

Q.10 Explain thermal conductivity and derive necessary formula for it.

Q.11 Explain normal mode enumeration . Show that expression for Debye characteristic frequency for solid is given in the following form:

$$W_D = \left(\frac{18N\pi^2}{V}\right)^{\frac{1}{3}}\left[\frac{2}{C_t^2}+\frac{1}{C_l^2}\right]^{-\frac{1}{3}}$$

where C_t= velocity of transverse wave and C_ℓ= velocity of longitudinal wave, V= Volume of crystal and N= number of atoms in crystal

8.17 Answers to Exercise

Ans.1: It is characteristic a temperature defined by $\theta_E = \frac{h\upsilon}{k}$, which is used in Einstein's model of specific heat. Here k is Boltzmann's constant.

Ans.2: The number of modes of vibrations per unit frequency range is known as density of modes.

Ans.3: According to Debye model, at low temperature, the specific heat is proportional to T^3. This is known as Debye's T^3 law and hold for $T < \frac{\theta_D}{10}$, where is θ_D is the Debye temperature.

References and Suggested Readings

1. Introduction to Solid State Physics by C. Kittel
2. Elementary Solid State Physics by Rama Swami
3. Solid State Physics by A.J. Dekker
4. Fundamentals of Solid State Physics by Saxena, Gupta and Saxena
5. Solid State Physics by S.O. Pillai

UNIT-9

Free Electron Model : Part-I

Structure of the Unit

9.0 Objectives

This unit contains the detailed description about the Free Electron Model. We study in this unit about Fermions and its energy known as Fermi Energy. The main objective of this unit is to give a overview about the free electron model and its related topic which are given or defined on the basis of this model. We are going to study in this unit about some important topic as the Fermi Dirac Distribution, heat capacity, electrical conductivity, and Matthissen's rule.

9.1 Introduction

Motion of charged elementary particles in solids is responsible for the manifestation of electrical resistivity in much the same way as the motion of uncharged particles in fluids is responsible for the manifestation of viscosity. It is known from elementary Physics that a metallic filament connected to the poles of a battery or any other source of electric current becomes hot and ends up by melting if the current is increased enough. Resistance to an electric current appears whenever the motion of charged particle in an electric field is being impeded by the motions of or collisions with other charged or neutral particles.

9.2 Free Electron Model

Free electron model is very important and simple model for the study of the behaviour of valence electron of a crystal structure of a solid which is mainly for the metal. **Somerfield** developed a model, by the combination of classical model of an electron and quantum mechanical Fermi-Dirac Statistics, known as **Free Electron Model.**

This model successfully explain some experimental phenomenon, which are given below;

1. On the basis of **Weidemann-Franz Law,** Electrical conductivity and Thermal conductivity,
2. Temperature dependence of the Heat capacity,
3. Shape of Electronic Density of States,
4. Thermal electron emission and Field electron emission.

9.3 Free Electron Fermi Gas

It consists of very large and those particles or electrons which obey the Pauli's exclusion principle, known as free electron Fermi gas and the Particles are known as **Fermions.** These particles also obey the Fermi-Dirac statistics. In the condition of the thermal equilibrium, Fermi-Dirac statistics determine the energy distribution of Fermions in a Fermi gas.

A Fermi gas having total energy at absolute zero larger than the sum of simple-particle ground states because of the Pauli's Exclusion principle. A Fermi gas have non zero pressure at zero temperature. Fermi gas of electron is also known as "**White Dwarf** " star.

9.4 Free Electron Gas in three Dimensions

In a solid state, a few loosely bound valence (outermost and not in completely filled shells) electrons become detached from atoms and move around throughout the material being a subject of the combined potential of the entire crystal lattice rather than initial atomic nucleus. Let us, consider two such models. In the first one, free electron gas, we ignore all forces except confining boundaries and treat our electrons as free particles in the three dimensional box with infinite walls.

We assume that our solid is a rectangular box with dimensions $l_x,\ l_y, and\ l_z$, and that the electron inside only experience the potential associated with impenetrable walls, i.e.

$$V(x,y,z) = 0, if\ 0 < x < l_x, 0 < y < l_y, 0 < z < l_z$$
$$= \infty \quad otherwise$$

The Schrödinger wave equation inside the walls is given by

$$\frac{-\hbar^2}{2m}\nabla^2\Psi = E\Psi$$

Separating in cartesian coordinates with a wave function written as

$$\Psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

$$\frac{-\hbar^2}{2m}\frac{d^2X}{dx^2}YZ - \frac{-\hbar^2}{2m}\frac{d^2Y}{dy^2}XZ - \frac{-\hbar^2}{2m}\frac{d^2Z}{dz^2}XY = E_x\,XYZ + E_y\,XYZ + E_zXYZ$$

Separating by parts ,we get

$$E_x\,X = \frac{-\hbar^2}{2m}\frac{d^2X}{dx^2}$$

and $E_y\,Y = \frac{-\hbar^2}{2m}\frac{d^2Y}{dy^2}$

and $E_z\,Z = \frac{-\hbar^2}{2m}\frac{d^2Z}{dz^2}$

Here $E = E_x + E_y + E_z$

Now making the following substitution

$$k_x = \frac{\sqrt{2mE_x}}{\hbar}, k_y = \frac{\sqrt{2mE_y}}{\hbar}\ and\ k_z = \frac{\sqrt{2mE_z}}{\hbar}$$

We get $\frac{d^2X}{dx^2} = -{k_x}^2X, \frac{d^2Y}{dy^2} = -{k_y}^2Y \; and \; \frac{d^2Z}{dz^2} = -{k_z}^2Z$

The solutions of the above equations are

$$X(x) = A_x \sin k_x x + B_x \cos k_x y$$
$$Y(y) = A_y \sin k_y y + B_y \cos k_y z$$
$$Z(z) = A_z \sin k_z z + B_z \cos k_z z$$

Now, we use our boundary conditions. At the infinite walls, our wave function is zero.

$$X(0) = Y(0) = Z(0) = 0$$
$$X(l_x) = Y(l_y) = Z(l_z) = 0$$

By applying first condition, we get that

$$B_x = B_y = B_z = 0$$

Now applying second condition, we get that

$k_x l_x = \pi n_x$ Here $n_x = 1, 2, 3, \dots \dots$

Similarly, we can get

$$k_y l_y = \pi n_y, \;\; n_y = 1, 2, 3, \dots \dots$$
$$k_z l_z = \pi n_z, \qquad n_z = 1, 2, 3, \dots \dots$$

The normalized wave functions are

$$\Psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{\pi n_x}{l_x}\right) \sin\left(\frac{\pi n_y}{l_y}\right) \sin\left(\frac{\pi n_z}{l_z}\right)$$

And the allowed energies are

$$E = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) = \frac{\hbar^2}{2m} k^2$$

Consider the figure (9.4.1) each block in this grid occupies a volume $\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$ of k-space. Suppose our solid contains N atoms with each atom contributing q free electrons and our solid is in its collective ground state (no thermal excitations).

If the electrons were distinguishable particles or bosons they all would have been in the ground state, Ψ_{111}. However, electrons are identical fermions and obey Pauli exclusion principal, so only two of them can occupy any particular state (two because of the spin, one being "spin up" and another one being "spin down".

We can say that electrons will fill up one octant (i.e. 1/8 part, see picture) of a sphere in k-space.

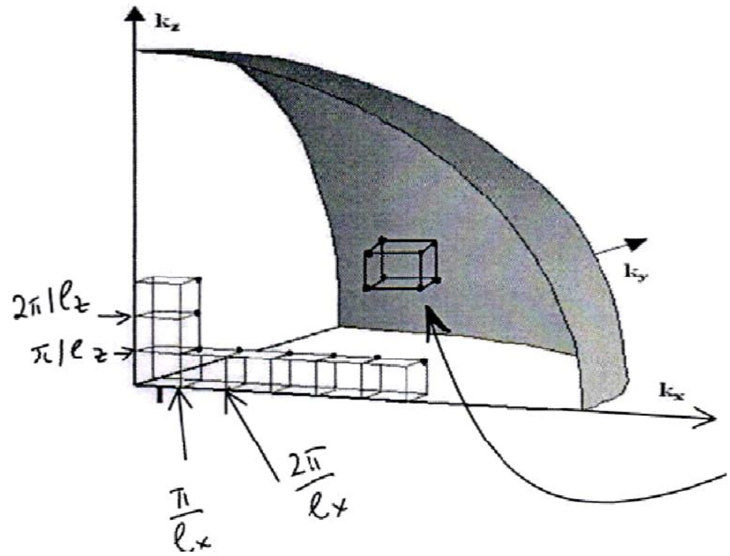


Figure 9.4.1: ***3D k-space with axes k_x, k_y, k_z. Each intersection point in this block represents a distinct one-particle size.***

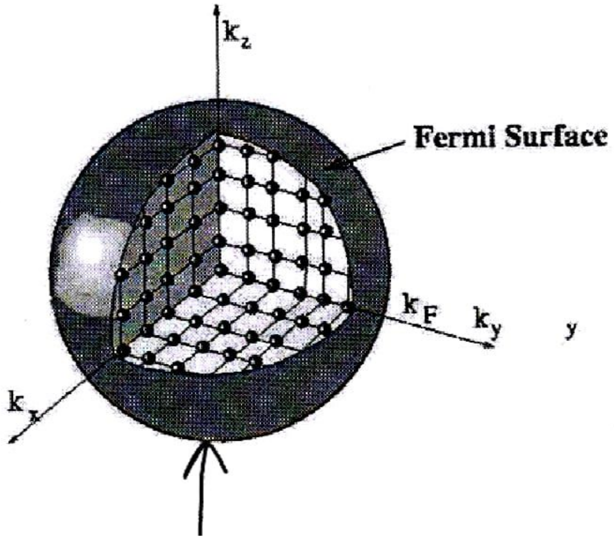


Figure 9.4.2: ***Fermi Surface***

The radius K_F of that sphere is determined by the volume required for each pair of electrons $\left(\frac{\pi^3}{V}\right)$:

$$\frac{1}{8}\left(\frac{4}{3}\pi k_f^3\right) = \frac{N_q}{2}\left(\frac{\pi^3}{V}\right)$$

We assume that we have N atoms with each atom contributing q free electrons. Each pair needs volume, we so need to divide N_q by 2.

We define the free electron density ρ

$$\rho = \frac{N_q}{V}$$

Hence $k_f^3 = (3\pi^2\rho)$

The boundary that separates occupied and unoccupied states in k-space is called the Fermi surface.

The corresponding Fermi energy, i.e. the energy of the highest occupied state, is

$$E_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{\frac{2}{3}}$$

9.5 Heat Capacity of the Electron Gas

Classical statistical mechanics predicts that particles in an assembly would be able to absorb energy, and so contribute to the heat capacity. Hence, the electronic contribution to the capacity of a monovalent metal will be $\frac{3}{2}(k_B N_A) = \frac{3}{2}R$. But the observed electronic contribution at room temperature is usually less than 0.01 of this value. This discrepancy is explained as follows:

When we heat the specimen from absolute zero temperature , not all the electrons gain energy of the order of K_BT as expected classically, but only those electrons in orbital within an energy range K_BT of the Fermi level can be excited thermally; these electrons are in orbital within an energy which itself is of the order of K_BT and go top higher unoccupied energy states. This gives an immediate qualitative solution to the problem of the heat capacity of the conduction electron gas. Thus the minimum energy required for exciting all the free electrons will be E_F. Hence the fraction of electrons that will be excited at T=300K is given by:

$$\frac{K_BT}{E_F} = \frac{0.025}{5} = 0.005 = 0.5\%$$

i.e. at ordinary temperatures, less than 1% of the valence electrons contribute to the heat capacity. This result contrasts with the classical view in which all the electrons in a system would absorb energy, and so contribute to the heat capacity.

Each of the electrons may absorb a kinetic energy of the order $\frac{3K_BT}{2}$. Hence the energy associated with a kmol of the metal will be

$$U = \left(\frac{3k_BT}{2}\right)\left[\frac{k_B\,T}{E_F}\right]N_A$$

$$U = \left(\frac{3T^2}{2}\right)\left[\frac{{k_B}^2 N_A}{E_F}\right]$$

$$[C_v]_{el} = \left(\frac{dU}{dT}\right) = \left[\frac{k_B\,T}{E_F}\right] 3N_A k_B$$

$$[C_v]_{el} = 3R_u[0.005]\; with\, k_B\,T = 0.025eV\; and\; E_F = 5eV$$

$$[C_v]_{el} = 0.015R_u \tag{9.5.1}$$

9.6 Effect of the temperature on the Fermi Dirac distribution

Here we assumed that the electron gas is at absolute zero degree and, in accordance with the Pauli's exclusion principle. The levels will be filled until by all the electrons up to the Fermi level energy E_f. But the kinetic energy of the electron gas increases as the temperature is increased and some energy levels are occupied which were vacant initially at absolute zero, and some levels gets vacant which were previously occupied at absolute zero.

The number of electrons dN having energy values lying between $E\; and\; E + dE$ is given by

$$dN = Z(E)dEf(E)$$

$$N = \int_0^\infty Z(E)dEf(E) \tag{9.6.1}$$

$$\bar{E} = \frac{1}{N}\int_0^\infty Z(E)Ef(E)dE \tag{9.6.2}$$

$$\bar{E} = \frac{1}{N}\int_0^\infty Z(E)\frac{EdE}{1+e^{\frac{E-Ef}{k_B\,T}}} \tag{9.6.3}$$

For the solution of this above integral, we shall evaluate the integral given by equation (9.6.2)

$$N = \int_0^\infty f(E)\frac{d}{dE}g(E)dE \tag{9.6.4}$$

Where f(E) is the Fermi distribution function and g(E) any other function, such that g(E)⟶0 as E⟶0.

Now integrating equation (9.6.4) by part

$$I = [f(E)g(E)]_0^\infty - \int_0^\infty g(E)f'(E)dE \tag{9.6.5}$$

In the above expression the first term on the right hand side vanishes at the upper limit because the probability of finding an electron with infinite energy is zero. The second term vanishes at the lower limit because we assume that g(0)=0.

Now expanding g(E) by *Taylor's series about* E_f as

$$g(E) = g(E_f) + (E - E_f)g'(E_f) + \frac{(E - E_f)^2}{2} g''(E_f) + \cdots \ldots \ldots \ldots$$

Now substituting the value of g(E) in equation (9.6.5), we have

$$I = -\int_0^\infty f'(E) \left[g(E_f) + (E - E_f)g'(E_f) + \frac{(E - E_f)^2}{2} g''(E_f) + \cdots \ldots \right] dE$$

$$I = L_0 g(E_f) + L_1 g'(E_f) + L_2 g''(E_f) + \cdots \qquad (9.6.6)$$

where $L_0 = -\int_0^\infty f'(E)dE$

$$L_1 = -\int_0^\infty (E - E_f) f'(E) dE$$

$$L_2 = -\left(\frac{1}{2}\right) \int_0^\infty (E - E_f)^2 f'(E) dE$$

However, at low temperatures such that $k_B T \ll E_f$, the derivatives $f'(E)$ is large only at energies near E_f as shown in given figure (9.1); it is negligible for other values of E, particularly for negative values of E. The lower limit on the integrals may thus be replaced by -∞; we shall now solve the integrals as follows:

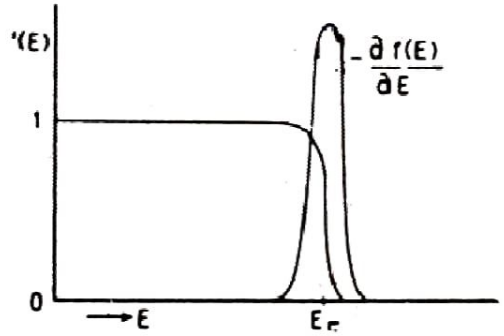


Figure 9.1 The function f(E) and$-\frac{\partial f(E)}{\partial E}$.

$$L_0 = \int_{-\infty}^{\infty} f'(E)dE = -[f(E)]_{-\infty}^{\infty}$$

$$L_0 = -[f(E)]_{-\infty}^{\infty} = \left[\frac{1}{1 + e^{\frac{E - Ef}{k_B T}}} \right]_{\infty}^{-\infty} = [1 - 0] = 1$$

$$L_1 = -\int_{-\infty}^{\infty} (E - E_f) f'(E) dE$$

Where $f(E) = \left[\frac{1}{1+e^{\frac{E-Ef}{k_B T}}}\right] = \left(1 + \exp\left(\frac{E-Ef}{k_B T}\right)\right)^{-1}$

Thus $f'(E) = -\left[\frac{1+e^{\frac{E-Ef}{k_B T}}}{k_B T}\right]^{-2} e^{\frac{E-Ef}{k_B T}}$

$$f'(E) = -\left(\frac{1}{kB\ T}\right) \frac{e^{\frac{E-Ef}{k_B T}}}{\left[1+e^{\frac{E-Ef}{k_B T}}\right]^2}$$

Thus $L_1 = \int_0^{\infty} (E - E_f) \left(\frac{1}{kB\ T}\right) \frac{e^{\frac{E-Ef}{k_B T}}}{\left[1+e^{\frac{E-Ef}{k_B T}}\right]^2} dE$

The integral vanishes because $f'(E)$ is an even function of $(E - E_f)$, and the integral is thus an odd function which when integrated from -∞ to ∞ will yield zero.

Now $L_2 = -\left(\frac{1}{2}\right) \int_{-\infty}^{\infty} (E - E_f)^2 f'(E) dE$

With $f'(E) = -\left(\frac{1}{kB\ T}\right) \frac{e^{\frac{E-Ef}{k_B T}}}{\left[1+e^{\frac{E-Ef}{k_B T}}\right]^2}$

Put $x = \frac{E-Ef}{k_B T}$

i.e. $(k_B T) dx = dE$

Substituting these values in L_2 relation,

$$L_2 = \frac{1}{2} \int_{-\infty}^{\infty} \frac{(k_B T)^2 x^2 e^x (k_B T) dx}{[1 + e^x]^2 (k_B T)}$$

$$L_2 = \frac{(k_B T)^2}{2} \int_{-\infty}^{\infty} \frac{x^2 e^x dx}{[1 + e^x]^2}$$

The solution of this standard integral is $\frac{\pi^2}{3}$, thus

$$L_2 = \frac{\pi^2 (k_B\, T)^2}{6}$$

Thus equation (9.6.6) becomes $I = \int_0^{\infty} f(E) g(E) dE$

$$I = g(E_f) + \frac{\pi^2 (k_B T)^2}{6} g''(E_f) + \cdots \qquad (9.6.7)$$

Equation (9.6.7) is a convenient form for working out Fermi integrals given by equations (9.6.1) and (9.6.3). but it is restricted by the condition g(E)=0 when E=0 and by the condition that $k_B T \ll E_f$.

Hence, to evaluate the integral given by equation (9.6.1), we choose

$$g(E) = \int_0^{E_f} Z(E) dE$$

With g'= Z(E) and g'' = Z'(E)

From equation (9.6.1) and (9.6.7), we write

$$N = \int_0^{\infty} f(E) Z(E) dE = \int_0^{E_f} Z(E) dE \ + \frac{\pi^2 (k_B\, T)^2}{6} \mathrm{Z'(E)} \qquad (9.6.8)$$

At 0K, F(E)=1 for $0 \leq E \leq E_f$ and thus

$N = \int_0^{\infty} f(E) dE Z(E)$with F(E)=1

i.e. $$N = \int_0^{E_f} Z(E) dE \qquad (9.6.9)$$

Now equating equations (9.6.8) and (9.6.9), we get

$$\int_{E_F}^{E_f} Z(E) dE \ + \frac{\pi^2 (k_B\, T)^2}{6} [\mathrm{Z'(E)}]_{E_f} = 0 \qquad (9.6.10)$$

Now we assume that Z(E) does not vary much in the interval from E_F to E_f, which for $k_B T \ll E_f$ will be only a small fraction of E_F. Hence we can write above equation as in the form

$$Z(E_f)(E_f - E_F) + \frac{\pi^2 (k_B\, T)^2}{6} \mathrm{Z'(E)} = 0$$

Since Z(E) is the form $C(E_f)^{\frac{1}{2}}(E_f - E_F) + \frac{\pi^2 (k_B\, T)^2}{6} \left[\frac{C(E)^{\frac{1}{2}}}{2}\right]_{E_f} = 0$

$$C(E_f)^{\frac{1}{2}}(E_f - E_F) + \frac{\pi^2 (k_B\, T)^2}{6} \left[\frac{C(E)^{\frac{1}{2}}}{2E}\right]_{E_f} = 0$$

$$(E_F - E_f) - \frac{\pi^2 (k_B\, T)^2}{12} = 0$$

$$E_f = E_F - \frac{\pi^2 (k_B\,T)^2}{12} \tag{9.6.11}$$

where $E_F$is the Fermi level at absolute zero and E_f that at higher temperature such that $k_B T \ll E_f$.

However, the second term of equation (9.6.11) is a very small correction term that should be subtracted from a relatively large term E_F. For example, the Fermi energy of copper is about 7eV. Thus

$$\frac{\pi^2}{12}\frac{(kB\;T)^2}{7} = \frac{\pi^2}{12}\frac{(0.023)^2}{7} = 10^{-4} eV$$

Now if E_f in equation (9.6.11) is replaced by E_F on the right hand side. Thus equation (9.6.11) can be written as

$$E_f = \left[E_F - \frac{\pi^2(kB\;T)^2}{12E_F}\right] = \left[E_F - \frac{\pi^2(k_BT)^2 E_F}{12{E_F}^2}\right]$$

$$E_f = E_F\left[1 - \frac{\pi^2(k_B\;T)^2}{12{E_F}^2}\right] \tag{9.6.12}$$

Equation (9.6.12) indicates that Fermi energy is not constant, but decreases slowly as the temperature rises. The result given by equation (9.6.12) is quite satisfactory, but while using it, we must remember that it is applicable only at temperatures such that $k_B T \ll E_f$, which includes the whole range of temperatures for which the metals are solids.

For determining the mean energy of an electron at other temperatures, we have to evaluate the integral given by equation (9.6.3) choosing

$$g(E) = \int_0^E EZ(E)dE$$

With $$g' = EZ(E) and\; g'' = \frac{\partial}{\partial E}[EZ(E)]$$

Referring from equation (9.6.8), the total energy of the electronic system written as

$$U = \int_0^\infty Z(E)EdEf(E) = \int_0^{E_f} EZ(E)dE \; + \frac{\pi^2(k_B\,T)^2}{6}\frac{\partial}{\partial E}[EZ(E)]_{E_f}$$

$$U = \int_0^{E_F} EZ(E)dE + \int_{E_F}^{E_f} EZ(E)dE \; + \frac{\pi^2(k_B\,T)^2}{6}\frac{\partial}{\partial E}[EZ(E)]_{E_f}$$

Or $$U = U_0 + \int_{E_F}^{E_f} EZ(E)dE \; + \frac{\pi^2(k_B\,T)^2}{6}\frac{\partial}{\partial E}[EZ(E)]_{E_f}$$

where $$U_0 = \int_0^{E_F} EZ(E)dE$$

The procedure which we used to solve the equation (9.6.10), is also used here to solve the above equation. In the last term Z(E) is evaluated at E_F, rather than E_f.

Thus $$U = U_0 + E_F Z(E_F)\int_{E_F}^{E_f} dE + \frac{\pi^2(k_B\,T)^2}{6}\frac{\partial}{\partial E}\left[EC(E)^{\frac{1}{2}}\right]_{E_f}$$

$$U = U_0 + E_F Z(E_F)\left(E_f - E_F\right) + \frac{\pi^2(k_B\,T)^2}{6}\left[C\frac{3}{2}(E)^{\frac{1}{2}}\right]_{E_f}$$

$$U = U_0 + E_F Z(E_F)\left(E_f - E_F\right) + \frac{\pi^2(k_B\,T)^2}{4} Z(E_F)$$

Now we substituting the value of $\left(E_f - E_F\right)$ from equation (9.6.12)

$$U = U_0 - E_F Z(E_F)\frac{\pi^2(k_B\,T)^2}{12E_F} + \frac{\pi^2(k_B\,T)^2}{4} Z(E_F)$$

$$U = U_0 + \frac{\pi^2(k_B\,T)^2}{6} Z(E_F) \tag{9.6.13}$$

When we put E = E_F, we have

$$Z(E_F) = \left(\frac{\pi}{2}\right)\left(\frac{8m}{h^2}\right)^{\frac{3}{2}} V(E_F)^{\frac{1}{2}} \tag{9.6.14}$$

and from relation $\frac{1}{(E_F)^{\frac{3}{2}}} = \left(\frac{\pi}{3N}\right)\left(\frac{8m}{h^2}\right)^{\frac{3}{2}} V$

i.e. $\left(\frac{\pi}{2}\right)\left(\frac{8m}{h^2}\right)^{\frac{3}{2}} V = \left(\frac{3N}{2}\right)\frac{1}{(E_F)^{\frac{3}{2}}}$

Substituting this in equation (9.6.14)

$$Z(E_F) = \left(\frac{3N}{2}\right)\frac{1}{(E_F)^{\frac{3}{2}}}(E_F)^{\frac{1}{2}} = \frac{3N}{2E_F}$$

Substituting this value of $Z\left(E_F\right)$ in equation (9.6.13)

$$U = U_0 + \frac{\pi^2(k_B\,T)^2}{6}\frac{3N}{2E_F}$$

$$\frac{U}{N} = \frac{U_0}{N} + \frac{\pi^2(kB\,T)^2}{4E_F}$$

$$\bar{E} = \bar{E}_0 + \frac{\pi^2(k_B\,T)^2}{4E_F}$$

We know that the relation between $\bar{E}_0$ and E_F is given by

$$E_F = \frac{5}{3}\bar{E}_0$$

Now substituting this value of E_F in the above equation, we have

$$\bar{E} = \bar{E}_0 + \frac{\pi^2}{4}\left(\frac{k_B T}{E_F}\right)^2 E_F$$

$$\bar{E} = \bar{E}_0 + \frac{\pi^2}{4}\left(\frac{k_B T}{E_F}\right)^2 \frac{5}{3}\bar{E}_0$$

$$\bar{E} = \bar{E}_0\left[\mathbf{1} + \frac{\mathbf{5\pi^2}}{\mathbf{12}}\left(\frac{\boldsymbol{k_B T}}{\boldsymbol{E_F}}\right)^{\mathbf{2}}\right] \tag{9.6.15}$$

In equations (9.6.12) and (9.6.15) E_F and $\bar{E}_0$ are referring to quantities at T=0 K. It is thus observed that as T increases E_F decreases and $\bar{E}$ increases slightly. The changes are small due to the occurrence of the factor $\left(\frac{k_B T}{E_F}\right)^2$. At room temperature, the factor $\left(\frac{k_B T}{E_F}\right)^2$ is only 2×10^{-5} for $E_F = 5eV$ and so for practical purposes, the Fermi level may be considered as a constant.

The significance of the above equations may be studied by considering the specific heat problem. The specific heat at constant volume is

$$[C_v]_{el} = \left[\frac{\partial \bar{E}}{\partial T}\right]_v = \frac{5}{6}\pi^2 \bar{E}_0\left[\frac{{k_B}^2 T}{{E_F}^2}\right]$$

Now we use relation $\bar{E}_0 = \frac{3}{5}E_F$, we have

$$[C_v]_{el} = \frac{\pi^2}{2}\left[\frac{k_B T}{E_F}\right] k_B$$

Thus for a monovalent metal, the heat capacity per k mol of the metal due to free electron is

$$[C_v]_{el} = \left(\frac{\pi^2}{2}\right)\left[\frac{k_B T}{E_F}\right] k_B N_A = \left(\frac{\pi^2}{2}\right)\left[\frac{k_B T}{E_F}\right] R_u \tag{9.6.16}$$

$$[C_v]_{el} = \left(\frac{\pi^2}{2}\right)\left[\frac{k_B T}{k_B T_F}\right] k_B N_A = \left(\frac{\pi^2}{2}\right)\left[\frac{T}{T_F}\right] R_u = AT \tag{9.6.17}$$

Where $A = \left(\frac{\pi^2}{2}\right)\left[\frac{{k_B}^2 N_A}{E_F}\right]$

For $\boldsymbol{E_F} = \mathbf{5}\boldsymbol{eV}$ and **300 K**

$$[C_v]_{el} = \left(\frac{\pi^2}{2}\right)\left[\frac{k_B T}{E_F}\right] R_u = \left(\frac{\pi^2}{2}\right)\left[\frac{0.025}{5}\right] R_u$$

$$[C_v]_{el} = 0.025 R_u \tag{9.6.18}$$

This value is higher than that predicted by equation $[C_v]_{el} = 0.015R_u$ and this result agrees with the value which calculates by the experiment. Expression (9.6.17) differs from classical result of $\frac{3}{2}R_u$ by a factor $\left(\frac{\pi^2}{2}\right)\left[\frac{T}{T_F}\right]$ which amounts to

0.025 for $E_F = 5eV$ at 30°C. Thus the quantum mechanical theory predicts a specific heat much smaller than the classical value of $\frac{3}{2}R_u$.

Ratio of electronic specific heat calculated quantum mechanically and classically is

$$\frac{[C_v]_{el}(Q.Mech)}{[C_v]_{el}(Classical)} = \frac{\left(\frac{\pi^2}{2}\right)\left[\frac{k_B\,T}{E_F}\right]R_u}{\frac{3}{2}R_u} = 0.57 \text{ X } 10^{-4}T \qquad (9.6.19)$$

The electronic specific heat together with the lattice specific heat gives the total specific heat of a solid. Equation(9.6.17) tells that the electronic contribution varies linearly with temperature whereas the lattice specific heat varies as the cube of absolute temperature at low temperature range. Thus the total specific heat at low temperature is given by

$$C_v(Total) = [C_v]_{el} + [C_v]_{iat}$$

$$[C_v]_T = AT + BT^3 \qquad (9.6.20)$$

where A and B are constants. But the lattice specific heat contribution at high temperature region is $3R_u$ and is independent of temperature. Equation (9.6.20) is thus written as

$$\frac{C_v}{T} = A + BT^2 \qquad (9.6.21)$$

Figure (9.2) indicates the lattice, electronic and total specific heats for the metal cobalt at low temperature range. It is clear from the graph that the electronic contribution to the total specific heat in this range is significant.

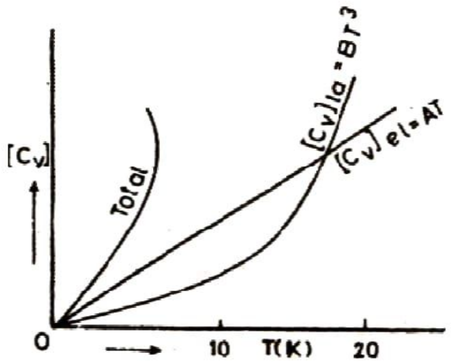


Figure 9.2: ***Different contribution to the total specific heat of cobalt.***

Figure (9.3) shows that a plot of $\frac{C_v}{T}$ as a function of T^2 gives a straight line. From this graph the values of the constants A and B can be determined, which are useful in checking the theoretically predicted specific heat values of metals.

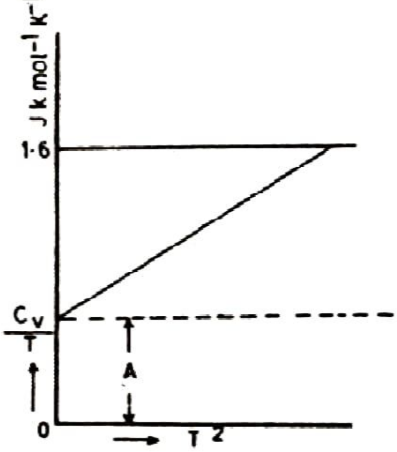


Fig. 9.3: ***Keesom plot for copper***

The plot for copper in figure (9.3) yields a value 0.695 for A. Using $E_F = 7.1eV$, one gets A = 0.508 using the equation (9.6.17). Thus calculated value is much smaller than observed value. This will be resolved if we remember that the free electrons in the system are not actually completely free, and that they rather move in a periodic potential. Hence if we use the effective mass $m*$ instead of m (for copper m*=1.5m) for calculating E_F, the expected agreement with the experimental results immediately appear.

9.7 Experimental Heat Capacity of Metals

We already know that one gram of water takes 4.18 joules of energy to increase its temperature by 1ºC. This is the most energy any substance takes to raise its temperature 1ºC. In contrast to taking the highest energy to raise its temperature by 1ºC, this means that it also take longest to cool it down. This means that water has the highest heat capacity. It must release 4.184 joules of energy in order to decrease its temperature by just 1 ºC. The water releases the heat absorbed by its environment. Knowing the heat capacity of water, it is possible to find how well its environment insulates it. Also using the heat capacity of water, one can figure out the heat capacity of an unknown substance by putting it in water and measure the temperature change of the water and of the unknown substance.

9.8 Electrical Conductivity

In equilibrium condition the valence electrons obeying classical free electron theory do random motion with no preferential velocity in any direction. It is now conveniently plotted the velocities of these free electrons in velocity (v_f) which is the maximum velocity that an electron can have i.e. v_f is the actual velocity value of the electron at the Fermi level. The shape having v_f as a radius represents, therefore, the Fermi surface. The velocity vectors cancel each other in pair at equilibrium and no net velocity of the electron exists.

It is very interesting to note that although all the electrons participate in the conduction mechanism, the relaxation time of only those electrons which are at the Fermi level occurs in the conductivity. The conductivity is proportional to the Fermi surface area. Thus, metals with large Fermi surface areas will have high electric conductivity; whereas insulators with zero Fermi surface areas will have zero conductivity.

Since, for a free electron $v = \left[\frac{\hbar k}{m}\right]$ (9.8.1)

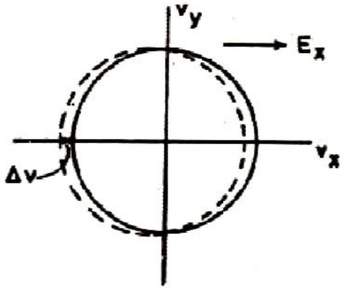


Fig 9.4: ***Displacement of Fermi surface with an electric field.***

The equation of motion of each electron in the Fermi surface under the influence of a static electric field of intensity, **E** is

$$\hbar\left[\frac{dk}{dt}\right] = Ee \tag{9.8.2}$$

This means that in the absence of collisions, the Fermi sphere will be at a constant rate in **k**-space.

The following approach yields the quantum mechanical expression for electrical conductivity. Now from the integration of above equation (9.8.2) is

$$\boldsymbol{k}(t) - \boldsymbol{k}(0) = \left[\frac{eEt}{\hbar}\right] \tag{9.8.3}$$

Thus if the electrical field is applied at time t=0 to a filled Fermi sphere centered at the origin of **k**-space, then in a characteristic time

$$\tau = \tau_F = \frac{\lambda_F}{v_F} \tag{9.8.4}$$

The sphere will have moved to a new centre at

$$\Delta\boldsymbol{k} = \frac{eE\lambda_F}{\hbar v_F} \tag{9.8.5}$$

Collisions create an opposing effect tending to restore the displaced surface back to its (t=0) equilibrium position: A steady current is ultimately reached with

$$J = \left[\frac{ne\hbar\Delta k}{m^*}\right] = \sigma\boldsymbol{E} \tag{9.8.6}$$

$$\left[\frac{ne\hbar}{m^*}\right]\frac{eE\lambda_F}{\hbar v_F} = \sigma\boldsymbol{E}$$

$$\sigma = \left[\frac{ne^2\lambda_F}{m^* v_F}\right] \tag{9.8.7}$$

$$\sigma = \left[\frac{ne^2\tau_F}{m^*}\right] \tag{9.8.8}$$

$$J = \sigma\boldsymbol{E} = \left[\frac{ne^2\tau_F}{m^*}\right]\boldsymbol{E}$$

The above treatment is based on the free electron approximation. A similar treatment may be given for the band approximation. The result of such a calculation is

$$\sigma = \left[\frac{n_{eff}e^2\tau_F}{m^*}\right] \text{ with } \tau_F = \frac{\lambda_F}{v_F} \tag{9.8.9}$$

The real picture of electrical conduction in metals is quite different from classical one,in which it was assumed that the current is carried equally by all electrons,each moving with an average drift velocity v_d. But quantum mechanical treatment tells us that current is in fact, carried out by the latter is more accurate.

The only quantity on the right hand side of above equation (9.8.9) which depends on temperature is the mean free path λ_F. Since this mean free path is inversely proportional to the temperature at high temperatures, it follows that $\sigma \propto \frac{1}{T}$; or $\rho \propto T$, in agreement with experimental conclusions. Thus the Fermi surface is very important in transport phenomenon. Since the flow of current is by electrons close to the Fermi surface, these phenomena are very sensitive to properties, shape etc. of this surface. Thus the inner electrons are irrelevant so far as conduction processes are concerned.

The mean free path of the electron in a metal may now be computed from the above said quantum mechanical treatment of conductivity. The resistivity of copper is $1.7\text{X}10^{-2}\Omega$-m. Thus

$$\rho = \left(\frac{m^*}{ne^2\tau_F}\right) \text{with } m^* = 1.01m$$

9.9 Matthiessen's Rule

This rule is simply based on resistivity of the metals. It is very easy task to explain the temperature dependence of resistivity using following model: we assume that the crystal is free from the deviation that the presence of impurity atoms and other point defects that will upset the lattice periodicity and estimate $\lambda_F \; and \; \tau_F$ as determined only by lattice vibrations. We, thus, proceed by assuming that the scattering of the electron wave is due to the finite size of the vibration amplitude of the atoms, that is , the vibrational amplitude produces a scattering cross-section; that mean free path is obtained directly by using kinetic theory formula. It is also assumed that at high temperatures, the lattice vibrations are essentially classical.

If M is the mass of the atom, and $(-fx)$ is the $restoring\,force$ on the displaced atom, the equation of the atomic oscillator is

$$M\frac{d^2x}{dt^2} + fx = 0$$

$$\frac{d^2x}{dt^2} + \left(\frac{f}{M}\right)x = 0$$

where $\omega = 2\pi\upsilon = (\frac{f}{M})^{\frac{1}{2}}$. x- is the amplitude of vibration.

The potential energy of the oscillator will be

$$\frac{1}{2}(M\omega^2x^2) = \frac{1}{2}M[4\pi^2\upsilon^2x^2]$$

$$P.E. = 2\pi^2M\upsilon^2x^2 = \frac{k_BT}{2} \tag{9.9.1}$$

It is PE per degree of freedom. At high temperatures, at the Einstein and the Debye frequencies are essential the same, and most of the modes are the high frequency modes, we write

$$\omega^2 = {\omega_E}^2 = {\omega_D}^2 \tag{9.9.2}$$

With $h\upsilon_D = k_B\theta_D$.

Thus $${\omega_D}^2 = (2\pi\upsilon_D)^2 = 4\pi^2\left(\frac{k_B\theta_D}{h}\right)^2$$

$${\omega_D}^2 = \left(\frac{2\pi k_B\theta_D}{h}\right)^2$$

From equation (9.9.1) $x^2 = \frac{k_BT}{4\pi^2M{\upsilon_D}^2}$

Now substituting v_D from equation (9.9.2)

$$x^2 = \left(\frac{k_B T}{4\pi^2 M}\right)\left(\frac{h}{k_B \theta_D}\right)^2$$

$$x^2 = \left(\frac{h^2 T}{4\pi^2 k_B M}\right)\left(\frac{1}{\theta_D}\right)^2$$

$$x^2 = \left(\frac{\hbar^2 T}{k_B M {\theta_D}^2}\right) \tag{9.9.3}$$

Since the scattering cross-sections are proportional to the squares of the amplitudes, we write scattering cross-section,

$$Q_f = constant\ x\ x^2$$

$$Q_f = constant\ x\ \frac{\hbar^2 T}{k_B M {\theta_D}^2}$$

From kinetic theory that the mean free path is given by

$$\lambda = \frac{1}{nQ_f} = \left(\frac{1}{n}\right)\frac{(constant)}{x^2}$$

$$\text{i.e. } \lambda \propto \frac{1}{nx^2}$$

here n is the number of atoms in one cubic metre.

We know that $\tau = \frac{\lambda}{v}$

Thus $\tau = (constant)\ x \frac{1}{nvx^2}$

From equation (9.9.3)

$$\tau = \frac{(constant)}{nv}\left[\frac{k_B M {\theta_D}^2}{\hbar^2 T}\right]$$

$$\tau_F = \frac{(constant)}{nv_F}\left[\frac{k_B M {\theta_D}^2}{\hbar^2 T}\right] \tag{9.9.4}$$

$$\tau_F v_F = \lambda_F = \frac{(constant)}{n}\left[\frac{k_B M {\theta_D}^2}{\hbar^2 T}\right](T \gg \theta_D)$$

i.e.

$$\lambda_F \propto \frac{1}{T} \tag{9.9.5}$$

Substituting this value of τ_F in equation (9.9.9), we get

$$\sigma = constant \times \left(\frac{e^2}{m^* v_F}\right)\left(\frac{k_B M {\theta_D}^2}{\hbar^2 T}\right)\ for\ (T \gg \theta_D) \tag{9.9.6}$$

Assuming there is one conduction electron per atom.

i.e.

$$\rho \propto T$$

The temperature dependence of resistivity given by equation (9.9.6) is in agreement with the experimental value. It is emphasized once again that the theory applies only to temperature $T \gg \theta_D$.

At low temperature, we use the model suggested by Bloch and Debye. At temperatures much lower than the Debye temperature ($T \gg \theta_D$), a relaxation time cannot be defined consistently. The above theory, therefore, cannot be extended to low temperatures, since the lattice vibrations begin to die out, the scattering cross-section would fall and we would therefore except that their contribution to the resistivity, usually denoted by ρ_P will decrease at low temperatures, eventually becoming zero at 0K. A detailed calculation shows that at low temperatures, ρ_P varies as T^5 and this changes over to a linear dependence on T at higher temperatures.

The larger the amplitude of vibration at any temperature, the greater will be ρ_P. Since this amplitude depends on the inverse of the Debye temperature (θ_D), it is to expect that ρ_P will be less for metals with a high θ_D, and vice versa, and this is confirmed by experiment. The arrangement of point defects in a crystal resistivity ρ_0, which they produce, would be expected to be constant. The contribution to the resistivity is temperature independent, but of course, increases with the impurity concentration.

The total resistivity ρ is therefore

$$\rho = \rho_0 + \rho_P(T) \tag{9.9.7}$$

This is shown in figure (9.4), in which it can be seen that ρ at first decreases linearly with T, and at low temperatures, it flattens off to a constant value, equal to ρ_0, which is called the *residual resistivity*. it is clear that, for a very pure sample, ρ_0 will be very small, whereas for an impure specimen, it will have a high value.

The probabilities of electrons being scattered by photons and by impurities are additive, since these two mechanisms are assumed to act independently. Therefore we may write

$$\frac{1}{\tau} = \frac{1}{\tau_P} + \frac{1}{\tau_0} \tag{9.9.8}$$

where the first term on the right is due to photons and second is due to impurities. The former is expected to depend on T and latter on impurities, but not on T. Thus

$$\rho = \rho_0 + \rho_P(T) = \frac{m^*}{ne^2\tau_0} + \frac{m^*}{ne^2\tau_P} = \frac{m^*}{ne^2}\left[\frac{1}{\tau_P} + \frac{1}{\tau_0}\right] \tag{9.9.9}$$

The simple addition of $\rho = \rho_0 + \rho_P(T)$ in equation (9.9.9) is often referred to as $\boldsymbol{Matthissen's\,rule}$ .The thermally induced part of the resistivity, ρ_P , is sometimes known as the $ideal\,resistivity,$ whereas the resistivity which has its origin in impurities and defects is summed up in the $residual\,resistivity, \rho_0$.Since the resistivity is inversely proportional to τ_F, associated with the electrons at the Fermi level, the impurity scattering leads to a constant term in Matthiessen's rule.

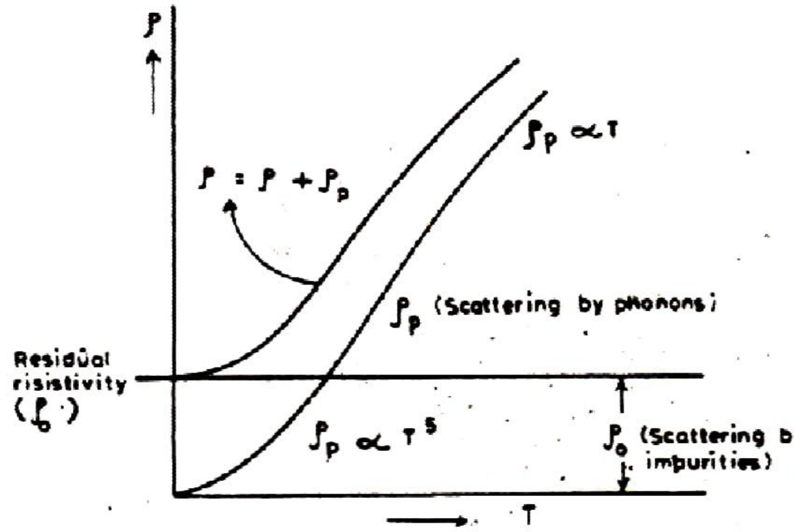


Fig: 9.5: ***The electrical resistivity,ρ, is the sum of two contributions. A constant ρ_0 due to scattering by impurities and ρ_P which is caused by electrons being scattered by photons.***

The resistivity of metals arises due to scattering of the conduction electrons by the lattice vibrations, by the impurities and by the structural imperfections. At low temperatures, the impurity scattering is dominant and the resistivity due to it is found to be practically temperature independent. The total $resistivity(\rho)$ of the metal can be given as the sum of the three components, ρ_l is resistivity due to lattice scattering which is temperature dependent, ρ_i is the resistivity due to scattering by impurities and ρ_d is the resistivity due to defects or dislocation in the structure. That is:

$$\rho = \rho_l + \rho_i + \rho_d$$

This is the $\boldsymbol{Matthissen's\,rule}$ in stick sense.

9.10 Umklapp Scattering

Suppose that two phonons collide and form third phonon. The probability of such a collision process is controlled by the magnitude of the anharmonic terms in the description of the energy. The properties of the resulting phonon are controlled by laws of energy conservation and of crystal momentum conservation.

We remarked earlier in connection with the inelastic scattering of slow neutrons by vibrations of a crystal momentum $\hbar k$ of a phonon is not the same thing as "ordinary" momentum. Thus a normal vibrational mode (a standing wave) in a finite crystal has zero momentum with respect to the crystal as a whole. Yet ordinary momentum is transferred to a crystal when phonons are created or destroyed by external stimulation such as the scattering of an incident neutron or $\beta - particle$. The question of whether crystal momentum $\hbar k$ must be conserved or not depends on the detailed circumstances of the transition being considered.

At any rate, crystal momentum is conserved when two phonons collide to produce a single phonon such that

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 \tag{9.10.1}$$

$$\text{and} \quad \hbar\boldsymbol{k}_1 + \hbar\boldsymbol{k}_2 = \hbar\boldsymbol{k}_3 \tag{9.10.2}$$

in the conservation of energy and momentum. Such a process is known as a $normal - process\ or\ N - process.$ As we can see, if we sketch the vector diagram of equation (9.10.2), an N-process does not alter the direction of energy flow; thus it makes no contribution towards the thermal resistance. If N-process were the only possible phonon-phonon interactions inside a perfect crystal, the lattice thermal conductivity would be infinite.

However, Peierls showed that thermalization of phonon population could proceed by process which satisfied equation 9.10.1 for energy conservation, and also the vector relationship

$$\boldsymbol{k}_1 + \boldsymbol{k}_2 = \boldsymbol{k}_3 + \boldsymbol{G} \tag{9.10.3}$$

Here G is a reciprocal lattice vector. Since a phonon of wave-vector $(\boldsymbol{k}_3 + \boldsymbol{G})$ is indistinguishable from a phonon of ave-vector k_3 in a periodic lattice. Equation (9.10.3) is evidently a valid conservation law. Peierls called such events $Umklapp - process, or\ U - process$.The intriguing aspect of a U-process is that it destroys momentum and changes the direction of energy flow (as given in figure 9.6 in which energy is carried to the right by $\boldsymbol{k}_1 and\ \boldsymbol{k}_2$, but to the left by the final state$\boldsymbol{k}_3$). Thus U-process provide thermal resistance to phonon flow and can thermalize a phonon distribution.

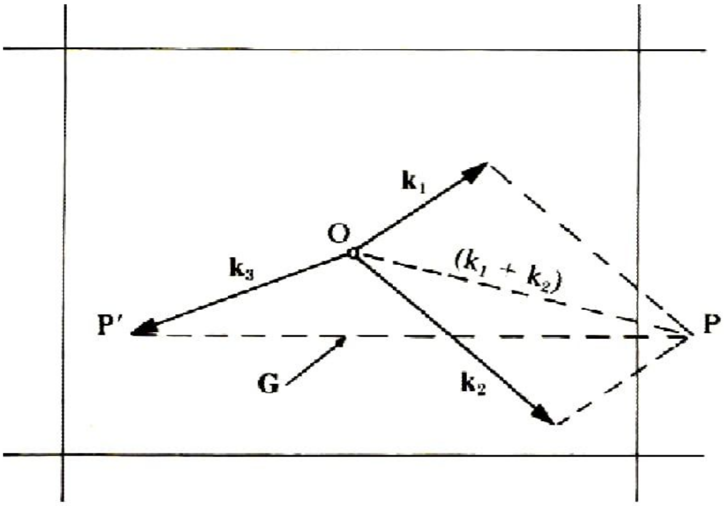


Figure 9.6: ***A section through k-space, showing the vector relationships of wave-vectors for an Umklapp process.***

Peierls noted that the mean free path set by U-processes would vary asT^{-1} at high temperatures, since the excitation of all lattice modes is proportional to T for temperature larger than θ_D. Interesting things happen when we consider the chances for U-processes at lower temperatures, only the regions of k-space close to centre of the Brillouin zone remain heavily populated with phonons; yet a U-process cannot occur unless $(\boldsymbol{k}_1 + \boldsymbol{k}_2)$ extends beyond the zone boundary. This requires that the probability of U-processes would fall off as $\exp\left(-\frac{\theta_u}{T}\right)$ at low temperature probability of N-processes, which should fall off as T^5 well below the Debye temperature.

Behaviour of the form

$$A \propto \exp\left(\frac{\theta_u}{T}\right) \tag{9.10.4}$$

It is indeed seen in numerous solids, though the value of θ_u required for a fit is usually smaller than $\theta_D/2$. Thus in sapphire (Al_2O_3) the Debye temperature θ_D~$1000\ K$ and Umklapp temperature θ_u~$250\ K$. The phonon mean free path on sapphire at 50 K is about is about 10^{-2} cm, some 30 times larger than would be given by extrapolation of the high temperature T^{-1} line.

Phonon-phonon processes more complicated than the ones we have considered so far also occur. Both N-processes and U-processes involving larger numbers of phonons have to be considered in more complete discussions of thermal resistance. These higher order processes affect the behaviour to an appreciable extent only at rather high temperatures.

9.11 Self Learning Exercise

Q.1 Given that one gram molecule of a gas at 0°C and a pressure of 760mm of mercury occupies a volume of 22.414 liters, compute the number of molecules in the gas at 0°C and 760mm of mercury.

Q.2 Compute the average kinetic energy of a gas molecule at 27°C. Express the result in electron volt. If the gas is hydrogen, what is the order of magnitude of the velocity of the molecules at 27°C?

Q.3 The relaxation time of conduction in copper is 2.5×10^{-14}sec. Find the thermal conductivity of copper at 0°C. Assume density of electrons to be 8.5×10^{28}.

Q.4 Calculate the number of energy states available for the electrons in a cubical box of side 1cm lying below an energy of 1 electron volt.

Q.5 Evaluate the temperature at which there is one percent probability that a state, with an energy 0.5 electron volt above the Fermi energy, will be occupied by an electron.

Q.6 The Fermi energy of silver is 5.51 electron volt. (a) What is the average energy of the free electrons is silver at 0 K?(b) What temperature is necessary for the average molecular energy in an ideal gas to have this value.? (c) What is the speed of the electron with this energy?

9.12 Summary

In this unit we study about the Fermi energy and free electron Fermi gas. This unit gives us very important information about some important topic as Free Electron Model, Matthissen's Rule, type of scattering, electrical conductivity of metals and Fermi Dirac Distribution.

9.13 Glossary

Electron Gas: The motion of electron in a metal is like perfect gas, so it constitutes the electron gas.

Fermions: These are the particle which obey Fermi-Dirac Statistics and fill in the electron shell according to Pauli's exclusion principle.

Fermi-Dirac Distribution: This distribution is according to the Pauli's exclusion principle.

Fermi Energy: The maximum kinetic energy of electron is known as Fermi energy. It depends upon the temperature.

Phonon: It is quanta of Lattice heat vibration.

9.14 Answers to Self Learning Exercise

Ans.1: $22.414 \times 10^3 (cm^3)$ of the gas will contain 6.02×10^{23} molecules.

Hence $1\ cm^3$ will therefore contain:

$$\frac{6.02 \times 10^{23}}{22.414 \times 10^3} = 2.69 \times 10^{19} = 2.69 \times 10^{25}/m^3$$

Ans.2: We know that the equation of kinetic energy is

$$E = \frac{1}{2}(mc^2) = \left(\frac{3}{2}\right) k_B T = 1.5 \times k_B T$$

With $k_B = 1.38 \times 10^{-23} \frac{joule}{kelvin}$, $T = 27 + 273 = 300\ K$

Thus, $E = 1.5 \times 1.38 \times 10^{-23} \times 300$

$E = 6.21 \times 10^{-21}$ joule or $E = \frac{6.21 \times 10^{-21}}{1.6 \times 10^{-19}}\ eV = 0.039 eV$

and now $c = \sqrt{\frac{3k_B\,T}{M_H}}$

With $k_B = 1.38 \times 10^{-23} \frac{J}{K}$, $T = 300\ K$

$M_H = 1.008 \times 2 \times 1.67 \times 10^{-27}\ kilogram$

Thus $c = \sqrt{\frac{3k_B\,T}{M_H}} = \sqrt{\left[\frac{3 \times 1.38 \times 10^{-23} \times 300}{2 \times 1.008 \times 1.67 \times 10^{-27}}\right]} = 1921\ metre\ /second$

Ans.3: $\sigma_T = \frac{k_B nc\,\lambda}{2}$,But $\lambda = \tau$ c

Thus $\sigma_T = \frac{k_B n \tau c^2}{2}$

With $c = \sqrt{\frac{3k_B\,T}{m}}$

Thus $\sigma_T = \left[\frac{k_B n\tau}{2}\right] \times \left[\frac{3k_B\,T}{m}\right] = \left[\frac{3{k_B}^2 n\tau T}{2m}\right]$

With $n = 8.5 \times \frac{10^{28}}{m^3}, \tau = 2.5 \times 10^{-14}\ sec,\ k_B = 1.38 \times 10^{-23} joule/kelvin$

$T = 273\ K, \qquad m = 9.1 \times 10^{-31} kilogram$

$$\sigma_T = \left[\frac{3 \times 8.5 \times 10^{28} \times 2.5 \times 10^{-14} \times (1.38 \times 10^{-23})^2 \times 273}{2 \times 9.1 \times 10^{-31}}\right]$$

$$\sigma_T = 182 \frac{W}{m - K}$$

Ans.4: $Z(E)dE = \left[\frac{\pi}{2}\right]\left[\frac{8ma^2}{h^2}\right]^{\frac{3}{2}} E^{\frac{1}{2}} dE$

Thus the number of energy states below one electron volt is:

$$\int_0^E Z(E)dE = \left[\frac{\pi}{2}\right]\left[\frac{8m}{h^2}\right]^{\frac{3}{2}} V \int_0^E E^{\frac{1}{2}} dE$$

With $m = 9.1 \times 10^{-31} kg\ \ , V = 10^{-6} m^3, E = 1 \times 1.6 \times 10^{-19} joule$

Thus the number of energy states is,

$$= \left[\frac{\pi}{2}\right]\left[\frac{8m}{h^2}\right]^{\frac{3}{2}} V \left[\frac{2}{3} E^{\frac{3}{2}}\right]_0^{1(eV)}$$

$$= \left[\frac{\pi \times 2}{2 \times 3}\right]\left[\frac{8 \times 9.1 \times 10^{-31}}{(6.62 \times 10^{-34})^2}\right]^{\frac{3}{2}} (10^{-6})[1.6 \times 10^{-19}]^{\frac{3}{2}} = 4.5\ \times\ 10^{21}$$

Ans.5: We know that $F(E) = \frac{1}{1+\exp\left[\frac{E-E_F}{k_B T}\right]}$

$$E = E_F + 0.5$$

Thus $F(E) = \frac{1}{100} = \frac{1}{1+\exp\left[\frac{0.5}{k_B T}\right]}$

i.e. 0.01 = 1/1+e^x where $x = \frac{0.5}{k_B T}$

Thus, $0.01 + 0.01e^x = 1$

$$0.01e^x = [1 - 0.01] = 0.99$$

$$e^x = \frac{0.99}{0.01}$$

i.e. $x = 2.303 \times log_{10}99$

$$\frac{0.5}{k_B T} = 2.303 \times log_{10}99$$

$$\frac{0.5}{2.303 \times log_{10}99} = k_B T$$

$$k_B T = 0.109\ electron\ volt$$

$$T = 0.109 \times 1.6 \times 10^{-19}/1.38 \times 10^{-23}$$

$$T = 1262\ kelvin$$

Ans.6: (a) The average electron energy at 0 K is given by

$$\bar{E}_0 = \frac{3}{5} E_F = \frac{3}{5} \times 5.51\bar{E}_0 = 3.306\ \ (eV)$$

(b) The average molecular energy in an ideal gas at temperature, T degree Kelvin is $\frac{3}{2} k_B T$.

i.e. $\bar{E}_0 = \frac{3}{2} k_B T$ or $T = \frac{2}{3} \frac{\bar{E}_0}{k_B}$

With $\bar{E}_0 = 3.306 \times 1.6 \times 10^{-19}\ joule,\ \ k_B = 1.38 \times 10^{-23} joule/kelvin$

Thus,

$$T = \frac{2}{3} \frac{\times 3.306 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} = 2.56 \times 10^4\ K$$

(c) Let the velocity of the electron be v metre/sec, then its kinetic energy is:

$\bar{E}_0 = \frac{1}{2} m v^2$ i.e. $v = \frac{\sqrt{2\bar{E}_0}}{\sqrt{m}}$

With $\bar{E}_0 = 3.306 \times 1.6 \times 10^{-19}\ joule\ \ , m = 9.1 \times 10^{-31} kilogram$

Now, $v = \sqrt{\left[\frac{3 \times 3.306 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}\right]} = 1.3 \times 10^6 m/s.$

9.15 Exercise

Q.1 What is Fermi energy? Write down its relation with the concentration of electrons in metals.

Q.2 What is the sources of electrical resistivity in metals?

Q.3 Explain Fermi-Dirac distribution function. Plot this function for various temperatures including 0 K.

Q.4 What is meant by density of energy states in metals?

Q.5 Discuss electrical conductivity in metals.

Q.6 How does Fermi energy change with temperature ?

Q.7 Give the brief description of heat capacity of electron gas.

Q.8 Give a brief account of effect of temperatures on Fermi Dirac distribution.

Q.9 What is Matthissen's Rule? Give related description.

Q.10 How do you explain the electrical conductivity of metals on the free electron gas model?

Q.11 Give the brief summary of Umklapp Scattering.

References and Suggested Readings

1. Solid State Physics by Neil W. Ashcroft and N. David Mermin
2. Introduction to Modern Solid State Physics by Yuri M. Galperin
3. Solid State Physics by R. J. Singh
4. Applied Solid State Physics by M R Srinivasan.

UNIT 10

Free Electron Model : Part-II

Structure of the Unit

10.0 Objectives

This unit is based on the thermal properties of metals mainly, such as thermal conductivity, Hall Effect, *Schottky* effect and some other properties of metals such as AC conductivity and optical properties & *paramagnetism* of metals. These all above written topic has explained on the basis of Free Electron Model.

10.1 Introduction

Metals are generally those materials which possess good electrical and thermal conductivities. The free electron theory, which was able to explain the conductivities of the materials, was proposed by *Drude* and further developed by Lorentz. Based on these free electron model *Drude* and Lorentz derived theoretical expressions for electrical and thermal conductivities and evaluated the ratio between them, which is well known as Lorentz number. This theory was applied to understand several other physical properties as well. Based on this theory, some metals, when subjected to combined electric and magnetic fields, showed positive values for the hall coefficient which proved the presence of positive charge carriers, contrary to the normal expectations as most possess negative Hall constants.

10.2 Free Electron Model

According to Rutherford and Bohr arguments, electrons revolve in the circular stationary orbit around the nucleus. All positive charge of the atom is concentrated in the nucleus. The electrons in outer orbit are known as valence electrons. In case of metals, these valence or outermost orbital electrons are loosely bound to the nucleus and they can move through the volume of the crystal in free manner. Hence, the valence electrons are also known as free electrons.

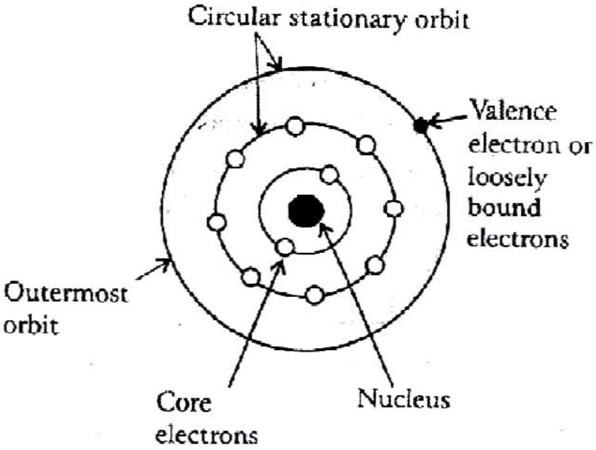


Figure: 10.1 Atomic structure of sodium

The behaviour of moving free electrons inside the metals is analogous to that of atoms or molecules in perfect gas and are called free electron gas. The free electron gas, however, differs from ordinary gas:

(1) The molecules of an ordinary gas are neutral while the free electron gas is negatively charged.

(2) The concentration of molecules in an ordinary gas is very small in comparison to the concentration of electrons in a free electron gas.

The classical theory of free electron gas (**Drude Lorentz Theory)** assumes that the free electron gas obeys M.B. statistics and explains various properties of metals such as;

Validity of Ohm's law, high thermal and electrical conductivity of metals $\left(\frac{\sigma}{K} = constant\right)$, complete opacity of metals etc. But the classical theory fails to explain the heat capacity & paramagnetic susceptibility of the conduction electrons. Sommerfeld explained these characteristics by treating the problem quantum mechanically using F.D. statistics. According to Sommerfeld, the potential energy for an electron in crystal is periodic.

10.3 Thermal Conductivity in Metals

Heat conduction is the transfer of thermal energy from a hot body to a cold body when both the bodies are brought into contact. For best visualization we consider a bar of a material of length x whose ends are held at different temperatures. The amount of thermal energy Q which crosses unit area of this bar per unit time (i.e. the heat flux J_Q) is proportional to the temperature gradient $\frac{dT}{dx}$. The proportionality constant is called as the Thermal Conductivity σ_T. We can write

$$J_Q = -\sigma_T \frac{dT}{dx} \tag{10.3.1}$$

The negative sign indicates that the heat flows from the hot to the cold end. The unit of heat conductivity is $Wm^{-1}K^{-1}$.The thermal conductivity decreases by 20% within a temperature range of 1000°C. In the same temperature region σ_T for iron decreases by 10%.

In insulators, heat is carried entirely by phonons, but in metals heat may be transported by both electrons and phonons. The conductivity σ_T is equal to the sum of the two contributions.

$$\sigma_T = \sigma_e + \sigma_p$$

In most metals, the contribution of the electrons greatly exceeds that of the phonons, because of the great concentration of electrons; typically $\sigma_p = 0.01\sigma_e$. Hence σ_p is usually neglected.

Here now question arises, as to what velocity do the electrons have, and do all the electrons participate in the heat conduction?

For the answer of this question we follow this model given as:

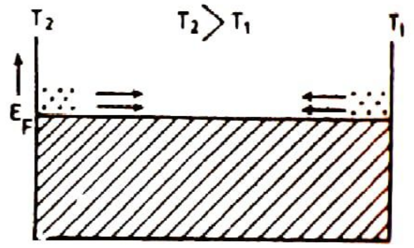


Figure 10.2: Energetic electrons on the left carry net energy to the right.

Electrons at the hot end travel in all directions, but a certain fraction travel to the right and carry energy to the cold end. Similarly, a certain fraction of electrons at the cold end travel to the left, and carry to the hot end. These oppositely travelling electron currents are equal but because those at the hot end are more energetic on the average than those on the right, a net energy is transported to the right, resulting in a current of heat. Note that heat is transported almost entirely by those electrons near Fermi levels, because those well below this level cancel each other's contributions. Once more it is seen that the electrons at the Fermi surface play primary role in transport phenomenon. The velocity of such electrons is calculated using the formula

$$\mathrm{E}_F = \frac{1}{2} m v_F{}^2 \tag{10.3.2}$$

For the evaluation the thermal conductivity σ_T, we use the expression $\sigma_T = \frac{1}{3}[C_v]_{el} c n \lambda$. In this expression, $[C_v]_{el}$ is the electronic specific heat per unit volume. In the present case $[C_v]_{el}$ should be substituted from equation

$$[C_v]_{el} = \left(\frac{\pi^2}{2}\right)\left[\frac{k_B\, T}{E_F}\right] k_B N_A = \left(\frac{\pi^2}{2}\right)\left[\frac{k_B\, T}{E_F}\right] R_u$$

Also R_u should be replaced by $R = nk_B$, since we are dealing here with unit volume rather than a kmol. In addition, c and λ should be replaced by v_F and λ_F, since only electrons at the Fermi levels are effective. Thus

$$\sigma_T = \frac{1}{3}[C_v]_{el} c n \lambda$$

$$\sigma_T = \frac{1}{3}\left[\left(\frac{\pi^2}{2}\right)\left[\frac{k_B\,T}{E_F}\right] k_B\right] v_F n \lambda_F$$

$$\sigma_T = \frac{\pi^2}{6}\left[\frac{n {k_B}^2\,T \lambda_F v_F}{E_F}\right]$$

Now from the equation (10.3.2), we have

$$\sigma_T = \frac{\pi^2}{3}\left[\frac{n {k_B}^2\,T \lambda_F v_F}{m {v_F}^2}\right]$$

$$\sigma_T = \left(\frac{\pi^2}{3}\right)\left[\frac{n {k_B}^2\,T \tau_F}{m}\right]$$

With $\tau_F = \frac{\lambda_F}{v_F}$

So we get $\sigma_T = \left(\frac{\pi^2}{3}\right)\left[\frac{n {k_B}^2\,T \tau_F}{m}\right]$ (10.3.3)

This equation expresses thermal conductivity in terms of the electronic properties of the metal. Substituting the usual values of the microscopic quantities in equation (10.3.3), we get

$$\sigma_T = 350\,Wm^{-1}K^{-1}.$$

Recalling that $\sigma = \frac{ne^2\tau_F}{m}$, we get

$$\frac{\sigma_T}{\sigma} = \left(\frac{\pi^2}{3}\right)\left[\frac{n {k_B}^2\,T \tau_F}{m}\right]\left(\frac{m}{ne^2\tau_F}\right)$$

$$\frac{\sigma_T}{\sigma} = \left(\frac{\pi^2}{3}\right)\left[\frac{k_B}{e}\right]^2 T \qquad (10.3.4)$$

This quantum mechanical equation gives a comparison of thermal conductivity with electrical conductivity. The relation is the $\boldsymbol{Wiedemann-Franz\ law}$ obtained using quantum theory. Thus $Lorentz\ number\ L$ is given by

$$L = \frac{\sigma_T}{\sigma T} = \left(\frac{\pi^2}{3}\right)\left[\frac{k_B}{e}\right]^2 = 2.45 \times 10^{-8}\ watt\ ohm\ kelvin^{-2} \qquad (10.3.5)$$

This remarkable result involves neither m nor n. It does not involve the relaxation time τ. This Lorentz number L, because it depends only on the universal constants k_B and e, should be the same for all metals. This conclusion suggests that the electrical and thermal conductivities are closely related, which is to be expected since both electrical and thermal current are carried by the same agent electrons. Experimental values of L at 0°C and 100°C is for $Ag\ are\ 2.31 \times 10^{-8}\ and\ \ 2.37 \times 10^{-8}$ respectively.

At low temperatures the Lorentz number tends to decrease. This is due to difference in the collision averages involved in the electrical and thermal conductivities; the thermal and electrical relaxation times are not identical.

The theory for low temperature region is very complicated; but it can be said that at very low temperatures τ becomes constant and σ_T, thus, has to go to zero as T⟶0. However, σ_T continues to rise as T goes down, because scattering is less likely even among the phonons that do exist. The thermal conductivity keeps rising as T goes down until the mean free path is limited by geometrical scattering; that is, the sample dimensions themselves finally set an upper limit to λ. Further reduction of temperature now causes σ_T to drop since $C_v \longrightarrow 0$. It may also be mentioned- impurity scattering. In such a case, if such a case, if the two types of scattering are independent, we may write for the total conductivity σ_T as

$$\frac{1}{\sigma_T} = \frac{1}{\sigma_i} + \frac{1}{\sigma_l}$$

where σ_l is the contribution arising from electron-lattice scattering and σ_i is the contribution from electron impurity scattering.

10.4 Cyclotron Resonance

According to Maxwell's equations, a magnetic field applied to an electron tends to change the electron's direction of motion without changing its energy. The Lorentz force is given by

$$F = -e(E + \frac{1}{c}(v \times H) \qquad (10.4.1)$$

Here e is the velocity of electron, H is magnetic field and E is electric field.

Thus magnetic field H_z affects motion in the XY plane without affecting motion in the z- direction. If the electron is not scattered, it executes an orbit in the XY plane, superimposed on any trajectory it may have in the z-direction.

For a quasi-free electron of scalar mass m^*, the orbit executed is a circular one, of radius r and angular frequency ω_c. These quantities are related by the requirement that the centrifugal force $(m^*\omega_c r)$ must balance the Lorentz force. Thus the angular frequency, known as the $cyclotron\ frequency$, is

$$\omega_c = \left(\frac{eH_z}{m^* c}\right) \tag{10.4.2}$$

For magnetic fields of the strength used in practice, this frequency lies in the range of microwave part of the electromagnetic spectrum, since in numerical terms

$$\nu_c = \left(\frac{\omega_c}{2\pi}\right) = 2.8\left(\frac{H_z m}{m^*}\right)\ MHz \tag{10.4.3}$$

for a magnetic field expressed in gauss.

The motion of the electron in real space under the influence of a magnetic field is accompanied by a precession through k-space on a path of $constant\ energy$ in the Brillouin zone. Of course, for the highly degenerate electron population in a metal, this motion is seen only for electrons at the Fermi energy, electrons which perform orbits in k-space around the Fermi surface. Since there is inevitably some scattering of electrons by phonons and defects even in a nearly perfect crystal at low temperatures, a well-defined cyclotron motion can be resolved only if $(\omega_c \tau_m) > 1$, so that an electron can move through a significant part of a magnetic orbit before it is scattered.

Experiments of $cyclotron\ resonance$ are based on the absorption of radio-frequency energy at a frequency ω when a steady magnetic field H is adjusted to make ω coincide with ω_c. Measured combinations of ω and H then allow us to deduce information about the tensor of effective mass at the Fermi energy. The theory of cyclotron resonance is in practice rather more complicated, both for semiconductors and for metals.

For a semiconducting material in which the free electron density is small, cyclotron resonance experiments can be carried out with e. m. waves penetrating throughout the solid. The complications which arise are associated with the topology of constant-energy surfaces, and with hybrid plasma resonances if the free electron density is not very small.

The frequencies used for cyclotron resonance studies in a metal are in variably much smaller than the plasma frequency, and the real part of the dielectric constant is negative. Accordingly, a metal is opaque for such frequencies, with a penetration depth δ much smaller than the probable thickness of a sample. The magnitude of the electronic mean free path λ then determines whether the surface electrical characteristics for R. F. waves are controlled by the *normal skin effect* or by the *anamalous skin effect*. The former situation holds if $\lambda < \delta$ and the latter when λ is large compared with the skin depth.

10.5 Hall Effect

This effect arises when a metal is subjected to a magnetic field. This effect sometimes also seems to contradict completely the classical picture of conduction. If a sample conducting material is placed in a uniform magnetic field and a current is passed along the length of the conductor as shown in figure 10.3, a voltage is found to develop at right angles to both the direction of the current flow and that of the magnetic field. This voltage is known as the *Hall voltage*, and its value is found to depend on the magnetic field strength and on the current passed. The mathematics of Hall effect is based on the simple dynamics of charges moving in electromagnetic fields.

Consider a specimen in the form of a rectangular cross-section as shown in figure 10.3 carrying a current I_x in $x-$direction. If a uniform magnetic field B_z is applied along z-axis, it is found that an emf develops along the y-axis i.e., in a direction perpendicular to I_x and B_z. This voltage is called Hall voltage.

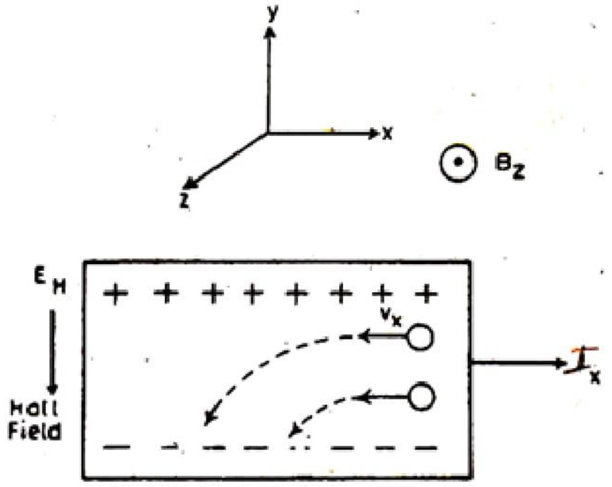


Figure 10.3: Origin of Hall field and Hall Effect.

Let us first consider the situation before the magnetic field is introduced. There is an electric current flowing in the positive $x-$direction, which means that the conduction electrons are drifting with a velocity v_x in the negative x −direction. When magnetic field is introduced, the $Lorentz\, force\; F_L$ causes the electrons to bend downward as shown in figure 10.3. As a result, electrons accumulate on the lower surface, producing a net negative charge there. Simultaneously a net positive charge appears on the upper surface, because of the deficiency of electrons there. This combination of positive and negative surface charges creates a down-ward electric field, which is called $Hall\ field$.

The Lorentz force F_L which produces the charge accumulation in the negative y-direction, has the value.

$$F_L = \mathrm{e}v_x B_z$$

Now the field created by the surface charges produces a force which opposes this Lorentz force. The accumulation process continues until the Hall force completely cancels the Lorentz force. Thus, in the steady state, $F_H = F_L$.

$$eE_H = ev_x B_z$$

$$\text{or} \quad E_H = v_x B_z \tag{10.5.1}$$

The current density, j_x is given by the equation

$$j_x = -nev_x \tag{10.5.2}$$

Dividing equation (10.5.1) by equation (10.5.2)

$$\frac{E_H}{j_x} = -\frac{B_z}{ne}$$

$$\text{or} \qquad E_H = -\left(\frac{1}{ne}\right) j_x B_z$$

The Hall field is thus proportional, both to the current, and to the magnetic field. The proportionality constant, that is $\frac{E_H}{j_x B_z}$ is known as the Hall constant and is usually denoted by R_H i.e.,

$$\frac{E_H/j_x}{B_z} = -\frac{1}{ne} = R_H \tag{10.5.3}$$

Now the Hall constant or Hall coefficient R_H is defined as the ratio of the electric field strength produced per unit current density to the transverse magnetic field. It will be noted that R_H depends on the sign of ‘e’ and the reader should verify that if E_H is in certain direction for a flow of negative charges, then it will be in the opposite sense for the same current when it is produced by a flow of positive charges in a reverse direction. In the $monovalent$ metals, R_H is negative, which is consistent with our belief that the current is produced by a flow of negatively charged particles; the magnitude of R_H is then such that there is of the order of one moving charge per atom. In more complicated metals, particularly those in which there is band overlap, R_H can be due to positive holes.

From equation (10.5.3), we have

$$R_H = \frac{E_H}{j_x B_z} = \left(\frac{V_y}{y}\right)\left(\frac{yz}{I_x}\right)\frac{1}{B_z} = \left(\frac{v_y z}{I_x B_z}\right) \qquad (10.5.4)$$

$$Unit\ of\ R_H = volt - m/amp - weber/m^2 = Vm^3A^{-1}wb^{-1}$$

Example: For silver and cadmium the Hall coefficient is -0.84 and +0.60, respectively.

The general expression for current density is

$$j_x = nev_x$$

i.e. electrical conductivity

$$\sigma = \frac{j_x}{E_x} = \frac{(ne)v_x}{E_x}$$

The drift velocity produced for unit electric field is called the mobility of charge carriers.

i.e. $$\sigma = \frac{j_x}{E_x} = ne\mu_e;\ \ or\ \ \mu_e = \left(\frac{1}{ne}\right)\sigma$$

$$\mu_e = R_H\sigma \quad ;\ or \quad \mu_e = \left(\frac{j_x}{E_x}\right)\frac{E_H}{j_x B_z}$$

$$\mu_e = \left(\frac{V_y}{B_z y}\right)\left(\frac{x}{V_x}\right) = \left(\frac{V_y}{V_x}\right)\left(\frac{x}{y}\right)\left(\frac{1}{B_z}\right) \qquad (10.5.5)$$

From above given equation, we can easily determine the mobility of electrons. Measurement of Hall voltage helps one to determine the following:

1. The sign of current-carrying charges can be determined.

2. The number of charge carriers present in unit volume can be calculated from the magnitude of R_H.

3. The mobility of the charge carriers may be obtained directly from the measurement of Hall voltage.

10.6 AC Conductivity and Optical Properties

If the D. C. conductivity of a superconductor is indeed infinite, then a current initiated in a closed loop of superconducting material should continue forever without any need for a driving electromotive force. On the other hand, if a superconducting loop of inductance L has a finite resistance R, then a persistent current should slowly decline in accordance with

$$I = I_0 \exp\left(-\frac{Rt}{L}\right) \tag{10.6.1}$$

Attempts to detect a decay rate in persistent currents were begun early in the history of superconductivity, and $Onnes\ and\ Tuyn$ concluded that the conductivity of lead was at least10^{16}/ohm-cm in the superconducting state. Compared with perhaps10^9/ohm-cm for highly pure lead just above T_c. Numerous experiments since then have extended the lower bound, and $Quinn\ and\ Ittner$ report that the lower limit conductivity is at least10^{23}/ohm-cm.

It is still important to draw a distinction between a superconductor, as a solid infinite D. C. conductivity, and a perfect conductor, as a solid which occupy Bloch states with zero scattering. Bardeen remarked that it is more fruitful to view a superconductor as an extreme case of diamagnetism rather than as a limiting case of infinite conductivity. At T=0, the conductivity is infinite only up to a limiting frequency, and at a finite temperature, there is a small A. C. loss at all frequencies.

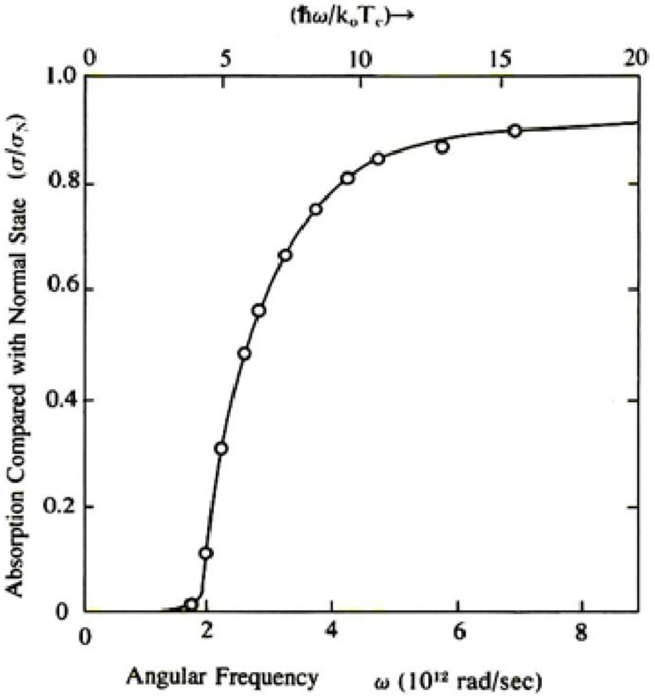


Figure 10.4: Frequency dependence of the electromagnetic absorption by a thin superconducting film of Indium.

The absence of superconductivity at optical frequencies was noted very early in the history of this subject and measurements in the 1930's showed that superconductivity disappeared at a frequency of more than $10^9\ Hz$ but less than $10^{14}\ Hz$. The more recent developments of far infrared techniques have permitted an accurate determination of the frequency dependence in the interesting region for a variety of superconductors. A typical occurs for a photon energy of about $4k_0T_c$ which is to be associated with an energy gap $\in_g$ between superconducting and "normal" electron states. Such an energy gap was postulated by F. London is an integral part of his phenomenological theory of superconductivity, and it lies at the heart of the BCS microscopic theory.

10.7 Paramagnetism of Free Electrons

Suppose we have a solid containing N magnetic atoms per unit volume, each with a magnetic moment $\boldsymbol{\mu}$ given by equation

$$\boldsymbol{\mu} = g\mu_B\boldsymbol{J} \tag{10.7.1}$$

For combination of applied field and ambient temperature which justifies a "weak-field" approximation, a paramagnetic susceptibility

$$\chi_m = \left(\frac{M}{H}\right) = \frac{N\mu^2}{3k_0T} = \frac{C}{T} \qquad \mu H \ll k_0 \tag{10.7.2}$$

This result is known as $Curie's\ Law$, and the quantity C is $Curie\ constant$ of the solid. Detail analysis is given in unit16.

10.8 Thermionic Emission and Richardson Equation

If we increase the temperature of any given metal, then it becomes heated and electrons are emitted from its surface, then this whole phenomenon is known as *thermionic emission.* This property is widely used in vacuum tubes, in which the metallic cathode is usually heated in order to supply the electrons required for the operation of the tube.

The given (10.6) figure shows the energy level scheme for electrons in metals, according to free electron model. At 0K, all the levels up to the Fermi level E_F are filled up, above which all levels are empty. Note also that an electron at E_F cannot escape from the metal because of the presence of an energy barrier at the surface. The height of this barrier, denoted by φ, is known as the *work function.*

This function varies from one metal to another, but generally falls in the range 1.5-5eV. At 0 K, no electrons can escape from the metal. But as the temperature of the metal is increased, the levels above E_F begin to be occupied because of the transfer of electrons from below E_F. Even the levels above than barrier, i.e. at energies higher than $(E_F + \phi)$ become populated to some extent. The electrons in these latter levels now have enough energy to overcome the barrier, and they are the ones responsible for the observed emission from the surface of the metals.

Let us consider the $x - direction$ perpendicular to the surface of the electron emitting solid. The critical value of the electron's momentum in the $x - direction$, so that it just escapes from the surface, is given by

$$\frac{p_{x_0}^2}{2m} = E_F + \phi = V_B \ or \ p_{x_0} = \sqrt{2m(E_F + \phi)} \qquad (10.8.1)$$

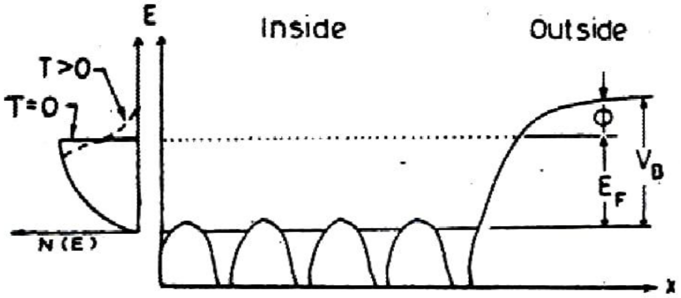


Figure10.6: Thermionic Emission

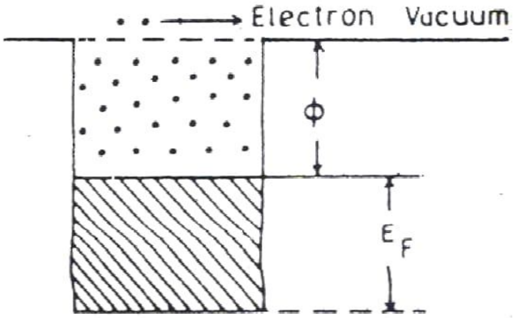


Figure 10.7: Ideal potential energy of an electron along a row of atoms near the surface, and the potential energy barrier at the surface which constrains the electrons to remain inside, the shaded area represents electron energy as given by the Fermi distribution shown on the left.

The height of the potential-energy barrier at the surface (V_B) is greater than that of the Fermi energy (E_F) by an amount φ, called the Work function.

The product of electronic charge and the number of electrons having a momentum in the $x-direction$ greater than its critical value, which strikes unit area of the surface in unit time, gives the thermionic current at a certain temperature. Let $N(P_x)$ represents the number of electrons per unit volume having momentum values $p_x \, and \, p_x + dp_x$ in the $x-direction.$ When the electron having momentum p_x arrives at the surface, its velocity will be $\frac{p_x}{m}$. Thus the number arriving at unit area of the surface in unit time is

$$\int_{p_{x_0}}^{\infty} \frac{p_x}{m} N(p_x)dp_x$$

Thus the $emission\ current\ density$ is

$$j = \frac{e}{m}\int_{p_{x_0}}^{\infty} p_x \, N(p_x)dp_x \tag{10.8.2}$$

Here $N(p_x)$ is the product of the number of possible states of momentum p_x and the probability that an electron is in each state. The number of states having momentum values lying between p and $p + dp$ may be written from the equation

$$Z'(E)dE = \frac{\pi}{2}\left[\frac{8m}{h^2}\right]^{\frac{3}{2}} E^{\frac{1}{2}}dE$$

Now we substitute $E = \frac{p^2}{2m}$ and $dE = p\left(\frac{dp}{m}\right)$ in above equation, we have

$$Z(p)dp = \left(\frac{\pi}{2}\right)\left[\frac{8m}{h^2}\right]^{\frac{3}{2}}\left(\frac{p^2}{2m}\right)^{\frac{1}{2}} p\left(\frac{dp}{m}\right)$$

$$Z(p)dp = \left(\frac{8\pi}{h^3}\right)p^2dp \tag{10.8.3}$$

This result gives the momentum values of p in any direction, but we are connected with momenta in the $x-direction$ specifically. We have now calculated the number of electrons that have a momentum lying in the range dp_x at p_x when p_y and p_z values are unrestricted. To do this, we construct a plot in $'momentum\ space'$ such that each point represents a particular combination of momentum components p_x, p_y and p_z with $p^2 = {p_x}^2 + {p_y}^2 + {p_z}^2$.

A spherical shell with $p = \sqrt{{p_x}^2 + {p_y}^2 + {p_z}^2}$ as radius and dp as thickness is drawn. Each momentum state with momentum between p and $p + dp$ lies in the shell. Thus the fraction of states at momentum which have momentum values lying in the interval p_x and $p_x + dp_x$, p_y and $p_y + dp_y$, p_z and $p_z + dp_z$ is given by the ratio of the volume $dp_x dp_y dp_z$ to the volume of spherical shell of radius p and thickness dp.

i.e., fraction of states in $dp_x dp_y dp_z = \frac{dp_x dp_y dp_z}{4\pi p^2 dp}$.

Hence the number of states in the momentum interval $dp_x dp_y dp_z$ is obtained by multiplying the above fraction by the total number interval dp at momentum p. Thus

$$Z(p_x p_y p_z) dp_x dp_y dp_z = \left(\frac{8\pi}{h^3}\right) p^2 dp \frac{dp_x dp_y dp_z}{4\pi p^2 dp}$$

$$= \left(\frac{2}{h^3}\right) dp_x dp_y dp_z \qquad (10.8.4)$$

Equation (10.8.4) gives the number of states per cubic metre with momentum component in the x-direction lying between the values p_x and $p_x + dp_x$ and, similarly, for p_y and p_z.

Now number of electrons per unit volume having momentum values p_x and $p_x + dp_x$ in the $x - direction$ is given by:

$$N(p_x)dx = \left(\frac{2}{h^3}\right) dp_x \int \frac{dp_y dp_z}{1 + e^{\frac{E - E_F}{k_B T}}}$$

$$N(p_x)dx = \left(\frac{2}{h^3}\right) dp_x \int_{p_y=-\infty}^{\infty} \int_{p_z=-\infty}^{\infty} \frac{dp_y dp_z}{1 + e^{\frac{E - E_F}{k_B T}}}$$

(10.8.5)

At 27°C (300 K), $E - E_F \gg k_B T$, hence 1 is neglected. We also know that

$$E = \frac{1}{2m}\left(p_x{}^2 + p_y{}^2 + p_z{}^2\right)$$

The equation (10.8.5) becomes

$$N(p_x)dx = \left(\frac{2}{h^3}\right) dp_x \int_{p_y=-\infty}^{\infty} \int_{p_z=-\infty}^{\infty} e^{-\frac{E}{k_B T}} e^{\frac{E_F}{k_B T}} dp_y dp_z$$

Now we solve the equation on Right Hand Side

$$R.H.S. = \left(\frac{2}{h^3}\right) dp_x \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{(p_x{}^2+p_y{}^2+p_z{}^2)}{2mk_BT}} e^{\frac{E_F}{k_BT}} dp_y dp_z$$

$$= \left(\frac{2}{h^3}\right) dp_x e^{\frac{E_F}{k_BT}} e^{\frac{-p_x{}^2}{2mk_BT}} \int_{-\infty}^{\infty} e^{\frac{-p_y{}^2}{2mk_BT}} dp_y \int_{-\infty}^{\infty} \exp\left[\frac{-p_z{}^2}{2mk_BT}\right] dp_z$$

The integrals have the standard form

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dp_z = \sqrt{\frac{\pi}{\alpha}}$$

Thus

$$N(p_x)dx = \left(\frac{2}{h^3}\right) e^{\frac{E_F}{k_BT}} e^{\frac{-p_x{}^2}{2mk_BT}} dp_x \sqrt{2\pi mk_BT}\sqrt{2\pi mk_BT}$$

$$N(p_x)dx = \left(\frac{4\pi mk_BT}{h^3}\right) e^{\frac{E_F}{k_BT}} e^{\frac{-p_x{}^2}{2mk_BT}} dp_x$$

Substituting the above value in equation (10.8.2), we have

$$j = \frac{e}{m}\left(\frac{4\pi mk_BT}{h^3}\right) \int_{p_{x_0}}^{\infty} e^{\frac{E_F}{k_BT}} e^{\frac{-p_x{}^2}{2mk_BT}} p_x dp_x$$

Now substituting the value of $\frac{-p_x{}^2}{2m}$ from the general equation (10.8.1), we have

$$j = \frac{e}{m}\frac{4\pi mk_BT}{h^3} \int e^{\frac{E_F}{k_BT}} e^{\frac{-E_F}{k_BT}} e^{\frac{-\phi}{k_BT}} m d\phi$$

$$j = \left(\frac{e}{m}\right)\left(\frac{4\pi mk_BT}{h^3}\right) m \int_{\phi}^{\infty} e^{\frac{-\phi}{k_BT}} d\phi$$

$$j = \left(\frac{4\pi emk_B{}^2T^2}{h^3}\right) e^{\frac{-\phi}{k_BT}}$$

$$j = \frac{4\pi emk_B{}^2}{h^3} T^2 e^{\frac{-\phi}{k_BT}}$$

$$j = AT^2 e^{\frac{-\phi}{k_BT}} \qquad (10.8.6)$$

This equation is commonly known as $\boldsymbol{Richardson - Dushman\ equation}$,with A the emission coefficient. Thus $A = \frac{4\pi emk_B{}^2}{h^3} = 1.20 \times 10^6\ amp\ m^{-2}K^{-2}$

Equation (10.8.6) indicates that the emission current is exponentially dependent upon the work function, and inversely dependent upon the absolute temperature; which means that the variation of emission with these quantities is very rapid.

$$\frac{j}{T^2} = Ae^{\frac{-\phi}{k_B T}}$$

Now taking 'log' both side in above equation, we have

$$log\frac{j}{T^2} = logA - \frac{\phi}{k_B}\left(\frac{1}{T}\right) \qquad (10.8.7)$$

$$log\frac{j}{T^2} = logA - \left(\frac{b}{T}\right)$$

A plot of $log\frac{j}{T^2}$ against 1/T is a straight line having slope $\left(\frac{\phi}{k_B}\right)$ and an intercept to $logA$.

For Calcium A=60×$10^4 amp\, m^{-2}K^{-2}$ and for Cesium A=162×$10^4 amp\, m^{-2}K^{-2}$.

When we compare the values of A with the value obtained theoretically from equation (10.8.6), one finds greater discrepancy. This discrepancy is related to the difficulties associated with experiment measurements. The theory does not assume the use of any external field to remove the electrons from the emitter. But if we do not use it, a space will be existing in the vicinity of the emitter, which intends to decrease the current. Thus, in order to prevent the decrease of current, the use of an electric field is a must. This field must be strong enough to remove all the electrons as soon as they are emitted.

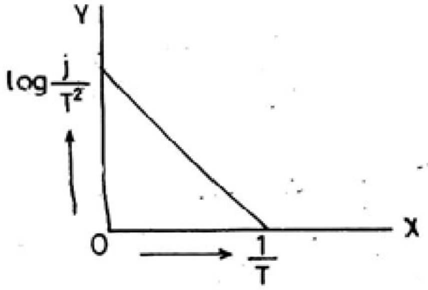


Figure 10.8: Graph between $1/T$ and j/T^2

However, the application of electric field changes the apparent work function; it decreases with increasing external field strength. Therefore, it is suggested to measure $j(T)$ for different electric fields and then extrapolated to get the correct value. Because of thermal expansion, the work function (ϕ) itself is a function of temperature. For metals $\frac{d\phi}{dT}$ is of order of $10^{-4} e\, V/K$. Therefore, φ should not be regarded as a constant, independent of temperature. The actual emission current is strongly dependent upon the surface conditions. Contamination of the surface may have a large effect on the value of φ and because of this; the exponential function may greatly modify the thermionic effect.

10.9 Schottky Effect

Here we shall study model for the process thermionic emission including (a) image force and (b) electric field.

An accelerating electric field is usually applied to the emitter, in order to remove the emitted electrons from the vicinity of the surface, and to accelerate them to the collector, where they constitute the *thermionic current*. This electric field besides doing this, also lowers the height of the potential energy barrier at the surface and hence increases the emission. This increase of emission and its dependence on the external electric field is called the *Schottky effect*.

Now we consider the following model of the potential energy barrier near the surface of the metal. The refinement is to add to the potential barrier the force on an electron outside the metal surface. Any charge when placed near the surface of a conductor experiences a force arising from the polarization of the conducting material. For distances that are large compared with the *interatomic* distances, the surface of the metal can be considered to be a plane perfect conductor for the present problem. The force on the electron can thus be calculated by *'method of images'* principle used in electrostatics problems. Now the force on the electron is equivalent to that of an equal positive charge placed at an equal distance behind the plane surface as the electron is in front. The force acting on the electron can be expressed as

$$F_{image} = \frac{1}{4\pi\epsilon_0}\left(\frac{e}{2x}\right)^2 = \frac{1}{4\pi\epsilon_0}\frac{e^2}{4x^2}$$

$$F_{image} = \frac{1 \times e^2}{16\pi\epsilon_0 x^2}$$

The *potential function* for this force is

$$V_{image} = \frac{e^2}{16\pi\epsilon_0}\int_{\infty}^{x}\frac{1}{x^2}dx$$

$$V_{image} = -\frac{e^2}{16\pi\epsilon_0 x}$$

The potential function is shown below in figure 10.9.

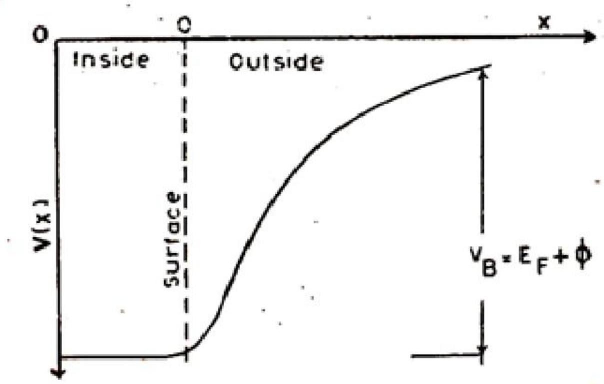


Figure 10.9: Actual form of the potential barrier near the surface of the metal.

Under the influence of an external electric field E_x, the potential experienced by the charge is the sum of the image potential and applied potential. The total potential is shown below in figure 10.10.

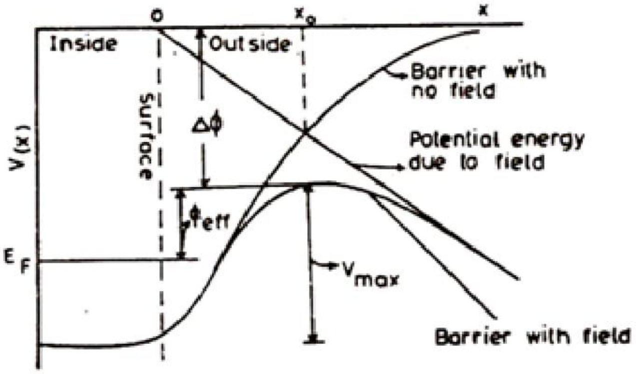


Figure 10.10: The total potential at the surface of a metal including both image forces and an external electric field.

The most important significance of this result is that the work function ϕ_{eff} in the field is less than that without the field. If the applied electric field is strong enough, it is clearly possible for ϕ_{eff} to vanish completely. When this happens, the top of the electron distribution is free to leave the metal without the necessity for *tunneling*. This reduction in work function is known as the *Schottky effect*. The magnitude of the reduction in the work function for a given system is obtained by following method:

The effective potential energy in the presence of the field is given by

$$V = -\frac{e^2}{16\pi\epsilon_0 x} - eEx \tag{10.9.1}$$

Since the work function is the difference between the barrier height and the position of the Fermi level, equation (10.9.1) represents the effective reduction in the work function due to the applied field. The maximum value of V may be obtained by differentiating the above equation with respect to x and putting $x = x_{max.}$ i.e.

$$\frac{dV}{dx} = 0 = \frac{e^2}{16\pi\epsilon_0 x_{max.}^2} - eE$$

$$\frac{e^2}{16\pi\epsilon_0 x_{max.}^2} = eE$$

$$\frac{e}{16\pi\epsilon_0 E} = x_{max.}^2$$

$$x_0 = x_{max.} = \frac{1}{\sqrt{16\pi\epsilon_0}}\left(\frac{e}{E}\right)^{\frac{1}{2}} \tag{10.9.2}$$

So now the equation (10.9.1) become

$$V_{max.} = -\frac{e^2}{16\pi\epsilon_0 x_{max.}} - eEx_{max.}$$

$$V_{max.} = -x_{max.}\left[\frac{e^2}{16\pi\epsilon_0 x_{max.}^2} + eE\right] \tag{10.9.3}$$

Substituting the value of $x_{max.}$ from equation(10.9.2) in equation (10.9.3), we have

$$V_{max.} = -\sqrt{\frac{e}{16\pi\epsilon_0 E}}\left[\frac{e^2}{16\pi\epsilon_0}\left(\frac{16\pi\epsilon_0 E}{e}\right) + eE\right]$$

$$V_{max.} = -\sqrt{\frac{e}{16\pi\epsilon_0 E}}\left[eE + eE\right]$$

$$V_{max.} = -2eE\sqrt{\frac{e}{16\pi\epsilon_0 E}}$$

$$V_{max.} = -e\sqrt{\frac{eE}{4\pi\epsilon_0}} \tag{10.9.4}$$

That is, the energy needed to escape from the metal is reduced by an amount $V_{max.}$. The effective work function is thus reduced from $\phi\ to\ \phi_{eff}$.

$$\phi_{eff} = \phi - e\left(\frac{eE}{4\pi\epsilon_0}\right)^{\frac{1}{2}}$$

Now substituting this value in equation (10.8.6), we get the new formula for thermionic emission as

$$j = [AT^2]\exp\left[\frac{\phi - e\sqrt{\left(\frac{eE}{4\pi\epsilon_0}\right)}}{k_B T}\right] \tag{10.9.5}$$

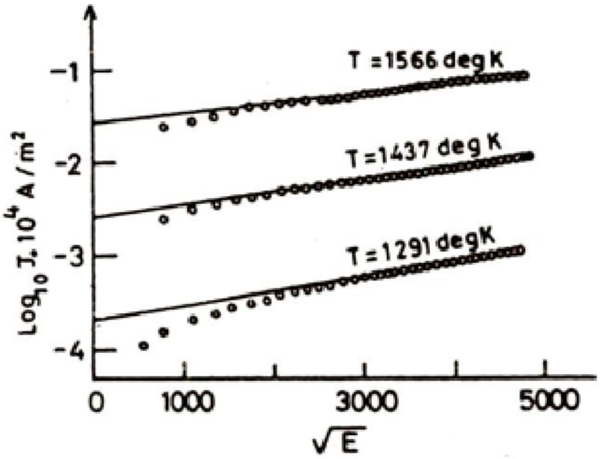


Figure 10.11: *Schottky* plots of the thermionic emission from uranium carbide at three temperatures.

Now if we shall plot the graph between $\log j$ against $\sqrt{E}$, we get the $Schottky\ line$.

A comparison with experimental results in figure 10.11. shows that above a certain value of electric field the relationship is quite accurate. The effect is ($\Delta\phi = 0.012eV\ for\ a\ field\ of\ 10^5Vm^{-1}$), but the effect on the emitted current may be appreciable.

10.10 Field Emission

In the discussion of thermionic emission, we have assumed that the potential of an electron jumps from zero inside a metal to $(\phi + \epsilon_F)$ immediately outside the surface, as is shown in figure 10.12 A. The quantum mechanical reflection factor is considerable for an abrupt barrier, even for electrons with energy larger than the barrier height.

The potential barrier encountered by a departing electron should be more gradual, as was first noted by Schottky. We might expect $V(x)$ to increase linearly with x at first; but when the electron is more than a few Å beyond the surface it should experience the attractive image force of a charge -e with respect to a homogeneous conducting plane, to give a potential energy

$$V(x) = (\phi + \epsilon_F) - \left(\frac{e^2}{4x}\right) \tag{10.10.1}$$

The correct asymptotic behaviour for very small and very large x is given in the form

$$V(x) = 0, x < 0$$

$$V(x) = \frac{(\phi+\epsilon_F)^2}{(\phi+\epsilon_F)+\left(\frac{e^2}{4x}\right)}, x > 0 \tag{10.10.2}$$

Which is illustrated in Figure 10.12 B. For an electron with an initial kinetic energy slightly larger than $(\phi + \epsilon_F)$, the quantum-mechanical probability of reflection is considerably smaller for a barrier represented by equation (10.10.2) than for a step function barrier.

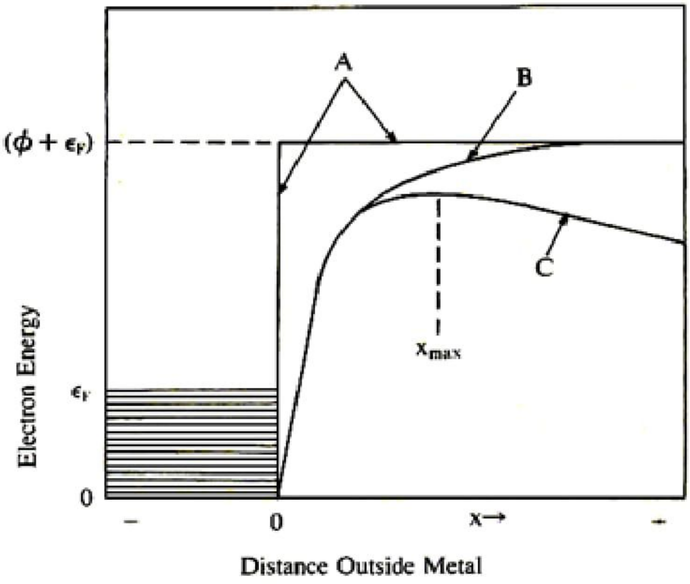


Figure 10.12: Electron energy inside a metal and in a vacuum surrounding the metal. The origin of energy is chosen as a state of rest inside the crystal.

Suppose that an electric field in the x-direction is created in the vacuum outside a heated metal crystal. This modifies the potential energy function to

$$V(x) = (\phi + \epsilon_F) - \left(\frac{e^2}{4x}\right) - exE \qquad (10.10.3)$$

For a locations more than a few Å outside the metal. A curve for the field-modified potential energy is shown as figure 10.12 C. differentiating V(x) with respect to x, we find that there is a maximum in the height of the potential barrier at

$$\left.\begin{aligned} x_{max} &= \left(\frac{e}{4E}\right)^{1/2} \\ V_{max} &= (\phi + \epsilon_F) - (e^3E)^{1/2} \end{aligned}\right\} \qquad (10.10.4)$$

Thus the presence of an external electric field produces a slight lowering of the effective work function. This is the phenomenon of Field Emission, or Schottky Emission. The lowering of the work function is small for fields of a few thousand volt/cm, and then the potential maximum is out many angstrom units from the crystal surface. Even a small reduction of work function makes thermionic emission possible for many electrons which are insufficiently energetic at zero field.

10.11 Failure of Free Electron Model

There are some satisfactory reasons for the failure of the free electron model, which are given below:

(1) By the help of Sommerfeld's quantum modification of free electron theory, we obtained a relation between electrical and thermal conductivities, known as $Lorentz\ number\ L$, but this expression is not satisfactory. This is due to the fact that this theory does not include mean free path. In order to obtain the correct values of conductivities, it is necessary to assume that the mean free path varies inversely as T, and its value at ordinary temperatures is of the order of 100 $interatomic$ distances. The existence of such a long mean free path cannot be explained on the basis of classical theory.

(2)This model also suggests that the electrical conductivity is proportional to electron concentration. But it is surprising that the $divalent$ metals($Be, Cd\ and\ Zn$), and even $trivalent$ metals (Al, In) are consistently low conductive than the *monovalent* metals. (Cu, Ag *and* Au), despite the fact that former has higher concentration of electrons.

(3) A very important testimony against this model is the fact that some metals exhibit positive Hall constants, for example, Be, Zn, Cd. The free electron model always predicts a negative hall constant.

(4)From the measurement of the Fermi surface, we saw that it is *nonspherical* in shape. This contradicts the model, which predicts a spherical Fermi surface. It is also a reason for failure of model.

(5) This theory is incapable of explaining why some crystals have metallic properties while other semiconductors and insulators.

(6)The most important feature of this theory is that it destroys the notion of classical theory that all free electrons are conduction electrons. According to *Sommerfeld's* theory only few electrons, whose energies lie in the vicinity of Fermi level, contribute to the mechanism of conduction and only those free electrons are called *conduction electrons*.

10.12 Self Learning Exercise

Q.1 A copper wire of length 0.5 metre and diameter 0.3 mm has a resistance 0.12Ω at 20°C. If the thermal conductivity of copper at 20°C is $390\ W\,m^{-1}K^{-1}$, calculate Lorentz number. Compare this value with the value predicted by classical free electron theory.

Q.2 The work function of tungsten is $4.5eV$. Calculate the thermionic emission of a filament 0.05 m long and 10^{-4} *metre* diameter that is at a temperature of 2400 K. How much the current increase if a field of would10^{7} *volt/meter* is applied to the surface?

Q.3 If the electrical resistivity of aluminium at 20°C is $2.87 \times 10^{-8}\Omega m$, calculate the electronic contribution of thermal conductivity of aluminium.

Q.4 Calculate the hall coefficient for sodium whose lattice constant is 0.428nm.

Q.5 If the Hall coefficient of silver is $-8.4\times10^{-11} m^3/C$, calculate the electron concentration.

Q.6 Give the Brief theory of Field Emission.

10.13 Summary

Basically in this unit, we study about the electrical and thermal properties of metals, such as Hall Effect, Cyclotron frequency, Thermionic Emission, $Schottky$ effect and Thermal conductivity of metals. Very important topic of this unit is that the expalnatory reasons which are responsible for failure of free electron model.

10.14 Glossary

Hall Effect: This effect arises when a current carrying metal/semiconductor is subjected to a magnetic field. This effect sometimes also seems to contradict completely the classical picture of conduction. If a sample conducting material is placed in a uniform magnetic field and a current is passed along the length of the conductor, this effect is known as Hall Effect.

Monovalent: These are defined as the atoms which having one valence electron.

Thermionic Emission: If we increase the temperature of any given metal, then it became heated and electrons are emitted from its surface, then this whole phenomenon is known as thermionic emission.

Thermionic Current: An accelerating electric field is usually applied to the emitter, in order to remove the emitted electrons from the vicinity of the surface, and to accelerate them to the collector, where they constitute the thermionic current.

10.15 Answers to Self Learning Exercise

Ans.1: We know that,

$$\rho = \frac{aR}{l}, \qquad or\ \sigma = \frac{l}{aR} = \frac{l}{(\pi r^2)R}$$

With $l = 0.5\, meter, r = 0.15 \times 10^{-3} meter,\ r = 0.12\Omega$

Thus,

$$\sigma = \frac{l}{(\pi r^2)R} = \frac{0.5}{\pi(0.15 \times 10^{-3})^2 \times 0.12}$$
$$\sigma = 5.89 \times 10^7 ohm^{-1}m^{-1}$$

Now, $\frac{\sigma_T}{\sigma T} = L = \frac{3}{2}\left(\frac{k_B}{e}\right)^2$

Theoretical value of Lorentz number from classical theory is calculated as follows:

$$L = \left[\frac{3}{2}\right]\left(\frac{k_B}{e}\right)^2$$

With $k_B = 1.38 \times 10^{-23}\, \frac{joule}{kelvin}\, , e = 1.6 \times 10^{-19}\, coulomb$

Thus, $L = \left[\frac{3}{2}\right]\left(\frac{1.38\times10^{-23}}{1.6\times10^{-19}}\right)^2$

The experimental value of L is obtained as follows:

$$L = \frac{\sigma_T}{\sigma(T)}$$

With $\sigma_T = 390\, Wm^{-1}K^{-1}, \sigma = 5.89 \times 10^7 ohm^{-1}m^{-1}\, , T = 293\, kelvin$

Thus, $L = \frac{390}{5.89\times10^7\times293}$

$$L = 2.26 \times 10^{-8}\, W\Omega K^{-2}$$

Thus, here we saw that the experimentally found value is twice the theoretically predicted classical value.

Ans.3: We know that $\sigma = \frac{1}{\rho}$

With $\rho = 2.87 \times 10^{-8}\Omega m$

So now $\sigma = \frac{1}{2.87\times10^{-8}}$

$$\sigma = 3.48 \times 10^7 ohm^{-1}m^{-1}$$

And we know that Lorentz number for Aluminium is

$$L = 2.02 \times 10^{-8} W\Omega K^{-2}$$

From the relation $L = \frac{\sigma_T}{\sigma(T)}$

$$\sigma_T = L\sigma(T)$$

$$\sigma_T = 2.02 \times 10^{-8} \times 3.48 \times 10^7 \times 293$$

$$\sigma_T = 205.9\, Wm^{-1}K^{-1} \approx 206 Wm^{-1}K^{-1}$$

Ans.4: Na will have two atoms per unit cell.

$$a = 0.428 \times 10^{-9}m$$

Two atoms occupy volumea^3,

Hence, the number of atoms/m^3 is

$$n = \frac{2}{a^3} = \frac{2}{(0.428 \times 10^{-9})^3} = 255 \times 10^{26}$$

As Na is monovalent each atom will contribute one free electron.

So, $n = 255 \times 10^{26}$

Now the Hall constant is:

$$R_H = -\frac{1}{ne} = -\frac{1}{255 \times 10^{26} \times 1.6 \times 10^{-19}} = -2.45 \times 10^{-10} m^3/C$$

Here the negative sign shows that the electrons are current carriers in the specimen.

Ans.5: We have for silver

$$R_H = -\frac{3\pi}{8ne} \ and\ n = -\frac{3\pi}{8R_H e}$$

Now substituting the value of e and R_H, in above equation, we get

$$n = -\frac{3 \times 3.14}{8 \times -8.4 \times 10^{-11} \times 1.6 \times 10^{-19}} = 8.8 \times 10^{28}/m^3$$

Ans.6: Here, we consider that the potential of an electron jumps from zero inside a metal to $(\phi + \epsilon_F)$ immediately outside the surface, as is shown in figure 10.12 A. The quantum mechanical reflection factor is considerable for an abrupt barrier, even for electrons with energy larger than the barrier height.

The potential barrier encountered by a departing electron should be more gradual, as was first noted by Schottky. We might expect $V(x)$ to increase linearly with x at first; but when the electron is more than a fewA^0 beyond the surface it should experience the attractive image force of a charge-e with respect to a homogeneous conducting plane, to give a potential energy

$$V(x) = (\phi + \epsilon_F) - \left(\frac{e^2}{4x}\right)$$

The correct asymptotic behaviour for very small and very large x is given in the form

$$\left.\begin{aligned} V(x) &= 0, x < 0 \\ V(x) &= \frac{(\phi + \epsilon_F)^2}{(\phi + \epsilon_F) + \left(\frac{e^2}{4x}\right)}, x > 0 \end{aligned}\right] -$$

Which is illustrated in Figure 10.12 B. For an electron with an initial kinetic energy slightly larger than$(\phi + \epsilon_F)$, the quantum-mechanical probability of reflection is considerably smaller for a barrier represented by equation (10.10.2) than for a step function barrier.

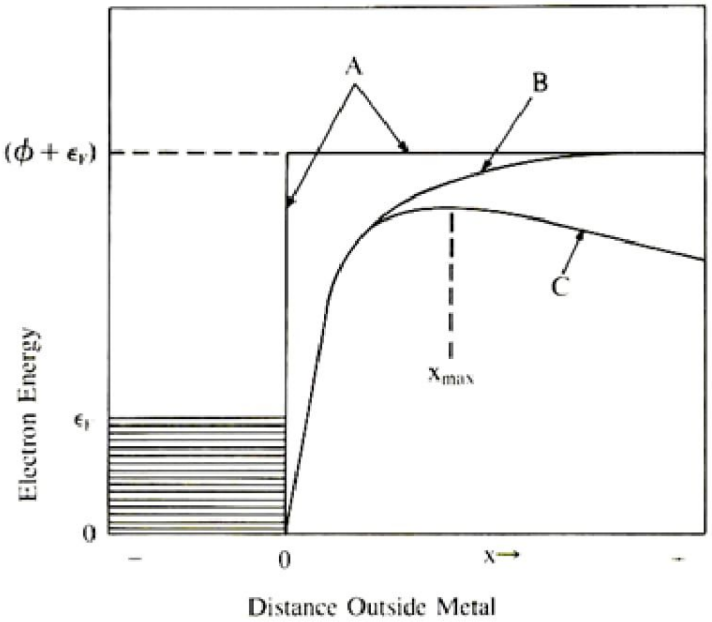


Figure 10.12: Electron energy inside a metal and in a vacuum surrounding the metal. The origin of energy is chosen as a state of rest inside the crystal.

Suppose that an electric field in the x-direction is created in the vacuum outside a heated metal crystal. This modifies the potential energy function to

$$V(x) = (\phi + \epsilon_F) - \left(\frac{e^2}{4x}\right) - exE$$

Curve for the field-modified potential energy is shown as figure 10.12 C. differentiating V(x) with respect to x, we find that there is a maximum in the height of the potential barrier at

$$\left.\begin{aligned} x_{max} &= \left(\frac{e}{4E}\right)^{\frac{1}{2}} \\ V_{max} &= (\phi + \epsilon_F) - (e^3E)^{1/2} \end{aligned}\right\} \qquad (10.10.4)$$

Thus the presence of an external electric field produces a slight lowering of the effective work function. This is the phenomenon of Field Emission, or Schottky Emission. The lowering of the work function is small for fields of a few thousand volt/cm, and the potential maximum is then many angstrom units out from the crystal surface. Even a small reduction of work function makes thermionic emission possible for many electrons which are insufficiently energetic at zero field.

10.16 Exercise

Q.1 Explain Wiedemann-Franz law.

Q.2 Describe the Hall Effect? Give an elementary theory of Hall Effect. Mention the important uses of Hall Effect.

Q.3 Show that Hall coefficient is independent of the applied magnetic field and is inversely proportional to the current density and electronic charge. Mention Some of the applications of this effect.

Q.4 Show that the Lorentz number obtained on the basis of quantum theory is equal to $\left(\frac{\pi^2}{3}\right)\left[\frac{k_B}{e}\right]^2$, where the symbols have their usual meaning. Compare this value with one predicted by classical theory.

Q.5 Discuss the phenomenon of thermionic emission in metals. Obtain Richardson-Dushman equation for the emission of current density.

Q.6 Derive an expression for thermal conductivity on the basis of classical theory and obtained Wiedemann-Franz law.

Q.7 The thermal conductivity of aluminium at 20 ^{0}C is $210\,Wm^{-1}K^{-1}$. Calculate the electrical resistivity of aluminium at this temperature. The Lorentz number for aluminium is 2.02×10^{-8}.

Q.8 Explain the reasons of failure of free electron model.

Q.9 Verify Equation of cyclotron frequency and how the radius of orbit described in real space is related to the electron energy.

Q.10 A set of paramagnetic atoms has all electrons except one per atom in paired states and this one is in an s-like state. What are the possible values for m_j?

References and Suggested Readings

1. Solid State Physics by Neil W. Ashcroft and N. David Mermin
2. Introduction to Modern Solid State Physics by Yuri M. Galperin
3. Solid State Physics by R. J. Singh
4. Applied Solid State Physics by M. R. Srinivasan.

UNIT-11

Energy Bands

Structure of the Unit

11.0 Objectives

The aim of this unit is to know about the formation of energy bands by free atom model and by nearly free electron model. To study motion of an electron in a periodic potential and to obtain Bloch function. Then to study the Bloch theorem and its proof. Then to study Kronig Penney model to explain energy bands. To study wave equation of electron in a periodic potential and calculate number of orbitals in a band.

11.1 Introduction

The free electron theory could successfully explain several properties of metals such as thermal conductivity, electrical conductivity, specific heat and paramagnetism, but this theory could not explain the distinction between conductors, insulators and semiconductors. In order to understand this distinction, more extended theory as band theory is to be studied now. We must extend the free electron model to take account of the periodic lattice of the solid. The possibility of a band gap is the most important new property that emerges from band theory.

11.2 Formation of Energy Bands in Crystals

In connection with origin of bands, two extreme theories which come across are as follows:

(1)Free Atom model and (2) Nearly free electron theory

First extreme model comes from atomic physics, in which electrons reside in bound state in isolated atoms and when these atoms came nearer to each other, then due to mutual interaction between them, perturbs the initial atomic levels.

In second extreme model electrons are supposed to be completely free in crystal, where potential is zero and Hamiltonian related to this is $H = \frac{p^2}{2m}$.

But in crystal there is periodic potential, which is produced due to mutual interaction between electrons and lattice ions. So the motion of crystal cannot be taken completely free. So Hamiltonian will change as

$$H = \frac{p^2}{2m} + V(r) \qquad \text{Classical} \qquad (11.1)$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad \text{Quantum Mechanical} \qquad (11.2)$$

Here V(r) is periodic potential

Now here question arises that which extreme model is correct? Whether solid is composed of free atoms or it is composed of free electrons and ions. Actually both models are not complete. In solid we cannot assume the electrons totally free, because electrons experience force with ions and similarly in solid we cannot assume the atoms to be free, because they interact with each other. Now we discuss energy bands on the basis of both models, which can solve most of the problems of solids.

11.2(a)Energy Bands from Isolated Atoms

We know that in an isolated atom, electrons are arranged in discrete energy levels whose energy increases as they go away from nucleus. In atom these energy levels are represented by horizontal straight lines. The gap between these lines decreases as we go to higher energy levels. The energy levels of two identical isolated atoms are shown in figure 11.1(a) and 11.1 (b) by identical energy levels. When these two atoms are brought nearer to each other then interaction takes place between these two, due to this each energy level of these atoms splits up into two energy levels as shown in figure 11.1 (c). In mutual interaction between N atoms, each energy level splits up into N sublevels. Since the number N is very large due to this, subenergy levels are situated very closer to each other, So it is very difficult to distinguish the sublevels .The group of these sublevels construct energy bands.

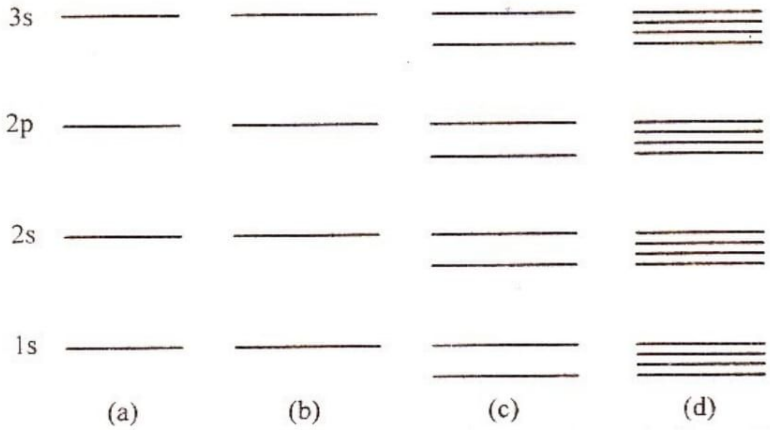


Figure11.1:*(a) and (b) , the energy levels of two identical isolated atoms which are separated by a large distance. Fig (c) each energy level of these atoms splits up into two energy levels when these atoms are brought nearer to each other. Fig (d) In mutual interaction between N atoms, each energy level splits up into N sublevels i.e. origin of energy bands.*

Here this to be noted that as energy of electron increases, then the width of energy band corresponding to that electron also increases, while opposite to this the forbidden energy gap between two successive energy band decreases. The region between two successive energy bands in which energy of electron is not allowed is known as forbidden energy gap .We know that electrons nearest to atomic nucleus are tightly bound with nucleus , so energy levels corresponding to these electrons are least effected in mutual interaction process. So the energy band of this electron is of minimum width . This is shown in figure (11.2). It is clear from graph that interaction between atoms takes place when the atoms are brought closer and as this distance decreases bandwidth starts increasing, due to this forbidden energy gap between two successive energy band decreases. When the distance between atoms is equal to real intermolecular distance "a" of a solid then bands corresponds to that crystal. It is also clear from figure that as electron energy increases, bandwidth also increases, while forbidden energy gap decreases.

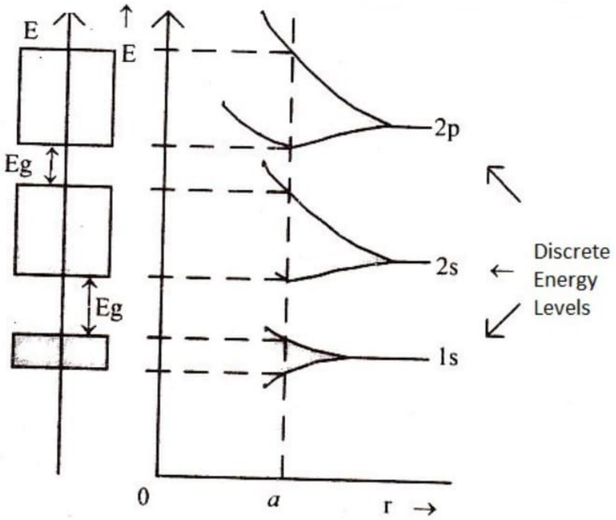


Figure (11.2): ***(Formation of energy bands in crystal having lattice constant "a")***

For example, we consider the origin of conduction band, valence band and forbidden energy gap in silicon semiconductor.

We know that the electronic configuration of Si atom is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^2$. The energy levels of isolated atoms i.e. 1s, 2s, 2p, 3s and 3p contains 2,2,6, 2 and 2 electrons respectively while their capacity is 2,2,6,2 and 6 electrons respectively. In a crystal of N atoms, when they interact, then degeneracy of s and p energy levels, split in 2N and 6N subenergy levels. According to figure (11.3), when the intermolecular distance between Si atoms is equal to *b* (i.e. *r*=*b*) ,then 3s and 3p energy bands overlap with each other. In this condition distinction between 3s and

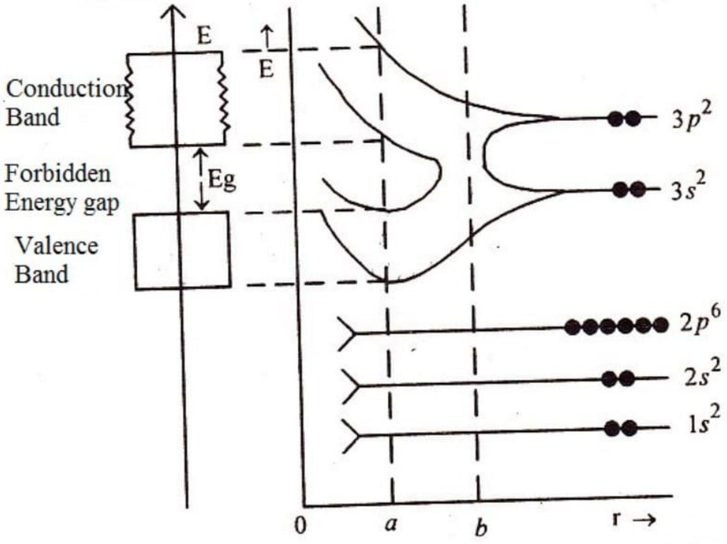


Figure (11.3): ***(origin of conduction and valence band in silicon crystal)***

3p vanishes and total sub energy levels become 2N s-level+6N p-level=8N levels. For these available electrons are 2N s-electrons+ 2N p-electrons=4Nstates. It is clear that from available 8N energy levels only 4N are filled while remaining 4N are unfilled. But at intermolecular distance of crystal i.e. r=a, these filled and unfilled energy levels are separated by forbidden gap E_g. The band corresponding to filled energy levels, associated with outermost electrons is known as valence band, while the band just above it which is perfectly empty is known as conduction band. All the bands 1s, 2s and 2p below valence band are completely, filled.

11.2 (b) Nearly Free Electron Model

In nearly free electron concept, the motion of electrons in perfectly free from binding forces. Hence electron is moving in constant potential field (Here V=0) and its total energy E is purely Kinetic. This kinetic energy of electron is related with wave vector of electron in the following way

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \tag{11.3}$$

where k_x, k_y and k_z are the x, y, and z components of *k*. If we draw dispersion curve according to equation (11.3), then we shall get parabolic curve as shown in figure (11.4).

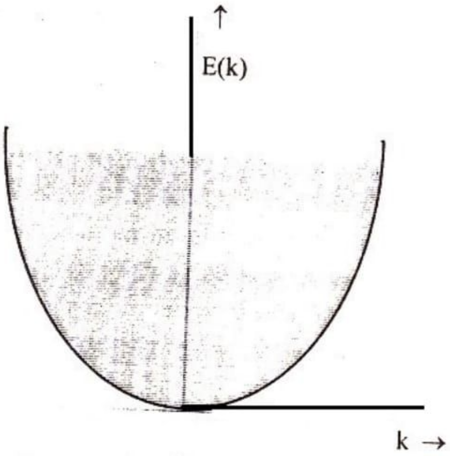


Figure (11.4): Variation of energy E(*k*) of free electron with *k* in the form of parabolic curve

Energies of electron exist from 0 to ∞ in approximate continuous form and there is very small energy interval between them. But on boundary lines the energy levels are discrete due to boundary condition.

It is clear from energy spectrum of free electron that this model is perfectly unsuccessful in explaining origin of energy bands and energy gap in crystals. The reason for this is that electron is not perfectly free in crystal and it is not moving in constant potential field (here V=0), but electrons in crystal are supposed to move in a region of periodically varying potential [V(x) =V(x+a)] where *a* is lattice constant of ion cores of the crystal.

The motion of electron in periodic potential field, gives rise to phenomenon of diffraction. Such electrons suffer diffraction in the same way as x-rays suffer diffraction from crystals and obey Bragg's law. Now, we will see that Bragg's reflection is responsible for the origin of energy bands and forbidden energy gap.

In figure (11.5) periodic arrangement of positive ions in crystal at intermolecular distance, "*a*" is shown. According to Bragg's law, an electron wave having wavelength λ incident on vertical plane YY' at an angle θ i.e. at glancing angle. The necessary Bragg's condition for diffraction, which should be obeyed by electron wave, is given by

$$2a\sin\theta = n\lambda \qquad (11.4)$$

where n= 1,2,3, …..

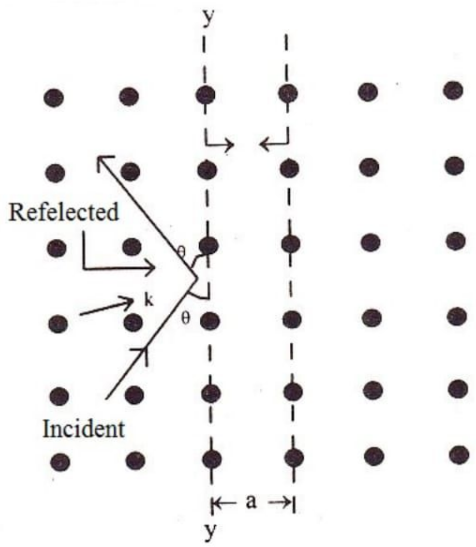


Figure (11.5): (The reflection of electron of wavevector $\vec{k}$ on YY' plane in two-dimensional regular arrangement of positive ions)

For first order diffraction and normal incidence putting n=1 and $\theta = \pi/2$ in equation (11.4) we shall get $2a = \lambda$, and with this wave vector ,

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{2a} = \frac{\pi}{a}$$

$$\text{or} \quad k = \pm\pi/a \tag{11.5}$$

Here ± sign is for moving electron in positive and negative direction. It is clear from this, that electron wave reflects at $k = \pm\pi/a$. Due to the presence of incident wave $e^{i\frac{\pi}{a}x}$ and reflected wave $e^{-i\frac{\pi}{a}x}$ on these points, the resultant wave is obtained by the superposition of these two waves, which is only standing wave but not progressive wave. These can be two types of standing waves which can be formed from the two traveling wave $e^{i\frac{\pi}{a}x}$ and $e^{-i\frac{\pi}{a}x}$

$$\psi_I = e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x} = 2\cos\left(\frac{\pi x}{a}\right) \tag{11.6}$$

and
$$\psi_{II} = e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x} = 2i\sin\left(\frac{\pi x}{a}\right) \tag{11.7}$$

The charge density associated with these standing waves is given by $\rho = |\psi|^2 e$, which gives the probability of finding the electrons at those points. So associated charge density will be:

$$\rho_1 = e|\psi_1|^2 = 4e\cos^2\frac{\pi x}{a} \tag{11.8}$$

$$\rho_2 = e|\psi_2|^2 = 4e\sin^2\frac{\pi x}{a} \tag{11.9}$$

while the charge density associated with progressive wave $\psi = e^{ikx}$ of free electron [$i.e.\ \rho = e|\psi|^2 = e$]remains constant.

$$\rho = e|\psi|^2 = e \tag{11.10}$$

It is clear from equations (11.8) and (11.9) that distribution of electrons near to positive ions due to standing wave is different from constant distribution of electrons in progressive wave (i.e. free electrons). Due to this ,electron potential changes.

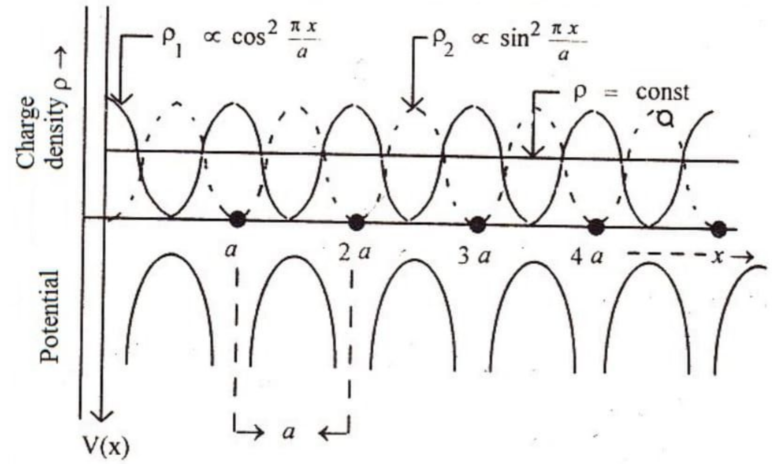


Figure (11.6):***The change in charge density due to periodic potential field produced by the regular arrangement of positive ions is plotted .***

From above figure ,the charge density ρ_1 and ρ_2 corresponding to standing waves ψ_1 and ψ_2 produced due to linear chain of positive ions in periodic potential V(x) are shown by solid and dashed line curve, while the constant charge density of progressive wave associated with free electrons, is shown by horizontal straight line.

According to figure (11.6) the maximum value of ρ_1 is obtained at x=0, a,2a,…..

which are the positions of positive ions. Hence the distribution of electrons is maximum, over these positive ions. The potential decreases as negative charges approach positive ions, hence the energy of electrons corresponding to standing wave ψ_1 decreases, while the value of ρ_2 is maximum at $x = \frac{a}{2}, \frac{3a}{2}, \frac{5a}{2}, ...$ So electron charge distribution is available at more distance from positive ions, due to this potential increases. So the energy of electrons corresponding to ψ_2 is more.

Hence, the energy difference E_g between ψ_1 and ψ_2 is the main cause of origin of forbidden energy gap E_g. The dispersion curve between E(*k*) versus *k* of free electron as shown in figure (11.4) is changed due to reflection of electron wave at $k = \pm\frac{\pi}{a}$. {The reflection of electron wave at $k = \pm\frac{\pi}{a}$, changes the dispersion curve between E(*k*) and *k* of free electron as shown in figure (11.4)} Due to this we observe discontinuity at $k = \pm\frac{\pi}{a}$ as shown in figure (11.7) . At $k = \pm\frac{\pi}{a}$ we obtain forbidden energy field whose gap is E_g.

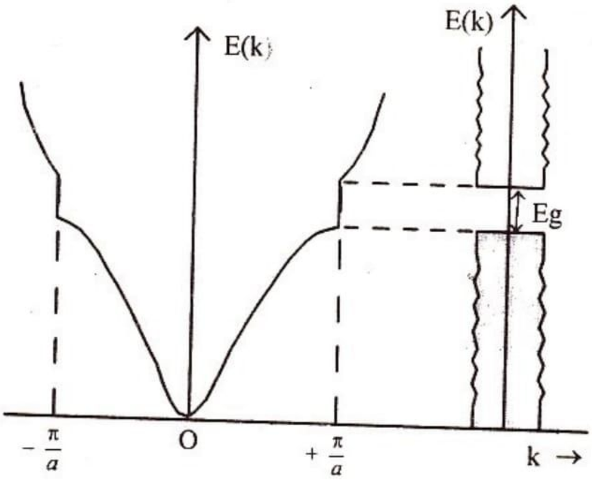


Figure (11.7):[The change of energy of electron in periodic potential field gives discontinuous energy interval E_g]

The curve is perfectly parabolic in region between $-\pi / a$ to π / a and in this region electron is free. This region is known as first Brillouin Zone. Mutual discontinuities are obtained at $k = \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}, ...$respectively.

Hence the nearly free electron model describes band structure of solid crystal in which band electrons in crystal move in a region of periodically varying potential due to the ion cores of the crystal.

11.3 Bloch Function and Bloch Theorem

The wave function $\psi(x)$ for total energy E, in potential field V(x) is obtained from the solution of one-dimensional Schrödinger's wave equation as given below:

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left[E-V(x)\right]\psi=0 \tag{11.11}$$

For free electron V(x) =0 and the solution of equation (11.11), is one dimensional plane wave as follows

$$\psi(x)=e^{\pm ikx} \tag{11.12}$$

But in a real crystal having lattice constant *a*, the motion of electron completes in one-dimensional periodic potential

$$V(x) = V(x+a) \tag{11.13}$$

Statement of Bloch Theorem: The solution of Schrödinger's equation (11.11) for moving electron in a periodic potential field V(x) defined by equation (11.13) is a plane wave $e^{\pm ikx}$, which is modified by periodic function $U_k(x)$. So for periodic function V(x) ,the solution of equation (11.11) is as follows.

$$\psi_{(x)}=e^{\pm ikx}U_k(x) \tag{11.14}$$

where $U_k(x)=U_k(x+a)$ (11.15)

The function $\psi(x)$ given by equation (11.14) is known as Bloch function. From this function $\psi(x+a)=e^{\pm ik(x+a)}\,U_k(x+a)=e^{\pm ika}\;e^{\pm ikx}U_{k(x)}$

or $\psi(x+a)=e^{\pm ika}\psi(x)$ (11.16)

Proof Bloch Theorem

Since Schrödinger's equation (11.11) is differential equation of second order, so it will have two real and independent solutions. Let f(x) and g(x) are two real and independent solutions. So general solution will be the simple sum of these solutions

$$\psi(x)=Af(x)+Bg(x) \tag{11.7}$$

where A and B are arbitrary constants. Since the potential is periodic i.e.

V(x)=V(x+a), therefore function f(x+a) and g(x+a) should also be solution of equation (11.11) . So functions f(x+a) and g(x+a) can be expressed as the linear addition of main solutions f(x) and g(x)

$$f(x+a)=\alpha_1 f(x)+\alpha_2 g(x) \tag{11.18}$$

$$g(x+a)=\beta_1 f(x)+\beta_2 g(x) \tag{11.19}$$

where α_1 , α_2 , β_1 and β_2 are real functions of energy E. Substituting equation (11.19) in equation (11.18) we shall get:

$$\psi(x+a)=(A\alpha_1+B\beta_1)f(x)+(A\alpha_2+B\beta_2)g(x) \tag{11.20}$$

Let $\psi(x+a)=Q\psi(x)$ (11.21)

or $\psi(x+a)=QAf(x)+QBg(x)$ from equation (11.17), --- (11.22)

Now comparing equation (11.22) with (11.20), we shall get

$$A\alpha_1+B\beta_1=QA \tag{11.23)(a}$$

and $A\alpha_2+B\beta_2=QB$ (11.23)(b)

where Q is constant. Equation (11.23)(a) and (11.23)(b) will give non zero values of A and B if the determinant of their coefficient vanishes i.e.

$$\begin{vmatrix} (\alpha_1-Q) & \beta_1 \\ \alpha_2 & (\beta_2-Q) \end{vmatrix}=0$$

or $Q^2-(\alpha_1+\beta_2)Q+(\alpha_1\beta_2-\alpha_2\beta_1)=0$ (11.24)

The quadratic equation of Q i.e. equation (11.24) will have two roots Q_1 and Q_2. The product of these two roots will be following

$$Q_1Q_2=(\alpha_1\beta_2-\alpha_2\beta_1) \tag{11.25}$$

In order to obtain the value of product Q_1 Q_2 ,we write Schrödinger's equation i.e. equation (11.11) for f(x) and g(x).

$$\frac{d^2 f(x)}{dx^2}+\frac{2m}{\hbar^2}\left[E-V(x)\right]f(x)=0 \tag{11.26}$$

$$\frac{d^2 g(x)}{dx^2}+\frac{2m}{\hbar^2}\left[E-V(x)\right]g(x)=0 \tag{11.27}$$

Multiplying equation (11.16) by g(x) and equation (11.27) by f(x) and then subtracting them we shall get

$$g(x)\frac{d^2 f(x)}{dx^2} - f(x)\frac{d^2 g(x)}{dx^2} = 0$$

or $$\frac{d}{dx}\left[g(x)\frac{df(x)}{dx} - f(x)\frac{d}{dx}g(x)\right] = 0$$

$$g(x)\frac{df(x)}{dx} - f(x)\frac{d}{dx}g(x) = \text{constant} \qquad (11.28)$$

The left hand side of equation (11.28) is called Wronskian, W(x). So

$$W(x) = g(x)f'(x)-f(x)g'(x) \qquad (11.29)$$

Similarly $W(x+a) = g(x+a)f'(x+a)-f(x+a)g'(x+a)$ (11.30)

By the use of equation (11.18) and (11.19), W(x+a) will have the following value

$$W(x+a) = (\alpha_1\beta_2 - \alpha_2\beta_1)W(x)$$

Since W(x+a)=W(x)

So $\alpha_1\beta_2 - \beta_1\alpha_2 = 1$ (11.31)

Putting the value from equation (11.31) in equation (11.25) we shall get

$$Q_1 Q_2 = 1 \qquad (11.32)$$

From equation (11.21), two solution or two equations corresponding to Q_1 and Q_2 will be obtained as follows.

$$\psi_1(x+a) = Q_1\psi_1(x) \qquad (11.33)$$

and $$\psi_2(x+a) = Q_2\psi_2(x) \qquad (11.34)$$

Special Cases:

(i) For imaginary values of Q_1 and Q_2,there are two possibilities for Q_1 and Q_2 ,as follow:

$Q_1 = e^{ika}$ and $Q_2 = e^{-ika}$ So $Q = e^{\pm ika}$

From this $\psi(x+a) = e^{\pm ika}\psi(a)$ (11.35)

which is the solution of Schrödinger's equation (11.11) as given by equation (11.16)

(ii) For real values of Q_1 and Q_2,there are also two possibilities for Q_1 and Q_2 as follows:

$Q_1 = e^{ua}$ and $Q_2 = e^{-ua}$,but these values are not allowed in wave mechanics because the wavefunctions obtained from these $\psi(x+a)=e^{\pm ua}\psi(x)$ or $\psi(x)=e^{\pm ux}U_k(x)$ are not bounded functions, since these functions become infinite at $\pm\infty$.

So the roots $Q_1=e^{ika}$ and $Q_2=e^{-ika}$ are allowed roots and roots $Q_1=e^{ua}$ and $Q_2=e^{-ua}$ are not allowed i.e. forbidden roots. Hence allowed roots correspond to allowed energy regions, while the forbidden (or disallowed) roots are associated with forbidden energy region. Hence it is clear that energy spectrum of an electron moving in a periodic potential in crystal consists of allowed and forbidden energy bands.

11.4 Kroning Penney Model

Kroning and Penney illustrated the main characteristics of the behaviour of electrons in one dimensional periodic potential region in this model in which the period of periodic potential is assumed as (a+b) . This is shown in figure (11.8). The periodic potential energy of valance electron is along x-direction.

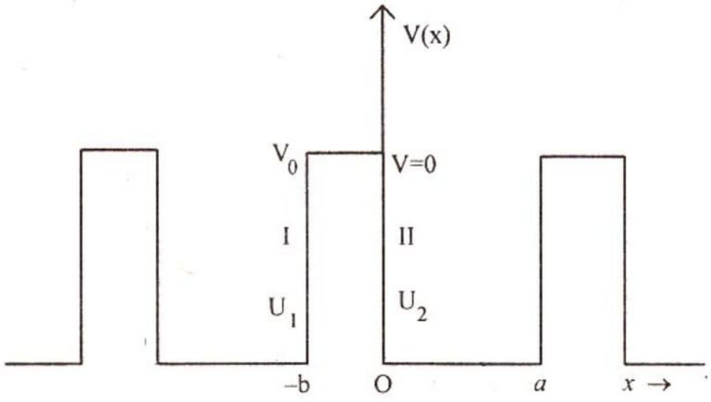


Figure (11.8): ***[one-dimensional Kroning Penney periodic potential with period (a+b)]***

It is assumed that the potential energy of an electron in a linear array of positive nuclei has the form of a periodic array of square wells with period (a+b). At the bottom of the well i.e. for $0<x<a$ the electron is supposed to be in the vicinity of a nucleus and the potential energy is zero, whereas outside the well i.e. $-b<x<0$,the potential energy is V_0.

In periodic potential as shown in figure (11.8)

$$V(x) = V_0, \quad -b < x < 0 \qquad \text{(i) and}$$

$$V(x) = 0, \; 0 < x < a \qquad \text{(ii)} \qquad (11.36)$$

The Schrodinger's equations for the above two regions are as follows

$$\frac{d^2\psi_1}{dx^2} + \frac{2m}{\hbar^2}\left[E - V_0\right]\psi_I = 0, \quad -b < x < 0 \qquad (11.37)$$

and $$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2}E\psi_2 = 0, \quad 0 < x < a \qquad (11.38)$$

Let the energy E of electron is less than V_0. Now taking two real quantities α and β in these equations as follows

$$\alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m}{\hbar^2}\left(V_0 - E\right) \qquad (11.39)$$

Then equations (11.37) and (11.38) will take the following form.

$$\frac{d^2\psi_I}{dx^2} - \beta^2\psi_{II} = 0, \quad -b < x < 0 \qquad (11.40)$$

and $$\frac{d^2\psi_2}{dx^2} + \alpha^2\psi_2 = 0, \quad 0 < x < a \qquad (11.41)$$

Since potential is periodic i.e. V(x) = V(x+a+b), where (a+b) is the period. Let the solutions of these equations are in the form of Bloch function

$\psi_I = e^{ilx}U_I(x)$ and $\psi_2 = e^{ikx}U_2(x)$. The second derivatives of these functions are

For Ist function $\dfrac{d^2\psi_1}{dx^2} = e^{ikx}\left[\dfrac{d^2U_1}{dx^2} + 2ik\dfrac{dU_1}{dx} - k^2\right]$

Similarly for 2nd function $\dfrac{d^2\psi_2}{dx^2} = e^{ikx}\left[\dfrac{d^2U_2}{dx^2} + 2ik\dfrac{dU_2}{dx} - k^2\right]$

Now putting the values of $\psi_1, \psi_2, \dfrac{d^2\psi_1}{dx^2}$ and $\dfrac{d^2\psi_2}{dx^2}$ in equations (11.40) and (11.41) we shall get

$$\frac{d^2U_1}{dx^2} + 2ik\frac{dU_1}{dx} - \left(\beta^2 + k^2\right)U_1 = 0, \quad -b < x < 0 \qquad (11.42)$$

and $$\frac{d^2U_2}{dx^2} + 2ik\frac{dU_2}{dx} - \left(\alpha^2 - k^2\right)U_2 = 0, \quad 0 < x < a \qquad (11.43)$$

The Solution of these equations are

$$U_1 = Ae^{(\beta - ik)x} + Be^{-(\beta + ik)x} \quad \text{for } -b < x < 0 \tag{11.44}$$

and $$U_2 = Ce^{i(\alpha - k)x} + De^{-i(\alpha + k)x} \quad \text{for } 0 < x < a \tag{11.45}$$

where A,B,C and D are constants. These constants can be determined by the following boundary conditions i.e. wave function U and its derivative $\frac{dU}{dx}$ are single valued and continuous.

$$U_1\big|_{x=0} = U_2\big|_{x=0} \text{ and } U_1\big|_{x=-b} = U_2\big|_{x=a} \tag{11.46}$$

$$\left.\frac{dU_1}{dx}\right|_{x=0} = \left.\frac{dU_2}{dx}\right|_{x=0} \text{ and } \left.\frac{dU_1}{dx}\right|_{x=-b} = \left.\frac{dU_2}{dx}\right|_{x=a}$$

The first two conditions are imposed because of the requirement of continuity and the other two conditions are required because of periodicity of U_k (x) .Using these boundary conditions in equations (11.44) and (11.45) ,we get

$$A+B= C+D \tag{11.47}$$

$$A(\beta - ik) - B(\beta + ik) = Ci(\alpha - k) - Di(\alpha + k) \tag{11.48}$$

$$Ae^{-(\beta - ik)b} + Be^{(\beta + ik)b} = Ce^{i(\alpha - k)a} + De^{-i(\alpha + k)a} \tag{11.49}$$

$$A(\beta - ik)e^{-(\beta - ik)b} - B(\beta + ik)e^{(\beta + ik)b} = Ci(\alpha - k)e^{i(\alpha - k)a} - Di(\alpha + k)e^{-i(\alpha + k)a} \tag{11.50}$$

These four equations have a non zero solution only if the determinant of the coefficients A,B,C and D vanishes. On expanding the determinant and after simplification, we get the following result:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a+b) \tag{11.51}$$

In order to obtain equation (11.51)in more simplified from, we put $\beta^2 - \alpha^2 = \frac{2m}{\hbar^2}(V_0 - 2E)$ in equation (11.51) we shall get

$$\frac{m(V_o - 2E)}{\hbar^2 \alpha\beta} \sinh \beta b \, \sin \alpha a + \cosh \beta b \, \cos \alpha a = \cos k(a+b)$$

or $$\frac{m(V_o b - 2Eb)}{\hbar^2 \alpha} \left(\frac{\sinh \beta b}{\beta b}\right) \sin \alpha a + \cosh \beta b \, \cos \alpha a = \cos k(a+b)$$

In this expression, we apply $V_0 \to \infty$ and $b \to 0$, but the product $V_o b$ has a finite value, i.e. periodic potential barriers become delta function as shown in figure

(11.9). So given model is modified in such a way that it represents a series of wells separated by infinitely thin potential barrier of infinitely large potential. The value $V_o b$ is known as barrier strength.

From above conditions $Lim_{b\to 0}\dfrac{\text{Sinh}\,\beta b}{\beta b}=1$, and $\text{Cosh}\,\beta b=1,\ Eb=0$

From these values, the simple form of above expression will be as follows

$$\frac{mV_o b}{\hbar^2\alpha}\text{Sin}\,\alpha a+\text{Cos}\,\alpha a=\text{Cos}\,ka$$

or $$P\frac{\sin\alpha a}{\alpha a}+\cos\alpha a=\cos ka \qquad (11.52)$$

where $$P=\frac{mV_o ba}{\hbar^2} \qquad (11.53)$$

Now if we plot a graph between $\left(P\dfrac{\text{Sin}\,\alpha a}{\alpha a}+\cos\alpha a\right)$ i.e. the left hand side quantity of equation (11.52) and αa for the value $P=\dfrac{3\pi}{2}$, we get the curve as shown in figure (11.9).

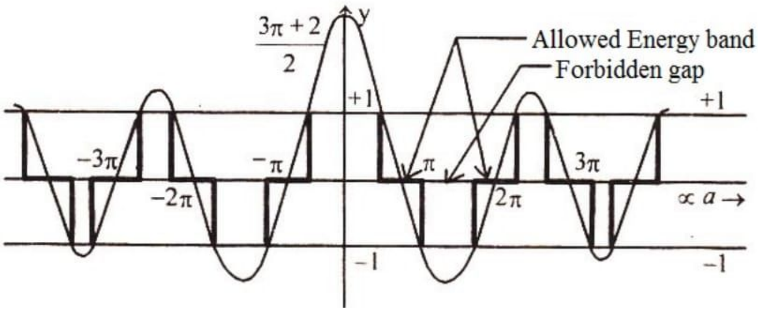


Figure (11.9)*:[Plot of curve,* $y=\dfrac{3\pi}{2}\dfrac{\text{Sin}\,\alpha a}{\alpha a}+\text{Cos}\,\alpha a$ *and on axis of x,* $x=\alpha a$*]*

In this along y axis ,we took the left hand side of equation (11.52) for $P=\dfrac{3\pi}{2}$ and along x-axis we have taken $x=\alpha a$. So equation of plot will be

$$y=\frac{3\pi}{2}\frac{\text{Sin}\,\alpha a}{\alpha a}+\text{Cos}\,\alpha a \qquad (11.54)$$

As $\alpha a\to 0,\dfrac{\text{Sin}\,\alpha a}{\alpha a}\to 1$

So the maximum value of y will be $y_{\max} = \frac{3\pi}{2} + 1 = \left(\frac{3\pi + 2}{2}\right)$ at $\alpha a = 0$

While at $\alpha a = \pm\pi, \pm 2\pi, \pm 3\pi, ...$ the value of y comes out to be -1, +1,-1. Equation (11.52) also gives the condition, which must be satisfied so that solutions of the wave equation may exist. Since cos*ka* lies between +1 and -1, the left hand side of equation (11.52) should take up only those values of αa for which its values lie between +1 and -1. The values of αa satisfying the equation (11.52) are obtained by drawing lines parallel to αa-axis at a distance cos*ka* from it and if ka is continuously varied from 0 to π i.e. cos*ka* from +1 to -1, we obtain all possible values of ka .These possible values of αa are shown by thick lines. Here it is to be noted that from equation (11.39), it is clear that $\alpha^2 \propto E$ i.e. energy of electron, therefore, the abscissa αa is a measure of energy.

From the study of plot (11.9), we obtain the following important results:

1. The width of allowed energy bands (thick lines) increases as αa increases i.e. as energy of electron E increases.
2. The interval between two successive energy bands i.e. forbidden energy regions decreases as αa increases or energy of electron E increases. So higher energy bands come closer to each other.
3. The width of allowed energy bands decreases with increasing value of P(i.e. as V_0 increases or binding energy of the electron increases) and at critical boundary i.e. when $P \to \infty$ i.e. $V_o \to \infty$ i.e. height of periodic potential is larger, then the allowed energy bands become infinitely narrow .Due to this band spectrum converts into line spectrum. In this condition, the first term of equation (11.52) becomes infinite. The value of first term $\frac{P \sin \alpha a}{\alpha a}$ should be finite at $P \to \infty$, for this it is necessary that $\sin \alpha a = 0$ but $\alpha a \neq 0$. So the value of αa will be.

   $$\alpha a = n\pi \text{ where n=1, 2, 3................} \qquad (11.55)$$

   or $\alpha^2 a^2 = n^2 \pi^2$ from equation (11.39) putting value of α^2

   $$\frac{2m}{\hbar^2} E_n a^2 = n^2 \pi^2 \text{ Or } E_n = \left(\frac{\pi^2 \hbar^2}{2ma^2}\right) n^2 \qquad (11.56)$$

This energy equation, represents, the energy spectrum of those particles confined into potential box of atomic dimensions, whose height is infinite and the probability of crossing the box is negligible. In this condition energy spectrum is linear. This case applies to crystal where the electrons are tightly bound with their nuclei. In the limit $P \to 0$ (no barrier), the electron can be considered to be moving freely througout the potential well. This case applies to crystals where the electrons are almost free from their nuclei.

4. From equation (11.52), electron energy can be determined in the form of function of k and the important results of this energy are shown in figure (11.10)

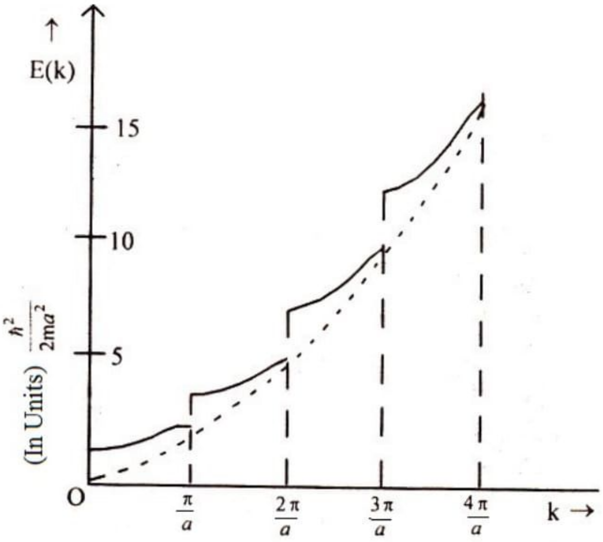


Figure-11.10: ***[A graph between E(k) and k for*** $P = \frac{3\pi}{2}$***, same type of graph is obtained in left side of E(k)]***

In the graph E(k) versus k discontinuities occur at $ka = \pi, 2\pi, 3\pi, ...n\pi$,where n=1,2,3,……… .The k values corresponding to these values of ka, define boundaries of 1st, 2nd, 3rd, etc. Brillouin Zones. The forbidden energy gap region are formed in these boundaries.

From $k = +\pi / a$ to $-\pi / a$, there exits the first Brillouin Zone. The second Zone consists of two parts, one from $+\pi / a$ to $\frac{2\pi}{a}$ in the right and second from $-\pi / a$ to $-\frac{2\pi}{a}$ in the left. Similarly other Brillioun Zones can be defined. These Zone boundaries represent the maximum energies that the electron can have without any discontinuity.

5. The total number of possible wavefunctions in any energy band is equal to the number of unit cells N. But according to Pauli's exclusion principle, each wavefunction can occupy maximum two electrons only. So in any band, total number of electrons will be double of number of unit cells i.e.2N.

11.5 Wave Equation of Electron in a Periodic Potential

In the above part of this chapter, we have considered the approximation for the solution of the Schrödinger equation that $k = \pm\pi / a$ i.e. wave vector k is at a zone boundary. Now we consider the wave equation for a general potential at general value of k. Let U(x) denotes the potential energy of an electron in a linear lattice of lattice constant *a*. As we have studied that the potential energy is invariant under a crystal lattice translation: U(x)=U(x+a). We know that if any function is invariant under a crystal lattice translation, that can be expanded as a Fourier series in terms of reciprocal lattice vector G, so we can write the Fourier series for the potential energy as:

$$U(x) = \sum_G U_G e^{iGx} \tag{11.57}$$

The values of the coefficients U_G for actual crystal potentials tend to decrease rapidly with increasing magnitude of G.

For the potential energy U(x) to be a real function:

$$U(x) = \sum_{G>0} U_G (e^{iGx} + e^{-iGx}) = 2\sum_{G>0} U_G \operatorname{Cos} Gx \tag{11.58}$$

For convenience we take $U_0 = 0$

We know that the wave equation of an electron in crystal is $H\psi = \varepsilon\psi$, where H is the Hamiltonian and ε is the energy eigenvalue. The solutions ψ are called eigenfunctions or orbitals. So explicitly, the wave equation can be written as:

$$\left[\frac{1}{2m} p^2 + U(x)\right]\psi(x) = \left(\frac{1}{2m} p^2 + \sum_G U_G e^{iGx}\right)\psi(x) = \varepsilon\psi(x) \tag{11.59}$$

Since equation (11.59) is written for one-electron approximation in which wavefunction $\psi(x)$ describes the motion of one electron in the potential of the ion cores i.e. in a periodic potential and in the average potential of the other conduction electron. Now the wavefunction $\psi(x)$ may be expressed as a Fourier series summed over all values of wave vector (k) permitted by the boundary conditions so that

$$\psi(x)=\sum_{k} C(k)e^{ikx} \tag{11.60}$$

Where k is real, the various values of k is in the form $\frac{2\pi n}{L}$, for these values satisfy the periodic boundary condition over the length L, here *n* is any integer, positive or negative. We can label a wavefunction ψ that contains a Fourier component k as $\psi(k)$ or equally well as $\psi(k+G)$, for if *k* enters the Fourier series then (k+G) also enters. The wavevector (k+G) running over G are a very restricted subset of wavevectors $\frac{2\pi n}{L}$,where G is any reciprocal lattice vector.

Now to solve the wave equation, put equation (11.60) in equation (11.50) to obtain a set of linear algebraic equations for the Fourier coefficients. The kinetic energy term is

$$\frac{1}{2m}P^2\psi(x)=\frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2\psi(x)=-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=\frac{\hbar^2}{2m}\sum k^2C(k)e^{ikx}$$

and the potential energy term is :

$$\left(\sum_{G} U_G e^{iGx}\right)\psi(x)=\sum_{G}\sum_{k} U_G\, e^{iGx}C(k)e^{ikx}$$

The wave equation is obtained as the sum:

$$\sum\frac{\hbar^2}{2m}k^2C(k)e^{iKx}+\sum_{G}\sum_{k} U_G C(k)e^{i(k+G)x}=\varepsilon\sum_{k} C(k)e^{ikx} \tag{11.61}$$

So each Fourier component must have the same coefficient on both sides of the equation. Thus

$$(\lambda_k-\varepsilon)C(k)+\sum_{G} U_G C(k-G)=0 \tag{11.62}$$

where $\lambda_k=\dfrac{\hbar^2k^2}{2m}$ (11.63)

Now the equation (11.62) is a useful form of the wave equation in a periodic lattice. The solutions of the wave equation in a periodic lattice are of the Bloch form $\psi_k(\vec{r}) = e^{i\vec{k}.\vec{r}}.U_k(\vec{r})$, where $U_k(\vec{r})$ is invariant under a crystal lattice translations. The k's which appear in a Fourier series expansion

$$\psi_k(r) = \sum_k C(k)\exp(i\vec{k}.\vec{r})$$

are all of the form (k+G), where G runs over all reciprocal lattice vectors. There are regions of energy for which no Bloch function solutions of the wave equations exist. These energies form forbidden regions in which the wavefunctions are damped in space and the values of the k's are complex. The existence of insulators is due to the existence of forbidden regions of energy. The energy bands may often be approximated by one or two plane waves. For example

$\psi_k(x) = C(k)e^{ikx} + C(k-G)e^{i(k-G)x}$ near the zone boundary at $\frac{1}{2}G$.

The values of k enters into the conservation laws for collision processes of electrons in crystals. For this region $\hbar k$ is called the crystal momentum of the electron.

11.6 Number of Orbitals in a Band

Let us consider a one dimensional crystal of N lattice points. If the distance between two successive lattice points is a ,then the length of the crystal is L= Na. In order to count states we apply periodic boundary conditions to the wave functions (orbital) over the length L of the crystal. We find that the wave function must be periodic in "L" .That is:

$$\psi(x) = \psi(x+L) \tag{11.64}$$

The wave function according to Bloch theorem

$\psi(x) = e^{ikx}U_k(x)$ and $\psi_{(X+L)} = e^{ik(x+L)}U_k(x+L)$

So $\quad e^{ikx}U_k(x) = e^{ik(x+L)}U_k(x+L)$.

$$e^{ikx}U_k(x) = e^{ik(x+L)}U_k(x)$$

Since according to Bloch theorem $U_k(x)$ function is also periodic

$$\therefore U_k = U_k(x+L)$$

So $\quad e^{ikx} = e^{ik(x+L)}$

$\therefore e^{ikL} = 1 = e^{i2\pi n}$ where $n = 0, \pm1, \pm2, \pm3, \ldots$

$$\therefore k = \frac{2\pi n}{L} \quad \text{or} \quad n = \frac{kL}{2\pi}$$

Thus the number of possible wavefunctions in the interval dk is

$$dn = \left(\frac{L}{2\pi}\right) dk$$

Hence total number of possible states in first Brillouin zone (in a band).

$$n = \int dn = \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk = \frac{L}{2\pi} \times \frac{2\pi}{a} = \frac{L}{a} = N = \text{Total number of unit cell.}$$

Thus the total number of allowed k values in the first Brillouin zone is equal to N. This shows that the total number of possible states or wavefunctions or orbitals in an energy band is equal to the number of primitive unit cells N. Taking into account two independent orientations of the electron spin and Pauli's exclusion principle, there are 2N independent orbitals in each energy band. If there is a single atom of valence one in each primitive cell, the band can be half filled with electrons. If each atom contributes two valence electrons to the band, the band can be exactly filled.

11.7 Self Learning Exercise

Q.1 How energy Bands are formed?

Q.2 What is Bloch function?

Q.3 Explain the difference in E-k curve in case of free electron theory and band theory.

11.8 Summary

In this unit we have studied that when a number of atoms are brought close together to form a crystal, the atomic energy levels are split into bands. We find that energy spectrum of the electron is comprised of a set of continuous bands separated by regions of forbidden energy gap. The solutions of the wave equation in the periodic lattice are of the Bloch form $\psi_k(x) = e^{ik.x}U_k(x)$ where $U_k(x)$ is invariant under a crystal lattice translation. The potential of the electron within lattice (potential well) is not constant but it will vary and is periodic. Kronig and Penney model illustrates the behaviour of electron in a periodic potential by assuming that the potential energy of an electron in a linear array of positive nuclei has the form of a periodic array of square wells. Then using Bloch function, Kroning Penney Model was successful in explaining band structure of solids. Then we have discussed wave equation of electron in a periodic potential and define crystal momentum and concept of reciprocal lattice vector G. In the last we calculated the number of orbitals in a band and it came out equal to 2N, where N is the number of unit cells in the crystal.

11.9 Glossary

Bragg's law: $2a\sin\theta = n\lambda$

Bloch's Function: $\psi(x) = e^{\pm ikx}U_k(x)$ where $U_k(x) = U_k(x+a)$

11.10 Answers to Self Learning Exercise

Ans.1: Energy bands are formed when a number of atoms are brought close together to form a crystal, the atomic energy levels are split into bands.

Ans.2: The wavefunction of the type $\psi(x) = e^{\pm ik.x}U_k(x)$ is called Bloch function. The wave vector $\vec{k}$ gives the direction of Bloch wave.

11.11 Exercise

Section-A (Very short answer type questions)

Q.1 What is Valence band?

Q.2 What is forbidden energy gap?

Q.3 What is the basic assumption in the Kronig –Penny model?

Section-B (Short answer type questions)

Q.4 What are energy bands in Solids? What is its origin?

Q.5 Explain the significance of Bloch theorem.

Q.6 What are the properties of Bloch functions?

Q.7 What are Brillouin Zones?

Section-C (Long answer type questions)

Q.8 Explain the periodicity character of the potential in crystals. State and prove Bloch theorem in this reference.

Q.9 Discuss Kronig Penny model. Using the model show that the energy spectrum of electron consists of a number of allowed energy bands separated by forbidden regions.

Q.10 What is the significance of E-k curve? Explain the various schemes to explain the E-k curve. Obtain an expression for the number of possible wavefunctions (orbitals) in an energy band.

Q.11 Given the solution of Schrodinger equation for a one-dimensional periodic lattice (with symbols having their usual meaning)

$\dfrac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$ with $\alpha = \left(\dfrac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$ .Discuss the formation of energy bands in a solid.

Q.12 Prove that the motion of an electron through the periodic potential of solid gives rise to band structure using nearly free electron model.

11.12 Answers to Exercise

Ans.1: The Highest filled energy band, which includes electrons shared in covalent bonds or electrons transferred in ionic bonds, is known as valence band.

Ans.2: The energy gap between the conduction band, and valence band is known as forbidden energy gap and it is denoted by E_g.

Ans.3: In this model it is assumed that the potential energy of an electron has the form of a periodic array of square wells.

References and Suggested Readings

1. Introduction to Solid state Physics by C. Kittel
2. Elementary Solid state Physics by Rama Swami
3. Solid State Physics by A.J. Dekkar
4. Fundamentals of Solid State Physics by Saxena, Gupta and Saxena
5. Solid State Physics by S.O. Pillai

UNIT-12

Semiconductor Physics

Structure of the Unit

12.0 Objectives

In this chapter we will discuss physical features of semiconductors such as band gap, carrier concentration and impurity conductivity. This chapter explains the direct and indirect absorption process in semiconductors. The chapter also deals with concept of effective mass of electrons in the energy bands of solids.

12.1 Introduction

The semiconductors are class of solids has resistivity in between those of metals and insulators. Semiconductors are quite different from the metals, in metals there are a large number of electrons available, responsible for thermal and electrical conductivity. Metals show the positive temperature coefficient of resistance. Meanwhile, the semiconductors and insulators are observed with negative temperature coefficient of resistance. Though, the electrical resistivity of semiconductor is found quite lower than the insulators at room temperature(at 300K). Quantum theory for a free electron gas was able to explain successfully electrical and thermal properties of metals but the band theory for solids is further required to explain the electrical properties of metals, insulators and semiconductors. Band theory of solids accounts the periodic potential due to periodically distributed ion cores throughout the crystal which gives rise the origin of band gap.

The band gap is general term, represents a range of frequency which is not allowed or particular allowed to pass through. In electronics, if a specific range of frequency propagates through the electronic circuits, circuit named as band pass filters. In materials, specifically, if a range of frequencies of elastic waves are not allowed to propagate through the crystalline materials, it is still defined as band gap, though related to vibrational frequencies of lattice. In regime of electrical properties in metals, semiconductors and insulators, it is related to transition of electrons and considered as energy band gap.

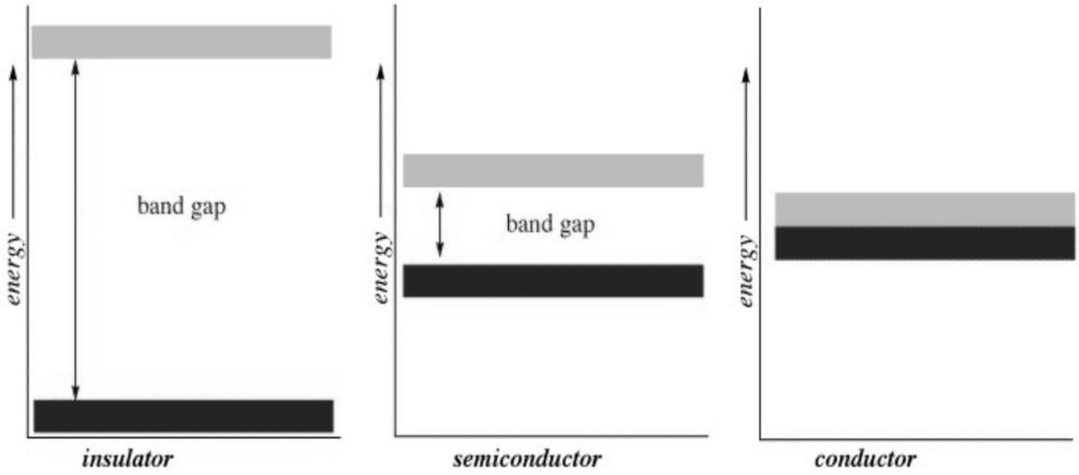


Figure 12.1: *Band scheme for insulator, semiconductor and conductor*

As per band theory of solids, the semiconductors are differentiated from the metals and insulators by its band gap energy. The band gap is considered as a forbidden energy gap between the highest energy point of valance band (valance band edge) and lowest energy point of conduction band (conduction band edge), where the electron is not permissible to exist. The materials with band gap energy range about $0 < \epsilon_g < 4\ eV$ are considered as semiconductors[1]. Semiconductors also defined with their four valence electrons available for bonding with neighboring atoms. According to octet rule, to be more stabilized atom tries to have eight or zero electrons in their valance shell. A semiconductor, as it has four valence electrons, it has equal tendency to give up or accept an electron (although it depends on size of element too). This special property of semiconductor allows it to achieve p-type or n-type behavior. Available intrinsic semiconductors are Silicon (Si) and Germanium (Ge), meanwhile there are several compound semiconductors are invented to fulfill the various purposes in device fabrication (solar cell, light emitting diodes, switches etc.) having two elements from different groups known as compound semiconductors such as III-V (GaN, GaAs, InN etc.), II-VI (ZnO, ZnS, CdS etc.) and IV-IV (SiC).

12.2 Band Gap in Semiconductors

As it has been already described that the energy difference between the valance band edge and conduction band edge is considered as band gap; in the semiconductor at 0K the conduction band is found empty. Only those electrons which are available in conduction band and as well as the holes in valance band can carry the current through the semiconductors and commonly known as ***charge carriers***. The generation of charge carriers in a semiconductor is possible by various processes mainly as an electron in valance band interact with other electrons, holes, photons, or the vibrating crystal lattice itself (thermally generated phonons).For an intrinsic semiconductor the number of charge carriers significantly controlled by $\frac{\epsilon_g}{k_B T}$, as much as this ratio will be lower, carrier concentration will be high.

If a photon equal to band gap energy (ϵ_g)incident on semiconductor, the transition of electron from valance band to conduction band is possible either by ***direct absorption process*** or ***indirect absorption process*** (figure 12.1). In a direct absorption process, the photon is absorbed by the crystal and one electron in conduction band as well as one hole in the valance band are generated. In such a process the valance band edge and conduction band edge are on same k values and such type of materials are commonly classified as ***direct band gap semiconductors***. Meanwhile, in an indirect absorption process the transition of electron from valance band to conduction band is possible only by the involvement of a phonon, it is because of that the both edges are widely separated in k-space ($\boldsymbol{k}_c$).Since, in the energy range of interest, the wave vector of incident photon is negligible ($\boldsymbol{k} \approx 0$) ,so by keeping the conservation of momentum, a phonon with energy $\hbar\Omega$ and wave vector $\boldsymbol{q}$ involves for such type of transition processes to be occurred. The momentum and energy conservation equations for indirect absorption process can be described as below

$$\hbar\boldsymbol{k} = \hbar\boldsymbol{k}_c + \hbar\boldsymbol{q} \approx 0 (\text{momentum conservation})$$

$$\hbar\omega = \epsilon_g \pm \hbar\Omega \ (\text{energy conservation})$$

such type of semiconductors is counted as ***indirect band gap semiconductors***. At lower temperatures, the threshold energy required for this process is in actual higher than the true band gap ($\hbar\omega > \epsilon_g$). However, at higher temperature, where the phonons are already thermally excited, instead of phonon creation, it may be possible a phonon is annihilated along with photon absorption.

Transition of electron from valance band to conduction band at threshold energy takes place from edge to edge meanwhile, if higher energy is provided than the threshold one, transition can occur between almost all points of the two bands for which the wave vector and energy are conserved (figure 12.2).

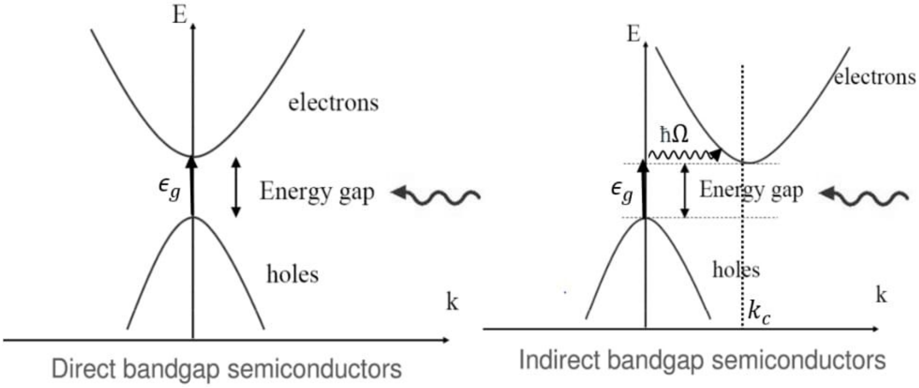


Figure 12.2: *Direct and indirect band gap semiconductors*

However, the transition of electron from the conduction band to valance band generally occurs from edge to edge. Electrons excited to the higher levels in conduction band first lose their energy in form of phonon by interacting with immobile ions and as soon as they arrived at the edge point of conduction point, they jump to the edge point of valance band by emitting a photon and/or by involvement of a phonon depends on the type of band gap (figure 12.3).

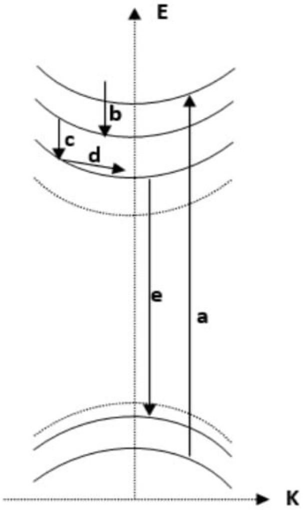


Figure 12.3: *possible transition of electron through band gap:*

(a) In an inter–band absorption process, photon absorption is followed by electron–hole pair generation.
(b) This type of transition attributed to jump of charge carriers from the continuum states in results of Electron–electron scattering, electron–hole scattering, or phonon scattering can result in this transition.
(c) Direct inter–sub–band transition, such as inter–sub–band relaxation or absorption, and usually corresponds to a relatively small energy transition.
(d) It is related to indirect intra sub band transition by involving of a phonon. Phonon scattering is usually included in this category
(e) Edge to edge transition of electron by emitting a photon and/or phonon (depend on type of band gap)

The band gap for various semiconductors are displayed in table 3.1.

Table 3.1: Energy band gap for various semiconductors [2]

S. No.	**Semi-conductor**	**Band gap**		**Type**	**S. No.**	**Semi-conductor**	**Band gap**		**Type**
		0 K	300 K				0 K	300 K	
1.	Si	1.17	1.11	Indirect	**9.**	SiC	3.0	-	Indirect
2.	Ge	0.744	0.66	Indirect	**10.**	PbS	0.286	0.34-0.37	Direct
3.	InSb	0.23	0.17	Direct	**11.**	PbTe	0.190	0.29	Indirect
4.	InAs	0.43	0.36	Direct	**12.**	CdS	2.582	2.42	Direct
5.	InP	1.42	1.27	Direct	**13.**	CdSe	1.840	1.74	Direct
6.	GaP	2.32	2.25	Indirect	**14.**	CdTe	1.607	1.44	Direct
7.	GaAs	1.52	1.43	Direct	**15.**	SnTe	0.3	0.18	Direct
8.	GaSb	0.81	0.68	Direct	**16.**	Cu_2O	2.172	-	Direct

12.3 Equation of Motion of an Electron in an Energy Band

We can describe the equation of motion of an electron exist in the energy band or more correctly under the periodic potential. Electron moving with velocity v can be considered as a wave packet of group velocity v_g and definitely:

$$v = v_g = \frac{d\omega}{dk}$$

where ω is angular frequency of the deBroglie waves associated with moving electron and k is wave vector. If the energy of electron in the particular band is ϵ then we can write the velocity of electron

$$v = \frac{1}{\hbar}\frac{d\epsilon}{dk} \tag{1}$$

For free electrons we know that the energy of electrons

$$\epsilon = \frac{\hbar^2 k^2}{2m} \tag{2}$$

In band theory velocity and ϵ varies with k as given below:

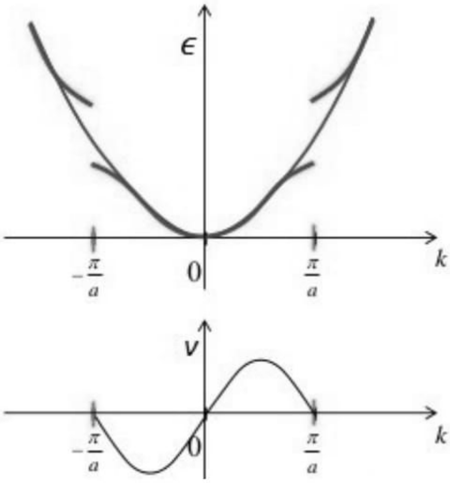


Figure 12.4: *Variation in energy and velocity of electron with k in the first Brillouin zone.*

So, we can observe that the velocity of electron in a band will be zero at the top and bottom of the energy band means at zonal boundaries of Brillouin zone (for $k = 0, \pm\frac{\pi}{a}$). Important conclusion is beyond the inflexion points ($k = k_0$) the velocity decreases while energy is increasing, which is indicating that the electron is not completely free in a band.

12.4 Effective Mass

A particle's **effective mass** (often denoted by m^*) is the mass that it seems to possess by the particle when responding to the applied forces, or the mass that it seems to have when it grouped with other identical particles in a thermal distribution.If the same magnitude of electric field is applied to both electrons, one in the vacuum and other one inside the crystal, the electrons will accelerate at a different rate from each other due to the existence of different potentials inside the crystal. So, the electron inside the crystal will behave as a particle having a different mass than that of the electron in vacuum. This altered mass is called as an effective-mass. The use of effective mass is an approach that simplifies the understanding of band structures by constructing an analogy to the behavior of a free particle with that mass.

Let's consider that if electric field E is applied on the motion of an electron present in the Brillouin zone, if *v* is the velocity of electron then the increment in the energy of the electron in the time interval *dt* will be

$$d\epsilon = evdt$$

Using the value of velocity of electron in a band from equation (1)

$$d\epsilon = \frac{eE}{\hbar}\frac{d\epsilon}{dk}dt$$

$$\frac{d\epsilon}{dk}dk = \frac{eE}{\hbar}\frac{d\epsilon}{dk}dt$$

So we can obtain

$$\frac{dk}{dt} = \frac{eE}{\hbar}$$

Or $$\hbar\frac{dk}{dt} = eE$$

$$\frac{d(\hbar k)}{dt} = F \qquad (3)$$

So $\hbar k$ represents the crystal momentum (often denoted by G). this equation is analogues to Newton's second law for electron in a periodic potential. Here,for an electron inside the crystal, force F is regarded as the total force on electron which includes the electrostatic force applied by lattice (F_{latt}) and external applied electric force (F_{ex}).

$$\frac{d(\hbar k)}{dt} = F_{latt} + F_{ex} \tag{4}$$

Furthermore, the acceleration of electron can be given by

$$a = \frac{dv}{dt} = \frac{1}{\hbar}\frac{d^2\epsilon}{dk^2}\frac{dk}{dt}$$

$$a = \frac{1}{\hbar}\frac{d^2\epsilon}{dk^2}\frac{eE}{\hbar}$$

$$a = \frac{eE}{\hbar^2}\frac{d^2\epsilon}{dk^2}$$

or

$$a = \frac{eE}{\left(\frac{\hbar^2}{\frac{d^2\epsilon}{dk^2}}\right)} \tag{5}$$

We know that the acceleration of a free electron with mass m moving under electrostatic force *eE* is given by

$$a = \frac{eE}{m} \tag{6}$$

So, comparing both of the equations (6) and (7), we can obtain the expression for effective mass of electron in a lattice

$$m^* = \frac{\hbar^2}{\left(\frac{d^2\epsilon}{dk^2}\right)} \tag{7}$$

This equation showing that effective mass of an electron moving in a periodic potential is not a constant, it is estimated from dispersion curve ($\epsilon - k$ diagram). If the slope of slope of curve $\frac{d^2\epsilon}{dk^2}$ is higher ,then it is corresponding to lighter mass and if the slope is lower, it indicates larger mass (explained in figure12.5).

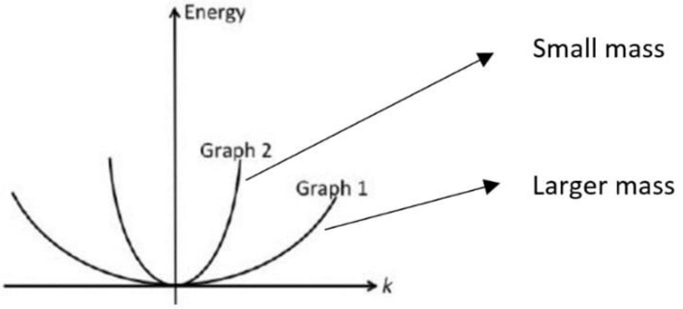


Figure 12.5: *Relation between mass and curvature of the energy band.*

A factor which is the ratio of mass of electron in vacuum to in a periodic potential can be introduced

$$f_k = \frac{m}{m^*} = \frac{\hbar^2}{\left(\frac{d^2\epsilon}{dk^2}\right)} \tag{8}$$

If the value of this factor is one, it indicates that the electron is a free . Moreover, if it is greater than one means a heavy particle and influenced by periodic potential and if it is less than unity which means that effective mass (*m**) is less than the real mass (*m*).

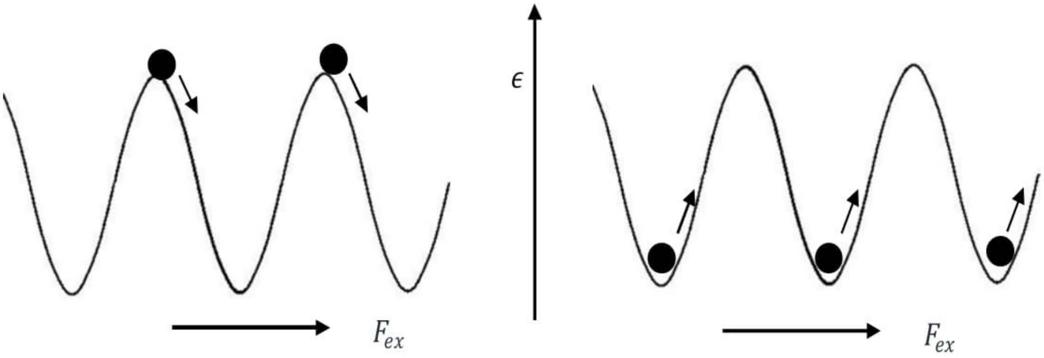


***Figure 12.6**: Electron spatial distribution (A) $f_k < 1$, (B) $f_k > 1$[3].*

If we applied an external electric field on crystal (F_{ext} = eE) and we study the behavior of particle we can readily express from equation (6)

$$a = \frac{eE}{m^*}$$

or

$$ma = m\frac{eE}{m^*}$$

$$ma = f_k F_{ex} \tag{9}$$

From equation (4) and (9)

$$f_k = \frac{F_{ex}+F_{latt}}{F_{ex}} \tag{10}$$

So we can see if the potential by lattice (F_{latt}) is zero then $f_k = 1$, hence electron will behave as a free particle.

Furthermore, if we plot the effective mass with wave vector *k* in a *Brillouin zone,* as shown figure 12.7

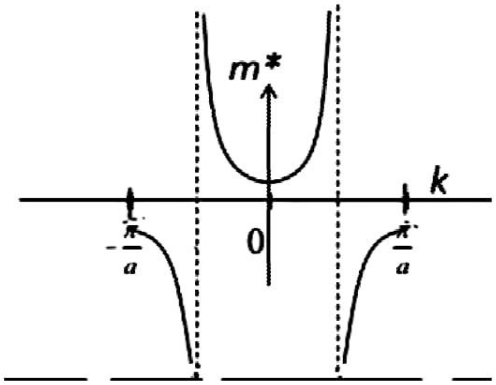


Figure 12.7: *Variation of effective mass with wave vector k.*

The upper half of this plot is indicates positive effective mass in the energy band while the lower half corresponds to negative effective mass. In regime of a parabolic $\epsilon - k$ curve, the electron can be treated as free particle and the energy of free particle is given by(from eq. 2)

$$\epsilon = \frac{1}{\hbar}\frac{k^2}{2m}$$

we can observe that energy is function of k^2

$$\epsilon \propto k^2$$

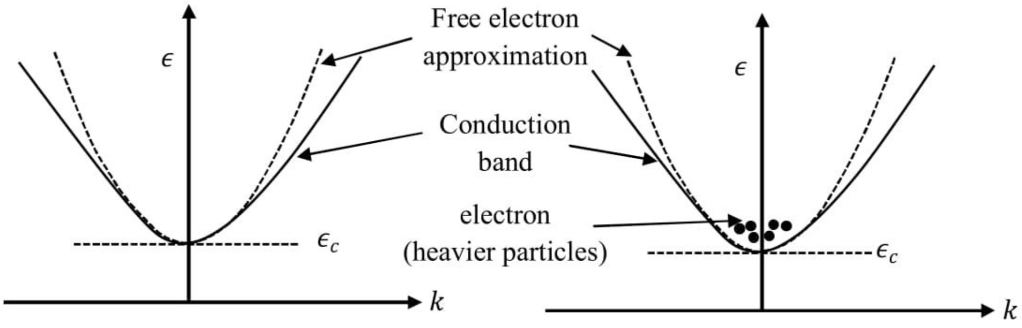


Figure 12.8: Electrons in conduction band with positive effective mass

For a particle exists anywhere in the conduction band

$$(\epsilon - \epsilon_c) \propto k^2$$
$$(\epsilon - \epsilon_c) = C_1 k^2$$

So we can obtain

$$\frac{d^2\epsilon}{dk^2} = C_2$$

Here,'C_1' and C_2 are any constants. So from equation (7) the effective mass of electron in conduction band can be given by

$$m_e^* = \frac{\hbar^2}{C_1}$$

Since $(\epsilon - \epsilon_c) > 0$, so surely $C_1 > 0$ and in results

$$m_e^* > 0$$

The electrons in conduction band have positive effective mass and are treated as heavier particles, and would like to stay at the bottom of conduction band.

Furthermore, for valance band where we have the energy of electron

$$(\epsilon_v - \epsilon) = C_3 k^2$$

Since $(\epsilon_v - \epsilon) > 0$, so surely $C_3 > 0$ and we can deduce

$$-\frac{d^2\epsilon}{dk^2} = C_4$$

By using equation (7) the effective mass of electron in valance band can be given by

$$m_h^* = -\frac{\hbar^2}{C_4}$$

Since C_4 will be also a positive quantity

$$m_h^* < 0$$

The electrons in valance band have negative effective mass and behave as lighter particles known as holes, these holes would like to stay at the top of the valance band.

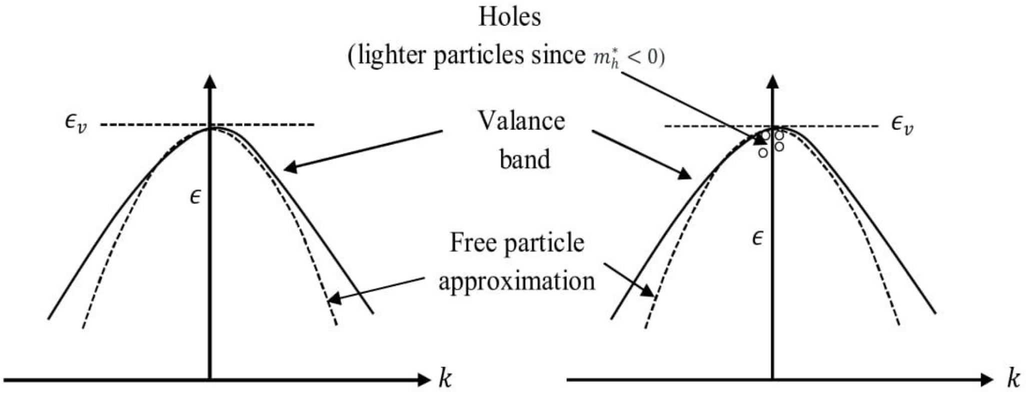


Figure 12.9: *Electrons in valance band with negative effective mass (holes).*

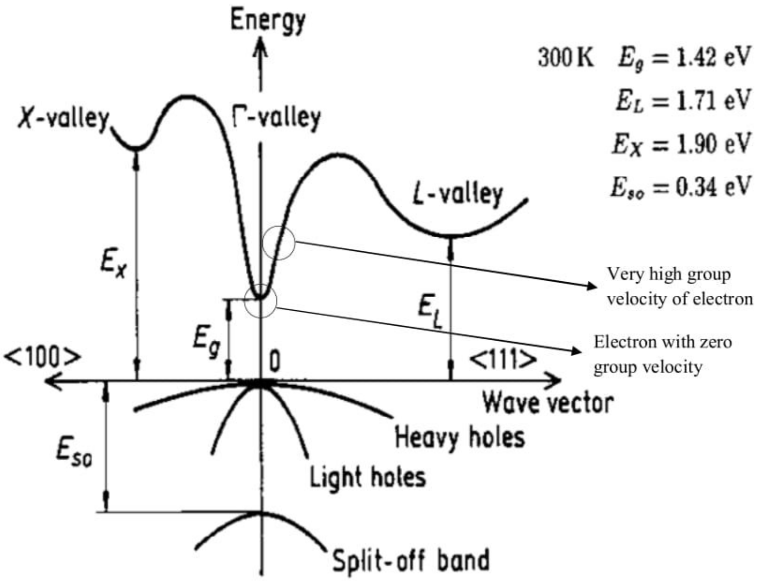


Figure 12.10: *Band structure of GaAs in <100> and <111> direction [4].*

In the given example of GaAs band structures, which is a direct band gap semiconductor, we can observe that at the bottom point of conduction band where the slope of curve is zero, electron possesses zero group velocity. At the edge of conduction band, the electron behaves like a heavy mass particle (as indicated in figure 12.10). Similarly, in this potential well of conduction band, where the slope is very high (as indicated in figure 12.10), corresponds to high group velocity, with electron having light effective mass. In a GaAs crystal at such position (indicated in figure 12.10) have effective mass around

$$m_e^* \approx 0.06\, m$$

Here *m* is mass of free electron (electron in vacuum). Similarly, for the holes in the valance band, for the example of GaAs, we can see that they have higher effective mass for the band where slope is lower and are lighter for the band having high slope in $\epsilon - k$ diagram.

12.5 Self Learning Exercises-I

Q.1 What are direct and indirect band gap semiconductors ?

Q.2 If the energy-wavenumber relationship for an electron in some material is

$$\epsilon = \frac{\hbar^2}{2m}\cos(k)$$

Determine the group velocity.

Q.3 Plot the variation of energy and group velocity of an electron with *k*, in first Brillouin zone.

Q.4 Plot the ϵ-k diagram for masses m_1 and m_2 (where $m_1 > m_2$)

Q.5 Give the name of direct and indirect energy band gap materials.

12.6 Intrinsic Carrier Concentration

The Intrinsic charge carrier concentration is simply means the number of electrons in the conduction band and the number of holes in the valance band in per unit volume which is available in form of free electrons and holes at a given temperature. It can be obtained by mathematical multiplication of the available states (of course in per unit volume, the volume which is actual available for free charge carriers) that can be occupied by the electron of energy ϵ (so called density of states) and the probability to occupy that energy level (ϵ) by the electron at given temperature T. This probability for electrons and holes (fermions) is determined by the Fermi-Dirac statistics (f_e for electrons and f_h for holes).

So the electron concentration in whole conduction bandrange at temperature T

$$n = \int_{E_c}^{\infty} \{D_e(\epsilon) \times f_e\,(\epsilon)\} d\epsilon \qquad (11)$$

Similarly, the hole concentration in whole valance band range at temperature T

$$p = \int_{-\infty}^{E_v} \{D_h(\epsilon) \times f_h\,(\epsilon)\} d\epsilon \qquad (12)$$

Here, D_e density of states for electrons in conduction band and D_h density of states for holes in valance band.

(A)To find out density of states for electrons and holes (D_e and D_h):

The density of states is calculated simply for parabolic band edges. Electrons in conduction band are located in the states at the edge and rest of the band remains empty. So, such electrons can be treated as a free charge carrier with effective mass m_e^* and hence, the total energy of electron is the kinetic energy

$$\epsilon_k = \frac{P^2}{2m_e^*}$$

Here *P* is the momentum in the energy band. To calculate the states available for the electron of energy E, quantum mechanically, taking in account the wave nature (with wavelength λ) of particle, the momentum of electron can be given by

$$P = \frac{h}{\lambda}$$

For calculation in the momentum space, introducing the wave vector which is defined by $k = 2\pi/\lambda$, energy of electron can be obtained (in free particle approximation the kinetic energy of electron will be total energy, as energy curve is parabolic)

$$\epsilon = \epsilon_k = \frac{\hbar^2 k^2}{2m_e^*}$$

If the component of k along the axis X, Y and Z are k_x, k_y and k_z then

$$k_x^2 + k_y^2 + k_z^2 = \frac{2m_e^*}{\hbar^2}\,\epsilon$$

This equation is analogues to the equation for a sphere having the radius $\sqrt{\frac{2m_e^*}{\hbar^2}\epsilon}$, indicating that in momentum space, a constant energy (ϵ) surface is spherical in shape, known as fermi surfaces. The volume of this fermi surface sphere will be

$$= \frac{4}{3}\pi\left(\sqrt{\frac{2m_e^*}{\hbar^2}\,\epsilon}\right)^3$$

On the other hand, if we consider a rectangular parallelepiped having sides L_x, L_y and L_z, the wavelengths which a free electron can have in X, Y and Z directions are $\lambda_x = \frac{L_x}{n_1}$, $\lambda_y = \frac{L_y}{n_2}$ and $\lambda_z = \frac{L_z}{n_3}$ respectively (n_1, n_2 and n_3 are integers, indicating number of states). If we change the integers by unity (which is corresponding to one quantum state) then by using the relation $k = 2\pi/\lambda$

$$\Delta k_x \Delta k_y \Delta k_z = \frac{8\pi^3}{L_x L_y L_z}$$

In momentum space it is related to volume of one quantum. $L_x L_y L_z = V$ can be taken as the volume of assumed parallelepiped. Hence, the volume of one quantum state is $\frac{8\pi^3}{V}$

The number of states upto energy ϵ can be obtained by dividing the total occupied volume of all quantum states upto energy ϵ with the volume of one quantum state. So, the number of states for an electron having energy upto ϵ

$$= \frac{\frac{4}{3}\pi\left(\sqrt{\frac{2m_e^*}{\hbar^2}\,\epsilon}\right)^3}{\frac{8\pi^3}{V}}$$

As each quantum state can have two electrons with opposite spin, so total number of states per unit volume (V = 1) which can be occupied by electron having energy up to ϵ will be

$$N = 2 \times \frac{\frac{4}{3}\pi\left(\sqrt{\frac{2m_e^*}{\hbar^2}\epsilon}\right)^3}{8\pi^3}$$

$$N = \frac{1}{3\pi^2}\left(\sqrt{\frac{2m_e^*}{\hbar^2}}\right)^3 \epsilon^{3/2}$$

Hence, the total possible number of states in a unit volume available for electrons those having energy in the range of ϵ to $\epsilon + d\epsilon$ will be

$$dN = \frac{1}{3\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \frac{3}{2}\epsilon^{1/2} d\epsilon$$

So, the total possible number of states per unit energy range in a unit volume available for electrons having energy in proximity ϵ, is so called density of states

$$\frac{dN}{d\epsilon} = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \epsilon^{1/2}$$

According to Shockley as the conduction band starts from its edge of lowest energy level ϵ_c and below this level there is forbidden energy gap where the electrons cannot exist. So, density of states in conduction band for electron having energy level ϵ

$$D_e(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} (\epsilon - \epsilon_c)^{\frac{1}{2}} \tag{13}$$

Similarly, density of states for holes having energy ϵ in valance band can be given by

$$D_h(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} (\epsilon_v - \epsilon)^{1/2} \tag{14}$$

Here, m_h^* is effective mass of hole in valance band and ϵ_v is highest energy level for holes at the edge of valance band and above it the free hole cannot exist.

(B) To find out the probability to have energy level ϵ for temperature T (f_e and f_h):

The probability that an electron can have energy ϵ at temperature T is given by Fermi-Dirac distribution function

$$f_e\,(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

Here, k_B is Boltzmann constant and μ is chemical potential. In semiconductor physics the more popular term is fermi energy (ϵ_f) instead of chemical potential (μ). At the temperature of interest (around room temperature), it can be assumed (approximation valid if $f_e\,(\epsilon) \ll 1$) for the conduction band of a semiconductor crystal that $(\epsilon - \epsilon_f) >> k_B T$(approximation valid if $f_e\,(\epsilon) \ll 1$). Hence,

$$f_e\,(\epsilon) \approx e^{(\epsilon_f-\epsilon)/k_B T} \tag{15}$$

(using term ϵ_f instead of μ)

The probability that a hole can have energy ϵ in valance band at temperature T is given by

$$f_h\,(\epsilon) = 1 - f_e\,(\epsilon)$$

(since the absence of electron is a hole)

$$f_h\,(\epsilon) = 1 - \frac{1}{e^{(\epsilon-\epsilon_f)/k_B T} + 1}$$

$$f_h(\epsilon) = \frac{1}{e^{(\epsilon_f-\epsilon)/k_B T} + 1}$$

With the similar approximation $\{(\epsilon_f - \epsilon) >> k_B T\}$we can obtain

$$f_h\,(\epsilon) \approx e^{(\epsilon-\epsilon_f)/k_B T} \tag{16}$$

(C)Equilibrium carrier concentration

The electron concentration in whole conduction band range at temperature T

$$n = \int_{\epsilon_c}^{\infty} \{D_e(\epsilon) \times f_e\,(\epsilon)\} d\epsilon$$

$$n = \int_{\epsilon_c}^{\infty} \left\{ \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} (\epsilon - \epsilon_c)^{\frac{1}{2}} \times e^{\frac{\epsilon_f - \epsilon}{k_B T}} \right\} d\epsilon$$

$$n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} e^{\frac{\epsilon_f}{k_B T}} \int_{\epsilon_c}^{\infty} \left\{ (\epsilon - \epsilon_c)^{\frac{1}{2}} e^{-\frac{\epsilon}{k_B T}} \right\} d\epsilon$$

Integration gives the result

$$n = 2\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} e^{\frac{\epsilon_f - \epsilon_c}{k_B T}} \tag{17}$$

Similarly, the equilibrium concentration for the holes

$$p = \int_{-\infty}^{E_v} \left\{ \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{\frac{3}{2}} (\epsilon_v - \epsilon)^{\frac{1}{2}} \times e^{\frac{\epsilon - \epsilon_f}{k_B T}} \right\} d\epsilon$$

Solving it, $$p = 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{\epsilon_v - \epsilon_f}{k_B T}} \tag{18}$$

Multiplying the electron carrier concentration and hole carrier concentration, we can obtain

$$np = 4 \left(\frac{k_B T}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{\frac{3}{2}} \times e^{-\frac{\epsilon_c - \epsilon_v}{k_B T}}$$

If the band gap energy of given semiconductor is ϵ_g defined as $\epsilon_g = \epsilon_c - \epsilon_v$ (as shown in figure 12.11),

$$np = 4 \left(\frac{k_B T}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{\frac{3}{2}} \times e^{-\frac{\epsilon_g}{k_B T}} \tag{19}$$

This relation holds for both intrinsic semiconductor and as well as for impurity ionization of semiconductor material, the only assumption is taken that the fermi energy level is far better from the edge of both bands in comparison with $k_B T$. It can be observed that it does not involve fermi energy and a constant term for a given temperature, most commonly known as *mass action law*.

$$np = n_i^2 \tag{20}$$

Here n_i is carrier concentration of electrons for intrinsic semiconductor and obviously for intrinsic semiconductor

$$n_i = \mathrm{p}_i$$

Hence, $n_i = \mathrm{p}_i = \sqrt{np}$

$$n_i = \mathrm{p}_i = 2 \left(\frac{k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} (m_e^* m_h^*)^{\frac{3}{4}} \times e^{-\frac{\epsilon_g}{2k_B T}}$$

as for intrinsic semiconductor at any given temperature T we have

$$n_i = \mathrm{p}_i$$

using from eq. (17) and eq. (18)

$$2 \left(\frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{\epsilon_f - \epsilon_c}{k_B T}} = 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{\epsilon_v - \epsilon_f}{k_B T}}$$

$$e^{\frac{2\epsilon_f}{k_B T}} = 2 \left(\frac{m_h^*}{m_e^*} \right)^{\frac{3}{2}} e^{\frac{\epsilon_g}{k_B T}}$$

which gives $$\epsilon_f = \frac{\epsilon_g}{2} + \frac{3}{4} k_B T ln \left(\frac{m_h^*}{m_e^*} \right) \tag{21}$$

As the effective mass of hole little bit higher than the effective mass of electron ($|m_h^*| > |m_e^*|$), in an intrinsic semiconductor, the fermi level will shift slightly towards conduction band with temperature. In practice if $m_h^* = m_e^*$, the fermi level, we can say, will lie exactly in the middle of forbidden energy gap of an intrinsic semiconductor.

12.7 Impurity Conductivity

Conductivity of semiconductor materials can be interpreted in terms of mobility and carrier concentration of charge carriers. Obviously, the electrical conductivity of a semiconductor is the sum of contributions from electrons as well as holes and given by:

$$\sigma = ne\mu_e + pe\mu_p$$

Here, μ_e and μ_h are the mobility of electrons and holes in semiconductor material respectively. Mobility of a charge carrier can be defined as the magnitude of the drift velocity of a charge carrier per unit electric field (E)[2]. Hence,

$$\mu = \frac{|v|}{E}$$

As the drift velocity of a charged particle with charge *q* in the electric field E is defined as

$$v = \frac{q\tau E}{m}$$

where m is the mass of charged particle and τ is the collision time. Hence, the mobility of electron and hole in a semiconductor material can be defined as

$$\mu_e = \frac{e\tau_e}{m_e^*}, \text{ and } \mu_h = \frac{e\tau_h}{m_h^*}$$

As the mobility depends on collision time and effective mass, further the effective mass of a hole is higher than electron in a given semiconductor material, so the mobility of holes is comparatively less than the mobility of electrons. Furthermore, with temperature the collision time will be reduced and it will affect the mobility.

However, the temperature dependence conductivity is dominated by carrier concentration instead of mobility.

Beyond the mobility, the other factor which is responsible to affect the conductivity of a semiconductor is the carrier concentration (*n* and *p*). The carrier concentration for an intrinsic semiconductor has already been described, which significantly depends upon the temperature of surrounding (T) and band gap (ϵ_g). Moreover, the carrier concentration significantly affected by the defects present in a semiconductor crystal. Crystal defects are broadly divided in two categories as line and point defects. Any kind of imperfection in the crystal expressively affects the electrical and optical properties of the crystal. Sometime, point defects are intentionally created in a semiconductor material to achieve desire level of electrical and optical properties; for example, at normal room temperature conductivity of an intrinsic semiconductor is noticed very poor, to enhance the conductivity for the purpose of device fabrication, foreign impurity atoms (other than the constituent elements of the crystal) are inserted in the semiconductor crystal. Intentionally addition of impurities to a semiconductor is known as doping[2].

In the crystal of silicon where each atom is attached by its four neighbors connected by four covalent bonds having the electrical conductivity ~ 10^5ohm-cm at 300 K. If an impurity atom with five valance electrons (P, As or Sb) doped in the silicon, there will be one electron extra after sharing its four electrons with nearby silicon atoms. This extra electron can be released by impurity atom after having sufficient amount of ionization energy and this electron contributes in the charge carrier concentration of semiconductor, obviously in electron concentration. In results, the conductivity significantly enhanced. Foreign element that can release an electron are known as ***donor***.

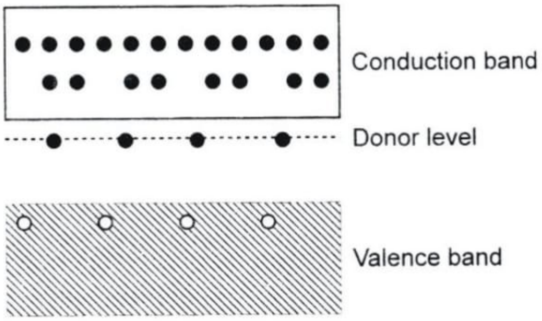


Figure 12.12: Band energy diagram of semiconductor with donor impurity[5].

These elements require less energy in comparison to the band gap energy (ϵ_g) to give up the electron and can be represented by a different energy level in the energy band diagram of semiconductor called **donor level (ϵ_d)**.

Similarly, if an impurity atom with three valance electrons (B, Al, Ga and In) added in silicon, this trivalent impurity atom will share it's all three electrons to nearby four silicon atoms. By sharing all three electrons by impurity atom, there will be lack of one electron to complete the octet of valance shell. This scarcity of one electron leaves behind a hole. Such impurities are known as **acceptors** and always eager to accept an electron to complete the covalent bond with nearby atoms. As the acceptor impurity accepts the electron it gets ionized. These impurities create own energy level in band gap near to the valance band as shown in the energy diagram of a semiconductor with acceptor impurities.

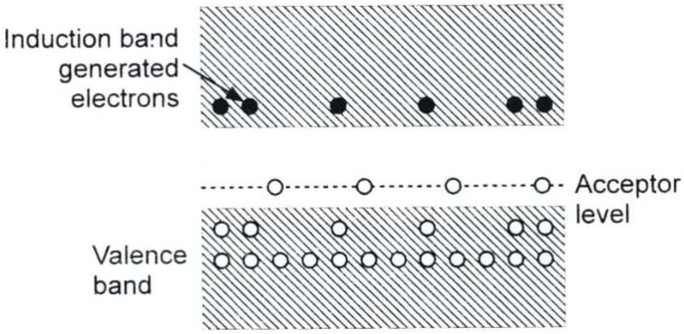


Figure 12.13: Band energy diagram of semiconductor with acceptor impurity [5].

12.8 Illustrative Examples

Example 1. Show that the period of Bloch oscillation for a one-dimensional crystal having lattice period a is $\tau = \frac{h}{eEa}$

Sol. $\hbar \frac{d\boldsymbol{k}}{dt} = -\boldsymbol{E}e$

and assume that $\tau/2$ is the time required for the electron to accelerate across the full Brillouin zone. Then,

$$\hbar \int_0^{\tau/2} \frac{dk}{dt} dt = \int_0^{\tau/2} \boldsymbol{E}e\, dt$$

$$\hbar \left[k\left(\frac{\tau}{2}\right) - k(0)\right] = \boldsymbol{E}e \frac{\tau}{2}$$

$$\hbar \left[\frac{\pi}{a} - 0\right] = \boldsymbol{E}e \frac{\tau}{2}$$

$$\frac{h}{2\pi} \frac{\pi}{a} = \boldsymbol{E}e \frac{\tau}{2} \qquad \therefore \tau = \frac{h}{eEa}$$

Example 2. What is the occupation probability of an electron at energy level $3k_B$T above the fermi level?

Sol. Occupation probability of an electron at energy level E is given by

$$f(\epsilon) = \frac{1}{1 + \exp\left(\epsilon - \epsilon_f / k_B T\right)} \qquad Here\ \epsilon - \epsilon_f = 3k_B T$$

$$f(3k_B T) = \frac{1}{1 + exp\ (3k_B T / k_B T)}$$

$$f(3k_B \mathrm{T}) = \frac{1}{1 + \exp\ (3)} = \frac{1}{1 + 20.09}$$

$$= .0474 = 4.74\%$$

12.9 Self Learning Exercise-II

Q.1 What do you mean doping of a semiconductor?

Q.2 Calculate the thermal equilibrium concentration of holes in silicon at 400 K.

Given: $\epsilon_f - \epsilon_v$=0.27eV , N_v=1.04 x 10^{19} cm^{-3}

Q.3 Plot the Fermi occupation function at temperature T=0K, T= T_1 and T=T_2> T_1

Q.4 What do you mean by curvature of the $\epsilon - k$ diagram?

Q.5 Draw the $\epsilon - k$ diagram for direct and indirect band gap semiconductors.

12.10 Summary

The semiconductors are class of solids has resistivity in between those of metals and insulators. Semiconductors can be differentiated from metals and insulator by band gap energy. The band gap for electronic transitions is considered as a forbidden energy gap between the highest energy point of valance band (valance band edge) and lowest energy point of conduction band (conduction band edge), where the electron is not permissible to exist. In well-established regime the materials with band gap energy $0 < \epsilon_g < 4\ eV$ are considered as semiconductors.

In a direct absorption process, the photon is absorbed by the crystal and one electron as well as one hole generated. In such a process the valance band edge and conduction band edge are on same value of k and such type of materials are Commonly classified as ***direct band gap semiconductors***. Meanwhile, in an indirect absorption process the transition of electron from valance band to conduction band is possible only by the involvement of a phonon. The variation in the energy of electron with its momentum are plotted as ϵ -k diagram.

A particle's **effective mass** (often denoted by m^*) is the mass that it seems to possess by the particle when responding to the applied forces, or the mass that it seems to have when it grouped with other identical particles in a thermal distribution. The group velocity and the mass of electron are decided by the slope of these curve.

Intrinsic semiconductors have poor conductivity at room temperature, to control the conductivity, to achieve n-type and p type characteristics we doped the impurity elements.

12.11 Glossary

Collision time: relaxation time between two collisions.

Line defects: Line defects, or dislocations, are lines along which whole rows of atoms in a solid are arranged anomalously. The resulting irregularity in spacing is most severe along a line called the **l**ine of dislocation.

Point defects: Point defects are where an atom is missing or is in an irregular place in the lattice structure. Point defects include self-interstitial atoms, interstitial impurity atoms, substitutional atoms and vacancies.

12.12 Answers to Self Learning Exercises

Answers to Self-Learning Exercise I

Ans.1: Semiconductors in which there is direct transition of electrons from conduction band to valance band called as direct band gap semiconductors and those involve a phonon for such transition known as indirect band gap semiconductors.

Ans.2: $v_g = \frac{1}{\hbar}\frac{dE}{dk} = -\frac{1}{\hbar}\frac{\hbar^2}{2m}\sin(\mathrm{k}) = -\frac{\hbar}{2m}\sin(\mathrm{k})$

Ans.3: See figure 12.4.

Ans.4: see figure 12.5.

Ans.5: Direct energy band gap: GaAs and Indirect energy band gap: Si

Answers to Self-Learning Exercise II

Ans.1: The deliberate addition of impurities like Al, B, As to a semiconductor like

Ge, Si, is called doping.

Ans.2: N_v=1.04 x $10^{19}(400/300)^{3/2}$ =1.6 x 10^{19}cm^{-3}

k_BT=0.0259(400/300)= 0.03453 eV

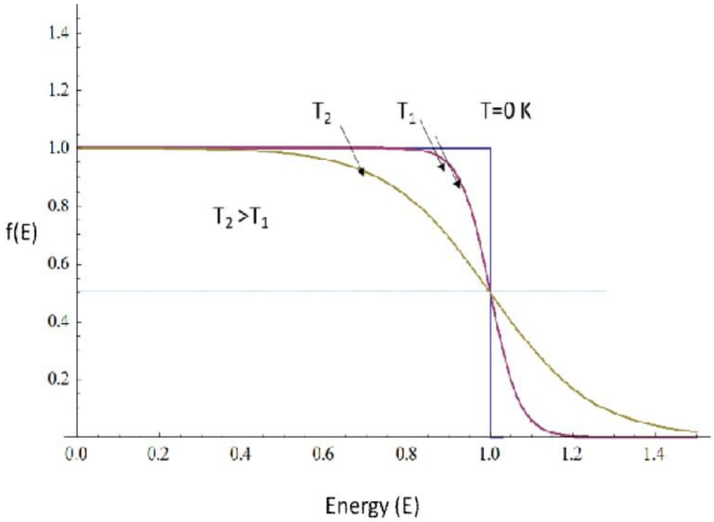
Hole concentration

$$p = N_v exp\left[\frac{-(E_F - E_v)}{kT}\right]$$

$$p = 1.6\ \times 10^{19} exp\left[\frac{-0.27}{.003453}\right]$$

$$p = 6.43\ \times 10^{15} cm^{-3}$$

Ans.3:



Ans.4: The curvature of E-k diagram provides information about group velocity and effective mass of an electron or a hole.

Ans.5: See figure 12.2

12.13 Exercise

Q.1 Is it possible to enhance the conductivity of a semiconductor by a laser?

Q.2 In As has donor energy E_d = 0.23 eV, dielectric constant ε = 18 and electron effective mass m* = 0.015 m. Then calculate donor ionization energy.

Q.3 Calculate the ground state radius of electron for InAs.

Q.4 In a semiconductor, there are 10^{13} donors/cm^3 of ionization energy 1meV and an effective mass 0.01 m. Then calculate the concentration of electrons at 4 K.

Q.5 What will be the wave-vector of a hole if an electron is missing from the state of wave-vector k_e?

Q.6 What is the effective mass of the electron in energy band

$$\epsilon_k = -\alpha - 6\gamma + \gamma k^2 a^2?$$

12.14 Answers to Exercise

Ans.1: Yes, if the energy of incident photon more than the band gap.

Ans.2: E_{ion}=(13.6 eV)($m^*/m\ \varepsilon^2$)=0.63meV

Ans.3: $r = a_H \varepsilon \left(\frac{m}{m^*}\right)$

$a_H = 0.53 \times 10^{-10} m$

$r = 6 \times 10^{-6}$ cm

Ans.4: $n = (n_0 N_d)^{1/2} e^{-E_d/2k_B T}$

$$n_0 = 2\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} \approx 4 \times 10^{13} cm^{-3}$$

$\frac{E_d}{2k_B T} = 1.45$; and $e^{-1.45}$=0.23, n=0.46 x 10^{13} electrons cm^{-3}

Ans.5: $k_h = -k$

Ans.6: Effective mass $m^* = \frac{\hbar^2}{d^2\epsilon_k/dk^2} = \frac{\hbar^2}{2\gamma a^2}$

References and Suggested Readings

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UNIT-13
Fermi Surfaces and Metals

Structure of the Unit

13.0 Objectives

The measurement of Fermi surface is very useful in metal physics. Shape of the Fermi surface gives information about electronic band structure. Therefore, in this section we will study the band structure calculation and experimental measurement of Fermi surface.

13.2 Introduction to Fermi Surfaces and Metals

The Fermi surface is defined by constant energy surface in ***k***-space at absolute zero temperature. It separates the filled orbitals from unfilled orbitals. The electrical conductivity of metals is determined by population of the electrons around Fermi level or changes in the occupancy of states of the Fermi surface. Therefore, the volume and shape of the Fermi surface give the electrical properties of the metal. The free electron Fermi surfaces in *k*-space is given by spheres of radii *k*. The radius depends on concentration of the valence electrons. The free electron Fermi surfaces in k-space is constructed by the reduced and the periodic zone schemes.

13.3 Reduced Zone Scheme

Consider a Bloch function $\psi_{\boldsymbol{k}'}(\boldsymbol{r}) = e^{i\boldsymbol{k}'.\boldsymbol{r}}u_{\boldsymbol{k}'}(\boldsymbol{r})$ having $\boldsymbol{k}'$ outside the first zone [Figure 1]. But it is always possible to choose a wavevector ***k*** for a Bloch function which lies within the first Brillouin zone. This procedure called as a mapping of the bands in the reduced zone scheme.

We can obtain a wave vector ***k*,** which is lies within the first Brillouin zone by choosing suitable reciprocal lattice vector **G** or $\boldsymbol{k} = \boldsymbol{k}' + \mathbf{G}$ [Figure 1] [1]. Then Bloch function

$$\begin{aligned}\psi_{\boldsymbol{k}'}(\boldsymbol{r}) &= e^{i\boldsymbol{k}'.\boldsymbol{r}}u_{\boldsymbol{k}'}(\boldsymbol{r}) \\ &= e^{\boldsymbol{k}.\boldsymbol{r}}\left(e^{-i\boldsymbol{G}.\boldsymbol{r}}u_{\boldsymbol{k}'}(\boldsymbol{r})\right) \qquad (1) \\ &= e^{\boldsymbol{k}.\boldsymbol{r}}u_{\boldsymbol{k}}(\boldsymbol{r})\end{aligned}$$

$$\psi_{\boldsymbol{k}'}(\boldsymbol{r}) = \psi_{k}(\boldsymbol{r}) \qquad (2)$$

where $u_{\boldsymbol{k}}(\boldsymbol{r}) = e^{-i\boldsymbol{G}.\boldsymbol{r}}u_{\boldsymbol{k}'}(\boldsymbol{r})$. Because $e^{-i\boldsymbol{G}.\boldsymbol{r}}$ and $u_{\boldsymbol{k}'}(\boldsymbol{r})$are periodic function of crystal lattice, therefore $u_{\boldsymbol{k}}(\boldsymbol{r})$ is also a periodic function and $\psi_{k}(\boldsymbol{r})$ is a Bloch function.

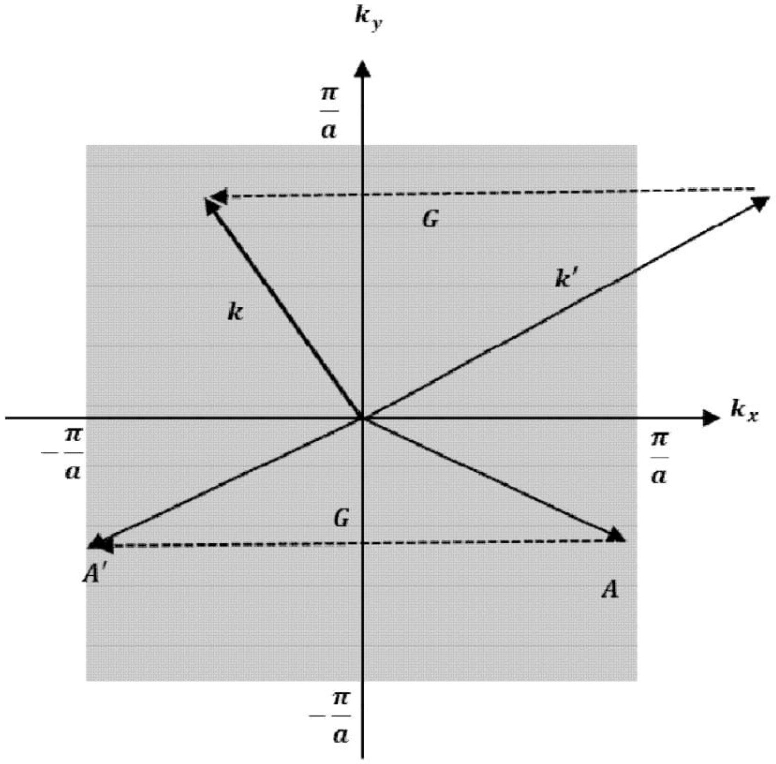

Figure 1: *First Brillouin zone for a lattice of side* ***a.*** *The wave vector* **k'** *mapped into the first zone with suitable reciprocal lattice vector* **G** *or* **k**=**k'** + **G***[1].*

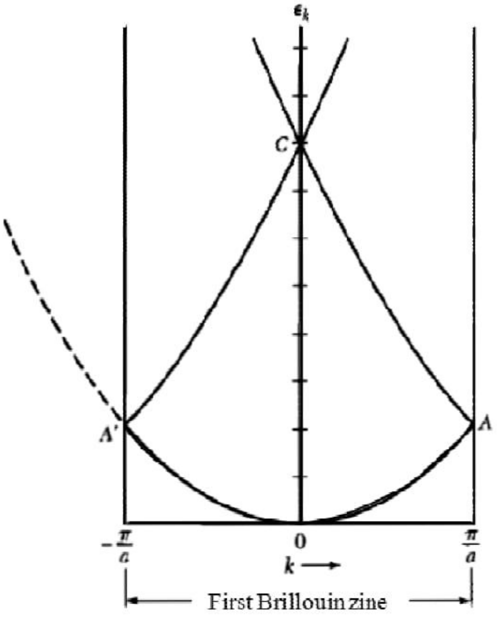

Figure 2 :*E-k diagram for free electrons in the reduced zone scheme [1].*

Because any energy $\epsilon_{k'}$ corresponding to k' which is outside the first zone have equal energy ϵ_k in the first zone with ***k*** = ***k'*** + **G**. Therefore, in reduced zone scheme we need the energy for each band only in the first Brillouin zone. Therefore, in the reduced zone scheme different energy band are represented at the same value of the ***k*.** Each different energy characterizes a different energy band [see Figure 2].

13.4 Periodic Zone Scheme

Brillouin zone of a lattice can repeat periodically in ***k***-space. This repetition can be achieved by translation of zone by **G**. As a result the energy $\epsilon_{\boldsymbol{k}}$ of bands also become a periodic function in **G**:

$$\epsilon_{\boldsymbol{k}} = \epsilon_{\boldsymbol{k+G}} \tag{3}$$

The periodically representation of energy bands in **k**-space is called as the **periodic zone scheme.**

For example, we can write an energy band for a simple cubic lattice:

$$\epsilon_k = -\alpha - 2\gamma(cosk_xa + cosk_xb + cosk_xc) \tag{4}$$

where α and γ are constants. For SC lattice, the reciprocal lattice vector is $\boldsymbol{G} = (2\pi/a)\hat{\boldsymbol{x}}$.

Now we replace ***k*** by ***k***+**G** then from Equation (3) we have

$$cosk_xa \longrightarrow \cos\left(k_x + \frac{2\pi}{a}\right)a = cos(k_xa + 2\pi) = cosk_xa \tag{5}$$

When ***k*** is increased by **G**, the energy ϵ_k remain same. Therefore, the band energy ϵ_k is a periodic function of ***k*** in ***k***-space.

Generally E-k diagram are constructed in different three zone schemes [see Figure3].

(a) In **extended zone scheme** the energy bands are represented in different zones in **k**-space.

(b) In **reduced zone scheme,** all energy bands are represented in the first Brillouin zone.

(c) In **periodic zone scheme** representation of energy band, every energy band is drawn in every zone of the lattice.

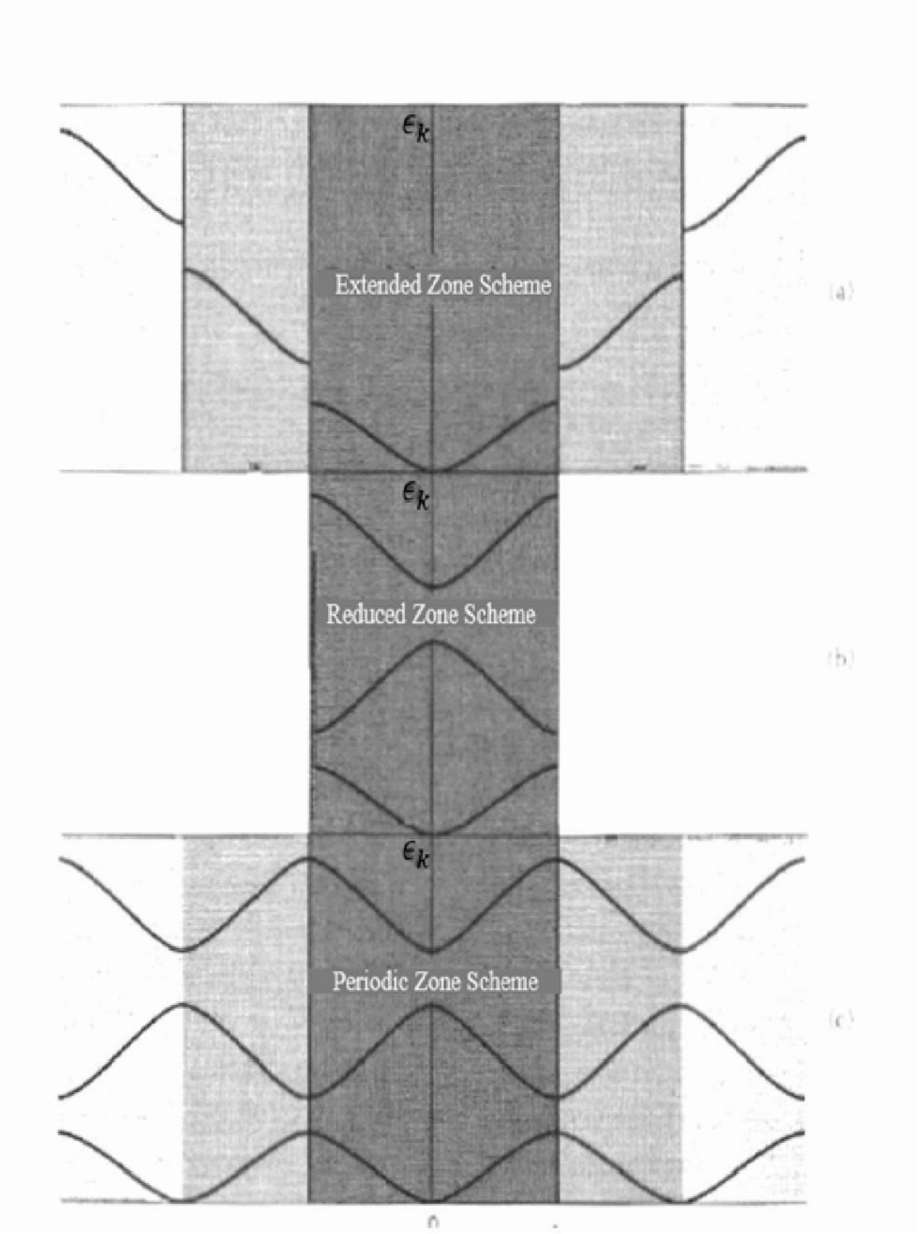

Figure 3: E-k diagram in different three zone schemes (a) the extended, (b) reduced, and (c) periodic zone schemes[1].

13.5 Construction of Fermi Surfaces

In **k**-space Brillouin zone related to diffraction condition $\mathbf{2k.G}+G^2=0$ or

$\mathbf{k}.(1/2\mathbf{G})=(1/2G)^2$. According to diffraction condition in reciprocal space, the zone boundaries given by a plane normal to **G** and passing through midpoint of **G**.

Now consider a square lattice [Figure 4(a)] having three reciprocal lattice vectors $\mathbf{G}_1$, $\mathbf{G}_2$ and $\mathbf{G}_3$. The first Brillouin zone can be construct from $\mathbf{G}_1$. Figure 4(b) shows the first Brillouin zone which is area enclosed by four vectors, normal to $\mathbf{G}_1$ and passing through midpoint of $\mathbf{G}_1$.

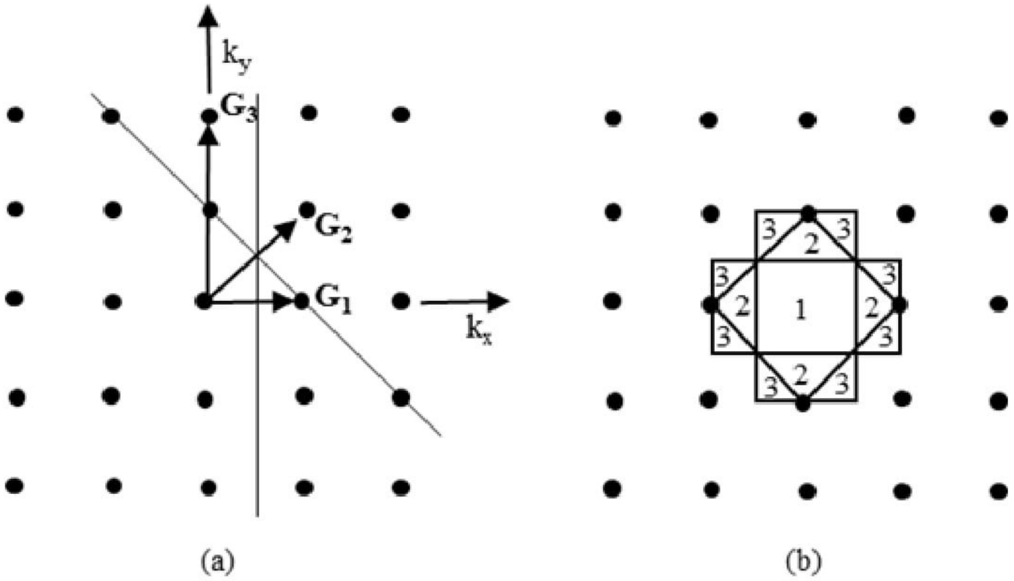

Figure 4: *(a) Three reciprocal lattice vectors* G_1, G_2 *and* G_3 *in k-space for a square lattice.(b) Construction of Brillouin zones in k-space for a square lattice [1].*

For square lattice these four reciprocal lattice vectors are written as $\pm(2\pi/a)\hat{\boldsymbol{k}}_x \pm (2\pi/a)\hat{\boldsymbol{k}}_y$. Similarly, second and third Brillouin zones can be construct from reciprocal lattice vectors $\mathbf{G}_2$ and $\mathbf{G}_3$. First, second and third Brillouin zones are shown in Figure 4(b).

We can also draw the free election Fermi surface for square lattice in two dimensional **k**-space with arbitrarily concentration of electron. Figure 5 shows a Fermi surface of square lattice which is a circle. The total filled area of k-space determined by free electron concentration and is independent of electron-lattice interaction. The Shape of Fermi surface may be deviated from exact circle depending on electron-lattice interaction.

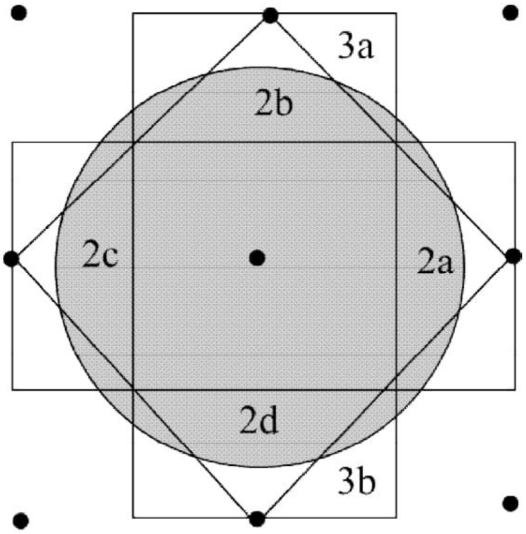

Figure 5: Brillouin zones diagram for a square lattice and circle represent free electron Fermi surface [1].

13.6 Nearly Free Electrons

Fermi surfaces for nearly free electrons can be calculated from free electrons Fermi surfaces by assuming following approximations:

(a) The energy gaps due to interaction between electron and periodic potential occurs at the zone boundaries.
(b) The intersect of Fermi surfaces at zone boundaries is almost perpendicular.
(c) Assuming that the crystal potential edges are rounded in the Fermi surfaces.
(d) The volume of Fermi surface is determined only by electron concentrations.

Figure 6 shows the free electron Fermi surfaces for a square lattice constructed by Harrison procedure. In this procedure, draw circles around each reciprocal lattice points in k-space. The radii of these circles are determined by free electron concentration. Any point inside one sphere represents an occupied state in the first zone. Points common to at least two spheres give occupied states in the second zone. Similarly, we can find occupied states in other zones. In alkali metals (Na) conduction electrons interactions with lattice is negligible, hence these metals have nearly spherical Fermi surfaces.

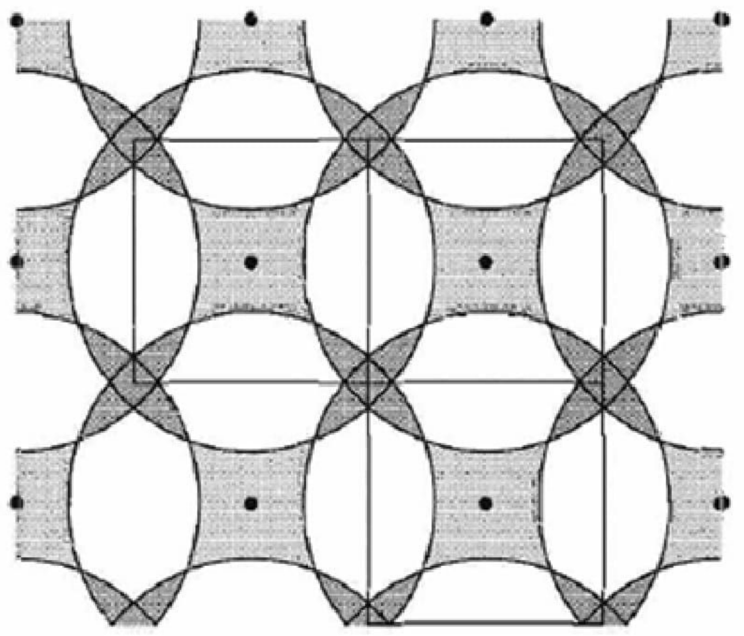

Figure 6: Construction of free electron Fermi surfaces for a square lattice [1].

13.7 Calculation of Energy Bands

In 1933 first time band structure calculations were performed by Wigner and Seitz. After that several methods developed to calculate the band structure of solids. But here we will discuss only an introductory methods called the tight-binding method.

13.8 Tight Binding Method for Energy Bands

A free atom characterized by discrete energy levels and energy level denoted by principal quantum number *n* [Figure 7(a)]. As free atoms come close to each other as a result the coulomb interaction between these atoms occurs. Due to coulomb interaction between these atoms their energy levels split and formation of the energy bands take place. Each energy state of free atom corresponding to quantum number n, gives a band of energies [s-band (n=1), p-band (n=2), d-band, (n=3) …], where width of energy band depends on strength of interaction between atoms.

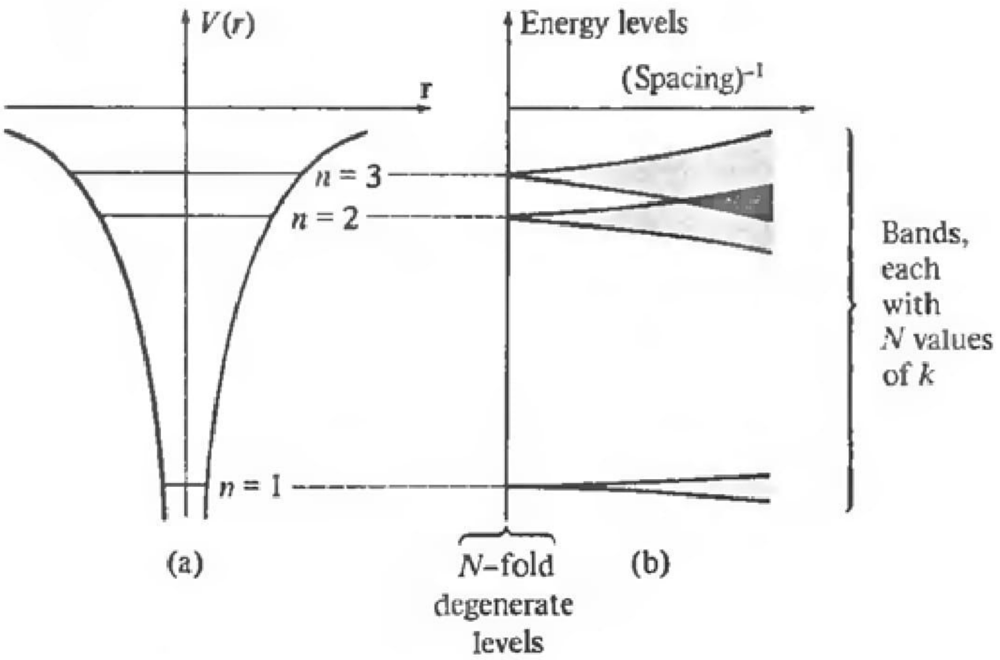

Figure 7.*(a) Energy levels of an atom. (b) Formation of bands in a solid corresponding to desecrate energy level of atom[2].*

In tight–binding model we assumed that the crystal potential is strong. When an electron is moving in such periodic potential it is captured by strong ionic potential. Therefore, electron spent a long time at that lattice site before tunneling to neighboring ion. During capturing process, wave function of the electron is considered as atomic orbital wave function which is unaffected by other nearest ions. In such approximation we can express one electron wavefunction for the whole crystal as the linear combination of atomic orbitals (LCAO)

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = N^{-1/2} \sum_j \exp\,(i\boldsymbol{k}.\boldsymbol{r}_j)\,\varphi(\boldsymbol{r} - \boldsymbol{r}_j) \tag{6}$$

Where $\varphi(\boldsymbol{r} - \boldsymbol{r}_j)$ atomic orbital at j$^{\text{th}}$ lattice site. For whole crystal $\psi_{\boldsymbol{k}}(\boldsymbol{r})$ is similar to Bloch function in periodic potential.

The first-order energy calculation is given by diagonal matrix elements of the Hamiltonian:

$$\epsilon_{\boldsymbol{k}} = \langle \boldsymbol{k}|\boldsymbol{H}|\boldsymbol{k}\rangle = N^{-1} \sum_j \sum_m \exp\,[i\boldsymbol{k}.(\boldsymbol{r}_j - \boldsymbol{r}_m)]\langle \varphi_m|H|\varphi_j\rangle \tag{7}$$

where $\varphi_m = \varphi(\boldsymbol{r} - \boldsymbol{r_m})$. Now we can write the distance between m^th^ and j^th^ lattice site as $\boldsymbol{\rho_m} = \boldsymbol{r_m} - \boldsymbol{r_j}$ then from Equation (7) we have

$$\langle \boldsymbol{k}|\boldsymbol{H}|\boldsymbol{k}\rangle = \sum_{\boldsymbol{m}} \exp(-i\boldsymbol{k}.\boldsymbol{\rho}_m) \int dV \varphi^* (\boldsymbol{r} - \boldsymbol{\rho_m})\boldsymbol{H}\boldsymbol{\varphi}(\boldsymbol{r}) \qquad (8)$$

We consider only neraest neighbour interaction as a result we neglect all other integral term in Equation (8) except corresponding to same atom and nearest neighbors separeted by $\boldsymbol{\rho}$. Then we have the first-order energy

$$\epsilon_{\boldsymbol{k}} = \langle k|H|k\rangle = -\alpha - \gamma \sum_m \exp(-i\boldsymbol{k}.\boldsymbol{\rho_m}) \qquad (9)$$

where $\int dV \varphi^* (\boldsymbol{r})\boldsymbol{H}\varphi(\boldsymbol{r}) = -\boldsymbol{\alpha}$ and $\int dV \varphi^* (\boldsymbol{r} - \boldsymbol{\rho})\boldsymbol{H}\varphi(\boldsymbol{r}) = -\gamma$.

13.9 Illustrative Examples

Example 1. Calculate first order band energy for simple cubic lattice in case ka <<1.

Sol. According to tight-binding method band energy

$$\epsilon_{\boldsymbol{k}} = -\alpha - \gamma \sum_m \exp(-i\boldsymbol{k}.\boldsymbol{\rho_m})$$

In simple cubic lattice position of nearest-neighbour atoms

$$\boldsymbol{\rho_m} : \quad (\pm a, 0,0); \quad (0, \pm a, 0); \quad (0,0, \pm a)$$

Then we have

$$\epsilon_{\boldsymbol{k}} = -\alpha - \gamma\, [(\exp(-ik_x a) + \exp(ik_x a)) + (\exp(-ik_y a) + \exp(ik_y a)) + (\exp(-ik_z a) + \exp(ik_z a))$$

or

$$\epsilon_{\boldsymbol{k}} = -\alpha - 2\gamma[\cos k_x a + cosk_y a + cosk_z a]$$

For ka <<1 we can expand cosx=1-x^2 ,then we have band energy

$$\epsilon_{\boldsymbol{k}} = -\alpha - 6\gamma + \gamma k^2 a^2$$

13.10 Self Learning Exercise-I

Q.1 What is the diffraction condition in **k**-space?

Q.2 Construct the first three Brillouin zones in k space for a square lattice.

Q.3 Draw the free electron Fermi surface for a square lattice.

Q.4 What is the effective mass of the electron in following energy band ?

$$\epsilon_{\boldsymbol{k}} = -\alpha - 6\gamma + \gamma k^2 a^2$$

13.11 Experimental Methods in Fermi Surface Studies

Experimentally measurement of Fermi surface gives details about band structure of the material. It also provided the information about crystal potential. The shape of the Fermi surface is useful in calculation of transport properties of metals. There are several experimental methods to determine Fermi surfaces. But the de Haas-van Alphan effect is most powerful and simple method for determination of Fermi surface.

13.12 Quantization Orbits in a Magnetic Field

When a particle of charge q and momentum **p** moving in a magnetic field **B** then its resultant momentum will be sum of kinetic momentum ($\mathbf{P}_{\text{kin}}$= m**v** = **ħk**) and the field momentum (**P$_{\text{field}}$= qA/c).**

$$\boldsymbol{P} = \boldsymbol{P}_{kin} + \boldsymbol{P}_{field} = \hbar\boldsymbol{k} + q\boldsymbol{A}/c \tag{10}$$

where the vector potential **A** and magnetic field **B** are related by **B** = curl **A.**

According to Onsager and Lifslutz the orbits of particle are quantized in magnetic field **B** and quantization given by the Bohr-Sommerfeld relation [1]

$$\oint \boldsymbol{P}.\boldsymbol{dr} = (n+\gamma)2\pi\hbar \tag{11}$$

where is *n* an integer and γ is a phase correction factor. Integrating Equation (10)for close path then we have

$$\oint \boldsymbol{P}.\boldsymbol{dr} = \oint \hbar\boldsymbol{k}.\boldsymbol{dr} + \frac{q}{c}\oint \boldsymbol{A}.dr \tag{12}$$

But we know that the equation of motion the particle in presence of magnetic field is $\hbar \boldsymbol{dk}/\boldsymbol{dt} = \boldsymbol{q}/\boldsymbol{c}[\boldsymbol{dr}/\boldsymbol{dt} \times \boldsymbol{B}]$and its integration with respect to time gives

$$\hbar \boldsymbol{k} = \frac{q}{c}\boldsymbol{r} \times \boldsymbol{B} \tag{13}$$

From first term of Equation (12) and Equation (13) we have

$$\oint \hbar \boldsymbol{k}.\boldsymbol{dr} = \frac{q}{c}\oint \boldsymbol{r} \times \boldsymbol{B}.d\boldsymbol{r} = -\frac{q}{c}\boldsymbol{B}.\oint \boldsymbol{r} \times d\boldsymbol{r} = -\frac{2q}{c}\Phi \tag{14}$$

where Φ magnetic flux within area of orbit and which is equal to

$\oint \boldsymbol{r} \times d\boldsymbol{r} = \boldsymbol{2}$ (area enclosed bythe orbit).

Again path integral of second term in Equation (12) can be written as

$$\frac{q}{c}\oint \boldsymbol{A}.d\boldsymbol{r} = \frac{q}{c}\int \boldsymbol{B}\,.\,d\boldsymbol{\sigma} = \frac{q}{c}\Phi \tag{15}$$

Finally, from Equation (12), Equation (14) and Equation (15) we have

$$\oint \boldsymbol{P}.d\boldsymbol{r} = -\frac{q}{c}\Phi = (n+\gamma)2\pi\hbar \tag{16}$$

Therefore quantized flux of electron in magnetic field is

$$\boldsymbol{\Phi_n} = (n+\gamma)(2\pi\hbar\mathrm{c}/\mathrm{e}) \tag{17}$$

Where unit of quantized flux is $2\pi\hbar\mathrm{c}/\mathrm{e}$= 4.14x 10^{-7} gauss cm^2 or Tm^2.

13.13 De Haas-Van Alphen Effect

For Fermi surface measurement by de Haas-van Alphen effect we required the area of the orbit in **k**-space. Equation (13) shows the relation between orbit element **Δr** in real space and **Δk** in **k**-space. Magnetic field perpendicular to line element of real space then $\boldsymbol{\Delta r} = (\hbar c/eB)\boldsymbol{\Delta k}$ and we can write

$$A_n = (\hbar c/eB)^2 S_n \tag{18}$$

where A_n is area of orbit in real space and S_n in k-space. Therefore, the flux in k-space one can write using Equation (17) and (18)

$$\Phi_n = (\hbar c/e)^2\frac{S_n}{B} = (n+\gamma)\frac{2\pi\hbar c}{e} \tag{19}$$

For experimental measurement of Fermi surface in **k**-space we can change the applied static magnetic field. The incremental change in magnetic field **ΔB**, such that two successive orbits (n and n+1) in k-space have equal area on the Fermi surface. or

$$S\left(\frac{1}{B_{n+1}} - \frac{1}{B_n}\right) = \frac{2\pi e}{\hbar c}$$

or $$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{S\hbar c} \tag{20}$$

Equation (20) is an important result which explain the equal increments of 1/B gives identical orbits and having periodicity in 1/B [see Figure 8]. For experimental measurement of Fermi surface requires the oscillation of the magnetic moment of pure specimens at low temperatures with a static magnetic field. Fermi surface of a metal reconstructed from period of these oscillations of magnetic moment of metal.

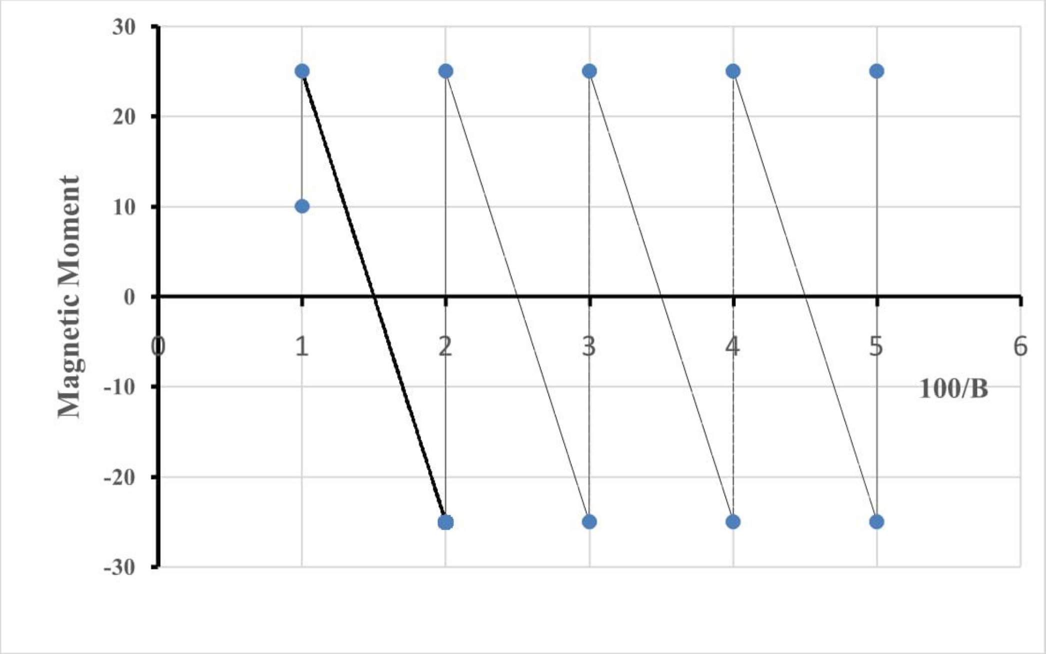

Figure 8: *Plot of oscillations of magnetic moment of a metal as a function of 1/B[1].*

13.14 Illustrative Examples

Example.1 According to free electron theory estimate the period of magnetic momentum oscillation with 1/B for potassium and calculate the area of orbit in real space at B = 10 kG = 1 T.

Sol. The period of oscillations of the magnetic moment of a metal with static magnetic field is

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{S\hbar c}$$

The area of orbit in k-space is $S = \pi k_F^2$ then

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\pi k_F^2 \hbar c} = \frac{2e}{k_F^2 \hbar c}$$

Putting $\frac{e^2}{\hbar c} = \frac{1}{137}$ then we have

$$\Delta\left(\frac{1}{B}\right) = \frac{2}{137 k_F^2 e}$$

For potassium $k_F = 0.75 \times 10^8\ \text{cm}^{-1}$ then the period of oscillations of the magnetic moment

$$\Delta\left(\frac{1}{B}\right) = 5.5 \text{ x } 10^{-9}\ \text{G}^{-1}$$

Area of orbit in real space is given by

$$A = (\hbar c/eB)^2 S$$

The area of orbit in k-space is $S = \pi k_F^2$ then

$$A = \pi k_F^2 (\hbar c/eB)^2 = \pi(\hbar c k_F/eB)^2$$

$$\frac{\hbar c k_F}{eB} = 5 \text{ x } 10^{-4}\ \text{cm}$$

$$A = 7 \text{ x } 10^{-7}\ \text{cm}^2$$

13.15 Self-Learning Exercise-II

Q.1 What will be the total momentum **p** of a particle of charge q moving in a magnetic field **B?**

Q.2 What is the quantized flux of an electron in **k**-space?

Q.3 In de Haas-van Alphen effect, plot the magnetic moment vs. 1/**B**?

Q.4 What is the period of oscillations of the magnetic moment of a metal in static magnetic field B?

13.16 Summary

1. In **k**-space a Fermi surface is a constant energy surface which separates filled and empty states at 0 K. The shape of the Fermi surface is best to represent in the reduced zone scheme, but the electrical properties are more clear in the periodic zone scheme.
2. The tight binding model is good for the inner electrons of atoms. Therefore, the d bands of the transition metals can be described approximately by this model.
3. In de Haas-van Alphan effect the oscillation of the magnetic moment of pure specimens with a static magnetic field allows the construction of Fermi surface.

13.17 Glossary

k-space diagram: The plot between energy gap of an electron in a crystal and wavevector k.

Femi energy: The energy which separates the filled states and empty states at T = 0 K.

13.18 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans. 1: In k-space diffraction condition is $\mathbf{2k.G}+G^2=0$

Ans. 2: See Figure 4

Ans. 3: See figure 5

Ans. 4: Effective mass $m^* = \frac{\hbar^2}{d^2\epsilon_k/dk^2} = \frac{\hbar^2}{2\gamma a^2}$

Answers to Self Learning Exercise-II

Ans. 1: When a particle of charge q and momentum **p** moving in a magnetic field **B** then its resultant momentum is sum of kinetic momentum ($\mathbf{P}_{kin}=$ m**v** $= \hbar\mathbf{k}$) and the field momentum ($\mathbf{P}_{field}=\mathbf{qA/c}$)

or $\boldsymbol{P} = \boldsymbol{P}_{kin} + \boldsymbol{P}_{field} = \hbar\boldsymbol{k} + q\boldsymbol{A}/c$

Ans. 2: Quantized magnetic flux in k-space is

$$\Phi_n = (\hbar c/e)^2 \frac{S_n}{B} = (n+\gamma)\frac{2\pi\hbar c}{e}$$

Ans. 3: See Figure 8

Ans. 4: The period of oscillations of the magnetic moment of a metal with static magnetic field is

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{S\hbar c}$$

13.19 Exercise

Q.1 Define the Fermi surface in k-space.

Q.2 Why construction of Fermi surface is important?

Q.3 How one can construct Fermi surfaces for free electrons from Fermi surfaces for nearly free electrons?

Q.4 What are the reciprocal lattice vector for simple cubic lattice?

Q.5 Draw the ***E-k*** diagram in different three zone scheme (a) the extended, (b) reduced, and (c) periodic zone schemes.

Q.6 What is the tight binding approximation?

Q.7 For what kind of material tight binding modal is applicable?

Q.8 Why de Haas-van Alphan effect can be observed in pure specimens at low temperatures in strong magnetic fields?

13.20 Answers to Exercise

Ans. 1: In **k**-space a Fermi surface is a constant energy surface which separates filled and empty states at 0 K.

Ans. 2: Experimentally measurement of Fermi surface gives details about band structure of the material. It also provides the information about crystal potential. The shape of the Fermi surface is useful in calculation of transport properties of metals.

Ans. 3: see section 13.4

Ans. 4: See figure 4

Ans. 5: For simple cubic lattice, six reciprocal lattice vectors: $\pm(2\pi/a)\widehat{\boldsymbol{k}}_{\boldsymbol{x}} \pm (2\pi/a)\widehat{\boldsymbol{k}}_{\boldsymbol{y}}.\pm(2\pi/a)\widehat{\boldsymbol{k}}_{\boldsymbol{z}}$.

Ans. 6: In tight–binding model we assumed that the crystal potential is strong. When an electron is moving in such periodic potential it captured by strong ionic potential. Therefore, electron spent a long time at that lattice site before tunneling to neighboring ion. During capturing, wave function of the electron is considered as atomic orbital wave function which is unaffected by other nearest ions.

Ans. 7: (a) For the d bands of the transition metals (b) valence bands of diamond like materials(c) crystals of inert gas.

Ans. 8: To avoid effect of collision and temperature on quantized orbits of the electron in static magnetic field.

References and Suggested Readings

1. C. Kittel "*Introduction to Solid State Physics*" ,John Wiley & Sons, Inc. (1996).
2. N. W. Ashcroft and N. D. Mermin "*Solid State Physics*" Harcourt. Inc. (1976).

UNIT-14

Dielectrics

Structure of the Unit

14.0 Objectives

The aim of this chapter is to let the readers know about the behaviour of the solid dielectric materials in the electric field. When such materials are placed in the external field then what happens at atomic or molecular levels. The phenomenon related to such response will be discussed. The different parameters of dielectric materials and the theories related to dielectric phenomenon will we explained in detail.

14.1 Introduction

The dielectric materials is one of the important class of solid materials. In this chapter the behaviour of such materials in external electric field i.e. polarization of the materials is discussed. The net electric field in the dielectric materials is evaluated. The dielectric parameters like electric polarizability, dielectric constant and electric susceptibility are explained in detail. The contribution due to electronic polarization of the polarizability and its frequency dependence has been discussed.

14.2 Introduction to Dielectric Materials

The dielectrics are the non-conducting materials of electricity due to bounding of positive and negatively charged particles. When electric field is applied on such materials, separation of positive and negative charges takes place. This phenomenon is called as polarization of dielectric materials. In the polarization process the whole material medium remains neutral. The polarize charges create their own electric field which oppose the applied electric field.

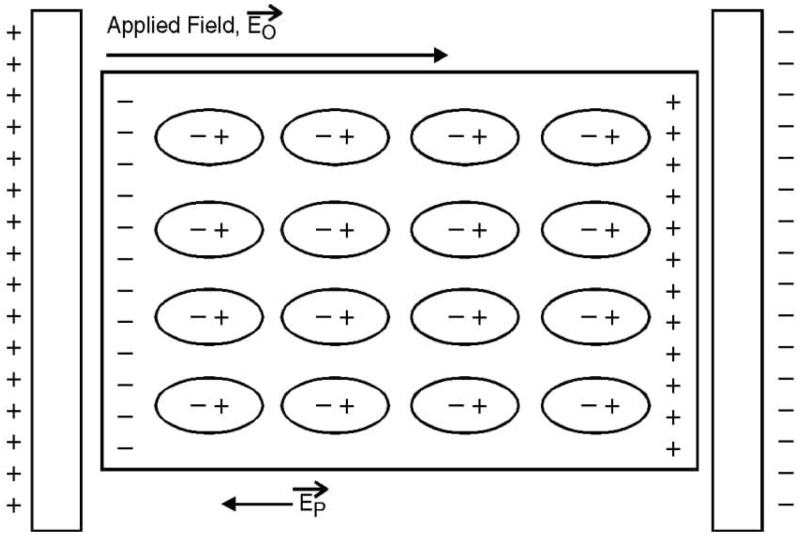

Figure14.1 Dielectric Polarization in external electric field

The polarization $\vec{P}$ (polarization vector) in a solid is defined as total dipole moment per unit volume.

$$\vec{P} = \frac{\vec{p}}{V} = \frac{\sum_i q_i \vec{r}_i}{V}$$

where $\vec{p}$ is the total dipole moment and V is the volume of the material medium. The characteristics of a dielectric medium are studied in term of dielectric constant.

$$\varepsilon = \frac{E_{vac}}{E} = \frac{C}{C_{vac}}$$

The dielectric constant is the representative of dielectric and optical properties of the medium.

14.3 Macroscopic Electric Field

One contribution to field inside the dielectric material is due to the applied external field produced by fixed charges. The other contribution to the electric field is the sum of all the charges that constitute the material body. If a body is neutral, the contribution to the average field is due to sum of electric fields of atomic dipoles. We define the average electric field as the average field over a volume of the crystal cell that contain the lattice point r_0

$$\vec{E}(\vec{r}_0) = \frac{1}{V_c} \int \vec{e}(\vec{r}) dV$$

where $\vec{e}(\vec{r})$ is the microscopic field at the point $\vec{r}$. To find the contribution of the polarization to the macroscopic field simplification will be done over all the dipoles in the sample. From the theorem of electrostatic the macroscopic electric field produced by uniform polarization is equal to the electric field in vacuum of a fictitious surface charge density on the surface of a body given by

$\sigma = \hat{n}.\vec{P}$, here $\hat{n}$ is the unit vector normal to the surface

We apply the result to a thin dielectric slab (Figure 14.2)with a uniform volume polarization $\vec{P}$. The electric field $\vec{E}(\vec{r})$ is equal to the field produced by the fictitious surface charge density $\sigma = \hat{n}.\vec{P}$ on the surface of a slab. On the upper surface the unit vector is in upward direction while in the lower surface it is in lower direction. The upper surface has charge +Q while lower has –Q charge or surface charge density $\sigma = \hat{n}.\vec{P} = P$ and $-\sigma = \hat{n}.\vec{P} = -P$.

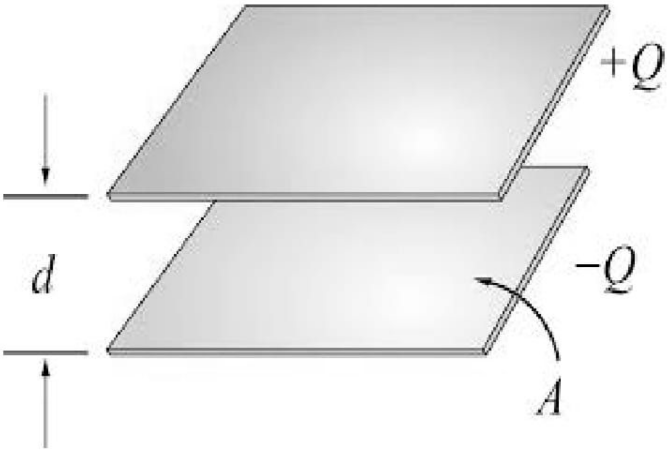

Figure 14.2 Charges due to polarization

The electric field $\vec{E}$ due to these charges has a simple form at any point between the plates. By Gauss law

$$\vec{E} = -\frac{|\sigma|}{\varepsilon_0}\hat{z} = -\frac{\vec{P}}{\varepsilon_0},$$

where $\hat{z}$ is the unit vector normal to plane of slab.

The total macroscopic electric field inside the slab is given by

$$\vec{E}_{macr} = \vec{E}_0 + \vec{E}$$

$$\Rightarrow \vec{E}_{macr} = \vec{E}_0 - \frac{\vec{P}}{\varepsilon_0}$$

Here $\vec{E}_0$ is the applied electric field and the electric field $\vec{E}$ due to polarized surface charge density which varies smoothly in space inside and outside the body and satisfies the Maxwell equation similar to macroscopic field. In the above equations the polarization is uniform throughout the whole body. The electric field $\vec{E}$ due to uniform polarization is called as depolarization field because ,it tends to oppose the applied electric field $\vec{E}_0$.

In case of sample in the form of ellipsoid like sphere, cylinder, disc, etc., the uniform polarization produces uniform depolarization field inside the body. If P_x, P_y and P_z are the components of polarization along the principal axes of the ellipsoid, then the components of the depolarization field are

$$E_x = -\frac{N_x P_x}{\varepsilon_0},$$

$$E_y = -\frac{N_y P_y}{\varepsilon_0} \quad \text{and}$$

$$E_z = -\frac{N_z P_z}{\varepsilon_0}$$

Here N_x ,N_y and N_z are called as depolarization factors and their values depend upon the ratio of principal axes. The values of these depolarization factors are positive and satisfy the equation as

$$N_x + N_y + N_z = 1$$

The polarization vector $\vec{P}$ is related to local electric field $\vec{E}_{macr}$ by the following equation as

$$\vec{P} = \varepsilon_0 \chi \vec{E}_{macr}$$

Here χ is called as dielectric susceptibility.

If $\vec{E}_0$ is uniform and parallel to the principal axis of the ellipsoid then

$$\vec{E}_{macr} = \vec{E}_0 + \vec{E} = \vec{E}_0 - \frac{N\vec{P}}{\varepsilon_0}$$

$$\vec{P} = \chi(\varepsilon_0 \vec{E}_0 - N\vec{P})$$

$$\vec{P} = \frac{\chi \varepsilon_0}{1 + N\chi} \vec{E}_0$$

The macroscopic electric field in a sphere

$$\vec{E}_{macr} = \vec{E}_0 + \vec{E} = \vec{E}_0 - \frac{\vec{P}}{3\varepsilon_0}$$

14.4 Local Electric Field at an Atom

The value of the local electric field that acts at the site of an atom is significantly different from the value of the macroscopic electric field. We consider here the local field at a site in the cubic crystal of spherical shape. The macroscopic electric field in a sphere

$$\vec{E}_{macr} = \vec{E}_0 + \vec{E} = \vec{E}_0 - \frac{\vec{P}}{3\varepsilon_0}$$

We now derive an expression for local field at a general lattice site not necessarily having cubic symmetry. The field at an atom is the sum of electric field from external source and from the dipoles inside the specimen. The local field can be written as

$$\vec{E}_{local} = \vec{E}_0 + \vec{E}_1 + \vec{E}_2 + \vec{E}_3$$

where

$\vec{E}_0$ is the applied electric field, $\vec{E}_1$ is depolarization field on the outer surface of the specimen, $\vec{E}_2$ is field due to polarization charges (Lorentz field) on inside of a spherical cavity cut from the specimen and $\vec{E}_3$ is the field of atoms within the cavity.

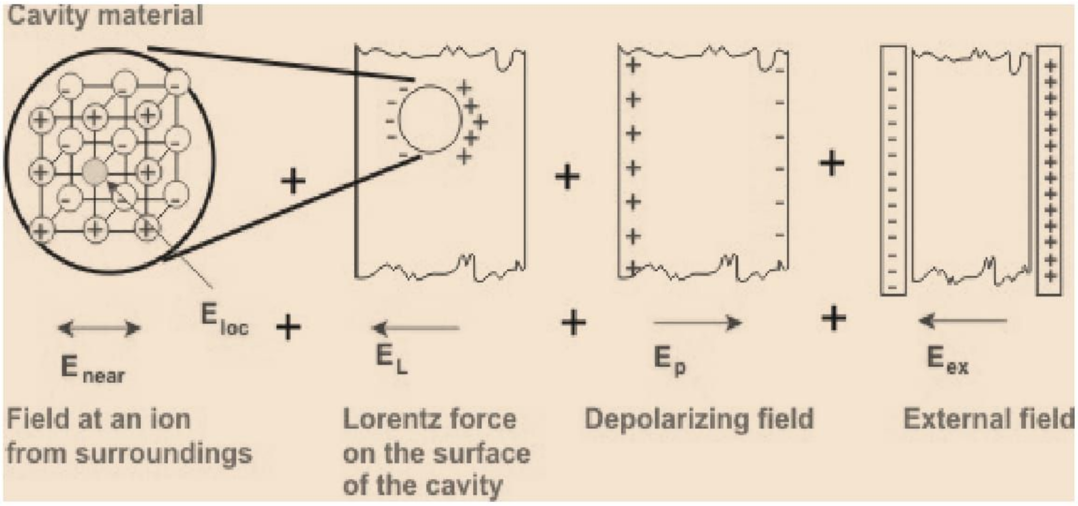

Figure 14.3: Electric field Contributors at an atom

The contribution of $\vec{E}_1 + \vec{E}_2 + \vec{E}_3$ to local field at any atom, caused by dipole moments of all the other atoms in the specimen is given by

$$\vec{E}_1 + \vec{E}_2 + \vec{E}_3 = \frac{1}{4\pi\varepsilon_0}\sum_i \frac{3(\vec{p}_i.\vec{r}_i)\vec{r}_i - r_i^2\vec{p}_i}{r_i^5}$$

The depolarization field is given by

$$\vec{E}_1 = -\frac{N\vec{P}}{\varepsilon_0}$$

For sphere it is given by

$$\vec{E}_1 = -\frac{\vec{P}}{3\varepsilon_0}$$

The Lorentz field is given by

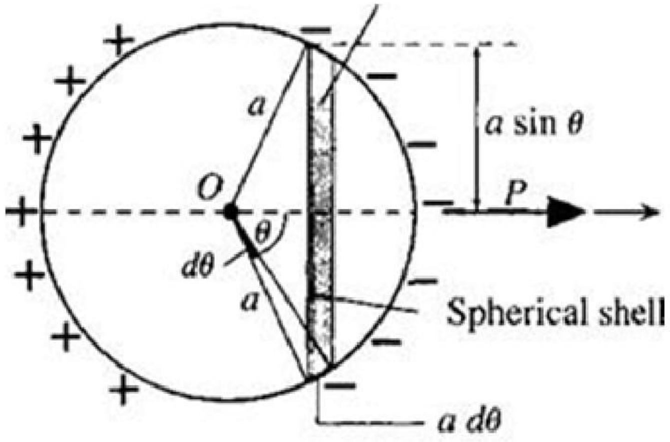

Figure 14.4: Lorentz Cavity

This field is due to polarization charges on the surface of an arbitrary cavity. This field was calculated by Lorentz and called as Lorentz field. Let θ is the angle of an elementary surface on the surface of cavity with respect to polarization direction $\vec{P}$. The surface charge density on the surface of cavity is –Pcosθ. So the electric field at the centre of spherical cavity of radius *a* is

$$E_2 = \frac{1}{4\pi\varepsilon_0}\int_0^{\pi} \frac{(2\pi a\sin\theta)(a d\theta)(P\cos\theta)(\cos\theta)}{a^2}$$

$$= \frac{1}{4\pi\varepsilon_0} \times \frac{4\pi}{3} P$$

$$= \frac{P}{3\varepsilon_0}$$

$$\Rightarrow \vec{E}_2 = \frac{\vec{P}}{3\varepsilon_0}$$

So the depolarization field and the Lorentz field cancel each other for a sphere.

$$\vec{E}_1 + \vec{E}_2 = -\frac{\vec{P}}{3\varepsilon_0} + \frac{\vec{P}}{3\varepsilon_0} = 0 \qquad \text{(For sphere)}$$

The field $\vec{E}_3$ is due to dipoles within the spherical cavity which depends upon the crystal structure. For cubic surrounding it is equal to zero.

$$\vec{E}_3 = 0$$

So the total local field at a cubic site is

$$\vec{E}_{local} = \vec{E}_0 + \vec{E}_1 + \vec{E}_2 + \vec{E}_3$$

$$= \vec{E}_0 + \vec{E}_1 + \frac{\vec{P}}{3\varepsilon_0}$$

$$\vec{E}_{local} = \vec{E}_{macr} + \frac{\vec{P}}{3\varepsilon_0}$$

It is the Lorentz relation for the electric field on an atom in cubic site.

14.5 Dielectric Constant and Polarizability

The dielectric constant ε of an isotropic or having cubic medium relative to vacuum is defined in term of macroscopic field as

$$\varepsilon = \frac{E_{macr} + \frac{P}{\varepsilon_0}}{E_{macr}}$$

$$= \frac{\varepsilon_0 E_{macr} + P}{\varepsilon_0 E_{macr}} = 1 + \chi$$

The susceptibility is related to dielectric constant as

$$\chi = \frac{P}{\varepsilon_0 E_{macr}} = \varepsilon - 1$$

The polarization of an atom in the material is due to local electric field. The dipole moment induced on an atom is proportional to the local electric field.

$$\vec{p} = \alpha \vec{E}_{local}$$

The polarization of a crystal may be expressed as the product of polarizability of the atoms times the local electric field.

$$\vec{P} = \sum_i N_i p_i$$

$$\Rightarrow \vec{P} = \sum_i N_i \alpha_i \vec{E}_{local}(i)$$

where, N_i is the number of atoms per unit volume, α_i is the polarizability of *i* atoms and $\vec{E}_{local}(i)$ is the electric field at the site of *i* atoms. The local electric field is given by

$$\vec{E}_{local} = \vec{E}_{macr} + \frac{\vec{P}}{3\varepsilon_0}$$

So the polarization is given by

$$\vec{P} = \sum_i N_i \alpha_i (\vec{E}_{macr} + \frac{\vec{P}}{3\varepsilon_0})$$

The electric susceptibility is given by

$$\chi = \frac{\vec{P}}{\varepsilon_0 \vec{E}_{macr}} = \frac{\sum_i N_i \alpha_i}{\varepsilon_0 (1 - \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i)}$$

As the dielectric constant is related to electric susceptibility as

$$\chi = \varepsilon - 1$$

$$\Rightarrow \chi = \frac{\sum_i N_i \alpha_i}{\varepsilon_0 (1 - \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i)}$$

which get converted into, $$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i$$

This equation is called as Clausius-Mossotti equation.

14.6 Electronic Polarizability

The total polarizability of a specimen has three contributions from electronic, ionic and dipolar. The electronic contribution arises from the displacement of the electron shell relative to the nucleus. The ionic contributions arise due to displacement of charged ions with respect to other ions. The dipolar contribution arises from molecules with a permanent electric dipole moment that can change orientation relative to applied electric field. In heterogeneous materials there is an interfacial polarization arising from accumulation of charges at structural interfaces.

The dielectric constant at optical frequencies arises due to mostly from electronic polarizability. The contributions from dipolar and ionic polarizability are small at high frequencies because of inertia of the molecules and ions. In optical frequencies the Clausius-Mossotti equation reduces to

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i (electonic)$$

where $n^2 = \varepsilon$, n is the refractive index of the material.

By using this equation for large number of crystals the electronic polarizabilities were found to reasonably consistent with observed values of refractive indices. But it not entirely consistent because the electronic polarizability of an ion depends upon the environment in which it is placed. The negative ions have high polarizability due to their large size.

14.6.1 Classical Theory of Electronic Polarizability (Static Case)

Suppose an electron is bound harmonically to an atom which show resonance absorption at a frequency at $\omega_0 = (\frac{\beta}{m})^{1/2}$, where β is the force constant. Let the displacement of the electron from mean position x on application of electric field E_{local}. The equation of motion of the electron in the local electric field is as

$$m\frac{d^2x}{dt^2} + m\omega_0^2 x = -eE_{local}\sin\omega t, \text{ (neglecting the damping effect)}$$

Let the solution of this equation is

$$x = x_0 \sin\omega t$$

So
$$m(-\omega^2 + \omega_0^2)x_0 = -eE_{local},$$

$$\Rightarrow x_0 = \frac{eE_{local}}{m(\omega_0^2 - \omega^2)}$$

The dipole moment induced is given by

$$p_0 = ex_0 = \frac{e^2 E_{local}}{m(\omega_0^2 - \omega^2)}$$

The electronic polarizability is given by

$$\alpha_{(electronic)} = \frac{p_0}{E_{local}} = \frac{e^2}{m(\omega_0^2 - \omega^2)}$$

The static electronic polarizability is given by

$$\alpha_{(electronic)} = \frac{e^2}{m\omega_0^2}$$

14.6.2 Frequency dependence of Electronic Polarizability

If in the above equation damping effect of the dielectric medium is also considered then the equation of motion of the electron in the A.C. local electric field is given by

$$m\frac{d^2x}{dt^2}+mg\frac{dx}{dt}+m\omega_0^2x=-eE_{local}e^{j\omega t},$$

where, $g=\frac{\gamma}{m}$, γ is the coefficient of damping,

$E_{local}e^{j\omega t}$ is the local A.C. electric field

Let the solution of this equation is

$$x=x_0e^{j\omega t}$$

So $$m(-\omega^2+ig\omega+\omega_0^2)x_0=-eE_{local},$$

$$x_0=\frac{eE_{local}}{m(\omega_0^2-\omega^2+ig\omega)}$$

The dipole moment induced is given by

$$p_0=ex_0=\frac{e^2E_{local}}{m(\omega_0^2-\omega^2+ig\omega)}$$

The electronic polarizability is given by

$$\alpha_{(electronic)}=\frac{p_0}{E_{local}}$$

$$\Rightarrow\alpha_{(electronic)}=\frac{e^2}{m(\omega_0^2-\omega^2+ig\omega)}$$

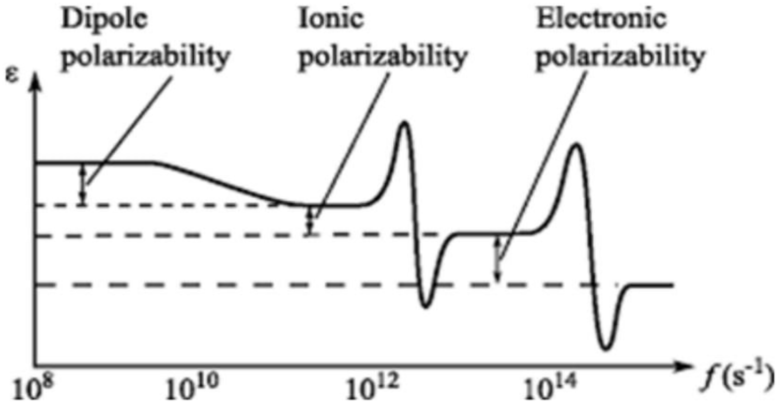

Figure14.5: Variation of Polarizability with Frequency

If N is the number of polarized electrons per unit volume, then polarization vector is given by

$$\vec{P} = N\,\vec{p}_0$$

The complex dielectric constant is given by

$$\begin{aligned}\varepsilon(\omega) &= 1 + \chi \\ &= 1 + \frac{\vec{P}}{\varepsilon_0 \vec{E}_{local}} \\ &= 1 + \frac{Ne^2}{m\varepsilon_0(\omega_0^2 - \omega^2 + ig\omega)}\end{aligned}$$

Let $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$

The real part of dielectric constant is given by

$$\varepsilon'(\omega) = 1 + \frac{Ne^2(\omega_0^2 - \omega^2)}{m\varepsilon_0[(\omega_0^2 - \omega^2)^2 + g^2\omega^2]}$$

and the imaginary part of the dielectric is

$$\varepsilon''(\omega) = \frac{Ne^2 g\omega}{m\varepsilon_0[(\omega_0^2 - \omega^2)^2 + g^2\omega^2]}$$

The real part of dielectric constant gives the value of dielectric constant while imaginary part gives the power dissipation or damping loss.

For frequency $\omega = \omega_0$ the value of $\varepsilon''(\omega)$ is maximum i.e. material absorbs energy at natural frequency; this phenomenon is called as resonance absorption.

14.7 Self Learning Exercise

Q.1 Write the relation between polarization, electric susceptibility, depolarization factor and applied electric field.

Q.2 Write the Clausius-Mossotti equation.

Q.3 Explain the polarizability. Discuss various types of polarizabilities.

Q.4 Write a short note on Lorentz field in dielectric material.

14.8 Summary

This unit deals with the study of dielectric materials. It deals with the basics of the dielectric materials. Here first the effect of applied electric field on the dielectric materials is discussed in terms of polarization i.e. dipole moment induced per unit volume. After this the concept of macroscopic field is discussed. Here the idea of depolarization field is discussed and also its dependence on geometry of the specimen is discussed in terms of depolarization factor. The relations of polarization, depolarization factor and the applied electric field are derived. The theory is developed to find the electric field at the site of an atom in the specimen of a dielectric. The different contributions are discussed and evaluated. After this the concept of polarizability is discussed and relations with various dielectric quantities are derived. The different kinds of polarizabilities and their variation with frequency are discussed.

Finally the electronic polarizability is discussed in detail and its classical theory is discussed. The frequency dependence of the electronic polarizability is discussed and variation of dielectric constant and loss factor with frequency are also discussed.

14.9 Glossary

Dielectric: Insulator

Dipole: The arrangement of two equal and opposite charges separated by a distance.

Polarization Vector : The total dipole moment per unit volume.

Depolarization : Opposing polarization

Specimen : Sample

Cavity : Geometry in the form of sphere

Heterogeneous : Different kind

Interface : Boundary

Accumulation : Collection

14.10 Answers to Self Learning Exercise

Ans.1: The relation between theses quantities is given by

$$\vec{P} = \frac{\chi\varepsilon_0}{1+N\chi}\vec{E}_0$$

Ans.2: The Clausius-Mossotti equation is given by

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i$$

or $$\frac{n^2-1}{n^2+2} = \frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i(electonic)$$

Ans.3: The polarizability of molecules means that the positive and negative charges are displaced relative to each on application of electric field. The polarizability has three major contributions as

(i) Dipolar or orientation polarizability

(ii) Ionic polarizability

(iii) Electronic polarizability

If the molecules of materials are ionic in nature then they have permanent dipole moment. In absence of external electric field ,the dipole moments of these molecules are randomly oriented. When electric field is applied then these dipole moments tends to align along the direction of field. This phenomenon is called as dipolar or orientation polarizability.

If the molecules of the material contain ions ,then the field tends to displace the positive and negative ions in opposite direction causing a change in the length of the bond. The effect of this change in length is to produce a net dipole in the unit cell as compared to earlier state having zero dipole moment. This phenomenon is called as ionic polarizability.

The polarizability of atoms or ions in the molecules due to displacement of the electrons with respect to nuclei is called as electronic polarizability. So the total polarizability is given by

$$\alpha = \alpha_{dip} + \alpha_{ion} + \alpha_{elect}$$

where α_{dip} is the dipolar polarizability, α_{ion} is the ionic polarizability and α_{elect} is the electronic polarizability.

14.11 Exercise

Q.1 Explain the polarization or polarization vector.

Q.2 What are dielectric materials ? Define the dielectric constant.

Q.3 Explain the macroscopic field and derive the formula for it.

Q.4 Explain the depolarization field. Express the depolarization field in terms of depolarization factors and also write the macroscopic field in terms of depolarization factor.

Q.5 Find the expression for local electric field at the site of an atom in the dielectric material.

Q.6 Discuss various types of dielectric materials and type of polarization processes.

Q.7 Derive the Clausius-Mossotti relation.

Q.8 Explain the variation of polarizability with frequency.

Q.9 Explain the electronic polarizability and discuss its classical theory.

14.12 Answers to Exercise

Ans.1: The total dipole moment induced per unit volume is called as polarization or polarization vector.

Ans.2: The materials in which the positive and negative charges are strongly bounded are called as dielectric materials. They behave like the insulating materials. When such materials are subjected to external electric field they get polarized. In these materials either electric dipole moment is induced or dipole moments get orientated in the direction of applied field. The later process is called as orientation polarization. The characteristic of dielectric materials are studied in terms of dielectric constant. The dielectric constant is defined as the ratio of permittivity of the medium to the permittivity of air.

Ans.3: The sum of applied external electric field and the field due to polarization on the surface of dielectric material is called as macroscopic field.

Ans.4: The electric field which is induced on the surface of the dielectric material which tends to oppose the applied electric field is called as depolarization field.

Ans.6: The dielectric materials are of two types: polar and non polar dielectric materials. The materials having molecules which have intrinsic electric dipole moment are called as called as polar dielectric materials. In the materials positively and negatively charges are strongly bounded. When such materials are subjected to external electric field the dipole moment of the molecule tends to get oriented in the direction of applied field. The non polar materials have molecules which have non polar molecules. When such materials are placed in external electric field then polarization of molecules takes place i.e. the centres of positives and negatives chares are displaced with respect to each other and electric dipole moment is induced on the molecules.

References and Suggested Readings

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2. A.J. Dekker, Solid State Physics, Macmillan India Limited, Delhi, 1986.

UNIT-15

Ferroelectrics

Structure of the Unit

15.0 Objectives

This chapter is aimed to understand the readers the one kind of dielectric materials known as ferroelectric. The basic theory of ferroelectricity, kind of ferroelectric materials and related theory will be presented here. The basic idea of other dielectric materials like anti-ferroelectric, piezoelectric and pyroelectric materials will be explained.

15.1 Introduction

Ferroelectric is one of the kinds of dielectric materials. In this chapter ,the basic characteristics of ferroelectric materials, theory of ferroelectricity and types of ferroelectric materials are presented. The examples of some of the ferroelectric materials and spontaneous polarization in ferroelectric materials are explained here. The overview of other class of dielectric materials like piezoelectric and pyroelectric materials is discussed.

15.2 Ferroelectricity

The ferroelectric materials are kind of dielectric materials which have following properties:

1. The static dielectric constant of these material changes with temperature according to following relation

   $\varepsilon = \dfrac{C}{T - T_C}$, where $T > T_C$

   here C is a constant which is independent of temperature and called as Curie's constant. This relation is known as Curie-Weiss law. C and T_C are the parameters which depend upon the material. T_C is called as Curie temperature.
2. These materials posses spontaneous electric polarization i.e. polarization in the absence of external electric field. This polarization only exits if the temperature $T < T_C$.

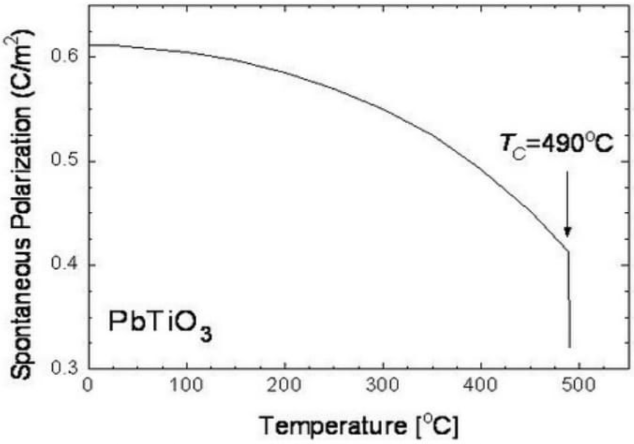


Figure 1. Spontaneous polarization with temperature

3. These materials show the property of hysteresis under the action of alternating electric field. The hysteresis loop can be obtained for such materials. This curve is obtained between polarization and the electric field (P-E curve). This curve is similar to the B-H curve for ferromagnetic materials.

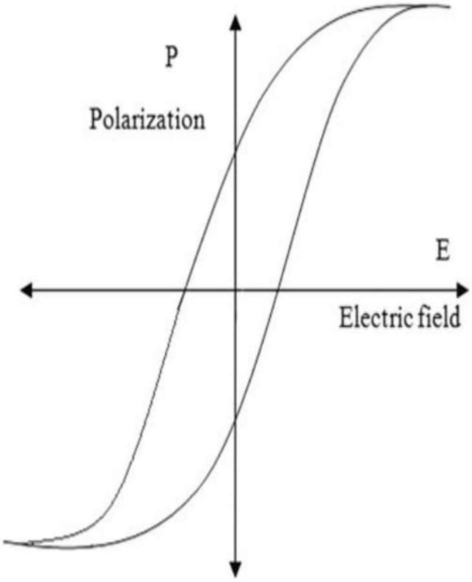


Figure 2: P-E curve for ferroelectrics

15.3 Dipolar Theory of Ferroelectricity

The most popular theory of Ferroelectricity is the dipolar theory. This theory is based on the fact that the ferroelectric substance consists of a system of freely rotating dipoles. The existence of spontaneous resulted due to orientation of dipole moments of different unit cells in a common direction. There is cooperation between different unit cells to align the dipoles in a common direction. So the cooperative phenomenon is observed in ferroelectrics. The dipole moment of a unit cell is contributed by electronic displacement, ionic displacements and from permanent dipoles. The local field which is responsible for rotation of the dipoles is given

$$E_{local} = E_0 + \gamma P \tag{1}$$

where E_0 is the externally applied field, P is the polarization and γ is the local field constant. This expresses the cooperative phenomenon because larger the value of P, larger the value of E_{local} and hence stronger will be the tendency of a dipole to align in the direction of polarization of other dipoles. In the high temperature region the local field given by above equation leads to Curie-Weiss law. The polarization far away from saturation polarization is given by the following equation

$$P = N\mu < \cos\theta >= \frac{N\mu^2}{3kT} E_{local} \tag{2}$$

where N is total no of electric dipoles per unit volume, μ is electric dipole moment of each dipole and θ is the angle between the orientations of dipole with respect to field. The electric susceptibility is given by

$$\chi = \frac{P}{E_0} = \frac{(N\mu^2 / 3kT)}{(1 - N\gamma\mu^2 / 3kT)}$$

$$= \frac{T_C / \gamma}{T - T_C}$$

$$\chi = \frac{C}{T - T_C} \tag{3}$$

where $C = T_C / \gamma$ is called as Curie's constant and $T_C = \frac{N\gamma\mu^2}{3k}$ is called as Curie's temperature.

In order to discuss the spontaneous polarization we will here make the use of Langevin's expression as

$$P = N\mu < \cos\theta >= N\mu L(\frac{\mu E_{local}}{kT}) \tag{4}$$

where $L(\frac{\mu E_{local}}{kT})$ is called as Langevin's function. For spontaneous polarization P we have to consider the external electric field to be zero i.e. E_0=0. So we can write the equation (4) as

$$\frac{P}{N\mu} = \frac{P}{P_{sat.}} = L(x) \tag{5}$$

where $P_{sat.} = N\mu$ is called as saturation polarization and $x = \frac{\mu\gamma P}{kT}$ since $E_{local} = \gamma P$

From equation (1)

$$\frac{P}{N\mu} = \frac{P}{P_{sat.}} = \left(\frac{kT}{N\mu^2\gamma}\right)x \tag{6}$$

The equations (5) and (6) should be satisfied simultaneously, which corresponds to a set of straight lines passing through origin and have slope equal to $\frac{kT}{N\mu^2\gamma}$.

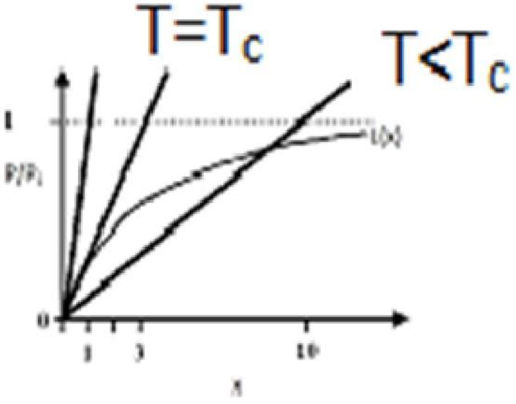


Figure 3:Temperature Dependence of Spontaneous Polarization

Thus the slope of these lines depends upon the temperature. The solution for $\frac{P}{P_{sat.}}$ corresponding to a temperature T_1 is determined by the intersection of L(x) and the line of slope $\frac{kT_1}{N\mu^2\gamma}$. The slope of the straight line decreases with decrease in temperature and solution $\frac{P}{P_{sat.}}$ approaches unity. At the critical temperature T_C ,the slope at the origin is

$$\frac{kT_C}{N\mu^2\gamma} = \frac{1}{3}, \text{ so the critical temperature is given by } T_C = \frac{N\mu^2\gamma}{3k}$$

For $T > T_C$ there is no spontaneous polarization.

15.4 Ferroelectric Crystals

The ferroelectric crystal exhibits an electric dipole moment even in the absence of an external field. In the ferroelectric state the centre of positive charge of the crystals does not coincide with the centre of negative charge. The plot of polarization versus electric field for a ferroelectric state shows hysteresis loop. A crystal in the normal dielectric state generally does not show significant hysteresis, when the electric field is increased and reversed thereafter slowly.

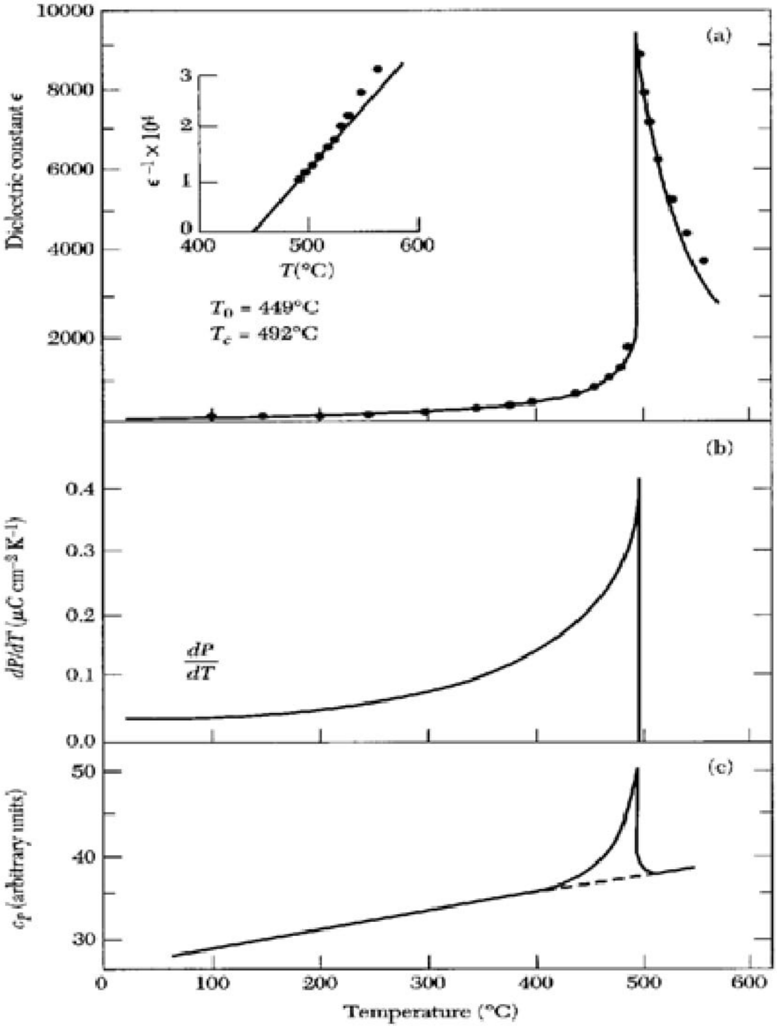


Figure 4.

In some ferroelectric crystals the ferroelectric dipole moment is not changed by an electric field of maximum intensity which it is possible to apply before causing electrical breakdown. In these crystals we often observe a change in the spontaneous moment when the temperature is changed. Such crystals are called as pyroelectric. For example $LiNbO_3$ is a pyroelectric crystal at room temperature. It has a very high transition temperature T_C = 1480 K and a high saturation polarization 50μC/cm^2.

Ferroelectricity disappears above a certain temperature called as transition temperature. Above the transition temperature the crystal is in paraelectric state.

15.5 Classification of Ferroelectric Crystals

The ferroelectric crystals may be classified into two main groups: Displacive transition and order-disorder transition ferroelectrics. If in the paraelectric phase the atomic displacements are oscillations about a non-polar site, then after displacive transition the oscillations are about a polar site. If in the paraelectric phase the displacements are about some double-well or multi-well configuration of sites then in an order-disorder transition the displacements are about an ordered subset of these wells.

The order-disorder class of ferroelectrics includes crystals with hydrogen bonds in which the motion of proton is related to ferroelectric properties. For example the crystals of dihydrogen Phosphate KH_2PO_4 and isomorphous salt KD_2PO_4. The substitution of hydrogen by deuterons nearly doubles the transition temperature.

The displacive class of ferroelectric includes ionic crystals structures closely related to the perovskite and ilmenite structure. The example of such ferroelectric is GeTe with sodium chloride structure and $LiNbO_3$, $BaTiO_3$, $SrTiO_3$, etc.

15.6 Theory of Displacive Transitions

This theory provides good information regarding these transitions in perovskite type crystal and it could explain the experimental data. Theses crystals generally undergo a displacive transition at the Curie point. There are two viewpoints to understand the ferroelectric displacive transition. In first viewpoint we talk about polarization catastrophe that refers to an unusual situation in which the polarization becomes infinitely large. In this situation the force exerted by local electric field is greater than the elastic restoring force. The shift is limited to a finite displacement by the anharmonic restoring force. The second point of view is the soft mode approach in which a transverse optical mode is frozen i.e. the frequency vanishes at some point in the Brillouin zone below the Curie temperature. This mode is called as soft mode. When $\omega_T = 0$, the crystal becomes unstable because of the absence of an effective restoring force.

15.6.1 Polarization Catastrophe

From the Clausius-Mossotti equation

$$\varepsilon = 1 + \frac{3(N_i\alpha_i + N_e\alpha_e)}{3\varepsilon_0 - (N_i\alpha_i + N_e\alpha_e)} \tag{1}$$

If $(N_i\alpha_i + N_e\alpha_e) = 3\varepsilon_0$, the dielectric constant becomes infinite giving the state of polarization catastrophe. Further

$$\vec{P} = (N_i\alpha_i + N_e\alpha_e)\vec{E}_{local} \tag{2}$$

$$\vec{P} = (N_i\alpha_i + N_e\alpha_e)(\vec{E} + \frac{\vec{P}}{3\varepsilon_0}) \tag{3}$$

where, $\vec{E} = E_0 + E_1$, E_0 is the applied electric field and E_1 is the depolarization field.

If $\vec{E} = 0$, then

$$\vec{P}\{\frac{N_i\alpha_i + N_e\alpha_e}{3\varepsilon_0} - 1\} = 0$$

In the polarization catastrophe, $\vec{P} \neq 0$

In order to understand the physical meaning of above situation ,we consider a highly polarisable ionic crystal having cubic symmetry. Let α be the total polarizability and $\vec{p}$ is the dipole moment of an ionic pair. A transient field is supposed to start polarization of the pair. The ionic pair will keep on polarizing until some resistance develops to stop the process. The resistance finally stop the process of polarization. The dipole moment of a single ion pair with ion separation y is

$$\vec{p} = q\vec{y} = \alpha\vec{E}_{local} = \frac{\alpha\vec{F}}{q} \tag{4}$$

where $\vec{F}$ is the restoring force that tends to bring the positive and negative ions together and q is the charge on the each ion. The work required to form such N dipoles per unit volume in the crystal is

$$w_1 = N\int \vec{F}.d\vec{y}$$

$$= \frac{Nq^2}{\alpha}\int \vec{y}.d\vec{y} = \frac{Np^2}{2\alpha}$$

$$\Rightarrow w_1 = \frac{P^2}{2N\alpha} \tag{5}$$

On the other hand the work done per unit volume by local electric field in displacement of ions is

$$w_2 = \int \vec{E}_{local}.d\vec{P}$$

$$w_2 = \int [\vec{E} + \frac{\vec{P}}{3\varepsilon_0}].d\vec{P}$$

$$w_2 = \frac{P^2}{6\varepsilon_0} + \int \vec{E}.d\vec{P} \tag{6}$$

So, the resultant work done per unit volume or the energy density of a polarized dielectric is

$$w_2 - w_1 = \frac{P^2}{2N\alpha}(\frac{N\alpha}{3\varepsilon_0} - 1) + \int \vec{E}.d\vec{P} \tag{7}$$

This shows that even $\vec{E}$ =0, $w_2 > w_1$, if $N\alpha \geq 3\varepsilon_0$. This can be written in general form

$$\sum_i (N_i\alpha_i) \geq 3\varepsilon_0$$

The equality sign describes the condition of polarization catastrophe. The minimum value of $\sum_i (N_i\alpha_i)$ for which the Ferroelectricity will be found is $3\varepsilon_0$.

Unfortunately in any real ferroelectric crystal ,the polarization catastrophe is not observed. A small deviation in the value of $\sum_i (N_i\alpha_i)$ from $3\varepsilon_0$ changes the value of ε by large amount. Let us consider

$$\sum_i (N_i\alpha_i) = 3\varepsilon - 3\beta, \text{ where } \beta <<1$$

So from equation (1) we get

$$\varepsilon \propto \frac{1}{\beta}$$

If we assume that β is a linear function of temperature near Curie point and it is given by

$$\beta = \frac{T - T_C}{\eta}, \ \eta \text{ is a constant then}$$

$$\beta \propto \frac{1}{(T - T_C)}$$

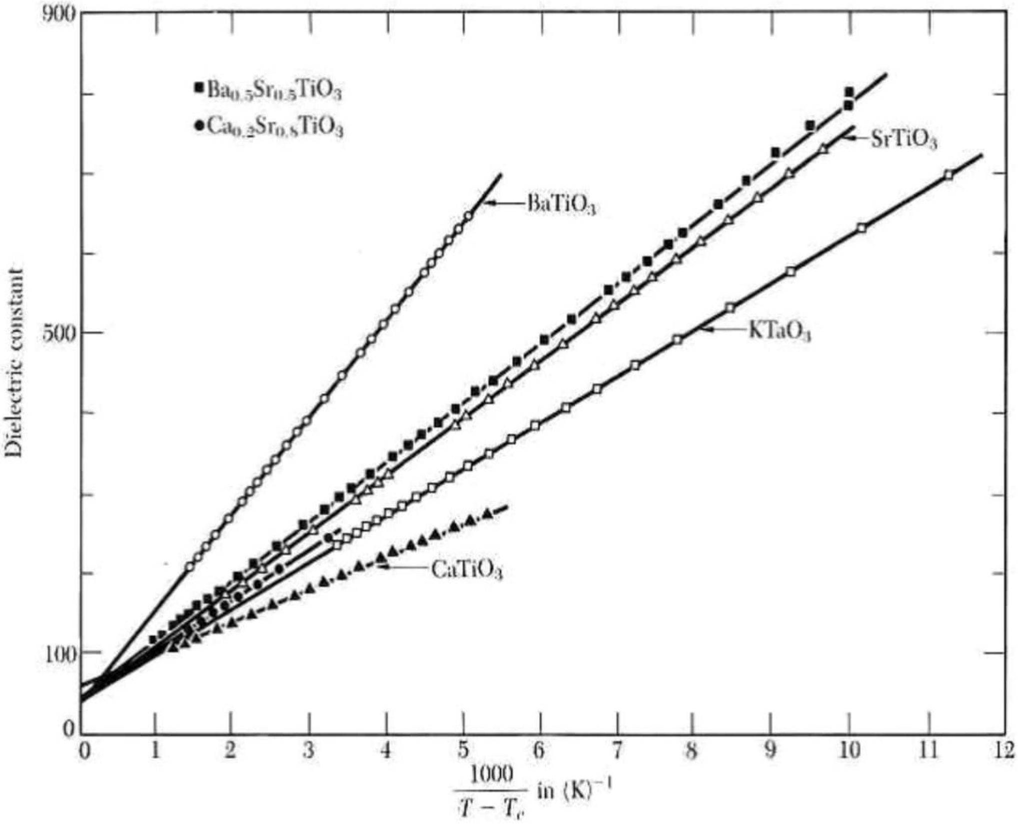


Figure 5. Dielectric constant and $1/(T-T_C)$ curve

The temperature variation of ε given by this equation is in excellent agreement with observed behaviour in several perovskite crystals.

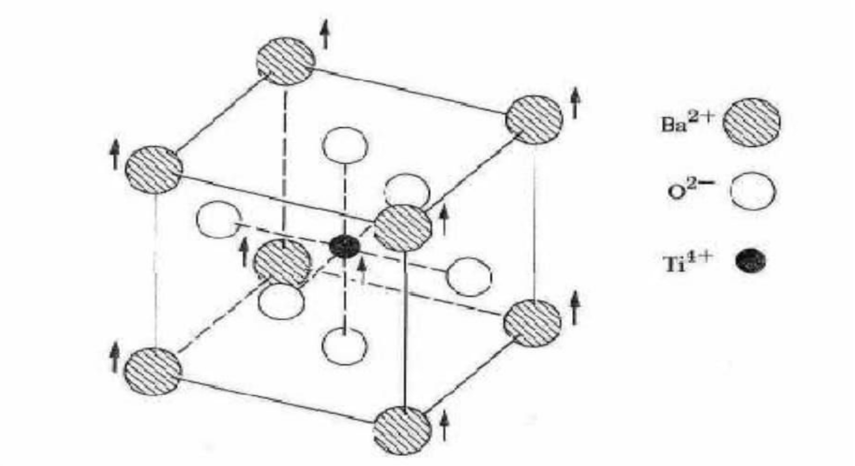


Figure 6. Structure of Barium Titanate

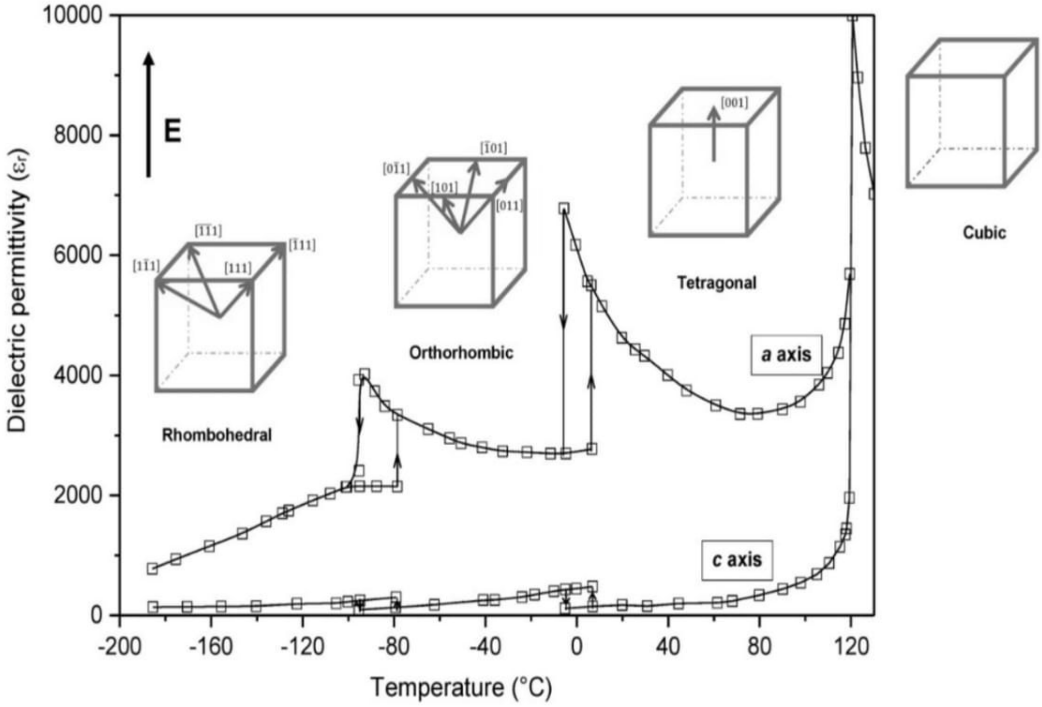


Figure 7. Spontaneous polarization of Barium Titanate with Temperature

15.6.2 'Frozen in' Transverse Optical Phonon

A ferroelectric state can be regarded as a 'Frozen In' Transverse Optical (TO) phonon. From the Lyddane-Sachs-Teller relation

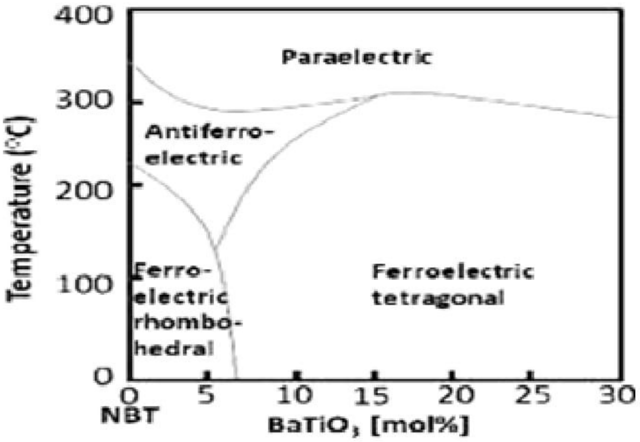
$\dfrac{\omega_{TO}^2}{\omega_{LO}^2} = \dfrac{\varepsilon_\infty}{\varepsilon_S}$, where TO stands for transverse optical and LO stands for longitudinal optical mode. ε_s is the static dielectric constant. It shows that when ε_S increases ,then ω_{TO} decreases. Thus for large value of ε_S which is observed at Curie temperature ω_{TO} may be zero. In actual practice ε_s remains finite, so the TO mode is called as soft mode. At the transition temperature T_C , when ω_{TO} approaches the zero value the crystal becomes unstable and anharmonic elastic forces come into play. So, in presence of anharmonic forces ω_{TO} show a following temperature dependence

$$\omega_{TO}^2 \propto (T-T_C) \text{ or } \frac{1}{\varepsilon_s} \propto (T-T_C)$$

The large value of static dielectric constant at low frequency TO phonon is supported by several perovskites ferroelectrics.

15.7 Antiferroelectricity

A ferroelectric displacement is not only the type of instability that is found in dielectric materials but some other types of deformations also occurs there. These types of deformations do not give any spontaneous polarization by them are accompanied by change in dielectric constant. One type of deformations are in which neighbouring lines of ions displaced in opposite sense called as antiferroelectrics. The perovskites structure appears to be susceptibility to many types of deformations often with a small difference in the energy between them.



The phase diagram of perovskite like $BaTiO_3$ shows transition between para-, ferro-, and antiferroelectrics states. Ordered antiferroelectic arrangement of permanent dipole moments occur at low temperatures in ammonium salt and in hydrogen halides.

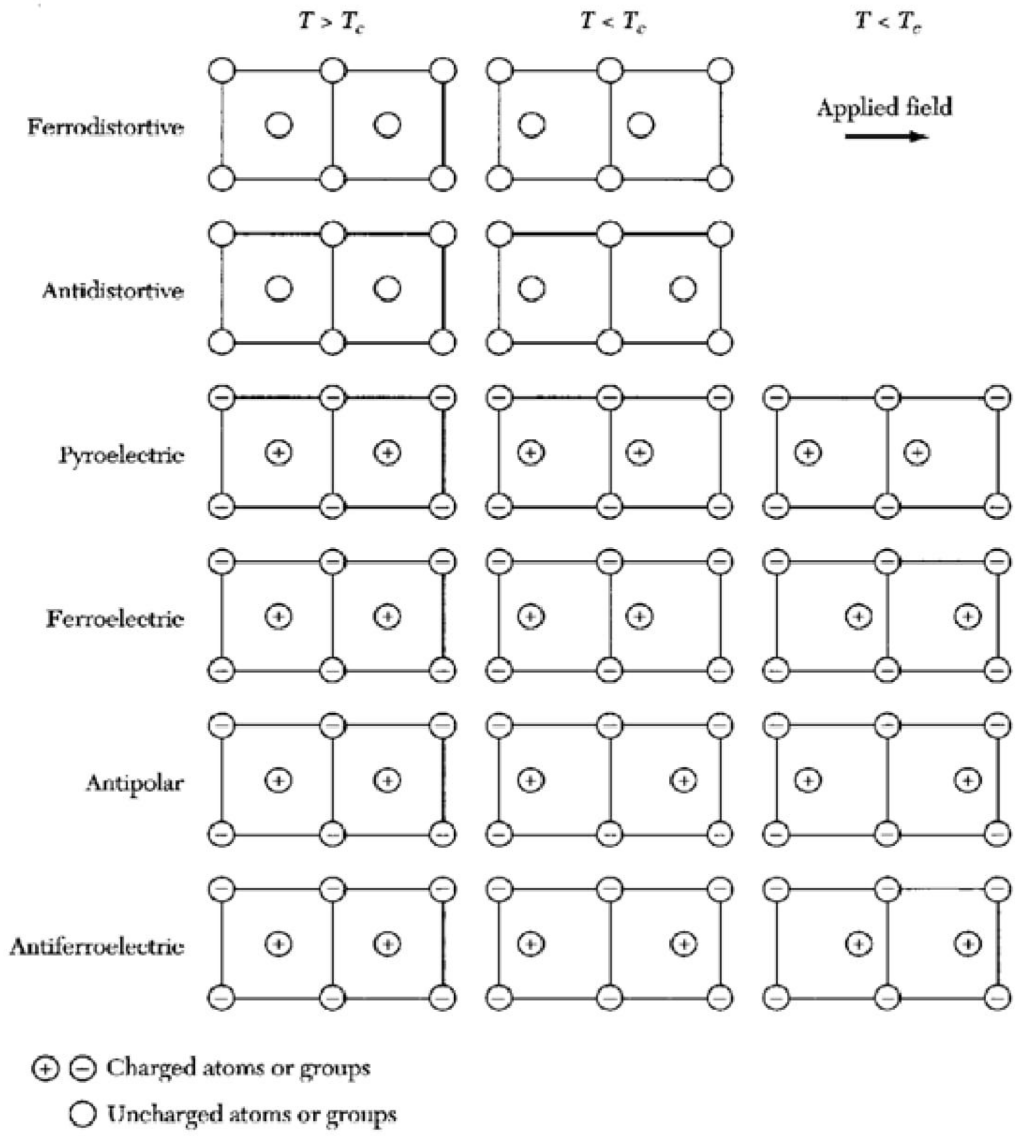


Figure 8 : Antiferroelectric transition and Displacement of ions in Ferroelectrics

15.7.1 Difference between Ferroelectric and Antiferroelectric

A ferroelectric crystal is defined as a crystal which belongs to the pyroelectric family i.e. It shows a spontaneous electric polarization and whose direction of spontaneous polarization can be reversed by an electric field. An antiferroelectric crystal is defined as a crystal whose structure can be considered as being composed of two sublattices polarized spontaneously in antiparallel directions and in which a ferroelectric phase can be induced by applying an electric field. Experimentally, the reversal of the spontaneous polarization in ferroelectrics is observed as a single hysteresis loop and the induced phase transition in antiferroelectrics as a double hysteresis loop, when a low-frequency ac field of a suitable strength is applied. The spontaneous polarization in ferroelectrics and the sublattice polarizations in antiferroelectrics are analogous to their magnetic counterparts. However, these polarizations are a necessary but not sufficient condition for ferroelectricity or antiferroelectricity. In other words, ferroelectricity and antiferroelectricity are concepts based not only upon the crystal structure, but also upon the dielectric behaviour of the crystal. It is a common dielectric characteristic of ferroelectrics and antiferroelectrics that, in a certain temperature range, the dielectric polarization is observed to be a two-valued function of the electric field.

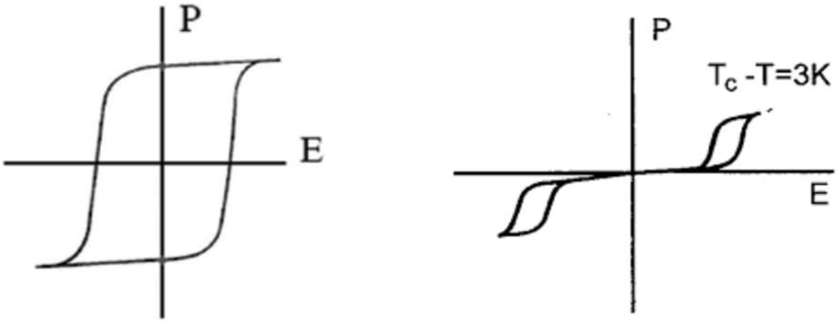


Figure 9: Hysteresis loop of ferroelectric and antiferroelectric material

15.8 Ferroelectric Domains

Let us a ferroelectric crystal of barium titanate in the tetragonal phase. In this phase of crystal the spontaneous polarization is either in upward direction or in the downward direction of the c axis of the crystal. So in the ferroelectric crystals the regions of spontaneously polarized called as domains are observed. Within each domain the polarization is in same direction. The direction of polarization is different in different domains. The net polarization in a volume depends upon the difference in the upward and downward directed domains. The crystal as whole is unpolarized since the volumes of oppositely polarized regions are same. The total dipole moment may be changed by the movement of walls between the domains or by the nucleation of new domains.

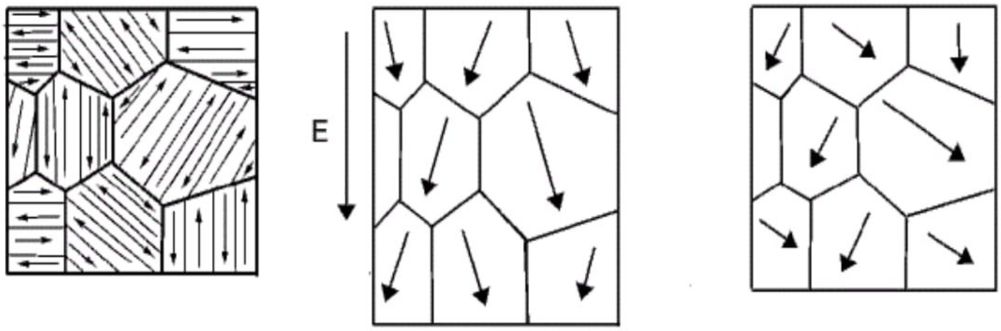


Figure 10: Spontaneous polarization without field, in presence of field, remanent polarization

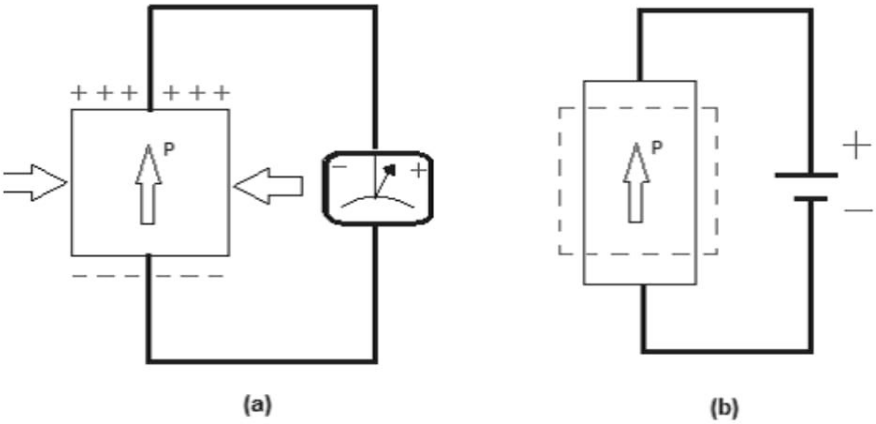
15.9 Piezoelectricity

The materials in the ferroelectric state also show the property of piezoelectricity i.e. when stress is applied on the crystal it will induce electric polarization. Similarly, on application of electric field on the crystal will induce a strain in it. In one dimension the polarization vector and elastic strain in the material are given by

$$P = dZ + \varepsilon_0 \chi E \quad \text{and} \qquad e = sZ + dE$$

where P is the polarization vector, Z is the stress, d is the polarization constant, E is the electric field, χ is the dielectric susceptibility, *e* is the elastic strain and *s* is the elastic compliance constant. These relations show the development of polarization by an applied stress and the development. A crystal may be piezoelectric even if it is not ferroelectric e.g. quartz is not ferroelectric. In quartz the order of magnitude of d is 10^{-3} m/V while in barium titanate it is of order of 10^{-1} m/V. The other examples of good piezoelectric materials are lead zirconate-lead titanate system (PZT) and polymer of polyvinylidenfluoride (PVF_2). The response of a piezoelectric crystal in transducer application is given by the electrochemical constant factor k, the square of this is given by

$$k^2 = \frac{\textit{mechnical}\text{ energy stored}}{\textit{electric}\text{ energy stored}}$$



(a) (b)

Figure 11:(a) Direct Piezoelectric Effect (b) Converse Piezoelectric Effect

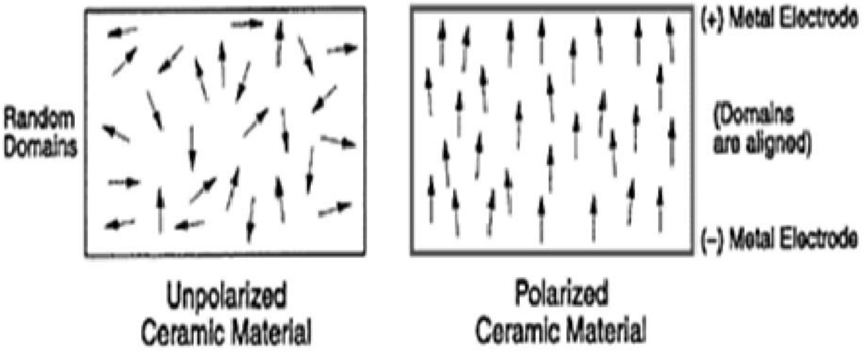


Figure 12: Polarization in Lead-Zirconate-Titanate (PZT) ceramic due to voltage.

The essential requirement for a crystal to be piezoelectric is the absence of centre of symmetry. In piezoelectric materials there is a lack of centre of inversion symmetry.

15.10 Pyroelectricity

Pyroelectricity is the ability of some materials to generate a voltage when they are subjected to heat or cold. Due to the variation in the temperature, slight changes occur in the position of atoms within the crystals as a result, the polarization of the crystal changes. This develops a voltage across the crystal. The voltage that develops across the crystal is not stable and when the temperature change remains as such, the voltage ceases due to leakage of current. This may be due to the movement of electrons in the crystals. The term pyroelectricity was originated from Greek word **'Pyr'** meaning **'fire'** and the term electricity.

Pyroelectricity is different from thermoelectricity in terms of the electric charge. In pyroelectricity, as the temperature changes the pyroelectric crystal as a whole and a voltage develops across the crystal whereas in thermoelectricity a voltage develops across the crystal when its one side is kept at one temperature while the other end at a different temperature. The electrical and thermal aspects of the Pyroelectric crystals represent the pyroelectric effect while the kinetic energy aspect &electrical aspect represents the piezoelectric property. All the pyroelectric materials also show the piezoelectric property. But some piezoelectric materials have a crystal symmetry which does not allow the pyroelectric property. Some pyroelectric crystals change their crystal property in response to very minute change in temperature level as seen in the crystals used to make the PIR Sensors. In these 'Passive Infra Red' sensors the passive infrared emissions due to the body heat of human beings generate voltage across the crystals.

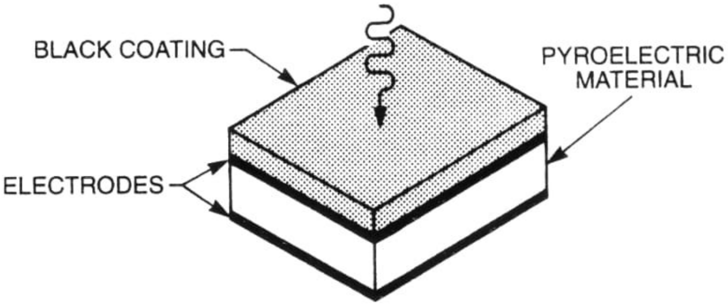


Figure 13: Pyroelectric crystal

The crystals generating pyroelectricity falls into thirty two classes based on the number of rotational axes and reflection planes. Out of the 32 classes of crystals, 21 classes are considered as non Centro metric which do not have centre symmetry. Out of these 21 classes, 20 classes exhibit direct piezoelectric property. Out of the 20 classes, crystals of 10 classes are polar in nature possessing a dipole and exhibits pyroelectricity. If the dipole of the crystal is reversed by applying an electrical field, the crystal shows ferroelectric property. Out of the 32 classes of pyroelectric crystals, only 10 are polar crystals showing charge separation even in the absence of an electric field. All the polar crystals are pyroelectric.

15.11 Self Learning Exercise

Q.1 Define the ferroelectric materials.

Q.2 Explain the characteristics of ferroelectric materials.

Q.3 Explain the Curie's temperature for ferroelectric materials.

Q.4 Write the examples of ferroelectric materials.

Q.5 Write a short note on antiferroelectric materials.

15.12 Summary

This unit deals with the study of a class of dielectric materials called as ferroelectrics. First of all the general characteristics are discussed i.e. spontaneous polarization, ferro-paraelectric transition and ferroelectric hysteresis. The most popular theory of ferroelectric materials known as dipolar theory is discussed in detail. In the next step the theory for displacive transition is discussed in detail to explain the transition in ferroelectric materials. The next section is related to antiferroelectric materials and the existence of spontaneous polarized regions called as domains. In both ferroelectric and antiferroelectric the existence of domain and the hysteresis is discussed. The last section of the unit deals with piezoelectric materials and pyroelectric materials. A brief discussion is presented here on both these materials.

15.13 Glossary

Dielectric: Insulator

Dipole: The arrangement of two equal and opposite charges separated by a distance

Polarization Vector: The total dipole moment per unit volume.

Spontaneously: Automatically (without electric field here)

Ferroelectric: A class of dielectric materials

Hysteresis: Property of materials (here of ferroelectric implying lagging of P with E)

Perovskites: Kind of structure name.

Cooperative: Combined

Orientation: Direction

Deformation: Related to some types of defects

Analogous: Similar

Counterpart: Similar to some in other stream.

Nucleation: Combining or get bigger.

15.14 Exercise

Q.1 Explain the dipole theory of ferroelectric materials in details.

Q.2 Discuss the theory of displacive transition of ferroelectric materials.

Q.3 Write a short note on ferroelectric domains.

Q.4 Explain the difference between ferroelectric and antiferroelectric materials.

Q.5 Write a short note on piezoelectric materials.

Q.6 Explain the concept of pyroelectricity.

References and Suggested Readings

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UNIT-16

Diamagnetism and Paramagnetism

Structure of the Unit

16.0 Objectives

In this unit we study the dia and para magnetic properties of materials. After going through this unit you will be able to explain the properties and classical and quantum mechanical model of diamagnetic and paramagnetic materials.

16.1 Introduction

Substances are classified into groups in terms of both the magnitude of their magnetic properties and the temperature dependence of these properties.

Magnetism originates from the magnetic moment due to the rotational motion of charged particles. An electron revolving in an orbit about the nucleus in an atom is equivalent to circular current and behaves like a magnetic shell or tiny magnetic doublet possessing a magnetic moment. Thus electronic orbits are associated with a magnetic moment. Since most of the atoms include several electronic orbits, their orbital planes are not usually parallel to each other and the sense of rotation is not essentially the same, two cases arise:-

1. The arrangement of orbits be such that the vector sum of magnetic moments is not zero and the atom as a whole has resultant magnetic moment. This effect gives rise to paramagnetic substance whose atoms or molecules are assumed to possess a permanent magnetic moment. Consequently, on the application of external fields, the atoms of such a substance will rotate in the field direction increasing there by the magnetic induction.
2. The number and orientation be such that the vector sum of magnetic moment is zero. Consequently, there should be no directive rotating action upon the atom when subjected to external field but actually the field will cause a rotating action owing to its influence on the individual electronic orbits. This action produces an induced magnetic moment which according to lenz's law will be in a direction opposite to the field and hence tend to decrease the magnetic induction. Substances built up of such molecules or atoms are diamagnetic .

16.2 Langvin Diamagnetism Equation

Electric orbits are associated with a magnetic moment. Since most of the atoms include several electronic orbits, their orbital planes are not usually parallel to each other and the sense of rotation is not essentially the same. When the number and orientation of the electronic orbits is such that the vector sum of magnetic moments is zero then there would be no directive rotating action upon the atom when subjected to external field, but actually the field will cause a rotating action owing to its influence on the individual electronic orbits. This action produces an induced magnetic moment which according to Lenz's law will be in a direction opposite to the field and hence tend to decrease the magnetic induction. This action is called diamagnetic action and the substance built up of such molecules are called diamagnetic substances.

A quantitative discussion of the effect of magnetic field on the motion of an electron in an atom will now be taken as follows:

Since any orientation of electronic orbits with respect to the applied field direction is possible, we take angular momentum L_a in any arbitrary direction relative to to the direction of H as shown in Fig. (2.1).

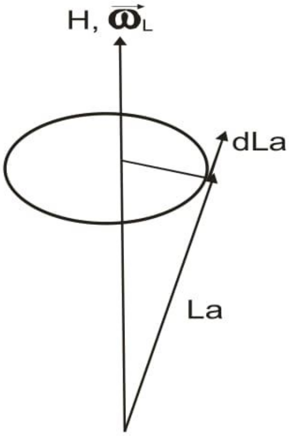

Fig. 16.1 : ***Precesion of angular momentum***

The magnetic dipole moment will be

$$\bar{\mu} = -\left(\frac{e}{2mc}\right) La \tag{1}$$

where m is the mass and e the charge vector around **H** on electron. The minus sign signifies that the dipole moment points in a direction opposite to L_a.

The magnetic field **H** exerts a torque $\bar{\mu} \times H$ on the dipole so that we may write

$$\frac{dL}{dt} = \bar{\mu} \times H$$

$$= -\left(\frac{e}{2mc}\right) \mathbf{L}_a \times \mathbf{H} \tag{2}$$

which is the equation of motion of vector $\mathbf{L}_a$ precessing about **H** with an angular frequency.

$$\overline{\omega_L} = \frac{eH}{2mc}$$

where ω_L is called the Larmor's frequency which is quite small even for high value of H as compared to the angular frequency of the electron in its orbit.

While deriving the relation for Larmor's frequency it has been assumed that $\mathbf{L}_a$ can assume any direction relative to **H** or $\mathbf{L}_a$ is independent of **H** which implies that orbit is not deformed under the influence of magnetic field. Equation (2) predicts that the plane of the orbit is not stationary but precesses about H. Since there is charge on the electron, this precession gives rise to an induced magnetic moment with a component opposite to the direction of applied field H. Suppose r_1 is the projection of radium r of an orbit on the plane perpendicular to the magnetic field. Then component of induced magnetic moment opposite to that of H will be,

$$(\mu)_{\text{induced}} = -\left(\frac{e}{2mc}\right) m\omega_L r_1^2 \tag{3}$$

For single electron, if an atom consists of z electronic orbits lying in all possible directions in space, the total induced magnetic moment is

$$(\mu)_{\text{ind}} = \left(\frac{e}{2mc}\right) m\omega_L \, \Sigma \overline{r_1^2} \tag{4}$$

where $\overline{r_1^2}$ represents the mean of the square of the projections of the orbits radii on a plane perpendicular to the field H. If x, y and z are the co-ordinates of any point on an orbit of radius r, then

$$\overline{r^2} = \overline{x^2} + \overline{y^2} + \overline{z^2}$$

For a spherically symmetric atom, we have

$$\overline{x^2} = \overline{y^2} = \overline{z^2}$$

Or $\quad \overline{r_1^2} = \overline{x^2} + \overline{x^2} + \overline{x^2}$

If z - axis lies in a plane perpendicular to the field H, then

$$\overline{r_1^2} = \overline{x^2} + \overline{y^2} = 2x^2 = 2/3\ \overline{r^2}$$

So that equiation (4) becomes

$$(\mu)_{ind} = -\left(\frac{e}{2mc}\right) m\omega_L \, \Sigma \frac{2}{3} r^2$$

$$= \frac{-He^2}{4mc^2} \frac{2}{3} \Sigma \overline{r^2} \quad \text{(on putting for WL)}$$

$$= \frac{He^2}{6mc^2} \Sigma \overline{r^2}$$

If there are z orbits (equal to the atomic numbers, i.e. each atom containing z electrons) ,then the total induced magnetic moment will be

$$(\mu)_{\text{ind}} = -\frac{ZHe^2}{6mc^2}\overline{r^2} \tag{5}$$

Therefore diamagnetic susceptibility is given by

$$\chi_{dia} = \frac{(\mu)_{ind}}{H} \quad \text{per atom}$$

$$= \frac{-Ze^2}{6mc^2}\overline{r^2}$$

If there are N atoms, each atom containing Z electrons, then susceptibility is given by

$$\chi_{\text{dia}} = -\frac{NZe^2}{6mc^2}\overline{r^2} \tag{6}$$

The following points are note worthy:

(i) From, $\overline{r_1^2} = \frac{2}{3}\left(\overline{r^2}\right)$ we get $(\overline{r^2}) = \frac{3}{2}\,(\overline{r_1^2})$ which represents the mean square distance of the electrons from the nucleus. This implies that susceptibility is thus determined essentially by the charge distribution in the atoms.

(ii) Equation (6) represents that diamagnetic susceptibility is independent of the field applied and the temperature, and is true according to experimental verification.

(iii) As stated in the beginning, the effect of field H on individual electron will be the same irrespective of the fact that the total magnetic moment of the atom is zero or not. This mean each electron orbit would acquire an additional induced moment opposite to the direction of applied field, modifying the magnetic moment of the atom as a whole in the same sense. Thus it predicts that all substances should exhibit diamagnetism.

16.3 Quantum Theory of Diamagnetism

We know that for a charged particle moving in an electromagnetic field, the Hamiltonian, H, is

$$H = \frac{1}{2m}\left(P + \frac{e}{c}A\right)^2 - e\phi$$

where P is the momenta of the particle, ϕ is magnetic scalar potential and A is magnetic vector potential. If we put P =− i ℏ ∇

According to schrodinger co-ordinate representation, then

$$\mathrm{H} = \frac{1}{2m}\left(-i\hbar\nabla + \frac{e}{c}A\right)^2 - e\phi$$

where $\nabla = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$ and $A = \hat{i}A_x + \hat{j}A_y + \hat{k}A_z$

Therefore

$$\left(-i\hbar v + \frac{e}{c}A\right)^2 = \left(-i\hbar + \frac{\partial}{\partial x} + \frac{e}{c}A_x\right)\left(-i\hbar + \frac{\partial}{\partial x} + \frac{e}{c}A_x\right)$$

x - component

$$= -\hbar^2\frac{\partial^2}{\partial x^2} - i\hbar\frac{\partial}{\partial x}\left(\frac{e}{c}A_x\right) - \frac{e}{c}A_x i\hbar\frac{\partial}{\partial x} + \frac{e^2}{C^2}A^2x$$

$$= \hbar^2\frac{\partial^2}{\partial x^2} - i\hbar\left\{A_x\frac{\partial}{\partial x}\left(\frac{e}{c}\right) + \frac{e}{c}\frac{\partial A_x}{\partial x}\right\} - \frac{e}{c}A_x i\hbar\frac{\partial}{\partial x} + e^2/c^2A^2x$$

$$= \hbar^2\frac{\partial^2}{\partial x^2} - i\hbar\frac{e}{c}\left(\frac{\partial Ax}{\partial x} + 2Ax\frac{\partial}{\partial x}\right) + \frac{e^2}{c^2}A^2x$$

in which we have implicity operated over some function, say Ψ.

Writing for all the three components, x, y and z, we have

$$\left(i\hbar\nabla + \frac{e}{c}A\right)^2 = -\hbar^2\nabla^2 - i\hbar\frac{e}{c}diva - 2i\hbar\frac{e}{c}\left(A_x\frac{\partial}{\partial x} + A_y\frac{\partial}{\partial x} + A_z\frac{\partial}{\partial z}\right) + \frac{e^2}{c^2}A^2$$

Thus the Hamiltonian becomes

$$H = -\frac{\hbar^2}{2m}\nabla 2 - \frac{i\hbar e}{mc} divA - \frac{i\hbar e}{mc}\left(Ax\frac{\partial}{\partial x}+A_y\frac{\partial}{\partial y}+A_z\frac{\partial}{\partial z}\right) + \frac{e^2}{2mc^2}A^2 - e\phi$$

Putting divA = $\frac{1}{c}\frac{\partial\phi}{\partial t}$

We get

$$H = \frac{\hbar^2}{2m}\nabla 2 - \frac{i\hbar e}{mc}\frac{\phi}{c} - \frac{i\hbar e}{mc}\left(A_x\frac{\partial}{\partial x}+A_y\frac{\partial}{\partial y}+A_z\frac{\partial}{\partial z}\right) + \frac{e^2}{2mc^2}A^2 - e\phi$$

If the external field **H** is uniform, we may choose **A** as

$$\vec{A} = \frac{1}{2}\vec{H}\times\vec{r}$$

If the field H lies in Z- direction only, then

$$H_x = H_y = 0 \quad \text{and } H = H_z$$

So that

$$A_x = -\frac{1}{2}y \quad H_z = -\frac{1}{2}yH$$

$$A_y = -\frac{1}{2}xH$$

So that $A_z = 0$

$$\left(Ax\frac{\partial}{\partial x}+Ay\frac{\partial}{\partial y}+Az\frac{\partial}{\partial z}\right) = \frac{1}{2}\,H\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$$

and $\dot{\phi} = \frac{\partial\phi}{\partial t} = \frac{\partial}{\partial t}\left(-\frac{e}{r}\right) = 0$

also $A^2 = A.\ A$

$$= \left[i\left(-\frac{1}{2}yH\right)+j\left(\frac{1}{2}yH\right)\right]\left[i\left(-\frac{1}{2}yH\right)+j\left(\frac{1}{2}xH\right)\right]$$

$$= \frac{1}{4} y^2 H^2 + \frac{1}{4} x^2 H$$

$$= \frac{1}{4} H^2 (x^2 + y^2)$$

Putting these values, we get for H,

$$\mathrm{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{i\hbar e}{2mc} H \left(x \frac{\partial}{\partial x} - y \frac{\partial}{\partial x} \right) + \frac{e^2}{8mc^2} H^2 (x^2 + y^2) - e\phi$$

Thus the additional term in Hamiltonian due to magnetic fields is

$$= \frac{i\hbar e}{2mc} H \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) + \frac{e^2 H^2}{8mc^2} (x^2 + y^2)$$

We note that :

(i) First term can be written as

$$= \frac{eH}{2mc} \left[x \left(-i\hbar \frac{\partial}{\partial y} \right) - y \left(-i\hbar \frac{\partial}{\partial x} \right) \right]$$

$$= \frac{eH}{2mc} \left[x p_y - y p_x \right]$$

$$= \frac{eH}{2mc} (r \times P)_Z$$

$$= \frac{eH}{2mc} \mathrm{L_Z}$$

where L_z is the Z- component of the angular momentum. So the term is

$$= \mu_z \mathrm{H}$$

$$= -(-\overline{\mu} . \mathrm{H})$$

which means that the electron motion is associated with a permanent magnetic dipole moment μ. Further the term is proportional to the orbital angular momentum compenent L_z and in mononuclear systems give rise only to paramagnetism.

(ii) The second term, if written for a unit volume of a substance containing N atoms, each atom containing z- electrons, would become

$$= ZN\frac{e^2H^2}{8mc^2}\sum_i(x_i^2+y_i^2)$$

$$= NZ\frac{e^2H^2}{8mc^2}\overline{\rho^2}$$

where $\overline{\rho^2}$ represents the mean squares of the radii of the projections of orbits on a plane perpendicular to H. Now, if the magnetic field produces induced dipole moments in the substance, then the corresponding energy term would be quadratic in H. Thus the above term is considered as the energy term associated with the diamagnetism of the solid.

Thus, comparing it with $-\frac{1}{2}\chi_{\text{dia}} H^2$ we get

$$\chi_{\text{dia}} = -NZ\left(\frac{e^2}{4mc^2}\right)\overline{\rho^2}$$

we know that $\overline{r_1^2} = \frac{2}{3}\overline{r^2}$

Here we have $\overline{\rho^2}$ instead of $\overline{r_1^2}$ so that

$$\overline{\rho^2} = \frac{2}{3}\overline{r^2}$$

Putting it, we have

$$\chi_{\text{dia}} = -NZ\left(\frac{e^2}{6mc^2}\right)\overline{r^2}$$

With the application of quantum orbital theory, the expression for χ_{dia} was corrected by substituting the value of $\overline{r^2}$. For hydrogen like atoms, $\overline{r^2}$ from Bohr's theory is given by $\overline{r^2} = a_o^2\frac{h^2}{Z^2}\left(\frac{5}{2}n^2-\frac{3}{2}k^2\right)$

where n is radial quantum number and k is azimuthal quantum number and z is the effective nuclear charge, a_o is the radius of the inner most orbit in the hydrogen atom (normal state) and is equal to 0.528 × 10^{-8} cm.

Therefore atomic diamagnetic susceptibility is given by

$$\chi_a = -0.79\times10^{-6}\frac{n^2}{z^2}\left(\frac{5}{2}n^2-\frac{3}{2}k^2\right)$$

Theoretical value of susceptibility, when put to experimental verification, was found to be much smaller than the experimental value. To make the expression of susceptibility move accurate, Van-Vleck modified the expressian as follows.

$$\chi_a = -0.79\times10^{-6}\frac{n^2}{z^2}\left(\frac{5}{2}n^2-\frac{3l(l+1)-1}{2}\right)$$

where l is orbital quantum number equal to (R-1) for molecular hydrogen, the susceptibility will be

$$\chi_m = 2\chi_a$$

$$= 2x-0.79\times10^{-6}\frac{n^2}{z^2}\left[\frac{5}{2}n^2-\frac{3l(l+1)-1}{2}\right]$$

$$= 2x-0.79\times10^{-6}\left[\frac{5}{2}+0+\frac{1}{2}\right]$$

or $\chi_m = -4.74\times10^{-6}$

The experimental value of χ_m, the molar susceptibility, For hydrogen is found to be - 4.00 × 10^{-6} and is thus quite in agreement with the above calculated value.

In 1927, Pauling extended the equation (2) to atoms with many electrons using the wave mechanical theory. He deduced the relation

$$\chi_a = -0.79\times10^{-6}\,\Sigma\frac{n^2}{(z-\sigma^2)}\left[\frac{5}{2}n^2-\frac{3l(l+1)-1}{2}\right]$$

where summation extends over all the electrons in the atom. σ is the screening constent. Later on in 1927 stoner evaluated the value of $\Sigma\bar{r}^{-2}$ by applying the result of Hartee self consistent field calculations. For helium predicted value χ_a= -1.86 × 10^{-6} whereas the experimental value is 1.906 × 10^{-6}. Slater, Augus and others gave other useful expressions.

16.4 Self Learning Exercise-I

Section A:Very Short Answer Type Questions

Q.1 Write the formula of Langevin diamagnetism.

Q.2 Write the formula of atomic diamagnetic susceptibility?

Q.3 What is the value of diamagnetic susceptibelity for copper?

Section B: Short Answer Type Questions

Q.4 What is Curie temperature?

Q.5 Define magnetic susceptibility?

Q.6 Explain the properties of diamagnetism material?

16.5 Langevin Theory of Paramagnetism

Some atoms and ions have permanent magenetic moments arising out of particular combination of orbital and spin magnetic moments of the electrons. These magnetic moments, in the absence of any external field, point in random directions so that there is no resultant external magnetic moment. This happens because the interaction energy between the dipoles is smaller than the thermal energy at that temperature (K_BT). Thus thermal agitation that gives rise to randomising effect predominates. When an external magnetic field is applied, the magnetic moments tend to line up along the field direction and produce a net magnetisation, counteracting the thermal agitation. When the atoms and ions are acted upon individually, with no mutual interaction between them, the effect is called paramagnetism.

On the basis of kinetic theory, for the explanation of paramagnetism property in material Langevin used the following postulates:-

1. Due to motion of electrons in an atoms of paramagnetism material are permanent magnetic moment, a atom in which odd number of electrons i.e. whose internal electron orbits are not filled, they has permanent magnetic moment. Permanent magnetic moment of atom is equivalent to the magnetic moment of short magnetic dipole.
2. In the absence of an external magnetic field, the probability of direction of

magnetic moment or magnetic dipoles of an atoms is equal in all directions. Hence at specified direction the sum of magnetic moment of the atoms is zero.

3. When an external magnetic field is applied which tends to produce alignment of the magnetic axes of atoms in its direction of external magnetic field. But the thermal agitation in material causes disorder and oppose the alignment of atoms. Since both effects are opposite, resultant state of matter is decided by the both effects.
4. According to kinetic theory, in equlbrium those atom whose magnetic axis lies between θ and $\theta + d\theta$ is directly proportional to sin θ dθ of its number.
5. According to equipartition of energy, the number of atoms (magnetic dipoles) whose magnetic potential energy is directly proportional to exp $(-u/k_BT)$.

Let us consider the unit volume of a paramagnetic material containing N atoms or molecules, each bearing a permanent magnetic moment μ. When the external magnetic field B is applied, the magnetic potential energy of magnetic dipoles or atoms whose magnetic axis makes an angle θ with the filled is

$$\mu = - \mu B \cos\theta \qquad (1)$$

According to kinetic theory, number of atoms inclined at an angle θ from the external magnetic field

$$dN = N \exp\left[\mu B \cos\theta / K_B T\right] \sin\theta \, d\theta \qquad (2)$$

where K_B is Boltzmann constant and T is temperature of the material.

The average component of the magnetic moment of all atoms along the external magnetic field isgiven as

$$<\mu>= \frac{\int_o^\pi \mu\cos\theta dN}{\int_o^\pi dN} = \frac{N\int_o^\pi \mu\cos\theta \exp\left[\mu B\cos\theta/K_B T\right]\sin\theta}{N\int_o^\pi \exp\left[\mu B\cos\theta/K_B T\right]\sin\theta}$$

Let

$$\frac{\mu B}{K_B T} = x$$

$$< \mu > = \frac{\int_{o}^{\pi} \mu \cos\theta e^{x} \cos\theta \sin\theta d\theta}{\int_{o}^{\pi} e^{x\cos\theta} \sin\theta d\theta}$$

Let $I = \int_{o}^{\pi} e^{x\cos\theta} \sin\theta d\theta$

$$\frac{dI}{dx} = \int_{o}^{\pi} \cos\theta e^{x\cos\theta} \sin\theta d\theta$$

$$< \mu > = \frac{\mu}{I}\frac{dI}{dx}$$

But $I = \int_{o}^{\pi} e^{x\cos\theta} \sin\theta d\theta = \left[-\frac{e^{x\cos\theta}}{x} \right]_{o}^{\pi}$

$$= \frac{e^{-x} - e^{-x}}{x}$$

and $\frac{dI}{dx} = \frac{e^{x} + e^{x}}{x} - \frac{e^{-x} - e^{-x}}{x^{2}}$

$$< \mu > = \mu \left[\frac{e^{x} + e^{-x}}{e^{x} - e^{-x}} - \frac{1}{x} \right]$$

$$= \mu \left[coth x - \frac{1}{x} \right] = \mu \text{ L } (x) \qquad (3)$$

where $L(x) = \left[coth x - \frac{1}{x} \right]$ is called the Langevin function.

Intensity of magnetisation of material

$$M = N < \mu > = N \mu L(x)$$

or $$M = M_s L(x) = M_s (\text{Coth}x - \frac{1}{x}) \qquad (4)$$

where $M_S = N \mu$ is called saturation intensity of magnetisation.

The graph plotted between Langevin's function L(x) and x is as shown in Fig. (16.2)

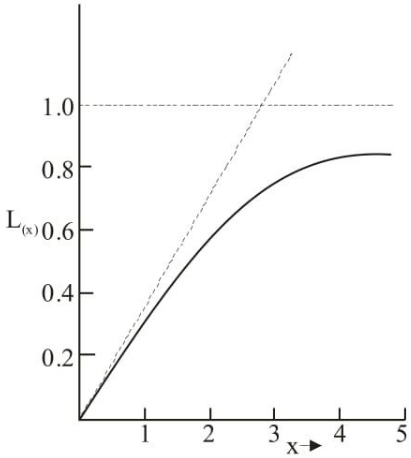

Fig. (16.2) : ***Variation of Langevins funcion L (x) with x***

Case-1: When $\mu B >> K_B T$ i.e. $x >> 1$,then for large value of x is obtained corresponding to strong intense field and at low temperature.

At $x >> 1$ Let $L(x) \approx 1$

$$M = M_S \tag{5}$$

i.e. at strong intense field and low temperature intensity of magnetisation is in saturation state.

Case-2. When $\mu B << K_B T$ i.e. $x << 1$ then this position is obtained at weak field and high temperature.

$$\text{At } x<<1, \qquad \text{Let } \coth x \approx \left(\frac{1}{x} + \frac{x}{3}\right) \tag{6}$$

Intensity of magnetisation $M = M_s \dfrac{x}{3} = \dfrac{N\mu\mu B}{3K_B T}$

Or $M = \dfrac{N\mu^2 B}{3K_B T}$

Magnetic Susceptibility

$$\chi = \frac{\mu_o M}{B} = \frac{\mu_o N \mu^2}{3K_B T} \qquad (7)$$

where $C = \frac{\mu_o N \mu^2}{3K_B T}$ is called Curie constant.

As the sucessful explanation of Langevin's theory for gases, dilute solution of paramagnetic material and temperature dependence (equation 7) of magnetic susceptitility of gadolinium sulphate (solid) but this is failure to explanation of compression and cooling gases, concentration solution of paramagnetic material, temperature dependence of magnetic susceptibility in solid and crystal ,because the following shortcoming in this theory.

(i) If the permanent magnetic moment is associated with and it is directly proportional to the angular momentum of moving electric charges then the magnetic moment cannot have a fixed magnitude but must take all values ranging from $-\infty$ to $+\infty$.

(ii) When the atom of permanent magnetic moment μ is placed in a weak magnetic field B, it cannot place itself at any angle θ to the external magnetic field as was supposed by Langevin.

16.6 Quantum Theory of Paramgnetism

According to classical theory, the permanent magnetic moment of a given atom rotates freely and can possess any orientation with respect to the external magnetic field. But According to quantum theory, the permanent magnetic moment of a given atom does not rotate freely, but limited, with respect to the external magnetic field to a finite set of orientations.

Let the permanent magnetic moment in atoms of a material Let N be the number of atoms per unit volume of a material and $\vec{J}$ be the total angular momentum in each atom. According to quantum mechanics, the possible number of components of its magnetic moment along magnetic field B is (2J+1) and the value of these component

$$(\mu_z)_J = -m_j g \mu_B$$

where m_J = J, (J-1), (J-2) ………… (J-1), - J

Here m_j is the magnetic quantum number, g the Lande splitting factor and the Bohr magneton.

The magnetic potential energy of atoms in magnetic field

$$u_B = -\vec{\mu}\vec{B} = -\mu_z B = mjg\mu_B B$$

∴ From the Maxwell - Boltzmann statistics, average of total magnetic moment along the external magnetic field in atom is

$$<\mu> = \frac{\sum_{-J}^{J}\left(\mu_z\right)_J \exp\left(-u_B/K_B T\right)}{\sum_{-J}^{J}\exp\left(-u_B/K_B T\right)}$$

$$= \frac{\sum_{-J}^{J}\left(m_j g\mu_B\right)\exp\left(m_j g\mu_B B/K_B T\right)}{\sum_{-J}^{J}\exp\left(m_j g\mu_B B/K_B T\right)}$$

Hence total intensity of Magnetisation in material is

$$M = N<\mu>$$

Let $y = \frac{g\mu_B B}{K_B T}$

$$M = \frac{Ng\mu_B \sum_{J}^{J} m_j \exp(m_j y)}{\sum_{-J}^{J}\exp(m_j y)}$$

$$= Ng\ \mu_B \frac{d}{dy}\left[\log\left(\sum_{-J}^{J}\exp(m_j y)\right)\right]$$

$$= Ng\ \mu_B \frac{d}{dy}\left[\log e\left(e^{Jy}+e^{(J-1)y}+.....+e^{-(J-1)y}+e^{-Jy}\right)\right]$$

$$= \text{Ng } \mu_B \frac{d}{dy}\left[\log e^{jy}\frac{\left(1-e^{-(2J+1)y}\right)}{(1-e^{-y})}\right]$$

$$=\text{Ng } \mu_B \frac{d}{dy}\left[\log e\frac{e\left(J+\frac{1}{2}\right)^{y}-e^{-(J+1/2)^{y}}}{e^{y/2}-e^{-y/2}}\right]$$

$$= \text{Ng } \mu_B \frac{d}{dy}\left[\log e\frac{\sinh(J+\frac{1}{2})^{y}}{\sinh y/2}\right]$$

$$\text{M} = \text{Ng } \mu_B \left[\left(J+\frac{1}{2}\right)\cot h\left(J+\frac{1}{2}\right)y-\frac{1}{2}\coth\frac{y}{z}\right]$$

$$\text{x} = \text{Jy} = \frac{Jg\mu_B B}{K_B T}$$

$$\text{M} = Ng\mu_B JB(x) \tag{1}$$

where $B(x) = \left[\left(\frac{2J+1}{2J}\right)\coth\left(\frac{2J+1}{2J}\right)x-\frac{1}{2J}\coth\frac{x}{2J}\right]$ (2)

is known as brillouin function.

Case-1:- When mjg μ_BB<<KT i.e. x<<1 then this condition is obtained at high temperature and weak magnetic field B. In this condition

$$\coth\alpha x\approx\frac{1}{\alpha x}\left(1+\frac{\alpha^2x^2}{3}\right)$$

Using above approximation in equation (2)

$$\text{B}(x) = \frac{x}{3}\,\frac{J(J+1)}{J}$$

Hence M = $\frac{Ng^2\mu_B^2 B}{3K_BT}J(J+1)$

Magnetic Susceptibility of material

$$\chi = \frac{\mu_o M}{B} = \frac{\mu_o N g^2 \mu_B^2 B}{3K_BT}J(J+1) \qquad (3)$$

If total magnetic moment μ_J is defined from following way:-

$$\mu_J = g\mu_B\sqrt{J(J+1)} = P_{eff}\,\mu_B$$

where $P_{eff} = g\sqrt{J(J+1)}$ is called effective number of Bohr magneton

$$\chi = \frac{\mu_o N\mu_j^2}{3K_BT}$$

The equation when compared with equation (7) of topic (16.5) is found to be identical with classical result with a difference that in quantum result μ_J replaces μ but from this theory Curie constant is C = $\frac{\mu_o N\mu_j^2}{2K_B}$. It is equivalent to experimental value.

Case-2 : When $m_J g\mu B >> K_BT$ i.e. $x>>1$ then condition is obtained at Low temperature and strong magnetic field B.

In this condition

$$\text{Coth } \alpha x = 1$$

Using of above approximation in equation (2), We have

$$B(x) = 1$$

Intensity of Magnetisation $M = Ng\mu_BJ = M_S$ (Intensity of Saturation)

Hence at low temperature applied strong magnetic field causes magnetisation of paramagnetic materials to be in saturation state. This is consistant with experiment.

(i) **Rare earth ions :-** The rare earth compound falls under the VI group of periodic table. These are 14 in number. The shells are complete upto $4d^{10}$ consisting of a Xenon core of 54 electrons. In this case most of the atoms are in lowest energy state and L-S coupling holds good.

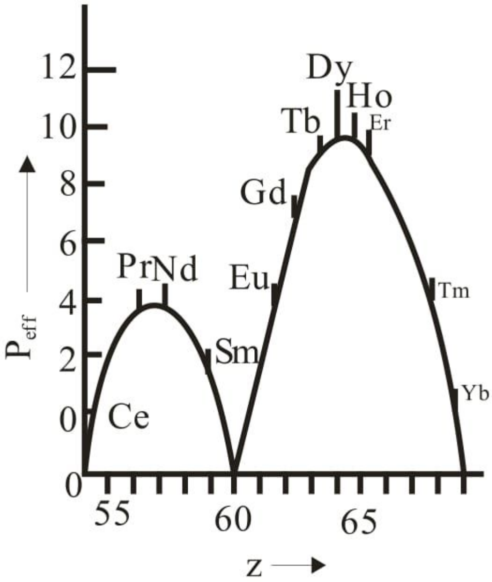

Fig. (16.3) : ***Calculated and observed value of P_{eff} (in the form of Z function) for the rare earth ions.***

The experimental data have been thoroughly examined by Vanvleck. He tabulated the mean value of P_{eff} obtained experimentally and those calculated from the expression $P_{eff} = g\sqrt{J(J+1)}$. The full curve represents the effective number of Bohr magnetons calculated from the above expression, and J and g values were obtained from Hund's rule and Lande's formula. The vertical lines correspond to observed values of P_{eff}. These values of P_{eff} delivered in the case of wide multiples, agree well with the experimental values except for Sm and Eu.

(ii) Iron- Group Ions :- The iron group elements fall under the IV group of the periodic table. They are 10 in number. The sub shells are completed filled up to $3p^6$ and such shells are partially filled upto 3d. The values of P_{eff} were calculated from $P_{eff} = g\sqrt{J(J+1)}$. But is was found that the result obtained from the ions did not agree. It has been found that the experimental values lie much closes to $P_{eff} = 2\sqrt{S(S+1)}$, the value which would be expected if there were no orbital angular momentum at all and the magnetism were due entirely due to the electron spin.

Stoner has suggested the following explanation in this respect. In the rare earth group, on the other hand, the paramagnetic 4f electrons are situated relatively deep inside the ions. Because of the outer electrons filled shells $5s^2$ $5p^6$,the electrons in these ions are therefore practically screened from the crystalline field. In the iron group, the paramagnetic 3d electrons are the outermost electrons and these are therefore fully exposed to crystalline field. Consequently, the orbital motion is locked into the field of neighbours and cannot orient itself in an external magnetic field. The electron spin has no direct interaction with electric static field. Thus orient itself freely in an external magnetic field. Similarly in the iron group ions ,the contribution of L in magnetic moment is neligible.

16.7 Self Learning Exercise-II

Section A : Very Short Answer Type Questions

Q.1 Write the formula of Langevin theory of paramagnetism ?

Q.2 Write the formula of quantum theory of paramagnetism ?

Q.3 What is the value of Curie constant?

Section B : Short Answer Type Questions

Q.4 Draw the graph between Langevin's function L(x) and x ?

Q.5 What are the postulates of Langevin theory of paramagnetism?

Q.6 The magnetic susceptibility 2×10^{-3} of a paramagnetic material at temperature 27^0C. If atomic concentration of material is 2.7×10^{25} per m^3 then calculate the stable magnetic moment of each atomic dipole in absence of magnetic field.

16.8 Summary

In this chapter we have discussed diamagnetism, Larmor-Langevin theory, quantum theory of diamagnetism. We have shown that for diamagnetic materials classical and quantum theories gives the exactly same expression for magnetic susceptibility. We have also explained paramagnetism and paramagnetic cooling.

16.9 Glossary

Paramagnetism: Magnetic property in certain iron bearing minerals that cause them to be weakly attracted to magnetic field.

Curie temperature: The temperature that a magnetic substance losses it magnetic properties.

Magnetic saturation: The maximum amount of magnetic energy that can be absorbed by a magnetic substance.

16.10 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: $x_{dia} = \frac{-ze^2}{6mc^2} r^{-2}$

Ans.2: $x_a = -0.79\times10^{-6}\frac{n^2}{z^2}\left(\frac{5}{2}n^2 - \frac{3}{2}k^2\right)$

Ans.3: -4.2×10^{-6}

Answer To Self Learning Exercise-II

Ans.1:

$$M = \frac{n\mu^2 H}{3K_B (T - \frac{\lambda\mu^2 N}{3K_B})}$$

Ans.2: M = $Ng\mu_B JB(x)$

Ans.3: $C = \frac{\mu_o N\mu^2}{3K_B}$

Ans.6: $-8.55\times10^{-22} A - m^2$

16.11 Exercise

Section-A (Very Short Answer Type Questions)

Q.1 Define diamagnetism.

Q.2 What is diamagnetism material ?

Q.3 Define paramagnetism.

Q.4 Explain the properties of paramagnetism material.

Q.5 Explain the difference between diamagnetism and paramagnetism**.**

Section-B (Short Answer Type Questions)

Q.6 What is magnetic susceptibility? How does it vary for different types of magnetic materials.

Q.7 Distinguish between the dia, para and ferromagnetic materials.

Q.8 What is physical significance of magnetic susceptibility?

Q.9 What is Larmor's precession?

Q.10 What is paramagnetic cooling ?

Section - C (Long Answer Type Questions)

Q.12 Explain Paramagnetism of rare earth ions and iron group ions. Explain the quenching of orbital angular momentum for iron group ions.

Q.12 Discuss Langevin's theory of paramagnetism for a magnetic material.

Q.13 Discuss Langevin's theory of diamagnetism for a magnetic material.

Q.14 On the basis of classical theory derive expression for the paramagnetism susceptibility of free electrons.

Q.15 Explain quantum theory of diamagnetism.

References and Suggested Readings

1. Introduction to Solid State Physics, 7e, Charles Kittle, Willey India Pvt. Ltd.
2. Solid State Physics, S. L. Gupta & V. Kumar, K. Nath & Co.
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UNIT-17
Ferromagnetism

Structure of the Unit

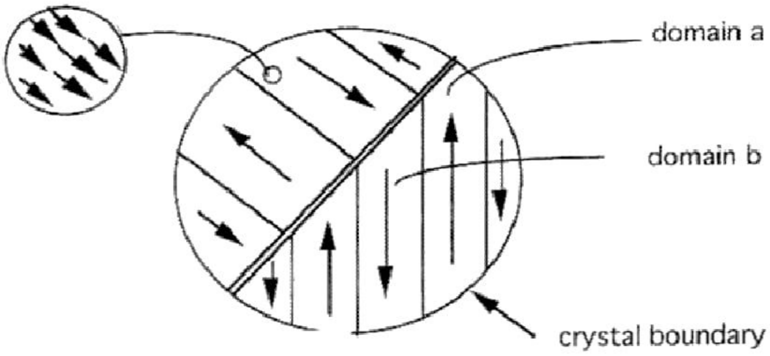
17.0 Objectives

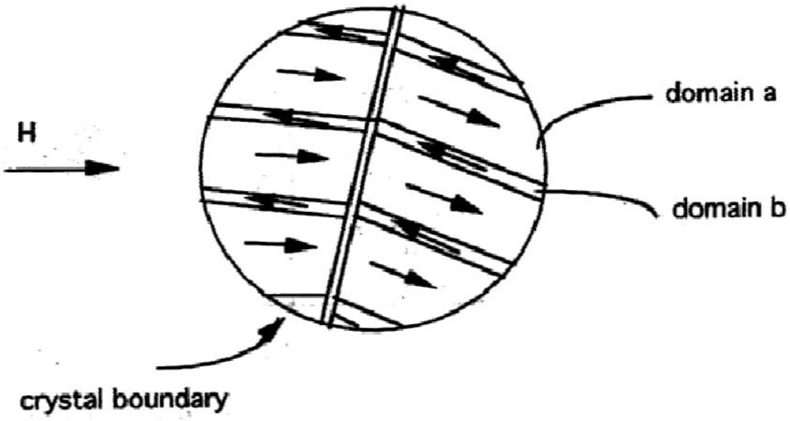
After interacting with the material presented here students will be able to understand

- Concept of Ferromagnetism
- Curie Point of Ferromagnetic material
- Temperature dependence of the saturation magnetization
- Magnons and thermal excitation of them

17.1 Introduction

Ferromagnetism is an extreme case of paramagnetism. If the permanent dipoles resulting from the electron spin are very close together in the medium, there is a quantum mechanical effect, called "exchange" which results in a strong tendency for the spins of adjacent atoms or molecules to line up parallel to each other, even in the absence of a magnetic field. This parallel orientation can extend, in an unmagnetized body, over volumes of a considerable atomic scale. Such a volume containing parallel orientation of magnetic dipoles, is called a "domain."





An ordinary unmagnetized ferromagnetic body contains many domains, each with a strong magnetic moment, but oriented in different directions. In the presence of an external magnetic field, the domains change the orientation of their permanent magnetic moments, lining up with the external magnetic field, until finally when the external magnetic field reaches a certain large value, the moment reaches a limit when all moments are parallel. This limit is called “saturation.” Reversing the external field reverses the moments, but this reorientation is countered by an effect similar to friction, so that by the time the external field is reduced to zero, there can still be a considerable magnetic moment. This is the origin of permanent magnetism. If the external field is reversed alternately between one direction and the other, the magnetic moment lags behind the field, resulting in the phenomenon of hysteresis.

Ferromagnetism tends to decrease with temperature, and the individual domains lose their magnetic moments at a critical temperature known as the “Curie temperature.” The origin of this temperature effect is thermal agitation which opposes the tendency toward orientation.

17.2 Properties of Ferromagnetism Material

1. Large and positive susceptibility.
2. Strong attraction to magnetic fields.
3. Retain their magnetic properties after the external field has been removed.
4. Some unpaired electrons so their atoms have a net magnetic moment.
5. Strong magnetic properties due to the presence of magnetic domains. In these domains, large numbers of atomic moments (10^{12} to 10^{15}) are aligned parallel so that the magnetic force within the domain is strong. When a ferromagnetic material is in the unmagnetized state, the domains are nearly randomly organized and the net magnetic field for the part as a whole is zero. When a magnetizing force is applied, the domains become aligned to produce a strong magnetic field within the part.
6. Iron, nickel, and cobalt are examples of ferromagnetic materials.
7. Magnetization is not proportional to the applied field.

$$B=\mu_0(H+M)$$

17.3 Curie Point and Exchange Integral

Ferromagnetism is the phenomenon of spontaneous magnetization – the magnetization exists in the ferromagnetic material in the absence of applied magnetic field.

Ferromagnetism appears only below a certain temperature, which is known as the ferromagnetic transition temperature or simply as the Curie temperature. This temperature depends on the substance, but its order of magnitude is about 1000°K for Fe, Co, Gd, Dy. It might be however much less. For example it is 70K for EuO and even less for EuS. Thus the ferromagnetic range often includes the whole of the usual temperature region.

Above the Curie temperature, the moments are oriented randomly, resulting in a zero net magnetization. In this region the substance is paramagnetic, and its susceptibility is given by

$$\chi = \frac{C}{T - T_c}$$

which is the Curie-Weiss law. The constant C is called the Curie constant and T_C is the Curie temperature.

The Curie-Weiss law can be derived using arguments proposed by Weiss. In the ferromagnetic materials the moments are magnetized spontaneously, which implies the presence of an internal field to produce this magnetization. Weiss assumed that this field is proportional to the magnetization, i.e.

$$B = \lambda M$$

where λ is the *Weiss constant.* Weiss called this field *the molecular field* and thought that this field results from all the molecules in the sample. In reality, the origin of this field is the *exchange interaction*. The exchange interaction is the consequence of the Pauli exclusion principle and the Coulomb interaction between electrons. Consider for example the system of two electrons. There are two possible arrangements for the spins of the electrons: either parallel or antiparallel. If they are parallel, the exclusion principle requires the electrons to remain far apart. If they are antiparallel, the electrons may come closer together and their wavefunctions overlap considerably. These two arrangements have different energies because, when the electrons are close together, the energy rises as a result of the large Coulomb repulsion. This is actually an explanation of the first Hund rule according to which the system of electrons tends to have a high possible spin, which is not forbidden by the Pauli principle. As we see from this example the electrostatic energy of an electron system depends on the relative orientation of the spins: the difference in energy defines the exchange energy. The exchange interaction is short ranged. Therefore, only nearest neighbor atoms are responsible for producing the molecular field. The magnitude of the molecular (exchange) field is very large – of the order of 10^7G or 10^3T. It is not possible to produce such field in laboratories.

Let us consider the paramagnetic phase: an applied magnetic field B_0 causes a finite magnetization. This in turn causes a finite exchange field B_E. If χ_P is the paramagnetic susceptibility, the induced magnetization is given by

$$M = \chi(B_0 + B_E) = \chi(B_0 + \lambda M)$$

Note that the magnetization is equal to a constant susceptibility times a field only if the fractional alignment is small: this is where the assumption enters that the specimen is in the paramagnetic phase. Above equation should be considered as a self-consistent equation for the magnetization. It can be solved explicitly for the magnitude of the magnetization so that

$$M = \frac{\chi B_0}{1 - \chi\lambda}$$

We know that the paramagnetic susceptibility is given by the Curie law $\chi_P = C/T$, where C is the Curie constant. We then find for the susceptibility of the ferromagnetic material.

$$\chi = \frac{M}{B_0} = \frac{C}{T - C\lambda} = \frac{C}{T - T_c}$$

The susceptibility has a singularity at $T_C = C\lambda$. At this temperature (and below) there exists a spontaneous magnetization, because if C is infinite so that we can have a finite M for zero B_0.

17.4 Temperature dependence of the Saturation Magnetization

The susceptibility of the ferromagnetic material is

$$\chi = \frac{M}{B_0} = \frac{C}{T - C\lambda} = \frac{C}{T - T_c}$$

Using the expression we obtained earlier for C (in paramagnetic material), i.e.

$$C = \frac{Np^2 \mu_B^2}{3k_B}$$

the Curie temperature is given by

$$T_c = \frac{N\lambda p^2 \mu_B^2}{3k_B}$$

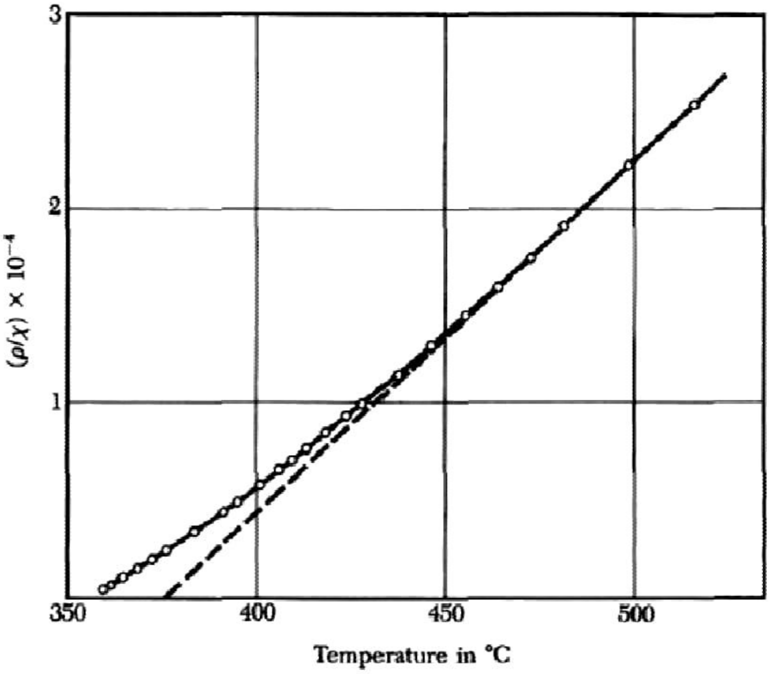


Figure 1: The reciprocal of the susceptibility per gram of nickel in the neighborhood of the Curie temperature (358°C). The dashed line is a linear extrapolation from high temperatures.

The Curie-Weis law describes fairly well the observed susceptibility variation in the paramagnetic region above the Curie point. Only in the vicinity of the Curie temperature a notable deviations are observed. This due to the fact that strong fluctuations of the magnetic moments close to the phase transition temperature can't be described by the mean field theory which was used for deriving the Curie-Weiss law. Accurate calculations predict that at temperatures very close to T_C

$$\chi \propto \frac{C}{(T - T_c)^{1.33}}$$

We can also use the mean field approximation below the Curie temperature to find the magnetization as a function of temperature. We can proceed as before but instead of the Curie law which is valid for not too high magnetic fields and not too low temperatures, we can use the complete Brillouin function. If we omit the applied magnetic field and replace *B* by the exchange field $B_E = \lambda M$ we find

$$M = NgJ\mu_B B_J\left(\frac{gJ\mu_B\lambda M}{kT}\right)$$

where $B_J(x)$ is the Brillouin function. This is a non-linear equation in *M*, which can be solved numerically.

Now we shall see that solutions of this equation with nonzero *M* exist in the temperature range between 0 and T_C. To solve above equation we write it in terms of the reduced magnetization

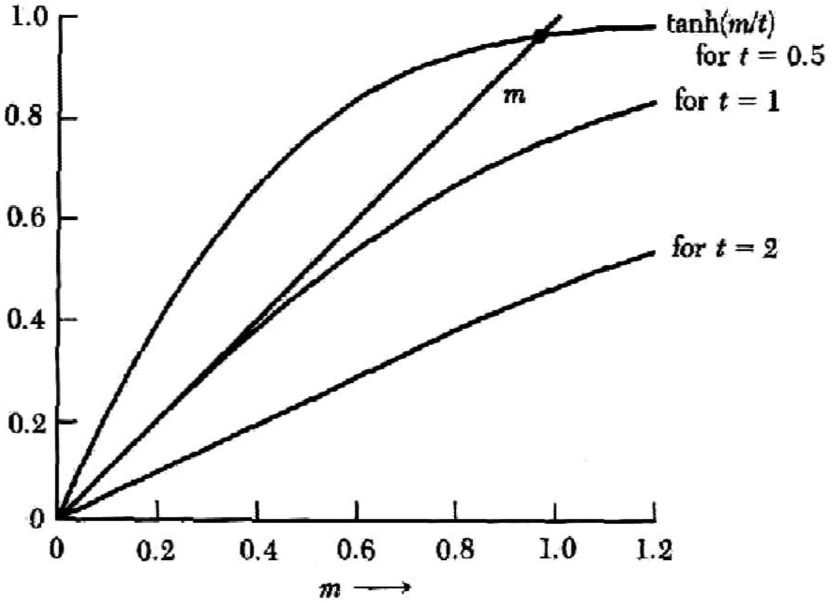
$$M = NgJ\mu_B M$$

and the reduced temperature

$$t = \frac{kT}{Ng^2J^2\mu_B{}^2\lambda}$$

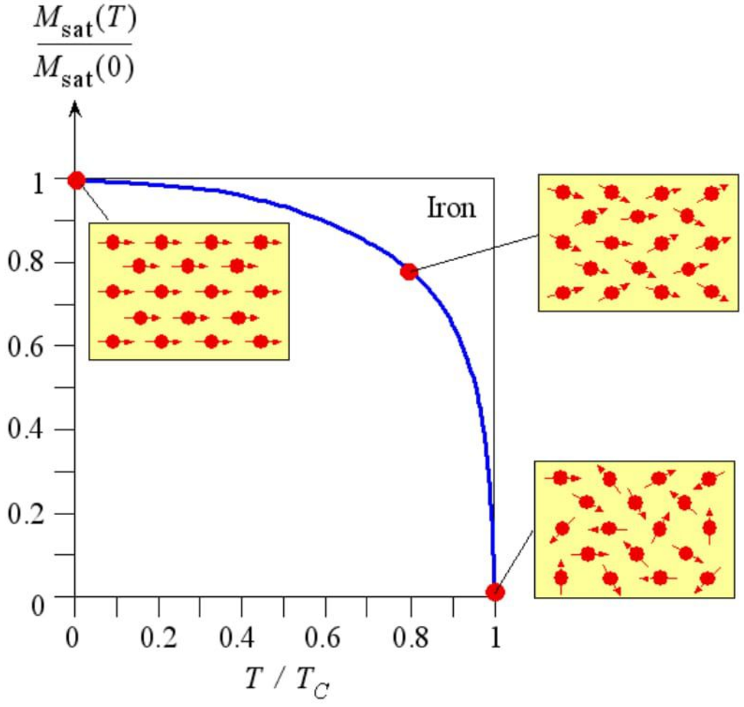
and $m = B_J\left(\frac{m}{t}\right)$

Graphical solution of above equation for the reduced magnetization *m* as a function of temperature. The left-hand side of Eq. is plotted as a straight line *m* with unit slope. The right-hand side Eq. is plotted vs. *m* for three different values of the reduced temperature *t*. The three curves correspond to the temperatures $2T_C$, T_C, and $0.5T_C$. The curve for $t = 2$ intersects the straight line *m* only at $m = 0$, as appropriate for the paramagnetic region (there is no external applied magnetic field). The curve for $t = 1$ (or $T = T_C$) is tangent to the straight line *m* at the origin; this temperature marks the onset of ferromagnetism. The curve for $t = 0.5$ is in the ferromagnetic region and intersects the straight line *m* at about $m = 0.94N\mu_B$,. As $t \rightarrow 0$ the intercept moves up to $m = 1$, so that all magnetic moments are lined up at absolute zero.



The curves of M versus T obtained in this way reproduce roughly the features of the experimental results, as shown in below figure for Iron. As T increases the magnetization decreases smoothly to zero at $T = T_C$.

The mean field theory does not give a good description of the variation of M at low temperatures.



17.5 Self Learning Exercise-I

Very Short Answer Type Questions

Q.1 State Curie-Weiss law.

Q.2 Define Ferromagnetism.

Short Answer Type Questions

Q.3 What is Curie temperature ?

Q.4 Write down any four properties of Ferromagnetism material.

17.6 Magnons-Quantized Spin Wave

In ferromagnetic materials the lowest energy of the system occurs when all spins are parallel to each other in the direction of magnetization. When one of the spins is tilted or disturbed, however, it begins to precess – due to the field from the other spins. Due to the exchange interaction between nearest neighbors the disturbance propagates as a wave through the system, as shown in Figure.

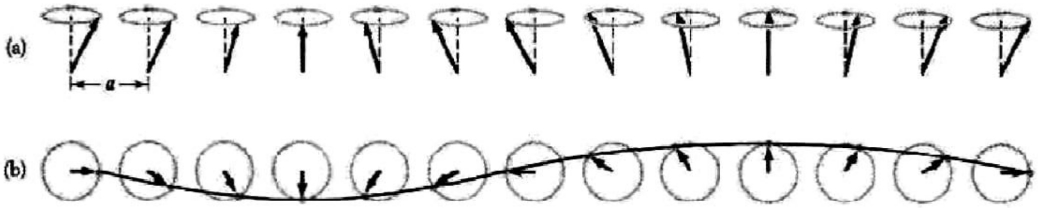


Figure 2 A spin wave on a line of spins, (a) The spins viewed in perspective, (b) Spins viewed from above, showing one wavelength. The wave is drawn through the ends of the spin vectors.

Spin waves are analogous to lattice waves. In lattice waves, atoms oscillate around their equilibrium positions, and their displacements are correlated through lattice forces. In spin waves, the spins precess around the equilibrium magnetization and their precessions are correlated through exchange forces.

Now we derive an expression for the frequency of the spin waves. We consider a linear chain of spins with nearest neighbor spins coupled by the Heisenberg interaction:

$$U = -2J\sum_{p=1}^{N} S_p.S_{p+1}$$

where J is the exchange integral and S_p is spin at site p. For simplicity we will use classical theory in which spin operators are replaces by classical vectors. According to above interaction which involves the p-th spin is

$$-2JS_p.(S_{p-1}+S_{p+1})$$

This interaction can be rewritten as $-\mu_p.B_p$, where $\mu_p=-g\mu_B S_p$ is the magnetic moment associated with spin S_p and B_p is an effective magnetic field or exchange field acting on this moment due to nearest neighbor spins:

$$B_p = -\frac{2J}{g\mu_B}(S_{p-1}+S_{p+1})$$

According to classical mechanics the rate of change of the angular momentum $\hbar S_p$ is equal to the torque $\mu_p \times B_p$ which acts on the spin, i.e.

$$\frac{\hbar dS_p}{dt} = \mu_p \times B_p$$

$$\frac{dS_p}{dt} = -\left(\frac{g\mu_B}{\hbar}S_p\right)\times\left[-\frac{2J}{g\mu_B}(S_{p-1}+S_{p+1})\right]B_p = \frac{2J}{\hbar}S_p \times\left[(S_{p-1}+S_{p+1})\right]$$

Normally the amplitude of excitation is very small, so that $S_p^z \approx S$ and $S_p^x, S_p^y << S$.

This allows to linearize Eqs:

$$\frac{dS_P^x}{dt} = \frac{2J}{\hbar}S\times\left[2S_P^y - S_{P-1}^y - S_{P+1}^y\right]$$

$$\frac{dS_P^y}{dt} = \frac{2J}{\hbar}S\times\left[2S_P^x - S_{P-1}^x - S_{P+1}^x\right]$$

$$\frac{dS_P^z}{dt} = 0$$

By analogy with the problem of lattice vibrations we look for traveling wave solutions of the form

$$S_P^x = u\exp[i(pka-\omega t)]$$

$$S_P^y = v\exp[i(pka-\omega t)]$$

where *u* and *v* are constants and *a* is the lattice constant. we obtain

$$-i\omega u = \frac{2J}{\hbar}S\left[2-e^{-ika}-e^{ika}\right]v = \frac{4J}{\hbar}S\left[1-\cos ka\right]v$$

$$-i\omega v = -\frac{2J}{\hbar}S\left[2-e^{-ika}-e^{ika}\right]u = -\frac{4J}{\hbar}S\left[1-\cos ka\right]u$$

These equations have a solution if the determinant of coefficients is equal to zero, i.e.

$$\begin{vmatrix} i\omega & \frac{4JS}{\hbar}(1-\cos ka) \\ -\frac{4JS}{\hbar}(1-\cos ka) & i\omega \end{vmatrix} = 0$$

This leads to the dispersion relation

$$\omega = \frac{4J}{\hbar}S\left[1-\cos ka\right]$$

With this solution we find that $v = -iu$. This corresponds to circular presession of each spin about the z axis. Then

$$S_P^x = u\cos[(pka-\omega t)]$$

$$S_P^y = u\sin[(pka-\omega t)]$$

In a long wave limit, $ka \ll 1$, we find

$$\omega \sim \frac{2JSa^2}{\hbar}k^2$$

The frequency is proportional to k^2. Note that in the same limit the phonon frequency is proportional to *k*.

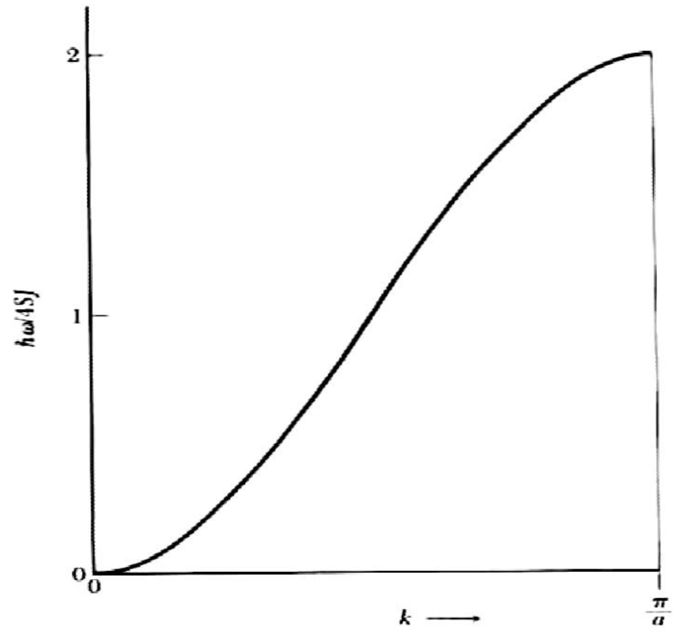


Figure 3: Dispersion relation for magnons in a ferromagnet in one dimension with nearest-neighbor interactions.

Generalization to a three dimensional cubic lattice with nearest neighbor interaction results in

$$\omega = \frac{4JS}{\hbar}\left[z - \sum_{\delta} \cos(k.\delta) \right]$$

where the summation is over the z vectors denoted by δ which join the central atom to its nearest neighbors. In the limit $ka \ll 1$ we find for all three cubic lattices

$$\omega \sim \frac{2JSa^2}{\hbar} k^2$$

which is the same result.

17.7 Thermal Excitation of Magnons

Spin waves can be quantized in a similar way as phonons. A quantized spin wave is called *magnon*. The energy of a magnon mode of frequency ω_k with n_k magnons is given by

$$E_k = \hbar\omega_k(n_k + \frac{1}{2})$$

In thermal equilibrium the average number of magnons excited in the mode k is given by the Planck distribution

$$\langle n_k \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

The total number of magnons excited at temperature T is

$$\sum_k n_k = \int d\omega D(\omega) \langle n(\omega) \rangle$$

where $D(\omega)$ is the number of magnon modes per unit frequency range. The integral is taken over allowed values of k lying in the first Brillouin zone. At sufficiently low temperatures we may carry the integral between 0 and ∞ ,because $<n(\omega)> \rightarrow 0$ exponentially as $\omega \rightarrow \infty$.

Magnons have a single polarization for each value of ***k***. In three dimensions the number of modes of wavevector less than k is $(1/2\pi)^3(4\pi k^3/3)$ per unit volume, whence the number of magnons $D(\omega)d\omega$ with frequency in $d\omega$ at ω is $(1/2\pi)^3(4\pi k^2)(dk/d\omega)d\omega$.

In the longwave limit [$\omega \sim (2JSa^2/\hbar)k^2$] (we can use a longwave limit here because at low temperatures only magnons which have low frequency and therefore small wavevector are thermally excited), we find

$$\frac{d\omega}{dk} = \frac{4JSa^2}{\hbar} k = 2\left(\frac{2JSa^2}{\hbar}\right)^{1/2} \omega^{1/2}$$

Therefore the density of magnon modes is

$$D(\omega) = \frac{1}{4\pi^2}\left(\frac{\hbar}{2JSa^2}\right)^{3/2} \omega^{1/2}$$

Thus the total number of magnons is

$$\sum_k n_k = \frac{1}{4\pi^2}\left(\frac{\hbar}{2JSa^2}\right)^{3/2}\int_0^\infty d\omega \frac{\omega^{1/2}}{\exp(\hbar\omega/k_BT)-1} = \frac{1}{4\pi^2}\left(\frac{k_BT}{2JSa^2}\right)^{3/2}\int_0^\infty dx \frac{x^{1/2}}{e^x-1}$$

The definite integral is equal to $(0.0587)(4\pi^2)$.

The number of N of atoms per unit volume is Q/a^3, where Q=1,2,4 for sc, bcc and fcc lattices. Since the excitation of a magnon corresponds to the reversal of one spin, $\sum_k n_k / NS$ is equal to the fractional change of magnetization $\Delta M / M$, whence

$$\frac{\Delta M}{M} = \frac{0.0587}{SQ}\left(\frac{k_BT}{2JS}\right)^{3/2}$$

The result is the *Bloch* $T^{3/2}$ *law* which is confirmed experimentally.

17.8 Self Learning Exercise -II

Short Answer Type Questions

Q.1 What is magnon?

Q.2 Draw the dispersion relation for magnons in a ferromagnet in one dimension with nearest-neighbor interactions.

Q.3 State *Bloch* $T^{3/2}$ *law.*

Long Answer Type Questions

Q.4 Explain thermal excitation of magnons.

17.9 Summary

In this chapter we firstly introduce Ferromagnetism and properties of Ferromagnetic materials followed by Curie Point of Ferromagnetic material, Temperature dependence of the saturation magnetization, Magnons and thermal excitation of them.

17.10 Glossary

Crystal Structure: For crystalline materials, the manner in which atoms or ions are arrayed in space. It is defined in terms of the unit cell geometry and the atom positions within the cell.

Curie Temperature: It is the temperature above which a ferromagnetic or ferrimagnetic material becomes paramagnetic.

Ferromagnetism: Permanent and large magnetizations found in some metals (e.g., Fe, Ni, and Co), which result from the parallel alignments of neighboring magnetic moments.

Hysteresis (magnetic): The irreversible magnetic flux density-versus-magnetic field strength (B-versus-H) behavior found for ferromagnetic and ferrimagnetic materials.

Magnetic Susceptibility: The proportionality constant between the magnetization M and the magnetic field strength H.

Magnetization: The total magnetic moment per unit volume of material. Also, a measure of the contribution to the magnetic flux by some material within an H field.

Relative Magnetic Permeability: The ratio of the magnetic permeability of some medium to that of a vacuum.

Resistivity : The reciprocal of electrical conductivity, and a measure of a material's resistance to the passage of electric current.

17.11 Answer to Self Learning Exercises

Answer to Self learning exercise-I

Ans.1: $\chi = \dfrac{C}{T - T_c}$

Ans.2: Ferromagnetism is the phenomenon of spontaneous magnetization – the magnetization exists in the ferromagnetic material in the absence of applied magnetic field.

Ans.3: Curie temperature is the temperature above which a ferromagnetic or ferrimagnetic material becomes paramagnetic.

Ans.4:

1. Large and positive susceptibility.
2. Strong attraction to magnetic fields.

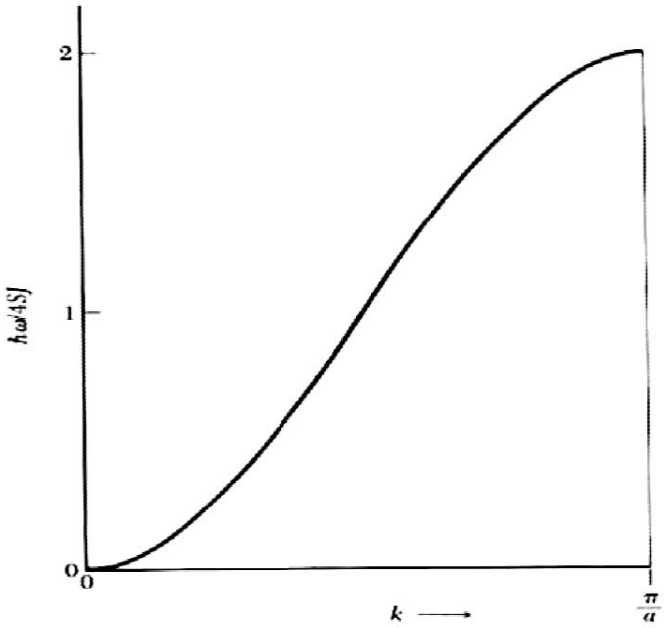
3. Retain their magnetic properties after the external field has been removed.

4. Some unpaired electrons so their atoms have a net magnetic moment.

Answer of Self Learning Exercise-II

Ans.1: A quantized spin wave is called *magnon*.

Ans.2:



Ans.3:

$$\frac{\Delta M}{M} = \frac{0.0587}{SQ}\left(\frac{k_B T}{2JS}\right)^{3/2}$$

Ans.4: Section 17.7

17.12 Exercise

Q.1 What is the origin of magnetic dipoles ?

Q.2 How does magnetic dipole relates to the orbital angular momentum and spin?

Q.3 What is saturation magnetization ?

Q.4 What is the physical origin of the exchange interaction ?

Q.5 What is the form of magnetic interaction Hamiltonian ?

References and Suggested Readings

1. Introduction to Solid State Physics(2004) by Charles Kittel.
2. Magnetic Properties of Solids by M. S. Dresselhaus.
3. Solid State Physics: Structure and Properties of Materials, 2009, by M. A. Wahab.
4. Solid State Physics: An Introduction to Solid State Electronic Devices, 2010, by A. K. Saxena

UNIT-18
Ferromagnetic Domain, Antiferromagnetism , Ferrimagnetism

Structure of the Unit

18.0 Objectives

After interacting with the material presented here students will be able to understand

1. Ferromagnetism
2. Antiferromagnetism
3. Ferrimagnetism
4. Origin of domains-Magnetic energy, Anisotropic energy, Bloch wall, Magnetostriction,

18.1 Ferrimagnetism

The Heisenberg model leads to ferromagnetism, if the constant *J* is positive. The parallel aligned state will then have a lower energy then the antiparallel state. The negative constant leads to antiferromagnetism or ferrimagnetism. Figure 1b illustrates an *antiferromagnetic* arrangement, in which the dipoles have equal moments, but adjacent dipoles point in opposite directions. Thus the moments balance each other, resulting in a zero net magnetization. Another type of arrangement commonly encountered is the *ferrimagnetic* pattern shown in Figure 1c. Neighboring dipoles point in opposite directions, but since in this case the moments are unequal, they do not balance each other completely, and there is a finite net magnetization.

Now we discuss the ferrimagnetic arrangement.

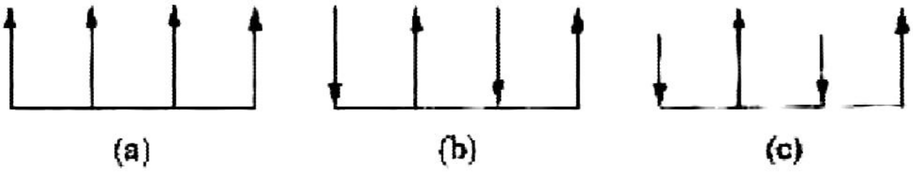


Figure 4: a. ferromagnetic, b. antiferromagnetic, c. ferrimagnetic

The most familiar example of a ferrimagnetic material is magnetite, Fe_3O_4. More explicitly, the chemical composition is $FeO.Fe_2O_3$, showing that there are two types of iron ions: ferrous (doubly charged), and ferric (triply charged). The compound crystallizes in the spinel structure. The unit cell contains 56 ions, 24 of which are iron ions and the remainder oxygen. The magnetic moments are located on the iron ions. If we study the unit cell closely, we find that the Fe ions are located in either of two different coordinate environments: A tetrahedral one, in which the Fe ion is surrounded by 4 oxygen ions, and an octahedral one, in which it is surrounded by 6 oxygen ions. Of the 16 ferric ions in the unit cell, 8 are in one type of position and 8 are in the other. Furthermore, the tetrahedral structure has moments oriented opposite to those of the octahedral one, resulting in a complete cancellation of the contribution of the ferric ions. The net moment therefore arises entirely from the 8 ferrous ions which occupy octahedral sites. Each of these ions has six 3d electrons,

whose spin orientations are $\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow$. Hence each ion carries a moment equal to 4 Bohr magneton.

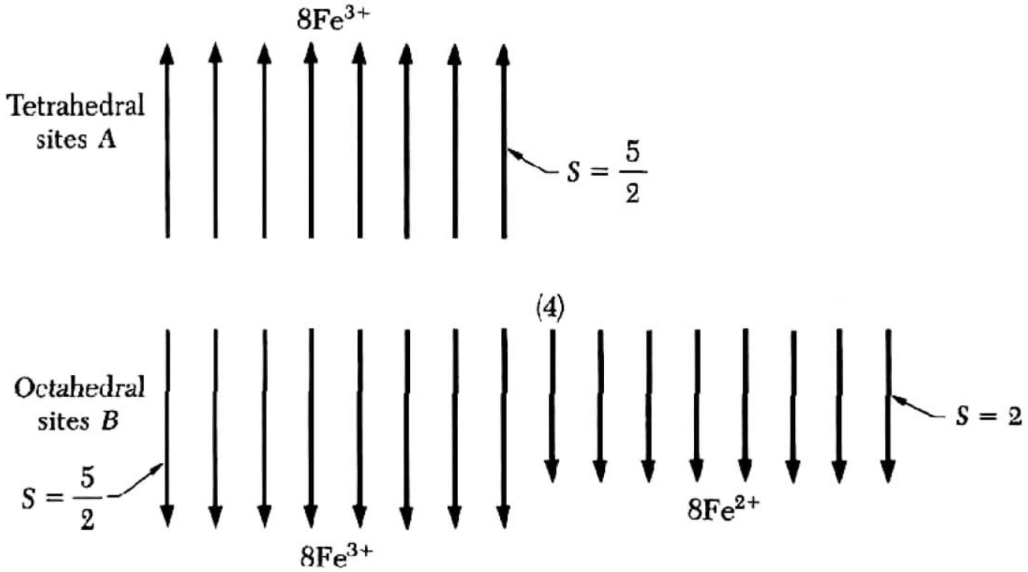


Figure 5: Spin arrangements in magnetite, FeO.Fe2O3, showing how the moments of the Fe3+ ions cancel out, leaving only the moments of the Fe2+ ions.

There are many other materials which have ferrimagnetic properties. An important class of magnetic oxides is known as ferrites. The usual chemical formula of a ferrite is $MO.Fe_2O_3$, where M is a divalent cation, often Zn, Cd, Fe, Ni, Cu, Co, or Mg.

Now we calculate the Curie temperature and susceptibility of ferromagnets using the mean field theory.

For this we assume that the lattice consists of two types of ions which have different magnetic moments and positions at sites A and B. We assume that there is an antiparallel interaction between the A and B sites so that $\mathbf{B}_A = -\lambda M_B$ and $B_\mathbf{B} = -\lambda \mathbf{M}_\mathbf{A}$, where λ is positive. We define Curie constants C_A and C_B for the ions on the A and B sites. Within the mean field approximation we obtain

$$M_A = \frac{C_A}{T}(B_0 - \lambda M_B)$$

$$M_B = \frac{C_B}{T}(B_0 - \lambda M_A)$$

where B_0 is the applied field. These equations have a nonzero solution for M_A and M_B in zero applied field if

$$\begin{vmatrix} T & \lambda C_A \\ \lambda C_B & T \end{vmatrix} = 0$$

So that the ferrimagnetic Curie temperature is given by

$$T_C = \lambda\sqrt{C_A C_B}$$

We solve above equation for M_A and M_B to obtain the susceptibility at $T > T_c$:

$$\chi = \frac{M_A + M_B}{B_0}$$

$$\therefore \chi = \frac{(C_A + C_B)T - 2\lambda C_A C_B}{T^2 - T_c^2}$$

This result is more complicated than that for ferromagnets. Experimental values for Fe_3O_4 are plotted in Figure3. The curvature of the plot of $1/\chi$ versus T *is* a characteristic feature of a ferrimagnet.

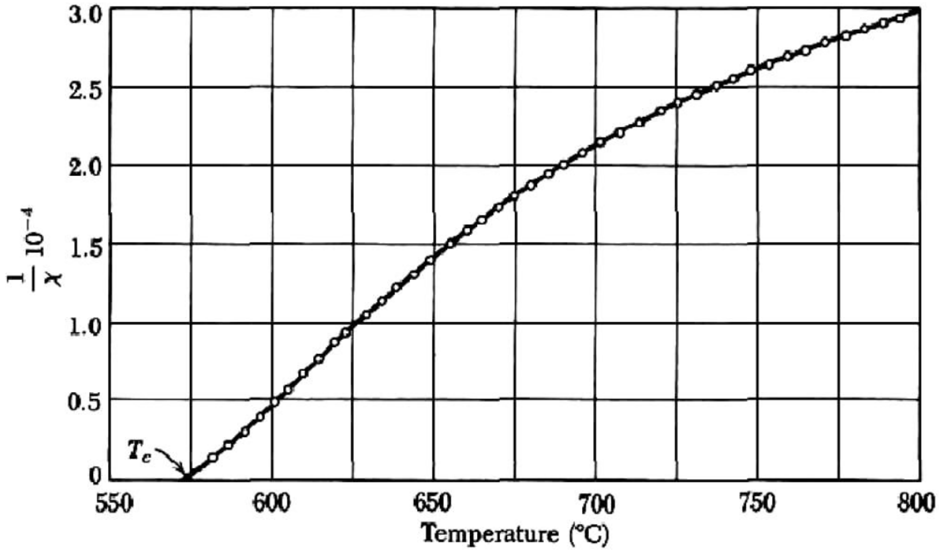


Figure 3

Many ferromagnets exhibit a very interesting behavior of the saturation magnetization versus temperature which is shown in Figure 4.

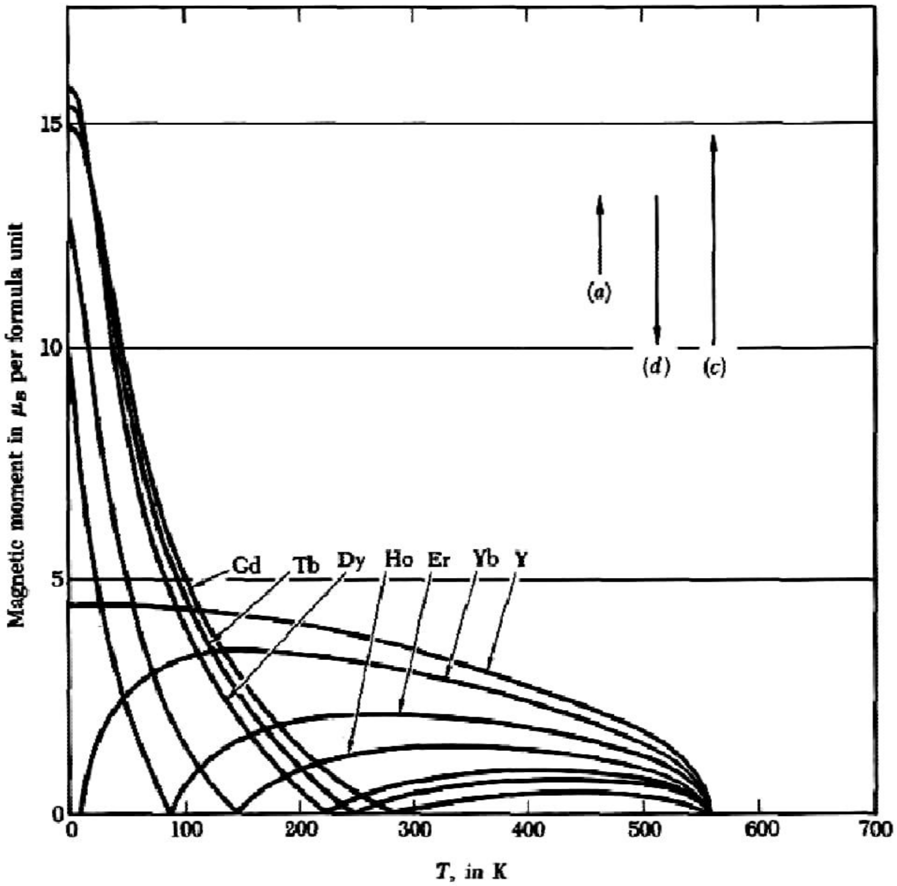


Figure 4

18.2 Antiferromagnetism

An antiferromagnet is a special case of a ferrimagnet for which both sublattices *A* and B have equal saturation magnetizations.

In an antiferromagnet the spins are ordered in an antiparallel arrangement with zero net moment at temperatures below the ordering temperature which is called the *Néel temperature*. Thus $C_A = C_B$, and $T_N=\lambda C$. where *C* refers to a single sublattice. This expression is identical to that we obtained earlier for ferromagnetic materials. However, in this case the susceptibility in the paramagnetic region behaves in a different fashion. For $T > T_N$ we obtain

$$\chi = \frac{2CT - 2\lambda C^2}{T^2 - (\lambda C)^2} = \frac{2C}{T + T_N}$$

At and above the Néel temperature the susceptibility is nearly independent of the direction of the field relative to the spin axis. However, below the Néel temperature the susceptibility of antiferromagnets depends strongly on the orientation of magnetic field. There are two situations: with the applied magnetic field perpendicular to the axis of the spins; and with the field parallel to the axis of the spins.

For B_0 perpendicular to the axis of the spins we can calculate the susceptibility from the energy density which is

$$U = \lambda M_A . M_B - B_0 .(M_A + M_B) \cong -\lambda M^2 \left(1 - \frac{1}{2}(2\varphi^2)\right) - 2B_0 M\varphi$$

where $M = |M_A| = |M_B|$, and the angle that the spins make with each other is 2φ (Figure 5a). In Figure Magnetic susceptibility parallel and perpendicular to the tetragonal axis.

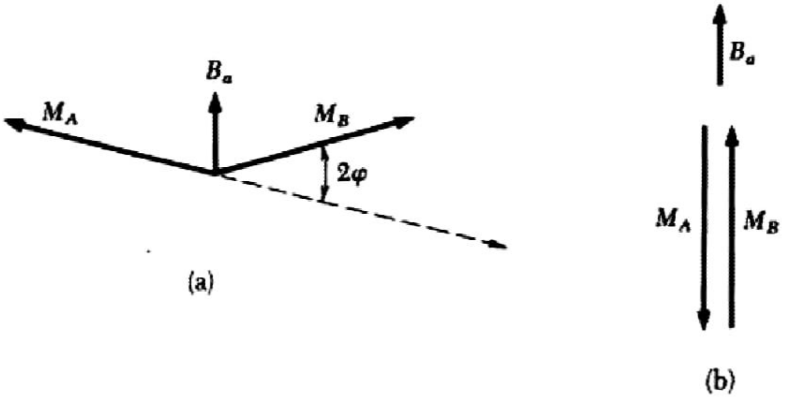


Figure 5

The energy is a minimum when

$$\frac{dU}{d\varphi} = 0 = 4\lambda M^2 \varphi - 2B_0 M$$

$$\varphi = \frac{B_0}{2\lambda M}$$

so that

$$\chi_\perp = \frac{2M\varphi}{B_0} = \frac{1}{\lambda}$$

In the parallel orientation (Figure 5b) the magnetic energy is not changed if the spins make equal angles with the field. Thus the susceptibility at T=0K is zero.

$$\chi_{\parallel} = 0$$

The parallel susceptibility increases smoothly with temperature up to T_N. The $\chi_{\perp}, \chi_{\parallel}$ for MnF_2 are shown in Figure6.

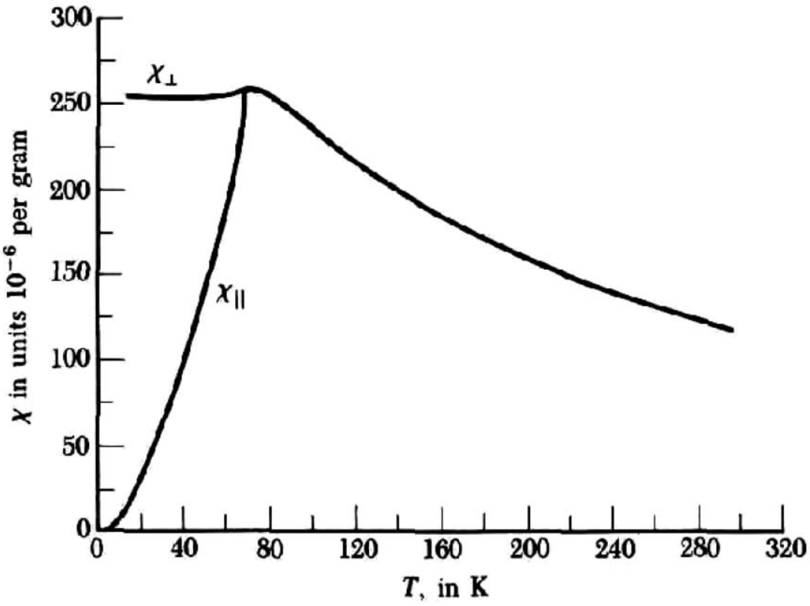


Figure 6

18.3 Self Learning Exercise -I

Very Short Answer Type Questions

Q.1 Write down example of ferrimagnetic material.

Short Answer Type Questions

Q.2 Design ferromagnetic, antiferromagnetic, ferrimagnetic pattern.

Q.3 Define *antiferromagnetic* arrangement.

Q.4 What is *Néel temperature*?

18.4 Magnetic Domains in Ferromagnetic Materials

Magnetization Curve

If we apply a magnetic field to a previously demagnetized ferromagnetic specimen its magnetization will gradually increase. Starting from point O, the magnetization increases relatively fast at first, then the increase becomes slower, until it reaches a constant value at point A. At this point, the specimen is saturated. This curve is *the initial magnetization curve*. The *saturation magnetization* M_s is equal to the *spontaneous magnetization*.

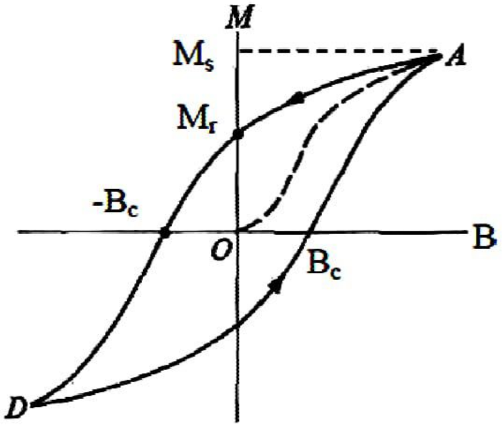


Figure 7: (Magnetization curve) The coercivity B_C is the reverse field that reduces M to zero. The remanence M_r is the value of M at B = 0. The saturation magnetization M_S is the limit of M at large B

If the field, *B* is now decreased, *M* does not retrace the initial magnetization curve, but decreases more slowly and when *B* reaches zero, *M* still has a non-zero value M_r. This is the largest magnetization we can get in zero field. It is called the *remanent magnetization* or *remanence*. In order to decrease *M* further, we must apply a field in the opposite direction. When the reverse field is sufficiently large, *M* passes through zero. The reverse field needed to bring the magnetization to zero from remanence is called the *coercive field* or *coercivity* B_c. A further increase of the reverse field results in increasing *M* in the direction in which *H* is now applied. Eventually, *M* reaches the saturation value M_s again. If we continue to change *B* between large values in opposite directions, *M* will vary repeatedly along the closed loop. This loop is called the *hysteresis loop*.

Magnetic Domains

Within each domain the magnetization is uniform and equal to the spontaneous magnetization. However different domains are magnetized in different directions. Now if we calculate the average magnetization of this sample it will not be equal to the spontaneous magnetization. The average magnetization of a specimen will be than M_S and could even be zero (if we have the appropriate domain configuration).

Why ferromagnetic materials are subdivided into domains rather than be uniformly magnetized ? We know that a system will always be in a state in which its energy is minimum. We have to explain therefore why a subdivided state has a smaller energy than a uniformly magnetized state. There are four types of energy which contribute to the total energy of the material.

1. ***Exchange energy***

This is the energy which is responsible for ferromagnetism of magnetic materials. The exchange coupling between nearest neighbors is significant and results in parallel alignment of the magnetizations in ferromagnetic materials. In a classical view of the Heisenberg representation the exchange coupling between nearest spins can be written as follows:

$$E_{ex} = -2JS_iS_j = -2JS_iS_j\cos\theta$$

where J is the exchange integral and $\mathbf{S}_i$ and $\mathbf{S}_j$ are two neighboring spins. The sign of the exchange integral determines whether we have ferromagnetic or antiferromagnetic coupling. For ferromagnetic materials J is positive.

If there were no other type of energy to consider, then obviously all magnetic materials would be magnetized to saturation all the time. In the presence of other interactions the exchange coupling tries to ensure that the angle between them is as small as possible. Because the exchange interaction is strong, we may assume that the angle between two spins $\delta\varphi$ is small. In this case

$$E_{ex} \sim 2JS^2\delta\varphi^2 / 2 + const$$

where we assumed that $S=S_i=S_j$. The constant is independent of angle and can be put equal to zero because we can measure all the energies relative to this constant.

Now consider a material with a simple cubic structure with a lattice constant a. Let x, y and z to be the Cartesian axes and assume for simplicity that the magnetic moments are parallel everywhere to yz plane. The orientation of magnetic moments varies with x so that φ is the angle between the magnetic moment and the y-axis and $\delta\varphi$ is the angle between neighboring moments. Because $\delta\varphi$ is normally very small ,we can regard it as a continuous function of x and therefore

$$\delta\varphi \sim a\frac{d\varphi}{dx}$$

Therefore the exchange energy per unit volume is

$$E_{ex} \sim \frac{JS^2a^2}{V}\left(\frac{d\varphi}{dx}\right)^2 = A\left(\frac{d\varphi}{dx}\right)^2$$

where A is the *exchange stiffness constant* which can serve as a characteristic of a ferromagnetic material. A typical value for the exchange stiffness constant in ferromagnetic metals is 10^{-6} erg/cm.

2. *Magnetostatic energy*

Why a magnetic material should not always be uniformly magnetized like as is shown in Figure 8a.

The state of uniform magnetization has the lowest possible exchange energy, since all adjacent spins are parallel to each other. However, the exchange energy is not the only type of energy that a magnetic material has. This state costs a large amount of magnetostatic energy. The magnetization generates north poles on the top surface and south poles on the bottom surface. These poles act as the source of magnetic field. They can be thought as "magnetic" charges. These poles produce a magnetic field which is shown in Figure 8a.

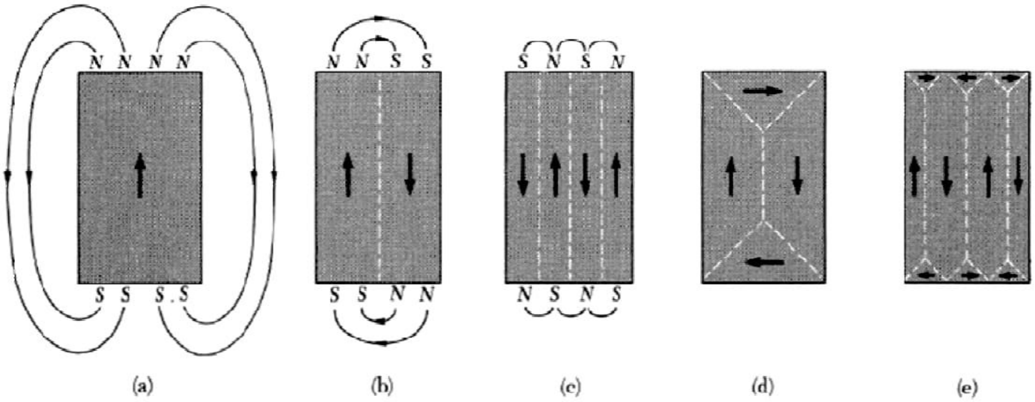


Figure 8

In addition to the field outside the specimen there is also field inside the specimen. This field is in the opposite direction to the magnetization. This field tries to demagnetize the specimen and is called the *demagnetization field* $\boldsymbol{B_d}$. The respective energy is called magnetostatic or demagnetization energy. The density of this energy is given by

$$E_m = -\frac{1}{2} M B_d$$

The value of $\boldsymbol{B}_d$ depends on the shape of the specimen, and is usually written as

$$B_{dy} = -N_y M_y$$
$$B_{dz} = -N_z M_z$$
$$B_{dx} = -N_x M_x$$

where N_x, N_y, and N_z are the *demagnetization factors.* This factor, which is large for a flat sample and small for an elongated sample, is equal to unity for a sample in the shape of a thin, flat disc normal to the field. The magnetostatic energy is of the order of 10^7 erg/cm^3. The fields which are produced by the uniformly magnetized sample are huge and the magnetic system will try to reduce them.

What happens if the specimen is subdivided into two domains (Figure 8b). In this case the top surface carries north poles on the left and south poles on the right, and the bottom surface carries south poles on the left and north poles on the right. The demagnetizing field does not extend from the top surface to the bottom, but it is confined to the region near the two ends of the specimen. As the specimen is further subdivided into smaller domains, the effect of the demagnetizing field becomes even smaller (Figure 8 c,d).

What happens with the exchange energy in a state where the magnetic sample is subdivided into domains. You see that this state does not correspond to a minimum of the exchange energy. The exchange energy is minimized for uniformly magnetized material. However, the exchange interaction is quite short-ranged. Therefore, only spins near domain boundaries will experience unfavorable exchange interactions with the nearby spins in the neighboring misaligned domain. On the contrary, the dipolar interaction is long-ranged. Therefore, all the spins in the sample are involved in the magnetic dipolar interactions. And therefore, subdivision into domains is energetically favorable.

We see therefore that the main reason for the subdivision into domains is magnetostatic energy.

3. *Anisotropy energy*

What is wrong with a configuration in which magnetization is gradually rotates? If the magnetization rotates very slowly, it has very little exchange energy. It appears however that this configuration does not normally exist.

There is usually a structure consisting of uniformly magnetized domains, separated by narrow boundaries. The reason is that there is another kind of energy which is called magnetic anisotropy. It arises from the crystalline nature of most magnetic materials. That is why it is often called *magnetocrystalline anisotropy*.

Due to crystalline structure of most magnetic materials the directions in which the magnetization is allowed to point are restricted. The magnetization prefers to be parallel to certain crystallographic directions. In this sense crystals are anisotropic. If the magnetization deviates from these directions there is an extra cost in energy which is called the *anisotropy energy*.

The origin of magnetocrystalline anisotropy is spin-orbit interaction. The magnetization of the crystal sees the crystal lattice through orbital overlap of the electrons: the spin interacts with the orbital motion by means of the spin-orbit coupling.

Magnetic anisotropy reflects the symmetry of the lattice. In cubic monocrystals the anisotropy energy can be expressed as

$$E_\alpha = K_1(\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2$$

where K_1 is the first order ,

K_2 is the second order anisotropy constants and

α_1, α_2, α_3 are the direction cosines referred to the cube axes.

This form of the expression comes from symmetry considerations. It can be shown that this expression is invariant under all transformation of the cubic symmetry. If constants K_1 and K_2 are positive (of the order of 10^5 erg/cm^3), the anisotropy energy has a minimum when the magnetization is aligned along (100) direction. This is the case for example for iron. (100) is called the easy axis because the magnetization can be very easily saturated if the magnetic field is applied in this direction.

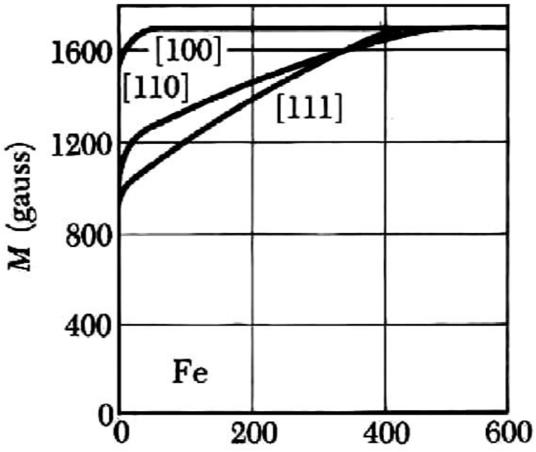


Figure 9: Magnetization curves for single crystal of iron. From the curves for iron we see that the [100] directions are easy directions of magnetization and the [110] and [111] directions are hard directions.

This can be seen from above Figure 9, where the magnetization of iron as a function of the magnetic field is shown. If the magnetic field is applied along (100) direction the magnetization very rapidly riches the saturation. On the contrary, if the magnetic field is applied along (110) or (111) directions ,the magnetizations reach the saturation only in a relatively high fields. That is why (110) and (111) axes are called the hard axes of magnetization.

In uniaxial crystals which have tetragonal, hexagonal and trigonal symmetries, the anisotropy per unit volume can be written as

$$E_\alpha = K_1 \sin^2\theta + K_2 \sin^4\theta$$

where θ is the angle between the magnetization and the main symmetry axis. If $K_1>0$ the magnetization prefers to be parallel to the symmetry axis. In this case this axis is called the easy axis. If $K_1<0$ it prefers to be perpendicular to the symmetry axis. In this case it is called the hard axis.

Now let us return to the domain structures. The domain configuration with gradually rotating magnetization is not possible because it would cost too much anisotropy energy because in a large part of the specimen the magnetization is not parallel to an easy direction. The magnetization prefers certain direction in crystals and can not rotate gradually over long distances. In order to reduce the anisotropy energy the domains have to have abrupt boundaries.

This configuration would have very little exchange, magnetostatic and anisotropy energy if this is a cubic crystal and this is (100) direction. It turns out however that simple structures with large domains do not usually occur. We usually have a much larger number of much smaller domains. In order to understand why it happens we have to consider the magnetoelastic energy.

4. *Magnetoelastic energy*

When the magnetization of the material is changed, there is a slight change in its dimensions, generally of the order of 10^{-5} or less. Some materials expand in the direction of the magnetization, others, for example nickel, contract. This effect is called *magnetostriction*. The materials which expend are said to have positive magnetostriction, the materials which contract are said to have negative magnetostriction. Therefore, the change in the magnetization of the material results in elastic distortions. The energy associated with these distortions is called the *magnetoelastic energy*. The larger the domains are, the more elastic energy is needed. It is therefore favorable to form smaller domains at the domain boundaries of larger domains. This costs less elastic energy to hold the domains together.

Domain walls

In order to complete the picture about domain structures we should consider the boundary between neighboring domains which called domain walls. Qualitatively it is clear that the width of the domain wall is determined by the balance between the exchange energy and the anisotropy energy. If the exchange is very strong and anisotropy is small ,we can expect that the width of the domain wall is large. On the contrary, in the case when the exchange energy is small and anisotropy is large, the width of the domain wall should be small.

In order to calculate the width of the domain wall we assume that we have a 180° domain wall as is shown in Figure10. That means that this wall separates two domains magnetized in opposite directions – the magnetization rotates by 180 degrees.

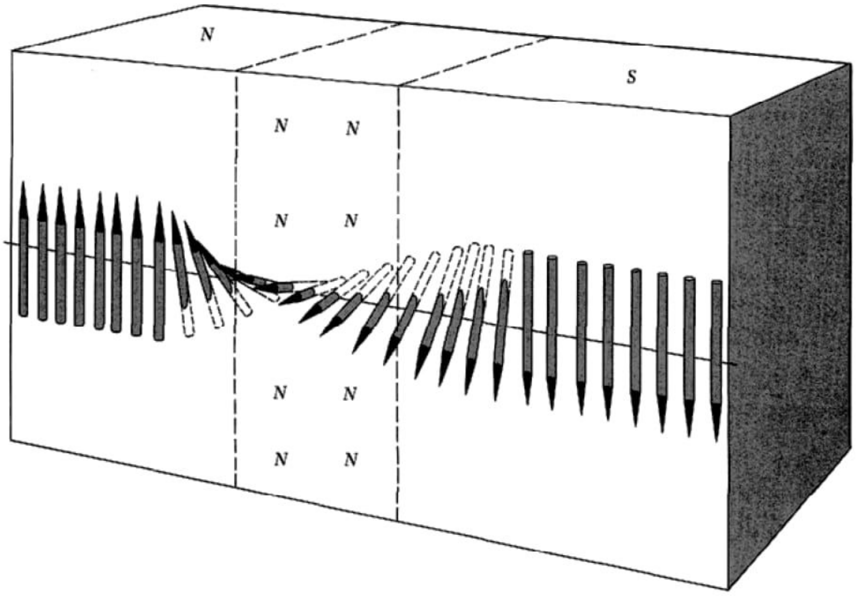


Figure 10

The exchange energy per unit area of the domain wall is

$$E_{ex} = A\left(\frac{d\phi}{dx}\right)^2 \delta$$

where δ is the domain wall width. For the case considered we can use estimate

$$\left(\frac{d\phi}{dx}\right)^2 = \left(\frac{\pi}{\delta}\right)^2$$

So that

$$E_{ex} = A\frac{\pi^2}{\delta}$$

For the anisotropy energy per unit area we take a rough estimate

$$E_{ex} = K\delta$$

where *K* is anisotropy constant. The total energy of the domain wall per unit area is

$$E = E_{ex} + E_a = A\frac{\pi^2}{\delta} + K\delta$$

In the equilibrium we have $\dfrac{dE}{d\delta} = 0$

which gives

$$\delta = \pi\sqrt{A/K}$$

and $$E = 2\pi\sqrt{AK}$$

For typical values $A \sim 10^{-6}$erg/cm and $K \sim 10^{5}$erg/cm^3 we have $\delta \sim 100$nm. The typical size of the domains is 1-100μm and therefore the width of the domain walls is much smaller. That is why the domain structure consists of uniformly magnetized domains separated by narrow boundaries.

The Effect of Applied Field and Domain Wall Motion

Now we consider qualitatively the effect of applied field on the domain structure. The applied magnetic field tends to align the magnetization parallel to the field. There are two ways to reduce the energy. First, the domain wall can move, thereby increasing the volume of the domain whose energy is lower and decreasing the volume of the other. Second, the magnetization direction of the two domains can change. Both these processes, i.e. the domain wall motion and the magnetization rotation, can occur in practice.

The position of the domain walls depends on the demagnetizing energy. When the external field is applied, the magnetic field inside the specimen is the sum of the demagnetizing field and the applied field. The domain walls will therefore generally move to new positions. On the other hand, the magnetization orientations are determined mainly by the anisotropy, which resists the rotation of the magnetization. In general therefore domain wall motion tends to occur in small applied fields, and the magnetization rotation only begins as the field is large enough.

Domain walls move reversibly in very small magnetic fields. In other words, the domain walls are displaced by a small amount when the field is applied, but if the field is removed, they return to their original positions. In larger fields the domain wall motion becomes irreversible - the walls do not return to their original positions when the field is removed. The main reason of that is that the domain wall energy is not a constant but varies in an irregular manner because of imperfections of the specimen. These imperfections are dislocations, grain boundaries, voids, lattice distortions, impurities. When the aligning field is removed, these defects may prevent the domain walls from returning to their original configuration. It then becomes necessary to apply a rather strong field in the opposite direction to restore the unmagnetized configuration. This is the origin of the *hysteresis* in ferromagnetic materials.

18.5 Self Learning Exercise-II

Very Short Answer Type Questions

Q.1 Why the magnetization can be much less than the saturation magnetization and even equal to zero?

Q.2 Write down the Heisenberg representation of the exchange coupling energy between nearest spins.

Short Answer Type Questions

Q.3 Draw *magnetization curve.*

Q.4 What is *coercive field* or *coercivity*, B_c ?

Q.5 Why a magnetic material should not always be uniformly magnetized?

18.6 Summary

The unit starts with the introduction of Ferromagnetism, Antiferromagnetism, and Ferrimagnetism followed by Origin of domains.

18.7 Glossary

Antiferromagnetism: A phenomenon observed in some materials in which complete magnetic moment cancellation occurs as a result of antiparallel coupling of adjacent atoms or ions. The macroscopic solid possesses no net magnetic moment.

Crystal Structure: For crystalline materials, the manner in which atoms or ions are arrayed in space. It is defined in terms of the unit cell geometry and the atom positions within the cell.

Curie Temperature: It is the temperatue above which a ferromagnetic or ferrimagnetic material becomes paramagnetic.

Ferroelectric: A dielectric material that may exhibit polarization in the absence of an electric field.

Ferromagnetism: Permanent and large magnetizations found in some metals (e.g., Fe, Ni, and Co), which result from the parallel alignments of neighboring magnetic moments.

Hysteresis (magnetic) : The irreversible magnetic flux density-versus-magnetic field strength (B-versus-H) behavior found for ferromagnetic and ferrimagnetic materials.

Magnetic Susceptibility : The proportionality constant between the magnetization M and the magnetic field strength H. In general it is tensor quantity.

Magnetization : The total magnetic moment per unit volume of material. Also, a measure of the contribution to the magnetic flux by some material within an H field.

Relative Magnetic Permeability : The ratio of the magnetic permeability of some medium to that of a vacuum.

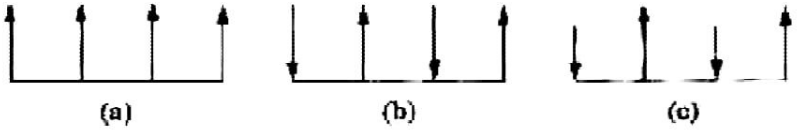
Resistivity : The reciprocal of electrical conductivity, and a measure of a material's resistance to the passage of electric current.

18.8 Answer To Self Learning Exercises

Answer To Self Learning Exercise-I

Ans.1: Fe_3O_4.

Ans.2: a. ferromagnetic, b. antiferromagnetic, c. ferrimagnetic



Ans.3: In *antiferromagnetic* arrangement the dipoles have equal moments, but adjacent dipoles point in opposite directions. Thus the moments balance each other, resulting in a zero net magnetization.

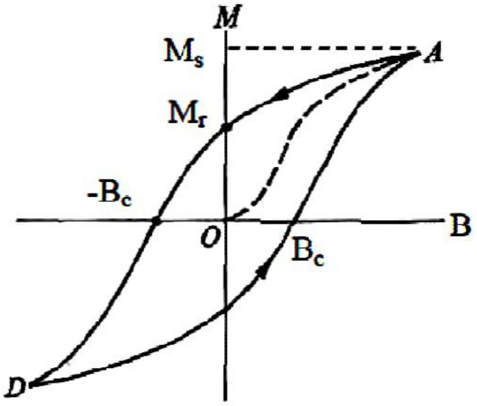
Ans.4: In an antiferromagnet the spins are ordered in an antiparallel arrangement with zero net moment at temperatures below the ordering temperature which is called the *Néel temperature*.

Answer To Self Learning Exercise-II

Ans.1: Magnetic domains.

Ans.2: $E_{ex} = -2JS_iS_j = -2JS_iS_j\cos\theta$

Ans.3:



Ans.4: The reverse field needed to bring the magnetization to zero from remanence is called the *coercive field* or *coercivity*, B_c.

Ans.5: The state of uniform magnetization has the lowest possible exchange energy, since all adjacent spins are parallel to each other.

18.9 Exercise

Short Answer Type Questions

Q.1 At what temperature do materials loose their ferro-, anti-ferro- and ferromagnetic properties?

Long Answer Type Questions

Q.2 How to classify materials with respect to exchange integral? What are the differences between ferromagnetic, anti-ferromagnetic and ferromagnetic materials?

References and Suggested Readings

1. Introduction to Solid State Physics (2004) by Charles Kittel
2. Magnetic Properties of Solids by M. S. Dresselhaus.
3. Solid State Physics: Structure and Properties of Materials, 2009, by M. A. Wahab.
4. Solid State Physics: An Introduction to Solid State Electronic Devices, 2010, by A. K. Saxena

UNIT-19

Superconductivity : Part-I

Structure of the Unit

19.0 Objectives

The objectives of this unit is to study the phenomenon of superconductivity. How superconductivity was discovered and to study which properties of superconductor changes from normal into superconducting state and which do not change. We also study influence of external factors on superconductivity. In the last we study various experimental observations in superconductors which are helpful in understanding the superconductivity phenomenon.

19.1 Introduction

We have studied that resistance of conductor increases with increase in temperature and decreases with decrease in temperature. In 1911 first of all Kamerlingh Onnes observed that when various metals and alloyes are cooled in the region of Helium liquid temperature, then their electric resistivity sharply decreases and in the end the resistivity becomes zero.

The sudden decrease of resistivity to zero, only possible when metals are cooled below a fixed temperature, which is known as critical temperature T_C .The phenomenon of decreasing resistivity to zero is known as Superconductivity. The concerned material under study is called Superconductor. The temperature at which the specimen undergoes a phase transition is called Super-Conducting transition temperature or critical temperature T_C. For example Ny, Pb, Vd and Al show Superconductivity at temperature 9.2K, 7.2K, 5.1K and 1.2K respectively. Different research scientists are trying to increase the Superconducting temperature because lowering the temperature to 4K or 1K is very cumbersome. Many scientists say that they have been able to raise the critical temperature to 100K. If by some mean the conductors could be changed into superconductors, we shall have vast applications of superconductivity, for example generation and transmission of electricity, exceptionally powerful electromagnets, supercomputers, fastest trains etc., shall be there.

In the study of superconductor it is found that those metals which are good conductors at normal temperatures like Ag, Cu,Au remain normal conductors even at temperatures down to 0.35K, 0.07 K and 0.05K respectively. It has been found that the superconducting properties of metals can be changed by varying temperature, magnetic field and impurity etc.

19.2 Experimental Survey

19.2 .1 Superconductivity and Transition Temperature

Superconductivity is the name given to a remarkable combination of electric and magnetic properties which appears in certain metals, when they are cooled to a sufficiently low temperature often a temperature in the liquid Helium range. Superconductivity was discovered in 1911 when Kamerlingh Onnes observed that the resistivity of Hg vanishes completely below 4.2^0K. At critical temperature T_C the specimen undergoes a phase transition from a state of normal electrical resistivity to a superconductivity state. The temperature at which the superconductor loses resistance is called its superconducting transition temperature or critical temperature T_C .The element Nobium has highest transition temperature i.e. 9.3^0K. The transition temperature is not very sensitive to small amount of impurities. The transition temperature varies from specimen to specimen. For a particular metallic element ,the transition and its transition point to superconducting state depend upon the degree of its purity. Less pure it is, transition temperature will be higher and the transition range will be broader and vice versa.

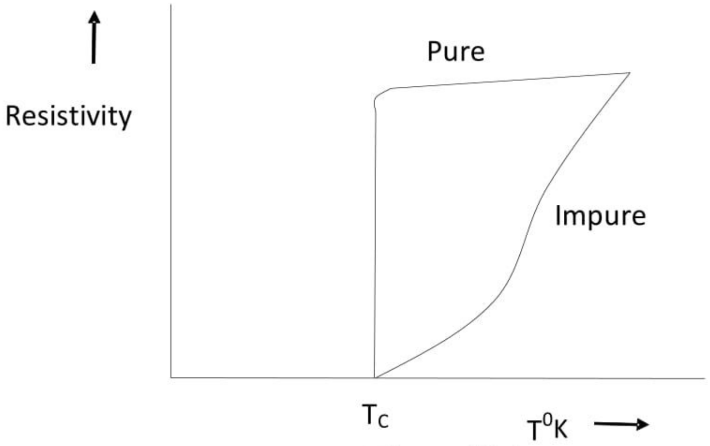


Figure 19.1

On cooling the transition to the super-conducting state may be extremely sharp if the specimen is pure and physically perfect as given in figure (19.1) which shows the transitions in pure and impure or disturbed crystal structure of Tin specimens.

19.2.2 Zero Resistance

As described earlier, that the disappearance of d.c. resistance at temperatures, below the transition temperature as shown in fig. (19.1) is the most important property of superconductor. The careful investigation have shown that the resistivity of a metal in the superconducting state drops to less than one part in 10^{17} of its value in the normal state. It may be noted that no general criteria for determining whether a given metal should become a superconductor has been developed so far. The abrupt loss of resistance appears because of some fundamental changes occur in the electronic or atomic structure of the metals. If d.c. current flows through a superconductor in the form of ring. It was observed that constant current flows for more than one year without decay because of zero resistance. This type of current is known as persistent current. Besides this, in some substances, which are used in superconducting magnets, decay time is observed.

19.3 Effect of Magnetic Field

If high magnetic fields are applied on superconductors, then their superconductivity is destroyed and substance becomes normal conductor again. We know that critical temperature is that temperature above which substance behave as normal conductor and below this temperature substance behaves as superconductor. If applied magnetic field is zero, the applied magnetic field which is required to destroy superconductivity is known as critical magnetic field H_C and it is function of temperature. The critical magnetic field H_C and temperature T are related with the following equation:

$$H_c = H_{co}[1 - \frac{T^2}{T_c^2}] \qquad (19.1)$$

Where H_{Co} is the critical magnetic field at $T=0^0K$. From equation (19.1) it is clear that the critical magnetic field increases as temperature decreases below T_C or $T< T_C$ or we can say that below critical temperature more magnetic field is required to destroy superconductivity.

This is demonstrated by graph in figure (19.2). The right side of upper portion of H_C - T curve shows normal state of Pb and the left side of lower portion represents superconducting state of Pb. For most of the superconductors it was observed experimentally that H_{C0} is related with critical temperature T_C by the following relation :

$$H_{C0} = AT_c^2 \qquad (19.2)$$

where $\alpha = 1.8$ and $H_C = \frac{B_C}{\mu_0}$ in S.I. System

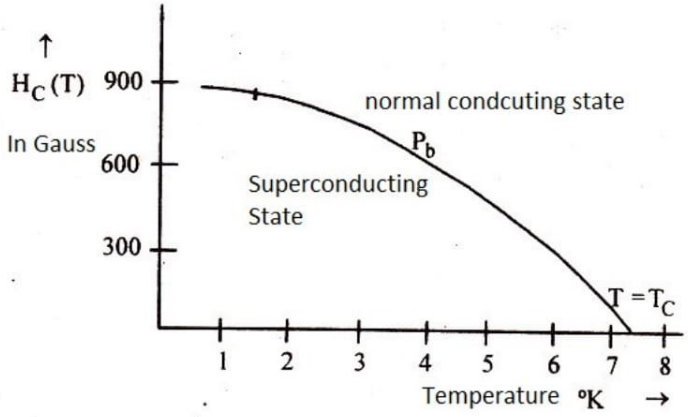


Figure (19.2): Variation graph of Critical magnetic field (H_C) with Temperature T for Pb

The original observation on the elimination of superconductivity by the application of magnetic field was made by K. Onnes by passing an electric current through a superconducting wire.

19.4 Meissener Effect

It was observed that when the value of applied magnetic field B_a is less than critical magnetic field B_C (= $\mu_0 H_C$), then below critical temperature, the superconductor behaves perfectly diamagnetic i.e. the magnetic flux originally present is ejected from the specimen i.e. the magnetic induction B inside superconducting substance is zero. This phenomenon is known as Meissner Effect.

At $T < T_C$, B =0 inside superconductor shows that below critical temperature (T_C), the superconducting material diverses total magnetic flux lying inside the substance. This is shown in diagram 19.3(a) for $T > T_C$ and in diagram 19.3 (b) for $T < T_C$.

If we take superconducting material in the form of a thin cylinder and we apply magnetic field ($B_a = \mu_0 H_a$) along its length then total magnetic induction will be:

$$B=B_0 + \mu_0 M \qquad (19.3)$$

where M is known as magnetization or intensity of magnetization. If applied magnetic induction B_a is less than critical magnetic induction then at $T<T_C$ superconductor shows Meissner Effect i.e. B=0.

So from equation (19.3)

$$B_a+\mu_0 M = 0$$

$$\text{or} \quad B_a = -\mu_0 M \qquad (19.4)$$

$$\text{or} \quad \mu_0 H = -\mu_0 M$$

$$\text{or} \quad \chi = \frac{M}{H} = -1 \qquad (19.5)$$

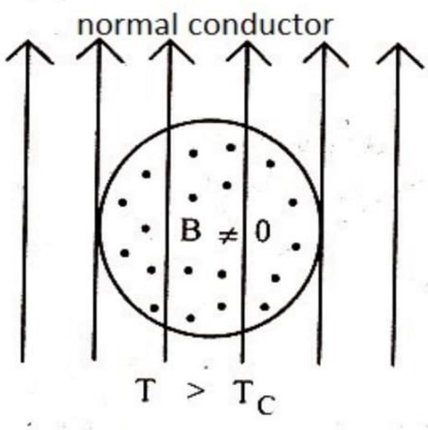


Figure 19.3 (a)

At $T > T_C$,the substance behaves as normal conductor and magnetic flux density B inside is not zero.

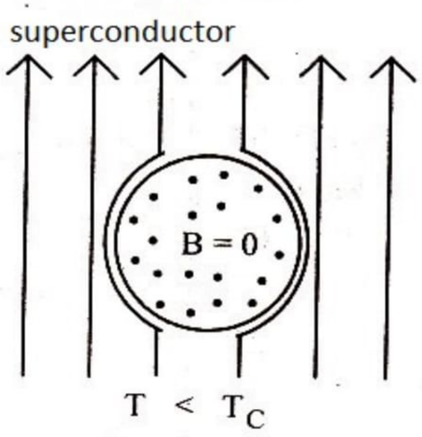


Figure 19.3 (b)

At $T<T_C$ the substance behaves as superconductor and it expells total magnetic flux from inside.

It is clear from eq.(19.5) that at $T < T_C$,superconductor is perfectly diamagnetic, whose magnetic susceptibility is negative i.e. $\chi = -1$

Hence it is necessary to note that for superconductor perfect diamagnetism and zero resistivity are two independent phenomenon. To understand this we consider the relation between current density J and intensity of Electric Field (E).

$$E = \rho J \tag{19.6}$$

We know that superconductor resistivity $\rho=0$ and current density J is finite, then from equation (19.6) $\vec{E}=0$

From Maxwell's equation $\nabla \times \vec{E} = \frac{-\partial \vec{B}}{\partial t}$

Since E=0 $\therefore \frac{\partial \vec{B}}{\partial t} = 0$

or $\vec{B}$ = Constant.

This result, in which magnetic induction is constant w.r. to time is against Meissner effect, in which at critical temperature the magnetic induction B suddenly drops to zero.

This concludes that perfect diamagnetism is an essential property of the superconducting state.

19.5 Type -I & Type - II Superconductors

If we draw magnetization curve below transition temperature or critical temperature, for many superconductors, those are obtained as shown in diagram 19.4 (a) and 19.4(b)

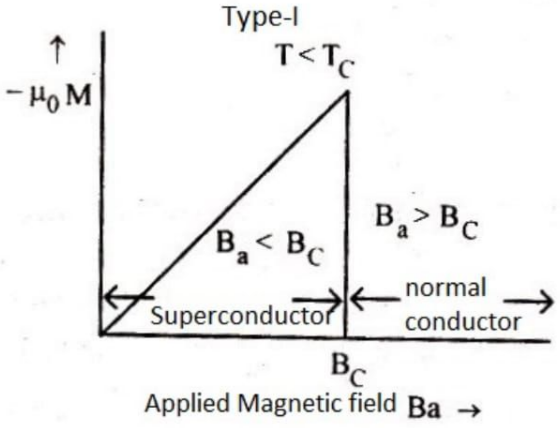


Figure 19.4(a)

Diagram 19.4(a) shows that magnetization curve at $B_a < B_c$, obeys Meissner effect perfectly and at $B_a > B_c$ substance behaves as normal conductor where B_a is applied external magnetic field.

Diagram 19.4(b) describes that penetration of magnetic flux starts when $B_a > B_c$ .For $B_{C_1} < B_a < B_{C_2}$ the substance remains in mixed state and at $B_a > Bc_2$ the substance acquires normal conducting state.

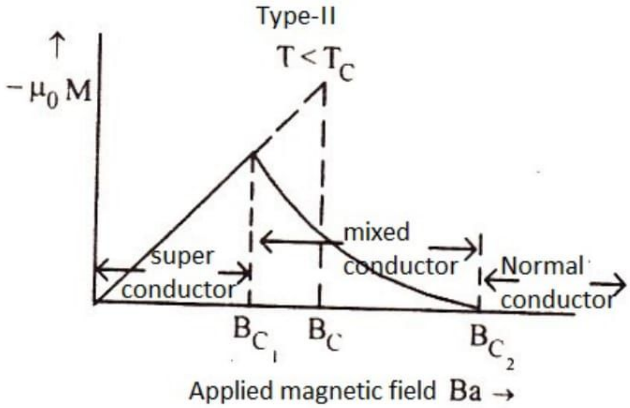


Figure 19.4(b)

19.5.1 Type – I Superconductor

When the value of applied magnetic field B_a is increased on superconductor then the value of Magnetic Intensity M increases proportionally to B_a , when applied magnetic field B_a is equal to critical magnetic field B_c then the value of M suddenly drops to zero and at $B_a > B_c$,the substance acquire normal conducting state. This is shown in diagram 19.4(a). Those Substances whose magnetization curve is according to diagram 19.4(a) are known as Type -I or soft superconductor. Pb, Sn and Hg are the examples of Type - I Superconductors. Such type of superconductors obey Meissner effect perfectly and their magnetization curve is according to the equation (19.4). They are called soft because of their tendency to permit magnetic field to penetrate fully above H_c. These are useful in coils for superconducting magnets.

19.5.2 Type – II Supercondcutor

The magnetization curve for Type-II superconductors are obtained as shown in fig. 19.4 (b) in which high and low critical magnetic fields Bc_2 and Bc_1 are obtained as shown in figure. When the applied magnetic field B_a is less than low critical magnetic field Bc_1 ,then the substance remains in superconducting state. When applied magnetic field B_a is more than Bc_1 then magnetic flux penetrates inside the substance and when B_a is equal to Bc_2 then magnetic flux totally enter into the substance.Due to this ,the super conductivity of the substance totally destroyed. when $B_a > Bc_2$, then substance returns to its normal conducting state. It is clear that when applied magnetic field B_a lies between Bc_1 and Bc_2 then substance remains in mixed state of superconductor and normal conductor. Hence it is noticeable that low critical magnetic field $Bc_1 < B_c$ and high critical magnetic field $Bc_2 > B_c$. Where B_c is that critical magnetic field which is at critical temperature T_c. The value of Bc_2 is 100 times B_c and even more than this. Between Bc_1 and Bc_2 we have intermediate state called vortex state.

In Type-II superconductors, we are having transition metals and alloys, whose electric conductivity in normal state is high. These are also known as hard superconductors. These superconductors are technically very usefull materials in contrast to type-I superconductors. These superconductors are used for naking strong field superconducting magnets.

19.6 Isotope Effect

Through experiments it was observed that the critical temperature T_c of superconductors changes with average isotopic mass M. This change occurs according to following equation :

$$M^{\alpha} T_c = \text{Constant} \tag{19.7}$$

where the value of α is different for different superconductors. It has been found through experiment that the superconducting critical temperature (T_c) for various isotopes of a superconductor is different. This is called Isotope effect.

For example the average atomic mass M of Hg superconductor varies from 199.5a.m.u. to 203.4 a.m.u. while the value of critical temperature T_C ,varies from 4.185K to 4.146K.

The dependence of critical temperature (T_c) on isotopic mass, proves that in superconductors electron-phonon interaction exists necessarily. There is no other reason due to which critical temperature (T_c) depends upon neutron number or isotopic mass.

For $\alpha = \frac{1}{2}$, the relation (19.7) can be obtained in the following manner :

From BCS Theory

$$T_C \propto \theta_{\text{Debye}}$$

But $\theta_{\text{Debye}} \propto$ phonon velocity

Phonon velocity $(V) \alpha\, M^{-\frac{1}{2}}$

$$T_C\, \alpha\, M^{-\frac{1}{2}}$$

or $T_C\, M^{\frac{1}{2}} = \text{Constant}$

or $M^{\frac{1}{2}} T_C = \text{Constant}$ (19.8)

When we compare equation (19.8) with (19.7) We obtain α=1/2 .It is clear that eq.(19.7) is the result of phonon -electron interaction, in which α=1/2. But when Coulombian interaction between electrons also involves then equation (19.8) will change.

From the dependence of T_c on isotopic mass ,we learn about lattice vibrations and hence electron-lattice interaction are deeply involved in superconductivity.

19.7 Thermodynamic Effects

As we know that transition from normal conducting state to superconducting state is a reversible process, this is analogous to phase transition of substance from liquid state to vapour state is reversible under the condition of slow evaporation .This is due to the fact that because the superconducting currents do not die away with the production of Joule heat when superconductivity is destroyed by the application of magnetic field. We can therefore apply thermodynamics to the phase transition and thereby obtain an expression for the difference of entropy between superconducting and normal states in terms of the critical field curve B_c versus T. We treat type I superconductor with a complete Meissner effect, so that B=0 inside the superconductor. We shall see that the critical field B_c is a quantitative measure of the energy difference between the normal and superconducting states at absolute zero. Hence we can apply thermodynamics argument to a superconductor using the temperature and magnetic field strength with the thermodynamical variable. There are a number of thermodynamic effects of interest in the superconducting and in the normal states, which are primarily important from the point of view of the development of the fundamental theory of superconductivity. These effects are essentially reversible in nature and all are predicted by phenomenological theories. Now we will discuss different thermodynamical effects e.g. entropy, specific heat, energy gap and thermal conductivity in detail.

19.8 Entropy

It is observed that in all superconductors entropy decreases remarkably on cooling below the critical temperature T_c. This decrease in entropy from normal to superconducting states tells us that the superconducting state is more ordered than normal state, brcause entropy is a measure of disorder. Although the difference in entropy is very small, it is of the order of 10^{-4} k_B per atom in the case of aluminum; This small difference shows that the rearrangement of the system on becoming superconducting is relatively small.

The entropy S of Al in normal and superconducting states as a function of temperature is plotted in figure (19.5). It is clear from figure that entropy is less in the case of superconducting state. It was observed that is simple superconductors (Type-I or soft superconductor) , there is a spatial order of super electrons which extends over a distance of the order of 10^{-6} meters.

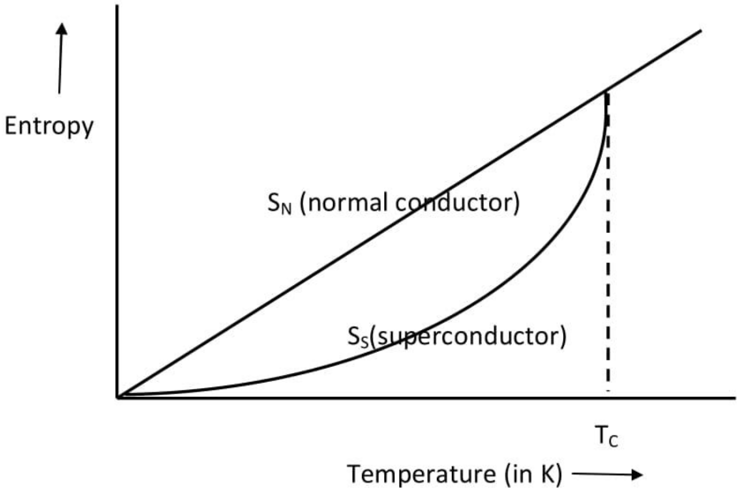


Figure 19.5: Variation of entropy with temperature (K) in normal state and superconducting state

19.9 Specific Heat

In superconductors the behavior of specific heat curves in superconducting state and normal conducting state is different. At $T<T_c$,the specific heat of superconductor decreases exponentially as temperature T decreases as shown in figure (19.6). The change in specific heat of superconductor with temperature is represented by the following relation:

$$C_S = A\exp\left(-\frac{\Delta}{k_B T}\right) \tag{19.9}$$

where $2\Delta = E_g$ is the energy gap which is obtained in superconductor. But this is not universal property of superconductor. There are such type of superconductors in which there are no energy gap. The specific heat of superconductor is mainly due to electrons.

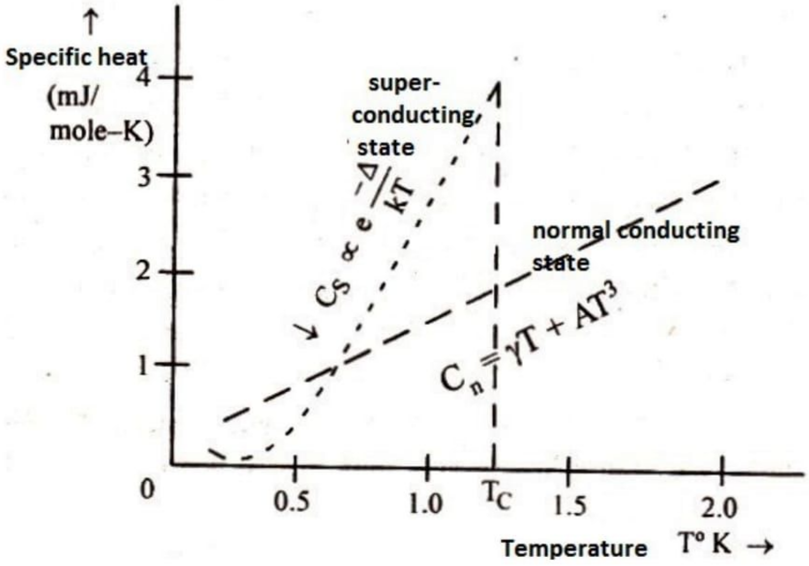


Figure (19.6: *[Specific heat curve for Al:- In superconducting state, specific heat varies as $e^{\left(-\frac{\Delta}{k_B T}\right)}$ and in normal conducting state at $T<T_c$,C_n is proportional to T]*

If at $T<T_c$,we apply magnetic field greater than critical magnetic field B_c on superconductor ,then this returns to normal conducting state. In this position its specific heat is equal to the sum of electronic specific heat C_{el} and lattice specific heat $C_{lattice}$, so total specific heat

$$C_n = C_{el} + C_{lattice}$$

$$= \gamma T + A\,T^3 \tag{19.10}$$

But at temperature $T<T_c$, electronic specific heat is more effective, due to this in normal conducting state specific heat C_n is proportional to T, as shown in figure (19.6)

For *Al*, whose critical temperature is T_c=1.19K, specific heat graph is shown in figure (19.6). It is clear from figure (19.6) ,that at $T=T_c$, discontinuity appears in specific heat and it is related with entropy. In conducting state electrons are in more disordered state, while in superconducting state electrons are in more ordered state. So as soon as substance acquires superconducting state from normal conducting state ,its entropy decreases. At low temperature close to T_c ,the specific heat of superconductor is more than specific heat in normal conducting state. But on decreasing temperature ,the value of C_s decreases more rapidly in comparison to C_n.

19.10 Thermal Conductivity

The value of thermal conductivity of a pure superconductor in superconducting state is less in comparison to thermal conductivity in normal conducting state. For this reason is that in pure superconductor electrons are in more ordered state. In normal conducting state electrons are in more disordered, due to this, they are more helpful in heat transfer, so thermal conductivity is more. While in perfect ordered state i.e. in superconducting state, the possibility of heat transfer is negligible, due to this thermal conductivity is very low.

If however, the superconductor is driven normal by the application of a magnetic field, thermal conductivity is restored to the value of the normal state. Hence thermal conductivity of the superconductor can be controlled by magnetic field, and this effect has been used in “Thermal Switches” at low temperature to make and break heat contact between specimen connected by a link of superconducting metals.

19.11 Energy Gap

It is observed through experiment that in superconductors energy gap exists. At transition temperature T_c ,the sudden increase in specific heat, clearly shows that energy gap $(E_g = 2\Delta)$ exists in superconductors. But its value $(-10^{-4} E_F)$ is very low. The nature of energy gap in superconductor is totally different than energy gap in insulators. In insulators energy gap separates valence electrons and conduction electrons while in superconductors it separates electrons in normal state and superconducting state and nearer to Fermi level. The energy gap E_g which exists in superconductor is function of temperature T. This energy gap initially decreases slowly with increase in temperature. But when temperature T, approaches T_c i.e. transition temperature, then energy gap decreases sharply and at $T=T_c$, it becomes zero. The dependence of E_g on temperature is given by the following equation :

$$E_g(T) = 1.74\, E_g(0)\left[1-\frac{T}{T_C}\right]^{\frac{1}{2}} \tag{19.11}$$

where $E_g(T)$ and $E_g(0)$ are the energy gap at temperature T and 0K respectively. The dependence of $E_g(T)$ on temperature is shown in figure (19.7). The value of $E_g(0)$ is maximum at T=0K and at $T=T_c$,the value of $E_g(T_c)$ is equal to zero.

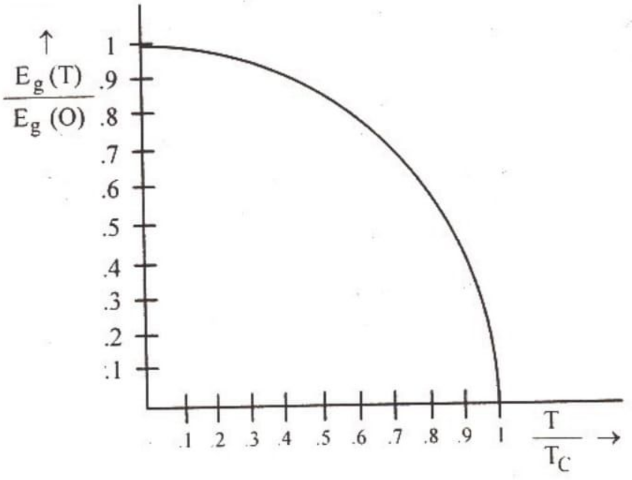


Figure 19.7 *(Variation of energy gap Eg(T) with respect to Temperature T in superconductor.*

In normal conductor at T=0K all energy level below Fermi level are completely filled and energy bandgap is zero as shown in figure 19.8(a). While in superconductor on Fermi level E_F, the energy gap is $(E_g = 2\Delta)$. At 0K any superconductor electron cannot cross this forbidden energy gap.

At 0K, the energy gap in V, Nb, Ta and Al, is 1.6, 3.05, 1.4 and 0.34 meV respectively.

We know that due to the presence of an energy gap, the superconductors respond only to high frequency electromagnetic radiation of a particular frequency. Thus energy gap is a characteristic feature of all superconductors which determines their thermal properties as well as their response to high frequency electromagnetic fields.

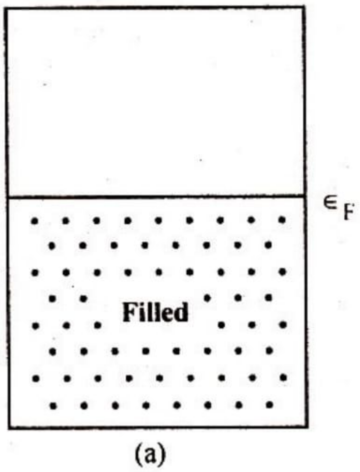


Figure 19.8(a)

[In normal conductor energy gap E_g =0 at 0K]

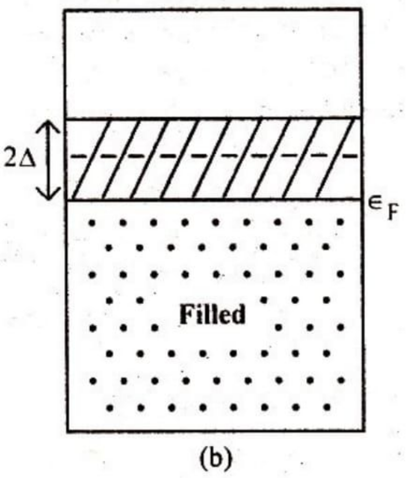


Figure 19.8(b)

[In Superconducting state Fermi level ϵ_F energy gap E_g =2Δ]

19.12 Self Learning Exercise

Q.1 What is a superconductor?

Q.2 What is Meissner effect?

Q.3 Distinguish between soft and hard superconductors.

Q.4 Explain isotope effect in superconductors.

19.13 Summary

In 1911 first of all Kamerling Onnes discovered superconductivity. Meissner and Ochsenfield found that the field distribution around the superconductor could only be explained if it were assumed that all magnetic flux was excluded from the metal. In other words a superconductor is perfect diamagnetic. The alloys and metals become superconductor at transition temperature T_c .As we know the characteristics of superconductors are its zero resistivity, persistent current, perfect diamagnetism and presence of energy gap($\Delta = \frac{E_g}{2}$). In superconducting state many thermodynamical properties as entropy, thermal conductivity and specific heat undergo changes. There are two type of superconductors i.e. soft (Type-I) and hard (Type-II). It has been found that the superconducting properties of metals can be changed by varying temperature, magnetic field, impurity, frequency of excitation and isotopic mass etc. Superconductivity can be destroyed by magnetic field. Superconductivity can be used in generation and transmission of electricity and making exceptionally powerful electromagnets supercomputers, fastest train etc.

19.14 Glossary

Isotope : atoms having same number of protons but different number of neutrons

Perfectly Diamagnetic: whose magnetic susceptibility is negative i.e. $\chi = -1$

Phonon : Quanta of Lattice Vibration

19.15 Answers to Self Learning Exercise

Ans.1: The conductor which offers almost zero resistance is called a superconductor.

Ans.2: A bulk specimen of metal in the superconducting state exhibits perfect diamagnetism, with the magnetic induction B=0, this is Meissner effect.

19.16 Exercise

Section - A (Very Short Answer Type Questions)

Q.1 What is transition temperature or critical temperature?

Q.2 What is energy gap in superconductors?

Q.3 What is vortex state?

Section - B (Short Answer Type Questions)

Q.4 Define transition temperature and critical magnetic field.

Q.5 What is Meissner effect? Give some applications of superconducting materials.

Q.6 Discuss the effect of external magnetic field on superconductors.

Section - C (Long Answer Type Questions)

Q.7 What is superconductivity? Describe the effect of magnetic field on a superconductor.

Q.8 What is Meissner effect ? Distinguish between Type-I and Type-II superconductors.

Q.9 Write brief notes on:

(a) Isotope Effect

(b) Entropy change in superconductors

(c) Thermal Conductivity and specific heat of superconductors.

Q.10 Explain the origin of energy gap in superconductors. Explain the relevant experimental observations in superconductors that confirms the existence of energy gap.

Q.11 What are important properties of superconductors, list them. How these properties can change? What are the uses of superconductors?

19.17 Answers to Exercise

Ans.1: The temperature at which the specimen undergoes a phase transition is called superconducting transition temperature or critical temperature.

Ans.2: In the superconducting state an energy gap $E_g=4K_BT_c$ separates superconducting electrons (below) from normal electrons (above) the gap. This gap is detected in specific heat.

Ans.3: In the region between Bc_1 and Bc_2 the superconductor is threaded by flux lines and is said to be in the vortex state.

References and Suggested Readings

1. Introduction to Solid State Physics by C.Kittel
2. Elementary Solid State Physics by Rama Swami
3. Solid State Physics by S.O. Pillai
4. Solid State Physics by A.J. Dekker
5. Fundamentals of Solid State Physics by Saxena, Gupta and Saxena
6. Introduction to super conductivity by A.C. Rose- Innes and E.H.E.H. Rhodrick

UNIT-20

Superconductivity : Part-II

Structure of the Unit

20.0 Objectives

The objective of this unit is to study the theoretical explanation of superconductivity in the form of London equations and BCS theory. We will also study coherence length, flux quantization in a superconducting ring, Josephson effect i.e. tunneling effects in superconductors. In the last ,we will study elements of high temperature superconductors and applications of superconductors.

20.1 Introduction

The explanation of various properties related to superconductivity phenomeno cannot be understood by only single principle. So far there are number of theories have been proposed to explain the phenomenon of superconductivity. Since thermodynamics and London's equations are useful in explaining free energy, stabilization energy and penetration depth. While Bardeen, Cooper and Schrieffer have given microscopic theory i.e. quantum theory for superconductivity and provide basis for progressive path. The B.C.S. theory is the most successful one and explains all the properties of superconductors. But it cannot explain high-T_C ceramic superconductors. Josephson and Anderson showed the importance of phase of superconducting wave function.

20.2 London Equations

As we know that in superconducting state zero resistivity (ρ=0) and Meissner effect both are observed independently. Since Meissner effect is perfectly applicable in type-I superconductors. This shows that magnetic field (B) inside the superconductors is zero ,which is the characteristic of perfectly diamagnetic property of superconductor i.e. χ =−1. But the penetration of magnetic flux in superconducting thin films cannot be understood with this effect. The penetration of magnetic flux in superconducting thin films was successfully explained by London's theory. This theory is based on Maxwell's equation and conductivity and it is very useful in finding penetration depth in superconductors. In 1935 London and London derived two equations by using Ohm's law and Maxwell's equation, known as London's equations considering two fluid model .They considered that in material there are two types of electrons (1) superconducting electrons and (2) normal electrons. In this theory it was supposed that the current in superconductor flows due to purely superconducting electrons and electron-lattice scattering is negligible. So that resistivity can be taken as zero .At 0K a superconductor contains only superconducting electrons but as temperature increases the ratio of the normal electrons to superconducting electrons increases, until at the transition temperature all the electrons become normal. Suppose below critical temperature there are *n* superconducting electrons/ions present in superconductor. The equation of motion of an electron in presence of electric field $\vec{E}$ is given by

$$m\frac{d\vec{v}}{dt} = -e\vec{E} \tag{20.1}$$

where m is the mass of electron and (-e) is charge of the electron.

Equation of current density

$$\vec{J} = -ne\vec{v} \tag{20.2}$$

Now putting the value of $\vec{v}$ from equation (20.2) in equation (20.1) we shall get

$$\frac{m}{ne}\frac{d\vec{J}}{dt} = e\vec{E}$$

or

$$\frac{d\vec{J}}{dt} = \frac{ne^2}{m}\vec{E} \tag{20.3}$$

Equation (20.3) is first London's equation. This equation represents absence of resistance in substance, in superconducting state. If E = 0, then from equation (20.3),

$$\frac{d\vec{J}}{dt} = 0$$

or $\vec{J}$ = const (w.r.t. to time). This shows that in the absence of electric field current flows continuously, which is characteristic property of superconducting state. While in normal conducting stage, $J = \sigma E$, if E = 0, then J = 0 which is the characteristic property of normal conductor .Now taking curl of equation (20.3) we shall get

$$\vec{\nabla}\times\frac{d\vec{J}}{dt} = \frac{ne^2}{m}\vec{\nabla}\times\vec{E}$$

or

$$\frac{d}{dt}(\vec{\nabla}\times\vec{J}) = \frac{ne^2}{m}\vec{\nabla}\times\vec{E} \tag{20.4}$$

From Maxwell's equation $\vec{\nabla}\times\vec{E}=-\frac{\partial\vec{B}}{\partial t}$, putting value of $(\vec{\nabla}\times\vec{E})$ in equation (20.4), we shall get

$$\frac{d}{dt}(\vec{\nabla}\times\vec{J})=\frac{ne^2}{m}\left(-\frac{\partial\vec{B}}{\partial t}\right)$$

or $$\vec{\nabla}\times\vec{J}=-\frac{ne^2}{m}\vec{B} \qquad (20.5)$$

Equation (20.5) is second London's equation. By putting $\vec{B}=\vec{\nabla}\times\vec{A}$, where $\vec{A}$ is vector potential, then equation (20.5) changes in the following form

$$\nabla\times\vec{J}=-\frac{ne^2}{m}\vec{\nabla}\times\vec{A}$$

or $$\vec{J}=-\frac{ne^2}{m}\vec{A} \qquad (20.6)$$

Now we will show how London's second equation (20.5) explains Meissner effect. Maxwell's equation in static state is given by

$$\vec{\nabla}\times\vec{B}=\mu_0\vec{J} \qquad \text{Since (E=0)} \qquad (20.7)$$

Now taking curl of equation (20.7) on both side we shall get

$$\vec{\nabla}\times\vec{\nabla}\times\vec{B}=\mu_0\vec{\nabla}\times\vec{J}$$

$$\vec{\nabla}(\vec{\nabla}.B)-\nabla^2\vec{B}=\mu_0\vec{\nabla}\times\vec{J}$$

Since $\vec{\nabla}.\vec{B}=0$, so

$$-\nabla^2\vec{B}=\mu_0\vec{\nabla}\times\vec{J} \qquad (20.8)$$

Now putting the value of $\vec{\nabla}\times\vec{J}$ from equation(20.5) into equation (20.8) we shall get

$$-\nabla^2\vec{B}=\mu_0\left(-\frac{ne^2}{m}\right)\vec{B}$$

or $$\nabla^2 \vec{B} = \left(\frac{\mu_0 n e^2}{m}\right)\vec{B}$$

or $$\nabla^2 \vec{B} = \frac{1}{\lambda_L^2}\vec{B} \qquad (20.9)$$

where $$\lambda_L = \sqrt{\frac{m}{\mu_0 n e^2}} \qquad (20.10)$$

Since the dimensions of λ_L is of length and it is known as London penetration depth. The solution of equation (20.9) cannot be B = constant i.e. magnetic field can not be uniform in superconductor and it is only possible when B = 0, inside superconductor, which is Meissner effect. So the possible solution of equation (20.9) is following :

$$B = B_0\, e^{-(x/\lambda_L)} \qquad (20.11)$$

where B_0 is the magnetic filed on the surface of superconductor and B is the magnetic field at a distance x inside the surface of superconductor. Equation (20.11) represents that magnetic field inside the substance decreases exponentially and λ_L measures the magnitude of penetration distance of magnetic field ,so it is known as London penetration depth. λ_L is the distance from surface of substance where the value of magnetic field reduced to $\left(\frac{B_0}{e}\right)$.

On observing equation (20.10) ,we found that λ_L is inversely proportional to square root of superconducting electron density (n). It is found that at T = 0 the penetration depth is minimum due to maximum superconducting electron density (n), while at $T = T_C$, penetration depth tending towards infinity, because at $T = T_C$, superconducting electrons density (n)tending towards zero. Since at $T = T_C$, superconducting electrons convert into normal conducting electrons.

20.3 BCS Theory

The phenomenon of superconductivity has been developed over many years. Various theories have been proposed to explain the phenomenon of superconductivity. Thermodynamics and London's Theory cannot explain superconductivity fully. In 1957 Bardeen, Cooper and Schrieffer formulated an effective quantum theory or microscopic theory to explain various properties of superconductors. This theory has a long list of experimental checkups and it is is called BCS theory. The important facts that provide the basis for this theory are (1) the isotope effect and (2) variation of specific heat of superconductors. By getting the clues from above facts Bardeen, Cooper and Schrieffer built up their theory using quantum mechanical concepts. An elementary qualitative treatment of BCS theory is given as follows.

As we know from the isotopes effect $(T_C M^{1/2} = const.)$ it is observed that the transition which produces the superconducting phase must involve thermodynamic of the ion motions or the lattice vibrations i.e. phonons. When the transition temperature tends to zero, then M tends to infinity or if the lattice points were really to be fixed. This suggests very strongly that non zero transition temperature is a consequence of the finite mass of the ions which can contribute phonons by their vibrations. To find out the part played by the phonons in producing superconducting transitions we have to very careful to observe the interaction process.

20.3 (A) Electron-Phonon-Electron Interaction and Formation of Cooper Pairs

Frohlic and Bardeen for the first time pointed out that an electron moving through a crystal lattice has a self energy accompanied with virtual phonons. It means that moving electron through lattice, distorts it and oscillatory distortion takes place. This oscillatory distortion of lattice is quantized in terms of phonons. This distorted lattice acts on electron by virtue of electrostatic forces between them. The interaction between electrons and lattice can be interpreted as the constant emission and re-absorption of phonons by the lattice. These are called virtual phonons because as a consequence of uncertainty principle their short life-time renders it unnecessary to conserve the energy in the process. Thus one can think of the electron moving through the lattice, as being accompanied, even at 0K, by a cloud of virtual phonons. This is responsible for the self energy of the electron. The energy is proportional to the square of the average phonon energy.

Bardeen, Cooper and Schrieffer succeeded in showing that the basic interaction responsible for superconductivity appears to be that of a pair of electrons by means of an interchange of virtual phonons. This means that the lattice is distorted by a moving electron. This distortion of lattice give rise to a phonon. A second electron is attracted by distorted lattice or vibrating ion core. This lowers the energy of the second electron. Hence two electron interact via the lattice distortion or phonon field. This type of interaction is called electron-lattice- electron interaction. Thus the basic postulate by B.C.S. theory is that when superconductivity appears, the attractive interaction between two electrons by means of phonon exchange, dominates the usual repulsive Coulomb interaction.

Cooper Pair :

In superconductor, Two electrons, whose momentum is equal and opposite, interacts by the exchange of phonon, form a pair and this pair of electrons is known as Copper pair. This interaction between electrons is a very rare interaction. The process of Copper pair formation is the result of lattice distortion. When an electron performs Columbian interaction with lattice ion, then it is scattered by emitting a phonon, due to this its momentum decreases. Another electron nearer to this distorted lattice absorbs this phonon and got scattered and both electrons form a Cooper pair.

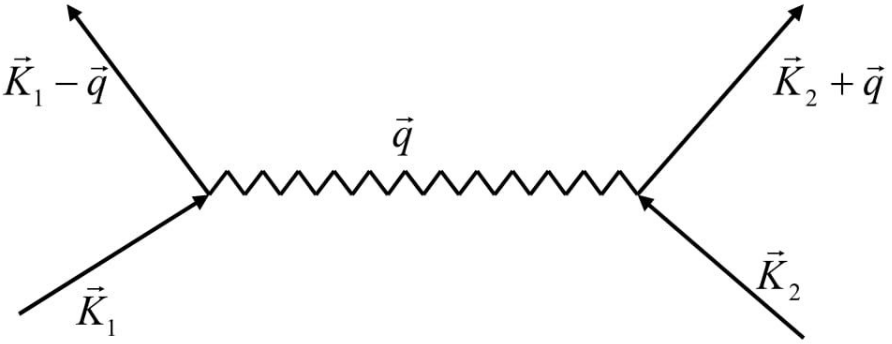


Figure 20.1: Electron-electron interaction through exchange of phonon

Although in electron-electron interaction it is not necessary that the momentum of both the electrons should be same. Even then for strongest attractive interaction momentum of both the electrons are equal and opposite. This interaction is shown in diagram (20.1) in which an electron of momentum $\vec{K}_1$, emits a phonon of momentum $\vec{q}$ and scattered with the momentum $\left(\vec{K}_1 - \vec{q}\right)$ while another electron of momentum $\vec{K}_2$ absorbs the phonon of momentum $\vec{q}$ and scattered with momentum $(\vec{K}_2 + \vec{q})$. In energy levels of BCS state, electrons reside in pair form whose momentum are $\vec{K}$ and $-\vec{K}$ and have spins opposite to each other. This pair behaves as boson particle. The energy of the pair of electrons in the bound state is less than the energy of the pair in the free state. The difference of energy of the two states is the binding energy of Cooper pair and therefore this amount of energy should be supplied if the pair is to be broken. Cooper pairs have certain aspects of single particle. At temperature less than critical temperature, electron lattice electron interaction is stronger than electron- electron Coulomb interaction. So the valence electrons tend to pair up and pairing completes at T = 0K and is completely broken at a critical temperature.

20.3 (B) The Energy Gap

The energy difference between the free state of the electron (normal state) and the paired state (superconducting state) appears as energy gap at the Fermi surface. The normal electron states are above the energy gap and superconducting electron states are below the energy gap at the Fermi surface. This energy gap unlike the constant energy gap in semiconductors and insulators, depends strongly on temperature. At absolute zero temperature the energy gap is maximum and at $T = T_C$ pairing is dissolved and energy gap reduces to zero. Across the energy gap there are many excited states for the superconducting Cooper pairs.

20.3 (C) Ground State:

As we know that BCS ground state differs from the ground state of the non-interacting Fermi gas. As we have studied earlier, the phonon assisted attractive interaction between electrons gives rise to the BCS ground state. The superconducting BCS theory states that the superconducting state is separated by a finite energy gap E_g from the lowest excited state. The BCS state appears to have a higher energy than the Fermi state. But the attractive potential energy of the BCS state, acts to decrease this total energy of the BCS state with respect to Fermi state and due to this BCS state becomes more stable than the Fermi state and superconductivity persists. In BCS state, the one particle orbitals are occupied in pairs. These are called Cooper pairs. If state with wave $\vec{K}$ and spin up $(\uparrow)$ is occupied, then the orbital with wave vector $-\vec{K}$ and spin down $(\downarrow)$ is also occupied. Similarly if one is vacant, then the other is also vacant.

20.3 (D) Coherence Length

According to BCS theory Cooper pairs (i.e paired electrons) are not scattered from lattice due to their special property of smoothly riding over the lattice imperfections without ever exchanging energy with them. These paired electrons keep their coupled motion up to a certain distance. This distance up to which they almost behaves as a single unit is called coherence length. The concept of coherence is the idea that superconductivity is due to the mutual interaction and correlation of the behavior of electrons .This corelation extends over a considerable distance. The maximum distance up to which the states of pair electrons are correlated to produce superconductivity is called coherence length (ξ) . In superconducting state coherence length (ξ) is of the order of $10^{-6} m$. The properties of a superconductor depend on the correlation of electrons within a volume of $(\xi)^3$ called the coherence volume. Since the large number of electrons in such a volume act together in superconductivity, so the transition is extremely sharp. The ratio of London penetration depth to the coherence length given by

$$K = \frac{\lambda}{\xi} \tag{20.12}$$

For type –I superconductors $K < \frac{1}{\sqrt{2}}$ and for type-II superconductors $K > \frac{1}{\sqrt{2}}$. It can be shown from BCS theory that intrinsic coherence length (ξ) is related to the energy gap as

$$\xi = \frac{\hbar V_F}{E_g} \tag{20.13}$$

where E_g is the energy gap.

It has also been shown by BCS theory that the energy gap decreases from a value of about 3.5 $K_B T_C$ at 0K to zero at transition temperature T_C.

20.4 Flux Quantization in a Superconducting Ring

When a superconducting ring is placed in magnetic field B at normal temperature, then flux of magnetic field will pass through all places as shown in figure 20.2 (a). If the temperature of the ring is decreased below critical temperature then magnetic flux will diverge from the material of the ring but it is concentrated in the hole of the ring. Now if the applied magnetic filed B is reduced to zero. Then induced current in the ring maintains magnetic flux in the hole of the ring. When induced current reduces then magnetic flux linked with hole of ring also decreases.

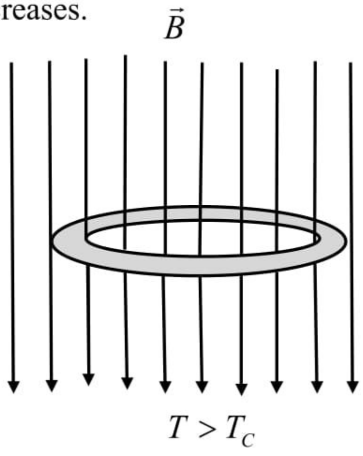


Figure 20.2(a)

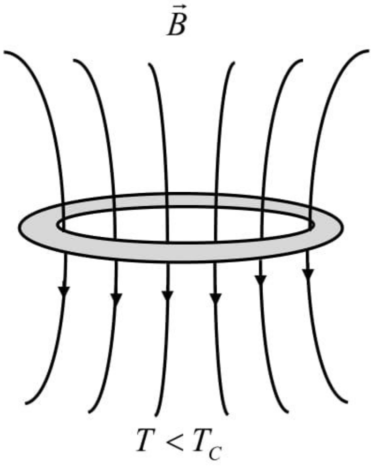


Figure 20.2(b)

Through supersensitive experiment it was observed that magnetic flux produced in a superconducting ring due to flow of superconducting current is quantized and it is perfect integer of $\frac{h}{q}$. Hence q is equal to 2e, i.e. charge of electron pair.

$$\text{Hence magnetic flux } = \phi = n\frac{h}{2e} \tag{20.14}$$

where n = 1, 2, 3…

The value of quantum of magnetic flux $= \phi_0 = \frac{h}{2e} = \frac{6.62\times10^{-34}}{2\times1.6\times10^{-19}}$

$$\therefore \ \phi_0 = 2.06\times10^{-15} \text{ weber-m}^2$$

The unit of flux is known as Fluxoid. The flux quantization has been confirmed experimentally. The quantization of flux is in accordance with modern theory of superconductivity in which electrons exists in pairs on Fermi level.

20.5 Josephson Effect

In 1962 B.D. Josephson predicated that a supercurrent consisting of correlated pairs of electrons (Cooper pair) can be made to flow across an insulating gap between two superconductors if the thickness of insulating layer is very thin of the order nm. This effect is known as Josephson's effect. If a Junction is made by joining a very thin insulator between two superconductors. Such an insulating layer forms a weak link between the superconductors which is referred to as the Josephson junction. The effects observed by Josephson are :

(i) The D.C. Josephson effect.

(ii) The A.C. Josephson effect.

Experimental arrangement to study Josephson effect

Consider the Josephson Junction with two superconductors S_1 and S_2 of the same kind separated by a very thin insulator (of the order of nanometer) as shown in figure (20.3) and no magnetic field shall be present. The object of insulating film separates the superconductors and leaving open a way of coupling them by tunneling.

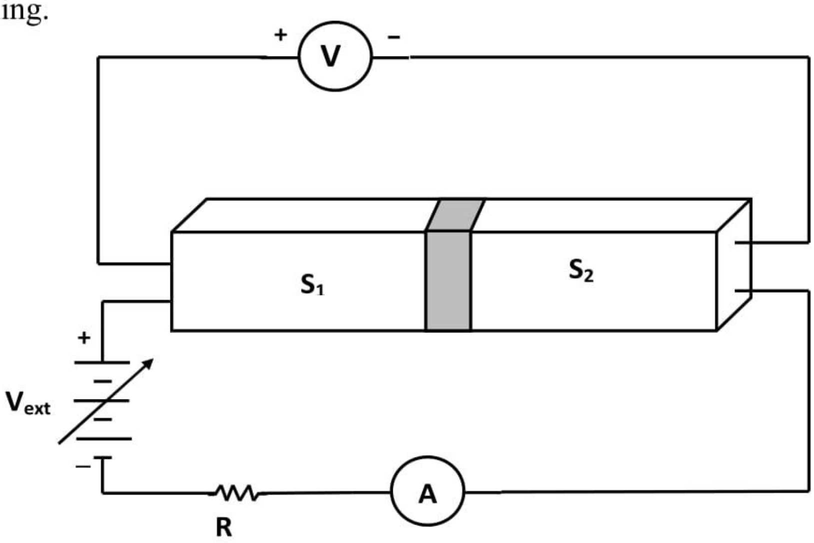


Figure 20.3 : Circuit to study Josephson effect

Now the temperature should be low enough so that it is assumed that all electrons are associated together in Cooper pairs and motion of electrons is correlated. The arrangement shown in figure (20.3) is referred as Josephson Junction. Now if the thickness of the insulating film is more ,then no current will flow and the voltmeter will indicate a voltage equal to the open circuit voltage of the current source. Now if the thickness of the insulating film is of the order of 1 nm, then voltmeter suddenly shows zero voltage showing thereby that a current flows across the junction in a superconducting way. This is known as the d.c. Josephson's effect. When a d.c. voltage is applied at the ends of the Junction ,the voltmeter indicates a voltage, but at the same time a very high frequency electromagnetic radiation emanates from the gap, indicating the presence of a very high frequency alternating current in the gap. This phenomenon is known as A.C. Josephson's effect. All these experimental observations show that BCS theory is gaining more grounds.

20.5 (A) The D.C. Josephson Effect :

As soon as the contact across the Junction is complete, a tunnel current of Cooper pairs flows. This d.c. current which flows through the Junction in absence of external magnetic field or electric field in a direction S_1 to S_2. The voltage drop V across the junction is zero though an external voltage is applied as shown in figure. The current flowing in the circuit in this condition is purely the tunnel current of Cooper pairs. This is called the d.c. Josephson effect.

20.5(B) The A.C. Josephson Effect :

On applying d.c. voltage at the ends of the Junction, it causes r.f. (radio frequency)current oscillation across the Junction. This phenomenon of generating an alternate current by applying a d.c voltage across a Josephson Junction is called a.c. Josephson effect. A d.c. voltage of 1 μV produces a frequency of 483.6 MHz. By the application of r.f. voltage alongwith the d.c. voltage can result in the flow of direct current through the junction.

20.6 Introduction to High Temperature Superconductors

We know that the property of superconductivity in many metals and alloys is obtained by cooling them up to critical temperature. Critical temperature of these were found from 0.5K to 23K (for NB_3Ge). The process of obtaining low temperature is very cumbersome and costly. So applications associated with superconductors are also very costly. So in last few years many attempt to discover superconductors of high critical temperature were performed. In present time to obtain superconductivity at high temperature ($T > 30$ K) by liquid helium or another cooling method is a subject of research.

In this reference in 1986 J.G. Bednorz and K.A. Muller for the first time discovered a new class of oxide ceramic superconductors having the critical temperature greater than 30 K. These are called high temperature superconductors. The first group of high temperature superconductor discovered was $La_{2-x} M_x CuO_4$ (where M = Ba, Ca, Sr) and critical temperature lies between 20K to 40 K. Both the scientists in their experiment measured critical temperature $T_C = 36$ K of compound $La_{1.85} Ba_{0.15} CuO_4$ in the system of Ba – La –CuO. This process was followed by the discovery of another important system having the general formula $LnBa_2Cu_3O_{7-x}$ (Ln =Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb) with x = 0.2. In 1988 several other non-rare earth based copper oxide system involving *Tl* and Bi were discovered which showed superconductivity between 60 K and 125 K. The critical temperature of these substances are more than critical temperature of liquid Nitrogen. So these can be converted into superconductors easily. Both these scientists were awarded Noble prize in 1987 for the discovery of high temperature superconductivity. Various families of high temperature superconductors with critical temperature limits are given below

Formula	**Symbol**	**Range of T_C in 0K**
(i) $La_{2-x} M_x CuO_4$	M = Ca, Sr, Ba	20 – 40
(ii) $Ln Ba_2 Cu_4O_8$	Ln = rare earth element	90
(iii) $Ti_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$	n = 1–4	80 –125
(iv) $Pb_2Sr_2ACu_3O_8$	A=rare earth or Ln + Sr or Ca	40 – 70

Recently it has been possible to design some ceramic superconductors which can act as such at temperature greater than 77 K, these high temperature oxide superconductors have advantage over low temperature superconductors in the sense that liquid nitrogen can be used as coolent, this arrangement is not only much cheaper but has better cooling due to high thermal capacity of liquid nitrogen. This also suggests strongly that with modified ceramic materials we may have superconducting materials at room temperature in future.

20.7 Application of Superconductors

Superconductivity finds a number of practical applications as follows.

(1) In making cryotron : It is a magnetically operated current switch. As we know superconductivity disappears for magnetic field exceeding the critical value, has been utilized in a cryotron. It was discovered by Buck. The Cryotron is used in digital computers.

(2) In making superconducting coils : Since superconducting rings can produce maximum magnetic field with the required homogeneity. Since the superconducting current density flowing through superconducting rings is maximum $(\sim 10^8 amp/m^3)$ so the magnetic field produced by this current is also more (B > 10Tesla). High magnetic fields are used in high energy physics.

(3) In making cables : In those works, where high alternating current is required, for power transmission niobium superconductor is used in making cables. In power transmission by superconductors, power loss is very small.

(4) Electromagnets : Electromagnets that carry heavy currents can be constructed and thereby large magnetic fields of the order of 5 to 10Tesla can be obtained. As thin superconducting wires can carry large currents as their resistivity is zero.

(5) Bearings : These use the Meissner effect. The mutual repulsion between two superconductors that expel the magnetic flux is used in the principle, the bearings operate without power loss and friction.

(6) The memory systems, logic units, cryotronic switches, oscillators, amplifiers, modulators, superconducting magnetometers, microwave detector,

superconducting computer and counters etc. are possible with superconductors.

20.8 Self Learning Exercise

Q.1 What is London penetration depth ?

Q.2 What is d.c. Josephson effect ?

Q.3 Explain electron-phonon-electron interaction.

Q.4 Explain the flux quantization in a superconducting ring.

20.9 Summary

In this chapter we have studied the phenomenon of superconductivity with theoretical explanation by London equations and B.C.S. theory. In London theory we studied coherence length and penetration depth. London theory can explain only Meissener effect but failed to explain the presence of energy gap in superconductors and other properties. The B.C.S. theory is able to explain all the experimental observations such as coherence length, flux quantization etc. in metallic superconductors. In 1986 Bednorz and Muller discovered a new class of oxide ceramic superconductors having the critical temperature more than 30 K. These are called high temperature superconductors. These are having a wide and variety of applications in various fields of science.

20.10 Glossary

Phonon : Quanta of Lattice Vibration

B.C.S. theory: Bardeen, Cooper and Schrieffer theory for superconductivity.

20.11 Answers to Self Learning Exercise

Ans.1: It is the distance from the surface of substance where the value of magnetic field reduces to $\left(\frac{1}{e}\right)$ of its initial value at the surface.

Ans.2: According to this effect, a d.c. current flows across the junction even when no voltage is applied across it.

20.12 Exercise

Section-A (Very Short Answer Type-Questions)

Q.1 What is cooper pair ?

Q.2 Write down London's first and second equations.

Q.3 What is coherence length ?

Section-B (Short Answer Type Questions)

Q.4 Describe the construction of cooper pair in short.

Q.5 Derive an expression for London penetration depth in superconductor.

Q.6 Describe the application of superconductors.

Section-C (Long Answer Type Questions)

Q.7 Derive London equations and hence discuss the Meissner effect.

Q.8 Give a qualitative description of the BCS theory. On the basis of this theory explain the energy gap and ground state in superconductors.

Q.9 What is Josephson effect ? Distinguish between d.c. and a.c. Josephson effects?

Q.10 What are high temperature superconductors? Write a note on them ?

Q.11 What is flux quantization ? Prove that the magnetic flux trapped inside the superconducting ring is an integer multiple of $\left(\frac{h}{q}\right)$,where h is Planck's constant and q is the charge of superconducting carrier.

20.13 Answers to Exercise

Ans.1: In superconductor, two electrons, whose momentum is equal and opposite, interacts by the exchange of phonon form a pair and this pair of two electrons is known as Cooper pair.

Ans.2: (i) First London's equation is given by

$$\frac{d\vec{J}}{dt} = \frac{ne^2}{m}\vec{E}$$

(ii) Second London's equations is given by

$$\vec{\nabla} \times \vec{J} = -\frac{ne^2}{m}\vec{B}$$

Ans.3: The paired electrons (i.e. Cooper pair) keep their coupled motion up to a certain distance. This distance up to which they almost behaves as a single unit is called coherence length.

References and Suggested Readings

1. Introduction to Solid State Physics by C. Kittel
2. Elementary Solid State Physics by Rama Swami
3. Solid State Physics by S.O. Pillai
4. Solid State physics by A.J. Dekker
5. Fundamentals of Solid State Physics by Saxena Gupta and Sexena.
6. Introduction to Superconductivity by A.C. Rose-Innes and EHEH Rhoderick.

UNIT-21

Nanoscience

Structure of the Unit

21.0 Objectives

Nanotechnology offers a paradigm that crosses scientific disciplines and therefore provides a unique motivation for exploring the intersections between traditional disciplines. The broad nanotechnology invests at the frontiers and intersections of many areas, including biology, chemistry, computer science, ecology, engineering, geology, materials science, medicine, physics and the social sciences. Activities targeted towards this goal span a broad continuum, form support for basic and fundamental research through use-inspired and application research and into technology development. Successful advancement and commercialization of nanotechnology will depend on the scientific quality of research.

21.1 Introduction

Nanoscience is one of the most exciting topics in the history of scientific research. The role of nanotechnology was given its due recognition by prominent academicians from all over the world and industry as well recognized its potential for a plethora of applications.

21.2 Background of Nanoscience and Nanotechnology

At the beginning of 20th century, when scientists felt that atoms were mere abstract entities used for the purpose of calculations, it was Albert Einstein who explained the “jittery dance of microscopic particles-Brownian motion”- with his original work tilted “On the movement of *small particles* suspended in stationary liquids required by the molecular-kinetic theory ” and provided the view point that the mathematical description of Brownian motion is the evidence for the true existence of atoms.

21.3 History of Nanoscience

After the prediction of Albert Einstein, Richard P. Feynman suggested that it should be possible to build machines small enough to manufacture objects with atomic precision. His talk, *There's plenty of Room at the bottom,* is widely considered to be the foreshadowing of nanotechnology.

Feynman said, “What I want to talk about is the problem of manipulating and controlling things on a Small Scale”. The term “nanotechnology” rapidly became popular.

Following this, a team of IBM physicist revealed that they could write the letters “IBM” using 35 individual atoms of Xenon. A book titled *Nanosystems: Molecular Machinary, Manufacturing and computation* was published by Eric Drexler where he outlined a way to manufacture extremely high-performance machines out of molecular carbon lattice. After some time Federal funding for nanotechnology in the United States began with the National Nanotechnology Initiative (NNI). The NNI-funded nanotechnology was defined as a new technology dealing with materials with sizes between 1 to 100 nanometres exhibiting novel properties. The broad definition covering cutting-edge semiconductor research, several developing families of physics and chemistry, deals with physics of low dimensional systems and other advanced materials. The government of India launched a mission on nanoscience and nanotechnology with an allocation of 1000 crores for the first five years. One of the main objective of this mission is to foster linkage between educational and research institutions and industry and promote public private partnerships.

21.4 Density of States at Low Dimensional Structures

The density of states (DOS) formulation describes the number of electronic states that are available in system. Therefore it is important from the viewpoints of carrier concentration of the system and energy distribution of the carriers. It is also useful for the determination of optical properties of a material such as a semiconductor. Here, we will find out the expressions for DOS for three-dimensional, two-dimensional, one-dimensional and zero-dimensional systems and see if the electronic DOS changes as a function of size reduction.

21.4.1 Density of States at One-Dimensional Structures:

In case of one-dimensional system (nanowire), the electron is confined in both the $x - and\ y - directions$, but the electron can move freely in the $z - direction$ (quantum wire). The DOS equation for 1D system is given by

$$g(k)dk = 2\frac{2dk}{2\left(\frac{\pi}{a}\right)} \tag{21.4.1}$$

where $2dk$ is the length of wire in $k - space$ and $2\left(\frac{\pi}{a}\right)$ is effective length of the wire and multiplication factor 2 is due to the spin degeneracy. Finally we get

$$g(k)\, dk = \frac{2a}{\pi} dk \tag{21.4.2}$$

We have

$$kdk = \left(\frac{m}{\hbar^2}\right)\, dE$$

By putting the value of $k = \sqrt{2mE/\hbar^2}$, we get

$$dk = \sqrt{\frac{\hbar^2}{2mE}}\left(\frac{m}{\hbar^2}\right)\,dE \tag{21.4.3}$$

Substituting dk in Equation (21.4.2), the number states in the energy range $E\ and\ E + dE$ can be written as

$$g(E)dE = \frac{2a}{\pi}\sqrt{\frac{\hbar^2}{2mE}}\left(\frac{m}{\hbar^2}\right)\,dE \tag{21.4.4}$$

Hence, DOS for the 1D case [DOS(1D)] is given by

$$DOS\ (1D) = \left(\frac{a}{\pi}\sqrt{\frac{2m}{\hbar^2}}\right)\sqrt{\frac{1}{E}} \tag{21.4.5}$$

which varies as $\sqrt{\frac{1}{E}}$. Figure 21.1 depicts the 1D Nano system (nanorod) and the corresponding DOS variation of the 1D system as a function of energy.

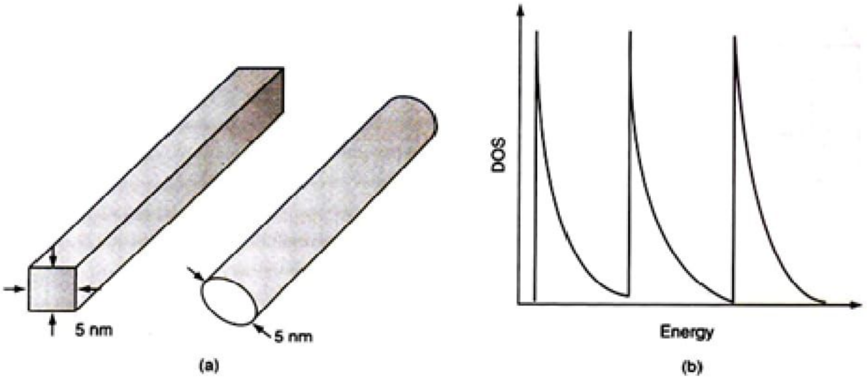


Figure 21.1: (a) Illustration of 1D system, (b) DOS variation of 1D system as function of energy.

21.4.2 Density of States at Zero-Dimensional Structures:

The DOS for a 0-D system (quantum box or a quantum dot) shows the variation like that of a δ-function as shown in Fig.21.2

Electronic levels and DOS determine the properties of materials including optical, magnetic and electronic properties and there functionalities. For nanoscale materials, the energy levels and the DOS vary as a function of size, resulting in dramatic changes in the material property. Thus, the DOS of a reduced dimensional system also changes significantly with decreasing size. As discussed above, for a 3-D bulk material, the DOS is proportional to the square root of energy ($\sqrt{E}$). For a 2D system (ultra thin film quantum wells), the DOS is a step function. For a 1D system (nanowire or quantum wire), the DOS is completely different (peculiar behaviour). For a 0-D system (quantum dot), The DOS has the shape for a δ-function (atom like) . Figure 21.2 shows a summary of the DOS for low-dimensional systems in comparison with the microscopic bulk material.

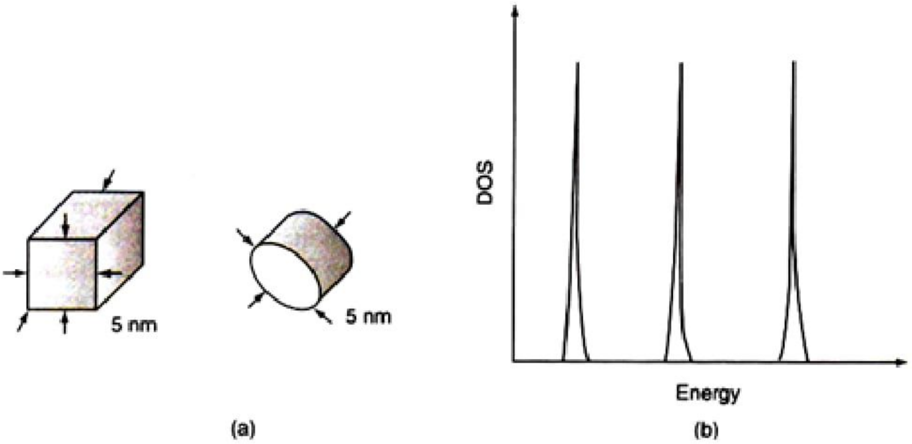


Figure 21.2: (a) Illustration of 0D system, (b) DOS variation of 0D system as function of energy.

21.5 Idea of Quantum Well Structure

If we consider initially an isolated thin semiconductor sheet of thickness L, the carrier motion is unrestricted in such a thin sheet along two orthogonal directions with in the plan of sheet. However, the motion is quantized perpendicular to the plane, forming a quantum well. The resultant quantized energy levels are found by solving the 1D form of the time independent Schrodinger equation given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2}+V(x)\psi_n(x)=E_n(x)\psi_n(x)$$

where V(x) is the potential and $\Psi_n(x)$ and E_n are the wave function and energy of the *n*th confined state respectively. The one dimensional potential [V(x)] can be constructed from alternating thin layers of dissimilar semiconductors in which electrons and holes can move in the plane of layers. For the present case, V(x) is zero within the semiconductor (which extends from x = 0 to x = L) and is infinite elsewhere; this is the infinite-depth potential well model.

Solving the Schrodinger equation and apply the boundary condition that the wave functions must be zero at the edges of the sheet results in the following energies and wave functions

$$E_n = \frac{h^2 n^2}{8mL^2} \tag{21.5.1}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{21.5.2}$$

Here n= 1, 2, 3, 4, ……..∞.

A thin free-standing semiconductor sheet would possess negligible mechanical strength, and practical quantum wells are formed by sandwiching a thin layer of a semiconductor between two layers of a second, larger bandgap semiconductor which forms the barriers. This results in a finite-depth potential (~25eV) well. The wave functions and energies of a confined state are again determined by the solution of the Schrodinger equation with the appropriate potential, which now remains finite outside the well.

In contrast to the infinite-depth well, in the case of a finite-depth potential well, the wave functions penetrate out of the well and into the barriers. For a finite-depth-well, it is not possible to obtain analytical forms for the confined energies and the Schrodinger equation must be solved numerically. However, for many applications, the energies and wave functions of an infinite-depth well can be used as reasonable approximations, particularly for states that lie close to the bottom of the well. For the semiconductor quantum well, both the electron and hole motions normal to the plane will be quantized, resulting in a series of confined energy states in the conduction and the valence bands.

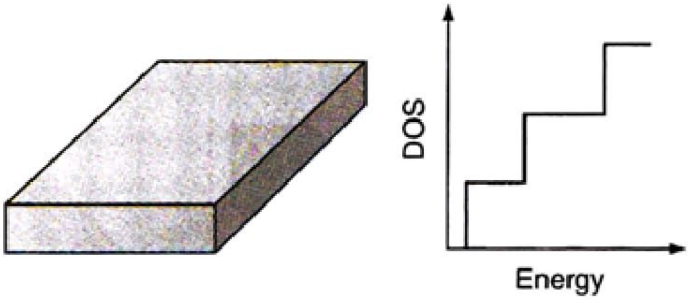


Figure 21.3: Quantum well

One consequence of this quantum confinement is that the effective bandgap of the semiconductor is increased from its bulk value by the addition and hole confinement energies corresponding to the states with $n = 1$ and is given by

$$E_g^{eff} = E_g + \frac{h^2}{8m_e L^2} + \frac{h^2}{8m_h L^2} \tag{21.5.3}$$

The effective bandgap will determine, for example, the energy of emitted photons and can be altered by varying the thickness of the well. If we consider the emission spectrum of a structure containing five quantum wells of different widths, each well emits photons of different energies; the energy increases as the width of the well decreases, in agreement with the predictions of the equation. Although the carrier energy is quantized for motion normal to the well, the motion is unrestricted. The total energy of a carrier is given by the sum of the energies due to this unrestricted motion plus the quantization energy. The motion in-plane is characterized by a wave vectors (k_{II}), which corresponds to the combination of the wavevectors for motion along the two mutually orthogonal in-plane directions.

If the z-axis is taken perpendicular to the plane of the well, then the two in-plane directions are x and y and hence we can write

$$k_{II} = \sqrt{k_x^2 + k_y^2} \tag{21.5.4}$$

From the relationship between momentum, p = mv and wave vector, p = $\hbar$k , where $\hbar$ = h/2π , the definition of kinetic energy is given by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{21.5.5}$$

The energy corresponding to in-plane motion can be written as

$$E = \left(\frac{\hbar^2 k_{II}^2}{2m}\right) \tag{21.5.6}$$

The total energy for a carrier in the *n*th confined states is therefore given by

$$E_{n,k_{II}} = \frac{\hbar^2 k_{II}^2}{2m} + \frac{h^2 n^2}{8mL^2} \tag{21.5.7}$$

Heisenberg uncertainty principal tells us that if we confine a particle with a mass *m* to a region of the z-axis of length Δz (e.g., thickness of a thin film quantum well), then we introduce an uncertainly in its momentum given by

$$\Delta p_z \sim \frac{\hbar}{\Delta z} \tag{21.5.8}$$

The confinement in the z-directions gives the particle's additional kinetic energy of magnitude is given by

$$E_{confinement} = \frac{(\Delta {p_z}^2)}{2m} \sim \frac{\hbar^2}{2m(\Delta z)^2} \qquad (21.5.9)$$

The confinement energy will be significant if it is comparable to or greater than the kinetic energy of the particle due to its thermal motion in the z-direction. Hence, Eq. (21.5.9) may be written as

$$E_{confinement} \sim \frac{\hbar^2}{2m(\Delta z)^2} \geq \frac{1}{2} k_B T \qquad (21.5.10)$$

Equation (21.5.10) gives us an idea that the size-dependent "*quantum confinement effect*" will be important if

$$\Delta z \sim \sqrt{\frac{\hbar^2}{m k_B T}} \qquad (21.5.11)$$

This is equivalent to saying that Δz must be of the same order of magnitude as the de Broglie wavelength $\lambda_{dB} \equiv p_z/h$ for the thermal motion. The criterion given in Eq. (21.5.11) gives us an idea of how small the structure must be if we are to observe "size dependent quantum confinement effects." For an electron in a typical semiconductor quantum well (ultrathin film), we find that we must have $\Delta z \sim 5\text{nm}$ (nearly 10-12 unit cell stacks). In other words, to observe the quantum confinement effect, we must grow thin enough layers by employing advanced growth techniques such as molecular beam epitaxy (MBE), metal-organic comical vapour deposition (MOCVD), pulsed laser deposition (PLD), etc.,

21.6 Quantum Wire

A quantum wire can be considered as a strip of a semiconductor. Unrestricted carrier motion is only possible along the length of the wire and is quantized along the two remaining orthogonal directions. For simple wire shapes (square or rectangular cross sections), it is possible to calculate the quantization energies for the two directions independently. These two quantization energies are then added to the energy resulting from the unrestricted motion along the wire. Using the infinite-depth approximation for the quantized energies, the total energies for a carrier in a quantum wire with z and y dimensions L_z and L_y respectively, is

$$E_{n,\ k_{II}} = \frac{h^2 n^2}{8m^* L_z^2} + \frac{h^2 m^2}{8m^* L_y^2} + \frac{\hbar^2 k_x^2}{2m^*} \qquad (n, m= 1, 2, 3, \ldots\ldots)$$

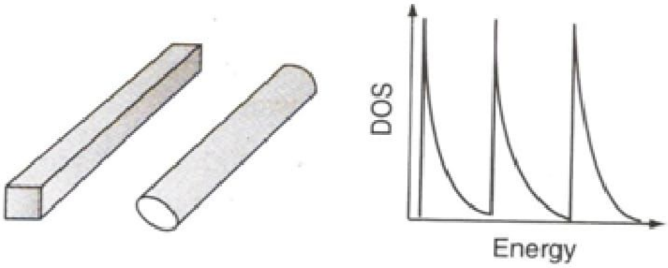


Figure 21.4: Quantum wire.

The total energy depends on the two quantum numbers n and m and the wavevector for free motion along the wire is k_x .Here m^* is the effective mass. For each confined state, given by a particular combination of *n* and *m*, there will be a sub-band of continuous states resulting from the unrestricted values of k_x.

In realty quantum wires have complex cross-sections. This prevents the confined energies from being calculated by separating them in two terms corresponding to the directions to the axis of the wire. Instead, the confined energies of a quantum wire must be obtained from a numerical solution of the appropriate Schrodinger equation.

21.7 Quantum Dots

In a quantum dot, the carrier motion is quantized along all three spatial directions and this means there is restricted carrier motion. For a simple shape such as cube or a cuboid or a cluster, confinement for the three spatial directions can be considered separately. In the infinite-depth well approximation, the energy for a carrier in cuboid-shaped dot of dimensions L_z, L_y, and L_x is a function of three quantum numbers *n, m,* and *l* and is given by

$$E_{n,m,l} = \frac{h^2 n^2}{8m^* L_z^2} + \frac{h^2 m^2}{8m^* L_y^2} + \frac{h^2 l^2}{8m^* L_x^2} \quad (n, m= 1, 2, 3, \ldots\ldots)$$

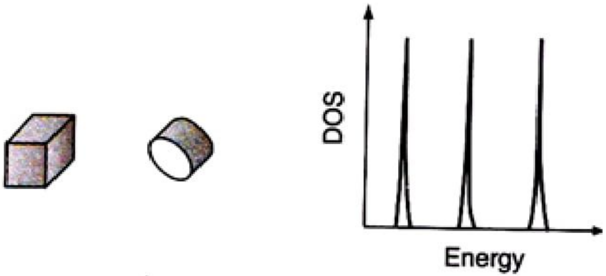


Figure 21.5: Quantum dots.

The energy is now fully quantized and the states are discrete, in a manner similar to those of an atom. The shapes of real quantum dots are more complex than simple cuboid and a calculation of the confined energy levels requires a numerical solution of the relevant Schrodinger equation.

21.8 Growth Techniques of Nanomaterials

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapour phase. On the basis of this, crystal growth may be classified into three categories as follows,

Solid Growth - Solid-to-Solid phase transformation

Liquid Growth - Liquid to Solid phase transformation

Vapour Growth - Vapour to Solid phase transformation

Based on the phase transformation process, crystal growth techniques are classified as solid growth, vapour growth, melt growth and solution growth.

The conversion of a polycrystalline piece of material into single crystal by causing the grain boundaries to be swept through and pushed out of the crystal takes place in the solid-growth of crystals. The above methods have been discussed in detail by several authors.

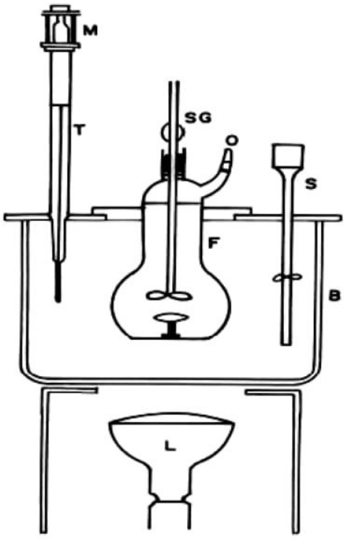
An efficient process is the one, which produces crystals adequate for their use at minimum cost. Better choice of the growth method is essential because it suggests the possible impurity and other defect concentrations. Choosing the best method to grow a given material depends on material characteristics.

In the above mentioned categories liquid growth includes both melt and solution growth. A survey of the methods of growth suggests that almost 80% of the single crystals are grown from the melt compared with roughly 5% from vapour, 5% from low temperature solution, 5% from high temperature solution, and 3% from the solid and only 2% by hydrothermal methods.

In contrast to the historical work, it seems that the essential task for the crystal growers at present is to gain basic knowledge about the correlation of crystal properties and the growth conditions defined to be special parameters. This basic understanding of the deposition of atoms onto a suitable substrate surface – crystal growth – the generation of faults in the atomic structure during growth and subsequent cooling to room temperature – crystal defect structure, are the input for the design of crystal growth systems and control of growth parameters. Though the fundamentals are relatively simple, the complexities of the interactions involved and the individualities of different materials, system and growth process have ensured that experimentally verifiable predictions from scientific principles have met with limited success – good crystal growth remains apart. As a result, crystal growth has long had the image of alchemy. The recent advances which include reduction of growth temperature, the reduction or elimination of reactant transport variables and the use of better controlled energy sources to promote specific reactions, coupled with increased development and application of *in-situ* diagnostic techniques to monitor and perhaps the ultimate control lead to simplified growth systems and the crystal growth process has transferred the field from an art to science, technique and to technology.

21.8.1 Growth From Solution

Materials, which have high solubility and have variation in solubility with temperature can be grown easily by solution method.



L : Heater Lamp ; B : Bath ; F : Flask ; S : Stirrer ;
O : Opening ; SG : Stirring Gland ; T : control Thermometer ;
M : Motor.

Figure21.6 Basic apparatus for solution growth

There are two methods in solution growth depending on the solvents and the solubility of the solute. They are

1. High temperature solution growth
2. Low temperature solution growth

21.8.1.1 High temperature solution growth:

In high-temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturation may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a cooler region. The high temperature crystal growth can be divided into two major categories:

1. Growth from single component system.
2. Growth from multi component system.

This method is widely used for the growth of oxide crystals. The procedure is to heat the container having flux and the solute to a temperature so that all the solute materials dissolve. This temperature is maintained for a 'soak' period of several hours and then the temperature is lowered very slowly.

21.8.1.2 Growth From Melt:

All materials can be grown inform of single crystal from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature. Depending on the thermal characteristics, the following techniques are employed.

1. Bridgman technique
2. Czochralski technique
3. Kyropoulos technique
4. Zone melting technique
5. Verneuil technique

1. In **Bridgman technique** the material is melted in a vertical cylindrical container, tapered conically with a point bottom. The container is lowered slowly from the hot zone of the furnace in to the cold zone. The rates of movement for such processes range from about 1 – 30 mm/hr. Crystallization begins at the tip and continues usually by growth from the first formed nucleus. This technique cannot be used for materials, which decompose before melting. This technique is best suited for materials with low melting point.

2. In **Czochralski method**, the material to be grown is melted by induction or resistance heating under a controlled atmosphere in a suitable non-reacting container. By controlling the furnace temperature, the material is melted. A seed crystal is lowered to touch the molten charge. When the temperature of the seed is maintained very low compared to the temperature of the melt, by suitable water cooling arrangement, the molten charge in contact with the seed will solidify on the seed. Then the seed is pulled with simultaneous rotation of the seed rod and the crucible in order to grow perfect single crystals.

Liquid encapsulated Czochralski abbreviated as LEC technique makes it possible to grow single crystals of materials, which consists of components that produce high vapour pressure at the melting point. This refined method of Czochralski technique is widely adopted to grow III-V compound semiconductors.

3. In **Kyropoulos technique**, the crystal is grown in a larger diameter. As in the Czochralski method, here also the seed is brought into contact with the melt and is not raised much during the growth, i.e. part of the seed is allowed to melt and a short narrow neck is grown. After this, the vertical motion of the seed is stopped and growth proceeds by decreasing the power into the melt. The major use of this method is growth of alkali halides to make optical components.

4. In the **zone melting technique**, the feed material is taken in the form of sintered rod and the seed is attached to one end. A small molten zone is maintained by surface tension between the seed and the feed. The zone is slowly moved towards the feed. Single crystal is obtained over the seed. This method is applied to materials having large surface tension. The main reasons for the impact of zone refining process to modern electronic industry are the simplicity of the process, the capability to produce a variety of organic and inorganic materials of extreme high purity, and to produce dislocation free crystal with a low defect density.

In the case of vertical normal freezing, the solid-melt interface is moved upwards from the cold bottom to the hot top so as to get better quality crystals. The method is more applicable in growing single crystals of materials with volatile constituents like GaAs.

5. In the **Verneuil technique**, a fine dry powder of size 1-20 microns of the material to be grown is shaken through the wire mesh and allowed to fall through the oxy-hydrogen flame. The powder melts and a film of liquid is formed on the top of the seed crystal. This freezes progressively as the seed crystal is slowly lowered. The art of the method is to balance the rate of charge feed and the rate of lowering of the seed to maintain a constant growth rate and diameter. By this method ruby crystals are grown up to 90 mm in diameter for use in jewelled bearings and lasers. This technique is widely used for the growth of synthetic gems and variety of high melting oxides.

21.8.2 Low Temperature Solution Growth

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. It is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures and also which undergo phase transformations below melting point. The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. A power failure or a contaminated batch of raw material can destroy months of work.

Materials having moderate to high solubility in temperature range, ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method. The mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process; temperature, pressure and solvent concentration. The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straight forward equipment design which gives a good degree of control of accuracy of ±0.01 ºC. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum.

The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique .The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent (Hooper et al 1979). The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the ease of solvent inclusion into the growing crystal. Under the controlled conditions of growth the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. After many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low.

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications.

In the low temperature solution growth, crystals can be grown from solution if the solution is supersaturated i.e., it contains more solute than it can be in equilibrium with the solid. Three principal methods are used to produce the required supersaturation:

i. Slow cooling of the solution

ii. Slow evaporation of the solvent

iii. The temperature gradient method.

Low temperature solution growth is a well-established technique due to its versatility and simplicity. It is possible to grow large crystals of high perfections as the growth occurs close to equilibrium conditions. It also permits the preparation of different morphologies of the same materials by varying the growth conditions.

21.8.2.1 Slow Cooling Technique

It is the best way to grow single crystals by solution technique. The Main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which such crystallization can begin is usually within the range 45 - 75 °C and the lower limit of cooling is the room temperature.

21.8.2.2 Slow Evaporation Method

This method is similar to the slow cooling method in view of the apparatus requirements. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.005°C and rates of evaporation of a few ml /hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials, which have very small temperature coefficient of stability.

21.8.2.3 Temperature Gradient Method

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are that

(a) Crystal grows at a fixed temperature.

(b) This method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change.

(c) Economy of solvent and solute.

On the other hand, changes in the small temperature differences between the source and the crystal zones have a large effect on the growth rate.

Excellent quality nanomaterials of ferroelectric and piezo-electric materials such as Ammonium dihydrogen phosphate (ADP), Potassium di-hydrogen phosphate (KDP) and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method.

21.8.3 Electrocrystallization:

Electrolysis of fused salts is normally used for the commercial production of metals such as aluminium and has great technological importance. The process of crystal growth from fused salts is analogous in many respects, except for the requirement of electron transfer in deposition of the metal. Fused salt electrolysis has been used to grow crystals of oxides in reduced valence states.

21.9 Plasma Arc Discharge Method

The synthesis setup consists of a stainless steel cylindrical vacuum chamber with a total volume of 4500cm^3 (27 cm in length and 14.5 cm in diameter). A pair of electrodes ,a cathode and anode, is installed along the vertical axis of the chamber. Both electrodes are made of POCO EDM-3 graphite. The cathode is a cylindrical rod with a diameter of 13 mm, while the anode is a hollow tube with inner and outer diameters of 3 and 5 mm respectively.

Figure 21.7a shows the schematic of the arc discharge synthesis setup. The anode and cathode were placed 2 mm apart, and the distance between the substrate and the cathode-anode assembly was about 1.5-2 cm. A shutter (shown in Figure 21.7b) made of molybdenum foil, with a quarter section cutout, allowed control of the substrate exposure time to the arc plasmas. The vacuum chamber was pumped to the pressure of about 13 Pa and then high purity helium (about 99.97%) was introduced into the chamber to the pressure around 67000 Pa.

A 1.5 x 14 mm^2, 0.1 mm thick copper foil was used as a substrate to collect sample. In order to heat the substrate, a nickel-chromium resistance wire was used. The resistance wire was wound into the shape of a spring, and the copper foil was then inserted inside. Voltage generated by a variable auto-transformer was applied to the heater during the synthesis. Before the experiment, the substrate was pre-cleaned using ethanol. It has to be noted that extreme requirements to residual vacuum and substrate cleaning were not applied in this work.

The arc electrodes were connected to an external DC power source at a fixed arc current of about 75A. Arc current and arc voltage were recorded by a digital oscilloscope. The anode motion was controlled by a linear drive system using a personal computer equipped with a National Instruments Data Acquisition card, and the program was written on the lab view platform. The arc was generated by mechanical contact of the arc electrodes followed by their immediate separation. A camera was utilized to record the whole process of the synthesis procedure.

The sample synthesized on the copper substrate was then characterized using a Horiba Lab RAM spectroscope, SIGMA VP-02-44 SEM and JEOL 1200 EX TEM. It has to be noted that there was no quantity of sample observed on the pre-heated substrate if the arc discharge was not initiated, indicating that possible production of sample as a result of decomposition of hydrocarbon oil utilized in the vacuum pumping system is negligible.

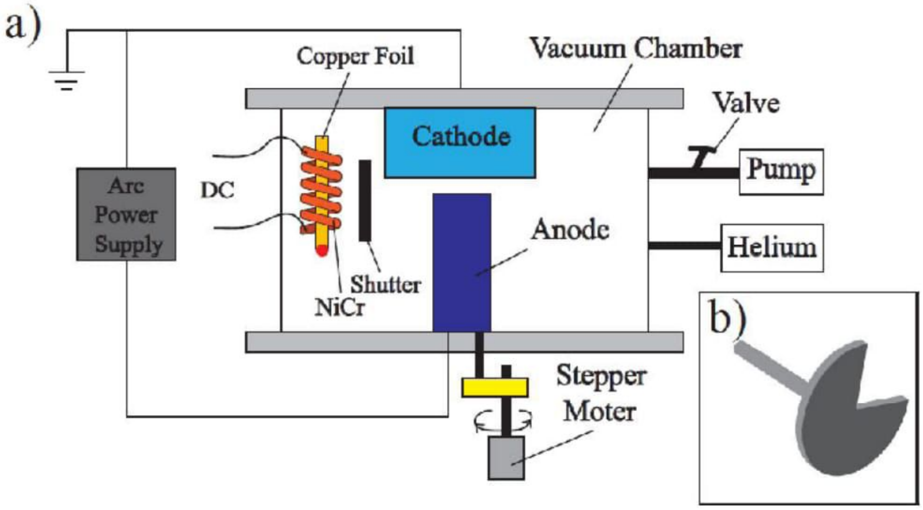


Figure21.7 Schematic of the set-up of the plasma based synthesis system using Shutter in between the substrate and arc.

The substrate was heated for 2 minutes before initiating the arc. Once the arc stabilized, a few seconds after initiation, the shutter then made one full revolution for one second. After a single revolution, the arc was then turned off. Heating of the copper foil was continued for an additional 3 minutes and then was also turned off.

21.10 Pulsed Laser Deposition

Transient and high speed events can be photographed using holographic methods. It is especially useful, when it is not clear, as to where in a given volume the event is taking place. So the techniques applied in particle size analysis can also be used in macrophotography. A ruby laser, both in conventional and Q switched mode was used by Brookers and his colleagues. The design was such that the path of the reference beam was carefully matched to the path of the illuminating beam. Here the output from the laser is slightly diverged and divided into two, by a beam divider.

21.11 Chemical Methods

If the crystal is in dynamic equilibrium with its parent phase ,the free energy is at a minimum and no growth will occur. For growth to occur this equilibrium must be disturbed by a change of the correct sign, in temperature, in pressure, chemical potential (e.g. saturation) electrochemical potential (e.g. electrolysis), or strain (solid state growth). The system may then release energy to its surrounding to compensate for the decrease in entropy occasioned by the ordering of atoms in the crystal and the evolution of heat of crystallization. In a well – designed growth process just one of these parameters is held minimally away from its equilibrium value to provide a driving force for growth.

Crystal growth then is a non-equilibrium process and thought must be given to the temperature and concentration and other gradients and the fact that heat of crystallization is evolved and must be removed to the surroundings. At the same time the crystal growth process must be kept as near equilibrium and as near to a steady state process as possible. This is why control of the crystal growth environment and a consideration of growth kinetics both at the macroscopic and the atomic levels are of vital importance to the success of a crystal growth experiment. It is particularly important to avoid constitutional supercooling and the breakdown of the crystal-liquid interface that this can cause.

In some growth techniques there is no crystal initially present. Here the nucleation problem is met which in essence is due to the fact that the surface-to-volume ratio of small particle is much higher than for a large crystal. Surfaces lose energy because of discontinuities in atomic bonding. Thus the nucleation of a new phase is a discontinuity, not a quasi equilibrium process. This is the reason why pure melts supercool and solutions become supersaturated. Thus the growth system departs considerably from equilibrium before a crystal nucleates, and when it comes the new born crystal grows very rapidly at first and is full of defects, some of which propagates into the later stages of near equilibrium growth. Crystal growers thus seek to use methods where a seed crystal can be introduced into the system to avoid the nucleation. In the last three decades great strides have been made toward achieving crystal perfection motivated by the needs of the electronics and optics industries. While thermodynamics excludes the possibility of growing a perfect crystal, gross defect like grain boundaries, voids, and even dislocations can be eliminated with care and point defects, like impurities, vacancies, interstitials, and antistructure disorder can be minimized by attention to growth environment and purity of reagents and apparatus.

There are some chemical methods present for the growth of the nano-materials

21.11.1 Gel Growth

It is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. Gel is a two-component system of a semisolid rich in liquid and inert in nature. The material, which decomposes before melting, can be grown in this medium by counter diffusing two suitable reactants. Crystals with dimensions of several mm can be grown in a period of 3 to 4 weeks. The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place at room temperature.

21.11.2 Hydrothermal Growth

Hydrothermal implies conditions of high pressure as well as high temperature. Substances like calcite, quartz is considered to be insoluble in water ,but at high temperature and pressure, these substances are soluble. This method of crystal growth at high temperature and pressure is known as hydrothermal method. Temperatures are typically in the range of 400°C to 600°C and the pressure involved is large (hundreds or thousands of atmospheres).

Growth is usually carried out in steel autoclaves with gold or silver linings. Depending on the pressure the autoclaves are grouped into low, medium and high-pressure autoclaves. The concentration gradient required to produce growth is provided by a temperature difference between the nutrient and growth areas. The requirement of high pressure presents practical difficulties and there are only a few crystals of good quality and large dimensions are grown by this technique. Quartz is the outstanding example of industrial hydrothermal crystallization. One serious disadvantage of this technique is the frequent incorporation of OH^- ions into the crystal, which makes them unsuitable for many applications.

21.11.3 Growth from Vapour

The growth of single crystal material from the vapour phase is probably the most versatile of all crystal growth processes. Crystals of high purity can be grown from vapour phase by sublimation, condensation and sputtering of elemental materials. To obtain single crystals of high melting point materials this method is used. Molecular beam techniques have also been applied recently to crystal growth problems. The most frequently used method for the growth of bulk crystals utilizes chemical transport reaction in which a reversible reaction is used to transport the source material as a volatile species to the crystallization region. Finding a suitable transporting agent is a formidable, problem in this technique. It is rarely possible to grow large crystals because of multi-nucleation.

The commercial importance of vapour growth is the production of thin layers by chemical vapour deposition (CVD), where usually irreversible reactions e.g. decomposition of silicon halides or of organic compounds are used to deposit materials epitaxially on a substrate. Doping can be achieved by introducing volatile compounds of dopant elements into the reaction region. The thickness of the doped layer can be controlled.

21.12 Thermolysis

Thermal decomposition, or **thermolysis**, is a chemical decomposition caused by heat. The **decomposition temperature** of a substance is the temperature at which the substance chemically decomposes.

The reaction is usually endothermic as heat is required to break chemical bonds in the compound undergoing decomposition. If decomposition is sufficiently exothermic, a positive feedback loop is created producing thermal runaway and possibly an explosion.

Example:

- Calcium carbonate (limestone or chalk) decomposes into calcium oxide and carbon dioxide when heated. The chemical reaction is as follows:

  $CaCO_3 \rightarrow CaO + CO_2$

The reaction is used to make quick lime, which is an industrially important product.

- Some oxides, especially of weakly electropositive metals decompose when heated to high enough temperatures. A classical example is the decomposition of mercuric oxide to give oxygen and mercury metal.

When metals are near the bottom of the reactivity series, their compounds generally decompose easily at high temperatures. This is because stronger bonds form between atoms towards the top of the reactivity series, and strong bonds break less easily. For example, copper is near the bottom of the reactivity series, and copper sulphate ($CuSO_4$), begins to decompose at about 200 °C, increasing rapidly at higher temperatures to about 560 °C. In contrast potassium is near the top of the reactivity series, and potassium sulphate (K_2SO_4) does not decompose at its melting point of about 1069 °C, nor even at its boiling point.

21.13 Self Learning Exercise

Q.1 What is nanotechnology ? Give the reason for their development.

Q.2 How is nanotech different from biotech ?

Q.3 Where is nanotechnology being developed ?

Q.4 Are there any safety or environmental issues with the nanotechnologies in use today ?

Q.5 What are some of the most interesting nanoparticles found in nature (not manufactured in the lab) ?

Q.6 What are nanomaterials ? Do they exist in nature ?

Q.7 What are nanotubes, nanoparticles and nanoplates ?

Q.8 What are uses of nanotechnology ?

21.14 Summary

In this chapter we have studied some important topics named as Quantum dot,Quantum well structures and growth techniques of nanomaterials. This is very important study in nanoscience because it gives us basic idea about the nanoscience.

21.15 Glossary

Quantum Dot: 0-D system (quantum box or a quantum dot).In a quantum dot, the carrier motion is quantized along all three spatial directions and this means there is restricted carrier motion.

DOS: The density of states (DOS) formulation describes the number of electronic states that are available in system.

21.16 Answer to Self Learning Exercise

Ans.1: On the basis of industrial use nano technology consists those structures, devices, and systems having novel properties and functions in which the arrangement of their atoms on the 1 to 100 nanometre scale. Many fields of endeavour contribute to nanotechnology, including molecular physics, materials science, chemistry, biology, computer science, electrical engineering, and mechanical engineering.

Due to the extreme breadth and generality of this definition, many prefer to use the term "nanotechnologies." For clarity, it is also useful to differentiate between near-term and long-term prospects, or to segment the field into first-generation through fourth-generation stages.

Gaining better control over the structure of matter has been a primary project of our species since we started chipping flint. The quality of all human-made goods depends on the arrangement of their atoms. The cost of our products depends on how difficult it is for us to get the atoms and molecules to connect up the way we want them. The amount of energy used - and pollution created - depends on the methods we use to place and connect the molecules into a given product. The goal of nanotechnology is to improve our control over how we build things, so that our products can be of the highest quality and while causing the lowest environmental impact. Nanotech is even expected to help us heal the damage our past cruder and dirtier technologies have caused to the biosphere.

Nanotechnology has been identified as essential in solving many of the problems facing humanity. Specifically, it is the key to addressing the Foresight Nanotech

Challenges:

1. Providing Renewable Clean Energy
2. Supplying Clean Water Globally
3. Improving Health and Longevity
4. Healing and Preserving the Environment
5. Making Information Technology Available To All
6. Enabling Space Development

Ans.2: On the basis of the definition of nanotech is defined as involves structures, devices, and systems having novel properties and functions due to the arrangement of their atoms on the 1 to 100 nanometer scale and biotech can be thought of as a subset of nanotech - "nature's nanotechnology." Biotech uses the molecular structures, devices, and systems found in plants and animals to create new molecular products. Nanotech is more general, not being limited to existing natural structures, devices, and systems, and instead designing and building new, non-biological ones. These can be quite different: harder, stronger, tougher, and able to survive a dry or hot environment, unlike biology. For example, nanotech products can be used to build an automobile or spacecraft.

Ans.4: Concerns have been raised regarding potential health and environmental effects of the passive nanostructures termed "nanoparticles." Regulatory agencies and standards bodies are beginning to look at these issues, though significantly more funding for these efforts is required. Foresight is working with the International Council on Nanotechnology to address these concerns.

Ans.5: Certainly, nanoparticles are a fact of life, and were long before humans were around. Anything that burns and many things that get very hot release nanoparticles – think fires and volcanoes. Liquid sprays that contain small amounts of dissolved substances can also produce nanoparticles as they evaporate – sea spray for instance is a great source of nanoparticles. Photochemical smog is a great example of man-made atmospheric “nanoparticle factories.” But nature was there before us – terpenes released by trees can form nanoparticles in the atmosphere (the blue haze associated with the Blue Ridge Mountains is a result of naturally occurring nanoparticles). These are all certainly interesting nanoparticles. But they usually differ from engineered nanoparticles in that they are usually complex mixtures of nanoparticles and other stuff.

Ans.7: These are different types of nanomaterials, named for their individual shapes and dimensions. Think of these simply as objects with one or more dimension at the nanoscale.

Nanoparticles are bits of a material in which all three dimensions of the object are within the nanoscale. Nanotubes have a diameter in the nanoscale, but can be several hundred nanometers long—or even longer. Nanoplates have a thickness at the nanoscale, but their other two dimensions can be quite large.

Ams.8: Nanotechnology is used in many commercial products and processes, for example, nanomaterials are used to manufacture lightweight, strong materials for applications such as boat hulls, sporting equipment, and automotive parts. Nanomaterials are also used in sunscreens and cosmetics.

Nanostructured products are used to produce space-saving insulators which are useful when size and weight is at a premium—for example, when insulating long pipelines in remote places, or trying to reduce heat loss from an old house. Nanostructured catalysts make chemical manufacturing processes more efficient, by saving energy and reducing waste.

In healthcare, nanoceramics are used in some dental implants or to fill holes in diseased bones, because their mechanical and chemical properties can be "tuned" to attract bone cells from the surrounding tissue to make new bone. Some pharmaceutical products have been reformulated with nanosized particles to improve their absorption and make them easier to administer. Opticians apply nanocoatings to eyeglasses to make them easier to keep clean and harder to scratch and nanoenabled coatings are used on fabrics to make clothing stain-resistant and easy to care for.

Almost all high-performance electronic devices manufactured in the past decade use some nanomaterials. Nanotechnology helps build new transistor structures and interconnects for the fastest, most advanced computing chips.

21.17 Exercise

Q.1 What do you mean by Nano? Define Nano Technology and Nano Science ?

Q.2 What is the difference between Nano Science & Nano Technology ?

Q.3 Define nano structured material ? Classify nanomaterials and give examples for them ?

Q.4 List any four day to day live commercial applications of nanotechnology ?

Q.5 What do you mean by quantum dots & nanocrystals ?

Q.6 List any four processes for growth of nanomaterial.

Q.7 What are the nanotubes ? Define carbon nanotubes ?

References and Suggested Readings

1. The Chemistry of Nanomaterials by C.N.Rao, A. Miller, A. K. Cheetham.
2. Nanoscience by Massimo Lazzari, Goujun Liu.
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4. Introduction to Nanoscience and Nanotechnology B. S. Murty.

UNIT-22

Some Special Topics in Nanotechnology

Structure of the Unit

22.0 Objectives

The objective of nanoscience is , as with other technical achievements, the nanoscale science too has to start from basic scientific research. Once a comprehensive understanding of the nanoworld has been established, nanotechnology with applications showing commercial potential will emerge. There are so many fields in nanotechnology like Nanobiotechnology is related to the science which gives us idea about diseases and other form of life. It mainly teaches us nanoscale things which are useful in our life.

22.1 Introduction

The term "nano" refers to the metric prefix 10^{-9}. It means one billionth of something. "Nano" can be ascribed to any unit of measure. For example, you may report a very small mass in nanograms or the amount of liquid in one cell in terms of nanoliters.

So Nanoscience is the study of structures and materials on the scale of nanometers. To give you an idea of how long a nanometer is, this printed page is about 75,000 nanometers thick. When structures are made small enough—in the nanometer size range—they can take on interesting and useful properties. Nanoscale structures have existed in nature long before scientists began studying them in laboratories. A single strand of DNA, the building block of all living things, is about three nanometers wide. The scales on a morpho butterfly's wings contain nanostructures that change the way light waves interact with each other, giving the wings brilliant metallic blue and green hues. Peacock feathers and soap bubbles also get their iridescent coloration from light interacting with structures just tens of nanometers thick. Scientists have even created nanostructures in the laboratory that mimic some of nature's amazing nanostructures.

22.2 Bukminster Fullerence

Buckminsterfullerene derives from the name of the noted futurist and inventor Buckminster Fuller. One of his designs of a geodesic dome structure bears great resemblance to C_{60}; as a result, the discoverers of the allotrope named the newfound molecule after him. The general public, however, sometimes refers to buckminsterfullerene, and even Mr. Fuller's dome structure, as buckyballs.

Buckminsterfullerene (or **bucky-ball**) is a spherical fullerene molecule with the formula C_{60}. It has a cage-like fused-ring structure (truncated icosahedron) which resembles a football (soccer ball), made of twenty hexagons and twelve pentagons, with a carbon atom at each vertex of each polygon and a bond along each polygon edge.

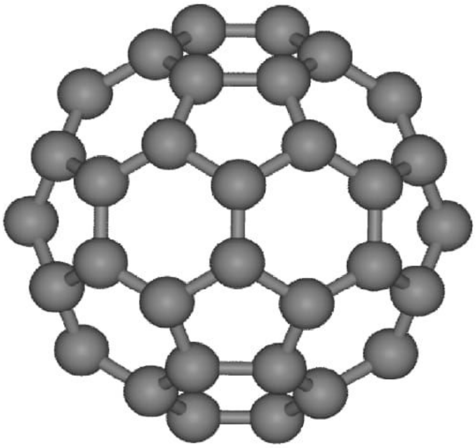


Figure 22.1: Buckyballs.

It was first generated by scientists Harold Kroto, James R. Heath, Sean O'Brien, Robert Curl, and Richard Smalley at Rice University. Some scientists were awarded the Nobel Prize in Chemistry for their roles in the discovery of buckminsterfullerene and the related class of molecules, the fullerenes. The name is a reference to Buckminster Fuller, as C_{60} resembles his trademark geodesic domes. Buckminsterfullerene is the most common naturally occurring fullerene molecule, as it can be found in small quantities in soot. Solid and gaseous forms of the molecule have been detected in deep space.

Buckminsterfullerene is one of the largest objects to have been shown to exhibit wave–particle duality; as stated in the theory every object exhibits this behaviour. Its discovery led to the exploration of a new field of chemistry, involving the study of fullerenes.

The structure of a buckminsterfullerene is truncated icosahedrons with 60 vertices and 32 faces (20 hexagons and 12 pentagons where no pentagons share a vertex) with a carbon atom at the vertices of each polygon and a bond along each polygon edge. The Vander Waals diameter of a C_{60} molecule is about 1.01 nanometres (nm). The nucleus to nucleus diameter of a C_{60} molecule is about 0.71 nm. The C_{60} molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5

bonds (between a hexagon and a pentagon). Its average bond length is 0.14 nm. Each carbon atom in the structure is bonded covalently with 3 others.

The C_{60} molecule is extremely stable, withstanding high temperatures and high pressures. The exposed surface of the structure can selectively react with other species while maintaining the spherical geometry. Atoms and small molecules can be trapped within the molecule without reacting.

C_{60} undergoes six reversible, one-electron reductions to C_{60}^{6-}, but oxidation is irreversible. The first reduction needs ~1.0 V showing that C_{60} is a moderately effective electron acceptor. C_{60} tends to avoid having double bonds in the pentagonal rings, which makes electron delocalization poor, and results in C_{60} not being "superaromatic". C_{60} behaves very much like an electron deficient alkene and readily reacts with electron rich species. A carbon atom in the C_{60} molecule can be substituted by a nitrogen or boron atom yielding $C_{59}N$ or $C_{59}B$ respectively.

In solid buckminsterfullerene, the molecules C_{60} stick together via the Vander Waals forces in the fcc (face-centred cubic) motif. At low temperatures the individual molecules are locked against rotation. Upon heating, they start rotating at about −20 °C. This results in a first-order phase transition to a fcc structure and a small, yet abrupt increase in the lattice constant from 1.411 to 1.4154 nm.

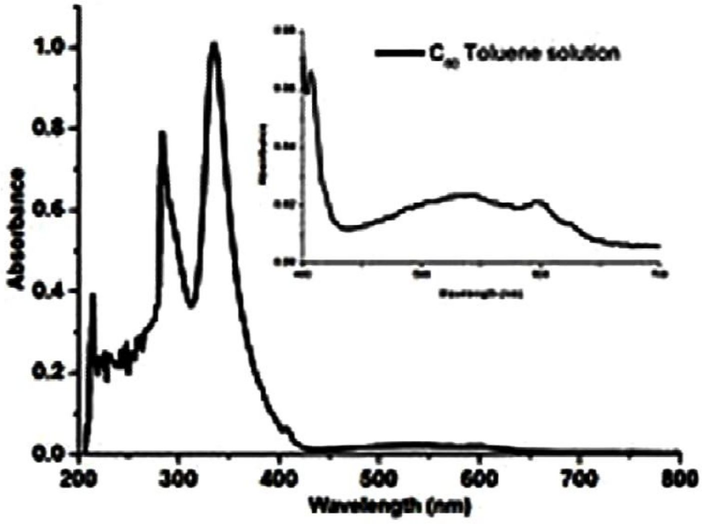


Figure 22.2: Optical absorption spectrum of C_{60} solution.

There is no application of C_{60} in commercial life. In the medical field, elements such as helium (that can be detected in minute quantities) can be used as chemical tracers in impregnated buckyballs.

Water-soluble derivatives of C_{60} were discovered to exert an inhibition on the three isoforms of nitric oxide synthase, with slightly different potencies.

The optical absorption properties of C_{60} match solar spectrum in a way that suggests that C_{60}-based films could be useful for photovoltaic applications because of its high electronic affinity. It is one of the most common electron acceptor used in donor/acceptor based solar cells. Conversion efficiencies up to 5.7% have been reported in C_{60}-polymer cells.

22.3 Carbon Nano Tubes

The terminology of nano tubes is no consensus on some terms describing carbon nanotubes in scientific literature: both -wall and -walled are being used in combination with single, double, triple or multi, and the letter C is often omitted in the abbreviation; for example, multi-walled carbon nanotube.

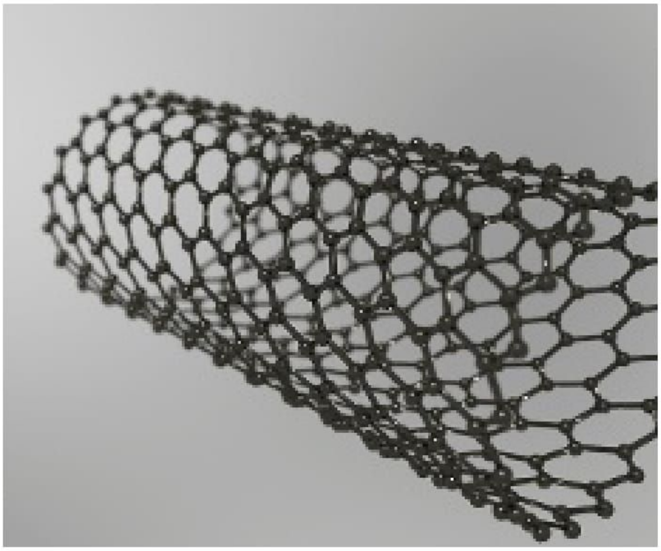


Figure 22.3: Carbon Nano tube.

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1 significantly larger than for any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. For instance, nanotubes form a tiny portion of the material(s) in some (primarily carbon fiber) baseball bats, golf clubs, car parts or damascus steel.

Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. These sheets are rolled at specific and discrete angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes and multi-walled nanotubes. Individual nanotubes naturally align themselves into ropes held together by Vander Waals forces, more specifically, pi-stacking.

Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes is composed entirely of sp^2 bonds, similar to those of graphite. These bonds, which are stronger than the sp^3 bonds found in alkanes and diamond, provide nanotubes with their unique strength.

Most single-walled nanotubes (SWNTs) have a diameter of close to 1 nanometer, and can be many millions of times longer. Multi-walled nanotubes (MWNTs) consist of multiple rolled layers (concentric tubes) of graphene. There are two models that can be used to describe the structures of multi-walled nanotubes, sheets of graphite are arranged in concentric cylinders, e.g., a (0,8) single-walled nanotube (SWNT) within a larger (0,17) single-walled nanotube. In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper.

Recently, several studies have highlighted the prospect of using carbon nanotubes as building blocks to fabricate three-dimensional macroscopic (>100 nm in all three dimensions) all-carbon devices. Lalwani et al. have reported a novel radical initiated thermal crosslinking method to fabricate macroscopic, free-standing, porous, all-carbon scaffolds using single- and multi-walled carbon nanotubes as building blocks. These scaffolds possess macro-, micro-, and nano-structured pores and the porosity can be tailored for specific applications. These

3D all-carbon scaffolds/architectures may be used for the fabrication of the next generation of energy storage, supercapacitors, field emission transistors, high-performance catalysis, photovoltaics, and biomedical devices and implants

22.3.1 Nitrogen Doped Carbon Nano Tubes

Nitrogen doped carbon nanotubes (N-CNTs) can be produced through five main methods, chemical vapor deposition, high-temperature and high-pressure reactions, gas-solid reaction of amorphous carbon with NH_3 at high temperature, solid reaction, and solvothermal synthesis.

Nitrogen doping plays a pivotal role in lithium storage, as it creates defects in the CNT walls allowing for Li ions to diffuse into interwall space. It also increases capacity by providing more favorable bind of N-doped sites. N-CNTs are also much more reactive to metal oxide nanoparticle deposition which can further enhance storage capacity, especially in anode materials for Li-ion batteries. However boron-doped nanotubes have been shown to make batteries with triple capacity

A carbon peapod is a novel hybrid carbon material which traps fullerene inside a carbon nanotube. It can possess interesting magnetic properties with heating and irradiation. It can also be applied as an oscillator during theoretical investigations and predictions.

22.3.2 Cup Stacked Carbon Nano Tube

Cup-stacked carbon nanotubes (CSCNTs) differ from other quasi-1D carbon structures, which normally behave as quasi-metallic conductors of electrons. CSCNTs exhibit semiconducting behaviors due to the stacking microstructure of graphene layers.

22.3.3 Extreme Carbon Nano Tube

The observation of the *longest* carbon nanotubes grown so far are over 1/2 m (550 mm long) was reported in 2013. These nanotubes were grown on Si substrates using an improved chemical vapor deposition (CVD) method and represent electrically uniform arrays of single-walled carbon nanotubes.

The *shortest* carbon nanotube is the organic compound cycloparaphenylene, which was synthesized in few years ago.

The *thinnest* carbon nanotube is the armchair (2, 2) CNT with a diameter of 0.3 nm. This nanotube was grown inside a multi-walled carbon nanotube. Assigning of carbon nanotube type was done by a combination of high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and density functional theory (DFT) calculations.

22.3.4 Properties of Carbon Nano Tubes

The *highest density* of CNTs was achieved in 2013, grown on a conductive titanium-coated copper surface that was coated with co-catalysts cobalt and molybdenum at lower than typical temperatures of 450 °C. The tubes averaged a height of 380 nm and a mass density of 1.6 g cm^{-3}. The material showed ohmic conductivity (lowest resistance ∼22 kΩ).

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms.

Standard single-walled carbon nanotubes can withstand a pressure up to 25 GPa without [plastic/permanent] deformation. They then undergo a transformation to super hard phase nanotubes. Maximum pressures measured using current experimental techniques are around 55 GPa. However, these new superhard phase nanotubes collapse at an even higher, albeit unknown, pressure.

The surface wet ability of CNT is of importance for its applications in various settings. Although the intrinsic contact angle of graphite is around 90°, the contact angles of most as-synthesized CNT arrays are over 160°, exhibiting a super hydrophobic property. By applying a low voltage as low as 1.3V, the extreme water repellent surface can be switched into super hydrophilic.

Multi-walled nanotubes are multiple concentric nanotubes precisely nested within one another. These exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell, thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already, this property has been utilized to create the world's smallest rotational motor.

22.3.5 Current Application

Current use and applications of nanotubes has mostly been limited to the use of bulk nanotubes, which is a mass of rather unorganized fragments of nanotubes. Bulk nanotube materials may never achieve a tensile strength similar to that of individual tubes, but such composites may, nevertheless, yield strengths sufficient for many applications. Bulk carbon nanotubes have already been used as composite fibres in polymers to improve the mechanical, thermal and electrical properties of the bulk product.

22.4 Nanoelectronics

Nanoelectronics refers to the use of nanotechnology in electronic components. The term covers a diverse set of devices and materials, with the common characteristic that they are so small that inter-atomic interactions and quantum mechanical properties need to be studied extensively. Some of these candidates include: hybrid molecular/semiconductor electronics, one-dimensional nanotubes/nanowires, or advanced molecular electronics. Recent silicon CMOS technology generations, such as the 22 nanometer node, are already within this regime. Nanoelectronics are sometimes considered as disruptive technology because present candidates are significantly different from traditional transistors.

It is observed that silicon transistors were undergoing a continual process of scaling downward, an observation which was later codified as Moore's law. Since his observation transistor minimum feature sizes have decreased from 10 micrometers to the 28-22 nm range in 2011. The field of nanoelectronics aims to enable the continued realization of this law by using new methods and materials to build electronic devices with feature sizes on the nanoscale. The volume of an object decreases as the third power of its linear dimensions, but the surface area only decreases as its second power.

22.4.1 Some Approaches of Nanoelectronics

Nanofabrication:

For example, single electron transistors, which involve transistor operation based on a single electron. Nanoelectromechanical systems also fall under this category. Nanofabrication can be used to construct ultradense parallel arrays of nanowires, as an alternative to synthesizing nanowires individually.

Nanomaterials electronics:

Besides being small and allowing more transistors to be packed into a single chip, the uniform and symmetrical structure of nanotubes allows a higher electron mobility (faster electron movement in the material), a higher dielectric constant (faster frequency), and a symmetrical electron/hole characteristic. Also, nanoparticles can be used as quantum dots.

Molecular Electronics:

Single molecule devices are another possibility. These schemes would make heavy use of molecular self-assembly, designing the device components to construct a larger structure or even a complete system on their own. This can be very useful for reconfigurable computing, and may even completely replace present some technology.

Molecular electronics is a new technology which is still in its infancy, but also brings hope for truly atomic scale electronic systems in the future. One of the more promising applications of molecular electronics was proposed by the IBM researcher Ari Aviram and the theoretical chemist Mark Ratner. This is one of many possible ways in which a molecular level diode / transistor might be synthesized by organic chemistry. A model system was proposed with a spiro carbon structure giving a molecular diode about half a nanometre across which could be connected by polythiophene molecular wires. Theoretical calculations showed the design to be sound in principle and there is still hope that such a system can be made to work.

22.5 Molecular Machine

A molecular machine, or nanomachine, is any discrete number of molecular components that produce quasi-mechanical movements (output) in response to specific input. The expression is often more generally applied to molecules that simply mimic functions that occur at the macroscopic level. The term is also common in nanotechnology where a number of highly complex molecular machines have been proposed that are aimed at the goal of constructing a molecular assembler. Molecular machines can be divided into two broad categories; synthetic and biological.

Molecular systems capable of shifting a chemical or mechanical process away from equilibrium represent a potentially important branch of chemistry and nanotechnology. As the gradient generated from this process is able to perform useful work these types of systems, by definition are examples of molecular machinery.

From a synthetic perspective, there are two important types of molecular machines: molecular switches (or shuttles) and molecular motors. The major difference between the two systems is that a switch influences a system as a function of state, whereas a motor influences a system as function of trajectory. Furthermore, switches cannot use chemical energy to repetitively and progressively drive a system away from equilibrium where a motor can.

22.5.1 Biological Molecular Machine

The most complex molecular machines are proteins found within cells. These include motor proteins, such as myosin, which is responsible for muscle contraction, kinesin, which moves cargo inside cells away from the nucleus along microtubules, and dynein, which produces the axonemal beating of motile cilia and flagella. These proteins and their nanoscale dynamics are far more complex than any molecular machines that have yet been artificially constructed.

Probably the most significant biological machine known is the ribosome. Other important examples include ciliary mobility. A high-level-abstraction summary is that, "in effect, the [motile cilium] is a nanomachine composed of perhaps over 600 proteins in molecular complexes, many of which also function independently as nanomachines." Flexible linker domains allow the connecting protein domains to recruit their binding partners and induce long-range allostery via protein domain dynamics.

This protein flexibility allows the construction of biological machines. The first useful applications of these biological machines might be in nanomedicine. For example, they could be used to identify and destroy cancer cells. Molecular nanotechnology is a speculative subfield of nanotechnology regarding the possibility of engineering molecular assemblers, biological machines which could re-order matter at a molecular or atomic scale. Nanomedicine would make use of these nanorobots, introduced into the body, to repair or detect damages and infections. Molecular nanotechnology is highly theoretical, seeking to anticipate what inventions nanotechnology might yield and to propose an agenda for future inquiry. The proposed elements of molecular nanotechnology, such as molecular assemblers and nanorobots are far beyond current capabilities.

22.6 Nanobiometrics

It is defined as the part of nanobiomechanics in which the measurement of the tiny forces that act on the cells and may be related to deseases and their cure.

Nanorobots have existed in nature since the beginning of life. They are called bacteria and viruses. Cells contain many sorts of nanomachines including 12 nm diameter rotating motors, called ATPase. Optical structures on butterfly wings that are highly metallic in appearance, yet contain no pigments; exquisitely sensitive chemical sensors based on 4 nm-sized ion channels; composite nanomaterials, such as spiders' silk or abalone shells, that are tougher or stronger than the best synthetic materials; and methods to convert sunlight into chemical energy. All of this is done without the use of toxic solvents, billion dollar factories and endless pollution.

Humans are inveterate tinkerers. We want these materials, but we want to have control and to make them suit our purpose, not nature's. Our needs are different to those of an abalone or a butter fly. We need to be able to make standard materials, since western society is not very good at dealing with products that are not identical. We can also produce materials that biology cannot make and so we may be able to develop new hybrid materials and structures to extend biology's proper ties. So, rightly or wrongly, for various reasons, we are not content with what nature provides. We want to develop our own nanotechnology.

Biology shows us that only a few basic building blocks can self assemble into more complex structures. These structures in turn can self-assemble into more complex hierarchical structures from which you can build devices ranging from the nanoscopic (such as nanoscale sensors based on proteins) to the gargantuan (for example, the Great Barrier Reef in Australia). The three basic structural units found in biology — lipids, proteins and DNA — and how these units can self assemble into structures and devices that can be used to develop areas of nanotechnology. It is important to remember that although we may want to mimic and to some extent imitate nature, we do not want to slavishly copy biology — hence the term biomimetic nanotechnology.

22.7 Self Learning Exercise

Q.1 What is Bukminster Fullerence ?

Q.2 What are Carbon Nano Tubes ?

Q.3 Give some future uses of nanotechnology.

Q.4 Give brief description about nano-electronics devices.

Q.5 Give the brief description about Lipid structure.

Q.6 What is Nano-scale ?

Q.7 What is Nanobiotechnology ?

Q.8 What is molecular manufacturing ?

22.8 Summary

This unit contains some important topics which are Fullerence, Nanobiometrics and nanoelectronics. These topics give us idea about the nanoscale development in our life. An important topic which is molecular machine gives us idea about the construction of molecules. Molecules are very important unit in our life. This unit contains all topics related to our life and our future uses.

22.9 Glossary

Fullerene : A fullerene is a molecule of cabon in the form of a hollo sphere, ellipsoid, tube, and many other shapes.

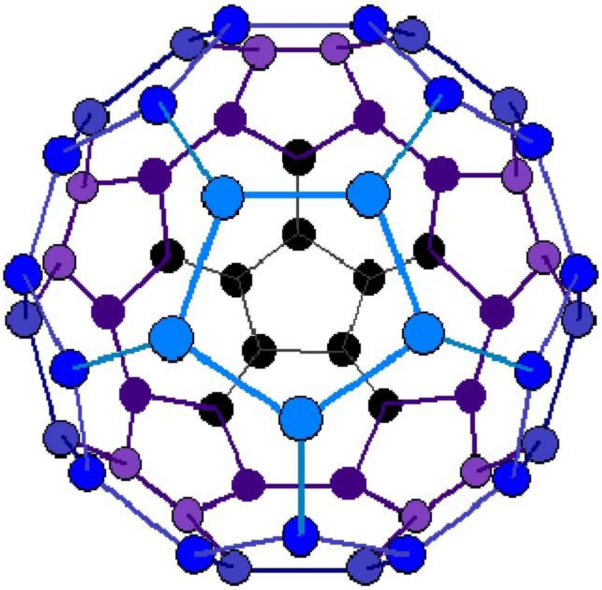
Nano tubes : It is nanometer scale tube like structure.

Carbon Nano-tubes : these are allotropes of carbon with a cylindrical nanostructure.

Nanoelectronics: it is refer to the use of nanotechnology in electronic component.

22.10 Answer to Self Learning Exercise

Ans.1: In 1985 a new allotrope of carbon (C_{60}) was discovered. Sixty carbon atoms form the shape of a ball like a football with a carbon atom at each corner of the 20 hexagons and 12 pentagons. Each carbon atom (shown below as a circle) has three bonds.



The size of the molecule is almost exactly 1nm in diameter. The ratio of the size of an ordinary soccer ball to the planet Earth is the same as the ratio of the size of a C_{60} molecule to a soccer ball. These are not called giant molecules because there are only sixty atoms. A large number of these molecules can fit together to form a transparent yellow solid called fullerite. This form of carbon was named after the American architect Buckminster Fuller, who was famous for designing a large geodesic dome which looked similar (sort of) to the molecular structure of C_{60}. Many other balls of carbon called fullerenes have since been made, including C_{70}, C_{76} and C_{84}. These molecules have become known as "buckyballs".

Fullerenes are used as catalysts and lubricants. They are also used in nanotubes for strengthening materials (for example sports equipment) and are sometimes used as a way of delivering drugs into the body.

Ans.2: Carbon nanotubes (CNTs) are best described as a seamless cylindrical hollow fibers, comprised of a single sheet of pure graphite (a hexagonal lattice of carbon, similar to a chain link fence), having a diameter of 0.7 to 50 nanometers with lengths generally in the range of 10's of microns. Being a hollow tube comprised entirely of carbon, they are also extremely light weight.

The type of bond holding the carbon atoms together is very strong, plus the hexagonal pattern of the atoms themselves gives rise to a phenomenon known as electron delocalization. This means that under the right conditions electrical charge can move freely in a nanotube. The regular arrangement of the atoms also can vibrate in ways that effectively move heat through the tube, so thermal conductivity is high as well as electrical.

When Carbon Nano Tubes were first discovered people believed that any length was good enough for real world applications. However, it was soon learned that the relatively short lengths of these tubes (a small fraction of a millimeter) meant that when tubes were combined with other materials, unless they were added in very high (and costly) amounts, they wouldn't connect and form a network. Without the tubes forming a network, it was practically impossible to make a material that delivered the electrical, thermal, and mechanical performance that the individual tubes exhibited.

Nanocomp resolved this problem by developing processes that generate tubes that are hundreds of times longer (>1mm) than those from other manufacturers formed into *bundles*. When tubes get very close to each other, some of the electrons in each of the tubes begin synchronizing their motion so that the tubes actually stick together. This attractive force – called a *dispersion force* - does more than simply hold the tubes together. As the tubes come together, the force also makes them intertwine with each other forming a network. This combined effect makes the sheets, yarns, and tapes made by Nanocomp much stronger than if they were made with the shorter tubes. While the bulk material properties of Nanocomp's Miralon products do not match those of the individual tubes described above, they are far superior to the loose tube powders being manufactured elsewhere.

Further, Miralon products are shipped as macro formats, comprised of many bundles of multi-millimeter long Carbon Nano Tubes that are too long to be inhaled or absorbed by the skin. Due to this, they are classified by the Environmental Protection Agency (EPA) as "articles", and "not" particles, unlike traditional Carbon Nano Tube powders and loose tubes, making them safe to handle and process in commercial, industrial, and military applications.

Ans.3: Exciting new nanotechnology-based medicines are now in clinical trials, which may be available soon to treat patients. Some use nanoparticles to deliver toxic anti-cancer drugs targeted directly to tumors, minimizing drug damage to other parts of the body. Others help medical imaging tools, like MRIs and CAT scans, work better and more safely. Nanotechnology is helping scientists make our homes, cars, and businesses more energy-efficient through new fuel cells, batteries, and solar panels. It is also helping to find ways to purify drinking water and to detect and clean up environmental waste and damage.

Nanomaterials are being tested for use in food packaging to greatly improve shelf life and safety. Nanosensors to detect food-borne pathogens are also being developed for food packaging. New nanomaterials will be stronger, lighter, and more durable than the materials we use today in buildings, bridges, automobiles, and more. Scientists have experimented with nanomaterials that bend light in unique ways that may enable the development of an "invisibility cloak." The possibilities seem limitless, and the future of nanotechnology holds great potential.

Ans.4: Current high-technology production processes are based on traditional top down strategies, where nanotechnology has already been introduced silently. The critical length scale of integrated circuits is already at the nanoscale (50 nm and below) regarding the gate length of transistors in CPUs or DRAM devices.

Computers:

Nanoelectronics holds the promise of making computer processors more powerful than are possible with conventional semiconductor fabrication techniques. A number of approaches are currently being researched, including new forms of nanolithography, as well as the use of nanomaterials such as nanowires or small molecules in place of traditional CMOS components. Field effect transistors have been made using both semiconducting carbon nanotubes and with heterostructured semiconductor nanowires.

Memory Storage:

Electronic memory designs in the past have largely relied on the formation of transistors. However, research into crossbar switch based electronic have offered an alternative using reconfigurable interconnections between vertical and horizontal wiring arrays to create ultra high density memories. Two leaders in this area are Nantero which has developed a carbon nanotube based crossbar memory called Nano-RAM and Hewlett-Packard which has proposed the use of memristor material as a future replacement of Flash memory.

Ans.5: The term lipid has been used in a variety of ways. Here the word lipid is generally used to refer to compounds that are extracted from, or are synthesised to mimic, the naturally occurring compounds. So what are lipids ? Lipids are molecules that possess a hydrocarbon tail that is hydrophobic or insoluble in water (just like oil is insoluble in water) and a polar head group that is hydrophilic, or water soluble. This is a rule of thumb for solubility: like dissolves like. Generally the total length of the lipid molecules is 2–4 nm. From these molecules we can build supermolecular structures that are hundreds of anometres to hundreds of microns in size.

These lipids, as well as synthetic compounds where the hydrophilic head-groups and hydrophobic tails are made up of groups that may never occur in nature, are also known as amphiphilic compounds or amphiphiles (literally amphi – both, phile – to love, that is, to be happy in both oil and water). It is possible to either extract naturally occurring lipids or to synthesize lipids using standard organic chemistry techniques. Literally thousands of different amphiphiles have been extracted, synthesized and studied.

Ans.6: The nanoscale is the dimensional range of approximately 1 to 100 nanometers. Matter such as gases, liquids, and solids can exhibit unusual physical, chemical, and biological properties at the nanoscale, differing in important ways from the properties of bulk materials and single atoms or molecules. Some nanostructured materials are stronger or have different magnetic properties compared to other forms or sizes or the same material. Others are better at conducting heat or electricity. They may become more chemically reactive or reflect light better or change color as their size or structure is altered.

Ans.7: Nanobiotechnology is an emerging field of research and development that seeks new solutions to pressing health and environmental problems by combining physical sciences and engineering with life sciences and medicine. This exciting frontier of discovery is generating new therapies, devices, diagnostic tools, and a better understanding of the relationship between cells and disease. For example, very small devices are now enabling new kinds of minimally invasive medical procedures. Nanobiotechnology represents the future of medicine and healthcare.

Ans.8 : Molecular manufacturing is the name given to a specific type of "bottom-up" construction technology. As its name implies, molecular manufacturing will be achieved when we are able to build things from the molecule up, and we will be able to rearrange matter with atomic precision. This technology does not yet exist; but once it does, we should have a thorough and inexpensive system for controlling of the structure of matter.

Other terms, such as molecular engineering or productive molecular nanosystems, are also often applied when describing this emerging technology. The central thesis of nanotechnology is that almost any chemically stable structure that is not specifically disallowed by the laws of physics can in fact be built. The possibility of building things with atomic precision was first introduced by Richard Feynman in a famous after-dinner talk in 1959 when he said: "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom."

Scientists have recently gained the ability to observe and manipulate atoms directly, but this is only one small aspect of a growing array of techniques in nanoscale science and technology. The ability to make commercial products may yet be a few decades away. But theoretical and computational models indicate that molecular manufacturing systems are possible - that they do not violate existing physical law. These models also give us a feel for what a molecular manufacturing system might look like. Today, scientists are devising numerous tools and techniques that will be needed to transform nanotechnology from computer models into reality. While most remain in the realm of theory, there appears to be no fundamental barrier to their development.

22.11 Exercise

Q.1 Define carbon nanotube ? What are the types of carbon nanotubes ?

Q.2 Highlight the properties of carbon nanotubes?

Q.3 What is the difference between nanotechnology & nanoscience ?

Q.4 What is the Lipid Structure ? Give briefly.

Q.5 What are the nanotubes ? Define carbon nanotubes ?

Q.6 Define nano structured material ? Classify nanomaterials and give examples for them?

Q.7 What is the difference between STM & AFM ?

Q.8 What are the induced effects due to increase in surface area of nanoparticles?

Q.9 Define nanocomposite ? What are the types of nanocomposites ?

Q.10 What is the difference between SEM & TEM?

References and Suggested Readings

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