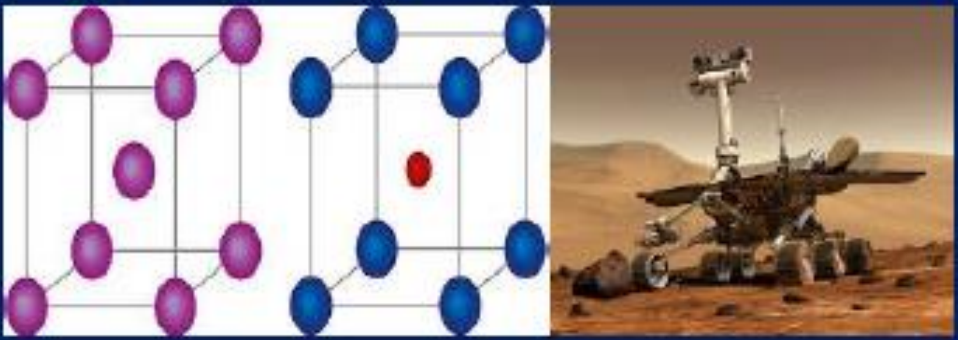
BSCPH203

B. Sc. II YEAR

Elementary Solid State Physics



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Elementary Solid State Physics

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Contents

Course 5: Elementary Solid State Physics

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Unit number	Block and Unit title	Page number
Block 1 CRYSTAL STRUCTURE		**1-64**
1	**Crystal structure :** Crystalline and amorphous solids, single crystal and poly crystal, elementary ideas about crystal structure, lattice and bases, unit cell, Bravais lattices, s.c., f.c.c. and b.c.c. lattices, characteristics of lattices cell, some crystal structures.	**1-14**
2	**Crystal symmetry:** Miller indices, lattice planes, spacing of planes in crystal lattices, symmetry operation, translational symmetry, basic idea about liquid crystal.	**16-37**
3	**Reciprocal lattice**: X ray diffraction, Bragg equations, Determination of crystal structure with X-rays, Laue and Powder method, Reciprocal lattice system, Ewald’s construction.	**38-51**
4	**Crystal bonding**: Crystal bonding, ionic crystal, potential and lattice energy crystal, Madelung constant, covalent bonding, Van der wall bonding, Lena potential, hydrogen bond, metallic bond.	**52-64**
BLOCK 2 BAND THEORY OF SOLIDS		**65-131**
5	**Free Electron theory:** Free electron theory of metals, Lorentz Drude theory, electrical conductivity, thermal conductivity. Wiedemann-Franz law	**65-86**
6	**Band theory of solids :** Band formation in solids, Band structure in conductors, Periodic potential and Bloch theorem, Kronig-Penny model, origin of band gap	**87-106**
7	**Semiconductors :** Semiconductors, effect of impurity on semiconductor, Fermi level, Electron and hole concentration, drift current, mobility and conductivity, Effective mass, Hall effect.	**107-131**
BLOCK3 SPECIFIC HEAT DIELECTRIC AND MAGNETIC PROPERTIES OF MATERIALS		**132-215**
8	**Specific heat:** Specific heat of solids, Dulong and Petit’s law, lattice heat capacity, Einstein theory of specific heat, Debye’s theory of specific heat, Density of state , lattice thrmal conductivity, normal and umklapp processes, paramagnetism of free electrons.	**132-166**
9	**Dielectric properties:** Electronic, ionic and dipolar polarizability, local fields, induced and oriented polarization, molecular field in a dielectric; Clausius-Mosotti relation.	**167-192**
10	**Magnetic properties:** magnetization, magnetic materials, Dia, para and ferro-magnetic properties of solids, magnetic moment, spin angular moment, Langevin’s theory of diamagnetism and paramagnetism, Quantum theory of paramagnetism, Curie’s law, Ferromagnetism, hysteresis and hysteresis loss, permanent magnet, spontaneous magnetization and domain structure, Weiss theory of ferromagnetism, anti- Ferromagnetism, ferrites, use of ferrites.	**193-215**
11	**Superconductivity** : Introduction,(Kamerlingh-Onnes experiment), effect of magnetic field, Type-I and type-II superconductors, Isotope effect, Meissner effect, Heat capacity, Energy gap, Basic Ideas about High-Tc superconductors, application.	**216-232**

UNIT 1 CRYSTAL STRUCTURE

Structure

1.1 INTRODUCTION

Matter, in general, occurs in three states- solid state, liquid state and gaseous state. As we move from the solid state to gaseous state, the distance between the neighbouring atoms increases and their structures vary too. The solids are classified on the basis of their electrical behaviour as conductors, semiconductors and insulators. The conductors are the materials which have a large number of free electrons. These free electrons are responsible for carrying current. On the other hand, the insulators have practically no free electron to conduct electric current. Between the conductors and insulators, we have semiconductors. A semiconductor behaves like an insulator at absolute zero but its conductivity increases as its temperature increases. In this unit, you will study about different states of solids. You will also study about lattice, bases, different types of lattices and crystal structures.

1.2 OBJECTIVES

After studying this unit, you should be able to-

- understand crystalline and amorphous solids
- understand lattice and bases
- understand different types of crystal structures

1.3 CRYSTALLINE AND AMORPHOUS

A most remarkable feature of matter in the solid state is the tendency of the constituent atoms of a great many solids to arrange themselves in an ordered periodic pattern. On the basis of the arrangements of its constituents, the solids are broadly classified into two categories- crystalline and amorphous.

A crystalline solid, commonly a crystal, is a solid material with such a regular arrangement. A crystalline solid is formed by regular and periodic repetition of identical building blocks in three dimensions. These building blocks may be a single atom or a group of atoms. These identical building blocks are called motif. Crystals which have regularity and periodicity in the arrangement of atoms or molecules only in one dimension or two dimensions are known as semi or partially crystalline solids. Metals, in general, are crystalline in nature. On melting, these lose their crystalline structure but their electrical properties remain almost the same. In a crystal, all the bonds have the same bond strength. The crystalline solids both organic and inorganic, therefore, melt (and solidify) at a given fixed temperature. Diamond, rock salt, sugar etc. are some examples of crystalline solids.

The amorphous solids are those in which there is no regularity and periodicity in the arrangement of atoms. All the bonds in an amorphous solid are not equally strong. When it is heated, the weak bonds are first to be broken. Thus, on heating, an amorphous solid gradually softens into a liquid. They, therefore, have no fixed melting point and freezing point. On cooling, the molten state of the amorphous solid gradually hardens into a solid at varying temperatures on account of its high viscosity or the fast rate of cooling. The disordered form, thus, retained even in the solid state of an amorphous body. Glass is the best example of an amorphous solid.

Thus, the presence of long range order is the defining property of a crystal while amorphous solids do exhibit short range order in their structures.

1.4 SINGLE CRYSTAL AND POLY CRYSTAL

In the single crystal, the periodicity extends throughout the material while in poly crystal (or polycrystalline crystal), the periodicity does not extend throughout the crystal but is interrupted at grain boundaries. The grains or crystallites are smaller than the size of the pattern unit which forms the periodicity. The size of the grains in which the structure is periodic may vary from macroscopic dimensions to several Angstroms. When the size of the grains or crystallites becomes comparable with the size of the pattern unit, the periodicity of structure is completely disturbed; it is no longer a crystal, single or polycrystalline but becomes an amorphous substance.

1.5 ELEMENTARY IDEAS ABOUT CRYSTAL STRUCTURE

Let us discuss some important terms in this section which play very important role in the formation of a crystal.

1.5.1 Periodic Array of Atoms and Basis

As you know that a crystal is a regularly repeated structure on an atomic scale i.e. a three-dimensional periodic array of atoms. An ideal crystal is constructed by the infinite repetition in space of identical structural units. In other words, you can say that there exists some smallest grouping that repeats itself exactly in all directions in the crystal so that the environment at one location is identical in all respects to the environment at a corresponding location somewhere else. In the simplest crystals such as silver, copper, aluminium etc., the structural unit is a single atom. The structure of all crystals is described in terms of a lattice with a group of atoms attached to each lattice point. The group is termed as the basis. The basis is repeated in space to form the crystal structure.

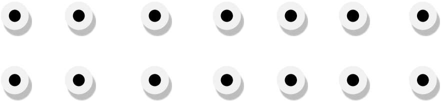
1.5.2 The Crystal Lattice and Crystal Structure

A crystal is constructed by the infinite repetition in space or identical structural units (atoms, molecules or ions). One can replace each unit by a geometrical point. The result is a pattern of points having the same geometrical properties as the crystal. This geometrical pattern is the crystal lattice or simply the lattice. The points are called lattice points. Thus, the regular pattern of points which describes the three-dimensional arrangement of particles, atoms, molecules or ions) in a crystal structure is called the crystal lattice or space lattice.

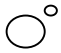
A crystal structure is formed by the addition of a basis to every lattice point i.e.

Lattice + Basis = Crystal Structure.

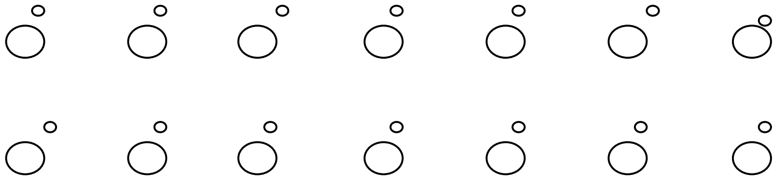
The crystal structure is real whereas the lattice is imaginary. The simple logical relation between lattice, basis and crystal structure can be expressed as in figure (1). The crystal structure is formed by the addition of the basis (b) to every lattice point of the lattice (a). By looking at (c), you can recognize the basis and then you can abstract the space lattice.



(a) space lattice



(b) basis containing two different ions



(c) crystal structure

Figure 1.1 : Crystal structure

1.5.3 Fundamental Translation Vectors

You have seen that a crystal is composed of atoms arranged at the lattice points. An ideal crystal is composed of atoms arranged on a lattice defined by three fundamental translation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ such that the atomic arrangement looks the same in every respect when viewed from any point $\vec{r}$ as when viewed from the point

$$\overrightarrow{r'} = \vec{r} + u\,\vec{a} + v\,\vec{b} + w\,\vec{c} \qquad (1)$$

where u, v, w are arbitrary integers. The set of points $\overrightarrow{r'}$ specified by equation (1) for all values of the integers u, v, w defines a lattice. The lattice and the translation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ are said to be primitive if any two points $\vec{r}$, $\overrightarrow{r'}$ from which the atomic arrangement looks the same always satisfy equation (1) with a suitable choice of the integers u, v, w. The definition of the primitive translation vectors shows that there is no cell of smaller volume that could serve as a building block for the crystal structure.

Often,the primitive translation vectors are used to define the crystal axes $\vec{a}$, $\vec{b}$, $\vec{c}$. The crystal axes $\vec{a}$, $\vec{b}$, $\vec{c}$ form three adjacent edges of a parallelepiped. If there are lattice points only at the corners of the parallelepiped, then it is a primitive parallelepiped.

Lattice translation operator T is defined in terms of three fundamental translation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ as follows-

$$\vec{T} = u\,\vec{a} + v\,\vec{b} + w\,\vec{c} \qquad (2)$$

A vector $\vec{T}$ connects any two lattice points.

You will see that the following figure 2gives the diagram of a two-dimensional lattice with lattice vector $\vec{a}$ and $\vec{b}$. The atomic arrangement in the crystal looks exactly the same to an observer at $\overrightarrow{r'}$as to an observer at $\vec{r}$, provided that the vector $\vec{T}$which connects $\overrightarrow{r'}$ and $\vec{r}$ may be expressed as an integral multiple of the vectors $\vec{a}$ and $\vec{b}$.

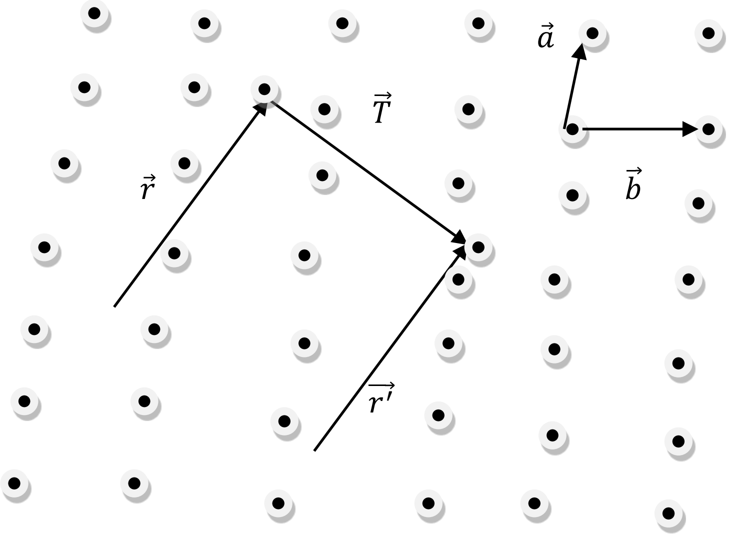


Figure 1.2 : Fundamental translational vector

1.5.4 Unit Cell

The smallest portion of a space lattice which can generate the complete crystal by repeating its own dimensions in various directions is called unit cell.

A unit cell is defined by the length of its edges and by the angles between them. In the figure 3, OA = a, OB = b and OC = c are the dimensions of the unit cell. The angles between a, b ,b, c and c, a are represented by γ, α and β respectively. They are called interfacial angles. The vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ define the axes of the crystal.

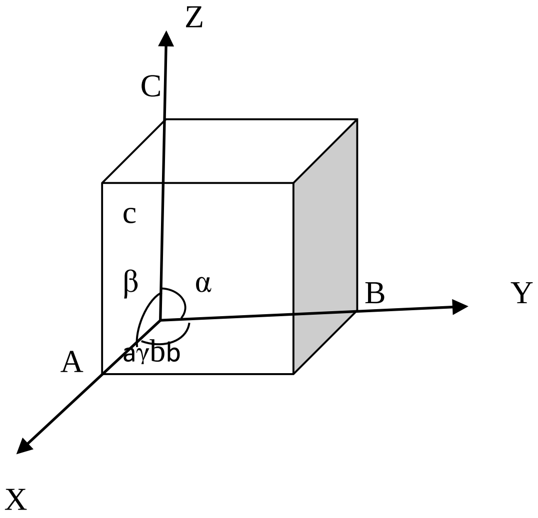


Figure 1.3: Unit cell

It is, however, traditional to choose a unit cell with minimum volume. A unit cell is thus a minimum volume cell which when repeated systematically in all the three directions gives the whole arrangement of atoms in the crystal.

1.6 PRIMITIVE LATTICE CELL

A unit cell is called a primitive cell or a simple cell, if it has atoms only at its corners. Thus, in figure 4, the unit cells ABCD is primitive cell but the unit cell PQRS is not a primitive cell.

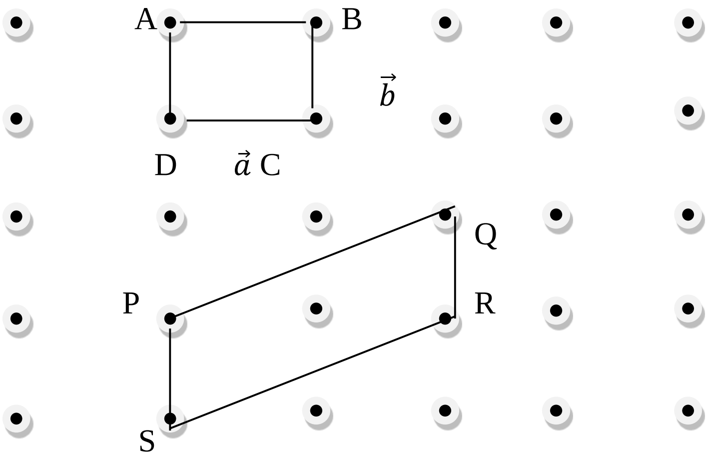


Figure 1.4: Primitive lattice cell

Each atom at a corner of a unit cell is shared equally by eight adjoining cells and hence any atom at a corner contributes only 1/8 atom to each adjoining cell. Thus, the number of atoms per unit cell is 8 × 1/8 = 1. In this way, you may define a primitive cell as one which has only one lattice point associated with it. You, therefore, conclude that all primitive cells are unit cells but all unit cells are not primitive cells.

The volume of a cell defined by $\vec{a}$, $\vec{b}$, $\vec{c}$ is-

$$V_c = \left|\vec{a}.\left(\vec{b} \times \vec{c}\right)\right| (3)$$

The basis associated with a lattice point of a primitive cell is called a primitive basis.

1.7 WIGNER-SEITZ CELL

Wigner and Seitz have developed a method for getting information about the behavior of valence electrons with ions in a lattice. This is another way of choosing a cell of equal volume V_c. Their method of constructing a primitive cell in a lattice is given below-

(i) Draw lines to connect a given lattice point to all nearby lattice points.
(ii) Bisect these lines by planes perpendicular to these lines.

The smallest volume enclosed in this way is the Wigner- Seitz primitive cell and is shown in figure 5. All space may be filled by these cells.

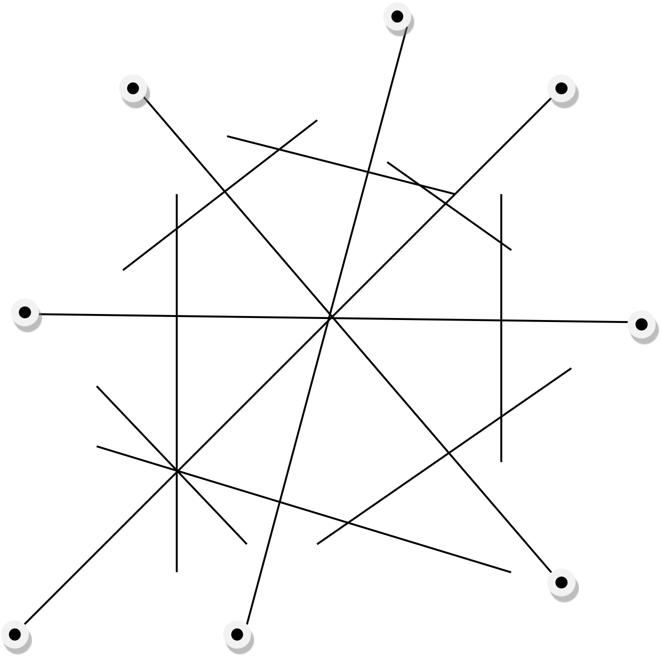


Figure 1.5: Wigner-seitz cell

1.8 ALLOWED ROTATIONS

Crystal lattices can be carried or mapped into themselves by the lattice translations $\vec{T}$ and by various other symmetry operations. A typical symmetry operation is that of rotation about an axis that passes through a lattice point. Lattices can be found such that one-, two-, three-, four- and six- fold rotation axes carry the lattice into itself, corresponding to rotations by 2π, 2π/2, 2π/3, 2π/4 and 2π/6 radians and by integral multiples of these rotations. The rotation axes are denoted by the symbols 1, 2, 3, 4 and 6. You cannot find a lattice that goes into itself under other rotations such as by 2π/7 or 2π/5 radians. One should not expect the lattice to have a five-fold rotation axis. If we try to construct a periodic lattice having five-fold symmetry, the pentagons do not fit together to fill all space, showing that we cannot combine five-fold point symmetry with the required translational periodicity.

1.9 BRAVAIS LATTICES

There are various ways of positioning structure less points in space such that all points have identical surroundings. These are called Bravais lattices. There are five Bravais lattices in two dimensions and fourteen in three dimensions. For a cubic system, you have the following three types of Bravais lattices-

1.9.1 Primitive or Simple Cubic (SC)

There is one lattice point at each of the eight corners of the unit cell.This type of cell is called primitive or simple cubic cell (P) of the system (Figure 6).

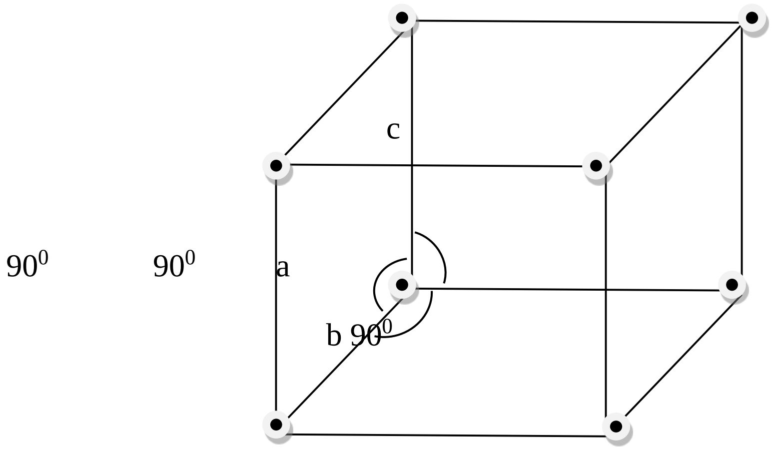


Figure 1.6: Primitive or Simple cubic

1.9.2 Body Centred Cubic (BCC)

There is one lattice point at each of the eight corners and one lattice point is at the centre of the cubic cell. This type of cell is called body centred cubic (BCC) cell (Figure 7).

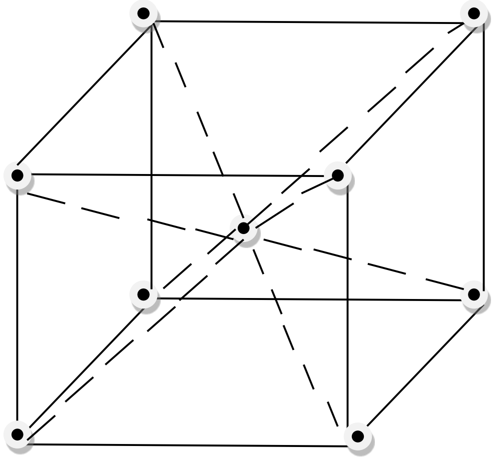


Figure 1.7: Body Centred Cubic

1.9.3 Face Centred Cubic (FCC)

There is one lattice point at each of the eight corners and one lattice point is at the centres of each of the six faces of the cubic cell. Such a cell is called face centred cubic (FCC) cell (Figure 8).

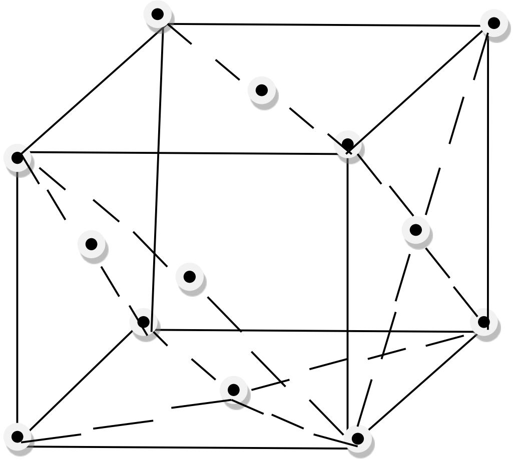


Figure 1.8: Face Centred Cubic

1.10 CRYSTAL-LATTICE SYSTEMS: COMMON CRYSTAL STRUCTURES

Depending upon the shape of the unit cells, all crystals are classified into seven systems. This classification can be conveniently expressed in terms of the relations between the axes of the unit cells. The axes are designated as a, b, c and the angles between them as α, β, γ (Figure 9).

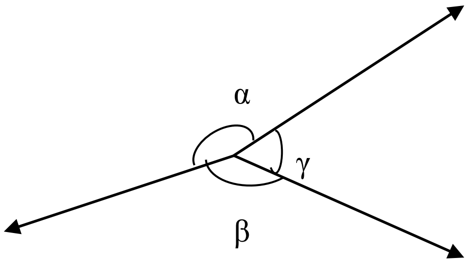


Figure1.9: Axes and angle representation in Common crystal structures

Seven systems of crystals are given in the following table-

S. No.	Name of the crystal system	Relation of lengths of axes of unit cell	Relation of angle between axes	Number of lattice types
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	3 (P, I, F)
2.	Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^0, < 120^0$	1 (P)
3.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0, \gamma = 120^0$	1 (P)
4.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	2(P, I)
5.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	4 (P, C, I, F)
6.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^0 \neq \beta$	2 (P,C)
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	1(P)

Here P means Primitive (simple), C means Base Centred, I means Body Centred, F means Face Centred

From the table, it is obvious that the cubic system is the simplest while the triclinic crystals are least symmetrical. Cubic crystals are the commonest and more than half of the naturally found crystals belong to this system. Obviously, the seven crystals system is divided into fourteen Bravais lattices.

(i) Cubic

In this case, all the sides are equal and all the angles are equal to 90^0 i.e. a = b= c and $\alpha = \beta = \gamma = 90^0$. The cubic crystal systems are of three types- simple (P), body centred (I) and face centred(F).

(ii) Trigonal

In this case, all the sides are equal and all the angles are equal and less than 120^0 but not equal to 90^0 i.e. a = b= c and $\alpha = \beta = \gamma \neq 90^0, < 120^0$. If all the angles become equal to 90^0, it becomes a cubic lattice. This crystal system is of one type- primitive or simple (P).

(iii) Hexagonal

In this case, two sides are equal and inclined at 120^0 and the third side is perpendicular to both of them. The repetitive intervals along the axes which are 120^0 apart are the same whereas the interval along the third axis is different i.e. $a = b \neq c$ and $\alpha = \beta = 90^0$, $\gamma =120^0$. This crystal system is of one type- primitive or simple (P).

(iv) Tetragonal

In this type of lattice, two sides are equal and all the axes are mutually perpendicular i.e. $a = b \neq c$ and $\alpha = \beta = \gamma = 90^0$. It is of two types- simple or primitive (P) and body centred (I)

(v) Orthorhombic

In this type of lattice, all the sides are unequal but all the angles are equal each equal to 90^0 i.e. $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^0$. It is of four types- simple or primitive (P), base centred (C), body centred (I) and face centred (F).

(vi) Monoclinic

In this case, all the three translation vectors of this lattice are unequal with one axis perpendicular to the other two i.e. $a \neq b \neq c$ and $\alpha = \gamma = 90^0 \neq \beta$. It is of two types- simple (P) and base centred (C).

(vii) Triclinic

It is the most general type of lattice in which $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$. It is the simple lattice (P).

Example 1: What are the seven crystal lattice systems?

Solution: There are seven crystal lattice systems-

(i) Cubic (ii) Trigonal (iii) Hexagonal (iv) Tetragonal (v) Orthorhombic (vi) Monoclinic (vii) Triclinic

Example 2: What are the cubical crystal systems?

Solution: In a cubical crystal system, the unit cell is a cube. All cubical systems have one atom each in all the corners of the cube. Each atom has 1/8th of its volume contained within the cube. In addition to this arrangement, each cubical system has its own extra atomic configuration. In general, there are three cubical crystal systems-

(i) Simple cubical lattice (ii) Body centred cubical lattice (iii) Face centred cubical lattice

Example 3: Fill in the blank-

The ....cell is the smallest unit cell that can be repeated to form the lattice.

Solution: primitive

Self-Assessment Question (SAQ) 1: Fill in the blank-

The seven crystal systems are...............

Self-Assessment Question (SAQ) 2: Fill in the blank-

A BCC system has...........atoms in its unit cell.

Self-Assessment Question (SAQ) 3: Fill in the blank-

An FCC system has............ atoms in its unit cell.

1.11 SUMMARY

In this unit, you have studied about crystalline, amorphous, single crystal, poly crystal etc. You have learnt that a solid material with an ordered periodic pattern and a regular arrangement is said to be crystalline whereas a solid material without such a structure is known as non-crystalline or amorphous. The unit has also covered crystal lattice and crystal structure, fundamental translation vectors, unit cell, primitive lattice cell, Wigner-Seitz cell. You have learnt that a crystal structure is formed by the addition of a basis to every lattice point. You have studied about Bravais lattices and learnt that there are five Bravais lattices in two dimensions and fourteen in three dimensions. For a cubic system, there are three types of Bravais lattices- SC, BCC and FCC. In the present unit, you have studied about seven systems of crystals.We have included examples and self-assessment questions (SAQs) to check your progress.

1.12 GLOSSARY

Array- arrangement.

Periodicity- the process of occurring something at equal intervals.

Disordered- tangled, lawless.

Macroscopic- visible to naked eye without use of any instrument.

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1.15 TERMINAL QUESTIONS

1. Write notes on-

   (i) crystalline (ii) unit cell

2. What do you mean by primitive basis?

3. What is meant by basis?

4. What are crystalline and amorphous solids? Explain.

5. Which rotations are allowed in a lattice?

6. What are the different types of Bravais lattices for a cubic system? Give their names.

7. How does a crystal differ from a lattice?

8. What is the maximum number of possible Bravais lattices?

9. What is the difference between single crystal and poly crystal?

10. Explain the following-

   (i) crystal lattice (ii) seven crystal system

11. What is primitive lattice cell? How are Wigner-Seitz cells formed? Discuss Bravais lattices. Give different types of crystal structure.

12. Fill in the blanks-

   (i) A ....crystal has one atom each on all its corners.

(ii) A ....crystal has one atom each on all its corners and an additional atom at the centre of the cube.

13. Choose the correct option-

(i) Long range order is found in-

(a) amorphous (b) crystalline (iii) in both (iv) none of these

(ii) Which relation is correct-

(a) Lattice + crystal structure = basis (b) lattice + basis = crystal structure

(c) lattice – basis = crystal structure (d) basis + crystal structure = lattice

(iii) In three dimensions, the number of Bravais lattice is-

(a) 7 (b) 5 (c) 10 (d) 14

1.16 ANSWERS

Self-Assessment Questions (SAQs):

1.cubic, trigonal, hexagonal, tetragonal, orthorhombic, monoclinic, triclinic

2. two

3. four

Terminal Questions:

12. (i) SCC (ii) BCC

13. (i) (b) crystalline

(ii) (b) lattice + basis = crystal structure

(iii) (d) 14

UNIT 2 CRYSTAL SYMMETRY

Structure

2.1 INTRODUCTION

In the previous unit, you have studied about crystalline, amorphous, single crystal, poly crystal, crystal structure, primitive lattice cell, Wigner-Seitz cell etc. You have also learnt about Bravais lattices, common crystal structures etc. in the previous unit. In this unit, you will study coordination number, Miller indices, spacing of planes in crystal lattices, translational symmetry, liquid crystal etc. You will establish the expression for interplanar spacing.You will also calculate coordination numbers in some cases. You will also learn about lattice constant of a space lattice, density of lattice points in a lattice plane.

2.2 OBJECTIVES

After studying this unit, you should be able to-

- understand crystal symmetry, Miller indices, liquid crystal etc.
- calculate coordination number or ligancy.
- to compute interplanar spacing.
- find Miller indices.
- distinguish between liquid crystal and glassy state.
- solve problems based on atomic radius and packing fraction.

2.3 COORDINATION NUMBER OR LEGANCY

You know that the cations and anions are the alternate lattice points in an ionic solid. The number of anions surrounding a cation is called the coordination number (CN) or the ligancy. The coordination number may also be defined as the number of nearest atoms which are directly surrounding a given atom is called the coordination number or simply the number of nearest neighbours to a given atom in a crystal lattice.

You know that usually the cation is smaller than anion in size. Each ion tends to surround itself with as many ions of opposite sign as possible so as to reduce the potential energy. The ligancy is a function of the size of an ion. You can work out from the space filling geometry when the following conditions are satisfied-

(a) Anion and cation are treated as hard spheres which touch each other.
(b) Anions are close enough to be in contact with one another.
(c) Maximum anions surround a central cation to reduce the electrostatic energy.

From the geometry, you can see that ligancies of 5, 7, 9, 10 and 11 are not permissible. The ratio of cation radius (r_c) to the anion radius (r_a) is known as radius ratio. When the anions just touch each other as well as the central cation, it is called the critical radius ratio.

Ligancy 3:

For ligancy 3, $OQ = r_a + r_c$

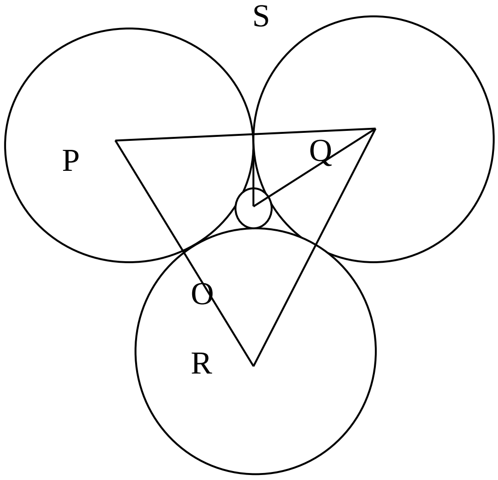


Figure 2.1: Pictorial representation of Ligancy 3

$<OQS = 30^0$

In right angled triangle OSQ, $\cos 30^0 = QS/QO = r_a/(r_a + r_c)$

or $\sqrt{3} / 2 = r_a/(r_a + r_c)$

or $r_c/r_a = 0.155$

Ligancy4 :

For ligancy 4, anions touch each other along face diagonal. Therefore, you have-

Face diagonal / Body diagonal = $\sqrt{2} / \sqrt{3}$

$= 2 r_a / 2 (r_a + r_c) = r_a / (r_a + r_c)$

or $r_c / r_a = 0.225$

Ligancy 6:

For ligancy6, $PR/PQ = \sqrt{2} / 1 = 2 (r_a + r_c) / 2 r_a$

Or $r_c / r_a = 0.414$

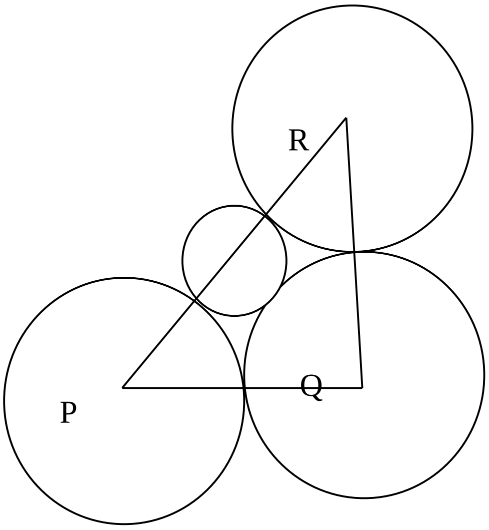


Figure 2.2: Pictorial representation of Ligancy 4

Ligancy 8 :

For ligancy8, eight anions at the corners of cube touch each other along the edge of the cube and cation touches two anions along body diagonal.

Therefore, $\sqrt{3} / 1 = 2 (r_a + r_c) / 2 r_a$

or $r_c / r_a = 0.732$

(a) Simple Cubic Structure (SC)

In this type of structure, there are atoms at each corner of unit cell. Any corner atom has four neighbours in the same plane plus two nearest neighbours are exactly above and other exactly below of that corner atom.

Therefore, coordination number (CN) = 4 + 2 = 6

(ii) Hexagonal Close Packed (HCP)

It contains two atoms per lattice point. In HCP structure, each sphere in a particular layer fits into the hollow formed by three spheres in the layer below it, hence each sphere is in contact with three spheres in the layers below and with three in the layers above it as well. Adding these six, it touches in its own layer, each sphere in close packed structure has 12 nearest neighbours hence coordination number is 12.

(iii) Face Centred Cubic (FCC)

In this type of structure, for any corner atom of the unit cell the nearest are the face centred atoms of the surrounding unit cells in its own plane, 4 face centred atoms below this and 4 face centred atoms above this plane.

Therefore, coordination number (CN) = 4 + 4+ 4 = 12

(iv) Body Centred Cubic (BCC)

In this structure for any corner atoms of the unit cell, the nearest atoms are the body centred atoms and corresponding to each corner atom of the unit cell there are 8 unit cells in neighbour which are having 8 body centred atoms.

Therefore, coordination number (CN) = 8

2.4 ATOMIC RADIUS

The atomic radius is defined as the half the distance between nearest neighbours in a crystal of a pure element. The atomic radius is calculated below for different type of structures-

(a) Simple Cubic (SC)

In this structure, there are 8 atoms at the corners and each of the 8 atoms is a member of 8 cells which enclose every corner. In such a lattice, $a = 2\,r$ and the radius r is therefore, $r = a/2$

(b) Hexagonal Close Packed (HCP)

In this structure, each atom touches 6 atoms at distance a that lie in the plane through the atom under consideration and 6 others at a distance $\left[\frac{a^2}{3} + \frac{c^2}{4}\right]^{\frac{1}{2}}$, three lying above and three below the base plane. But for ideal case, you have-

$a^2 = a^2/3 + c^2/4$ and $r = a/2$

(c) Face Centred Cubic (FCC)

For face centred cubic structure such as NaCl, the face diagonal is four times the radius of the atom. The lattice constant ‘a’ is related to the radius of the atom as-

$$(AC)^2 = (AB)^2 + (BC)^2$$

$$(4r)^2 = a^2 + a^2$$

or $$16\,r^2 = 2a^2$$

or $$a = 4\,r/\sqrt{2}$$

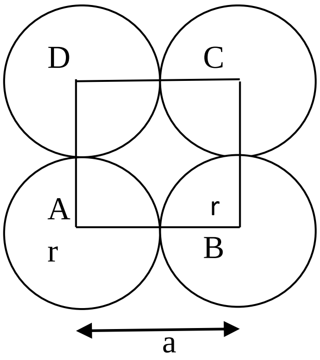


Figure 2.3: Face Centred Cubic

(d) Body Centred Cubic

In this structure, which has one atom at the centre and 8 at corners, the body diagonal is 4 times the radius of the atom. Therefore,

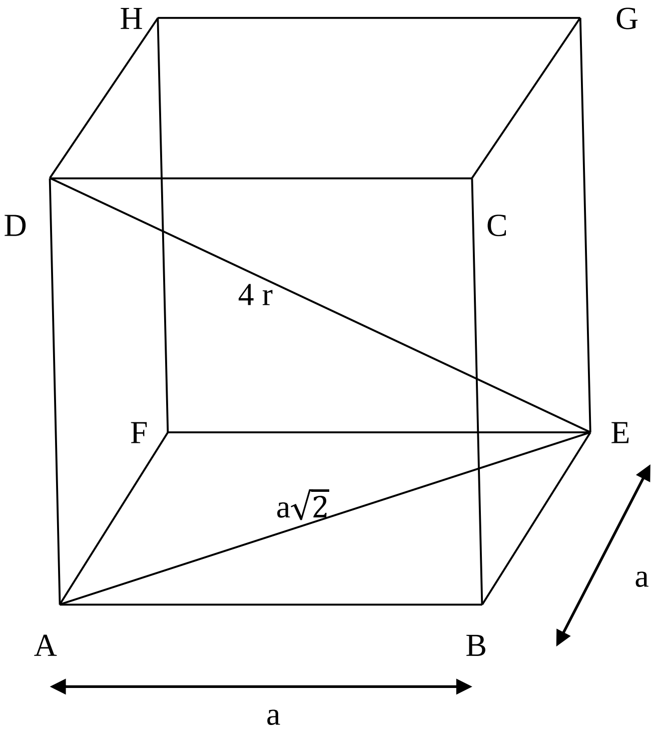


Figure 2.4: Body Centred Cubic

$(ED)^2 = (AD)^2 + (AE)^2$

$= (AD)^2 + (AB)^2 + (BE)^2$

$(4\,r)^2 = a^2 + a^2 + a^2$

or $16\,r^2 = 3\,a^2$

or $a = 4\,r/\sqrt{3}$

2.5 PACKING FRACTION

Packing fraction is defined as the ratio of the volume of the atoms per unit cell to the total volume occupied by the unit cell i.e.

Packing Fraction (P.F.) = $\frac{\text{Ratio of the volume of the atoms per unit cell}}{\text{Total volume occupied by the unit cell}}$

Volume of the atom is the ratio of the volume per unit cell to the volume of the unit cell. Now let us calculate the packing fraction for all the structures.

(a) Simple Cubic (SC)

You know, for SC atoms per unit cell = 1

Volume of one atom = $4/3\ \pi\ r^3$

Atomic radius $r = a/2$, where a is the edge of the cube.

Therefore, packing fraction (P.F.) = $\frac{1\times\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \pi/6 = 0.52 = 52\%$

(b) Hexagonal Close Packed (HCP)

Atoms per unit cell = 2

Volume of one atom = $4/3\ \pi\ r^3$

Atomic radius $r = a/2$

Therefore, packing fraction (P.F.) = $\frac{2\times\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{\frac{1}{2}\sqrt{3}a^2c} = 0.74 = 74\%$ (with $c/a = \sqrt{8/3}$)

(c) Face Centred Cubic (FCC)

Atoms per unit cell = 4

Volume of 4 atoms = $4 \times (4/3\ \pi\ r^3)$

Radius of atoms r = $\frac{\sqrt{2}}{4}a$

Therefore, packing fraction (P.F.) = $\frac{4\times\frac{4}{3}\pi\left(\sqrt{2}\frac{a}{4}\right)^3}{a^3}$ = $\pi\sqrt{2}$ /6 = 0.74 = 74%

(d) Body Centred Cubic

In this structure, atoms per unit cell = 2

Volume of 2 atoms = 2 × ($4/3\ \pi\ r^3$)

Radius of atom r = $\frac{\sqrt{3}}{4}a$

Therefore, packing fraction (P.F.) = $\frac{2\times\frac{4}{3}\pi\left(\sqrt{3}\frac{a}{4}\right)^3}{a^3}$ = $\pi\sqrt{3}$ /8 = 0.68= 68%

2.6 LATTICE CONSTANT OF A SPACE LATTICE

You know that the smallest unit cell is Wigner-Seitz primitive cell. Let the lattice constant for cubic crystals be ‘a’. Obviously, the each side of the cube will be ‘a’.

The volume of unit cell = a^3

If ρ be the density of the crystal then the mass of each unit cell = $a^3\ \rho$.

If M be the molecular weight and N the Avogadro number, then the mass of each molecule = M /N

Let ‘n’ be the number of molecules (lattice points) per unit cell, then the mass in each unit cell = $\frac{nM}{N}$

Therefore, $a^3\ \rho = \frac{nM}{N}$

or $\quad a = \left(\frac{nM}{N\rho}\right)^{\frac{1}{3}}$ .....(1)

The above expression gives the lattice constant of a space lattice.

Example 1: NaCl crystals have fcc structure. The density of NaCl is 2.18 gm/cm^3. Determine the distance between two adjacent atoms.

Solution: Given ρ = 2.18 gm/cm^3, M = 23 + 35.5 = 58.5, n = 4

Using $a = \left(\frac{nM}{N\rho}\right)^{\frac{1}{3}} = \left(\frac{4\times58.5}{2.18\times6.02\times10^{23}}\right)^{\frac{1}{3}} = 5.628\times10^{-8}$ cm

The distance between two adjacent atoms i.e. interplanar spacing d = a/2 = $5.628\times10^{-8}/2$

$= 2.814\times10^{-8}$ cm

Self Assessment Question (SAQ) 1: Calculate the density of copper crystal. Copper has fcc structure. Atomic weight of Cu = 63.54, Lattice constant of Cu = 3.61 A^0

2.7 DENSITY OF LATTICE POINTS IN A LATTICE PLANE

Let us consider N successive parallel lattice planes in a lattice having spacing ‘d’ and area of cross-section ‘A’.

The volume of the part of lattice under consideration = NAd

Let ‘V’ be the volume of each unit cell.

The number of unit cells in this part of the lattice = $\frac{NAd}{V}$

Let ‘n’ be the number of lattice points per unit cell, then the total number of lattice points in this part of lattice = $\frac{NAd}{V}\ n$

If ρ is the density of lattice points in these planes i.e. the number of lattice points per unit area then the total number of lattice in the same part of lattice = AρN

Therefore, $\quad A\ \rho\ N = \frac{NAd}{V}\ n$

or $\quad \rho = \frac{nd}{V}$ .....(2)

In the case of cubic, tetragonal and orthorhombic lattices, V = a b c

Therefore, $\quad \rho = \frac{nd}{abc}$ .....(3)

For primitive lattice in each of these systems, there is one lattice point per unit cell, i.e. n = 1.

Therefore, $\quad \rho = \frac{d}{abc}$ .....(4)

2.8 MILLER INDICES

In crystal structure analysis, it is very important to describe certain direction or position and orientation of a crystal plane. The direction is specified by coordinates of a first point through which a line is passing such that coordinates are whole numbers. Usually, square brackets are used to describe the directions e.g. Y-axis [0 1 0], Z-axis [0 0 1], negative X-axis [1 0 0] etc. The position and orientation of a plane is determined by any three points which are not collinear. Miller first used this index system to describe the crystal faces. Now, these are known as Miller indices. In general, a plane is inclined to all the crystallographic axes. The point of intersection of a plane on the axis is determined in terms of the lattice constants.

The Miller indices are a set of integers in the ratio of the reciprocals of the fractional intercepts which the plane makes with the three axes. Usually, these are specified as (h k l). The plane has fractional intercepts of$\frac{1}{h}$, $\frac{1}{k}$ and $\frac{1}{l}$ with the axes and intercepts are $\frac{a}{h}$, $\frac{b}{k}$ and $\frac{c}{l}$.

Following the simple procedure given below, you can find the Miller indices of a plane-

(i) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes X, Y and Z.

X	Y	Z
3a	4b	2c
pa	qb	rc

with p = 3, q= 4 and r = 2

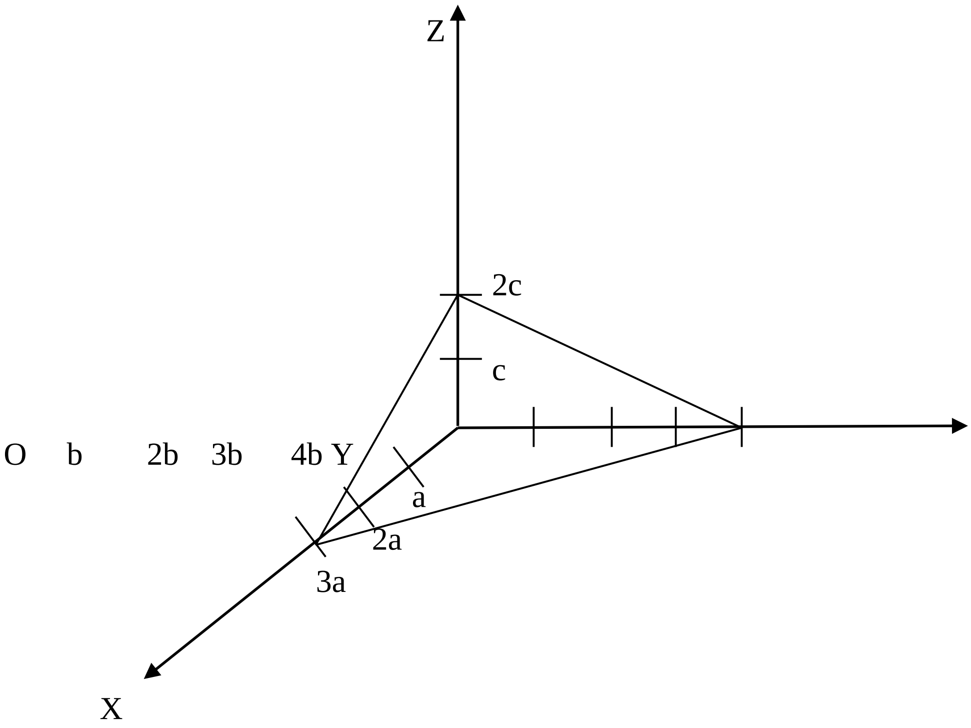


Figure 2.5: Representation of Miller Indices

(ii) Express the intercepts as multiples of the unit cell dimensions or lattice parameters along axes i.e.

$$\frac{3a}{a}\frac{4b}{b}\frac{2c}{c}$$

3 4 2

(iii) Obtain the reciprocals of these numbers

$$\frac{1}{3}\frac{1}{4}\frac{1}{2}$$

(iv) Reduce these reciprocals to the smallest set of integral numbers and enclose them in bracket

$$12\times\frac{1}{3} \qquad 12\times\frac{1}{4} \qquad 12\times\frac{1}{2}$$

(4 3 6)

Or (4 3 6)

Thus, (4 3 6) is the Miller indices of this hypothetical plane.

In general, it is represented by (h k l)

If the intercept is on negative direction, then put the sign of bar on the corresponding indices e.g. if the plane cuts an intercept on negative X-axis, then Miller indices are ($\bar{4}$ 3 6). If a plane is parallel to a given axis, its intercept on that axis is infinite.

Characteristics of the Miller indices

Following are the important characteristics of the Miller indices-

(i) The Miller indices denote a single plane or a set of parallel planes.

(ii) If the Miller indices of two planes have the same ratio, then the planes are parallel to each other. Thus, the planes (2 2 2) and (3 3 3) are parallel planes.

(iii) If (h k l) are the Miller indices of a plane, then the plane cuts the X-, Y- and Z-axes into h, k and l equal segments respectively.

Example 2: Obtain the Miller indices of a plane with intercept at a, b/3, 3c in a simple cubic unit cell.

Solution: Step I: Determine the coordinates of the intercepts made by the plane along the three crystallographic axes X, Y and Z- axes

X	Y	Z
a	$\frac{b}{3}$	3c

Step II: Let us express the intercepts as the multiples of the unit cell dimensions

$$\frac{a}{a}\,\frac{\frac{b}{3}}{b}\,\frac{3c}{c}$$

$$1 \qquad \frac{1}{3} \qquad 3$$

Step III: Let us get the reciprocals of these numbers

$$\frac{1}{1}\,\frac{1}{\frac{1}{3}}\,\frac{1}{3}$$

or $1 \qquad 3 \qquad \frac{1}{3}$

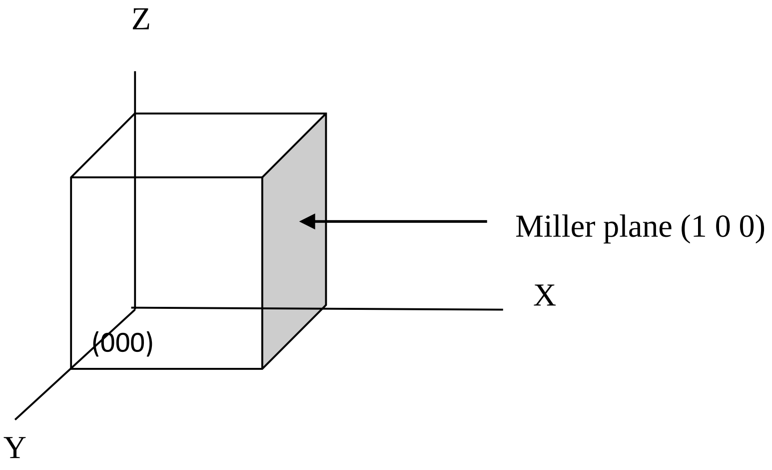
Step IV: Let us reduce the reciprocals to the smallest set of integral numbers and enclose them in bracket

$$1\times3 \qquad 3\times3 \qquad \frac{1}{3}\times 3$$

$$3 \qquad 9 \qquad 1$$

Therefore, the Miller indices are (3 6 1)

Example 3: Obtain the Miller indices of the lattice plane shown in the following figure-



Solution: Obviously, you observe that the plane cuts the X-axis at 1. There are no intercepts on the Y- and Z-axes as the plane is parallel to the Y-Z plane. Therefore, X-intercept = 1, Y-intercept = ∞ and Z-intercept = ∞. Now let us follow the following steps-

Here, the coordinates of the intercepts are already as the multiples of the unit cell dimensions.

$$1 \qquad \infty \qquad \infty$$

Let us get the reciprocals of these numbers-

$$\frac{1}{1}\frac{1}{\infty}\frac{1}{\infty}$$

$$1 \qquad 0 \qquad 0$$

Therefore, the Miller indices are: (1 0 0)

Self Assessment Question (SAQ) 2: In an orthorhombic crystal a lattice plane cuts intercepts of 3a, - 2b and 3c/2 along three axes. Deduce the Miller indices of the plane where a, b, c are primitive vectors of the unit cell.

Self Assessment Question (SAQ) 3: Find the Miller indices of a plane that makes an intercept of 3a, 2b and c along the three crystallographic axes where a, b, c being the primitive vectors of the lattice.

2.9 SPACING OF PLANES IN CRYSTAL LATTICES

Let us consider O as origin and OX, OY and OZ as three rectangular axes. Let a reference plane passes through O and consider a set of parallel planes defined by Miller indices (h k l). Besides reference plane through O, if next plane passes through A, B and C then the respective intercepts are a/h, b/k and c/l as shown in figure 7. If ON, as shown, is the normal between this plane and reference plane, then ON =d is the inter-planar spacing.

Let the normal ON makes angles α, β and γ with crystal axes such that < NOX = α, <NOY= β and <NOZ = γ.

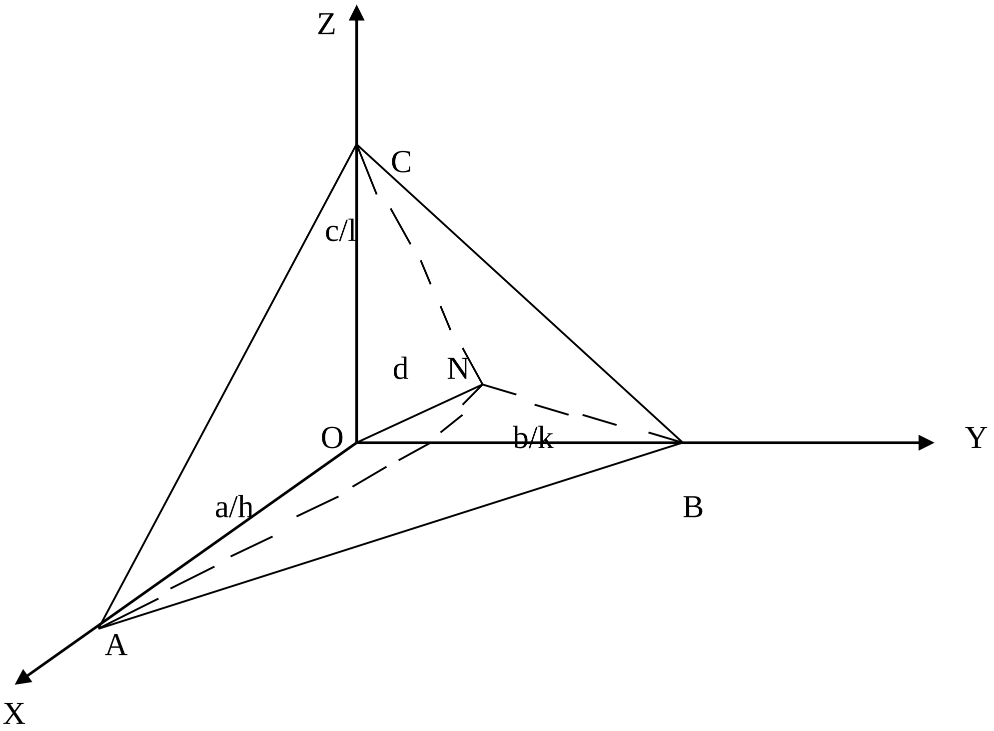


Figure 2.6: Spacing of planes in crystal lattices

By geometry,

$$d = a\cos\alpha/h = b\cos\beta/k = c\cos\gamma/l$$

or $\cos\alpha = \frac{d}{\left(\frac{a}{h}\right)}, \cos\beta = \frac{d}{\left(\frac{b}{k}\right)}, \cos\gamma = \frac{d}{\left(\frac{c}{l}\right)}$

But, you know that $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$ .....(5)

Putting for cosα, cosβ and cosγ in the above relation, you get-

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

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

or $$d = \frac{1}{\left[\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2\right]^{\frac{1}{2}}} \qquad .....(6)$$

Spacing of planes (or inter-planar spacing) d is also written as d_{hkl}.

The above equation is applicable to primitive lattices and for cubic, orthorhombic and tetragonal systems only where the axes are mutually perpendicular ($\alpha = \beta = \gamma = 90^0$). In the case of cubic system, a = b = c, then relation (6) becomes-

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \qquad .....(7)$$

Obviously, planes with low index numbers have wide inter-planar spacing compared with those with higher index numbers.

For a tetragonal crystal a =b, therefore,

$$d = \frac{1}{\left[\left(\frac{h}{a}\right)^2+\left(\frac{k}{a}\right)^2+\left(\frac{l}{c}\right)^2\right]^{\frac{1}{2}}} = \frac{1}{\left[\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right]^{\frac{1}{2}}} \qquad .....(8)$$

The spacing between (1 0 0), (1 1 0) and (1 1 1) planes in the case of a simple cubic lattice from equation (7) are given by-

d_{100}= a, $d_{110}= \frac{a}{\sqrt{2}}$, $d_{111} = \frac{a}{\sqrt{3}}$

Obviously, the ratio of spacing of the possible lattice planes in a simple cubic lattice are given by-

$d_{100} : d_{110} : d_{111} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$

Similarly, for bcc lattice, $d_{100} = \frac{a}{2}$, $d_{110}= \frac{a}{\sqrt{2}}$, $d_{111} = \frac{a}{2\sqrt{3}}$

For fcc lattice, $d_{100} = \frac{a}{2}$, $d_{110}= \frac{a}{2\sqrt{2}}$, $d_{111} = \frac{a}{\sqrt{3}}$

2.10 SYMMETRY OPERATION

Let us discuss the symmetry operations for a two-dimensional crystal. If a body attains its initial configuration after undergoing a particular operation, it is said to possess a symmetry corresponding to that operation. Let us consider an example. You may consider rotating a book by 360^0 about an axis passing through its centre and perpendicular to its plane. After this rotation, the book will assume its initial position. For an observer who is not aware of the rotation of the book, it will appear as if the book has not been subjected to any operation. Thus, a symmetry operation may be defined as one which leaves the crystal environment invariant.

The symmetry operation performed about a point or a line constitute point group elements and the symmetry operations performed by a combination of rotation and translation constitute the space group elements. The symmetry operations include the following-

(i) translation operation which applies only to lattice
(ii) point operation which includes- rotation operation about an axis, reflection in a plane and inversion about a point. These apply to all objects.
(iii) Compound operation which includes translation operation and point operation.

You should remember that in two-dimension, an axis of rotation is a point and a plane of reflection is a line.

2.10.1 Translational Symmetry

You have seen that a crystal is composed of atoms arranged at the lattice points. An ideal crystal is composed of atoms arranged on a lattice defined by three fundamental translation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ such that the atomic arrangement looks the same in every respect when viewed from any point $\vec{r}$ as when viewed from the point

$$\overrightarrow{r'} = \vec{r} + \mathrm{u}\,\vec{a} + \mathrm{v}\,\vec{b} + \mathrm{w}\,\vec{c} \qquad \text{.....(9)}$$

where u, v, w are arbitrary integers. The set of points $\overrightarrow{r'}$ specified by equation (9) for all values of the integers u, v, w defines a lattice. The lattice and the translation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ are said to be primitive if any two points $\vec{r}$, $\overrightarrow{r'}$ from which the atomic arrangement looks the same always satisfy equation (9) with a suitable choice of the integers u, v, w. The definition of the primitive translation vectors shows that there is no cell of smaller volume that could serve as a building block for the crystal structure.

Often, the primitive translation vectors are used to define the crystal axes $\vec{a}$, $\vec{b}$, $\vec{c}$. The crystal axes $\vec{a}$, $\vec{b}$, $\vec{c}$ form three adjacent edges of a parallelepiped. If there are lattice points only at the corners of the parallelepiped, then it is a primitive parallelopiped.

Lattice translation operator$\vec{T}$ is defined in terms of three fundamental translation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ as follows-

$$\vec{T} = \mathrm{u}\,\vec{a} + \mathrm{v}\,\vec{b} + \mathrm{w}\,\vec{c} \qquad \text{.....(10)}$$

A vector $\vec{T}$ connects any two lattice points.

You will see that the following figure 8 gives the diagram of a two-dimensional lattice with lattice vector $\vec{a}$ and $\vec{b}$. The atomic arrangement in the crystal looks exactly the same to an observer at $\overrightarrow{r'}$ as to an observer at $\vec{r}$, provided that the vector $\vec{T}$ which connects $\overrightarrow{r'}$ and $\vec{r}$ may be expressed as an integral multiple of the vectors $\vec{a}$ and $\vec{b}$.

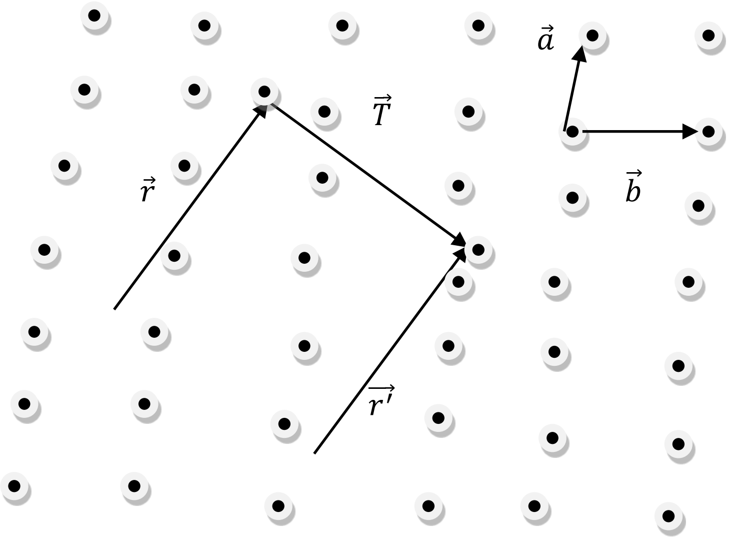
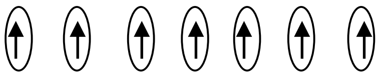


Figure 2.7: Translational Symmetry

2.11 LIQUID CRYSTALS

Some crystalline substances convert from solid to liquid phase during heating, not instantly but first passing into a thermodynamically stable transitional state in which the substances still retain the anisotropy in the properties such as dielectric, optical, magnetic and others, inherent in a crystal, although they simultaneously acquire the properties specific to liquids-fluidity, ability to form droplets etc. The substances exhibiting such an intermediate, mesomorphic, phase are known as liquid crystals. All liquid crystals are organic materials composed of rigid, moderately large rod-like molecules typically 1 to 3 mm in length and 0.3 to 1.0 mm across. At the end of molecules there are clusters of atoms exhibiting high polarizability. The ordered arrangement of molecules in the liquid crystalline state is provided by relatively weak Vander Waal’s force. Depending upon magnitude of these forces, three types of mesophase originate- smectic,nematic and cholesteric. The most ordered smectic crystals have layered structure. Molecules align themselves in parallel layers gliding one relative to the other, thereby promoting fluidity (Figures 9, 10).



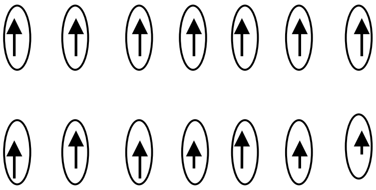


Figure 2.8: Liquid crystals

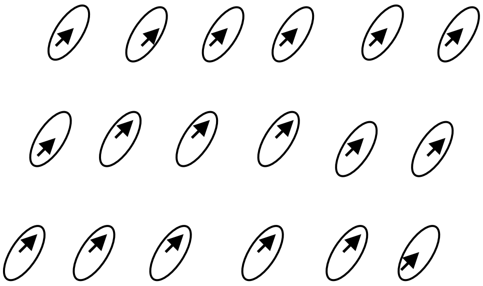


Figure 2.9: Liquid crystals

In a nematic mesophase, the molecules also have their axes parallel to each other but the location of their centres of gravity is as irregular as in conventional liquids (Figure 11). A cholesteric mesophase has its structure twisted about the helical axis lying perpendicular to the orientation of molecules (Figure 12). A cholesteric mesophase has its structure twisted about the helical axis lying perpendicular to the orientation of molecules (Figure 13).

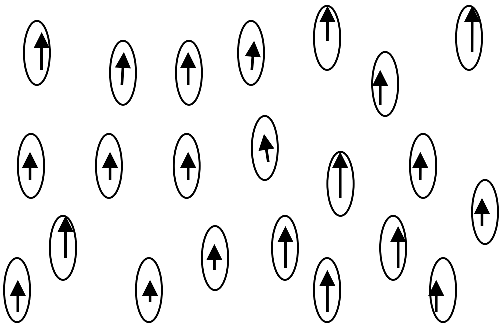


Figure 2.10: Nematic mesophase

The interest in these crystals continuously grows because they are useful in various display applications. Liquid crystalline cells consume less power, are cheap and easy to manufacture in any size and shape and a variety of colours. But these cells also present some disadvantages, namely, they operate in a limited temperature range, have comparatively large response times, short life etc. During last some years, many drawbacks of liquid crystals have been overcome and possibilities have been explored for the use of liquid crystals not only in displays but also in other systems.

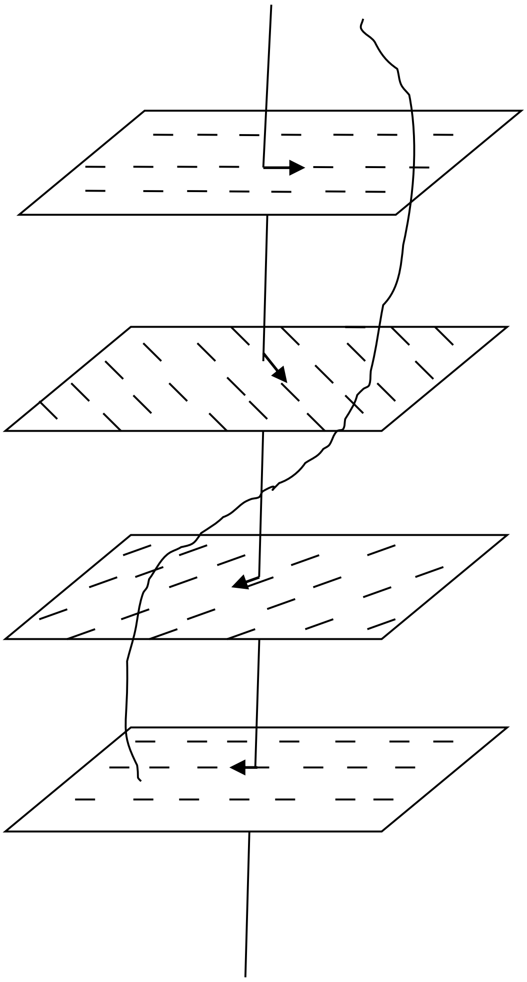


Figure 2.11: Twist in cholesteric mesophase

2.12 SUMMARY

In this unit, you have studied about coordination number (or ligancy), atomic radius, packing fraction, lattice constant of a space lattice, density of lattice points in a lattice plane. In some cases, you have calculated coordination number, atomic radius and packing fraction. The number of anions surrounding a cation is called the coordination number (CN) or the ligancy. The coordination number may also be defined as the number of nearest atoms which are directly surrounding a given atom is called the coordination number or simply the number of nearest neighbours to a given atom in a crystal lattice. You have defined the packingfraction as the ratio of the volume of the atoms per unit cell to the total volume occupied by the unit cell. In the unit, you have established the expressions for lattice constant of a space lattice and density of lattice points in a lattice plane. In the present unit, you have also learnt about Miller indices and its characteristics. You have also learnt the methods to find out Miller indices. You have learnt about spacing of planes in crystal lattices and derived the expression for this. You have learnt about symmetry operation for two-dimensional crystal and known that the symmetry operation performed about a point or a line constitute point group elements and the symmetry operations performed by a combination of rotation and translation constitute the space group elements. You have also studied about liquid crystals. We have included examples and self assessment questions (SAQs) to check your progress.

2.13 GLOSSARY

Lattice- web, network, pattern

Ordered- well-organized

Anisotropy- properties of a substance showing different physical properties in different directions

Dielectric- non-conductor of electricity in which an electric field persists in the presence of an inducing field.

Optical- ocular, visual, related to light

2.14 REFERENCES

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3. Introduction to Solid State Physics, Charles Kittel, John Wiley & Sons (ASIA) Pte Ltd, Singapore

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1. Solid State Devices, B. Somanathan Nair, S.R. Deepa, PHI Learning Private Limited, New Delhi.

2. Fundamentals of Solid State Physics, B.S. Saxena, R.C. Gupta, P.N. Saxena, Pragati Prakashan Meerut.

2.16 TERMINAL QUESTIONS

1. What is coordination number? Find out the coordination numbers of SC, HCP,FCC and BCC structure.

2. Define atomic radius. Calculate atomic radius in case of SC.

3. What is meant by atomic radius? Determine the relationship between the lattice parameter ‘a’ and the atomic radius ‘r’ for mono-atomic SC, BCC and FCC structures.

4. What do you understand by packing fraction? Compute the packing fraction of-

   (i) SCC structure

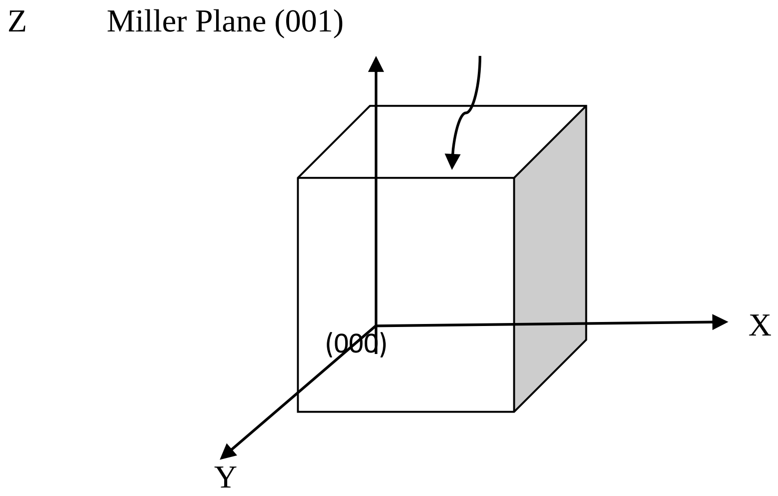
   (ii) BCC structure

   (iii) FCC structure

   (iv) HCP structure

5. Calculate the lattice constant of rock salt (NaCl) crystal. The molecular weight of NaCl = 58.45, $\rho = 2170$ Kg/m^3

6. Obtain the Miller indices of the lattice plane shown in figure 7-



7. Estimate the inter-planar spacing for a (3 2 1) plane in a simple cubic lattice where lattice constant is 4.2×10^{-10} m.

8. What is lattice constant of a space lattice? Derive an expression for lattice constant of a space lattice.

9. What do you mean by density of lattice points in a lattice plane? Establish an general expression for it.

10. What are the Miller indices and how are they computed? Illustrate your answer with a suitable example.

11. Define the Miller indices of a plane. What is its importance in the determination of inter-planar spacing of a crystal? Show that the [h k l] direction is normal to the plane (h k l) in a cubic crystal.

12. Show that the distance between successive planes of Miller indices (h k l) is given by-

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

where a, b, c have their usual meanings. Hence show that for a cubic lattice, this expression reduces to-

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

13. Explain symmetry operation. Discuss translational symmetry.

14. What are liquid crystals? Explain their importance.

15. Fill in the blanks-

(a) The plane with the Miller indices of (2 0 0) is designed as the ....plane.

(b) The distance between two neighbouring atoms touching each other is called................

(c) Given that the Miller indices h = 2, k = 1 and l = 2 is designed as ....plane.

16. Write notes on-

(i) Ligancy (ii) Packing fraction (iii) Liquid crystal (iv) Symmetry operation

17. What are Miller planes and directions?

2.17 ANSWERS

Self Assessment Questions (SAQs):

1. We know that $a = \left(\frac{nM}{N\rho}\right)^{\frac{1}{3}}$

or $\rho = \frac{nM}{a^3 N} = \frac{4\times 63.54}{(3.61)^3 \times 6.02\times 10^{23}}$ = 8.973 gm/cc

2. Step I: Determine the coordinates of the intercepts made by the plane along the three crystallographic axes X, Y and Z- axes

X Y Z

3 a -2b $\frac{3c}{2}$

Step II: Let us express the intercepts as the multiples of the unit cell dimensions

$\frac{3a}{a}$-$\frac{2b}{b}$ $\frac{\frac{3c}{2}}{c}$

3 - 2 $\frac{3}{2}$

Step III: Let us get the reciprocals of these numbers

$\frac{1}{3}$-$\frac{1}{2}$ $\frac{1}{\frac{3}{2}}$

or $\frac{1}{3}$-$\frac{1}{2}$ $\frac{2}{3}$

Step IV: Let us reduce the reciprocals to the smallest set of integral numbers and enclose them in bracket

$\frac{1}{3}\times 6$-$\frac{1}{2}\times 6$ $\frac{2}{3}\times 6$

2 - 3 4

Therefore, the Miller indices are (2 $\bar{3}$ 4)

3. Step I: Determine the coordinates of the intercepts made by the plane along the three crystallographic axes X, Y and Z- axes

X Y Z

3 a 2b c

Step II: Let us express the intercepts as the multiples of the unit cell dimensions

$$\frac{3a}{a}\frac{2b}{b}\frac{c}{c}$$

3 2 1

Step III: Let us get the reciprocals of these numbers

$$\frac{1}{3}\frac{1}{2}\frac{1}{1}$$

or $\frac{1}{3}\frac{1}{2}$ 1

Step IV: Let us reduce the reciprocals to the smallest set of integral numbers and enclose them in bracket

$$\frac{1}{3} \times 6 \frac{1}{2} \times 61 \times 6$$

$$2 \qquad\qquad 3 \qquad\qquad 6$$

Therefore, the Miller indices are (2 3 6)

Terminal Questions:

5. Given, The molecular weight of NaCl, M = 58.45, $\rho = 2170$ Kg/m^3

Here, n = 4

Using $a = \left(\frac{nM}{N\rho}\right)^{\frac{1}{3}} = \left(\frac{4\times 58.45}{6.02\times 10^{23}\times 2170}\right)^{\frac{1}{3}} = 5.64\times 10^{-10}$ m = 5.64 A^0

6. Obviously, you observe that the plane cuts the Z-axis at 1. There are no intercepts on the X- and Y-axes as the plane is parallel to the X-Y plane. Therefore, X-intercept = ∞, Y-intercept = ∞ and Z-intercept = 1. Now let us follow the following steps-

Here, the coordinates of the intercepts are already as the multiples of the unit cell dimensions.

$$\infty \qquad \infty \qquad 1$$

Let us get the reciprocals of these numbers-

$$\frac{1}{\infty}\frac{1}{\infty}\frac{1}{1}$$

$$0 \qquad\quad 0 \qquad\quad 1$$

Therefore, the Miller indices are: (0 0 1)

7. You know, for a simple cubic lattice, a = b = c, Given a = 4.2× 10^{-10} m

Using $d = \frac{1}{\left[\left(\frac{h}{a}\right)^2+\left(\frac{k}{a}\right)^2+\left(\frac{l}{c}\right)^2\right]^{\frac{1}{2}}}$

$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$

Therefore, $d_{321} = \frac{4.2\times 10^{-10}}{\sqrt{3^2+2^2+1^2}} = 1.123\times 10^{-10}$ m

15. (a) 200   (b) lattice constant   (c) (2 1 2)

UNIT 3 RECIPROCAL LATTICE

Structure

3.1 INTRODUCTION

In the preceding unit, you have studied about coordination number, atomic radius, packing fraction, lattice constant of a space lattice, density of lattice points in a lattice plane. In the previous unit, you have calculated coordination number, atomic radius and packing fraction in some cases. You have learnt about the Miller indices, inter-planar spacing in crystal lattices, symmetry operation etc. In the present unit, you will study about reciprocal lattice, X-ray diffraction, Bragg's law and learn about the determination of crystal structure. In the unit, you will also study of Laue and powder method for crystal structure.

3.2 OBJECTIVES

After studying this unit, you should be able to-

- understand reciprocal lattice, Bragg's law.
- calculate primitive translation vectors of reciprocal lattice.
- to compute atomic spacing.
- solve problems based on Bragg's law.

3.3 RECIPROCAL LATTICE

Every crystal structure has two lattices associated with it the crystal lattice and the reciprocal lattice. Vectors in the direct lattice have the dimensions of length while the vectors in the reciprocal lattice have the dimensions of $\frac{1}{\text{length}}$. The reciprocal lattice is a lattice in the Fourier space associated with the crystal.

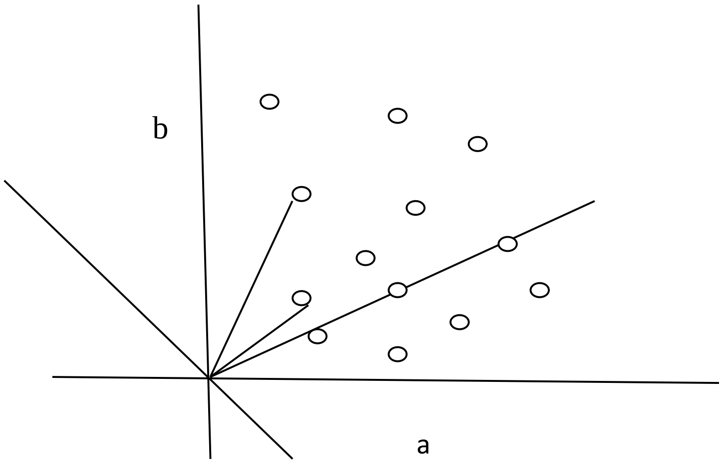


Figure 3.1: Reciprocal lattice

A reciprocal lattice can be constructed by proceeding as follows-

(i) The normal to each plane from a common origin have been drawn.

(ii) A point on the normal at a distance from the origin equal to $\frac{1}{d_{hkl}}$ has been placed. The collection of such points form a periodic array (a net like structure). This array is called the reciprocal lattice because distances in this lattice are reciprocal to those in the crystal.

Properties of Reciprocal Lattice Vectors

(i) A general representation of reciprocal lattice vector is-

$\overline{\sigma_{hkl}} = \frac{1}{d_{hkl}}$

The reciprocal of $\vec{a}$, $\overrightarrow{a^*} = \frac{\vec{b}\times\vec{c}}{\vec{a}.\vec{b}\times\vec{c}} = \frac{\vec{b}\times\vec{c}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]}$

The reciprocal of $\vec{b}$, $\overrightarrow{b^*} = \frac{\vec{c}\times\vec{a}}{\vec{a}.\vec{b}\times\vec{c}} = \frac{\vec{c}\times\vec{a}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]}$

The reciprocal of $\vec{c}$, $\overrightarrow{c^*} = \frac{\vec{a}\times\vec{b}}{\vec{a}.\vec{b}\times\vec{c}} = \frac{\vec{a}\times\vec{b}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]}$

(ii) The following relations hold good-

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

Here$\overrightarrow{a^*}$, $\overrightarrow{b^*}$ and $\overrightarrow{c^*}$ are reciprocal lattice vectors.

(iii) $\overline{\sigma_{hkl}} = \frac{1}{d_{hkl}}$

Where $\overline{\sigma_{hkl}}$ = h $\overrightarrow{a^*}$ + k $\overrightarrow{b^*}$ + l $\overrightarrow{c^*}$ and h, k, l are the Miller indices of the planes concerned.

(iv) Volume of unit of reciprocal lattice is inversely proportional to the volume of direct lattice.

Volume of unit of reciprocal lattice, $\overrightarrow{a^*} \,.\overrightarrow{b^*}\times\overrightarrow{c^*} = [\overrightarrow{a^*}\overrightarrow{b^*}\overrightarrow{c^*}]$

$$= \frac{(\vec{b}\times\vec{c}).\{(\vec{c}\times\vec{a})\times(\vec{a}\times\vec{b})\}}{\{\vec{a}.(\vec{b}\times\vec{c})\}^3}$$

$$= \frac{(\vec{b}\times\vec{c}).[\{\vec{c}.(\vec{a}\times\vec{b})\}-\{\vec{c}.(\vec{a}\times\vec{b})\}\vec{b}]}{\{\vec{a}.(\vec{b}\times\vec{c})\}^3} = \frac{1}{\{\vec{a}.\vec{b}\times\vec{c}\}}$$

$$= \frac{1}{\text{Volume of unit cell of direct lattice}}$$

(v) Also, $\overrightarrow{a^*}.\, \vec{a} = 1, \overrightarrow{b^*}.\, \vec{b} = 1, \overrightarrow{c^*}.\, c = 1$

In some texts on Solid State Physics, the primitive translation vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ of a direct lattice are related to the primitive translation vectors $\overrightarrow{a^*}$, $\overrightarrow{b^*}$ and $\overrightarrow{c^*}$of the reciprocal lattice as-

$\overrightarrow{a^*}.\, \vec{a} = \overrightarrow{b^*}.\, \vec{b} = \overrightarrow{c^*}.\, c = 2\pi$

These equations can be satisfied by choosing the reciprocal lattice vectors as-

$$\overrightarrow{a^*} = 2\pi \frac{\vec{b}\times\vec{c}}{\vec{a}.\vec{b}\times\vec{c}} = 2\pi \frac{\vec{b}\times\vec{c}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]} \overrightarrow{b^*} = 2\pi \frac{\vec{c}\times\vec{a}}{\vec{a}.\vec{b}\times\vec{c}} = 2\pi \frac{\vec{c}\times\vec{a}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]}, \overrightarrow{c^*} = 2\pi \frac{\vec{a}\times\vec{b}}{\vec{a}.\vec{b}\times\vec{c}} = 2\pi \frac{\vec{a}\times\vec{b}}{[\overrightarrow{a}\vec{b}\vec{c}]}$$

The factor 2π are not used by crystallographers but are convenient in Solid State Physics.

$\overrightarrow{a^*}\,.\vec{b}\times\vec{c}$ can be written as $[\vec{a}\vec{b}\vec{c}]$ which represents the volume of the unit cell.

Example 1: The primitive translation vectors of a two-dimensional lattice are-
$\vec{a} = 2\, i^{\wedge\,+} j^{\wedge}$, $\vec{b} = 2\, j^{\wedge}$ and $\vec{c} = k^{\wedge}$
Determine the primitive translation vectors of its reciprocal lattice.
Solution: Given- $\vec{a} = 2\, i^{\wedge\,+} j^{\wedge}$, $\vec{b} = 2\, j^{\wedge}$ and $\vec{c} = k^{\wedge}$
The primitive translation vectors of reciprocal lattice are given by-

$$\overrightarrow{a^*} = 2\pi \frac{\vec{b}\times\vec{c}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]}\, \overrightarrow{b^*} = 2\pi \frac{\vec{c}\times\vec{a}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]}\ ,\overrightarrow{c^*} = 2\pi \frac{\vec{a}\times\vec{b}}{[\overrightarrow{a}\overrightarrow{b}\overrightarrow{c}]}$$

$$[\vec{a}\vec{b}\vec{c}] = \begin{vmatrix} 2 & 1 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{vmatrix} = \left| 2 \begin{vmatrix} 2 & 0 \\ 0 & 1 \end{vmatrix} - 1 \begin{vmatrix} 0 & 0 \\ 0 & 1 \end{vmatrix} + 0 \begin{vmatrix} 0 & 2 \\ 0 & 0 \end{vmatrix} \right|$$

$= 4$ units

$\vec{b}\times\vec{c} = 2\, i^{\wedge} \times k^{\wedge} = 2\, i^{\wedge}$, $\vec{c}\times\vec{a} = k^{\wedge}\times(2\, i^{\wedge\,+} j^{\wedge}) = 2j^{\wedge} - i^{\wedge}$, $\vec{a}\times\vec{b} = (2\, i^{\wedge\,+} j^{\wedge}) \times 2\, j^{\wedge} = 4\, k^{\wedge}$

Therefore, $\overrightarrow{a^*} = 2\pi\ \frac{2\hat{\imath}}{4}$, $\overrightarrow{b^*} = 2\pi\ \frac{2\pi(2\hat{\jmath} - \hat{\imath})}{4} = \frac{\pi(2\hat{\jmath} - \hat{\imath})}{2}$,$\overrightarrow{c^*} = 2\pi\left(\frac{4\hat{k}}{4}\right) = 2\pi\, k^{\wedge}$

Self Assessment Question (SAQ) 1: Find out reciprocal lattice vectors for a space lattice defined by the following primitive translation vectors-

$\vec{a} = 5\, i^{\wedge} + 5j^{\wedge} - 5\, k^{\wedge}$, $\vec{b} = -5\, i^{\wedge} + 5\, j^{\wedge} + 5\, k^{\wedge}$ and $\vec{c} = 5\, i^{\wedge} - 5\, j^{\wedge} + 5\, k^{\wedge}$

3.4 X-RAY DIFFRACTION AND LAUE METHOD

Soon after the discovery of X-rays in 1895, the nature of X-rays became a matter of concern. Results of early experiments indicated that if X-rays consisted of waves, their wavelengths were of the order of 10^{-8} to 10^{-9} cm. Laue suggested that the ordered arrangement of atoms in a crystal must make it to act as a three-dimensional grating. Since the spacing between the layers of these atoms in a crystal is of the order of 10^{-8} cm (which is of the order of wavelength of X-rays), therefore a crystal would be suitable for the diffraction of X-rays.

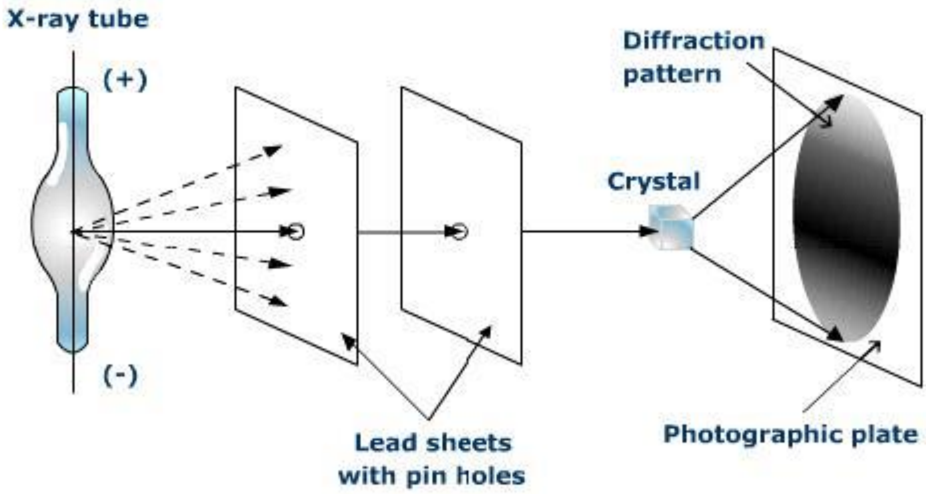


Figure 3.2: Experimental arrangement of Laue

The experimental arrangement of Laue and his co-workers is shown in Figure 2. A thin pencil of X-rays after passing through aligned slit was allowed to pass through a thin plate of crystal of zinc blende. The transmitted beam is received on a photographic plate. After the exposure of several hours, when the plate was developed, it had been found that in addition to the central spot, it consists of other fainter spots arranged regularly. These spots are called Laue spots (Figure 2). Each spot in the Laue pattern arises due to the constructive interference between the waves reflected from one of the various sets of parallel planes in the crystal. Figure 3 shows two such sets of planes by means of continuous and dotted lines. The corresponding planes will be perpendicular to the plane of the paper. A simple interpretation was given by W.L. Bragg.

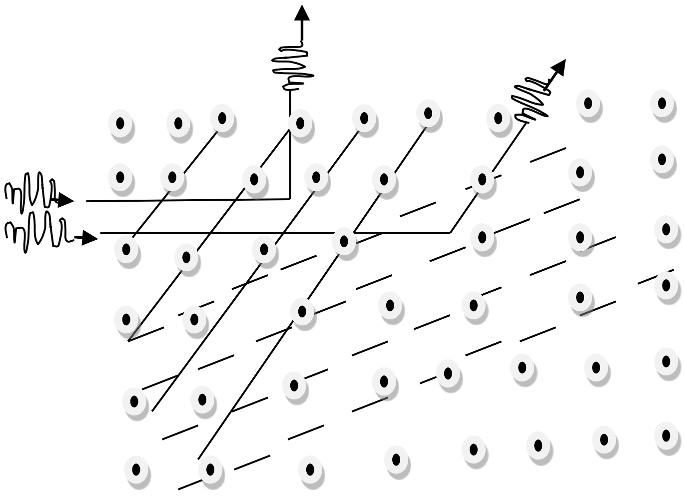


Figure 3.3: Lau Pattern

3.5 BRAGG'S LAW AND DETERMINATION OF CRYSTAL STRUCTURE

Let us consider a set of parallel planes of the crystal, separated by spacing d. The crystal acts as a series of parallel reflecting planes. Let a beam of monochromatic X-rays strike the crystal. Since X-rays can penetrate the crystal, there would be partial reflection from every plane till it would be absorbed completely. The rays reflected from various planes will interfere constructively if they are in same phase.

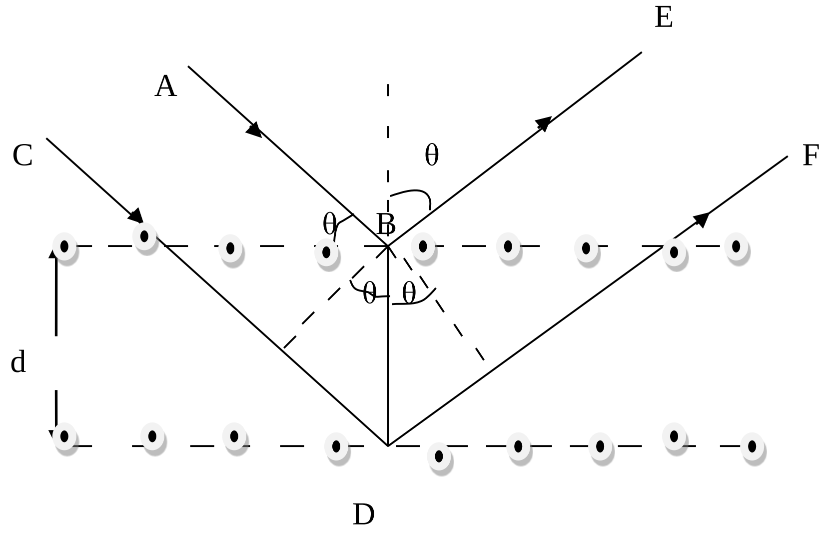


Figure 3.4: Bragg's law

Let us consider two parallel rays AB and CD incident over the planes at glancing angle θ. Corresponding reflected rays from atoms B and D are BE and DF.

The path difference between the rays = MD + DN

M and N are the feet of perpendiculars from B on CD and DF respectively.

MD = DN = d sin θ

Therefore, the path difference = d sin θ + d sin θ = 2 d sin θ

The two sets of scattered waves reinforce each other when the path difference is an integral multiple of wavelength λ i.e.

$$2\,d \sin\theta = n\,\lambda \qquad \text{….. (1)}$$

Here n = 1, 2, 3, …………… (an integer), θ = glancing angle, d = interlayer spacing

The equation (1) is known as Bragg's law.

For first order reflection, n = 1

Therefore, $2\, d \sin \theta = \lambda$

Similarly, n = 2, 3, 4, ….. for second, third, fourth order reflection……… respectively.

Using Bragg's equation and knowing lattice space d, you can determine the wavelength λ of X-rays. Alternatively, if you know the wavelength of X-rays, then you can determine the crystal lattice spacing. By Bragg's law, you can study the crystal structure.

Example 2:X-rays of wavelength 0.36 A^0 diffracted in a Bragg spectrometer at an angle of 4^0 48'. Determine the effective value of atomic spacing.

Solution: Given- $\lambda = 0.36\ A^0 = 0.36 \times 10^{-10}$ m, $\theta = 4^0\ 48'$

Now using Bragg's equation- $2\, d \sin \theta = n \lambda$

or $d = n \lambda / 2 \sin \theta = 1 \times 0.36 \times 10^{-10} / (2 \times \sin 4^0\ 48')$

$= 2.15 \times 10^{-10}$ m $= 2.15\ A^0$

Self Assessment Question (SAQ) 2: Estimate the longest wavelength that can be analysed by a rock salt crystal of spacing d = 2.82 A^0 in the (i) first order and (ii) second order

3.6 POWDER METHOD

When an X-ray is shined on a crystal, it diffracts in a pattern characteristic of the structure. In powder X-ray diffraction, the diffraction pattern is obtained from a powder of the material, rather than an individual crystal. Powder diffraction is often easier and more convenient than single crystal diffraction since it does not require individual crystals be made. Powder X-ray diffraction (XRD) also obtains a diffraction pattern for the bulk material of a crystalline solid, rather than of a single crystal, which doesn't necessarily represent the overall material. A diffraction pattern plots intensity against the angle of the detector, 2θ

Since most materials have unique diffraction patterns, compounds can be identified by using a database of diffraction patterns. The purity of a sample can also be determined from its diffraction pattern, as well as the composition of any impurities present. A diffraction pattern can also be used to determine and refine the lattice parameters of a crystal structure. A theoretical structure can also be refined using a method known as Rietveld refinement. The particle size of the powder can also be determined by using the Scherrer formula, which relates the particle size to the peak width. The Scherrer formula is

$$t = \frac{0.9\, \lambda}{\sqrt{B_M^2 - B_S^2 \cos \theta}} \qquad \text{…..(2)}$$

withλ , the X-rays wavelength; B_M ,the observed peak width; B_S, the peak width of a crystalline standard and θ the angle of diffraction.

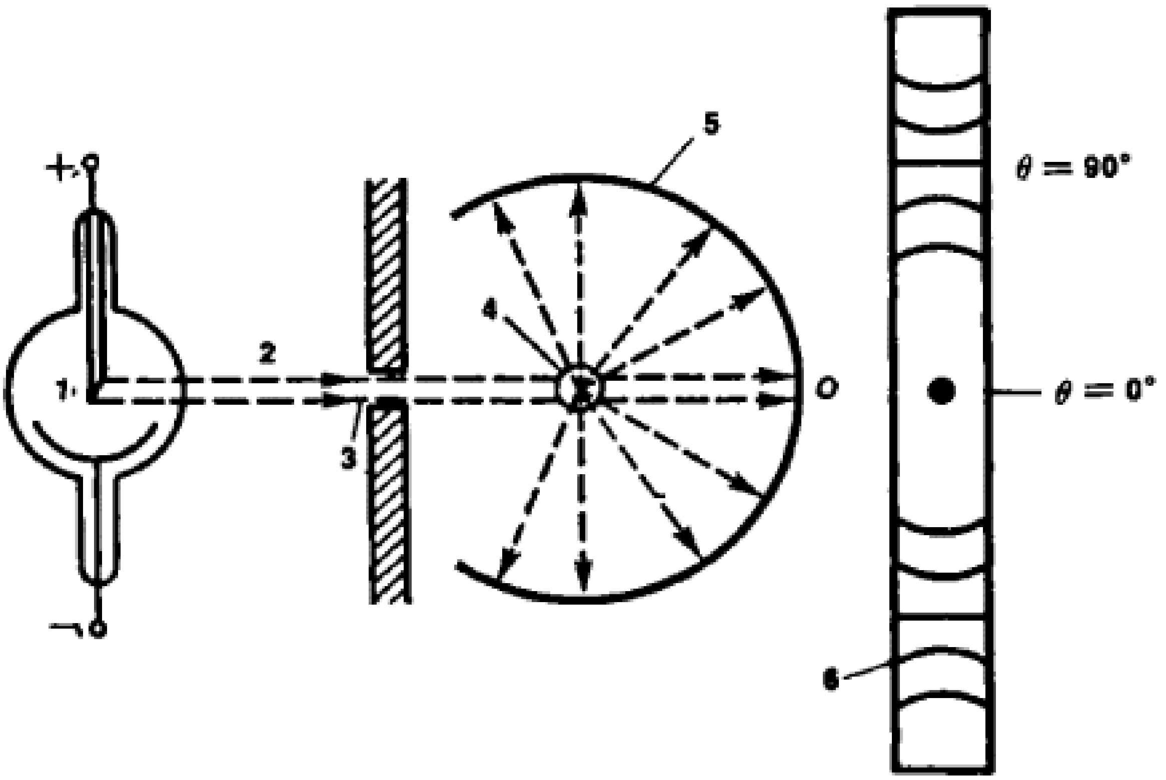


Figure 3.5: Experimental set up of Powder Method

3.7 EWALD'S CONSTRUCTION

Intensity of diffraction spots

The observed intensity I of the diffraction spots can be thought of as corresponding to the 'size' of the reciprocal lattice point (I(hkl) is proportional to $|F(hkl)|^2$). Clearly, either depends on the contents of the unit cell, and we already suspect that the space group symmetry will thus have some implications on the diffraction pattern symmetry. Before we investigate further, it may be useful to understand how the diffraction pattern can be derived from the reciprocal lattice. Let us look at a reciprocal lattice with spots in it.

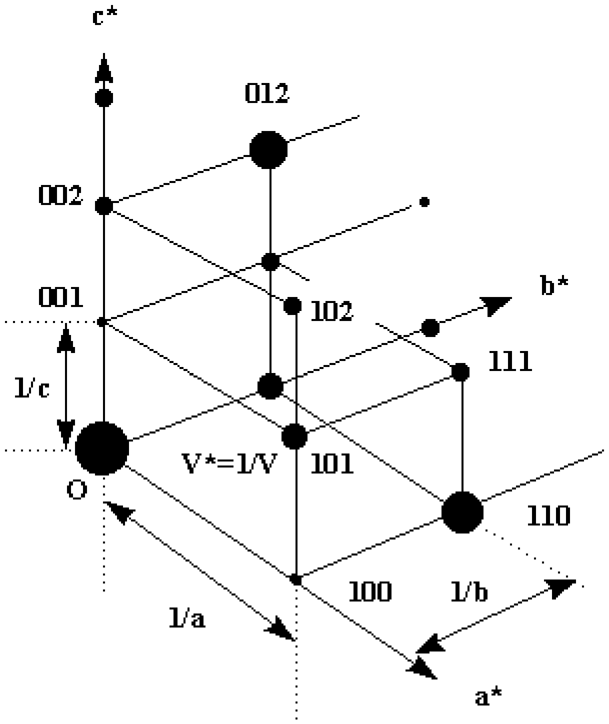


Figure 3.6: Reciprocal Lattice in Ewald's construction

Here we see different magnitudes for the lattice points. The largest spot is at the origin corresponding to F(000), which we know already is the sum of all electrons in the unit cell. The reflection itself is at zero diffraction angle, i.e., in the primary beam path and not observable. Now, where do we expect all the other diffraction spots to appear?

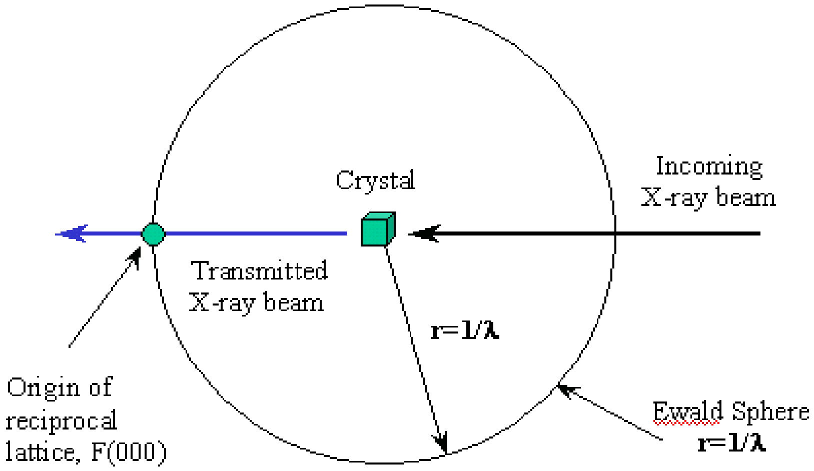


Figure 3.7: Ewald sphere

A most useful means to understand the occurrence of diffraction spots is the Ewald construction. Let's begin slowly: We draw a sphere of radius 1/lambda, in the center of which we imagine the real crystal. The origin of the reciprocal lattice (see above) lies in the transmitted beam, at the edge of the Ewald sphere.

We know already that diffraction maxima (reflections, diffraction spots) occur only when the 3 Laue equations, or equivalent, the Bragg equation in vector form, are satisfied. This condition occurs whenever a reciprocal lattice point lies exactly on the Ewald sphere.

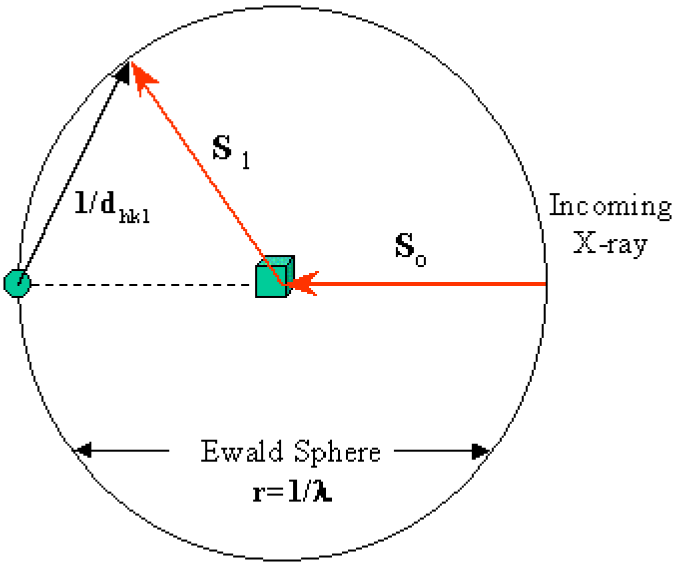


Figure 3. 8: Ewald sphere

As you may have assumed already, the chance for this to occur is modest, and we need to rotate the crystal in order to move more reciprocal lattice points through the Ewald sphere. In the following, I have drawn a reciprocal lattice in the origin, and we rotate it along the vertical axis of the drawing. We actually accomplish this by rotating the crystal along the same axis.

Just imagine turning the reciprocal lattice through the Ewald sphere: in the beginning, only (101) and (10-1) give rise to a reflection. After you turned the reciprocal lattice a bit (which actually means turning the crystal around the same axis), the reciprocal lattice point 201 will enter the sphere and create a diffraction spot.

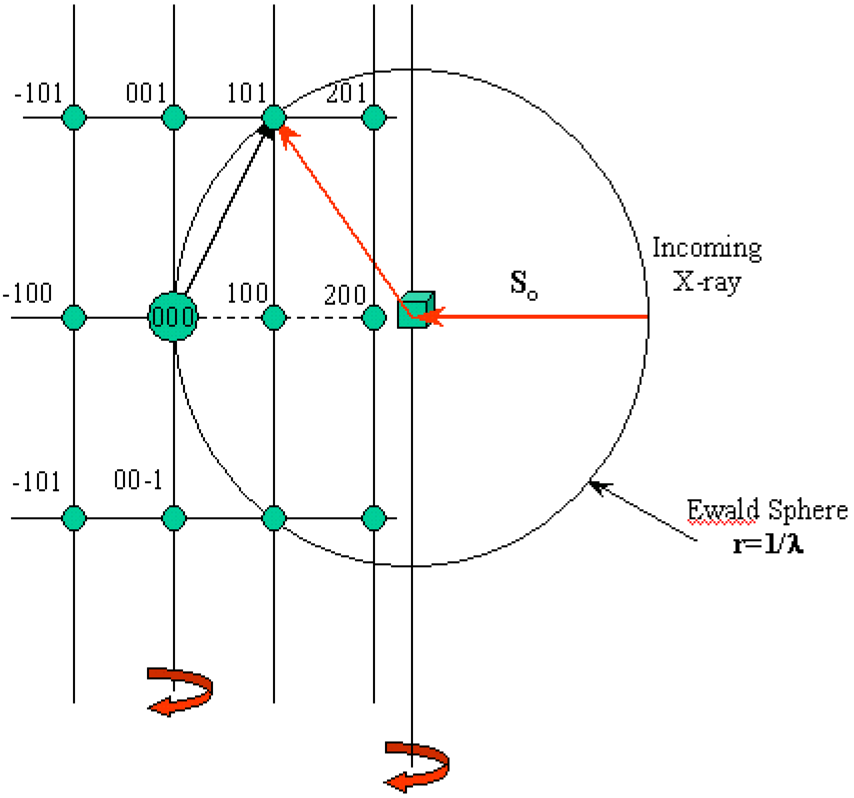


Figure 3.9: Ewald sphere and reciprocal lattice

3.8 SUMMARY

In the present unit, you have learnt about reciprocal lattice, X-ray diffraction and Laue method. You have known that the reciprocal lattice is a lattice in the Fourier space associated with the crystal. You have studied the method to construct the reciprocal lattice. You have also studied Bragg's law and learnt about the determination of crystal structure.Using Bragg's equation and knowing lattice space d, you can determine the wavelength λ of X-rays or alternatively you can say that if you know the wavelength of X-rays, then you can determine the crystal lattice spacing. By Bragg's law, you can study the crystal structure. You have also studied the powder method for the determination of crystal structure. In this unit, you have also learnt about Ewald's construction. Some solved examples are given in the unit to make the concepts clear. To check your progress, self assessment questions (SAQs) are given place to place.

3.9 GLOSSARY

Lattice- pattern, net, web.

Diffraction- bending of waves at the corners of the object in their path whose size is one of the order of wavelength of wave.

Transmitted- passed on, sent out.

Refinement- improvement, modification.

Intensity- strength, the average amount of energy of a wave transported by the wave per unit area of cross-section of the medium per second.

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2. Fundamentals of Solid State Physics, B.S. Saxena, R.C. Gupta, P.N. Saxena, Pragati Prakashan Meerut.

3.12 TERMINAL QUESTIONS

1. Describe Laue’s experiment for X-rays diffraction. Give its significance.

2. Give mathematical definition of Bragg’s law.

3. What is reciprocal lattice? How will you construct reciprocal lattice? Give its properties.

4. What is Bragg’s law? Derive Bragg’s equation. How will you use Bragg’s law to determine the crystal structure?

5. Describe powder method for the determination of crystal structure.

6. Discuss Ewald’s construction. Give its importance and uses.

7. Write note on-

(a) Bragg's law (b) Reciprocal lattice

8. A set of crystal planes reflects X-rays of wavelength 1.32 A^0 at a glancing angle of 9^0 30'. Determine the possible spacing of this set of planes.

9. Explain Laue pattern.

10. State True or False-

(i) Bragg's equation will have no solution if $\lambda > 2$ d

(ii) Laue spots show the diffraction property of X-rays.

(iii) The volume of unit of reciprocal lattice is inversely proportional to the volume of direct lattice.

3.13 ANSWERS

Self Assessment Questions (SAQs):

1. Given- $\vec{a} = 5\,i^{\wedge} + 5j^{\wedge} - 5\,k^{\wedge}$, $\vec{b} = -5\,i^{\wedge} + 5\,j^{\wedge} + 5\,k^{\wedge}$ and $\vec{c} = 5\,i^{\wedge} - 5\,j^{\wedge} + 5\,k^{\wedge}$
The primitive translation vectors of reciprocal lattice are given by-

$$\overrightarrow{a^*} = 2\pi \frac{\vec{b}\times\vec{c}}{[\vec{a}\vec{b}\vec{c}]}\overrightarrow{b^*} = 2\pi \frac{\vec{c}\times\vec{a}}{[\vec{a}\vec{b}\vec{c}]}, \overrightarrow{c^*} = 2\pi \frac{\vec{a}\times\vec{b}}{[\vec{a}\vec{b}\vec{c}]}$$

$$[\vec{a}\vec{b}\vec{c}] = \begin{vmatrix} 5 & 5 & -5 \\ -5 & 5 & 5 \\ 5 & -5 & 5 \end{vmatrix}$$

$$= 5\begin{vmatrix} 5 & 5 \\ -5 & 5 \end{vmatrix} - 5\begin{vmatrix} -5 & 5 \\ 5 & 5 \end{vmatrix} - 5\begin{vmatrix} -5 & 5 \\ 5 & -5 \end{vmatrix}$$

= 500 units

$\vec{b} \times \vec{c} = (-5\,i^{\wedge} + 5\,j^{\wedge} + 5\,k^{\wedge}) \times (5\,i^{\wedge} - 5\,j^{\wedge} + 5\,k^{\wedge}) = 50(i^{\wedge} + j^{\wedge})$

$\vec{c} \times \vec{a} = (5\,i^{\wedge} - 5\,j^{\wedge} + 5\,k^{\wedge}) \times (5\,i^{\wedge} + 5j^{\wedge} - 5\,k^{\wedge}) = 50(-i^{\wedge} + j^{\wedge} + k^{\wedge})$

$\vec{a} \times \vec{b} = (5\,i^{\wedge} + 5j^{\wedge} - 5\,k^{\wedge}) \times (-5\,i^{\wedge} + 5\,j^{\wedge} + 5\,k^{\wedge}) = 50(i^{\wedge} + k^{\wedge})$

Therefore, $\overrightarrow{a^*} = \pi\,(i^{\wedge} + j^{\wedge})/5, \overrightarrow{b^*} = \pi\,(j^{\wedge} + k^{\wedge})/5, \overrightarrow{c^*} = \pi\,(k^{\wedge} + i^{\wedge})/5$

2. Given- d = 2.82 $A^0 = 2.82\times10^{-10}$ m, for longest wavelength, $\sin\theta = 1$ (maximum value)

Using Bragg's equation- $2\,d \sin\theta = n\,\lambda$

Or $\lambda = 2\,d \sin\theta / n$

(i) For first order, n = 1, therefore $\lambda = 2\times2.82\times10^{-10} \times 1 / 1 = 5.64\times 10^{-10}$ m = 5.64 A^0

(ii) For second order, $n = 2$, therefore $\lambda = 2\times 2.82\times10^{-10} \times ½ = 2.82\times 10^{-10}$ m = 2.82 A^0

Terminal Questions:

8. Given- $\lambda = 1.32\ A^0 = 1.32 \times 10^{-10}$ m, $\theta = 9^0\ 30'$

Using Bragg's equation- $2\ d \sin\theta = n\ \lambda$

Or $d = n\lambda / (2 \sin\theta)$, $n = 1, 2, 3$……….

Or $d = n \times (1.32 \times 10^{-10}) / (2 \sin 9^0\ 30') = 4\ n \times 10^{-10}$ m = $4\ n\ A^0$, $n = 1, 2, 3$, ………

Thus possible spacing $d = 4\ A^0, 8\ A^0, 12\ A^0$, ………………..

10. (i) True (ii) True (iii) True

UNIT 4 CRYSTAL BONDING

Structure

4.1 INTRODUCTION

In the previous unit, you have studied about reciprocal lattice, X-ray diffraction, Laue method, Bragg's law and determination of crystal structure, powder method and Ewald's construction. You know that in solids, the different molecules are bound together by means of certain forces. Similarly, in a molecule, the atoms are bound to each other by means of some forces. Generally, the atoms and molecules are bound to each other by electrical forces. These forces are responsible for the cohesion of solids. Most of the physical properties of the solids can be explained on the basis of electron distribution in them. Depending upon the way in which the electrons are distributed in atoms, different types of bonds are formed between the atoms in a solid.In this unit, you will discussthe different types of bonding in crystals and their properties. Besides these, you will also study about Madelung constant, cohesive energy of an ionic crystal and Lennard-Jones potential.

4.2 OBJECTIVES

After studying this unit, you should be able to-

- understand different types of bonding in crystal.
- understand cohesive energy of an ionic crystal.
- solve problems based on cohesive energy.

4.3 BONDING IN CRYSTALS

Crystals may be classified in terms of the dominant type of chemical binding force keeping the atoms together. All these bonds involve electrostatic forces, with the chief differences among them lying in the ways in which the outer electrons of the structural elements are distributed. The distinct types of bonds that provide the cohesive forces in crystals can be classified as follows-

(i) Ionic bond.
(ii) Covalent bond.
(iii) Metallic bond.
(iv) Vander Waals bond.
(v) Hydrogen bond.

4.4 IONIC BOND AND COHESIVE ENERGY OF AN IONIC CRYSTAL AND MADELUNG CONSTANT

Ionic bonds are formed when atoms that have low ionization energies and hence lose electrons readily, interact with other atoms that tend to acquire excess electrons. The former atoms give up electrons to the latter. Thus, the atoms become positive and negative ions respectively. These ions come together in an equilibrium configuration in which the attractive forces between positive and negative ions predominate over the repulsive forces between similar ions.

Sodium chloride (NaCl) is an example of ionic crystal. In Na, the total number of valence electrons is 1 while in the case of Cl, the total number of valence electrons is 7. Here, a single valence electron is transferred from sodium (Na) atom to the chloride (Cl) atom. The Na^+ and Cl^- ions so formed are arranged in a face-centered cubic structure.

The cohesive energy of an ionic crystal is the energy that would be liberated by the formation of the crystal from individual neutral atoms. The main contribution to the cohesive energy of an ionic crystal is the electrostatic potential energy $U_{coulomb}$ of the ions.

Let us consider an Na^+ ion in NaCl. Its nearest neighbours are six Cl^- ions, each one the distance r away. Therefore, the potential energy of Na^+ ion due to 6 Cl^- ions-

$$U_1 = -\frac{1}{4\pi\varepsilon_0}\frac{(6e)\times e}{r} = -\frac{6e^2}{4\pi\varepsilon_0 r} \qquad \text{.....(1)}$$

The next nearest neighbours are 12 Na^+ *ions, each one distance* $\sqrt{2}\,r$ *away.*

The potential energy of the Na^+ *ion due to 12* Na^+ *ions-*

$$U_2 = +\frac{12e^2}{4\pi\varepsilon_0\sqrt{2}r} \qquad \text{.....(2)}$$

Then, there are 8 Cl^- *ions at* $\sqrt{3}r$ *distance, 6* Na^+ *ions at 2r distance and so on. When the summation is continued over all the +ve and –ve ions in a crystal of infinite size, the result is-*

$$U_{coulomb} = -\frac{6e^2}{4\pi\varepsilon_0 r} + \frac{12e^2}{4\pi\varepsilon_0\sqrt{2}r} - \frac{8e^2}{4\pi\varepsilon_0\sqrt{3}r} + \frac{6e^2}{4\pi\varepsilon_0(2r)} - \dots\dots\dots\dots\dots$$

$$= -\frac{e^2}{4\pi\varepsilon_0 r}\left[\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots\dots\dots\dots..\right]$$

$$= -1.748\,\frac{e^2}{4\pi\varepsilon_0 r}$$

In general, $U_{coulomb} = -\alpha\frac{e^2}{4\pi\varepsilon_0 r} \qquad \text{.....(3)}$

This result holds for the potential energy of a Cl^- *ion also.* α *is called Madelung constant of the crystal. It has the same value for all crystals of the same structure. For simple crystal structure-*

$$1.6 \leq \alpha \leq 1.8$$

Madelung constant is a property of crystal structure. It is very difficult to calculate its exact value although it can be approximated easily for simple *structure. Generally, the higher values of the Madelung constant indicate the stronger Madelungcontribution to the cohesive energy and hence greater stability of the structure.*

Two ions cannot continuously approach each other under coulomb attraction on account of Pauli's exclusion principle. When they are at a certain small distance apart, they start to repel each other with aforce which increases rapidly with decreasing inter-nuclear distance r. The potential energy contribution of the short range repulsive forces can be expressed approximately in the form-

$$U_{repulsive} = \frac{B}{r^n} \qquad \text{.....(4)}$$

Where B is a constant and n is a number (n≈ 9). Therefore, the total potential energy U of each ion due to its interactions with all the other ions is-

$$U = U_{coulomb} + U_{repulsive}$$

$$= -\alpha\frac{e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \qquad \text{.....(5)}$$

At equilibrium $r = r_0$, *U is minimum.*

Therefore, at $r= r_0$, $\frac{dU}{dr} = 0$

or $$\alpha\frac{e^2}{4\pi\varepsilon_0 r_0^2} + \frac{nB}{r_0^{n+1}} = 0$$

or $$B = \alpha\frac{e^2}{4\pi\varepsilon_0 n} r_0^{n-1} \qquad \text{.....(6)}$$

The total potential energy at the equilibrium separation is-

$$U=-\frac{e^2}{4\pi\varepsilon_0 r_0} + \alpha\frac{e^2}{4\pi\varepsilon_0 n r_0^n} r_0^{n-1} = -\alpha\frac{e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right) \qquad \text{.....(7)}$$

This is the magnitude of the energy needed to separate an ionic crystal into individual ions.

For NaCl crystal, $r_0 = 2.81 \times 10^{-10}$ *m,* $\alpha = 1.748$, $n = 9$

and $\frac{1}{4\pi\varepsilon_0} = 9 \times 10^9\ Nm^2C^{-2}$

The potential energy of an ion of either sign is-

$$U = -\alpha\frac{e^2}{4\pi\varepsilon_0 r}\left(1-\frac{1}{n}\right) = \frac{-(9\times10^9)\times(1.748)\times(1.60\times10^{-19})^2}{2.81\times10^{-10}}\left(1-\frac{1}{9}\right)$$

$$= -1.27\times 10^{-18} \text{ Joule} = -7.96 \text{ eV}$$

The contribution per ion to the cohesive energy of the crystal = $-\frac{7.96}{2}$ = - 3.98 eV

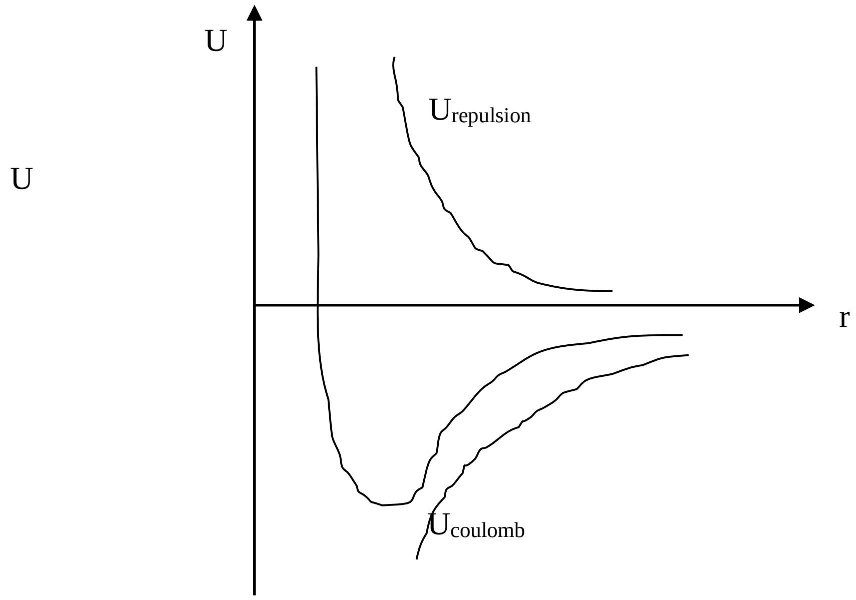

Figure 4.1: Variation of potential energy with distance

The energy needed to transfer an electron from a Na atom to a Cl atom to form a Na^+- Cl^- ion pair = Ionization energy of Na- electron affinity of Cl

= (+ 5.14 eV) – (3.61 eV) = 1.53 eV

Contribution of each atom to the cohesive energy = $+\frac{1.53}{2}$ = + 0.77 eV

Therefore, total cohesive energy per atom in NaCl crystal is-

$E_{cohesive}$ = (- 3.98 + 0.77) eV/atom = - 3.21 eV/atom

Properties of Ionic Bond

The following are the properties of ionic bond-

(i) Most ionic solids are hard, brittle and have high melting point.
(ii) These are soluble in polar liquids like water.
(iii) Their electrical conductivity is much smaller than that of metals at room temperature but with increase in temperature, the conductivity of these crystals increases.
(iv) These solids crystallize in close-packed structures of which the NaCl and CsCl structures are the commonest.

4.5 COVALENT BOND

In covalent bond, atoms are held together by the sharing of electrons. Each atom participating in a covalent bond contributes an electron to the bond. These electrons are shared by both atoms rather than being the virtually exclusive property of one of them as in an ionic bond. Diamond is an example of a crystal whose atoms are linked by covalent bonds. Other examples of covalent bonds are H_2, HCl etc. This bond is also known as homopolar.

$$H^* + {}^*H \Longrightarrow H \overset{*}{\underset{*}{\,}} H \Longrightarrow H - H \Longrightarrow H_2$$

Properties of Covalent Bond

The following are the properties of covalent bond-

(i) Covalent bond is a strong bond.
(ii) All covalent crystals are hard, have high melting points and are insoluble in all ordinary liquids.
(iii) These bonds are strongly directional.
(iv) These bonds have saturation property.
(v) The conductivity of covalent crystals varies over a wide range. Some crystals are insulators (diamond) and some are semiconductors (Ge). The conductivity increases with the increase in temperature.
(vi) These crystals are transparent to long wavelength radiation but opaque to shorter wavelengths.

4.6 METALLIC BOND

In metallic crystals, the metallic bond arises when all of the atoms share all of the valence electrons. The valence electrons of the atoms comprising a metal are common to the entire aggregate so that a kind of gas of free electrons saturates it. The crystal is held together by the electrostatic attraction between the negative electron gas and the positive metal ions. The best example of a metallic crystal is sodium. The cohesion of the metallic crystal results from a combination of forces-

(i) The attraction of the electron cloud for the ion cores.
(ii) The mutual repulsion of the electrons.
(iii) The mutual repulsion of the ion cores.

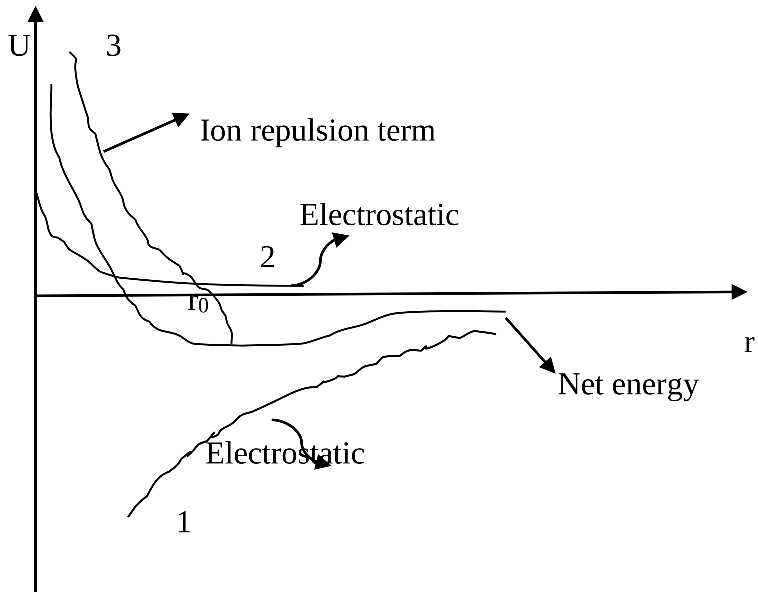

Figure 4.2: Potential energy contribution as a function of nuclear spacing

Figure 2 shows a sketch of a reasonable form for the potential (free) energy contribution, as a function of nuclear spacing, from each of these charge interactions.

Properties of Metallic Bond

The following are the properties of metallic bond-

(i) These have high electrical and thermal conductivities due to the presence of free electrons.
(ii) Metallic crystals have high optical reflection and absorption coefficients.
(iii) Metallic bonds are weaker than ionic and covalent bonds.
(iv) Ductility and metallic luster are the other characteristic properties of metals.

4.7 VANDER WAALS BOND (LONDON INTERACTION)

Vander Walls bond is also known as molecular bond. All atoms and molecules, even inert gas atoms such as those of helium and argon, exhibit weak, short range attractions for one another due to Vander Waals forces. These forces were proposed over a century ago by the Dutch physicist Johannes Vander Waals to explain the departures of real gases from the ideal gas law.

Vander Waals forces are responsible for the condensation of gases into liquids and the freezing of liquids into solids in the absence of ionic, covalent or metallic bonding mechanisms. Such familiar aspects of the behavior of matter in bulk as friction, surface tension, viscosity, adhesion, cohesion and so on, also arise from these forces. The Vander Waals attraction between two molecules the distance r apart is proportional to r^{-7} so that it is significant only for molecules very close together. Vander Waals interaction is also known as London interaction or induced dipole-dipole interaction. It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules. The Vander Waals interaction does not depend for its existence on any overlap of the change densities of the two atoms. The Vander Waals energy varies as - $\frac{A}{r^6}$, A is a constant.

Properties of Vander Waals Bond

The following are the properties of Vander Waals bond-

(i) The cohesive or binding energy of a molecular crystal is small.
(ii) They have poor conductivity.
(iii) They have low melting and boiling points.
(iv) They are transparent to electromagnetic radiations.
(v) The energy gap of a molecular crystal is large.

4.8 LENNARD-JONES POTENTIAL

The Pauli Exclusion Principle prevents multiple occupancy and electron distributions of atoms with closed shells can be overlap only if accompanied by the partial promotion of electrons to unoccupied high energy states of the atoms. Thus, the electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction.

The repulsive potential is of the form $\frac{B}{r^{12}}$, where B is a positive constant. Experimental data on the inert gases can be fitted well by an empirical repulsive potential of the form $\frac{B}{r^{12}}$, where B is a positive constant, when used together with a long range attractive potential of the form of -$\frac{A}{r^6}$. The constants A and B are empirical parameters determined from independent measurements made in the gas phase; the data used include the virial coefficients and the viscosity. It is usual to write the total potential energy of two atoms at separation r as-

$$U(r) = 4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \text{.....(8)}$$

Where ε and σ are the new parameters with $4\varepsilon\sigma^2 \equiv A$ and $4\varepsilon\sigma^{12} \equiv B$. The potential given by equation (8) is known as Lennard-Jones potential. The force between two atoms is given by-

$$F = -\frac{dU}{dr}$$

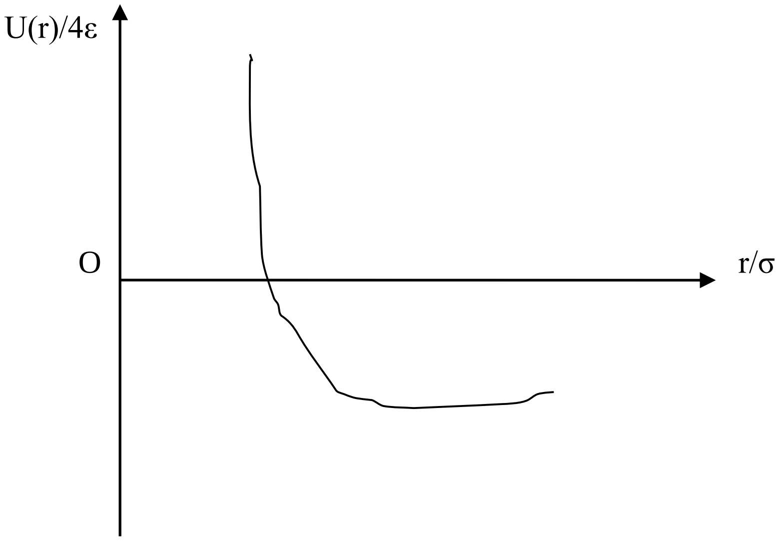

Figure 4.3: Lennard-Jones potential

4.9 HYDROGEN BOND

A hydrogen bond is a special type of Vander Waals bond which occurs between certain molecules containing hydrogen atoms. A hydrogen atom is electropositive as well as electronegative in character and as such, it can lose one electron or gain one electron to form inert gas configuration. Hydrogen bond is believed to be largely ionic in character, being formed only between the most electronegative atoms, oxygen, nitrogen in particular. In the extreme ionic form of hydrogen bond, the hydrogen atom loses its electron to one of the other atoms with the result that the probability of finding this electron on either atom or the hydrogen ion are equal. The positive hydrogen ion then attracts the two atoms more closely than their normal separation in the crystal. A hydrogen bond connects only two atoms because the two atoms adjacent to the hydrogen ion (proton) are so close that more than two atoms would get in each other's way.

Water molecules are exceptionally prone to be formed by hydrogen bonds because the electrons around the oxygen atom in H_2O are not symmetrically distributed but are more likely to be formed in certain regions of high probability density. These regions of high probability density are at the vertices of a tetrahedron as shown (Figure 4).

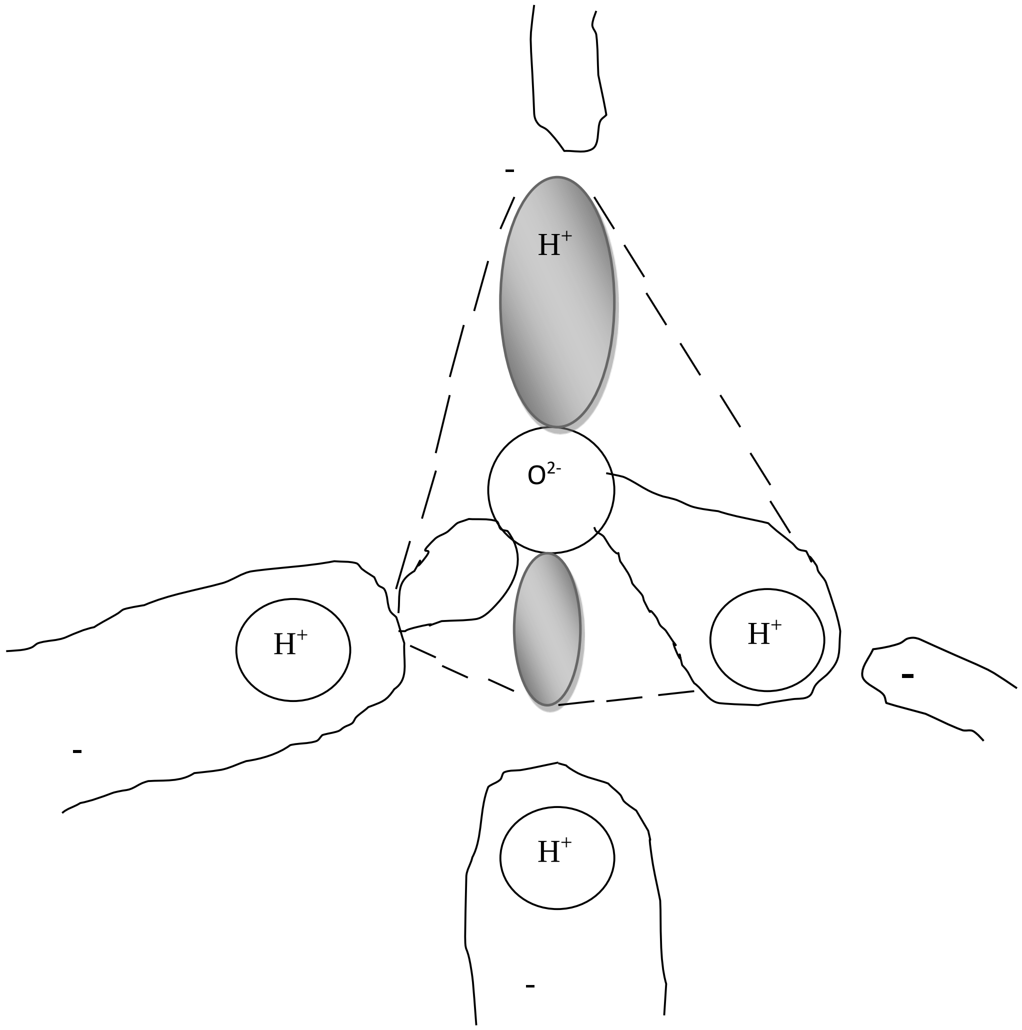

Figure 4.4: Hydrogen bond in water molecule

Obviously, hydrogen atoms are at two of its vertices which accordingly exhibit localized positive charges while the other two vertices exhibit somewhat more diffuse negative charges. Each water molecule (H_2O) can, therefore, form hydrogen bonds with four other H_2O molecules. In two of these bonds, the central molecule provides the bridging protons while in the other two the attached molecules provide them.

Properties of Hydrogen Bond

The following are the properties of hydrogen bond-

(i) The hydrogen bond is much weaker than a covalent bond.
(ii) This bond occurs in substances like protein, molecular genetics, hydrogen fluoride (HF), ice, water etc.

Example 1: How Vander Waals force varies?

Solution: That Vander Waals force varies as r^{-7}.

Self Assessment Question (SAQ) 1: Choose the correct option-

Ionic bond is formed due to-

(i) sharing of electrons (ii) transference of electrons (iii) both (i) and (ii) (iv) none of these

Self Assessment Question (SAQ) 2: Choose the correct option-

NaCl is an example of-

(i) covalent crystal (ii) ionic crystal (iii) metallic crystal (iv) hydrogen bonded crystal

Self Assessment Question (SAQ) 3: Fill in the blank-

For simple crystal structure ……..$\leq \alpha \leq$ ………..

4.10 SUMMARY

In the present unit, you have learnt about crystal bonding and known how different types of crystals are formed due to different types of bonding. According to their bonding, crystals have been divided into different groups- ionic crystals, covalent crystal or homopolar crystals, metallic crystals, Vander Waals or molecular crystals and hydrogen bonded crystals. In this unit, you have studied about cohesive energy which is defined as the energy of an ionic crystal that would be liberated by the formation of the crystal from individual neutral atoms. The main contribution to the cohesive energy of an ionic crystal is the electrostatic potential energy $U_{coulomb}$ of the ions. You have also learnt the importance of *Madelung constant which is a property of crystal structure.You have studied about* Lennard-Jones potential.*You have also discussed various types of bonding and their properties.* To check your progress, self assessment questions (SAQs) are given in the unit.

4.11 GLOSSARY

Ionization- the process of forming ions.

Cohesive energy- the energy due to the force of attraction between two similar molecules i.e. of the same substance.

Electron affinity- the energy released when an electron is attached to an atom or molecule.

Condensation- a change fromvapour to liquid the reverse of evaporation.

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4.14 TERMINAL QUESTIONS

1. Write an essay on bonding in crystals.

2. What is bonding in crystals? Describe different types of bonding that exhibit in crystals.

3. What is meant by cohesive energy? Establish the expression for cohesive energy of an ionic system.

4. Describe Lennard-Jones potential.

5. What are metallic bonds? Give their properties.

6. How are covalent bonds formed? List the properties of covalent bonds.

7. What are ionic crystals? Give some examples. What are the characteristics of ionic crystals.

8. What is Madelung constant? Give its significance.

9. Choose the correct option-

   The unit of Madelung constant is-

   (i) m (ii) cm (iii) N/m (iv) unitless

10. Fill in the blank-

    Diamond is ……….

4.15 ANSWERS

Self Assessment Questions (SAQs):

1. (ii) transference of electrons

2. (ii) ionic crystal

3. 1.6, 1.8

UNIT 5 FREE ELECTRON THEORY OF SOLIDS

Structure

5.1 INTRODUCTION

In lattice vibrations theory, we ignored the effects occurring due to electrons in crystals. We supposed that the electrons surrounding the nucleus of an atom are tightly bound. This assumption is valid for insulators, but not for metal and semiconductors. To understand the properties of metal and semiconductors, it is essential to understand the behavior of electrons. In this unit we shall focus mainly on the nature of the existence of the role of electrons to discuss the properties of metals. The free electron theory was successful in explaining the properties such as electrical conductivity, thermal conductivity etc. Although, it was unable to explain even the observed facts that why some solids are conductors and some insulators. We know several types of energies associated with the atom, like heat energy, electrical energy, light energy and so on and so forth. But we know that the atoms and molecules can be described by quantum mechanics. The quantum mechanics is very tricky and complex field. In the quantum mechanics the scientists trust on the Fermi energy to define the energy of the electrons or protons. In 1927, Pauli applied quantum statistics to explain the weak Para magnetism of alkali metals, that was the first success of the theory. The very subsequent year Sommerfeld published an improved free electron theory by switching classical statistics of Maxwell Boltzmann by Fermi Dirac statistics. The Sommerfeld free electron theory of metal could be better explained as the statistical behavior of the gas obeying Fermi Dirac statistics. In this unit, we shall study concept of free electron theory, Lorenz Drude theory, electrical conductivity, thermal conductivity, Fermi energy, Density of states, heat capacity of free electrons.

5.2 OBJECTIVE

After studying this unit, you should be able to-

- Define free electron theory.
- Apply free electron theory to calculate electrical conductivity, thermal conductivity.
- Ohm’s law from free electron theory.
- Fermi energy and density of states.
- Solve problems using Fermi energy and density of states.
- Concept of electronic heat capacity.

5.3 FREE ELECTRON THEORY

The Drude theory model of electrical conduction was proposed in 1900 by Paul Drude to explain the transport properties of electrons in materials especially metals. The model, which is an application of kinetic theory, assumes that the microscopic behaviour of electrons in a solid may be treated classically and looks much like a pinball machine, with a sea of constantly jittering electrons bouncing and re-bouncing off heavier, relatively immobile positive ions. The metals consist of positive ion cores with valence electrons moving freely among these cores. The electrons are however bound to move within the metal due to electrostatic attraction between the positive ion cores and the electrons. The potential field of these ion cores, which is responsible for such an interaction, is assumed to be constant throughout the metal and mutual repulsion among the electrons is neglected. The behaviour of free electron moving inside the metals considered to be similar to that of atoms or molecules in the perfect gas. These free electrons are therefore referred to as free electron gas and the theory is named as free electron gas model. These free electrons are known as the conduction electrons. The total energy of conduction electron is equal to its kinetic energy. Also, since the movement of conduction electrons is restricted to within the crystal only, the potential energy of a stationary electron inside metals is less than the potential energy of identical electrons just outside it. This energy difference serves as the potential barrier and stops the inner electrons from leaving the surface of the metal. Thus, in free electron Gas model, the movement of free electrons in a metal is equivalent to the movement of free electron gas inside a potential energy box.

5.4 LORENTZ DRUDE THEORY

The Drude model is a purely classical model and treats both electrons and ions as solid spheres. On the basis of Drude considerations that the electron gas behaves as perfect gas, Lorentz postulated in 1909 that the electrons constituting the electron gas obey Maxwell Boltzmann statistics under the equilibrium conditions. These shared ideas of Drude and Lorentz establish the Drude Lorentz theory. The basic assumptions of Lorentz Drude theory are

(i) in metals, there is large number of free electrons. These electrons are free to move about the volume of the metal as the molecules of a perfect gas in a container,

(ii) Free electron motion in a metal is similar to the thermal agitation of a perfect gas. The assembly of free electrons in a metal is called the electron gas. The electrical and thermal conductivity of metals is due to these free electrons.

(iii) In metals, the free electrons move randomly in all possible directions with different velocity like the molecules of a perfect gas. The average kinetic energy of an electron is 3kT/2, where k is Boltzmann’s constant and T absolute temperature.

(iv) In the lattice, the free electrons make collisions from time to time with fixed positive ions.

(v) In the absence of external electrical field, the random motion of free electrons is equally probable along all directions. In presence of external electric field, the electrons drift slowly with some average velocity, known as average drift velocity, in the direction opposite to that of electric field.

(vi) The free electrons are accelerated and gain some additional kinetic energy in the presence of external electric field. The accelerated free electron on collision with positive ion fixed in the lattice loses its additional kinetic energy. Such a collision is called inelastic collision.

(vii) Between two successive collisionswith the positive ions, the average distance traversed by the free electron is known as mean free path denoted by λ.

5.5 ELECTRICAL CONDUCTIVITY

Let the time taken between two successive collisions be τ and velocity along one direction u, then

$\tau = \frac{\lambda}{u}$, where λ is the mean free path

If the applied field on the electron of charge –e be E, then the equation of motion of electron is

$$m\frac{d^2x}{dt^2} = -eE$$

or, $\frac{d^2x}{dt^2} = -eE/m$

Integrating it, we get

$$\frac{dx}{dt} = -\frac{eE}{m}t + C$$

At t=0, dx/dt=0

Therefore C=0

Hence, $\dot{x} = \frac{dx}{dt} = -\frac{eE}{m}t$

Average velocity between two collisions is defined as

$$\bar{x} = -\frac{1}{\tau}\int_0^\tau \frac{eE}{m}tdt$$

On solving we get

$$\bar{x} = \frac{eE}{m}\frac{\tau}{2}$$

If *J* is the current density and n the number of electrons per unit volume, then we have

$J = -ne\dot{x}$, putting the values, we get,

$$J = \frac{1}{2}\frac{ne^2E}{m}\frac{\tau}{u} \qquad (1)$$

Since we know $\frac{1}{2}mu^2 = 3kT$ (2)

Therefore from eq.(1) and eq. (2), we get

$$J = \frac{ne^2 E\lambda u}{6kT} \tag{3}$$

or $J = \sigma E$

where $\sigma = \frac{ne^2 \lambda u}{6kT}$ (4)

which is defined as electrical conductivity.

5.6 THERMAL CONDUCTIVITY

Thermal conductivity is a process in which heat is transferred from one part of the body to another as a result of temperature gradient. In order to calculate the thermal conductivity, les us draw three parallel planes at E X and F, as shown in figure 5.1, normal to the direction of heat flow which are separated by mean free path λ, if two temperatures are equal, $T_1=T_2$, then there is no exchange of energy.

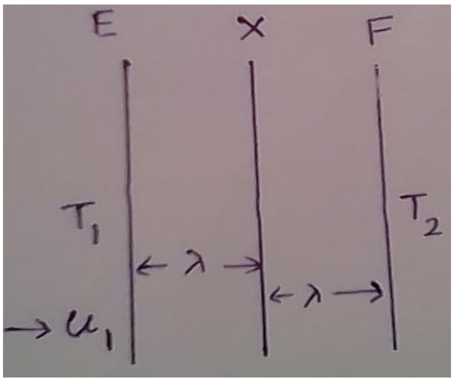

Figure 5.1: Heat conduction from one part of body to another

If $T_1$is greater than T_2, there is an exchange of energy from E to F, therefore the number of electrons per unit area per unit time is $\frac{nu}{6}$ and each electron has energy $\frac{mu_1^{\,2}}{2}$.

Thus, Energy transferred from E to F

$$= \frac{nu}{6}\frac{mu_1^2}{2}$$

$$= \frac{nu}{6}\frac{3k_BT_1}{2}$$

$$= \frac{1}{4}nuk_BT_1$$

Likewise, the energy transferred from F to E

$$= \frac{1}{4}nuk_BT_1$$

Therefore, the net energy transferred from E to F per unit area per unit time

$$= \frac{1}{4} nuk_B (T_1 - T_2)$$

Therefore, the transfer of energy per unit area per unit time, when K is the thermal conductivity

$$= \frac{K(T_1 - T_2)}{2\lambda}$$

On solving

$$K \frac{(T_1 - T_2)}{2\lambda} = \frac{1}{4} nuk(T_1 - T_2)$$

$$K = \frac{1}{2} \lambda nuk_B \qquad (5)$$

where k_B is Boltzmann constant.

Dividing (5) by (4), we get $\frac{K}{\sigma} = \frac{1}{2} \lambda nuk_B / \frac{ne^2 \lambda u}{6kT}$

$$\text{or} \frac{K}{\sigma} = 3(k_B / e)^2 T \qquad (6)$$

or $\frac{K}{\sigma} \propto T$, or $\frac{K}{\sigma} = LT$ .This is known asWiedemann-Franz relationwhere the constant of proportionality L is called the Lorenz number. Formetals, the thermal conductivity is quite high, and those metals which are the best electrical conductors are also the best thermal conductors. At a given temperature, the thermal and electrical conductivities of metals are proportional, but raising the temperature increases the thermal conductivity while decreasing the electrical conductivity. This behaviour is viewed in the Wiedemann-Franz Law.

Qualitatively, this relationship is based upon the fact that the heat and electrical transport both involve the free electrons in the metal. The thermal conductivity increases with the average particle velocity since that increases the forward transport of energy. However, the electrical conductivity decreases with particle velocity increases because the collisions divert the electrons from forward transport of charge. This means that the ratio of thermal to electrical conductivity depends upon the average velocity squared, which is proportional to the kinetic temperature.

Self-Assessment Question (SAQ) 1: A uniform copper wire of length 0.5 m and diameter 0.3 mm has a resistance of 0.12 Ohm at 293 k. If the thermal conductivity of the specimen at the same temperature is 390 $Wm^{-1}K^{-1}$, calculate the Lorentz number. Compare the value with the theoretical value.

5.7 OHM'S LAW FROM FREE ELECTRON THEORY

We know from Lorentz-Drude theory, $J = \sigma E = \frac{ne^2\lambda}{mv_F}$, if I is the current flowing through a conductor of *l* length and area of cross section A and potential difference V, then

$J = I/A$ and $E = V/l$

or, $I/A = \frac{ne^2\lambda V}{mv_F l}$

or. $I = \frac{ne^2\lambda AV}{mv_F l}$ for a given conductor, if the physical conditions do not change *l*, A, λ , v_F are constant.

Hence, $I \propto V$, that is at given physical conditions the current flowing through a conductor is proportional to the potential difference across it. That is Ohm's law.

5.8 ELECTRICAL CONDUCTIVITY OF METALS

The mechanism of electrical conductivity of metal can be understood by the free electron theory. The crystal lattice of a metal consists of positive ions at the lattice points and the valence electrons free to move inside the crystal. When there is no electric field applied, the free electrons move in the random direction inside the crystal. It is because of that the electrons collide frequently with the imperfection in the crystal lattice, which occurs with the thermal vibrations of the ions about their equilibrium positions in the lattice and also from the presence of impurity ions. Following each collision, the electron is scattered in the new directions with new speeds, which makes their random motion. Let τ be the average time between successive collisions of an electron, which gives $\tau = \frac{\lambda}{v_F}$. Where λ is the average distance between collisions and v_F is the speed of those electrons whose kinetic energy is equal to the Fermi energy. It should be noted that electrons which are near the Fermi level contribute to the conductivity. In the presence of applied the electric field to the metal, the electrons modify their random motion in such a way that on an average they drift slowly in the direction opposite to that of the field (since electrons have negative charge) with a small speed, which is known as drift velocity, v_d. When electric field is applied to an electron in the metal exerts on it a force eE, which gives acceleration to electron, that is

$a = \frac{eE}{m}$, where e and m are the charge and mass of electron respectively. Consider an electron that has just collided with the lattice imperfection. The drift speed of electron has become momentarily zero and it would now move in a purely random direction, gaining a drift speed $a\tau$ just before its succeeding collision. Therefore, the average drift speed during the interval of τ is given as

$$v_d = \frac{a\tau}{2}$$

or, $v_d = \dfrac{eE\tau}{2m}$

placing the value of τ , we get

$$v_d = \frac{eE\lambda}{2mv_F}$$

If n is the number of electrons per unit volume in the conduction band of the metal, then the current density j is given as

$$j = nev_d$$

or, $j = \dfrac{ne^2E\lambda}{2mv_F}$

We know the resistivity ρ of the metal, which is defined as

$$\rho = \frac{E}{j}$$

Hence, we obtain

$$\rho = \frac{2mv_F}{ne^2\lambda}$$

This form is a sort of Ohm's law, since the quantities v_F and λ which determine ρ do not depend on the applied field. Therefore, at given temperature the resistivity ρ is a constant for a given metal.

Since conductivity of metal is defined as

$$\sigma = 1/\rho$$

or, $\sigma = \dfrac{ne^2\lambda}{2mv_F}$ (7)

Mobility is defined as

$$\mu = v_d / E$$

or, $\mu = \dfrac{e\lambda}{2mv_F}$

Putting this expression in equation (7), we get

$$\sigma = ne\mu$$

This is the general expression for conductivity. If the conductivity is due to holes and electrons, then the expression becomes

$$\sigma = n_e e\mu_e + n_h e\mu_h$$

Where, μ_h and μ_e are the mobility due to holes and electrons respectively.

5.8.1 Effect of Temperature on Conductivity of Metals

On increasing temperature of the metals, its conductivity decreases and the resistivity increases. In the metallic lattice, metals have electrical resistivity due to the scattering of free electrons by the imperfections. There are two types of imperfections.

1. Occurring due to the thermal vibrations of the positive ions about their equilibrium positions in the lattice.
2. Occurring due to structural defects as presence of impurity ions. Hence the resistivity of a metal can be given as

   $$\rho = \rho_t + \rho_i$$

Here ρ_t the resistivity due to thermal imperfections and ρ_i is caused by impurity or structural imperfections. As the temperature increases, the amplitude of ion vibrations increases, because of that the scattering cross section of the ions increases. Hence, the resistivity ρ_t increases. The vibration of ρ_t with temperature is of the form $\rho_t \propto T^5$ at low temperature and $\rho_t \propto T$ at high temperatures. We can explain metallic resistivity by this expression

$$\rho \propto \frac{v_F}{\lambda}$$

On rising temperature, the electron speed v_F increases and the mean free path λ decreases, therefore, the resistivity ρ increases.

On the other hand, the resistivity ρ_i is independent upon the temperature. The variation of resistivity is shown in figure.

5.9 FERMI ENERGY

The Fermi energy is a concept in quantum mechanics usually referring to the energy difference between the highest and lowest occupied single-particle states in a quantum system of non-interacting fermions at absolute zero temperature. In a Fermi gas, the lowest occupied state is taken to have zero kinetic energy, whereas in a metal, the lowest occupied state is typically taken to mean the bottom of the conduction band.

5.9.1 Fermi Dirac Distribution of Energy in an Electron Gas in Metal

In a metallic solid, the valence electrons are loosely bound to the individual atoms; we can treat these electrons as an ideal electron gas. Since electrons are Fermi particles, they obey Pauli's exclusion principle and Fermi Dirac distribution law.

According to this law, the number of electrons n_i with energy ε_i is given by

$n_i = \frac{g_i}{e^{\varepsilon - \varepsilon_F / k_B T} + 1}$, where g_i is the number of quantum states having the energy ε_i

In a solid, there are 10^{22} to 10^{23} atoms/ cm^3 and the same number of valence electrons. As such there are an enormous number of quantum states which the electron can occupy.

So, the number of electrons in energy ranges ε to $\varepsilon + d\varepsilon$

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{e^{\varepsilon - \varepsilon_F / k_B T} + 1}$$

where $g(\varepsilon)d\varepsilon$ is the number of quantum states available to these electrons.

It can be shown that the number of allowed energy values between ε to $\varepsilon + d\varepsilon$ is

$g(\varepsilon)d\varepsilon = \frac{4\sqrt{2}}{h^3}\pi V m^{3/2}\varepsilon^{1/2}d\varepsilon$, where m is the mass of electron and V is the volume of the electron gas. Since there are two possible spin states $(+\frac{1}{2}, -\frac{1}{2})$ for an electron, each energy value can have by two electrons.

Therefore,the number of energy states available to the electrons having energy between ε to $\varepsilon + d\varepsilon$ is given by

$$g(\varepsilon)d\varepsilon = \frac{8\sqrt{2}}{h^3}\pi V m^{3/2}\varepsilon^{1/2}d\varepsilon$$

Hence $n(\varepsilon)d\varepsilon = \frac{8\sqrt{2}}{h^3}\pi V m^{3/2}\varepsilon^{1/2}\frac{1}{e^{(\varepsilon - \varepsilon_F / k_B T)} + 1}d\varepsilon$

$n(\varepsilon)$, is known as Fermi Dirac distribution function.

At absolute zero, there are two cases

Case I: $\varepsilon \langle \varepsilon_F$, $n(\varepsilon)d\varepsilon = \frac{8\sqrt{2}}{h^3}\pi V m^{3/2}\varepsilon^{1/2}d\varepsilon$

Which represents a parabolic curve.

Case II: $\varepsilon \rangle \varepsilon_F$, $n(\varepsilon)d\varepsilon = 0$

This means that no electrons have energy greater than Fermi energy at absolute temperature. Fermi energy is the maximum energy that a free electron in the metal can have at absolute zero.

5.9.2 Calculation of Fermi Energy

Suppose a given metal contains N free electrons. We can calculate its Fermi energy by filling up its energy states. At T=0, starting from $\varepsilon = 0$, all quantum states upto $\varepsilon = \varepsilon_F$ are filled.

That is

$$N = \int_0^{\varepsilon_F} n(\varepsilon)d\varepsilon$$

or, $N = \frac{8\sqrt{2}}{h^3}\pi V m^{3/2}\int_0^{\varepsilon_F} \varepsilon^{1/2} d\varepsilon$

or we get, $\varepsilon_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}$

This is the expression for the Fermi energy of a metal at T=0, the N/V is the density of free electrons. Thus, the Fermi energy is independent of the size of metal. Fermi energy can be written in terms of Fermi temperature defined as $\varepsilon_F = kT_F$, where k is the Boltzmann'sconstant.

5.9.3 Density of States for Free Electron Gas in Three Dimensions

Consider the behavior of free electron gas in 3D metallic crystal. The potential of the electrons inside the crystal is constant and may be taken zero, whereas it has a large value outside the crystal. For simplicity, the 3D crystal may be regarded as a cubical box having length of the edge equal to L. the free particle Schrodinger equation in 3D is given as

$$\nabla^2\psi_k(r) + \frac{2m}{\hbar}E_k\psi_k(r) = 0 \tag{8}$$

The solution of it given by

$$\psi_k(x) = Ae^{i\vec{k}.\vec{r}} = Ae^{i(k_x x + k_y y + k_z z)} \tag{9}$$

Where, A is an arbitrary constant. Such wave function must satisfy the periodic boundary conditions. They must be periodic in x, y, z with period equal to L. these boundary conditions are

$$\psi_k(x+L, y, z) = \psi_k(x, y, z) \tag{10}$$

$$\psi_k(x, y+L, z) = \psi_k(x, y, z)$$

$$\psi_k(x, y, z+L) = \psi_k(x, y, z)$$

An application of the first boundary condition in (10) to the wave function (9) gives

$$e^{ik_x L} = 1$$

or, $k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, ...$

Similar results are obtained for k_y, k_z

The allowed Eigen values of the state or orbital with wave vector k are obtained

$$E_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(K_x^2 + k_y^2 + k_z^2)$$

Where the magnitude of the wave vector k is related to the wavelength λ as

$$k = \frac{2\pi}{\lambda}$$

Thus, it is easy to see the energy spectrum consists of discrete energy levels. These energy levels are very close to each other.

In a system of N free electrons, the occupied states or orbitals in the ground state may be represented by points inside a sphere in the k space. The energy corresponding to the surface of the sphere represents the Fermi energy as shown in figure 5.2. Let k_F be the wave vector from the origin of the k space to the surface of the sphere. Then the Fermi energy is written as

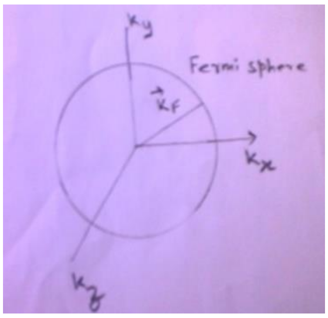

Figure 5.2: Density of states sphere

$$E_F = \frac{\hbar^2 k_F^2}{2m} \qquad (11)$$

Fermi sphere volume is given by

$$\frac{4}{3}\pi k_F^3$$

Volume occupied by one state in k space

$$(\frac{2\pi}{L})^3$$

The total number of electronic states or orbitals is (the number of states is equal to number of electrons)

$$N = (2)\frac{4}{3}\pi k_F^3 / (\frac{2\pi}{L})^3 \qquad (12)$$

Where a factor 2 appears because there are two allowed values for each orbital. So, we get

$$k_F = (\frac{3\pi^2 N}{V})^{1/3} \qquad (13)$$

Therefore, eq (12) and (13), we get the expression of Fermi energy

$$\varepsilon_F = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3}$$

The electron velocity v_F at the Fermi surface is obtained

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}(\frac{3\pi^2 N}{V})^{1/3}$$

(Particle velocity is given by $v_F = \hbar k_F / m$)

The density of state function is obtained by using the fact that at absolute zero, all the energy states below Fermi energy are occupied and the total number of states is equal to the number of electrons.

$$N = \int_0^{\varepsilon_F} D(\varepsilon) f(\varepsilon) d\varepsilon \tag{14}$$

So, from (14) and (12), on solving we get

$$D(\varepsilon) == \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{3/2}\varepsilon^{1/2} \tag{15}$$

5.9.4 Average Kinetic Energy

Av Kinetic Energy is defined as

$$\bar{\varepsilon} = \frac{1}{N}\int_0^{\varepsilon_F} \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon$$

Putting the values of $D(\varepsilon)$ and Fermi function and integrating we get

$$\bar{\varepsilon} = \frac{3}{5}\varepsilon_F$$

or we can write at absolute zero as

$$\bar{\varepsilon}_0 = \frac{3}{5}\varepsilon_{F_0} \tag{16}$$

5.10 HEAT CAPACITY OF FREE ELECTRON GAS

Electron heat capacity or electronic specific heat describes the contribution of electrons to the heat capacity. Heat is transported by phonons and by free electrons in solids. For pure metals, however, the electronic contributions dominate in the thermal conductivity. In impure metals, the electron mean free path is reduced by collisions with impurities, and the phonon contribution may be comparable with the electronic contribution. Theoretically the specific heat of metal shall get contribution from the atoms as well as free electrons

$$c = c_{atomic} + c_{electronic}$$

Since the T_F (Fermi Temperature) is of the order of 10^4K, as the temperature increase some of the electrons close to the Fermi energy level are moved to occupy higher energy states due to the thermal excitation (around 100K). As is seen by the figure 5.3, only those particles that are indicated in graph by dots contribute the specific heat. It is only a fraction of electrons with energy near Fermi energy which can be excited. For most electrons, the states to which they will be excited are already occupied and because of the Pauli exclusion principal, they cannot be excited into these states.

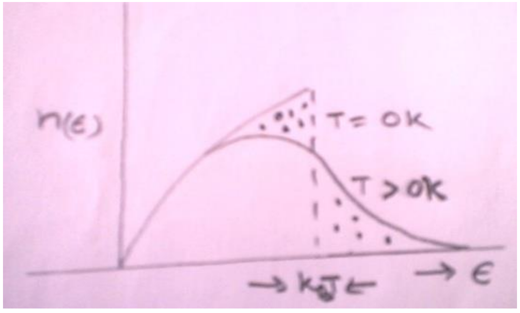

Figure 5.3: Contribution of electrons to the heat capacity

The electrons in the metal which contribute to conduction are very close to the Fermi level. But to contribute to bulk specific heat, all the valence electrons would have to receive energy from the thermal energy $k_B T$. But the Fermi energy ($k_B T_F$) is much greater than thermal energy, and the majority of the electrons cannot receive such energy since there are no available energy levels within of their energy.

The small fraction of electrons which are within $k_B T$ of the Fermi level does contribute a small specific heat, and this electron specific heat becomes significant at very low temperatures. Using Fermi-Dirac statistics (as opposed to Einstein-Bose for phonons), a small fraction of the electrons is available to participate in specific heat. This fraction contributes a specific heat.

Excited electrons will be only fraction given by

$$k_B T / k_B T_F$$

$k_B T_F$ Corresponds to all the states and $k_B T$ corresponds to the energy of thermal excitation. $k_B T / k_B T_F = T / T_F$, These are the fraction of electrons excited thermally. And each of them has the excitation of $k_B T$. Therefore, the excitation energy is of the order of

$$k_B T (T / T_F)$$

Or, $\varepsilon = k_B T^2 / T_F$

By definition of specific heat

$$c_e = \frac{d}{dT}(k_B T^2 / T_F)$$

$c_e = 2k_B T / T_F$, or we can write

$c_e = \gamma T$, where $\gamma = (2k_B / T_F)$ is constant.

We know by Debye theory the specific heat due to lattice vibration

$$c_{atomic} = \beta T^3$$

Thus, the total specific heat as shown in figure 5.4, is given by the sum of these two

$$c = c_{atomic} + c_{electronic} = \beta T^3 + \gamma T$$

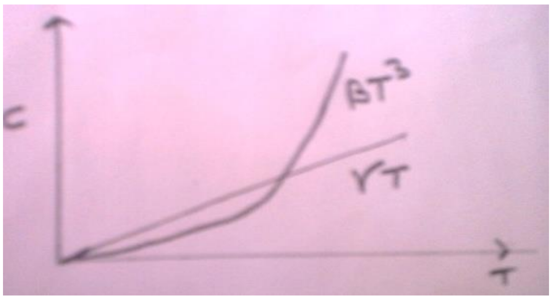

Figure 5.4: Specific heat with temperature

At very low temperature the atomic specific heat becomes small and the electronic specific heat becomes relatively high. For, example the atomic heat of silver becomes very small compared to its electronic specific heat from the temperature range 3K. In specific heat measurement Keesom and Cock found that in the range from 1.5 to 3K the specific heat varies according to $c_e = \gamma T$. This suggests that below the 3K for silver, free electrons become the chief contributor to the specific heat. Thus, the Fermi Dirac statistics has solved the problem of specific heat of metals.

Examples 1: Calculate the Fermi energy in electron volts for sodium assuming that it has one free electron per atom. (Atomic weight of sodium= 23, density of sodium= 0.97 g cm^{-3}

Solution: we have the expression of Fermi energy $\varepsilon_F = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3}$ or

$$\varepsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}$$

First calculate $N/V = \dfrac{N_A\rho}{W}$

We know $N_A = 6\times10^{26} atoms/kg.mole$

Given $\rho = 0.97 g.cm^{-3}$

or, $\rho = 0.97\times10^3 kg/m^3$

$N/V = \dfrac{N_A\rho}{W} = 2.53\times10^{28} electrons/m^3$

Planck's constant h= 6.62 x 10^{-34} joule sec, mass of the electron m= 9.1 x 10^{-31}kg

Putting all these values in $\varepsilon_F = \dfrac{\hbar^2}{2m}(\dfrac{3\pi^2 N}{V})^{2/3}$, we get

$\varepsilon_F = 5.032\times10^{-10} jules$

Or, $\varepsilon_F = 5.032\times10^{-10}/1.6\times10^{-19} = 3.14eV$

Example 2: There are 2.54 x 10^{22} free electrons per cm^3 in sodium. Calculate its Fermi energy, Femi velocity and Fermi temperature. (h= 6.67 x 10^{-34} Jsec, m=9.1 x 10^{-31} kg, k=1.38 x 10^{-23}J/K,

1eV=1 x 10^{-19}joule)

Solution: $\varepsilon_F = \dfrac{\hbar^2}{2m}(\dfrac{3\pi^2 N}{V})^{2/3}$

First calculate N/V= 2.54 x 10^{28} / m^3, putting in above equation, with the values of m and h, we get

$\varepsilon_F = 5.0\times10^{-19} J = 3.1eV$

At absolute zero, this is the maximum kinetic energy of the free electron

$\dfrac{1}{2}mv_F^2 = 5.0\times10^{-19} J$

Therefore, on solving $v_F = 1.05\times10^6 m/s$

Fermi temperate is defined as $T = \dfrac{\varepsilon_F}{k} = \dfrac{5.0\times10^{-19}}{1.38\times10^{-23}} = 3.6\times10^4 K$

Example 3: The Fermi energy in silver is 5.51 eV. What is the average energy of the electrons in silver at 0K? At what temperature a classical free particle will have this kinetic energy.

Solution: At 0K the average energy of an electron is $\bar{\varepsilon}_0 = \dfrac{3}{5}\varepsilon_{F_0}$

$$\bar{\varepsilon}_0 = \frac{3}{5}\times 5.51 = 3.31eV$$

The kinetic energy of a classical particle is

$$\frac{3}{2}kT$$

So, $\frac{3}{2}kT = 3.31eV = 3.31\times 1.6\times 10^{-19}J$

On solving for T we get

$$T = \frac{2}{3}\times\frac{3.31\times 1.6\times 10^{-19}}{1.38\times 10^{-23}} = 2.56\times 10^{4}K$$

Example 4: The Fermi energy of copper is 7eV. Calculate the average distance (mean free path) travelled by the conduction electrons between collisions. (conductivity of copper 6 x 10^7/ ohm m, concentration of valence electrons 8.5 x 10^{28}/ m^3)

Sol: The velocity of electrons is given by $v_F = \sqrt{\frac{2\varepsilon_F}{m}}$, putting the given values you may get $v_F = 1.6\times 10^6 m/s$, Conductivity is given as $\sigma = \frac{ne^2\lambda}{2mv_F}$ or $\lambda = \sigma 2mv_F / ne^2$, putting the given values you may get $\lambda = 8\times 10^{-8}m$

Example 5: What would be the mobility of electrons in copper if there are 9 x 10^{28} valence electrons per metre^3 and the conductivity of copper is 6 x 10^7 mho/meter

Solution: conductivity of metal is given as $\sigma = ne\mu$ or $\mu = \frac{\sigma}{ne}$, putting the given values you may get $\mu = 4.16\times 10^{-3} m^2/Vs$

Example6: Find the average drift velocity of electrons in copper conductor with a cross-sectional area of 10^{-6} m^2 carrying a current of 4 x 10^{-10}meter. The atomic weight of copper is 63.6 and the density is 8.9 gram/cm^3. Avogadro's number N_A= 6.02 x 10^{23}.

Solution: $\frac{N_A\rho}{M} = 8.42\times 10^{28} atoms/m^3$, you know the relation $j = nev_d$, therefore $v_d = \frac{j}{ne} = \frac{i}{neA} = 3.0\times 10^{-4}m/s$

Self-Assessment Question (SAQ) 2: Calculate the Fermi energy in electron volts for sodium assuming that it has one free electron per atom. Given density of sodium = 0.97 g cm^{-3}, atomic weight of sodium = 23.

Self-Assessment Question (SAQ) 3: Consider silver in metallic state with one free conduction electron per atom. Calculate its Fermi energy. The density of silver is 10.5 gram/cm^3 and its atomic weight is 108. The Avogadro's number is 6.02 x 10^{23} atoms/mole.

Self-Assessment Question (SAQ) 4: The Fermi energy for lithium is 4.72 eV at absolute zero. Calculate the number of conduction electrons per unit volume in lithium. (h= 6.67 x 10^{-34} J-sec, m=9.1 x 10^{-31} kg, k=1.38 x 10^{-23}J/K)

5.11 SUMMARY

In this unit, we have briefly reviewed classical kinetic theories of an electron gas both by Drude and by Lorentz as simple models of metals. The free electron model explains successfully some of the properties of solids, such as electrical and thermal conductivities etc. We have also reviewed electrical conductivity of metals in terms of electron collisions and mean free path. The Fermi energy is useful in determining the thermal and electrical characteristics of the solids. It is the very important concepts in the quantum mechanics and the superconductor physics. It is used to metal, insulators and semi-conductors. We learned that the Fermi Level is the highest energy level which an electron can occupy at the absolute zero temperature. Since at absolute zero temperature the electrons are all in the lowest energy state hence the Fermi level is in between the valence band and the conduction band. Free electrons are associated with a continuous energy spectrum and bound electrons with a discrete energy spectrum. Moreover, you have learned Fermi Dirac energy distribution among free electrons in metals. Now, we understand that at low temperature the electronic specific heat of solid is found to be predominant and varies linearly with T.

5.12 GLOSSARY

Assumption- supposition.

Randomly-arbitrarily.

Collision–accident.

Bouncing-Recoiling.

Trust-Belief.

Immobile-Steady.

Imperfection-deficiency.

Exclusion- rejection.

Mobility- flexibility.

Contribute-provide.

Residual-remaining.

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5.15 TERMINAL QUESTIONS

1. What is the relation of electrical conductivity and the thermal conductivity agreeing to free electron theory?

2. What is Fermi energy?

3. What is the value of Fermi energy at absolute Zero?

4. What is the value of mean energy in terms of Fermi energy at absolute zero?

5. How does Fermi energy depends upon temperature?

6. How does electrical conductivity of a metal depends upon on temperature?

7. Write the relation of Fermi energy ε_F with Fermi temperature T_F

8. Why do metals have high electrical conductivity?

9. Why does metallic resistivity increase with rise in temperature?

10. True or False statement?
    (i) Fermi energy of a metal depends upon the size of the metal.
    (ii) Fermi energy does not change when two identical metals are joined together.
    (iii) Only electrons near the Fermi level contribute to the conductivity.
    (iv) Conductivity of metals increase with rice in temperature.
    (v) Pure metals have some residual resistivity at absolute zero temperature.
    (vi) Electron, proton and neutron are fermions.

11. Fill in the Blanks
    (i) In Quantum Physics, two or more identical particles are ……...

(ii) Fermions have…...spin.

(iii) The highest energy level that can be occupied by an electron in a metal at 0K is called……level.

(iv) The maximum energy that a free electron in a metal can have at absolute zero is called….

(v) The Fermi energy of a metal at 0 K temperatures depends on …. per unit volume in the metal.

(vi) The ratio of Fermi energy to Fermi temperature equals to…

(vii) In metals, the average distance covered by free electrons between collisions is called…

12. The electrical and thermal conductivities of silver at 20°C are 6.22 x 10^7 / ohm / meter and 423 W/m/K, respectively. Calculate the Lorentz number on the basis of free electron theory.

13. Calculate the heat capacity of electron gas at room temperature in copper assuming one free electron per atom. Compare this with the lattice specific heat value of 2.4 x 10^4 J/ kmol/K. the Fermi energy of copper is 7eV.

14. A copper wire of cross sectional area 5 x 10^{-2} sq. cm. carries a study current of 50 ampere. Assume one electron per atom; calculate the density of free electrons, the average drift velocity and the relaxation time. Given: the resistivity of copper 1.7 x 10^{-8}/ ohm m.

15. Objective questions

(i) The formula relating the thermal conductivity and electrical conductivity is

(a) $K/\sigma T = const$ (b) $K/\sigma T^2 = const$ (c) $\sigma/KT = const$ (d) $\sigma/KT^2 = const$

(ii) Fermi level is.

(a) Lowest level filled with electrons
(b) Highest level containing electrons
(c) Sometimes
(d) Highest vacant level

(iii) The drift speed of an electron in presence of an electric field E across a metal, having relaxation time τ is

(a) $eE/2m$ (b) $e\tau E/2m$ (c) $eE/2m\tau$ (d) $2mE/e\tau$

(iv) The current density in a metal in terms of drift speed and electron concentration per unit volume n is

(a) ne/v_d (b) v_d/ne (c) nev_d (d) ev_d/n

(v) The resistivity of a metal

(a) Increases linearly with absolute temperature t at high temperatures
(b) Decreases linearly with temperature T at high temperatures
(c) is proportional to T^3 at high temperatures
(d) is proportional to $T^{1/3}$ at high temperatures.

5.16ANSWERS

Self-Assessment Question (SAQ) :

1. Given: *l*=0.5 m, d = 0.3 mm, r = 0.15 x 10^{-3} m, R = 0.12 W, Lorentz Number =?

   $$R = \rho\frac{1}{\pi r^2} = \frac{1}{\sigma\pi r^2}$$

   $$\sigma = 5.89\times10^7 / \Omega m$$

   $$L = \frac{K}{\sigma T} = \frac{390}{5.89\times10^7\times293}$$

   $$L = 2.26\times10^{-8} W\Omega K^{-2}$$

2. The Fermi energy is given by $\varepsilon_F = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3}$

   First, we calculate electron density. Assuming one electron per sodium atom N/V is given by

   $$\frac{N}{V} = \frac{N_A\rho}{W}$$

   $$\frac{N}{V} = \frac{6\times10^{26}\times0.97\times10^3}{23}$$

   $$= 2.53\times10^{28} electrons/m^3$$

   $$\varepsilon_F = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3} = 5.02\times10^{-19}\ jules$$

   $$\varepsilon_F = 3.145 eV$$

3. Use the formula $\varepsilon_F = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3}$

   Here $N/V = 58.4\times10^{27} atoms/m^3$

   Putting these values in eq $\varepsilon_F = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3}$

   We get $\varepsilon_F = 8.8\times10^{-19} J$

   or, $\varepsilon_F = 5.5 eV$

4. $\varepsilon_F = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3}$

   Here N is the number of conduction electrons in a volume V of lithium metal. The number of conduction electrons per unit volume is given as

   $$N/V = 4.64\times10^{28}/m^3$$

Terminal Questions

1., $\frac{K}{\sigma T} = Const$, σ electrical conductivity and, K thermal conductivity

2. Fermi energy is the highest energy level containing electrons.

3. $\varepsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}$

4. $\bar{\varepsilon}_0 = \frac{3}{5}\varepsilon_{F_0}$

5. Fermi energy increases with increasing temperature.

6. On increasing temperature, the thermal agitation of electrons increases so electrons collide more frequently, thus leading to decrease in relaxation time consequently electrical conductivity decreases with increase in temperature.

7. $\varepsilon_F = kT_F$, where k is the Boltzmann constant.

8. Metals contain free electrons in abundance which is charge carriers.

9. The metallic resistivity is expressed as $\rho = \frac{2mv_F}{ne^2\lambda}$

As temperature increases, v_F increases and λ decreases, so ρ increases.

10. (i) F, (ii) T, (iii) T, (iv) F, (v) T, (vi) T

11. (i) indistinguishable (ii) half integral (iii) Fermi (iv) Fermi energy (v) Number of electrons (vi) Boltzmann constant k (vii) mean free path

12. 2.32 x 10^{-8} W ohm K^{-2}.

13. 146 X 10^{2} J $kmol^{-1}$ K^{-1}, 0.608 %.

14. 8.4 x 10^{28} / m^3, 7.4 x 10^{-4} m/s, 2.46 x 10^{-4} s.

15. (i) a (ii) b (iii) b (iv) c (v) a

UNIT 6 BAND THEORY OF SOLIDS

Structure

6.1 INTRODUCTION

The electronic band structure of a solid describes the range of energies that an electron within the solid may have, named as energy bands, allowed bands, or simply bands and ranges of energy that it may not have named as band gaps or forbidden bands. Band theory derives these bands and band gaps by examining the allowed quantum mechanical wave functions for an electron in a large, periodic lattice of atoms or molecules. Band theory has been successfully used to explain many physical properties of solids. In this division, the one-electron energy band theories for the crystalline solids are proposed. The significance of energy band theories for a crystalline solid is due to the fact that many important physical and optical properties of a solid can be described using its energy band structure. In broad, the energy band structure of a solid can be raised by solving the one-electron Schrödinger equation for electrons in a crystalline solid that contains a large number of interacting electrons and atoms. To simplify the complex work of solving the Schrödinger equation for the many-body problems in a crystal, the results that arise from the motion of atomic nuclei must beignored;it is supposed that the nuclei are at rest in the equilibrium positions at each lattice site. In this unit, we shall study how the bands are formed and their classification on the basis of energy band gap. We shall use the concept of Bloch function to discuss the Kronig-Penney model for the behavior of an electron in periodic potential and describe how it leads to the origin of the energy bands and the forbidden bands in solids.

6.2 OBJECTIVES

After studying this unit, you should be able to-

- Define origin of energybands.
- Apply the theory to classify bands.
- Understand Bloch function.
- Motion of an electron in one dimensional periodic potential.
- Kronig Penney Model and its consequences.
- Apply the theory to solve problems.

6.3 WHY BANDS AND BAND GAPS OCCUR

To understand the physics of energy band, consider a solid enclosing a huge number of atoms packed closely together. Each atom when isolated has a discrete set of electron energy levels 1s, 2s, 2p, 3s, 3p……. If we consider all the N atoms of the solids to be isolated from one another, then they would have completely coinciding sets of energy levels. That is each of the energy levels of the N atoms system would have N fold degeneracy. They fill the energy levels in each atom independently. As the atom approach one another to form the solid, a continuous increasing interaction occurs between them which causes each of the levels to split into N distinct levels. In practice, N is very large, therefore the split energy levels become so numerous and so close together that they form an almost continuous energy band. The amount of splitting is different for different energy levels as shown in figure 6.1. In general the lower levels are splitted less than the higher levels, the lowest levels remaining almost unsplitted. The reason is that the electrons in the lower levels are the inner electrons of the atoms. which are not significantly influenced by the presence of nearby atoms. On the other hand, the electrons in the higher levels are the valence electrons whose wave functions overlap appreciably. The formation of energy levels for some of the higher energy levels of isolated sodium atoms are shown in figure. The 2p level does not split until the interatomic distance become smaller than actually found in the solid sodium, the level 1s and 2s do not split at all. The 3s level is the first occupied level to be splitted into a band. The energy bands in the solid correspond to energy levels in an atom. An electron in a solid can have only energies that fall within these energy bands. The various energy bands in solids may or may not be overlapping depending upon the structure of the solid. If they do not overlap then the intervals between them represents energies which the electrons in the solid cannot have. These intervals are called forbidden band gap or the energy band gap. If there is overlapping between the bands then they have the continuous distribution of allowed energies.

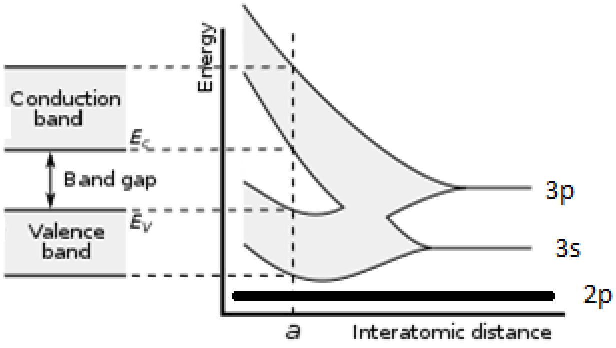

Figure 6.1: Splitting of Energy levels

In a single isolated atom, the electrons in each orbit have definite energy associated with it. But in case of solids all the atoms are close to each other, so the energy levels of outermost orbit electrons are affected by the neighbouring atoms.

When two single or isolated atoms are bring close to each other than the outermost orbit electrons of two atoms are interact or shared with each other. i.e., the electrons in the outermost orbit of one atom experience an attractive force from the nearest or neighbouring atomic nucleus. Due to this the energies of the electrons will not be in same level; the energy levels of electrons are changed to a value which is higher or lower than that of the original energy level of the electron. The electrons in same orbit exhibit different energy levels. The grouping of these different energy levels is called energy band. However, the energy levels of inner orbit electrons are not much affected by the presence of neighbouring atoms.

There are number of energy bands in solids but three of them are very important as revealed in figure 6.2. These three energy bands are important to understand the behaviour of solids. These energy bands are

1. Valence Band
2. Conduction Band
3. Forbidden Band

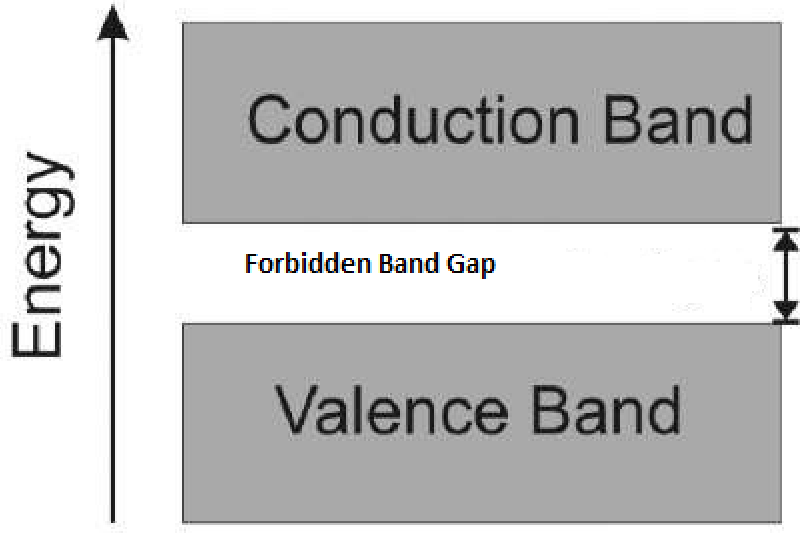

Figure 6.2: Classification of bands

6.3.1 Valence Band

The energy band which is formed by grouping the range of energy levels of the valence electrons or outermost orbit electrons is called as valence band. Valence band is present below the conduction band as shown in figure. Electrons in the valence band have lower energy than the electrons in conduction band. The electrons present in the valence band are loosely bound to the nucleus of atom.

6.3.2 Conduction Band

The energy band which is formed by grouping the range of energy levels of the free electrons is called as conduction band. Generally, the conduction band is empty but when external energy is applied the electrons in the valence band jumps in to the conduction band and becomes free electrons. Electrons in the conduction band have higher energy than the electrons in valence band. The conduction band electrons are not bound to the nucleus of atom.

6.3.3 Forbidden Band

The energy gap which is present between the valence band and conduction band by separating these two energy bands is called as forbidden band or forbidden gap. In solids, electrons cannot stay in forbidden gap because there is no allowed energy state in this region. Forbidden gap is the major factor for responsible of electrical conductivity of a solid. The classification of materials as insulators, conductors and semiconductors are mainly depends on forbidden gap. The energy associated with forbidden band is called energy gap and it is measured in unit electron volt, eV (1 eV = 1.6×10^{-19} J). The applied external energy in the form of heat or light must be equal to the forbidden gap in order to push an electron from valence band to the conduction band.

6.4 Classification of Solids on the basis of Band Structure

The electrical properties of a solid depend upon its energy band structure. In common, each energy band has a total of N individual levels, and each level can hold $2(2l+1)$ electrons. In this way each band has $2(2l+1)$ N electrons. It means that the 1s, 2s, 2p, 3s…. bands can hold 2N, 2N, 6N, 2N……electrons respectively. The classification of solids is based upon the nature of band occupation by electrons and the width of forbidden bands.

A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials as displayed in figure 6.3. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically. An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperatures. The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.

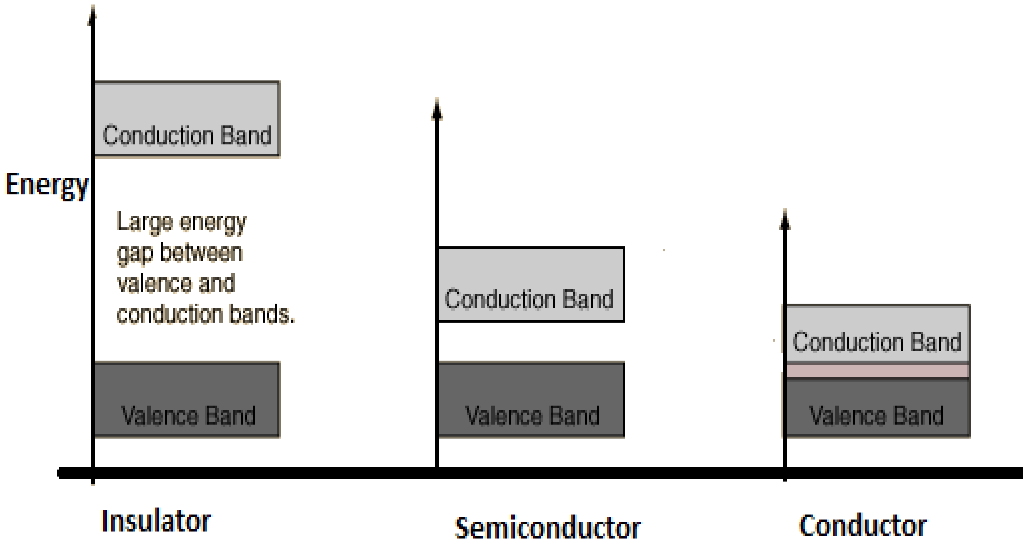

Figure 6.3: Comparative study of insulator, semiconductor and conductor

6.4.1 Conductors

In some solids, there is partially filled band above the completely filled lower bands. Such a band is formed from partially filled atomic levels as in case of Sodium. A sodium atom has a single valence electrons in its outer 3s level. Therefore, out of N atoms in a solid material of sodium, each contributes only one 3s electron to the solid, and so there are only N valence electrons in the 3s band. Thus the balance band 3s is only half full. A partially filled band may also be the result of overlapping of a completely filled band and an empty band, as in case of alkaline earth metals. As shown in figure the energy band of beryllium in which there is an overlap of the lower energy levels of the empty 2p band with the upper energy levels of the completed 2s band. Those electrons which would occupy the highest energy levels in the 2s band will actually go into the lowest levels of the overlapping 2p band. Thus, levels of the top of 2s band become unoccupied and the band is only partially filled.

When an electric field is applied across a piece of solid sodium, the electrons in the partially filled valence band easily acquire additional energy to move to the higher unoccupied energy levels within the same band as depicted in figure 6.4, without crossing the energy gap. Thus, a partially filled valence band is a feature of conductors. As we know a conduction band is an empty band just above the valence band into which electrons can pass. So, in conductors the balance band itself is a conduction band.

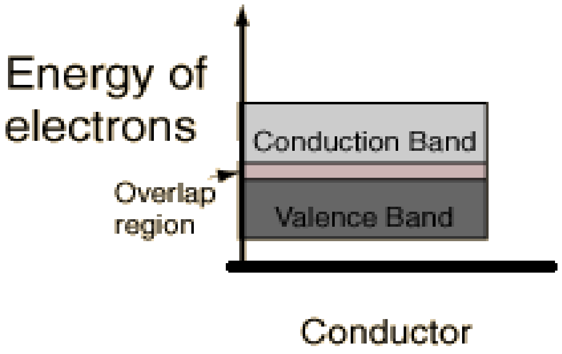

Figure 6.4: Overlapping of bands in conductor

6.4.2Semiconductor

In semiconductor as shown in figure 6.5, the band gap is small enough that the thermal energy can bridge the gap for the small fraction of the electrons.

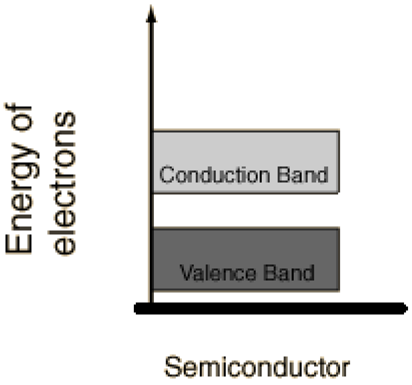

Figure 6.5: Band gap in semiconductor

For intrinsic semiconductors like silicon and germanium, the Fermi level is essentially halfway between the valence and conduction bands. Although no conduction occurs at 0 K, at higher temperatures a finite number of electrons can reach the conduction band and provide some current. In doped semiconductors, extra energy levels are added. The increase in conductivity with temperature can be modelled in terms of the Fermi function, which allows one to calculate the population of the conduction band. However, the doping of semiconductors has a much more dramatic effect on their electrical conductivity and is the basis for solid state electronics.

6.4.3 Insulator

In insulators, there is a big gap between valence band and conduction band. Figure6.6 shows the energy bands of diamond. There is an energy band completely filled with electrons and above is the empty band separated by a gap of around 7 eV. At least 7eV of energy must be supplied to an electron in order to reach the conduction band where it can move freely.

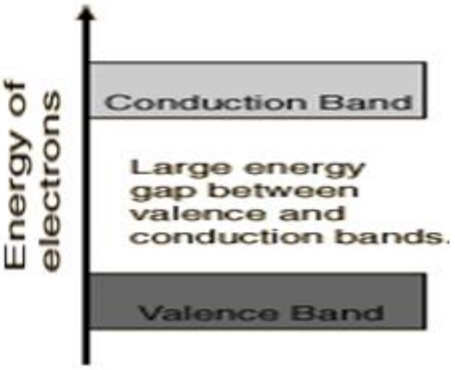

Figure 6.6: Band gap in insulator

Most solid substances are insulators, and in terms of the band theory of solids this implies that there is a large forbidden gap between the energies of the valence electrons and the energy at which the electrons can move freely through the material (the conduction band). Glass is an insulating material which may be transparent to visible light for reasons closely correlated with its nature as an electrical insulator. The visible light photons do not have enough quantum energy to bridge the band gap and get the electrons up to an available energy level in the conduction band. The visible properties of glass can also give some insight into the effects of doping on the properties of solids. A very small percentage of impurity atoms in the glass can give it colour by providing specific available energy levels which absorb certain colours of visible light. The ruby mineral (corundum) is aluminium oxide with a small amount (about 0.05%) of chromium which gives it its characteristic pink or red colour by absorbing green and blue light. While the doping of insulators can dramatically change their optical properties, it is not enough to overcome the large band gap to make them good conductors of electricity.

6.5 BLOCH THEOREM

A periodic potential appears because the ions are arranged with a periodicity of their Bravais lattice, given by lattice vectors *a*.

$V(x + a) = V(x)$

The Bloch theorem is a mathematical statement regarding the form of the solutions of the Schrodinger equation of an electron moving in a region of periodic potential, such as crystal lattice. It states that the eigenfunction of the electronic Schrodinger equation for a periodic potential are of the form $\psi(\vec{r}) = e^{i\vec{k}.\vec{r}} u_k(\vec{r})$, where the function $u_k(\vec{r})$ has the period of the crystal lattice and $\vec{k}$ is the wave vector. This is the statement of Bloch theorem which means that the eigenfunctions of the wave equation for a periodic potential are of the form of plane waves $e^{i\vec{k}.\vec{r}}$, modulated by a function $u_k(\vec{r})$ with the periodicity of the crystal lattice.

6.6 EXTENDED, REDUCED AND PERIODIC ZONE SCHEME

In Bloch function, $\psi(\vec{r}) = e^{i\vec{k}.\vec{r}} u_k(\vec{r})$, we have labeled the modulating factor $u_k(\vec{r})$ by a subscript $\vec{k}$ to indicate that the form of this factor depends on the wave vector $\vec{k}$. There are three ways called zone schemes to states in different energy bands.

6.6.1Extended Zone Scheme

Different energy bands are drawn in different Brillouin zones in the wave vector space.

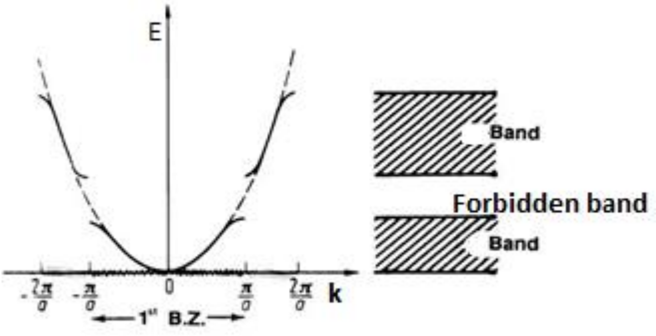

Figure 6.7: Energy versus wave vector in extended zone scheme

Three energy bands of a linear lattice have shown in figure 6.7for the first three Brillouin zones. The first zone is the region of k space with in the first energy gap; the second zone is the region between the first and the second energy gap and so on.

6.6.2 Reduced Zone Scheme

The representation using $E_k = \frac{\hbar^2 k^2}{2m}$ shows all bands in the first Brillouin zone only and is known as the **reduced zone scheme**.

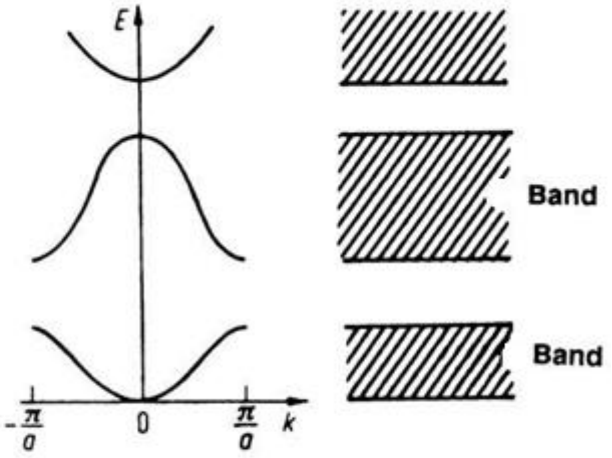

Figure 6.8: Energy vs wave vector in reduced zone scheme

6.6.3 Periodic zone Scheme

In this pattern, energy band is drawn in every zone as shown in figure 6.9. We repeat a given Brillouin zone periodically through whole of k space. If we translate a band from other zones into the first zone, than we can translate a band in the first zone into every other zone. Therefore, in this pattern the energy E of the band is a periodic function in the reciprocal lattice.

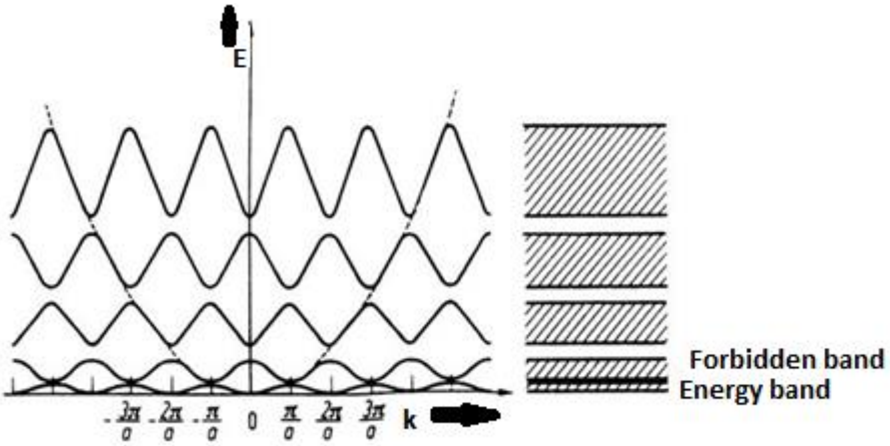

Figure 6.9: Energy vs wave vector in periodic zone scheme

6.7 BEHAVIOR OF AN ELECTRON IN PERIODIC POTENTIAL

The free electron model of metals assumes the conduction electrons to move freely in a region of constant potential without interacting with the crystal lattice. Although this model explains certain properties of metals, such as conductivity, specific heat, Para magnetism etc., but it fails to explain satisfactorily properties of solids in general. Hence it needs to be modified.

In general an electron in solid moves in a region of periodically varying potential caused by the ion cores situated at the lattice points.

6.8 THEORY OF BAND STRUCTURE IN SOLIDS (KRONIG PENNEY MODEL)

Kronig and Penney assumed that an electron experiences an infinite one dimensional array of finite potential well. Each potential well model attraction to an atom in the lattice, so the side of the wells must corresponds roughly to the lattice spacing as exposed in figure 6.10.

In order to find the allowed energies of electrons in solids, we must solve the Schrodinger equation for an electron in a crystal lattice. The figure shows the actual potential as seen by the electron in the crystal lattice in one dimension. Kronig-Penney suggested a simplified model potential consisting of an infinite row of rectangular potential wells separated by barriers of width *b*, with space periodicity *a* is the periodicity of the lattice. The solution to the Schrodinger equation for an electron in a periodic lattice can be found by Bloch theorem. According to this, the eigenfunction of the free electron travelling wave $\psi_k(x) = e^{ikx}$ is modified by the periodic potential to be of the form $\psi_k(x) = u_k(x)e^{ikx}$.

Where $u_k(x) = u_k(x+a)$

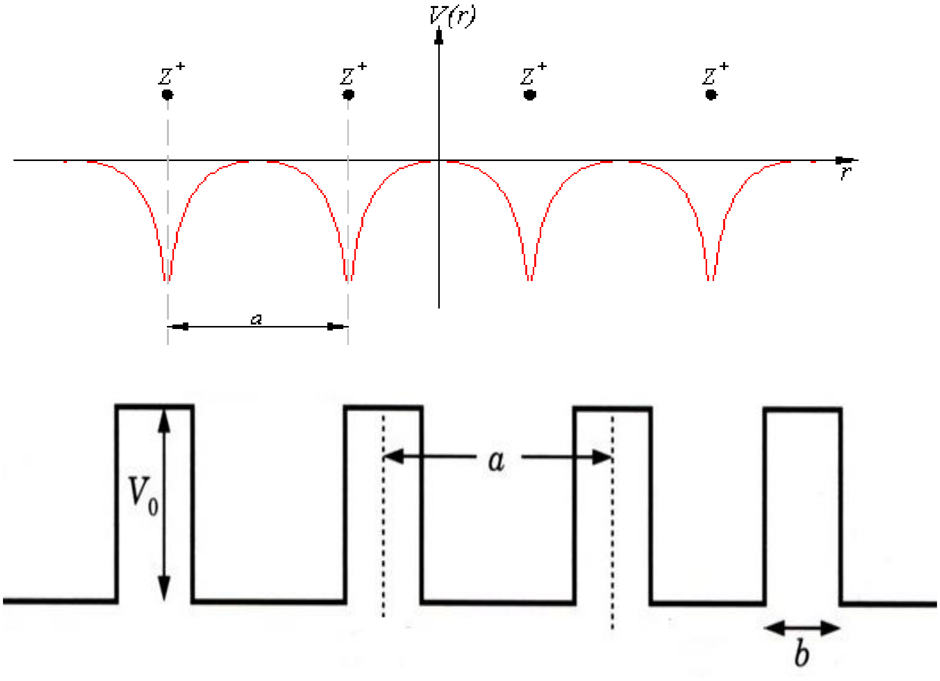

Figure 6.10: Kronig and Penney square well potential

On solving Schrodinger equation of the electron for the Kronig-Penney potential under the condition that ψ and $d\psi / dx$ must be continuous at the boundaries of the well, a complicated expression for the allowed energies in terms of k of the electron is obtained which shows that the gap in the energy occur at values given by

$$k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}, ...$$

Figure 6.11 shows the relationship between energy ε and wave number k for a one-dimensional lattice. The dashed curve is the free electron parabola.

At the above value of k we get energy gap, whereas for values of k not near these values the energy are much like that of free electron. The origin of the allowed energy bands are forbidden gaps are seen in figure.

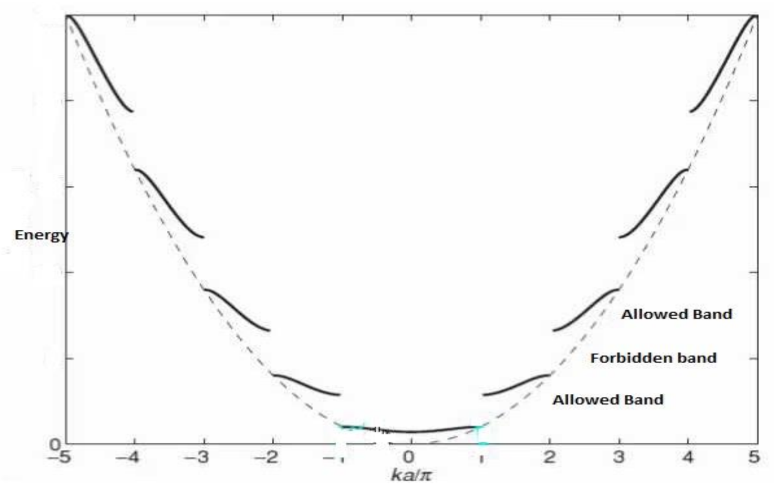

Figure 6.11: Allowed and forbidden bands

The occurrence of gaps can be understood in terms of Bragg reflection. The Bragg's condition is

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

Where a is the spacing between the ions of the lattice. Since we are considering the lattice in one dimension only, the above equation becomes

$$2a = n\lambda$$

or $2a = n\lambda 2\pi / 2\pi$

or, $k = n\frac{\pi}{a} = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}.....$

These are just the values of k at which the gaps in the $\varepsilon - k$ curve occur. The waves corresponding to values of k not satisfying the above condition travel almost freely and those satisfying the condition are reflected resulting in standing waves.

6.9 ORIGIN OF BAND GAP

The wave function associated with Kronig-Penney modelmay be calculated on solving Schrodinger wave equation in two sections.

We have $\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0$ for 0 < x < a

or we can write $\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0$

Where the value of $\alpha^2 = \frac{8\pi^2 mE}{h^2}$

Also, $\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V_0)\psi = 0$ for -b < x < a

or we can write $\frac{d^2\psi}{dx^2} - \beta^2\psi = 0$

Where $\beta^2 = \frac{8\pi^2 m}{h^2}(V_0 - E)$

Expected solutions of these Schrodinger equations should have the form of Bloch function, which requires that ψ and $d\psi / dx$ to be continuous throughout the crystal. Let us consider the general solutions of these Schrodinger equations

$$\psi_1(x) = A\exp(i\alpha x) + B\exp(-i\alpha x)$$

And $\psi_2(x) = C\exp(\beta x) + D\exp(-\beta x)$

Here, A, B, C, and D are the constant in region I and II. Values of these constant can be obtained using the boundary conditions as

$$\psi_1(x)\big|_0 = \psi_2(x)\big|_0$$

$$d\psi_1 / dx\big|_{x=0} = d\psi_2 / dx\big|_{x=0}$$

And $\psi_1(x)\big|_{x=0} = \psi_2(x)\big|_{x=-b}$

Because for the periodic lattice that is $V(x+a) = V(x)$, it is supposed that the wavefunction will also show the same periodicity. Hence, the expected solution of the above said Schrodinger equation must have the same form as that of the Bloch function.

So, we can write

$$\psi_k(x+a+b) = \psi_k(x)\exp(ik(a+b))$$

$$\psi_k(x) = \psi_k(x+a+b)\exp(-ik(a+b))$$

Now applying the boundary conditions we get the following relations

$$A + B = C + D$$

$$i\alpha(A - B) = \beta(C - D)$$

On simplifying these equation one can get

$$\cos k(a+b) = \left[\frac{\beta^2 - \alpha^2}{2\alpha\beta}\right]\sin\alpha a \sinh\beta b + \cos\alpha a \cosh\beta b$$

To solve above equation, Kronig-Penney supposed that the potential energy is zero at lattice sites and equal V_0 in side. Also assumed that, as the height of the potential barrier V tends to infinity and the width of the barrier b tends to zero so that the product V_0 b remains finite. Under these assumptions

$$\sinh\beta b \to \beta b$$

$$\cosh\beta b \to 1 \text{ as } b \to 0$$

Therefore

$$\cos ka = \left[\frac{\beta^2 - \alpha^2}{2\alpha\beta}\right]\beta b \sin\alpha a + \cos\alpha a$$

Hence on solving we get

$$\cos ka = \left[\frac{8\pi^2 m}{2\alpha\beta h^2}\right]V_0 \beta b \sin\alpha a + \cos\alpha a$$

or, $\cos ka = P \sin\alpha a / \alpha a + \cos\alpha a$

Where $P = \left[\frac{4\pi^2 ma}{h^2}\right]V_0 b$

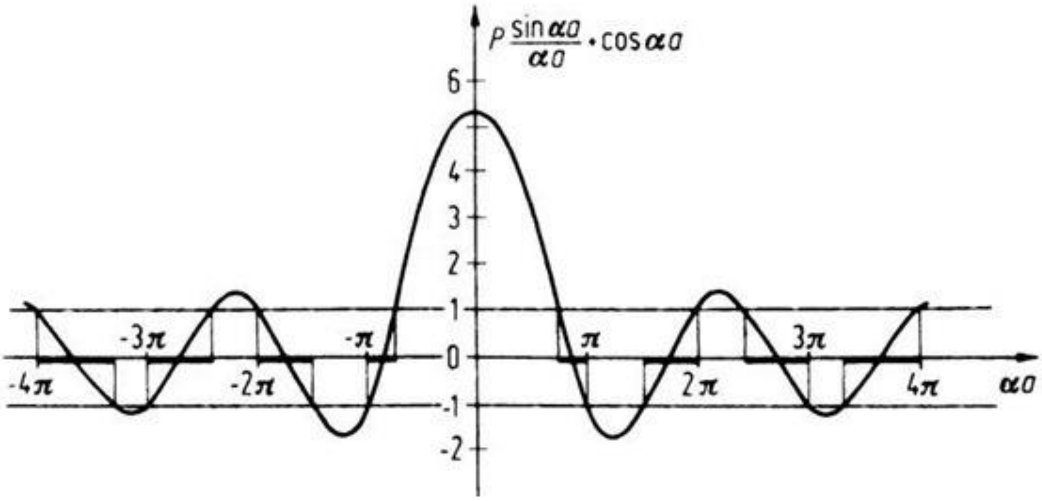

Figure 6.12: Origin of band gap

This is the condition for the solutions of the wave equation to exist. As you see from figure 6.12 that this is satisfied only for those value of αa for which its left-hand side lies between +1 and -1. It is because its right hand side must lie in range. Such values of αa represent the wave like solution and are reachable. On the other hand, the other values of αa will be inaccessible. The significances of this can be agreed very well by the figure. the part of vertical axis lying between the horizontal lines represents the range acceptable. Since α^2 is proportional to the energy so αa will be measure of energy. It is clear that the region for αa where the value of $P\sin\alpha a/\alpha a+\cos\alpha a$ does not lie between -1 and +1. Therefore, these values of αa and henceforth of energy E, there is no solution. Such region of energy is disallowed and is named forbidden bands. This analysisled to the following inferences

1. The energy spectrum of the electronconsists of alternate regions of allowed energy that is continuous band and forbidden energy band. Usually these bands are referred as allowed and forbidden energy bands.
2. As the value of αa increases the width of the allowed energy bands increases.
3. The quantity P, which is noted as a measure of potential barrier strength. If P is large, means the potential barrier V_0 b is large. For the infinite deep well the electron can be considered as confined into a single potential well. It is applied to the crystals where the electrons are very tightly bound with their nuclei. In second case, when P is small, the barrier strength is small that is $P \to 0$, the electron can be considered to be moving freely through the potential well. It is the case of crystal where the electron is almost free of their nuclei. Hence we conclude that the width of particular allowed band decreases as P increases. As $P \to \infty$, the allowed bands are compressed into energy levels and the energy spectrum is thus a line spectrum. Whereas $P \to 0$, we have the free electron model of the energy spectrum. It is known as quasi continuous. In between these limits, the position and the width of the allowed and forbidden bands for any value of P are obtained.
4. To calculate the energy spectrum in extreme cases ($P \to \infty$), we have

$$\alpha a = n\pi$$

or we can write $\frac{2mE}{\hbar^2}a^2 = n^2\pi^2$

or you can write, $E = \frac{\pi^2\hbar^2}{2ma^2}n^2$

It is the physically expected result because the large P makes the tunneling through the barrier nearly unlikely. In second case when $P \to 0$

We get $\cos\alpha a = \cos ka$

Which implies $\alpha = k$

or, $\alpha^2 = k^2$

Which gives $E = \frac{\hbar^2k^2}{2m}$, this is equivalent to the case of free particle. Thus no allowed energy level exists.

Example 1: Show that for the Kronig-Penney potential with $P \leq 1$, the energy of the lowest energy band at k=0 is given by $E = \frac{h^2P}{4\pi^2ma^2}$

Solution: for k=0 $P\sin\alpha a/\alpha a+\cos\alpha a = \cos ka$ becomes

$P\sin\alpha a/\alpha a+\cos\alpha a = 1$

or we may write

$P/\alpha a = 1 - \cos\alpha a / \sin\alpha a$

On expanding sine and cosine function

where $\cos\alpha a = 1 - \frac{\alpha^2 a^2}{2}$

And $\sin\alpha a = \alpha a$

so, we can write $P/\alpha a = \frac{\alpha^2 a^2}{2}$

we know $\frac{8\pi^2 mE}{h^2} = \alpha^2$

hence, we get $P = \frac{8\pi^2 mE}{h^2}(a^2/2)^2$

or $E = \frac{h^2 P}{4\pi^2 ma^2}$

Example 2: In germanium the energy gap is about 0.75 eV. Show that the crystal behaves as a transparent medium only for light of wavelength above 16533 Å. (given h= 6.63 x 10^{-34} J s, vel of light c= 3.0 x 10^8 m/s)

Solution: first we calculate the energy of 16533 Å photon

$E = hc/\lambda$

On putting the values we get

$E = hc/\lambda = \frac{6.63\times10^{-34}\times3.0\times10^{8}}{16533\times10^{-10}}$

= 1.2x 10^{-19} Joule

or =1.2x 10^{-19} Joule/ 1.6 x 10^{-19}= 0.75 eV

Since the photon energy for light of wavelength above 16533 Å will be less than 0.75 eV which is energy band gap in case of germanium. Therefore, these photons will not be absorbed and the light will be transmitted through the crystal. Those photons for light below 16533 Å will have energy more than the energy gap of 0.75 eV and so they will be absorbed in exciting the electrons from the valence band to the conduction band. So, the crystal is opaque for the light below 16533 Å.

Example 3: The energy gap in silicon is 1.1eV and in diamond it is 6eV. State the transparency of these substances to visible light.

Solution: the wavelength of light corresponding to photon energies 1.1 eV

$E = hc/\lambda = \frac{6.63\times10^{-34}\times3.0\times10^{8}}{1.1\times1.6\times10^{-19}}$

= 11.3 x 10^{-7} m

= 11300 Å

And for 6 eV

$E = hc/\lambda = \frac{6.63\times10^{-34}\times3.0\times10^{8}}{6\times1.6\times10^{-19}}$

=2072 Å

So, we conclude the silicon is transparent only to radiation of $\lambda \geq 11300$ Å. Because, it absorbs photons of shorter wavelength, and so it is opaque to visible light. Since diamond is transparent to radiation of $\lambda \geq 2072$ Å, therefore it is transparent to visible light.

6.10 SUMMARY

In this unit, you have studied about the origin of the energy band theory in solids. The large energy gap between the valence band and conduction bands in an insulator says that at ordinary temperature, no electron can reach the conduction band. It is discussed that, in semiconductor the band gap is small enough that the thermal energy can bridge the gap for the small fraction of the electrons. In, conductors, there is no band gap since the valance band overlap the conduction band. Making use of the Bloch theorem and the Kronig-Penney model, the energy spectrum of the electron is found to comprise a set of continuous band, separated by the region of forbidden energies which are called energy gaps. This can be understood from the construction of Brillouin zones. The first Brillouin zone is defined as the region in k space. The energy levels of an electron in a crystal can be determined by solving Schrödinger's equation for a periodic potential and by studying changes to the electron energy structure as atoms are pushed together from a distance. The energy structure of a crystal is characterized by continuous energy bands and energy gaps. The ability of a solid to conduct electricity dependenceson the energy structure of the solid. In solids, the discrete energy levels of the individual atoms merge to form energy bands Energy gaps arise in solids because they contain standing wave states. The size of the energy gap between the valence and conduction bands determines whether a substance is a conductor, an insulator or a semiconductor. To check your progress, examples and terminal questions are given.

6.11 GLOSSARY

extended – extensive.
Periodic- cyclic.
Forbidden – prohibited.
Contribute– provide.
Crucial– critical.
Doping– fixing.
Dramatically–noticeably.
Translate– interpret.
Assumption– supposition.
Accessible– reachable.
Transmit– convey.
Discrete - isolated.

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6.14TERMINAL QUESTIONS

1. How does the electrical conductivity of a pure semiconductor change with rice in temperature?
2. Why does the electrical conductivity of a pure semiconductor increase on heating?
3. Name the charge carriers at room temperature in a conductor, an intrinsic semiconductor and an insulator.
4. 16. The energy gaps in the energy band diagram of a conductor, an insulator and a semiconductor are E_1, E_2 and E_3, arrange them in increasing order.
5. Describe in what sense an insulator with infinite band gap cannot be a perfect insulator.
6. Calculate the energy gap of a crystal which is transparent only for light of wavelength greater than 12345 Å.
7. An insulator has an optical absorption only for wavelengths shorter than 1800 Å. Find the width of the forbidden band for the insulator. What is the order of magnitude of the forbidden gap in a semiconductor?
8. The energy gaps of Si, Ge and Ag are 1.1, 0.7 and 0 eV respectively. Find the wavelength of electromagnetic radiation to which these solids are opaque. (given h= 6.63 x 10-34 J s, vel of light c= 3.0 x 108 m/s)
9. What are the two main approaches used to determine the energy levels of electrons in a crystal?
10. How does the number of energy levels in a band correspond to the numberN of atoms?
11. What is the main difference between an insulator and a semiconductor?
12. A valence electron in a crystal absorbs a photon of wavelength, λ=0.300nm, this is just enough energy to allow the electron to jump from the valence band to the conduction band. What is the size of the energy gap?

13. In a band theory of solids, there are an infinite number of bands. If T = 0 K, the uppermost band to contain electrons is partially filled, and the gap between the band and the next lowest band is 0.8 eV, is the material a metal, an insulator, or a semiconductor.

14. In a band theory of solids, there are an infinite number of bands. If T = 0 K, the uppermost band to contain electrons is completely filled and the gap between the band and the next lowest band is 8 eV, is the material a metal, an insulator, or a semiconductor? What if the gap is 0.8 eV?

15. **True/ False statements**

(a) When the large number of atoms is brought close together, the energy levels split and form energy band.

(b) The conduction band of an insulator is empty.

(c) The forbidden energy band in Si is 1.1 eV.

(d) The conduction band of a conductor is empty.

(e) Insulators are opaque to visible light.

(f) All one electron configurations in an ideal crystal are Bloch functions.

(g) Conductivity of semiconductors decreases with rice in temperature.

(h) At temperature near absolute zero, the semiconductors become insulators.

(i) Kronig-Penny model explains the behaviour of an electron in non-uniform magnetic field.

16. **Fill in the Blanks**

(a) Conductors have ……………..valence energy band.

(b) The motion of electron in the periodic crystal lattice gives rise to …………

(c) The band energy of solids deals with electron motion in the ………..field of crystal.

(d) In metals, there is an overlapping of ……..and…….bands.

(e) The energy gap for a semiconductor is………..than for an insulator.

(f) A solid having a band completely field and the next allowed band completely empty is called…….

(g) Insulators are transparent to …….light.

(h) Kronig-Penney model explain the behaviour of an electron moving in a periodically varying……...

(i) Semiconductors are opaque to visible light but transparent to …..

6.15 ANSWERS

2. Around absolute zero, a pure semiconductor is an insulator because the valence band is full and there are no free electrons in the conduction band. As the temperature rises, more and more of the electrons in the valence band gain energy to cross the energy gap and enter the conduction band, hence the conductivity increases.

3. Free electrons, free electrons and holes, no charge carriers.

4. $E_1 < E_2 < E_3$.

5. As long as band gapis finite, an electron can be elevated to the conduction band, resulting is conduction

6. 1.0 eV

7. 6.9 e V

8. For Si, λ = 0-11300 Å, For Ge, λ = 0- 17760 Å, For Ag, λ = 0- ∞ Å

9. (1). Solve Schrödinger's equation for the allowed states and energies. (2) Determine energy levels for the case of very large lattice spacing and then determine the energy levels as this spacing is reduced.

10. For N atoms spaced far apart, there are N different wave functions, all with the same energy (similar to the case of an electron in the double well of H2).
As the atoms are pushed together, the energies of these N different wave functions are split. By the exclusion principle, each electron must each have a unique set of quantum numbers, so the N atoms bringing N electrons together must have at least N states.

11. For an insulator, the energy gap between the valence band and the conduction band is larger than for a semiconductor.

12. 4.13 keV.

13. Metal.

14. Insulator, semiconductor.

15. (a) T, (b) T,(c) T, (d) F, (e) F, (f) T, (g) F, (h) T, (i) F.

16. (a) partially filled, (b) energy gap, (c) periodic, (d) valence, conduction, (e) smaller (f) insulator (g) visible (h) potential (i) infrared radiation.

UNIT 7 SEMICONDUCTORS

Structure

7.1 INTRODUCTION

Generally, solids can be classified into two broad categories, conductors and insulators. Conductors are those across which electric charge can flow very easily. While insulators are those through which, there is no electric charge or difficult to flow the charge. This difference between the conductors and insulators can be described on the basis of the number of free electrons in them. In conductors, there are large numbers of free charge carriers while insulators have nearly no free charge carriers. The electrical resistance increases with rise in temperature meaning that the temperature coefficient of resistance of conductor is positive. However, there are certain solids whose electrical conductivity is intermediate between conductors and insulators. These are called semiconductors. Ge, Si and C are some examples of semiconductors. The outermost valence shell electrons of semiconductors are neither so tightly bound with the atom as in insulator, nor so loosely bound as in case of conductors. The electrical resistance in case of semiconductors decreases with the increase in temperature that is why, the temperature coefficient of semiconductors is negative. At absolute zero temperature all the semiconductors become insulators. Some solids have a much smaller energy gap that is of the order of 1 eV, between valence band and the conduction band are known as the semiconductors.

It may be explained in other way as in an ordered periodic crystal lattice, electrons as the carriers of electrical current are not allowed to move around freely. Instead, they have to obey certain rules enforced by quantum mechanics. As a consequence, electrons have to occupy certain energy bands which are separated from each other by small or large band gaps. This situation can be compared to a two-floor building consisting of a ground floor and a first floor. In the language of solid state physics, these two floors are called valence band and conduction band, respectively. Both floors are covered by a well-ordered array of quadratic tiles, representing the periodic lattice of atoms in a semiconductor crystal. The movement of electrons in a crystal is then analogous to the movement of citizens in our building, whose most important purpose is to transport charge from one end of the building to the other end.

In this unit, we shall begin here by the overview of semiconductors. We shall study *p* type and *n* type semiconductors. Also, you will study, why the Fermi level shifted towards conduction band or valence band on doping the *p* type or ntype impurities in the semiconducting specimen. Also, in this unit, you shall also review electron hole concentration, drift current, mobility and conductivity, effective mass and Hall Effect.

7.2 OBJECTIVES

After studying this unit, you should be able to-

- ✓ define semiconductor
- ✓ what are the difference between intrinsic and extrinsic semiconductors
- ✓ what are the difference between n type and p type extrinsic semiconductors
- ✓ how does temperature affect each type of semiconductor?
- ✓ what are the difference between conductivity equation of intrinsic and extrinsic semiconductors
- ✓ what are the relation of electron and hole mobility to conductivity
- ✓ explain drift current
- ✓ what is effective mass
- ✓ understand Hall effect
- ✓ solve problems using law of conservation of charges
- ✓ apply Hall effect to calculate the number of charge carriers

7.3 WHAT ARE SEMICONDUCTORS?

The semiconductors are the solids whose conductivity lies between the very high conductivity of conductors and very low conductivity of insulators. The energy band gap between the conduction band and the valence band is narrow, which is of the order of 1 eV. At absolute zero the semiconductor has the energy band structure of an insulator with the difference that the forbidden band gap. But at room temperature a semiconductor is considered as

1. A partially filled conduction band
2. Partially unoccupied valence band
3. A small energy gap of the order of 1eV

7.4 PROPERTIES OF SEMICONDUCTORS

Followings are some properties of semiconductors.

1. The resistance of semiconductors decreases with the increase of temperature that is semiconductor have negative temperature coefficient.
2. Electrical properties of semiconductors changes on adding some impurities.
3. The bonding between valence electrons of semiconductors is covalent which are formed by sharing of valence electrons.

7.5 TYPES OF SEMICONDUCTORS

The semiconductors are the solids whose electrical conductivity lies between the very high conductivity of metals and the very low conductivity of insulators. They are characterized by the narrow gap of the order of 1 eV between the valence band and the conduction band. Germanium and silicon have the energy gaps of around 0.7 eV and 1.1 eV respectively. Pure semiconductors are insulators at low temperatures. At room temperature, although, some of the valence electrons acquire thermal energy greater than forbidden band gap and cross over to the conduction band. A vacancy is created in the valence band at each place where an electron was present before moving to the conduction band as shown in figure 7.1. This vacancy is called the hole. The free electrons in the conduction band and the holes in the valence band can move about even under a small field. Therefore, semiconductors are slightly conducting. As the temperature increases, more and more electrons are reaching to the conduction band, leaving behind equal number of holes in the valence band. Consequently, the conductivity of semiconductors increases with the increase in temperature.

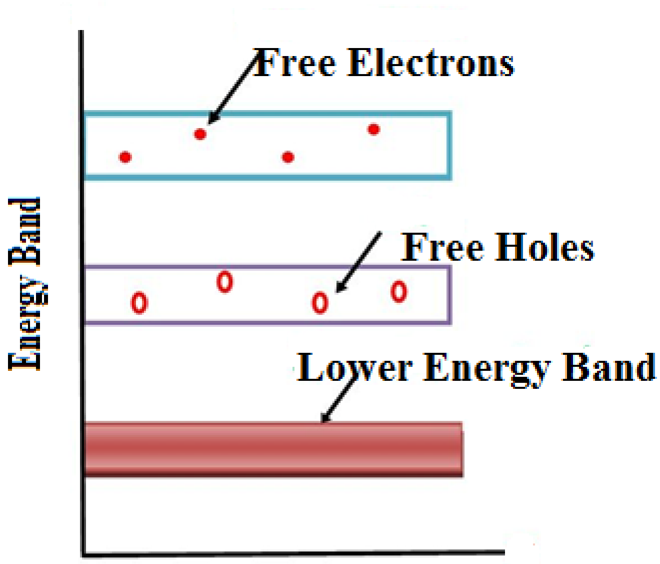


Figure 7.1: Energy Band gap

Depending upon the conductivity, there are two types of semiconductors: -

1. Pure semiconductors (intrinsic semiconductors)
2. Impure semiconductors (extrinsic semiconductors)

7.5.1 Intrinsic Semiconductor

A semiconductor in pure form is called an intrinsic semiconductor. The electrical conductivity of these semiconductors arises by the thermal excitation of electrons from the valence band to the conduction band. Pure Si and pure Ge are notable examples of intrinsic semiconductors. The electronic configurations of these semiconductors are as follows:

$$_{14}Si = 1s^2, 2s^2 2p^6, 3s^2 3p^2$$

$$_{32}Ge = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^2$$

Since, atoms of Si and Ge both have four valence electrons, because of that, these are tetravalent.

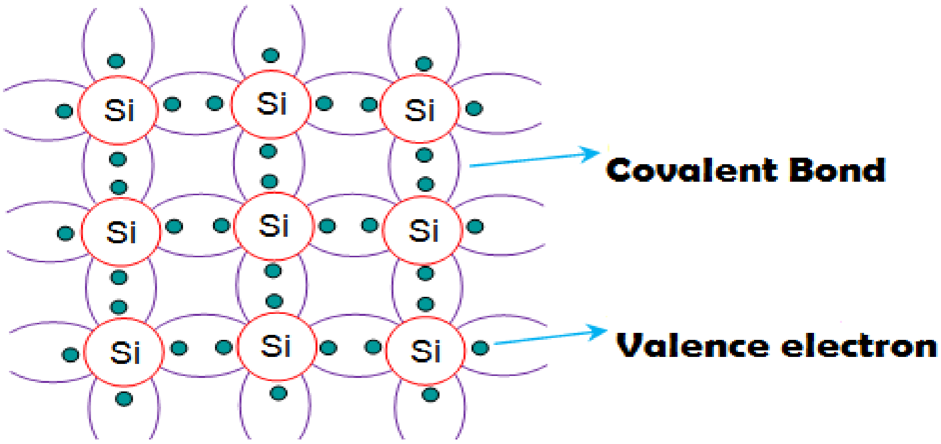


Figure 7.2: Intrinsic semiconductor

The atoms of Si and Ge have four valence electrons surrounding an inner core as shown in figure 7.2. Each of the four valence electrons of an atom is shared by an electron of its four nearestneighoursatoms and formed the covalent bonds. At temperature near to zero, all valence electrons are tightly bound to the inner core and there are no free electrons available toconduct electricity through the specimen. At room temperature, although, some of the valence electrons are thermally excited into the conduction band and become free to move about. These excited electrons leave holes in the valence band as shown in figure 7.3. Greater the temperature, more is the number of electron-hole pairscreated. On applying the electric field, the free electrons in the conduction band move in a direction opposite to the field and holes in the valence band move in the direction of the field also both give growth to the electric current. Therefore, in a semiconductor electrons and holes both establish current. Thus, in an intrinsic semiconductor the conduction is due to electrons and holes both and the total current is the sum of currents due to free electrons and holes. The conductivity of an intrinsic semiconductor is very poor.At normal temperature, only one covalent bond breaks in 10^9 atoms of Ge. Meaning that, only one atom in 10^9 atoms is available for conduction. So, practically there is no use of intrinsic semiconductor.

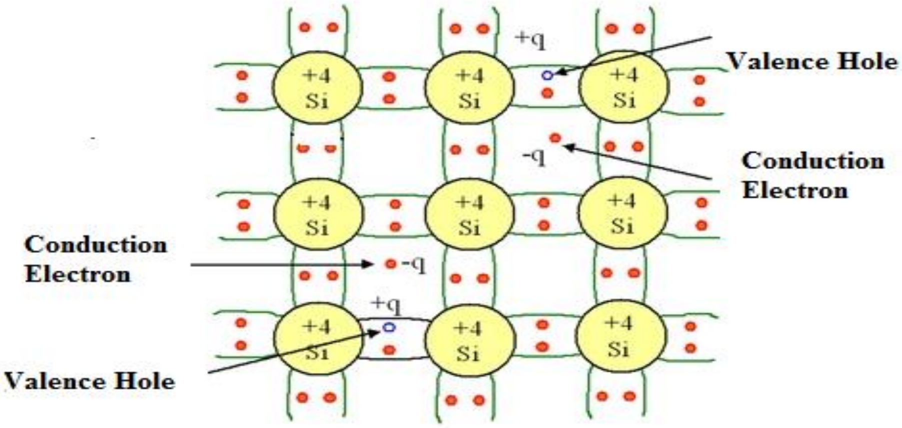


Figure 7.3: Bond formation in intrinsic semiconductor

In case of intrinsic semiconductor, the concentration of electrons in conduction band and holes in valence band are equal at a given temperature. If n_e and n_h are the electrons and holes concentration respectively, we have $n_e = n_h = n_i$, where n_i is called the intrinsic concentration. The rate of destruction of electron hole pairs by recombination is given by $-\frac{dn}{dt} \propto n_e n_h$ or, we can write as $-\frac{dn}{dt} = Qn_e n_h = Qn_i^2$, where Q is the constant of proportionality also known as recombination coefficient. Here, negative sign shows that there is decrease in electron hole pairs with time due to recombination process.

The rate of creation of electron hole-pairs per unit volume is related to

1) Density of electrons available for thermal excitation, that is given as $N - n_i$, where N is the total number of covalent electrons per unit volume
2) The Boltzmann factor $e^{-(E_C - E_V)} / k_B T$

   We take forbidden energy gap $E_g = E_C - E_V$, therefore we can write

$$e^{-(E_C - E_V)} / k_B T = e^{-E_g} / k_B T$$

Therefore, the rate of creation of electron hole pairs is

$$\frac{dn}{dt} \propto (N - n_i) e^{-E_g} / k_B T$$

or, $$\frac{dn}{dt} = L(N - n_i) e^{-E_g} / k_B T$$

Where, L is the constant of proportionality. Thus, we can write

$$Rn_i^2 = L(N - n_i) e^{-E_g} / k_B T$$

As, at normal temperature only a small fraction of covalent electrons is excited to the conduction band, therefore N >>n_i , hence we neglect n_i from the term $(N - n_i)$

Hence $$n_i^2 = \frac{L}{R} N e^{-E_g} / k_B T$$

or we can write,

$$n_i = De^{-E_g} / 2k_B T$$

Where,*D*is a constant (D=*LN/R*).

7.5.1.1 Density of electron hole pair in an intrinsic semiconductor

According to Quantum Mechanics, the density of energy states per unit volume in the conduction band is given by $D(E)=(1/2\pi^2)\left[\frac{2m_e^*}{\hbar^2}\right]^{3/2}(E-E_C)^{1/2}$, where m_e^* is the effective mass of an electron. We know the Fermi function

$$F_e(E)=\frac{1}{e^{(E-E_F)/k_BT}+1}$$

If $E - E_F = k_BT$, the Fermi function becomes

$$F_e(E)=\frac{1}{e^{(E-E_F)/k_BT}}$$

or, $$F_e(E)=e^{-(E-E_F)/k_BT}$$

This is known as the Boltzmann approximation which says that all electrons in the conduction band are in narrow region at the bottom of conduction band. Now we can calculate the number of electrons per unit volume in the energy interval E and E +dE in the conduction band by this relation

$$n_e(E)dE=D(E)F_e(E)dE$$

On putting the values of Fermi function and density of states, we get

$n_e(E)d(E)=(1/2\pi^2)\left[\frac{2m_e^*}{\hbar^2}\right]^{3/2}(E-E_C)^{1/2}e^{-(E-E_F)/k_BT}dE$, on integrating it between the limits E and ∞, we obtain

$$n_e(E)d(E)=\int_{E_C}^{\infty}(1/2\pi^2)\left[\frac{2m_e^*}{\hbar^2}\right]^{3/2}(E-E_C)^{1/2}e^{-(E-E_F)/k_BT}dE$$

or, $$n_e(E)=(1/2\pi^2)\left[\frac{2m_e^*}{\hbar^2}\right]^{3/2}e^{-(E_F-E_C)/k_BT}\int_{E_C}^{\infty}(E-E_C)^{1/2}e^{-(E-E_C)/k_BT}dE$$

On substitution, $x=\frac{E-E_C}{k_BT}$ and differentiation it, $dx=\frac{dE}{k_BT}$

On putting in the above equation we get

$$n_e(E)=(1/2\pi^2)\left[\frac{2m_e^*}{\hbar^2}\right]^{3/2}(k_BT)^{3/2}e^{-(E_F-E_C)/k_BT}\int_{0}^{\infty}x^{1/2}e^{-x}dx$$

Where, $\int_0^\infty x^{1/2} e^{-x} dx$ is the standard integral, whose integration is $\pi^{1/2}/2$

Therefore,

$$n_e(E) = (1/2\pi^2)\left[\frac{2m_e^*}{\hbar^2}\right]^{3/2} (k_B T)^{3/2} e^{-(E_F - E_C)/k_B T} \pi^{1/2}/2$$

or, $$n_e(E) = 2\left[\frac{2\pi m_e^* k_B T}{h^2}\right]^{3/2} e^{(E_F - E_C)/k_B T}\text{, where } \hbar = h/2\pi$$

This is the equation of hole concentration in the conduction band. Similarly, we can calculate the concentration of holes in the valence band. Hence, the concentration on holes in the valence band is written as $n_h(E) = 2\left[\frac{2\pi m_h^* k_B T}{h^2}\right]^{3/2} e^{(E_V - E_F)/k_B T}$, Multiplying these two equations, we have

$$n_e n_h = 4\left[\frac{2\pi k_B T}{h^2}\right]^3 (m_e^* m_h^*)^{3/2} e^{(E_V - E_C)/k_B T}$$

or we can write

$$n_e n_h = 4\left[\frac{2\pi k_B T}{h^2}\right]^3 (m_e^* m_h^*)^{3/2} e^{-E_g/k_B T}$$

where, $E_g = E_C - E_V$ is the forbidden energy gap. It shows that the electron and hole densities at thermal equilibrium is independent upon the Fermi level and depends only upon the forbidden energy band gap. For intrinsic semiconductors, $n_e = n_h = n_i$, therefore the above equation becomes

$$n_i = \sqrt{4\left[\frac{2\pi k_B T}{h^2}\right]^3 (m_e^* m_h^*)^{3/2} e^{-E_g/k_B T}}$$

7.5.1.2 Fermi Energy

It is the energy of latest occupied level below which all the states are completely occupied and above it is completely unoccupied.

In intrinsic semiconductor, the electron and hole concentrations are given as

$$n_e(E) = 2\left[\frac{2\pi m_e^* k_B T}{h^2}\right]^{3/2} e^{(E_F - E_C)/k_B T}$$

And $$n_h(E) = 2\left[\frac{2\pi m_h^* k_B T}{h^2}\right]^{3/2} e^{(E_V - E_F)/k_B T}$$

In intrinsic case $n_e = n_h = n_i$

Therefore, $$2\left[\frac{2\pi m_e^* k_B T}{h^2}\right]^{3/2} e^{(E_F - E_C)/k_B T} = 2\left[\frac{2\pi m_h^* k_B T}{h^2}\right]^{3/2} e^{(E_V - E_F)/k_B T}$$

On solving, we have $e^{\frac{2E_F - E_C - E_V}{k_B T}} = (m_h^* / m_e^*)^{3/2}$, taking log on both sides, we have

$$\frac{2E_F - E_C - E_V}{k_B T} = (3/2)\log(m_h^* / m_e^*)$$

which gives, $$2E_F = E_C + E_V + (3/2)k_B T \log(m_h^* / m_e^*)$$

or, $$E_F = (E_C + E_V)/2 + (3/4)k_B T \log(m_h^* / m_e^*)$$

If effective mass of an electron is equal to the effective mass of holes ($m_h^* = m_e^*$), putting these values in above equation, we get

$$E_F = (E_C + E_V)/2$$

It shows that in case of intrinsic semiconductor, Fermi level lies in middle of valence band and the conduction band.

EXAMPLE: Show that the electron and hole concentrations in intrinsic semiconductor is constant, also called Law of Mass Action.

Solution: We have electrons and hole concentrations as

$$n_e(E) = 2\left[\frac{2\pi m_e^* k_B T}{h^2}\right]^{3/2} e^{(E_F - E_C)/k_B T}$$

$$n_h(E) = 2\left[\frac{2\pi m_h^* k_B T}{h^2}\right]^{3/2} e^{(E_V - E_F)/k_B T}$$

On multiplying both equations, we get

$$n_e n_h = n_i^2 = 2\left[\frac{2\pi m_e^* k_B T}{h^2}\right]^{3/2} e^{(E_F - E_C)/k_B T}\, 2\left[\frac{2\pi m_h^* k_B T}{h^2}\right]^{3/2} e^{(E_V - E_F)/k_B T}$$

or, $$n_e n_h = n_i^2 \propto T^3 e^{-E_g/k_B T}$$

or, $n_i \propto e^{-E_g/2k_BT}$

where, $A = 4\left[\frac{2\pi m_e^* k_B T}{h^2}\right]^{3/2}\left[\frac{2\pi m_h^* k_B T}{h^2}\right]^{3/2}$ is a constant and k_B is the Boltzmann constant.

This equation shows that at a given temperature and certain band gap, n_i^2 is a constant. It does not depend upon the impurities introduced in it. This equation is known as law of mass action. For pure semiconductors conductivity increases with increasing temperatures, also increases on impurity doping.

7.5.2 Extrinsic Semiconductors

Extrinsic semiconductor is an impure semiconductor formed from a pure semiconductor by adding a small quantity of impurity atoms called dopants. The process of adding impurities to the semiconductor solid is known as doping. This added impurity is very small of the order of one atom per million atoms of pure semiconductor. Depending upon the type of impurity added to the extrinsic semiconductors are categorized as

1. n type semiconductor.
2. p type semiconductor.

7.5.2.1 n-type Semiconductor

To describe the formation of n-type semiconductor, consider that a pentavalent impurity (As), is added to a pure Ge semiconductor.As shown in figure 7.4, Four of the five valence electrons of the impurity atom form covalent bonds with one each valence electrons of four Ge atoms nearby it. The fifth valence electron of the impurity atom requires little energy to leaves its atom. Therefore, it becomes free to move about in the crystal and acts as a free charge carrier. Therefore, on adding thepentavalent impurity to the intrinsic semiconductor, the number of free charge carriers increases, henceforth, the conductivity of semiconductors increases. The impure Si or Ge semiconductor is called the n-type semiconductor since it has an excess of negative charge carriers. The impurity atoms are called the donor atoms because they donate the electrons to the crystal.

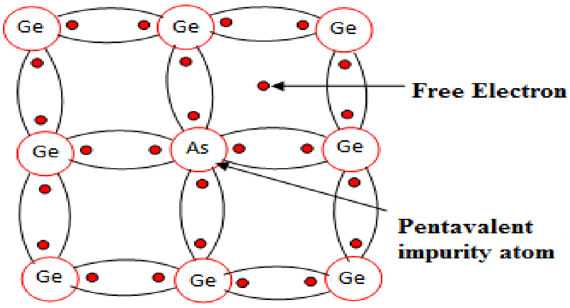


Figure 7.4: n type semiconductor

n-type semiconductor energy band diagram is shown above. The valence electron of the impurity atoms occupies the energy level just below the conduction band. This is called the donor level. This level is around 0.01 eV below the conduction band. At normal temperature, nearly all the electrons in the conduction band come from the donor levels, only a few come from the valence band. therefore, in n type semiconductor, majority charge carriers are the electrons donated by donors. Because of the thermal excitation, there are few holes in the valence band, hence small current contributed due to holes also. Therefore, in an n type semiconductor the electrons are the majority charge carries and holes are the minority charge carriers. The Fermi level in the n type crystal, which is measure of top filled energy state, shifts from the energy gap towards the conduction band. Let the density of ionized donor atoms is N_d and the density of electron hole pairs in the intrinsic semiconductors is n_i at any temperature T, we have $N_d = n_i$ because of recombination of electron hole in the presence of surplus electrons. Hence, we have

$$N_d = 2\left[\frac{2\pi m_e^* kT}{h^2}\right]^{3/2} e^{(E_F - E_C)/k_B T}$$

or,

$$N_d = N_C e^{(E_F - E_C)/k_B T}$$

Where,

$$N_C = 2\left[\frac{2\pi m_e^* kT}{h^2}\right]^{3/2}$$

or, from above equations we get,

$$N_C / N_d = e^{-(E_F - E_C)/k_B T}$$

Taking log on both sides, we get

$$\log(N_C / N_d) = -\frac{(E_F - E_C)}{k_B T}$$

or, it become

$$E_F = E_C - k_B T \log(N_C / N_d)$$

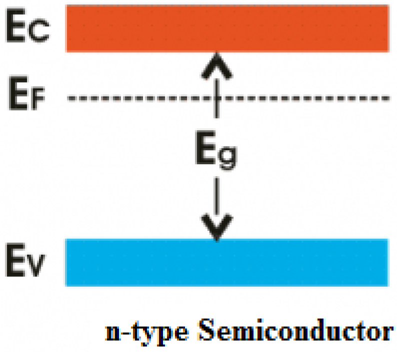


Figure 7.5: Fermi level in n type semiconductor

It shows in figure 7.5, that in n type semiconductor the Fermi level lies below the bottom of conduction band. As we increase the temperature, the Fermi level goes on falling below the conduction band (E_C). On application of potential difference across the n type semiconductor, the free electrons in the crystal are attracted towards the positive terminal and few holes towards the negative terminals. Thus, the current flow takes place. The current flow in the n type semiconductor is mainly due to the free electrons and hence in n type the majoritycharge carries are the electrons. In n type semiconductor, minority charge carriers are given as

$$n_h = n_i^2 / n_e$$

or,
$$n_h = n_i^2 / N_d$$

Since, the density of free electrons is $n = n_i + N_d$, where N_d is the density of donor impurity electron and n_i is the density of intrinsic semiconductor electrons.

7.5.2.2 p-type semiconductor

In a pure (intrinsic) Si or Ge semiconductor, each nucleus uses its four valence electrons to form four covalent bonds with its neighbors as shown in figure. Each ionic core, consisting of the nucleus and non-valent electrons, has a net charge of +4, and is surrounded by 4 valence electrons. Since there are no excess electrons or holes in this case, the number of electrons and holes present at any given time will always be equal.

Now, if one of the atoms in the semiconductor lattice is replaced by an element with three valence electrons, as shown in figure 7.6, such as a Group 3 element like Boron B or Gallium Ga, the electron-hole balance will be changed. This impurity will only be able to contribute three valence electrons to the lattice, therefore leaving one excess hole as shown in figure. Since holes will accept free electrons, a Group 3 impurity of periodic table, is also called an acceptor. Sincean acceptor donates excess holes, which are considered to be positively charged, a semiconductor that has been doped with an acceptor is called a p-type semiconductor, *p* stands for positive. It is observed that the material as a whole remains electrically neutral. In p-type semiconductor, the population of holes in valence band is more, whereas the population of free electrons in conduction band is less. So, current conduction is mainly because of holes in valence band. Free electrons in conduction band constitute little current. Hence in p-type semiconductor, holes are called majority carriers and free electrons are called minority carriers.

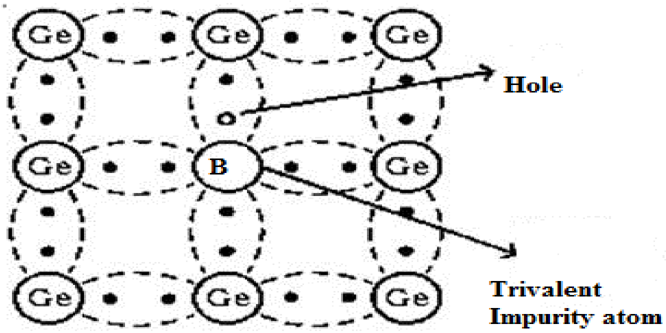
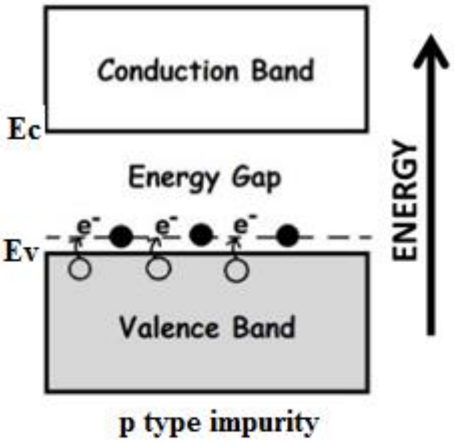


Figure 7.6: p type semiconductor

At room temperature, the number of holes in the valence band is greater than the number of electrons in the conduction band. Hence, the probability of occupation of energy levels by the holes in the valence band is greater than the probability of occupation of energy levels by the electrons in the conduction band. This probability of occupation of energy levels is represented in terms of Fermilevel. Therefore, the Fermi level in the p-type semiconductor lies close to the valence band. The expression for Fermi energy in p type semiconductor is given as

$$E_F = E_V + k_B T \log(N_V / N_a),$$

Where, $N_a$is the density of acceptor atoms and $N_V = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2}$, the equation shows that the Fermi level lies above the top of the valence band as shown in figure 7.7 and 7.8. The Fermi level depends upon the number of impurity atoms and the temperature of the specimen. On increasing the number of impurity atoms, the number of holes in the valence increases and the Fermi level shifts towards the valence band. As temperature increases, the electrons from the valence band excited to the conduction band and the crystal behaves like an intrinsic semiconductor when the number of electrons in the conduction band is equal to the number of holes in the valence band. At very high temperature, Fermi level shift towards the middle of the forbidden energy band gap.



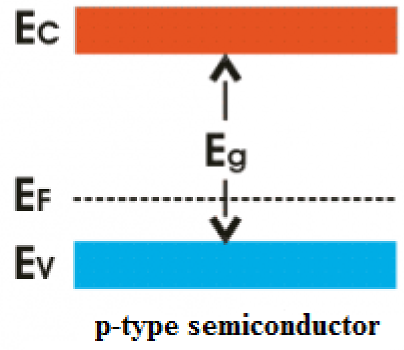


Figure 7.7: p type impurity semiconductor

Figure 7.8: Fermi level in p type

Example 1: Pure Si at 300K has equal electron n_e and n_h concentration of 1.5×10^{16} /m^3. Doping of Boron increases hole concentrations n_h to 4.5×10^{22}/ m^3. Calculate n_e in the doped Si.

Solution: We have in doped semiconductor, $n_e n_h = n_i^2$

Where, n is the intrinsic concentration in a pure semiconductor.

$n_h = 4.5 \times 10^{22}/\ m^3$

$n_i = 1.5 \times 10^{16}\ /m^3$

Putting these values in the above equation we get,

$$n_e = n_i^2 / n_h = \frac{(1.5\times10^{16})^2}{4.5\times10^{22}}$$

$= 5.0 \times 10^9/m^3$

Example 2: The number of electron hole pair in an intrinsic semiconductor is 2 x $10^{19}/m^3$ at 27^0C. if this semiconductor is doped by a donor impurity such as the number of conduction electrons becomes 2 x $10^{24}/m^3$, calculate the number of holes. Also calculate the dopant concentration.

Solution: for doped semiconductor, we know $n_e n_h = n_i^2$

$n_e = 2 \times 10^{24}/\ m^3$

$n_i = 2 \times 10^{19}\ /m^3$

$$n_h = n_i^2 / n_e = \frac{(2\times10^{19})^2}{2\times10^{24}}$$

$= 2 \times 10^{14}/m^3$

On doping it becomes an n type semiconductor.

Therefore, the number of dopant

$$N_d = n_e = 2\times10^{24} / m^3$$

7.6 DIFFERENCE BETWEEN INTRINSIC AND EXTRINSIC SEMICONDUCTORS

Intrinsic Semiconductors	**Extrinsic Semiconductors**
1. It is pure form. Pure Si or Ge is known as the intrinsic semiconductor 2. Holes and electrons are equal. These are not practically used	1. It formed by adding trivalent or pentavalent impurity to the pure semiconductor. 2. Number of holes are more in p type and number of electrons are more in n type as shown in figure 7.9.
3. Fermi level lies in between valence and conduction band	3.Fermi level lies near valence band in *n* type and near conduction band in *p* type as shown in figure 7.10

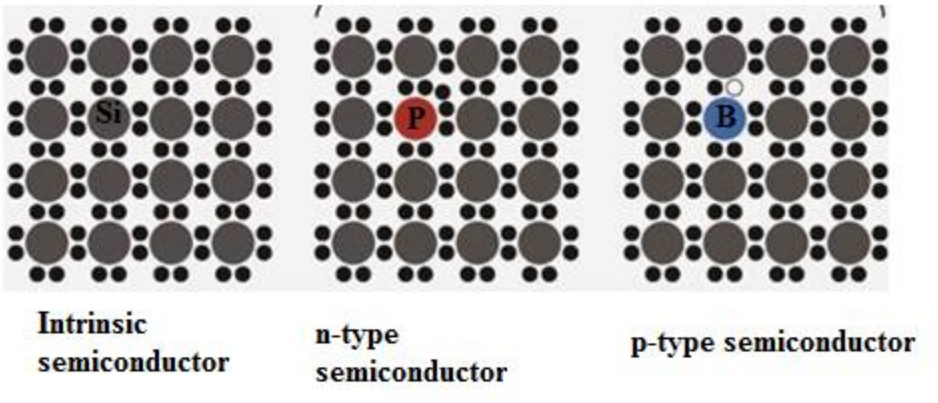


Figure 7.9: Difference between intrinsic and extrinsic semiconductor

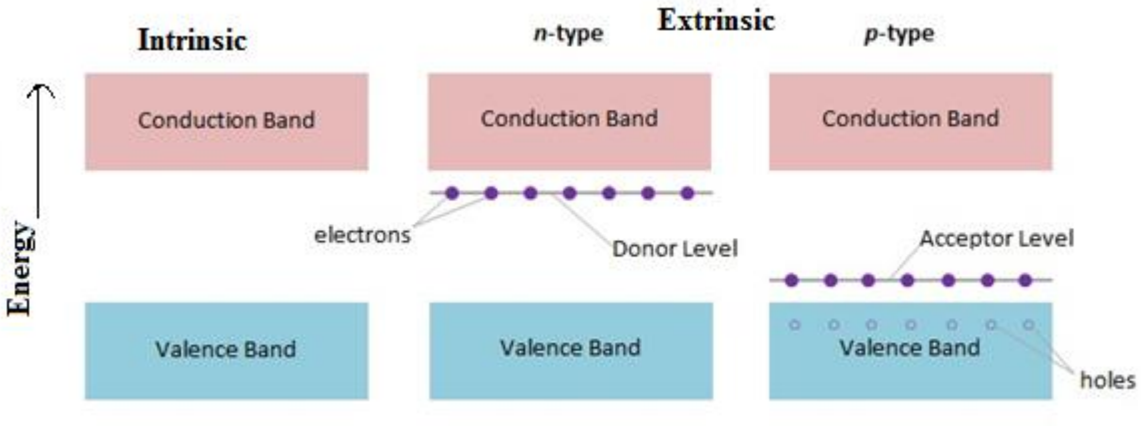


Figure 7.10: Band gap diagram of semiconductors

7.7 DRIFT CURRENT

Drift current is defined as the flow of electric current due to the motion of the charge carriers under the influence of an external electric field.

In a semiconductor, there are two types of charge carriers, they are electrons and holes. When the voltage is applied to a semiconductor, the free electrons move with drift velocity v_d towards the other end as indicated in figure 7.11.

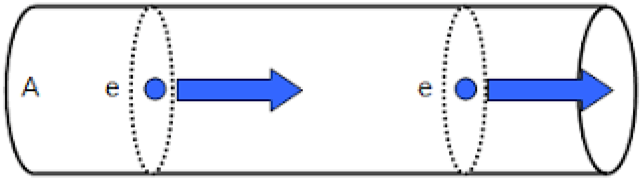


Figure 7.11: Flow of charge carriers

If q is the charge carried through the section of wire in time t, then then current is given as

$$i = q / t$$

Let *n* be the charge density per unit volume, therefore the total number of charge carriers in passing per second through the cross-section of wire is nAv_d . So, $nAv_d t$ electrons will pass through the cross section of wire in *t* second. Thus, charge passing through anycross-section of wire in *t* second is given as

$$q = (nAv_d t)e$$

Therefore, by definition

$$i = \frac{nAv_d t}{t}$$

or, $$i = neAv_d$$

It is well known relation between electric current and the drift velocity.

We may define current density,

$$j = i / A = nev_d ,$$

This is the relation of current density and drift velocity.

In vector form, $\vec{j} = ne\vec{v}_d$

7.8 MOBILITY

The ability of an electron to move through a semiconductor, in the presence of applied electric field is called electron mobility.

Let us consider a specimen of length *l*, area of cross section A and having electron concentration n_e and hole concentration $n_h$as displayed in figure 7.12. If a potential difference *V* is applied across thesample semiconductor, it creates an electric field, given as

$$E = V / l$$

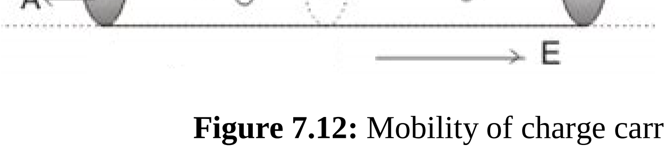


Figure 7.12: Mobility of charge carriers

Due to the electric field, electrons and holes both drift in opposite direction with velocity $\vec{v}_d$ and creates the current i_e and i_h respectively.

Hence, $$i_e = n_e eAv_d$$

And

$$i_h = n_h eAv_d$$

Therefore, total current due to both charge carriers

$$i = i_e + i_h = n_e eAv_d + n_h eAv_d$$

or, current density $$i / A = n_e ev_d + n_h ev_d$$

If, R is the resistance of semiconducting specimen and ρ is the resistivity, we have a relation

$$R = \rho l / A$$

Therefore dividing $E = V / l$ by $R = \rho l / A$, we get

$$E / \rho = i / A$$

On substituting the value of $i / A = n_e ev_d + n_h ev_d$ in the above expression, we get

$$E / \rho = e(n_e v_d + n_h v_d)$$

or, $$1/\rho = e(n_e v_d + n_h v_d) / E$$

Let us define $\mu_e = v_d / E$, mobility due to electrons and $\mu_h = v_d / E$ mobility due to holes, hence above equations become as

$$1/\rho = e(n_e \mu_e + n_h \mu_h)$$

or $$\sigma = e(n_e \mu_e + n_h \mu_h),$$

Where σ is reciprocal of resistivity, therefore defined as conductivity of semiconductor. Hence, the electrical conductivity of semiconductor is written as

$$\sigma = e(n_e \mu_e + n_h \mu_h)$$

This is the expression of electrical conductivity of semiconductor, which depends upon the concentration and mobility of charge carriers. I would like to mention here; the mobility of electron is higher than the nobility oh holes.

Example 3: Find the conductivity of *p* type Ge crystal which is doped with acceptor atoms of concentration 2 x 10^{17} atoms/ cm^3 and all acceptor atoms are active. Ignore minority concentration, given $\mu_h = 1900 cm^2 / volt\sec$

Solution: In a *p* type semiconductor, the hole concentration is roughly equal to the acceptor concentration

That is

$$n_h = N_a = 2\times10^{17} / cm^3$$

We know the expression of conductivity as

$$\sigma = n_e e\mu_e + n_h e\mu_h$$

In p type semiconductor

$n_h > n_e$ and holes are the majority charge carriers, so we have $\sigma = n_h e\mu_h$

On putting the given values, we get

= 6100/ ohm meter

Example4: The mobility of electrons and holes sample intrinsic germanium at room temperature is 0.36 and 0.17 m^2/Volt/s respectively. If the electron and hole densities are each equal to 2.5 x 10^{19}/ m^3, calculate the electrical conductivity and resistivity of germanium.

(a) $\sigma = n_e e\mu_e + n_h e\mu_h$

$$n_e = n_h = n_i$$

$$\sigma = 2.12 / ohm / m$$

Resistivity

$$\rho = \frac{1}{\sigma} = 0.47\Omega m$$

7.9 THE HALL EFFECT

It isGiven by American Physicist Hall in 1879 a graduate student. When a magnetic field is applied perpendicular to the current carrying conductor, a potential difference is developed between those points on opposite sides of the conductor. This is called the Hall Effect. This phenomenon tells us how the charges constituting electric current moves through a conductor and what these charges are.

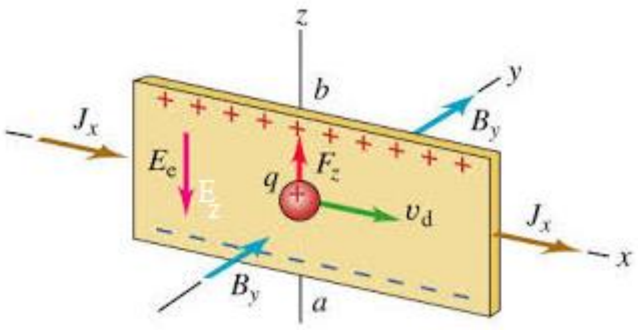


Figure 7.13: Hall effect

Let us consider a conductor in the form of flat strip as shown in figure 7.13. If the charge carriers are positive (+q). Let I (or, current density J= I /A) be the current flowing in the conductor which is placed in magnetic field as shown in figure. The force is exerted on the charge carriers due to this magnetic field and current. The moving charge is driven towards the upper edge of the strip given by the magnetic force

$$F_z = qv_d B_y ,$$

where v_d is the drift velocity of chargecarriers. Due to this an excess positive charge accumulates at the upper edge of the strip leaving an excess negative charge to its lower edge. This accumulation continues until the resulting transverse electrostatic field E becomes large enough to cause a force $\vec{F}_z = q\vec{E}_z$, that is equal and opposite the magnetic force $F_z = qv_d B_y$. This electrostatic field causes a transverse potential difference between opposite edges of the strip, called the Hall Voltage.

The polarity depends upon whether the moving charges are positive or negative.

In steady state

$$qE_z = qv_d B_y$$

We know the current density

$$J_x = nqv_d$$

From these equations, we get

$$n = \frac{J_x B_y}{E_z q},$$

Where, n is the number of charge carriers.

or,

$$R_H = \frac{1}{nq} = \frac{E_z}{J_x B_y},$$

The factor *1/nq* is called the Hall coefficient R_H of the material of the conducting strip.

Example5: The carrier concentration in n type semiconductor is $10^{19}/\text{m}^3$. What is the value of Hall coefficient?

Solution: $R_H = \frac{1}{nq}$

$$R_H = \frac{1}{10^{19} \times 1.6 \times 10^{-19}}$$

= 0.262 m^3/C

7.10 EFFECTIVE MASS OF AN ELECTRON

The electrons in a crystal are not free, but instead interact with the periodic potential of the crystal lattice. The behavior of interacting electron with crystal concerning the external forces is different from that of free electron. In the crystal lattice, the variation of the electron behavior can be grasped into account simply by seeing the electron to have an effective mass $m*$rather than its free space mass m.It differs with the direction of the motion of the electron in the lattice. Consider an electron moving along x direction in electric field $\vec{E}$. Let the electron acquires velocity *v* in time *dt* over a distance *dx*. Work done by the force is given as

$$dW = d\varepsilon = eEdx = eEvdt$$

or, $$d\varepsilon = eEv_g dt \quad \text{(considering, } v = v_g \text{ group velocity)}$$

We have Einstein De Broglie relation

$\varepsilon = h\nu = h\omega / 2\pi$, On differentiating it, we get

$$d\varepsilon = h/2\pi(\frac{d\omega}{dk})dk$$

or, $$d\varepsilon = \frac{h}{2\pi} v_g dk$$

or, $$\frac{dk}{dt} = \frac{h}{2\pi} eE$$

We know, $$v_g = \frac{d\omega}{dk} = \frac{2\pi}{h}\frac{d\varepsilon}{dk},$$

Differentiating it with respect to *t*, we get

$$\frac{dv_g}{dt} = (\frac{2\pi}{h})^2 \frac{d^2\varepsilon}{dk^2} eE \text{ ,}$$

or,

$$\frac{dv_g}{dt} / eE = (\frac{2\pi}{h})^2 \frac{d^2\varepsilon}{dk^2}$$

Left hand side is nothing but the dimension of inverse of mass, so we can write as

$$\frac{1}{m^*} = \frac{4\pi^2}{h^2} \frac{d^2\varepsilon}{dk^2}$$

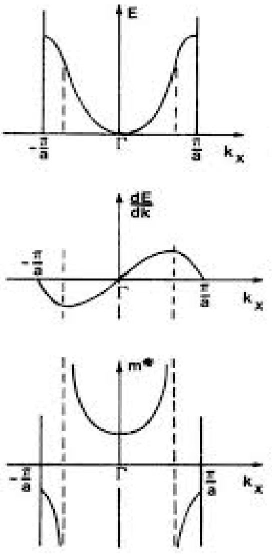


Figure 7.14: Electrons in periodic potential

Where, $m*$is define as the effective mass of an electron. The effective mass is a new concept and causes because of the interaction of the electron wave packet with the periodic lattice as shown in figure 7.14. The effective mass of an electron may be positive or negative as shown in figure. It is evident that the effective mass is positive in the lower part of the band and negative close to the zone boundary. The effective mass may be equal to m, only when the energy is not close the edge of the band and E versus k curve is parabolic. In case of semiconductor, where full or almost full valence bands are concerned, effective mass varies with the mass m.

7.11. SUMMARY

In this unit, you have studied about the types of semiconductors such as intrinsic semiconductor and extrinsic semiconductor. To present it clear, valence band, conduction band and forbidden band are discussed in details. You have studied how on adding trivalent impurity pure semiconductor becomes p type semiconductor and on adding pentavalent impurity pure semiconductor become n type semiconductor. You have also understood how the Fermi level shifted towards the valence band (due to trivalent impurity) or towards the conduction band (due to pentavalent impurity). You have seen that that in pure semiconductor, Fermi level is just in middle in valence band and conduction band. Here, you have learned that on increasing the temperature conductivity increases of semiconductor. You have also reviewed about the mobility and conductivity of the charge carriers. A new concept of electron effective mass is debated and it is shown that how the effective mass becomes negative or positive. You have also skilled about the Hall Effect and its applications. Many solved examples are given in this unit to make the concept clear. To check your progress, some conceptual questions are given at the end.

7.12 GLOSSARY

Across –through.

Intrinsic– basic.

Extrinsic – impure.

Drift – flow.

Specimen – sample.

Characteristic – specific.

Categorized – classified.

Minority – lesser.

Majority – bulk.

Surrounded – bounded.

Doped - fixed.

Ignore – overlook.

Donor – contributor.

Phenomenon – fact.

Effective – actual.

Periodic – cyclic.

Concerned– affected.

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7.15 TERMINAL QUESTIONS

1. How does the energy gap in an intrinsic semiconductor vary, when doped with pentavalent impurity?
2. Why is Ge preferred over Si for making semiconductor devices?
3. What is hole? How does it behave?
4. What is the purpose of making extrinsic semiconductor by adding impurity in intrinsic semiconductor?
5. What is the effect of temperature rise on the resistivity and conductivity of a pure semiconductor?
6. Why is semiconductor damaged when a strong current is passed through it?
7. Why? Semiconductor is opaque to visible light, but transparent to infra-red radiation.
8. Calculate the intrinsic conductivity and resistivity of pure Si at room temperature, assuming intrinsic carrier (electron hole pair) density at this temperature to be 1.5 x 10^{16}/ m^3. The electron and hole mobilities in Si are 0.135 and 0.048 m^2/V s respectively.
9. The semiconductor has 6 x 10^{19} electrons and 7 x 10^{20} holes/m^3. If the mobilities of electrons and holes are 0.10 m^2/ V s and 0.06 m^2/V s respectively. Calculate the conductivity of the semiconductor.
10. A Ge crystal is doped with 10^{14} donor atoms/ cm^3. Assuming that all the donors are ionized determine the resistivity of the doped sample. ($\mu_e = 0.39 m^2 / Vs$).

Select the right choice

11. Silicon has 14 electrons. Its outermost orbit is
    (a) Empty
    (b) Completely filled
    (c) Half filled
    (d) None of the above
12. Main current in an intrinsic semiconductor is due to
    (a) Conduction band electrons
    (b) Valence band holes
    (c) Valence band electrons
    (d) Thermally generated electrons
13. When Ge is doped with indium, it becomes
    (a) N type semiconductor
    (b) P type semiconductor
    (c) An insulator
    (d) Photo transistor
14. The energy gap between the valence and conduction bands in a semiconductor is of the order of
    (a) 0.025 eV
    (b) 1 eV
    (c) 6 eV
    (d) Negligible
15. An example of p type semiconductor is
    (a) pure Ge
    (b) germanium doped with arsenic
    (c) silicon doped with boron
    (d) germanium doped with carbon

7.16 ANSWERS

1. Energy gap decreases.

2. The energy gap for Ge is only about 0.7 eV while for Si it is about 1.1 eV.

3. A hole indicates a vacancy left by an electron in the p type semiconductor. It behaves like a positively charged particle.

4. Since the conductivity of intrinsic semiconductor is very small. By introducing impurity in it, the conductivity of semiconductor is increased.

5. The resistivity decreases, conductivity increases.

6. Since at room temperature, a semiconductor has a finite resistance. When a strong current is passed through it, it gets heated and the covalent bonds break up. This give rise to a very

large number of free electrons. The semiconductor then behaves like a conductor that is why; it ceases to be a conductor.

7. Valence band of semiconductor is full; above it there is an empty conduction band with a very small gap of around 1 eV in between them. Photons of visible light have energies roughly between 1 and 3 eV and so they are absorbed by the valence electrons which are excited to the conduction band. Thus, the semiconductor is opaque to the visible light. The photons of infra-red radiation are of much smaller energies and fail to excite the electrons in the valence band. So, the infra-red radiation passes through the semiconductor, because of that, the semiconductor is transparent to it.

8. Conductivity = 4.4 x 10^{-4} / ohm meter, resistivity = 2.27 x 10^{3} ohm meter

9. Conductivity = 7.68 / ohm meter

10. Resistivity = 0.16 ohm meter

11. c

12. a

13. b

14. c

15. c

UNIT 8 LATTICE VIBRATIONS AND SPECIFIC HEAT OF SOLIDS

Structure

8.1 INTRODUCTION

A lattice may be considered as a periodic arrangement of atoms, ions or molecules which are joined together by elastic springs as shown in figure 1. The displacement of any atom is shared by all the surrounding atoms. The lattice may vibrate in normal modes due to their internal energy or may experience forced vibrations under the effect external forces which may be mechanical or electromagnetic in nature. The vibration of first type gives information about the thermal properties of solids like specific heat, thermal conductivity etc, while the second types of vibrations gives the optical or acoustical properties of solids.

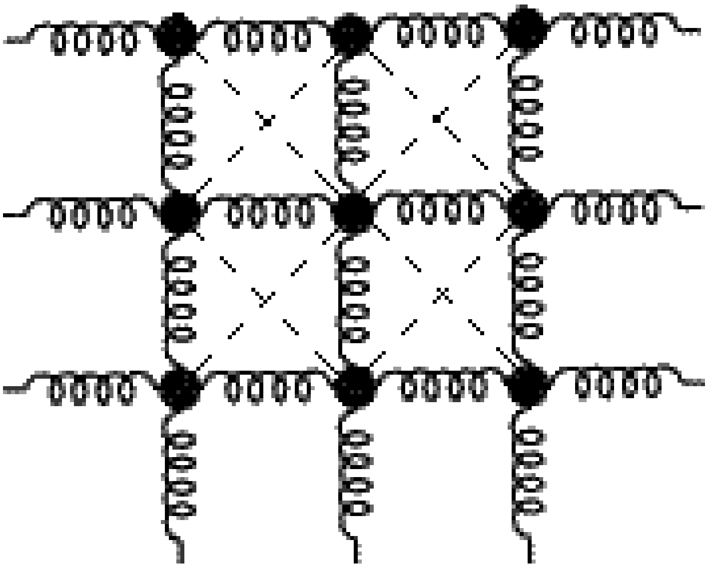

Figure 1

8.2 OBJECTIVES

This chapter includes the study of interactions between atoms and molecules of the solids via phonon as a mediator. After the study of this chapter we shall be able to know

- The lattice vibrations in monoatomic lattices.
- Lattice vibrations in diatomic lattices.
- What is phonon and how to calculate its momentum?
- Classical model of specific heat.

- Quantum model of specific heat.
- Limitations of classical and quantum models.
- Specific heat of gases.
- Contribution of vibrational motion to the specific heat etc.

8.3 VIBRATIONS OF ONE DIMENSIONAL MONOATOMIC LATTICE

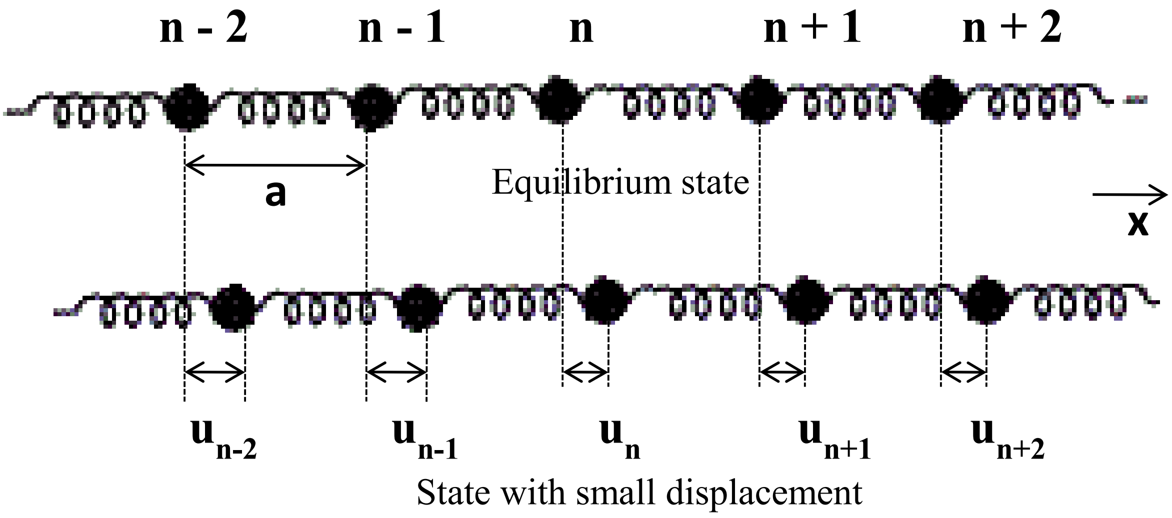

Figure 2

Consider a one dimensional array of atoms with each atom of having mass m and these masses are attached to one another by massless springs. Consider the equilibrium state of the atoms when these are situated at equal spacing, atomic sites are represented by n-1, n-2, n, n+2 etc. as shown in figure 2. In the state of vibratory motion along the x-axis the atom will execute periodic motion about their equilibrium position and become source of elastic wave which propagate through the medium. Suppose at any instant of time the displacement of nth, (n+1)th, (n+2)th etc. atoms from their mean position be u_n, u_{n+1}, u_{n+2} etc. respectively. Assuming the imaginary springs are perfectly elastic, the force between any two atoms will follow Hooke's law i.e. the force required to produce an atomic displacement is proportional to the displacement itself. If u is the displacement of a spring with spring constant γ, the force exerted by any spring on the atom is given by

$$F = \gamma u \qquad (1)$$

Since the nth atom is attached to (n-1)th and (n+1)th atoms by two springs. The net force on nth atom is

$$F = \gamma\{(u_{n+1} - u_n) - (u_n - u_{n-1})\}$$

$$= \gamma(u_{n+1} - 2u_n + u_{n-1}) \qquad (2)$$

By Newton's second law

$$Force = mass \times acceleration$$

Hence

$$m\frac{d^2u_n}{dt^2} = \gamma(u_{n+1} - 2u_n + u_{n-1}) \qquad (3)$$

where $\frac{d^2u_n}{dt^2}$ represents the accelerations of the nth atom. The periodic solution of this equation is given by

$$u_n = u_o e^{i(\omega t - Kna)} \qquad (4)$$

where K is wave vector or propagation vector and ω is the angular frequency of the wave. Similarly the solutions of (n+1)th and (n-1)th atoms may be written as

$$u_{n+1} = u_o e^{i\{\omega t - K(n+1)a\}} \qquad (5)$$

$$u_{n-1} = u_o e^{i\{\omega t - K(n-1)a\}} \qquad (6)$$

FromEquation (4) we get$\frac{d^2u_n}{dt^2} = -\omega^2 u_o e^{i(\omega t - Kna)}$ (7)

Putting the value of $\frac{d^2u_n}{dt^2}$, u_{n+1} and u_{n-1} in Equation (3)

$$-m\omega^2 u_o e^{i(\omega t - Kna)} = \gamma\left(u_o e^{i\{\omega t - K(n+1)a\}} - 2u_o e^{i(\omega t - Kna)} + u_o e^{i\{\omega t - K(n-1)a\}}\right)$$

$$-m\omega^2 = \gamma(e^{iKa} - 2 + e^{-iKa})$$

$$-m\omega^2 = \gamma(e^{iKa/2} - e^{-iKa/2})^2 \qquad (8)$$

since

$$\sin Ka = \frac{e^{iKa} - e^{-iKa}}{2i} \quad (9)$$

$$\sin^2 Ka = -\frac{\left(e^{iKa} - e^{-iKa}\right)^2}{4} \qquad (10)$$

Using this expression in equation (8),

$$m\omega^2 = 4\gamma sin^2\left(\frac{Ka}{2}\right) \qquad (11)$$

$$\omega = \pm\sqrt{\frac{4\gamma}{m}}sin\left(\frac{Ka}{2}\right) \qquad (12)$$

If

$$q = \gamma a \quad (13)$$

and $\rho = m/a$ (14)

where q is longitudinal stiffness and ρ is the mass per unit length of atomic chain. Therefore equation (12) becomes

$$\omega = \pm\frac{2}{a}\sqrt{\frac{q}{\rho}}sin\left(\frac{Ka}{2}\right) \qquad (15)$$

$$\omega = \frac{2}{a}v_s sin\left(\frac{Ka}{2}\right)(frequency\ is\ always\ positive\ ) \qquad (16)$$

where v_s is a constant for a given lattice and represents the velocity of sound in lattice.Since the value of frequency ω is always positive or we can say its magnitude does not depend on the sign of K i.e.

$$\omega = \frac{2}{a}v_s\left|sin\left(\frac{Ka}{2}\right)\right| \qquad (17)$$

Equation(17) is known as dispersion relation and is plotted in figure 3.

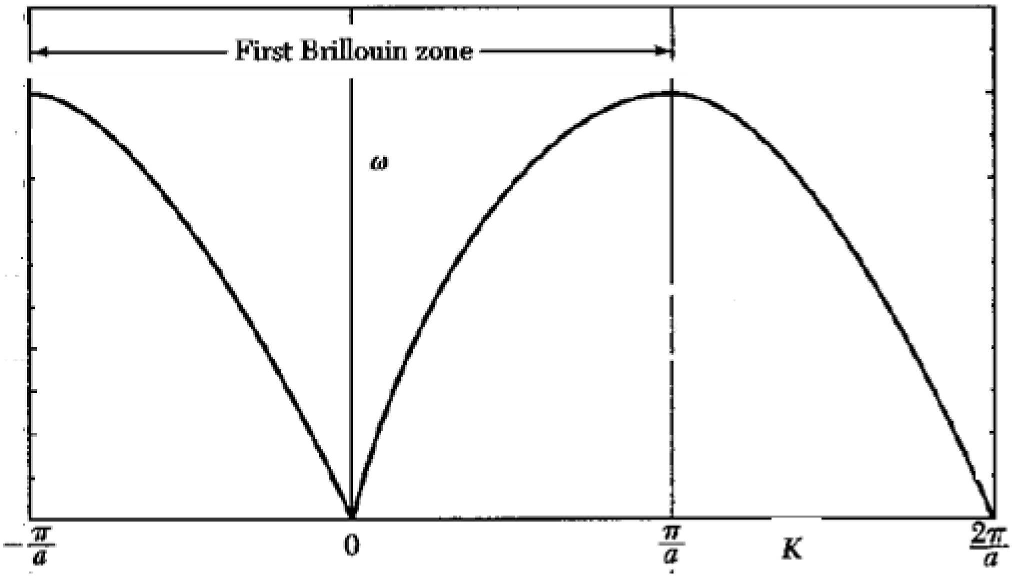

Figure 3

The following important results are obtained from this relation: -

1. At low frequencies,

$$\lim_{K\to 0} sin\left(\frac{Ka}{2}\right) = \frac{Ka}{2} \qquad (18)$$

Equation (17) gives

$$\omega = Kv_s \qquad (19)$$

The phase velocity of the wave is defined as the ratio of frequency with wave vector and is given by

$$v_p = \frac{\omega}{K} \qquad (20)$$

The group velocity is defined as the velocity of a group of waves and is given by

$$v_g = \frac{d\omega}{dK} \qquad (21)$$

2. At high frequencies, phase and group velocities are different and can be obtained from equation (17) as

$$v_p = \frac{\omega}{K} = \frac{2v_s}{aK} sin\left(\frac{Ka}{2}\right) \qquad (22)$$

and

$$v_g = \frac{d\omega}{dK} = v_s cos\left(\frac{Ka}{2}\right) \quad (23)$$

Thus, both v_p and v_g are the function of frequencies. This is referred to as the phenomenon of dispersion and the medium is called dispersive medium.

8.4. VIBRATIONS OF ONE DIMENSIONAL DIATOMIC LATTICE

Consider a chain of one dimensional primitive lattice consisting two atoms of masses m and M which are placed alternatively along the x-axis with an inter atomic spacing ‘a’. Suppose the atoms are located at sites represented by 2n-2, 2n-1, 2n, 2n+1, 2n+2, 2n+3 etc as shown in figure 4. Let u_{2n} is the displacement of an atom corresponding to the 2nth site at any time. Using the atom similar to monoatomic lattice we can obtain the equation of motion for lighter and heavier atoms separately.

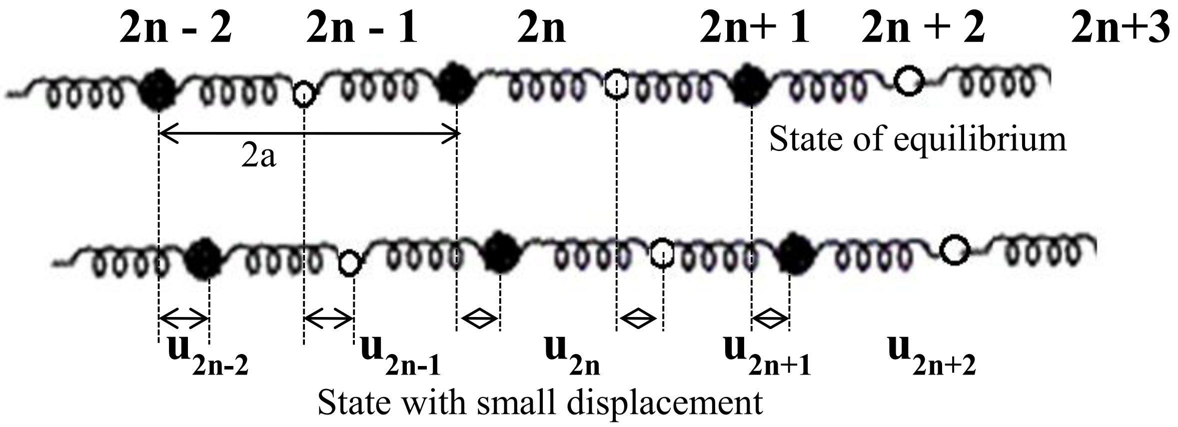

Figure 4

Equation of motion for mass ‘m’ is

$$m\frac{d^2u_{2n}}{dt^2} = \gamma(u_{2n+1} - 2u_{2n} + u_{2n-1}) \quad (24)$$

and equation of motion for mass ‘M’ is

$$M\frac{d^2u_{2n+1}}{dt^2} = \gamma(u_{2n+2} - 2u_{2n+1} + u_{2n}) \quad (25)$$

where $\frac{d^2u_{2n}}{dt^2}$ represents the accelerations of the 2nth atom. The periodic solution of these equations are given by

$$u_{2n} = Ae^{i(\omega t-2Kna)} \quad (26)$$

and $$u_{2n+1} = Be^{i(\omega t-(2n+1)Ka)} \quad (27)$$

where K is wave vector or propagation vector and ω is the angular frequency of the wave. Here we assumed that the vibrational frequency of both type of atoms is same. A and B are the amplitude of vibrations.

Substituting the values of u_{2n} and u_{2n+1} from equation (26) and (27) in equation (24) and (25) we get

$$-m\omega^2 A = \gamma B(e^{iKa}+e^{-iKa}) - 2\gamma A \quad (28)$$

or $(2\gamma - m\omega^2)A - 2\gamma\cos Ka\, B = 0$ (29) $-M\omega^2 B = \gamma A(e^{iKa}+e^{-iKa}) - 2\gamma B$

or $-2\gamma\cos Ka\, A + (2\gamma - M\omega^2)B$(30)

Equation (29) and (30) are the homogeneous equations. The nonzero solution for A and B only if

$$\begin{vmatrix} 2\gamma - m\omega^2 & -2\gamma\cos Ka \\ -2\gamma\cos Ka & 2\gamma - M\omega^2 \end{vmatrix} = 0 \quad (31)$$

or $$(2\gamma - m\omega^2)(2\gamma - M\omega^2) - 4\gamma^2\cos^2 Ka = 0 \quad (32)$$

$$(4\gamma^2 - 2\gamma m\omega^2 + mM\omega^4 - 2\gamma M\omega^2) - 4\gamma^2\cos^2 Ka = 0$$

$$mM\omega^4 - (2\gamma m + 2\gamma M)\omega^2 + 4\gamma^2(1-\cos^2 Ka) = 0$$

$$\omega^4 - \frac{2\gamma(m+M)}{mM}\omega^2 + \frac{4\gamma^2\sin^2 Ka}{mM} = 0 \quad (33)$$

We can solve this equation exactly for ω^2, but it is simpler to examine the limiting case Ka<<1 and $Ka = \pm\pi$ at the zone boundary. For small Ka we have $\sin^2 Ka \cong K^2a^2$, and the two roots are

$$\omega^2 = 2\gamma\left(\frac{1}{m}+\frac{1}{M}\right)\text{(Optical branch)(34)}$$

$$\omega^2 = \frac{\gamma}{2}\left(\frac{K^2a^2}{m+M}\right)\text{(Acousticalbranch)(35)}$$

The extant of the first Brillouin zone is $-\frac{\pi}{a} \leq K \leq +\frac{\pi}{a}$ where 'a' is lattice constant. At $K_{max} = \pm\frac{\pi}{a}$ the roots are

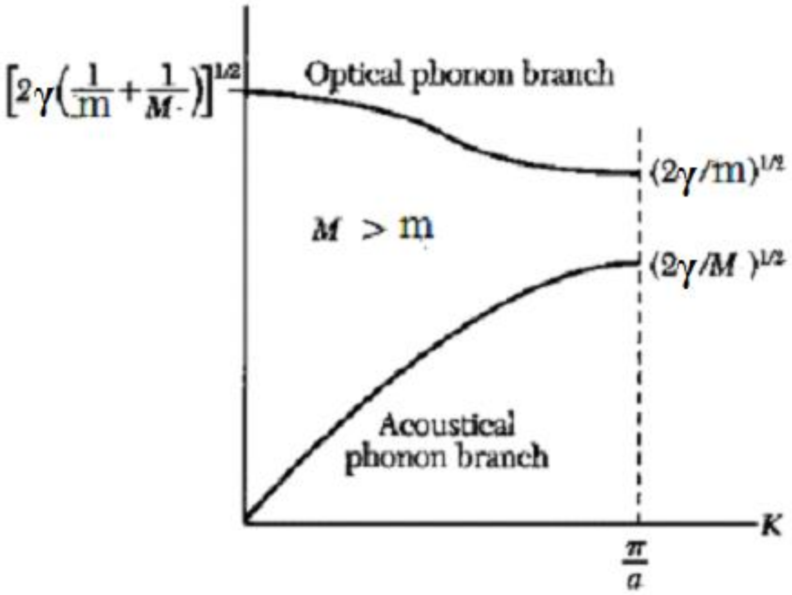

Figure 5

$$\omega^2 = \frac{2\gamma}{M}(36) \qquad and \qquad \omega^2 = \frac{2\gamma}{m} \qquad (37)$$

The dependence of ω on K is shown in fig. 5 for M > m

The particle displacement of transverse acoustical (TA) and transverse optical (TO) branches is shown in fig 6. For the K = 0 we find

$$\frac{u_{2n+1}}{u_{2n}} = -\frac{m}{M} \qquad (38)$$

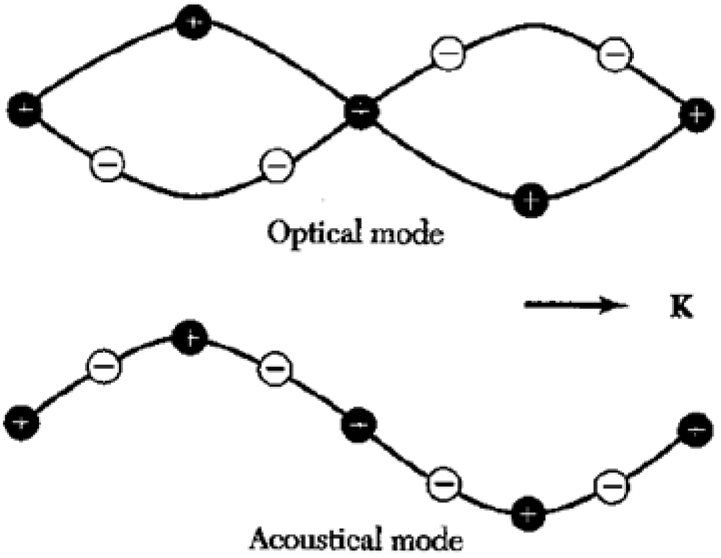

Figure 6

The atoms vibrate against each other, but their centre of mass is fixed.

8.5 CONCEPT OF PHONON

The energy of lattice vibrations is quantized and the quantum of this energy is called phonon. Phonon is analogues to photon, the quanta of electromagnetic wave. All types of lattice vibrations in crystals comprise phonons, thermal vibrations are thermally excited phonons, sound waves are acoustical phonons and excitations of optical branch generate optical phonons. If n is the number of phonons in a particular mode of vibration the total energy of the mode is written as

$$\epsilon = \left(n + \frac{1}{2}\right)\omega\hbar \tag{39}$$

n can be zero or positive integer. Since the number of phonon may change with temperature, the average number of phonons in a vibrational mode is given by

$$\bar{n} = \frac{1}{\exp\left(\frac{\omega\hbar}{k_B T}\right) - 1} \tag{40}$$

where k_B is the Boltzmann’s constant and T is absolute temperature of the crystal. Hence the number of phonons can be increased and decreased by raising or lowering of the temperature. The frequency of the phonon waves may vary from 10^4 to 10^{12} Hz. The concept of wave particle duality, which applies to photons, applies equally well as to photons. There is however no experimental evidence that the energy of an elastic wave is quantized but it does exist for photons e.g. photoelectric effect. Despite this we have following evidences.

1. The approach of the lattice heat capacity to zero as the temperature approaches zero can be explained only if the lattice vibrations are quantized.
2. X-rays and neutrons are scattered inelastically by crystals. The change of energy and momentum in this process corresponds to the gain or loss of one or more quanta of energy.

8.6 MOMENTUM OF PHONON

A lattice phonon does not carry any momentum, but it interacts with other particles as if it has a momentum $\hbar K$, where K is wave vector of the phonon. Using de Broglie relation we can write

$$p = \frac{h}{\lambda} = \hbar K \tag{41}$$

The quantity $\hbar K$ is sometimes called the crystal momentum. The physical significance of $\hbar K$ is provided by the momentum conservation law in crystal.

8.7 SPECIFIC HEAT OF SOLIDS:

According to first law of thermodynamics, the amount of heat dQ given to a system must be equal to the sum of increase in energy dE of the system and work done by the system. We may write this process mathematically as

$$dQ = dE + p\,dV \tag{42}$$

The energy added to the system may be expressed as

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \tag{43}$$

Using this equation, (42) may be expressed as

$$dQ = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + p\,dV \tag{44}$$

$$dQ = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right] dV \qquad (45)$$

The specific heat of any substance is defined as the quantity of heat required to raise the temperature of unit mass of substance through 1°C. The specific heat of same substance is different at different temperatures; generally the specific heat determined experimentally is the mean specific heat. There exists an infinite number of specific heats but here we are interested in only two

1. Specific heat at constant volume C_V.
2. Specific heat at constant pressure C_P.

If dQ units of heat raise the temperature of mass m of a substance dT, at constant volume, then the mean specific heat of the substance using equation (45) is

$$C_V = \frac{1}{m}\left(\frac{dQ}{dT}\right)_V = \frac{1}{m}\left(\frac{dE}{dT}\right)_V \qquad (46)$$

For solids at low temperature only specific heat at constant volume C_V exists while for liquid and gases both C_V *and* C_P exist. In following figure 7 C_V *and* C_P as a function of temperature for copper are shown. It is clear that at low temperature their difference becomes very small and both go to zero at absolute zero of temperature.

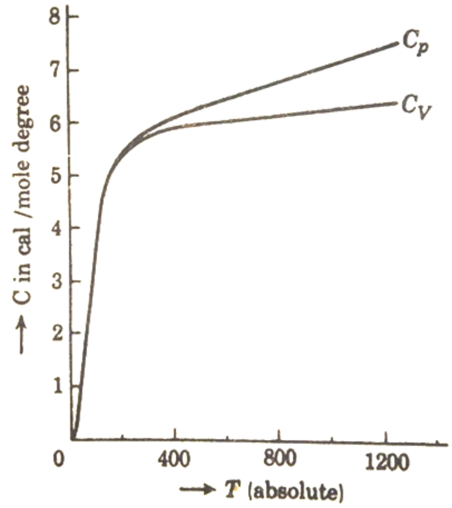

Figure 7. Variation of specific heat of copper.

8.8 CLASSICAL THEORY OF SPECIFIC HEAT (DULONG PETIT'S LAW)

According to this law "the product of atomic weight and the specific heat of an element at constant volume is constant for a number of elements in solid state and is equal to 5.96". This value agrees with the value derived from kinetic molecular theory.

According to classical kinetic theory of the atoms of a solid are at rest at absolute zero of temperature. The energy of solids in this state is assumed to be zero. When the temperature of the substance is raised, the atoms are set into vibrations about their position of equilibrium symmetrically. Thus the vibrations of the atoms are simple harmonic in nature. In this case total energy of atom is given by

$$K.E.+P.E.$$

$$\frac{1}{2}m\dot{x}^2 - \frac{1}{2}Kx^2 \qquad (47)$$

where K is force constant and x is displacement. But in this case the average K.E. is equal to the average potential energy. Hence the average energy corresponding to one mode of vibration is equal to twice the kinetic energy corresponding to one degree of freedom. Thus the vibration of an atom in an elastic solid along one co-ordinate is equivalent to two degree of freedom.

Thus, according to law of equipartition of energy the average energy associated with the motion of an atom along one co-ordinate kT, where k is Boltzmann's constant.

As we know each atom is free to vibrate along three co-ordinate axes, the total average energy of each atom $= 3kT$

The total energy of one gram atom of solid containing N atoms is given by

$$E = 3NkT$$

$$= 3RT \qquad (48)$$

where $R = Nk$ is gas constant for one-gram atom. If the whole energy given to the solid is used to increase the energy of vibrations of atoms and during the rise in temperature the volume of the substance remains constant, then the atomic heat at constant volume, i.e. the energy required to raise the temperature of one gram atom through 1°C will be given by

$$C_V = \frac{dE}{dT} = 3R \qquad (49)$$

Clearly the atomic heat of solid at constant volume is

1. constant and independent of temperature.
2. equal to three times the gas constant R.

   The numerical value of R= 1.9856 cal. per gm. atom, the value of atomic heat at constant volume

   $$= 3\,R$$

   $$= 5.9568$$

   which is Dulong and Petit's law.

8.9 EINSTEIN'S THEORY OF SPECIFIC HEAT

A great step to explain the variation of specific heat with temperature was made by Einstein in 1906 on the basis of quantum theory. According to quantum theory heat energy is radiated in the form of discrete particles called photons, whose energy is equal to $nh\nu$, where h is Planck's constant and ν is the frequency of heat radiation and $n = 0,1,2,3 \ldots \ldots$.

Einstein's assumed that

1. The energy of the solid at absolute zero temperature state is zero. As the solid is heated the atoms are set into simple harmonic vibrations about their position of equilibrium.
2. Each atom of solid has three degrees of freedom like a molecule of monoatomic gas. The mean energy per degree of freedom is not kT as given by equilibrium law but equal to $\frac{h\nu}{e^{h\nu/kT} - 1}$.

The energy of one atom $= \frac{3h\nu}{e^{h\nu/kT}-1}$.

Energy of one-gram atoms containing N atoms $= \frac{3Nh\nu}{e^{h\nu/kT}-1}$.

Atomic specific heat at constant volume

$$C_V = \frac{dE}{dT}$$

$$= 3Nh\nu \left[\frac{-1}{(e^{\frac{h\nu}{kT}}-1)^2}\right] e^{\frac{h\nu}{kT}} \left(\frac{-h\nu}{kT^2}\right) \quad (50)$$

$$= \left(\frac{3Nk(h\nu)^2}{(kT)^2}\right) \left[\frac{e^{\frac{h\nu}{kT}}}{(e^{\frac{h\nu}{kT}}-1)^2}\right] \quad (51)$$

$$= 3Nk \left(\frac{h\nu}{kT}\right)^2 \left[\frac{e^{\frac{h\nu}{kT}}}{(e^{\frac{h\nu}{kT}}-1)^2}\right] \quad (52)$$

It is convenient to introduce the Einstein temperature θE defined by $\theta_E = \frac{h\nu}{k}$. The frequency corresponding to θ_E is called Einstein's frequency.

$$C_V = 3R \left(\frac{\theta_E}{T}\right)^2 \left[\frac{e^{\frac{\theta_E}{T}}}{(e^{\frac{\theta_E}{T}}-1)^2}\right] \quad (53)$$

$$where, \qquad \theta_E = \frac{h\nu}{k}$$

This is Einstein's equation for the atomic heat of solid at constant volume. The equation represents that the atomic heat is a function of temperature. The behaviour of atomic heat in two temperature regions is as follows.

Case 1- At high temperatures, $\frac{\theta_E}{T}$ approaches very small values and so we have

$$(e^{\frac{\theta_E}{T}}-1)^2 = \left[1+\frac{\theta_E}{T}+\frac{1}{2!}\left(\frac{\theta_E}{T}\right)^2+\frac{1}{3!}\left(\frac{\theta_E}{T}\right)^3+\cdots\ldots\ \ -1\right]^2$$

$$= \left(\frac{\theta_E}{T}\right)^2 \qquad (54)$$

putting this value in equation (i)

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2\left[\frac{1+\frac{\theta_E}{T}+\frac{1}{2!}\left(\frac{\theta_E}{T}\right)^2+\frac{1}{3!}\left(\frac{\theta_E}{T}\right)^3+\cdots}{\left(\frac{\theta_E}{T}\right)^2}\right] \qquad (55)$$

$$C_V = 3R\left[1+\frac{\theta_E}{T}+\frac{1}{2!}\left(\frac{\theta_E}{T}\right)^2+\frac{1}{3!}\left(\frac{\theta_E}{T}\right)^3+\cdots\right] (56)$$

$$C_V = 3RF_E\left(\frac{\theta_E}{T}\right) \qquad (57)$$

where F_E is called Einstein function, it determines the ratio of the specific heat at temperature T and the classical value 3R

as T→ ∞, $\frac{\theta_E}{T}$→0

Hence $C_V = 3R$ (58)

Thus, according to Einstein’s theory at high temperature the specific heat approaches 3R, which is in good agreement with experiments and Dulong’s and Petit’s law.

Case 2-When the value of temperature is very low i.e. $T \to 0, \frac{\theta_E}{T} \to \infty$, thus 1 may be neglected in the denominator of equation (52).Hence

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2\left[\frac{e^{\frac{\theta_E}{T}}}{(e^{\frac{\theta_E}{T}})^2}\right] \qquad (59)$$

$$= 3R\frac{\left(\frac{\theta_E}{T}\right)^2}{e^{\frac{\theta_E}{T}}} \qquad (60)$$

$$= 3R\frac{\left(\frac{\theta_E}{T}\right)^2}{\left[1+\frac{\theta_E}{T}+\frac{1}{2!}\left(\frac{\theta_E}{T}\right)^2+\frac{1}{3!}\left(\frac{\theta_E}{T}\right)^3+\cdots\right]} \qquad (61)$$

$$= 3R\frac{1}{\left[\frac{1}{\left(\frac{\theta_E}{T}\right)^2}+\frac{1}{\frac{\theta_E}{T}}+\frac{1}{2!}+\frac{1}{3!}\frac{\theta_E}{T}+\cdots\right]} = 0 \qquad (62)$$

Therefore, as the temperature tends to absolute zero the specific heat also tends to zero.

It is obvious from equation (52) that specific heat of different substances differs only because of difference in characteristic frequency ν. At corresponding temperature ν/T is same for all elements. Hence the experimental curve for all substances has same form.

Thus, the Einstein's theory is in good agreement with experiments.

Example1. Calculate Einstein's frequency if $\theta_E = 236K$. Given $k = 1.4 \times 10^{-23} J/K$ and $h = 6.6 \times 10^{-34} J.sec$.

Solution: Einstein's temperature is defined as

$$\theta_E = \frac{h\nu}{k}$$

or

$$\nu = \frac{k\theta_E}{h} = \frac{1.4 \times 10^{-23} \times 236}{6.6 \times 10^{-34}} = 5 \times 10^{12} Hz$$

Example 2. **(a)** For copper Einstein frequency is $2.49 \times 10^{12} Hz$, calculate the characteristic temperature θ_E.

(b) Specific heat C_V for copper is $23.8 \frac{joule}{mole.K}$ and for diamond it is $6.1 \frac{joule}{mole.K}$. Why this difference is? Given that $k = 1.4 \times 10^{-23} J/K.\ h = 6.6 \times 10^{-34} J.sec$

Solution: (a) Einstein's temperature is given by

$$\theta_E = \frac{h\nu}{k}$$

$$= \frac{6.6 \times 10^{-34} \times 2.49 \times 10^{12}}{1.4 \times 10^{-23}}$$

$$= 117.4 \text{ K}$$

(b) According to Einstein's theory of specific heat

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2\left[\frac{e^{\frac{\theta_E}{T}}}{(e^{\frac{\theta_E}{T}}-1)^2}\right]$$

For same temperature T the value of C_V are different due to their different values of characteristic frequency ν.

8.10 DEBYE'S THEORY OF SPECIFIC HEAT

The Einstein's theory could provide a definitely much better explanation of the variation of specific heat with temperature than the classical theory. But the agreement is not perfect in low temperature region. Figure 8 represents the variation with temperature of atomic heat at constant volume of two solids gold and cobalt. This discrepancy between the theory and low temperature experimental region is because of oversimplified model employed by Einstein in which he assumed that all the atomic oscillators vibrate independently at the same frequency. In fact they are coupled oscillators, and thus there is a range of possible values of the vibration frequencies rather than just a single frequency. This is taken into account by Debye's theory, which gives excellent agreement with experiment over the whole observable temperature range.

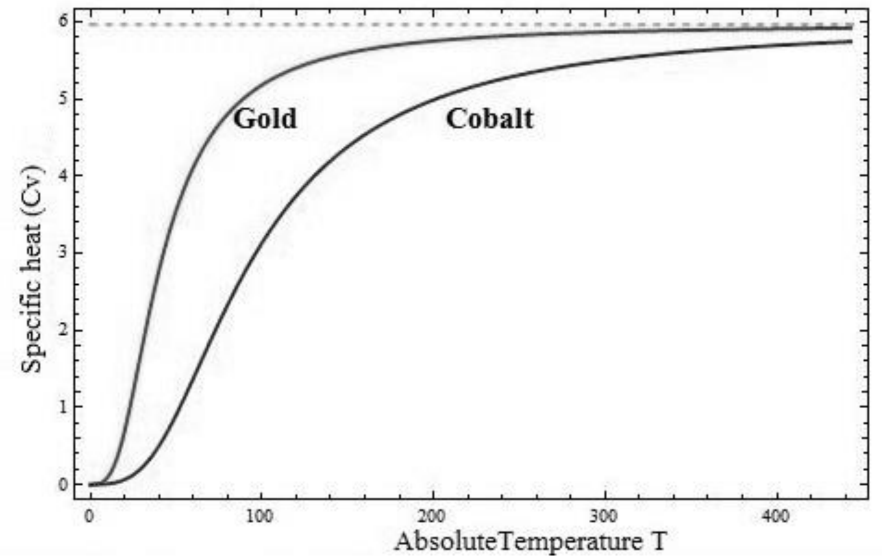

Figure 8- The variation of specific heat with temperature for Gold and Cobalt.

Debye assumed that any solid is capable of vibrating elastically in many different modes, the frequency varying from one mode to another mode and the numbers of modes of vibration of solids are limited in numbers. When a solid is subjected to elastic vibrations, two kinds of vibrations are produced:

1. transverse vibrations and
2. longitudinal vibrations.

The numbers of modes of longitudinal vibrations per unit volume with frequencies between $\nu \; and \; \nu + d\nu$ are

$$= \frac{4\pi\nu^2 \, d\nu}{c_l^3}$$

where c_l being the velocity of longitudinal vibrations.

The number of modes of transverse vibrations per unit volume with frequencies between $\nu \; and \; \nu + d\nu$ are

$$= \frac{4\pi\nu^2 \, d\nu}{c_t^3} \qquad (63)$$

where c_t being the velocity of transverse vibrations.

Since transverse vibrations have two independent directions of vibrations or we may say they are equivalent to two waves polarized at right angles to each other. Therefore, the number of independent vibrations per unit volume with frequency between $\nu \; and \; \nu + d\nu$ is

$$= 4\pi \left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right] \nu^2 \, d\nu$$

If V is the volume of one-gram molecule of any solid, then the number of modes of vibrations for this amount within the same frequency range is

$$= 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right] \nu^2 \, d\nu$$

The total number of modes of vibrations is given by

$$= \int_0^{\nu_m} 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right] \nu^2 \, d\nu$$

Debye assumed that the frequencies can only reach a definite upper limit ν_m. Since each atom has three degrees of freedom. If there are N atoms in volume V then the total number of vibrations will be equal to 3N. Hence

$$\int_0^{\nu_m} 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right] \nu^2 \, d\nu = 3N \qquad (63)$$

or

$$4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right] \frac{{\nu_m}^3}{3} = 3N \qquad (64)$$

$$4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right] {\nu_m}^3 = 9N \qquad (65)$$

Quantum mechanically energy associated with each degree of freedom is $\frac{h\nu}{e^{h\nu/kT} - 1}$.

Thermal energy of one-gram atom of solid between frequency ranges $\nu \; and \; \nu + d\nu$ will be

$$= \frac{h\nu}{e^{h\nu/kT} - 1} . 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right] \nu^2 \, d\nu$$

Using Eq. (65)

$$= \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} . \frac{9N}{{\nu_m}^3} \, \nu^2 \, d\nu$$

$$= \frac{9N}{{\nu_m}^3} . \frac{h \, \nu^3}{e^{\frac{h\nu}{kT}} - 1} . d\nu$$

Total thermal energy for one-gram atom is given by

$$E = \int_0^{\nu_m} \frac{9N}{{\nu_m}^3} . \frac{h \, \nu^3}{e^{\frac{h\nu}{kT}} - 1} . d\nu \qquad (66)$$

Let

$$\frac{h\nu}{kT} = p, then\ \nu = \frac{kT}{h}p$$

$$d\nu = \frac{kTdp}{h}$$

$E = \frac{9N}{{\nu_m}^3}\int_0^{\frac{h\nu_m}{kT}}\left(\frac{kT}{h}\right)^3\frac{p^3}{e^p-1}kTdp$(67)

Quantity $\frac{h\nu_m}{k}$ has the dimension of temperature. Here as in Einstein's theory, it is convenient to introduce a characteristic temperature θ_D, called as Debye temperature $\frac{h\nu_m}{k} = \theta_D$, thus equation (66) becomes

$$E = 9Nk\frac{T^4}{{\theta_D}^3}\int_0^{\frac{\theta_D}{T}}\frac{p^3}{e^p-1}dp \qquad (68)$$

The upper limit of integration is equal to $\frac{\theta_D}{T}$. It is observed that for high temperature (T>>θ_D), p is small compared with unity for the whole range of integration. In that case the denominator of the integration in equation (v) by be replaced in first approximation by x, i.e.

$$E = 9Nk\frac{T^4}{{\theta_D}^3}\int_0^{\frac{\theta_D}{T}}\frac{p^3}{1+p+\frac{1}{2!}p^2+\frac{1}{3!}p^3+\cdots-1}dp \qquad (69)$$

$$= 9Nk\frac{T^4}{{\theta_D}^3}\int_0^{\frac{\theta_D}{T}}\frac{p^3}{p}dp \qquad (70)$$

$$= 9Nk\frac{T^4}{{\theta_D}^3}\int_0^{\frac{\theta_D}{T}}p^2dp \qquad (71)$$

$$= 9Nk\frac{T^4}{{\theta_D}^3}\left[\frac{p^3}{3}\right]_0^{\frac{\theta_D}{T}} \qquad (72)$$

$$= 3Nk\frac{T^4}{{\theta_D}^3}\frac{{\theta_D}^3}{T^3} = 3NkT \qquad (73)$$

Thus, the specific heat

$$C_V = \frac{dE}{dT} = 3Nk = 3R\ \ for\, T \gg \theta_D(74)$$

this is identical with the classical theory.

In case of very low temperature such that $T \ll \theta_D$, the upper limit of integration may be replaced by infinity in equation (68), i.e.

$$E = 9Nk\frac{T^4}{{\theta_D}^3}\int_0^\infty \frac{p^3}{e^p-1}dp \qquad (75)$$

Now the quantity $\int_0^\infty \frac{p^3}{e^p-1}dp$ is a standard integration, and the solution of this integration comes out to be $\frac{\pi^4}{15}$, thus

$$E = 9Nk\frac{T^4}{{\theta_D}^3}\frac{\pi^4}{15} = \frac{3}{5}\pi^4 NkT\frac{T^3}{{\theta_D}^3}, forT \ll \theta_D \qquad (76)$$

The specific heat at low temperature according to Debye theory is

$$C_V = \frac{dE}{dT} = \frac{12}{5}\pi^4 Nk\frac{T^3}{{\theta_D}^3} forT \ll \theta_D \qquad (77)$$

This is a famous Debye T^3 law. The general expression for specific heat as a function of temperature may be obtained by differentiating equation (68) with respect to T.

$$C_V = 3RF_D\left(\frac{\theta_D}{T}\right) \qquad (78)$$

where F_D is the Debye function. The comparison between Debye theory and experimentally observed specific heat curve are shown in following figure 9.

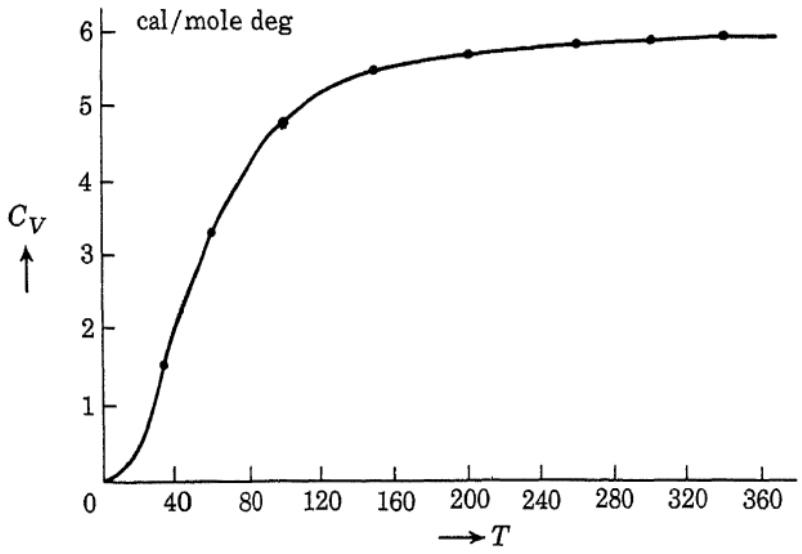

Figure 9- Debye specific heat is shown by curve and experimental values are shown by dots.

From such curves it is possible to calculate the Debye temperature of the solid involved.

8.11 LIMITATIONS OF DEBYE MODEL

1. The theory completely ignores the interactions among the atoms and the contributions of electrons to the specific heat.
2. Debye temperature θ_D is independent of temperature T, whereas really it is found to vary up to an extant of 10% or more.
3. This theory does not take into account the actual crystalline nature of the solid. The theory cannot be applied to the crystals containing more than one type of atoms.
4. Debye model is valid for long wavelengths or shorter frequencies only.
5. Cut off frequency is same for both transverse and longitudinal waves, while the velocities of longitudinal and transverse waves have different values for different frequencies.

8.12 THERMAL CONDUCTIVITY

There are three ways by which heat may travel from one place to another (i) conduction, (ii) convection and (iii) radiation. In the process of conduction, heat flows from one particle to another particle in the direction of fall of temperature without any visible movement of the particles.

The basic experimental fact is that the heat current Q that is, the amount of thermal energy crossing a unit area per unit time is proportional to the temperature gradient $\frac{dT}{dx}$:-

$$Q = -K\left(\frac{dT}{dx}\right) \tag{79}$$

A theory of thermal conductivity of insulators was developed in 1914 by Debye as in his theory of specific heat. He assumed that lattice vibrations may be described by a model in which elastic waves are propagated through a continuum. Since solids expand upon heating, these waves cannot be purely harmonic but must be anharmonic. The various normal modes of the system are not completely independent; they are rather coupled with each other. In terms of the phonons we may say that phonons corresponding to the various normal modes now interact with one another. It is clear from the discussion that the finite value of the thermal conductivity is associated essentially with the anharmonicity of the lattice vibrations. Now since the magnitude of anharmonicity increases with increase in the vibration amplitude. This effect is quite generally observed experimentally at sufficiently high temperatures.

We shall first develop a formula for the thermal conductivity of an ideal monoatomic gas and then examine how it may be applied to the lattice of a crystalline solid. Suppose now $n(v)dv$ represents the number of particles per unit volume having velocity in the range $v \ and \ v + dv$ we have for the desired number

$$dn = \frac{1}{2}v.n(v)dv\frac{4\pi sin\theta d\theta}{4\pi}\ ds\ cos\theta \tag{80}$$

$$= \frac{1}{2}v.n(v)\ sin\theta\ cos\theta\ dv\ d\theta\ ds \tag{81}$$

The factor $\frac{4\pi sin\theta d\theta}{4\pi}$ is the ratio of the two solid angles.

Using Maxwell-Boltzmann distribution

$$n(v)dv = 4\pi n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{\left(-\frac{mv^2}{2kT}\right)} dv \qquad (82)$$

Putting this value in equation (81)

$$dn = \frac{1}{2}.4\pi n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^3 e^{\left(-\frac{mv^2}{2kT}\right)} sin\theta\ cos\theta\ dv\ d\theta\ ds \qquad (83)$$

Integrating this expression over v we may write

$$n(\theta)d\theta = \frac{1}{2}.4\pi n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}.\frac{1}{2}\left(\frac{2kT}{m}\right)^2 sin\theta\ cos\theta\ d\theta\ ds \qquad (84)$$

$$= \frac{1}{2}.n.\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} sin\theta\ cos\theta\ d\theta\ ds \qquad (85)$$

$$= \frac{1}{2}.n.\bar{v} sin\theta\ cos\theta\ d\theta\ ds \qquad (86)$$

where $\bar{v}$ is the average thermal velocity of a particle. Now suppose the situation as shown in following figure 10, a temperature gradient is exist along x-axis. The particles at origin have average energy E and those at a short distance to the left have average energy.

$$E + \Delta E \approx E + \left(\frac{\partial E}{\partial x}\right)\Delta E \qquad (87)$$

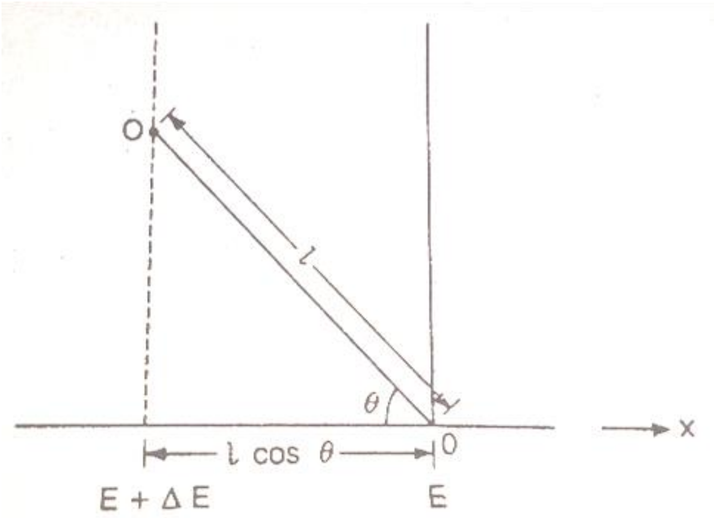

Figure 10

The energy of particle at a distance *l* away from the origin in a direction θ may be expressed as

$$E + \Delta E \approx E + (l\,cos\theta)\frac{\partial E}{\partial x} \qquad (88)$$

If we assume that this particle gives up whole of its energy to the distribution at the origin through a collision, then there will be a particle leaving the origin and thus carrying energy E. The net transport of energy is thus

$$E + \Delta E \approx E + (l\,cos\theta)\frac{\partial E}{\partial x} \qquad (89)$$

The average value of *l* is simply the mean free path λ between randomising collision. The net energy transport per particle averaged over the distribution of path lengths *l* is $\overline{\Delta E} = (\lambda\,cos\theta)\frac{\partial E}{\partial x}$. Extending this result for the number of particles represented by equation (82) we get

$$\overline{\Delta E}\,n(\theta)d\theta = (\lambda\,cos\theta)\frac{\partial E}{\partial x}.\frac{1}{2}.n.\bar{v}sin\theta\,cos\theta\,d\theta\,ds \qquad (90)$$

$$= \frac{1}{2}.n.\bar{v}\lambda\frac{\partial E}{\partial x}.sin\theta\,cos^2\theta\,d\theta\,ds \qquad (91)$$

The net energy flux is thus

$\Delta F = \frac{1}{2}.n.\bar{v}\lambda\frac{\partial E}{\partial x}.sin\theta\ cos^2\theta\ d\theta\ ds$ (92)

Integrating over the angle θ between limits of $0$and π, total energy flux comes out to be

$$\frac{1}{3}.n.\bar{v}\lambda\frac{\partial E}{\partial x}$$

But from the definition of thermal conductivity this quantity must be equal to

$\frac{1}{3}.n.\bar{v}\lambda\frac{\partial E}{\partial x} = K\left(\frac{dT}{dx}\right)$ (93)

$K = \frac{1}{3}.n.\bar{v}\lambda\frac{\partial E}{\partial T}$ (94)

$K = \frac{1}{3}.\bar{v}\lambda C_V$ (95)

where $C_V = n\frac{\partial E}{\partial T}$ is specific heat.

Debye showed that the equation (95) is also good for a gas of phonons, provided for the velocity $\bar{v}$ is understood to refer to an average phonon velocity i.e. to an average sound velocity in the crystal.

8.13 SPECIFIC HEAT OF GASES

As we discussed earlier that heat can be added to a gaseous system in two different conditions either at constant pressure or at constant volume.

The specific heat of a gas at constant volume is the amount of heat required to raise the temperature of one gram of gas through 1°C, keeping volume constant. It is denoted by C_V. In this case the whole heat supplied to the system increases the internal energy of the gas only. The specific heat of the gas at constant pressure is the amount of heat required to raise the temperature of one gram of gas through 1°C, keeping pressure constant. It is denoted by C_P. In this case the gas is allowed to expand against a constant pressure and in doing so it does external work in addition to the work done in increasing the temperature by 1°C. Hence the specific heat at constant pressure is greater than the specific heat at constant volume by an amount to the external work done by the gas. Therefore

$$C_P - C_V = W \qquad (96)$$

If $C_P\ and\ C_V$ are the molar specific heats at constant pressure and constant volume, which are defined as $C_P = MC_P$ and $C_V = MC_V$, where M is molecular weight of gas, then

$$C_P - C_V = R \qquad (97)$$

This expression is known as Mayer's formula.

8.13.1Contribution of vibrational motion to specific heat

At high temperatures vibrational motion comes into existence in addition to rotational motion. The actual motion is very complicated, but it may be imagined that the motion is simple harmonic. According to Maxwell-Boltzmann's distribution law the number of simple harmonic resonators having energy E_ν are given by

$$N_\nu = N_o e^{-\frac{E_\nu}{kT}} \qquad (98)$$

*(where ν is frequency)*According to Planck's quantum theory energy is quantized as

$$E_\nu = nh\nu \qquad (99)$$

Substituting Eq. (99) in Eq. (98)

$$N_\nu = N_o e^{-\frac{nh\nu}{kT}} \qquad (100)$$

The observation of wave mechanics shows that

$$E_\nu = \left(n + \frac{1}{2}\right) h\nu \qquad (101)$$

According to wave mechanics the total vibrational energy of N_ν (number of oscillators) is

$$W_\nu = \sum_\nu N_\nu E_\nu \qquad (102)$$

$$= \sum_\nu N_\nu \left(n + \frac{1}{2}\right) h\nu \qquad (103)$$

$$= \frac{1}{2} N_\nu h\nu + \sum_\nu N_\nu n h\nu \qquad (104)$$

$$= \frac{1}{2} \sum_\nu N_\nu\, h\nu + N_o \sum_\nu nh\nu e^{-\frac{nh\nu}{kT}} \qquad (105)$$

$$= \frac{1}{2} Nh\nu + N_o \sum_\nu nh\nu e^{-\frac{nh\nu}{kT}} \qquad (106)$$

where N is number of oscillators.

Partition function for harmonic oscillator is defined as

$$F_\nu = \sum_n^\infty e^{-\frac{nh\nu}{kT}} \qquad (107)$$

Nowsince $N = \sum N_\nu = N_o \sum e^{-\frac{nh\nu}{kT}} = N_o F_\nu$

Assuming$\frac{h\nu}{kT} = p$, we have

$$F_\nu = \sum_n^\infty e^{-np} \qquad (108)$$

hence

$$\frac{\partial F_\nu}{\partial p} = -n \sum_n^\infty e^{-np} \quad (109)$$

Now Equation (107) becomes

$$W_\nu = \frac{1}{2} Nh\nu - N_o h\nu \frac{\partial F_\nu}{\partial p} (110)$$

$$= \frac{1}{2} Nh\nu - \frac{N_o h\nu F_\nu}{F_\nu} \frac{\partial F_\nu}{\partial p} \qquad (111)$$

$$W_\nu = \frac{1}{2}Nh\nu - Nh\nu\frac{\partial(\log F_\nu)}{\partial p} \qquad (112)$$

Therefore, the contribution of vibrational motion to specific heat

$$C_\nu = \frac{dW_\nu}{dT} = -Nh\nu\frac{d}{dT}\left\{\frac{\partial(\log F_\nu)}{\partial p}\right\} \qquad (113)$$

$$= -Nh\nu\frac{\partial^2(\log F_\nu)}{\partial p^2}\left(\frac{dp}{dT}\right) \qquad (114)$$

$$= -Nh\nu\frac{\partial^2(\log F_\nu)}{\partial p^2}\left(-\frac{kp^2}{h\nu}\right) \qquad (115)$$

$$= Nkp^2\frac{\partial^2(\log F_\nu)}{\partial p^2} \qquad (116)$$

$$= Rp^2\frac{\partial^2(\log F_\nu)}{\partial p^2} \qquad (117)$$

Using and simplifying equation (107)

$$C_\nu = R\frac{p^2e^p}{(e^p-1)^2} \qquad (118)$$

The translational energy per gram molecule is same as in classical theory, i.e.

$$E_t = \frac{3}{2}RT \qquad (119)$$

The contribution of translational motion to the specific heat is given by

$$C_t = \frac{dE_t}{dT} = \frac{3}{2}R \qquad (120)$$

In case of diatomic molecule, the contribution of rotational motion in specific heat is given by

$$C_r = R \qquad (121)$$

Therefore the value of specific heat of diatomic gases may be summarized as

$$C_V = C_t + C_r + C_\nu \qquad (122)$$

$$C_V = \frac{3}{2}R + R + R\frac{p^2 e^p}{(e^p - 1)^2} \tag{123}$$

$$C_V = \frac{5}{2}R + R\frac{p^2 e^p}{(e^p - 1)^2} \quad , where\ p = \frac{h\nu}{kT} \tag{124}$$

At very low temperatures the total energy of the molecules is very small and is less than the minimum energy needed to set up the rotational and vibrational motions. Hence the specific heat is due to only translational motion equal to $\frac{3}{2}R$. Consequently, at very low temperatures the specific heat for all diatomic gases is equal to $\frac{3}{2}R$.

As the temperature increases slightly, rotational motion arises. As the energy required to set up rotational motion is supplied gradually, and the specific heat becomes $C_t + C_r$. After that the specific heat remains constant until the energy supplied to the gas is sufficient to set up the vibrational motion. As the temperature of the gas increases and hence the specific heat again increases and finally becomes $C_V = C_t + C_r + C_v$. Figure 11 shows the variation for diatomic hydrogen gas.

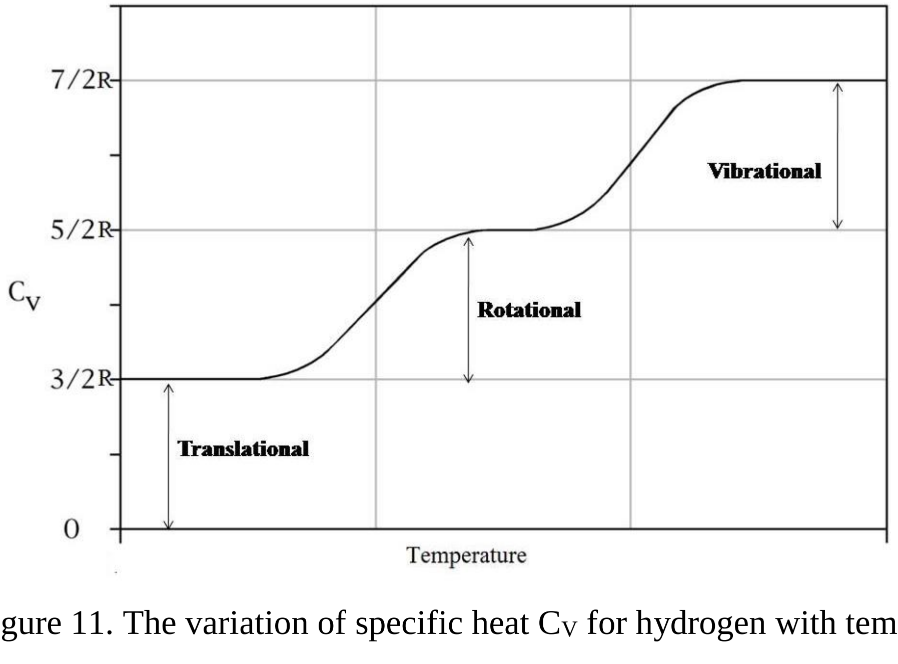

Figure 11. The variation of specific heat C_V for hydrogen with temperature.

Example 3. It is assumed that the molecule of an ideal is rigid but free to rotate about its two mutually perpendicular axes. Determine C_p, C_v and γ for such a gas and compare with the experimental values of γ for diatomic gases.

Solution. Here the molecules of diatomic gas are rigid; there exist only five degree of freedom, three of translation and two of rotation.

The kinetic energy per degree of freedom according to equipartitional principle of energy is equal to $\frac{1}{2}kT$. Therefore the kinetic energy associated with five degree of freedom is equal to $\frac{5}{2}kT$.

Thus the kinetic energy per molecule $= \frac{5}{2}kT$

and the kinetic energy per gram molecule $E = \frac{5}{2}NkT$

hence specific heat is $C_V = \frac{dE}{dT} = \frac{5}{2}Nk = \frac{5}{2}R$

and $C_p = C_V + R = \frac{7}{2}R$

therefore $\gamma = \frac{7}{5} = 1.40$

The experimentally observed values of γ at 15^0C are given in the following table

Diatomic gas	Values of γ
H_2	1.41
N_2	1.404
O_2	1.401

8.14 SUMMARY

In this chapter we studied the vibration of atoms in monoatomic and diatomic lattices. The phonon is the mediator for energy transfer. In monoatomic lattice there exists only one mode of vibration while in diatomic lattice there exist two modes of vibrations i.e. optical mode and acoustical mode.

In this chapter we also studied the different models to determine the specific heat of solids and gases. Dulong and Petit's law is the classical model of specific heat.

According to this law specific heat is not the characteristic of substance it is same for all materials and equal to 3R. This law fails to explain the decrease of specific heat in low temperature region. Einstein’s theory of specific heat is quantum mechanical theory. This theory is successful to explain the variation of specific heat with temperature up to a great extent. Debye’s modified Einstein’s theory of specific heat which gives excellent agreement with experiment over the whole measurable range of temperature. In monoatomic substances heat supplied is used only electronic transition while in diatomic or polyatomic substances heat supplied is used in electronic as well as in vibrational and rotational motions of the molecules.

8.15 GLOSSARY

Latent – Hidden

Mode of vibrations – kinds of oscillations

Specific – characteristic

Phonon – quanta of lattice vibrations (equivalent to photon)

Lattice – array of atoms or molecules

Equipartition – equal distribution

Thermal properties – heat related properties

8.16 TERMINAL QUESTIONS

1. The specific heat C of a certain substance at very low temperature is found to depend on the absolute temperature T according to the relation $C = AT^3$ where A is a constant .

   (i) If units are in calorie, gram and degree Kelvin, so what should be the unit of constant A.

   (ii) How much heat must be added to raise the temperature of a mass m of the material from T_1 to T_2?

2. Consider diatomic gas with two rotational degree of freedom and one vibrational degree of freedom. Find C_p, C_v and γ. It may be assumed that the vibrations of molecules are simple harmonic in nature.

[Ans. 7/2R, 9/2R and 9/7]

3. The bond length of HCl molecule is 13×10^{-8} cm. Calculate

(i) First five excited rotational energy states.

[Ans. 3.7×10^{-15} ergs. 10.8×10^{-15} ergs. 2.28×10^{-15} ergs. 3.6×10^{-14} ergs. 5.4×10^{-14} ergs]

(ii) The rotational energy gap between first five consecutive states.

[Ans. 3.6×10^{-15} ergs. 7.2×10^{-15} ergs. 1.2×10^{-14} ergs . 1.32×10^{-14} ergs. 1.8×10^{-14} ergs]

4. Calculate the specific heat at constant volume for air given that specific heat at constant pressure is equal to 0.23. Density of air at 27^0C and normal atmospheric pressure is equal to 0.18 gm/litre and J=4.2 joule/calori.

[Ans. 1618]

5. copper has an atomic weight 63.5, a density of 8.9×10^3 kg/m^3, and $c_t = 2.32\times10^3$ m/s and $c_l = 4.76\times10^3$ m/s. Determine the specific heat at low temperature say 30K. [Ans.1.328Jmole^{-1}K^{-1}]

6. Estimate the relative contribution of electrons and lattice to the specific heat at constant volume of sodium at 20K. The Fermi temperature of sodium is 3.6×10^4 K and its Debye temperature is 150K.

[Ans. $(C_v)_{el}$ = 22.78 J/kmole/K, $(C_v)_{la}$ = 4.6×10^3J/kmole/K]

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8.18 SUGGESTED READINGS

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UNIT 9 DIELECTRIC PROPERTIES OF MATERIALS

Structure

9.1 INTRODUCTION:

A conducting material generally refers to the material consisting of a large number of mobile free electrons, such as a metal in which the concentration of free electrons is of the same order as that of atoms, i.e., about 10^{22} to 10^{23} cm^{-3}. In these conducting materials, the electrostatic induction phenomenon occurs. But in other materials the number of mobile charge carriers is very less than the number of atoms; such materials are called dielectric materials. In other words, we can say that dielectrics are the materials in which all the electrons are tightly bound to the nuclei of the atoms and no free electrons to carry current. All the dielectrics are classified into two main categories:

1. Polar dielectric, e.g. HCl, NaCl, H_2O etc.
2. Non-polar dielectric, e.g. H_2, N_2, O_2 etc.

9.2 OBJECTIVE:

After studying this chapter,we shall be able to know

- ✓ What are dielectric materials?
- ✓ What is displacement vector?
- ✓ Ferroelectricity.
- ✓ The different ways of polarization of materials.
- ✓ The temperature dependence of dielectric constant.

9.3 DIELECTRIC CONSTANT:

Faraday discovered that when a dielectric material is placed between the plates of a capacitor, the capacitance of the capacitor increases. The ratio of the capacitance of a given capacitor when dielectric is fully filled between the plates to the capacitance of the same capacitor in vacuum is called dielectric constant of that dielectric. Thus, if C_o is the capacitance in vacuum and C is the capacitance with dielectric, then dielectric constant

$$K = \frac{C}{C_o} \tag{1}$$

Since it is a ratio of two same quantities hence it is dimensionless quantity. It is independent of the shape and size of the capacitor, but its value is different of different materials. For vacuum $K = 1$, for distilled water $K = 80$ for air $K = 1.0006$ etc.

In the S.I. system of units, the capacitance is measured in farad. The capacitance of a conductor is 1 farad (1f) if a charge of 1 coulomb raises its potential by 1 volt. The farad is too large unit. Hence in practice, smaller units are used. They are microfarad and picofarad.

1 microfarad$(1\mu f) = 10^{-6}f$

1 picofarad $(1pf) = 10^{-12}f$

Example1: Can a parallel plate air capacitor of 1 farad capacitance having plate separation 1mm be constructed in laboratory?

Solution: the capacitance of a parallel-plate capacitor is

$$C = \frac{K\varepsilon_o A}{d}$$

$$A = \frac{dC}{K\varepsilon_o}$$

Here C = 1f, d = 1mm, K =1 and $\varepsilon_o = 8.85 \times 10^{-12} Coul^2/(Nm^2)$

Hence

$$A = \frac{1 \times 1 \times 10^{-3}}{1 \times 8.85 \times 10^{-12}}$$

$$= 1.13 \times 10^8 \quad m^2$$

$$= 113 \quad km^2$$

A capacitor of plate area of about 133 km^2 cannot be constructed in laboratory.

9.4 POLAR AND NON-POLAR MOLECULES

A system of two charges, q and – q separated by a certain distance l, is called electric dipole e.g. HCl, NaCl etc. The electric dipole moment of an electric dipole is defined as

$p = q \times l$ (2)

The dipole moment is a vector quantity and its direction is towards positive charge from negative charge.

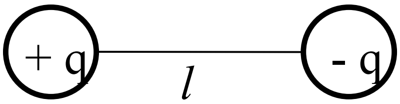

Figure 1: Schematic of a dipole

The molecules having dipole moment greater than zero are called polar molecules and those molecules having dipole moment zero are called non-polar. Water molecule has a triangular structure: two H-O bonds have dipole moments p_1 as shown in following figure, hence the resultant dipole moment p is directed from O towards H-H base. Thus, H_2O molecule is a polar molecule. On the other hand, CO_2 molecule has a linear symmetrical structure hence the resultant dipole moment is zero. Thus, CO_2 is a non-polar molecule.

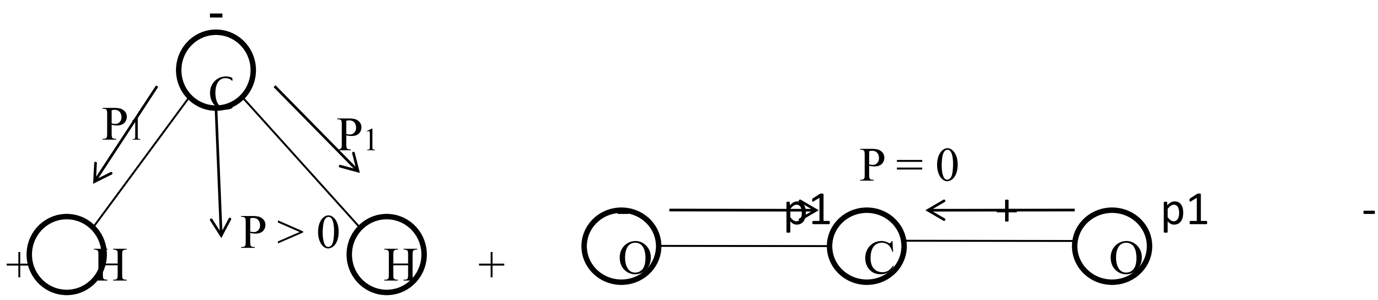

Figure 2: polar and non-polar molecules

9.5 TYPES OF ELECTRIC POLARIZATION IN A MATTER

A dielectric material is made up of atoms or molecules. When a dielectric material is placed in an electric field the positive and negative charges experience electrostatic forces in opposite directions. Electric polarization refers to a phenomenon of the relative displacement of the negative and positive charges of atoms or molecules, the orientation of existing dipoles toward the direction of the field, or the separation of mobile charge carriers at the interfaces of impurities or other defect boundaries, caused by an external electric field.

All dielectrics possess one or more of five basic types of electric polarization.

1. Electronic or optical polarization.
2. Atomic or ionic polarization.
3. Orientation polarization.
4. Spontaneous polarization.
5. Space charge polarization.

Each type of polarization takes some time to perform properly. That is why the degree of polarization depends on the frequency of polarizing electric field.

9.5.1 Electronic polarization or optical polarization:

When a dielectric (non-polar) material is placed in an electric field the positive and negative charges of its molecules or atoms experience electrostatic force in opposite direction.

Center of the gravity of the two charges are separate from each other, and the molecules thus acquire an induced electric dipole moment in the direction of field. The noble gas atoms, such as He, Ne, Ar, Kr, Xe, and Ra, whose shells are completely filled have the lowest polarizabilities for their atomic numbers. The elements, such as H, Li, Na, K, Rb, and Cs, with only one electron in the outermost shell, have the highest polarizabilities for their atomic numbers, possibly due to the ease of polarization of a single electron in the outermost orbit.

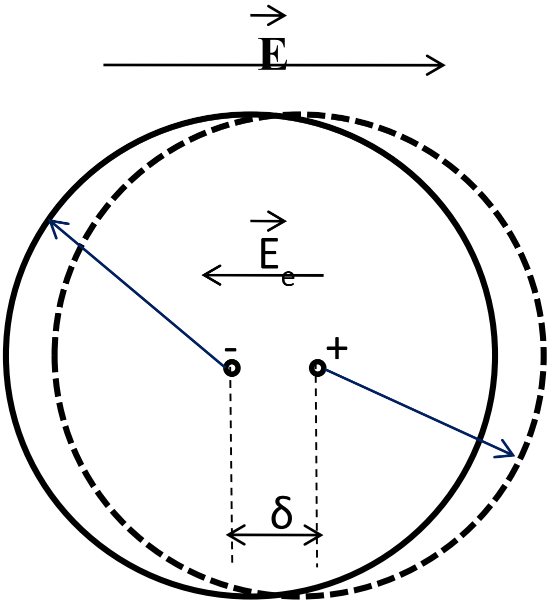

Figure 3: Displacement of electron cloud relative to nucleus due to external electric field.

If the external field E produces a displacement δ of the electron cloud relative to the nucleus of positive charge eZ due to the polarization. Then induced dipole moment δeZ arises in the molecule of atom.Suppose that the electron cloud of charges –*Zq* is uniformly distributed in a sphere of radius *R* and that its center of gravity originally coincided with that of the nucleus and suppose that it is displaced by the field to a distance δ from the center of the nucleus, as shown in Figure 3. There is a Coulombic restoring force tending to bring the electron cloud back to its initial position. According to Gauss's law, the Coulombic force is only exerted on the electron cloud that does not surround the positive nucleus charges +*Zq*. This part of the electron cloud is contained in the sphere of radius δ and it is

$$Q = \frac{Zq(4\pi\delta^3 / 3)}{(4\pi R^3 / 3)}$$

$$= Zq\frac{\delta^3}{R^3} \qquad (3)$$

Thus, Coulombic force is

$$F = \frac{Zq.Zq\frac{\delta^3}{R^3}}{4\pi\varepsilon_o\delta^2} = \frac{(Zq)^2\delta}{4\pi\varepsilon_o R^3} \qquad (4)$$

This force must balance the displacement force

$$F = Zq.E \qquad (5)$$

Comparing equation (4) and (5)

$$ZqE = \frac{(Zq)^2\delta}{4\pi\varepsilon_o R^3} \qquad (6)$$

$$\delta = \frac{4\pi\varepsilon_o R^3}{Zq}E \qquad (7)$$

Dipole moment produced will be given by

$$p_e = Zq.\delta = 4\pi\varepsilon_o R^3 E \qquad (8)$$

Therefore, the electronic polarizability is

$$\alpha_e = \frac{p_e}{E} = 4\pi\varepsilon_o R^3 = 3\varepsilon_o V_a \qquad (9)$$

where V_a is the volume of the atom, α_e is proportional to the volume of the atom. For the hydrogen atom, *R* is about 0.50Å, α_e= 1.57×$10^{-24}\varepsilon_o$cm^3. For *E* = 10^4Vcm^{-1}, δ = 10^{-14} cm. The displacement distance δ is extremely small.

9.5.2 Atomic or Ionic polarization:

This type of polarization is also called vibrational polarization. If we have a solid whose molecules are made up of ions there is a relative motion of positive and negative ions i.e. cations and anions in an ionic crystal are displaced with respect to each other resulting an induced dipole moment.

In general, there are two types of ionic solids. One type does not possess permanent dipoles, such as NaCl, which forms a simple cubic lattice so that the lattice symmetry and the overall charge neutrality ensure that electric dipoles formed by each ion pair everywhere cancel each other. The other type possesses permanent dipoles, because the crystal lattice in this case is less symmetrical, as with HCl. In fact, the internal field at the positive ion sites is generally different from that at the negative ion sites. Commonly, most ionic solids are asymmetrical and the electronegativities of both ions are different. They possess permanent dipoles, but these dipoles are tightly bound in the solid and cannot be aligned by an electric field. Therefore, in most ionic solids belonging to this group; the permanent dipole moments do not contribute to the polarizability in the solid state although the materials possess them.

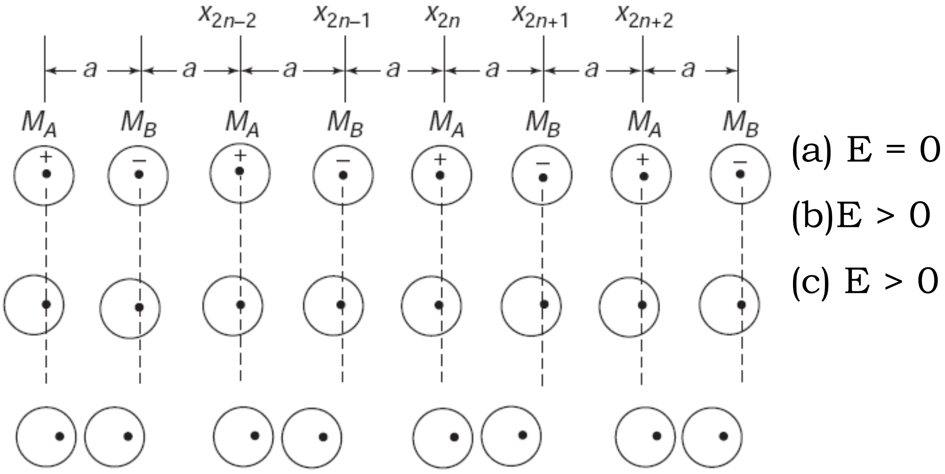

Figure 4: Schematic of atomic or ionic polarization

Suppose a linear chain of ions *A* and ions *B* placed at equal distances along the *x* direction, as shown in Figure 4(a). In thermal equilibrium and in the absence of an electric field, the positive ions *A* at x_{2n}, x_{2n+2}, x_{2n-2}, etc., and the negative ions *B* at x_{2n+1}, x_{2n+3}, x_{2n-1}, etc., will always undergo lattice vibrations, but their interatomic distance is $x_{2n+1}-x_{2n}=a$, on average. Now if a step-function electric field is applied in the *x* direction, the electron clouds immediately shift to the left, and it takes only about 10^{-15} sec to produce electronic polarization, as shown in Figure 4(b).After about 10^{-13} sec of the application of the field, the positive ion at $x_{2n}$and the negative ion at x_{2n+1} tend to attract and move toward each other, making the interatomic distance $\Delta x_1= x_{2n+1}- x_{2n}<a$ and $\Delta x_2= x_{2n}- x_{2n-1}>a$. The same tendency prevails in other ions. The displacement in both the electron clouds and the ions themselves produces electronic polarization, as well as ionic polarization, as shown in Figure 4(c). Displacement of atoms or ions from their equilibrium sites will generate a force which tends to bring them back to their original position. We can write the equation of motion for ions M_A and M_B

$$M_A \frac{d^2 x_{2n}}{dt^2} = \beta_i [x_{2n+1} + x_{2n-1} - 2x_{2n}] \quad (10)$$

$$M_B \frac{d^2 x_{2n-1}}{dt^2} = \beta_i [x_{2n} + x_{2n-2} - 2x_{2n-1}] \quad (11)$$

where β_i is the restoring force constant and its value is given by

$$\beta_i = \frac{2Z^2q^2}{4\pi\varepsilon_o a^3} \tag{12}$$

The solutions of equations (10) and (11) comes out as

$$x_{2n} = x_A \exp[jk(2n)a] \tag{13}$$

$$x_{2n-1} = x_B \exp[jk(2n-1)a] \tag{14}$$

where $x_A$and $x_B$are periodic functions of time and the exponential is a phase factor and k is wave number. Therefore equations (10) and (11) modified as

$$M_A \frac{d^2x_A}{dt^2} = -2\beta_i[x_A - x_B] \tag{15}$$

$$M_B \frac{d^2x_B}{dt^2} = -2\beta_i[x_B - x_A] \tag{16}$$

Simplifying equations (15) and (16)

$$M_r \frac{d^2\Delta x}{dt^2} = -2\beta_i\Delta x - \gamma\frac{d\Delta x}{dt} - ZqE \tag{17}$$

where $M_r = \frac{M_A M_B}{M_A + M_B}$ is the reduced mass and$\Delta x = \Delta x_B - \Delta x_A$ is the relative displacement of positive and negative ions.We can express $\beta_i$in terms of natural frequency (lattice vibration) ω_o as $2\beta_i = M_r\omega_o^2$. If applied electric field is alternating field with the frequency ω, then the solution of equation (17) gives

$$\Delta x = \frac{ZqE}{M_r(\omega_o^2 - \omega^2) + j\gamma\omega} \tag{18}$$

The induced dipole moment is

$$\mu_i = Zq.\Delta x = \frac{(Zq)^2E}{M_r(\omega_o^2 - \omega^2) + j\gamma\omega} \tag{19}$$

Thus, ionic or atomic polarizability is

$$\alpha_i = \frac{(Zq)^2}{M_r(\omega_o^2 - \omega^2) + j\gamma\omega} \tag{20}$$

In steady state $\omega = 0$, therefore static ionic polarizability

$$\alpha_i = \frac{(Zq)^2}{M_r\omega_o^2} \tag{21}$$

The time required for electronic polarization is about 10^{-15}sec, and that required for the ionic polarization is about 10^{-13} sec, simply because ions are heavier than electrons by more than 10^3 times. Therefore, the resonances for these two polarizations occur in different frequency regions.

9.5.3 Orientational polarization:

If there are molecules with permanent dipole moments randomly oriented, they tend to align in the direction of applied field thus producing a net dipole moment. This is called dipolar or orientational polarization. A dielectric whose molecules are polar and thus have a permanent electric dipole moment. In the absence of any external electric field the individual dipoles are oriented at random and no net dipole moment is observed in the dielectric. When the dielectric is placed in an electric field, The molecules tend to be aligned in the direction of the field. The alignment is, however incomplete due to the thermal agitation of the molecules. Hence a net dipole moment is produced in the dielectric.

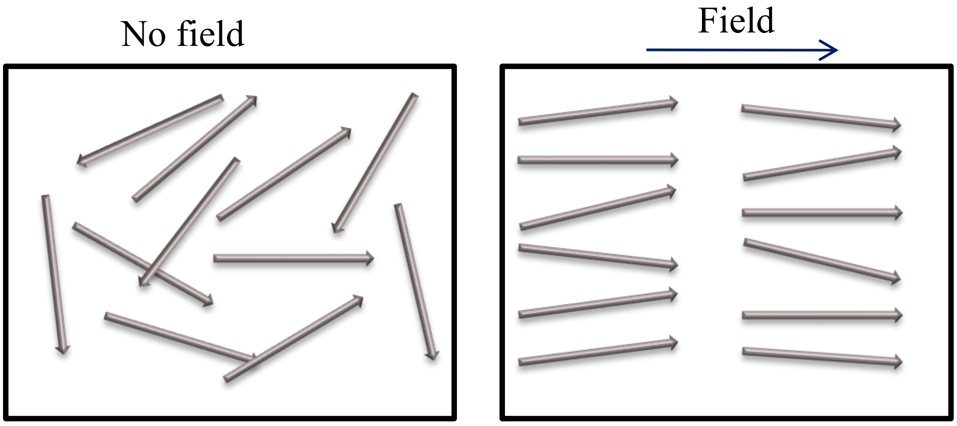

Figure 5: Schematic of orientational polarization

This process is generally referred to as the relaxation process. This polarization involves the inelastic movement of particles, and its interaction is an intermolecular phenomenon; hence, orientational polarizability is strongly temperature-dependent.

Suppose the permanent dipole moment p_o of the molecule, unaffected by external field and temperature. Component of dipole moment in the direction of field as shown in figure 6 is given by

$$p_E = p_o cos\theta \tag{22}$$

where θ is the angle between dipole moment and applied field.

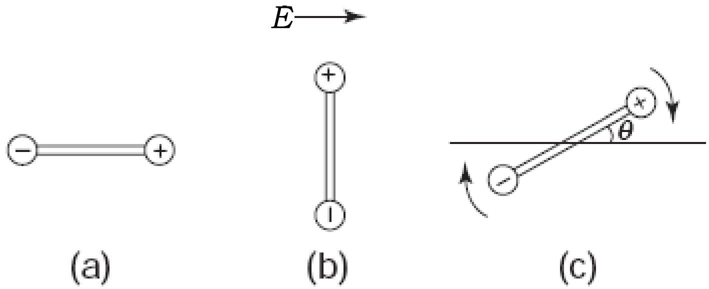

Figure 6: the orientation of a dipole: (a) stable position (b) unstable position and (c) orienting to the field direction.

At zero applied field, the number of dipoles having an inclination of their axes to the axes lying between θ and θ + dθ as shown in figure 7, is

$$dN = N\frac{1}{2}sin\theta d\theta \tag{23}$$

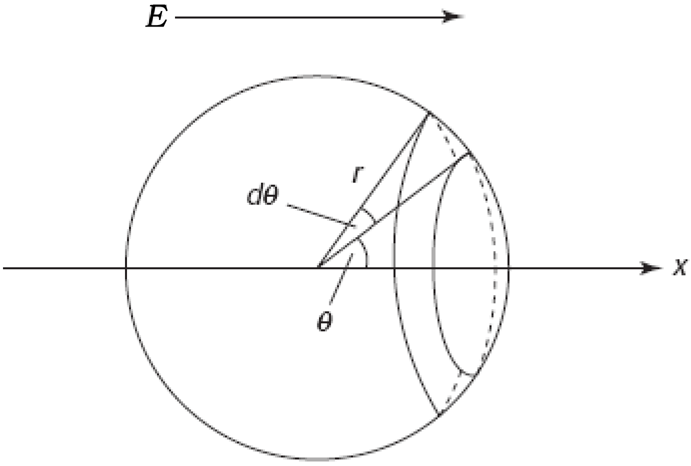

Figure 7: calculation of the number of dipoles having the inclination of their axes to the x-axis between θ and θ + dθ.

with an applied electric field E and the effect of temperature using Boltzmann's statistics equation (23) modifies as

$$dN = Aexp\left(-\frac{U}{kT}\right)\frac{1}{2}sin\theta d\theta \qquad (24)$$

Where U is the potential energy of dipole in electric field E at angle θ, i.e.

$$U = p_o Ecos\theta \qquad (25)$$

The average dipole moment in the field direction is

$$< p_E >= p_o < cos\theta > \qquad (26)$$

Introducing $y = cos\theta$ and $x = p_o E/kT$ we obtain

$$< cos\theta > \; = \; cothx - \frac{1}{x} = L(x) \qquad (27)$$

The function $L(x)$ is called Langevin's function which is shown in figure 8. At low value of x, $L(x)$ varies linearly with the relation

$$L(x) =< cos\theta > = \frac{p_o E}{3kT} \qquad (28)$$

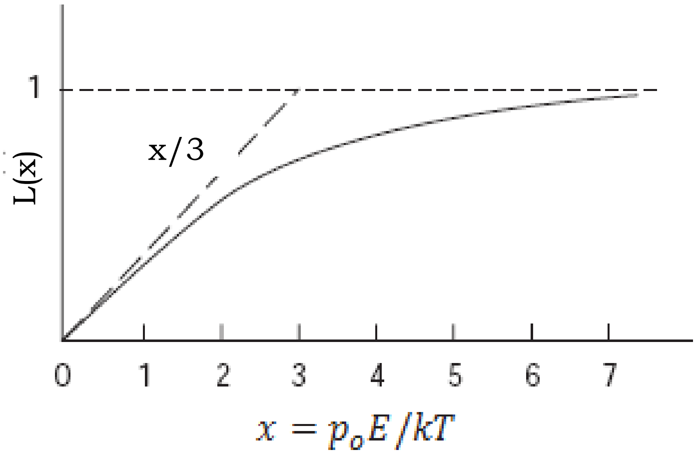

Figure 8: The Langevin function

For x>>1, $L(x)$ can be estimated by

$$L(x) = 1 - \frac{1}{x} \qquad (29)$$

Substituting equation (28) in equation(26) we obtain

$$< p_E > = \frac{{p_o}^2 E}{3kT} \tag{31}$$

and orientational polarizability is

$$\alpha_o = \frac{< p_E >}{E} = \frac{{p_o}^2}{3kT}$$

In general, orientational polarizability is much larger than electronic and atomic polarizabilities at normal conditions, since α_e and α_i are practically independent of temperature but α_o is strongly temperature dependent.

9.5.4 Spontaneous Polarization:

There is another kind of polarization, called spontaneous polarization. Spontaneous polarization occurs in materials whose crystalline structure exhibits electrical order. By analogy to magnetization, electric polarization can be grouped into two major polarizations:

a. Paraelectric polarization, which includes mainly electronic, ionic, and orientational polarizations, with χalways positive.

b. Ferroelectric polarization, with χ very large, like ferromagetization.

In ferroelectric materials, electric polarization occurs spontaneously due to a phase transition at a critical temperature called the Curie temperature, T_c, without the help of an external electric field. At and below T_c, the crystal undergoes a phase transition, usually from a nonpolar cubic structure to a polar structure. $BaTiO_3$ is a typical example of a ferroelectric crystal.

In a single crystal or a crystallite, there are many domains with moments pointing in various directions. But the vector sum of the dipole moments of all domains vanishes. Each domain can be considered as a large dipole. Under an external electric field, all of these randomly arranged domains tend to move toward the direction of the field, resulting in a net total spontaneous polarization. Upon the removal of the field, spontaneous polarization does not vanish but remains inside the material. The electric field and polarization forms a hysteresis loop, called p-E loop, similar to the hysteresis loop for ferromagnetic materials. This is discussed in Ferroelectricity section of this chapter.

9.5.5 Space charge polarization:

This occurs mainly in amorphous or polycrystalline solids or in materials consisting of traps. At higher fields, carrier injection becomes important. For materials consisting of a high concentration of charge carriers, polarization due to the migration of charge carriers to form space charges at interfaces or grain boundaries becomes important.

There are two possible ways in which space charge polarization may result.

a. Hopping Polarization.

b. Interfacial Polarization.

Since these two types of polarization involve the movement of charged particles, there is no easy experimental method to separate these two different mechanisms.

Example2: Assuming that the negative charge in a hydrogen atom is uniformly distributed in a sphere of radius 0.5×10^{-10} meter around the proton. This atom is placed in an electric field of 10^6V/m. Determine the separation produced between the positive and negative charges of the atom due to the electric field.

Solution: Each of the positive and negative charge in the hydrogen atom is e. Let d be the equilibrium separation produced by the electric field E. At this separation, the force eE on the positive charge due to the field is balanced by electrostatic force of attraction between the two charges. i.e.

$$\frac{1}{4\pi\varepsilon_o}\frac{e^2 d}{R^3} = eE$$

$$d = \frac{R^3 4\pi\varepsilon_o}{e}E$$

$$d = \frac{(0.5\times10^{-10})^3\times(10^6)}{(9\times10^9)(1.6\times10^{-19})}$$

$$d = 8.7\times10^{-17}m$$

9.6 ELECTRIC SUSCEPTIBILITY

When a dielectric is placed in an electric field, it becomes electrically polarized. For most materials the polarization vector $\vec{P}$ is proportional to the electric field, i.e.

$$\vec{P} = \chi_e\vec{E} \qquad (32)$$

χ_e is called the electric susceptibility of the dielectric material.

The electric susceptibility χ_e of a dielectric material is a measure of how easily it polarizes in response to an electric field.

9.7 ELECTRIC DISPLACEMENT $\vec{D}$

If σ is the surface charge density of free charges and σ′is the surface charge density due to induced charge on the capacitors plate and dielectric surface. The magnitude of electric fields due to σ and σ′at any point between the plates of the capacitor are

$E_o = \sigma/\varepsilon_o$ and $E' = \sigma'/\varepsilon_o$ (33)

These are oppositely directed. The magnitude of resultant field within the dielectric is therefore

$E = E_o - E'$ (34)

putting the values of E_o and E from above relations

$E\varepsilon_o = \sigma - \sigma'$

$\sigma = E\varepsilon_o + \sigma'$ (35)

the term σ′is induced charge density which is equal to the magnitude of electric polarization vector P. hence

$\sigma = E\varepsilon_o + P$ (36)

Quantity $E\varepsilon_o + P$ has a significance in electrostatics and is known as electric displacement vector D

$$\vec{D} = \vec{E}\varepsilon o + \vec{P} \tag{37}$$

Or $D = \sigma$ (38)

σ is also called free charge density. The units of D are also same as of surface charge density i.e. coulomb/m^2. Since D is a vector quantity hence it has the same direction as of E and P. From the definitions and nature of D, E and P we reach on following conclusions.

1. D is linked with free charge only. This quantity can be represented by lines of electrical displacement similar to electric line of forces. The electric displacement lines arise and end at free charges only.
2. P is associated with polarization charges. The lines of polarization begin and end on the polarization charges only.

3. E vector is related to all kinds of charges present in the system.

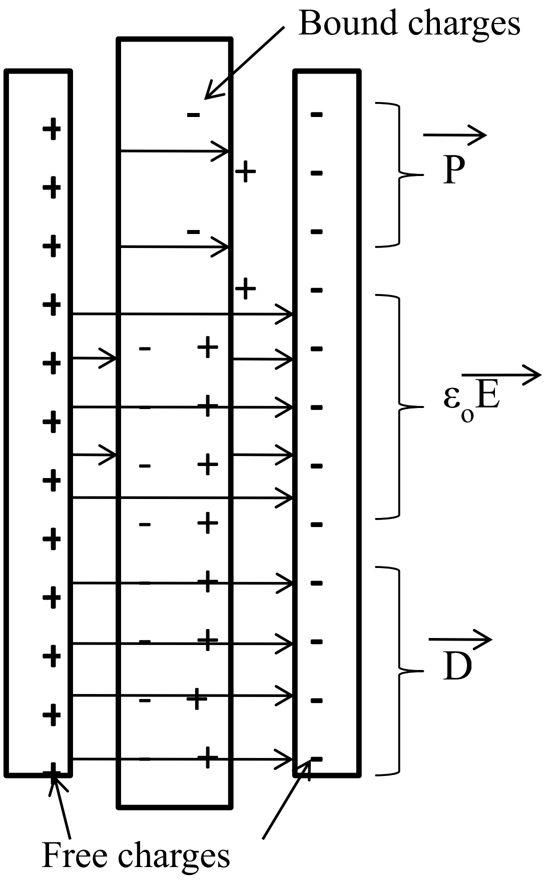

Figure 9: Dielectric inside the plates of a capacitor

For a homogeneous and isotropic dielectric D, E and P are in same direction.

again, if we assume a relation

$$\sigma = \epsilon_o \left(\frac{\sigma}{\epsilon_o}\right) \tag{39}$$

Now in vacuum

$$\sigma = \mathrm{D} \text{ and } \left(\frac{\sigma}{\epsilon_o}\right) = \mathrm{E_o}(\text{electric field in vacuum}) \tag{40}$$

Hence

$$\mathrm{D} = \mathrm{E_o}\epsilon_o \tag{41}$$

If K is dielectric constant of the material and E is the field in dielectric, then

$$\mathrm{E_o} = \mathrm{KE} \tag{42}$$

putting this value in above equation

$$\mathrm{D} = \mathrm{KE}\epsilon_\mathrm{o} \qquad (43)$$

Comparing equation (37) and (43)

$$\mathrm{KE}\epsilon_\mathrm{o} = \mathrm{E}\epsilon_\mathrm{o} + P$$

$$P = \mathrm{E}\epsilon_\mathrm{o}(\mathrm{K} - 1) \qquad (44)$$

in vacuum K=1, thus P = 0, i.e. polarization is not possible in vacuum.

Example 3: The dielectric constant of neon gas at NTP is 1.000134. Calculate the dipole moment induced in each atom of the gas when it is placed in an electric field of intensity 90kV/m. Also find the atomic polarizability of neon. Avogadro number is $6.023 \times 10^{26} \frac{atoms}{kg-mole}$.

Solution: let p be the dipole moment induced in each neon atom and *n* the number of neon atoms per meter^3. Then the electric polarization of the gas is given by

$$\mathrm{P} = \mathrm{np} = (\mathrm{K} - 1)\varepsilon_o E$$

$$p = \frac{(\mathrm{K}-1)\varepsilon_o E}{n} \qquad \text{(i)}$$

Now at NTP 1kg-atom of neon gas occupies a volume of 22.4meter^3 and contains 6.023×10^{26} atoms. Therefore the number of neon atoms in 1 m^3 is given by

$$n = \frac{6.023 \times 10^{26}}{22.4} = 2.69 \times 10^{25}$$

Substituting $K = 1.000134$, $E = \frac{90kV}{m}$ and $n = 2.69 \times 10^{25}$ in eq.(i) we have

$$p = \frac{(1.000134 - 1) \times 8.85 \times 10^{12} \times 90000}{2.69 \times 10^{25}}$$

$$= 3.97 \times 10^{-36} coul - m$$

The atomic polarizability is given by

$$\alpha = \frac{\mathrm{p}}{E} = \frac{3.97 \times 10^{-36}}{90000}$$

$$= 4.4 \times 10^{-41} \frac{(coul - m^2)}{volt}$$

9.8 MOLECULAR POLARIZABILITY AND ELECTRICAL SUSCEPTIBILITY

When a nonpolar molecule is placed in an electric field the center of gravity of positive and negative charges becomes separate from each other. The molecule or atom thus acquires an induced electric dipole moment. It is found that for most atoms or molecules the dipole moment is proportional to the applied electric field.

$$p \propto E$$

$$p = \alpha E \tag{45}$$

p and E both are vector quantities. Constant α is known as atomic or molecula
polarizability.

Again, polarization vector P is proportional to the electric field, thus

$$\vec{P} = \chi_e \vec{E}$$

$$\chi_e = \frac{P}{E} \tag{46}$$

where χ_e is a constant called electrical susceptibility of the dielectric material.

Thus, in a dielectric electric susceptibility is defined as the ratio polarizationto the electric field intensity. As we know there is no polarization occurs in vacuum hence value of χ_e is zero. The dielectrics having molecules of permanent dipole moment, their χ_e depends on temperature while for non-polar dielectrics χ_e is temperature independent.

Example4: the polarizability of NH_3 molecule is found experimentally by the measurement of dielectric constant as $2.5 \times 10^{-39} \frac{c^2-m}{N}$ at 300K and $2.0 \times 10^{-39} \frac{c^2-m}{N}$ at 400K. Calculate for each temperature the polarizability due to permanent dipole moment and that due to deformation of the molecules.

Solution: the total polarizability α of a polar molecule is the sum of deformation polarizability and orientational polarizability. Thus

$$\alpha = \alpha_d + \alpha_o \tag{i}$$

α_d is independent of temperature, but α_o inversely proportional to the absolute temperature, so that we may write.

$$\alpha_o = \frac{\beta}{T} \qquad \text{(ii)}$$

where β is constant. Thus we can write eq.(i) for temperature 300K and 400K as

$$2.5 \times 10^{-39} = \alpha_d + \frac{\beta}{300} \qquad \text{(iii)}$$

$$2.0 \times 10^{-39} = \alpha_d + \frac{\beta}{400} \qquad \text{(iv)}$$

subtracting eq(iv) from (iii), we get

$$0.5 \times 10^{-39} = \frac{\beta}{300} - \frac{\beta}{400} = \frac{\beta}{1200}$$

$$\beta = 0.5 \times 10^{-39} \times 1200 = 6 \times 10^{-37}$$

substituting this value of β in eq.(iii), we get

$$2.5 \times 10^{-39} = \alpha_d + \frac{6 \times 10^{-37}}{300}$$

$$\alpha_d = 2.5 \times 10^{-39} - 2 \times 10^{-39}$$

$$\alpha_d = 0.5 \times 10^{-39} \ \frac{c^2 - m}{N}$$

Again, substituting the value of β in eq.(ii), we get

$$\alpha_o \ at\ 300K = \frac{6 \times 10^{-37}}{300} = \ 2 \times 10^{-39} \ \frac{c^2 - m}{N}$$

$$\alpha_o \ at\ 400K = \frac{6 \times 10^{-37}}{400} = \ 1.5 \times 10^{-39} \ \frac{c^2 - m}{N}$$

9.9 RELATION BETWEEN DIELECTRIC CONSTANT AND SUSCEPTIBILITY

As we know displacement vector

$$\vec{D} = \vec{E}\varepsilon_o + \vec{P} \qquad (47)$$

But polarization vector

$$\vec{\mathrm{P}} = \chi_{\mathrm{e}}\vec{\mathrm{E}} \qquad (48)$$

Hence

$$\vec{D} = \vec{E}\varepsilon_o + \chi_{\mathrm{e}}\vec{\mathrm{E}} \qquad (49)$$

$$\vec{D} = \vec{E}(\varepsilon_o + \chi_{\mathrm{e}}) \qquad (50)$$

$$\vec{D} = \vec{E}\varepsilon_o\left(1 + \frac{\chi_{\mathrm{e}}}{\varepsilon_o}\right) \qquad (51)$$

The quantity $1 + \frac{\chi_{\mathrm{e}}}{\varepsilon o}$ is known as dielectric constant of the substance. Therefore

$$K = 1 + \frac{\chi_{\mathrm{e}}}{\varepsilon_o} \qquad (52)$$

For vacuum susceptibility is zero thus $K = 1$.

Now eq.(51) becomes

$$\vec{D} = \vec{E}K\varepsilon_o \qquad (53)$$

$$E = \frac{\mathrm{D}}{K\varepsilon_o} \qquad (54)$$

The term $K\varepsilon_o$is known as permittivity of the substance and denoted by ε.i.e.

$$\varepsilon = K\varepsilon_o \qquad (55)$$

In vacuum $K = 1$

Hence $\varepsilon = \varepsilon_o$called permittivity of free space. We can write the Eq.(55) as

$$\frac{\varepsilon}{\varepsilon_o} = K \tag{56}$$

Thus, dielectric constant of the material also known as relative permittivity of the material.

9.10 CLASSIUS-MOSSOTTI RELATION

Dielectric properties of any substance are macroscopic properties. Classius-Mossotti made a relation between dielectric constant of any dielectric and its microscopic parameters like molecular polarizability and electron density etc.

As we discussed already in this chapter that when we place a non-polar molecule in any external electric field its molecules get induced polarization. An internal electric field is setup in dielectric. The resultant electric field at any point inside the dielectric is called local field. Clausius and Mossotti found that induced dipole moment p is proportional to the local field. That is

$$p \propto E_{local} \tag{57}$$

$$p = \alpha E_{local} \tag{58}$$

'α' is the polarizability of a molecule. If n numbers of atoms or molecules per unit volume, then the polarization is given by

$$P = n\alpha E_{local} \tag{59}$$

E_{local} is given by

$$E_{local} = E + \frac{P}{3\varepsilon_o} \tag{60}$$

Hence

$$P = n\alpha\left(E + \frac{P}{3\varepsilon_o}\right) \tag{61}$$

As we proved earlier that polarization is,

$$P = E\epsilon_o(K - 1) \tag{62}$$

Comparing above two expressions (61) and (62) we have

$$\mathrm{E}\epsilon_{\mathrm{o}}(\mathrm{K}-1)=\mathrm{n}\alpha\left(\mathrm{E}+\frac{\mathrm{E}\epsilon_{\mathrm{o}}(\mathrm{K}-1)}{3\varepsilon_{o}}\right) \qquad (63)$$

$$\epsilon_{\mathrm{o}}(\mathrm{K}-1)=\mathrm{n}\alpha\left(\frac{(\mathrm{K}+2)}{3}\right) \qquad (64)$$

$$\frac{K-1}{K+2}=\frac{n\alpha}{3\varepsilon_{0}} \qquad (65)$$

This is the Clausius-Mossotti relation in terms of number of molecules or atoms per unit volume. ‘α’ can be determined easily because all the parameters are generally known or can be measured. This relation is true only for non-polar molecules. When $\frac{n\alpha}{3\epsilon_{\mathrm{o}}}$ approaches to unity, K becomes infinite. Hence the equation (65) is reasonable for low ρ and low ‘α’ for non-polar materials.

9.11 DIELECTRIC STRENGTH

Very high electric fields can free electrons from atoms and accelerate them to such high energies that they can, in turn, free other electrons, in an avalanche process (or electrical discharge). This is called dielectric breakdown, and the field necessary to start is called the dielectric strength or breakdown strength. The theoretical dielectric strength of a material is an intrinsic property of the bulk material and is independent of the configuration of the material or the electrodes with which the field is applied. Breakdown occurs quite abruptly (typically in nanoseconds), resulting in the formation of an electrically conductive path and a disruptive discharge through the material. For solid materials, a breakdown event severely degrades, or even destroys, its insulating capability.

Factors affecting apparent dielectric strength.

1. It decreases with increased operating temperature.
2. It decreases with increased frequency.
3. For gases it normally decreases with increased humidity.
4. For air, dielectric strength increases slightly as the absolute humidity increases but decreases with an increase in relative humidity.

Substance	**Dielectric Strength (10^6 V/m)**
Air	3.0
Alumina	13.4
Window glass	9.8 - 13.8
Borosilicate glass	20 - 40
Benzene	163
Distilled water	65 - 70
Mica	118
Diamond	2000
Vacuum	10^{12}

9.12 DIELECTRIC CONSTANT OF A CONDUCTOR

As we know that conductor is a material having large number of free electrons. When we put this conductor between the plates of a capacitor the free electrons in the conductor moves towards the surface facing positive plate and another surface of the conductor becomes positive. This motion continues until the electric field due to the induced charge becomes equal to the external applied field. Thus, inside the conductor electric field is zero everywhere.

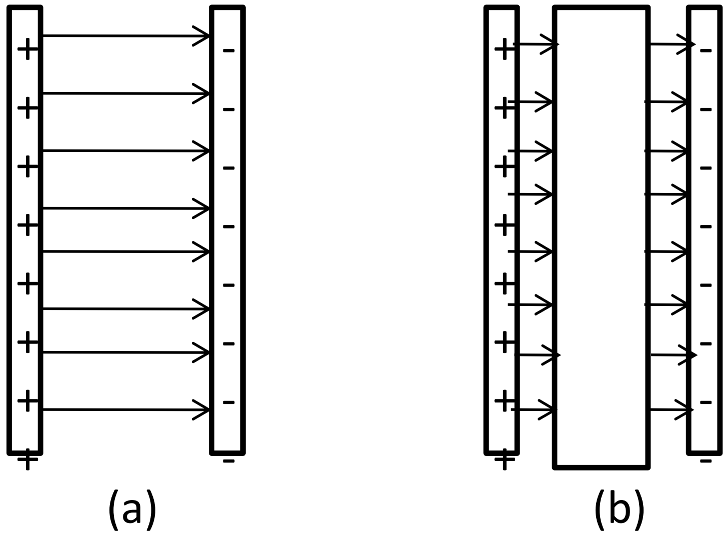

Figure 10: A conductor inside the plates of a capacitor

In figure 10(a) field lines starting from positive plate ends at negative plate. In figure 10(b) all the lines of force leaving the positive plate of the capacitor terminate on the induced negative charge on the left face of the conductor.

Similarly, the equal number of lines produced at the induced positive charges on the right face of the conductor and terminate on the negative charge on another plate of the capacitor. The induced charge produced on the face of the conductor are equal and opposite to the original charges on the capacitor plates. Since $E = 0$ inside the conductor, hence $K = \infty$, thus dielectric constant of a conductor is infinite**.**

9.13 FERROELECTRICITY

Since the dielectric behavior of some materials is in many respects analogous to the magnetic behavior of ferromagnetic materials, they are called ferroelectric solids or ferroelectrics. It is spontaneously polarized in the absence of external electric field. The direction of spontaneous polarization may be altered under influence of an applied electric field. In general, the direction of spontaneous polarization is not the same throughout in a macroscopic crystal. Rather, the crystals consist of a number of domains. Within each domain the polarization has a specific direction. In figure 11 consider a crystal which initially has an over-all polarization equal to zero. When an electric field is applied to the crystal, the domains with polarization components along the applied field direction grows at the expense of the antiparallel domains; thus, the polarization increases (OA). When all domains are aligned in the directions of the applied field, the polarization saturates (BC) and the crystal has become a single domain. Extrapolation of the linear part BC to zero external field gives the spontaneous polarization P_s. when the applied field for the crystal corresponding to point B is reduces the polarization of the crystal decreases, but for zero applied field there remain the remanent polarization P_r.

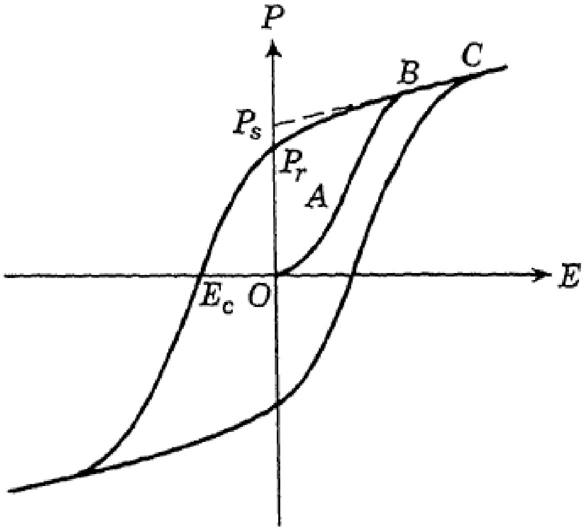

Figure 11: Representation of hysteresis in the electric polarization versus applied electric field.

To remove the remanent polarization, the polarization of about half the crystal must be reversed and this occurs only when a field in the opposite direction is applied. The field requires to make the polarization zero again is called the coercive field E_c.

The ferroelectric properties of a ferroelectric disappear above a critical Temperature T_c, this temperature is called ferroelectric curie temperature. Associated with the transition from the ferroelectric to the non-ferroelectric phase. The dielectric constant of ferroelectrics is not a constant but depends on the field strength at which it measured. The best example of ferroelectric material is barium titanate.

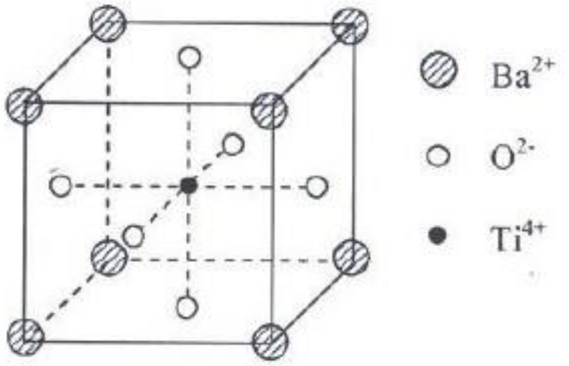

Figure 12: Structure of $BaTiO_3$, for $T>T_C$.

9.14 SUMMARY

In this chapter we studied various types of electric polarization and polarizability of dielectric solids. In electronic polarization (also called optical polarization) the electric field causes deformation or translation of the originally symmetrical distribution of the electron clouds of atoms or molecules. This is essentially the displacement of the outer electron clouds with respect to the inner positive atomic cores. In atomic or ionic polarization, the electric field causes the atoms or ions of a polyatomic molecule to be displaced relative to each other. This is essentially the distortion of the normal lattice vibration and this is why it is sometimes referred to as vibrational polarization. In orientational polarization the polarization occurs only in materials consisting of molecules or particles with a permanent dipole moment. The electric field causes the reorientation of the dipoles toward the direction of the field. Ferromagnetic materials are those which exhibit spontaneous electric dipole moment in the absence of applied electric field. These are analogous to ferromagnetic material. Ferroelectric materials possess a Curie point and exhibit hysteresis loop. This occurs mainly in amorphous or polycrystalline solids or in materials consisting of traps.

9.15 GLOSSARY

Polarization – separation of charges

Monoatomic substance – containing one atom in its molecule e.g. He, Ne, Ar etc

Diatomic substance - containing two atoms in its molecule e.g. H_2, N_2, HCl etc

Dielectric breakdown – loss of dielectric properties

Bound charge – the charge which cannot move

Non polar molecule – molecules having symmetrical structure

9.16 TERMINAL QUESTIONS

1. Find the total polarizability of CO_2, if its susceptibility is 0.985×10^{-3}. Density of carbon dioxide is 1.977 kg/m^3. [Ans. 3.24×10^{-40} Fm^2]

2. The relative permeability of argon at 0°C and atmosphere pressure is 1.000435. Calculate the polarizability of the atom. [Ans. 1.43×10^{-40} Fm^2]

3. Prove that the gravitational force is negligible in comparison to electrostatic force in the hydrogen atom in which the electron and proton are about 0.53Å apart.

4. The polarizability of neon gas is 0.35×10^{-40} Fm^2. If the gas contains 2.7×10^{25} atoms/m^3 at 0^{o}C and one atmosphere pressure; calculate its relative dielectric constant.

[Ans. 1.000108]

5. There are 1.6×10^{20} NaCl molecules/m^3 in a vapour. Determine the orientational polarization at room temperature if the vapour is subjected to an electric field 5000V/cm. Assume that the NaCl molecule consists of Na^+ and Cl^- ions separated by 0.25nm.

[Ans. 10^{-11}C/m^2]

6. One gram molecule of a certain polar substance is dissolved into 1000cm^3 of a nonpolar liquid. The liquid itself has a dielectric constant 3.000 at 27^{o}C, whereas the solution has a dielectric constant of 3.200 at that temperature. Calculate the dipole moment of polar molecule. [Ans. 0.355×10^{-29} Cm]

7. A parallel plate has an area of 8cm^2 with a separation of 0.08 mm. The space is filled with polystyrene. The real part of the relative dielectric constant is 2.56 and the loss tangent is 0.7×10^{-4} at a frequency of 1 MHz. Calculate the capacitance and the equivalent parallel loss resistance. [Ans. 226μF, 10MΩ]

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2. Solid State Physics, A. J. Dekker, Printed in USA.
3. Solid State Physics, S. O. Pillai, New Age International Publishers.
4. Solid State Physics, Puri and Babbar.

9.18 SUGGESTED READINGS

1. Introduction to Solid State Physics. Charles Kittel.

UNIT 10: MAGNETIC PROPERTIES OF MATERIALS

Structure

10.1 INTRODUCTION:

Magnetic materials fascinated human beings for over 4000 years. Magnetism is a phenomenon through which materials assert an attractive or repulsive force or influence on other materials. In the modern concept all materials are said to exhibit magnetism, though of different nature.

When a substance is placed in a magnetic field **H** substance gets magnetized. The magnetic moment per unit volume **M** is produced inside the substance **M** is called magnetization. The relation between magnetization and magnetic field is given by the equation

$$\vec{M} = \chi_m \vec{H} \qquad (1)$$

The constant $\chi_m$is called magnetic susceptibility of the material. It may be defined as the ratio of magnetization M and magnetic field intensity H. The value of χ_m for vacuum is zero because there is no magnetization in vacuum.

In this unit we shall discuss the various types of magnetic materials and their characteristics. We shall also discuss the different theories of magnetization broadly. In last we will discuss the temperature dependence of susceptibility using Langevin's function.

10.2 OBJECTIVES:

After studying this unit, you should be able to-

- Know magnetic permeability, susceptibility, retentivity etc.
- Know the difference between magnetic and non-magnetic materials.
- Differentiate the paramagnetic, diamagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic materials.
- Understand the hysteresis curve and hysteresis losses.
- Understand the domain theory of ferromagnetism.
- Learn the Langevin's theory of diamagnetism and paramagnetism.

10.3 MAGNETIC PERMEABILITY

When a specimen is placed in a magnetic field H it is magnetized due to alignments of current loops. The magnetic flux density within the specimen is the resultant of magnetizing field and intensity of magnetization M. The relation is given by

$$\vec{B} = \mu_o\overrightarrow{(H + \vec{M})} \qquad (2)$$

By susceptibility equation, we know that

$$\vec{M} = \chi_m\vec{H} \qquad (3)$$

Hence$\vec{B} = \mu_o\overrightarrow{(H + \chi_m\vec{H})}$

$$\vec{B} = \mu_o(1 + \chi_m)\vec{H} \qquad (4)$$

If we write

$$\mu = \mu_o\ (1 + \chi_m)$$

Then we have

$$\vec{B} = \mu\vec{H} \qquad (5)$$

The constant μ is called magnetic permeability if the material. Magnetic permeability may be defined as the ratio of magnetic induction to the magnetic intensity. For vacuum, it is denoted by $\mu_o(4\pi \times 10^{-7}\frac{Wb}{A-m})$ and called permeability of vacuum. Hence magnetic induction in vacuum will be

$$\overrightarrow{B_o} = \mu_o\vec{H} \qquad (6)$$

The ratio

$$\frac{B}{B_o} = \frac{\mu}{\mu_o} = \mu_r \qquad (7)$$

is called relative permeability.

Example 1: A magnetic field of 20 CGS units produces a flux of 2400 CGS units in a bar of iron of cross section 0.2cm^2. Calculate the permeability, intensity of magnetization and susceptibility of a bar.

Solution: the flux density in a bar is

$$B = \frac{\emptyset}{A} = \frac{2400}{0.2} = 12000\ gauss$$

Therefore, the permeability of the bar is

$$\mu = \frac{B}{H} = \frac{12000}{20} = 600\ CGS\ units$$

The intensity of magnetization is

$$I = \frac{B - H}{4\pi} = \frac{12000 - 20}{4 \times 3.14} = 953.8$$

The relation between permeability μ and susceptibility χ_m is

$$\chi_m = \frac{\mu - 1}{4\pi} = \frac{600 - 1}{4 \times 3.14} = 47.7\ CGS\ units$$

10.4 TYPES OF MAGGNETISM

According to modern theories, magnetism in solids arises due to orbital and spins motion of electrons as well as spin motion of nuclei. The motion of electrons is equivalent to an electric current which produces magnetic effect. The major contribution in magnetism comes from the spin of unpaired valence electrons which produces permanent magnetic moments. A number of such magnetic moments align themselves in different directions to generate a net non-zero magnetic moment. Therefore, the nature of magnetization produced depends on the number of unpaired valence electrons present in the atoms of the solid and on the relative orientations of the neighboring magnetic moments. The magnetism in solid materials can be classified into five main groups according to their magnetic properties.

1. Diamagnetism.
2. Paramagnetism.
3. Ferromagnetism.
4. Antiferromagnetism.
5. Ferrimagnetism.

Diamagnetism is a very weak magnetic effect and is found in those solids which do not contain any permanent magnetic moments.

10.4.1 Diamagnetism:

Diamagnetic materials do not have unpaired electrons in them. In these materials electron spin moments are mutually cancelled and there is no interaction between individual magnetic moments. These materials are weakly repelled in a magnetic field because they have a weak, negative magnetic susceptibility. Examples of diamagnetic materials are MgO, Cu, Ag, Au etc. The behavior of diamagnetic material in external magnetic field is shown in figure 1.

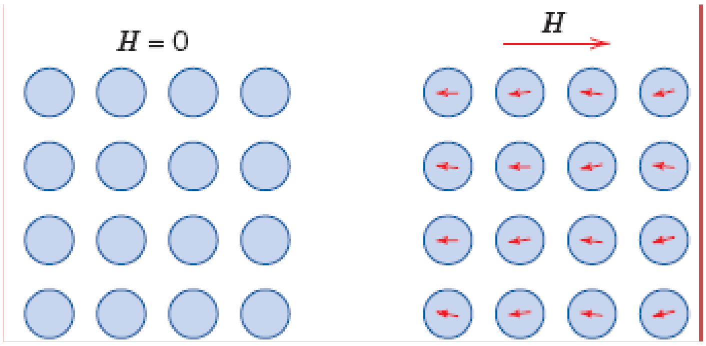


Figure 1: Atomic dipole configuration for a diamagnetic material without and with magnetic field.

10.4.2 Paramagnetism:

For some materials, each atom possesses a permanent dipole moment by virtue of incomplete cancellation of electron spin and/or orbital magnetic moments e.g. Mg, Mo, Li etc. In the absence of an external magnetic field, the orientations of these atomic magnetic moments are random, such that a piece of material possesses no net macroscopic magnetization. Paramagnetism results when they preferentially align, by rotation, with an external field as shown in figure 2. The susceptibility of the paramagnetic materials depends on temperature,

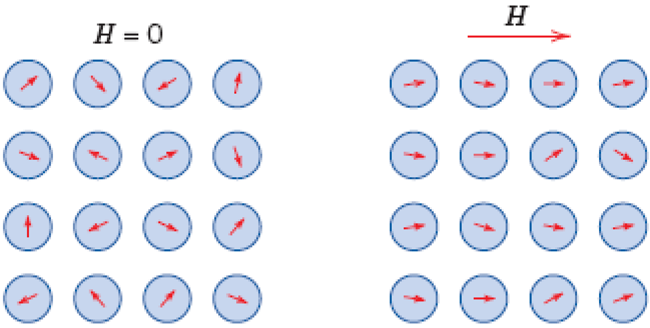


Figure 2: Atomic dipole configuration for a paramagnetic material without and with magnetic field.

following the *Curie law*:

$$\chi = \frac{C}{T} \tag{8}$$

where C is called Curie constant. In real systems interactions between the magnetic moments are present, and the susceptibility dependence on the temperature follow the *Curie-Weiss law*:

$$\chi = \frac{C}{T-\theta} \qquad (9)$$

where θ is called *Curie Weiss temperature* and it is related to the strength of the interactions between moments.

10.4.3 Ferromagnetism:

Certain metallic materials possess a permanent magnetic moment in the absence of an external magnetic field (figure 3), and exhibit very large and permanent magnetizations e.g. Fe, Co, Ni etc. Permanent magnetic moments in ferromagnetic materials result from atomic magnetic moments due to uncancelled electron spins as a consequence of the electron structure. Above a particular temperature called Curie temperature (T_c) the ferromagnetic material exhibits paramagnetism.

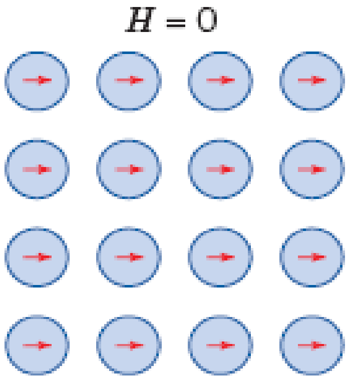


Figure 3: The orientation of atomic dipoles for a ferromagnetic material.

According to Weiss theory of ferromagnetism a specimen of ferromagnetic material contains a number of small regions called domains which are spontaneously magnetized. The magnitude of spontaneous magnetization of the specimen as a whole is determined by the vector sum of the magnetic moments of individual domains. The spontaneous magnetization of each domain is due to the presence of an exchange field, $\boldsymbol{B_E}$, which tends to produce a parallel alignment of the atomic dipoles. The field $\boldsymbol{B_E}$ is assumed to be proportional to the magnetization $\boldsymbol{M}$ of each domain, i.e.

$$B_E = \lambda M \qquad (10)$$

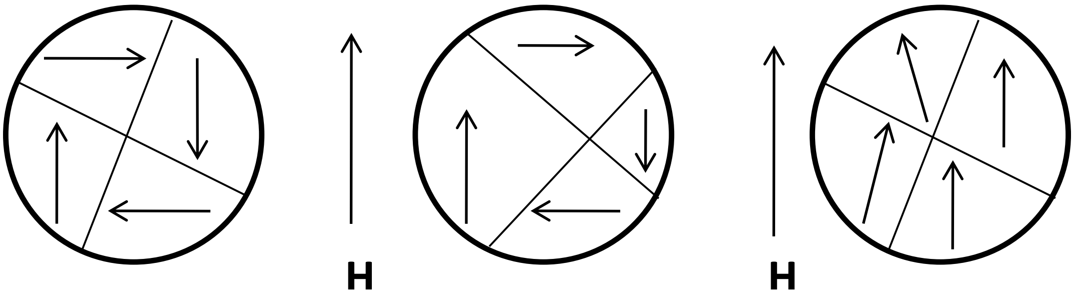
where λ is a constant called Weiss-field constant and is independent of temperature. The field B_E is also called the molecular field, it is generally quite strong as compared to the applied field B. B_E =1000Tesla for iron. Thus, the effective magnetic field on atom becomes

$$B_{eff} = B + \lambda M \qquad (11)$$

The magnetization produced in the ferromagnetic material in the presence of an external magnetic field may be attributed to

1. Growth in the size of domains having favourable orientation and corresponding shrink in the size of domains having unfavourable orientations with respect to the applied field.
2. Rotation of the directions of magnetizations of various domains along the direction of applied field.

These two magnetization processes are illustrated below in figure 4



(a) Unmagnetized Specimen

(b) Magnetization by domain growth

(c) Magnetization by domain rotation

Figure 4: two fundamental processes of magnetization in ferromagnetic materials.

In weak fields, the magnetization usually takes place by means of domain boundary displacement so that the favourably oriented domains increase in size. In strong field the magnetization occurs by the rotation of domains. When the field is removed the domain boundary do not move completely back to their original position, and the substance remains still magnetized. Now the substance becomes permanent magnet. At high temperature the domains are broken up and the ferromagnetic substance becomes paramagnetic having individual atomic dipoles.

Above the Curie temperature, T_C, the susceptibility of a ferromagnetic material obeys the Curie-Weiss law i.e.

$$\chi = \frac{C}{T - T_C} \tag{12}$$

where C is the Curie- Weiss constant

In figure 5 the variation of flux density with magnetic field strength is shown for diamagnetic, paramagnetic, ferromagnetic materials and vacuum. Flux density is maximum for ferromagnetic and minimum for diamagnetic materials.

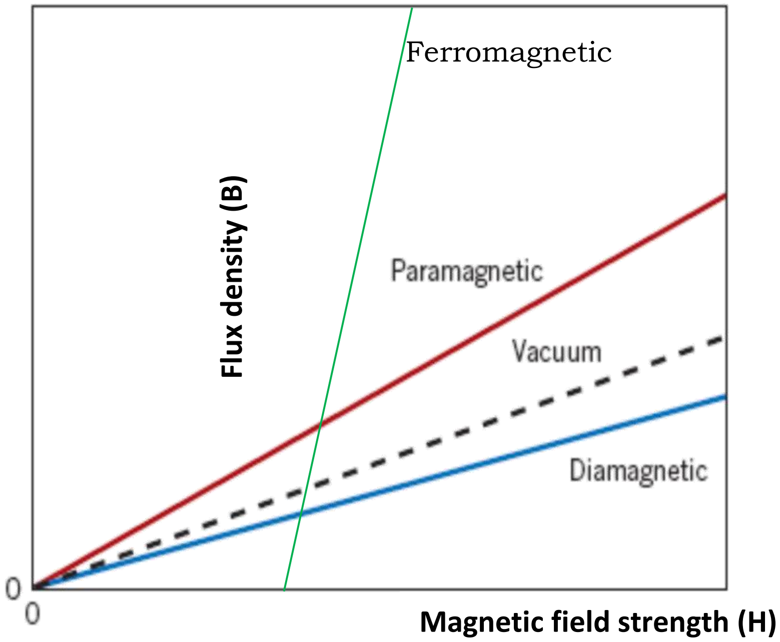


Figure 5: Flux density B versus the magnetic field strength H for different magnetic materials.

10.4.4 Antiferromagnetism:

This phenomenon of magnetic moment coupling between adjacent atoms or ions occurs in materials other than those that are ferromagnetic. In one such group, this coupling result in an antiparallel alignment; the alignment of the spin moments of neighboring atoms or ions are in exactly opposite directions, is termed antiferromagnetism. Manganese oxide(MnO) is one material that displays this behavior (figure 6). Antiferromagnetism occurs below a critical temperature called Neel temperature T_N. Above T_N, antiferromagnetic material becomes paramagnetic.

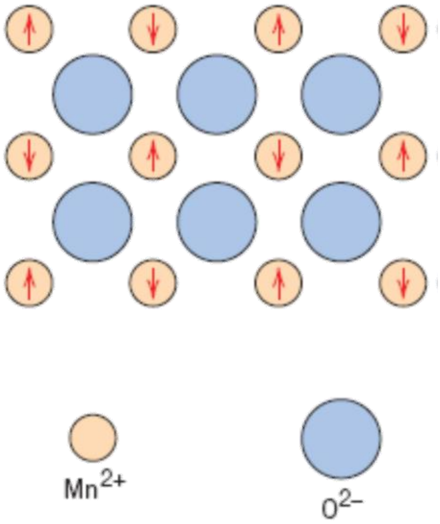


Figure6: Antiparallel alignment of spin magnetic moments for antiferromagnetic manganese oxide.

10.4.5 Ferrimagnetism:

The macroscopic magnetic characteristics of ferromagnets and ferrimagnets are similar; the distinction lies in the source of the net magnetic moments. These materials may be represented by the chemical formula MFe_2O_4 in which M represents any one of several metallic elements. The prototype ferrite is Fe_3O_4, the mineral magnetite, sometimes called lodestone. The formula for Fe_3O_4 may be written as $(Fe^{+2})[Fe^{+3}]_2O^{-2}_4$ in which the Fe ions exist in both +2 and +3 valence states in the ratio of 1:2. A net spin magnetic moment exists for each Fe^{+2} and Fe^{+3} ions, which corresponds to 4 and 5 Bohr magnetons, respectively. There are antiparallel spin-coupling between the Fe ions, similar in character to antiferromagnetism. However, the net moment arises from the incomplete cancellation of spin moments. Figure 7 shows the opposing magnetic moments of two different sites. As a result, the solid as a whole possesses some net magnetic moment.

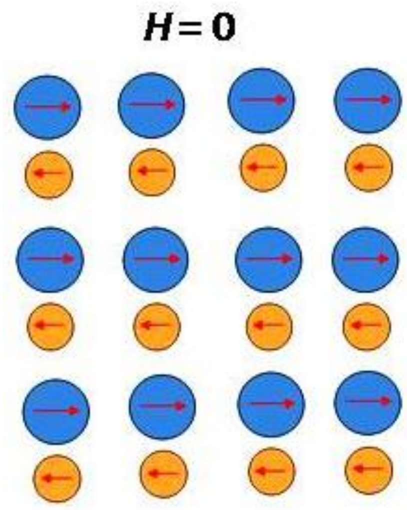


Figure 7: Antiparallel alignment of spin magnetic moments for ferrimagnetic materials.

10.5 RETENTETIVITY, COERCIVITY AND HYSTERESIS:

When a specimen of ferromagnetic material is placed in an external magnetic field the specimen is magnetized by induction. As the magnetic field intensity is varied the flux density in the material does not varies linearly which means the permeability is not constant. Permeability depends not only on the value of H but also on the past history of the material. The variation of **B** with the variation of **H** is shown in following figure 8. Point *O* represents an initially unmagnetised specimen at zero magnetic field intensity. As **H** is increased **B** also increased but not uniformly, and a point such as ‘*a*’ is reached where **B** becomes constant, and substance is called magnetically saturated. Magnetization corresponding to this point is called saturation magnetization $M_{S.}$

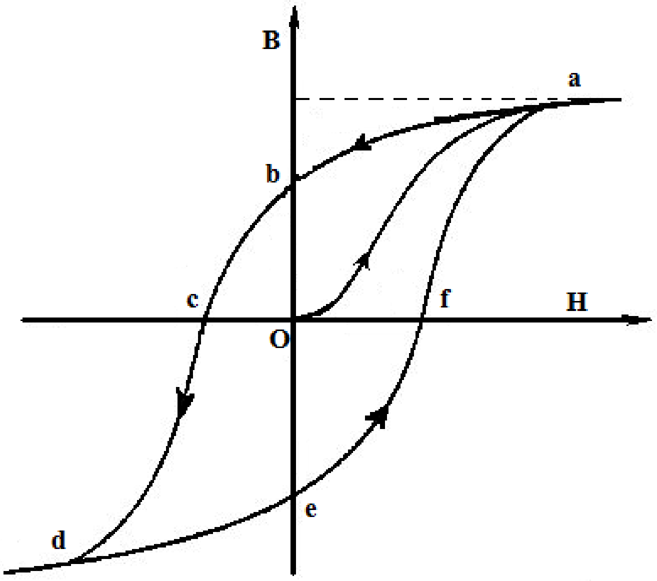


Figure 8: Hysteresis loop of a ferromagnetic material.

If **H** is now decreased, **B** also decreases but following a different path *abc*, thus **B** lags behind **H**. when **H** becomes zero **B** still has a value *Ob*. This magnetic flux density remaining in the specimen in the absence of any external field is called residual magnetism. The property of bearing this magnetism is called retentivity or remanence of the material. If the magnetic field intensity **H** is increased in reversed direction, the value of **B** further decreased, still lagging behind **H**, and becomes zero when magnetic field intensity **H** has a value equal to *Oc*. This value of magnetic intensity is called the coercivity of the specimen. Thus, coercivity is a measure of the magnetic intensity required to destroy the residual magnetism of a specimen.

When **H** is increased beyond *Oc* the specimen is strongly magnetized in opposite direction and a point such as *d* is reached after which magnetization becomes constant. Magnetization corresponding to this point is also called saturation magnetization $\mathbf{M_s}$ .reducing **H** from this point **d** to zero and again increasing in another direction a similar curve *defa* is obtained at point *b* and *e* where substance consist magnetization in the absence of external magnetic field, is said to be permanent magnet.

The closed curve *abcdefa* is known as hysteresis curve of the substance. Hysteresis curve shows that **B** always lags behind **H** when **H** changes.

Example 2: the hysteresis loop for a specimen of 12 kg is equivalent to 3000 ergs/cm^3. Find the loss of energy per hour at a frequency of 50 cycle/ sec, if density of iron is 7.5 gm/cm^3.

Solution: the energy dissipated per cm^3 per hysteresis loop is given to be 3000 ergs. The volume of the core is mass/ density.

$$\frac{12000}{7.5} = 1600\ cm^3$$

Therefore the energy dissipated in the specimen per cycle

$$= 1600 \times 3000 = 4.8 \times 10^6\ ergs$$

The number of cycles in one hour is

$$= 50 \times 60 \times 60 = 1.8 \times 10^5$$

$$\text{energy loss per hour} = 1.8 \times 10^5 \times 4.8 \times 10^6$$

$$= 8.64 \times 10^{11} ergs$$

10.6 SOFT AND HARD MAGNETIC MATERIALS

The wide variety of magnetic materials can be sharply divided into two groups, the magnetically soft (easy to magnetize and demagnetize) and the magnetically hard (hard to magnetize and demagnetize). The distinguishing characteristic of the first category is high permeability. Magnetically hard materials, on the other hand, are made into permanent magnets; here a high coercivity is a primary requirement because a permanent magnet once magnetize must be able to resist the demagnetizing action. Most widely used permeable materials are iron and iron alloys. Almost pure iron is used as the magnetic core for direct current applications. The maximum permeability is obtained for a composition of about 79% nickel and the balance is iron. Such an alloy shows zero magnetostriction and zero anisotropy and that is why the permeability is high. The addition of molybdeneum or chromium increases as the electrical resistivity thereby reducing the eddy current losses.

The most widely used permanent magnetic materials are low alloy steels containing 0.6 to 1% carbon which are hardened by quenching. The permanent magnetic materials usually hard, brittle and difficult to shape so that they must be cast and finished by grinding.

For many applications a permanent magnet is the better choice, because it provides a constant field without the continuous expenditure of electric power and without the generation of heat. A magnet can be regarded as an energy storage device. This energy is put into it when it is first magnetized and it remains in the magnet. In short the magnetism is permanent. Moreover, the energy of a magnet, which is chiefly the energy of its external field, is always available for use and is not drained away by repeated use, like the energy of a battery, because a magnet does no net work on its surroundings.

10.7 SUPERPARAMAGNETISM:

Superparamagnetism is a phenomenon by which magnetic materials may exhibit a behavior similar to paramagnetic material at temperatures below the Neel or the Curie temperature. In the absence of external magnetic field net magnetic moment is zero (figure 9). Normally, coupling forces in magnetic materials cause the magnetic moments of neighboring atoms to align, resulting in very large internal magnetic fields. At temperatures above the Curie temperature or the Neel temperature, the thermal energy is sufficient to overcome the coupling forces, causing the atomic magnetic moments to fluctuate randomly. Because there is no longer any magnetic order, the internal magnetic field no longer exists, and the material exhibits paramagnetic behavior. Superparamagnetism occurs when the material is composed of very small crystallites (lower than 100 nm). In this case even though the temperature is below the Curie or Neel temperature and the thermal energy is not sufficient to overcome the coupling forces between neighboring atoms, the thermal energy is sufficient to change the direction of magnetization of the entire crystallite. The material behaves in a manner similar to paramagnetic, except that instead of each individual atom being independently influenced by an external magnetic field, the magnetic moment of the entire crystallite tends to align with the magnetic field. The energy required to change the direction of magnetization of a crystallite is called the crystalline anisotropy energy and depends both on the material properties and the crystallite size.

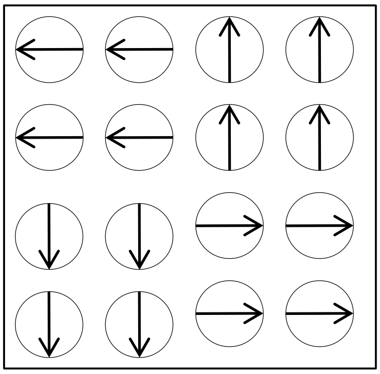


Figure 9: Ordering of the atomic dipoles in a superparamagnetic material.

10.8 ATOMIC MODEL OF MAGNETISM

It is impossible to separate the north and south poles of a magnet. When a magnet is divided into small pieces, each piece is a complete magnet. Every matter is made up of atoms. According to atomic model of magnetism, each atom is a complete magnetic dipole. Each atom consists of a positively charged nucleus at the center and electrons revolve around the nucleus in definite orbits. The motion of electrons around the nucleus is identical to that of earth around the sun. Accordingly electron revolving nucleus has two types of motion.

(i). **Orbital Motion**: electrons revolve around the nucleus in a definite obit (this motion is identical to the motion of earth around the sun).

(ii). **Spin Motion**: electrons spin about its own axis. This spin motion may be clockwise or anticlockwise (this motion is identical to the rotation of earth about its own axis).

As electron has negative charge, therefore the revolving electron is a current loop. A current loop is equivalent to a magnetic dipole and possesses a magnetic moment. This magnetic moment is resultant of both due to orbital motion and spin motion of the electron. However, the most of magnetic moment is produced due to spin motion and a very small contribution due to orbital motion.

$$\vec{m}_l = -\frac{e}{2m_e}\vec{L} \tag{13}$$

In addition to orbital angular momentum **L**, electron possesses spin angular momentum **S**. which contribute to spin magnetic moment, given by

$$\vec{m}_s = -\frac{e}{m_e}\vec{S} \tag{14}$$

Therefore, the total magnetic moment will be

$$m = \vec{m}_l + \vec{m}_s \tag{15}$$

$$= -\frac{e}{2m_e}\vec{L} - \frac{e}{m_e}\vec{S} \tag{16}$$

$$= -\frac{e}{2m_e}[\vec{L} + \overrightarrow{2S}] \tag{17}$$

10.9 LANGEVIN’S THEORY OF DIAMAGNETISM:

Those substances which are weakly magnetized in the opposite direction to the applied field are known as diamagnetic materials. According to Langevin’s theory an electron revolving in orbit behaves as a current loop, and the value of the current equals the rate at which charge passes any given point of the loop. Thus

$$i = ev \tag{18}$$

where v is the angular frequency of the motion of the electron and $v = \frac{\omega}{2\pi}$. The magnetic dipole moment associated with this current would be

$$p = iA = evA \tag{19}$$

where A is the area of the orbit and $A = \pi r^2$, r is the radius of the orbit. Thus

$$p = e(\frac{\omega}{2\pi})\,(\pi r^2) = \frac{1}{2}e\omega r^2 \tag{20}$$

In a diamagnetic material the number and orientations of electron orbits in each atom are such that the net magnetic moment of the atom is zero. Whenever a diamagnetic material is placed in a magnetic field the electronic currents in each atom are modified in such a way that a magnetic moment is induced whose direction is opposite to the applied field. In the absence of magnetic field, the Coulomb force on the electron by atomic nucleus is the required centripetal force, that is

$$F_c = m\omega_o^2 r \tag{21}$$

where ω_o is the angular velocity of the electron of mass m in its orbit. When an external magnetic field is applied perpendicular to the plane of the orbit, an external magnetic force acts on the electron. This force, being perpendicular to the direction of motion of the electron as well as to the magnetic field. Hence the new centripetal force on the electron is

$$electrostaticforce \pm magneticforce$$

$$F_c \pm F_m \tag{22}$$

a change in centripetal force requires a change in the angular velocity of the electron. if ω be the new angular velocity, then we have

$$F_e \pm F_m = mr\omega^2 \qquad (23)$$

$$m\omega_o^2 r \pm Bev = mr\omega^2 \qquad (24)$$

$$\pm Ber\omega = mr\omega^2 - m\omega_o^2 r \qquad (25)$$

$$\pm Be\omega = m(\omega^2 - \omega_o^2) = m(\omega - \omega_o)(\omega + \omega_o) \qquad (26)$$

The quantity $(\omega - \omega_o)$ is $(\Delta\omega)$ change in angular frequency of the electron. $(\omega + \omega_o)$ is approximately 2ω because ω differs slightly from ω_o even in high magnetic field. Thus

$$\pm Be\omega = m\Delta\omega\, 2\omega \qquad (27)$$

$$\Delta\omega = \pm \frac{Be}{2m} \qquad (28)$$

This change in angular velocity results a change in magnetic moment whose magnitude is given by modifying equation (20)

$$\Delta p_m = \frac{1}{2} er^2 \Delta\omega \qquad (29)$$

$$= \frac{1}{2} er^2 \frac{Be}{2m} \qquad (30)$$

$$= e^2 r^2 \frac{B}{4m} \qquad (31)$$

If an atom consists j electrons, the total induced magnetic moment is

$$\sum_j \Delta p_m = \frac{e^2 B}{4m} \sum_j {r_j}^2 \qquad (32)$$

If n be number of atoms of the material per unit volume, then magnetic moment per unit volume will be

$$I = n \sum_j \Delta p_m \qquad (33)$$

$$I = n \frac{e^2 B}{4m} \sum_j {r_j}^2 \qquad (34)$$

Now $B = \mu_o(H + I)$. Since I is very small for diamagnetic material, hence $B = \mu_o H$, thus

$$I = n\frac{e^2\mu_o H}{4m}\sum_j {r_j}^2 \qquad (35)$$

in vector form this equation will be written as

$$\vec{I} = -n\frac{e^2\mu_o}{4m}\sum_j {r_j}^2\,\vec{H} \qquad (36)$$

Negative sign indicates that $\vec{I}$ *and* $\vec{H}$ are in opposite directions. Magnetic susceptibility of the diamagnetic material is therefore given by

$$\chi = \frac{\vec{I}}{\vec{H}} = -\mu_o\frac{ne^2}{4m}\sum_j {r_j}^2 \qquad (37)$$

This expression shows that for a diamagnetic material the magnetic susceptibility is negative and is independent of the temperature. Thus, diamagnetism is a universal property of the material.

10.10 LANGEVIN’S THEORY OF PARAMAGNETISM

A paramagnetic material is one which when placed in a magnetic field becomes weakly magnetized in the same direction as the field. Langevin explained paramagnetism on the basis that the atoms or molecules of a paramagnetic material have a net intrinsic magnetic moment due to the spin and orbital motion of electrons in it. In the absence of magnetic field, a macroscopic amount of paramagnetic material is not magnetized because molecules are randomly oriented due to thermal vibrations so that the net magnetic moment of the specimen is zero.

When paramagnetic material is placed in an external magnetic field the molecule experience torque which tries to align them in the direction of the field. But the alignment is not complete because the thermal motion of the molecule which favors random orientation. The average alignment gives raise a net magnetic moment per unit volume in the direction of the field. If the temperature of the specimen is raised the magnetization becomes smaller due to the increase of thermal agitation.

Let us now calculate the net magnetic moment per unit volume produced by alignment of the molecules at certain temperature T. suppose n be the number of molecules per unit volume of the specimen and θ the angle which the magnetic moment $\overrightarrow{p_m}$ of a molecule makes with the external magnetic field $\vec{B}$ the potential energy of the molecule in the field is

$$U = -\mathrm{p_m}\,\mathrm{B}\cos\theta \tag{38}$$

Statistically the number of molecules having energy U at a temperature T is proportional to$e^{-U/kT}$, where k is Boltzman's constant. The number of molecules per unit volume dn, having energy U and oriented at angles between $\theta and\ \theta + d\theta$with respect to the direction of $\vec{B}$ is given by

$$dn = Ce^{-U/kT}d\omega \tag{39}$$

Where C is a constant and $d\omega$ is solid angle between two hollow cones of semi vertex angles $\theta and\theta + d\theta$ and is given by

$$d\omega = 2\pi\sin\theta d\theta \tag{40}$$

substituting the value of U and $d\omega$ in equation (39) using equation (38) and (40) we get

$$dn = Ce^{\mathrm{p_m}\,\mathrm{B}\cos\theta/kT}2\pi\sin\theta d\theta$$

or

$$dn = Ae^{\mathrm{x}\cos\theta}\sin\theta d\theta \tag{41}$$

where

$$x = \frac{\mathrm{p_m B}}{kT} \tag{42}$$

and $A = C2\pi$is a new constant. Integrating equation (41) from $\theta = 0$ to $\theta = \pi$, we get the total number of molecules per unit volume i.e.

$$n = A\int_0^\pi e^{\mathrm{x}\cos\theta}\sin\theta d\theta \tag{43}$$

putting $\cos\theta = r$, $\sin\theta d\theta = -dr$ we have

$$n = -A\int_1^{-1} e^{xr}dr \tag{44}$$

$$= -A\left[\frac{e^{xr}}{x}\right]_1^{-1} \quad (45)$$

$$= -\frac{A}{x}(e^{-r} - e^{r}) \quad (46)$$

$$= \frac{A}{x}(e^{r} - e^{-r}) \quad (47)$$

$$= \frac{2A}{x}(\sinh x) \quad (48)$$

Since each molecule of dn has a component of magnetic moment $p_m \cos\theta$ along the direction of magnetic field. Thus, the magnetic moment of dn molecules along the direction of magnetic field $p_m \cos\theta\, dn$. The total magnetic moment I along the direction of field due to all molecules per unit volume is given by

$$I = \int_0^{\pi} p_m \cos\theta\, dn \quad (49)$$

using equation (48)

$$I = Ap_m \int_0^{\pi} e^{\mathrm{x}\cos\theta} \cos\theta \sin\theta d\theta \quad (50)$$

Assuming $\cos\theta = r$so that $\sin\theta d\theta = -dr$ we have

$$I = -Ap_m \int_1^{-1} re^{rx} dr \quad (51)$$

$$= -Ap_m\left[r\frac{e^{rx}}{x} - \int_1^{-1}\frac{e^{rx}}{x}dr\right]_1^{-1} \quad (52)$$

$$= -Ap_m\left[r\frac{e^{rx}}{x} - \frac{e^{rx}}{x^2}\right]_1^{-1} \quad (53)$$

$$= -Ap_m\left[\left\{-\frac{e^{-x}}{x} - \frac{e^{-x}}{x^2}\right\} - \left\{\frac{e^{x}}{x} - \frac{e^{x}}{x^2}\right\}\right] \quad (54)$$

$$= \frac{Ap_m}{x}\left[\left\{e^{-x} + \frac{e^{-x}}{x}\right\} + \left\{e^{x} - \frac{e^{x}}{x}\right\}\right] \quad (55)$$

$$= \frac{Ap_m}{x}\left[\{e^{x} + e^{-x}\} - \frac{1}{x}\{e^{x} - e^{-x}\}\right] \quad (56)$$

$$= \frac{2Ap_m}{x}\left[\cosh x - \frac{\sinh x}{x}\right] \tag{57}$$

Using Eq. (48), $\frac{2A}{x} = \frac{n}{\sinh\, x}$, we have

$$I = np_m\left[\coth x - \frac{1}{x}\right] \tag{58}$$

$\left[\coth x - \frac{1}{x}\right]$ is termed as Langevin's function and is denoted by $L(x)$. Hence

$$I = np_m L(x) \tag{59}$$

where

$$x = \frac{Bp_m}{kT} \tag{60}$$

for small value of x the series expansion of $L(x)$ shows that

$$L(x) = \coth x - \frac{1}{x} \simeq \frac{x}{3} \tag{61}$$

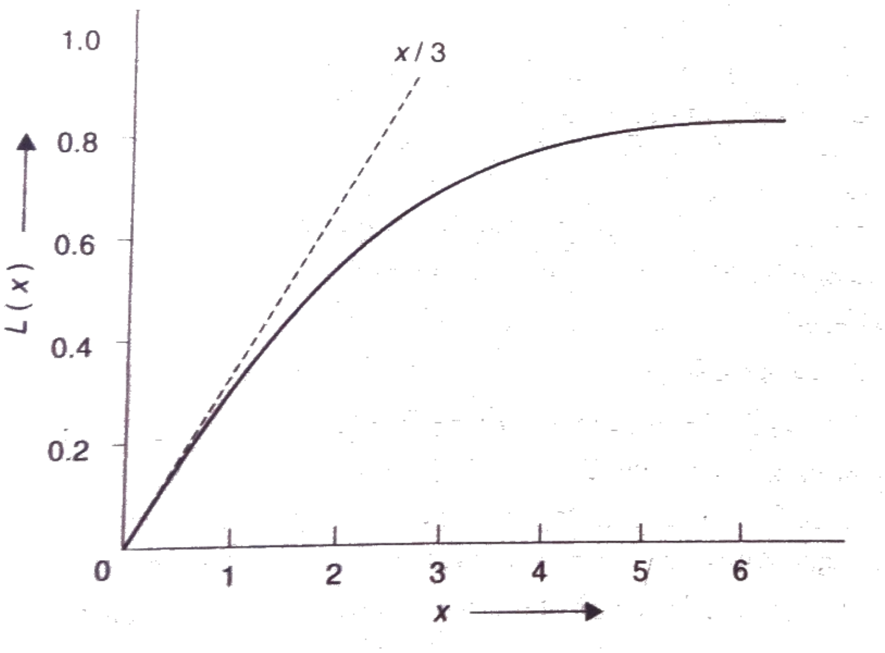


Figure 10: Variation of Langevin function with x

so that

$$I = np_m \frac{x}{3} = \frac{np_m{}^2}{3kT}B \tag{62}$$

we know that $B = \mu_o(H + I)$, $I$is very small for paramagnetic substances hence $B = \mu_o H$. Then we have $I = \mu_o \frac{n{p_m}^2}{3kT} H$

Since magnetization is a vector quantity, hence

$$\vec{I} = \mu_o \frac{n{p_m}^2}{3kT} \vec{H} \qquad (63)$$

In paramagnetic materials $\vec{I} and \vec{H}$ are in same direction. The magnetic susceptibility of a paramagnetic material is given by

$$\chi = \frac{\vec{I}}{\vec{H}} = \mu_o \frac{n{p_m}^2}{3kT} \qquad (64)$$

$$\chi \propto \frac{1}{T} \qquad (65)$$

Thus, for a paramagnetic material the magnetic susceptibility is inversely proportional to the absolute temperature. This relation is known as Curie's law.

10.11 SUMMARY

In this chapter we concluded that diamagnetism is a very weak magnetic effect. It is observed in those solids which do not contain any permanent magnetic moment. The small non-zero magnetic moment in these materials is due to the orbital motion of electrons. This magnetic moment is always directed to the opposite of applied magnetic field. Paramagnetism is also a weak magnetic effect, unlike diamagnetism, the magnetic moments are aligned in the directions of the field. Ferromagnetism a strong magnetic effect and arises when the adjacent magnetic moments align themselves in the same direction. In antiferromagnetism, the adjacent magnetic moments are equal and opposite of each other and hence complete cancellation of magnetic moments takes place. Ferrimagnetism is similar to antiferromagnetism except that adjacent magnetic moments are unequal in magnitude therefore the complete cancellation of moments does not take place. It is also found that above a certain temperature the difference in magnetic properties disappears and all the materials becomes paramagnetic.

10.12 GLOSSARY

Specimen – sample

Flux density – Flux passing through per unit volume

Domain – small regions

Orientation - direction

Susceptibility – sensitivity

Retentivity – tendency to retain

Saturation magnetization – limit to be magnetized

Remanence – residual magnetism

Hysteresis – tendency to remember their magnetic history.

10.13 TERMINAL QUESTIONS

1. What is hysteresis? Discuss a brief laboratory method for determining the hysteresis curve of a sample of iron. What is the utility of the curve? Derive an expression for the energy dissipated in hysteresis cycle.
2. Write short notes on (i) Hysteresis, (ii) magnetic circuit and (iii) Magnetic reluctance.
3. A paramagnetic substance of volume 40 cm^3 is placed in a magnetic field of intensity 500 oersted. Find (i) the magnetization, (ii) permeability and (iii) mass susceptibility. Given that susceptibility $= 0.3 \times 10^{-3}$ and density $= 5.0\,\frac{g}{cm^3}$.

   [Ans. (i) 150 joule/ weber-m^3, (ii) 1.0038, (iii) $6 \times 10^{-8} kg - m^3$]
4. Two rectangular blocks of length 20 cm and 10 cm, each of area 3cm×5cm are connected in series. Assuming magnetic induction uniform throughout the blocks, find the net reluctance and permeance. The relative permeabilities of blocks are 500 and 2000 respectively. [Ans. 1.59×10^5 h^{-1}, 6.3×10^{-6}h]
5. Consider a typical magnetic field of 10^4 gauss and compare the magnetic potential energy of an electron spin dipole moment with kT at room temperature. [Ans. $\frac{\mu H}{kT} \approx 2.3 \times 10^{-3}$]
6. A magnetic material has magnetization of 3300 ampere/meter and flux density of 0.0044 Wb/m^2. Calculate the magnetizing field and the relative permeability of the material. [Ans. 203A/m, 17.3]
7. The magnetic field intensity in a piece of ferric oxide is 10^6 ampere/ meter. If the susceptibility of the material at room temperature is 1.5×10^{-3}, compute the flux density and magnetization of the material. [Ans. 1.259Wb/m^2,1500A/m]

10.14 REFERENCES

1. Introduction to Solid State Physics. Charles Kittel.
2. Solid State Physics, S.O. Pillai.
3. Solid State Physics, Puri and Babbar.
4. Solid State Physics, R.L.Singhal.

10.15 SUGGESTED READINGS

1. Introduction to magnetic materials, B.D. Cullity.

UNIT 11 SUPERCONDUCTIVITY

Structure:

11.1 INTRODUCTION

When certain materials or alloys are cooled to sufficiently low temperatures (say beyond the critical temperature T_C), the electrical resistivity of many material and alloys suddenly drop to zero. This critical temperature is of the range of temperature of liquid helium. Such materials and alloys are termed as superconductors and this phenomenon is called superconductivity. The zero resistance of the material leads to the maximum conduction in the material. Thus, it is named as superconductors. At critical temperature T_C, a phase transition is observed in the specimen from normal conducting state to superconducting state.

In superconducting state, the dc resistivity of a superconducting specimen is zero or very close to zero thus the electric current in a superconducting loop can flow for many years without any attenuation. The variation of the superconducting behaviour of superconductor and metals (pure or impure) is shown in Fig.14.1.

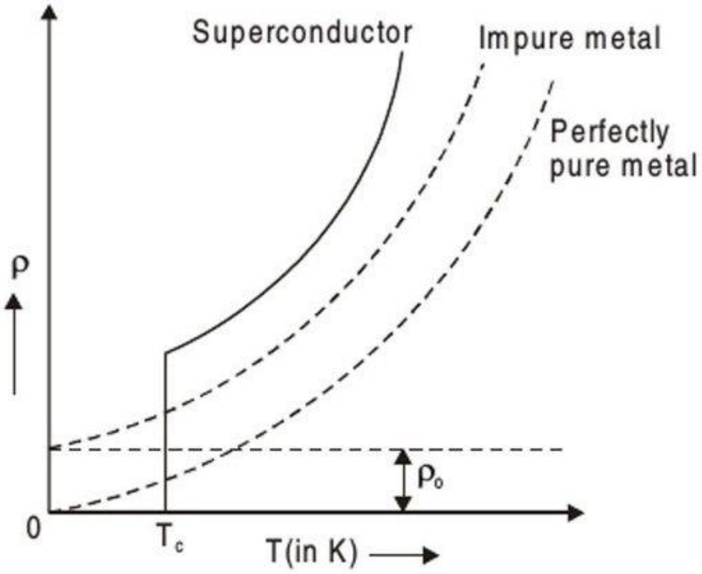


Figure 11.1 Variation of resistance of a metal and a superconductor with temperature.

Following are some important features of superconductivity:

- The crystal structure did not get altered during transition from normal state to superconducting state. This can be proved by X-ray diffraction. This also validates that the superconductivity is a phenomenon related to free electrons and not the atoms.
- The photoelectric properties did not change.
- Thermal expansion and elastic properties remained unchanged.
- Latent heat and volume remain unchanged.
- During the phase transition, the magnetic flux is fully ejected out of the material and it behaves as a perfect diamagnetic material.
- If the field equal to critical field H_c is applied to the material, it loses its superconductivity.

- Specific heat shows exponential change with temperature.

11.2 OBJECTIVE

After studying this unit, we should be able to understand-

- Superconductivity
- Critical field and critical temperature
- Meissner Effect
- Thermodynamic properties of superconductor
- London Equation
- London Penetration depth
- Coherence length
- BCS Theory

11.3 DISCOVERY OF SUPERCONDUCTIVITY AND OBSERVATIONS

In 1908, Kamerlingh Onnes was first liquidify the helium. He used an ingenious apparatus to cool helium and converts it in liquid form. This liquid helium and its properties were studied. Based on this theory, cooling of different substances and framing their properties at low temperatures was also done. Later, this theory became base for the generating of the new theory of superconductors. In 1911, Kamerlingh Onnes observed that the electrical resistance of mercury dropped abruptly and completely disappeared at temperatures a few degrees above the absolute zero, and named this phenomenon as superconductivity. Kamerlingh demonstrated the superconducting phases for 25 elements. Many alloys and intermetallic compounds have also been shown to be superconductors. A few of them are mentioned in Table 1.

Table 1: Some elements and compounds show superconductivity

Element	**T_C (K)**	**Compound**	**T_C (K)**
Niobium	9.46	Nb_3Ge	23.2
Lead	7.18	Nb_3Ga	20.3
Mercury	4.15	Nb_3Sn	18.05
Indium	3.41	NbN	16
Aluminium	1.19	Mo_3Lr	8.8
Cadmium	0.56	$PdSb_2$	1/25
Titanium	0.40	AuBe	2.64
Iridium	0.14	$AuSb_2$	0.58
Tungsten	0.01	$ZrAl_2$	0.30

In case of the superconductors, the resistance decreases with the decrease in temperature and when the metal became a superconductor the resistivity abruptly drops to 0 at T_c. This temperature is termed the critical temperature. As predicted by Cohen, superconductivity had been observed in semiconductor crystals with large free electron densities. There is a possibility of every pure element showing superconducting behaviour below critical temperature, though it may take a long time for the transition to occur. The monovalent alkali and noble metals had been investigated to less than 0.1K without showing any evidence of superconductivity. Superconductivity is also absent in the ferromagnetic metals, and it is well known that magnetic impurities have a deleterious effect on superconductivity in their host solid. This is easy to reconcile with the startling magnetic behaviour of a superconductor.

11.4 DESTRUCTION OF SUPERCONDUCTIVITY BY MAGNETIC FIELD

In 1913, Kammerlingh observed that superconductivity is destroyed if sufficient strong magnetic field is applied. In other words, we can say that the electrical resistivity of any material remains unaltered or restored due to the presence of a strong magnetic field. The externally applied magnetic field necessary to destroy the superconductivity of any material is called the critical magnetic field $H_C(T)$. $H_C(T)$ is the function of temperature and is expressed by the equation given as:

$$H_C(\mathrm{T}) = H_C(0)\left[1-\left(\frac{T}{T_C}\right)^2\right] \qquad (1)$$

Where $H_C(0)$ is the critical magnetic field at absolute zero.

This expression is often called Tuyn's law. The relation between critical field and temperature is shown in figure 14.2 which is result of this expression. It shows the phase boundary between the superconducting and normal state.

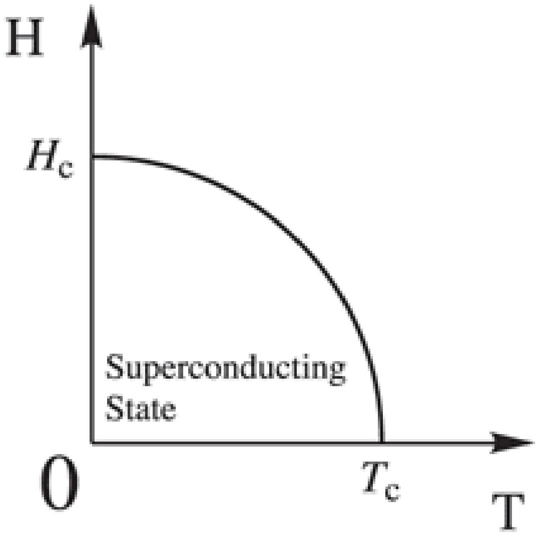


Figure 14.2 Variation of critical magnetic field with temperature.

11.5 MEISSNER EFFECT

In 1933, Meissner and Ochsenfeld found that if a superconductor is cooled in a magnetic field below the transition temperature, the magnetic field lines are pushed out from the bulk superconductor. They named this phenomenon “Meissner effect”. In other words, the bulk superconductor behaves as the inside of superconductor B = 0. The relatively weak magnetic fields are entirely repulsed from the interior of superconductors. The Fig 14.3 shows the behaviour of magnetic field lines when a superconductor is placed in magnetic field.

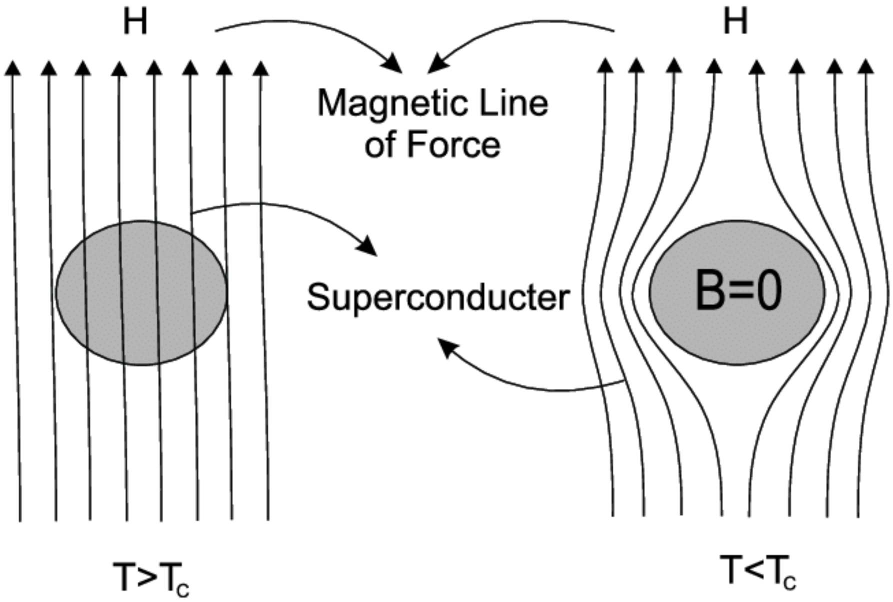


Figure 3 Meissner effect in Superconductors.

The Meissner effect can be understand by assuming that the destruction of magnetic field inside the bulk superconductor is due to an electric current flowing inside the material, which produces a magnetic field which cancel the applied magnetic field. Thus the net magnetic field inside the superconducting material is zero as

$$B = 0 \tag{2}$$

$$B = \mu_0(H + M) \tag{3}$$

$$H = -M$$

And, magnetic susceptibility is given as

$$\chi = \frac{M}{H} = -1 \tag{4}$$

This gives the negative magnetic susceptibility of which show the superconductivity behaves as perfect diamagnetic material.

11.6 TYPES OF SUPERCONDUCTIVITY

Superconductors have been classified as the type I and type II depending upon their behaviour in an external magnetic field, i.e., how they follow the Meissner effect.

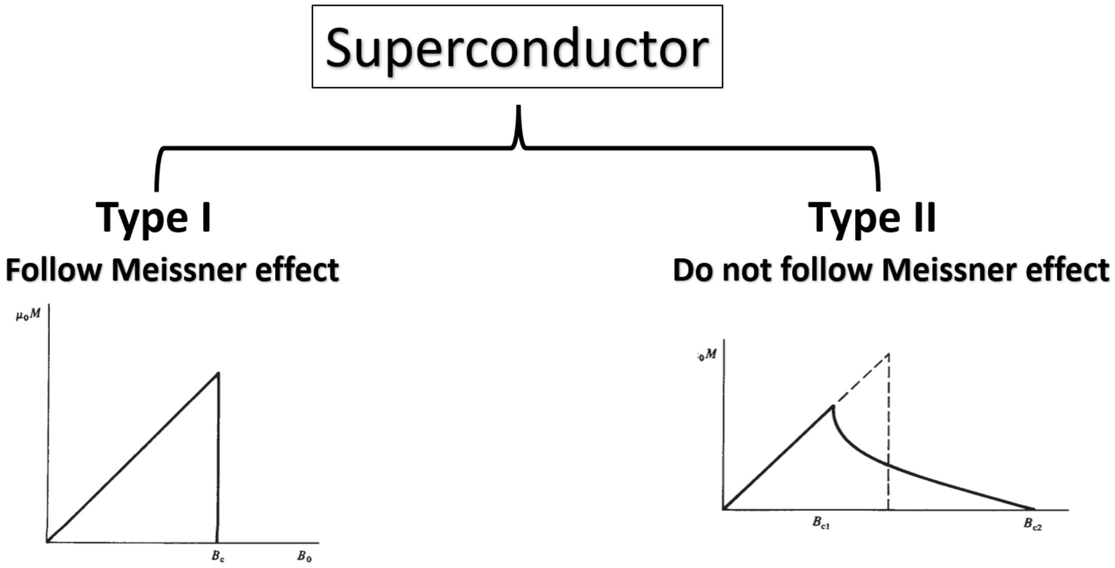


Figure 11.4 Types of superconductors and magnetization curves.

Type I superconductors:

In type I superconductor, as critical field reaches the superconductivity destroyed suddenly and entire specimen change to normal state. Figure 14.4(a) shows the magnetization curve. At critical field the magnetization suddenly becomes zero and superconductivity destroyed. Material exhibits such behavior is call type I superconductors or soft superconductor. These superconductors easily lose the superconducting state by low-intensity magnetic field. Therefore, Type-I are also known as soft superconductors. Some properties of Type I superconductors are:

- Low critical temperature (typically in the range of 0K to 10K)
- Perfectly obey the Meissner effect and magnetic field cannot penetrate inside the material.
- The transition from a superconducting state to a normal state due to the external magnetic field is sharp and abrupt for type-I superconductors.
- Type-I superconductors are generally pure metals.
- These are completely diamagnetic.
- Pure metals like Hg, Pb, Zn, etc. are few examples.

Type II superconductors have the following properties:

In type II superconductor, as critical field H_{C1} reaches the superconductivity start destroying gradually. Figure 14.4 shows the magnetization curve for Type II. There are two critical fields, at critical field H_{C1} the magnetization start decreasing and gradually becomes zero at critical field H_{C2} and superconductivity totally destroyed. The state between lower critical magnetic field H_{C1} and upper magnetic field H_{C2} is known as an intermediate state or mixed state. Material exhibits such behavior is call type II superconductors. These materials do not easily lose the superconducting state by external magnetic field thus also called as Hard Superconductors.Type-II superconductors are generally alloys and complex oxides of ceramics. These are also called as High-temperature Superconductors. The critical temperature is typically greater than 10K. Some features of type II superconductors are:

- Partly obey the Meissner effect but not completely: Magnetic field can penetrate inside the material.
- Due to the high critical magnetic field, type-II superconductors can be used for manufacturing electromagnets used for producing strong magnetic field.
- Slight impurity greatly affects the superconductivity of type-II superconductors.
- Due to the high critical magnetic field, type-II superconductors have wider technical applications.
- Compounds like Nb, Ta, Nb_3Sn, etc. are few examples.

11.7 THERMODYNAMIC PROPERTIES OF SUPERCONDUCTOR

Thermodynamic properties are defined as characteristic features of a system, capable of specifying the system's state. There are free electrons pairs present in conductors which are the reason of the conduction. In normal conductors these conduction electrons are scattered by impurities, dislocations, grain boundaries, and lattice vibrations (phonons). Unlike normal conductors there is an ordering among the conduction electrons that prevents this scattering. This ordering is named as cooper pairs. The thermodynamic parameters have direct relation with the cooper pairs. Some thermodynamic properties of superconductors are mentioned below.

11.7.1 Entropy

The disorderness and the randomness of the particles of any system is explained by the entropy of the system. The entropy of the normal conductors increases with the rise in temperature. But in case of superconductors, the entropy decreases on cooling below the critical temperature. This validates the ordering of the superconducting state. Figure 14.5 shows the variation of entropy of a normal conductor and a superconductor with temperature.

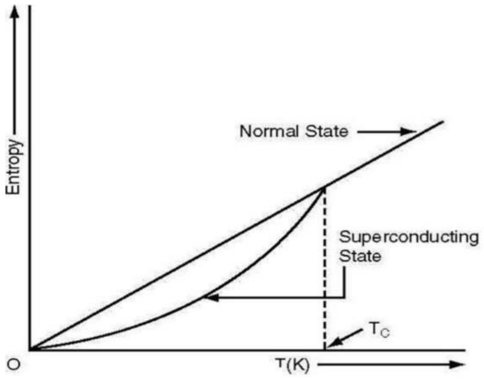


Figure 14.5: Change of entropy of normal conductor and superconductor with temperature.

11.7.2 Thermal Conductivity

Thermal conductivity accounts the level of conduction in superconductors due to the rise in temperature. A continuous change between the two phases is observed in the thermal conductivity of superconductors (Fig. 14.6). A superconductor is a perfect conductor of charge, but it cannot conduct heat. At normal temperature, electronic heat conduction of a superconductor goes to zero, as there are no thermally-excited quasiparticles to carry heat Therefore, the superconducting electrons possibly playing no part in heat transfer.

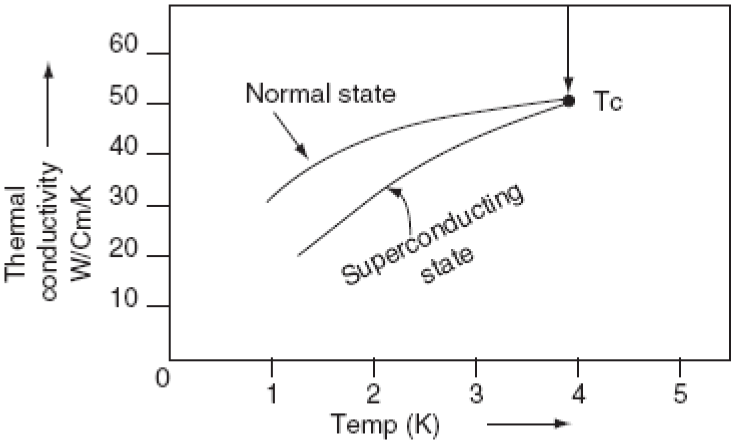


Figure 14.6: Thermal conductivity of normal conductor and a superconductor with temperature.

11.7.3 Isotopic Effect

It has been observed that the critical temperature T_C of superconductors varies with isotopic mass. The Isotope effect is one of the major properties of the superconductors. Higher T_C is found in lighter nuclei. The transition temperature T_C of superconductors found to have the dependency on the isotopic mass as

$$T_c \propto M^{-\alpha}$$

$$T_c M^{\alpha} = constant \qquad (5)$$

Where M is atomic mass and $\alpha = 0.5$ which is valid for most of the materials. It is also observed that transition temperature changes smoothly when we mix different isotopes with same element. For example, T_c for mercury varies from 4.18 K to 4.14 K as the isotopic mass varies from 199.5 to 203.4. Isotopic mass is involved in the formation of the superconducting phase of any material.

11.7.4 Heat Capacity and Specific Heat

Electronic specific heat for superconducting materials is found to vary with temperature. Lattice specific heat variation of superconductor however remains unaltered by change in temperature (proportional to T^3). The given equation shows the variation of specific heat of superconductivity.

$$C_n(T) = AT + BT^3 \qquad (6)$$

In this relation the first term is specific heat contribution due to electrons and the second term is contribution due to lattice vibration. When a small amount of heat is given to a superconductor system, some of the energy is used to increase the lattice vibrations, and the remained energy is used to increase the energy of the conduction electrons. The electronic specific heat ($C_e=AT$) of the electrons is defined as the ratio of that portion of the heat used by the electrons to the rise in temperature of the system. Superconductivity affects electrons mainly thus we assume that lattice vibration part remains same for both superconducting and normal states. The specific heat of the electrons in a superconductor varies with the absolute temperature (T_c) in the normal and in the superconducting state as shown in the Fig. 14.7.

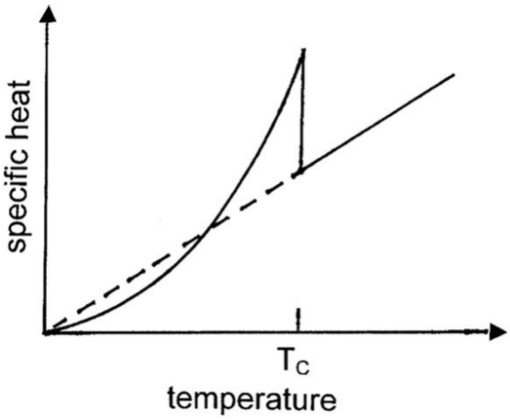


Figure 14.7: Specific Heat of normal conductor and a superconductor

11.7.5 Energy Gap

In a superconductor the important interaction is electron-electron interaction. These electrons are paired and known as cooper pair, may be considered as the single-particle of the system with zero spins. All the electrons related to the Cooper pair can be considered as the bosons. At T=0, all the electrons in the superconducting states are cooper pairs in the ground state. The energy can be absorbed or emitted only when the Cooper pair will break. This can be compared with the energy associated with the dissociation of atoms. The bonds of the atoms need the energy to break. Thus, the energy required to break up the Cooper pairs of the superconductors is defined as the superconducting energy gap E_g.

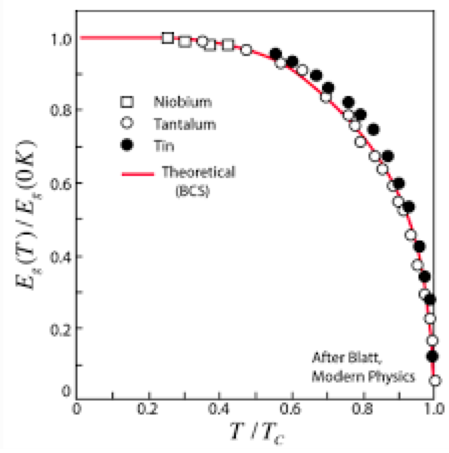


Figure 11.8: Energy gap as a function of temperature.

The energy gap in superconductor is entirely different that the nature of band gap of semiconductor. In semiconductor band gap arises due to electron lattice interaction and prevent the flow of electron. Energy needed to move the electron from valance band to conduction band. But in superconductor, this interaction ties the electron to lattice and the electrons flow in ordered way in the presence of this energy gap. The existence of energy gap can be confirmed by number of experiment and theoretically explained by BCS theory. The energy gaps of some superconductors are given in table 14.2. As temperature increases, the energy gap increases as shown in figure 14.8.

Table 11.2: Energy gaps and transition temperature of some superconductors

Elements	Energy gap $E_g(0)$ in 10^{-4}eV	T_C	$2\ E_g(0)/k_TT$
Nb	3.05	9.5	3.8
Ta	1.40	4.48	3.6
Al	0.34	1.2	3.3
Sb	1.15	3.72	3.5

11.8 LONDON EQUATIONS

Maxwell equations of electromagnetism were not sufficient to explain the zero resistivity and perfect diamagnetic nature of superconductors. Following this array, F. London and M. London came up with two equations in 1934. These equations are termed as London equations and explain the Meissner effect and zero resistivity and superconductors. In superconductors, the conduction is due to the superconducting electrons. Superconducting electrons (cooper pairs) are different than free electron. As Temperature decreases, the numbers of free electrons decrease and superconducting electrons increase.

The equation of motion of superconducting electron is given as

$$m\frac{dv_s}{dt} = F = -eE \qquad (7)$$

Where E is electric field. The current density is

$$J = -n_s e v_s \qquad (8)$$

Where n_s is the number of superconducting electrons per unit volume and v_s is the velocity corresponding to superconducting electrons.

From derivation of eq. (8)

$$\frac{dJ}{dt} = -n_s e\frac{dv_s}{dt}$$

Put the value of $\frac{dv_s}{dt}$ from eq. (7) $\quad \frac{dJ}{dt} = -n_s e\frac{-eE}{m}$

$$\frac{dJ}{dt} = \frac{n_s e^2}{m}E \qquad (9)$$

This is first London equation. The superconducting electrons act like free electrons to the electric field. Taking curl of the first London equation

$$curl\ \frac{dJ}{dt} = \frac{n_s\, e^2}{m}\ curl(E) \qquad (10)$$

Using Maxwell 3rd equation $\left\{curl\ E = -\mu_0\frac{\delta H}{\delta t}\right\}$ eq. 10 becomes

$$curl\ \frac{dJ}{dt} = \frac{n_s\, e^2}{m}\left[-\mu_0\frac{\delta H}{\delta t}\right]$$

$$curl\ \frac{dJ}{dt} = \frac{-\mu_0 n_s\, e^2}{m}\left[\frac{\delta H}{\delta t}\right] \qquad (11)$$

Integrating the above eq. (11)

$$curl\, J = \frac{-\mu_0 n_s\, e^2}{m}\; H - H_0 \tag{12}$$

For the Meissner effect, the field inside the material is zero, i.e., H_0=0. Then

$$curl\, J = \frac{-\mu_0 n_s\, e^2}{m}\; H \tag{13}$$

According to the Maxwell's 4th equations:

$$curl\, H = (J + J_D) \tag{14}$$

where J is the current density related to the material and J_D is the displacement current. If the applied external field is varying, then the J_D is very small as compared to the J value. Thus, for superconductor, Maxwell's eq. 4 can be written as above can be written as$curl\ H = J$
Putting this value of J in eq. 13 we get

$$-\nabla^2 H = \frac{-\mu_0 n_s\, e^2}{m}\; H$$

$$\nabla^2 H = \frac{\mu_0 n_s\, e^2}{m}\; H \tag{15}$$

$$\nabla^2 H = \frac{1}{\lambda^2} H \tag{16}$$

$$\text{Where}\lambda^2 = \frac{m}{\mu_0 n_s\, e^2} \tag{17}$$

Where λ is another constant. This is known as London's second equation which explains Meissner's effect.

11.8.1 London Penetration Depth

Equation (16) is second order differential equation. The standard solution of this equation can be given as

$$H(x) = H_0 e^{-x/\lambda} \tag{18}$$

where H_0 is defined as the externally applied magnetic field and $H(x)$ is the magnetic field present inside the material at a distance x from the surface. λ is named as London penetration depth. The London penetration depth can be defined as the measure of the distance from the surface of a superconductor at which the magnetic field decays to 1/e of its value and the surface of the superconductor as shown in figure 14.9. The penetration depth did not remain constant and vary with temperature. At low temperature the depth remains constant but when the temperature is raised, the depth increases rapidly. When the temperature reaches its transition value, the depth approaches to infinite. The dependency of temperature on penetration depth is given by the equation

$$\lambda(x) = \frac{\lambda(0)}{\sqrt{\left[1 - \left(\frac{T}{T_c}\right)^4\right]}} \tag{19}$$

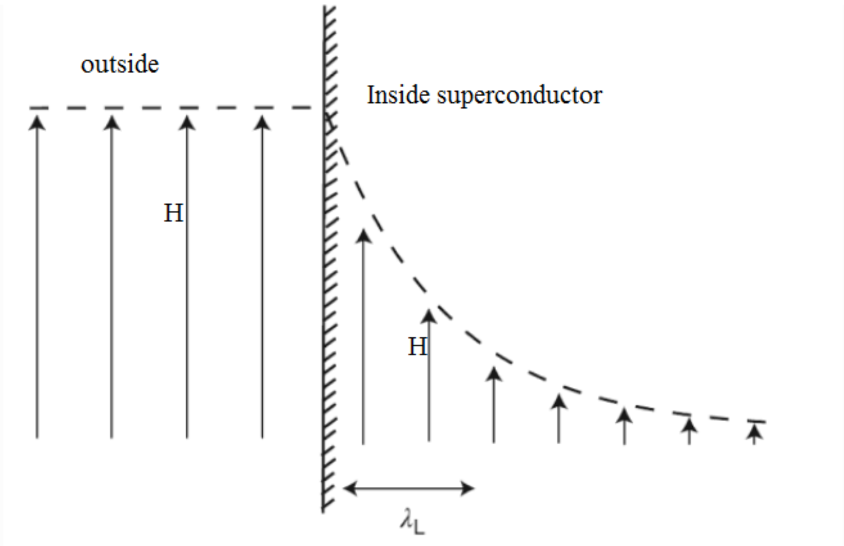


Figure 14.9: Decay of magnetic field inside a superconductor

11.8.2 Coherence Length

The coherence length is the characteristic exponent of the variations of the density of superconducting component. In eq. (18) the x component in the exponent term is coherence length. The average distance between the two electrons in a Cooper pair is known as the coherence length. It is represented by ξ. The coherence length depends upon the particular superconducting material.

11.9 BCS THEORY

BCS theory gave a satisfactory explanation for the Superconductivity of the material. In 1957 Bardeen, Cooper, and Schrieffer (BCS) gave an explanation for the superconductor based on the formation of cooper pairs. In normal state the force between the electrons is observed to be repulsive. Superconductors the force between two electrons becomes attractive due to the formation of the Cooper pairs. The BCS theory postulated that the electrons present inside the superconductor experience a special kind of neutral attraction. This attraction dominates over the coulombic repulsion and results in the formation of cooper pairs at very low temperature. Cooper pairs move within the letters without catering and result in the transition of material from normal conductor to superconductor. BCS theory has very wide range of applicability as for He, Type I, Type II and high temperature superconductors. It is assumed that there is a BCS wave function composed of particle pairs $k\uparrow$ and $k\downarrow$. The BCS theory can be understood with the help of following accomplishments.

(1) Attractive interaction of electrons:

An attractive interaction among the electrons in a superconductor results a ground state separation from excited state by energy gap E_g. The critical field thermal properties are due to this energy gap.

(2) Electron – Lattice – Electron Interaction

The electron pair experiences an attractive force. The ion core undergoes a slight displacement due to the attractive force. This displacement is termed as **lattice distortion**. Similar thing happens with the nearby electrons which ever came in the field of this attractive force. This process is known as **Electron–Lattice–Electron Interaction.** Any two electrons can interact via lattice distortions**.** The interaction leads to the subsequent reduction of energy of the electron. Thus, the interactions between electrons give results in attractive forces.

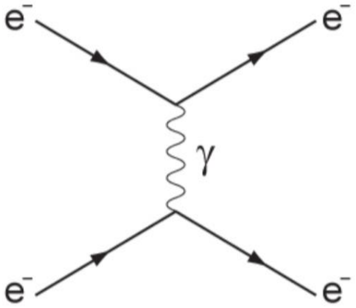


Figure 11.10: Electron – Lattice – Electron Interaction due to phonon field.

(3) Cooper Pair

The lattice distortions result in the generation of momentum of lattice which leads to the generation of phonons. These phonons interact to give free electrons called cooper pairs. Thus, Cooper pairs are the pair of free electrons formed by the interaction between the electrons in the phonon field. The cooper pairs do not experience any scattering and flow with zero resistance.

(4) Penetration depth and coherence length:

The penetration depth and coherence length are the natural consequences of BCS theory. If we go in detail, we will find the explanation of out the results as penetration depth and coherence length Meissner effect.

(5) Transition temperature:

The transition temperature depends on the density of state $D(\epsilon_F)$ and lattice interaction energy. BCS theory predicts that

$$T_C = 1.14\theta \, exp[-1/U \, D(\epsilon_F)] \tag{20}$$

Where θ is Debye temperature and U is attractive interaction energy.

(6) Magnetic Flux quantization:

The magnetic flux through a superconducting loop is quantised in terms of 2e in place of e. The superconducting state contains electron pair thus the charge is quantised in term of 2e.

11.10 HIGH TEMPERATURE SUPERCONDUCTORS

High temperature superconductors (HTS) are mainly oxides with high transition temperature and critical field. The discovery of high temperature superconductors had given new field of research in superconducting materials. The chemical bonding and physical properties at high temperature vary from low transition temperature. A minor hindrance in the oxygen atoms and cations doping converts the material into low carrier density metal first and then into the superconducting one. Some high temperature oxide superconductors are:

$\mathrm{BaPb_{0.75}Bi_{0.25}O_3}$	(BPBO)	$T_C = 12K$
$\mathrm{La_{1.85}Ba_{0.15}CuO_4}$	LBCO)	$T_C = 36K$
$\mathrm{YBa_2Cu_3O_7}$	(YBCO)	$T_C = 12K$
$\mathrm{Tl_{0.75}Ba_2Ca_2Cu_3O_{10}}$	(TBCO)	$T_C = 120K$

The high temperature oxide semiconductors can have the following properties:

- They are derived from ideal perovskite composition ABX_3 here A is larger cation, B is smaller cation, and X is anion.
- Copper is present in the mixed valance state involving a partial oxidation of Cu^{2+} into Cu^{3+}.
- There is a charge transfer to and from CuO_2 layer which is induced by doping near the metal-insulator phase boundary existing in all oxide high temperature superconductors.
- The crystal structures of all these are highly anisotropic. The bonding in these materials is highly directional and covalent.
- The coherence length and the penetration depth are also highly anisotropic.
- The lower critical field H_{c1}, and upper field H_{c2} are highly anisotropic.

14.11 APPLICATIONS

In practical and applied physics, superconductors have wide applicability. A few of them are mentioned below:

A. **Power transmission:** Electrical power transmission through any conductor is always accompanied by energy loss I^2R. If superconductors are used for power transmission, the losses will be eliminated and the power transmission can be done at a lower voltage level with much higher efficiency.

B. **Superconducting magnets:** An Electromagnet is made by using superconducting wire is called a superconducting magnet. The advantage of such wires or cables is that once the current is set up the coil requires no source of electromotive force to derive the current. Superconducting magnets are used in Magnetic resonance imaging (MRI) employed to generate images of bodies. This technique has very less harmful and can be used over X-rays.

C. **Electrical applications in cryotron**: Cryotron consists of a wire of superconducting material A around which another wire of superconducting material B is bound in the form of a solenoid. The cryotron Based on the principle of activity above the critical temperature. At 4.4 K temperature, both A and B materials are in the superconducting state. Cryotron has wide applications in fast-acting switches.

D. **Very strong magnetic fields**: The strong magnetic field is of the order of 50 Tesla by consuming only 10 KV can be generated with the poles made of superconducting material. Such coils are cost-effective than the regular conventional electromagnets. High magnetic fields are required in many areas of research and in pharmaceutical science.

E. **Superconducting quantum interference devices**: Superconducting Quantum interference devices (SQID) are fundamentally superconducting rings that act as storage devices for magnetic flux they are used to detect very minute changes in the magnetic field of a human brain or body or any other part.

F. **In computer technology:** Due to heat generated (loss I^2R), there is a limit to which the components can be crowded on a chip of given size. The use of superconductors in makes it possible to assemble more circuit in the given area of the chip.

11.12 SUMMARY

1. When certain materials or alloys are cooled to sufficiently low temperatures (say beyond the critical temperature T_C), the electrical resistivity of many material and alloys suddenly drop to zero. Such materials and alloys are termed as superconductors and this phenomenon is called superconductivity.

2. Kammerlingh observed that superconductivity is destroyed if sufficient strong magnetic field is applied. The externally applied magnetic field necessary to destroy the superconductivity of any material is called the critical magnetic field $H_C(T)$ is the function of temperature.

$$H_C(\mathrm{T}) = H_C(0)\left[1 - \left(\frac{T}{T_C}\right)^2\right]$$

3. Meissner and Ochsenfeld found that if a superconductor is cooled in a magnetic field below the transition temperature, the magnetic field lines are pushed out from the bulk superconductor. They named this phenomenon “Meissner effect”.

4. The transition temperature T_C of superconductors found to have the dependency on the isotopic mass as

$$T_c M^\alpha = constant$$

5. The specific heat of superconductivity

$$C_n(T) = AT + BT^3$$

6. This is first London equation

$$\frac{dJ}{dt} = \frac{n_s e^2}{m} E$$

Second London equation

$$\nabla^2 H = \frac{1}{λ^2} H \quad \text{where} λ^2 = \frac{m}{μ_0 n_s e^2}$$

7. London penetration depth

$$H(x) = H_0 e^{-x/λ}$$

$$λ(x) = \frac{λ(0)}{\sqrt{\left[1 - \left(\frac{T}{T_c}\right)^4\right]}}$$

8. F*lux quantization:*

$$\phi = \oint \vec{B} . d\vec{s} = \mathrm{n} \frac{\mathrm{h}}{2e} = \mathrm{n}\ \phi_0$$

where $\phi_0 = \frac{\mathrm{h}}{2e} = 2.07 \times 10^{-15}\mathrm{weber}$ *, is a constant called fluxon or fluxoid.*

11.13 GLOSSARY

Superconductivity: Zero resistance ability.

Critical: Involving a deep analysis.

Hard superconductor: These materials do not easily lose the superconducting state by external magnetic field.

Soft superconductor: These superconductors easily lose the superconducting state by low-intensity magnetic field.

11.14 REFERENCES

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14.19 TERMINAL QUESTIONS

Short answer type questions:

Q1. At what temperature is $H_c(T) = 0.1\ H_c(0)$ for Lead having Tc equals to 7.2K?

Q2. Why do superconductors expel magnetic fields?

Q3. Is plasma a superconductor?

Q4. Prove that the value of magnetic susceptibility for diamagnetic materials is -1.

Q5. Do all superconductors expel magnetic flux?

Q6. What happens to the magnetic field when a superconductor is placed in a weak external magnetic field H, and cooled below its transition temperature?

Q7. Describe the physical meaning of the coherence length (ξ) in superconductors.

Long answer type questions:

Q1. What is Type 1 and Type 2 superconductors? Mention important differences.

Q2. Explain the occurrence of superconductivity.

Q3. Explain and derive the London equations.

Q4. Why do various superconductors have different Tc?

Q5. The critical temperature of mercury is 4.153 k for its one isotope of mass 200.59 amu. Calculate the critical temperature of Mercury for its one isotope of mass 20 amu.

Answers:

Short Answer – 1. 6.83K