

## ENGINEERING PHYSICS-II

### UNIT I - CONDUCTING MATERIALS

#### Introduction

The conductivity of a material depends on the presence of free electrons. The materials which conduct electricity due to free electrons when an electric potential difference is applied across them are known as conducting materials. The conducting materials play an important role in Engineering and Technology. Conducting materials are good conductors of electricity and heat. Gold, silver, copper, aluminium are the examples of conducting materials.

#### Classical free electron theory

##### Assumptions of Free electron gas model:

- A metal contains a large number of free electrons which are free to move about in entire volume of the metal like the molecules of a gas in a container.
- The free electrons move in random directions and collide with either positive ions fixed in the lattice or other free electrons. All the electrons are elastic and there is no loss of energy.
- The velocity and the energy distribution of free electrons obey the classical Maxwell Boltzmann statistics.
- The free electrons are moving in a completely uniform potential field due to the ions fixed in the lattice.
- In the absence of electric field the random motion of free electrons is equally probable in all directions so that the current density vector is zero.
- When the external electric field is applied across the ends of a metal, the electrons drift slowly with some average velocity known as drift velocity in the direction opposite to that of electric field. This drift velocity is superimposed over the random velocity. This drift velocity is responsible for the flow of electric current in a metal.

#### Drift velocity

The average velocity of the free electrons with which they move towards the positive terminal under the influence of the electrical field.

#### Mobility

It is defined as the drift velocity of the charge carrier per unit applied electric field.

### Collision time

The average time taken by a free electron between two successive collisions is called collision time.

### Mean free path

The average distance travelled by a free electron between two successive collisions is called mean free path.

### Relaxation time

It is defined as the time taken by a free electron to reach its equilibrium position from the disturbed position in the presence of an electric field.

### Electrical conductivity.

**Electrical conductivity  $\sigma$**  is defined as the rate of charge flow across unit area in a conductor per unit potential (voltage) gradient.

$$\sigma = \frac{J}{E}. \text{ Its unit is } \Omega^{-1}\text{m}^{-1} \text{ or } \text{Sm}^{-1}.$$

### Expression for the electrical conductivity.

When an electrical field (E) is applied to an electron of charge 'e' of a metallic rod, the electron moves in opposite direction to the applied field with a velocity  $v_d$ . This velocity is known as drift velocity.

$$\text{Lorentz force acting on the electron } F = eE \dots \dots (1)$$

This force is known as the driving force of the electron.

Due to this force, the electron gains acceleration 'a'.

From Newton's second law of motion,

$$\text{Force } F = ma \dots \dots (2)$$

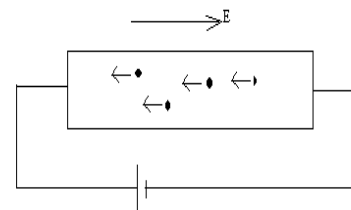
From the equation (1) and (2),

$$ma = eE \quad \text{or} \quad a = \frac{eE}{m} \dots \dots (3)$$

$$\text{Acceleration (a)} = \frac{\text{Drift velocity}(v_d)}{\text{Relaxation time}(\tau)} \text{ or } a = \frac{v_d}{\tau}$$

$$v_d = a\tau \dots \dots (4)$$

Substituting equation (3) in (4)



$$v_d = \left( \frac{e\tau}{m} \right) E \dots\dots\dots( 5)$$

The Ohms' law states that current density (J) is expressed as

$$J = \sigma E \text{ or } \sigma = \frac{J}{E} \dots\dots(6)$$

Where  $\sigma$  is the electrical conductivity of the electron.

But, the current density in terms of drift velocity is given as

$$J = nev_d \dots\dots\dots (7)$$

Substituting equation (5) in equation (7), we have

$$J = ne \left( \frac{e\tau}{m} \right) E$$

$$\text{or } \frac{J}{E} = \frac{ne^2\tau}{m} \dots\dots(8)$$

On comparing the equation (6) and (8) , we have

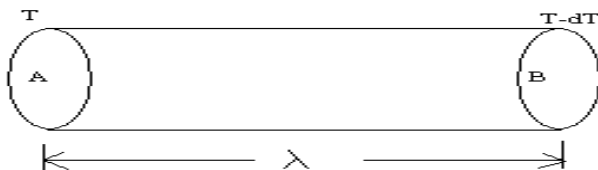
$$\text{Electrical conductivity } \sigma = \frac{ne^2\tau}{m} \dots\dots(9)$$

### Thermal conductivity

**Thermal conductivity K** is defined as the amount of heat flowing per unit time through the material having unit area of cross-section per unit temperature gradient.  $Q = K \frac{dT}{dx}$ .

### Expression for Thermal Conductivity of a Metal

Consider two cross-sections A and B in a uniform metallic rod AB separated by a distance  $\lambda$ . Let A at a high temperature (T) and B at low temperature (T-dT). Now heat conduction takes place from A and B by the electrons. The conduction electron per unit volume is n and average velocity of these electrons is v. During the movement of electrons in the rod, collision takes place. Hence, the electrons near A lose their kinetic energy while electrons near B gain kinetic energy.



$$\text{At A, average kinetic energy of an electron} = \frac{3}{2} kT \dots\dots(1)$$

$$\text{At B, average kinetic energy of the electron} = \frac{3}{2} k(T - dT) \dots\dots(2)$$

The excess of kinetic energy carried by the electron from A to B is,

$$\frac{3}{2}kdT.....(3)$$

Number of electrons crossing per unit area per time from A and B is,

$$\frac{1}{6}nv$$

The excess of energy carried from (A to B) per unit area in unit time is  $= \frac{1}{4}nvkdT....(4)$

Similarly, the deficient of energy carried from B to A per unit area per unit time is

$$= -\frac{1}{4}nvkdT.....(5)$$

Hence, the net amount of energy transferred from A to B per unit area per unit time is,

$$Q = \frac{1}{2}nvkdT.....(6)$$

But from the basic definition of thermal conductivity, the amount of heat conducted per unit area per unit time is,

$$Q = K \frac{dT}{\lambda} \text{ i.e., } \frac{1}{2}nvkdT = K \frac{dT}{\lambda}; \therefore K = \frac{1}{2}nvk\lambda.....(7)$$

We know that for the metals i.e.  $\tau = \tau_c = \frac{\lambda}{v} = \tau v = \lambda.....(8)$

Substituting the equation (8) in equation (7), we have

$$K = \frac{1}{2}nv^2k\tau.....(9)$$

### **Wiedemann – Franz law:**

The law states that the ratio of thermal conductivity to electrical conductivity of the metal is directly proportional to the absolute temperature of the metal.

We know that,

$$\sigma = \frac{ne^2\tau}{m}.....(1) \quad \text{and}$$

$$K = \frac{1}{2}nv^2k\tau.....(2)$$

$$\frac{\text{Thermal conductivity}}{\text{Electrical conductivity}} = \frac{K}{\sigma} = \frac{\frac{1}{2} n v^2 k \tau}{\frac{n e^2 \tau}{m}}; \frac{k}{\sigma} = \frac{1}{2} \frac{m v^2 k}{e^2} \dots\dots (3)$$

We know that the kinetic energy of an electron,

$$\frac{1}{2} m v^2 = \frac{3}{2} k T \dots\dots (4)$$

Substituting the equation (4) in the equation (3). We have

$$\frac{k}{\sigma} = \frac{3}{2} \frac{k T \times k}{e^2} = \frac{3}{2} \frac{k^2 T}{e^2}, \text{ or } \frac{K}{\sigma} = \frac{3}{2} \left[ \frac{k}{e} \right]^2 T, \text{ or } \frac{K}{\sigma} = L T \dots\dots (5)$$

Where  $L = \frac{3}{2} \left[ \frac{k}{e} \right]^2$  is a constant and it is known as Lorentz number.

$$\frac{K}{\sigma} \propto T \dots\dots (6)$$

Hence, it is proved that the ratio of thermal conductivity of a metal is directly proportional to the absolute temperature of the metal.

### Fermi-Dirac distribution function

#### Fermi function F (E):

Fermi-Dirac distribution function represents the probability of an electron occupying a given energy level at absolute temperature. It is given by

$$F(E) = \frac{1}{1 + e^{(E-E_F)/K_B T}}$$

Where  $K_B \rightarrow$  Boltzmann Constant

T  $\rightarrow$  Temperature

#### Effect of temperature on Fermi Function:

##### Case (i) Probability of occupation for $E < E_F$ at $T = 0K$

$$F(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

When  $T = 0K$  and  $E < E_F$ , we have

$$F(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1 + 0} = \frac{1}{1} [\because e^{-\infty} = 0]; \therefore F(E) = 1$$

*Thus at  $T = 0K$ , there is 100 % chance for the electrons to occupy the energy levels below the Fermi level.*

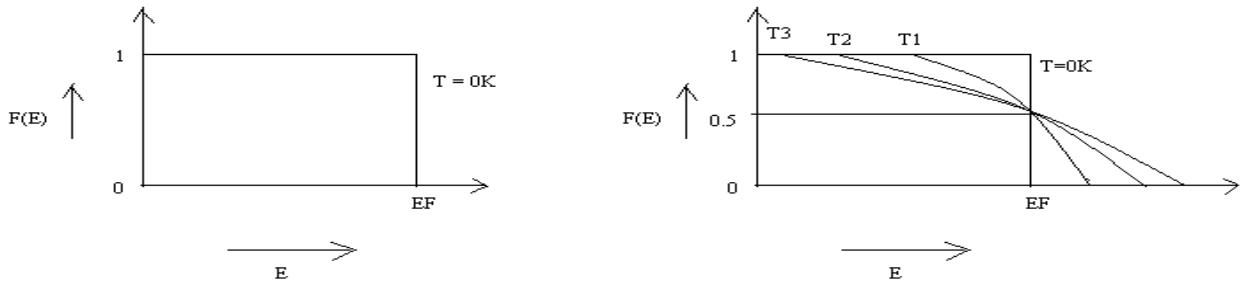
**Case (ii) Probability of occupation for  $E > E_F$  at  $T = 0K$**

When  $T = 0K$  and  $E > E_F$ ,

we have 
$$F(E) = \frac{1}{1 + e^{(+ve/0)}} = \frac{1}{1 + e^{\infty}} = \frac{1}{1 + \infty} = \frac{1}{\infty} = 0 \therefore F(E) = 0$$

*Thus, there is 0 % chance for the electrons to occupy energy levels above the Fermi energy level.*

From the above two cases, at  $T = 0K$  the variation of  $F(E)$  for different energy values becomes a step function.



*Variation of Fermi distribution function with  $E$  at different temperatures*

**Case (iii) Probability of occupation at ordinary temperature:**

At ordinary temperature, the value of probability starts reducing from 1 for values of  $E$  slightly less than  $E_F$ . With the increase of temperature, i.e.,  $T > 0K$ , Fermi function  $F(E)$  varies with  $E$ .

At any temperature other than  $0K$  and  $E = E_F$ ,

$$F(E) = \frac{1}{1 + e^0} = \frac{1}{1 + 1} = \frac{1}{2} = 50\%$$

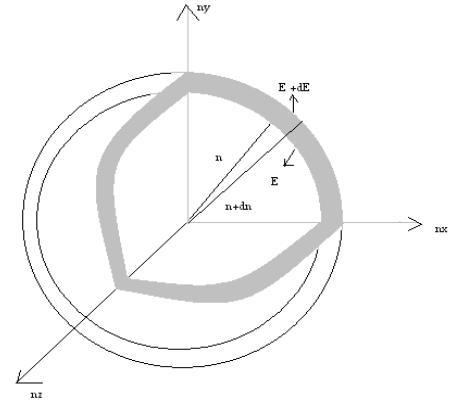
*Hence, there is 50 % chance for the electrons to occupy Fermi level. Further, for  $E > E_F$  the probability value falls off rapidly to zero.*

**Case (iv) At high temperature:**

When  $kT \gg E_F$ , the electrons lose their quantum mechanical character and Fermi distribution function reduces to classical Boltzmann distribution.

## Density of energy states.

**Definition:** It is defined as the number of available electron states per unit volume in an Energy interval  $E$  and  $E + dE$ . It is denoted by  $Z(E)dE$ .



## Expression for density of energy states.

Let us consider a cubical sample with side 'a'. A sphere is constructed with three quantum numbers  $n_x, n_y, n_z$  as coordinate axes in three-dimensional space as shown.

A radius vector  $n$  is drawn from origin 'O' to a point with co-ordinates  $n_x, n_y, n_z$  in this space. All the points on the surface of that sphere will have the same energy  $E$ . Thus,  $n^2 = n_x^2 + n_y^2 + n_z^2$  denotes the radius of the sphere with energy  $E$ . This sphere can be further divided into a many shells. Each shell represents a particular combinations of quantum numbers ( $n_x, n_y, n_z$ ). Therefore, it denotes a particular energy value with a particular radius. In this space, unit volume represents one energy state.

$$\text{Number of energy states within a sphere of radius 'n'} = \frac{4}{3}\pi n^3 \dots (1)$$

Since the quantum numbers  $n_x, n_y, n_z$  can have only positive integer values, we have to take only one octant of the sphere, i.e.,  $\frac{1}{8}$ th of the spherical volume.

Therefore, the number of available energy states within one octant of the sphere of radius 'n'

$$\text{corresponding to energy E is } = \frac{1}{8} \left[ \frac{4}{3} \pi n^3 \right] \dots (2)$$

Similarly, the number of available energy states within one octant of the sphere of radius 'n + dn'

$$\text{corresponding to energy E + dE } = \frac{1}{8} \left[ \frac{4}{3} \pi (n + dn)^3 \right] \dots (3)$$

Now, the number of available energy states between the shell of radius  $n$  and  $n + dn$  i.e., between the energy values  $E$  and  $E + dE$ ,

$$N(E) dE = \frac{1}{8} \left( \frac{4\pi}{3} \right) (n + dn)^3 - \frac{1}{8} \left( \frac{4\pi}{3} \right) n^3 = \frac{1}{8} \left( \frac{4\pi}{3} \right) [(n + dn)^3 - n^3]$$

$$N(E)dE = \left(\frac{\pi}{6}\right) \left[ n^3 + dn^3 + 3n^2 dn + 3ndn^2 - n^3 \right]$$

Since  $dn$  is very small, higher powers of  $dn$  terms  $dn^2$  and  $dn^3$  can be neglected.

$$N(E) dE = \frac{\pi}{6} 3n^2 dn = N(E)dE = \frac{\pi}{2} n^2 dn = N(E)dE = \frac{\pi}{2} n(ndn).....(4)$$

We know that the energy of an electron in a cubical metal piece of sides 'a' is given by

$$E = \frac{n^2 h^2}{8ma^2} \dots(5) \text{ or }; n^2 = \frac{8ma^2 E}{h^2} \dots\dots(6) \text{ or }; n = \left[ \frac{8ma^2 E}{h^2} \right]^{1/2} \dots\dots(7)$$

**Differentiating the equation (6), we get**

$$2ndn = \frac{8ma^2 dE}{h^2} \text{ or }; ndn = \frac{8ma^2 dE}{h^2} \dots\dots(8)$$

Substituting equations (7) and (8) in equation (4), we have

$$\begin{aligned} N(E)dE &= \frac{\pi}{2} \left( \frac{8ma^2 E}{h^2} \right)^{1/2} \left[ \frac{8ma^2 dE}{2h^2} \right] = \frac{1}{2} \frac{\pi}{2} \left( \frac{8ma^2 E}{h^2} \right)^{1/2} \left[ \frac{8ma^2 dE}{h^2} \right] \\ &= \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{1/2} E^{1/2} \left( \frac{8ma^2}{h^2} \right) dE = N(E)dE = \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{3/2} E^{1/2} dE \dots\dots(10) \end{aligned}$$

Pauli's exclusion states principle states that two electrons of opposite spins can occupy each state and hence the number of energy states available for electron occupancy is given by

$$\begin{aligned} N(E)dE &= 2 \times \frac{\pi}{4} \left[ \frac{8ma^2}{h^2} \right]^{3/2} E^{1/2} dE = \frac{\pi}{2} \left( \frac{8m}{h^2} \right)^{3/2} a^3 E^{1/2} dE \\ &= \frac{\pi}{2} (8m)^{3/2} \left( \frac{a^3}{h^3} \right) E^{1/2} dE = N(E)dE = \frac{\pi}{2} \left( \frac{a}{h} \right)^3 (8m)^{3/2} E^{1/2} dE \\ N(E)dE &= \frac{\pi}{2} \left( \frac{a}{h} \right)^3 8(2m)^{3/2} E^{1/2} dE = \frac{4\pi}{h^3} (2m)^{3/2} a^3 E^{1/2} dE \end{aligned}$$

Density of states is given by the number of energy states per unit volume,

$$\begin{aligned} Z(E)dE &= \frac{N(E)dE}{V} \\ \text{i.e., Density of states } Z(E)dE &= \frac{4\pi}{h^3} \frac{(2m)^{3/2} a^3 E^{1/2} dE}{a^3} ; ; [ \because \text{Volume } V = a^3 ] \\ Z(E)dE &= \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \dots\dots(11) \end{aligned}$$

This is the expression for the density of charge carriers in the energy interval  $E$  and  $E + dE$ .



**Carrier Concentration:** Carrier Concentration, i.e., the number of electrons per unit volume in a given energy interval is calculated by assuming the product of the density of states  $Z(E)$  and the occupancy probability  $F(E)$ .

$$\text{i.e. } n_c = \int Z(E)F(E)dE$$

Substituting the expressions for  $Z(E)$  and  $F(E)$ , we have

$$n_c = \int \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} \frac{1}{1 + e^{(E-E_f)/kT}} dE \dots (12)$$

## UNIT- II. SEMICONDUCTING MATERIALS

### Introduction

A semiconducting material has electrical conductivity considerably greater than that of an insulator but significantly lower than that of a conductor. The value of resistivity varies from  $10^{-4}$  to 0.5 ohm metre.

### Properties of a semiconductor.

1. The resistivity lies between  $10^{-4}$  to 0.5 ohm metre.
2. At 0K, they behave as insulators.
3. The conductivity of a semiconductor increases both due to the temperature and impurities.
4. They have negative temperature coefficient of resistance.
5. In semiconductors both the electron and holes are charge carries and will take part in condition.

### Types of Semiconductors

#### (i) Intrinsic semiconductor:

Semiconductor in a pure form is called intrinsic semiconductor. Here the charge carries are produced only due to thermal agitation. They are low electrical conductivity. They have low operating temperature.

#### (ii) Extrinsic semiconductor:

Semiconductor which are doped with impurity is called extrinsic semiconductor. Here the charge carries are produced only due to impurities and may also be produced due to thermal agitation. They are high electrical conductivity.

### Density of electrons in the conduction band

The number of electrons per unit volume in the conduction band for the energy range E and E + d E is given by

$$d n = Z (E) F (E) d E \dots\dots (1)$$

$$\int d n = n = \int_{E_c}^{\infty} Z(E)F(E)dE\dots\dots(2)$$

Density of states in the conduction band between the energy range E and E + d E is given by,

$$Z(E) dE = \frac{4\pi}{h^3} (2m_e^*)^{3/2} E^{1/2} dE \dots (3)$$

$E - E_c$  is the kinetic energy of the conduction electron at higher energy levels.

Thus in equation (3),  $E$  is replaced by  $(E - E_c)$

$$Z(E) dE = \frac{4\pi}{h^3} (2m_e^*)^{3/2} (E - E_c)^{1/2} dE \dots (4),$$

The probability of electrons occupation is given by

$$F(E) = \frac{1}{1 + e^{(E - E_F)/kT}} \dots (5),$$

Substituting the equations (4) & (5) in (2), we get,

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} \int_{E_c}^{+\infty} \frac{(E - E_c)^{1/2}}{1 + e^{(E - E_F)/kT}} dE \dots (6),$$

Since  $(E - E_F)$  is greater than  $kT$ ,  $e^{(E - E_F)/kT}$  is very large compared to '1'

i.e.,  $1 + e^{(E - E_F)/kT} \approx e^{(E - E_F)/kT}$ , now the equation (6) becomes,

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} \int_{E_c}^{\infty} \frac{(E - E_c)^{1/2} dE}{e^{(E - E_F)/kT}}, \quad n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} \int_{E_c}^{+\infty} (E - E_c)^{1/2} e^{(E_F - E)/kT} dE$$

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{E_F/kT} \int_{E_c}^{\infty} (E - E_c)^{1/2} e^{-E/kT} dE \dots (7),$$

To solve the integral in the equation (7), let us assume

$E - E_c = x$	When	when
$E = E_c + x$	$E = E_c$	$E = +\infty$
$dE = dx$	$E_c - E_c = x$	$+\infty - E_c = x$
	$\therefore x = 0$	$\therefore x = +\infty$

Substituting the above values in equation (7),

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{E_F/kT} \int_0^{\infty} x^{1/2} e^{-(E_c + x)/kT} dx$$

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{(E_F - E_c)/kT} \int_0^{\infty} x^{1/2} e^{-x/kT} dx \dots (8),$$

Using the gamma function, it is shown that

$$\int_0^{\infty} x^{1/2} e^{-x/kT} dx = \frac{(kT)^{3/2} \pi^{1/2}}{2} \dots (9),$$

Substituting the equation (9) in the equation (8), we have

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{(E_F - E_c)/kT} \left[ \frac{(kT)^{3/2} \pi^{1/2}}{2} \right] \text{ or } n = 2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} e^{(E_F - E_c)/kT} \dots (10)$$

### Density of holes in the valence band of an intrinsic semiconductor

Let  $dp$  be the number of holes per unit volume in the valence band between the energy  $E$  and  $E + dE$ .

$$dp = Z(E) (1-F(E)) dE \dots (1)$$

$1-F(E)$  is the probability of an unoccupied electron state, i.e., presence of a hole.

$$1-F(E) = 1 - \frac{1}{1 + e^{(E-E_F)/kT}} ; 1-F(E) = \frac{e^{(E-E_F)/kT}}{1 + e^{(E-E_F)/kT}} \dots (2)$$

Since  $E$  is very small when compared  $E_F$ , in the valence band  $(E-E_F)$  is a negative quantity.

Therefore  $e^{(E-E_F)}$  is neglected in the denominator.

$$\therefore 1-F(E) = e^{(E-E_F)/kT} \dots (3),$$

Density of states in the valence band,

$$Z(E)dE = \frac{4\pi}{h^3} (2m_h^*)^{3/2} E^{1/2} dE \dots (4)$$

Here,  $m_h^*$  is the effective mass of the hole in the valence band.  $(E_v - E)$  is the kinetic energy of the hole at level below  $E_v$ . So the term  $E^{1/2}$  is replaced by  $(E_v - E)$  in equation (4).

$$\therefore Z(E)dE = \frac{4\pi}{h^3} (2m_h^*)^{3/2} (E_v - E)^{1/2} dE \dots (5)$$

Substituting the equations (3) & (5) in (1), we get  $dp = \frac{4\pi}{h^3} (2m_h^*)^{3/2} (E_v - E)^{1/2} e^{(E-E_F)/kT} dE \dots (6)$

The number of holes in the valence band for the entire energy range is obtained by integrating the equation (6) between the limits  $-\infty$  to  $E_v$ .

$$\int dp = p = \frac{4\pi}{h^3} (2m_h^*)^{3/2} e^{(-E_F/kT)} \int_{-\infty}^{E_v} (E_v - E)^{1/2} e^{(E/kT)} dE \dots (7),$$

To solve the above integral in equation (7),

let us assume,

$E_v - E = x$	When	when
$E = -x + E_v$	$E = -\infty$	$E = E_v$
	$E_v + \infty = x$	$x = E_v - E_v$

$$\therefore dE = - dx$$

$$\therefore = \infty$$

$$\therefore x = 0$$

Substituting these values in equation (7), we have,

$$p = \frac{4\pi}{h^3} (2m_h^*)^{3/2} e^{(E_F - E_F)/kT} \int_0^{\infty} x^{1/2} e^{(-x/kT)} dx \dots (9),$$

Using the gamma function, it is shown that

$$\int_0^{\infty} x^{1/2} e^{(-x/kT)} dx = \frac{(kT)^{3/2} \pi^{1/2}}{2} \dots (10),$$

Substituting the equation (10) in the equation (9), we have

$$p = \frac{4\pi}{h^3} (2m_h^*)^{3/2} e^{(E_F - E_F)/kT} \left[ \frac{(kT)^{3/2} \pi^{1/2}}{2} \right] \text{or..} p = 2 \left( \frac{2\pi m_h^* kT}{h^2} \right)^{3/2} e^{(E_v - E_F)/kT} \dots (11).$$

### Intrinsic carrier concentration

In an Intrinsic carrier concentration, number of electrons and holes are same.

Hence,  $n = p = n_i$

Where  $n_i$  is the Intrinsic carrier concentration,

$$n_i^2 = n \times p$$

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{(E_F - E_c)/kT} \left[ \frac{(kT)^{3/2} \pi^{1/2}}{2} \right] \text{or..} n = 2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} e^{(E_F - E_c)/kT} \dots (10)$$

$$p = \frac{4\pi}{h^3} (2m_h^*)^{3/2} e^{(E_F - E_F)/kT} \left[ \frac{(kT)^{3/2} \pi^{1/2}}{2} \right] \text{or..} p = 2 \left( \frac{2\pi m_h^* kT}{h^2} \right)^{3/2} e^{(E_v - E_F)/kT}$$

$$n_i^2 = 2 \left[ \frac{2\pi kT}{3/2} \right]^{3/2} (m_e^* m_h^*)^{3/4} e^{\frac{-E_g}{2kT}}$$

### Fermi energy of an intrinsic semiconductor

Fermi energy level is the energy level which distinguishes the filled and empty states (or) it is the maximum energy level up to which the electrons are filled.

At 0K,

The Fermi energy of an intrinsic semiconductor is  $E_F = \frac{E_c + E_v}{2}$  i.e., the Fermi energy level exactly lies between the lowest energy level of conduction band and highest energy level of valence band.

## Elemental semiconductor and Compound semiconductor

### Elemental semiconductors:

Semiconductor elements of fourth group, which are doped with pentavalent or trivalent impurities, in order to get n-type semiconductors, are called elemental semiconductors.

### Compound semiconductors:

Semiconductors formed by combining fifth and third group or sixth and second group are called compound semiconductors.

### **Extrinsic semiconductor:**

Semiconductor which are doped with impurity is called extrinsic semiconductor. Here the charge carriers are produced only due to impurities and may also be produced due to thermal agitation. They are high electrical conductivity.

Extrinsic semiconductors are further subdivided into

- (i) N- TYPE semiconductor
- (ii) P-TYPE semiconductor

### **Distinguish between P-type & N-type Semiconductors.**

S.No.	N- TYPE	P-TYPE
1.	Pentavalent impurity is added	Trivalent impurity is added
2.	Electrons are majority charge carriers	Holes are minority charge carriers
3.	Impurity is called donor impurity	Impurity is called acceptor impurity
4.	Fermi level decreases with increase in temperature	Fermi level increases with increase in temperature

### **Fermi energy of an Extrinsic semiconductors at 0k.**

Fermi energy level is the energy level which distinguishes the filled and empty states (or) it is the maximum energy level up to which the electrons are filled.

- (i) The Fermi energy of 'n'-type semiconductor is a  $E_F = \frac{E_c + E_d}{2}$  i.e., the Fermi energy level exactly lies between minimum energy level of conduction band and donor energy level.
- (ii) The Fermi energy of 'p'-type semiconductor is a  $E_F = \frac{E_c + E_d}{2}$  i.e., the Fermi energy level exactly lies between top of the valence band and acceptor energy level.

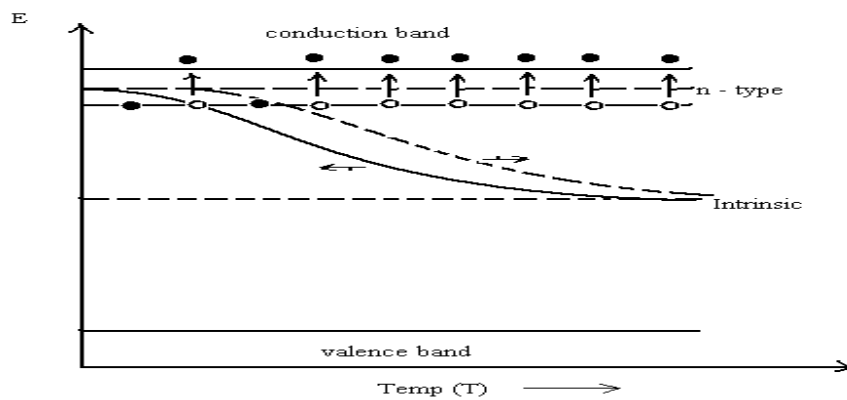
### Donor energy level

A donor is an atom or group of atoms whose highest filled atomic orbital or molecular orbital is higher in energy than that of a reference orbital.

### Acceptor energy level

An acceptor is an atom or group of atoms whose lowest unfilled atomic or molecular orbital is lower in energy than that of a reference orbital.

### Variation of Fermi level with temperature in the case of n-type semiconductor.



**Concentration of Holes in the Valence Band of n-type Semiconductor :**

In n-type semiconductor, donor energy level ( $E_d$ ) is just below the conduction band and  $N_d$  denotes the number of donor atoms per unit volume. Density of electrons per unit volume in the conduction band is given by

$$n = 2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} e^{(E_f - E_c)/kT} \dots\dots\dots(1)$$

Density of ionized donors =  $N_d F(E_d)$

$$= \frac{N_d}{1 + e^{(E_d - E_f)/kT}} = \frac{1}{1 + e^{(E_d - E_f)/kT}} \dots\dots\dots(2)$$

Since  $E_d - E_f$  is very large when compared to  $kT$ ,  $e^{(E_d - E_f)/kT}$  is a large quantity and thus ‘1’ from the denominator of R.H.S. of the equation (2) is neglected.

Now, the equation (2) is modified as,  $N_d e^{(E_f - E_d)/kT} \dots\dots\dots(3)$

At equilibrium,

Density of holes in valence band = Density of ionized donors.

$$2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} e^{(E_f - E_c)/kT} = N_d e^{(E_d - E_f)/kT} \dots\dots\dots(4)$$

Taking log on both sides of the equation (4), we have

$$\log_e \left[ 2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} \right] + \frac{E_f - E_c}{kT} = \log_e N_d + \frac{E_d - E_f}{kT} \dots\dots\dots(5)$$

Rearranging the expression (5), we have

$$\frac{E_f - E_c - E_d - E_f}{kT} = + \log_e N_d - \log_e \left[ 2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} \right] \dots\dots\dots(6)$$

$$E_f = \frac{E_d + E_c}{2} + \frac{kT}{2} \log_2 \left[ \frac{N_d}{2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2}} \right] \dots\dots\dots(7)$$

Substituting the expression of  $E_f$  from (7) in (1), we get



$$n = 2 \left( \frac{2 \pi m_e^* kT}{h^2} \right)^{3/2} \exp \left\{ \frac{E_d - E_c}{2} + \frac{kT}{2} \log_e \frac{N_d}{2 \left[ \frac{2 \pi m_e^* kT}{h^2} \right] - E_c} \right\}$$

$$n = 2 \left( \frac{2 \pi m_c^* kT}{h^2} \right)^{3/2} \exp \frac{E_c + E_d - 2E_c}{2kT} + \frac{1}{2} \log_e \left[ \frac{N_d}{2 \left( \frac{2 \pi m_c^* kT}{h^2} \right)^{3/2}} \right] \dots\dots\dots(8)$$

$$n = 2 \left( \frac{2 \pi m_c^* kT}{h^2} \right)^{3/2} \frac{\left( \frac{N_d}{2} \right)^{1/2}}{\left( \frac{2 \pi m_c^* kT}{h^2} \right)^{3/4}} e^{(E_d - E_c) / 2kT}$$

$$n = (2 N_d)^{1/2} \left( \frac{2 \pi m_c^* kT}{h^2} \right)^{3/4} e^{(E_d - E_c) / 2kT} \dots\dots\dots( 9)$$

$$n = (2 N_d)^{1/2} \left( \frac{2 \pi m_e^* kT}{h^2} \right)^{3/4} e^{-\Delta E / 2kT} \dots\dots\dots( 10)$$

Where  $\Delta E = E_c - E_d$

### Fermi energy of a P – type semiconductor

In p-Type semiconductor, acceptor energy level ( $E_a$ ) is just above the valence band and  $N_a$  denotes the number of acceptor atoms per unit volume. Density of holes per unit volume in the valence band is given by

$$p = 2 \left( \frac{2 \pi m_h^* kT}{h^2} \right)^{3/2} e^{(E_v - E_F) / kT} \dots\dots\dots (1)$$

$$\text{Density of ionized acceptors} = N_a F(E_a) = \frac{N_a}{1 + e^{(E_a - E_F) / kT}} = \frac{1}{1 + e^{(E_a - E_F) / kT}} \dots\dots\dots(2)$$

Since  $E_a - E_F$  is very large when compared to  $kT$ ,  $e^{(E_v - E_F) / kT}$  is a large quantity and thus ‘1’ from the denominator of R.H.S. of the equation (2) is neglected.

$$\text{Now, equation (2) is modified as, } N_a e^{(E_F - E_a) / kT} \dots\dots\dots(3)$$

At equilibrium,

Density of holes in valence band = Density of ionized acceptors.

$$2 \left( \frac{2\pi m_h^* kT}{h^2} \right)^{3/2} e^{(E_v - E_F)/kT} = N_a e^{(E_F - E_a)/kT} \dots (4)$$

Taking log on both sides of the equation (4), we have

$$\log_e \left[ 2 \left( \frac{2\pi m_h^* kT}{h^2} \right)^{3/2} \right] + \frac{E_v - E_F}{kT} = \log_e N_a + \frac{E_F - E_a}{kT} \dots (5)$$

Rearranging the expression (5), we have

$$\frac{E_F - E_a - E_v + E_F}{kT} = -\log_e N_a + \log_e \left[ 2 \left( \frac{2\pi m_h^* kT}{h^2} \right)^{3/2} \right] \dots (6)$$

$$E_F = \frac{E_a + E_v}{2} - \frac{kT}{2} \log_e \left[ \frac{N_a}{2 \left( \frac{2\pi m_h^* kT}{h^2} \right)^{3/2}} \right] \dots (7)$$

When T = 0 K, Then  $E_F = \frac{E_a + E_v}{2}$ , the Fermi level lies at the middle of the acceptor energy level and the top most energy level of the valence band.

### Hall effect

When a conductor (metal or semiconductor) carrying a current (I) is placed perpendicular to a magnetic field (B), a potential difference (electric field) is developed inside the conductor in a direction perpendicular to both current and magnetic field.

### Expression of Hall coefficient.

**Statement:** When a conductor (metal or semiconductor) carrying a current (I) is placed perpendicular to a magnetic field (B), a potential difference (electric field) is developed inside the conductor in a direction perpendicular to both current and magnetic field.

### Hall Effect in an n-type semiconductor:

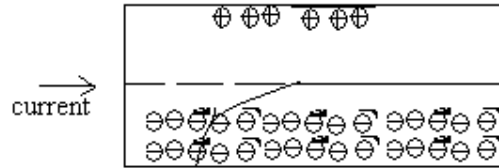
Let us consider an n-type semiconducting material in the form of rectangular slab. In such a material, current flows in X-direction and magnetic field B is applied in Z-direction. As a result,

Hall voltage is developed along Y-direction as shown. The current flow is entirely due to the flow of electrons moving from right to left along X-direction as shown. When a magnetic field (B) is applied in Z-direction, the electrons moving with velocity v will experience a downward force.

Downward force experienced by the electrons =  $Bev$ ,

Where e is the charge of an electron; ... (1)

This downward force deflects the electrons in downward direction.



This causes the bottom face to be more negative with respect to the top face. Therefore, a potential difference is developed between top and bottom of the specimen. This potential difference causes an electric field  $E_H$  called Hall field in negative Y-direction. This electric field develops a force which is acting in the upward direction on each electron.

Upward force acting on each electron =  $eE_H$  ..... (2),

At equilibrium, the downward force  $Bev$  will balance the upward force  $eE_H$

$$\therefore Bev = eE_H \text{ or } E_H = Bv \dots\dots (3).$$

The current density ( $J_x$ ) acting along the X-direction is related to the velocity v as

$$J_x = -nev,$$

$$v = \frac{-J_x}{ne} \dots\dots(4)$$

Substituting the equation (4) in the equation (3), we have

$$E_H = \frac{-BJ_x}{ne} \dots(5); E_H = R_H J_x B \dots\dots(6) \text{ or, } R_H = \frac{E_H}{J_x B}$$

$$\text{Where } R_H = -\frac{1}{ne} \text{ (for, electrons)}$$

$R_H$  is a constant and it is known as Hall coefficient.

### Hall Coefficient in terms of Hall Voltage:

If 't' is the thickness of the sample and  $V_H$  the voltage developed, then

$$V_H = E_H t \dots\dots(7)$$

Where  $E_H$  is Hall field.

Substituting the equation (6) in the equation (7), we have

$$V_H = R_H J_x B t \dots\dots (8),$$

Area of the sample (A) = Breadth (b) × Thickness (t) = bt.

$$\text{Current density, } J_x = \frac{I_x}{\text{Area.of.the.sample.(A)}} = \frac{I_x}{bt} \dots(9)$$

Substituting the equation (9) in the equation (8), we have  $V_H = \frac{R_H I_x B t}{bt}$  or  $V_H = \frac{R_H I_x B}{b}$

$$\text{Hall coefficient } R_H = \frac{V_H b}{I_x B} \dots\dots(11)$$

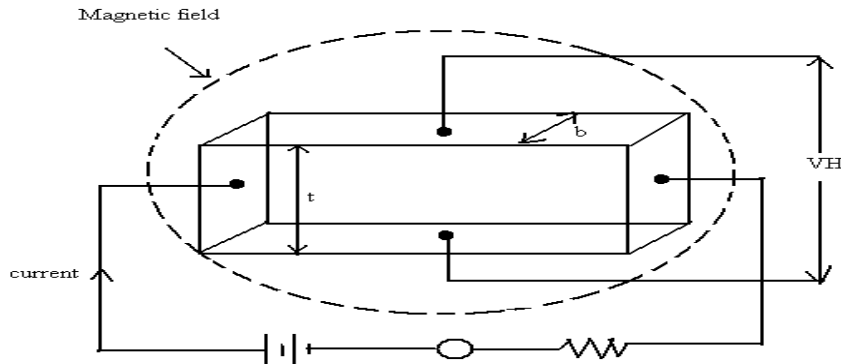
**Hall voltage.**

- Hall voltage is the voltage developed across a conductor or semiconductor, when an electric and magnetic fields are applied perpendicular to each other in the specimen

**Experimental setup for the measurement of the Hall voltage**

**Determination of Hall Coefficient:**

The experimental set up for the measurement of Hall-Coefficient is shown.



A Semi conducting material is taken in the form of a rectangular slab of thickness ‘t’ and breadth ‘b’ current  $I_x$  is passed through this sample along X-axis by connecting it to a battery.

This sample is placed in between two poles of an electromagnet such that the magnetic field is applied along Z-axis. Due to Hall Effect, Hall voltage ( $V_H$ ) is developed in the sample.

This voltage is measured by fixing two probes at the centers of the bottom and top faces of the sample. By measuring Hall voltage, Hall coefficient is determined from the formula,

$$R_H = \frac{V_H b}{I_x B}$$

From Hall coefficient, carrier concentration and mobility can be determined.

### Application of Hall effect.

1. The sign of charge carriers (electrons or holes) are determined.

2. The carrier density (concentration) is determined

$$n = - \frac{1}{R_H e}$$

$$p = \frac{1}{R_H e}$$

3. Mobility of charge carriers are measured.

Mobility of electron  $\mu_n = R_H e$

Mobility of hole  $\mu_h = R_H h$

4) Electrical conductivity of the material is determined

5) Magnetic flux density is measured from known Hall coefficient and measured Hall voltage.

## UNIT- III. MAGNETIC MATERIALS AND SUPER CONDUCTORS

### Introduction

Magnetism arises in the materials mainly due to orbital and spinning motion of electrons. Magnetic materials are of great use in equipments such as transformers, alternators, motors, electromagnets and magnetic tapes. The materials Ferrites and Metallic glasses find special applications in the memory of computer cores, magnetic shielding and recording devices.

### Basic Definitions

#### Bohr magneton

The magnetic moment contributed by an electron with angular momentum quantum number  $n=1$  is known as bohr magneton

**Bohr magneton** is the elementary electromagnetic moment of value.

$$\mu_B = \frac{eh}{4\pi m} = 9.274 \times 10^{-24}$$

#### Magnetic susceptibility

It is defined as the intensity of magnetization produced in the substance per unit magnetic field strength.

#### Magnetic permeability

Magnetic permeability of a substance measures degree to which the magnetic field can Penetrate through the substance

### Classification of Magnetic materials

The different types of magnetic materials are

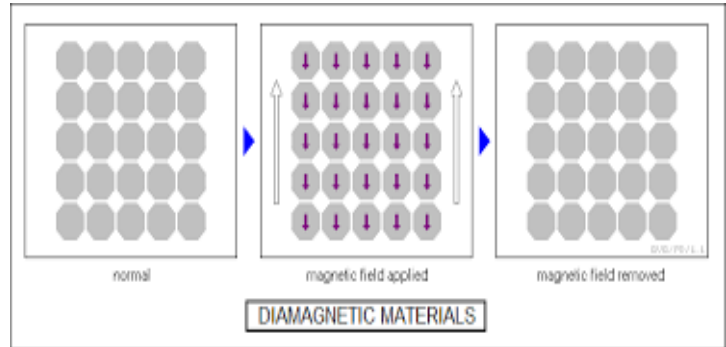
- (i) Diamagnetic materials
- (ii) Paramagnetic materials
- (iii) Ferromagnetic materials

(iv) Antiferromagnetic materials

(V) Ferrimagnetic materials

### Diamagnetic materials

- Diamagnetic materials do not have permanent dipoles.
- In an external magnetic field  $H$ , the orbital motion of electrons undergoes changes and the atoms acquire induced magnetic moment in the direction opposite to the field.
- Its susceptibility is negative  $\chi$  and independent on temperature

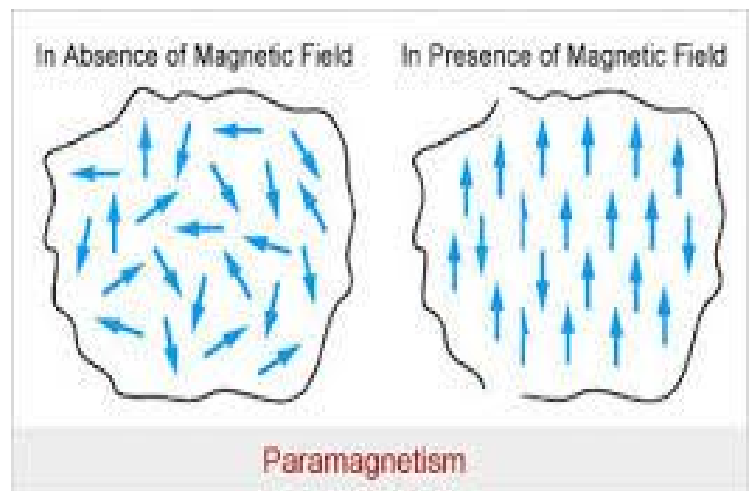


$$\kappa = \frac{M}{H} = -1$$

The induced dipoles and magnetization vanishes as soon as the field is removed. Diamagnetism is a universal property of all the substances. But other magnetic property dominates it.

### Paramagnetism

- Paramagnetic materials have permanent dipoles.
- The dipoles are randomly oriented. Therefore, the net magnetic moment is zero. In the external magnetic field  $H$ , the dipoles are tending to align in the direction of the field.
- The material becomes magnetized. Its susceptibility  $\chi$  is positive and inversely proportional to the temperature  $T$ .



$$\chi = \frac{C}{T} > 1 \quad (\text{Curie-Weiss law})$$

Where C – Curie’s constant.

### Ferromagnetism

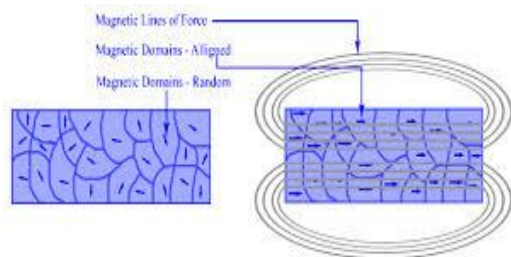
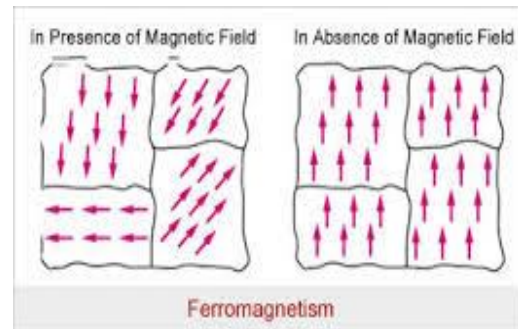


Fig. Ferromagnetism (a) Unmagnetized Material (b) Magnetized Material



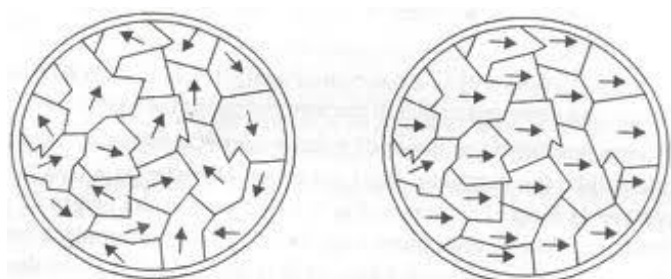
- Ferromagnetic materials have permanent dipoles.
- The dipoles are parallel to each other within the domain.
- The net magnetic moment of the domain is zero due to intermolecular field.
- The spin magnetic moments of unpaired electrons are responsible for it. They have spontaneous magnetization.
- Its susceptibility is very large and depends on temperature.

$$\chi = \frac{C}{T - \theta} \gg 1$$

When the temperature T increases its susceptibility  $\chi$  decreases and shows paramagnetic behaviour above the paramagnetic Curie temperature  $\theta$ .

### **Ferromagnetic domain theory**

- It states that a ferromagnetic material consist of large number of small





regions of spontaneous magnetization called domains.

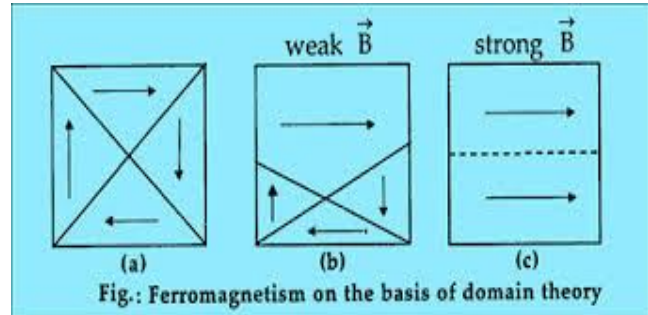
- Within each domain, the magnetic moments are aligned parallel to one another.
- The direction of magnetization varies from domain to domain and thus net macroscopic magnetization is zero in a virgin specimen.

When we apply an increasing external magnetic field, initially, the areas of the domains which are parallel to the field are increased. In the final saturation stage, the other domains are rotated parallel to the field.

### Process of domain magnetization:

#### 1. By the motion of domain walls:

When small magnetic field is applied the domain with magnetization direction parallel or near by parallel to the field ,grow at the expense of others as show below picture



#### 2. By rotation of domains :

As the magnetic field increased to large value further domain growth becomes impossible through domain wall movement

### Types of energy involved in the process:

1. Exchange energy
2. Magnetstatic energy
3. Crystal anisotropy energy

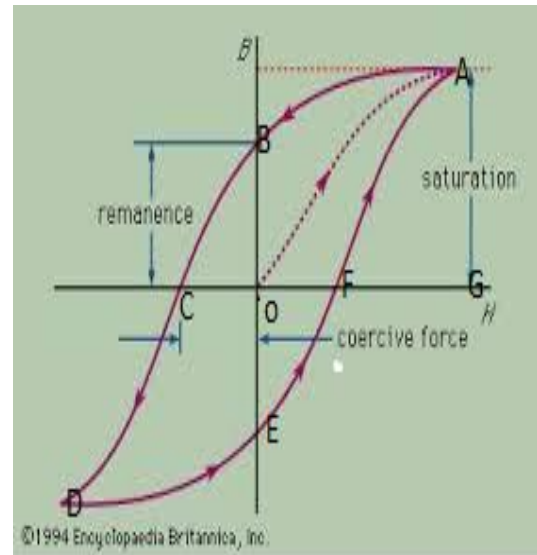
### The hysteresis on the basis of domain theory of ferromagnetism

**Hysteresis** is the lagging of magnetic induction  $B$  behind the applied magnetic field  $H$ .

## Hysteresis loop

A B-H curve is drawn by taking magnetization  $H$  in the x-axis and magnetic induction  $B$  of the ferromagnetic material in the y-axis.

1.  $H$  is increased then  $B$  increased and reached saturation at A.
2.  $H$  is decreased then  $B$  decreased and reached retentivity at B.
3.  $H$  is increased in the reverse direction then  $B$  decreased and reached zero at C known as coercivity.
4.  $H$  is further increased then  $B$  increased in the reverse direction and reached saturation at D.
5.  $H$  is decreased then  $B$  decreased and reached retentivity at E.
6.  $H$  is increased in the reverse direction then  $B$  decreased and reached zero at F.
7.  $H$  is increased further then  $B$  reached saturation again at A.



The obtained loop ABCDEA as in the figure is called **Hysteresis loop**.

The area occupied by the loop indicates the **Hysteresis energy loss** during the magnetization cycle of ferromagnetic material.

- **Retentivity or residual magnetism** is the amount of magnetic induction retained at B in the material after the removal of the applied magnetic field ( $H = 0$ ).
- **Coercitivity or coercive force** is the required amount of magnetizing field  $H$  in the reverse direction to remove the residual magnetism completely from the material ( $B=0$ ).

## Types of Magnetic materials

There are two types of magnetic materials. They are

- (i) Soft magnetic materials
- (ii) Hard magnetic materials

### Soft and hard magnetic materials

<b>Soft magnetic materials</b>	<b>Hard magnetic materials</b>
They are easily magnetized and demagnetized.	They cannot be easily magnetized
They have large permeability and susceptibility	They have low permeability
Hysteresis loss is low	Hysteresis loss is high.
Low retentivity	High retentivity
Low coercitivity	High coercitivity
Low eddy current loss	High eddy current loss

### **Energy Product**

The Energy product is defined as the product of retentivity and coercivity. The energy product gives the maximum amount of energy stored in the specimen. The value of energy product should be very large for manufacturing permanent magnets. Hard magnetic materials are having large energy product.

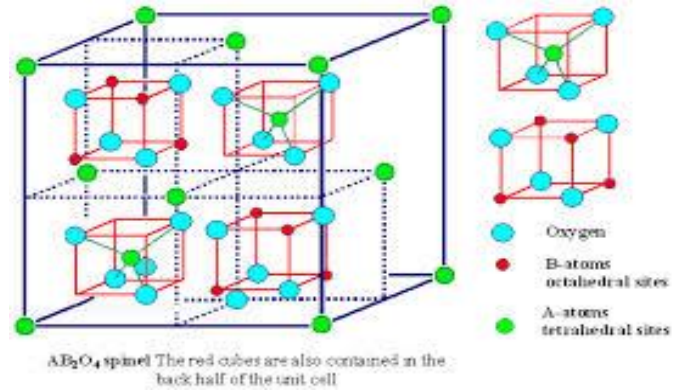
### **Anti ferromagnetism**

Antiferromagnetic materials containing two types of dipoles in the adjacent sites. The electron spin of neighboring dipoles are aligned antiparallel. So net magnetization is zero at 0 K. Its susceptibility initially increases slightly with temperature T and decreases beyond the Neel temperature  $T_N$ .

- The dipole alignment is antiparallel
- The susceptibility is very small and is antiparallel
- Initially, the susceptibility increases slightly as the temperature increases. Beyond a particular temperature known as Neel temperature, the susceptibility decreases with temperature.
- Example : Ferrous oxide, Manganese oxide.

## The structure and application of Ferrites

- They are compounds of iron oxides with oxides of other metals.
- Magnetic moment of sub-lattices are antiparallel of different magnitude. Mechanically it has pure iron character.
- They have high permeability and retentivity.
- They have low hysteresis and eddy current losses. Its susceptibility is very large and positive



C

$$\chi = \frac{C}{T \pm \theta}$$

Where C – Curie constant and  $\theta$ - paramagnetic Curie's temperature

### Applications of ferrites

1. Soft magnetic ferrites are used to make cores for transformer.
2. Soft Ferrite rods are used to produce ultrasonic sound by magnetostriction principle.
3. Soft Ferrite rods are used to increase the sensitivity and selectivity of the radio receiver.
4. To make ferrite coated magnetic film, magnetic discs, magnetic tapes and microwave drivers.
5. Hard magnetic ferrites are used to make permanent magnet.

## SUPER CONDUCTORS

### Introduction

The electrical resistivity of many metals and alloys drops suddenly to zero when the materials are cooled to a sufficiently low temperature called critical or transition temperature. This phenomenon is known as superconductivity.

Superconductivity was first observed in 1911 by a Dutch Physicist, H.K. Onnes in the course of his experiment on measuring the electrical conductivity of metals at low temperature. He observed that when purified mercury was cooled to 4.2 K its resistivity suddenly dropped to zero. Superconductivity occurs in metallic elements and also in alloys and semiconductors.

## Transition temperature

The temperature at which a normal conductor loses its resistivity and becomes a super conductor is known as transition temperature.

## Meissner effect

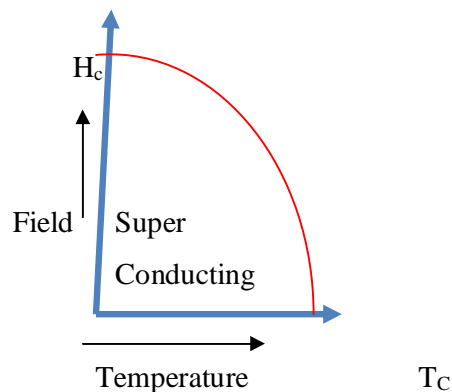
When a super conducting material is kept in an external magnetic field under the condition when  $T \leq T_c$  and  $H \leq H_c$ , the magnetic flux lines are completely excluded from the material and the phenomenon is known as Meissner effect.

## Critical magnetic field in superconductor.

When a super conductor is kept in magnetic field, the super conductor becomes normal conductor. The magnetic field required to destroy the super conducting property is called critical field ( $H_c$ ). It is given by

$$H_c = H_o \left[ 1 - \frac{T^2}{T_c^2} \right]$$

Where  $H_o$  Critical field at 0K  
 $T_c$  Transition temperature.



## Persistent Current

The steady current which flows through a superconducting ring without any decrease in its strength as long as the material is in the superconducting state even after the removal of the magnetic field is called persistent current.

## Types of Super conductors:

There are two types of Superconductors. They are,

- Type I superconductors
- Type II superconductors

When a super conductor is kept in a external magnetic, if the super conductors becomes normal conductor suddenly at critical magnetic field. It is called as type I super conductors.

When a super conductor is kept in a external magnetic, if the super conductors becomes normal conductor gradually with respect to various critical fields, it is called as type II super conductors.

### **Type I and Type II superconductors**

S.No	Type I (soft) superconductor	Type II (Hard) superconductor
1.	The Type I super conductor becomes a normal conductor abruptly at critical magnetic field.	Type II super conductor loses its super conducting property gradually, due to increase in magnetic field.
2.	Here we have only critical field ( $H_c$ )	Here we have two critical fields (i.e.) Lower critical fields ( $H_{c1}$ ) and Upper critical fields ( $H_{c2}$ ).
3.	No mixed state exists	Mixed (or) vortex state is present.
4.	Highest known critical field is 0.1 Tesla	The critical field is greater than Type I (i.e) Upto 30 Teslas.
5.	Examples:Pb, Zn, Al, Ga, Hg,	Examples:Niobium, Vanadium.

### **BCS Theory**

- The BCS theory relies on the assumption that superconductivity arises when the attractive Cooper pair interaction dominates over the repulsive Coulomb force.
- A Cooper pair is a weak electron-electron bound pair mediated by a phonon interaction. Although somewhat ambiguous, one can visualize this pairing by the following explanation. Imagine an electron moving within a material.
- The Coulomb attraction between the electron and the positively charged cores of ions in the material will leave a net positive charge in the vicinity.
- A “paired “electron is one with opposite momentum and spin that is attracted to this force.

The BCS Theory is, in its simplest form, actually contradictory to our crude macroscopic view expressed earlier. As discussed earlier, superconductivity arises because electrons do not interact destructively with atoms in the crystal lattice of the material.

The BCS Theory says that electrons do actually interact with the atoms, but constructively. The BCS Theory makes a crucial assumption at the beginning: that an attractive force exists between electrons. In typical Type I superconductors, this force is due to Coulomb attraction between the electron and the crystal lattice.

- An electron in the lattice will cause a slight increase in positive charges around it. This increase in positive charge will, in turn, attract another electron. These two electrons are known as a Cooper pair.
- Cooper pairs are formed by Coulomb interactions with the crystal lattice.
- As the Cooper pair flows, the leading electron causes this increase of charge, and the trailing electron is attracted by it. This is illustrated below.

### **High $T_c$ Superconductors**

High temperature superconductors are the one which has the transition temperature above 77 K. Here crossing 77 K is very important, because cooling can be made by liquid nitrogen instead of liquid helium, which is costly than nitrogen.

Example:

- (i)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  [YBCO] [ $T_c=90\text{K}$ ]
- (ii)  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  [TBCO] [ $T_c=120\text{K}$ ]

### **High $T_c$ super conductor**

- High-temperature superconductors (abbreviated high- $T_c$  or HTS) are materials that have a [superconducting](#) transition temperature ( $T_c$ ) above 30 K ( $-243.2^\circ\text{C}$ ).
- "High-temperature" has three common definitions in the context of superconductivity: Technological applications benefit from both the higher critical temperature being above the boiling point of liquid nitrogen and also the higher critical magnetic field (and critical current density) at which superconductivity is destroyed.
- In magnet applications the high critical magnetic field may be more valuable than the high  $T_c$  itself. Some cuprates have an upper critical field around 100 teslas. However, cuprate materials are brittle ceramics which are expensive to

**High temperature superconductors** have transition temperature  $T_c$  above 24 K.

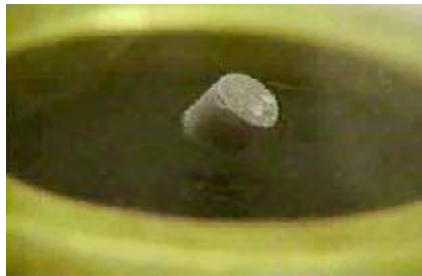
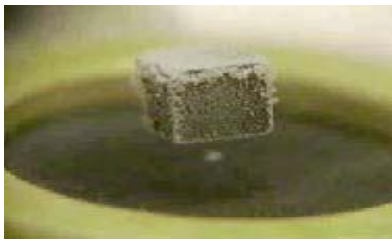
Eg:  $\text{YBa}_2\text{Cu}_3\text{O}_7$   $T_c = 95 \text{ K}$ .

### Properties of high temperature superconductors

1. They obey **Resonating Valence Bond RVB theory**
2. They are oxides of copper in combination with other elements
3. Their superconducting property is direction dependent.

### Magnetic Levitation

- Magnetic fields are actively excluded from superconductors (Meissner effect). If a small magnet is brought near a superconductor, it will be repelled because induced super currents will produce mirror images of each pole.
- If a small permanent magnet is placed above a superconductor, it can be levitated by this repulsive force. The black ceramic material in the illustrations is a sample of the yttrium based superconductor.
- By tapping with a sharp instrument, the suspended magnet can be caused to oscillate or rotate. This motion is found to be damped, and will come to rest in a few seconds.



- Magnetically levitated (MAGLEV) trains are considered as a future application of HTS development. To understand why, we must look briefly at the history of the railroads. The development of trains and rails began in the early 1800s. The modern conventional train is no faster (~110 mph) than those of the late 1890s.
- So conventional trains have reached the end phase of their development. France, Germany, and Japan have developed "high-speed" or "bullet" trains capable of speeds of 150-180 mph. This improvement in speed is based upon improved rails and controls.

However, this technology has also reached the end phase of its development. One limiting factor for these trains is the expensive and time-consuming maintenance of the rails. So it is the mechanical friction between train wheels and metal tracks that limit this technology. This leads us to the development of the magnetically levitated (no friction) trains. We briefly describe the history of this development.

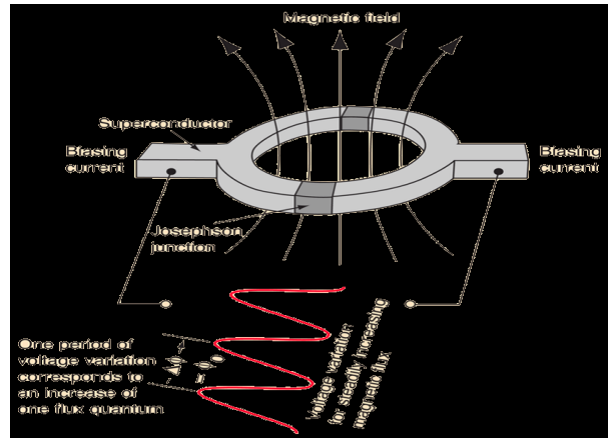


Two basically different concepts of magnetic suspension have evolved.

1. The attractive electromagnetic suspension (EMS) uses electromagnets on the train body which are attracted to the iron rails. The vehicle magnets wrap around the iron guideways and the attractive upward force lifts the train.
2. The electrodynamic suspension (EDS) levitates the train by repulsive forces from the induced currents in the conductive guideways.

## SQUIDS

- The superconducting quantum interference device (SQUID) consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions.
- The device may be configured as a magnetometer to detect incredibly small magnetic fields -- small enough to measure the magnetic fields in living organisms.
- Squids have been used to measure the magnetic fields in mouse brains to test whether there might be enough magnetism to attribute their navigational ability to an internal compass.
- The great sensitivity of the SQUID devices is associated with measuring changes in magnetic field associated with one flux quantum. One of the discoveries associated with Josephson junctions was that flux is quantized in units.
- If a constant biasing current is maintained in the SQUID device, the measured voltage oscillates with the changes in phase at the two junctions, which depends upon the change in the magnetic flux. Counting the oscillations allows you to evaluate the flux change which has occurred.



### Application of superconductors.

#### Engineering applications:

- (i) It is used in magnetic levitation, cryotrons, Josephson devices, SQUIDS etc.
- (ii) It is used in computers transmission lines etc.

#### Medical applications:

- (i) Super conductors are used in NMR (Nuclear Magnetic Resonance) imaging equipments.
- (ii) Super conducting solenoids are used in magneto hydrodynamic power generation to maintain plasma in the body.

## UNIT- IV - DIELECTRIC MATERIALS

### INTRODUCTION

Insulators are those substances which resist the flow of current through them when a potential difference is applied across them. Dielectrics are basically insulators. There are no free charge carriers in a dielectric since the electrons are tightly bound to the atoms or molecules of the dielectric material. When a dielectric material is placed in an electric field, dipoles are created. This phenomenon is called polarization. Hence, dielectrics are mainly used to store electric charges and as electric insulators.

### Properties

- Dielectric materials are insulators with band gap energy more than 3 eV.
- All the electrons are tightly bound to the atoms or molecules and there are no free charges.
- The electrons cannot be dislodged either by thermal vibrations or by ordinary applied voltage
- The dielectric materials are non metallic materials of high specific resistance and have negative temperature coefficient of resistance.
- Glass, ebonite, mica, rubber, wood and paper are examples

### Dielectric constant

Dielectric constant ( $\epsilon_r$ ) is the measure of the polarization produced in the material. It is the ratio between the absolute permittivity ( $\epsilon$ ) and the permittivity of free space ( $\epsilon_0$ ).

$$\text{(i.e.) } \epsilon_r = \frac{\epsilon}{\epsilon_0}$$

### Polarization of a dielectric material.

The process of producing electric dipoles inside the dielectric when placed in external electric field (E) is called electric polarization.

(i.e.) The induced dipole moment ( $\mu$ ) =  $\alpha E$ ; where  $\alpha \rightarrow$  electric polarizability.

### Types of polarization mechanisms involved in dielectric.

The four types of polarization mechanisms are:

- (i) Electronic polarization
- (ii) Ionic polarization

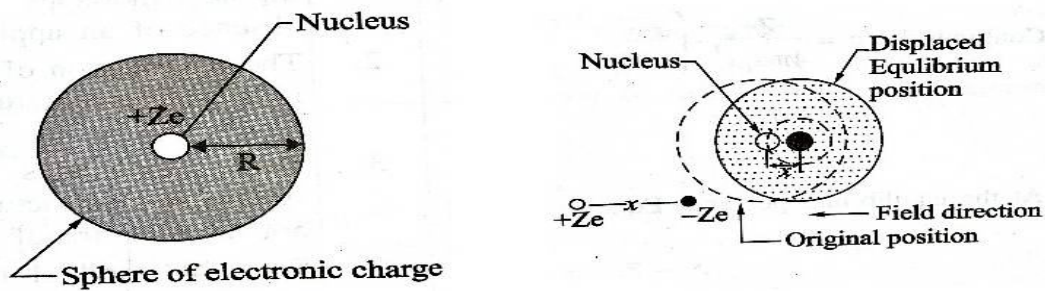
- (iii) Orientation polarization
- (iv) Space-charge polarization

**Electronic polarization**

Electronic polarization occurs due to the displacement of the positively charge nucleus and negative electrons of an atom in opposite direction by an electric field.

$$\text{The induced dipole moment } \mu = \alpha_e E$$

Where  $\alpha$  is the electronic polarizability. Electronic polarizability is proportional to the volume of the atoms and is independent of temperature.



**Calculation of Electronic polarizability**

**Without field**

Consider an atom. Assume the charge of nucleus of that atom is  $Ze$ . The nucleus is surrounded by an electron cloud of charge  $-Ze$ , which is distributed in a sphere of radius  $R$ .

$$\text{The charge density of the charged sphere} = \frac{-Ze}{\frac{4}{3}\pi R^3} \dots\dots(1)$$

**With Field**

When the dielectric is placed in a d.c electronic field  $E$ , two phenomenon occur.

- (i) Lorentz force due to the electric field tends to separate the nucleus and the electron cloud from their equilibrium position.
- (ii) After separation, an attractive coulomb force arises between the nucleus and electron cloud which tries to maintain the original equilibrium position.

Let  $x$  be the displacement made by the electron cloud from the positive core. Since the core is heavy, it will not move when compared to the movement of electron cloud. Here  $x \ll R$ , where  $R$  is

radius of the atom. Since Lorentz and Coulomb forces are equal and opposite in nature, equilibrium is reached.

$$\text{Lorentz forces} = \text{Coulomb force} = -ZeE \quad (-\text{ve sign indicates repulsive force}) \quad \dots 2$$

$$\text{Coulomb force} = \text{Charge} \times \text{Field}$$

$$= Ze \times \frac{Q}{4\pi\epsilon_0 x^2}$$

$$\text{Coulomb force} = \text{Charge} \times \frac{\text{Total negative charge (Q) enclosed in the sphere of radius x}}{4\pi\epsilon_0 x^2} \quad (3)$$

$$Q = \text{Charge density of electron} \times \text{volume of the sphere}$$

From equation (1)

$$\text{Total number of negative charges enclosed in sphere of radius x} = \frac{-3}{4} \times \frac{Ze}{\pi R^3} \times \frac{4}{3} \pi x^3$$

$$Q = \frac{-Zex^3}{R^3} \quad (4)$$

Substitute eqn (4) in (3) we get

$$\begin{aligned} \text{Coulomb force} &= \frac{Ze}{4\pi\epsilon_0 x^2} \times \frac{-Zex^3}{R^3} \\ &= \frac{-Z^2 e^2 x}{4\pi\epsilon_0 R^3} \quad (5) \end{aligned}$$

At equilibrium position, Equation (2) = Equation (5).

$$-ZeE = \frac{-Z^2 e^2 x}{4\pi\epsilon_0 R^3}$$

$$x = \frac{4\pi\epsilon_0 R^3 E}{Ze} \quad (6)$$

### Dipole Moment

Now the two electric charges  $+Ze$  and  $-Ze$  are displaced by a distance  $x$  under the influence of applied field.

Induced dipole moment = Magnitude of the charge  $\times$  displacement

Substitute the value of  $x$  from eqn (6)

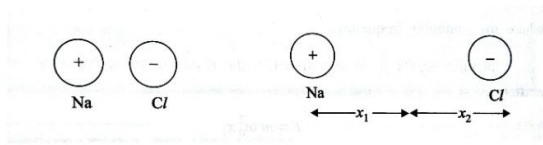
$$\mu_e = 4\pi\epsilon_0 R^3 E$$

$$\mu_e = \alpha_e E$$

$\alpha_e$ - electronic polarizability

### Ionic polarization:

**Ionic polarization** occurs due to the displacement of the cat ion and anion in opposite direction by an electric field. This occurs only in ionic solids.



When the electric field is applied, let  $x_1$  and  $x_2$  be the distance to which the positive and negative ions move from their equilibrium position.

Induced dipole moment = Magnitude of the charge  $\times$  displacement.

$$\mu_i = e(x_1 + x_2) \quad (1)$$

When the field is applied, restoring force is produced proportional to the displacement.

**For +ve ion,**

$$\text{Restoring force } F \propto x_1 \text{ or } F = \beta_1 x_1 \quad (2)$$

For -ve ion,

$$\text{Restoring force } F \propto x_2 \text{ or } F = \beta_2 x_2 \quad (3)$$

Here  $\beta_1$  and  $\beta_2$  are restoring force constant which depend on the masses of the ion and the angular frequency of the molecule in which the ions are present.

If 'm' is the mass of +ve ion and 'M' is the mass of -ve ion and  $\omega_0$  is the angular frequency, then

$$\beta_1 = m\omega_0^2 \quad (4)$$

$$\beta_2 = M\omega_0^2 \quad (5)$$

Substituting for  $\beta_1$  in eqn (2), the restoring force for +ve ion can be written as

$$F = m\omega_0^2 x_1 \quad (6)$$

$$\text{We know } F = eE \quad (7)$$

Equating equation (6) and (7), we get

$$eE = m\omega_0^2 x_1$$

$$x_1 = \frac{eE}{m\omega_0^2} \quad (8)$$

Similarly for the negative ion we can write

$$x_2 = \frac{eE}{M\omega_0^2} \quad (9)$$

Adding equation (8) and (9) we get

$$x_1 + x_2 = \frac{e^2}{\omega_0^2} \left\{ \frac{1}{m} + \frac{1}{M} \right\} \quad (10)$$

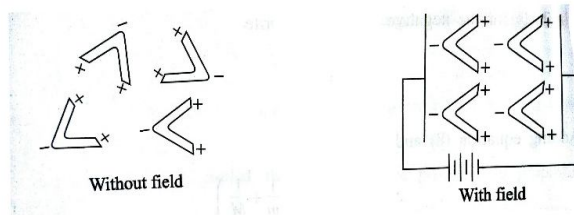
Substituting equation (10) in eqn (1), we get

$$\mu_i = \frac{e^2 E}{\omega_0^2} \left\{ \frac{1}{m} + \frac{1}{M} \right\}$$

$\mu_i = \alpha_i E$  where  $\alpha_i$  -ionic polarizability.

### Orientation Polarization

Orientation polarization arises due to the presence of polar molecules in the dielectric medium. Polar molecules are the molecules which have permanent dipole moment even in the absence of an electric field. Example methyl chloride.



Now when the field is applied, positive portion align themselves along the direction of field and the negative portion align in opposite direction of the field. This kind of polarization is called as orientation polarization.

This depends on temperature. When temperature is increased, the thermal energy tends to randomize the alignment.

From the Langevin's theory of paramagnetism, net intensity of magnetisation

$$= \frac{N\mu^2 B}{3K_B T}$$

Since, the same principle can be applied to the application of electric field we can write,

$$\text{Orientation polarization } P_o = \frac{N\mu^2 E}{3K_B T}$$

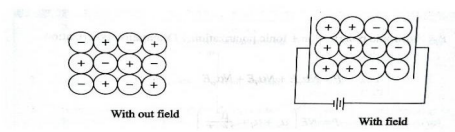
Where N is the number of atoms.

$$P_o = N\alpha_o E$$

Where  $\alpha_o$  is orientational polarizability.

### Space charge polarization

Space charge polarization occurs due to diffusion of ions, along the electric field direction and giving rise to redistribution of charges in the dielectrics. This occurs only in ferrites and semiconductors and will be very small.

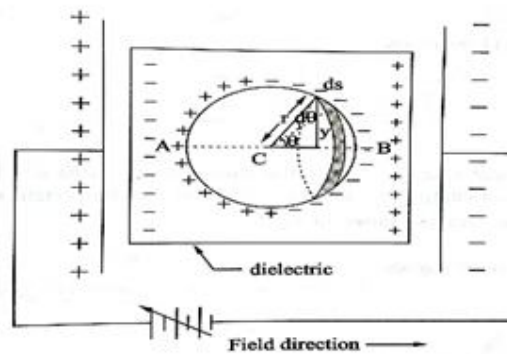


### Local field in a dielectric

When a dielectric is kept in an external electric field ( $E$ ), two fields are exerted due to (i) External field and (ii) dipole moment created. These long range of coulomb forces which are created due to the dipoles are called local field (or) internal field dielectric.

It is given by  $E_{int} = E + \frac{P}{\epsilon_0}$ ; where  $P$  polarization;  $(\epsilon_0) \rightarrow$  Permittivity in free space.

### Internal / Local field



When a dielectric material is kept in an external electric field it exerts a dipole moment in it. Therefore two fields are exerted,

- (i) Due to external field
- (ii) Due to dipole moment

Internal / Local field at any point inside a dielectric is the sum of the applied electric field and the fields created by the neighbouring dipoles. Lorentz method for finding the internal or local field for a cubic structure.

A dielectric material is placed in an external electric field  $E$  between the parallel plates as shown in the figure. Consider an imaginary spherical sphere around an atom at  $C$ .

The internal field at  $C$ ,  $E_{int} = E_1 + E_2 + E_3 + E_4$  (1)

Where,

$E_1$  is the field intensity due to free charge density on the plates

$E_2$  is the field intensity due to the induced charge density on the plane surface of the dielectric.

$E_3$  is the field intensity due to charges on the surface of the sphere.

$E_4$  is the field intensity due to the atomic dipole inside the sphere considered.

If the dielectric is highly symmetric then the dipoles will cancel with each other therefore we can write

$$E_4 = 0, \text{ Macroscopically, } E = E_1 + E_2$$

Therefore equation (1) becomes,

$$E_{\text{int}} = E + E_3 \quad (2)$$

Consider elementary area  $ds$  on the surface of the sphere and  $q'$  be the charge on it. Let  $r$  be the radius of the sphere.  $d\theta$  be angle subtended by the area with the atomic site.  $P$  direction of polarization and  $P_N$  component normal to the area.

Then  $P_N = P \cos \theta$ . Then  $P_N = q'/ds$ .

Therefore  $q' = P \cos \theta ds$ .

According the coulomb's law, the electric field at  $C$  due to  $q'$  is given by

$$\begin{aligned} E &= q' / (4\pi\epsilon_0 r^2) \\ &= P \cos \theta ds / (4\pi\epsilon_0 r^2) \end{aligned} \quad (3)$$

X component of the electric field  $E_x = E \cos \theta = P \cos^2 \theta ds / (4\pi\epsilon_0 r^2)$  (4)

Y component  $E_y = 0$ . X components is parallel to electric field and Y components perpendicular to the field direction hence cancel each other.

Consider an elementary ring of area  $dA$  lying between  $\theta$  and  $\theta + d\theta$ . Where  $\theta$  is direction with respect to the applied field direction..

$$\begin{aligned} dA &= \text{circumference} \times \text{Thickness of the ring} \\ &= 2\pi y \times ds \\ &= 2\pi r \sin \theta \times r d\theta \quad (\text{since } y = r \sin \theta \quad ds = r d\theta) \\ &= 2\pi r^2 \sin \theta d\theta \end{aligned} \quad (5)$$

where  $r$  is the radius of the sphere

$$\text{Electric field intensity at } C \text{ due to } dA = \frac{P \cos^2 \theta \sin \theta dA}{4\pi\epsilon_0 r^2}$$

Substituting equation (5) in equation (4), we get

$$= \frac{2 r^2 P \cos^2 \theta \sin \theta d\theta}{4 \pi \epsilon_0 r^2} = \frac{P \cos^2 \theta \sin \theta d\theta}{2 \epsilon_0} \quad (6)$$

Electric field intensity at  $c$  due to charges on the whole surface of the sphere can be derived by integrating equation (6) within limits  $0$  to  $\pi$



$$E_3 = \int_0^\pi \frac{P \cos^2 \theta \sin \theta d\theta}{2\epsilon_0} = \frac{2}{3} \left\{ \frac{P}{2\epsilon_0} \right\} = \frac{P}{3\epsilon_0} \quad (7)$$

Substituting equation (7) in equation (2)

$$E_{\text{int}} = E + E_3; E_{\text{int}} = E + \frac{P}{3\epsilon_0} \quad (8)$$

This shows the internal field is larger than the macroscopic field intensity E.

### Clausius- Mosotti relation

Consider a dielectric solid in an external electric field E, dipoles are formed in the material. The polarizability  $\alpha$  of an atom or molecule is,  $\alpha = P/(N E_{\text{int}})$

Where P is the total polarization, N is the number of atoms or molecules or dipoles per unit volume and  $E_i$ - Local electrical field.

$$P = N\alpha E_{\text{int}}; E_{\text{int}} = \frac{P}{N\alpha};$$

We know.

$$D = \epsilon E = \epsilon_0 E + P$$

$$(\epsilon - \epsilon_0)E = P$$

$$E = \frac{P}{\epsilon - \epsilon_0}$$

$$E_{\text{int}} = E + \frac{P}{3\epsilon_0} = \frac{P}{\epsilon - \epsilon_0} + \frac{P}{3\epsilon_0}$$

$$\frac{P}{N\alpha} = \frac{P}{\epsilon - \epsilon_0} + \frac{P}{3\epsilon_0} = \frac{P(3\epsilon_0 + \epsilon - \epsilon_0)}{3\epsilon_0(\epsilon - \epsilon_0)}$$

$$\frac{3\epsilon_0}{N\alpha} = \frac{2\epsilon_0 + \epsilon}{\epsilon - \epsilon_0}; \text{multiply .and .Divide .by .}\epsilon_0 \text{ in .right .side .we .have .} \frac{3\epsilon_0}{N\alpha} = \frac{2 + \epsilon_r}{\epsilon_r - 1}$$

$$\frac{N\alpha}{3\epsilon_0} = \frac{\epsilon_r - 1}{2 + \epsilon_r}$$

Clausius mosotti equation relates the microscopic parameters (atomic polarizability  $\alpha$ ) with the macroscopic dielectric constant  $\epsilon_r$ .

### Dielectric loss

When a dielectric material is subjected to electric field, the electrical energy is absorbed by the dielectric and certain amount of electrical energy is dissipated in the form of heat energy. This loss in energy in the form of heat is called dielectric loss.

## Dielectric breakdown

When a dielectric is placed in an electric field and if the electric field is increased, when the field exceeds the critical electrical field, the dielectric loses its insulating property and becomes conducting. This phenomenon is called dielectric breakdown.

### Different types of breakdown mechanism

- (i) Intrinsic breakdown
- (ii) Thermal breakdown
- (iii) Discharge breakdown
- (iv) Electrochemical breakdown
- (v) Defect breakdown

### Types of dielectric breakdown

- Above the critical electric field, electrons in the valence band jump to conduction band and cause for large flow of current that leads to **intrinsic dielectric break down**.
- When the applied electric field is further large the accelerated electrons in the conduction band breaks the covalent bonds and produce large current that leads to **avalanche dielectric breakdown**.

### Characteristics

It can occur even at lower temp.

It requires relatively large electric fields.

It occurs within a short span of time

- If the applied electric field is sufficient to melt the dielectric due to dissipated heat energy. This cause for large amount of current flow that leads to **thermal dielectric breakdown**.

### Characteristics

(a) It occurs at higher temp.

(b) It requires moderate electric fields.

(c) It occurs in the order of millisecond.

- When the temperature of dielectric increases, the mobility of ions increases and hence chemical reaction takes place and leads to leakage current that leads to **chemical dielectric breakdown**.

### Characteristics

(a) It can occur even at lower temp.

(b) It depends on concentration of ions, magnitude of leakage currents.

- If any air bubbles inside the dielectric is subjected to ionization and produce discharge of large ionization current that leads to **discharge dielectric breakdown**.

### **Characteristics**

- (a) It occurs at low voltages.
- (b) It depends upon the frequency of the applied voltage.
- (c) It occurs due to presence of occluded gas bubble.

## UNIT- V. MODERN ENGINEERING MATERIALS

### METALLIC GLASSES

Metallic glasses is an amorphous metal having the properties of both metals and glasses. They are strong, ductile, malleable, opaque and brittle. They have good magnetic properties and high corrosion resistance. Temperature at which transition from liquid to solid occurs is known as glass transition temperature ( $T_g$ ).

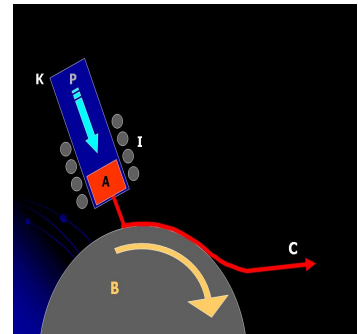
#### Preparation of Metallic Glasses

##### **Principle:**

The Principle used in making metallic glasses is extreme rapid cooling of the molten metal alloy. This technique is called as rapid **quenching**.

##### **Melt spinning system:**

- A melt spinner consists of a copper roller over which a refractory tube with fine nozzle is placed.
- The refractory tube is provided with induction heater.
- The metal alloy is melted under inert gas atmosphere.
- The super heated molten alloy is ejected through the fine nozzle at the bottom of the refractory tube.
- The molten alloy falls on the copper roller which is rotated at high speed.
- Thus, the alloy is suddenly cooled to form metallic glass.



##### **Other Techniques:**

The other techniques used for producing ribbons of metallic glasses include.

##### **(i) Twin roller system**

In twin roller system, the molten alloy is passed through 2 rollers rotating in opposite directions.

##### **(ii) Melt extraction system**

In melt extraction system, a fast moving roller sweeps off molten droplet into a strip from a solid rod.

##### **Types of Metallic Glasses**

- Metal – Metal metallic glasses:** They are combination of metals. Eg: Nickel (Ni) – Niobium (Nb)
- Metal – Metalloid metallic glasses:** These are combinations of metals and metalloids.

Eg: Fe, Co, Ni – B, Si, C

### **Properties of Metallic Glasses:**

#### **Structural properties:**

1. They do not have any crystal defects such as grain boundaries, dislocation etc.
2. Metallic glasses have tetrahedral close packing.

#### **Mechanical properties:**

They have extremely high strength, high elasticity and highly ductile.

#### **Electrical properties:**

1. They have high electrical resistivity and the eddy current loss is very small.
2. The temperature coefficient is zero or negative.

#### **Magnetic properties:**

1. Metallic glasses have both soft and hard magnetic properties.
2. They exhibit high saturation magnetization, less core losses and narrow hysteresis loop.

#### **Chemical properties:**

They are highly resistant to corrosion and are highly reactive and stable.

### **Applications of Metallic Glasses:**

1. They are used as reinforcing elements in concrete, plastic and rubber.
2. They are used to construct large fly wheels for energy storage and are used to make razor blades and different kinds of springs.
3. They are used in tape recorder heads, cores of high-power transformers.
4. They are used to produce high magnetic fields and magnetic levitation effect.
5. They are useful in preparing containers for nuclear waste disposal and are used in inner surfaces of reactor vessels, etc.
6. They are used to make surgical instruments.
7. They are used as prosthetic materials for implantation in human body.

## SHAPE MEMORY ALLOYS

Metallic alloys which has the ability to return to their original shape or size when they are subjected to heating or cooling are called shape memory alloys.

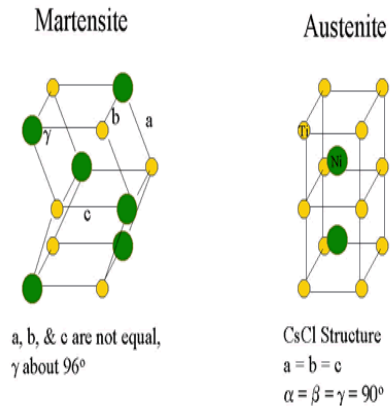
### Phases of shape memory alloys:

- (i) **Martensite** is relatively soft and it is easily deformable phase which exists at low temperature.
- (ii) **Austenite** is a phase that occurs at high temperature having a crystal structure and high degree of symmetry.

### Types of Shape memory alloys:

- (i) **One-way shape memory alloy**
- (ii) **Two-way shape memory alloy**

- A material which exhibits shape memory effect only upon heating is known as **one-way shape memory**.
- A material which shows a shape memory effect during both heating and cooling is called **two-way shapememory**.



**Examples: Ni – Ti alloy, Cu – Al – Ni alloy.**

### Methods of Processing:

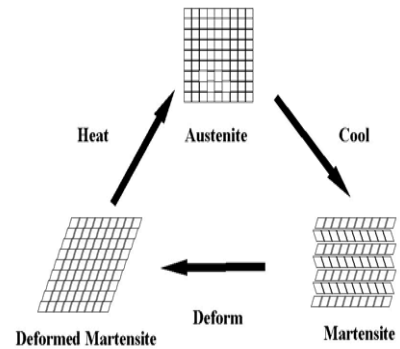
The shape memory alloys are generally prepared in vacuum or in an inert gas atmosphere. Methods such as plasma arc melting, electron beam melting, etc., are used for the preparations of shape memory alloys.

### Characteristics of SMA

#### 1. Shape memory effect

- The change of shape of a material at low temperature by loading and regaining of original shape by heating it, is known as **shape memory effect**.

- While loading, twinned martensite becomes deformed martensite at low temperature.
- On heating, deformed martensite becomes austenite and upon cooling it gets transformed to twinned martensite.



2. SMAs exhibit changes in electrical resistance, volume and length during the transformation with temperature.
3. **The mechanism involved in SMA is reversible.**
4. **Stress and temperature have a great influence on martensite transformation.**
5. The phenomenon of deformation of a SMA on application of large stress and regaining of shape on removal of the load is known as **Pseudo elasticity. This occurs without a change in temperature.**
6. The difference between the transition temperature upon heating and cooling is called **hysteresis**. The temperature range for the martensite to austenite transformation which takes place upon heating is somewhat higher than that for the reverse transformation upon cooling.

### **APPLICATIONS OF SHAPE MEMORY ALLOYS:**

1. They are used as blood clot filters and are used in artificial hearts.
2. They are used to make toys and ornamental goods.
3. They are used to make eye glass frames as they provide good comfort and durability.
4. They are used as couplings for metal pipes.
5. They are used in aircraft engines and other high temperature environments.
6. Digital SMA stepping motors are used for robotic control.

### **NANO MATERIALS**

Nano materials are newly developed materials with grain size at the nanometer range ( $10^{-9}$ m). They contain a very large number of grain boundaries which increases their magnetic and chemical properties. They exhibit different properties such as tremendous strength, hardness, formability and toughness.

#### **Different forms of nanomaterials:**

1. Nano particles
2. Nano dots
3. Nano rods
4. Nano tubes
5. Nanowires
6. Fullerenes
7. Nanocomposites
8. Cluster
9. Colloids

## **Synthesis of Nanomaterials:**

The methods for the synthesis of nanomaterials are broadly classified into two ways

- (i) **Top-down process:** In this process, the bulk materials are broken into nano sized particle.  
Eg: Mechanical alloying (or) Ball milling.
- (ii) **Bottom-up process:** In this process, nano materials are produced by building of atom by an atom. Eg: Chemical vapour deposition.

## **Preparation Of Nanomaterials:**

There are few widely known methods to produce nanomaterials. They are

- (i) Ball milling (ii) Plasma arcing (iii) Chemical vapour deposition (iv) Sol-Gels
- (v) Electro-deposition (vi) Laser synthesis (vii) Inert gas condensation.

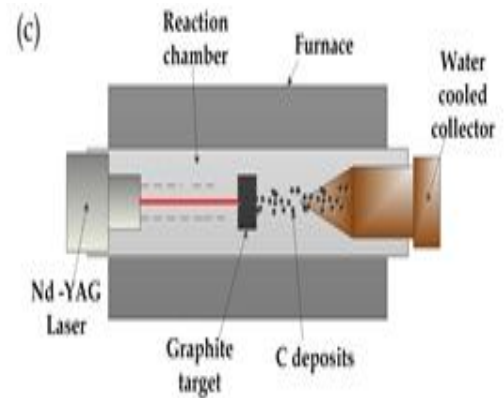
## **Pulsed Laser Deposition**

### **Principle:**

The laser pulse of high intensity and energy is used to evaporate carbon from graphite. These evaporated carbon atoms are condensed to form nanotubes.

### **Description:**

- A quartz tube which contains a graphite target is kept inside a high temperature muffle furnace.
- This quartz tube is filled with argon gas and it is heated to 1473 K.
- A water cooled copper collector is fitted at the other end of the tube.
- The target material graphite contains small amount of nickel and cobalt as a catalyst to nucleate the formation of nanotubes.



### **Working:**

- When an intense pulse of laser beam is incident on the target, it evaporates the carbon from the graphite.



- The evaporated carbon atoms are swept from the higher temperatures argon gas to the colder copper collector.
- The carbon atoms reach the colder copper collector, they condense into nanotubes.

### Advantages:

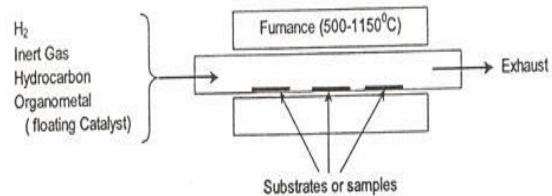
1. Single walled carbon nanotubes of 10-20nm can be produced by this technique.
2. The nanotube diameter can be controlled by the reaction temperature.

### Chemical Vapour Deposition:

**Principle:** Material is heated to gaseous state and then it is deposited on a solid surface under vacuum condition to form nano powder by chemical reaction with the substrate.

### Description and Working:

- It involves the flow of gas with diffused reactants over a hot substrate surface.
- The gas flows over the hot solid surface, the heat energy increases chemical reactions of the reactants that form film during and after the reactions.
- The byproduct of the chemical reactions are then removed.
- The thin films of desired compositions can thus be formed over the surface of the substrate.



Schematic of catalytic CVD operated either as floating catalyst or substrate catalyst

### Advantages:

1. This method is used to produce defect free nanoparticles.
2. The scaling up of the unit for mass production in industry is achieved without any major difficulties.

### **Properties and applications of nano materials**

#### Properties:

The mechanical, electrical, chemical, magnetic and structural properties of nanophase materials change with the reduction in the particle size of the material.

#### **(a) Physcial properties:**

- (i) Interparticle spacing decreases with decrease in grain size for metal clusters.
- (ii) Melting point reduces with decrease in cluster size
- (iii) Ionisation potential changes with cluster size of the nanograins.

**(b) Magnetic properties:**

- (i) Bulk magnetic moment increases with decrease in co-ordination number.
- (ii) The nano-materials shows variation in their magnetic property when they change from bulk state to cluster state.
- (iii) Non- magnetic materials become magnetic when the cluster size reduces to 80 atoms.

**(C) Mechanical properties:**

- (i) In nanophase materials, the elastic strength is low however, its plastic behaviour is high.
- (ii) Higher hardness and mechanical strength when grain size reduces from  $1\mu\text{m}$  to  $10\text{nm}$
- (iii) It has high ductility and superplastic behavior at low temperatures.

**Applications Of Nanophase Materials:**

1. They are used in underwater nanosensor networks.
2. They are used in transmission lines for the fabrication of filters, delay lines and switches etc.
3. They are used in Nanomicro-Electro Mechanical Systems (Nano MEMS).
4. They are used in Molecular Nano-Technology (MNT) to develop robotic machines, called assemblers.
5. Nanoparticles are used in the coating for eye glasses to protect from scratch or breakage.
6. Metal nanoparticles are very useful in fabrication of ionic batteries.
7. Nanoparticulate zinc oxide is used to manufacture effective sunscreens.

**ORIGIN OF NON LINEAR OPTICS**

- A light wave is electromagnetic in nature .
- When the light propagates through a material, it changes the properties of the medium, such as the refractive index.
- It depends on the electric and magnetic fields associated with the light.
- We could not observe nonlinear effects with the ordinary light beam of low intensity,
- With the invention of laser, it is now possible to have electric fields which are strong enough to observe interesting non linear effects.

- Thus if electric and magnetic fields are strong enough, the properties of the medium will be affected which in turn will affect the propagation of the light beam.

### Non linear properties

Few of the nonlinear phenomena observed are

1. Second harmonic generation
2. Optical mixing
3. Optical phase conjugation
4. Soliton

### Second Harmonic Generation

In a linear medium, polarization  $P$  is directly proportional to the electric field  $E$

$$P \propto E$$

$$P = \epsilon_0 \chi E$$

Where  $\epsilon_0$  - permittivity of free space

$\chi$  - electrical susceptibility

In nonlinear medium for higher fields i.e., higher intensities of light the non linear effects are observed.

$$P = \epsilon_0 (\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \dots) \quad (1)$$

Where  $\chi_1$  is the linear susceptibility and  $\chi_2, \chi_3 \dots$  are higher order non linear susceptibilities.

The electric field passing through the medium with amplitude  $E_0$  is

$$E = E_0 \cos \omega t \quad (2)$$

Substituting value of (2) in (1) we have

$$P = \epsilon_0 (\chi_1 E_0 \cos \omega t + \chi_2 E_0^2 \cos^2 \omega t + \chi_3 E_0^3 \cos^3 \omega t) \quad (3)$$

We know that

$$\left. \begin{aligned} \cos^2 \omega t &= \frac{1 + \cos 2\omega t}{2} \\ \cos^3 \omega t &= \frac{3 \cos \omega t + \cos 3\omega t}{4} \end{aligned} \right\} \quad (4)$$

Substituting equation (4) in (3), we have

$$\begin{aligned}
 P &= \epsilon_0 \left[ \chi_1 E_0 \cos \omega t + \chi_2 E_0^2 \left( \frac{1 + \cos 2\omega t}{2} \right) + \chi_3 E_0^3 \left( \frac{\cos 3\omega t + 3 \cos \omega t}{4} \right) \right] \\
 &= \epsilon_0 \left[ \chi_1 E_0 \cos \omega t + \chi_2 E_0^2 \left( \frac{1}{2} \right) + \chi_2 E_0^2 \left( \frac{\cos 2\omega t}{2} \right) \right] + \chi_3 E_0^3 \left( \frac{\cos 3\omega t}{4} \right) + \chi_3 E_0^3 \left( \frac{3}{4} \cos \omega t \right) \\
 &= \epsilon_0 \left[ \frac{1}{2} \chi_2 E_0^2 + \chi_1 E_0 \cos \omega t + \frac{3}{4} \chi_3 E_0^3 \cos \omega t + \chi_2 \frac{E_0^2 \cos 2\omega t}{2} + \chi_3 \frac{E_0^3 \cos 3\omega t}{4} \right] \\
 &= \epsilon_0 \left[ \frac{1}{2} \chi_2 E_0^2 + \left( \chi_1 + \frac{3}{4} \chi_3 E_0^2 \right) E_0 \cos \omega t + \frac{1}{2} \chi_2 E_0^2 \cos 2\omega t + \frac{1}{4} \chi_3 E_0^3 \cos \omega t \right] \\
 P &= \frac{1}{2} \epsilon_0 \chi_2 E_0^2 + \epsilon_0 \left( \chi_1 + \frac{3}{4} \chi_3 E_0^2 \right) E_0 \cos \omega t + \frac{1}{2} \epsilon_0 \chi_2 E_0^2 \cos 2\omega t + \frac{1}{4} \epsilon_0 \chi_3 E_0^3 \cos \omega t + \dots \quad (5)
 \end{aligned}$$

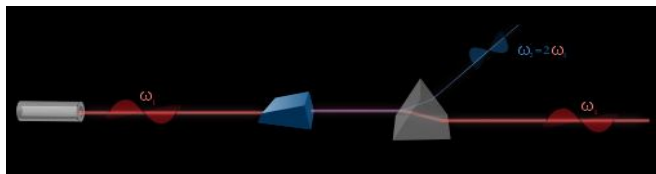
In the above equation, I term gives rise to dc field across the medium, the second term gives external polarisation and is called **first** or **fundamental harmonic polarisibility**.

The third term which oscillates at a frequency  $2\omega$  is called **second harmonic of polarisation** and other term are referred as higher harmonic polarisation.

Both the first term (dc field) and third term (second harmonic of polarisation) added together is called **optical rectification**.

The second harmonic generation is possible only in the crystals lacking inversion symmetry. SHG crystals are quartz, potassium dihydrogen phosphate (KDP), Ammonium dihydrogen phosphate (ADP), Barium titanate ( $\text{BaTiO}_3$ ) and Lithium Iodate ( $\text{LiIO}_3$ )

The observation of second harmonic generation by KDP is shown in fig.



## **BIOMATERIAL AND ITS MODERN APPLICATIONS IN THE FIELD OF MEDICINE.**

- The materials which are used for structural applications in the field of medicine are known as **Biomaterials**.
- These materials are used to make devices to replace damaged or diseased body parts in human and animal bodies.

### **CLASSIFICATION OF BIOMATERIALS**

Based on the applications in the field of medicine, biomaterials are classified as

1. Metals and alloys biomaterials
2. Ceramic biomaterials
3. Polymer biomaterials
4. Composite biomaterials

### **METALS AND ALLOYS**

Metals and alloys are used as biomaterials due to their excellent electrical and thermal conductivity and mechanical properties.

#### **Types of Biomaterials using metals and alloys**

1. Cobalt based alloys
2. Titanium
3. Stainless steel
4. Protosal from cast alloy
5. Conducting metals such as Platinum.

### **APPLICATIONS**

The metals and alloys biomaterials are used in **implant** and **orthopedic** applications.

1. Stainless steel is the predominant implant alloy.
2. Ni-Ti shape memory alloy is used in dental arch wires, micro surgical instruments, blood clot filters, guide wires etc.

**Ceramics:** These are used as biomaterials due to their high mechanical strength and biocompatibility.

**Types of Bio-Ceramic materials:** Tricalcium phosphate, Metal oxides such as  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , Apatite ceramics, Porous ceramics and Carbons and Alumina.

**Applications:**

1. Tricalcium phosphate is used in bone repairs.
2. Ceramic implants such as  $\text{Al}_2\text{O}_3$  with some  $\text{SiO}_2$  and alkali metals are used to make femoral head.
3. Carbon coating find wide applications in heart valves, blood vessel grafts because of high compatibility with soft tissues and blood.

**Bio Polymers:**

- These are macromolecules formed in nature during the growth cycles of all organisms.
- The most prominent Bio Polymer are **collagens**, muco-polysaccharides - chitin, collagens and its derivatives.
- **Collagens** which are major animal structural proteins are used in variety of forms such as solution, gel, fibers and tubing.
- These are used for large number of biomedical applications like drug delivery system, vessels, wound dressing and dental applications.

**Biomaterials in Opthamology:**

- They are used to improve and maintain vision.
- Eye implants are used to restore functionality of cornea, lens, etc, when they are damaged or diseased.
- The biomaterials include contact lenses, eye shields, artificial tears, correction of corneal curvature.

**Dental Materials**

- Polymers, composites, ceramic materials and metal alloys are four main groups of materials used for dental applications.
- The dental applications include impression materials, repair of cavities, artificial teeth, repair of alveolar bone, support for mandible.