

## 1.1 Introduction

Electronic materials are the type of materials which are typically used as core elements in a variety of device applications.

These elements can be, for example, memories, displays, LEDs and could be easily seen in daily electronic gadgets such as mobile phones, computers, laptops, tablets, GPS devices, LED bulbs, TVs and monitors.

## 1.2 Free electrons theory

Free electrons

Electrons which are not attached to ions or atoms or molecules and are free to move under the influence of applied electric field are called free electrons.

Free electron theory is classified into

Classical free electron theory.

Quantum free electron theory.

Band theory.

## 1.3 Classical free electron theory

It is macroscopic theory.

It is proposed by Drude and Lorentz in 1900.

It explains free electron in lattice.

It obeys laws of classical mechanics.

According to this theory metal consists of electron which are free to move about in the crystal-like molecules of gases in container.

### 1.3.1 Postulates of classical free electron theory.

A metal is composed of positive metal ion fixed in the lattice.

All the valence electrons are free to move among the ionic array. Such freely moving electrons contribute towards conduction in metals.

There are a large number of free electrons in a metal and they, move about the whole volume like the molecules of a gas.

The free electrons collide with the positive ions in the lattice and also among themselves. All the collisions are elastic.

The electrostatic force of attraction between the free electrons and the metallic ions are neglected, i.e., there is no loss of energy.

All the free electrons in metal have wide range of energies and velocities.

In the absence of electric field, the random motion of free electron is equally probable in all directions. So, net current flow is zero.

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When an electric field is applied, the electrons gain a velocity called drift velocity and moves in opposite direction to the field resulting in a current flow in the direction of field.

Thus, drift velocity is the average velocity acquired by an electron on applying an electric field.

Relaxation time - it is defined as the time required for the drift velocity to reduce to  $1/e$  times its initial value, just when the field is switched off. OR it is defined as the time taken by the free electron to reach its equilibrium position from its disturbed position just when the field is switched off.

Mean collision time - the average time between two consecutive collisions of an electron with the lattice points is called collision time.

Mean free path - it is the average distance travelled by the conduction electron between successive collisions with the lattice ions.

## 1.3.2 Electrical conductivity.

Let  $E$  be the applied electric field,  $m$  be the mass of the electron and  $e$  be the charge on the electron. The force  $F$  due to applied field will be  $F = eE$ .

Also,  $F = ma$

Comparing both, acceleration  $a = eE/m$ . -----1

Because of collisions of electrons during motion, the electrons will get accelerated momentarily as their velocity falls to zero.

If  $\tau$  be the relaxation time then the average electronic velocity known as drift velocity is given by

$$v_d = a\tau = \frac{eE}{m}\tau \quad \text{-----2}$$

We know Current density is

$$J = \frac{I}{A} = nev_d \quad \text{-----3}$$

Where  $n$  is the number of free electrons per unit volume.

Hence substituting 2 in 3 we get,

$$J = ne \left( \frac{eE}{m} \tau \right) = \frac{ne^2 \tau E}{m} \quad \text{-----4}$$

But  $J$  is also expressed as

$$J = \sigma E \quad \text{-----5}$$

Comparing 4 and 5

$$\frac{ne^2 \tau E}{m} = \sigma E \quad \text{-----6}$$

$$\sigma = \frac{ne^2 \tau}{m} = ne\mu = \frac{1}{\rho}$$

Where  $\mu = \frac{e\tau}{m} = \frac{v_d}{E}$ , is mobility of electrons.

Thus, the above expression relates the electrical conductivity to the number of free electrons per unit volume.

The relaxation time  $\tau$  in terms of the mean free path  $\lambda$  and average thermal velocity is given by

$$\tau = \frac{\lambda}{v}$$

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The kinetic energy of an electron based on kinetic theory is given by

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

Where  $k_B$  is the Boltzmann constant.

$$m = \frac{3k_B T}{v^2}$$

-----8

Using equation 8 and 7 in 6

$$\sigma = \frac{ne^2 \lambda v^2}{3k_B T v}$$

$$\sigma = \frac{ne^2 \lambda v}{3k_B T}$$

-----9

Thus, from the above expression of it is observed that, the electrical conductivity  $\sigma$  of a metal decreases with increase of temperature.

### 1.3.3 Thermal conductivity 'K'

It is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.

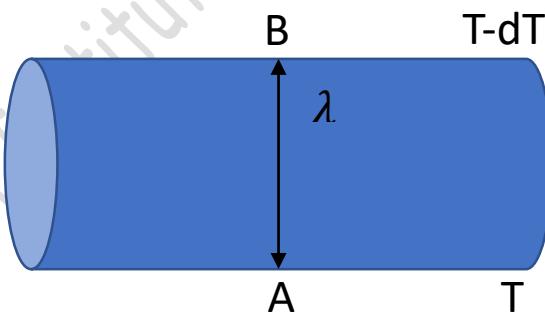
$$K = -\frac{Q'}{A \frac{dT}{dx}}$$

-----1

Where  $Q'$  is rate of heat flow,  $A$  is cross sectional area and  $dT/dx$  is the temperature gradient.

Unit of thermal conductivity is W/mK.

Consider a uniform metallic rod AB. Let the surface A be at a higher temperature T, and the surface B



be at a lower temperature  $T-dT$  as shown in figure.

Let the distance of separation between the surface be  $\lambda$  (mean free path). The electrons conduct heat from A to B. During collision, the electrons near A lose their kinetic energy while, the electrons near B gain the energy.

Let the density of electrons = n, the average thermal velocity = v.

Based on kinetic theory, the average kinetic energy of an electron at A =  $3k_B T/2$  and at B =  $3k_B(T-dT)/2$ .

Therefore, the excess kinetic energy carried by electrons from A to B is  $3k_B dT/2$ .

Electrons can move in any of the six directions equally.

The number of electrons crossing unit area in unit time from A to B is  $nv/6$ .

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The excess energy transferred from A to B per unit area in unit time is

$$\frac{1}{6}nv \times \frac{3}{2}k_BdT = \frac{1}{4}nvk_BdT$$

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

$$-\frac{1}{4}nvk_BdT$$

Since, the net energy transferred from A to B per unit area per unit time is the rate of heat flow Q.

$$Q = \frac{1}{4}nvk_BdT - \left( -\frac{1}{4}nvk_BdT \right)$$

$$= \frac{1}{2}nvk_BdT \quad \text{----- 2}$$

Using equation 2 and  $dx = \lambda$  in equation 1 we get,

$$K = \frac{\frac{1}{2}nvk_BdT}{A \frac{dT}{\lambda}}$$

$$K = \frac{nvk_B\lambda}{2}$$

## 1.3.4 Wiedemann-Franz law

The ratio of thermal to electrical conductivity is directly proportional to the absolute temperature.

$$\frac{K}{\sigma} \propto T$$

$$\frac{K}{\sigma} = \frac{3}{2} \left( \frac{k_B}{e} \right)^2 T = LT$$

Theoretical value of  $L = 1.11 \times 10^{-8} W\Omega K^{-2}$ .

Experimental value of  $L = 2.44 \times 10^{-8} W\Omega K^{-2}$ .

Theoretical and experimental value of L doesn't agree with each other. Hence assumption is wrong that all electrons contribute to thermal conductivity.

## 1.3.5 Success of classical free electron theory.

It verifies ohm's law.

It explains the thermal and electrical conductivities of metals.

It is used to deduce Wiedemann-Franz law.

It explains the optical properties of metals.

## 1.3.6 Drawbacks of classical free electron theory.

The theoretical value obtained for specific heat and electronic specific heat of metals based on this theory ( $3R/2$ ) is not in agreement with the experimental value ( $10^{-4}RT$ ).

The classical free electron theory is not able to explain the electrical conductivity of semiconductors and insulators.

According to classical theory,  $\frac{K}{\sigma T}$  is constant at all temperatures. But, this is not constant at low temperature.

It failed to explain the superconductivity and magnetic susceptibility.

The theoretical value of paramagnetic susceptibility  $\chi$  is greater than the experimental value and ferromagnetism cannot be explained.

The phenomena such as photoelectric effect, Compton effect and black body radiation could not be explained by this theory.

It failed to give correct mathematical expression of electrical conductivity of metals.

## 1.4 Quantum free electron theory of electrical conduction

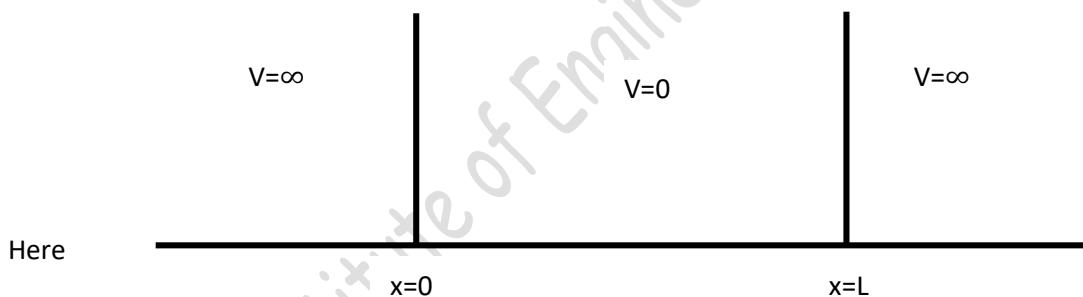
It is microscopic theory. It is proposed by Sommerfield in 1928.

It obeys the quantum laws.

According to this theory free electrons moves with a constant potential inside the metal and they are prevented from escaping the metal by a high potential barrier.

This means that free electrons of metals are trapped in a constant potential well.

Let us consider an electron of mass  $m$  confined in a box of length  $L$  as shown in fig.



$$x < 0 \Rightarrow V = \infty$$

$$0 \leq x \leq L \Rightarrow V = 0$$

$$x > L \Rightarrow V = \infty$$

We know the time independent Schrodinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0$$

Here inside the potential well  $V=0$ , therefore Schrodinger equation will become

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi(x)$$

— — — — — 1

Solution of the above equation will be

$\psi(x) = A\sin(kx) + B\cos(kx)$ , where  $k$  = wave vector

— — — — — 2

Differentiating above equation w.r.t. to x we get

$$\frac{d\psi}{dx} = Ak\cos(kx) - Bk\sin(kx)$$

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Differentiating above equation w.r.t. to x we get

$$\frac{d^2\psi}{dx^2} = -Ak^2 \sin(kx) - Bk^2 \cos(kx)$$

Using equation 2 in above equation

$$\frac{d^2\psi}{dx^2} = -k^2\psi \quad \dots \dots \dots \quad 3$$

From equation 1 and 3 we get

$$\frac{\hbar^2 k^2}{2m} = E \quad \therefore k = \frac{\sqrt{2mE}}{\hbar} \quad \dots \dots \dots \quad 4$$

Now as per the initial assumption  $\psi(x)$  must satisfy the following boundary condition, to be a valid wave function

$$x = 0 \Rightarrow \psi(x) = 0 \quad \text{and} \quad x = L \Rightarrow \psi(x) = 0$$

Therefore, at  $x=0$  we have,  $\psi(x) = A\sin(0) + B\cos(0) = B \Rightarrow B = 0$

And at  $x=L$  we have,  $\psi(x) = A\sin(kL) = 0$

$$\therefore kL = n\pi \quad (n = 1, 2, 3, \dots \dots \dots) \quad \dots \dots \dots \quad 5$$

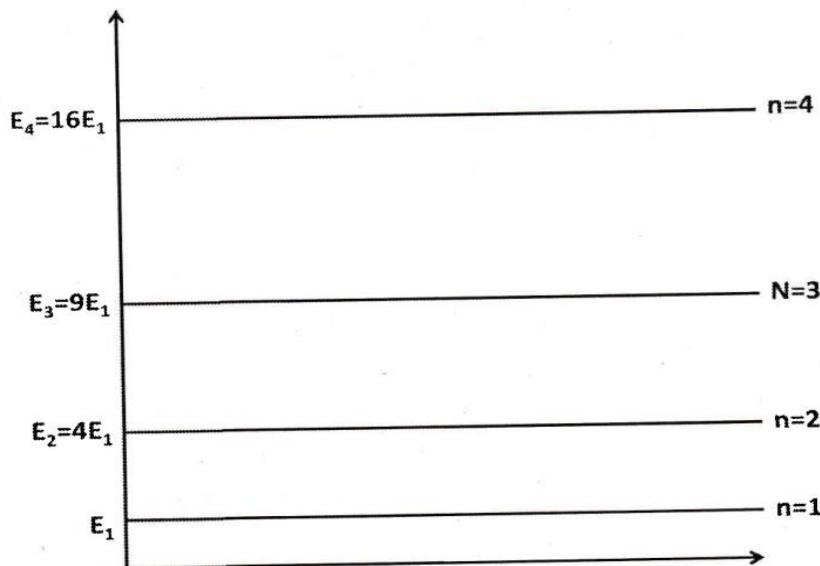
Therefore, the wave function will be valid only if

$$\psi(x) = A\sin\left(\frac{n\pi x}{L}\right) \quad \dots \dots \dots \quad 6$$

And from equation 4 and 5 we have,

$$\begin{aligned} E &= \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \left(\frac{n\pi}{L}\right)^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2m L^2} = \frac{\hbar^2 n^2 \pi^2}{4\pi^2 2m L^2} \\ E &= \frac{\hbar^2 n^2}{8m L^2} \quad (n = 1, 2, 3, \dots \dots \dots) \quad \dots \dots \dots \quad 7 \end{aligned}$$

This means inside an infinitely deep potential well; a particle can have only a discrete set of energy values. In other the energy of particle is quantized. Moreover, the lowest energy level is not  $E=0$ . Values of  $E_n$  obtained using equation 7 are known as eigen values of energy and the corresponding wave function as eigen functions of the particles. Above fig. shows energy level diagram for the particle.



One more assumption of Quantum free electron theory is wave function must be normalized. Value of constant A in equation 6 can be obtained by applying the normalization condition as

$$\int_0^L \psi * \psi dx = \int_0^L |\psi(x)|^2 dx = 1$$

$$\therefore \int_0^L A^2 \sin^2 \left( \frac{n\pi x}{L} \right) dx = 1$$

$$\therefore A^2 \int_0^L \sin^2 \left( \frac{n\pi x}{L} \right) dx = 1$$

$$\therefore A^2 \int_0^L \frac{1}{2} \left[ 1 - \cos \left( \frac{2n\pi x}{L} \right) \right] dx = 1$$

$$\therefore \frac{A^2}{2} \left[ x - \frac{L}{2n\pi} \sin \left( \frac{2n\pi x}{L} \right) \right]_0^L = 1$$

$$\therefore \frac{A^2}{2} [L] = 1$$

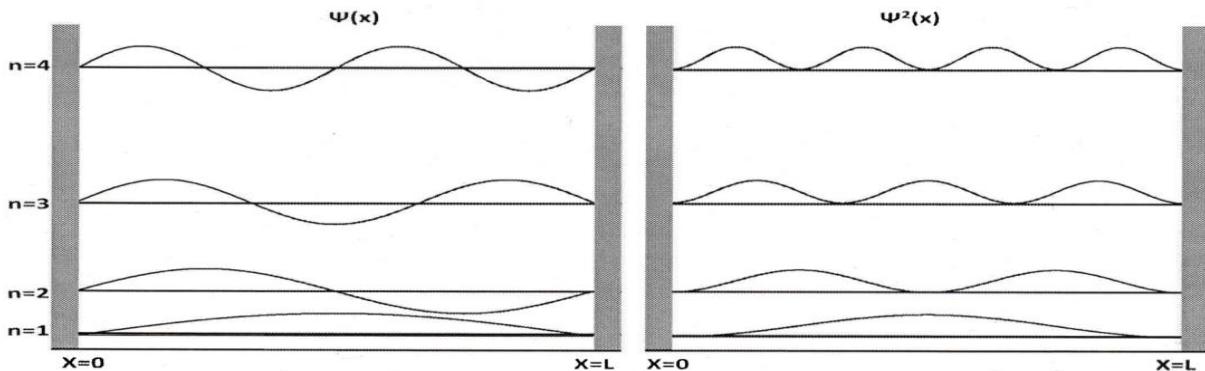
$$\therefore A = \sqrt{\frac{2}{L}}$$

Using this in equation 6 we get

$$\therefore \psi(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right)$$

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Equation 8 represents, the wave function of a particle enclosed in an infinitely deep potential well. The wave functions corresponding to four lowest states for different values of  $n$  and probability of finding the particle are shown in fig.



## 1.4.1 Advantages of quantum free electron theory

- It explains the specific heat of materials.
- It explains Compton effect, photoelectric effect, blackbody radiation, Zeeman effect.
- It gives the correct mathematical expression for the thermal conductivity of metals.
- It explains the superconductivity.

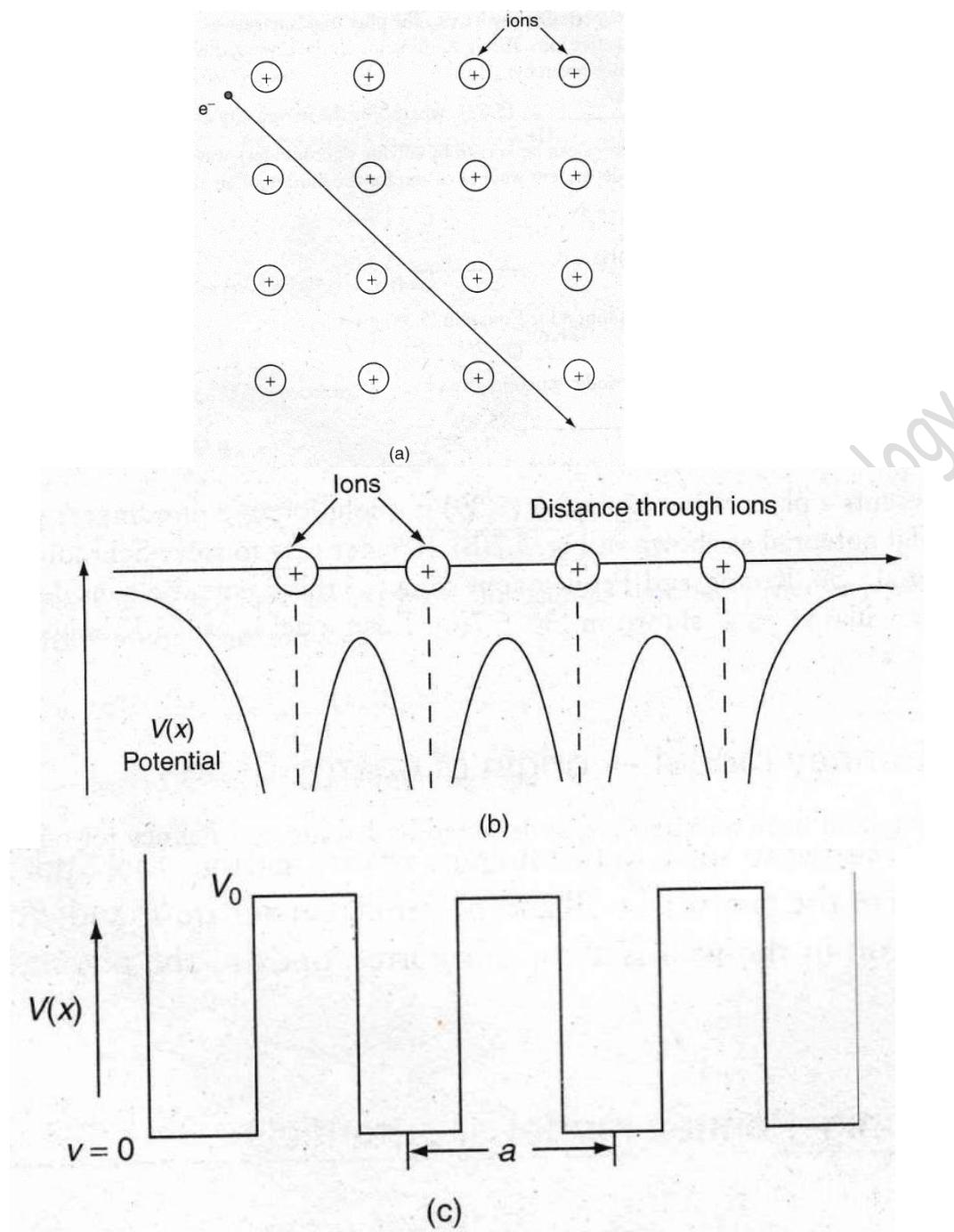
## 1.4.2 Drawbacks of quantum free electron theory

- This theory fails to explain the positive value of Hall coefficients.
- It failed to distinguish metal, semiconductor and insulator.
- It failed to explain lower conductivities of divalent metals than monovalent metals.

# 1.5 Band theory of solids

This theory was developed by Bloch in 1928. It is also known as Brillouin zone theory. However, the quantum free electron theory successfully explained several metallic properties, but still it has some limitations. The basic assumption of quantum free electron theory (positively charged ions in a metal crystal do not influence the motion of free electrons) seems to oversimplify the real situation in crystalline solids including metals. In order to overcome the limitations of quantum free electron theory, a more realistic model of solid was proposed in band theory of solids. It was proposed that in a solid, electrons move under the influence of a periodic potential due to ions arranged along a periodic lattice. The energy spectrum of such electrons consists of allowed and forbidden energy bands.

As shown in fig., if an electron moves through these ions, it experiences varying potentials. The potential of an electron at the positive ion site is zero and is maximum in between two ions. The potential experienced by an electron, when it passes along the line through the positive ions is shown in fig. We see that the potential experienced by an electron varies periodically with the same period as the lattice. The potential is negative because of an attractive force between electrons and positive ions.



(a) Electron motion; (b) The potential experienced by an electron in a row of ions; (c) Rectangular Potentials

In a periodic crystal lattice, the potential experienced by an electron will be periodic in nature. For the simplicity, let us consider a case of electron moving in one dimensional crystal lattice. The 1-D Schrodinger time-independent wave equation for an electron in a periodic potential is given by

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)]\psi(x) = 0$$

----- 1

Where  $V(x)$  is the periodic potential experienced by an electron in the crystal. If 'a' is the lattice constant then the periodicity of potential  $V(x)$  can be expressed as  $V(x) = V(x + a)$

Bloch showed a type of solution for above equation given by :  $\psi(x) = u_k(x)e^{\pm ikx}$  ----- 2

Where  $u_k(x)$  is a periodic function with periodicity of the lattice and is given by :  $u_k(x) = u_k(x + a)$

Equation 2 is called Bloch function and the result that  $\psi(x)$  can be expressed as a plane wave modulated by a periodic function is called Bloch theorem. Further, Bloch function is modulated by the periodic of lattice  $\psi(x + a) = u_k(x + a)e^{\pm ik(x+a)}$

$$\psi(x+a) = u_k(x)e^{\pm ikx}e^{\pm ika}$$

$$\psi(x+a) = \psi(x)e^{\pm ika}$$

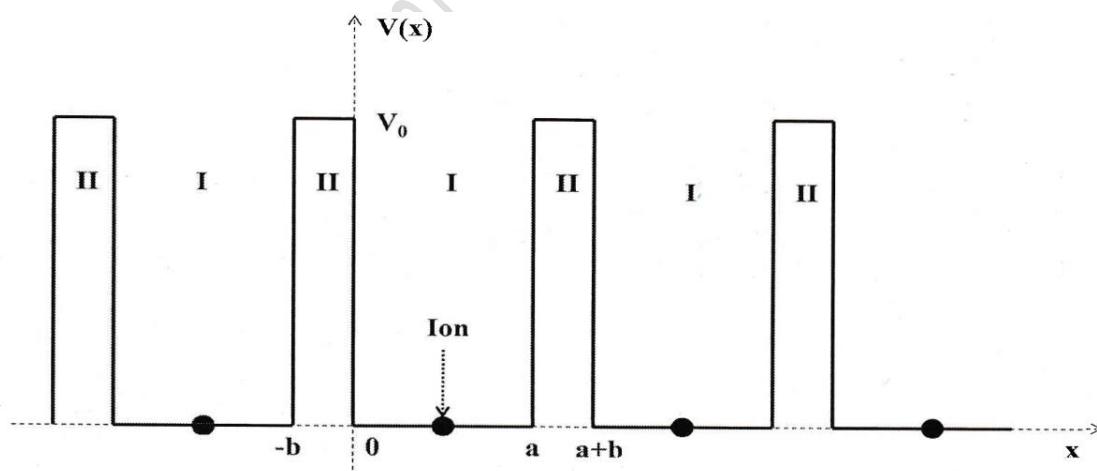
Here,  $k = \frac{2\pi}{\lambda}$  is propagation vector,  $\lambda$  is wavelength of de Broglie wave associated with the moving electron,  $e^{ikx}$  represents a plane wave. It is not easy to solve Schrodinger's equation with these potentials. So, Kronig and Penney approximated these potentials inside the crystal to the shape to rectangular steps. This model is known as Kronig-Penney model of potentials.

## 1.6 Kronig-Penney model – origin of energy bands

The rectangular potential wells and barriers, as assumed by Kronig and Penney for one dimensional lattice in 1931, are best suited to solve Schrodinger's wave equation. These potentials are shown in fig. below., in which the width of the potential well and potential barrier are 'a' and 'b' respectively. The potential energy of an electron in the well is zero, this corresponds to the potential in the vicinity of the nucleus and in barrier it possesses a constant value represented by  $V_0$ . The periodicity of the potential is  $(a+b)$ . This is an approximate model but close to reality.

The energies and wave functions of electrons associated with this model can be calculated by solving time-independent one dimensional Schrodinger's equations for the two regions I and II as shown in fig.

Each potential well (regions I) represents the potential of an electron in the vicinity of an ion. Each of these regions is of width "a" and the value of potential is zero.



Two consecutive potential wells are separated by a distance "b" (regions II) and the value of the potential in each of these regions is " $V_0$ ".

Therefore, potential of electron for the two regions can be expressed as  $V(x) = 0$  for region I and  $V(x) = V_0$  for region II

The Schrodinger's equations are:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \text{for region I } (0 < x < a) \quad \text{--- --- --- --- --- 1}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V_0(x)]\psi = 0 \quad \text{for region I } (-b < x < 0) \quad \text{----- 2}$$

Now let us assume that the system is at room temperature and electrons do not acquire sufficient thermal energy to escape from the crystal. It means energy  $E$  of electron is less than the height of the potential barrier " $V_0$ ". Let us define two real quantities  $\alpha$  and  $\beta$  such that:

$$\alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m(V_o - E)}{\hbar^2}$$

Hence equations 1 and 2 becomes:

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad \text{for } 0 < x < a \quad \text{--- --- --- --- --- 4}$$

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad \text{for } -b < x < 0$$

----- 5

The solution (according to Bloch theorem) that will be appropriate for both the regions will be of the form of a plane wave  $e^{ikx}$  modulated with a periodic function  $u_k(x)$ :

Where  $k = \frac{2\pi}{\lambda}$  is propagation vector or wave vector

Differentiating equation 6 twice, we get:

$$\frac{d\psi}{dx} = ike^{ikx} u_k(x) + e^{ikx} \frac{du}{dx}$$

$$\frac{d^2\psi}{dx^2} = -k^2 e^{ikx} u_k(x) + 2ike^{ikx} \frac{du}{dx} + e^{ikx} \frac{d^2u}{dx^2}$$

Substituting these values in equation 4 and 5 we get:

$$-k^2 e^{ikx} u_k(x) + 2i k e^{ikx} \frac{du}{dx} + e^{ikx} \frac{d^2 u}{dx^2} + \alpha^2 e^{ikx} u_k(x) = 0$$

$$\frac{d^2 u_k(x)}{dx^2} + 2ik \frac{d u_k(x)}{dx} + (\alpha^2 - k^2) u_k(x) = 0 \quad \text{for } 0 < x < a \quad \text{--- --- --- --- --- 7}$$

$$\frac{d^2 u_k(x)}{dx^2} + 2ik \frac{du_k(x)}{dx} - (\beta^2 + k^2) u_k(x) = 0 \quad \text{for } -b < x < 0 \quad \dots \quad 8$$

Solving above equations and using Dirac delta function we get,

Now to solve these differential equations, assume the solution of the form:  $u(x) = e^{mx}$  —— 9

so that  $\frac{du(x)}{dx} = me^{mx}$  and  $\frac{d^2u(x)}{dx^2} = m^2e^{mx}$  ----- 10

Substitution above equations in equation 7 gives:

$$m^2 e^{mx} + 2ikme^{mx} + (\alpha^2 - k^2)e^{mx} \equiv 0$$

$$m^2 + 2ikm \pm (\alpha^2 - k^2) = 0 \quad \text{for } 0 < x < a$$

$$m = \frac{-2ik \pm \sqrt{(-4k)^2 - 4(\alpha^2 - k^2)}}{2}$$

$$m = -ik + j\alpha$$

$$m_1 \equiv i(\alpha - k) \quad \text{and} \quad m_2 \equiv -i(\alpha + k)$$

Hence (using above in 9) the general solution is:

$$y_1(x) = Ae^{m_1 x} + Be^{m_2 x}$$

$$u_1(x) = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x} \quad \text{for } 0 < x < a \quad \text{--- --- --- --- --- 11}$$

Similarly,

Where  $u_1(x)$  and  $u_2(x)$  represent  $u_k(x)$  in region I and II, respectively.

Here A, B, C and D are constants. These constants may be obtained by applying the following boundary conditions.

$$[u_1(x)]_{x=0} = [u_2(x)]_{x=0} \quad \text{and} \quad \left[ \frac{du_1}{dx} \right]_{x=0} = \left[ \frac{du_2}{dx} \right]_{x=0} \quad \dots \quad 13$$

$$[u_1(x)]_{x=a} = [u_2(x)]_{x=-b} \quad \text{and} \quad \left[ \frac{du_1}{dx} \right]_{x=a} = \left[ \frac{du_2}{dx} \right]_{x=-b} \quad \dots \dots \dots - 14$$

The boundary conditions represented in equation 13 shows that the wave functions and their first derivatives are equal at  $x=0$  because of the continuity of wave functions at that point.

The boundary conditions represented in equation 14 show that the wave function and its first derivatives at  $x=a$  is equal to that at  $x=-b$ , because of the periodicity of wave functions.

Applying boundary conditions 13 and 14 on equation 11 and 12 gives four equations involving the constants A, B, C and D.

$$A + B = C + D \quad \text{-----} \quad 15$$

$$Ai(\alpha - k) - Bi(\alpha + k) = C(\beta - ik) - D(\beta + ik) \quad \dots \dots \dots \quad 16$$

$$Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)b} + De^{(\beta+ik)b} \quad \text{--- --- --- --- --- 17}$$

$$Ai(\alpha - k)e^{i(\alpha - k)a} - Bi(\alpha + k)e^{-i(\alpha + k)a} = C(\beta - ik)e^{-(\beta - ik)b} - D(\beta + ik)e^{(\beta + ik)b} \quad --- 18$$

The constants A, B, C and D can be determined by solving equation 13 to 16, and thus the wave function  $u_1$  and  $u_2$  can be obtained. The four equations 13 to 16 have solution only if the determinant of the coefficients of A, B, C and D vanishes. The above condition leads to the following equation.

This equation is quite complicated. To express it in a more simplified form, Kronig and Penney suggested the case such as  $V_0 \rightarrow \infty$  and  $b \rightarrow 0$  but the product  $V_0 b$  remain finite. Under these circumstances,  $\sinh\beta b \rightarrow \beta b$  and  $\cosh\beta b \rightarrow 1$  as  $b \rightarrow 0$ . Hence equation 17 becomes:

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

$$\frac{\frac{2m(V_o - E)}{\hbar^2} - \frac{2mE}{\hbar^2}}{2\alpha} b \sin \alpha a + \cos \alpha a = \cos ka$$

$$\left(\frac{mV_o b}{\hbar^2 \alpha}\right) \sin aa + \cos aa = \cos ka \quad (\text{since } V_o \gg E) \quad \dots \dots \dots -20$$

We define the quantity  $P = \frac{mV_0ba}{\hbar^2}$ , then equation 20 reduces to:

Where  $P = \frac{mV_o ba}{\hbar^2}$

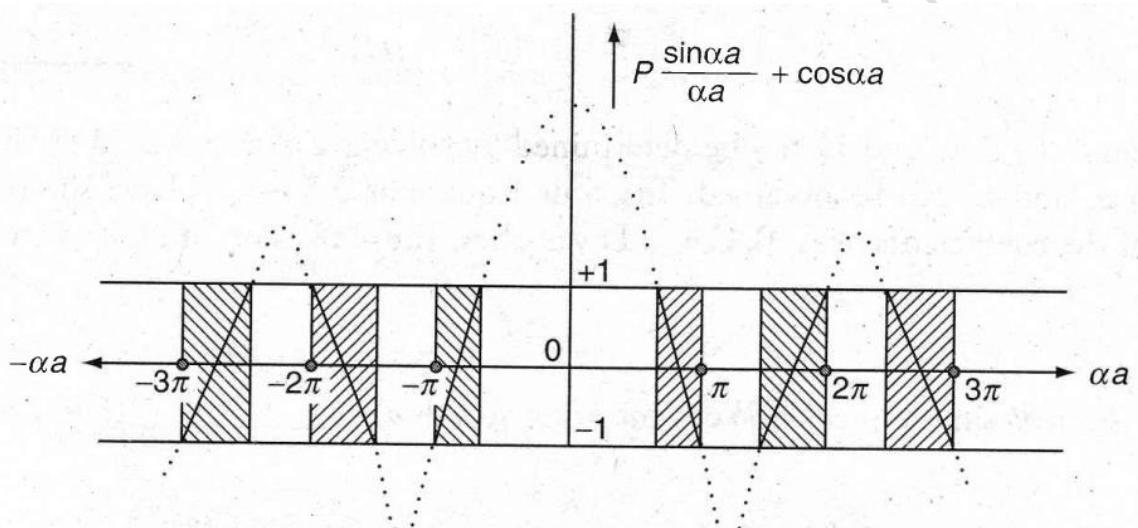
Equation 21 represents a condition for the wave function.  $P$  is referred to as the scattering power of the potential barrier. It represents the strength with which electrons in a crystal are attracted to the ions. The term  $V_0 b$  is called barrier strength. With an increase of  $P$ , an electron is bound more strongly to a potential well, when  $P \rightarrow 0$ , the electrons are free.

## 1.7 Conclusion of Kronig-Penney model

The right-hand side of equation 21 can take values between  $\pm 1$ , but the left-hand side exceeds this value.  $\therefore \cos ka = \pm 1$        $\therefore ka = \pm n\pi$  ( $n = 1, 2, 3, \dots$ )

$$\therefore k = \pm \frac{n\pi}{a}$$

By plotting the left-hand side of equation 21 for a finite value of  $P$  say  $3\pi/2$  against  $\alpha a$ , it is possible to determine the allowed values of  $\alpha a$ . To find the allowed parts of the curve, horizontal lines are drawn at  $\pm 1$  on vertical line as shown in fig. The parts of curve, which lies between the  $\pm 1$  horizontal line, are acceptable to the left-hand side of equation 21.



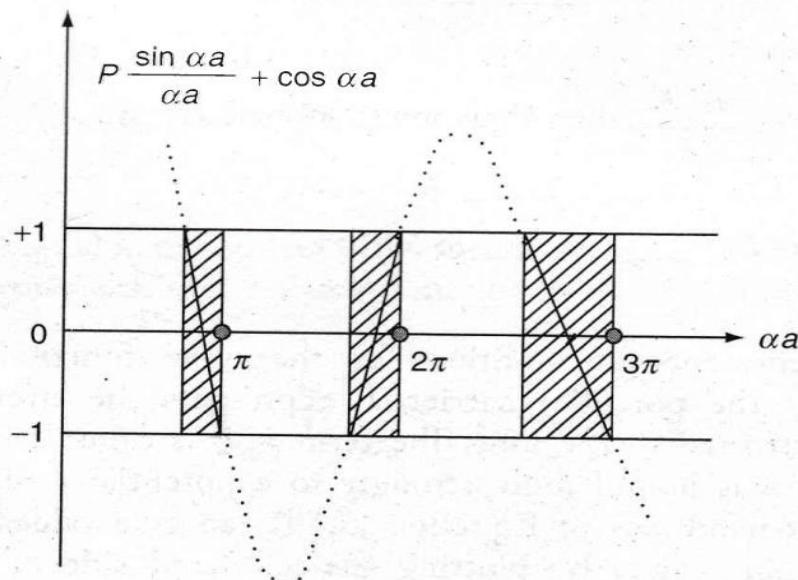
From the graph following conclusion may be drawn. (conclusion of Kronig-Penney model)

- i) The allowed values of  $\alpha a$  (and hence energy, since  $\alpha^2 = \frac{2mE}{\hbar^2}$ ) for which wave mechanical solutions exist are shown by the shadow portions. From the graph, we know that the conduction electrons in periodic potentials of lattice ions possess the bands of allowed energy (shaded region) separated by forbidden regions (unshaded region). Therefore we can conclude that the energy spectrum of electron consists of groups or bands of energy levels comprising allowed energy bands and forbidden energy bands.

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- ii) As the value of  $\alpha a$  increases, the width of allowed energy bands increases and the width of forbidden bands decreases.

**Shows the decrease of allowed energy bands width for large value of  $P$**



- iii) Now, we will see the effect of varying  $P$ . If  $P$  is large, then curve crosses  $\pm 1$  line steeply so that the allowed bands are narrower and forbidden bands are wider as shown in fig.

Case 1 : When  $P \rightarrow 0$ , then the left-hand side of equation will not cross  $\pm 1$  line as shown in fig. Hence, all the energies are allowed to the electrons. Thus, by varying  $P$  from zero to infinity, the energies of electrons will vary from continuous to bound, i.e., free electrons to bound electrons.

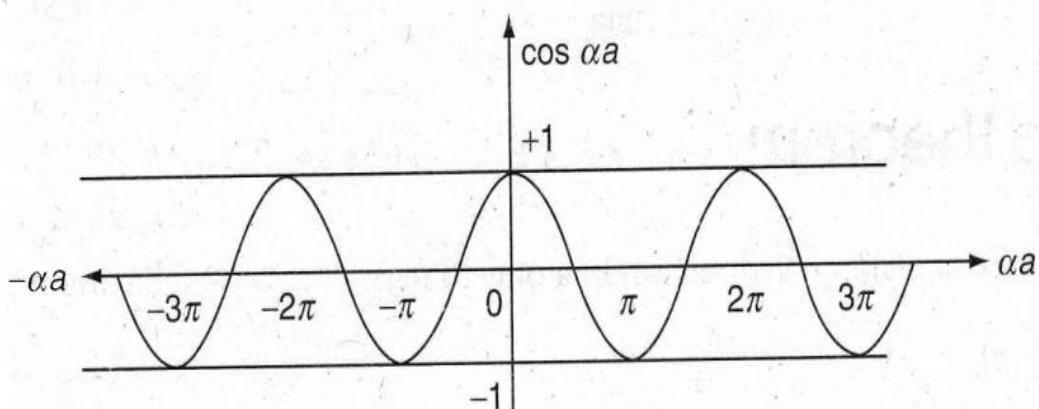
Using this limit in equation 21 we have,

$$\cos ka = \cos \alpha a \Rightarrow \alpha a = ka \Rightarrow \alpha = k$$

Using this in equation 3

$$k^2 = \frac{2mE}{\hbar^2} \Rightarrow E = \frac{\hbar^2 k^2}{2m} \Rightarrow E = \frac{p^2}{2m}$$

**Shows that all energies are allowed to the electrons as  $P \rightarrow 0$**



This expression gives the energy of a free electron and all energies are allowed. This situation corresponds to classical free electron theory.

Case 2 : In the limit  $P \rightarrow \infty$ , the allowed energy bands reduce to single energy levels as shown in fig. the energy levels in this case are discrete and similar to the energy levels of a particle in a constant potential box of atomic dimensions

Using this limit in equation 21 we have,

$$\sin \alpha a = \frac{\alpha a (\cos ka - \cos \alpha a)}{P}$$

$$\therefore P \rightarrow \infty \Rightarrow \sin \alpha a = 0$$

$$\alpha a = n\pi \quad \text{where } n = \pm 1, \pm 2, \pm 3, \dots \dots$$

$$\alpha^2 = \frac{n^2 \pi^2}{a^2}$$

-----22

Using equation 22 in 3

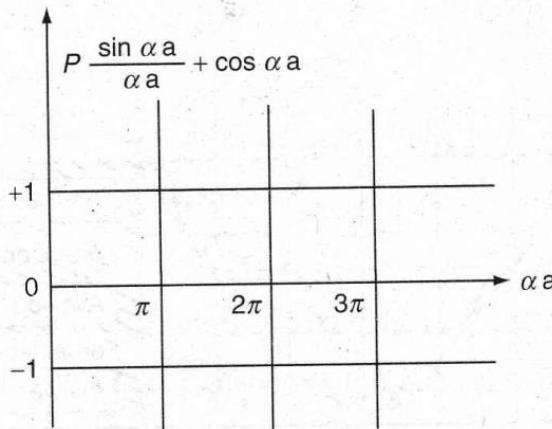
$$\frac{n^2 \pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$$E = \frac{n^2 \hbar^2}{8ma^2}$$

-----23

Thus using  $P \rightarrow \infty$  in Eq. (21) leads to Quantum free electron theory.

**Shows that the allowed energy bands reduces to single energy levels as  $P \rightarrow \infty$**



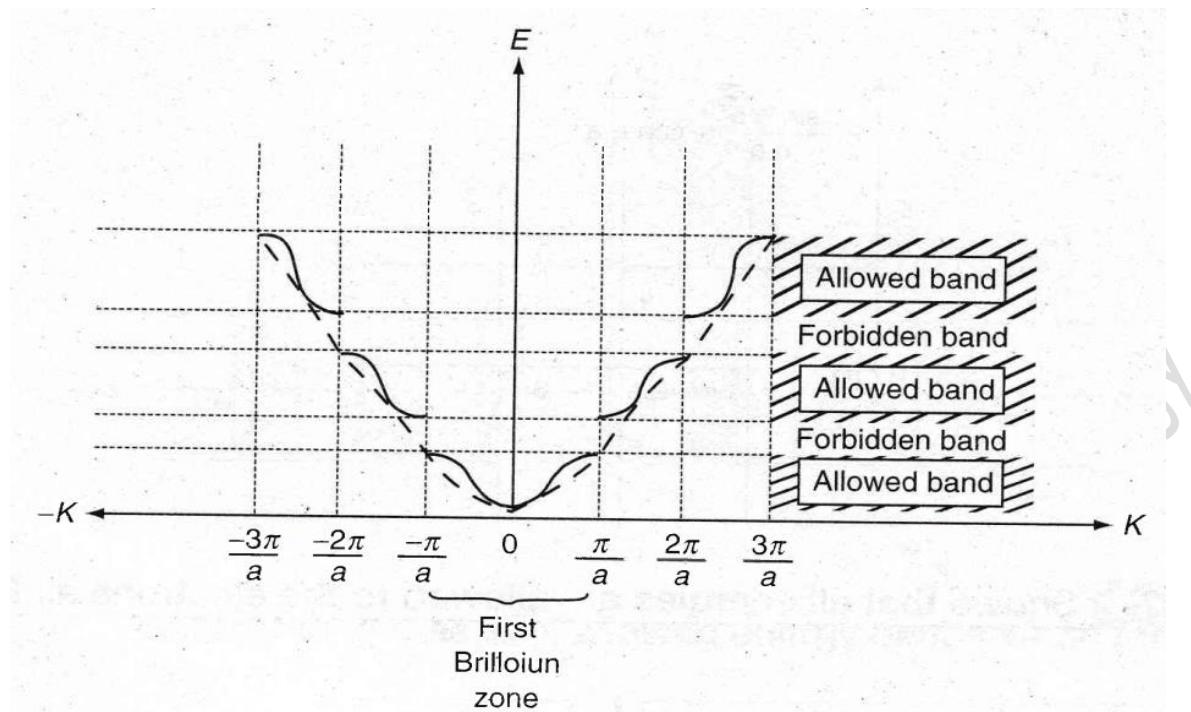
## 1.8 Ek diagram:

One more conclusion of Kronig-Penney model relates to dispersion relation ( $E$  vs.  $k$  curve) for electrons in a periodic potential. It is obvious from Eqn. (21) that for a given value of  $\alpha a$  (and hence energy  $E$ ), the RHS can take only one value. But, cosine function is an even periodic function. Therefore,  $\cos ka$  will have the same value for " $\pm ka$ " as well as for " $\pm ka \pm 2n\pi$ " (where  $n=1,2,3,\dots$ ). It suggests that the energy of an electron is an even periodic function of  $k$  with period  $2\pi$ . It can also be noticed here discontinuities in the energy spectrum will appear for  $\cos ka = \pm 1 = \cos(\pm n\pi) \Rightarrow ka = \pm n\pi$

$$k = \frac{n\pi}{a} \quad \text{where } n = \pm 1, \pm 2, \pm 3, \dots \dots$$

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Above result indicates that the first forbidden gap will appear at  $k = \pi/a$ , second forbidden gap will appear at  $k = 2\pi/a$  and so on. The E-k diagram for an electron in a periodic potential is shown in fig.



From the graph, it is clear that electrons have allowed energy values in the region or zone extending from  $k = -\pi/a$  to  $\pi/a$ . This is called first Brillouin zone. After a break in energy values, called forbidden band, the electrons have another allowed zone of energy values in the region extended from  $k = -\pi/a$  to  $-2\pi/a$  and from  $k = \pi/a$  to  $2\pi/a$ . This zone is called the second Brillouin zone. Similarly, the higher order Brillouin zones can be defined.

The discontinuities occur at the boundaries of the Brillouin zones. Each portion of the curve gives a number of allowed energies called allowed band of energies. The curves are horizontal at the top and bottom and they are parabolic near the top and bottom with curvatures in opposite directions. As P decreases the discontinuities in E-k graph will reduce to a continuous parabolic graph as shown by dotted lines and forbidden band disappears. Then, the energy values are practically continuous.

## 1.9 Origin of Energy bands

The origin of an energy gap can be explained by considering the formation of energy bands in solids.

The concentration of atoms in a gaseous medium is very low compared to the concentration of atoms in solid medium. Due to this large inter-atomic distance, the interaction between any two atoms of a gaseous substance is very weak. While in case of solid substances, very small inter-atomic distance allows a strong interaction between any two successive atoms.

Now consider a case two electrons possessing a particular energy level in two different non-interacting atoms. When these two atoms are arranged in a successive manner, a single energy level will split into two separate (having very small energy difference) energy levels to maintain the Pauli's exclusion principle (Pauli's exclusion principle: No two electrons in interacting atoms can have same energy state). As a solid is composed of a large number of interacting atoms, any single energy level will convert into several closely spaced energy levels, which can be collectively termed as an energy band. Therefore, in a solid, energy levels of all the electrons form several energy bands separated by energy gap/forbidden gap.

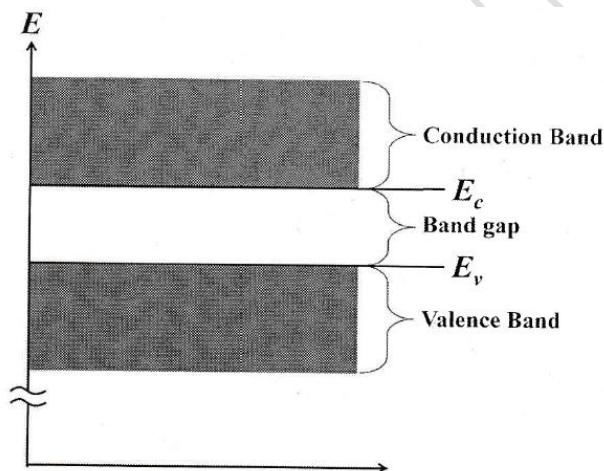
The highest partially or completely filled band is known as valence band and the next allowed unfilled band is known as conduction band. Note that only these two bands are of interest to us. It is because

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all other bands remain unaffected at ordinary temperatures and electrical fields; you should, however, keep in mind that other bands also exist. Energy gap between valence band and conduction band is called Band gap ( $E_g$ ).

Electrons in valence band and conduction are known as valence electrons and conduction electrons respectively. Valence electrons are bound to respective atoms through coulomb forces exerted by nucleus. Conduction electrons are free to move inside the solid as they are not affected by the coulomb force of nucleus due to relatively larger distance.

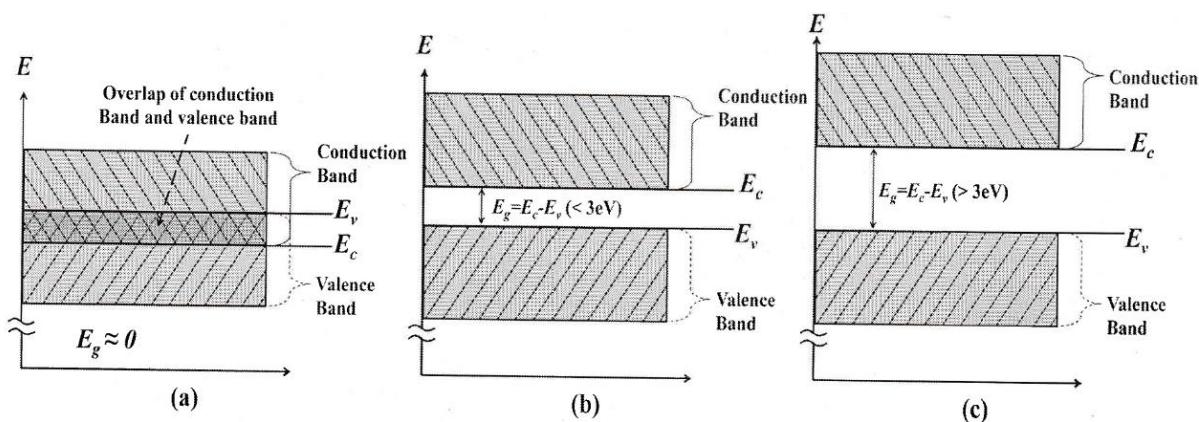
Valence electron can jump to the conduction band by absorbing the minimum energy equal to the band gap from the external sources like heating, light radiation, electric field etc. Such electron now acts as a conduction electron. When a valence electron is ejected from valence band it leaves a positively charged hole in the valence band. Similarly, a conduction electron can emit the energy equal to the band gap and recombine with a hole in the conduction. In this way, it returns back to the valence band and becomes valence electron. Figure below gives a visual idea about the relative position of valence band, band gap and conduction band. Highest energy level of valence band is denoted as  $E_v$  and lowest energy level of conduction band is denoted as  $E_c$ .



Typical energy bands in solid.

### 1.10 Classification of solids (metals, semiconductor and insulator)

On the basis of band gap, solids can be classified as Metal, semiconductor and insulator. According to the relative position of valence band and conduction band three distinct possibilities can be defined as shown in figure shown below



In the case of metals, valence band is partially filled. Therefore, valence band and conduction band overlaps each other as shown in figure (a). Due to these metals do not have band gap. Valence electrons can move easily to conduction levels at room temperature. This situation makes metals to have large number of free electrons resulting in high electrical and thermal conductivity. Metals typically possess resistivity of the order of  $10^{-8} \Omega\text{m}$  and carrier density of the order of  $10^{23} \text{ m}^{-3}$ .

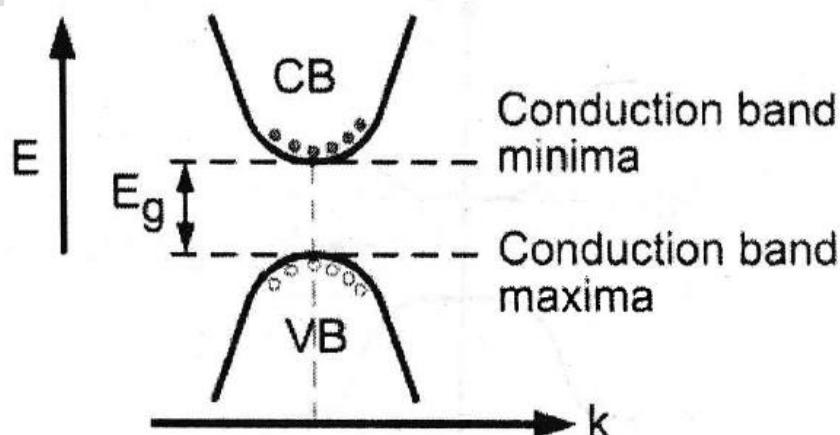
In the case of semiconductors, valence band is completely filled and energy gap between valence band and conduction band is relatively small as shown in figure (b). Due to these semiconductors have moderate value of band gap (typically less than 3eV). Valence electrons can jump to conduction band if the energy equal to or more than the band gap is applied externally. Actually, a semiconductor material is one whose electrical properties lie between insulators and good conductors. At 0 K there are no electrons in conduction band and valence band is completely filled. When a small amount of energy is supplied, the electron can easily jump from valence band to conduction band. Semiconductors typically possess resistivity in the range from  $10^{-8} \Omega\text{m}$  to  $10^3 \Omega\text{m}$  and carrier density of the order of  $10^{14} \text{ m}^{-3}$ .

In the case of insulators Band gap is very high (typically greater than 3eV). Therefore, it is very difficult for the valence electrons to cross the band gap and to reach to conduction band. Insulators typically possess resistivity of the order of  $10^3$  to  $10^{17} \Omega\text{m}$  and negligible carrier density.

## 1.11 Direct and Indirect bandgap semiconductor

### 1.9.1 Direct bandgap semiconductor

A direct semiconductor is the one in which maximum energy level of valence band aligns with the minimum energy level of conduction band with respect to momentum. e.g., GaAs.



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In a semiconductor, the minimum energy state in conduction band and maximum energy state in valence band is characterized by crystal momentum and wave vector 'k'.

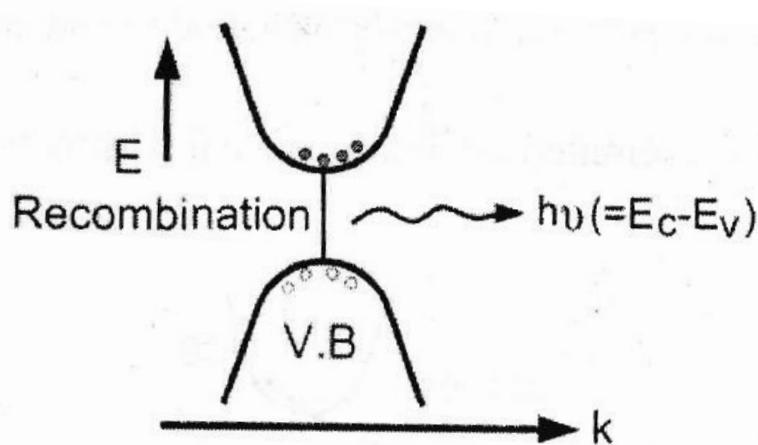
In a direct bandgap semiconductor, the k-vectors are same for conduction band minima and valence band maxima.

Whenever an electron from conduction band recombines with a hole from valence band, the energy and momentum, both should be conserved.

The energy difference between conduction band and valence band is released in the form of a photon.

The k-vectors of electron and hole are same. So, we say that momentum is also conserved.

We say the energy is conserved by emitting a photon.



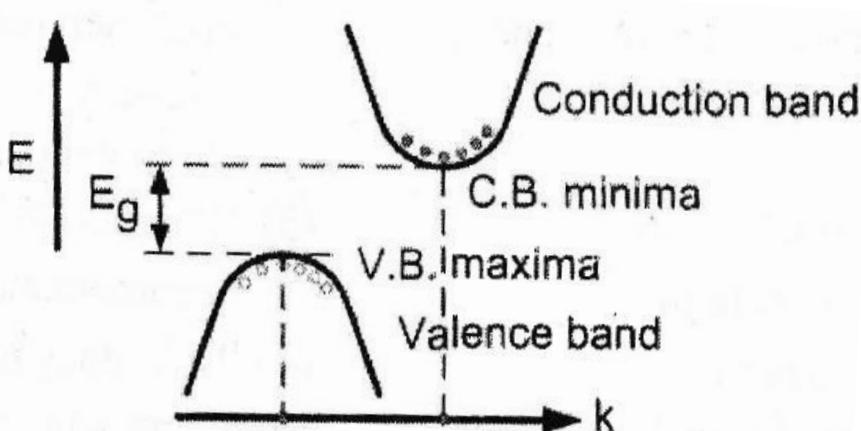
## 1.9.2 Indirect bandgap semiconductor

An indirect bandgap semiconductor is the one in which maximum energy level of valence band and minimum energy level of valence band and minimum energy level of conduction band are not aligned with respect to momentum. e.g., Si, Ge.

In an indirect bandgap semiconductor, the k-vectors are different for conduction band minima and valence band maxima.

In an indirect bandgap semiconductor, there is a difference in momentum. The recombination process can occur only after the momentum aligns.

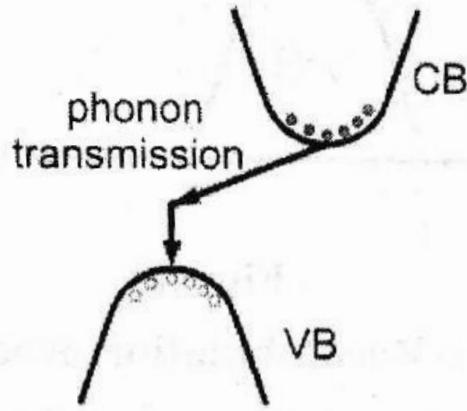
Due to crystal imperfections in certain semiconductors, the electron in the conduction band loses



energy and momentum at the same time.

The electron actually passes through an intermediate state and transfers its momentum to the crystal lattice.

In this case, the energy is emitted in the form of heat. The transition is non-radiative in nature.



### 1.9.3 Difference between direct and indirect bandgap semiconductor

DBG semiconductor	IBG semiconductor
It is one in which maximum energy level of valence band aligns with the minimum energy level of conduction band with respect to momentum.	It is the one in which maximum energy level of valence band and minimum energy level of valence band and minimum energy level of conduction band are not aligned with respect to momentum.
In this direct recombination takes place with energy equal to the difference between energy of recombining particles.	In this due to a difference in momentum, first momentum is conserved by release of energy and only when the two momenta are aligned, recombination occurs.
The probability of radiative recombination is very high.	The probability of radiative recombination is almost negligible.
Efficiency factor is high.	Efficiency factor is low.
They are preferred for making optical devices like LED's	Cannot be used to make optical device.

## 1.12 Density of states

Energy levels of electrons in a case of single atom are sharp, while in the case of a solid, energy levels of electrons will spread out over a range called energy band due to presence of huge number of atoms. Each energy band consists of a number of closely spaced energy levels. To determine the number of available states at each energy level to be occupied by electrons, it is necessary to understand the concept of the density of states. The density of states,  $g(E)$ , is defined as the number of energy levels available per unit volume per unit energy centered at  $E$ . (The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy).

Let us denote the number of states per unit volume between the energy levels  $E$  and  $E+dE$  as  $\rho(E)dE$ .

From the discussion of an electron in one-dimensional potential well of width  $L$ , we know that the allowed energies are given by

$$E = \frac{\hbar^2 n^2}{8mL^2} \quad (n = 1, 2, 3, \dots \dots \dots)$$

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Since a free electron in a solid experience a three-dimensional potential well, the above equation can be written as

$$E = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Here  $n_x$ ,  $n_y$  and  $n_z$  are non-zero positive numbers. Each set of  $(n_x, n_y, n_z)$  indicates the permitted energy value.

Now let

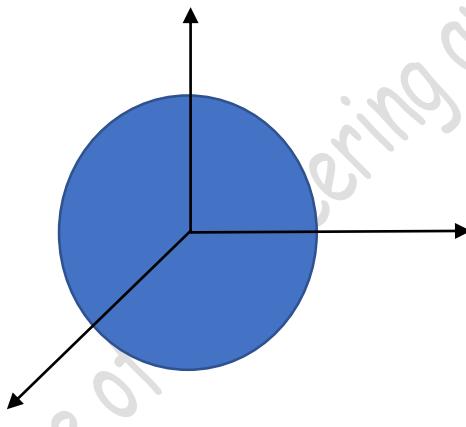
$$E_0 = \frac{h^2}{8mL^2} \text{ and } R^2 = n_x^2 + n_y^2 + n_z^2$$

Then,

$$E = E_0 R^2$$

----- 1

Here  $R^2 = n_x^2 + n_y^2 + n_z^2$  represents a sphere of radius  $R$  formed by the points  $(n_x, n_y, n_z)$  with  $n_x$ ,  $n_y$  and  $n_z$  as three mutually perpendicular coordinate axes. Since  $n_x$ ,  $n_y$  and  $n_z$  can take only the positive integer values, above equation represents only 1/8 portion of the sphere called the octane as shown in figure.



The number of allowed energy values  $N(E)$  in a small energy range between  $E$  and  $E+dE$  is equal to the product of 1/8<sup>th</sup> of the volume of sphere between the shells of radius  $R$  and  $R+dR$ , and number of points per unit volume which is 1.

$$N(E)dE = \frac{1}{8} \times 4\pi R^2 dR \times 1$$

$$N(E)dE = \frac{1}{2}\pi R^2 dR$$

Since, each such energy value can accommodate two states of electrons according to Pauli's exclusion Principle, therefore

$$N(E)dE = \pi R^2 dR$$

----- 2

Now from equation 1 we can write,

$$R = \sqrt{\frac{E}{E_0}} \quad \text{and} \quad dE = 2E_0 R dR$$

From above equations

$$\sqrt{\frac{E}{E_0}} dE = 2E_0 R^2 dR$$

$$R^2 dR = \frac{1}{2} \sqrt{\frac{E}{E_0^3}} dE$$

-----3

Using 3 in 2 we get,

$$N(E)dE = \frac{\pi}{2} \sqrt{\frac{E}{E_0^3}} dE$$

$$N(E)dE = \frac{\pi}{2} \sqrt{\frac{E}{E_0^3}} dE$$

$$N(E)dE = \frac{\pi}{2} \sqrt{\frac{E}{\left(\frac{h^2}{8mL^2}\right)^3}} dE$$

because  $E_0 = \frac{h^2}{8mL^2}$

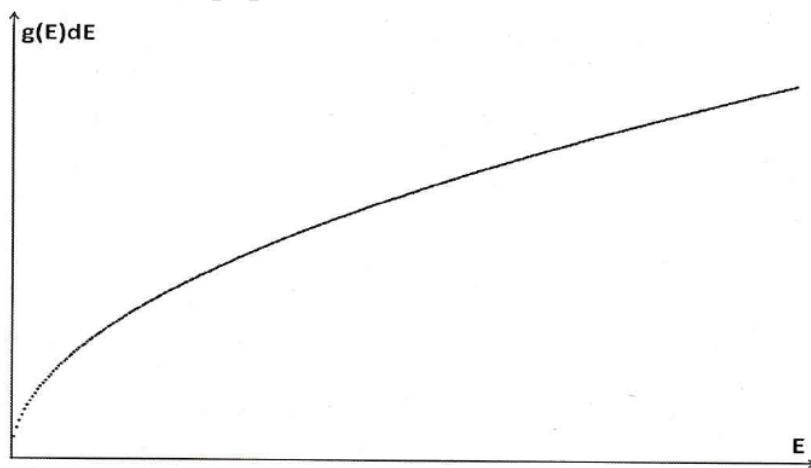
$$N(E)dE = 4\pi \left(\frac{2m^3}{h^3}\right)^{3/2} E^{1/2} dE = \frac{8\pi L^3 \sqrt{2m^3}}{h^3} \sqrt{E} dE$$

Here  $L^3$  represents the volume of the solid and since the density of states is the number of energy states per unit volume, we can write

$$\rho(E)dE = \frac{N(E)dE}{L^3}$$

$$\rho(E)dE = 4\pi \left(\frac{2m^3}{h^3}\right)^{3/2} E^{1/2} dE = \frac{8\pi \sqrt{2m^3}}{h^3} \sqrt{E} dE$$

The plot of  $\rho(E)dE \rightarrow E$  is shown below.



### 1.13 Fermi level, fermi energy and fermi function (Fermi-Dirac distribution function)

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In a single atom, there will be many allowed energy levels whereas in a solid each such energy level will spread over a range of few eV. If there are N atoms, there will be N closely spaced energy levels in each energy band of the solid.

According to Pauli's exclusion principle, each such energy level can accommodate two electrons.

At absolute zero temperature, two electrons with least energy with opposite spins occupy the lowest available energy level.

The next two electrons with opposite spins will occupy next energy level and so on.

In this way electrons will get accommodated up to certain energy level.

The top most energy level occupied by electrons at absolute zero temperature is called Fermi energy level. Energy corresponding to Fermi energy level is called Fermi energy.

This Fermi energy,  $E_F$ , can be defined as the energy at absolute zero temperature, corresponding to the highest filled energy level, below which all energy levels are completely occupied and above which all the energy levels completely empty. OR The energy possessed by electrons in the fermi level at absolute zero is called fermi energy.

Fermi energy represents maximum energy that electrons can have at absolute zero temperature.

At absolute zero all energy levels below Fermi energy are completely filled and above it are completely empty. But at any given temperature, the electrons get thermally excited and move up to higher energy levels. As a result, there will be many vacant energy levels below as well as above Fermi energy level. Under thermal equilibrium, the distribution of electrons among various energy levels can be given by a statistical function  $f(E)$ . The function  $f(E)$  is called the Fermi factor and this gives the probability of occupation of a given energy level under thermal equilibrium.

$$f(E) = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

Where  $f(E)$  is fermi distribution function,  $E_F$  is fermi energy, E is energy of level in which electron is present, T is absolute temperature and  $k_B$  is Boltzmann constant.

For filled energy level  $f(E) = 1$  and for an unfilled level,  $f(E) = 0$  [1-f(E)=1].

## Case 1: At T = 0 K

At absolute zero electrons occupy the lowest energy level first, followed by next higher levels as per Pauli's principle.

(a) At T = 0K,  $E < E_F$

For energy levels E, lying below  $E_F$ ,  $E - E_F$  takes a negative value

$$f(E) = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

This implies that all energy levels below  $E_F$  are completely filled.

(b) At T = 0K,  $E > E_F$

For energy levels E, lying above  $E_F$ ,  $E - E_F$  takes a positive value

$$f(E) = \frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = 0$$

This implies that all energy levels above  $E_F$  are completely vacant.

### Case 2: At $T > 0 \text{ K}$

At room temperature, the probability starts reducing from 1 for values of  $E$  close to  $E_F$ , but larger than  $E_F$ .

At  $T > 0\text{K}$ , for  $E = E_F$ ,

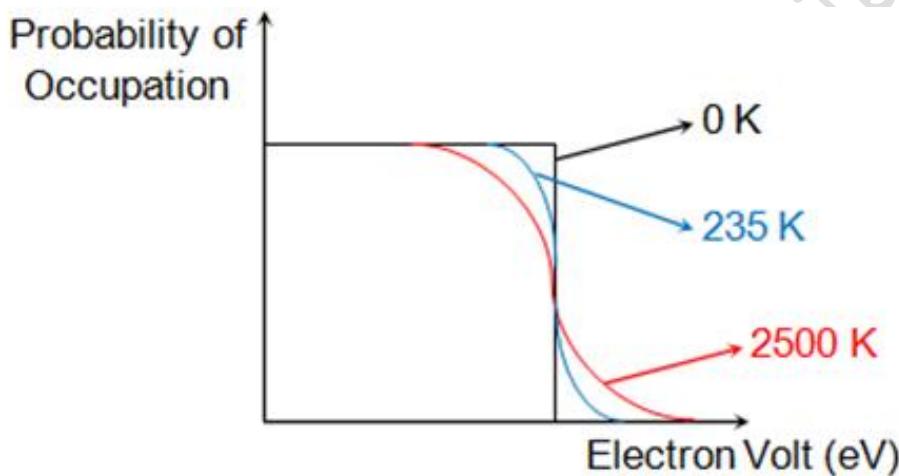
$$f(E) = \frac{1}{e^0 + 1} = \frac{1}{1 + 1} = 0.5$$

$f(E) = 0.5$  implies that probability of occupancy of an electron is 50 % at any temperature above 0K.

### Case 3: At very high temperatures.

At very high temperatures, it can be seen from the figure below that the transition between completely filled states and completely empty states is rather gradual than abrupt. i.e.,  $f(E)$  changes from 1 to 0 more gradually.

As temperature  $T$  increases, electron may get an energy of an order of  $k_B T$  and go to the higher vacant state. As a result, fermi function falls.



### Fermi-Dirac Distribution Function at Different Temperatures

## 1.14 Variation in fermi energy with temperatures

Now let us see how Fermi energy varies with temperature. Number of electrons per unit volume of the solid 'n' can be defined as a product of density of states and occupation probability of electrons in various energy levels up to Fermi level  $E_F$

$$n = \int_0^{E_F} f(E) \cdot \rho(E) dE$$

### Case 1: for $T = 0 \text{ K}$

We know that for  $T = 0\text{K}$ , we have  $f(E) = 1$ . Let the fermi energy for such a case be denoted as  $E_{F0}$ . Then above equation becomes

$$n = \int_0^{E_F} \frac{8\pi\sqrt{2m^3}}{h^3} \sqrt{E} dE$$

$$n = \frac{8\pi\sqrt{2m^3}}{h^3} \int_0^{E_F} \sqrt{E} dE$$

$$n = \frac{8\pi\sqrt{2m^3}}{h^3} \left[ \frac{2}{3} E_F^{\frac{3}{2}} \right]_0^{E_{F0}}$$

$$n = \frac{8\pi\sqrt{2m^3}}{h^3} \left( \frac{2}{3} E_{F0}^{\frac{3}{2}} \right)$$

$$E_{F0}^{\frac{3}{2}} = \frac{3h^3 n}{(8m)^{\frac{3}{2}} \pi}$$

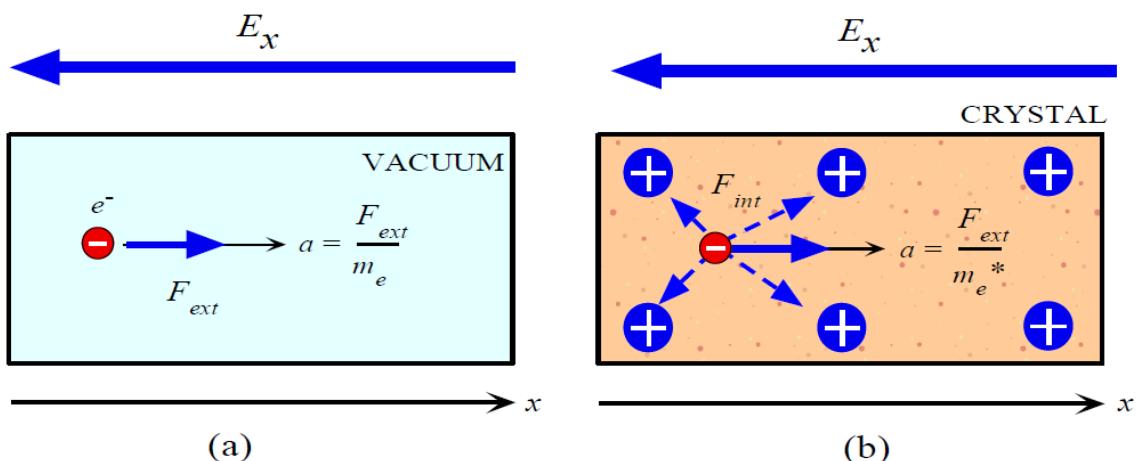
$$E_{F0} = \frac{h^2}{8m} \left( \frac{3n}{\pi} \right)^{\frac{2}{3}}$$

**Case 2: For  $T > 0$  but small**

$$E_F \approx E_{F0}$$

## 1.15 Effective mass of an electron

Under the influence of an electric field, electrons experience a force and get accelerated, stronger the applied field, higher is the acceleration. Effective mass of electron in a crystal placed in the electric field is different from its free mass. To appreciate the concept of effective mass, let us consider an electron of mass  $m$  moving under the influence of a periodic potential.



When an electron in a periodic potential accelerated by an electric field or magnetic field, then the mass of the electron is called effective mass  $m^*$ . Let an electron of charge 'e' and mass 'm' moving inside a crystal lattice of electric field 'E'. Acceleration  $a = \frac{eE}{m}$  is not a constant in the periodic lattice (potential) of the crystal. It can be considered that its variation is caused by the variation of mass of electron when it moves in the crystal lattice.

$$\therefore \text{acceleration}, a = \frac{eE}{m^*}$$

$$\therefore \text{Electric force}, F = m^* a$$

Considering the free electron as a wave packet, the group velocity  $v_g$  corresponding to the particle's velocity can be written as

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$$v_g = \frac{d\omega}{dk} = \frac{2\pi df}{dk} = \frac{2\pi}{h} \frac{dE}{dk} = \frac{1}{\hbar} \frac{dE}{dk} \quad (\because \omega = 2\pi f \text{ and } E = hf)$$

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d^2E}{dkdt} = \frac{1}{\hbar} \frac{d^2E}{dk^2} \frac{dk}{dt}$$

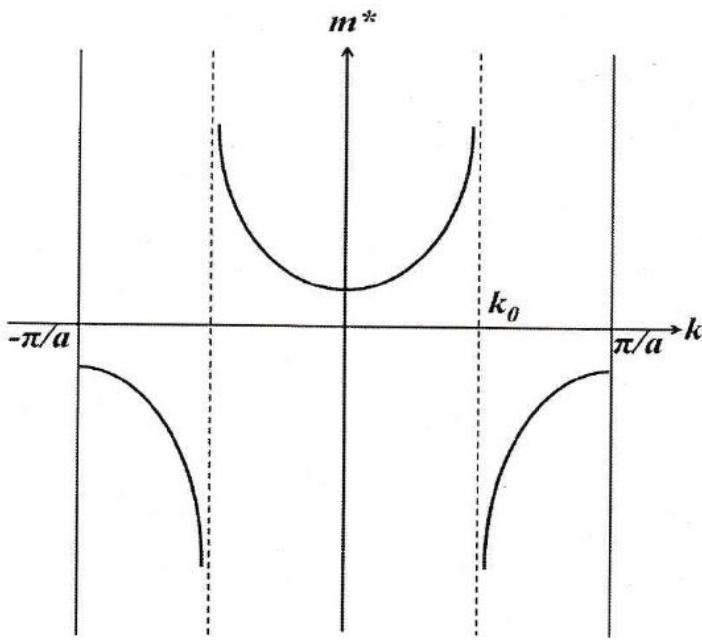
In quantum theory, the momentum of an electron is given by:  $p = \hbar k$

$$F = \frac{dp}{dt} \Rightarrow F = \hbar \frac{dk}{dt} \Rightarrow m^* a = \hbar \frac{dk}{dt} \Rightarrow m^* \frac{1}{\hbar} \frac{d^2E}{dk^2} \frac{dk}{dt} = \hbar \frac{dk}{dt} \quad (\because F = m^* a)$$

$$m^* = \frac{\hbar^2}{d^2E/dk^2}$$

Thus, effective mass of an electron in a crystalline solid depends on the variation of energy with the wave vector. For the relation between energy and wave number of a completely free electron  $\frac{\hbar^2 k^2}{2m} = E$  ( $m^*$  is equal to  $m$  the rest mass of the electron). The effective mass comes into play when electron is acted upon by the external field.

Variation of effective mass with wave vector is shown in figure below. At  $k=0$  effective mass of electron approaches to its rest mass. As  $k$  increases  $m^*$  increases and reaches to its maximum value at inflection point ( $k=k_0$ ).



Note that in the lower half of the energy band ( $k < k_0$ ),  $m^*$  is positive. However, in the upper half of the band ( $k > k_0$ ) i.e., beyond the point of inflection,  $m^*$  is negative.

The electric field which accelerates the electrons for ( $k < k_0$ ), deaccelerates it for ( $k > k_0$ ).

It is as if the deceleration is caused by the negative effective mass of the electron. In other words, beyond the point of inflection, the electron behaves as if it is a positively charged particle (called hole)! The concept of hole-electron with negative effective mass-has made significant contribution in our understanding about semiconductors.

## 1.16 Phonons

A solid crystal consists of atoms bound into a specific three-dimensional pattern called lattice.

The atoms behave as if they are connected by tiny springs and so their own thermal energy or outside forces makes the lattice vibrate.

This generates mechanical waves that carry heat and sound through the material.

A packet of these waves can travel throughout the crystal with a definite energy and momentum. These waves are treated as a particle called Phonons.

Thus, a phonon can be defined as a discrete unit of vibrational mechanical energy.

Phonons exist with discrete amount of energy, given by  $E = \hbar\omega = hf$

Phonons can carry heat and sound and they play a major role in determining heat capacities of solids and liquids.

## 1.17 Question bank

1. Give assumption of classical free electron theory.
2. Derive expression for electrical conductivity.
3. Derive expression for thermal conductivity.
4. State and deduce Wiedemann-Franz law.
5. Give success and drawbacks of classical free electron theory.
6. Derive expression for energy and wavefunction in case of one dimensional box(well) model. (quantum free electron theory).
7. Give success and drawbacks of quantum free electron theory.
8. Explain Kronig Penney model.
9. Give conclusion of Kronig Penney model. (don't write E-k diagram)
10. Explain E-k diagram.
11. How energy bands are formed? (energy bands)
12. Give classification of solids. (conductors, semiconductors and insulators).
13. Explain direct and indirect band gap semiconductors.
14. Define and derive density of states.
15. Explain probability of occupancy (fermi function)
16. Derive equation of fermi energy (OR explain variation of fermi energy with temperature).
17. Write a note on effective mass.
18. Write a note on phonons.

## 2.1 Introduction:

A semiconductor is a material that has a resistivity value in between that of a conductor and an insulator. The conductivity of a semiconductor material can be varied under an external electric field. Devices made from semiconductor materials are the foundation of modern electronics, including ratio, computers, telephones, and many other devices. The resistivity of semiconductors varies from  $10^{-5}$  to  $10^4$  ohm-m as compared to the values ranging from  $10^{-8}$  to  $10^{-6}$  ohm-m for conductors and from  $10^7$  to  $10^8$  ohm-m for insulators.

There are elemental semiconductors such as Ge and Si which belong to IV group of the periodic table and have resistivity of about  $0.6 \times 10^3$  to  $1.5 \times 10^3$  ohm-m respectively. Besides, there are certain compound semiconductors such as Gallium Arsenide, Indium phosphide, Cadmium sulphide, etc. which are formed from the combinations of the elements of groups III or V or groups II and VI. Semiconductors have a small band gap. The band gap of semiconductors varies from 0.2 to 2.5 eV which is quite small as compared to that of insulators. This property determines the wavelength of radiation which can be emitted or absorbed by the semiconductors and hence helps to construct devices. The conductivity and the effective band gaps of these materials can be modified by the introduction of impurities which strongly affect their electronic and optical properties.

In a metallic conductor, current is carried by the flow of electrons. In semiconductors, current can be carried either by the flow of electrons or by the flow of positively charged holes in the electron structure of the material. Silicon is used to create most semiconductors commercially. Semiconductor devices include the transistor, many kinds of diodes including the light emitting diode, the silicon controlled rectifier, and digital and analog integrated circuits. Solar photovoltaic panels are large semiconductor devices that directly convert light energy into electrical energy. So many other materials are used, including germanium, gallium arsenide.

Depending upon the nature of impurities added, the semiconductors are classified as pure or intrinsic semiconductors and Impure or extrinsic semiconductors. A pure semiconductor is often called an intrinsic material and then allowing the melt to solidify into a new and different crystal. This process is called doping.

Semiconductors with predictable, reliable electronic properties are necessary for mass production. The level of chemical purity needed is extremely high because the presence of impurities even in very small proportions can have large effects on the properties of material. High degree of crystalline perfection is also required, since faults in crystal structure (such as dislocations, twins and stacking faults) interfere with the semi-conducting properties of the material. Crystalline faults are a major cause of defective semiconductor devices. The larger the crystal, the more difficult it is to achieve the necessary perfection. Convert mass production processes use crystal ingots between 100 nm and 300 nm (4-12 inches) in a diameter which are grown as cylinders and sliced into wafers.

Because of the required level of chemical purity and the perfection of the crystal structure which are needed to make semiconductor devices, special methods have been developed to produce the initial semiconductor material.

### 2.1.1 Conduction band:

The conduction band in the range of electron energy, higher than that of the valence band, sufficient to make the electrons free to accelerate under the influence of an applied electric field and thus constitutes an electric current. Semiconductors may cross this conduction band when they are excited.

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### 2.1.2 Valence band:

The valence band is the highest range of electron energies where electrons are normally present at absolute zero. In semiconductors and insulators, there is a band gap above the valence band, followed by conduction band above that. In metals, the conduction band has no energy gap separating it from the valence band.

Semiconductors and insulators owe their high conductivity to the properties of the valence band in those materials. It just so happens that the number of electrons is precisely equal to the number of states available up to the top of the valence band. There are no available states in the band gap. This means that when an electric field is applied, the electrons cannot increase their energy because there are no states available to the electrons where they would be moving faster than they are already going. There is some conductivity in insulators, however this is due to thermal excitation of some of the electrons getting enough energy to jump the band gap in one go. Once they are in the conduction band, they can conduct electricity, as the hole they left behind in the valence band. The hole is an empty state that allows electrons in the valence band some degree of freedom.

### 2.1.3 Concept of holes

If we have a number of electrons in the band and the electron is moving with a velocity  $v_i$  then  $I = -e a_i v_i$ . If a band is completely filled, the current is zero, since for every electron moving with a velocity  $v_i$ , there is one moving in the opposite direction with the same speed; this is so because in a filled band, for every electron with a wave vector  $k$ , there is another electron with a wave vector  $-k$ . Thus, for a filled band  $I = -e \sum v_i = 0$ . Now, if the  $j^{\text{th}}$  electron is missing from the upper part of the band and a current  $I$  is flowing, then

$$I = -e \sum_{i \neq j} v_i = -e \sum_i v_i \pm ev_j = ev_j$$

As  $\sum v_i = 0$  for a filled band. The missing electron thus behaves like a positive charge. Such a positive charge is called a hole.

### 2.1.4 Filling up of the Energy levels

Consider the building up of a free-electron gas by filling electrons into a box, one by one. The first electron will take the minimum kinetic energy  $E_0$  ( $\approx 10^{-55}$  eV). The next electron will also be able to take the same minimum kinetic energy provided it (due to Pauli's exclusion principle). Thus, when added, this electron goes into the next slightly higher energy level (say  $E_0 + \delta$ ). The fourth electron will take the energy ( $E_0 + \delta$ ) provided it orients its spin antiparallel to the other electron in this energy state. In this way, addition of electron continues until all the available, say  $N$  electrons have been used, thus first  $N/2$  levels will be filled and the higher levels will be completely empty (for the system in ground state at  $T = 0$ ). The  $N/2$  level in this case (i.e. the level which divides the filled and the empty levels or the highest filled level) is known as the Fermi level and the corresponding energy, the Fermi energy.

## 2.2 Intrinsic and Extrinsic Semiconductors

### 2.2.1 Intrinsic semiconductors:

Intrinsic semiconductors are those in which impurities are not present and therefore called pure semiconductors. In these semiconductors, few crystal defects may be present. Fermi level exists exactly at mid-way of the energy gap. When a semiconductor is taken at 0 K then it behaves as an insulator and conduction occurs at higher temperature due to thermal excitation of electrons from the valence band to the conduction band. Examples: Germanium and Silicon. Figure shows the intrinsic semiconductors at  $T = 0$  K and  $T > 0$  K

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In order to get insight view of an intrinsic semiconductor, let us consider silicon, which has four valence electrons. In order to gain stability, it has to make four covalent bonds. In this regards each silicon atom makes four covalent bonds with four other silicon atoms. The electrons which are participating in the covalent bonds are known as valence electrons. If some energy is supplied then covalent bonds break, electrons will come out and move freely, resulting in the formation of vacant sites in the covalent bonds. These are known as positive charge carriers named as holes. The electrons which came out from the valence bands move freely without any constraints and have more energy than the electron in the covalent bonds or valence bond. The number of conduction electrons will be equal to the number of vacant sites in the valence band.

For an intrinsic material  $n = p = n_i$  or  $n_p = n_i^2$

At a given temperature there is certain concentration of electron-hole pair  $n_i$  and at the same time there is recombination of electron hole pairs. Recombination occurs when an electron in the conduction band makes a transition to an empty state in the valence band.

### 2.2.2 Extrinsic semiconductors:

In intrinsic or pure semiconductors, the carrier concentration of both electrons and holes at normal temperatures very low, hence to get appreciable current density through the semiconductor, a large electric field should be applied. This problem can overcome by adding suitable impurities (1 in 10<sup>8</sup>) into the intrinsic semiconductors.

The extrinsic semiconductors are those in which impurities of large quantity are present. In general, the impurities can be either III group elements or V group elements. Based on the impurities present in the extrinsic semiconductors, they are classified into two categories.

- (i) n-type semiconductors and
- (ii) p-type semiconductors

### 2.2.3 n-type semiconductors:

In order for silicon crystal to conduct electricity, we need to introduce an impurity atom such as Arsenic, Antimony or phosphorus into the crystalline structure. These atoms have five outer electrons in their outermost co-valent bond to share with other atoms and are commonly called pentavalent impurities. This allows four of the five electrons to bond with its neighboring silicon atoms leaving one free electron to move about when electrical voltage is applied. As each impurity atom donates one electron, pentavalent atoms are generally known as donors. Antimony (Sb) is frequently used as pentavalent additive as it has 51 electrons arranged in 5 shells around the nucleus. The resulting semiconductor material has an excess of current carrying electrons, each with a negative charge, and is therefore referred to as n-type material with the electrons called majority carriers and the resultant holes minority carriers.

Donor energy level, the localized electronic states or levels introduced by the donor atoms because of the presence of an extra electron is generated. And donor energy is defined as the energy difference between the bottom of the conduction band and the donor energy level.

The block diagram of n-type impurity doping and corresponding band diagram is shown in figure 1.

### 2.2.4 p-type semiconductors:

In contrast to n-type of semiconductor, if we introduce a trivalent (3 electron) impurity into the crystal structure, such as aluminum, Boron or indium, only three valence electrons are available in the outermost covalent bond meaning that the fourth bond cannot be formed. Therefore, a complete connection is not possible, giving the semiconductor material an abundance of positively charged carriers known as holes in the structure of the crystal. As there is a hole an adjoining free electron is

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attracted to it and will try move into the hole to fill it. However, the electron filling the hole leaves another hole behind, and is forth giving the appearance that the holes are moving as a positive charge through the crystal structure (conventional current flow). As each impurity atom generates a hole, trivalent impurities are generally known as acceptors as they are continually accepting extra electrons. Boron (B) is frequently used as trivalent additive as it has only 5 electrons arranged in 3 shells around the nucleus. Addition Boron causes conduction to consists mainly of positive charge carriers results in a p-type material and the positive holes are called majority carriers while the free electrons are called minority carriers.

It is usual for semiconductors to contain both the donor type and the acceptor type impurities simultaneously. When this happens, the hydrogenic impurity levels for both types of impurity appear in the band gap. However, the bound donor electrons and the bound acceptor holes do not represent the ground state of the crystal. In fact, the ground state of the donor electrons would be in the empty acceptor states, thus tending to fill the later. Since the acceptor levels are below the donor levels, a lower state of energy of the crystal will be reached if electrons from the donors fill the acceptor levels. It is called the neutralization or the compensation of the carriers with each other. Now, if there is an equal number of acceptors and donors present in the crystal, then this process would lead to all the acceptor levels being occupied and all the donor levels being empty. Under this condition, the Fermi level is halfway between the two impurity levels which, if  $m_e = m_h$ , is exactly as  $E_g / 2$  and the crystal then behaves identically as if it is an intrinsic semiconductor. Such specimen are said to be compensated.

This result is technologically important in the preparation of intrinsic semiconductors i.e., we may prepare samples with comparable number of donors and acceptors rather than with just zero concentration of these. The former preparation is much easier and at the same time gives the desired sample. Generally, it is difficult to add equal number of donors and acceptors and the sample is, therefore, essentially an extrinsic one, i.e. either n-type or p-type – depending upon whether donors exceed to acceptors or acceptors exceed the donors.

### 2.3 Fermi Distribution Function:

The fermi distribution function, also called the fermi function gives the probability of occupancy of energy levels by fermions in terms of fermi energy, temperature and Boltzmann constant. Fermions are half integer spin particles like electrons which obey Pauli exclusion principle.

The probability of an electron definitely occupying an energy state is given by  $f(E) = 1$ .

The probability of an electron not occupying an energy state i.e. the inoccupancy of an energy state is given by  $1 - f(E)$ .

Consider a system of electrons in thermal equilibrium at a temperature T K. The probability  $f(E)$  of an electron occupying a particular energy level (state) E is given by

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$

where  $f(E)$  is the fermi function

$E_F$  is the fermi energy (also called fermi level)

$k_B$  is the Boltzmann constant

T is the absolute temperature

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The uppermost filled energy level is referred as fermi level and the energy of the electrons in the fermi level at absolute zero degree is called the fermi energy. Thus, a system is characterized by its temperature and its fermi energy  $E_F$ . For a filled energy level,  $f(E) = 1$  and for an unfilled level  $f(E) = 0$

The dependence of fermi function under different conditions of temperature and the effect on occupancy of energy levels are as follows.

**1. At  $T = 0 \text{ K}$**

At absolute zero temperature, the electrons occupy the lowest energy level first, followed by the next higher ones as per Pauli's exclusion principle i.e. a pair of electrons, one with spin up and the other with spin down occupy the lowest level. The next pair of electrons occupy the next higher level and so on, till all the electrons of the metal are accommodated.

**Special Cases**

**(a) Probability of occupation At  $T = 0 \text{ K}$  for  $E < E_F$**

For energy levels  $E$  lying below  $E_F$ , the term  $(E - E_F)$  takes a negative value. Hence, the argument  $\left(\frac{E-E_F}{k_B T}\right)$  in the exponential function becomes  $-\infty$ .

$$\therefore f(E) = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

Therefore  $f(E) = 1$  implies that all the energy levels below  $E_F$  are occupied by electrons.

**(b) Probability of occupation At  $T = 0 \text{ K}$  for  $E > E_F$**

For energy levels above  $E_F$ , the term  $(E - E_F)$  takes a positive value. Hence the argument  $\left(\frac{E-E_F}{k_B T}\right)$  in the exponential function becomes  $\infty$

$$\therefore f(E) = \frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = 0$$

Therefore  $f(E) = 0$  implies that all the energy levels above  $E_F$  are vacant i.e. there is no chance of an electron occupying an energy level above  $E_F$ .

**2. Probability of occupation at  $T > 0 \text{ K}$**

At room temperature, the value of probability starts reducing from 1 for values of  $E$  close to but larger than  $E_F$ . At  $T > 0 \text{ K}$  for  $E = E_F$ , the argument in the exponential function becomes zero.

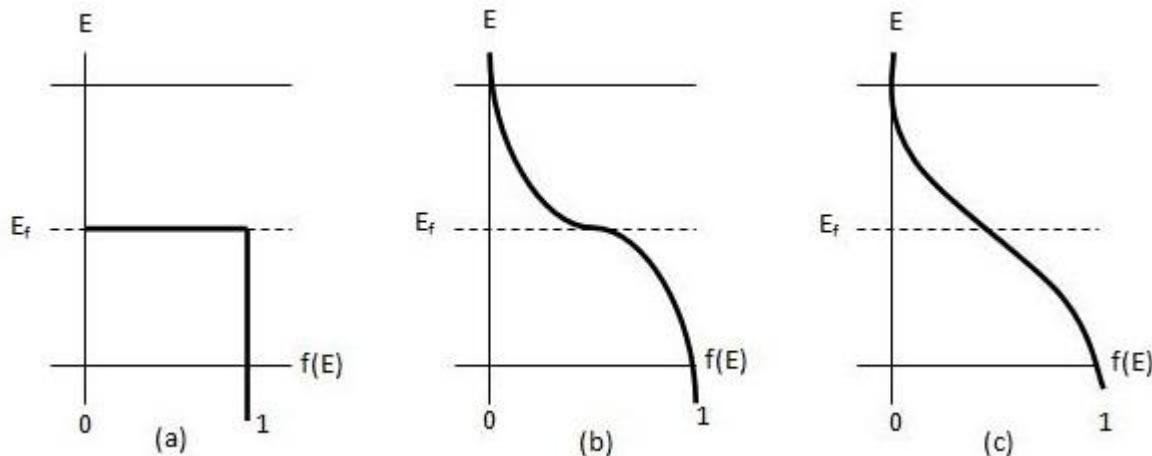
$$f(E) = \frac{1}{e^0 + 1} = \frac{1}{1 + 1} = 0.5$$

Therefore  $f(E) = \frac{1}{2}$  implies that the probability of occupancy of an electron is 50% at any temperature above 0 K. Further, for  $E > E_F$ , the  $f(E)$  value falls off to zero rapidly.

**3. Probability of occupation at very high temperatures**

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At very high temperatures, it is observed that the transition between completely filled states and completely empty states is gradual rather than abrupt, i.e.  $f(E)$  changes from 1 to 0 more and more gradually. For temperature of the order of 1000 K, we have  $kBT \approx 0.086$  eV, thus high temperatures alone are insufficient to make conduction electron energies close to EF. This however becomes feasible by applying an electric field. Still, at sufficiently high temperatures, fermions from even the lowest energy states will begin to be excited to energies  $\geq EF$ , then  $f(E)$  near  $E = 0$  will drop below the value 1. There are more filled states just above the Fermi energy in the partially filled band, consequently lesser number of unoccupied levels, so resistivity increases with temperature.  $f(E)$  will then assume the shape as shown. As a result, fermi function falls.



## 2.4 Quasi Fermi Level:

Quasi Fermi level describes the population of electrons separately in the conduction and valence band when their population is disturbed from the equilibrium state. This disturbance is generally caused by the external biasing, by light of suitable energy (more than energy band gap), etc. The displacement from equilibrium state is such that the carrier population can no longer be illustrated by a single Fermi level, rather it is possible to explain the same by using the concept of individual quasi Fermi levels (QFL) for each conduction and valence band. In thermal equilibrium, there is no need to distinguish between conduction band QFL and valence band QFL as both are equal to the Fermi level. A slight deviation from thermal equilibrium can disturb the population of electrons in the conduction and valence band.

If this disturbance is not changing too fast, both the bands relax to a state of quasi thermal equilibrium. Since the relaxation time for electrons within the conduction band is smaller than that for electrons in band gap, we can assume electrons are in the state of thermal equilibrium in the conduction band. This is also equally applicable for holes in the valence band. Thus, quasi Fermi level is defined as the thermal equilibrium state of electrons/holes in the conduction/valence band.

## 2.5 Carrier concentration for intrinsic semiconductor:

### 2.5.1 Electron concentration in the Conduction Band:

The concentration of electrons and holes in a semiconductor can be obtained from the knowledge of the densities of states in the valence band and the conduction band which also depends upon the Fermi-Dirac distribution function.

The number of free electrons per unit volume in an energy range  $E$  and  $E + dE$  can be obtained by

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$$d_n = D(E) f(E) dE$$

where  $D(E)$  is the density of states function defined as the total number of allowed electronic states per unit volume per electron volt in a semiconductor and  $f(E)$  is the Fermi distribution function representing the probability of occupation of a state with energy  $E$ . The expression for  $f(E)$  is given by

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$

the density of states is given by

$$D(E) = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2}$$

We assume that the effective mass is a scalar quantity and the energy curve is parabolic. Using above equations, we get

$$d_n = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} f(E) dE$$

It is clear from band diagram that an electron occupying an energy state  $E$  in the conduction band possesses the kinetic energy  $(E - E_c)$ . Therefore,  $E$  must be replaced by  $(E - E_c)$

$$d_n = \frac{4\pi}{h^3} (2m_n^*)^{3/2} (E - E_c)^{1/2} \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} dE$$

where  $m_n^*$  is the effective mass of the electron in the conduction band. The concentration of electrons,  $n$ , in the conduction band is obtained by integrating the above equation

$$d_n = \frac{4\pi}{h^3} (2m_n^*)^{3/2} \int_{E_c}^{\infty} \frac{(E - E_c)^{1/2}}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} dE$$

Therefore, for energies greater than  $E_c$ , we have

$$\begin{aligned} \exp\left(\frac{E - E_F}{k_B T}\right) + 1 &\cong \exp\left(\frac{E - E_F}{k_B T}\right) \\ d_n &= \frac{4\pi}{h^3} (2m_n^*)^{3/2} \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left[-\left(\frac{E - E_F}{k_B T}\right)\right] dE \end{aligned}$$

Adding and subtracting  $E_c$  and rearranging terms

$$\begin{aligned} \exp\left[-\left(\frac{E_c - E_c + E - E_F}{k_B T}\right)\right] &= \exp\left[\left(\frac{-E_c + E_c - E + E_F}{k_B T}\right)\right] \\ &= \exp\left[\left(\frac{-E_c + E_F}{k_B T}\right)\right] \exp\left[\left(\frac{E_c - E}{k_B T}\right)\right] \\ &= \exp\left[\left(\frac{E_F - E_c}{k_B T}\right)\right] \exp\left[-\left(\frac{E - E_c}{k_B T}\right)\right] \end{aligned}$$

Putting above equation in equation for density of states,

$$d_n = \frac{4\pi}{h^3} (2m_n^*)^{3/2} \exp\left[\left(\frac{E_F - E_c}{k_B T}\right)\right] \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left[-\left(\frac{E - E_c}{k_B T}\right)\right] dE$$

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Let us consider

$$\frac{E - E_c}{k_B T} = x$$

$$dE = k_B T dx$$

For limits  $E = E_c$  and at  $x = 0$

$$d_n = \frac{4\pi}{h^3} (2m_n^*)^{3/2} \exp\left[\left(\frac{E_F - E_c}{k_B T}\right)\right] \int_{E_c}^{\infty} (x)^{1/2} (k_B T)^{1/2} \exp[-(x)] k_B T dx$$

$$d_n = \frac{4\pi}{h^3} (2m_n^* k_B T)^{3/2} \exp\left[\left(\frac{E_F - E_c}{k_B T}\right)\right] \int_{E_c}^{\infty} (x)^{1/2} e^{-x} dx$$

Solving the equation

$$\int_{E_c}^{\infty} (x)^{1/2} e^{-x} dx = \left(\frac{\pi}{4}\right)^{1/2}$$

$$d_n = 2 \left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} \exp\left[\left(\frac{E_F - E_c}{k_B T}\right)\right]$$

Thus, the probability of occupancy of level  $E_c$  is given by

$$f(E_c) = \frac{1}{\exp\left(\frac{E_c - E_F}{k_B T}\right) + 1} = \exp\left(-\frac{E_c - E_F}{k_B T}\right)$$

$$d_n = 2 \left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} f(E_c)$$

$$d_n = N_c \exp\left(-\frac{E_c - E_F}{k_B T}\right)$$

where

$$N_c = 2 \left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2}$$

Here  $N_c$  represents the effective density of states of electrons at the conduction band edge.

### 2.5.2 Hole concentration in the valence Band

The number of holes per unit volume in an energy range  $E$  and  $E + dE$  can be obtained by

$$d_p = D(E) [1 - f(E)] dE$$

where  $D(E)$  is the density of states defined as the total number of allowed electronic states per unit volume in a semiconductor.  $1 - f(E)$  is the probability of an energy state  $E$  not to be occupied by an electron. The expression for  $1 - f(E)$  is given by

$$1 - f(E) = 1 - \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} = 1 - \left[\exp\left(\frac{E - E_F}{k_B T}\right) + 1\right]^{-1}$$

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Using binomial series  $(1+x)^{-1} = 1 - x + x^2 - x^3 + \dots$  with  $x = \exp\left(\frac{E-E_F}{k_B T}\right)$  and neglecting higher powers, we get

$$1 - f(E) = 1 - \left[1 - \exp\left(\frac{E-E_F}{k_B T}\right)\right] = -\left[-\exp\left(\frac{E-E_F}{k_B T}\right)\right]$$

$$1 - f(E) = \exp\left(\frac{E-E_F}{k_B T}\right)$$

From the above equation it is clear that, in valence band  $E < E_F$ , i.e. the fermi level  $E_F$  is again assumed to lie a few  $k_B T$  above  $E_v$ . Therefore, the function  $1 - f(E)$  decreases exponentially. Also, it implies that holes reside near the top of the valence band. This shows that the probability of finding holes decreases exponentially with increase in depth into the valence band. Also, the kinetic energy of a hole in the energy state  $E$  in the valence band is  $(E_v - E)$ . Therefore, the density of states per unit volume in the valence band can be written as

$$D(E) = \frac{4\pi}{h^3} (2m_p^*)^{3/2} (E_v - E)^{1/2}$$

Using above equations, we get

$$d_p = \frac{4\pi}{h^3} (2m_p^*)^{3/2} (E_v - E)^{1/2} [1 - f(E)] dE$$

where  $m_p^*$  is the effective mass of the hole in the valence band. The concentration of holes,  $p$ , in the valence band is obtained by integrating the above equation from  $E = -\infty$  to  $E_v$ .

$$d_p = \frac{4\pi}{h^3} (2m_p^*)^{3/2} \int_{-\infty}^{E_v} \frac{(E_v - E)^{1/2}}{1} * \exp\left(\frac{E-E_F}{k_B T}\right) dE$$

Let us consider

$$\frac{E_v - E}{k_B T} = x$$

$$E_v - E = k_B T x$$

$$E_v - k_B T x = E$$

$$dE = -k_B T dx$$

For limits  $E = E_v$  and at  $x = 0$  OR  $E = -\infty$  and  $x = \infty$ . Substituting the above equations, we get

$$d_p = \frac{4\pi}{h^3} (2m_n^*)^{3/2} \int_{E_c}^{\infty} (x)^{1/2} (k_B T)^{1/2} e^{\left[\frac{E_v-x k_B T - E_F}{k_B T}\right]} (-k_B T dx)$$

$$d_p = \frac{4\pi}{h^3} (2m_p^* k_B T)^{3/2} e^{\left[\frac{E_v-E_F}{k_B T}\right]} \int_{\infty}^0 (x)^{1/2} e^{-x} (-dx)$$

$$d_p = \frac{4\pi}{h^3} (2m_p^* k_B T)^{3/2} e^{\left[\frac{E_v-E_F}{k_B T}\right]} \int_0^{\infty} (x)^{1/2} e^{-x} dx$$

Solving the equation

$$\int_0^\infty (x)^{1/2} e^{-x} dx = \left(\frac{\pi}{4}\right)^{1/2}$$

$$d_p = 2 \left( \frac{2\pi m_p^* k_B T}{h^2} \right)^{3/2} \exp \left[ \left( \frac{E_v - E_F}{k_B T} \right) \right]$$

The above equation is the expression for the density of holes in the valence band for an intrinsic semiconductor.

### 2.5.3 Fermi Level and its variation with Temperature (Intrinsic Semiconductor)

We know that for an intrinsic semiconductor  $n_e = n_h$

i.e. density of electrons in conduction band = density of holes in valence band

Thus,

$$2 \left( \frac{2\pi m_n^* k_B T}{h^2} \right)^{3/2} \exp \left[ \left( \frac{E_F - E_c}{k_B T} \right) \right] = 2 \left( \frac{2\pi m_p^* k_B T}{h^2} \right)^{3/2} \exp \left[ \left( \frac{E_v - E_F}{k_B T} \right) \right]$$

$$\therefore (m_n^*)^{3/2} \exp \left[ \left( \frac{E_F - E_c}{k_B T} \right) \right] = (m_p^*)^{3/2} \exp \left[ \left( \frac{E_v - E_F}{k_B T} \right) \right]$$

Rearranging the terms, we obtain

$$\exp \left[ \frac{2E_F}{k_B T} \right] = \left( \frac{m_p^*}{m_n^*} \right)^{3/2} \exp \left[ \left( \frac{E_v + E_c}{k_B T} \right) \right]$$

Taking logarithm on both sides,

$$\frac{2E_F}{k_B T} = \frac{3}{2} \ln \frac{m_p^*}{m_n^*} + \frac{E_v + E_c}{k_B T}$$

To evaluate the variation in Fermi energy with temperature, find EF, we get,

$$E_F = \frac{3k_B T}{4} \ln \frac{m_p^*}{m_n^*} + \frac{E_v + E_c}{2}$$

Under a situation where  $m_p^* = m_n^*$ ;  $\ln(1) = 0$  reduces the above equation to

$$E_F = \frac{E_v + E_c}{2}$$

Thus, the fermi level is in the middle of the band gap i.e.  $E_F = \frac{E_g}{2}$ .

Thus,  $E_g$  lies half way between the top of valence band and bottom of conduction band.

### 2.5.4 Dependence of Fermi Energy on Temperature for intrinsic semiconductor

The variation of fermi level with temperature for an intrinsic semiconductor shows that at  $T = 0$  K, the fermi level lies exactly in the middle of forbidden gap. At low temperature region,  $E_F$  is practically independent of temperature. But, there is a slight variation in  $E_F$  in the high temperature region. The reason is, in actual case,  $m_n^* > m_p^*$ . Thus, the term,  $\ln \frac{m_p^*}{m_n^*}$  has a small value. This results in small increase in the magnitude of  $E_F$ . Thus, the fermi level gets raised slightly as  $T$  increases.

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### 2.5.5 Carrier Concentration in n-type semiconductor

Let  $N_d$  be the donor concentration i.e., the number of donor atoms per unit volume of the material and  $E_d$  is the donor energy level in an n-type semiconductor. Let us assume that  $E_c - E_F > k_B T$ . Then, in that case, density of electrons in the conduction band is given as

$$n_e = 2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \exp \left[ \left( \frac{E_F - E_c}{k_B T} \right) \right]$$

At 0 K, the fermi level  $E_F$  lies between  $E_c$  and  $E_d$ . Also, at very low temperature, all donor levels will be filled with electrons (donor atoms). With increase of temperature, more and more donor atoms get positively ionized due to electron donation to the conduction band and hence, the density of electrons in the conduction band increases.

If we assume that  $E_F$  lies more than a few  $k_B T$  above the donor level  $E_d$ , then the density of ionized donor atoms  $N_d^+$  must equal to the product of density of the donor atoms  $N_d$  and the probability function  $[1 - f(E_d)]$  for an electron absence in the donor energy level.

$$\text{i.e. } N_d^+ = N_d [1 - f(E_d)]$$

$$\text{But } [1 - f(E_d)] = \exp \left( \frac{E_d - E_F}{k_B T} \right)$$

from the above equation, it is clear that  $E_d < E_F$ , i.e.  $E_d - E_F$  is negative.

$$\text{Hence substituting equation we get } N_d^+ = N_d \exp \frac{E_d - E_F}{k_B T}$$

At very low temperature, since no electron hole pair is generated due to breaking of covalent bonds, the density of electrons  $n_e$  in the conduction band must be equal to the density of positively ionized donor atoms  $N_d^+$ .

$$n_e = N_d^+$$

$$2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \exp \left[ \left( \frac{E_F - E_c}{k_B T} \right) \right] = N_d \exp \frac{E_d - E_F}{k_B T}$$

Taking natural logarithm on both sides

$$\ln \left[ 2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \right] + \frac{E_F - E_c}{k_B T} = \ln N_d + \frac{E_d - E_F}{k_B T}$$

On rearranging the above equation reduces to

$$\frac{E_F - E_c}{k_B T} - \frac{E_d - E_F}{k_B T} = \ln N_d - \ln \left[ 2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \right]$$

Simplifying the above equation, we get

$$2E_F - (E_d + E_c) = k_B T \ln \left[ \frac{N_d}{2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}} \right]$$

$$E_F = \frac{(E_d + E_c)}{2} + \frac{k_B T}{2} \ln \left[ \frac{N_d}{2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}} \right]$$

At 0 K temperature, we get

$$E_F = \frac{(E_d + E_c)}{2}$$

Thus, above equation implies that, the fermi level  $E_F$  lies exactly at the middle of the donor level and the bottom of the conduction band  $E_c$  as shown.

### 2.5.6 Expression for carrier Concentration of Electrons in the conduction Band

The density of electrons in the conduction band is given by

$$n_e = 2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \exp \left[ \left( \frac{E_F - E_c}{k_B T} \right) \right]$$

Substituting for  $E_F$  from above equation, we get an expression for the density of electrons in the conduction band. Let us first simplify the term  $E_F - E_c$  in  $\exp \left[ \left( \frac{E_F - E_c}{k_B T} \right) \right]$  factor

$$E_F - E_c = \frac{(E_d + E_c)}{2} + \frac{k_B T}{2} \ln \left[ \frac{N_d}{2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}} \right] - E_c$$

$$E_F - E_c = \frac{(E_d - E_c)}{2} + \frac{k_B T}{2} \ln \left[ \frac{N_d}{2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}} \right]$$

On dividing the above equation by  $k_B T$ , we get

$$\frac{E_F - E_c}{k_B T} = \frac{(E_d - E_c)}{2 k_B T} + \frac{1}{2} \ln \left[ \frac{N_d}{2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}} \right]$$

$$\frac{E_F - E_c}{k_B T} = \frac{(E_d - E_c)}{2 k_B T} + \ln \left[ \frac{N_d^{1/2}}{\left( \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \right)^{1/2}} \right]$$

Using equation for density of electrons in the conduction band

$$n_e = 2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \exp \left[ \frac{(E_d - E_c)}{2 k_B T} + \ln \left[ \frac{N_d^{1/2}}{\left( \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \right)^{1/2}} \right] \right]$$

Simplifying the exponential term,

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$$n_e = 2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \exp \left[ \frac{(E_d - E_c)}{2 k_B T} \right] \frac{N_d^{1/2}}{\left( 2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \right)^{1/2}}$$

$$n_e = (2N_d)^{1/2} \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/4} \exp \left[ \frac{(E_d - E_c)}{2 k_B T} \right]$$

Hence, the density of electrons in the conduction band is proportional to the square root of the donor concentration  $N_d$ .

This equation holds good only at low temperatures and at high temperatures, the intrinsic carrier concentration must also be taken into account. Thus, at very high temperatures, the n-type semiconductor behaves like an intrinsic semiconductor.

The ionization energy of donors is given by  $\Delta E = E_c - E_d$ . It is the amount of energy required to transfer an electron from the donor energy level  $E_d$  to the conduction band.

### 2.5.7 Variation of Fermi level with Temperature

The fermi level increases with increase of temperature as per equation

$$E_F = \frac{(E_d + E_c)}{2} + \frac{k_B T}{2} \ln \left[ \frac{N_d}{2 \left( \frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}} \right]$$

As the temperature gets slowly increased, more and more donor atoms get ionized due to transfer of electrons to the conduction band, and the fermi level  $E_F$  lies in between  $E_c$  and  $E_d$ .

At a particular temperature, all the donor atoms would have been ionized. Hence, beyond this temperature, electron hole pairs get generated due to breaking of covalent bonds; and, the material tends to behave as an intrinsic semiconductor.

### 2.5.8 Carrier Concentration in p-type semiconductor

Let  $N_a$  be the acceptor concentration i.e., the number of acceptor atoms per unit volume of the p-type material and  $E_a$  is the acceptor energy level in an p-type semiconductor. Let us assume that  $E_a - E_F > k_B T$ . Then, in that case, density of holes in the valence band is given as

$$n_h = 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \exp \left[ \left( \frac{E_v - E_F}{k_B T} \right) \right]$$

At 0 K, the fermi level  $E_F$  lies between  $E_v$  and  $E_a$ . Also, at very low temperature, all acceptor levels remain empty. With increase of temperature, more and more acceptor atoms get negatively ionized due to electron transfer from the valence band to the acceptor energy level  $E_a$ . Hence, the density of holes in the valence band increases.

If we assume that  $E_F$  lies below the acceptor energy level  $E_a$  then, the density of negatively ionized, then the density of ionized acceptor atoms  $N_a^-$  must equal to the product of density of the acceptor atoms  $N_a$  and the probability function  $f(E_a)$  for an electron occupancy.

$$\text{i.e. } N_a^- = N_a f(E_a)$$

$$\text{But } f(E_a) = \frac{1}{1 + \exp \left( \frac{E_a - E_F}{k_B T} \right)}$$

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It is clear that  $E_a < E_F$ , i.e.  $E_a - E_F$  is positive. Therefore, the term in the denominator can be neglected, compared to  $\exp\left(\frac{E_a - E_F}{k_B T}\right)$ . Thus, we obtain  $f(E_a) = \exp\left(\frac{E_F - E_a}{k_B T}\right)$

Hence substituting equation, we get  $N_d^- = N_a \exp\left(\frac{E_F - E_a}{k_B T}\right)$

At very low temperature, the density of holes  $n_h$  in the valence band must be equal to the density of negatively ionized acceptor atoms  $N_a^-$ .

$$n_h = N_a^-$$

$$2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \exp\left[\left(\frac{E_v - E_F}{k_B T}\right)\right] = N_a \exp\frac{E_F - E_a}{k_B T}$$

Taking natural logarithm on both sides

$$\ln \left[ 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \right] + \frac{E_v - E_F}{k_B T} = \ln N_a + \frac{E_F - E_a}{k_B T}$$

On rearranging the above equation reduces to

$$\frac{E_v - E_F}{k_B T} - \frac{E_F - E_a}{k_B T} = \ln N_a - \ln \left[ 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \right]$$

Simplifying the above equation, we get

$$-2E_F + (E_v + E_a) = k_B T \ln \left[ \frac{N_a}{2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2}} \right]$$

$$E_F = \frac{(E_v + E_a)}{2} - \frac{k_B T}{2} \ln \left[ \frac{N_a}{2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2}} \right]$$

At 0 K temperature, we get

$$E_F = \frac{(E_v + E_a)}{2}$$

Thus, above equation implies that, the fermi level  $E_F$  lies exactly at the middle of the acceptor level  $E_a$  and the top of the valence band  $E_v$ .

### 2.5.9 Expression for carrier Concentration of Holes in the Valence Band

The density of holes in the valence band is given by

$$n_h = 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \exp\left[\left(\frac{E_v - E_F}{k_B T}\right)\right]$$

Substituting for  $E_F$  from above equation, we get an expression for the density of holes in the valence band. Let us first simplify the term  $E_v - E_F$  in  $\exp\left[\left(\frac{E_v - E_F}{k_B T}\right)\right]$  factor

$$E_v - E_F = \textcolor{red}{E_v} - \frac{(E_v + E_a)}{2} + \frac{k_B T}{2} \ln \left[ \frac{N_a}{2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2}} \right]$$

$$E_v - E_F = \frac{(E_v - E_a)}{2} + \frac{k_B T}{2} \ln \left[ \frac{N_a}{2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2}} \right]$$

On dividing the above equation by  $k_B T$ , we get

$$\frac{E_v - E_F}{k_B T} = \frac{(E_v - E_a)}{2 k_B T} + \frac{1}{2} \ln \left[ \frac{N_a}{2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2}} \right]$$

$$\frac{E_v - E_F}{k_B T} = \frac{(E_v - E_a)}{2 k_B T} + \ln \left[ \frac{N_a^{1/2}}{\left( 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \right)^{1/2}} \right]$$

Using equation for density of holes in the valence band

$$n_h = 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \exp \left[ \frac{(E_v - E_a)}{2 k_B T} + \ln \left[ \frac{N_a^{1/2}}{\left( 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \right)^{1/2}} \right] \right]$$

Simplifying the exponential term,

$$n_h = 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \exp \left[ \frac{(E_v - E_a)}{2 k_B T} \right] \frac{N_a^{1/2}}{\left( 2 \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \right)^{1/2}}$$

$$n_h = (2N_a)^{1/2} \left( \frac{2\pi m_h^* k_B T}{h^2} \right)^{3/4} \exp \left[ \frac{(E_v - E_a)}{2 k_B T} \right]$$

Hence, the density of holes in the valence band is proportional to the square root of the acceptor concentration  $N_a$ .

At very high temperatures, the p-type semiconductor behaves like an intrinsic semiconductor.

The ionization energy of acceptors is given by  $\Delta E = E_a - E_v$ . It is the amount of energy required to transfer an electron from the valence band to acceptor energy level  $E_a$ .

## 2.6 Carrier Generation and Recombination:

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**Carrier Generation:** It is the process where electron-hole pairs are created by exciting an electron from valence band to conduction band, thereby creating a hole in valence band.

**Carrier Recombination:** It is the process where electron-hole pairs recombine by an electron from conduction band and hole from valence band.

Carrier generation and recombination can occur through various techniques

1. Photon Transition OR Optical generation and recombination

This is also known as direct recombination or band to band transition. An electron from conduction band falls back to valence band and releases energy in the form of photon. The reverse process i.e. generation of electron hole pairs is triggered by sufficiently energetic photon, which transfers its energy to a valence band electron, moving it to conduction band and leaving behind a hole in valence band.

Energy of incident photon has to be atleast of the magnitude of band gap energy. For transitions from excited states to lower energy states, momentum has to be conserved. As the momentum of photon is very small, no momentum transfer is possible, so only direct band to band transitions are possible, where no change of momentum is required.

The process of recombination is directly proportional to the amount of available holes and electrons. The process always tries to achieve thermal equilibrium. In case of excess carrier concentration;  $n_e n_h - n_i^2 > 0$ , carrier recombination dominate and for low carrier concentration  $n_e n_h - n_i^2 < 0$ , carrier generation dominates.

2. Phonon Transition OR Shockley-Read-Hall recombination OR Non-radiative recombination

This is also called indirect or Trap-assisted recombination. This process is trap assisted, passing through a lattice defect at energy level Et within the semiconductor band gap. The trap can be caused by presence of any foreign atom or structural defect.

- a) Electron capture: An electron from conduction band is captured by an empty trap in the band gap. This excess energy  $E_c - E_t$  is transferred to the crystal lattice viz phonon transmission.
- b) Hole capture: The trapped electron moves to valence band and neutralizes a hole. A phonon with energy  $E_t - E_v$  is generated.
- c) Hole emission: An electron from valence band is trapped, leaving a hole in the valence band. Energy required is  $E_t - E_v$ .
- d) Electron emission: A trapped electron moves from the trap energy level to conduction band.

The electron capture rate is proportional to the electron concentration in conduction band and hole capture rate is proportional to the hole concentration in valence band.

The hole and electron emission rates are proportional to concentration of empty traps and filled traps respectively.

### 2.6.1 Drift and Diffusion current:

#### Drift Current:

The flow of charge carriers, which is due to applied voltage or electric field is called drift current.

In a semiconductor, there are two types of charge carriers i.e. holes and electrons. When voltage is applied to a semiconductor, free electrons move towards the positive terminal of battery and holes move

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towards the negative terminal of the battery. But due to continuous collisions with atoms, they change the direction of flow.

During the transition, electron would not be able to travel on a straight path due to collisions with atoms. During each such collision, the electron bounces in a random direction. The applied voltage does not stop the collisions, but causes the electrons to drift towards the positive terminal.

The average velocity that an electron or hole achieves, due to applied voltage or electric field is called drift velocity.

$$\text{Drift velocity of electrons } v_e = \mu_e E$$

$$\text{Drift velocity of holes } v_h = \mu_h E$$

$$\text{Drift current density due to free electrons is given by } J_e = n_e E \mu_e$$

$$\text{Drift current density due to free electrons is given by } J_h = n_h E \mu_h$$

$$\text{Total drift current density is given by } J = J_e + J_h$$

$$J = n_e E (\mu_e + \mu_h)$$

### **Diffusion current:**

The process by which charge carriers in a semiconductor move from a region of higher concentration to a region of lower concentration is called Diffusion. Region having more number of electrons is called higher concentration region and that with less number of electrons is called lower concentration region. Current produced due to the motion of charge carriers from a region of higher concentration to a region of lower concentration is called diffusion current.

The above process occurs in semiconductors that are non-uniformly doped. Let us consider an n-type semiconductor with non-uniform doping. As shown, due to non-uniform doping, more number of electrons are present on the left side, whereas lesser number of electrons are present on the right side.

The number of electrons on the left side is more, as a result of which they will experience a repulsive force from each other; i.e. they tend to move to the right side to achieve uniform concentration of electrons.

Electrons move from left side to right side and thus constitute a current, called Diffusion current.

Both Drift and Diffusion currents occur in semiconductors.

Diffusion current occurs without an external voltage or electric field applied. Drift current occurs on application of an external electric field.

## 2.7 Metal – Semiconductor Junction (Ohmic and Schottky)

Whenever a metal and a semiconductor are in intimate contact, there exists a potential barrier between the two that prevents most charge carriers (electrons or holes) from passing from one to the other.

Only a small number of carriers have enough energy to get over the barrier and cross to the other material. When a bias is applied to the junction, it can have one of two effects: it can make the

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barrier appear lower from the semiconductor side, or it can make it appear higher. The bias does not change the barrier height from the metal side.

The result of this is a Schottky Barrier (rectifying contact), where the junction conducts for one bias polarity, but not the other. Almost all metal-semiconductor junctions will exhibit some of this rectifying behavior.

Schottky Contacts make good diodes, and can even be used to make a kind of transistor, but for getting signals into and out of a semiconductor device, we generally want a contact that is Ohmic. Ohmic contacts conduct the same for both polarities. (They obey Ohm's Law).

There are two ways to make a metal-semiconductor contact look ohmic enough to get signals into and out of a semiconductor (or doing the opposite makes a good Schottky contact).

Lower the barrier height

The barrier height is a property of the materials we use. We try to use materials whose barrier height is small.

Annealing can create an alloy between the semiconductor and the metal at the junction, which can also lower the barrier height.

Make the barrier very narrow

One very interesting property of very tiny particles like electrons and holes is that they can "tunnel" through barriers that they don't have enough energy to just pass over. The probability of tunneling becomes high for extremely thin barriers (in the tens of nanometers).

We make the barrier very narrow by doping it very heavily ( $10^{19}$  dopant atoms/cm<sup>3</sup> or more).

## 3.1 Introduction

Electrons in semiconductors tend to stay in lowest energy state as it is most stable. If additional energy is supplied to electrons by heating, light, or electron beams, it absorbs these energies and jump(transit) to high energy state.

Such transitions of electrons from lower to higher energy states by absorbing external energy are called excitations.

But higher energy states are unstable therefore to gain stability the electrons in higher energy states transit to lower energy states in certain lifetimes. Such transitions of excited electrons from higher energy states to lower energy states are called relaxations.

In semiconductors, transitions of electrons from higher energy states to lower energy states is also called electron hole recombination.

During relaxation electrons release additional energy in form of light or heat.

Therefore electron hole recombinations are of two types : radiative recombination's and non- radiative recombinations.

Radiative recombinations emit photons and energies of photons correspond to a difference in the energies between initial and final energy states related to the transitions.

In contrast, in the non-radiative recombination, phonons are emitted to crystal lattices or electrons are trapped in the defects, and the transition energy is transformed into forms other than light. However, our discussion in this chapter will be focused on transitions with involvement of light.

## 3.2 Interaction of light with semiconductor

Different mechanisms in which absorption and emission of light/photons takes place in a semiconductor are as follows:

### 3.2.1 Band to band (inter band) transitions

In this process incident photon is absorbed in the semiconductor material. Energy of incident photon is transferred to the electron in the valence band of semiconductor. This lead to an upward transition of electron from valence band to conduction band, thereby creating an electron hole pair.

Inverse of this process is also called inter band transition in which electron hole recombination results in the emission of a photon.

Band to band transition may be assisted by one or more phonons. A phonon is a quantum of the lattice vibrations that results from thermal vibrations of the atoms in the material.

### 3.2.2 Impurity to band transitions.

In this process, an absorbed photon results in a transition between a donor (or acceptor) level and a band in a doped semiconductor. For example, in a p type material, a low energy photon can transit an electron from valence band to the acceptor level, where it becomes trapped by an acceptor atom.

As a result, hole is created in the valence band and the acceptor atom is ionized. Again, the inverse process is called impurity to band transition in which electron decays from the acceptor level to recombine with the hole. In such transition energy may be released radiatively (in form of emitted photon) or non-radiative (in form of phonons).

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The transition may also be assisted by traps in defect states.

### 3.2.3 Free carrier (intra band) transitions.

In this process, an absorbed photon imparts its energy to an electron in the given band, causing it to move higher within the band. For example, an electron in the conduction band, absorbs a photon and move to a higher energy level within the conduction band. Such process generally results in thermalization of the electrons. (A process in which an electron relaxes down to the bottom of the conduction band by releasing its energy in form of lattice vibrations).

### 3.2.4 Phonon transitions.

In this process, low energy (long wavelength) photons absorbed in semiconductor imparts their energy to produce lattice vibrations. i.e., by creating phonons.

### 3.2.5 Excitonic transitions.

In this process absorption of a photon results in the formation of an electron and a hole at some distance from each other but bound together by their mutual Coulomb interaction. This entity, which is much like a hydrogen atom but with a hole rather than a proton, is called exciton. Recombination of such electron and hole is often called annihilation of exciton, which results in emission of photons.

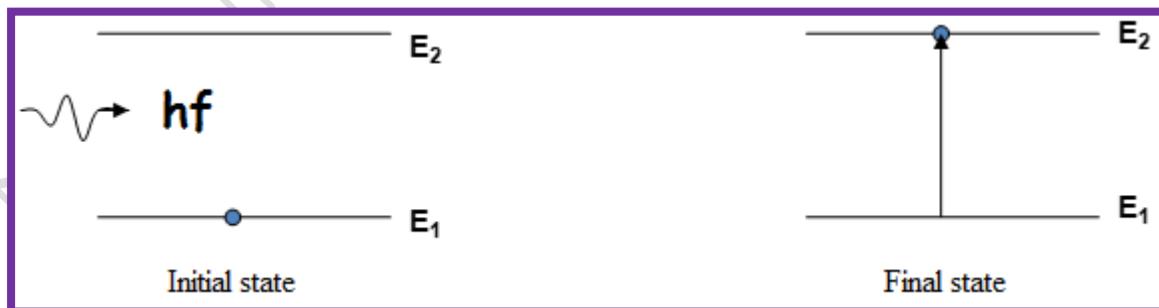
## 3.3 Optical transitions in bulk semiconductors

According to Einstein, whenever there is interaction between radiation and matter, there can be three main processes than can occur. One is absorption and other two are emissions.

### 3.3.1 Induced absorption

An atom has infinite number of quantized energy states. Initially an atom is in the ground state, i.e. all of its electrons possess the lowest possible energy states. If an atom transits from ground state (lowest energy level) to higher energy level by absorbing energy of incident photons then the process is called absorption (induced absorption or stimulated absorption).

**For absorption:** Atom + Photon  $\rightarrow$  Atom\*.

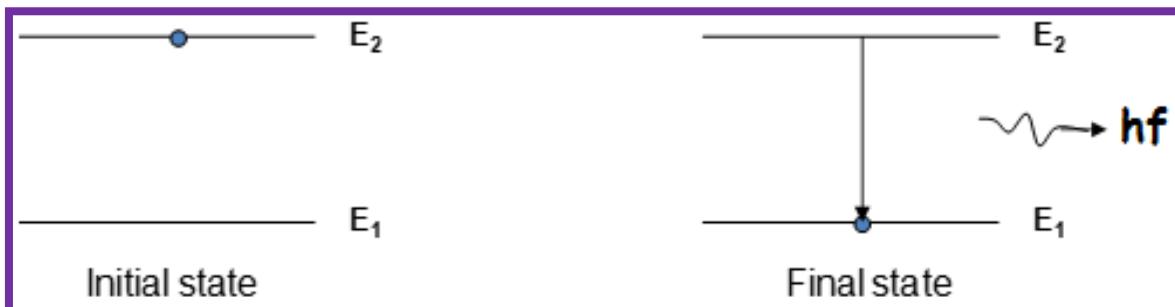


If  $E_1$  and  $E_2$  are the energies of an electron in the initial and final states respectively and  $f$  the frequency of absorbed radiation, then  $E_2 - E_1 = hf$  or  $f = (E_2 - E_1)/h$ , where  $h$  is Planck's constant. The rate of absorption depends on the properties of states 1 and 2 and is proportional to the photon density ( $\rho$ ) and to the number of atoms per unit volume  $N_1$  in the ground state. Thus  $R_{12} \propto N_1 \rho$  OR  $R_{12} = B_{12} N_1 \rho$ , where  $B_{12}$  is called the (probability of absorption per unit time) Einstein's coefficient for absorption of radiation.

### 3.3.2 Spontaneous emission (Natural emission)

The process of emission of photons when an atom transits from higher energy level to lower energy level without use of external agency (source) is called spontaneous emission.

**For spontaneous emission:** Atom\*  $\rightarrow$  Atom + Photon.

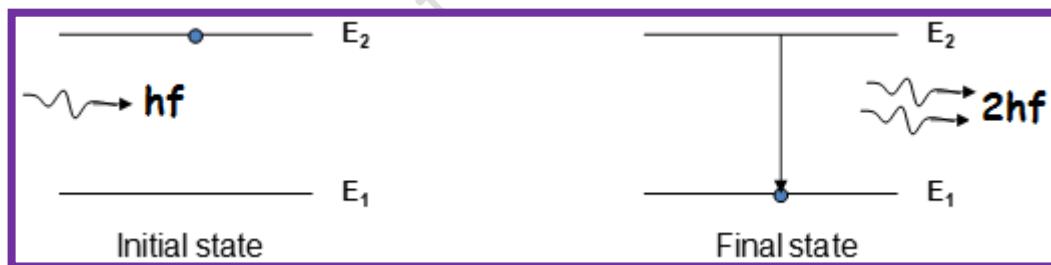


If  $E_1$  and  $E_2$  are the energies of an electron in the initial and final states respectively and  $f$  the frequency of emitted photons, then  $E_2 - E_1 = hf$  or  $f = (E_2 - E_1)/h$ , where  $h$  is Planck's constant. The rate of spontaneous emission is proportional to the number of atoms per unit volume in the excited state, i.e.  $R_{21(sp)} \propto N_2$  or  $R_{21(sp)} = A_{21}N_2$ , where  $A_{21}$  is called the (probability of spontaneous emission per unit time) Einstein's coefficient of spontaneous emission of radiation.

### 3.3.3 Stimulated emission (Forced emission)

The process of emission of photons when an atom transits from higher energy level to lower energy level, with use of external agency (source) is called stimulated emission. (When the atom is in the excited state, then an incident photon of correct energy may cause the atom to transit to lower energy state, emitting an additional photon of the same frequency. Thus, now two photons of the same frequency are present.)

**For stimulated emission:** Atom\* + Photon  $\rightarrow$  Atom + Photon + Photon



If  $E_1$  and  $E_2$  are the energies of an electron in the initial and final states respectively and  $f$  the frequency of emitted photons, then  $E_2 - E_1 = hf$  or  $f = (E_2 - E_1)/h$ , where  $h$  is Planck's constant. The rate of stimulated emission depends both on the external radiation and on the number of atoms per unit volume in the upper level  $E_2$ , i.e.  $R_{21(st)} \propto N_2\rho$  or  $R_{21(st)} = B_{21}N_2\rho$ , where  $B_{21}$  is called the (probability of stimulated emission per unit time) Einstein's coefficient of stimulated emission of radiation.

### 3.3.4 Difference between Spontaneous and Stimulated Emission

Sr. No.	Spontaneous Emission	Stimulated Emission
1.	Definition	Definition
2.	$R_{21(sp)} = A_{21}N_2$	$R_{21(st)} = B_{21}N_2\rho$
3.	It is natural emission.	It is forced emission.

Sr. No.	Spontaneous Emission	Stimulated Emission
4.	It is a random process.	It is not a random process.
5.	Emission takes place in all directions.	Emission takes place in specific direction.
6.	Intensity is low.	Intensity is high.
7.	Polychromatic light is emitted	Monochromatic light is emitted.
8.	Photons will not be multiplied by chain reaction.	Photons will be multiplied by chain reaction.
9.	It is uncontrollable process.	It is a controllable process.

### 3.4 Density of states for photons/Joint density of states

We know that density of states defines the number of allowed energy states per unit volume.

To know or find the number of transitions or emissions we need to know the emissions per unit volume.

This can also give an idea of the power emitted.

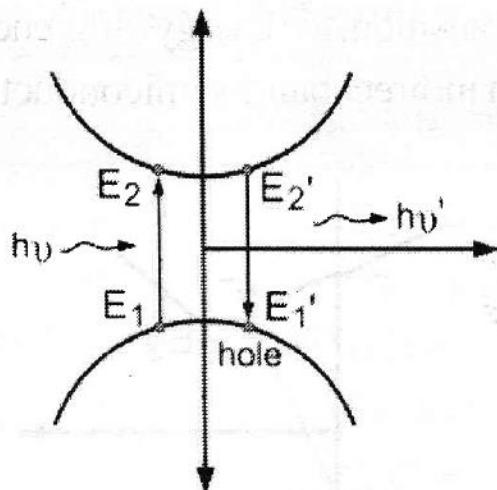
The number of emissions per unit volume can be found by multiplying density of states and probability of occupations.

Concentration of electrons in conduction band is given by

$$n_e = \int f(E) \cdot \rho_c(E) dE$$

Concentration of holes in valence band is given by

$$n_h = \int [1 - f(E)] \cdot \rho_v(E) dE$$



Suppose a radiation of energy ' $h\nu$ ' is incident on an electron sitting at certain level in valence band  $E_1$ , it makes a transition to a vacant state in conduction band  $E_2$ .

This means that absorption involves a certain energy level in valence and a corresponding vacant level in conduction band.

Similarly, if there is an electron at certain energy level  $E_2$  in conduction band and it makes a transition at a vacant level  $E_1$  in valance band, a photon with energy 'hf' is emitted.

We can thus say that absorption and emission involve a state in valance band and conduction band.

For a photon interaction, we have one state in valence band and one state in conduction band and so we define joint density of states that takes care of number of states for a given energy 'hf'.

For a fixed incident energy 'hf', if  $E_2$  is fixed then  $E_1$  will also be fixed.

For a given energy 'hf' there are several pairs of  $E_2 - E_1$  and so there are number of pairs of states available for a photon of energy 'hf' to interact and this is given by density of states.

Since the absorption or emission takes place from the top of valence band and bottom of conduction band respectively, we can have a parabolic approximation for any level in conduction and valance band resp.

$$E_2 = E_c + \frac{\hbar^2 k^2}{2m_c} \quad \text{--- --- --- --- --- 1}$$

$$E_1 = E_v - \frac{\hbar^2 k^2}{2m_v} \quad \text{--- --- --- --- --- 2}$$

The energy of photon 'hf' is given by  $hf = E_2 - E_1$

$$hf = E_c + \frac{\hbar^2 k^2}{2m_c} - E_v + \frac{\hbar^2 k^2}{2m_v}$$

$$hf = E_c - E_v + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_c} + \frac{1}{m_v} \right)$$

$$hf = E_g + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_r} \right)$$

where  $E_g$  is energy gap and  $m_r$  is reduced mass

$$k^2 = (hf - E_g) \left( \frac{2m_r}{\hbar^2} \right)$$

## Using 3 in 1 and 2

$$E_2 = E_c + \frac{\hbar^2}{2m_c} (hf - E_g) \left( \frac{2m_r}{\hbar^2} \right)$$

$$E_2 = E_c + \left( \frac{m_r}{m_c} \right) (hf - E_g) \quad \text{--- --- --- --- --- 4}$$

In above equation only  $E_2$  and  $f$  are variables and all others are constants.

$$E_1 = E_v - \frac{\hbar^2}{2m_r} (hf - E_g) \left( \frac{2m_r}{\hbar^2} \right)$$

$$E_1 = E_v - \left( \frac{m_r}{m_v} \right) (hf - E_g) \quad \text{--- --- --- --- --- 5}$$

In above equation only  $E_1$  and  $f$  are variables and all others are constants.

As there is a one-one correspondence between ' $E_2$ ' and ' $f'$ ' and also between ' $E_1$ ' and ' $f'$ ', so we have

$$\rho_c(E_2)dE_2 = \rho(f)df$$

where  $\rho(f)df$  is the number of states per unit volume available for photons of energy between  $hf$  and  $h(f+df)$  to interact (either absorb or emit).

Once we find out  $\rho(f)df$ , i.e., density of states available for interaction and multiply it by probability of emission or absorption, we can obtain total number of emission or absorption per unit volume.

## Using 6

$$\rho(f) = \rho_c(E_2) \frac{dE_2}{df} \quad \text{--- --- --- --- --- 7}$$

Using equation 4, i.e.,

$$E_2 = E_c + \left( \frac{m_r}{m_c} \right) (hf - E_g)$$

$$\frac{dE_2}{df} = \left(\frac{m_r}{m_c}\right) h \quad \text{----- 8}$$

Using equation 8 and  $\rho(E)dE = \frac{8\pi\sqrt{2m^3}}{h^3}\sqrt{E}dE = 4\pi\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}dE$  in 7 we get

$$\rho(f) = 4\pi \left(\frac{2m_c}{h^2}\right)^{3/2} (E_2 - E_c)^{1/2} \left(\frac{m_r}{m_c}\right) h \quad - - - - - 9$$

From equation 4 we get

$$(E_2 - E_c)^{1/2} = \left( \frac{m_r}{m_c} \right)^{1/2} (hf - E_g)^{1/2}$$

Using above in equation 9

$$\rho(f) = 4\pi \left(\frac{2m_c}{h^2}\right)^{3/2} \left(\frac{m_r}{m_c}\right)^{1/2} \left(hf - E_g\right)^{1/2} \left(\frac{m_r}{m_c}\right) h$$

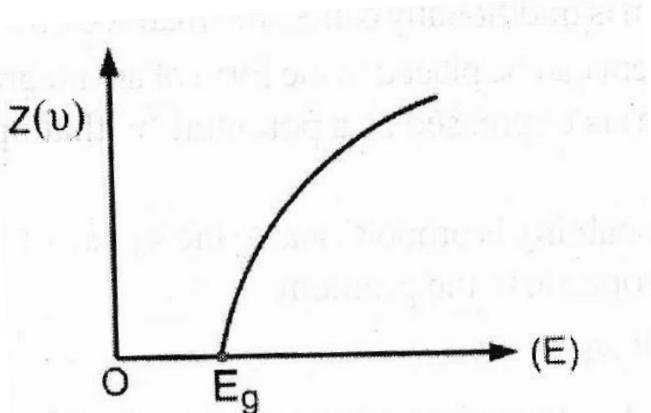
$$\rho(f) = \frac{4\pi h}{h^3} (2m_r)^{3/2} (hf - E_g)^{1/2}$$

$$\rho(f) = \frac{4\pi}{\hbar^2} (2m_r)^{3/2} (hf - E_g)^{1/2} = \rho(f) = \frac{1}{\pi\hbar^2} (2m_r)^{3/2} (hf - E_g)^{1/2} \quad \dots \quad 10$$

This is expression for optical joint density of states.

For band to band or inter band transitions it is required that  $h\nu > E_g$ .

The plot of  $\rho(f) \rightarrow E$  is as below.



As per graph, for every  $hf > E_g$ , we will have inter band transitions (emission or absorption)

## 3.5 Transition rates (Fermi golden rule)

In quantum physics, Fermi's golden rule is used to calculate transition rates.

The transition rate depends upon the strength of coupling between the initial and final state of a system and upon the number of ways the transition can happen (joint density of states)

The transition probability is given by

$$\lambda_{if} = \frac{2\pi}{\hbar} |M_{if}|^2 \rho_f$$

Where  $\lambda_{if}$  is transition probability,  $|M_{if}|^2$  is matrix element for interaction and  $\rho_f$  is joint density of final state.

The above equation is known as fermi's golden rule.

The transition probability  $\lambda$  is called the decay probability and is related to mean lifetime  $\tau$  of the state.

$$\lambda = \frac{1}{\tau}$$

The general form of fermi's golden rule can be applied to atomic transitions. Nuclear decay and scattering.

The transition can proceed more rapidly if coupling between initial and final states is stronger.

This coupling term is traditionally called the matrix element for the transition.

This matrix element can be placed in the form of an integral, where the interaction (that causes transition) is expressed as a potential  $V$  that operates on initial state wave function.

The transition probability is proportional to the square of integral of interaction over all of the space appropriate to the problem.

$$M_{if} = \int \psi_f^* \cdot V \psi_i df$$

Where  $V$  is operator for physical interaction that couples initial and final states,  $\psi_f^*$  is wave function for final state and  $\psi_i$  is wave function for initial state.

The transition probability is also proportional to the joint density of states.

## 3.6 Optical gain and optical loss

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## 3.7 Photovoltaic effect

The effect due to which light energy is converted into electrical energy is called photovoltaic effect.

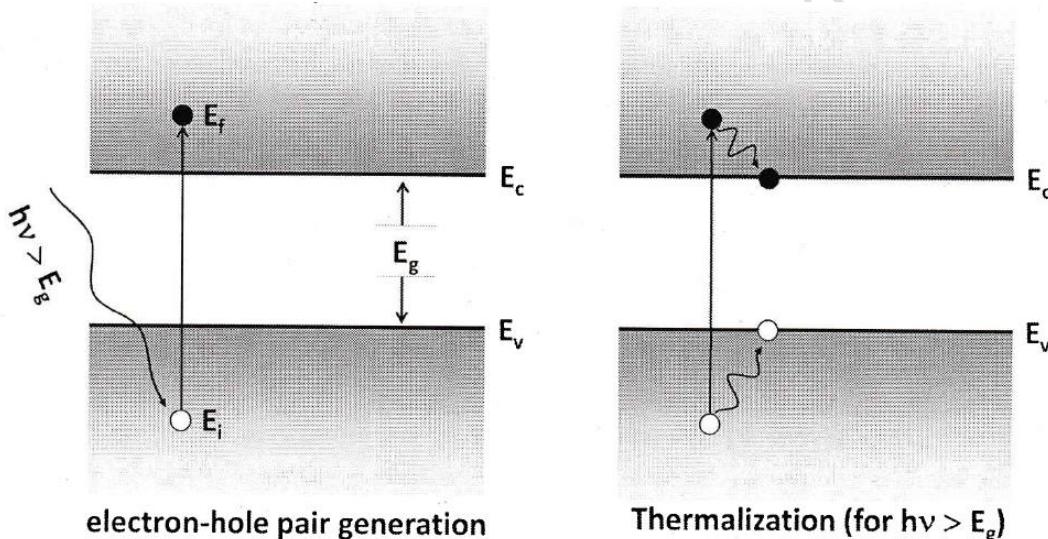
It was first discovered by Edmund Becquerel in 1839.

The photovoltaic effect can be divided into three basic processes:

## Module 3 - Light-semiconductor interaction

### 3.6.1. Generation of charge carriers due to the absorption of photons in the materials that form a junction.

Absorption of a photon in a material transfers the energy of photon to electron of the material. This excites an electron from an initial energy level  $E_i$  to a higher energy level  $E_f$ , as shown in Fig. Photons can only be absorbed if electron energy levels  $E_i$  and  $E_f$  are present so that their difference equals the photon energy,  $h\nu : E_f - E_i$ . In an ideal semiconductor, electrons can exist in energy levels below the valence band edge  $E_v$ , and above the conduction band edge  $E_c$ . Between those two bands there is no allowed energy state. This energy difference is called the band gap,  $E_g = E_c - E_v$ . If a photon with energy less than  $E_g$  is incident on an ideal semiconductor, it will not be absorbed but will pass through the material without interaction. In a real semiconductor, the valence and conduction bands are not flat, but vary with k-vector that describes the momentum of an electron in the semiconductor. If valence band maxima and conduction band minima occur at the same k-vector, an electron can be excited from the valence to the conduction band without a change in the momentum. Such a semiconductor is called a direct band gap semiconductor. If the electron cannot be excited without changing its momentum, it is called indirect band gap semiconductor. The electron can only change its momentum by momentum exchange with the crystal, i.e. by receiving momentum from or giving momentum to vibrations of the crystal lattice.



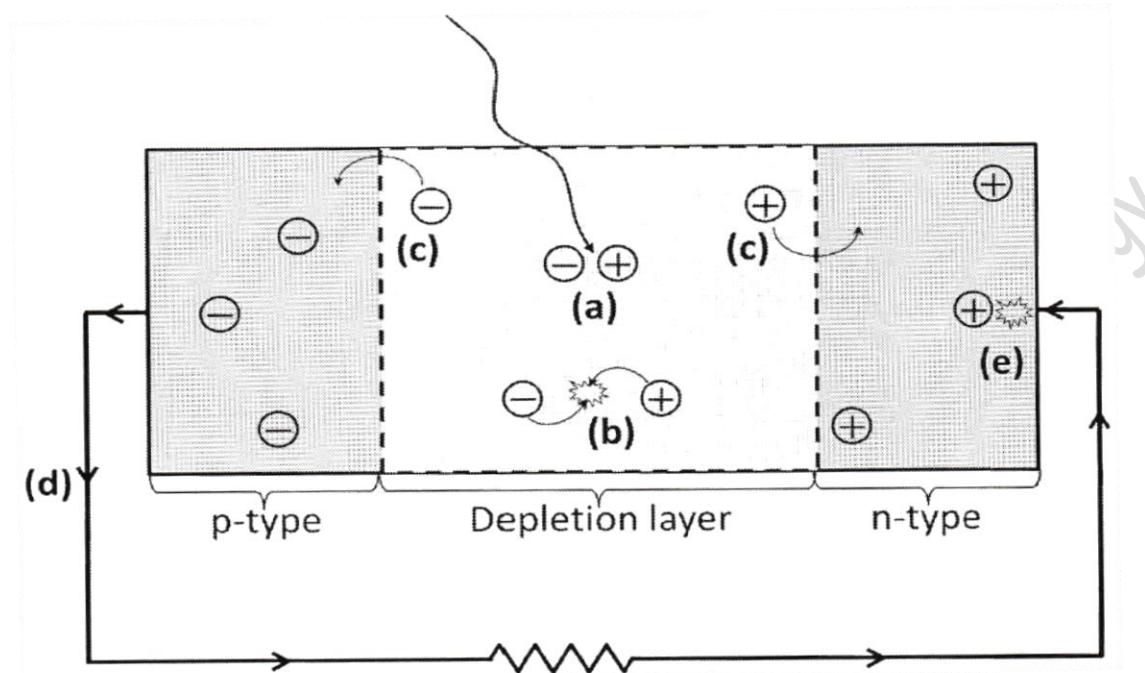
If an electron is excited from  $E_i$  and  $E_f$ , a void is created at  $E_i$ . This void behaves like a particle with a positive elementary charge and is called a hole. The absorption of a photon therefore leads to the creation of an electron-hole pair, as illustrated in Fig. If energy of incident photon is more than band gap of material, additional energy mostly gets consumed in Thermalization of carriers through intra-band transitions.

### 3.6.2. Subsequent separation of the photo-generated charge carriers in the junction.

Usually, the electron-hole pair will recombine, i.e. the electron will fall back to the initial energy level  $E_i$ , as illustrated in Figure. The energy will then be released either as photon (radiative recombination) or transferred to other electrons or holes or lattice vibration (non radiative recombination). If one wants to use the energy stored in the electron-hole pair for performing work in an external circuit, semi-permeable membranes must be present on both sides of the absorber, such that electrons only can flow out through one membrane and holes only can flow out through the other membrane, as illustrated in Figure. In most solar cells, these membranes are formed by n-type and p-type materials.

## Module 3 - Light-semiconductor interaction

A solar cell has to be designed such that the electrons and holes can reach the membranes before they recombine, i.e. the time it requires the charge carriers to reach the membranes must be shorter than their lifetime. Such arrangement can be made by creating a p-n junction, in which internal field of depletion region push the photo generated electrons towards n-type material and photons towards p-type material.



Typical mechanism involved in photo-voltaic effect: (a) electron-hole pair generation by incident photon of sufficient energy, (b) electron hole recombination, (c) separation of charge carriers, (d) electron travelling through external circuit and (e) recombination of electrons on completion of circuit with holes at metal-semiconductor interface.

### 3.6.3. Collection of the photo-generated charge carriers at the terminals of the junction.

Finally, the charge carriers are extracted from the solar cells with electrical contacts made on both side of junction, so that they travel through an external circuit. In this way, light energy gets converted to electric energy. After the passing through the circuit, electrons will recombine with holes at a metal-semiconductor interface.

## 3.8 Solar cell/Photovoltaic cell

Solar cell is the device that converts sunlight into electrical energy. It operates on the principle of photovoltaic action i.e. voltage generating capability. Since the voltage, they generate is proportional to the intensity of the sunlight, they are also called photovoltaic cells. They provide electrical energy with high efficiency of conversion and can provide nearly permanent power at low operating cost, and free of pollution. The efficiency of a solar cell depends on the band gap of the semiconductor materials.

### 3.7.1. Construction of solar cell.

It is a simple type of p-n junction made from semiconductor materials like silicon.

A thin layer of n-type material is diffused with p-type material, forming a simple p-n junction.

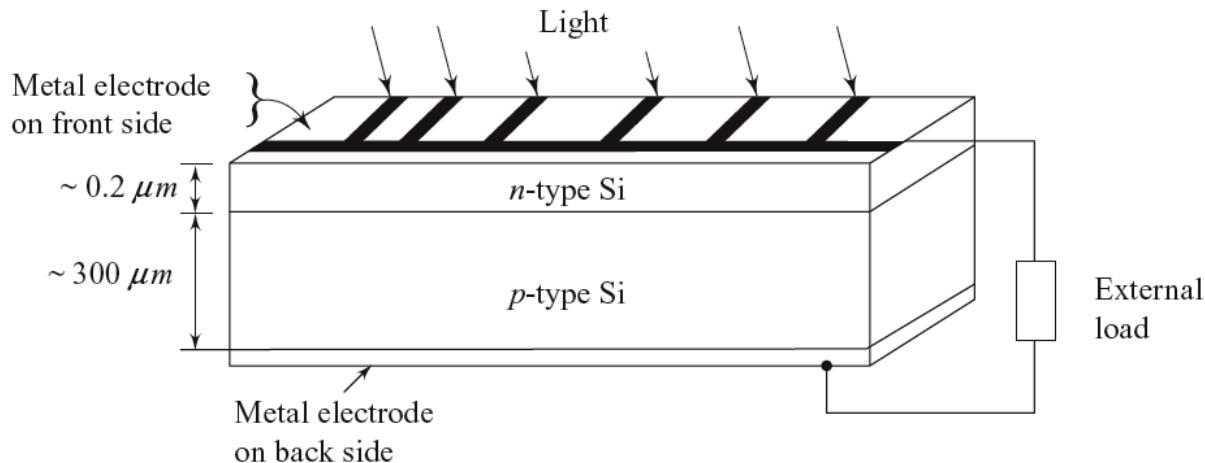
The thickness of n-layer is very small

## Module 3 - Light-semiconductor interaction

As seen in the figure, the upper surface of the solar cell is made by thin layer of n-type material, for the light to reach the junction easily.

To enhance the absorption of light by the material, there is an anti-reflection coating on the top of n-type material.

Metal contacts are made on the both type of material which act as positive and negative terminal respectively.



### 3.7.2. Working

When sunlight is incident on a solar cell, the electrons in the valence band gain energy and are excited to conduction band, thereby creating electron hole pairs. The electron hole pairs are generated, provided the incident photons has an energy greater than band gap energy.

The minority carriers i.e., electrons in p-type and holes in n-type, exist for a short time before recombination. If the carriers recombine electron hole pairs are lost and no current is generated.

The p-n junction prevents this recombination due to the internal electric field.

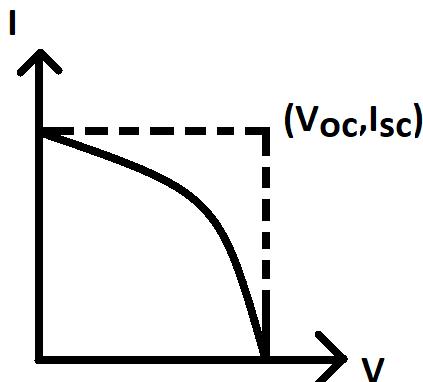
When these light generated electron hole pair reach the p-n junction, they are swept across the junction holes toward p-type and electrons towards n-type.

If the solar cell is connected through load, current starts flowing.

Thus, solar cell behaves as a battery with N-side as the negative terminal and P-side as positive terminal.

### 3.7.3. Parameters of solar cell.

The VI characteristics can be studied with the help of below diagram.



The output voltage from solar cell when load impedance is very high (i.e., infinite) is called open circuit voltage ( $V_{oc}$ ).

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The current output when the load impedance is very small (i.e., zero) is called the short circuit current ( $I_{sc}$ ).

The product of open circuit voltage and short circuit current gives the ideal power output from the solar cell. i.e.,  $P_{max} = I_{sc}V_{oc}$ .

But the actual power output is less than the ideal output power and is given by  $P_{max} = I_m V_m$

### 3.7.3.1. Efficiency of a Solar Cell

It is defined as the ratio of the total power converted by the solar cell to the total solar power available for energy conversion.

$$\eta = \frac{P_{max}}{\text{incident light power}}$$

Fill factor

### 3.7.3.2. Fill factor

The fill factor of solar cell is found to be 0.65 to 0.8

$$\text{Fill factor, } f = \frac{\text{Maximum output power}}{\text{ideal output power}}$$

## 3.7.4. Applications

Telecommunication photovoltaic systems are difficult to access at areas like mountain tops, islands and deserts

To prevent corrosion of pipelines, bridges, etc., a small direct current is impressed on the structures at regular intervals

PV systems are also used to power railway signals, alarm systems, fog, fire and flood hazard warnings, traffic lights and highway telephones

Mobile telephone, remote instrumentation, remote radar, water purifier, etc., are powered by PV systems

Remote radio and light beacons are powered by PV systems.

Interval of time, meteorological stations are powered by PV systems.

To provide electric power to remote villages and to power refrigerators at community health centres for keeping vaccines at low temperatures.

Some consumer products, such as pocket calculators, watches, torches, garden lights, portable fans for cars and houses, radios, toys, electric fences, etc., are powered by PV solar systems.

## 3.7.5. Merits

Cost is less

Process is free from pollution.

## 3.7.6. Demerits

Input energy is not always constant.

Efficiency is low

Requires large area for installation.

Various materials used for solar cells show varying efficiencies and have varying costs. Semiconductor materials like silicon, gallium arsenide, indium arsenide, cadmium arsenide, copper indium selenide are used for manufacturing solar cells.

Cadmium Telluride Solar cells: It uses thin film of cadmium telluride, a semiconductor layer to absorb and convert sunlight into electricity.

Copper Indium Gallium Selenide Solar Cells: It is a direct bandgap material with highest efficiency (~20%) among thin film materials.

Gallium Arsenide Multi-Junction Solar Cells: High efficiency multi-junction cells were originally developed for special applications such as satellites and space exploration. GaAs based multi-junction devices are the most efficient solar cells to date.

Organic/Polymer Solar Cells

Indium Gallium Nitride Solar Cells

Quantum Dot Solar Cell}}

## 3.9 Exciton

The concept of excitons was first proposed by Yakov Frenkel in 1931.

The absorption of a photon by an inter band transition in a semiconductor creates an electron in conduction band and a hole in valence band.

These oppositely charged particles attract each other through Coulomb interaction and there may be a probability of formation of a neutral electron hole pair called exciton.

An exciton is a bound state of an electron and hole which are attracted to each other by an electrostatic force.

When the photon is absorbed by a semiconductor, an electron hole pair is created. The electron in the conduction band is now attracted to the localized hole by repulsive Coulomb forces from the large number of electrons surrounding the hole and excited electrons. This attraction provides a stabilizing energy balance.

Two basic types:

### 3.8.1. Wannier – Mott excitons (free exciton):

When the electron hole separation is much larger to the lattice constant, then the exciton is called Wannier-Mott exciton.

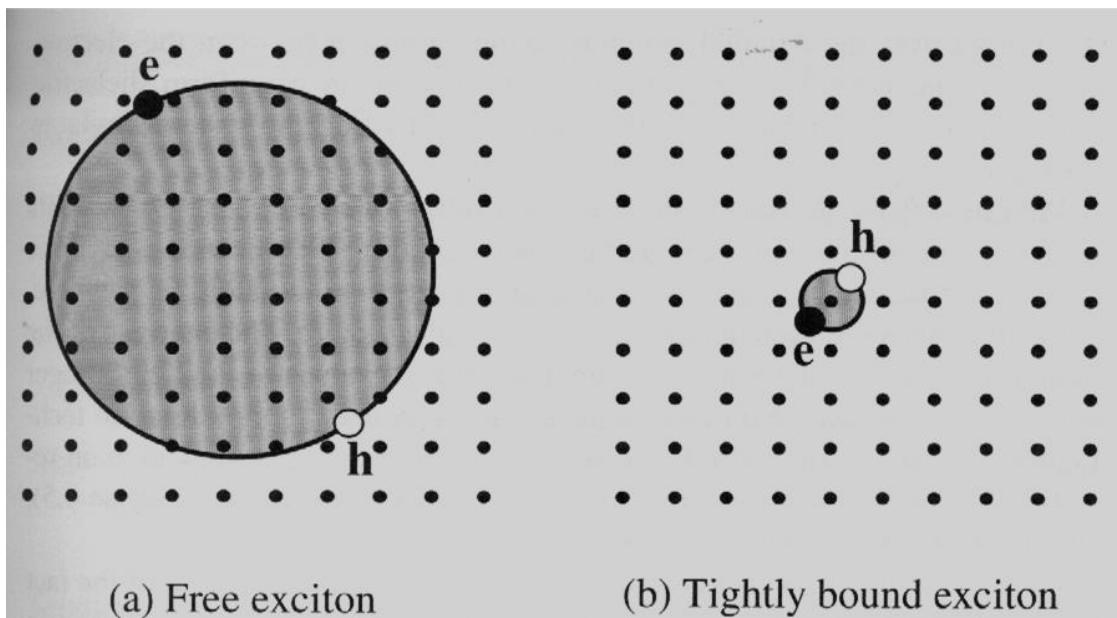
In this, the electron hole pair is weakly bound.

Mainly exist in semiconductors, have a large radius, are delocalized states that can move freely throughout the crystal, the binding energy  $\sim 0.01$  eV; stable at cryogenic temperature.

### 3.8.2. Frenkel excitons (tight bound excitons):

When there is a strong electron hole attraction, like in ionic crystals, the electrons and holes are tightly bound to each other, this type of exciton is called Frenkel exciton.

Found in insulator and molecular crystals, bound to specific atoms or molecules and have to move by hopping from one atom to another, the binding energy  $\sim 0.1$  - $1$  eV. stable at room temperature.



## 3.10 Drude model

The Drude model was proposed in 1900 by Paul Drude to explain the transport properties of electrons in materials.

The free electron theory aims to explain structure and properties of solids by their electronic structure.

They consider valence electrons to form an electron gas surrounding the ion cores and are free to move anywhere in the metals.

If we apply electric field then force on electron is given by

$$m \frac{dv}{dt} = -qE$$

Also, we have  $J = -nqv$

From above equations, we can say that as  $v$  changes with time so  $J$  will also change with time.

But it is not true in practice ( $J = \sigma E$ )

So we get,

$$m \frac{dv}{dt} + \gamma v = -qE$$

$$\gamma v_{sat} = -qE$$

$$v_{sat} = \frac{-qE}{\gamma}$$

$$J = -\frac{nq^2 E}{\gamma}$$

Where  $\gamma$  could be lattice atoms, impurities, grain boundaries or anything that give imperfection to lattice

### 3.9.1. Basic assumptions of Drude model

Between the collisions, the electrons move in a straight line in absence of electromagnetic field.

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The effect of electron-electron and electron-ion interaction is ignored.

Mean free time between collisions is  $\tau$ . It is independent of electrons position and velocity.

Electrons achieve thermal equilibrium by collisions with lattice.

After the collisions, they move in random directions with a speed that depends on the temperature of the region where collision occurred i.e., hotter the region higher is the speed of emerging electrons.

## 3.9.2. Applications of Drude model

### 3.9.2.1. DC electrical conductivity of metal

In absence of electric field average velocity of electrons is zero.

In presence of external electric field suppose velocity of an electron after collision is  $v_0$ .

In time  $t$  after collision velocity changes by  $-\frac{eE}{m}t$ .

As electron is moving randomly after collisions so we should take the average velocity.

Since average of this time  $t$  is  $\tau$ , we have  $v_{avg} = -\frac{eE}{m_e}\tau$

{Velocity of electron when electric field is applied is given by}

$$v = v_0 + at$$

$$\langle v \rangle = \langle v_0 \rangle - \left( \frac{eE}{m} \tau \right)$$

$$v = -\frac{eE}{m} \tau \quad ----- 3$$

As  $\langle v_0 \rangle = 0$  as it is initial velocity which is random.}}

We know  $J = -nev_{avg}$

$$J = ne \frac{eE}{m_e} \tau$$

$$J = \frac{ne^2 E \tau}{m_e}$$

Using  $J = \sigma E$  in above we get

$$\sigma E = \frac{ne^2 E \tau}{m_e}$$

$$\sigma = \frac{ne^2 \tau}{m_e}$$

This is the expression for DC conductivity in Drude Model.

### 3.9.2.2. General equation of motion under the effect of force $f(t)$

Momentum at any time  $t$  is  $p(t)$ . Two things can happen in the next time interval  $dt$ :

a. They can undergo collision with probability  $dt/\tau$ ; lose all momentum and emerge with a random momentum  $f(t)dt$ .

b. They do not undergo collision with probability  $(1 - dt/\tau)$  after time  $dt$  their momentum is  $p(t) + f(t)dt$ .

## Module 3 - Light-semiconductor interaction

Thus, the net momentum at time  $t + dt$  is:  $p(t + dt) = (1-dt/\tau) \{p(t) + f(t)dt\} + \text{random component} + f(t)(dt)^2/\tau$ .

Neglecting higher order term in  $dt$  we get,

$$p(t + dt) - p(t) = -p(t)dt/\tau + f(t)dt.$$

Dividing with  $dt$

$$\frac{dp(t)}{dt} = -\frac{p(t)}{\tau} + f(t)$$

$$\frac{dp(t)}{dt} + \frac{p(t)}{\tau} = f(t)$$

Collision acts as friction; dampens the motion of the electrons.

### 3.9.2.3. Hall Effect and magnetoresistance

Current density  $J_x$ , magnetic field  $B_z$ , Lorentz force  $ev \times B$  same on +ve and -ve charges; hence they move on the same side; Hall voltage has different sign for the two types of carriers. Can measure two quantities:

a. magnetoresistance,  $\rho(H) = E_x/J_x$

b. Hall coefficient,  $R_H = E_y/J_x B_z$

Hall co-efficient can determine the sign of the charge carriers – sometimes it was found to be +ve; not explained by Drude theory.

Equations of motion with  $B_z$ :

$$\frac{dp(t)}{dt} + \frac{p(t)}{\tau} = -e \left( E + \frac{p \times B}{m} \right) \Rightarrow \frac{dp(t)}{dt} = -e \left( E + \frac{p \times B}{m} \right) - \frac{p(t)}{\tau}$$

In steady state the current is independent of time and therefore  $p_x$  and  $p_y$  will satisfy

$$0 = -eE_x - \omega p_y - \frac{p_x}{\tau}$$

$$0 = -eE_y + \omega p_x - \frac{p_y}{\tau}, \text{ where } \omega = \frac{eB}{m}$$

Multiplying by  $\frac{n e \tau}{m}$  and  $J = n e v$ , we get

$$\sigma_0 E_x = \omega \tau J_y + J_x$$

$$\sigma_0 E_y = -\omega \tau J_x + J_y$$

In steady state  $J_y = 0$ , so we get

$$\sigma_0 E_y = -\omega \tau J_x \Rightarrow E_y = -\frac{\omega \tau J_x}{\sigma_0}$$

$$E_y = -\frac{\frac{eB}{m} \tau J_x}{\frac{ne^2 \tau}{m}} = -\frac{B}{ne} J_x$$

$$R_H = -\frac{1}{ne}$$

### 3.9.2.4. AC electrical conductivity

Equation of motion

$$\frac{dp(t)}{dt} = -eE - \frac{p(t)}{\tau}$$

$$p(t) = Re(p(\omega)e^{-i\omega t})$$

Steady state solution

$$-i\omega p(\omega) = -\frac{p(\omega)}{\tau} - eE(\omega)$$

$$\frac{p(\omega)}{\tau} - i\omega p(\omega) = -eE(\omega)$$

$$\left(\frac{1}{\tau} - i\omega\right)p(\omega) = -eE(\omega)$$

$$p(\omega) = -\frac{eE(\omega)}{\left(\frac{1}{\tau} - i\omega\right)}$$

$$J(\omega) = -nev = -\frac{nep(\omega)}{m} = \frac{ne}{m} \frac{eE(\omega)}{\left(\frac{1}{\tau} - i\omega\right)}$$

$$J(\omega) = \frac{ne^2\tau E(\omega)}{m(1 - i\omega\tau)}$$

$$J(\omega) = \sigma(\omega)E(\omega)$$

$$\sigma(\omega) = \frac{\sigma_0}{(1 - i\omega\tau)}, \quad \text{where } \sigma_0 \text{ is DC conductivity}$$

Useful for studying em wave propagation.

## 3.11 Question bank

1. Explain optical transitions in bulk semiconductors.
2. Explain Density of states for photons/Joint density of states.
3. Explain Transition rates (Fermi golden rule).
4. Explain optical loss and gain.
5. Explain Photovoltaic effect.
6. Write a note on Solar cell/Photovoltaic cell.
7. Write a note on Exciton.
8. Discuss Drude model.

## 4.1 Introduction

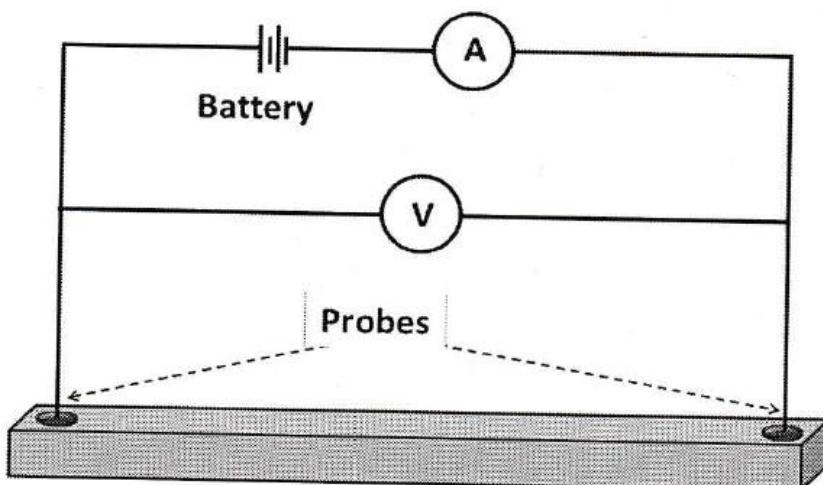
The properties of the bulk material used for the fabrication of transistors and other semiconductor devices are essential in determining the characteristics of the devices. Resistivity, determination of type (n-type or p-type), carrier concentration, carrier life time, band gap etc., measurements are generally made on sample (here our discussion is focused on semiconductors) to determine their suitability for a particular device application.

## 4.2 Two probe method

For a long sample having uniform cross-section, resistivity is generally determined by measuring the potential drop across the sample by passage of known current as shown in figure. Battery supplies current (in through probe 1 and out through probe 2). Let "I" be the current passing through sample. Potential difference between two contacts (probe 1 and probe 2) at the ends of sample is "V". Then the resistance of sample will be  $R=V/I$ .

Now if length of sample is "l" and cross-sectional area is "A" then resistance can be calculated as

$$R = \frac{\rho l}{A}$$



### 4.2.1 Drawback of two probe method

The major problem in such method is error due to contact resistance of measuring leads.

The above method cannot be used for materials having random shapes.

For some type of materials soldering the test leads would be difficult.

In case of semiconductors, the heating of samples due to soldering results in injection of impurities into the materials thereby affecting the intrinsic electrical resistivity.

In case of semiconductors, contacts between metallic probes and semiconducting sample are not ohmic in nature (rather they are of Schottky nature) works as barrier.

## 4.3 Four-point probe method

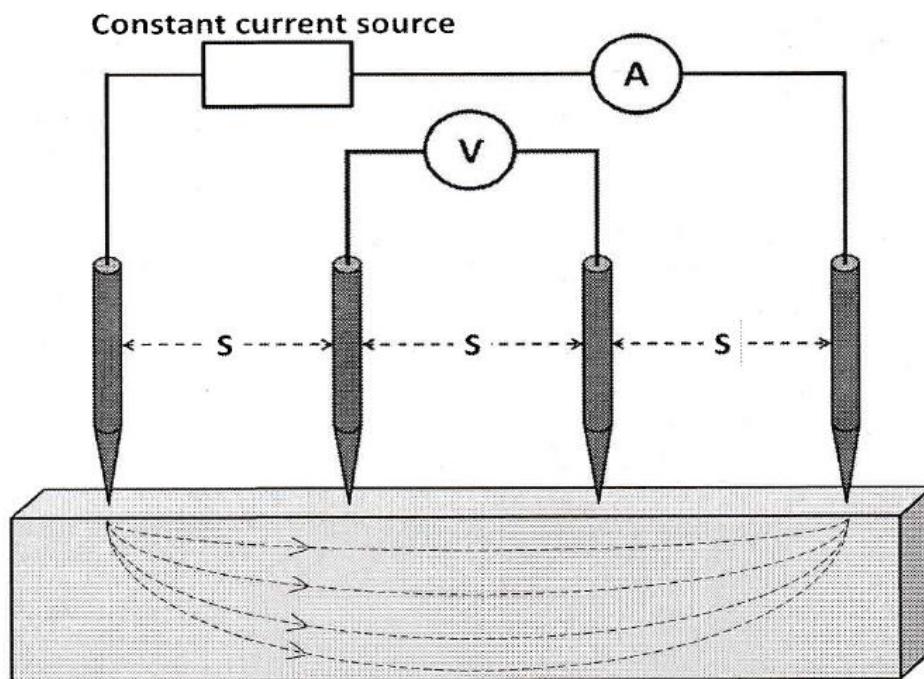
First two problem with two probe method can be eliminated by using four collinear equidistant probes for the measurement of resistivity (known as four probe method). This method provides the measurement of the resistivity of sample having wide variety of shapes but with uniform cross section.

## Module 4 - Measurements

The soldering contacts are replaced by pressure contacts to eliminate the impurity injection by heating while soldering and Schottky barrier between metal probes and semiconducting sample.

It is also known as 4 terminal sensing or 4 wire sensing. It is an electrical impedance measuring technique, that uses separate pairs of current carrying and voltage sensing electrodes to make more accurate measurements.

Four probe arrangement as shown in figure, consists of four equidistant metallic tips having finite radius. Each tip is supported by springs on the end to minimize sample damage during probing. The four metal tips are part of an auto mechanical stage which travels up and down during measurements. A high impedance current source is used to supply current through outer two probes and a voltmeter measures the voltage across inner two probes to determine the sample resistivity. Here inner probes draw no current because of the high input impedance voltmeter in the circuit. Thus unwanted voltage drop at point B and C caused by contact resistance between probes and sample is eliminated.



Fairly accurate measurement of resistivity of semiconductor samples can be achieved under the following conditions:

Resistivity of the material is uniform in the area of measurement.

If there is minority carrier injection into the semiconductor by the current carrying electrodes most of the carriers recombine near the electrodes so that their effect on the conductivity is negligible.

Surface of the sample flat with no surface leakage.

All the four probes touch the sample in a straight line.

Diameter of the contact between the metallic probes and the semiconductor sample should be small compared to the distance between nearby probes.

Boundary between current carrying electrodes and sample is hemispherical and small in diameter.

### 4.3.1 Resistivity measurements of a large sample.

Let us assume that the size of probe tip is very small compared to the lateral dimensions of sample. For such bulk samples where the sample thickness is much larger compared to probe spacing ( $t \gg s$ ), a current emanating from the outer probe tips as shown in the figure can be assumed.

## Module 4 - Measurements

The resistivity is then computed to be

$$\rho_0 = \left(\frac{V}{I}\right) 2\pi s$$

Here V is potential difference between inner probes, I is current passing through outer pair of probes and s is spacing between point probes.

**{we know,**

$$dR = \rho \frac{dx}{A}$$

**Integrating both sides,**

$$R = \int_{x_1}^{x_2} \rho \frac{dx}{A}$$

$$R = \int_{x_1}^{x_2} \rho \frac{dx}{2\pi x^2}$$

Current is injecting through the outer probes it travels outwards from the point of contact through concentric hemispherical shells of equipotential.

$$R = \frac{\rho}{2\pi} \int_{x_1=s}^{x_2=2s} \frac{dx}{x^2}$$

$$R = \frac{\rho}{2\pi} \left[ -\frac{1}{x} \right]_s^{2s}$$

$$R = \frac{\rho}{2\pi} \left( -\frac{1}{2s} + \frac{1}{s} \right)$$

$$R = \frac{\rho}{2\pi} \left( \frac{1}{2s} \right)$$

$$R = \frac{\rho}{4\pi s}$$

Due to super position of current, at the outer two probes, we have

$$R = \frac{V}{2I}$$

**Comparing above two we get,**

$$R = \frac{\rho}{4\pi s} = \frac{V}{2I}$$

$$\rho = 2\pi s \left( \frac{V}{I} \right)$$

This expression applies only to semi-infinite volume and not to thin film.}}

### 4.3.2 Resistivity measurement of a thin sheet ( $t \ll s$ )

For a very thin sample, we get current rings instead of hemispheres. i.e., current travels in short cylindrical shell of equipotential.

So the area will be the area of the cylinder i.e.,  $A = 2\pi t x t$

## Module 4 - Measurements

we know,

$$dR = \rho \frac{dx}{A}$$

$$dR = \rho \frac{dx}{2\pi xt}$$

Integrating both sides,

$$R = \int_{x_1}^{x_2} \rho \frac{dx}{2\pi xt}$$

$$R = \frac{\rho}{2\pi t} \int_{x_1}^{x_2} \frac{dx}{x}$$

$$R = \frac{\rho}{2\pi t} [\ln x]_s^{2s}$$

$$R = \frac{\rho}{2\pi t} [\ln x]_s^{2s}$$

$$R = \frac{\rho}{2\pi t} \ln 2$$

Due to super position of current, at the outer two probes, we have

$$R = \frac{V}{2I}$$

Comparing above two we get,

$$R = \frac{\rho}{2\pi t} \ln 2 = \frac{V}{2I}$$

$$\rho = \frac{\pi t}{\ln 2} \left( \frac{V}{I} \right)$$

$$\rho = 4.53t \left( \frac{V}{I} \right)$$

### 4.4 Van Der Pauw method

The resistivity of the semiconductor material is often determined using a four-probe method. Another common method for determining the resistivity and hall coefficient of a semiconductor material is the van der Pauw method.

The van der Pauw method involves applying a current and measuring voltage using four small contacts on the circumference of a flat, arbitrarily shaped sample of uniform thickness.

This method is particularly useful for measuring very small samples because geometric spacing of the contacts is unimportant. Effects due to a sample's size, which is the approximate probe spacing, are irrelevant.

From the measurement made, the following properties of a material can be calculated

- 1) Resistivity of the material
- 2) Doping type
- 3) Carrier density of majority charge carriers
- 4) Mobility of charges carriers.

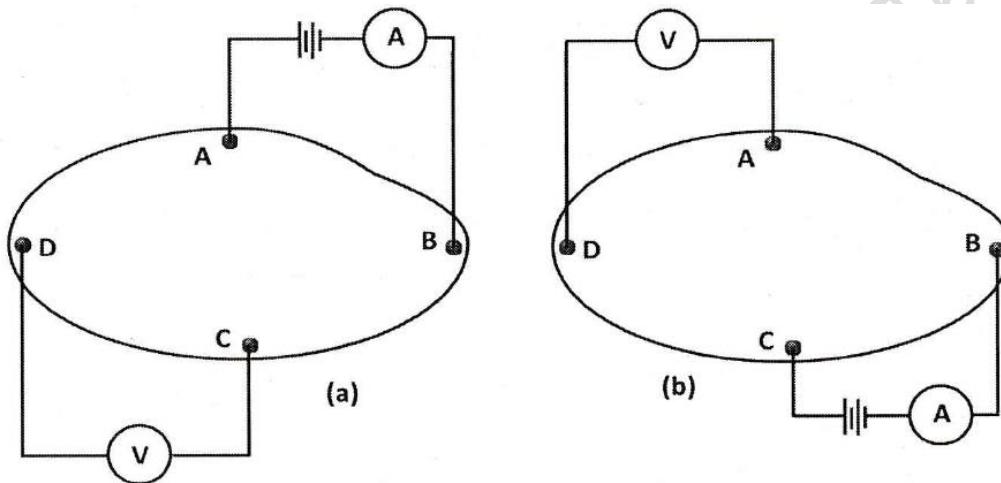
## Module 4 - Measurements

The basic requirements of the method are as under:

- 5) All the contacts should be at the periphery of the sample.
- 6) Size of the contacts should be negligibly small as compared to that of the sample.
- 7) All the contacts should be ohmic.
- 8) Sample should be very thin as compared to its area.
- 9) Surface of the sample should be singly connected i.e. the sample should be free from steps and discontinuities.
- 10) Sample should be flat so that the sample surface and contacts lie in the sample plane.
- 11) Applied field should be low so that breakdown does not occur.

If the contacts are not taken perfectly, the observed results may be associated with some error. This error will be proportional to the dimensions of the contact and can be given as  $\frac{\partial \rho}{\rho} = \frac{d}{D}$ , where d is the size of contact, D is the size of sample,  $\rho$  is the resistivity of sample and  $\partial \rho$  is the change in resistivity.

Figure shows typical circuit diagram used to measure the resistivity of material using Van der Pauw method.



Resistance  $R_1 = R_{AB,CD}$  can be determined by measuring potential difference between points 'D' and 'C' while passing current between points 'A' and 'B'.

$$R_1 = R_{AB,CD} = \frac{V_D - V_C}{I_{AB}}$$

$$R_2 = R_{BC,DA} = \frac{V_A - V_D}{I_{BC}}$$

Van der Pauw showed that in such case following equation holds good.

$$e^{\frac{\pi R_1 t}{\rho}} + e^{\frac{\pi R_2 t}{\rho}} = 1$$

Here, t is thickness of sample and  $t/\rho$  is sheet resistance  $R_s$ .

Simplification of above equation gives,

$$\rho = \frac{\pi t}{\ln 2} \left( \frac{R_1 + R_2}{2} \right) f \left( \frac{R_1}{R_2} \right)$$

Here 'f' is the geometrical correction factor and its value depends on ratio of ' $R_1$ ' and ' $R_2$ '.

'f' can be calculated from the following formula

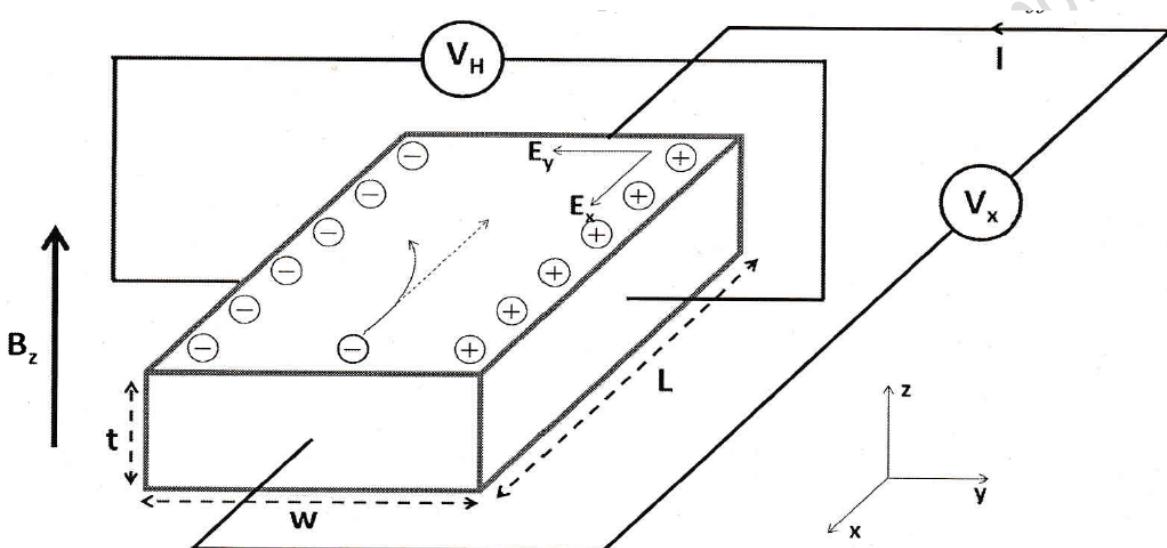
$$\frac{1}{2} \exp\left(\frac{\ln 2}{f}\right) = \cosh\left(\frac{\frac{R_1}{R_2} - 1}{\frac{R_1}{R_2} + 1} \cdot \frac{\ln 2}{f}\right)$$

For symmetric sample,  $R_1 = R_2$

$$\rho = \frac{\pi t}{\ln 2} R_1$$

## 4.5 Hall effect

Hall Effect was named after Edwin Hall, its discoverer. When a current 'I' is passed through a conductor placed in a transverse magnetic field 'B', an electric field 'E' is induced in the conductor perpendicular to both 'I' and 'B'. This phenomenon is called Hall Effect.



Let us take a sample having length 'L' along x-axis, width 'w' along y-axis and thickness 't' along z-axis. Magnetic field vector 'B' is applied on this sample along z-axis. Now if a current 'I' is passed through the sample in the direction of x-axis, charge carriers (in this case we assume electrons) will drift with drift speed ' $v_d$ ' in the opposite direction '-x'. Magnetic force ' $F_B$ ' acts on each drifting electron, pushing it toward the negative y-direction (left edge of the sample).

$$\vec{F}_B = e(\vec{v} \times \vec{B}) = ev_x B_z \quad \dots \dots \dots \quad 1$$

As time goes on, electrons move to the left piling up on the left edge of the sample, leaving uncompensated positive charges in fixed positions at the right edge. The separation of positive and negative charges produces an electric field ' $E_y$ ' within the sample pointing in negative  $y$ -direction. It will produce a potential difference ' $V_H$ ' (Hall voltage) between two edges along  $y$ -direction.

$$V_H = E_Y w \quad \text{---} \quad -2$$

This field creates an electric force ' $F_E$ ' in the opposite direction.

Thus, a Lorentz force acting on electrons can be given as

$$F_L = e(\vec{E} + \vec{v} \times \vec{B}) = e(E_Y + v_x B_z)$$

Eventually an equilibrium situation will be developed when electric force ' $F_E$ ' balances the magnetic force ' $F_B$ ' so as to keep current flowing along the x-direction.

$$\overrightarrow{F}_E = \overrightarrow{F}_B$$

$eE_Y = ev_x B_z$  —————— 4

Now the current density according to Ohm's law can be given as  $j_x = nev_d = nev_x$

$$v_x = \frac{j_x}{ne} \quad \dots \quad 5$$

Using 5 in 4 we get,

$$E_Y = \frac{j_x}{ne} B_z = R_H j_x B_z \quad \text{where } R_H = \frac{1}{ne} \quad \dots$$

Using 2 in 7 we get,

$$R_H = \frac{V_H}{wj_x B_z} = \frac{V_H A}{wI_x B_z} = \frac{V_H wt}{wI_x B_z}$$

$$R_H = \frac{V_H t}{I_x B_z} - \dots - 8$$

Thus, when a current carrying sample is placed in a transverse magnetic field, by measuring the Hall voltage ' $V_H$ ', it is possible to determine the Hall coefficient ' $R_H$ '. Then it is possible to calculate the carrier density 'n' using Eqn. (6). More over in this method, measured value of Hall voltage ' $V_H$ ' will be negative if the majority charge carriers are electrons and positive if the majority charge carriers are holes. Thus, if the sample under consideration is semiconductor, from the sign of Hall voltage, it is possible to determine the type of semiconductor (n-type or p-type). Now, we know that the electron velocity ' $v_d$ ' varies linearly with the electric field ' $E_x$ '. Then in case of Ohmic condition we can write

$$v_d = v_x = \mu E_x$$

Using 5 in above

$$\mu = \frac{j_x}{neE_x} = \frac{j_x}{E_x} R_H \quad - - - - - \quad 9$$

## Using 7 in 9

$$\mu = \frac{j_x}{E_x} \cdot \frac{E_Y}{j_x B_z} = \frac{1}{E_x} \cdot \frac{E_Y}{B_z} = \frac{L}{V_s} \cdot \frac{V_H}{w} \cdot \frac{1}{B_z}$$

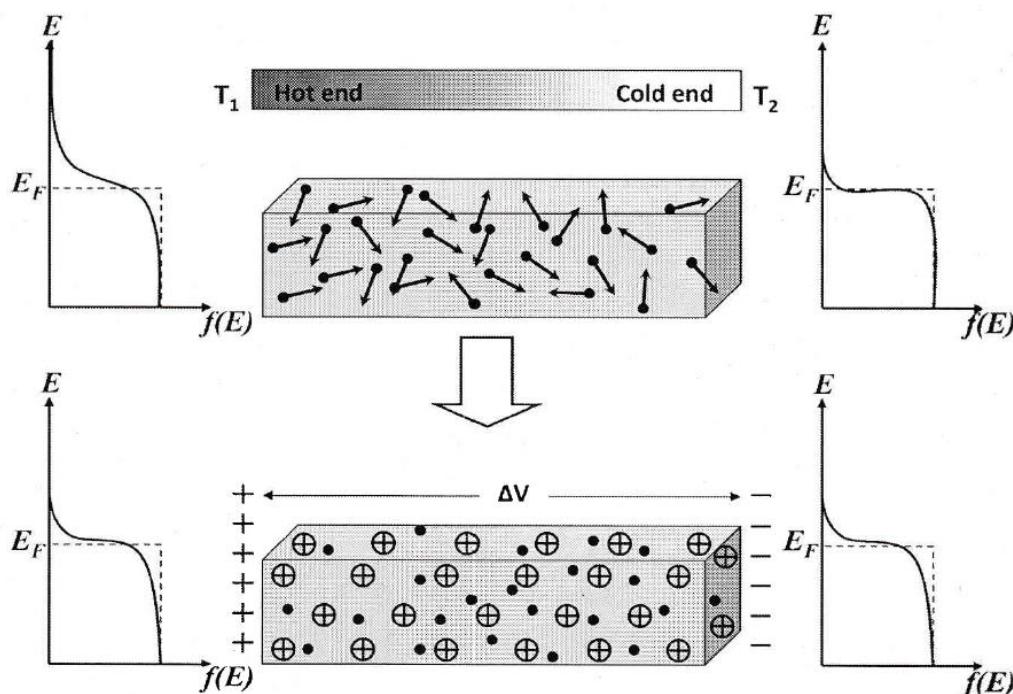
$$\mu = \frac{1}{B_z} \cdot \frac{V_H}{V_S} \cdot \frac{L}{w} \quad \text{--- --- --- --- --- 10}$$

Eqn. (10) represents the Hall mobility of the sample.

## 4.6 Hot probe method

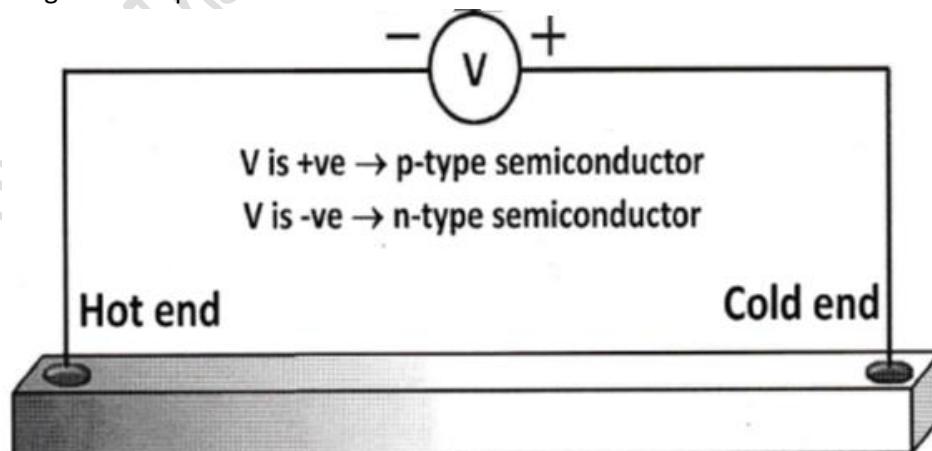
The hot probe method is simplest and quick method for the determination of type of majority charge carrier in semiconductor sample. Basic principle lying behind the hot probe method is Seebeck Effect.

## Module 4 - Measurements



Let us assume that two ends of a metal slab are subjected to different temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ ). In this condition electrons at the hot end will jump to higher energy levels (compared to those at cold end) by absorbing the energy from applied heat. Therefore, they will find state of lower energy at the cold end and try to diffuse towards cold end.

Electrons at the hot end become more energetic and therefore get greater velocities than those in the cold end. Consequently, there is a net diffusion of electrons from hot end towards cold end which leaves behind exposed positive ions in the hot end and accumulates electrons in the cold end. This situation prevails until the electric field developed between the two ends prevents further electron motion from hot end to cold end. A potential difference is therefore developed between two ends of the sample. This phenomenon is known as Seebeck effect and potential difference developed in this way is known as thermo-emf. This phenomenon for metallic sample is expressed in figure. If the sample is semiconducting with n-type conductivity, then (due to electrons as majority charge carriers) hot end will become positive compared to cold end. But in case of p-type semiconductor majority charge carriers are holes. Therefore, diffusion of positively charged holes from hot end to cold end will make hot end negative compared to cold end.



Suppose we are measuring thermo-emf of a semiconducting sample for which the type of majority carriers are unknown. In this case if negative terminal of voltmeter is connected at hot end and positive terminal is connected at cold end then negative value of measured thermo-emf indicates n-type semiconductor and positive value of measured thermo-emf indicates p-type semiconductor.

## 4.7 Capacitance Voltage Measurements

Capacitance–voltage profiling (or C–V profiling, sometimes CV profiling) is a technique for characterizing semiconductor materials and devices.

Hillibrand and Gold first described the use of capacitance –voltage (C–V) methods to determine the majority carrier concentration in semiconductors. C–V measurements are capable of yielding quantitative information about the diffusion potential and doping concentration in semiconductor materials.

The technique employs p-n junctions, metal-semiconductor (MS) junctions (Schottky barriers), electrolyte-semiconductor junctions, metal-insulator-semiconductor (MIS) capacitors, and MIS field effect transistors (MISFETs).

The applied voltage is varied, and the capacitance is measured and plotted as a function of voltage. The technique uses a depletion region, a region which is empty of conducting electrons and holes, but may contain ionized donors and electrically active defects or traps.

The depletion region with its ionized charges inside behaves like a capacitor. By varying the voltage applied to the junction it is possible to vary the depletion width.

The dependence of the depletion width upon the applied voltage provides information on the semiconductor's internal characteristics, such as its doping profile and electrically active defect densities.

Measurements may be done at DC, or using both DC and a small-signal AC signal (the conductance method), or using a large-signal transient voltage.

## 4.8 DLTS

This mainly identifies the crystal defects or traps in pn junction and Schottky diodes.

DLTS was introduced by D V Lang in the year 1974.

It is an efficient method to observe and identify deep level impurities in the semiconductors.

It is a capacitance transient thermal scanning technique which uses the capacitance of PN junction to monitor and find out the defects.

DLTS helps to distinguish between the majority and minority carrier traps.

When the voltage across a p-n junction is changed, there is a corresponding change in the depletion layer width. This change in width causes a change in number of free charge carriers on both sides, resulting in the change in junction capacitance.

Consider a pn junction with the deep level present, having its energy as  $E_T$ .

In steady state, there is no net flow of charges carriers across the trap.

The total density of deep level states  $NT$  can be given by  $NT = \pi r^2$

When the voltage across a p-n junction is changed, there is a corresponding change in the depletion layer width. This change in width causes a change in number of free charge carriers on both sides, resulting in the change in junction capacitance.

Consider a pn junction with the deep level present, having its energy as  $ET$ .

## Module 4 - Measurements

In steady state, there is no net flow of charges carriers across the trap.

### 4.9 UV Vis Spectroscopy

Spectroscopy is related to the interaction of light with matter.

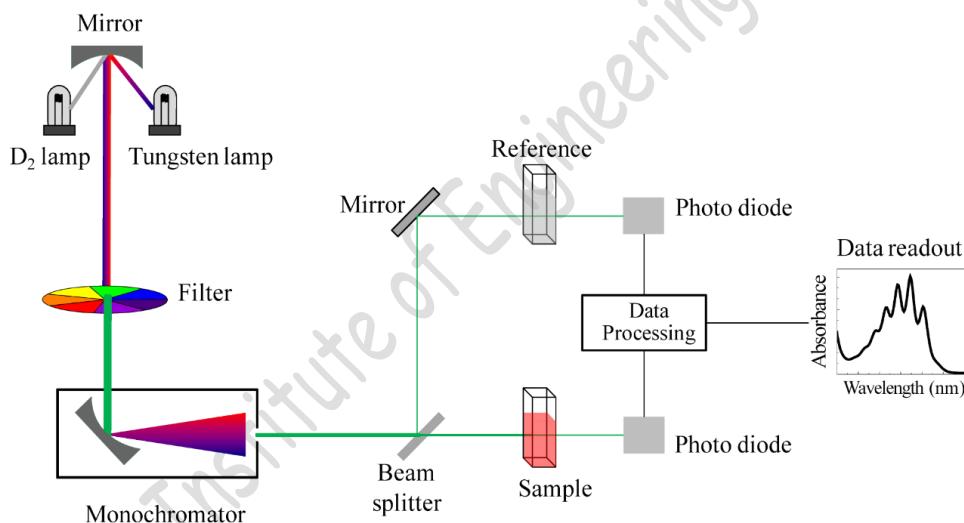
As light is absorbed by matter, the result is an increase in the energy content of the atoms or molecules. The absorption of visible light or ultraviolet light by a chemical compound will produce a distinct spectrum.

When ultraviolet radiations are absorbed, this results in the excitation of the electrons from the ground state towards a higher energy state.

Ultraviolet-visible spectroscopy is used for the qualitative analysis and identification of chemicals.

However, its main use is for the quantitative determination of different organic and inorganic compounds in solution.

UV spectrophotometer principle is that whenever a beam of monochromatic light is passed through a solution with an absorbing substance, the decreasing rate of the radiation intensity along with the thickness of the absorbing solution is actually proportional to the concentration of the solution and the incident radiation.



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UV spectrophotometer principle is that whenever a beam of monochromatic light is passed through a solution with an absorbing substance, the decreasing rate of the radiation intensity along with the thickness of the absorbing solution is actually proportional to the concentration of the solution and the incident radiation.

#### 4.9.1 Applications

This is used to detect a functional group in the given sample.

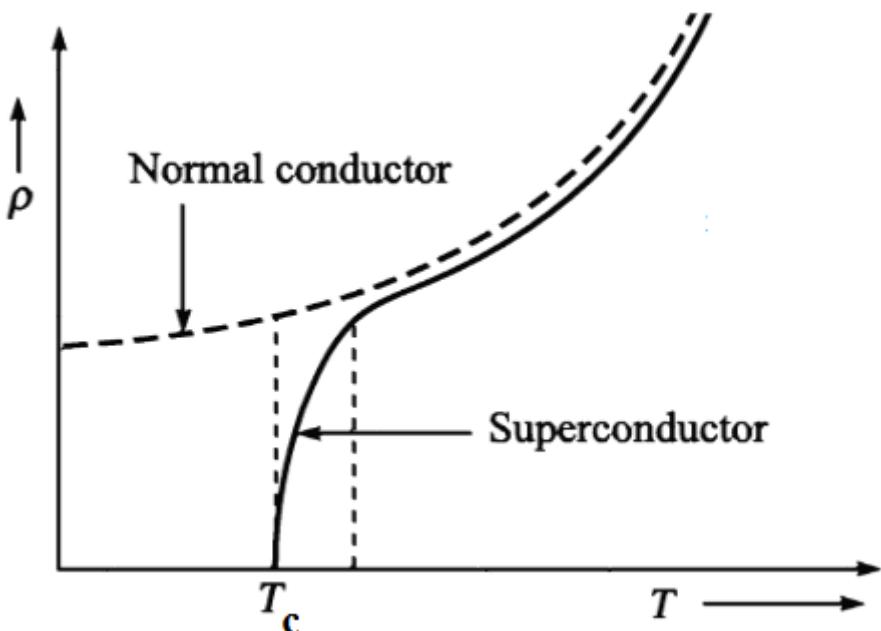
It can be used to detect the absence or the presence of chromophore in a complex compound.

UV spectroscopy may be used to identify unknown compounds

## 5.1 Introduction:

Helium gas - was liquefied at 4.2 K by Dutch Physicist Heike Kamerlingh Onnes in 1908. Superconductivity was discovered by K. Onnes in 1911. Liquid Helium has a temperature of 4.2 K. It was observed that the resistance of mercury dropped from  $0.08 \Omega$  at about 4.3 K to less than  $3 * 10^{-6} \Omega$  at 4.2 K. A large number and wide variety of metals, alloys, binary and ternary chemical compounds have been found to show superconductivity at various temperatures.

Superconductivity is a state in which quantum mechanics operates on a macroscopic scale of the order of many atomic distances rather than the usual atomic and subatomic scale. The superconducting state is influenced by the temperature, magnetic field and current. All these three parameters have critical values, above which material enters into normal state. Every superconductor has its own transition temperature.



Good electrical conductors such as silver, gold, and copper are not good superconductors because the resistivity of these conductors at low temperatures is limited to low resistivity i.e. residual resistivity, value due to scattering of electrons from crystal defects and impurities. Similarly, good superconducting materials like zinc and lead are not good electrical conductors.

## 5.2 Definitions

### 5.2.1 Superconductor:

It is a material that loses all its resistance (offers zero resistance) to the flow of electric current when it is cooled below a certain temperature called the critical temperature or transition temperature  $T_c$ .

Eg: Mercury, Zinc, Niobium, etc

### 5.2.2 Critical temperature:

The temperature at which a material's electrical resistivity drops to absolute zero is called the critical temperature or transition temperature. It is denoted by  $T_c$ .

# Module 5 - Superconductivity

## 5.2.3 Superconductivity:

It is a phenomenon in which certain metals, alloys and ceramics conduct electricity without resistance when it is cooled below a certain temperature called the critical temperature.

# 5.3 Properties of Superconductors

## 5.3.1 Electrical Resistance:

The electrical resistance of a superconducting material is very low and is of the order of  $10^{-7} \Omega$ .

## 5.3.2 Effect of impurities:

When impurities are added to superconducting elements, the superconducting property is not lost but the  $T_c$  value is lowered

## 5.3.3 Isotope Effect:

The critical temperature of a superconductor is found to vary with its isotopic mass. The atomic mass of Hg varies from 199.5 to 203.4. Due to this variation in atomic mass, the transition temperature of isotopes of Hg varies from 4.185 to 4.146 K. They are related as  $T_c \propto \frac{1}{\sqrt{M}}$  where M is the isotopic mass.

## 5.3.4 Magnetic field effect:

If a sufficiently strong magnetic field is applied to a superconductor at any temperature below critical temperature  $T_c$ , the superconductor is found to undergo a transition from the superconducting state to the normal state. OR This minimum magnetic field required to destroy the superconducting state is

called critical magnetic field  $H_c$ .  $H_c = H_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$  where  $H_0$  is the applied magnetic field at 0 K.

## 5.3.5 Effect of pressure and stress:

Certain materials are found to exhibit the superconductivity phenomena on increasing the pressure over them. For eg. Cs shows superconductivity at  $T_c = 1.5$  K and 110 kbar

Also, in Superconductors, an increase in stress results in increase of the  $T_c$  value.

## 5.3.6 Critical current density:

It is defined as the maximum current that can be permitted in a superconducting material without destroying its superconductivity state. OR Minimum current required to destroy the superconducting state is called critical current density  $J_c$  and this current is called critical current  $I_c$ . The equation relating

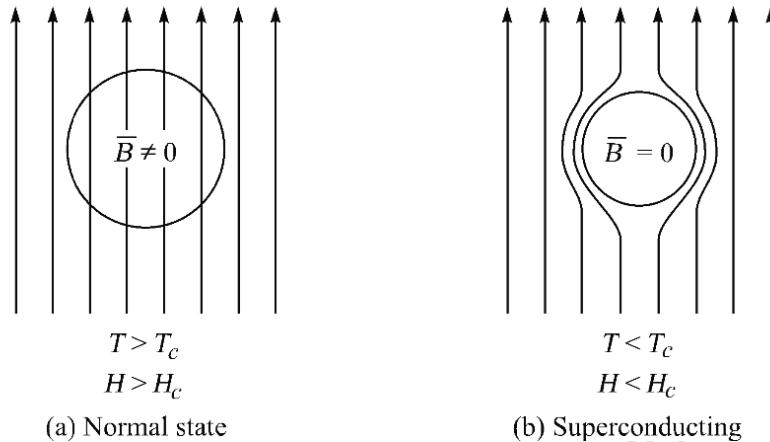
$$J_c = \frac{I_c}{A} \text{ and } I_c = 2\pi r H_c.$$

## 5.3.7 Persistent current:

If current is made to flow through a superconducting ring then it is observed that the current flows through the material without any significant loss. This steady flow of current in a superconducting ring without any potential deriving is called the persistent current.

### 5.3.8 Meissner effect:

The complete expulsion of all the magnetic field lines by a superconductor material is called Meissner effect. The Meissner effect is a distinct characteristic of a superconductor from a normal perfect conductor. In addition, this effect is exhibited by the superconducting materials only when the applied field is less than the critical field  $H_c$ .



To Prove that  $\chi_m = -1$  for superconductors

We know that for a magnetic material the magnetic induction or magnetic flux density  $B$  is given by the equation  $B = \mu_0(M + H)$  where  $\mu_0$  is the permeability of free space;  $M$  is the intensity of magnetization;  $H$  is the applied magnetic field.

But for the superconductors, we know that  $B = 0$ , thus the above equation can be written as

$$\text{i.e. } 0 = \mu_0(M + H)$$

$$\text{i.e. } 0 = (M + H) \text{ since } \mu_0 \neq 0$$

$$\text{i.e. } M = -H$$

$$\text{OR } \frac{M}{H} = -1 = \chi_m$$

where  $\chi_m$  is called as the magnetic susceptibility. This means that for a superconductor, the susceptibility is negative and maximum, i.e., a superconductor exhibits perfect diamagnetism. For all other magnetic materials, the susceptibility values are positive.

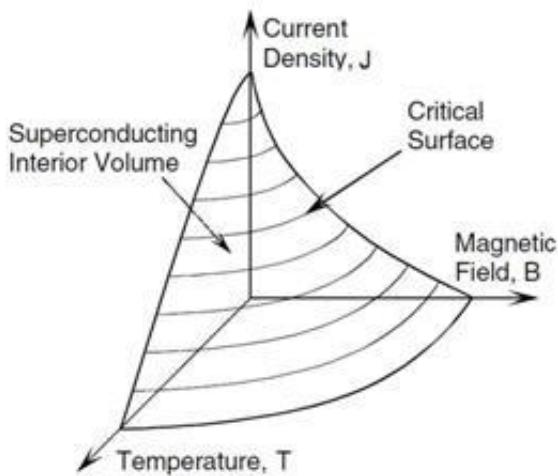
## 5.4 Factors to define a Superconducting State

Critical temperature

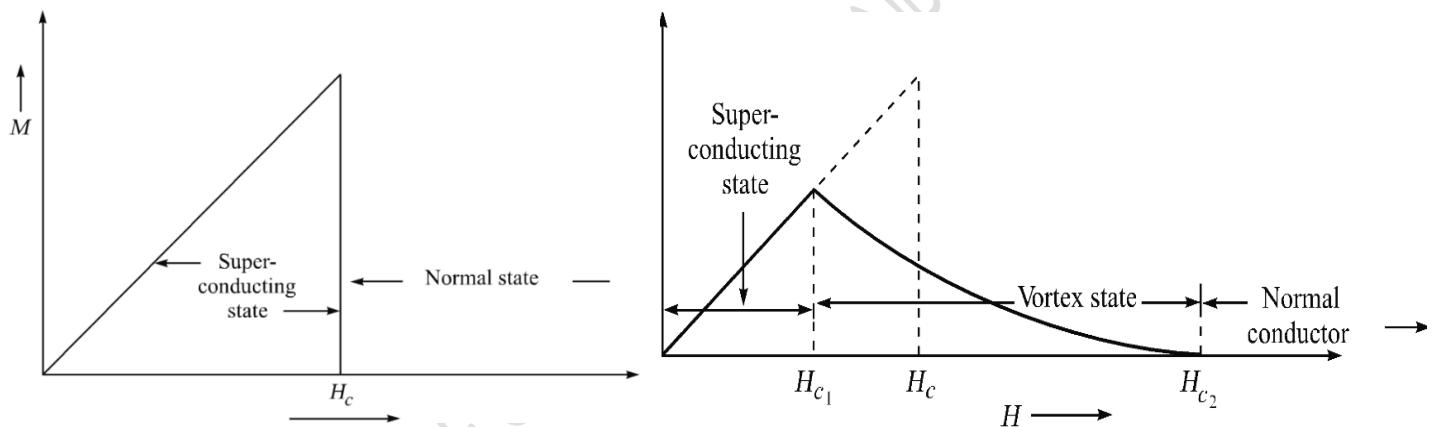
Critical current density

Critical magnetic field

## Module 5 - Superconductivity



Each of the above three parameters is very dependent on the other two properties. The highest values for  $H_c$  and  $J_c$  occur at 0 K; while the highest value for  $T_c$  occurs when  $H$  and  $J$  are zero. Thus the plot of all these three parameters represents a critical surface. Within the surface, the material is superconducting and outside the surface, the material is said to be in the normal state.



Graph of  $-M$  (Magnetization) vs  $H$  (Applied Magnetic Field) for Type I and II superconductors

Sr. No.	Type I superconductor	Type II superconductor
1	These superconductors are called as soft superconductors.	These superconductors are called as hard superconductors.
2	Only one critical field exists for these superconductors.	Two critical fields $H_{c1}$ (lower critical field) and $H_{c2}$ (upper critical field) exists for these superconductors.
3	The critical field value is very low.	The critical field value is very high.
4	These superconductors exhibit perfect and complete Meissner effect.	These do not exhibit a perfect and complete Meissner effect.
5	These materials have limited technical applications because of very low field strength value.	These materials have wider technological applications because of very high field strength value.
	Examples: Pb, Hg, Zn, etc.	Examples: $Nb_3Ge$ , $Nb_3Si$ , $Y_1Ba_2Cu_3O_7$ , etc.

## 5.5 Applications

### 5.5.1 Magnetic Levitation

Magnetic levitation or maglev is the process by which an object is suspended above another object with no other support but magnetic fields. We know that a diamagnetic substance repels a magnetic field. Thus, the perfect diamagnetic property of superconductors make them suitable for achieving frictionless motion in motors and bearing. The phenomena of magnetic levitation is based on Meissner effect.

#### 5.5.1.1 How to achieve magnetic levitation?

The magnetic levitation is brought about by enormous repulsion between two highly powerful magnetic fields. If a small magnet is brought near a superconductor, it will be repelled. This repulsion takes place due to the induced currents in the superconductor which is being generated by the magnetic field of the magnet. Because of zero resistance property of the superconductor this current persists, and thus the field due to this induced current repels the field due to the magnet. As a result, the magnet floats freely above the superconductor. Maglev demonstrates zero resistance and Meissner effect properties for superconductors.

Magnetically levitated vehicles are called maglev vehicles. The utility of such levitation in vehicles is that in the absence of contact between the moving and stationary systems, the friction is eliminated. With such an arrangement, great speeds could be achieved with very low energy consumption. This levitation is based on:

**Electromagnetic suspension (EMS)** - In attractive EMS, the electromagnets installed on the train bogies attract the iron rails. The vehicle magnets wrap around the iron guide-ways and the attractive upward force lifts the train.

**Electrodynamic suspension (EDS)** - In EDS, levitation is achieved by creating a repulsive force between the train and guide-ways.

The basic idea of maglev train is to levitate it with magnetic fields so that there is no physical contact between the train and the rails. Consequently the maglev train can travel at a very high speed. Maglev trains travel at speed of about 500 kmph. A similar magnetic propulsion system is being used to launch the satellite into orbits directly from the earth without the use of rockets.

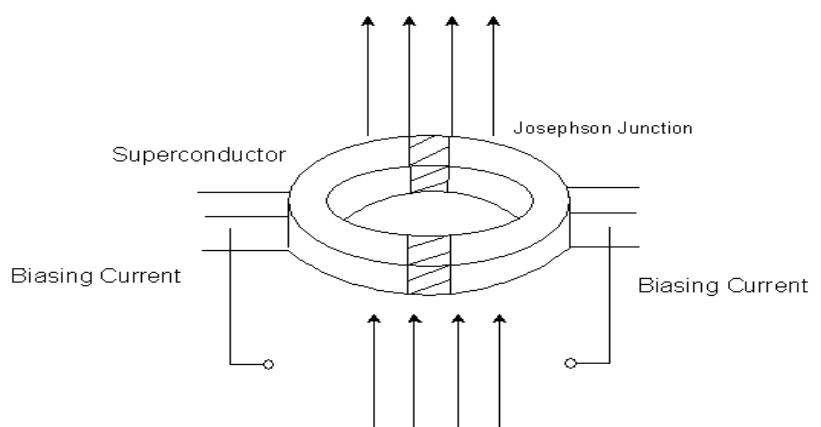
### 5.5.2 Josephson Effect

Two superconductors separated by a very thin strip of an insulator forms a Josephson junction.

The wave nature of moving particles makes the electrons to tunnel through the barrier (insulator) i.e. the electrons can tunnel from one superconductor to the other forming a current through the junction.

As a consequence of the tunneling of electrons across the insulator, there is a net current across the junction. This is called as dc Josephson Effect. This current flows even in the absence of a potential difference.

On the other hand, when a potential difference is applied between the two sides of the junction, there will be an oscillation of the tunneling current with



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angular frequency  $f = 2eV/h$ . This is called ac Josephson Effect.

### 5.5.2.1 Application of Josephson junction

Josephson junctions are used in sensitive magnetometers called SQUID – Superconducting Quantum Interference Device. A SQUID is formed by connecting two Josephson junctions in parallel. When current is passed into this arrangement, it splits flowing across the two opposite arc. The current through the circuit will have a periodicity which is very sensitive to the magnetic flux passing normally through the closed circuit. As a result, extremely small magnetic flux can be detected with this device. This device can also be used to detect voltages as small as  $10^{-15}$  V. Magnetic field changes as small as  $10^{-21}$  T can be detected. Weak magnetic fields produced by biological currents such as those in the brain can also be detected using SQUIDs. SQUID detectors are used to measure the levels of iron in liver – so that iron built up can be treated before much harm is done to the body.

## 5.6 Other Applications

To transmit electrical power over very large distances without any power loss or voltage drop.

Superconducting generators has the benefit of small size and low energy consumption than the conventional generators.

Used in NMR for scanning the whole body to diagnose medical problems.

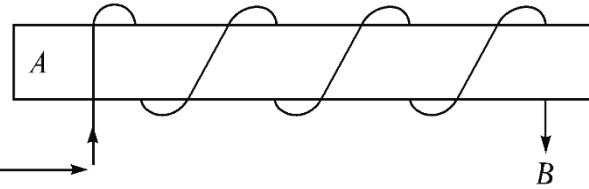
To generate very strong magnetic fields.

Superconductors can act as relay or switching system in a computer and also as a memory or storage element.

Very fast and accurate computer can be generated that consumes low power.

Ore separation can be done efficiently.

**Cryotron:** A small size relay or switch made of superconductors. They consume very less current. Let the critical field of the material A be  $H_{cA}$  and that of B be  $H_{cB}$  and also  $H_{cA} < H_{cB}$ . If a current  $I$  is passed through the material B,



the current induces a magnetic field  $H$ . If this induced field  $H$  happens to be greater than  $H_{cA}$  then the superconducting property of the material A gets destroyed. Hence the resistivity increases and the contact is broken. Thus, the current in A can be controlled by the current in B and hence this system can act as a relay or switch element.

## 5.7 London Penetration Depth

Maxwell's equations could not explain the zero resistance and perfect diamagnetism observed as main characteristics of superconductivity.

F. London and H. London (London brothers) suggested that motion of superconducting electrons in the presence of applied electric field  $E$ .

If a magnetic field is applied to a superconductor which is initially in zero field, the magnetic field is a function of time.

According to the Maxwell equation,

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$$\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t}$$

The time-varying magnetic field gives rise to an electric field.

In a normal metal this will induce eddy currents, but in a superconductor the electric field will give rise to persistent currents (i.e. supercurrents).

The induced supercurrents will in turn generate a magnetic field of their own which opposes the applied magnetic field.

If the applied magnetic field is weak, the flux is totally screened from the bulk of the superconductor.

This phenomenon is often described as "perfect diamagnetism".

From Newton's law, the equation of motion for a superconducting carrier with mass  $m$  and charge  $-e$  in the presence of an electric field  $E$  is

$$F = m \frac{dvs}{dt} = -eE$$

where  $v_s$  is the velocity of the superconducting carrier. The field-induced supercurrent density is given by

$$Js = -ns e v_s$$

where  $n_s$  is the local density of the superconducting carriers.

Thus we get

$$v_s = -\frac{Js}{ns e}$$

Thus the substitution gives

$$\frac{dJs}{dt} = \frac{nse^2}{m} E$$

which is called as the first London equation.

Taking curl on both sides, we get

$$\frac{m}{nse^2} \left( \nabla \times \frac{dJs}{dt} \right) = \nabla \times E$$

which can be rewritten using the Maxwell's equation as

$$\frac{mc}{nse^2} \left( \nabla \times \frac{dJs}{dt} \right) + \frac{dB}{dt} = 0$$

In order to obtain the Meissner effect, they removed the time derivative. Thus the equation becomes

$$\frac{mc}{nse^2} (\nabla \times Js) + B = 0$$

which is called as second London equation.

The supercurrent density and magnetic field  $B$  are related as per Maxwell's equation

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$$Js = \frac{c}{4\pi} (\nabla \times B)$$

This substitution gives

$$\frac{mc}{nse^2} \times \frac{c}{4\pi} (\nabla \times (\nabla \times B)) + B = 0$$

which gives

$$\lambda_L^2 (\nabla \times \nabla \times B) + B = 0$$

Where

$$\frac{1}{\lambda_L^2} = \frac{4\pi n_s e^2}{mc^2}$$

$\lambda_L$  is called the London penetration depth. It is a measure of magnetic field penetration inside the superconductor.

OR

$$\nabla \times J = \frac{ne^2}{m} B$$

These equations are called first and second London equations which explains Meissner effect or Perfect diamagnetism.

Their equation also predicts the penetration of super current and magnetic flux in a superconductor.

The penetration depth is the depth where the current drops to  $1/e$  times of its value at the surface.