

### Unit III INTRODUCTION TO SOLIDS

#### Conduction electrons

The valence electrons or free electrons which are freely moving in the metallic boundary and produces current in a metal are called conduction electrons.

#### Assumptions of classical free electron theory

- 1) In a metal there are freely moving valence electrons called free electrons confined to its body. It is these electrons which produce current in a metal hence called as conduction electrons.
- 2) The free electrons are treated equivalent to gas molecules, and thus assumed to obey the law of kinetic theory of gases.
- 3) The electric potential due to the ionic cores is taken to be essentially constant throughout the metal.
- 4) The attraction between the free electrons and the lattice ions and the repulsion between the electrons themselves are considered insignificant.

#### Terminologies

- (a) **Resistance**: It is the physical effect brought about by the vibrating lattice in a material by the virtue of which the accelerating effect of an applied field on the conduction electrons is annulled so that the electrons settle into a state of constant velocity which is proportional to the strength of the applied field.
- (b) **Relaxation time**: In a metal, electrons moves in different direction in the absence of an electric field, the probability of finding an electron moving in any given direction is equal to finding some other electron moving in exactly the opposite direction. The average velocity of the electrons is zero.

$$v_{av} = 0$$

When the external field is applied to the metal, then the drift velocity is developed

$$v_{av} = v'_{av}$$

If the field is turned off, the average velocity  $V_{av}$  starts reducing exponentially from the value  $V'_{av}$  as shown in the fig.

The process follows the equation.

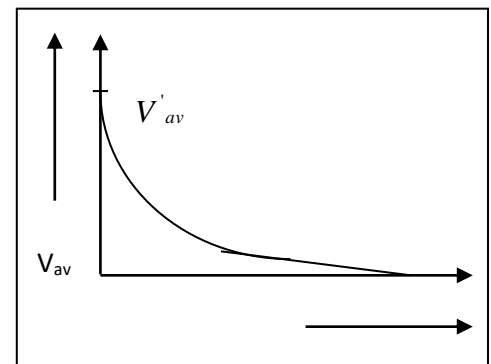
$$v_{av} = v'_{av} e^{-t/\tau_r} \text{ ----- (1)}$$

$t \rightarrow$  Time counted from the instant the field is turned off

$\tau_r \rightarrow$  Relaxation time

If  $t = \tau_r$ , then equation (1) becomes

$$v_{av} = \frac{1}{e} v'_{av}$$



Hence relaxation time is defined as “consequent to the sudden disappearance of an electric field across a metal, the average velocity of its conduction electrons decays exponentially to zero, and the time

required in this process for the average velocity to reduce to  $\frac{1}{e}$  times its value just when the field is turned off”.

- (c) **Mean free path:** It is the average distance travelled by the electrons between successive collisions with the lattice ions.
- (d) **Mean collision time:** The average time that elapses between two consecutive collisions of an electron with the lattice points.

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

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

(f) **Drift velocity:** When the electric field is applied the free electrons move with the constant velocity in the direction opposite to that of the applied field is called as drift velocity.

If  $m$ , is the mass of the electron,  $V_d$  is the drift velocity,  $\tau$  is mean collision time, then the resistance force  $F$  is given based on Newton's II law.

$$F = ma \Rightarrow F = \frac{mV_d}{\tau} \text{----- (1)}$$

If  $e$  is the charge on the electron, and  $E$  is the strength of the applied field, then the driving force.

$$F = eE \text{----- (2)}$$

On equating (1) and (2),

$$\frac{mV_d}{\tau} = eE$$

Therefore,

$$V_d = \frac{eE\tau}{m}$$

(d) **Mobility of electrons:** The mobility of electrons is defined as the magnitude of drift velocity acquired by the electrons in a unit field.

If  $E$  is the applied field,  $V_d$  is the drift velocity, then mobility of the electrons,

$$\mu = \frac{V_d}{E} \Rightarrow \mu = \frac{e\tau}{m}$$

#### **Expression for conductivity in a conductor:**

Consider the motion of a free electron in a conductor subjected to the influence of an electric field. If  $e$  is the charge of an electron and  $E$  is the strength of the field, then Force acting on the electron is

$$F = eE \text{----- (1)}$$

If  $m$ , is the mass of the electron, then from Newton's II law, Force on the electron is

$$F = ma \Rightarrow F = \frac{mdv}{dt} \text{-----} (2)$$

From (1) = (2)

$$eE = \frac{mdv}{dt} \Rightarrow dv = \frac{eE}{m} dt$$

On integrating the above equation,

$$v = \frac{eE}{m} t$$

where t is the time of traverse. Let  $t = \tau$ , then  $v = v_d$

$$v_d = \frac{eE\tau}{m} \text{-----} (3)$$

We know that  $J = \sigma E$

$$\sigma = \frac{J}{E} = \frac{I}{AE}$$

$$\sigma = \frac{nev_d A}{AE} \quad \therefore I = nev_d A$$

$$\sigma = \frac{ne}{E} \left[ \frac{eE\tau}{m} \right] \quad \therefore v_d = \frac{eE\tau}{m}$$

$$\boxed{\sigma = \frac{ne^2\tau}{m}}$$

### Failures of classical free electron theory.

#### 1) Specific heat:

The molar specific heat of gas molecules at constant volume is

$$C_V = \frac{3}{2} R$$

As per the theory, free electrons are treated as gas molecules, then the above equation must be applicable to free electrons;

But,  $C_V = 10^{-4} RT$

Which is not only lower than the expected value but also depends on temperature.

## 2) Temperature dependence on electrical conductivity

We know that,  $\sigma \propto \frac{1}{T}$  ----- (1)

But according to the assumption of classical free electron theory,

$$\frac{3}{2}kT = \frac{1}{2}mv_{th}^2$$

$$v_{th} = \sqrt{\frac{3kT}{m}} \Rightarrow v_{th} \propto \sqrt{T} \text{ ----- (2)}$$

Since mean collision time is,  $\tau = \frac{\lambda}{v_{th}} \Rightarrow \tau \propto \frac{1}{v_{th}} \propto \frac{1}{\sqrt{T}}$

$$\therefore \tau \propto \frac{1}{\sqrt{T}} \text{ ----- (3)}$$

But,  $\sigma = \frac{ne^2\tau}{m} \Rightarrow \sigma \propto \tau$

Therefore, from eqn. (3)

$$\sigma \propto \frac{1}{\sqrt{T}} \text{ ----- (4)}$$

Comparison of (1) and (4) indicates the failure of classical free electron theory.

## 3) Dependence of electrical conductivity on electron concentration

We know that  $\sigma = \frac{ne^2\tau}{m} \Rightarrow \sigma \propto n$

Let us consider the specific cases.

| Metal | Valency | $\sigma / (\Omega m)$ | N                      |
|-------|---------|-----------------------|------------------------|
| Cu    | 1       | $5.88 \times 10^7$    | $8.45 \times 10^{28}$  |
| Ag    | 1       | $6.3 \times 10^7$     | $5.85 \times 10^{28}$  |
| Zn    | 2       | $1.09 \times 10^7$    | $13.10 \times 10^{28}$ |
| Cd    | 2       | $0.15 \times 10^7$    | $9.28 \times 10^{28}$  |

When the electron concentration of Zn & Cd is compared with Cu & Ag, we can see that Zn & Cd have higher electron concentration but less conductivity compared to that of Cu & Ag which have high conductivity with less electron concentration.

Thus  $\sigma \propto n$  is not true.

**Assumptions of quantum free electron theory and based on it explain density of states.**

- 1) The energy values of the conduction electrons are quantized. The allowed energy values are realized in terms of set of energy levels.
- 2) The distribution of electrons in the various allowed energy levels occurs as per Pauli's Exclusion Principle.
- 3) The electric potential due to the ionic cores is taken to be essentially constant throughout the metal.
- 4) The attraction between the free electrons and the lattice ions and the repulsion between the electrons themselves are considered insignificant.

**Density of states**

The permitted energy levels for electrons in case of solid material will be in terms of bands. Each band is spread over an energy range of few electron volt.

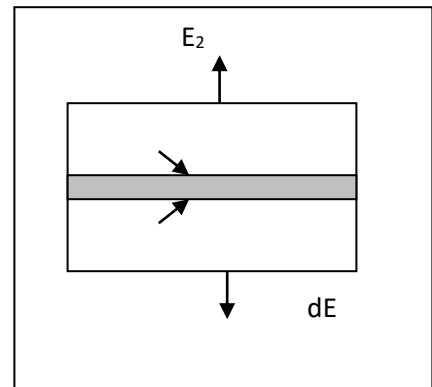
Let us consider a solid material of  $1\text{mm}^3$  volume, there will be more than a thousand billion permitted energy levels in an energy range, from the fig.

Let  $E_1$  and  $E_2$  be the allowed energy range. Let  $E$  be the energy, which takes small increment of  $dE$  which is negligible.

Then the no. of allowed energy levels between  $E$  and  $E+dE$  is given as density of states.

**Density of states** is defined as "the no. of available states per unit energy range  $E$  in the Valence band of a material of unit volume.

It is a mathematically continuous function and the product  $g(E) dE$  gives the no. of states in the energy  $y$  interval  $dE$  at  $E$ ".



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

$g(E)dE \rightarrow$  density of states in the interval of  $dE$

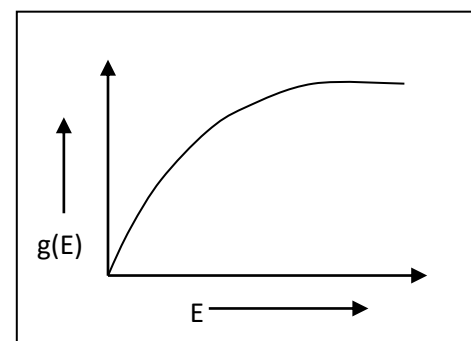
$m \rightarrow$  mass of the particle

$h \rightarrow$  Planck's constant

$E \rightarrow$  Energy

$dE \rightarrow$  small increment in the energy

From the eqn. we can notice that  $g(E)$  increases with  $E$

**Fermi energy and dependence of Fermi factor on temperature.**

**Fermi energy:** The energy corresponding to the highest occupied level at zero Kelvin absolute is called the Fermi energy and energy level is called as Fermi level.

At absolute  $T=0K$  the valence band is completely filled by the electrons, based on Pauli's exclusion principle that in each energy level there are maximum two electrons, one with spin up and other with spin down. The conduction band above the fermi level is completely empty at  $T=0K$ .

At  $0K$  the energy possessed by the electrons in the valence band is the highest energy called as the fermi energy.

**Fermi factor:** It is the probability of occupation of a given energy state for a material in thermal equilibrium.

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

**Dependence of Fermi factor on temperature:**

**Probability of occupation for  $E < E_f$  at  $T=0K$**

We know that

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

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

$f(E) = 1 \Rightarrow$  Energy level **below**  $E_f$  is **occupied**.

**1) Probability of occupation for  $E > E_f$  at  $T=0K$**

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

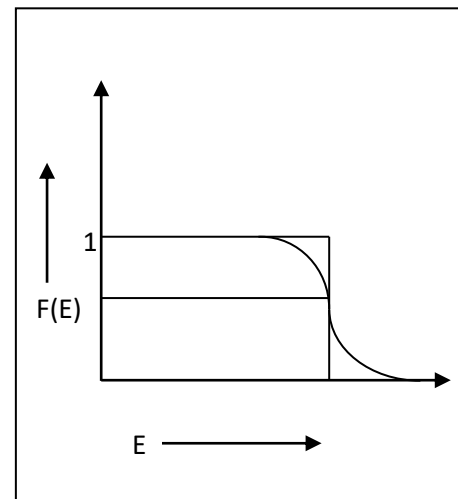
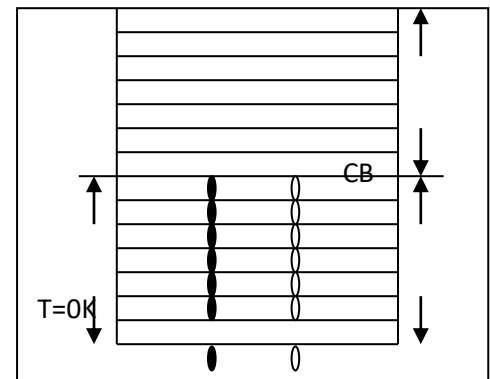
$f(E) = 0 \Rightarrow$  Energy level **above**  $E_f$  is **Unoccupied**.

**2) Probability of occupation at ordinary temperatures.**

At  $T > 0K$ , probability remains 1 for  $E \ll E_f$ , starts decreasing from 1 as the value becomes  $E = E_f$  and tends to zero for  $E > E_f$  as shown in the graph.

$$f(E) = \frac{1}{e^0 + 1} = \frac{1}{2} \text{ or } 0.5$$

Further for  $E > E_f$ ,  $f(E) = 0$



**Fermi temperature, Fermi velocity and Fermi Dirac distribution.**

**Fermi Temperature:** The temperature at which the average thermal energy of the free electron in a solid becomes equal to the fermi energy.

$$T_f = \frac{E_f}{k}$$

**Fermi velocity:** The velocity of the electrons which occupy the Fermi level.

$$v_f = \sqrt{\frac{2E_f}{m}}$$

**Effective mass.**

When a metal is subjected to an external field, free electrons in the metal moves under the combined influence of the applied electric field and that of a periodic potential due to lattice ions. Because of such a superposed effect the electrons responds as if it possesses a mass called Effective mass, which is different from true mass( $m^*$ ).

As per Sommerfeld's Quantum free electron theory, the movement of free electron in the metal is considered not as moving particle but as passage of periodic lattice. As a result, a moving electron is considered as a wave packet and the velocity is treated as group velocity. But free electron is totally free as the one in vacuum. Thus in vacuum the effective mass is same as that of true mass.

$$m^* = m$$

**Expression for Density States**

Let us consider a free electron is bound within a cube of side 'a'.

According to Quantum mechanics, the energy of an electron confined within a one dimensional potential well is given by

$$E = \frac{n^2 h^2}{8ma^2} \dots\dots\dots(1)$$

Where,  $n = 1, 2, 3, \dots, h$  = Planck's constant,  $m$  = mass of electron,  $a$  = width of potential well.

If we extend the above equation for 3 dimension,

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

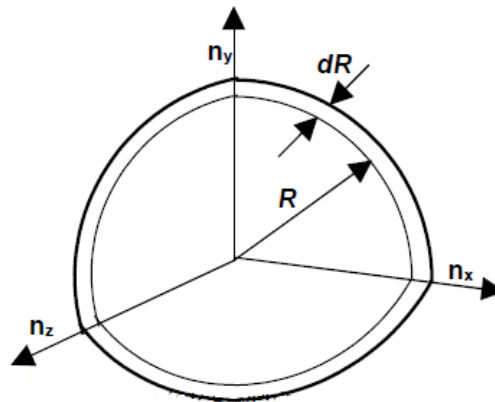
Where  $n_x, n_y, n_z$  are positive integers greater than zero.

The above equation can be written as

$$E = E_0 R^2 \dots\dots\dots (2)$$

$$\text{Where } E_0 = \frac{h^2}{8ma^2} \quad \text{and } R^2 = (n_x^2 + n_y^2 + n_z^2) \dots\dots\dots (3)$$

Now, the number of energy states with a particular value of  $E$  can be obtained by constructing a space in which each point is represented by  $n_x, n_y$  and  $n_z$ . Then all allowed energy states are within a sphere of radius  $R$  bound by three mutually perpendicular axes  $n_x, n_y$  and  $n_z$ . Since  $n_x, n_y$  and  $n_z$  can take only integer values, we can consider only an octant as shown in figure.



Therefore number of energy states within an octant of radius  $R$  is given by

$$\frac{1}{8} \left( \frac{4}{3} \pi R^3 \right)$$

III<sup>iv</sup> The number of energy states within a sphere of radius  $R+dR$  is given by

$$\frac{1}{8} \left\{ \frac{4}{3} \pi (R + dR)^3 \right\}$$

The number of energy states having energy values between  $E$  and  $E+dE$  is given by

$$\begin{aligned} g(E)dE &= \frac{1}{8} \left\{ \frac{4}{3} \pi (R + dR)^3 \right\} - \frac{1}{8} \left\{ \frac{4}{3} \pi R^3 \right\} \\ &= \frac{\pi}{6} \left\{ (R + dR)^3 - R^3 \right\} \\ &= \frac{\pi}{6} \left\{ R^3 + dR^3 + 3RdR^2 + 3R^2dR - R^3 \right\} \\ g(E)dE &\cong \frac{\pi}{6} (3R^2dR) \\ &= \frac{\pi}{2} (R^2dR) = \frac{\pi}{2} R(RdR) \dots\dots (4) \end{aligned}$$



From equation (2)  $\Rightarrow R^2 = \frac{E}{E_0} \Rightarrow R = \sqrt{\frac{E}{E_0}} \dots\dots (5)$

Differentiating  $R^2 \Rightarrow 2RdR = d\left(\frac{E}{E_0}\right) \dots\dots (6)$

Substitute equations (5) and (6) in (4)

$$(4) \Rightarrow g(E)dE = \frac{\pi}{2} \times \sqrt{\frac{E}{E_0}} \times \frac{dE}{2E_0} = \frac{\pi}{4} \frac{\sqrt{E}}{E_0^{3/2}} dE$$

$$g(E)dE = \frac{\pi}{4} \left[ \frac{8ma^2}{h^2} \right]^{3/2} \sqrt{E} dE$$

Since Pauli's exclusion principle allow two electrons in each state

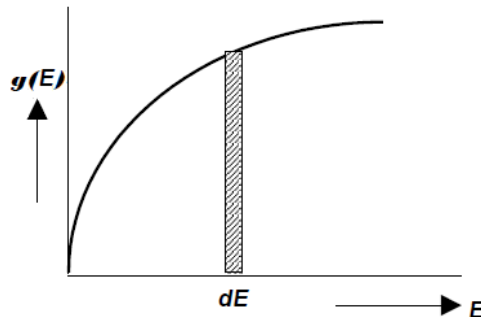
$$g(E)dE = 2 \times \frac{\pi}{4} \left[ \frac{8ma^2}{h^2} \right]^{3/2} \sqrt{E} dE$$

$$g(E)dE = \frac{\pi}{2} \left[ \frac{8ma^2}{h^2} \right]^{3/2} \sqrt{E} dE$$

In the above equation  $a^3$  represents the volume of the solid. If we consider the solid to be of unit volume (i.e.,  $a^3 = 1$ ), then,

$$g(E)dE = \frac{\pi}{2} \left[ \frac{8m}{h^2} \right]^{3/2} \sqrt{E} dE$$

The above equation represents the number of states in an energy range  $E$  and  $(E+dE)$  for the electrons in 3-dimensional solid of unit volume, called Density of states. The graph of  $g(E)$  against  $E$  is as shown in figure.



### Fermi-Dirac Distribution:

Fermi-Dirac Distribution gives the distribution of electrons among the permitted energy levels in a given solid.

The number of electrons occupying the energy levels between the energies  $E$  and  $E+dE$  is given by

$$N(E)dE = g(E)dE \times f(E)$$

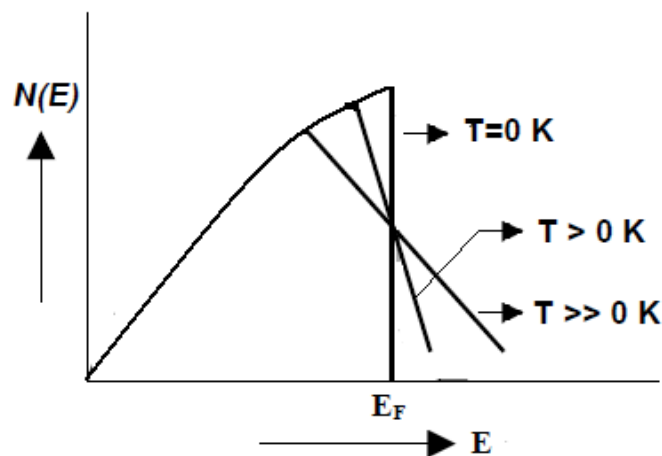
Where  $g(E)dE$  is called density of states given by

$$g(E)dE = \frac{\pi}{2} \left[ \frac{8m}{h^2} \right]^{3/2} \sqrt{E} dE$$

and  $f(E)$  is called Fermi factor given by

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

The graph of  $N(E)dE$  against  $E$  gives the distribution of electrons among the available energy levels in the solid at the given temperature. The distribution is known as Fermi-Dirac Distribution. The graph representing the distribution is shown below.



It is clear that from graph that  $N(E)$  increases with the temperature becomes maximum for  $E = E_F$  and then decreases to zero for the energies  $E > E_F$ , at the temperature  $T = 0 \text{ K}$ . At higher temperatures some of the electrons occupying energy levels below Fermi energy absorb energy and move to higher energy levels above  $E_F$ . It is clear from the graph that even at very high temperature only few electrons occupying energy levels closer to Fermi energy absorb energy and move to higher energy levels above Fermi energy. Electrons at lower energy levels are not at all disturbed.

**Differences between Classical free electron theory and Quantum free electron theory.**

| <b>Classical free electron theory</b>   | <b>Quantum free electron theory</b>   |
|---|---|
| 1) The energy levels of the free electron are continuous.                                 | 1) The energy levels of the free electron are discontinuous.                                    |
| 2) Free electrons may possess same energy.  | 2) Free electrons obeys Pauli's Exclusion Principle so no two electrons can possess same energy |
| 3) The distribution of energy among the free electrons obeys Maxwell-Boltzmann statistics | 3) The distribution of energy among the free electrons obeys Fermi-Dirac statistics             |

**Success of Quantum free electron theory.****Specific Heat**

According to classical free electron theory, all the free electrons in a metal absorb the heat energy, when the metal is heated. It results in a large value of the specific heat as predicted. But as per quantum free electron theory, only few electrons occupying energy levels close to Fermi level  $E_f$  absorb the heat energy and get excited to the higher energy level. Hence the value of specific heat is very small.

According to Quantum free electron theory

$$C_V = \left( \frac{2k}{E_f} \right) RT$$

Since the order of magnitude of the Fermi energy for metals is about 5eV, we get

$$\frac{2k}{E_f} = 0.345 \times 10^{-4} \approx 10^{-4}$$

$$C_V = 10^{-4} RT$$

The above equation agrees with experimental value.

**Temperature Dependence on Electrical Conductivity**

We know that  $\sigma \propto \frac{1}{T}$

From the Quantum free electron theory

$$\sigma = \frac{ne^2 \lambda}{mv_f} \text{-----} > (1) \qquad \therefore \tau = \frac{\lambda}{v_f}$$

$v_f$  is independent of temperature, but  $\lambda$  is dependent on temperature. As the electrons get scattered by lattice ions, which are vibrating in such a way that displacement of ions takes place in all directions. Hence ions are assumed to have a circular cross-section of area  $\pi r^2$  which blocks the path of electron. Here 'r' is the amplitude of vibration, as the temperature increases, the energy of the vibrating ions increases, increasing the amplitude of vibration and decreasing the mean free path.

$$\therefore T \propto \pi^2 \text{ and } \pi^2 \propto \frac{1}{\lambda}$$

$$\therefore T \propto \frac{1}{\lambda} \text{----- (2)}$$

From (1) we know that  $\sigma \propto \lambda$

From (1) and (2)  $\sigma \propto \frac{1}{T} \Rightarrow$  which holds good with the experimental result.

### **Electrical Conductivity and Electron concentration**

According to Quantum free electron theory,

$$\sigma = \frac{ne^2 \lambda}{mv_f}$$

$$\sigma \propto n \text{ also } \sigma \propto \frac{\lambda}{v_f}$$

$$(n_{Al} = 18.66 \times 10^{28} / m^3) > (n_{Cu} = 8.45 \times 10^{28} / m^3)$$

Though electron concentration of Aluminium is 2.137 times higher than Copper. The value of  $\frac{\lambda}{v_f}$  of

Copper is 3.73 times more than that of Aluminium. Hence Conductivity of Copper exceeds that of Aluminium.

### **Band theory of solids**

The energy band structure of a solid determines whether it is a conductor, an insulator, or a semiconductor.

The electron of an isolated atom has certain definite energies such as 1s, 2s, 3p, 3s, etc. Between two consecutive allowed values of energy there is forbidden gap. As we bring together large number of identical atoms to form a solid, significant changes take place in the energy levels. The energy levels of each atom will interact with the other identical atoms. The wave functions of each atom will overlap and as a result the energy levels of each atom are distributed slightly and split into a number of levels corresponding to the number of atoms. The split energy levels are very close to each other and they form a narrow band known as energy band.

The range of energies possessed by electrons in a solid is known as energy band.

The energy band formed by the energy levels of the valence electrons is called valence band. The energy band immediately above the valence band where the conduction electrons are present is called conduction band.

The separation between the upper level of valence band and the bottom level of conduction band is known as forbidden energy gap,  $E_g$ .

The forbidden energy gap is a measure of the bondage of valence electrons to the atom. The greater the energy gap more tightly valence electrons are bound. When energy is supplied, electrons from the valence band jump to the conduction band and thereby the material starts conducting.

### Semiconductors

Semiconductors are the class materials with the conductivity in the range intermediate between those of good conductors and insulators. The resistivity of semiconductors lies in the range  $10^{-6}$  to  $10^8$  ohm-m. The energy band gap of a semiconductor is of the order of 1 eV.

### Extrinsic and Intrinsic semiconductors

By adding a very small amount of impurities to a semiconductor, a large increase in the conductivity can be achieved. This process is called 'Doping'. The impurity added is called a 'dopant'. Doped semiconductors are called 'Extrinsic semiconductors'.

On the other hand, the pure semiconductors are called 'Intrinsic semiconductors'. The conductivity in intrinsic semiconductors is due to the thermal excitation only.

There are two types of extrinsic semiconductors:

1. n-type semiconductors- electrons are the majority charge carriers and
2. p-type semiconductors- holes are the majority charge carrier

### Intrinsic Semiconductors

A semiconductor in an extremely pure form is known as an intrinsic semiconductor.

Intrinsic carriers in pure semiconductors

At room temperature in pure semiconductors, a single event of breaking of bonds leads to two carriers; namely electron and hole. The electron and hole are created as a pair & the phenomenon is called electron-hole pair generation. At any temperature  $T$  the number of electrons generated will be equal to the number of holes generated. If ' $n$ ' denotes number density of electrons in the conduction band & ' $p$ ' is the number of holes in the valence band then  $n = p = n_i$  where, ' $n_i$ ' is called intrinsic concentration or the intrinsic density

After the generation, the carriers move independently; the electrons move in the conduction band & the holes move in the valence band. The motion of these two carriers is random in their respective band as long as no external field is applied.

### Concept of effective mass of the electron and holes

Consider an isolated electron of mass  $m$  and charge  $-e$  in an electric field of strength  $E$ . The electric force acting on it is  $-eE$ . The electron gets accelerated, then  $-eE = ma$ . However, an electron within a crystal is in a periodic potential due to positive ion cores. The neighboring ions and electrons in the crystal do exert some force on the electron in a crystal. Then  $ma = -eE + \text{force due to neighboring ions}$

and electrons. Since the latter force is not known quantitatively, we can write the above equation as  $m_e^*a = -eE$  or  $m_e^* = -eE/a$  where  $m_e^*$  is called the effective mass of the electron within the crystal. Thus it is inferred that the effective mass of an electron depends on its location in the energy band. Electrons near the bottom of the conduction band have an effective mass which is almost equal to the effective mass of a free electron. Electrons near the bottom of the valence band have negative effective mass. The removal of an electron with a negative effective mass is identical to creating a particle of positive mass. Thus hole is given the status of particle with positive effective mass  $m_h^*$ .

Carrier concentration in intrinsic semiconductor

Expression for electron concentration (n)

The actual number of electron in the conduction band is given by

$$n = \int_{E_c}^{\text{top of the band}} f(E) g_c(E) dE \quad (1)$$

Since F-D function describes the probability of occupancy of energy state. Under thermal equilibrium condition, the electron concentration obtained from eqn. (1) is the equilibrium concentration.

As  $f(E)$  rapidly approaches zero for higher energies, the integral in eqn. (1) can be re-written as

$$n = \int_{E_c}^{\infty} f(E) g_c(E) dE$$

We have

$$g_c(E) = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} (E - E_c)^{\frac{1}{2}} dE \quad \text{Where } E \text{ is the kinetic energy of the electron.}$$

In the above fig. the bottom edge of conduction band  $E_c$  corresponds to the potential energy of an electron at rest in conduction band. Therefore the quantity  $(E - E_c)$  represents the kinetic energy of conduction level electron at high energy level.

$$g_c(E) = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} (E - E_c)^{\frac{1}{2}} dE \quad (2)$$

$$n = \int_{E_c}^{\infty} \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} \frac{(E - E_c)^{\frac{1}{2}}}{1 + \exp\left[\frac{(E - E_F)}{kT}\right]} dE \quad (3)$$

$$\text{As } E > E_F : e^{\frac{E - E_F}{kT}} \gg 1 : 1 + e^{\frac{E - E_F}{kT}} \cong e^{\frac{E - E_F}{kT}}$$

$$\text{Therefore } \frac{1}{1 + e^{\frac{E-E_F}{kT}}} \cong e^{\frac{-(E-E_F)}{kT}}$$

Using this eqn in eqn. (3) we get

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

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

Let  $E - E_c = x$  then  $dx = dE$

Lower limit when  $E = E_c$   $x = E_c - E_c = 0$

Upper limit when  $E = \infty$   $x = \infty - E_c = \infty$

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

The integral is similar to standard integral.

The solution of eqn.(4) is given by

$$\int_0^{\infty} x^{1/2} e^{-ax} dx = \frac{\sqrt{\pi}}{2a\sqrt{a}}, \quad \text{where } a = 1/kT$$

$$\therefore n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{(E_F-E_c)/kT} \left( \frac{\sqrt{\pi}}{2} (kT)^{3/2} \right)$$

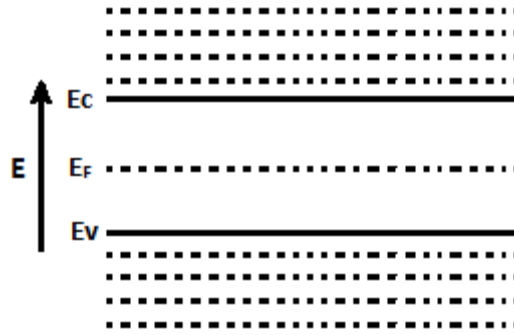
Rearranging the term we get

$$n = 2 \left[ \frac{2\pi m_e^* kT}{h^2} \right]^{3/2} e^{-(E_c-E_F)/kT} \quad (5)$$

$$\text{Let } N_c = 2 \left[ \frac{2\pi m_e^* kT}{h^2} \right]^{3/2}$$

$$\therefore n = N_c e^{-(E_c-E_F)/kT} \quad (6)$$

$N_c$  is temperature-dependent material constant known as effective density of states in the conduction band.



### Expression for hole concentration (p)

If  $f(E)$  is the probability for occupancy of an energy state at  $E$  by an electron, then probability that energy state is vacant is given by  $[1 - f(E)]$ . Since hole represents the unoccupied state in valence band, the probability for occupancy of state at  $E$  by a hole is equal to probability of absence of electron at that level. The hole concentration in valence band is therefore given by

$$p = \int_{\text{bottomband}}^{E_v} [1 - f(E)] g_v(E) dE \quad (7)$$

1-  $f(E)$  rapidly approaches to zero for lower energy levels, the above equation rewritten as

$$p = \int_{-\infty}^{E_v} [1 - f(E)] g_v(E) dE$$

$$p = \int_{-\infty}^{E_v} [1 - f(E)] \frac{4\pi}{h^3} (2m_h^*)^{\frac{3}{2}} (E_v - E)^{\frac{1}{2}} dE$$

$$\text{Now } 1 - f(E) = 1 - \frac{1}{1 + e^{\left(\frac{E - E_F}{kT}\right)}} = \frac{e^{\frac{E - E_F}{kT}}}{1 + e^{\left(\frac{E - E_F}{kT}\right)}} \quad (8)$$

For  $E < E_F$  ( $E - E_F$ ) is negative. Therefore  $e^{\frac{E - E_F}{kT}} \cong 0$

Therefore  $1 + e^{\left(\frac{E - E_F}{kT}\right)} \cong 1$  and equation 8 reduces to  $1 - f(E) = e^{\frac{-(E_F - E)}{kT}}$

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



$$p = \frac{4\pi}{h^3} (2m_h^*)^{\frac{3}{2}} e^{-\left(\frac{E_F - E_v}{kT}\right)} \int_{-\infty}^{E_v} (E_v - E)^{\frac{1}{2}} e^{-\left(\frac{E_v - E}{kT}\right)} dE$$

Let  $E_v - E = x$  then  $-dE = dx$  or  $dE = -dx$

LowerLt

UpperLt

$$x = E_v - (-\infty)$$

$$E = E_v$$

$$x = E_v + \infty$$

$$x = E_v - E_v = 0$$

$$x = \infty$$

$$x = 0$$

$$p = \frac{4\pi}{h^3} (2m_h^*)^{\frac{3}{2}} e^{-\left(\frac{E_F - E_v}{kT}\right)} \int_{\infty}^0 (E_v - E)^{\frac{1}{2}} e^{-\left(\frac{E_v - E}{kT}\right)} (-dE)$$

$$p = \frac{4\pi}{h^3} (2m_h^*)^{\frac{3}{2}} e^{-\left(\frac{E_F - E_v}{kT}\right)} \int_0^{\infty} (E_v - E)^{\frac{1}{2}} e^{-\left(\frac{E_v - E}{kT}\right)} dE$$

Above equation is of the standard form  $\int_0^{\infty} x^{\frac{1}{2}} e^{-ax} dx = \frac{\sqrt{\pi}}{2a\sqrt{a}}$  where  $E_v - E = x$  and  $a = \frac{1}{kT}$

$$p = \frac{4\pi}{h^3} (2m_h^*)^{\frac{3}{2}} e^{-\left(\frac{E_F - E_v}{kT}\right)} \frac{\sqrt{\pi}}{2} (kT)^{\frac{3}{2}}$$

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

Let  $N_v = 2 \left[ \frac{2\pi m_h^* kT}{h^2} \right]^{\frac{3}{2}}$  where  $N_v$  is temperature-dependent material constant known as effective

density of states in the valence band.

$$p = N_v e^{-\frac{(E_F - E_v)}{kT}}$$

### Fermi level in an intrinsic semiconductor

In an intrinsic semiconductor electron and hole concentrations are equal.

Therefore

$$n = p$$

$$N_c e^{-\frac{(E_C - E_F)}{kT}} = N_v e^{-\frac{(E_F - E_v)}{kT}}$$

Taking logarithm on both side and rearranging the term, we get

$$\Rightarrow \frac{-(E_C - E_F)}{kT} = \ln \left( \frac{N_v}{N_c} \right) - \frac{-(E_F - E_v)}{kT}$$

Multiplying by  $kT$  throughout

$$\Rightarrow -E_C + E_F = kT \ln\left(\frac{N_V}{N_C}\right) - E_F + E_V$$

$$\Rightarrow 2E_F = kT \ln\left(\frac{N_V}{N_C}\right) + E_C + E_V$$

$$\Rightarrow E_F = \left(\frac{E_C + E_V}{2}\right) + \frac{1}{2}kT \ln\left(\frac{N_V}{N_C}\right)$$

Substituting the values of  $N_V$  and  $N_C$  and after simplification we get

$$E_F = \left(\frac{E_C + E_V}{2}\right) + \frac{3}{4}kT \ln\left(\frac{m_h^*}{m_e^*}\right) \quad (1)$$

As  $kT$  is small and the effective mass  $m_e^*$  and  $m_h^*$  do not differ much, the second term in the eqn. (1) may be ignored.

If  $m_e^* = m_h^*$ , then we get

$$E_F = \left(\frac{E_C + E_V}{2}\right) \quad (2)$$

we can write eqn. (2) as

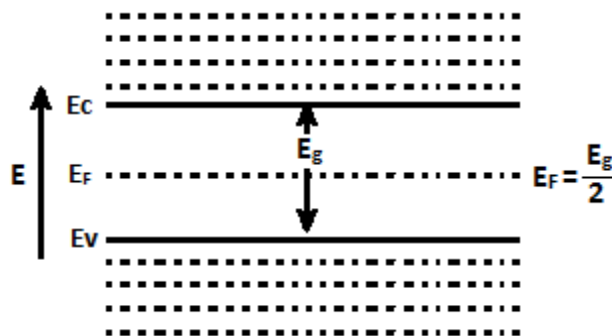
$$E_F = \left(\frac{E_C + E_V + E_V - E_V}{2}\right) = \frac{E_C - E_V}{2} + E_V$$

$$\text{but } E_C - E_V = E_g$$

$$\therefore E_F = \frac{E_g}{2} + E_V$$

If top of the valence band  $E_V$  is taken as zero level, then  $E_F = \frac{E_g}{2}$

Thus Fermi level in the intrinsic semiconductor lies at the centre of the energy gap as shown below:



**Intrinsic carrier density ( $n_i$ )**

In an intrinsic semiconductor at  $T = 0K$ , the electron concentration in the conduction band is identical to hole concentration in the valence band.

$$n = p = n_i$$

From this, we get

$$np = n_i^2$$

$$\begin{aligned} n_i^2 &= N_C e^{-\frac{(E_C - E_F)}{kT}} N_V e^{-\frac{(E_F - E_V)}{kT}} \\ &= (N_C N_V) e^{-\frac{(E_C - E_V)}{kT}} \end{aligned}$$

But  $E_C - E_V = E_g$

$$\begin{aligned} n_i^2 &= (N_C N_V) e^{-E_g / kT} \\ n_i &= (N_C N_V)^{1/2} e^{-E_g / 2kT} \end{aligned}$$

Substituting the values of  $N_C$  and  $N_V$  we get,

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

The following important points may be inferred from the above relation

1. The intrinsic density is independent of Fermi level position.
2. The intrinsic density is a function of band gap  $E_g$ , which represents the energy needed to break a bond.

The intrinsic density strongly depends on the temperature. The contribution of temperature increase to  $n_i$  is mostly due to the exponential term and only to a marginal extent due to the term  $T^{3/2}$ .

**Extrinsic semiconductor**

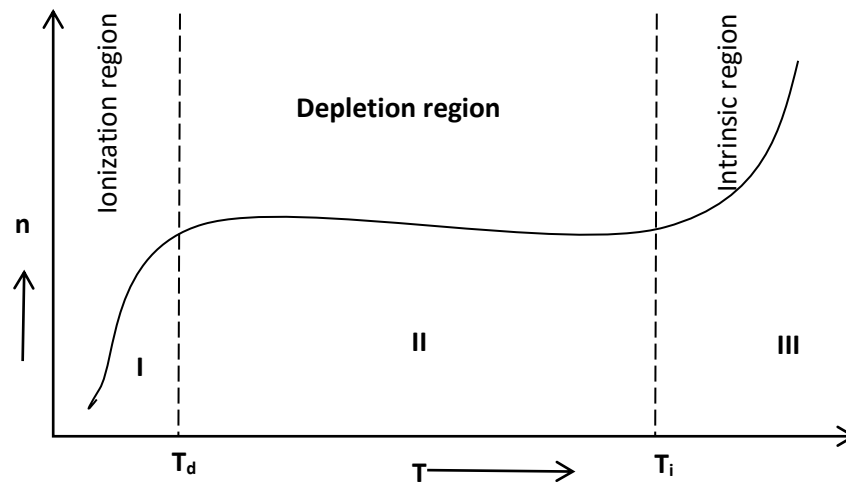
The intrinsic semiconductor has low conductivity which is not amenable to control. However, a judicious introduction of impurity atoms in a intrinsic semiconductor produces useful modification of its electrical conductivity. The method of introduction of controlled quantity of impurity into an intrinsic semiconductor is called doping. The impurity added is called dopant. The semiconductor doped with impurity atoms is called extrinsic semiconductor. There are two types of extrinsic semiconductor namely p-type & n-type which are produced depending on the group of impurity atoms.

n-type semiconductors are produced when pure semiconductors are doped with pentavalent impurity atoms such Phosphorous, Arsenic etc.

p-type semiconductors are produced when pure semiconductors are doped with trivalent impurity atoms such as Aluminum, Boron etc.

### Temperature variation of carrier concentration in extrinsic semiconductor

The dependence of electron concentration on temperature for n-type semiconductor is as shown in the figure below.



At 0K the donor levels are filled which means that all the donor electrons are bound to the donor atoms. At low temperature, corresponding to region- I, there is not enough energy to ionize all the donors and not at all enough to break covalent bond. As temperature increases, the donor atoms get ionized and donor atoms go into the conduction band. The region-I is known as ionization region. Occasionally a covalent bond may be broken out, but number of such events will be insignificantly small. At about 100K all donor atoms are ionized, once all electrons from donor level are excited into conduction band, any further temperature increase does not create additional electrons and the curve levels off. The region (region-II) is called depletion region. In the depletion region the electron concentration in the conduction band is nearly identical to the concentration of dopant atom.

If  $N_D$  is donor concentration then  $n_n = N_D$  (depletion region) where  $n_n$  – electron concentration in n-type

As temperature grows further, electron transitions from valence band to conduction band increases. At high temperature (region-III) the number of electron transition becomes so large that the intrinsic electron concentration exceeds the electron concentration due to donor. This region is therefore called intrinsic region. In intrinsic region,  $n_n = n_i$

Similarly in p-type semiconductor, the acceptor levels are vacant at 0K & valence band is full. As temperature increases in the ionization region, the electrons from the valence band jump into acceptor level. However the electrons do not acquire enough energy to jump into conduction band levels. At the temperature  $T_s$ , the acceptor levels are saturated with electrons. The region- II lying between  $T_s$  (saturation temperature) and  $T_i$  is called the saturation region. In case of p-type materials within this temperature interval the hole concentration remains constant as thermal energy is not yet sufficient to cause electron transition from valence band to conduction band. In the saturation region, the hole concentration is equal to the acceptor impurity concentration. Thus  $p_p = N_A$

With increase of temperature beyond  $T_i$ , electron transition due to intrinsic process commence & hole concentration due to intrinsic process far exceeds that due to impurity atom.

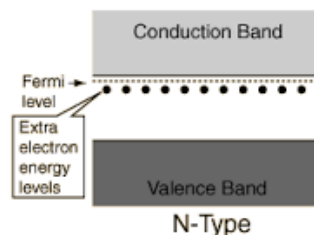
In region-III ,  $p_p = n_i$

### Fermi Energy in an extrinsic semiconductor

#### n-type semiconductor

n-type semiconductor consists of free electrons given by donor impurities. Energy levels for donor electrons will be much higher than the valence band and hence lie in the energy gap very close to the conduction band. These energy levels are called donor levels. The energy difference between the top of valence band and the donor level is  $E_d$ .

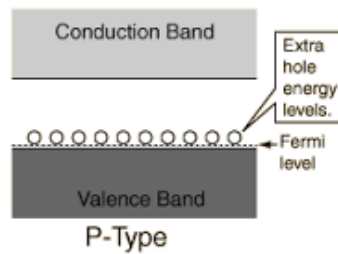
At low temperatures, electrons cannot be elevated from valence to conduction band. But to elevate electrons from donor level to conduction band, very small energy is sufficient since  $E_g - E_d$  is small. Hence the electrons from donor level occupy the bottom of the conduction band after excitation and returns to donor level on de-excitation. This is a continuous process.



Therefore, the average energy of the conduction electrons is  $E_d + \frac{1}{2}(E_g - E_d)$ . Thus Fermi level in n-type semiconductor at low temperature lie in the energy gap at the level  $\frac{1}{2}(E_g + E_d)$

#### p-type semiconductor

In case of p-type materials, acceptor atoms give rise to holes, which are free compare to the holes in the conduction band. The energy of the holes due to acceptor impurities are less and hence lie in an acceptor level  $E_a$  which is very close to valence band. Since the energy  $E_a$  is small, very small amount of thermal energy suffices to transfer the holes from acceptor to valence band.



At low temperature the conduction holes undergo excitation and de-excitation between the acceptor level and top of the valence band. Hence the average energy of conduction holes is  $\frac{1}{2} E_a$ . Therefore, the Fermi level in p-type semiconductor lies in the forbidden gap at  $\frac{1}{2} E_a$ .

### Law of mass action

From equations 1 & 2, it is clear that,  $N_e$  and  $N_h$  depends on  $E_F$ .

Consider the product of 1 & 2.

$$N_e N_h = \frac{32}{h^6} (\pi kT)^3 (m_e^* m_h^*)^{3/2} e^{\frac{E_g}{kT}}$$

The above equation shows that the product  $N_e N_h$  does not depend on  $E_F$ , but remains constant at a given temperature. i.e.,

$$N_e N_h = \text{a constant}$$

The above condition is applicable for both intrinsic and extrinsic semiconductor and is known as law of mass action. It states that 'for a given semiconductor, the product of charge carrier concentration remains a constant at any given temperature, even if the doping is varied'.

In case of an intrinsic semiconductor, if  $n_i$  is the charge carrier density, then

$$N_e = N_h = n_i$$