

## **Free electron theory:**

In solids, electrons in outer most orbits of atoms determine its electrical properties. Electron theory is applicable to all solids, both metals and non metals. In addition, it explains the electrical, thermal and magnetic properties of solids. The structure and properties of solids are explained employing their electronic structure by the electron theory of solids.

It has been developed in three main stages:

1. Classical free electron theory
2. Quantum Free Electron Theory.
3. Zone Theory.

# Classical Free Electron Theory

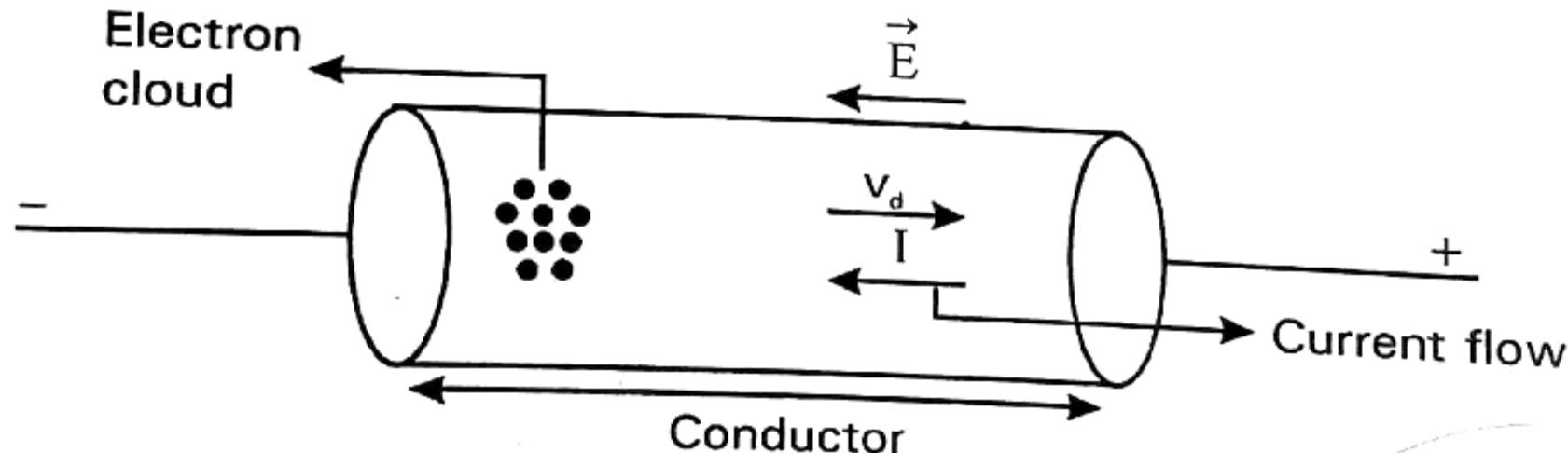
This theory was developed by Drude and Lorentz. Even though it is a macroscopic theory it successfully explained most of the properties of metals.

In this theory, the free electrons in a metal are treated like molecules in a gas; and, Maxwell-Boltzmann statistics is applied.

***The main assumptions or postulates of this theory are***

1. A metal is composed of positive metal ion fixed in the lattice.
2. All the valence electrons are free to move among the ionic array. Such freely moving electrons contribute towards conduction (electrical and thermal) in metals.
3. There are a large number of free electrons in a metal and they, move about the whole volume like the molecules of a gas.
4. The free electrons collide with the positive ions in the lattice and also among themselves. All the collisions are elastic, i.e., there is no loss of energy.

5. The electrostatic force of attraction between the free electrons and the metallic ions are neglected, i.e., The total energy of free electron is equal to its kinetic energy.
6. All the free electrons in metal have wide range of energies and velocities.
7. In the absence of electric field, the random motion of free electron is equally probable in all directions. So, the net current flow is zero.
8. When an electric field is applied as shown in figure 7.1 the electrons gain a velocity called drift velocity  $v_d$  and moves in opposite direction to the field resulting in a current flow in the direction of field.



**Figure : Conduction of electrons in a metal**

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

## **9. Relaxation time $\tau$**

**Definition - 1 :** 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.

**Definition - 2 :** 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.

## **10. Mean collision time $\tau_c$**

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

## **11. Mean free path $\lambda$**

It is the average distance travelled by the conduction electron between successive collisions with the lattice ions.

## **Electrical Conductivity $\sigma$**

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

$$\text{i.e.,} \quad \sigma = \frac{J}{E} \quad \text{-----[1]}$$

Its unit is **mho-m<sup>-1</sup>** or  **$\Omega^{-1} m^{-1}$** .

### **Expression for Electrical conductivity**

Electrical conductivity of a conductor is the property by which it allows the flow of electric current. *In a metal, the valence electrons are not attached to the individual atoms and are free to move about within the lattice. Hence, the valence electrons are also called free electrons or conduction electrons.*

In the absence of an electric field, the motion of the free electrons are completely random like those of the molecules of a gas in a container. But, when an electric field is applied to a metal, the electrons modify their random motion in such a way that, they drift slowly in the opposite direction to that of the applied field with an average velocity called the drift velocity  $v_d$ .

When an electric field  $E$  is applied, the free electrons in a metal experiences a force  $eE$ . Due to this force, the acceleration " $a$ " gained by the electron is

$$F = eE$$

$$ma = eE \quad [\because F = ma]$$

or 
$$a = \frac{eE}{m}$$
 -----[2]

Consider an electron that has just collided with an ion core. The collision momentarily destroys the tendency to drift and the electron will have truly random direction after this collision. In the next collision, the electrons velocity would have changed, to an average value  $v_d$  given by

$v_d = a\tau$

where  $\tau$  is called the mean free time.

----- [3]

Substituting equation (2) in (3), we get

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

The current density is given by

----- [4]

$$J = nev_d$$

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

----- [5]

Hence, substituting equation (4) in (5), we get

$$J = ne \times \frac{eE\tau}{m}$$

$$\therefore J = \frac{ne^2\tau}{m} \cdot E$$

But,  $J$  is also expressed as

$$J = \sigma E$$

----- [6]

Therefore, substituting for  $J$  in equation (6) from equation (7)

----- [7]

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

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

----- [8]

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

## **Expression for $\sigma$ in terms of $k_B T$**

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

$$\tau = \frac{\lambda}{v} \quad \text{---- [9]}$$

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)

$$\text{or } m = \frac{3k_B T}{v^2} \quad \text{---- [10]}$$

Substituting equation (10) for  $m$  and equation (9) for  $\tau$  in equation (8)

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

$$\therefore \sigma = \frac{ne^2 \lambda v}{3k_B T} \quad \text{---- [11]}$$

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

# Thermal Conductivity

*The thermal conductivity is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.*

$$\text{i.e., } K = - \frac{Q'}{A \left( \frac{dT}{dx} \right)}$$

where  $Q'$  is the rate of heat flow given by  $\left( \frac{dQ}{dt} \right)$

$A$  is the cross sectional area of the conductor

$\frac{dT}{dx}$  is the temperature gradient.

The –ve sign is optional, which indicates that, the heat flows from higher to lower temperature side.

The unit for thermal conductivity is  $\text{W m}^{-1}\text{K}^{-1}$ .

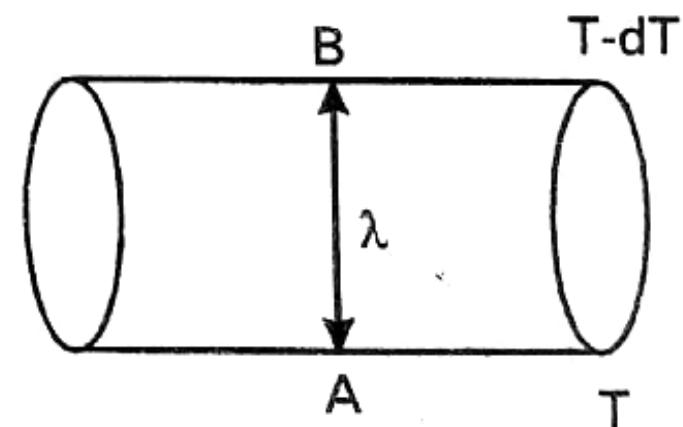
In solids, heat transfer takes place by conduction. In the process of heat transfer both electrons and phonons take part. Hence in general, the total thermal conductivity can be written as

$$K_{\text{Total}} = K_{\text{electron}} + K_{\text{phonon}}$$

Since, thermal conductivity due to electrons is greater than the thermal conductivity due to phonons in the case of pure metals, the total thermal conductivity is given by  $K_{\text{Total}} = K_{\text{electron}}$ .

### Expression for thermal conductivity K

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 7.2. Let the distance of separation between the surfaces 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.



*Figure*

Let,

The density of electrons =  $n$

The average thermal velocity =  $v$ .

Based on kinetic theory,

The average kinetic energy of an electron at A =  $\frac{3}{2} k_B T$  -----[1]

Similarly, the average kinetic energy of an electron at B =  $\frac{3}{2} k_B (T - dT)$  -----[2]

Therefore, the excess kinetic energy carried by electrons from A to B

$$\begin{aligned}
 &= \frac{3}{2} k_B T - \frac{3}{2} k_B (T - dT) \\
 &= \frac{3}{2} k_B dT
 \end{aligned} \quad \text{---- [3]}$$

Since, there is equal probability for the electrons to move in all the six directions ( $x, y, z$ ) and ( $-x, -y, -z$ ).

$$\text{The number of electrons crossing unit area in unit time from A to B} = \frac{1}{6} nv \quad \text{---- [4]}$$

$\therefore$  The excess energy transferred from A to B per unit area in unit time

$$= \frac{1}{6} nv \times \frac{3}{2} k_B dT = \frac{1}{4} nv k_B dT \quad \text{---- [5]}$$

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

$$= -\frac{1}{4} nv k_B dT \quad \text{--- [6]}$$

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

$$\begin{aligned} Q &= \frac{1}{4} nv k_B dT - \left( -\frac{1}{4} nv k_B dT \right) \\ &= \frac{1}{2} nv k_B dT. \end{aligned} \quad \text{--- [7]}$$

But, from the definition of thermal conductivity

$$K = \frac{Q}{\left(\frac{dT}{dx}\right)}$$

In this case,  $dx = \lambda$

$$\therefore K = \frac{Q}{\frac{dT}{\lambda}}$$

-----[8]

Hence, substituting for Q from equation (7) in equation (8), we get

$$K = \frac{\left(\frac{1}{2}\right)nvk_B dT}{\frac{dT}{\lambda}}$$

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

----- [9]

The value of K obtained with the above expression is verified experimentally and the free electron theory is found to be successful in explaining the thermal conductivity.

# Wiedemann-Franz Law

**Statement :** This law states that, the ratio of thermal conductivity to the electrical conductivity is directly proportional to the absolute temperature.

i.e.,  $\frac{K}{\sigma} \propto^a T$

or  $\frac{K}{\sigma} = LT$

where  $L$  is a constant called the Lorentz number. Its value is  $2.44 \times 10^{-8} W\Omega K^{-2}$ .

## Derivation

The electrical conductivity from equation (11) is

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

The thermal conductivity from equation (9) is

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

$$\therefore \frac{K}{\sigma} = \frac{nvk_B\lambda}{2\left(\frac{ne^2\lambda v}{3k_B T}\right)} = \frac{nvk_B\lambda \cdot 3k_B T}{2ne^2\lambda v} = \frac{3}{2} \frac{k_B^2}{e^2} T$$

$$\therefore \frac{K}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e}\right)^2 T = L T, \text{ where } L = \frac{3}{2} \left(\frac{k_B}{e}\right)^2.$$

Thus, Wiedemann-Franz law is obtained.

$$L = \frac{3}{2} \left(\frac{k_B}{e}\right)^2 = 1.12 \times 10^{-8} W\Omega K^{-2} \text{ is known as the Lorentz number.}$$

The above value of Lorentz number obtained based on classical concept does not agree with the experimental value. Hence, the assumption that all the free electrons of a metal participate in thermal conductivity is not correct.

The actual experimental value of the Lorentz number is  $2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ . Thus, there is a discrepancy in the value of L between classical theory and the experimental value. This discrepancy gets eliminated on applying quantum theory.

## **Success of Free Electron Theory**

1. It verifies ohm's law.
2. It explains the thermal and electrical conductivities of metals.
3. It is used to deduce Wiedemann-Franz law.
4. It explains the optical properties of metals.

## **Drawbacks of Classical Free Electron Theory**

1. The theoretical value obtained for specific heat and electronic specific heat of metals based on this theory is not in agreement with the experimental value.
2. The classical free electron theory is not able to explain the electrical conductivity of semiconductors and insulators.
3. According to classical theory,  $\frac{K}{\sigma T}$  is constant at all temperatures. But, this is not constant at low temperature.
4. The theoretical value of paramagnetic susceptibility  $\chi$  is greater than the experimental value and ferromagnetism cannot be explained.
5. The phenomena such as photoelectric effect, compton effect and black body radiation could not be explained by this theory.

## **Quantum free electron theory of metals:**

### **Advantages:**

1. All the electrons are not present in the ground state at 0 K, but the distribution obeys Pauli's exclusion principle. At 0 K, the highest energy level filled is called Fermi-level.
2. The potential remains constant throughout the lattice.
3. Collision of electrons with positive ion cores or other free electrons is independent of charges and is elastic in nature.
4. Energy levels are discrete.
5. It was successful to explain not only conductivity, but also thermionic emission paramagnetism, specific heat.

### **Drawbacks:**

1. It fails to explain classification of solids as conductors, semiconductors and insulators.

## Bloch Theorem:

According to free electron model, a conduction electron in metal experiences constant potential. But in real crystal, there exists a periodic arrangement of positively charged ions through which the electrons move. As a consequence, the potential experienced by electrons is not constant but it varies with the periodicity of the lattice. In zone theory, as per Bloch, potential energy of electrons considered as varying potential with respect to lattice 'a'.

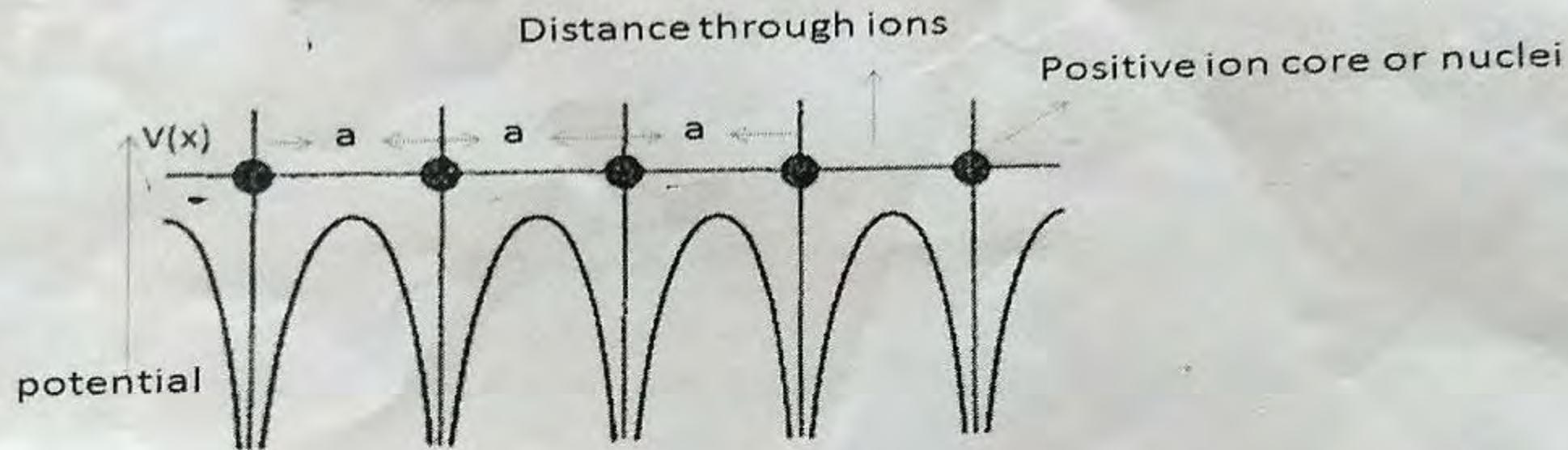


Fig: Variation of potential energy in a periodic lattice.

Let us examine one dimensional lattice as shown in figure. It consists of array of ionic cores along X-axis. A plot of potential V as a function of its position is shown in figure.

**From graph:**

At nuclei or positive ion cores, the potential energy of electron is minimum and in-between nuclei, the P.E. is considered as maximum w.r.to. Lattice constant 'a'.

This periodic potential  $V(x)$  changes with the help of lattice constant  $a$ ,

$$V(x) = V(x + a) \quad (\text{'a' is the periodicity of the lattice})$$

To solve, by considering Schrodinger's time independent wave equation in one dimension,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} [E - V(x)]\psi = 0 \dots \dots \quad (1)$$

Bloch's 1D solution for Schrodinger wave equation (1)  $\psi_k(x) = u_k(x)\exp(ikx) \dots \dots \dots \quad (2)$

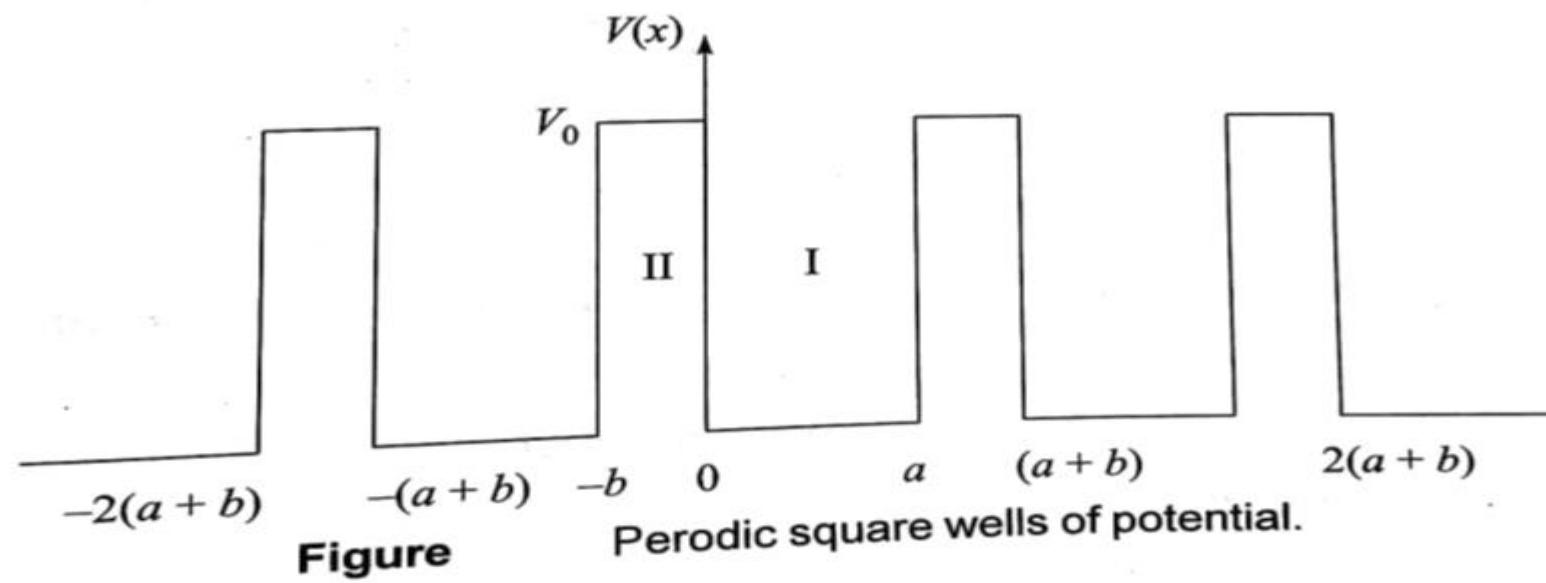
where  $u_k(x) = u_k(x + a)$

Here  $u_k(x)$  -periodicity of crystal lattice, modulating function, k- propagation vector  $= \frac{2\pi}{\lambda}$   $e^{ikx}$  is plane wave.

By applying eq.n (2) to eq.n (1), it is not easy to solve Schrodinger wave equation and Bloch cannot explains complete physical information about an  $e^-$  in periodic potential field. Then Kronig Penny model was adopted to explains the electrical properties of an  $e^-$ .

# Kronig-Penney Model

The Kronig–Penney model is a simplified model for an electron in a one-dimensional periodic potential. It explains the behaviour of an electron in a periodic potential. This model assumes that the potential energy of an electron in a linear array of positive nuclei has the form of a periodic square well potential of period  $(a + b)$  such that in the region  $0 < x < a$ , the



potential energy is equal to zero and in the region  $b < x < 0$ , the potential energy is  $V_0$ , i.e.

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ V_0 & \text{for } -b < x < 0 \end{cases} \quad (14.1)$$

The possible states that the electron can occupy in such a square well potential can be determined by one-dimensional Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0 \quad (14.2)$$

Here  $m$  is the mass of electron.

To obtain the meaningful results, we solve above Eq. (14.2) in the two regions I and II as shown in Figure 14.3. Equation (14.2) for the two regions I and II takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad [\text{for region } 0 < x < a] \quad (14.3)$$

and

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V_0]\psi = 0 \quad [\text{for region } b < x < 0] \quad (14.4)$$

Now we define two real quantities  $\alpha$  and  $\beta$  such that

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

$$\beta^2 = \frac{2m}{\hbar^2}[V_0 - E]$$

and

[Here we assume that  $E < V_0$ ]

Then Eqs. (14.3) and (14.4) become

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad [\text{for region } 0 < x < a] \quad (14.5)$$

and

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad [\text{for region } b < x < 0] \quad (14.6)$$

Since  $\psi(x)$  is the periodic function, it can be expressed as

$$\psi(x) = \exp(ikx)\varphi(x)$$

If  $\varphi_1$  and  $\varphi_2$  are the values of  $\varphi(x)$  in the two regions I and II, then Eqs. (14.5) and (14.6) take the form

$$\frac{d^2\varphi_1}{dx^2} + 2ik \frac{d\varphi_1}{dx} + (\alpha^2 - k^2)\varphi_1 = 0 \quad (14.7)$$

and

$$\frac{d^2\varphi_2}{dx^2} + 2ik \frac{d\varphi_2}{dx} + (\beta^2 + k^2)\varphi_2 = 0 \quad (14.8)$$

The general solutions of Eqs. (14.7) and (14.8) are

$$\varphi_1 = A \exp[i(\alpha - k)x] + B \exp[-i(\alpha + k)x] \quad (14.9)$$

and

$$\varphi_2 = C \exp[(\beta - ik)x] + D \exp[-(\beta + ik)x] \quad (14.10)$$

Here  $A$ ,  $B$ ,  $C$  and  $D$  are constants to be determined by the following conditions:

$$(\varphi_1)_{x=0} = (\varphi_2)_{x=0}; \left( \frac{d\varphi_1}{dx} \right)_{x=0} = \left( \frac{d\varphi_2}{dx} \right)_{x=0}$$

and

$$(\varphi_1)_{x=a} = (\varphi_2)_{x=-b}; \left( \frac{d\varphi_1}{dx} \right)_{x=a} = \left( \frac{d\varphi_2}{dx} \right)_{x=-b}$$

Applying these conditions in Eqs. (14.9) and (14.10) and solving, we get a significant expression in the form

$$\gamma \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad (14.11)$$

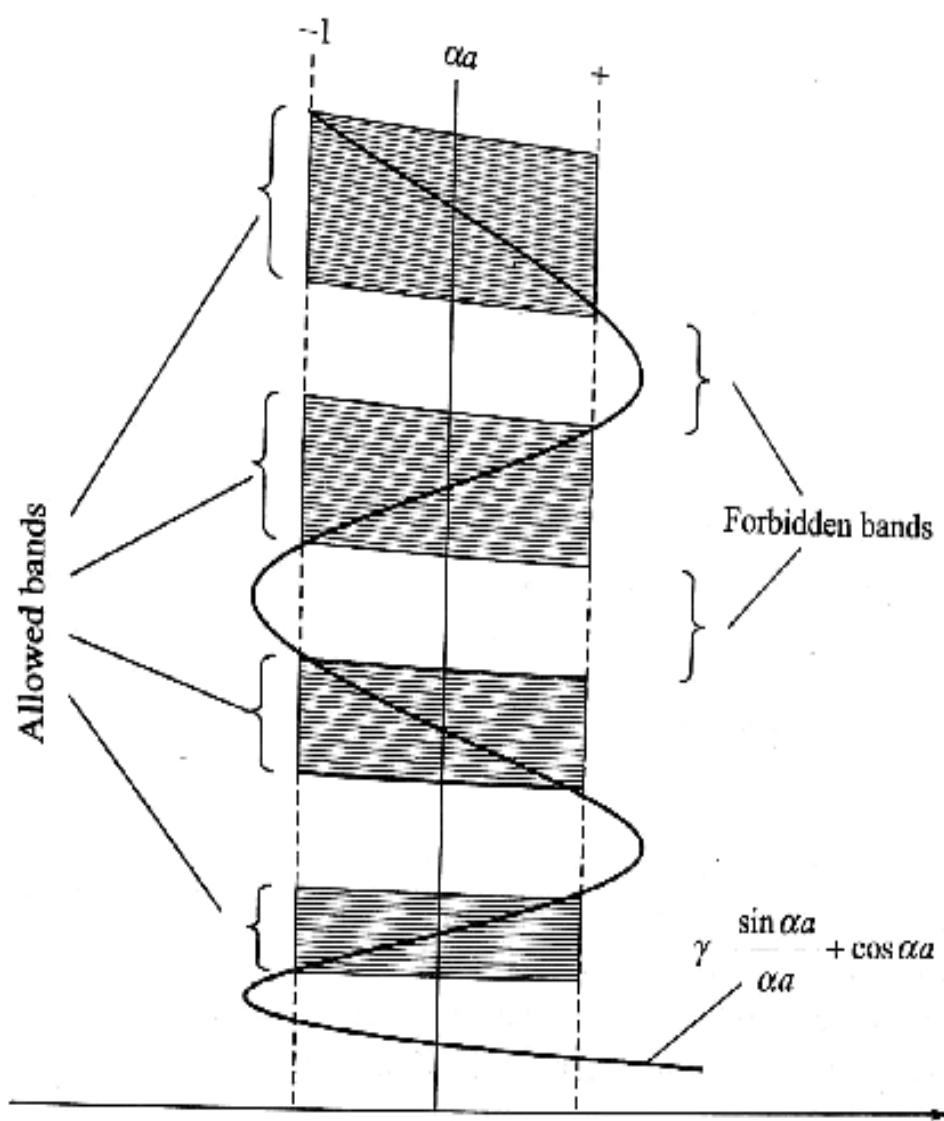
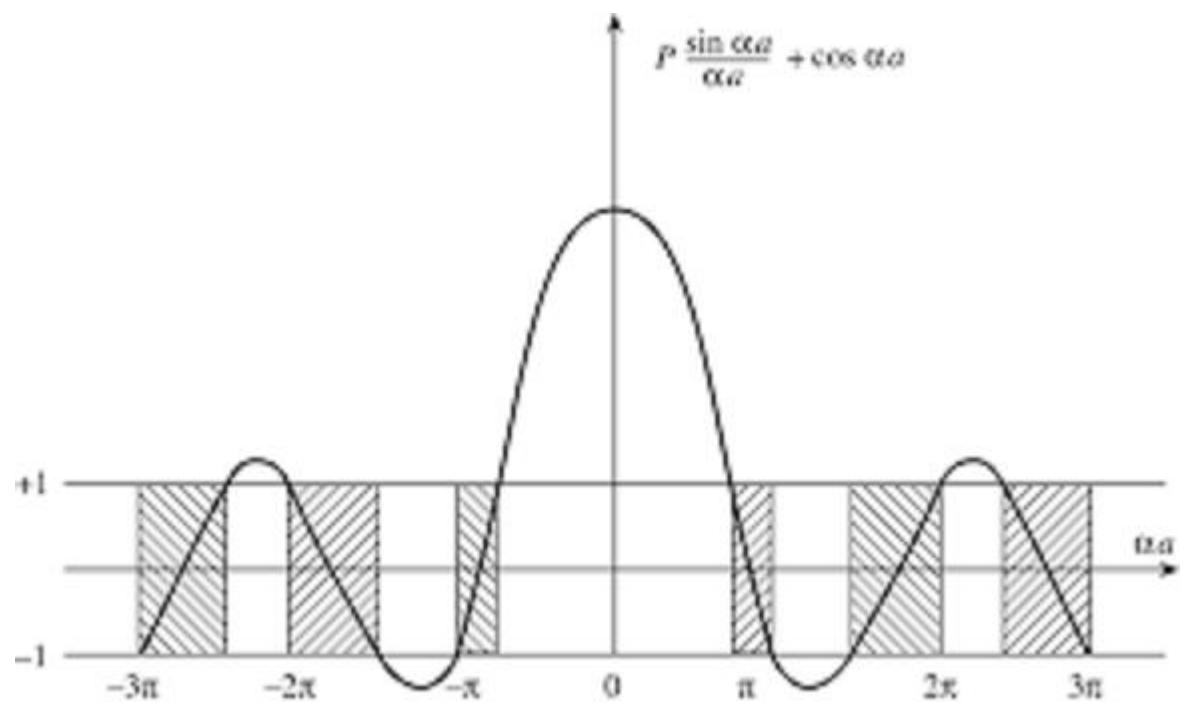
Here quantity  $\gamma$  is defined as

$$\gamma = \frac{mV_0 ab}{\hbar^2} \quad (14.12)$$

The solution of Eq. (14.11) for finite values of quantity  $\gamma$  results in an alteration of energy for real and imaginary values of  $k$ . The plot of L.H.S. of Eq. (14.11) is shown in Figure 14.4.

This curve shows that:

- (i) The energy spectrum of electrons consists of a number of allowed energy bands separated by forbidden energy bands.
- (ii) The width of the allowed energy bands increases with increase in value of  $\alpha$ , i.e. with increase in lattice parameter  $a$ .



Now let us consider two important cases:

**Case (i):** When  $\gamma \rightarrow \infty$ , then Eq. (14.12) has a solution only if

$$\sin \alpha a = 0$$

or

$$\sin \alpha a = \sin n\pi \quad [\text{here } n \text{ is an integer}]$$

or

$$\alpha a = n\pi$$

or

$$\alpha^2 a^2 = n^2 \pi^2$$

or

$$\frac{2mE}{\hbar^2} a^2 = n^2 \pi^2 \quad \left[ \text{since } \alpha^2 = \frac{2mE}{\hbar^2} \right]$$

or

$$E = E_n \text{ (say)} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

This expression represents the energy levels of a particle in one-dimensional box of atomic dimension. This is an expected result, since for large values of  $\gamma$ ; the electrons cannot tunnel through the potential barrier.

**Case (ii):** When  $\gamma \rightarrow 0$ , then Eq. (14.11) reduces to  
 $\cos \alpha a = \cos ka$

or

$$\alpha a = ka$$

or

$$\alpha^2 = k^2$$

or

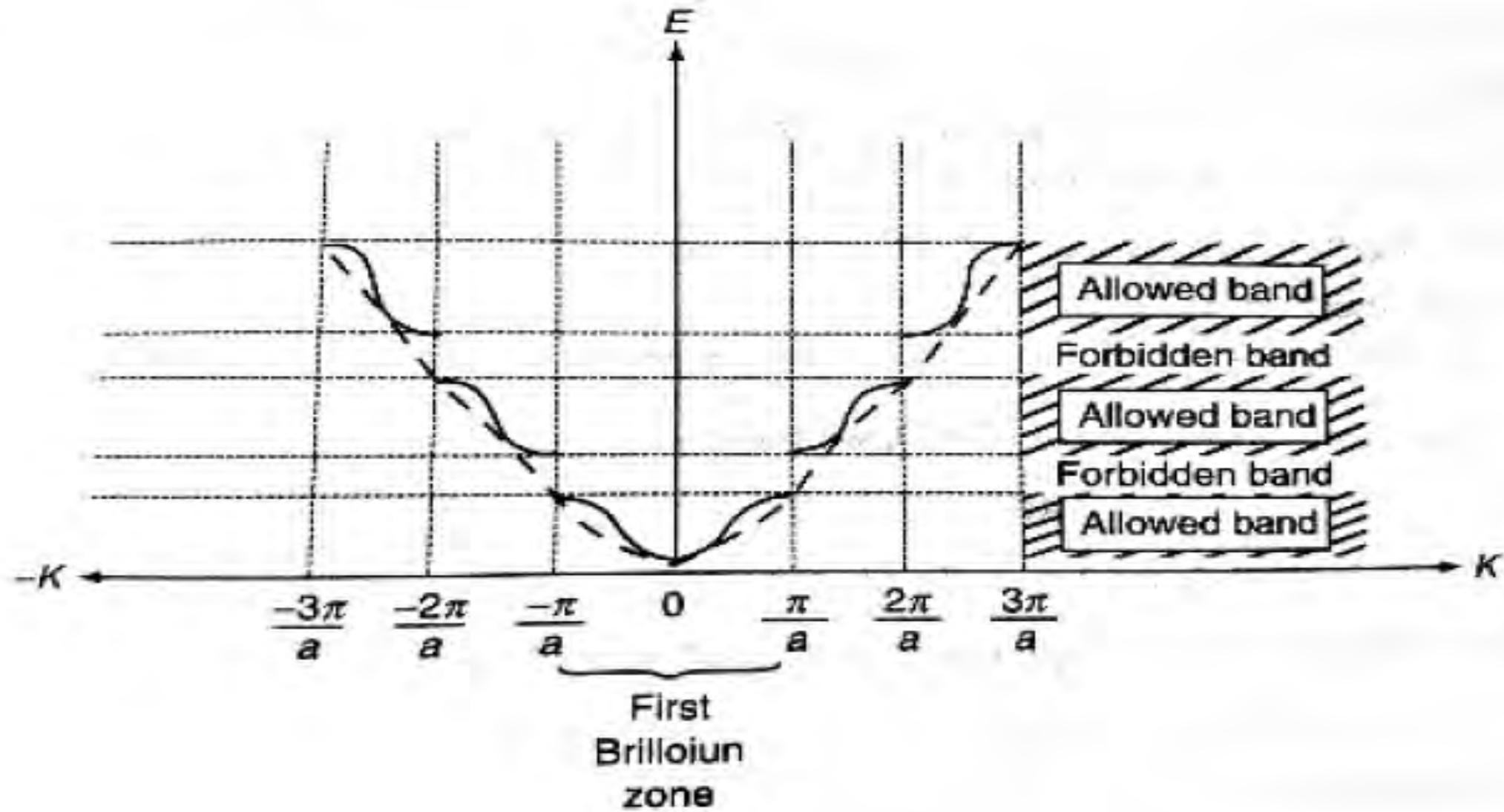
$$\frac{2mE}{\hbar^2} = k^2$$

or

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

This expression represents the energy of a completely free particle. In this case, the allowed energy bands of electrons are continuous. This is also an expected result which agrees with the free electron theory.

## EK Diagram



The Brillouin zone are the boundaries that are marked by the values of wave vector  $k$ , in which electrons can have allowed energy values. These represent the allowed values of  $k$  of the electrons in 1D, 2D,&3D.

We have ,the energy of the electron in a constant potential box is,

$$E = \frac{n^2 h^2}{8ma^2} \dots \dots \dots (1) \text{ where } a = \text{length of the box.}$$

But,

$$k = \frac{n\pi}{a} \Rightarrow k^2 = \frac{n^2 \pi^2}{a^2}$$

$$\frac{n^2}{a^2} = \frac{k^2}{\pi^2} \dots \dots \dots (2)$$

Substitute eqn (2) in (1) ,we get  $E = \frac{k^2 h^2}{8m\pi^2}$  ;  $E \propto k^2$ . It represents parabolic equation.

A graph is drawn between the total energy (E) and the wave vector  $k$ ,for various values of  $k$ .

i.e. $k = \frac{n\pi}{a}$  ;  $n = \pm 1, \pm 2, \pm 3, \dots \dots$

It is the energy spectrum of an electron moving in presence of a periodic potential field and is divided into allowed energy regions (allowed zones) or forbidden energy gaps (forbidden zones).

Allowed energy values lie in the region  $k = -\pi/a$  to  $=\pi/a$ . This zone is called the first Brillouin zone. After a break in the energy values, called forbidden energy band, we have another allowed zone spread from  $k = -\pi/a$  to  $-2\pi/a$  and  $+\pi/a$  to  $+2\pi/a$ . This zone is called the second Brillouin zone. Similarly, higher Brillouin zones are formed

# Effective Mass

When an electron is moving inside a solid material, the force between other atoms will affect its movement and it will not be described by Newton's law. So we introduce the concept of effective mass to describe the movement of electron in Newton's law. The effective mass can be negative or different due to circumstances.

Let us consider an electron inside a crystal in a state  $k$  with the electronic wave function  $\exp(ik)$ . For a wave packet the group velocity is given by

$$v = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{d(\hbar\omega)}{dk} = \frac{1}{\hbar} \frac{dE}{dk} \quad (14.13)$$

In presence of an electric field  $\xi$ , the force experienced by the electron is

$$F = \frac{dp}{dt} = m \frac{dv}{dt}$$

Here  $p$  is the electron's momentum.

Now since  $p = \hbar k$ , so we can say that

$$\hbar \frac{dk}{dt} = m \frac{dv}{dt}$$

or

$$\frac{\hbar}{m} \frac{dk}{dt} = \frac{dv}{dt} \quad (14.14)$$

Substituting the value of  $v$  from Eq. (14.13) to Eq. (14.14), we get

$$\frac{\hbar}{m} \frac{dk}{dt} = \frac{d}{dt} \left( \frac{1}{\hbar} \frac{dE}{dk} \right)$$

or

$$\frac{\hbar}{m} \frac{dk}{dt} = \frac{1}{\hbar} \frac{d}{dt} \left( \frac{dE}{dk} \right)$$

or

$$\frac{\hbar}{m} \frac{dk}{dt} = \frac{1}{\hbar} \frac{d}{dk} \left( \frac{dE}{dk} \right) \frac{dk}{dt}$$

or

$$\frac{1}{m} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

Replacing  $m$  by  $m^*$  in above equation, we get

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

This is the expression for the effective mass of electron.

### ***Significance of effective mass of electron***

Effective mass of electron has a special importance in solid state electronics because the results of free electron theory can be applied in band theory of solids by replacing the rest mass  $m$  of electron by effective mass of electron. The effective mass is used in transport calculations, such as transport of electrons under the influence of fields or carrier gradients in different semiconductors. It is also used to calculate the density of states.

# 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.

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

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

where

$f(E)$  is the fermi function.

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

$k_B$  is the Boltzmann constant

and,

$T$  is the absolute temperature.

Thus, a system is characterised 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.

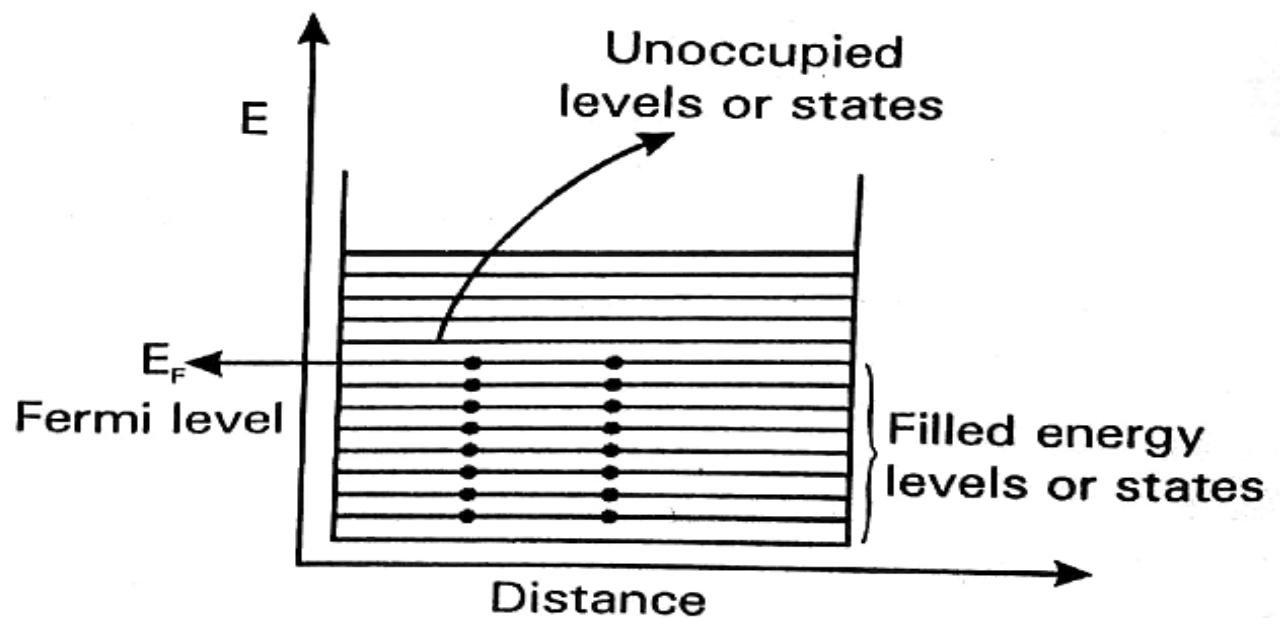
## Case 1:

### At T = 0K

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 as shown in figure 9.4.

*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, at a temperature of absolute zero, all the energy levels lying above the fermi level are empty and those lying below are completely filled. Hence, fermi level helps to distinguish between an occupied and an unoccupied state. Since there are two electrons in each energy level, out of the N allowed energy levels,  $\frac{N}{2}$  of them will be occupied.



*Figure 9.4 : Distribution of electrons in a band.  
Electrons occupy all the levels below  $E_F$ .*

**Special cases :- Probability of occupation**

(a) At  $T = 0K$  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,

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

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

(b) At  $T = 0K$  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,

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

$\therefore f(E) = 0$  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  $E_F$ .

Thus, the variation of  $f(E)$  at  $T = 0K$  for different energy values takes a step function as shown in figure 9.5.

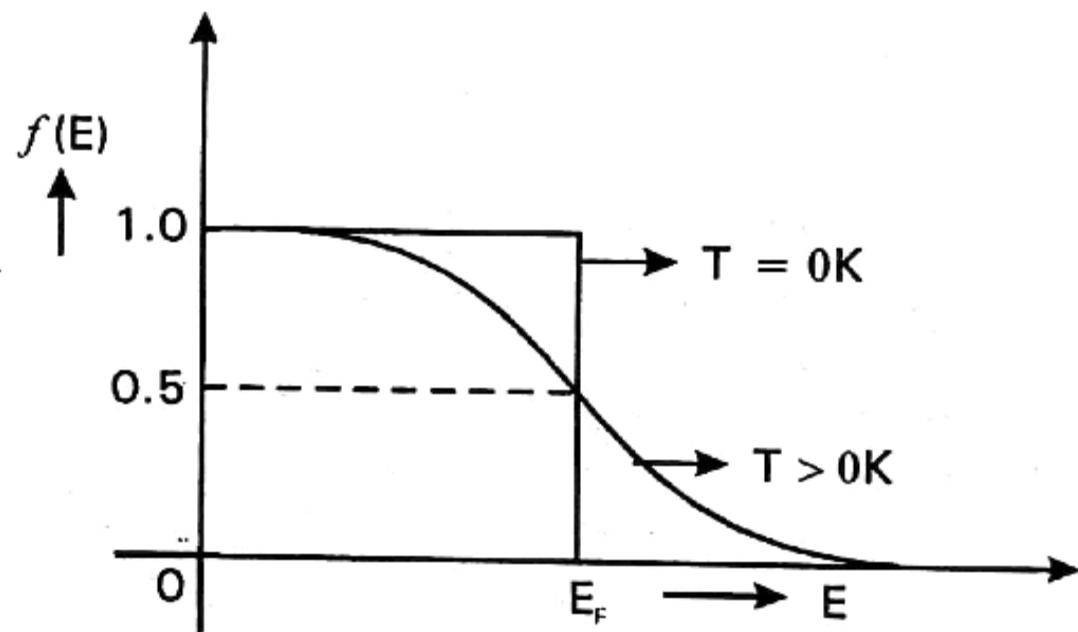


Figure 9.5 : Fermi function at 0K

**Case 2 :**

***Probability of occupation at  $T > 0K$***

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

At  $T > 0K$  for  $E = E_F$ , the argument in the exponential function becomes zero.

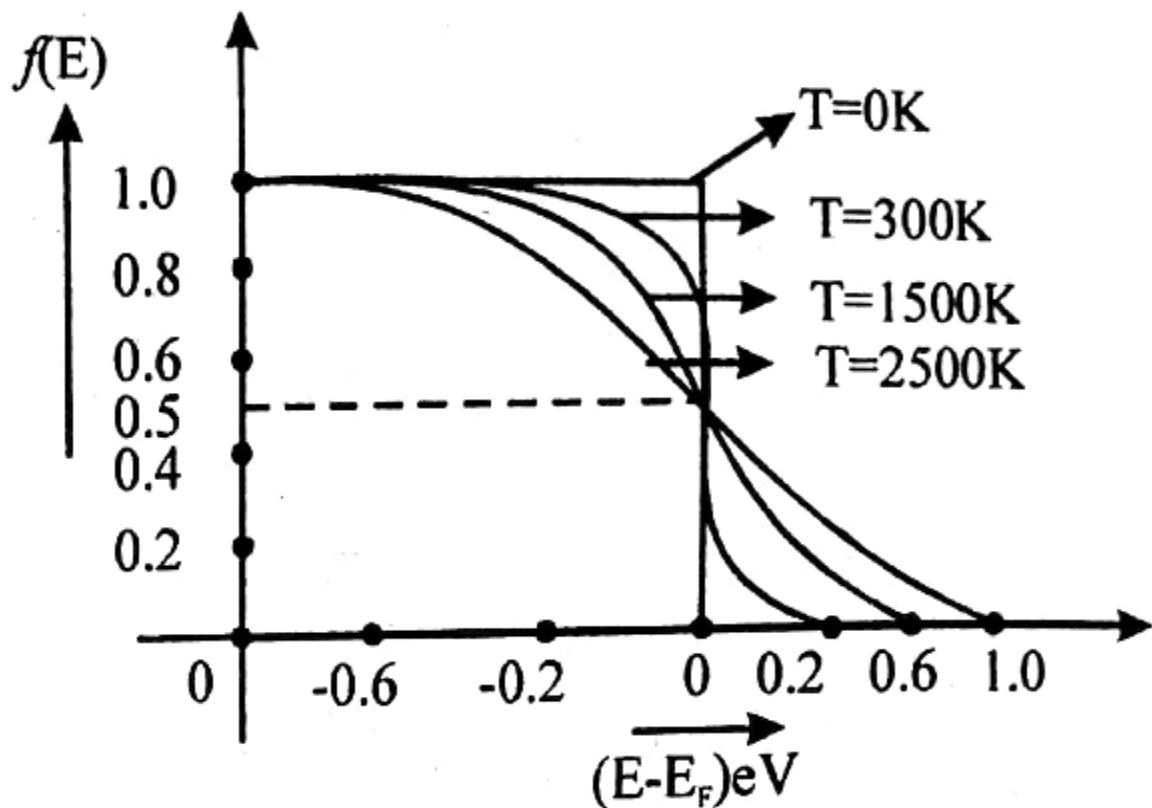
$$\therefore f(E) = \frac{1}{1+e^0} = \frac{1}{1+1} = \frac{1}{2} = 0.5 \quad [ \because e^0 = 1 ]$$

Thus  $f(E) = \frac{1}{2}$  implies that, the probability of occupancy of an electron is 50% at any temperature above 0K. Further for  $E > E_F$ , the  $f(E)$  value falls off to zero rapidly as shown in figure 9.5.

### Case 3 :

#### *Probability of occupation at very high temperatures*

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. Hence, as temperature increases an electron may get energy of the order of  $k_B T$  and go to higher vacant state. As a result, fermi function falls. But, for energies below  $E_F$ , such that  $(E_F - E) \gg k_B T$  the value of  $f(E)$  will be unity i.e., only in the region of  $E_F$ ,  $f(E)$  begins to fall as shown in figure 9.6.



*Figure 9.6 : The Fermi function at very high temperatures*

## Density of States

The fermi function gives us only the probability of occupation of an energy state by an electron. But, it does not give the actual number of electrons with a given energy.

Hence, to know the actual number of electrons with a given energy, the number of available energy states in the system with a particular energy has to be determined first. Then, by multiplying the number of energy states by the probability occupation we get the actual number of electrons.

If  $Z'(E)dE$  is the number of available states and  $f(E)$  the probability of occupation of any given energy state by the electron; then, the number of electrons  $N(E)$  in a system with energy  $dE$  is given by

$$N(E)dE = Z'(E)dE f(E)$$

----- [1]

Derivation to determine the number of available of energy states  
 Density of states  $Z(E)dE$  is defined as the number of energy states  $Z'(E)dE$  per unit volume in an energy interval  $dE$ .

### To find $Z'(E)dE$

We know that, the equation for the energy of a particle in 3d potential well is given by

$$E = \frac{h^2}{8m\alpha^2} (n_x^2 + n_y^2 + n_z^2) \quad [2]$$

where  $n_x$ ,  $n_y$  and  $n_z$  are positive integers and  $m$  is the mass of the electron.

Let us take  $n_x^2 + n_y^2 + n_z^2 = n^2$  [3]

$\therefore$  Equation (2) becomes,

$$E = \frac{h^2}{8m\alpha^2} n^2 \quad [4]$$

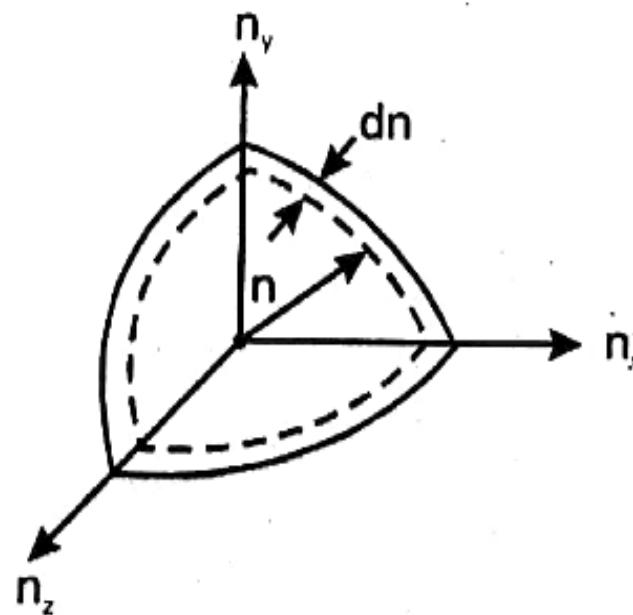
The allowed energy states are governed by the values of  $n_x$ ,  $n_y$  and  $n_z$ . For a single set of  $n_x$ ,  $n_y$  and  $n_z$  we get one energy value as per equation (2).

Since, equation  $n^2 = n_x^2 + n_y^2 + n_z^2$  represents a sphere, and if we take  $n_x$ ,  $n_y$  and  $n_z$  along three mutually perpendicular axes of a co-ordinate system then, each set of such values can be represented as a point in the system. Hence, for a very large number of such set of values we get a spherical distribution of points.

Therefore, to know the actual number of energy states with all possible energies a sphere of radius  $n$  is constructed. Thus, every point within this sphere represents an energy state, i.e., a unit volume of this sphere contains exactly one state. Also, since the values of  $n_x$ ,  $n_y$  and  $n_z$  are restricted to be positive; only one octant [i.e., (1/8)] of the sphere is available. Therefore,

*The number of allowed energy states in any volume = (Numerical value of) volume of one octant of the sphere of a definite radius*

----- [5]



*Figure : An octant of a sphere*

Hence, in order to calculate the number of energy states with small energy  $dE$ , we construct two spheres, one with radii  $n$  and the other with radii  $n + dn$  with energies  $E$  and  $E + dE$  respectively. Within the sphere and octant is considered as shown in figure.

Therefore, the number of available states with sphere of radius  $n$  is  $\frac{1}{8} \times \frac{4\pi}{3} n^3$

Applying equation (5)

$$= \frac{1}{6} \pi n^3$$

----- [6]

Similarly, the number of available states with sphere of radius  $(n + dn)$  is  $\frac{1}{8} \times \frac{4}{3} \pi(n + dn)^3$

$$= \frac{1}{6} \pi(n + dn)^3$$

Thus, the number of allowed energy states in an energy range  $E$  and  $E + dE$  (i.e., in the energy interval  $dE$ ) is ----- [7]

$$\begin{aligned} Z'(E)dE &= \frac{1}{6}\pi(n + dn)^3 - \frac{1}{6}\pi n^3 \\ &= \frac{\pi}{6} (n^3 + dn^3 + 3n^2dn + 3dn^2n - n^3) \end{aligned}$$

[Neglecting higher power of  $dn$  and on simplification]

$$Z'(E)dE = \frac{\pi}{6} [3n^2dn] ----- [8]$$

$$Z'(E)dE = \frac{\pi}{2} n^2dn$$

or

$$Z'(E)dE = \frac{\pi}{2} n (ndn) ----- [9]$$

From equation (4)

$$E = \frac{n^2 h^2}{8m\alpha^2}$$

$$n^2 = \frac{8m\alpha^2 E}{h^2}$$

---- [10]

Therefore,

$$n = \left( \frac{8m\alpha^2}{h^2} E \right)^{\frac{1}{2}}$$

---- [11]

On differentiating equation (10) we get,

$$2ndn = \frac{8m\alpha^2}{h^2} dE$$

$$\therefore ndn = \frac{8m\alpha^2}{2h^2} dE$$

---- [12]

substituting equation (11) and (12) in equation (9)

$$Z'(E)dE = \frac{\pi}{2} \left( \frac{8m\alpha^2 E}{h^2} \right)^{\frac{1}{2}} \frac{8m\alpha^2}{2h^2} dE$$

or  $Z'(E)dE = \frac{\pi}{4} \left( \frac{8m\alpha^2}{h^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$

---- [13]

According to Pauli's exclusion principle, since there can be two electrons, one with spin up and the other with spin down in a single energy state, The actual number of available energy states is

$$Z'(E)dE = 2 \times \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{3/2} E^{1/2} dE$$

$$Z'(E)dE = \frac{\pi}{2} \left( \frac{8ma^2}{h^2} \right)^{3/2} E^{1/2} dE \quad \text{----- [14]}$$

or  $Z'(E)dE = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \quad \text{----- [15]}$

Therefore, the density of states i.e., the number of energy states per unit volume with energy interval  $dE$  is

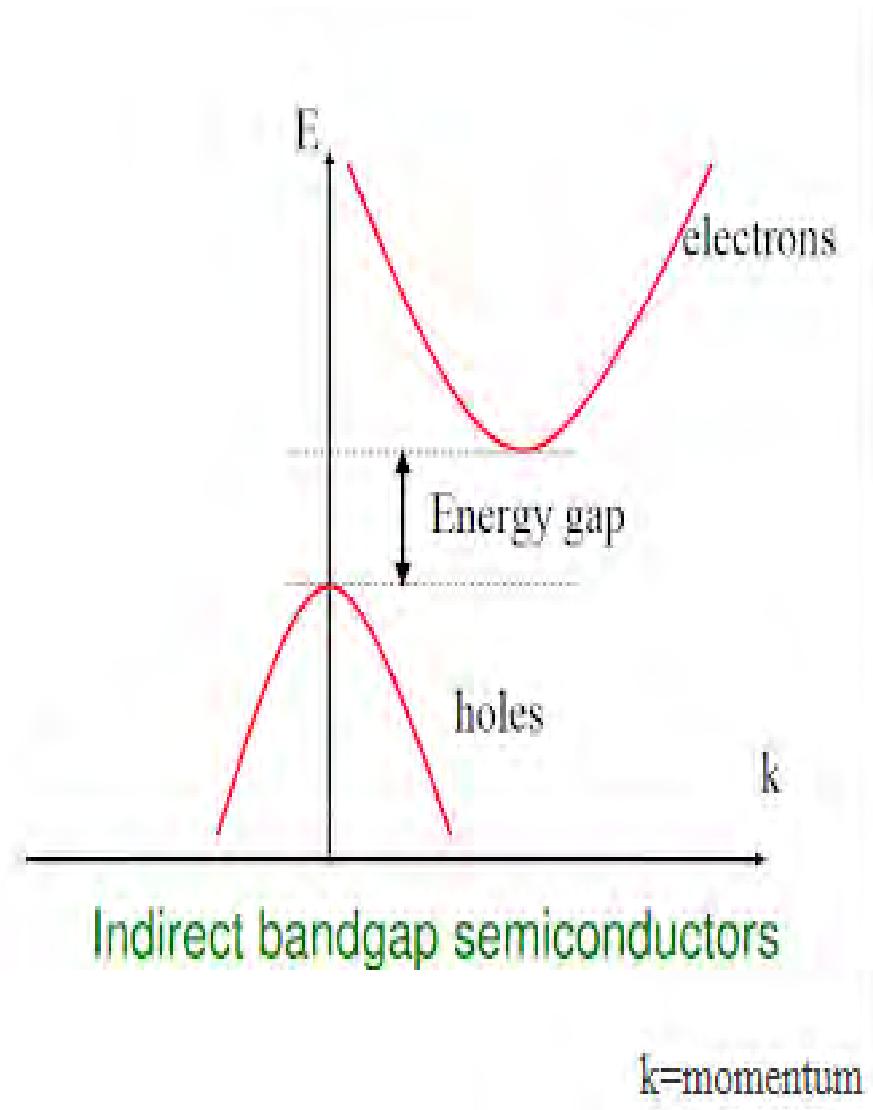
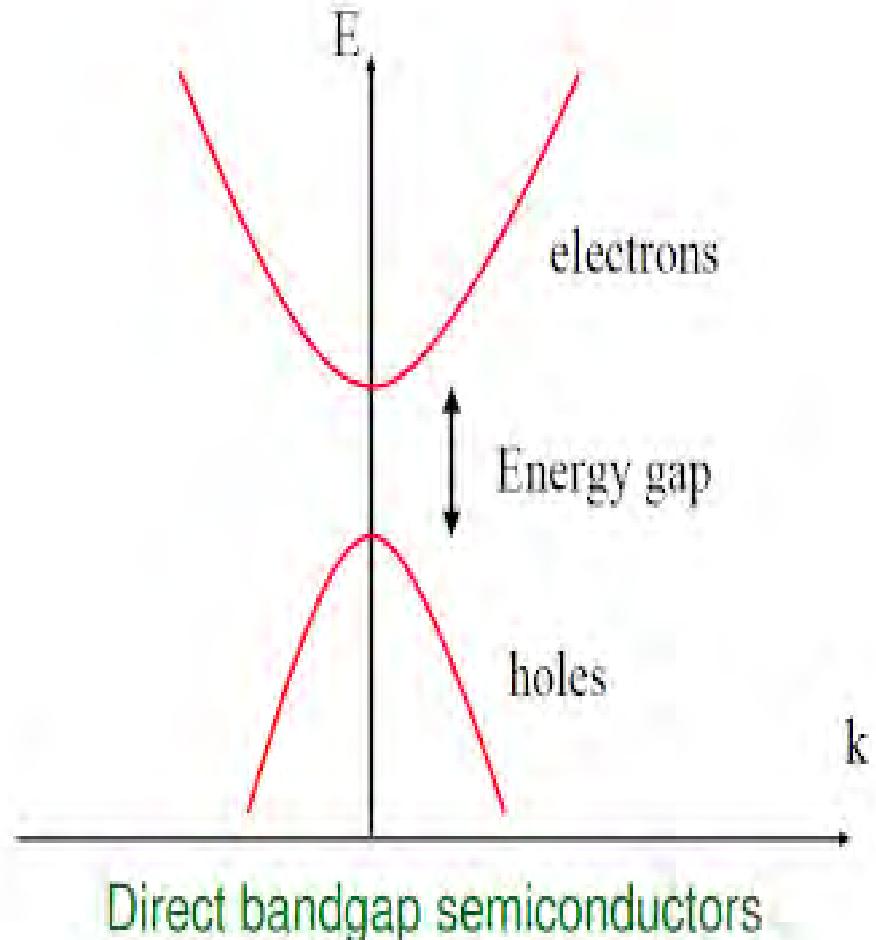
$$Z(E) dE = \frac{Z(E)dE}{\text{Volume}} = \frac{\frac{\pi}{2} \left( \frac{8m}{h^2} \right)^{3/2} a^3 E^{1/2} dE}{a^3}$$

or  $Z(E) dE = \frac{\pi}{2} \left( \frac{8m}{h^2} \right)^{3/2} E^{1/2} dE.$  ----- [16]

*Equation (16) is the expression for density of states, in a 3d solid of unit volume.*

## Differentiate between direct and indirect band gap semiconductors.

Direct band-gap (DBG) semiconductor	Indirect band-gap (IBG) semiconductor
<p>A direct band-gap (DBG) semiconductor is one in which the maximum energy level of the valence band aligns with the minimum energy level of the conduction band with respect to momentum.</p> <p>In a DBG semiconductor, a direct recombination takes place with the release of the energy equal to the energy difference between the recombining particles.</p> <p>The probability of a radiative recombination is high.</p> <p>The efficiency factor of a DBG semiconductor is higher. Thus, DBG semiconductors are always preferred over IBG for making optical sources.</p> <p>Example, Gallium Arsenide (GaAs).</p>	<p>An Indirect band-gap (IBG) semiconductor is one in which the maximum energy level of the valence band and the minimum energy level of the conduction band are misaligned with respect to momentum.</p> <p>In case of a IBG semiconductor, due to a relative difference in the momentum, first, the momentum is conserved by release of energy and only after the both the momenta align themselves, a recombination occurs accompanied with the release of energy.</p> <p>The probability of a radiative recombination is comparatively low.</p> <p>The efficiency factor of a IBG semiconductor is lower.</p> <p>Example, Silicon and Germanium</p>



## \* Phonon :

- 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 (internal energy present in a system by virtue of its temperature) 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'.*

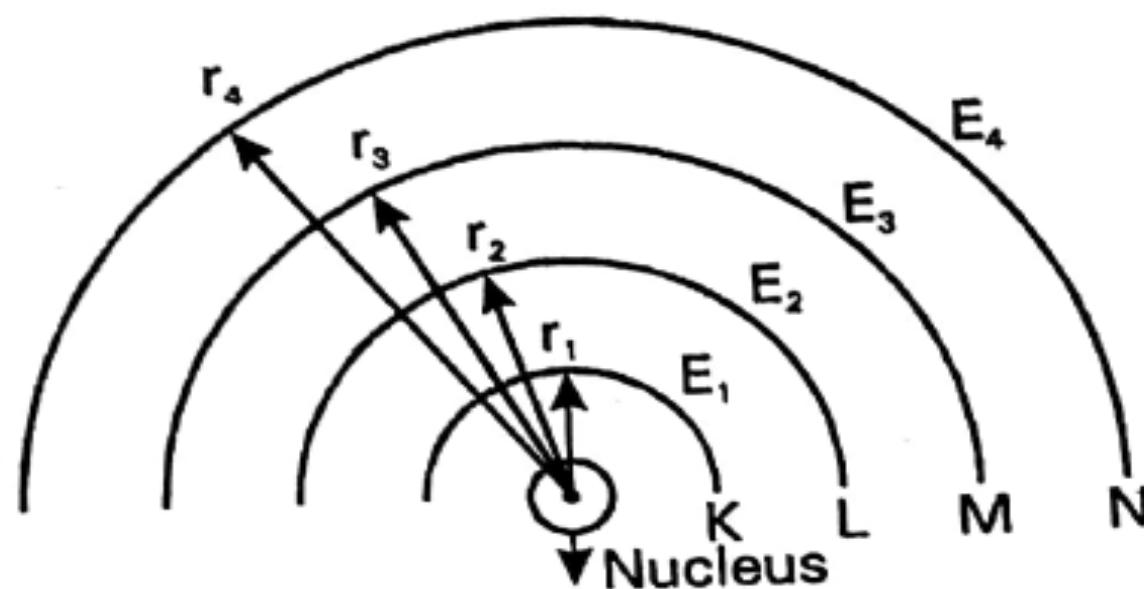
- Thus a phonon can be defined as a discrete unit of vibrational mechanical energy.
- Phonons act like bosons, they can be created or destroyed in collisions.
- Phonons exist with discrete amount of energy, given by

$$E = \hbar\omega = h\nu$$

where,  $\omega / 2\pi$  = frequency of vibrations,  $\hbar$  = planck constant

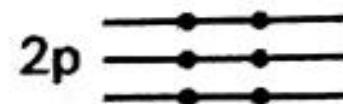
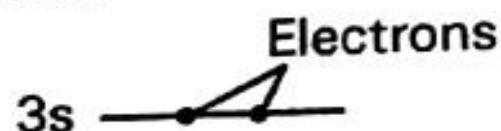
- Phonons can carry heat and sound and they play a major role in determining heat capacities of solids and liquids.

# Discuss –Band Theory of Solids



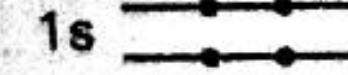
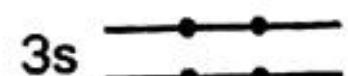
**Figure** : *The energy levels of a single isolated atom*

The pauli exclusion principle allows each energy level to contain only two electrons. For example, the 2s level of a single atom contains one energy level with two electrons and 2p level contains 3 energy levels with two electrons in each level thus, with a total of six electrons as shown in figure 9.2a.



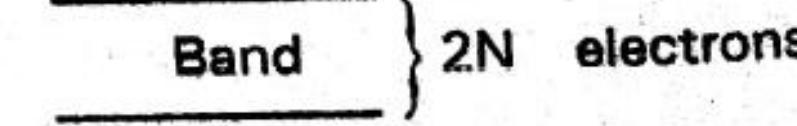
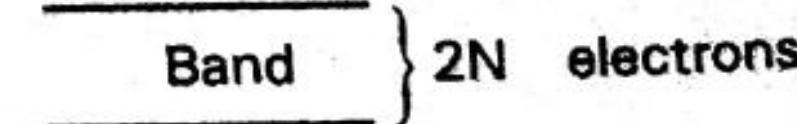
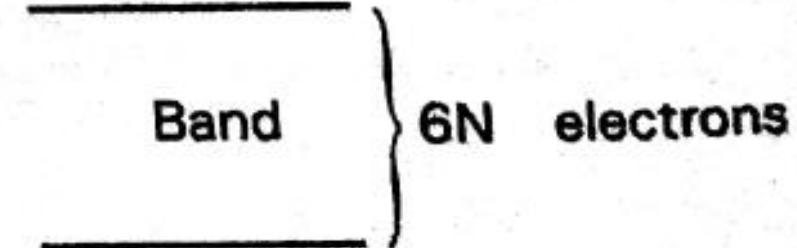
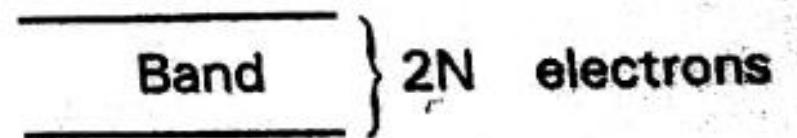
1 atom

(a)



2 atoms

(b)



$N$  atoms

(c)

Figure 2 : The energy levels broaden into energy bands

## **Energy Bands in Solids**

As explained in the case of solid sodium, the discrete energy levels of an atom becomes bands during the formation of solid due to the influence of the constituent atoms. Each band consists of a large number of energy levels which correspond to a range of energy values. The energies within the bands depend on the spacing between the atoms.

*The highest occupied band is called the valence band below which all the lower bands are occupied fully. The valence band may even be partially filled.* In the case of sodium, the 3s energy levels are the valence band which is partially filled.

*The empty band which is immediately above the valence band is called the conduction band.* In the case of sodium atom the empty 3p energy levels which are separated from the 3s band by an energy gap is the conduction band.

*The gap between the valence band and conduction band is called the forbidden band or the energy gap.*

## **Explain the formation of energy bands in solids. On the basis of energy bands distinguish between a metal, a semiconductor and an insulator.**

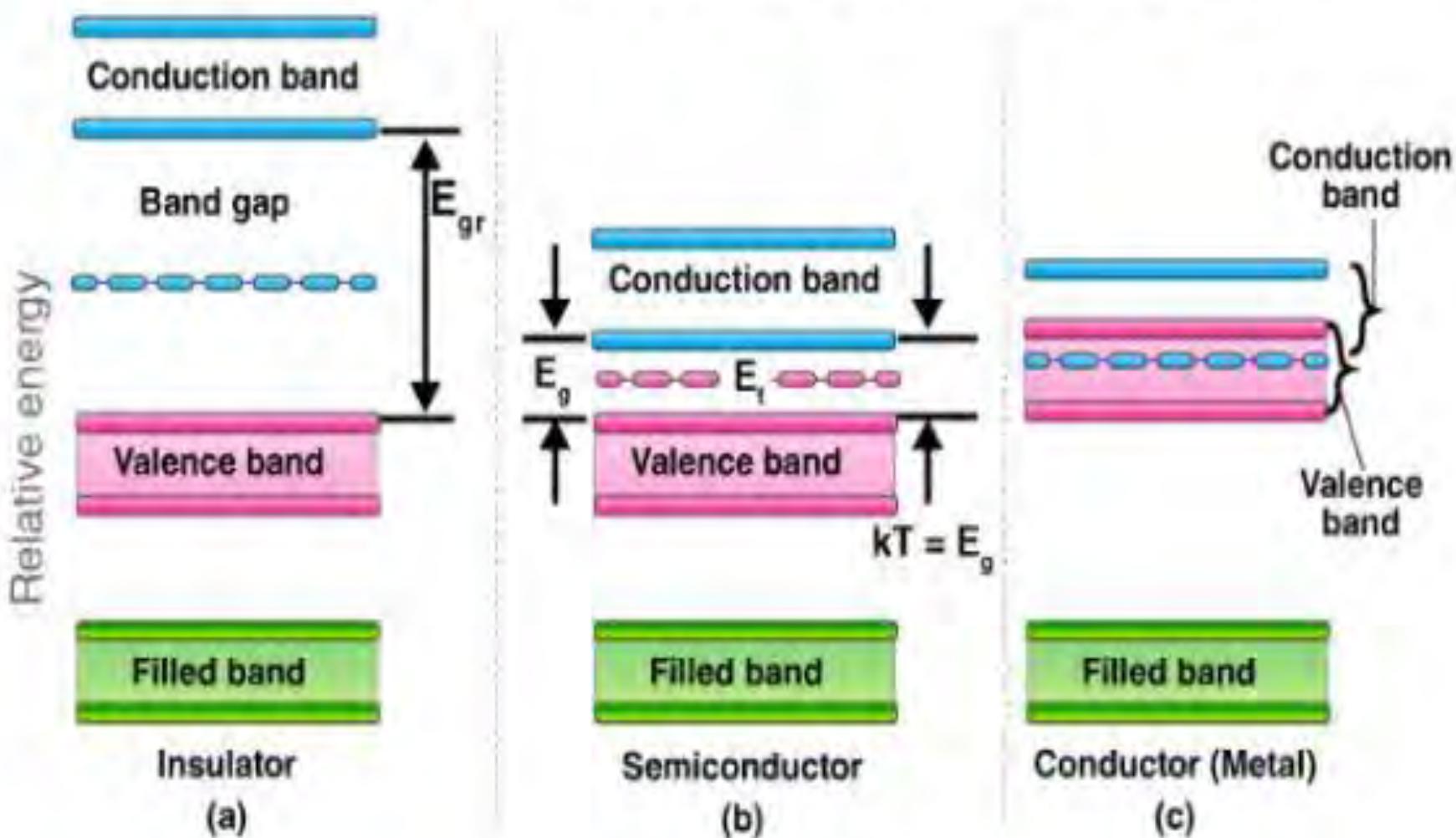
The band theory of solids is different from the others because the atoms are arranged very close to each other such that the energy levels of the outermost orbital electrons are affected. But the energy level of the innermost electrons is not affected by the neighboring atoms. The three energy bands in solids are

- Valence band
- Conduction band
- Forbidden band

### **Bond theory solids**

- In atoms, electrons are filled in respective energy orbits following Pauli's exclusion principle.
- In molecules, Two atomic orbitals combine together to form a molecular orbit with two distinct energy levels.
- In solids,  $10^{23}$  stacked up lines confined in a tiny space would look like a band. Thereby forming energy continuum called energy bands.
- This theory helps to visualise the difference between conductor, semiconductors and insulator by plotting available energies for an electron in a material.

# ENERGY BAND GAPS IN MATERIALS



## **Conductors:**

Metals are conductors in which there is no forbidden energy gap between the conduction band (CB) and valence band (VB). No extra energy required to transfer the electron from VB to CB.

## **Semiconductors:**

In a semiconductor, the valence band is completely filled with electrons while the conduction band is empty. The energy gap between the bands is less. For electrons to jump from the valence band to the conduction band, room temperature needs to be maintained. If the temperature is 0K, there is no transfer of electrons from the valence band to the conduction band.

## **Insulators:**

In insulators, the valence band is completely filled while the conduction band is empty. This results in a large energy gap. Since the energy gap between the conduction band and the valence band is more, there is no movement of electrons from the valence band to the conduction band.

## CONDUCTIVITY OF CONDUCTORS, INSULATORS AND SEMICONDUCTORS

Conductivity range for the different types of materials typically lie in the range as listed in the following table:

Material	Conductivity, $\sigma$ (in $\text{Sm}^{-1}$ )
----------	---

Insulator	$10^{-19} - 10^{-11}$
-----------	-----------------------

Semiconductor	$10^{-6} - 10^5$
---------------	------------------

Conductor	$10^2 - 10^8$
-----------	---------------

## BAND GAPS FOR CONDUCTORS, SEMICONDUCTORS AND INSULATORS

Materials can be classified on the basis of their band-gaps as follows:

1. Insulators:  $E_g > 3 \text{ eV}$

2. Semiconductors:  $E_g < 3 \text{ eV}$

3. Metals:  $E_g = 0 \text{ eV}$

Note: Band-gap is a function of the material, impurities, doping, temperature, etc.

## ENERGY GAPS IN SEMICONDUCTORS - DEFINITION

Semiconductors have a finite but small bandgap (< 3 eV). Because of this, at room temperature some electrons from valence band can acquire enough energy to cross the energy gap and enter the conduction band. Hence, resistivity of semiconductors is not high as insulators.

## CONDUCTORS, INSULATORS AND SEMICONDUCTORS - DEFINITION

Conductors	Insulators	Semiconductors
There are no band gaps.	Large gap between the lower energy levels (the valence band) and the upper conduction band.	The gap between the valence band and conduction band is smaller.
Electrons can move easily using a continuous, partially filled conduction band.	The valence band is full as no electrons can move up to the conduction band which is empty as a result. The material can't conduct as only the electrons in a conduction band can move easily.	At room temperature there is sufficient energy available to move some electrons from the valence band into the conduction band allowing some conduction to take place.

## COMPARISON BETWEEN CONDUCTORS, INSULATORS AND SEMICONDUCTORS

S.No	Conductors	Semiconductors	Insulators
1	Easily conducts the electrical current.	Conducts the electric current less than conductor and greater than insulator.	Does not conduct any current.
2	Has only one valence electron in its outermost orbit	Has four valence electron in its outermost orbit.	Has eight valence electron in its outermost orbit
3	Conductor formed using metallic bonding.	Semiconductors are formed due to covalent bonding.	Insulators are formed due to ionic bonding.
4	Valence and conduction bands are overlapped.	Valence and conduction bands are separated by forbidden energy gap of 1.1eV.	Valence and conduction bands are separated by forbidden energy gap of 6 to 10eV.
5	Resistance is very small	Resistance is high	Resistance is very high
6	It has positive temperature coefficient	It has negative temperature coefficient	It has negative temperature coefficient
7	Ex: copper, aluminium, etc	Ex: silicon, germanium, etc	Ex: Mica, Paper, etc

## BAND GAP FOR CONDUCTOR, SEMICONDUCTOR AND INSULATOR - DIAGRAM

