

Silicon	2300.00	4.35×10^{-4}
Aluminium glass	10^{10} to 10^{12}	10^{-10} to 10^{-12}
Borosilicate glass	10^{13}	10^{-13}
Polyethylene	10^{13} to 10^{15}	10^{-13} to 10^{-15}

It is seen from Table-1 that materials differ greatly in their conductivity. However, they may be broadly classified into three groups.

- Metals and alloys exhibit large conductivity of the order of 10^8 S/m and are therefore, called **conductors**.
- Materials such as metal oxides, glasses, plastics are found to possess very low conductivity of the order less than 10^{-12} S/m. They are called **insulators**.
- Materials such as silicon and germanium have values of conductivity, of the order of 10^4 to 10^{-4} S/m, intermediate to those of conductors and insulators. They are hence called **semiconductors**.

28.4 FREE ELECTRON MODEL OF SOLIDS

Electrical conduction is one of the important properties of solids. It was generally accepted that the valence electrons are involved in electrical conduction in metals and alloys. The evidence was provided at a later stage by the experiments of Stewart and Tolman. Much earlier to the experimental confirmation, the free electron model of solids was proposed by Paul Drude. He assumed that the valence electrons become *free* in solids and move about randomly within the solids much the same way as molecules in a gas confined to a container. This is the **free electron model** which is applicable to all the three categories of solids. This model is used in explaining not only the electrical properties but also the thermal, optical and magnetic properties of solids.

The free electron theory underwent successive modifications in an attempt to explain the electrical behaviour and the distinction between the three types of solids.

- Classical free electron theory:** This theory was proposed by Paul Drude in 1900 and later was extended by Lorentz. Therefore this theory is also known as the **Drude-Lorentz theory**. In this theory it was assumed that valence electrons become free in metals and move about randomly within the metal. In this theory it was assumed that the free electrons move in a region of constant potential. Just as the velocities of molecules in a container, the velocities of electrons in a solid obey the classical Maxwell-Boltzmann distribution. This theory successfully explained the Ohm's law and the high electrical conductivity of metals. However, the theory failed to explain other features and the distinction between conductors, insulators and semiconductors.
- Quantum free electron theory:** This theory was developed by Sommerfeld in 1928. Unlike neutral molecules, electrons are charged particles and obey Pauli Exclusion Principle. An assembly of free electrons obeys Fermi-Dirac statistics. Sommerfeld took into account these facts and modified the Drude's classical free electron theory. However, in this theory also it was assumed that the free electrons move in a region of constant potential. This theory is based on the particle character of electron and did not take into account of its wave character. The theory failed to explain other features and the distinction between conductors, insulators and semiconductors.

3. **Band theory of solids:** This theory was formulated by Felix Bloch in 1928. This theory takes into account that electrons exhibit wave character as they move between atoms in a solid. It further assumed that the potential varies in a periodic manner in the solid. This theory successfully explained the classification of solids into three groups, namely conductors, insulators and semiconductors.

28.5 CLASSICAL FREE ELECTRON THEORY OF METALS

Free electron gas

After the discovery of electron by J.J.Thomson in 1897, Drude developed the free electron theory of metals. According to this theory, metals consist of positive ion cores and valence electrons. The ions cores are immobile and consist of positive nucleus and the bound electrons. The valence electrons get detached from the parent atoms during the process of formation of the metal and move randomly among these cores. Hence they are known as **free electrons**. The potential field of the ion cores is assumed to be constant throughout the metal and the mutual repulsion among the electrons is neglected. The behaviour of free electrons moving within the metal is considered to be similar to that of atoms in perfect gas. These free electrons are therefore referred to as **free electron gas**. As the potential energy of a stationary electron inside the metal is less than the potential energy of an identical electron just outside it, the movement of free electrons is restricted to the boundaries of the metal. This energy difference serves as a potential barrier and stops the free electrons from leaving the surface of the metal. Thus, the free electron gas is confined to a potential energy box. The free electrons are called **conduction electrons** as they are responsible for conduction of electricity in the metals.

Thermal motion of free electrons

The free electrons keep moving randomly in all directions through the lattice structure of the metal due to thermal energy. The average speed is very high and is of the order of 10^6 m/s. As free electrons in a metal move through a maze of positive ion cores, they suffer repeated collisions with the ion cores or other electrons and get deflected. The direction of motion of each free electron changes on every collision and the electron moves along a zigzag path. On the average for every electron moving in a particular direction, there is another electron moving in the opposite direction. Therefore, the thermal motion of free electrons does not cause flow of current through the metal. The electron motion between two collisions is linear and uniform.

Drift motion of free electrons

When the ends of a piece of metal are connected to the terminals of a battery, an electric field is impressed across the metal and the equilibrium condition is disturbed. The electric field accelerates the electrons. The electrons acquire velocity and move in a direction opposite to that of electric field. The directional motion of electrons due to the action of electric field is called **drift**. The drift velocity gained by an electron due to acceleration is lost completely whenever a collision occurs. After that, the electron gets accelerated once again and loses its velocity at the next collision. The process goes on repeating and the electron moves on an average with a **mean drift velocity** v_d . The magnitude of the drift velocity is limited by the decelerations caused by collisions. Thus, the collisions play the role of a frictional force.

The drift speed is typically of the order of 10^{-2} m/s, which is very small compared to the thermal speed, 10^6 m/s. Thus, the motion of a free electron in the presence of electric field consists of a much slower directional drift motion superposed over random zigzag motion.

The drift motion is directional and causes current flow in a conductor called **drift current** or **conduction current**.

Mean Collision time, τ

An electron moving in a particular direction inside a metal encounters another electron or fixed positive ion and deviates from its direction through some angle with the initial direction. This is the process of **scattering** of electrons. For simplicity we say that electron underwent a collision during its motion. After some time another collision occurs and the electron deviates in another direction and this goes on. The time elapsed between two successive collisions is not a constant but varies. The number of collisions per second that an electron makes with the ion cores is proportional to its speed. The average duration of time that elapses between two successive collisions is called **mean collision time**, τ of the electron. It means that the electron on the average travels for a time τ before its next collision, and has traveled for a time τ since its last collision. The collision time is given by

$$\tau = \frac{\lambda}{\bar{v}} \quad (28.7)$$

where λ is known as mean free path and \bar{v} the *rms* (root mean square) velocity.

Mean free path, λ

The average distance traveled by an electron between any two consecutive collisions is known as **mean free path**, λ . The mean free path is given by the product of rms velocity of electrons and mean collision time.

$$\lambda = \bar{v}\tau \quad (28.8)$$

28.6 DRIFT VELOCITY

When an electric field E is impressed on a metal the electrons in it experience a force $-eE$.

If v is the velocity of free electron and τ is the average time between two consecutive collisions, the frictional force opposing the continuous acceleration of the electron may be written as $-mv/\tau$. Using Newton's second law, the equation of motion of free electron may be written as

$$m \frac{dv}{dt} = -eE - m \frac{v}{\tau} \quad (28.9)$$

where m is the mass of the electron and E is the intensity of the applied electric field.

Under the steady state condition, $\frac{dv}{dt} = 0$, and the electron attains a steady value of velocity v_d in dynamic equilibrium. Therefore, under steady state condition, eqn.(28.9) reduces to

$$0 = -eE - m \frac{v_d}{\tau}$$

$$\therefore v_d = -\frac{eE\tau}{m} \quad (28.10)$$

where v_d is the steady state velocity of the electron and is known as **drift velocity**. The drift motion of electrons causes current flow in a conductor.

28.7 ELECTRICAL CONDUCTIVITY

Let n be the number of free electrons per unit volume of the conductor, S (Fig. 28.1). n is called the **free electron density** or **free electron concentration** in the solid.

collision and gained energy of that place. Now we calculate the energy E_1 carried by electrons that drift from the left into the selected volume.

$$E_1 = \text{Number of electrons} \times \text{average energy of an electron} = z \times \frac{3}{2} k T_1$$

Let n be the electron concentration in the material and v be the velocity of electrons. From the kinetic theory of gases, z is given by

$$\begin{aligned} z &= \frac{1}{6} n v \\ \therefore E_1 &= \frac{n v}{6} \cdot \frac{3}{2} k \left[T_0 + \lambda \left(-\frac{dT}{dx} \right) \right] = \frac{n v}{6} \cdot \frac{3}{2} k \left[T_0 - \lambda \frac{dT}{dx} \right] \end{aligned} \quad (28.27)$$

The same number of electrons drifts from right to left through the volume under consideration. These electrons carry a lower energy E_2 because of the lower temperature of the particles at the site of interaction. Thus,

$$E_2 = \frac{n v}{6} \cdot \frac{3}{2} k \left[T_0 + \lambda \frac{dT}{dx} \right] \quad (28.28)$$

The excess thermal energy transferred per unit time into the unit volume is

$$J = E_1 - E_2 = \frac{n v}{6} \cdot \frac{3}{2} k \left[2 \lambda \frac{dT}{dx} \right] \quad (28.29)$$

Comparing equ. (28.29) with equ. (28.25), we obtain the expression for thermal conductivity as

$$K = \frac{n v k \lambda}{2} \quad (28.30)$$

As $\lambda = v \tau$, the above equation may be expressed as

$$K = \frac{n v^2 k \tau}{2} \quad (28.31)$$

28.11 WIEDEMANN-FRANZ LAW

If free electrons are responsible for both electrical and thermal conduction in metals, then the ratio should be of K/σ should be a universal constant, the same for all metals. In 1853, Wiedemann-Franz observed experimentally such a simple connection between K and σ . Wiedemann-Franz law states that **the ratio of thermal to electrical conductivity of a metal is proportional to the absolute temperature and the ratio is constant for all metals at a given temperature.**

That is,

$$\frac{K}{\sigma} \propto T \quad (28.32)$$

or

$$\frac{K}{\sigma T} = L \quad (28.33)$$

where L is a constant called the **Lorentz number**.

Derivation

Let us consider a metal. The thermal conductivity of the metal is given by

$$K = \frac{n v^2 k \tau}{2}$$

And its electrical conductivity is given by

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

The ratio of thermal conductivity to electrical conductivity is given by

$$\frac{K}{\sigma} = \frac{mv^2 k}{2e^2} \quad (28.34)$$

But $\frac{1}{2}mv^2$ = kinetic energy = $\frac{3}{2}kT$.

$$\frac{K}{\sigma} = \frac{3}{2}kT \cdot \frac{k}{e^2}$$

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

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

(28.35)

where

$$L = \frac{3}{2} \left(\frac{k}{e} \right)^2 \quad (28.36)$$

Thus, it is seen from eq. (28.35) that the ratio of thermal to electrical conductivity of a metal is proportional to the absolute temperature and the ratio is a constant.

Wiedemann-Franz law confirmed that the motion of the free electrons is mainly responsible for both electrical and thermal conductivity.

28.12 LORENTZ NUMBER

The Lorentz number is the ratio of thermal conductivity of a metal to the product of its electrical conductivity and its absolute temperature.

Thus,

$$L = \frac{K}{\sigma T}$$

Using the classical theory, we find that

$$L = \frac{3}{2} \left(\frac{k}{e} \right)^2$$

Now substituting the values of k and e in the above expression, we get the value of L .

$$L = \frac{3}{2} \left(\frac{1.38 \times 10^{-23} J/K}{1.602 \times 10^{-19} C} \right)^2 = 1.12 \times 10^{-8} \text{ watt.ohm/deg}^2$$

This classical value is only half of the experimental value. Using the expressions derived from quantum theory, we find that L is given by

$$L = \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2 \quad (28.37)$$

Substituting the values of k and e into the above expression, we get

$$L = 2.45 \times 10^{-8} \text{ watt.ohm/deg}^2$$

The above value agrees well with the experimental value.

Example 28.4. The electrical resistivity of copper at 27°C is $1.72 \times 10^{-8} \Omega\text{m}$. Compute its thermal conductivity if the Lorentz number is $2.26 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$.

spectrum and phonon concentration are strongly dependent on temperature. At low temperatures, phonon number reduces considerably. At low temperatures, the specific heat of metallic lattice is proportional to T^3 and therefore, the density of phonons and the probability of scattering are proportional to T^3 . In addition to this, the relaxation time is dependent on the scattering angle that would give rise to resistivity variation with temperature as T^2 . Consequently, $\rho_{ph} \propto T^3 \cdot T^2 = T^5$. At much higher temperatures, the electrical resistivity increases linearly with temperature. The relaxation time, τ_{ph} can be assigned to phonon scattering.

The total resistivity of a metal at any given temperature is a sum of resistivity due to impurity scattering, ρ_i , and phonon scattering, ρ_{ph} . Thus,

$$\rho(T) = \rho_i + \rho_{ph} \quad (28.38)$$

The above equation is known as "**Matthiessen's rule**".

As $\rho = \frac{m}{ne^2\tau}$, we can write equ. (28.38) as

$$\begin{aligned} \frac{m}{ne^2\tau} &= \frac{m}{ne^2\tau_i} + \frac{m}{ne^2\tau_{ph}} \\ \frac{1}{\tau} &= \frac{1}{\tau_i} + \frac{1}{\tau_{ph}} \end{aligned} \quad (28.39)$$

28.14 DRAWBACKS OF CLASSICAL FREE ELECTRON THEORY

The free electron model is highly successful in explaining many physical properties of metals such as their high electrical and thermal conductivities, their high luster etc. However, it failed to account for some of the other properties. We cite some important failures of the model here.

1. Monovalent metals (copper, silver etc) have been found to have higher electrical conductivity than divalent (cadmium, zinc etc) and trivalent (aluminum, indium etc) metals. If the conductivity is proportional to electron concentration, then monovalent metals should have lesser electrical conductivity compared to the divalent and trivalent metals.
2. The model cannot explain the classification of materials into conductors, semiconductors and insulators.
3. Metals are expected to exhibit negative Hall coefficient since the current carriers in them are electrons. However, some of the metals such as zinc have positive values for Hall coefficient. The free electron model cannot explain why zinc and other metals have positive Hall coefficient.
4. According to the classical theory, the conductivity of a metal is given by the expression (28.19). Thus, the resistivity is given by

$$\rho = \frac{m}{ne^2\tau} \quad (28.40)$$

When the above expression is used to calculate the mean free path of electron in metals, we find it to be the order of about 3 \AA and is consistent with the assumption of classical theory that the origin of resistivity is due to frequent collisions of electrons with the lattice ions. However, the experimentally measured values are very high and are of the order of 50 \AA . The experimental results suggest that electrons pass a long distance through the lattice without collisions.

5. According to classical free electron theory, all the valence electrons can absorb thermal energy. According to the law of equipartition energy, each free electron possesses an average kinetic energy of $(3/2)kT$. If we consider a monoatomic crystal,

each atom contributes one valence electron to the electron gas and there will be N free electrons per unit volume of the crystal. Then the total energy of electrons is given by

$$E = \frac{3}{2} N k T$$

When the metal is heated, the free electrons also absorb part of the heat energy and the electronic specific heat is given by

$$[C_v]_{\text{el}} = \left(\frac{dE}{dT} \right) = \frac{3}{2} N k \quad (28.41)$$

Substituting the values of N and k , we get $[C_v]_{\text{el}} = 12.5 \text{ kJ/kmol/K}$. This value is about hundred times greater than the experimentally measured value. This result implies that free electrons do not contribute significantly to the heat capacity of the metal. We conclude that the law of equipartition and hence Maxwell-Boltzmann statistics is not applicable to the free electrons in a metal.

28.15 QUANTUM FREE ELECTRON THEORY

The quantum theory for the assembly of free electrons in a metal was first advanced by Sommerfeld in 1928. He had retained the vital features of classical free electron theory and included (i) the Pauli Exclusion Principle and (ii) the Fermi-Dirac statistics to formulate his quantum free electron theory.

The main assumptions of this theory are:

- (i) The eigen values of conduction electrons are quantized and are realized in terms of a set of energy levels.
- (ii) The distribution of electrons in various allowed energy levels takes place according to Pauli's exclusion principle.
- (iii) The electrons move in a constant potential inside the metal and are confined within defined boundaries.
- (iv) Mutual attraction between electrons and lattice ions and the repulsion between individual electrons may be ignored.

28.16 DENSITY OF ENERGY STATES

Number of Energy States

Let us consider a specimen of a metal. For the sake of simplicity, we consider it to have the shape of a cube with the side L . We assume that the free electrons travel absolutely freely within the volume of the specimen. The sea of electrons obeying the Pauli Exclusion Principle is called **Fermi gas**. Since the electrons are confined inside the specimen, their wave properties limit the energy values that they may take. The application of Schrödinger equation to the electron motion in the three directions reveals that the electron energy is quantized. The quantized value of energy is given by

$$E = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (28.42)$$

The state of a free electron is determined by the four quantum numbers n_x , n_y , n_z and by the spin quantum number $m_s = \pm \frac{1}{2}$.

Equ. (28.42) indicates that the energy of an electron is determined by the sum of the squares of the quantum numbers n_x , n_y , and n_z . We get the same value for energy for several different combinations of these three quantum numbers. Corresponding to each set we can

find a specific energy state (or energy level) E . We can therefore represent a *quantum state* by a point in quantum number space (Fig. 28.4 a). Quantum number space is an imaginary space where the values of quantum numbers are denoted along the three axes respectively.

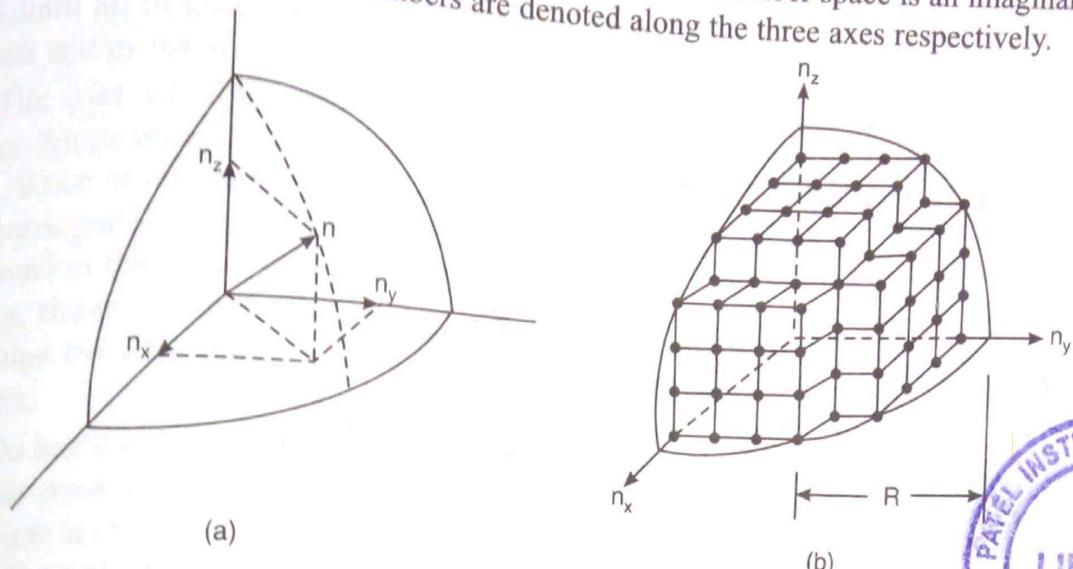


Fig. 28.4



In this space, a radius vector n may be drawn from the origin of the coordinate system to a point (n_x, n_y, n_z) where

$$n^2 = n_x^2 + n_y^2 + n_z^2 \quad (28.43)$$

It is easy to see that all points on the surface of a sphere of radius n will correspond to the same energy. All points within the sphere represent quantum states with energies smaller than E .

$$\text{Number of energy states within a sphere of radius } n = \text{Volume of the sphere} = \frac{4\pi}{3} n^3.$$

Since the quantum numbers can have only positive integer values, the n -values can only be defined in the positive octant of the sphere (Fig. 28.4 b).

Therefore, the number of quantum states with energy equal to or smaller than E is proportional to the first octant of the sphere.

$$\text{Number of energy states within one octant of the sphere of radius } n = \frac{1}{8} \times \frac{4\pi}{3} n^3 \quad (28.44)$$

Similarly, the number of energy states within one octant of a sphere of radius $(n + dn)$ corresponding to energy $(E + dE)$

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

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

$$N(E) dE = \frac{1}{8} \left[\frac{4\pi}{3} (n + dn)^3 \right] - \frac{1}{8} \left(\frac{4\pi}{3} \right) n^3 \approx \frac{\pi}{6} (3n^2 dn)$$

Terms corresponding to higher powers of dn are negligibly small and are hence neglected.

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

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

We know that

$$\therefore n^2 = \frac{8mL^2}{h^2} E \quad (28.46)$$

or

$$n = \left[\frac{8mL^2}{h^2} \right]^{1/2} E^{1/2}$$

Differentiating the equation (28.46), we get

$$\begin{aligned} n \, dn &= \frac{4mL^2}{h^2} dE \\ \therefore N(E)dE &= \frac{\pi}{2} n^2 dn = \frac{\pi}{2} n(n \, dn) \\ &= \frac{\pi}{2} \left[\frac{8mL^2}{h^2} \right]^{1/2} E^{1/2} \times \frac{4mL^2}{h^2} dE \\ &= \frac{\pi}{4} \left[\frac{8mL^2}{h^2} \right]^{3/2} E^{1/2} dE \end{aligned} \quad (28.47)$$

There are two spin states $m_s = \pm \frac{1}{2}$ for an electron. According to Pauli Exclusion Principle, two electrons of opposite spin can occupy each state. Hence, the number of energy states available for electron occupancy is double the above value (28.47) and equals to

$$\begin{aligned} N(E)dE &= \frac{\pi}{2} \left[\frac{8mL^2}{h^2} \right]^{3/2} E^{1/2} dE \\ \text{or } N(E)dE &= \frac{4\pi}{h^3} (2m)^{3/2} L^3 E^{1/2} dE \end{aligned} \quad (28.48)$$

Density of Energy States

The *density of states* is given by the number of available electron states per unit volume per unit energy range at a certain energy level, E .

$$\therefore Z(E)dE = \frac{N(E)dE}{L^3} = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \quad (28.49)$$

$Z(E)$ is called the **density of states function**. It may be noted that $Z(E)$ is independent of the dimensions (L) of the potential box and hence is applicable for any case. We define $Z(E)$ as *the number of available states per unit energy interval centered around E* .

28.16.1 Energy Distribution of Electrons

Density of energy states in the energy interval E and $E + dE$ is given by

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

The density of states plotted against the energy gives a parabola (Fig. 28.5). The area under the curve represents the number of electrons in the metal. Note that *the number of available energy levels at the lower end of the parabola is considerably less than at higher energies*.

The plot of $Z(E)$ versus E at $T = 0$ drops abruptly to zero at $E = E_F$. This distribution of electron energies is understandable. The electrons cannot crowd in the lower energy levels

The individual valence electrons no longer belong to individual atoms; but they now belong to all nuclei in the solid.

29.3 THE BAND THEORY OF SOLIDS—QUANTUM MECHANICAL EXPLANATION

In order to find the allowed energies of electrons in solids, we have to apply Schrödinger wave equation for an electron in a crystal lattice. Fig. 29.4(a) shows the actual potential as seen by an electron in the crystal lattice in one dimension.

29.3.1 The Kronig-Penny Model

Kronig and Penny suggested a simplified model consisting of an infinite row of rectangular potential wells separated by barriers of width b . This one-dimensional representation of periodic lattice is known as *Kronig-Penny model* and is shown in Fig. 29.4 (b). Each well has a width b and a depth V_0 .

The period of the potential is $(a + b)$. In regions where $0 < x < a$, the potential energy is assumed to be zero and in regions such as $-b < x < 0$, it is V_0 . Through this model, Schrodinger equation can be solved explicitly in terms of elementary functions.

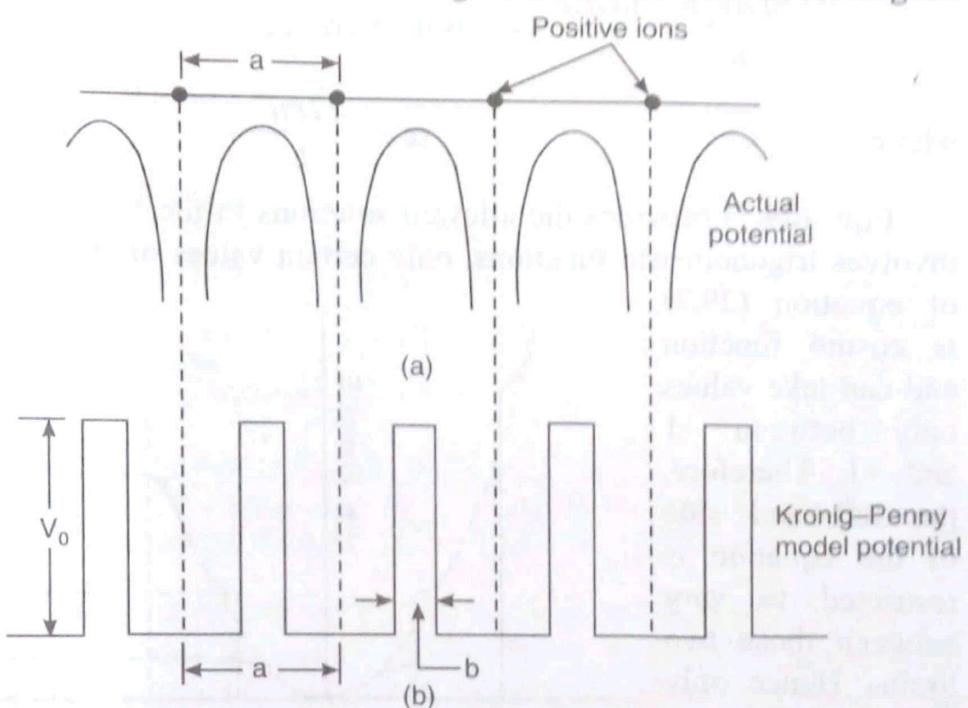


Fig. 29.4. Kronig-Penny Model

29.3.2 Bloch Theorem

The Schrodinger equation for the two regions can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E \psi = 0 \quad \text{for } 0 < x < a \quad (29.1)$$

and

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V_0) \psi = 0 \quad \text{for } -b < x < 0 \quad (29.2)$$

We rewrite the above equation as

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0 \quad \text{for } 0 < x < a \quad (29.3)$$

and

$$\frac{d^2\psi}{dx^2} + -\beta^2 \psi = 0 \quad \text{for } -b < x < 0 \quad (29.4)$$

There is an important theorem known as the **Bloch theorem**. According to this theorem, the solution of the Schrodinger equation for a periodic potential would be of the form of a plane wave modulated with the periodicity of the lattice. It means that the solution can

be represented as the product of two functions: a free particle wave function and a periodic function $u(x)$ that has the same period as the lattice. Thus

$$\psi(x) = u(x)e^{ikx} \quad (29.5)$$

with

$$u(x) = u(x + a) \quad (29.6)$$

The wave functions of the above type are known as **Bloch functions** which change periodically with increasing x .

29.3.3 Energy Bands

We substitute the above wave functions into the Schrodinger equation and solve it in the usual way. When we apply the periodic boundary condition, we get the following expression.

$$\frac{maV_0b}{\hbar^2} \cdot \frac{\sin \alpha a}{a} + \cos \alpha a = \cos k a \quad (29.7)$$

where

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

Equ. (29.7) provides the allowed solutions to the Schrodinger equation. As the relation involves trigonometric functions, only certain values of α are possible. The right hand side of equation (29.7)

is cosine function and can take values only between -1 and $+1$. Therefore, the left-hand side of the equation is restricted to vary between those two limits. Hence, only certain values of α are allowed. It means that energy E is restricted to lie within certain ranges.

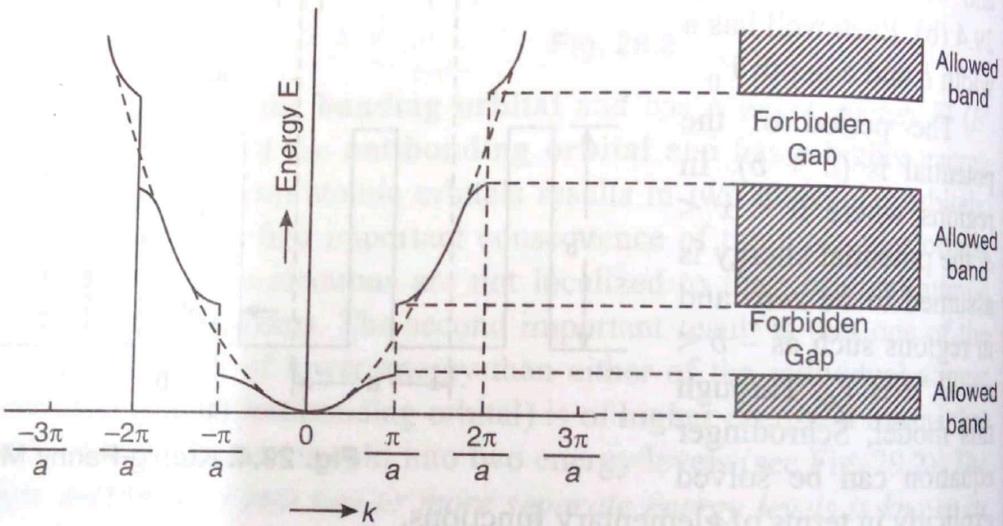


Fig. 29.5. Electron energy, E versus wave number, k plot for a solid

This concept is best understood by drawing the plot of energy E as a function of the wave number, k . The plot is shown in Fig. 29.5. The parabolic relation between E and k obtained in case of free electron is interrupted at certain values of k , as shown by the broken curve.

Fig. 29.5 shows discontinuities in E . The discontinuities occur at $ka = \pm n\pi$ i.e., at

$$k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}, \dots \quad (29.8)$$

The origin of the allowed energy bands and forbidden gaps is clear from Fig. 29.5.

29.4 ENERGY BAND STRUCTURE OF A SOLID

A crystal (i.e., solid) consists of an enormous number of atoms arranged in a regular periodic structure. The extent of energy level splitting in the solid depends on the nearness of atoms in it. Let us assume that N identical atoms form the crystal. The energy levels of the isolated atoms are shown in Fig. 29.6(c). All the N atoms have identical sets of energy levels. The electrons fill the energy levels in each atom independently. Fig. 29.6 (b) shows an atom sitting

at the origin of the coordinate system. Now let us imagine that other atoms approach this atom along the three axial directions and halt at the distance a_0 , which is the lattice constant of the crystal. As the atoms approach, a continuously increasing interaction occurs between the atoms. Each of the energy levels splits into many distinct levels and form energy bands, as shown in Fig. 29.6 (b). Fig. 29.6 (a) depicts the effect of slicing of Fig. 29.6 (b) at a_0 and it represents the *energy band structure* of the crystal. It is seen that corresponding to each allowed energy level of an isolated atom, there forms an allowed energy band; and that the allowed energy bands are separated by forbidden bands of energy.

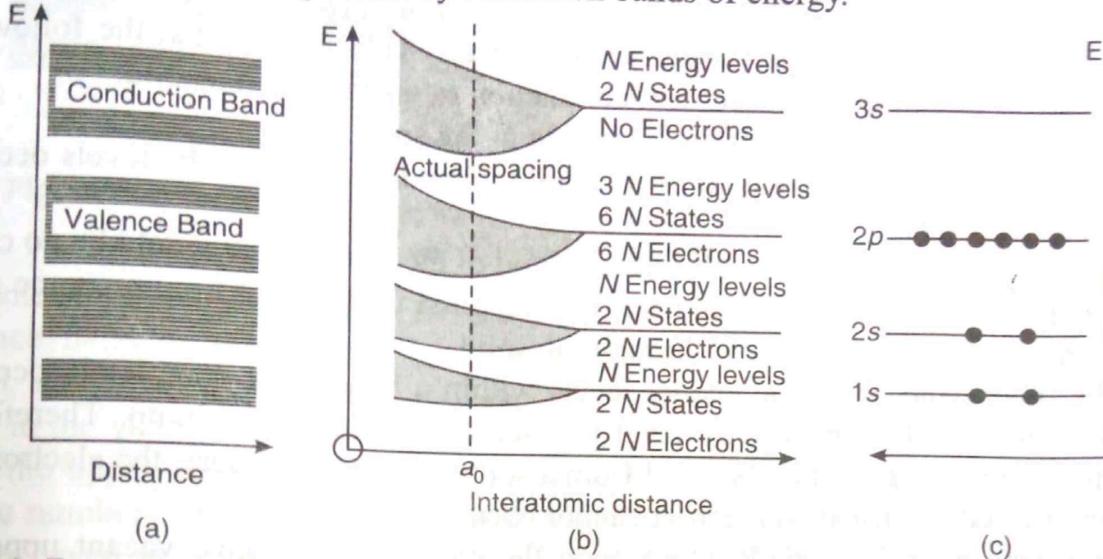


Fig. 29.6. Energy level splitting in a solid as a function of interatomic distance (a) Energy band structure of the solid corresponding to the actual spacing of atoms in the solid. (b) Energy level splitting as a function of distance. (c) Discrete energy levels in an isolated atom.

The degree of splitting of energy levels depends on their depth in the atom. The electrons in outer shells screen the core electrons belonging to inner shells. Consequently, the energy levels of inner shell electrons are split to a lesser degree. They form narrow core bands. They are always completely filled and do not participate in electrical conduction. In contrast the energy levels of valence electrons are split more and form wider bands.

In general, N interacting atoms cause an energy level to split into $(2l + 1)N$ levels. Thus, s -level ($l = 0$) splits into N levels whereas the p -level, consisting of three sublevels p_x , p_y and p_z , splits into $3N$ levels. Thus, in a solid each level of an individual atom splits into $(2l + 1)N$ number of levels where N is the number of atoms in the system. Consequently, the maximum electron capacity of an s -band is $2N$ electrons whereas the capacity of a p -band is $6N$ electrons.

While occupying an energy band, electrons start from the lowest energy level in the band and fill the levels one after the other in the ascending order of energy. When $2N$ electrons occupy the N levels available in the band, the band is said to be **completely filled**. In case of non-availability of $2N$ electrons, the energy band gets **partially filled**. When there are no electrons to occupy the levels, the energy band remains **vacant**.

The width of an allowed or forbidden energy band is generally of the order of a few electron-volts. As N is very large, the energy separation between successive energy levels in an allowed band is very small and is of the order of 10^{-27} eV. At room temperature, the kinetic energy of the electrons of the order of $kT (\approx 0.026 \text{ eV})$ which is very large compared to the energy level separation in an allowed band. Consequently, electrons can easily move into higher vacant levels within the allowed energy band either due to thermal energy or due to a small externally applied electric field. On the other hand, electrons cannot jump across a

forbidden band under normal thermal energy possessed by them or due to an applied electric field. High temperatures are required to cause inter-band electron transitions.

29.5 ELECTRICAL CONDUCTION FROM THE VIEW POINT OF BAND THEORY

In a solid, the allowed values of electron energy are distributed into bands (Fig. 29.6), each band consisting of a sequence of closely spaced discrete energy levels arranged in a manner akin to the rungs of a ladder. The electrons are distributed in the energy levels according to the Pauli exclusion principle. The motion of an electron corresponds to its transition from a lower energy level to an upper vacant energy level. This implies that the following two conditions are to be fulfilled for electrical conduction to take place in a solid:

- (i) There should be free electrons available in the solid.
- (ii) Vacant energy levels should be available immediately above the levels occupied by free electrons.

If a band has vacant energy levels but is devoid of electrons, there would be no carriers to move through the vacant levels when energy is supplied to the solid from a source such as a battery. Hence current does not flow through the solid.

On the other hand, if all the energy levels within a band were completely occupied by electrons, there would be no energy level to which an electron can jump. Therefore, even though the energy is supplied to the solid from a source such as a battery, the electrons cannot acquire energy and electrical conduction cannot occur in the solid.

If an energy band is partially filled, then the electrons will have vacant upper energy levels into which they can jump. On acquiring energy from the electric field applied across the solid, the electrons move into successive upper energy levels and cause electrical conduction. Thus, *partially filled energy band is required for electrical conduction in a solid*.

29.6 ENERGY BAND DIAGRAM

An energy band diagram is a graphic representation of the energy levels associated with top energy band and the next lower energy band in a solid. The energy band diagram shows two bands with a gap in-between (see Fig. 29.7). The upper band is called the **conduction band** and the lower energy band is called the **valence band**. These two bands are separated by a *forbidden gap*. This energy gap is more popularly called **band gap** and is denoted by the symbol E_g . The conduction band corresponds to the energy values of *free electrons* that have broken their valence bonds, and hence have become free to move in the crystal. The bottom of the conduction band represents the smallest energy that the electron must possess to become free. Only the free electrons can move in the crystal under the influence of the externally applied electric field. Hence, these electrons are called **conduction electrons** and the energies of such electrons constitute the **conduction band**. The band showing the energy values of **valence electrons** that are engaged in covalent bonding is called the **valence band**.

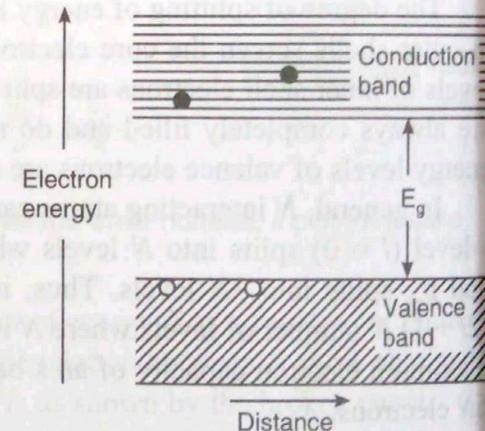


Fig. 29.7. Energy band diagram

29.7 CLASSIFICATION OF SOLIDS

The concept of energy bands helps us in understanding the division of solids into three groups. The nature of the energy bands determines whether the solid is an electrical conductor

or insulator. According to the band theory, the electrical conductivity of a solid is characterized by the energy gap E_g separating the outermost energy bands namely, the valence band and the conduction band. The ability of electrical conduction is decided by the order of magnitude of the energy gap E_g .

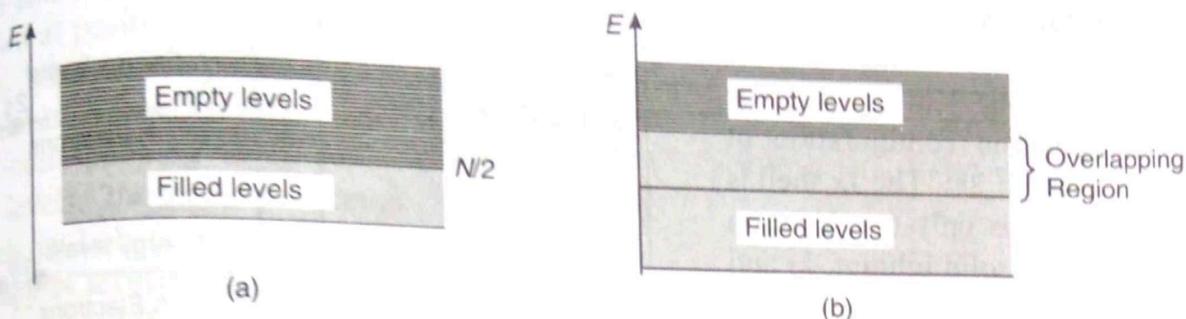


Fig. 29.8. Energy band formation in a conductor (a) Half filled conduction band.
(b) Empty upper band overlaps on a totally filled lower band.

In some solids, an upper vacant band overlaps the valence band or the valence band itself is half-filled, as shown in Fig. 29.8. It means that electrons in the valence band have easy access to levels in the upper vacant band. For this reason, very large numbers of electrons are available for conduction, even at extremely low temperatures. When electric field is impressed across the solid, electrons readily jump into upper unoccupied energy levels of the vacant band and current flows in a large measure in the solid. Therefore, these solids exhibit good electrical conductivity and are called **conductors**.

In some solids the band gap is narrow and of the order of 2 eV or less, as shown in Fig. 29.9. Acquisition of small amounts of energy from the vibrations of atom can raise electrons from the valence band to the conduction band. The conduction band is then partially filled. If a potential is applied across the material, it causes the electrons in the conduction band to move to upper levels. As a result, current flows in a modest measure in the solid. Such solids are called **semiconductors**.

Some solids (Fig. 29.10) have band gaps that are very wide ($E_g > 3$ eV). It would require the acquisition of very large amounts of energy to cause an electron to jump from the valence band to the conduction band. Very few electrons can get this large amount of energy to jump from valence band to conduction band at ambient temperature. Hence, there are very few electrons in the conduction band. When a voltage is applied across

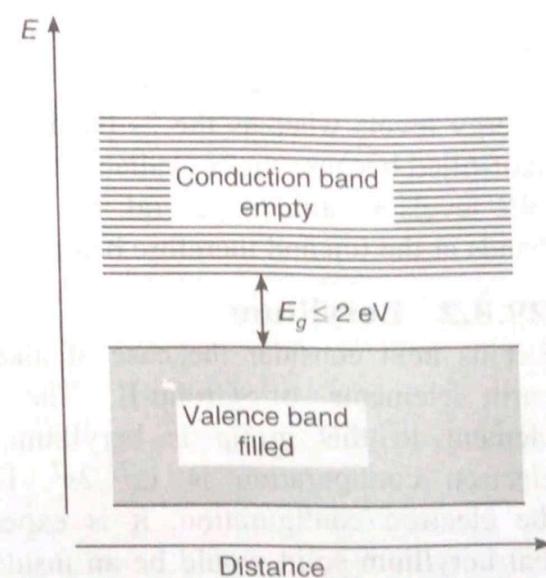


Fig. 29.9. Energy band structure of a semiconductor

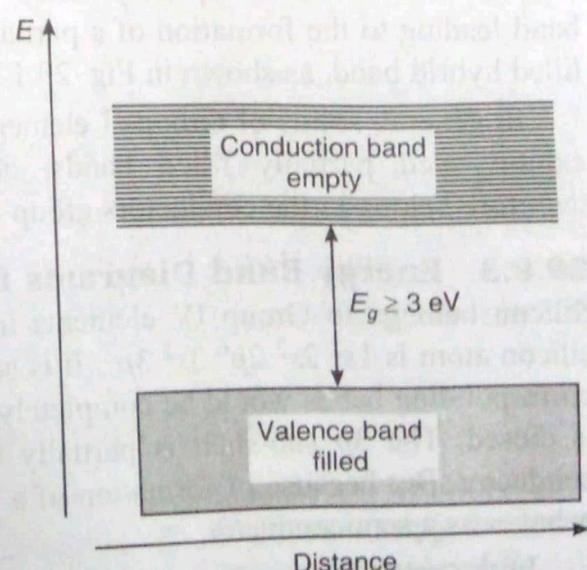


Fig. 29.10. Energy band structure of an insulator

Statistics and Band Theory of Solids

OBJECTIVES

- To derive the Fermi Dirac statistics for the energy states
- To study the probability of occupation of electrons
- To explain the density of states in metal or semiconductors
- To study the effect of temperature on Fermi energy function

17.1

I N T R O D U C T I O N The classical free electron theory could not explain specific heat capacity, electronic specific heat etc. But they are well explained using quantum free electron theory. On the other hand, quantum free electron theory fails to explain the distinction among metals, semiconductors and insulators, the positive value of Hall Effect and some transport properties. All the above failures are overcome by the energy band theory of solid. The band theory of the solids is used to explain the band structure and the electrical properties of solids. The outcome of quantum mechanics, Pauli's exclusion principle and Bohr's atom model are results in the band theory of solids.

The statistics mainly used to derive the velocity and the energy distribution of particles is of three types namely, (i) Maxwell-Boltzmann statistics, (ii) Bose-Einstein statistics and (iii) Fermi-Dirac statistics. The Maxwell – Boltzmann statistics deals with particles having no spin (Eg. Gaseous particles). The Bose-Einstein statistics explains the particles like photon having integral spins, while the particle with half integral spin was dealt by the Fermi-Dirac statistics. Examples for Fermi-Dirac statistics are the particles like electrons which have half integral spin and hence, these particles are known as Fermi particles or Fermions. The Fermi-Dirac statistics, Fermi energy and density of static band theory of solids are briefly discussed in this chapter.

17.2 FERMI-DIRAC STATISTICS

The distribution of energy states in a semiconductor is explained by Fermi-Dirac statistics since it deals with the particles having half integral spin like electrons. Consider that the assembly of electrons as electron gas which behaves like a system

of Fermi particles or Fermions. The Fermions obeying Fermi-Dirac statistics i.e., Pauli's exclusion principle.

Therefore, the probability function $f(E)$ of an electron occupying an energy level E is given by,

$$f(E) = \frac{1}{1 + \exp[(E - E_F)/KT]} \quad (17.1)$$

where E_F is known as Fermi energy, K the Boltzmann constant and T the absolute temperature.

Eq.(17.1), the probability function $f(E)$ lies between 0 and 1. Hence, there are three possible probabilities namely:

- $f(E) = 1$ 100 % Probability to occupy the energy level by electrons
- $f(E) = 0$ No probability to occupy the energy levels by electrons and hence, it is empty
- $f(E) = 0.5$ 50 % Probability of finding the electron in the energy level.

A detailed explanation for the above three cases are given by considering the temperature dependence of Fermi distribution function and its effects on the occupancy of energy level by electrons is shown in Fig. 17.1.

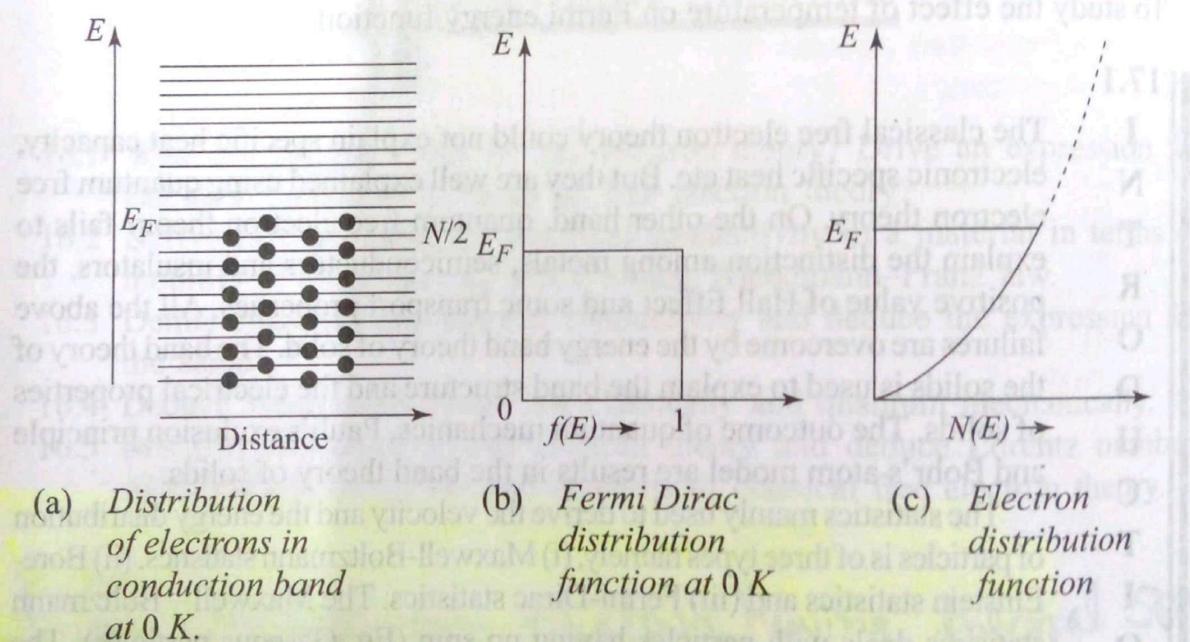


Fig. 17.1 Fermi-Dirac distribution function

Case I Probability of occupation at $T = 0\text{ K}$, and $E < E_F$

Substituting the above condition in Eq. (17.1). We get,

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

$$= \frac{1}{1} = 1$$

Therefore, $f(E) = 1$ (17.2)

Eq. (17.2), clearly indicates that at $T = 0\text{ K}$, the energy level below the Fermi energy level E_F is fully occupied by electrons leaving the upper levels vacant. Therefore, there is a 100 % probability that the electrons to occupy energy level below Fermi energy. Generally, a single energy band namely conduction band diagram as shown in Fig. 17.1 a is used to characterise the conductors. The conduction band have more energy levels than free electrons. Fig. 17.1 a indicates that conduction band is filled up to certain energy level marked as E_F , while the energy levels above the highest filled level is empty. Fermi energy level is defined as the upper most filled energy level in a conduction band at 0 K . In other words, the highest energy level occupied by an electron in a conductor at 0 K is the Fermi energy level.

Case II Probability of occupation at $T = 0\text{ K}$ and $E > E_F$

Substituting the above condition in Eq. (17.1) We get,

$$\begin{aligned} f(E) &= \frac{1}{1+e^\infty} \\ &= \frac{1}{1+\infty} \end{aligned}$$

or $= \frac{1}{\infty} = 0$

$$f(E) = 0 \quad (17.3)$$

Therefore,

Eq. (17.3) clearly indicates that at $T = 0\text{ K}$, the energy levels above the Fermi energy level E_F is unoccupied i.e., vacant. Therefore, there is a 0 % probability for the electrons to occupy the energy level above the Fermi energy level. Fig. 17.1 b shows that the variation of $f(E)$ for different energy values is a step function.

Case III Probability of occupation at $T = 0\text{ K}$ and $E = E_F$

Substituting the above condition in Eq. (17.1) We get,

$$\begin{aligned} f(E) &= \frac{1}{1+e^0} \\ &= \frac{1}{1+1} \\ &= \frac{1}{2} = 0.5 \\ \text{or } &= \frac{1}{2} = 0.5 \end{aligned} \quad (17.4)$$

Therefore, $f(E) = 0.5$ or $1/2$

Eq. (17.4) clearly indicates that at $T = 0 \text{ K}$, there is a 50 % probability for the electrons to occupy Fermi energy level. Therefore, the Fermi energy level is defined as the energy level at any temperature, the probability of electron is 50 % or $\frac{1}{2}$. Similarly, it is also defined as E_F the average energy occupied by the electrons which participate in conduction process in conductor at temperature above 0 K .

Case IV At High temperature ($T > 0 \text{ K}$) i.e., $KT \gg E_F$ or $T = \infty$

At higher temperature, electrons are excited above the Fermi energy level which is vacant. Therefore, most of the electrons are lying in the deep conduction band, without any disturbance. Since, the energy KT is not sufficient to make any transition to an unoccupied level. This energy is sufficient to make a jump to higher level those electrons lie in the energy level adjunct to Fermi level. At higher temperatures, the electron lost the quantum mechanical properties and the traditional classical Boltzmann distribution function.

17.2.1 Density of States

The energy distribution of electrons in a metal or semiconductor is determined using Fermi Dirac statistics. The n_x, n_y, n_z are quantum numbers used to construct the point in the sphere.

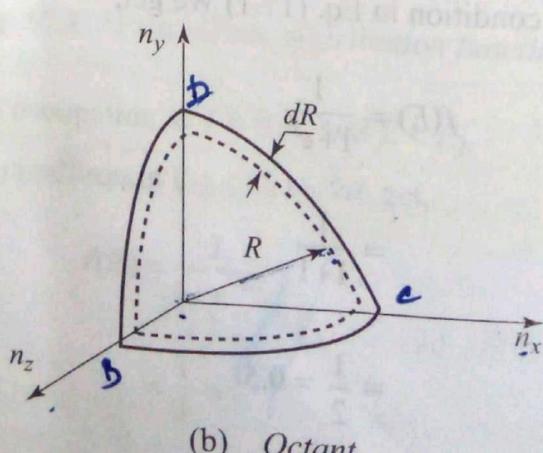
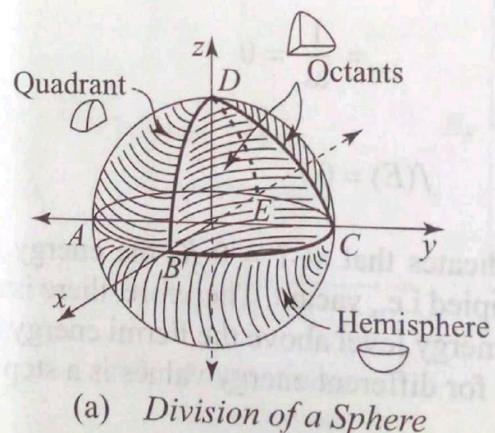


Fig. 17.2 Density of States

band increases at temperatures greater than 0K, the probability function is blurred and tapers off towards higher energy in the conduction band. Similarly, the probability of hole occupancy of the valence band increases, and the probability curve is blurred near the top edge of the valence band. The extent of blurring of probability curve in both the bands is equal indicating that the concentration of electrons in the conduction band and that of holes in the valence band are equal. Secondly, the probability function $f(E)$ rapidly approaches zero value with increasing E . It suggests that the electrons in the conduction band are clustered very close to the bottom edge of the band. In a similar way, the holes are grouped very close to the top edge of the valence band. Therefore, it may be approximated that electrons are located right at the bottom edge of the conduction band whereas the holes are at the top edge of the valence band.

The Fermi level represents the average energy of charge carriers participating in conduction. Both electrons and holes participate in conduction in semiconductor and they lie in two different bands separated by a forbidden gap. Therefore, it is expected that the Fermi level lies in the middle of the forbidden gap. If the Fermi level is located elsewhere, it would mean that the number of electrons in the conduction band would be different from the number of holes in the valence band. It, in turn, would imply that the material does not exhibit overall neutrality which is not at all true.

29.12 EFFECTIVE MASS

We generally assume that the mass of an electron in a solid is the same as the mass of a free electron. However, experimentally measured values indicate that in some solids the electron mass is larger while for others it is slightly smaller than the free electron mass. The experimentally determined electron mass is called the **effective mass m^*** .

The cause for the deviation of the effective mass from the free electron mass is due to the interactions between the drifting electrons and the atoms in a solid.

It has been found that the effective mass is inversely proportional to the curvature of an allowed energy band. It means that the effective mass depends on the location of an electron in the allowed energy band (Fig. 29.19). Considering the electron as a wave packet having a group velocity, v_g , an expression for the effective mass is derived as

$$m^* = \frac{\hbar^2}{d^2 E / dk^2} \quad (29.10)$$

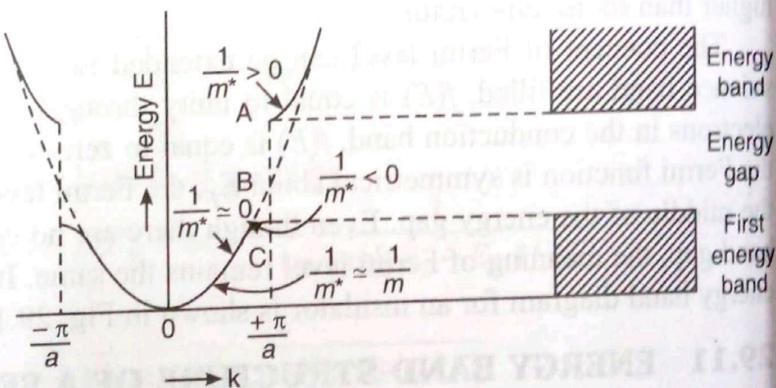


Fig. 29.19. The effective mass of electron in a solid depends on electron's location in the band.

- (i) Near the bottom of the band, the form of the $E - k$ curve does not differ much from the curve for free electron. Therefore, in these regions $m^* \approx m$.
- (ii) At the point of inflection B, the derivative $d^2E/dk^2 = 0$. Therefore, in these regions $m^* \approx \infty$. It means that an external field cannot exert any action on the motion of the electron in the region.