

Module 5: Solid and Semiconductors

❖ **Free electron theory of metals:** According to this model the most weakly bound electrons of the constituent atoms of metals, i.e. valance electrons move about freely through the volume of the metal. Thus the valance electrons of the metal become the conduction electrons. The forces between the conduction electrons and ion cores are neglected. The total energy is all kinetic. Therefore, the conduction electron move freely without any collision within the metals similar to the molecules of an ideal gas and hence it is also called free electron gas model.

For example Na atom has spectroscopic notation $1s^2 2s^2 2p^6 3s^1$ the valance electron is in a 3s state. In the metal this electron becomes as a conduction electron moving throughout the metal crystal. The remaining 10 electrons of Na^+ ion core fill the 1s, 2s and 2p state having 2, 2 and 6 electrons respectively in the free ion, the distribution of core electrons being essentially the same in the free ion as in the metal.

The metal crystal is thus supposed to consists of positive metal ions with free electron gas of valance electrons of the atom permeating the space between the positive ions. These free electrons behave like the atoms or molecules in a perfect gas and are, therefore, sometimes known as free electron gas or Fermi gas or electron cloud.

Free electron Fermi gas: It is a free electron gas of non-interacting electrons which obey Pauli's exclusion principle.

Interpretation of metallic properties on the basis of classical free electron model:

The interpretation of metallic properties in terms of free electron gas model was developed by Drude and Lorentz on the basis of classical theory applying Maxwell Boltzmann statistics to the electron gas. The mutual repulsion between the electrons are neglected and the potential field due to the positive ion core was assumed to be constant everywhere. Thus theory could explain:

- (i) Ohm's law, i.e., the current i through a conductor is proportional to the potential difference applied to the conductor i.e., V

$$i \propto V$$

- (ii) For pure metals electrical conductivity σ is inversely proportional to absolute temperature T .

$$\sigma \propto \frac{1}{T}$$

but for impure metals, electrical conductivity is inversely proportional to the square root of absolute temperature T .

$$\sigma \propto \frac{1}{\sqrt{T}}$$

- (iii) For most of the metals the resistivity ρ is inversely proportional to pressure P

$$\rho \propto \frac{1}{P}$$

- (iv) The ratio of thermal conductivity K to electrical conductivity σ is proportional to absolute temperature

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

This is known as Wiedemann-Franz law.

Besides these successes, the theory also met with a number of failures:

- (i) It could not explain the photoelectric effect, Compton scattering and black body radiation.
- (ii) Ferromagnetism could not be explained by this theory. The theoretical value of paramagnetic susceptibility is greater than the experimental value.
- (iii) According to classical free electron theory the specific heat of metals is given by $4.5R$ where as the experimental value is given by $3R$.
- (iv) According to classical free electron the electronic specific heat is equal to R while the actual value is $0.01R$.

Thus, the failures of the classical free electron theory were first corrected by Sommerfeld's quantum free electron model upon application of Fermi-Dirac or quantum Statistics.

❖ **Quantum free electron theory:** Considering the free nature of valance electrons as assumed in the classical theory, Sommerfeld treated the problem quantum mechanically using Fermi-Dirac Statistics rather than the classical Maxwell-Boltzmann Statistics. The possible electronic energy states in the potential box and the distribution of in these states are then determined using quantum statistics.

Free Electron Gas in One-Dimensional Box

Consider an electron of mass m which is bound to move in a one dimensional crystal of length L . The electron is prevented from leaving the crystal by the presence of a large potential energy barrier at its surfaces. The problem is identical to that of an electron moving in a one dimensional potential box which is represented by line and is bounded by infinite potential energy barriers as shown in Figure 1. The potential energy within the crystal or box is assumed to be zero. Thus,

$$V(x) = 0 \quad \text{for } 0 < x < L$$

$$V(x) = \infty \quad \text{for } x \leq 0 \text{ and } x \geq L$$

The wave function Ψ_n of the electron occupying the n^{th} state is determined from the solution of the Schrodinger equation, i.e.,

$$\frac{\delta^2 \Psi_n}{\delta x^2} + \frac{2m}{\hbar^2} (E_n - V) \Psi_n = 0 \quad \dots\dots\dots (1)$$

Where E_n represents the kinetic energy of the electron in the n^{th} state and V is its potential energy. Since $V = 0$ inside the box equation (1) becomes

$$\frac{\delta^2 \Psi}{\delta x^2} + \frac{2m}{\hbar^2} E \Psi = 0 \quad \dots\dots\dots (2)$$

Where p_x is the momentum of the electron

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

Where k is the propagation constant given by

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

Therefore, equation (1) can be written as

$$\frac{\delta^2 \Psi}{\delta x^2} + k^2 \Psi(x) = 0 \quad \dots\dots\dots (3)$$

The general solution of the equation (3) is

$$\Psi(x) = A \sin kx + B \cos kx \quad \dots\dots\dots (4)$$

Where A and B are two constants, the values of which can be calculated using from the boundary condition.

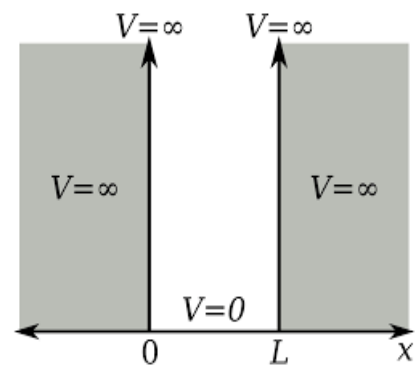


Fig. 1: One dimensional potential wall.

As the probability of findings the electron across the walls is zero

Therefore, $\Psi(x) = 0$ When $x = 0$

$\Psi(x) = 0$ When $x = L$

Substituting, $\Psi(x) = 0$, when $x = 0$ in equation (iii), we get

$$B = 0$$

Equation (iii) now becomes

$$\Psi(x) = A \sin kx \quad \dots\dots\dots (5)$$

Substituting, $\Psi(x) = 0$, when $x = L$ in equation (4), we have, $A \sin kl = 0$

$$kl = n\pi, \quad \text{or} \quad k = \frac{n\pi}{L}, \text{ where } n = 1, 2, 3 \dots\dots$$

Hence, equation (5) becomes

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

Now, $\int_0^L \Psi(x)^2 dx = 1$

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = 1$$

$$\frac{A^2}{2} \int_0^L 2 \sin^2 \frac{n\pi x}{L} dx = 1$$

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

$$\frac{A^2}{2} L = 1 \quad \text{or,} \quad A = \sqrt{\frac{2}{L}}$$

Substituting in equation (6), we will get

$$\Psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L}x$$

This is the expression for the wave function.

Eigen values of energy according to equation (6)

$$\Psi(x) = A \sin \frac{n\pi}{L}x$$

$$\frac{\delta \Psi}{\delta x} = A \left(\frac{n\pi}{L} \right) \cos \left(\frac{n\pi}{L}x \right)$$

$$\frac{\delta \Psi^2}{\delta x^2} = -A \left(\frac{n\pi}{L} \right)^2 \sin \left(\frac{n\pi}{L}x \right)$$

Substituting in equation (1), We get

$$-A \left(\frac{n\pi}{L} \right)^2 \sin \left(\frac{n\pi}{L}x \right) + \frac{2mE_n}{\hbar^2} A \sin \left(\frac{n\pi}{L}x \right) = 0$$

$$\left(\frac{n\pi}{L} \right)^2 = \frac{2mE_n}{\hbar^2}$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \dots\dots\dots (7)$$

i.e., Eigen values of energy E of the electrons

❖ **Fermi Level:**

The energy of the highest occupied level at 0K is called the Fermi Energy and the energy level is referred to as the Fermi level.

Fermi Dirac Distribution: A metal piece contains very large number of electrons. Each electron possesses quantized energy states and obeys Pauli's exclusion principle. Hence they satisfy Fermi-Dirac statistics. The probability $F(E_i)$ of an electron occupying energy level E_i is given by

$$F(E_i) = \frac{1}{\exp \left(\frac{E_i - E_f}{kT} \right) + 1}$$

Where $F(E_i)$ is called Fermi function which is defined as the probability of electron occupation in the given energy state (E_i) at thermal equilibrium E_f is Fermi energy, k is Boltzmann constant.

The plot of $f(E)$ vs E is shown in figure 2 and the following conclusions are made

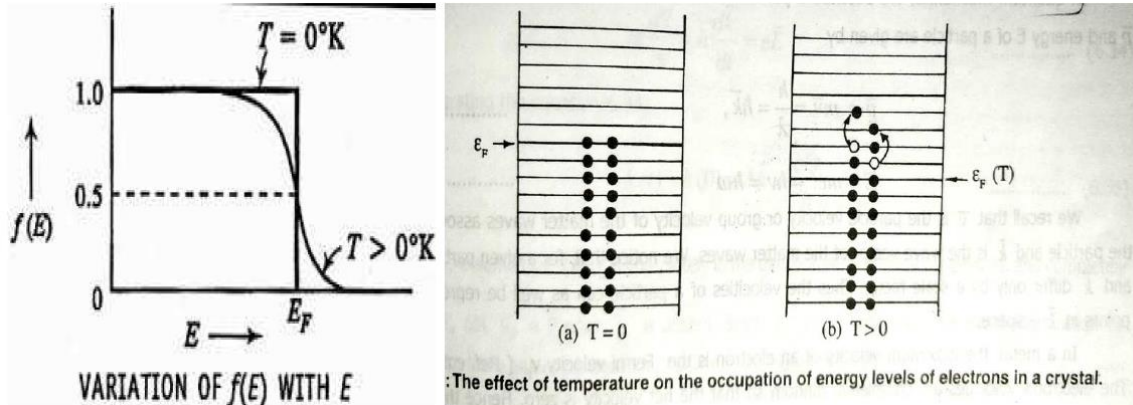


Fig. 2: Variation of probability $f(E_i)$ with E and occupation of electron in energy levels at $T=0\text{K}$ and $T>0\text{K}$.

At $T=0\text{K}$, the Fermi Dirac distribution of electrons can be understood mathematically from the following two cases.

Case I: If $E > E_F$, $\exp\left(\frac{E_i - E_F}{kT}\right) = \infty$

Therefore, $F(E_i) = 1/\infty$ then $F(E_i) = 0$. It indicates that energy levels above Fermi level are empty.

Case II: If $E < E_F$, $\exp\left(\frac{E_i - E_F}{kT}\right) = 1$ then $F(E_i) = 1$. It indicates that energy levels below Fermi levels are full of electrons. The Fermi level is a boundary energy level which separates the filled energy state and empty states at 0K . The energy of the highest filled state at 0K is called Fermi Energy E_F and the energy level is known as Fermi Level.

At $T > 0\text{K}$

if $E_i = E_F$ then $F(E_i) = 1/2$. i.e 50%. Therefore Fermi level is the energy level for which the probability of filled states is 50% at any temperature.

❖ **Density of states:** The number of electronic states or quantum states per unit energy range is defined as density of states. Let us consider spherical systems of radius n and it represents a vector to a point n_x , n_y and n_z in 3 dimensional space.

Consider a sphere of radius n and another sphere of radius $n + dn$ in which energy values are E and $E + dE$ respectively as shown in Figure 3

Number of energy states available in sphere of radius n is $\frac{1}{8} \left(\frac{4}{3} \pi n^3 \right)$ (1)

Number of energy states available in sphere of radius $n + dn$ is $\frac{1}{8} \left(\frac{4}{3} \pi (n + dn)^3 \right)$ (2)

E and dE are the energy values of above two regions respectively from equation (1) and (2)

we can write number of energy states available in dn or dE

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

$$= \frac{\pi}{6} [(n + dn)^3 - n^3]$$

By neglecting higher order terms we get

$$g'(E)dE = \frac{\pi}{6} 3n^2 dn$$

$$= \frac{\pi}{2} (n(n dn)) \dots \dots \dots (3)$$

The expression for nth energy level can be expressed as

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

$$n^2 = \frac{8mL^2}{\hbar^2} E \dots \dots \dots (4)$$

$$n = \sqrt{\frac{8mL^2}{\hbar^2} E} \dots \dots \dots (5)$$

Differentiating equation (4) and taking n and E are variables, we get

$$2n dn = \frac{8mL^2}{\hbar^2} dE$$

$$n dn = \frac{1}{2} \frac{8mL^2}{\hbar^2} dE \dots \dots \dots (6)$$

Substituting equation (5) & (6) in equation (3), we get

$$g'(E)dE = \frac{\pi}{2} \left(\frac{8mL^2}{\hbar^2} \right)^{1/2} E^{1/2} \frac{1}{2} \left(\frac{8mL^2}{\hbar^2} \right) dE$$

$$= \frac{\pi}{4} \left(\frac{8mL^2}{\hbar^2} \right)^{3/2} E^{1/2} dE$$

According to Pauli Exclusion Principal each energy level contain two states

$$\text{Therefore, } g(E)dE = 2 \frac{\pi}{4} \left(\frac{8mL^2}{\hbar^2} \right)^{3/2} E^{1/2} dE$$

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

Density of states $g(E)dE = \frac{g'(E)dE}{V}$, as length of the energy level is L,

Therefore, $V = L^3$, So density of states can be expressed as

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

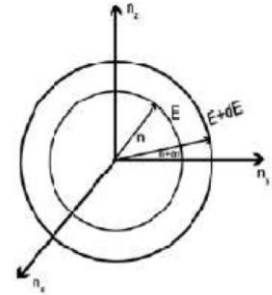


Fig. 3: Sphere of radius n and n+dn with corresponding energy E and E +dE