

- CONDUCTING MATERIALS

Introduction

The conductivity of a material depends on the presence of free electrons. The materials which conduct electricity due to free electrons when an electric potential difference is applied across them are known as conducting materials. The conducting materials play an important role in Engineering and Technology. Conducting materials are good conductors of electricity and heat. Gold, silver, copper, aluminium are the examples of conducting materials.

Classical free electron theory

Assumptions of Free electron gas model:

- A metal contains a large number of free electrons which are free to move about in entire volume of the metal like the molecules of a gas in a container.
- The free electrons move in random directions and collide with either positive ions fixed in the lattice or other free electrons. All the electrons are elastic and there is no loss of energy.
- The velocity and the energy distribution of free electrons obey the classical Maxwell Boltzmann statistics.
- The free electrons are moving in a completely uniform potential field due to the ions fixed in the lattice.
- In the absence of electric field the random motion of free electrons is equally probable in all directions so that the current density vector is zero.
- When the external electric field is applied across the ends of a metal, the electrons drift slowly with some average velocity known as drift velocity in the direction opposite to that of electric field. This drift velocity is superimposed over the random velocity. This drift velocity is responsible for the flow of electric current in a metal.

Drift velocity

The average velocity of the free electrons with which they move towards the positive terminal under the influence of the electrical field.

Mobility

It is defined as the drift velocity of the charge carrier per unit applied electric field.

Collision time

The average time taken by a free electron between two successive collisions is called collision time.

Mean free path

The average distance travelled by a free electron between two successive collisions is called mean free path.

Relaxation time

It is defined as the time taken by a free electron to reach its equilibrium position from the disturbed position in the presence of an electric field.

Electrical conductivity.

Electrical conductivity σ is defined as the rate of charge flow across unit area in a conductor per unit potential (voltage) gradient.

$$\sigma = \frac{J}{E}. \text{ Its unit is } \Omega^{-1}\text{m}^{-1} \text{ or } \text{Sm}^{-1}.$$

Expression for the electrical conductivity.

When an electrical field (E) is applied to an electron of charge 'e' of a metallic rod, the electron moves in opposite direction to the applied field with a velocity v_d . This velocity is known as drift velocity.

$$\text{Lorentz force acting on the electron } F = eE \dots\dots(1)$$

This force is known as the driving force of the electron.

Due to this force, the electron gains acceleration 'a'.

From Newton's second law of motion,

$$\text{Force } F = ma \dots\dots(2)$$

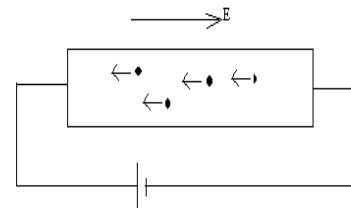
From the equation (1) and (2),

$$ma = eE \quad \text{or} \quad a = \frac{eE}{m} \dots\dots(3)$$

$$\text{Acceleration (a)} = \frac{\text{Driftvelocity}(v_d)}{\text{Relaxationtime}(\tau)} \text{ or } a = \frac{v_d}{\tau}$$

$$v_d = a\tau \dots\dots(4)$$

Substituting equation (3) in (4)



$$v_d = \left(\frac{e\tau}{m} \right) E \dots\dots\dots(5)$$

The Ohms' law states that current density (J) is expressed as

$$J = \sigma E \text{ or } \sigma = \frac{J}{E} \dots\dots(6)$$

Where σ is the electrical conductivity of the electron.

But, the current density in terms of drift velocity is given as

$$J = nev_d \dots\dots (7)$$

Substituting equation (5) in equation (7), we have

$$J = ne \left(\frac{e\tau}{m} \right) E$$

$$\text{or } \frac{J}{E} = \frac{ne^2\tau}{m} \dots\dots(8)$$

On comparing the equation (6) and (8) , we have

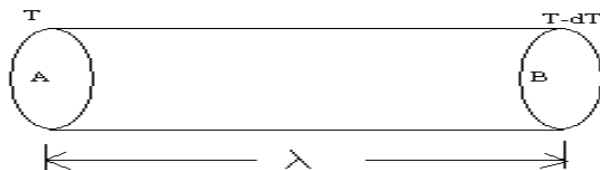
Electrical conductivity $\sigma = \frac{ne^2\tau}{m} \dots\dots(9)$

Thermal conductivity

Thermal conductivity K is defined as the amount of heat flowing per unit time through the material having unit area of cross-section per unit temperature gradient. $Q = K \frac{dT}{dx}$.

Expression for Thermal Conductivity of a Metal

Consider two cross-sections A and B in a uniform metallic rod AB separated by a distance λ . Let A at a high temperature (T) and B at low temperature (T-dT). Now heat conduction takes place from A and B by the electrons. The conduction electron per unit volume is n and average velocity of these electrons is v. During the movement of electrons in the rod, collision takes place. Hence, the electrons near A lose their kinetic energy while electrons near B gain kinetic energy.



At A, average kinetic energy of an electron = $\frac{3}{2} kT \dots\dots(1)$

At B, average kinetic energy of the electron = $\frac{3}{2} k(T - dT) \dots\dots(2)$

The excess of kinetic energy carried by the electron from A to B is,

$$\frac{3}{2}kT.....(3)$$

Number of electrons crossing per unit area per time from A and B is,

$$\frac{1}{6}nV$$

The excess of energy carried from (A to B) per unit area in unit time is $= \frac{1}{4}nVkdT....(4)$

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

$$= -\frac{1}{4}nVkdT.....(5)$$

Hence, the net amount of energy transferred from A to B per unit area per unit time is,

$$Q = \frac{1}{2}nVkdT.....(6)$$

But from the basic definition of thermal conductivity, the amount of heat conducted per unit area per unit time is,

$$Q = K \frac{dT}{\lambda} \text{ i.e., } \frac{1}{2}nVkdT = K \frac{dT}{\lambda}; \therefore K = \frac{1}{2}nVk\lambda.....(7)$$

We know that for the metals i.e. $\tau = \tau_c = \frac{\lambda}{v} = \tau v = \lambda.....(8)$

Substituting the equation (8) in equation (7), we have

$$K = \frac{1}{2}nV^2k\tau.....(9)$$

Wiedemann – Franz law:

The law states that the ratio of thermal conductivity to electrical conductivity of the metal is directly proportional to the absolute temperature of the metal.

We know that,

$$\sigma = \frac{ne^2\tau}{m}.....(1) \quad \text{and}$$

$$K = \frac{1}{2}nV^2k\tau.....(2)$$

$$\frac{\text{Thermal conductivity}}{\text{Electrical conductivity}} = \frac{K}{\sigma} = \frac{\frac{1}{2} n v^2 k \tau}{\frac{ne^2 \tau}{m}}; \frac{k}{\sigma} = \frac{1}{2} \frac{m v^2 k}{e^2} \dots\dots(3)$$

We know that the kinetic energy of an electron,

$$\frac{1}{2} m v^2 = \frac{3}{2} k T \dots\dots(4)$$

Substituting the equation (4) in the equation (3). We have

$$\frac{k}{\sigma} = \frac{3}{2} \frac{k T \times k}{e^2} = \frac{3}{2} \frac{k^2 T}{e^2}, \text{ or } \frac{K}{\sigma} = \frac{3}{2} \left[\frac{k}{e} \right]^2 T, \text{ or } \frac{K}{\sigma} = L T \dots\dots(5)$$

Where $L = \frac{3}{2} \left[\frac{k}{e} \right]^2$ is a constant and it is known as Lorentz number.

$$\frac{K}{\sigma} \propto T \dots\dots(6)$$

Hence, it is proved that the ratio of thermal conductivity of a metal is directly proportional to the absolute temperature of the metal.

Fermi-Dirac distribution function

Fermi function F (E):

Fermi-Dirac distribution function represents the probability of an electron occupying a given energy level at absolute temperature. It is given by

$$F(E) = \frac{1}{1 + e^{(E-E_F)/K_B T}}$$

Where $K_B \rightarrow$ Boltzmann Constant

T \rightarrow Temperature

Effect of temperature on Fermi Function:

Case (i) Probability of occupation for $E < E_F$ at $T = 0K$

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

When $T = 0K$ and $E < E_F$, we have

$$F(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1 + 0} = \frac{1}{1} [\because e^{-\infty} = 0]; \therefore F(E) = 1$$

Thus at $T = 0K$, there is 100 % chance for the electrons to occupy the energy levels below the Fermi level.

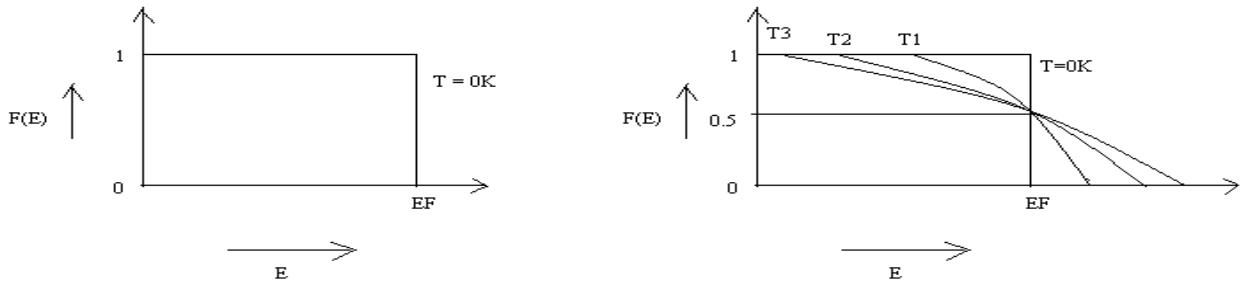
Case (ii) Probability of occupation for $E > E_F$ at $T = 0K$

When $T = 0K$ and $E > E_F$,

we have
$$F(E) = \frac{1}{1 + e^{(+ve/0)}} = \frac{1}{1 + e^{\infty}} = \frac{1}{1 + \infty} = \frac{1}{\infty} = 0 \therefore F(E) = 0$$

Thus, there is 0 % chance for the electrons to occupy energy levels above the Fermi energy level.

From the above two cases, at $T = 0K$ the variation of $F(E)$ for different energy values becomes a step function.



Variation of Fermi distribution function with E at different temperatures

Case (iii) Probability of occupation at ordinary temperature:

At ordinary temperature, the value of probability starts reducing from 1 for values of E slightly less than E_F . With the increase of temperature, i.e., $T > 0K$, Fermi function $F(E)$ varies with E .

At any temperature other than $0K$ and $E = E_F$,

$$F(E) = \frac{1}{1 + e^0} = \frac{1}{1 + 1} = \frac{1}{2} = 50\%$$

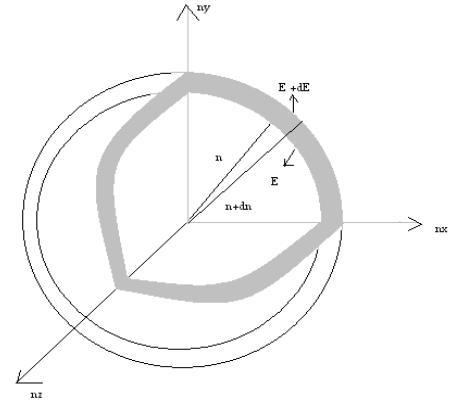
Hence, there is 50 % chance for the electrons to occupy Fermi level. Further, for $E > E_F$ the probability value falls off rapidly to zero.

Case (iv) At high temperature:

When $kT \gg E_F$, the electrons lose their quantum mechanical character and Fermi distribution function reduces to classical Boltzmann distribution.

Density of energy states.

Definition: It is defined as the number of available electron states per unit volume in an Energy interval E and $E + dE$. It is denoted by $Z(E)dE$.



Expression for density of energy states.

Let us consider a cubical sample with side 'a'. A sphere is constructed with three quantum numbers n_x, n_y, n_z as coordinate axes in three-dimensional space as shown.

A radius vector n is drawn from origin 'O' to a point with co-ordinates n_x, n_y, n_z in this space. All the points on the surface of that sphere will have the same energy E . Thus, $n^2 = n_x^2 + n_y^2 + n_z^2$ denotes the radius of the sphere with energy E . This sphere can be further divided into a many shells. Each shell represents a particular combinations of quantum numbers (n_x, n_y, n_z). Therefore, it denotes a particular energy value with a particular radius. In this space, unit volume represents one energy state.

$$\text{Number of energy states within a sphere of radius 'n'} = \frac{4}{3}\pi n^3 \dots (1)$$

Since the quantum numbers n_x, n_y, n_z can have only positive integer values, we have to take only one octant of the sphere, i.e., $\frac{1}{8}$ th of the spherical volume.

Therefore, the number of available energy states within one octant of the sphere of radius 'n'

$$\text{corresponding to energy } E \text{ is } = \frac{1}{8} \left[\frac{4}{3} \pi n^3 \right] \dots (2)$$

Similarly, the number of available energy states within one octant of the sphere of radius 'n + dn'

$$\text{corresponding to energy } E + dE = \frac{1}{8} \left[\frac{4}{3} \pi (n + dn)^3 \right] \dots (3)$$

Now, the number of available energy states between the shell of radius n and $n + dn$ i.e., between the energy values E and $E + dE$,

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

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

Since dn is very small, higher powers of dn terms dn^2 and dn^3 can be neglected.

$$N(E) dE = \frac{\pi}{6} 3n^2 dn = N(E)dE = \frac{\pi}{2} n^2 dn = N(E)dE = \frac{\pi}{2} n(ndn).....(4)$$

We know that the energy of an electron in a cubical metal piece of sides 'a' is given by

$$E = \frac{n^2 h^2}{8ma^2} \dots(5) \text{ or }; n^2 = \frac{8ma^2 E}{h^2} \dots\dots(6) \text{ or }; n = \left[\frac{8ma^2 E}{h^2} \right]^{1/2} \dots\dots(7)$$

Differentiating the equation (6), we get

$$2ndn = \frac{8ma^2 dE}{h^2} \text{ or }; ndn = \frac{8ma^2 dE}{h^2} \dots\dots(8)$$

Substituting equations (7) and (8) in equation (4), we have

$$\begin{aligned} N(E)dE &= \frac{\pi}{2} \left(\frac{8ma^2 E}{h^2} \right)^{1/2} \left[\frac{8ma^2 dE}{2h^2} \right] = \frac{1}{2} \frac{\pi}{2} \left(\frac{8ma^2 E}{h^2} \right)^{1/2} \left[\frac{8ma^2 dE}{h^2} \right] \\ &= \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{1/2} E^{1/2} \left(\frac{8ma^2}{h^2} \right) dE = N(E)dE = \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} E^{1/2} dE \dots\dots(10) \end{aligned}$$

Pauli's exclusion states principle states that two electrons of opposite spins can occupy each state and hence the number of energy states available for electron occupancy is given by

$$\begin{aligned} N(E)dE &= 2 \times \frac{\pi}{4} \left[\frac{8ma^2}{h^2} \right]^{3/2} E^{1/2} dE = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{3/2} a^3 E^{1/2} dE \\ &= \frac{\pi}{2} (8m)^{3/2} \left(\frac{a^3}{h^3} \right) E^{1/2} dE = N(E)dE = \frac{\pi}{2} \left(\frac{a}{h} \right)^3 (8m)^{3/2} E^{1/2} dE \\ N(E)dE &= \frac{\pi}{2} \left(\frac{a}{h} \right)^3 8(2m)^{3/2} E^{1/2} dE = \frac{4\pi}{h^3} (2m)^{3/2} a^3 E^{1/2} dE \end{aligned}$$

Density of states is given by the number of energy states per unit volume,

$$\begin{aligned} Z(E)dE &= \frac{N(E)dE}{V} \\ \text{i.e., Density of states } Z(E)dE &= \frac{4\pi}{h^3} \frac{(2m)^{3/2} a^3 E^{1/2} dE}{a^3} ; ; [\because \text{Volume } V = a^3] \\ Z(E)dE &= \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \dots\dots(11) \end{aligned}$$

This is the expression for the density of charge carriers in the energy interval E and $E + dE$.

Carrier Concentration: Carrier Concentration, i.e., the number of electrons per unit volume in a given energy interval is calculated by assuming the product of the density of states $Z(E)$ and the occupancy probability $F(E)$.

$$\text{i.e. } n_c = \int Z(E)F(E)dE$$

Substituting the expressions for $Z(E)$ and $F(E)$, we have

$$n_c = \int \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} \frac{1}{1 + e^{(E-E_F)/kT}} dE \dots (12)$$