

UNIT – 1

ELECTRICAL PROPERTIES OF MATERIALS

CONTENTS

1.5. Classical Free Electron theory

1.5.1. Postulates of classical free electron theory

1.5.2. Electrical Conductivity

1.5.3. Thermal Conductivity

1.5.4 Wiede- Mann – Franz Law

1.5.5. Lorentz number

1.5.6. Success of classical free electron theory

1.5.7. Drawbacks of classical free electron theory

1.5. Classical Free Electron theory

After the discovery of electron, Drude and Lorentz proposed classical free electron theory in 1900. It is a macroscopic theory and explains electrical and thermal properties of solids based on classical laws.

1.5.1. Postulates of classical free electron theory

In the absence of electrical field

- ❖ The electrons are moves freely in the boundaries of the metal, similar to the gas molecules moving in a vessel.
- ❖ The forces between the conduction electrons and ion core in neglected.
- ❖ The electrons possess kinetic energy only.
- ❖ Free electrons are elastically collides with each.

In the presence of field

- ❖ The free electrons move in the opposite direction to the applied electrical field direction.
- ❖ It is obey the classical Maxwell-Boltzmann distribution of velocities.
- ❖ All free electrons gain equal amount of thermal energy and involved for thermal conduction.

Mean free path

The average distance travelled by a free electron in any two successive collisions is known as mean free path.

$$\lambda = V_d r_c$$

Collision time

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

$$r_c = \lambda / V_d$$

Relaxation time

Average time taken by a free electron to reach its equilibrium state from disturbed state due to the application of an electrical field is known as relaxation time. It is approximately equal to 10^{-14} s.

Mobility

The drift velocity acquired by the electron per unit applied electrical field to it.

$$\mu = \frac{V_d}{E} \quad (m^2 V^{-1} S^{-1})$$

1.5.2. Electrical Conductivity

The amount of electrical charges conducted per unit time across unit area per unit applied electrical field is known as electrical conductivity.

$$\sigma = \frac{Q}{tAE}$$

$$\sigma = \frac{I}{AE} \quad (\because Q/t = I)$$

$$\sigma = \frac{J}{E} \quad (\because I/A = J)$$

$$J = \sigma E$$

Derivation of Electrical Conductivity of metals

Consider a metal conductor of 'XY' and 'E' is the applied electric field to it. The electron moves in opposite directions to the applied field with a velocity V_d .

Let 'n' be the number of free electrons per unit volume.

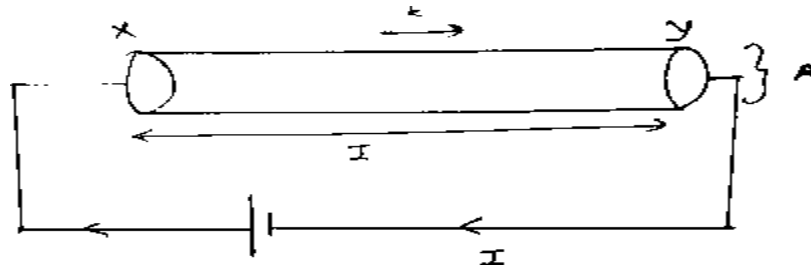


Fig 1.5.1 Movement of free electrons in a metal rod

Current density of a conducting material is given by,

$$J = -enV_d \dots\dots\dots (1)$$

Force experienced by the electron is

$$F = -eE \dots\dots\dots (2)$$

This force accelerates the electron

$$a = \frac{\text{Drift Velocity}}{\text{Collison time}}$$

$$a = \frac{V_d}{c}$$

$$V_d = ar \dots\dots\dots (3)$$

From the Newton's second law of motion, the force on the electron,

$$F = ma \dots\dots\dots (4)$$

Equate equations (2) and (4) we have,

$$-eE = ma$$

$$a = \frac{-eE}{m} \dots\dots\dots (5)$$

Substitute Eqn. (5) in Eqn. (3) we get,

$$V_d = \frac{-eEc}{m} \dots\dots\dots (6)$$

Substituting eqn. (6) in eqn. (1) we have,

$$J = \frac{(-e)n(-eEc)}{m}$$

$$J = \frac{nEe^2r}{m}$$

$$\frac{J}{E} = \frac{ne^2r}{m}$$

$$\sigma = \frac{ne^2c}{m} \dots\dots\dots (7) (\because \sigma = J/E)$$

We find that with increase of electron concentration ‘n’, the conductivity ‘σ’ is increases. As ‘m’ increases the motion of the electron becomes slow and hence the conductivity ‘σ’ decreases.

Co-efficient of electrical conductivity

The quantity of electricity flowing per unit area per unit time maintained at unit potential gradient.

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

If A=1; E=1, then,

$$I = \sigma$$

1.5.3. Thermal Conductivity

The amount of heat conducted by the conductor is

$$Q = KA \frac{dT}{dx} t$$
$$K = \frac{Q}{A \left(\frac{dT}{dx}\right) t} \dots \dots \dots (1)$$

Where,

K → is the thermal conductivity

A → is the area of cross section

t → is the time of flow of heat

$\frac{dT}{dx}$ → Temperature gradient

The amount of heat conducted per unit time per unit area of cross section per unit temperature gradient.

If A = 1; t = 1, then eqn. (1) becomes

$$K = \frac{Q}{\frac{dT}{dx}}$$
$$Q = K \frac{dT}{dx} \dots \dots \dots (2)$$

Expression for thermal conductivity of a metal

Consider a metal rod 'AB' with the length of ' λ '. Let 'A' be at higher temperature and 'B' at a low temperature. Now, heat flows from A to B by the free electrons.

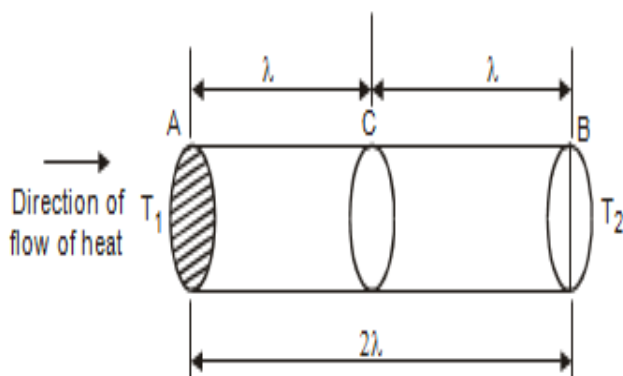


Fig 1.5.2 Thermal conductivity of a metal

Free electron per unit volume = n

Average velocity of the electrons = v

Average kinetic energy of electron at 'A' is

$$= \frac{3}{2} K_B T \dots \dots \dots (3)$$

Where,

$K_B \rightarrow$ is the Boltzmann constant

$T \rightarrow$ is the temperature at A

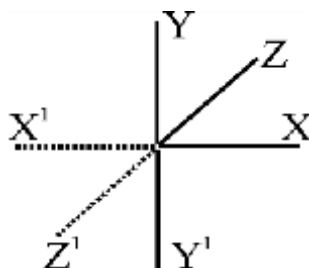
Average kinetic energy of an electron at 'B' is

$$= \frac{3}{2} K_B (T - dT) \dots \dots \dots (4)$$

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

$$\begin{aligned} &= \frac{3}{2} K_B T - \frac{3}{2} K_B (T - dT) \\ &= \frac{3}{2} K_B T - \frac{3}{2} K_B T + \frac{3}{2} K_B dT \\ &= \frac{3}{2} K_B dT \dots \dots \dots (5) \end{aligned}$$

Let us assume that, there is an equal probability for the electrons to move in all six directions shown in given figure.



Each electrons travels with thermal velocity 'v' and 'n' is the free electrons per unit volume. Then 1/6 nv electrons travel in any one of the directions per unit area per unit time.

Number of electrons crossing per unit area per unit time A to B is

$$= \frac{1}{6}nv$$

The excess of energy carried from A to B per unit area in unit time is

$$\begin{aligned} &= \frac{1}{6}nv \times \frac{3}{2}K_BdT \\ &= \frac{1}{4}nvK_BdT \quad \dots \dots \dots (6) \end{aligned}$$

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

$$= -\frac{1}{4}nvK_BdT \quad \dots \dots \dots (7)$$

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

$$\begin{aligned} Q &= \frac{1}{4}nvK_BdT - \left(-\frac{1}{4}nvK_BdT\right) \\ Q &= \frac{1}{2}nvK_BdT \quad \dots \dots \dots (8) \end{aligned}$$

Compare eqn. (2) and (8), we get

$$\begin{aligned} K \frac{dT}{dx} &= \frac{1}{2}nvK_BdT \\ K &= \frac{1}{2}nvK_Bdx \\ K &= \frac{1}{2}nvK_B\lambda \quad \dots \dots \dots (9) \quad (\because \lambda = dx) \end{aligned}$$

We know that for the metals, the collision time is equal to the relaxation time.

$$\lambda = vr \quad \dots \dots \dots (10)$$

Substitute eqn. (10) in eqn. (9) we have,

$$\begin{aligned} K &= \frac{1}{2}nvK_Bvr \\ K &= \frac{1}{2}nv^2K r \quad \dots \dots \dots (11) \end{aligned}$$

This is the expression of thermal conductivity and it is directly proportional to the square of the velocity of the electrons.

1.5.4. Wiedemann – Franz Law

The ratio between the thermal conductivity and electrical conductivity of a metal is directly proportional to the absolute temperature of the metal. This ratio is a constant for all metals at given temperature.

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

Where, 'L' is proportionality constant. It is known as Lorentz number. Its value is $2.44 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$ at $T=293 \text{ K}$.

From classical theory, the electrical thermal conductivity of a metal is given as

$$\sigma = \frac{ne^2c}{m} \dots\dots\dots (1)$$

$$K = \frac{1}{2} nv^2 K_B r \dots\dots\dots (2)$$

$$\frac{K}{\sigma} = \frac{\frac{1}{2} nv^2 K_B r}{\frac{ne^2r}{m}}$$

$$\frac{K}{\sigma} = \frac{\frac{1}{2} mv^2 K_B}{e^2} \dots\dots\dots (3)$$

We know that the kinetic energy of the electron is

$$\frac{1}{2} mv^2 = \frac{3}{2} K_B T \dots\dots\dots (4)$$

Substituting eqn. (4) in eqn.(3), we have

$$\frac{K}{\sigma} = \frac{3K_B T K_B}{2e^2}$$

$$\frac{K}{\sigma} = \frac{3K_B^2 T}{e^2}$$

$$\frac{1}{\sigma} = \frac{1}{2} \left(\frac{1}{e} \right) T$$

$$\frac{K}{\sigma} = LT \dots\dots\dots (5) (\because L = \frac{3 K_B}{2} \frac{1}{e})$$

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Where 'L' is a constant and it is known as **Lorentz number**. According to this law it can be concluded that if a metal has high thermal conductivity, it will also have high electrical conductivity.

1.5.5. Lorentz number

The ratio between the thermal conductivity (K) to the product electrical conductivity (σ) and absolute temperature (T) of the metal is a constant. The constant value is known as Lorentz number.

$$L = \frac{K}{\sigma T} \dots\dots\dots (1)$$

According to classical theory,

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

Substitute the values of $K_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ and $e = 1.602 \times 10^{-19} \text{ C}$ in equation (2), we have,

$$L = \frac{3}{2} \left(\frac{1.38 \times 10^{-23}}{1.602 \times 10^{-19}} \right)^2$$

$$L = 1.12 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \dots\dots\dots (3)$$

Hence, it was found that the classical value of Lorentz number is only half of the experimental value, i.e., $L = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$. This discrepancy in the experimental and theoretical value of Lorentz number is the failure of classical theory. This was rectified by quantum theory.

According to the quantum theory, electrons near the Fermi level alone contribute towards thermal and noble conduction. Using quantum free electron theory model, the electronic specific heat value is given by

$$C_v = \frac{n\pi^2 K^2 T}{m v^2} \dots\dots\dots (4)$$

Thermal conductivity is

1

$$v^2 r \dots \dots \dots (5)$$

$$= \frac{K}{3v}$$

Substitute equation (4) in (5) we get,

$$K = \frac{n\pi^2 K_B^2 T v^2 r}{3mv^2}$$

$$K = \frac{n\pi^2 K_B^2 T r}{3m} \dots \dots \dots (6)$$

The electrical conductivity is

$$\sigma = \frac{ne^2 r}{m} \dots \dots \dots (7)$$

From equations (6) and (7) we get,

$$\frac{K}{\sigma} = \frac{\frac{n\pi^2 K_B^2 T r}{3m}}{\frac{ne^2 r}{m}}$$

$$\frac{K}{\sigma} = \frac{m n \pi^2 K_B^2 T r}{3 m n e^2 r}$$

$$\frac{K}{\sigma} = \frac{\pi^2 K_B^2}{3} \left(\frac{1}{e}\right)^2 T$$

$$\frac{K}{\sigma T} = \frac{\pi^2 K_B^2}{3} \left(\frac{1}{e}\right)^2$$

$$\frac{K}{\sigma T} = L \dots \dots \dots (8)$$

$$L = \frac{\pi^2 K_B^2}{3} \left(\frac{1}{e}\right)^2$$

Substitute the values of $K_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ and $e = 1.602 \times 10^{-19} \text{ C}$ in equation (2), we have,

$$L = \frac{(3.14)^2 \cdot 1.38 \times 10^{-23}^2}{3} \left(\frac{1}{1.602 \times 10^{-19}}\right)^2$$

$$L = 2.44 \times 10^{-8} W \Omega K^{-2} \dots \dots \dots (9)$$

This value is in good agreement with the experimental value. The Widemann Franz law is not appreciable at very low temperature.

1.5.6. Success of classical free electron theory

1. It verifies ohm's law
2. It explains the electron and thermal conductivity.
3. It derives Widemann – Franz law.
4. It explains optical properties of metals.

1.5.7. Drawbacks of classical free electron theory

1. It is failed to explain photoelectric effect, Compton Effect, Para magnetism, ferromagnetism and black body radiation.
2. It is a macroscopic theory.
3. It cannot explain the electrical conductivity of semiconductors or insulators using this model.
4. It states that all the free electrons will absorb energy, but quantum theory states that only free electrons will absorb energy.
5. In classical free electron theory, theoretical and experimental value of Lorentz number is not matched. It is rectified by quantum theory.
6. Theoretical and experimental value of specific heat ($4.5R \neq 3R$) and electronic specific heat ($3/2 R \neq 0.01R$) is not matched.

UNIT-1

ELECTRICAL PROPERTIES OF MATERIALS

CONTENTS

1.9. Density of Energy States

1.9.1. Calculation of Carrier Concentration at 0 K

1.9.2. Calculation of Fermi Energy

1.9. Density of Energy States

A parameter of interest in the study of conductivity of metals and semiconductors is the density of states. The Fermi function $F(E)$ gives only the probability of filling up of electrons in a given energy state. It does not give the information about the number of electrons that can be filled in a given energy state, to know that we should know the number of available energy states called density of state

Density of states $Z(E)dE$ is defined as the number of states per unit volume in an energy interval E and $E+dE$.

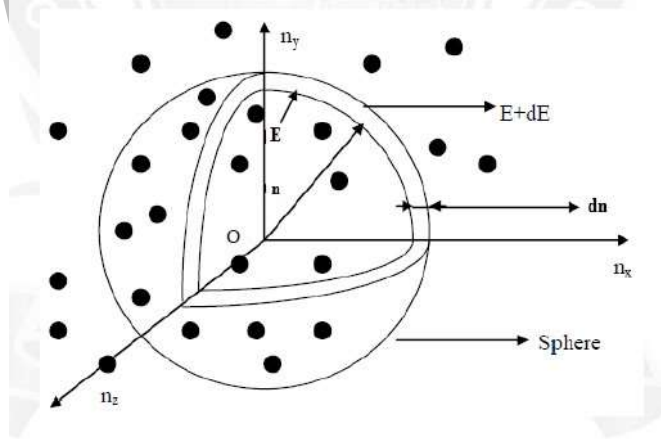


Fig 1.9.1-Density of States

$$\text{Density of states } Z(E) dE = \frac{N(E) dE}{\text{Volume of the metal piece } (V)}$$

The number of available energy levels can be obtained for various combinations of quantum numbers n_x, n_y and n_z . i.e.

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

Let us construct a three dimensional space of points which represents the quantum numbers n_x, n_y and n_z as shown in above figure. Each point in this space represents an energy level. Let us consider a cubical sample with side 'a'. A sphere is constructed with the quantum numbers n_x, n_y and n_z as three coordinate axes in three dimensional space, as shown in above figure. A radius 'n' is drawn from the origin 'O' to a point n_x, n_y and n_z in space and all the points on the surface of the sphere will have the same energy 'E'. Thus, $n^2 = n_x^2 + n_y^2 + n_z^2$ denotes

the radius 'n'. Any change in n_x, n_y and n_z will change 'E' and hence the radius 'n'.

Therefore, the number of energy states with in a sphere of radius 'n'

$$n = \frac{4}{3}\pi n^3 \dots \dots \dots (1)$$

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

Number of available energy states within one octant of sphere of radius 'n' corresponding to energy 'E'

$$n = \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right) \dots \dots \dots (2)$$

Hence, the number of available energy states between the spheres of radius $n+dn$ corresponding to energy $E+dE$ is

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

The number of available energy states between the shell of radius 'n' and 'n+dn' corresponding energy between 'E' and 'E+dE' is determined by subtracting equation (2) from equation (3), we have

$$\begin{aligned} N(E)dE &= \frac{1}{8} \left(\frac{4}{3} \pi (n + dn)^3 \right) - \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right) \\ &= \frac{1}{8} \left(\frac{4}{3} \pi \right) [(n + dn)^3 - n^3] \\ N(E) dE &= \frac{1}{8} \left(\frac{4}{3} \pi \right) (dn^3 + 3n^2dn + 3ndn^2) \dots \dots \dots (4) \end{aligned}$$

Since dn is very small, the higher powers dn^2 and dn^3 terms are neglected. Equation (4) becomes,

$$N(E)dE = \frac{1}{8} \left(\frac{4}{3} \pi \right) 3n^2dn \dots \dots \dots (5)$$

Number of available energy states between interval E and $E+dE$ is given by

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

$$N(E) dE = \frac{\pi}{2} n^2 (ndn) \dots\dots\dots (6)$$

From the application of Schrodinger wave equation, the energy of the electron in a cubical metal piece of side 'a' is given by

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

$$n^2 = \frac{8mEa^2}{h^2} \dots\dots\dots (7)$$

Take the square root of the above equation we get,

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

Differentiate the equation (7), we get,

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

$$ndn = \frac{8ma^2}{2h^2} dE \dots\dots\dots (9)$$

Substitute eqn. (8) and(9) in eqn. (6) we have

$$N(E) dE = \frac{\pi}{2} \left(\frac{8ma^2 E}{h^2} \right)^{1/2} \left(\frac{8ma^2 dE}{2h^2} \right)$$

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

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

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

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

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

$$N(E) dE = \frac{4\pi}{h^3} a^3 (2m)^{3/2} E^{1/2} dE \dots\dots\dots (11)$$

The density of states is equal to the number of states per unit volume in the energy range in E and E+dE

$$Z(E) dE = \frac{N(E) dE}{V}$$

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

$$Z(E) dE = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \dots\dots\dots (12)$$

This is the expression for the density of states and it is used to calculate the carrier concentration of metals and semiconductors.

1.9.1. Calculation of Carrier Concentration at 0 K

The number of electrons per unit volume is called carrier concentration. It is calculated by summing up the product of the density of states Z(E) and Fermi distribution function F(E).

$$\text{Carrier concentration } n_c = \int Z(E) F(E) dE$$

Substituting Z(E) and F(E) in the above equation, we get,

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

For metals at T = 0 K, the upper most occupied level is E_F and F(E) = 1. Now the equation (1) becomes,

$$\begin{aligned} n_c &= \int_0^{E_F} \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \\ &= \frac{4\pi}{h^3} (2m)^{3/2} \int_0^{E_F} E^{1/2} dE \\ n_c &= \frac{4\pi}{h^3} (2m)^{3/2} \left[\frac{E^{3/2}}{3/2} \right]_0^{E_F} \\ n_c &= \frac{8\pi}{3h^3} (2mE_F)^{3/2} \dots\dots\dots (2) \end{aligned}$$

This equation is the carrier concentration or density of charge carrier at 0 K in terms of Fermi energy.

1.9.2. Calculation of Fermi Energy

Fermi energy is calculated from the expression of carrier concentration.

$$\begin{aligned} n_c &= \frac{8\pi}{3h^3} (2mE_F)^{3/2} \\ (E_F)^{3/2} &= \frac{3h^3 n_c}{8\pi (2m)^{3/2}} \end{aligned}$$

Multiply the power of 2/3 on both sides of the above equation, we have

$$E_F = \left[\frac{3h^3 n_c}{8\pi(2m)^2} \right]^{\frac{2}{3}}$$

$$E_F = \left[\frac{3h^3 n_c}{\pi(8m)^2} \right]^{\frac{2}{3}} \quad (\because (8m)^2 = 8(2m)^2)$$

Rearrange the above equation, we get

$$E_F = \frac{h^2}{8} \left(\frac{3n_c}{\pi} \right)^{\frac{2}{3}} \frac{1}{m}$$

This is the expression for Fermi energy of electrons in solids at absolute zero temperature. It is depends only on the density of electrons of metals.

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MODULE – 1

ELECTRICAL PROPERTIES OF MATERIALS

CONTENTS

1.14. Effective mass of Electron and Hole

1.14.1 Effective mass of Electron

1.14.2. Concept of hole (or) Effective or Negative mass of electron:

1.14.1. Effective mass of Electron

The mass acquired by an electron when it is accelerated in a periodic potential is called effective mass of an electron. It is denoted by m^* .

Explanation:

When an electron is accelerated the mass of the electron is not constant, but it varies.

This varying mass is called effective mass (m^*).

Derivation of effective mass of electron:

When electric field is applied to a crystal the electron gains velocity described by wave vector k .

$$\text{Group velocity } v_g = \frac{d\omega}{dk} \text{-----(1)}$$

Where ω – angular frequency of the electron.

k - wave vector

we know that $E = \hbar\omega$

$$\begin{aligned} E &= \frac{h\omega}{2\pi} \\ &= \hbar\omega \\ \omega &= \frac{E}{\hbar} \text{-----(2)} \end{aligned}$$

Substituting (2) in(1)

$$v_g = \frac{d}{dk} \left(\frac{E}{\hbar} \right)$$

$$v_g = \frac{1}{\hbar} \frac{dE}{dk}$$

The acceleration 'a' is

$$a = \frac{d}{dt} (v_g)$$

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

$$= \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt} \text{-----(4)}$$

Momentum 'p' of an electron

$$p = \frac{h}{\lambda}$$

$$= \frac{h}{2\pi} \frac{2\pi}{\lambda}$$

$$= \hbar k \text{-----(5)}$$

Differentiating (5) w.r.t 't'

$$\frac{dp}{dt} = \hbar \frac{dk}{dt}$$

Or

$$F = \hbar \frac{dk}{dt}$$

$$\frac{dk}{dt} = \frac{F}{\hbar} \text{-----(6)}$$

Substituting (6) in (4)

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

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

$$F = \left[\frac{\hbar^2}{d^2 E} \right] a \text{-----(7)}$$

When an electrical field is applied ,acceleration is

$$a = \frac{eE}{m^*} = \frac{F}{m^*}$$

$$F = m^* a \text{ _____ (8)}$$

Comparing (7) & (8)

$$m^* a = \left[\frac{\hbar^2}{d^2 E} \right] a$$

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

From (9) effective mass is not constant but depends on $\frac{d^2 E}{dk^2}$

Special Cases:

Case i :

If $\frac{d^2 E}{dk^2}$ is positive then m^* is also positive.

Case ii :

If $\frac{d^2 E}{dk^2}$ is negative then m^* is also negative.

Case iii :

If $\frac{d^2 E}{dk^2}$ is more then electrons behave as light particles.

Case iv :

If $\frac{d^2 E}{dk^2}$ is very small, then the electrons behave as heavy particles.

1.14.2. Concept of hole (or) Effective or Negative mass of electron:

The effective mass m^* is negative near the zone edges of filled valence bands. The electrons in these regions are accelerated in a direction opposite to the direction of the applied field. This is called the negative mass behavior of the electrons.

The electrons with negative effective mass is considered as the same positive mass of that of an electron, but with positive charge. This new entity is given the name "hole".

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The positive hole conduction and effective negative electron mass conduction are in equilibrium. The calculation made on the hole appear to be more convenient and hence the hole concept is retained.

Several phenomena like Hall effect, Thomson Effect etc find explanation on the basis of the hole concept.

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MODULE – 1

ELECTRICAL PROPERTIES OF MATERIALS

CONTENTS

1.1 Introduction

1.2 Basic Definitions

1.3. Relationship between Current Density and Drift velocity

1.4. Electron theory of solids

1.1 Introduction

Conductors are nothing but a material having ability to conduct electricity (or) conduct free electrons. It has high thermal and electrical conductivity.

Examples: Al, Ag, Cu, Alloys etc.

The resistance of the conductor is the order of $10^{-8}\Omega$. This conductivity is mainly based on the available free or valence electrons in the material.

Valence electrons

The electrons in the outer most orbit of an atom in the material are known as valence electrons. It is loosely bounded with the nucleus.

In band theory, the conduction and valence bands are overlap with each other, and there is no band gap.

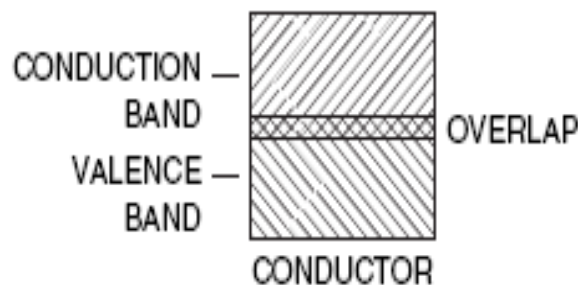


Fig 1.1-Band gap of metal

Classification of conducting materials

The conducting materials based on their conductivity, are classified into the major categories.

- Zero resistivity materials
- Low resistivity materials and
- High resistivity materials.

(i) Zero resistivity materials

Superconductors like alloys of aluminum, zinc, gallium, nichrome, niobium, etc., are a special class of materials that conduct electricity almost with zero resistance

below transition temperature. These materials are known as zero resistivity materials.

They are used for saving energy in the power systems, super conducting magnetism memory storage elements etc.,

(ii) Low Resistivity Materials

The metals like silver, aluminum and alloys have very high electrical conductivity. These materials are known as **low resistivity materials**.

They are used as conductors, electrical contact, in electrical devices, electrical power transmission distribution, winding wires in motors and transformers.

(iii) High Resistivity Materials

The materials like tungsten, platinum, nichrome etc., have resistivity and low temperature co-efficient of resistance. These materials are known as **high resistivity materials**.

Such metals and alloys are used in the manufacturing of resistors, heating elements, resistance thermometers etc. The conducting properties of a solid are not a function of the total number of the electrons of the atoms can take part in conduction. These valence electrons are called **free electrons or conduction electrons**.

1.2. Basic Definitions

1.2.1. Current

The rate of flow of charges across any cross sectional area of a conductor is called current. The rate of flow of charges is not uniform and it varies with respect to time.

$$I = \frac{q}{t} \Rightarrow I = \frac{dq}{dt}$$

1.2.2. Ohm's Law

At constant temperature, the steady current flowing through a conductor is directly proportional to the potential difference (voltage) between its ends.

$$V \propto I$$

$$V = IR$$

1.2.3. Resistivity

Resistance of a conductor (metal) is directly proportional to the length and inversely proportional to the area of cross section.

$$R \propto \frac{L}{A}$$
$$R = \rho \frac{L}{A}$$
$$\rho = \frac{RA}{L} (\Omega m)$$

Where, ρ is the electrical resistivity and it's inversely proportional is called electrical conductivity.

$$\sigma = \frac{1}{\rho} (\Omega^{-1} m^{-1})$$

1.2.4. Current Density

The current per unit area of cross section of a current carrying conductor is known as current density. It is perpendicular to the flow of charges.

$$J = \frac{I}{A} (Am^{-2})$$

1.2.5. Drift Velocity

The average velocity is required to drift the free electrons in the conductor towards the application of an electrical field is called drift velocity.

$$V_d = \frac{\lambda}{\tau_c}$$

1.2.6. Electrical Field

In a uniform cross section of a conductor, potential drop per unit length is known as electrical field.

$$E = \frac{V}{L} (Vm^{-1})$$

1.3. Relationship between Current Density and Drift velocity

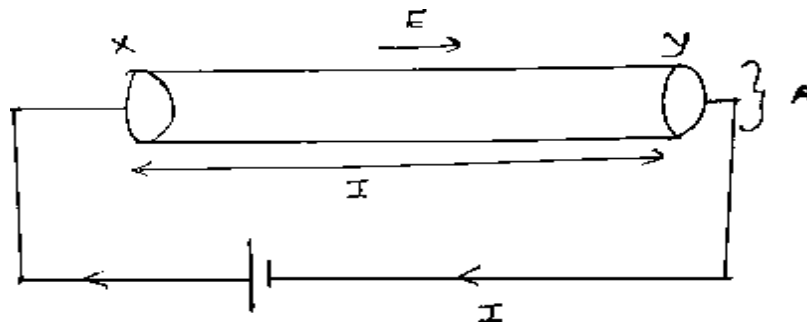


Fig 1.3.1- Movement of free electrons in a metal rod

Consider a conductor 'XY' of length (l) and area of cross section 'A'. An electric field 'E' is applied between its ends. Let 'n' be the number of free electrons per unit volume and V_d is the drift velocity.

The number of free electrons in the conductor is $= nAl$

The charge of an electron $= e$

Total charges passing through the conductor is

$$q = (nAl)e \dots\dots\dots (1)$$

The time taken by the charges pass through the conductor is

$$t = \frac{l}{V_d} \dots\dots\dots (2)$$

$$\therefore \text{Current } I = \frac{q}{t} \dots\dots\dots (3)$$

Substitute equations (1) and (2) in equation (3), we get,

$$I = \frac{nAle}{\frac{l}{V_d}}$$

$$= \frac{nAleV_d}{l}$$

$$I = nAeV_d$$

$$\frac{I}{A} = neV_d$$

$$J = neV_d \dots (4) (\because J = \frac{I}{A})$$

From this expression we obtained, the current density is directly proportional to the drift velocity and number of free electrons in the conductor.

Electron theory of solids

The electron theory of solids aims to explain the structures and properties of solids through their electronic structures. The electron theory is applicable to all solids both metals and non-metals. The electron theory of solids explains the following concepts,

- ❖ Structural, electrical and thermal properties of solids.
- ❖ Elasticity, cohesive force and binding in solids.
- ❖ Behavior of conductors, semiconductors and insulators etc.,

There are three types of electron theories have been proposed. They are,

- ❖ Classical Free Electron theory
- ❖ Quantum Free Electron theory
- ❖ Brillouin Zone theory (or) Band theory.

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UNIT – 1

ELECTRICAL PROPERTIES OF MATERIALS

CONTENTS

1.8. Fermi - Dirac Distribution Function

1.8.1. Effect of Temperature on Fermi Function

1.8. Fermi - Dirac Distribution Function

In a metal at zero Kelvin temperature, the highest filled energy level is called the **Fermi level** and the energy possessed by the electrons in that level is known as **Fermi energy**.

Fermi-Dirac statistics deals with the particles having half integral spin like electron. Fermi distribution function gives information about the distribution of electrons among the various energy levels as a function of temperature. It is given by,

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

Where,

$F(E)$ - is the Fermi distribution function.

E_F - is the Fermi energy.

K_B - is the Boltzmann constant.

T - is the temperature.

E - is the total energy.

The probability value $F(E)$ lies between 0 and 1.

- ❖ If $F(E) = 1$, the energy level is occupied by an electron.
- ❖ If $F(E) = 0$, the energy level is vacant.
- ❖ If $F(E) = 0.5$, then there is a 50% chance for finding the electron in the energy level.

Significance of Fermi energy

- It gives information about the velocities of the electrons which participate in ordinary electrical conduction.
- Fermi velocity of conduction electron is can be calculated from it.
- It is used to understand the specific heat capacity of solids at ordinary temperature.

1.8.1. Effect of Temperature on Fermi Function

The Fermi level varies with respect to temperature as given below

At 'T' is equal to zero Kelvin temperature (T = 0 K)

At T=0 K, the electrons are filled up to a maximum energy level called Fermi energy level E_F . All the energy levels above the Fermi energy levels are empty.

Case (i)

At T = 0 k and $E < E_F$

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

Therefore 100% chance for the electron to be filled with in the Fermi energy level.

Case (ii)

At T = 0 K and $E > E_F$

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

Therefore 0% chance for the electron not to be filled within the Fermi energy level. At T = 0 K and $E = E_F$

Case (iii)

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

Therefore 50% chance for the electron to be filled and not to be filled with in the Fermi energy level. The Fermi function at '0' Kelvin can also be graphically represented in given figure. The graph clearly shows that the curve has step like character at '0' Kelvin. Electrons with Fermi energy move with Fermi velocity and the same is related to the Fermi temperature by the relation.

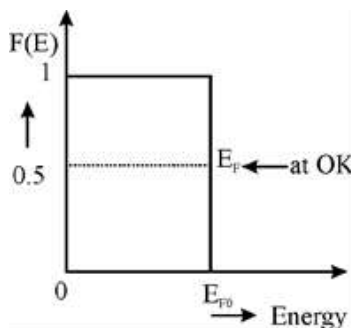


Fig 1.8.1 Fermi level variation with temperature at T=0K

At any temperature other than zero

When temperature is raised slowly from absolute zero, the Fermi distribution function smoothly decreases to zero. The electrons lose their quantum mechanical character and it reduces to classical Boltzmann distribution.

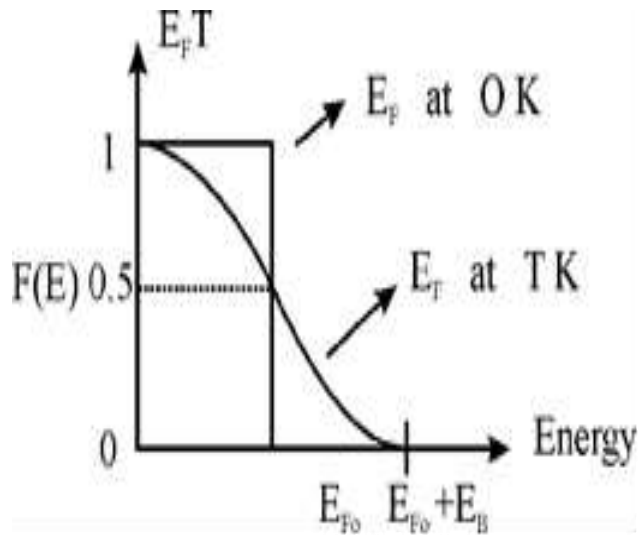


Fig 1.8.2 Fermi level variation with temperature at T

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UNIT – 1

ELECTRICAL PROPERTIES OF MATERIALS

1.10 Electron in Periodic Potential:

1.10.1 Bloch Theorem

1.11. Tight Binding approximation

1.10 Electron in Periodic Potential:

The free electron theory fails to explain why some solids are conductors, insulators and others are semiconductors.

A solution to this problem was given by band theory of solids and is called

Zone Theory.

Postulates:

Potential energy of electron within the crystal is periodic that is free electrons move inside periodic lattice field.

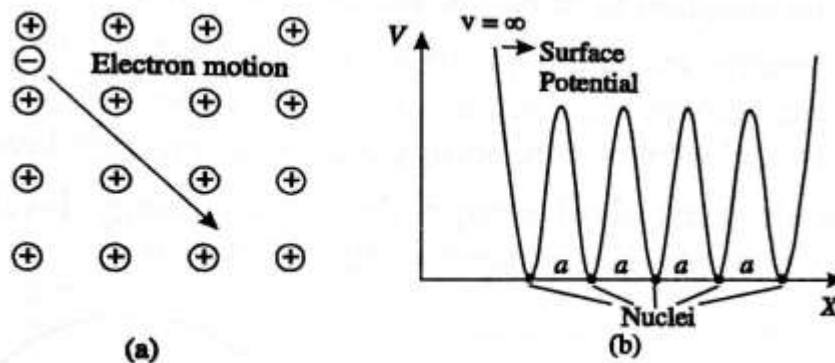


Fig 1.10.1-One dimensional periodic potential distribution for a crystal

Therefore, the potential energy of the electron near by the Centre of positive ion is maximum and will not be able to move freely, but the electrons which are above these potential peaks are free to move inside the metal and hence they are termed as free electrons.

1.10.1 Bloch Theorem

Bloch theorem is a mathematical statement of an electron wave function moving in a perfectly periodic potential. These functions are called Bloch functions. Let us consider an electron moving in a periodic potential. The Schrodinger equation

is

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\Psi = 0 \text{ -----(1)}$$

Solution for this equation is

$$\Psi(x) = e^{\pm ikx}u_k(x) \text{ -----(2)}$$

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

The solutions are plane waves modulated by the function $U_k(x)$. This theorem is known as the Bloch Theorem or Floquet's theorem.

The functions (2) are known as Bloch function and can be decomposed into sum of travelling waves.

1.11 Tight Binding approximation:

In solids, there exist the ionic core which are tightly bounded to the lattice location while the electrons are free to move here and there. This is called free electron approximation.

In free electron approximation

- 1.The potential of the electron is assumed to be lesser than its total energy.
- 2.The width of the forbidden bands are smaller than the allowed bands as in fig.
- 3.Therefore the interaction between the neighboring atoms will be very strong.
- 4.As the atoms are closer to each other, the inter atomic distance decreases and hence the wave function overlap with each other.

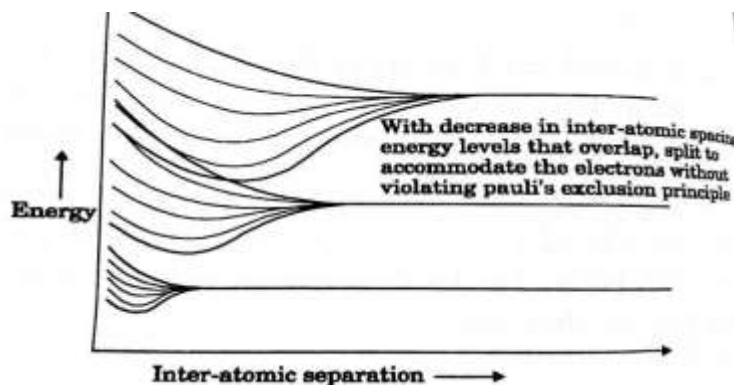


Fig 1.11.1-Tight binding approximation

UNIT – 1

ELECTRICAL PROPERTIES OF MATERIALS

CONTENTS

1.6. Quantum Free Electron Theory

1.6.1. Basic assumptions of Quantum free electron

1.6.2. Merits of Quantum theory

1.6.3. Demerits of Quantum theory

1.6. Quantum Free Electron Theory

The drawbacks of classical free electron theories were removed by **Sommerfeld in 1928**. Quantum concepts are used in classical theory and hence it is known as quantum free electron theory.

He applied Schrodinger's wave equation and De-Broglie's concept of matter waves to obtain the expression for electron energies. He substituted the quantum statistics of Fermi-Dirac in place of the classical statistics and hence, it is known as the quantum free electron theory.

1.6.1. Basic assumptions of Quantum free electron theory

- The electrons are considered as free electron gas.
- The electrons possess wave nature.
- Free electrons obey Fermi-Dirac statistics and Pauli's exclusion principle.
- The free electron is fully responsible for electrical conduction.
- The allowed energy levels of an electron are quantized.
- The correct values of electrical conductivity, thermal conductivity, specific heat, optical absorption, ferromagnetic susceptibility are determined by quantum free electron theory of solids.

1.6.2. Merits of Quantum theory

- ❖ In this theory, the electrons are treated quantum mechanically rather than classically.
- ❖ Quantum theory successfully explains the ohm's law.
- ❖ It explains the electrical conductivity, thermal conductivity, photoelectric effect, Compton effect and specific heat capacity of metals.

1.6.3. Demerits of Quantum theory

- ❖ It fails to explain the classification between metals, semiconductors and insulators.
- ❖ It fails to give the reason for positive value of Hall coefficient.
- ❖ It can't be able to explain the transport properties of metals.

1.7.1. Particle in a Three dimension box:

The solution of one dimension potential well is extended for a three dimensional potential box.

In a three dimensional potential box the particle can move in any direction .so we use three quantum numbers n_x, n_y and n_z to the three coordinate axes namely x,y and z respectively. If a,b,c are the lengths of the box along x,y and z axes then,

$$E_{n_x, n_y, n_z} = \frac{n_x^2 h^2}{8m a^2}$$

If a= b = c as for a cubical box then

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2] \text{-----(1)}$$

The corresponding normalized wave function is

$$\begin{aligned} \Psi_{n_x, n_y, n_z} &= \sqrt{\left(\frac{2}{a}\right)} \sqrt{\left(\frac{2}{a}\right)} \sqrt{\left(\frac{2}{a}\right)} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a} \sin \frac{n_z \pi z}{a} \\ &= \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a} \sin \frac{n_z \pi z}{a} \text{-----(2)} \end{aligned}$$

From the equations (1), (2)we understand that several combinations of the three quantum numbers(n_x, n_y, n_z) lead to different energy eigen values and eigen function.

1.7.2. Degenerate states:

For several combinations of quantum numbers,we have the same energy eigen value but different eigen function.Such a state of energy levels is called degenerate state.

The three combinations of quantum numbers (1,1,2),(1,2,1) and (2,1,1) which give the same Eigen value but different Eigen functions are called 3- fold degenerate state.

Example:

If (n_x, n_y, n_z) is (1,1,2) ,(1,2,1) and (2,1,1)

Then

$$E_{112} = \frac{h^2}{8ma^2} (1^2 + 1^2 + 2^2) = \frac{6h^2}{8ma^2}$$

$$E_{121} = \frac{6h^2}{8ma^2}$$

$$E_{211} = \frac{6h^2}{8ma^2}$$

The corresponding wave functions are

$$\psi_{112} = \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{2\pi z}{a}$$

$$\psi_{121} = \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{\pi x}{a} \sin \frac{2\pi y}{a} \sin \frac{\pi z}{a}$$

$$\psi_{211} = \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{2\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{\pi z}{a}$$

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