

## Content

*Failures of classical free electron theory, Mechanisms of electron scattering in solids, Matheissen's rule, Assumptions of Quantum Free Electron Theory, Density of States, Fermi Dirac statistics, Fermi Energy, Variation of Fermi Factor With Temperature and Energy, Expression for carrier concentration, derivation of electron concentration in an intrinsic semiconductor, Expression for electron and hole concentration in extrinsic semiconductor, Fermi level for intrinsic(with derivation) and extrinsic semiconductor (no derivation), Hall effect, Numerical Problems*

## Introduction:

Conducting materials play a vital role in Engineering. It is very essential to know the electrical properties of materials for specific application of the materials. The properties of metals such as electrical conduction, thermal conduction, specific heat etc., are due to the free electrons or conduction electrons in metals. The first theory to explain the electrical conductivity of metals is Classical free electron theory and it was proposed by Drude in the year 1900 and later developed and refined by Lorentz. Hence classical free electron theory is known as Drude-Lorentz theory.

## Assumptions of Classical Free Electron Theory:

1. A metal is imagined as a three-dimensional ordered network of positive ions with the outermost electrons of the metallic atoms freely moving about the solid. The electric current in a metal, due to an applied field, is a consequence of drift velocity of the free electrons in a direction opposite to the direction of the field.
2. The free electrons are treated as equivalent to gas molecules and thus assumed to obey the laws of kinetic theory of gases. As per kinetic theory of gases, in the absence of the field the energy associated with each electron at a temperature  $T$  is  $\frac{3}{2}kT$ , where  $k$  is Boltzmann constant. It is related to the kinetic energy through the relation.

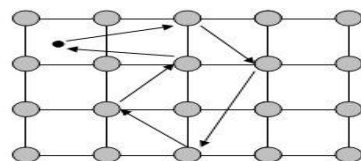
$$\frac{3}{2}kT = \frac{1}{2}mv_{th}^2$$

where  $v_{th}$  is the thermal velocity of the electrons.

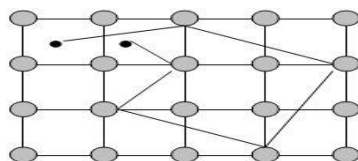
3. The electric potential due to the ionic core (lattice) is taken to be essentially constant throughout the metal.
4. The attraction between the free electrons and the lattice ions and the repulsion between the electrons are considered insignificant.

## Drift Velocity

Initially the electrons in the metal which are in thermal equilibrium will move in random directions and often collide with ions with no net displacement. When electric field is applied, the equilibrium condition is disturbed and there will be net displacement in randomly moving free electron's positions, with time in a direction opposite to the direction of the field. This displacement per unit time is called **drift velocity** which will be constant for the free electrons in the steady state. This accounts for the current in the direction of the field.



Random motion without the electric field.  
 In all probability the electron comes back to a position close to the earlier position if not the same position.



Direction of the electric field  
 Random motion in the presence of the electric field.  
 Notice the drift of the electron

If 'E' is the electric field applied to the metal, ' $\tau$ ' is mean collision time, then drift velocity for conduction electron in a metal is given by

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

Where 'e' and 'm' are charge and mass of electron respectively.

### **Current density (J):**

It is the current per unit area of cross section of an imaginary plane held normal to the direction of current in a current carrying conductor.

i.e.  $J = I/A$  where  $A$  is the area of cross section.

### **Electric Field (E):**

Electric field across homogeneous conductor is defined as the potential drop per unit length of the conductor.

If 'L' is the length of a conductor of uniform cross section and uniform material composition and 'V' is the potential difference between its two ends, then electric field 'E' is given by

$$E = V/L$$

### **Mean Free Path ( $\lambda$ ):**

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

### **Mean Collision Time ( $\tau$ ):**

It is the average time that elapses between two consecutive collisions of an electron with the lattice ions.

### **Relation between $v$ , $\tau$ and $\lambda$ :**

If ' $v$ ' is the total velocity of the electrons, then the mean collision time ' $\tau$ ' is given by

$$\tau = \frac{\lambda}{v}$$

### **Resistivity ( $\rho$ ):**

For a material of uniform cross section, the resistance 'R' is directly proportional to length 'L' and inversely proportional to area of cross section 'A'

$$\text{i.e.} \quad R \propto \frac{L}{A} \quad \therefore R = \rho \left( \frac{L}{A} \right)$$

Where ‘ $\rho$ ’ is called resistivity. It is the property of the material and gives the measure of opposition offered by the material during the current flow in it.

$$\therefore \rho = \frac{RA}{L}$$

### **Conductivity ( $\sigma$ ):**

It is reciprocal of resistivity. It is a physical property that characterizes conducting ability of a material.

$$\sigma = \frac{1}{\rho} = \frac{L}{RA}$$

### **Relation between J, $\sigma$ and E:**

From ohms law

$$V = IR = I \cdot \frac{\rho l}{A}$$

$$\frac{I}{A} = \frac{V}{l} \cdot \frac{1}{\rho}$$

$$\frac{I}{A} = J \text{ and } \frac{1}{\rho} = \sigma$$

$$J = \sigma E$$

### **Expression for electric current in a conductor: (I)**

$$I = nev_d A$$

$n$  - Number of free electrons in unit volume of the conductor

$v_d$  - Drift velocity of electrons

$A$  - Area of cross section of the conductor

$e$  - Charge of an electron

### Expression for Conductivity:

The current through the conductor is given by  $I = neAv_d$

We know that drift velocity ( $v_d$ ) is given by  $v_d = \frac{eE\tau}{m}$

Substituting for  $v_d$  in the above equation  $I = \frac{ne^2\tau}{m} AE$

$$I = \frac{ne^2\tau A}{m} \left(\frac{V}{L}\right)$$

where 'L' is the length of the conductor

Rearranging the terms of the above equation  $\frac{m}{ne^2\tau} = \frac{A}{L} \left(\frac{V}{I}\right)$

$$\frac{m}{ne^2\tau} = \frac{A}{L} R = \rho$$

$\frac{1}{\rho} = \sigma$ , Therefore **Conductivity**  $\sigma = \frac{ne^2\tau}{m}$

### Mobility of electrons:

Mobility of electrons ( $\mu$ ) is defined as the magnitude of drift velocity acquired by the electron in unit field.

$$\text{i.e. } \mu = \frac{v_d}{E} = \frac{1}{E} \left( \frac{eE\tau}{m} \right) = \frac{eE}{m}$$

### Failures of classical free electron theory:

Although electrical and thermal conductivity in metals can be explained successfully through classical free electron theory, it failed to account for many other experimental facts such as specific heat, temperature dependence of conductivity and dependence of electrical conductivity on electron concentration.

1. The molar specific heat of a gas at constant volume is  $C_v = \frac{3}{2} R$ ,

where R is a universal constant. But the experimental value of electronic specific heat is  $C_v = 10^{-4} RT$  which the classical theory

could not explain. Also, the experimental value shows that the electronic specific heat is temperature dependent, whereas the classical free electron theory says that it is temperature independent.

2. The electrical conductivity of a metal is inversely proportional to temperature. According to classical free electron theory, electrical conductivity is inversely proportional to the square **root of temperature, i.e.,**  $\sigma \propto \frac{1}{\sqrt{T}}$ .

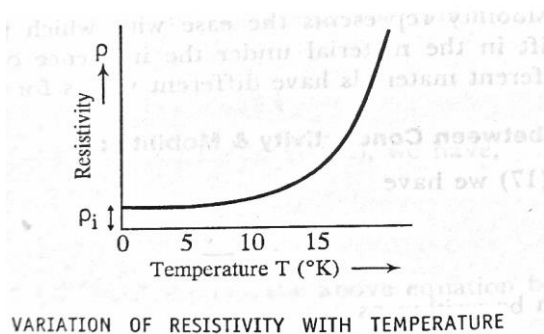
3. Electrical conductivity is given as  $\sigma = \frac{ne^2\tau}{m}$

According to classical electron theory electrical conductivity is directly proportional to the electron concentration. But monovalent metals like copper found to have high electrical conductivity than the divalent & trivalent metals like Zinc and Aluminium. Hence CFET fails to explain the observation.

4. Though metals are expected to exhibit negative Hall co-efficient since the charge carriers in them are electrons, some metals like zinc have positive Hall co-efficient. The free electron theory could not explain the positive Hall co-efficient of metals.

## Effect of Temperature and Impurity on Electron Resistivity of metals:

The variation of electrical resistivity  $\rho$  with temperature  $T$  in the low temperature region for sodium is as shown in the graph below.



Except for metals that are superconducting, the variation shown in the above graph applies to all conductors. The resistivity does not become zero at  $T = 0$  kelvin but has a small constant value. The resistivity increases slowly with temperature, later it assumes linear with a faster variation. The linearity in variation is continued throughout till the metal's melts.

### Mechanisms of electron scattering in solids and Matheissen's rule

In metals, the resistivity is attributed to the scattering of conduction electrons. It takes place under two mechanisms which give rise to two components of resistivity which are described below:

- 1) Resistivity  $\rho_{ph}$  due to scattering of electrons by lattice vibrations (phonons) increases with temperature. It is the resistivity exhibited by a pure specimen that is free of all defects, and hence called the ideal resistivity.

- 2) Resistivity  $\rho_i$  due to scattering of conduction electrons by the presence of impurities, and imperfections such as dislocation vacancies and grain boundaries.  $\rho_i$  is called residual resistivity. This type of scattering is independent of temperature and contributes to resistivity even at temperature  $T=0$  kelvin.

If  $\rho$  is the total resistivity of the metal, then  $\rho$  is given by

$$\rho = \rho_{ph} + \rho_i \dots\dots\dots(1)$$

The above equation is called **Matthiessen's rule**. It states that the total resistivity of a metal is the sum of resistivity due to phonon scattering which is temperature dependent and the resistivity due to scattering by impurities which is temperature independent.

Since the resistivity  $\rho = \frac{1}{\sigma}$  and  $\sigma = \frac{ne^2\tau}{m}$ , the equation for  $\rho$  can be written as,  $\rho = \frac{m}{n\tau e^2}$

If  $\tau_{ph}$  is the mean collision time, assuming there is no scattering by impurities, then  $\rho_{ph} = \frac{m}{n\tau_{ph}e^2}$

Similarly, if  $\tau_i$  is the mean collision time assuming there is no scattering by lattice vibrations, then,  $\rho_i = \frac{m}{n\tau_i e^2}$

Therefore equation (1) can be written as,  $\rho = \frac{m}{n\tau_{ph}e^2} + \frac{m}{n\tau_i e^2}$

At low temperatures, the amplitude of vibration becomes small because of which, the scattering of electrons by lattice ions becomes less. This results in  $\tau_{ph}$  becoming larger, and  $\rho_{ph}$  tends to zero at very low temperatures. It essentially means  $\rho = \rho_i$  at very low temperatures.

Accordingly, it is observed from the graph that the resistivity has a residual value  $\rho_i$  at  $T=0$  kelvin. On the other hand, when the temperature becomes high, the amplitude of lattice vibration increases



proportionately which results in large scale scattering of electrons. Consequently, the resistance curve takes an upswing, and the resistivity becomes linearly dependent on temperature. At sufficient high temperatures, the scattering effect due to phonons swamps the effect due to scattering by impurities. Thus, at temperatures near room temperatures, the resistivity curve is essentially linear.

### **Note: Concept of Phonon**

In condensed matter physics, a unit of vibrational energy that arises from oscillating atoms within the crystal is called phonon. Any solid crystal consists of atoms bound into a specific repeating three-dimensional spatial pattern called a lattice. Because the atoms behave as if they are connected by tiny springs, their own thermal energy or external forces make the lattice vibrate. A packet of these waves can travel throughout the crystal with a definite energy and momentum, so in quantum mechanical terms the waves can be treated as a particle, called a phonon. A phonon is a definite unit or quantum of vibrational mechanical energy, just as a photon is a quantum of electromagnetic or light energy.

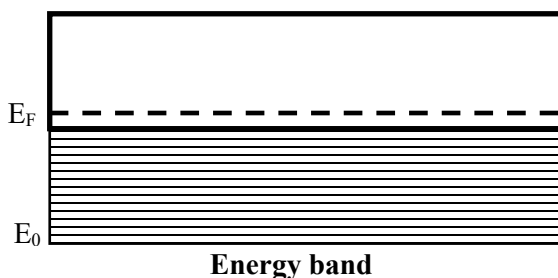
### **Assumptions of quantum free electron theory:**

The main assumptions of quantum free electron theory are.

1. The energy values of free electrons are quantized. The allowed energy values are realized in terms of a set of energy levels.
2. The distribution of electrons in the various allowed energy levels, follows Pauli's Exclusion Principle.
3. Distribution of electrons in energy states obey Fermi-Dirac statistics.
4. The free electrons travel in a constant potential inside the metal but stay confined within its boundaries.
5. The attraction between the free electrons and lattice ions, the repulsion between the electrons themselves are ignored.

## Fermi level and Fermi energy:

If we assume the number of electrons per unit volume as  $n_e$  then these electrons should be accommodated in the various energy levels. At absolute zero temperature, the electrons occupy the lowest available energy levels. The highest occupied level in metals at zero Kelvin is called as the **Fermi level** and the corresponding energy value of that level is called as the **Fermi energy**, it is denoted by  $E_F$ . Thus, at 0K all levels up to the Fermi level are occupied while the levels above it are vacant.



The dotted level is the Fermi level. Levels from  $E_0$  up to  $E_F$  are occupied while levels above  $E_F$  are empty.

## Fermi-Dirac statistics:

Under thermal equilibrium the free electrons are distributed in various available energy states. The distribution of electrons among the energy levels follows statistical rule known as Fermi-Dirac statistics.

Fermi-Dirac statistics is applicable to fermions. Fermions are indistinguishable particles with half integral spin. Since electron has half spin they obey Fermi-Dirac statistics, and they are called Fermions.

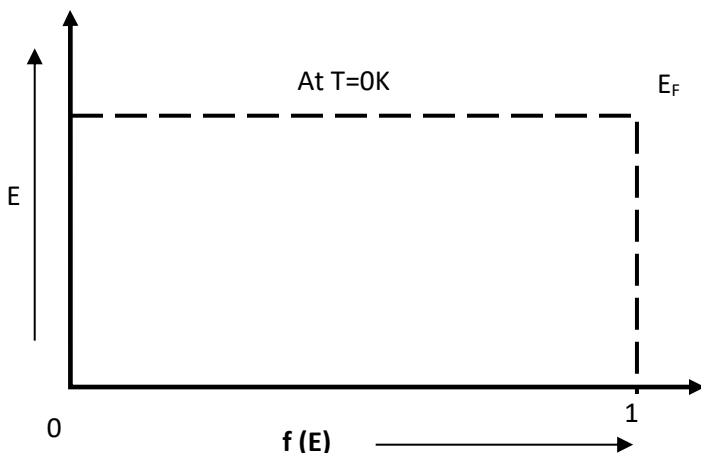
Fermi factor represents the probability that a quantum state with energy  $E$  is occupied by an electron, is given by Fermi-Dirac distribution function,

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Where  $k$  is the Boltzmann's constant,  $T$  is the temperature in Kelvin,  $E$  is the energy and  $E_F$  is the Fermi energy.

### Dependence of Fermi factor on temperature:

The dependence of Fermi factor on temperature at  $T=0K$  is given in the figure.



### Case 1: the probability of occupation for $E < E_F$ at $T = 0K$

Substituting the value of  $T = 0K$  in the Fermi function we get

$$f(E) = \frac{1}{e^{\left(\frac{E - E_F}{kT}\right) + 1}} = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

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

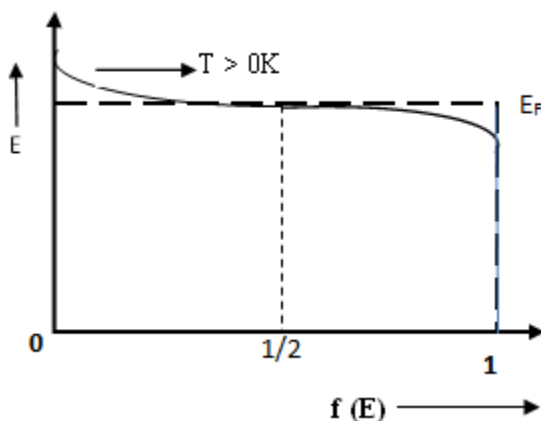
### Case 2: the probability of occupation for $E > E_F$ at $T = 0K$ .

Substituting the value of  $T = 0K$  in the Fermi function, we get

$$f(E) = \frac{1}{e^{(E-E_F/kT)+1}} = \frac{1}{e^{\infty} + 1} = \frac{1}{\infty} = 0.$$

This shows that all energy levels above  $E_F$  are vacant.

### Case 3: Probability of occupation at temperature $> 0K$



1. At ordinary temperatures, though the value of probability is 1 for  $E \ll E_F$ , it starts decreasing from 1 as the values of  $E$  become closer to  $E_F$ .
2. The value of  $f(E)$  becomes  $1/2$  at  $E = E_F$ . This is because at  $E = E_F$

$$f(E) = \frac{1}{e^{(E-E_F/kT)+1}} = \frac{1}{e^0 + 1} = \frac{1}{1+1} = \frac{1}{2}$$

3. For values just beyond  $E_F$ ,  $f(E) > 0$
4. Further above  $E > E_F$ , the probability value falls off to zero rapidly. It implies that the probability of occupancy of Fermi level at any temperature other than  $0K$  is  $0.5$ .

*Hence Fermi level is defined as the energy level at which the probability of electron occupancy is half. Also, Fermi energy,  $E_F$  is the average energy possessed by the electrons which participate in conduction process in conductors at temperatures above 0K.*

### **Density of states $g(E)$ :**

The permitted energy levels for electrons in a solid will be in terms of bands. Each energy band spread over an energy range of few eV. The number of energy levels in each band will be extremely large and hence the energy values appear to be virtually continuous over the band spread. Each energy level consists of two states and each state accommodates only one electron. Therefore, energy level can be occupied by two electrons only, having opposite directions of spin. The exact dependence of density of energy states on the energy is realized through a function denoted as  $g(E)$  and is known as **density of states function**.

*It is defined as, the number of available states per unit volume per unit energy interval.*

The number of states lying in the range of energies between  $E$  and  $E+dE$  is given by

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

Where  $E$  is the kinetic energy of the electron in the energy level  $E$ .

### **Carrier concentration in metals and Fermi energy at 0K**

Number of free electrons /unit volume which possess energy in the range  $E$  and  $E+dE$  is given by  $N(E) dE = g(E) \times dE \times f(E)$

The number of free electrons/unit volume of the material, i.e.,  $n$  is equal to the total number of electrons that are distributed in various energy levels upto  $E_F$ . Thus, we have

$$n = \int_{E=0}^{E_F} N(E) dE$$

$$n = \int_{E=0}^{E_F} g(E) f(E) dE$$

But  $f(E) = 1$ , at  $T = 0K$

$$n = \int_{E=0}^{E_F} g(E) dE$$

$g(E) dE$  is given by,  $g(E) dE = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE$

$$n = \frac{4\pi}{h^3} (2m)^{3/2} \int_{E=0}^{E_F} E^{1/2} dE$$

$$n = \frac{4\pi}{h^3} (2m)^{3/2} \frac{2}{3} (E_F)^{3/2}$$

$$n = \frac{8\sqrt{2}}{h^3} \pi m^{3/2} \times \frac{2}{3} (E_F)^{3/2}$$

$$n = \frac{8\pi}{3h^3} (2m)^{3/2} (E_F)^{3/2}$$

This is the equation of concentration of electrons in a metal at 0K.

Expression for the Fermi energy at 0K is given by  $E_F = \frac{h^2}{8m} \left(\frac{3n}{\pi}\right)^{2/3}$

$E_F = Bn^{2/3}$  Where  $B = \left(\frac{h^2}{8m}\right) \left(\frac{3}{\pi}\right)^{2/3}$  is a constant  $= 5.85 \times 10^{-38} J$ .

### Success of Quantum Free Electron theory

1. The theory could successfully explain the specific heat capacity of metals.
2. It could also explain temperature dependence of electrical conductivity.
3. It explained the dependence of electrical conductivity on electron concentration.
4. It also explained photoelectric effect, Compton effect, Black body radiation, Zeeman effect etc.,

### BAND THEORY OF SOLIDS:

**The energy band structure of a solid determines whether it is a conductor, an insulator, or a semiconductor.**

The electron of an isolated atom has certain definite energies such as 1s, 2s, 3p, 3s, etc. Between two consecutive allowed values of energy there is forbidden gap. As we bring together large number of identical atoms to form a solid, significant changes take place in the energy levels. The energy levels of each atom will interact with the other identical atoms. The wave functions of each atom will overlap and as a result the energy levels of each atom overlap slightly and split into several levels corresponding to the number of atoms. The split energy levels are very close to each other, and they form a narrow band known as energy band.

*The range of energies possessed by electrons in a solid is known as energy band.*

The energy band formed by the energy levels of the valence electrons is called valence band. The energy band immediately above the valence band where the conduction electrons are present is called conduction band.

*The separation between the upper level of valence band and the bottom level of conduction band is known as forbidden energy gap,  $E_g$ .*

The forbidden energy gap is a measure of the bondage of valence electrons to the atom. The greater the energy gap more tightly valence electrons are bound. When energy is supplied, electrons from the valence band jump to the conduction band and thereby the material starts conducting.

## SEMICONDUCTORS

Pure semiconductors are the materials having electrical conductivity greater than that of insulators but significantly lower than that of a conductor at room temperature. They have conductivity in the range of  $10^{-4}$  to  $10^4$  S/m. The interesting feature about semiconductors is that they are bipolar, and current is transported by two types of charge carriers of opposite sign namely electrons and holes. The number of carriers can be drastically enhanced by doping the semiconductor with suitable impurities. The doped semiconductor which exhibits higher conductivity is called an extrinsic semiconductor. The conductivity of an extrinsic semiconductor depends on the doping level which is amenable to control. The current transportation in extrinsic semiconductor occurs through two different processes namely drift and diffusion. Pure semiconductors are of relatively less importance whereas extrinsic semiconductors are widely used in fabricating devices. These devices are more generally known as solid-state electronic devices.

## INTRINSIC SEMICONDUCTORS

*A semiconductor in an extremely pure form is known as an intrinsic semiconductor.*

### *Intrinsic carriers in pure semiconductors*

At room temperature in pure semiconductors, a single event of breaking of bonds leads to two carriers: namely electron and hole. The electron and hole are created as a pair & the phenomenon is called electron-hole pair generation. At any temperature  $T$  the number of electrons generated will be equal to the number of holes generated. If 'n' denotes number density of electrons in the conduction band & 'p' denotes the number of holes in the 'valence band then  $n = p = n_i$  where, ' $n_i$ ' is called intrinsic concentration or the intrinsic density

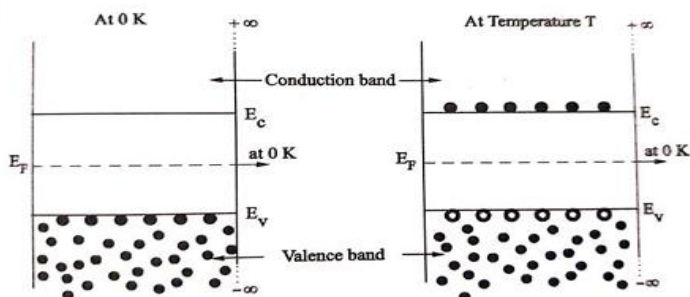


After the generation, the carriers move independently; the electrons move in the conduction band & the holes move in the valence band. The motion of these two carriers is random in their respective band if no external field is applied.

### ***Concept of Effective Mass of the Electron and Holes:***

Consider an isolated electron of mass  $m$  and charge  $-e$  in an electric field of strength  $E$ . The electric force acting on it is  $-eE$ . The electron gets accelerated, then  $-eE = ma$ . However, an electron within a crystal is in a periodic potential due to positive ion cores. The neighbouring ions and electrons in the crystal do exert some force on the electron in a crystal. Then  $ma = -eE$  plus force due to neighbouring ions and electrons. Since the latter force is not known quantitatively, we can write the above equation as  $m_e^*a = -eE$  or  $m_e^* = -eE/a$  where  $m_e^*$  is called the effective mass of the electron within the crystal. Thus, it is inferred that the effective mass of an electron depends on its location in the energy band. Electrons near the bottom of the conduction band have an effective mass which is almost equal to the effective mass of a free electron. Electrons near the bottom of the valence band have negative effective mass. The removal of an electron with a negative effective mass is identical to creating a particle of positive mass. Thus, hole is given the status of particle with positive effective mass  $m_h^*$ .

### **Carrier concentration in intrinsic semiconductor**



The actual number of electrons in the conduction band is given by

$$n = \int_{E_c}^{\text{top of the band}} f(E) g_c(E) dE \quad (1)$$

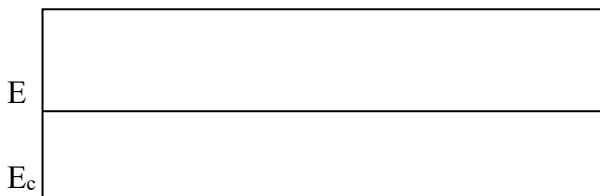
Since F-D function describes the probability of occupancy of energy state. Under thermal equilibrium condition, the electron concentration obtained from eqn. (1) is the equilibrium concentration.

As  $f(E)$  rapidly approaches zero for higher energies, the integral in eqn. (1) can be re-written as

$$n = \int_{E_c}^{\infty} f(E) g_c(E) dE$$

$$g_c(E) = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} (E - E_c)^{\frac{1}{2}} dE$$

Where, E is the kinetic energy of the electron.



### Conduction band

In the above fig. the bottom edge of conduction band  $E_c$  corresponds to the potential energy of an electron at rest in conduction band. Therefore the quantity  $(E - E_c)$  represents the kinetic energy of conduction level electron at high energy level.

$$g_c(E) = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} (E - E_c)^{\frac{1}{2}} dE \quad (2)$$

$$n = \int_{E_c}^{\infty} \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} \frac{(E - E_c)^{\frac{1}{2}}}{1 + \exp\left[\frac{(E - E_F)}{kT}\right]} dE \quad (3)$$

As  $E > E_F$ :  $e^{\frac{E-E_F}{kT}} \gg 1$  :  $1 + e^{\frac{E-E_F}{kT}} \cong e^{\frac{E-E_F}{kT}}$

Therefore  $\frac{1}{1 + e^{\frac{E-E_F}{kT}}} \cong e^{\frac{-(E-E_F)}{kT}}$

Using this equation in eqn. (3) we get

$$n = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} \int_{E_c}^{\infty} (E - E_c)^{\frac{1}{2}} e^{\frac{-(E-E_F)}{kT}} dE$$

Add and subtract  $E_c$  to the exponential term in the above equation.

$$n = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} e^{\frac{(E_F-E_c)}{kT}} \int_{E_c}^{\infty} (E - E_c)^{\frac{1}{2}} e^{\frac{-(E-E_c)}{kT}} dE$$

Let  $E - E_c = x$  then  $dx = dE$

Lower limit when  $E = E_c$   $x = E_c - E_c = 0$

Upper limit when  $E = \infty$   $x = \infty - E_c = \infty$

Therefore  $n = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} e^{\frac{(E_F-E_c)}{kT}} \int_0^{\infty} x^{\frac{1}{2}} e^{-ax} dx$  (4)

The integral is similar to standard integral.

The solution of eqn.(4) is given by

$$\int_0^{\infty} x^{1/2} e^{-ax} dx = \frac{\sqrt{\pi}}{2a\sqrt{a}}, \quad \text{where } a = 1/kT$$

$$\therefore n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{(E_F-E_c)/kT} \left( \frac{\sqrt{\pi}}{2} (kT)^{3/2} \right)$$

Rearranging the term, we get

$$n = 2 \left[ \frac{2\pi m_e^* kT}{h^2} \right]^{3/2} e^{-(E_c-E_F)/kT} \quad (5)$$

$$\text{Let } N_c = 2 \left[ \frac{2\pi m_e^* kT}{h^2} \right]^{3/2}$$

$$\therefore n = N_c e^{-(E_c - E_F)/kT} \quad (6)$$

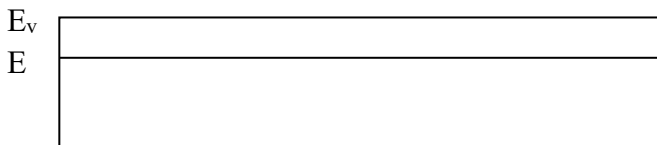
$N_c$  is temperature-dependent material constant known as effective density of states in the conduction band.

### Expression for hole concentration in valence band

If  $f(E)$  is the probability for occupancy of an energy state at  $E$  by an electron, then probability that energy state is vacant is given by  $[1 - f(E)]$ . Since hole represents the unoccupied state in valence band, the probability for occupancy of state at  $E$  by a hole is equal to probability of absence of electron at that level.

The hole concentration in valence band is therefore given by

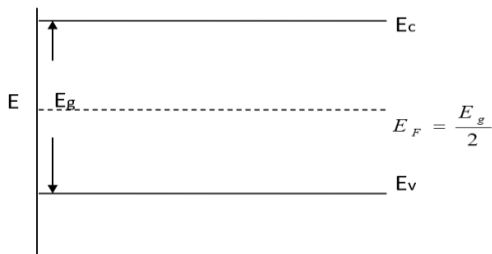
$$p = \int_{\text{bottomband}}^{E_v} [1 - f(E)] g_v(E) dE \quad (7)$$



Solving equation 7 we arrive at hole concentration,  $p = N_v e^{\frac{-(E_F - E_v)}{kT}}$  where,  $N_v$  is temperature-dependent material constant known as

effective density of states in the valence band. Let  $N_v = 2 \left[ \frac{2\pi m_h^* kT}{h^2} \right]^{3/2}$

## Fermi level in intrinsic semiconductor



In an intrinsic semiconductor electron and hole concentrations are equal.

Therefore  $n = p$

$$N_c e^{\frac{-(E_c - E_F)}{kT}} = N_v e^{\frac{-(E_F - E_v)}{kT}}$$

Taking logarithm on both side and rearranging the term, we get

$$\Rightarrow \frac{-(E_c - E_F)}{kT} = \ln\left(\frac{N_v}{N_c}\right) - \frac{(E_F - E_v)}{kT}$$

Multiplying by  $kT$ , throughout

$$\begin{aligned} \Rightarrow -E_c + E_F &= kT \ln\left(\frac{N_v}{N_c}\right) - E_F + E_v \\ \Rightarrow 2E_F &= kT \ln\left(\frac{N_v}{N_c}\right) + E_c + E_v \\ \Rightarrow E_F &= \left(\frac{E_c + E_v}{2}\right) + \frac{1}{2} kT \ln\left(\frac{N_v}{N_c}\right) \end{aligned}$$

Substituting the values of  $N_v$  and  $N_c$  and after simplification we get

$$E_F = \left(\frac{E_c + E_v}{2}\right) + \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*}\right) \quad (1)$$

As  $kT$  is small and the effective mass  $m_e^*$  and  $m_h^*$  do not differ much, the second term in the eqn. (1) may be ignored.

If  $m_e^* = m_h^*$ , then we get

$$E_F = \left( \frac{E_C + E_v}{2} \right) \quad (2)$$

we can write eqn. (2) as

$$E_F = \left( \frac{E_C + E_v + E_v - E_v}{2} \right) = \frac{E_C - E_v}{2} + E_v$$

$$\text{but } E_C - E_v = E_g$$

$$\therefore E_F = \frac{E_g}{2} + E_v$$

If top of the valence band  $E_v$  is taken as zero level, then  $E_F = \frac{E_g}{2}$

## Extrinsic semiconductor

The intrinsic semiconductor has low conductivity which is not amenable to control. However, a judicious introduction of impurity atoms in an intrinsic semiconductor produces useful modification of its electrical conductivity. The method of introduction of controlled quantity of impurity into an intrinsic semiconductor is called doping. The impurity added is called dopant. The semiconductor doped with impurity atoms is called extrinsic semiconductor. There are two types of extrinsic semiconductor namely p-type & n-type which are produced depending on the group of impurity atoms.

n-type semiconductors are produced when pure semiconductors are doped with pentavalent impurity atoms such Phosphorous, Arsenic etc.

p-type semiconductors are produced when pure semiconductors are doped with trivalent impurity atoms such as Aluminum, Boron etc.

## Expression for electron and hole concentration in extrinsic semiconductors

Extrinsic semiconductors are obtained by introducing a small amount of impurity atoms into a pure semiconductor. These impurities drastically influence the carrier concentration. When a pentavalent impurity such as arsenic is added, it donates extra electrons, making electrons the majority carriers and forming an n-type semiconductor. For partial ionization, the electron concentration is given by

$$n = (2N_D)^{1/2} \left[ \frac{2\pi m_e^* kT}{h^2} \right]^{3/4} e^{\left( \frac{E_D - E_C}{2kT} \right)}$$

Where:  $N_D$  - Donor impurity concentration,  $m_e^*$  - Effective mass of electrons in the conduction band,  $E_D$  - Donor impurity energy level,  $E_C$  - Energy of the conduction-band edge.

Similarly, when an acceptor impurity such as gallium is added, it creates vacant states (holes) in the valence band, making holes the majority carriers and producing a p-type semiconductor. The corresponding hole concentration for partial ionization is

$$p = (2N_A)^{1/2} \left[ \frac{2\pi m_h^* kT}{h^2} \right]^{3/4} e^{\left( \frac{E_V - E_A}{2kT} \right)}$$

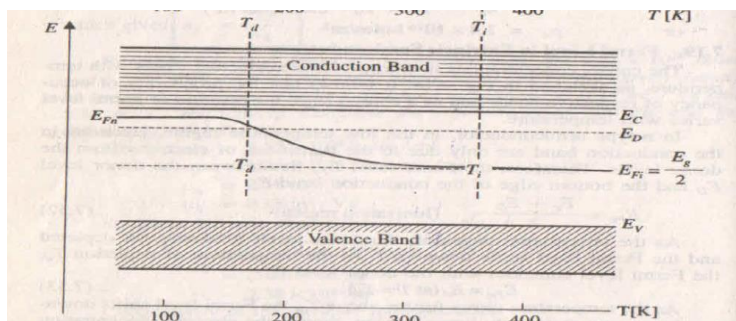
Where:  $N_A$  - Acceptor impurity concentration,  $m_h^*$  - Effective mass of electrons in the conduction band,  $E_A$  - Acceptor impurity energy level,  $E_V$  - Energy of the valence-band edge.

## Fermi level in extrinsic semiconductor

### N-type semiconductor

The carrier concentration in extrinsic semiconductors varies with temperature as discussed earlier. It follows that the probability of occupancy of respective bands & position of Fermi level varies with temperature.

In n-type semiconductor, in low temperature region the electron in the conduction band is only due to the transition of electrons from donor levels. Therefore, Fermi level lies between the donor level  $E_D$  & the bottom edge of conduction band.



As temperature increases the donor level gradually gets depleted & the Fermi level shifts downward. At the temperature of depletion  $T_d$ , the Fermi level coincides with the donor level  $E_D$

$$\text{i.e., } E_{Fn} = E_D.$$

As temperature increases further above  $T_d$ , the Fermi level shifts downward approximately in a linear fashion, though electron concentration in the conduction band remains constant. This is in

accordance with the relation  $E_{Fn} = \frac{E_C + E_D}{2} - \frac{kT}{2} \ln \frac{N_c}{N_D}$ .

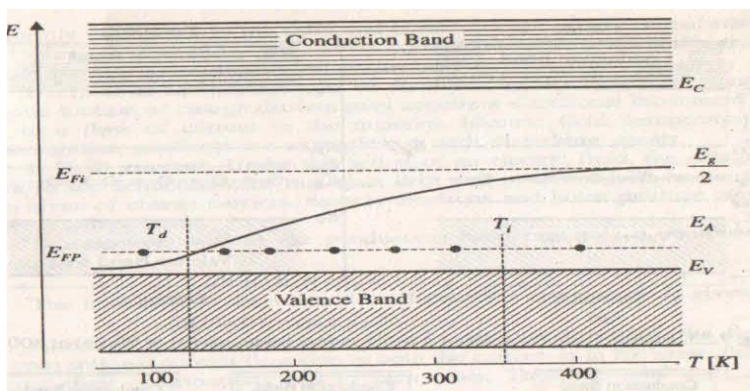


At temperature  $T_i$ , where intrinsic process contributes to electron concentration significantly, the Fermi level approaches the intrinsic value  $E_{Fi} = E_g/2$ . With further increase in temperature the behaviour of extrinsic semiconductor transitions into that of an intrinsic type & Fermi level stay at  $E_{Fi}$ . Thus

$$E_{Fn} = E_{Fi} = E_g/2.$$

## P-type semiconductor

In case of p-type semiconductor the Fermi level  $E_{Fp}$  rises with increasing temperature from below the acceptor level to intrinsic level  $E_{Fi}$  as shown in fig 2.



$$\therefore E_{Fp} = \frac{E_A + E_v}{2} \quad (\text{ionization region})$$

As temperature increases further above  $T_s$ , the Fermi level shifts upward approximately in linear fashion, though hole concentration in the valence band remains constant. This is in accordance with the relation

$$E_{Fp} = \frac{E_v + E_A}{2} + \frac{kT}{2} \ln \frac{N_v}{N_A}.$$

$$E_{Fp} = E_A \quad \text{at } T=T_s$$

$$\text{And } E_{Fp} = E_g/2.$$

## HALL EFFECT:

When a transverse magnetic field 'B' is applied perpendicular to current carrying conductor or semiconductor a potential difference is developed across the specimen in a direction perpendicular to both current and the magnetic field. This phenomenon is called the **Hall effect**. The Voltage so developed is called **Hall voltage**.

Hall effect helps to i) determine the sign of charge carrier in the material 2) determine the charge carrier concentration and iii) determine the mobility of charge carrier if conductivity of material is known. Hall effect measurement showed that the negative charge carriers, that is the electrons are responsible for conduction in metal and it also showed that there exist two types of charge carriers in a semiconductor.

To explain Hall Effect in **metals** or n-type semiconductor, consider a rectangular plate of a metal having, width  $w$  and thickness  $t$ . When, potential difference is applied across its ends, a current 'I' flows through it along x direction that is opposite to the direction of flow of electrons. The current passing through the metal is given by.

$$I = nAev_d \quad (1)$$

where  $n$ - concentration of electrons

$A$ - Area of cross section of end face

$e$ - charge on the electron

$v_d$ - drift velocity of electron

$n$  – concentration of electrons

$$\text{Therefore } v_d = I/nAe = I/nwte \quad (2)$$

where  $A=wt$  ( $w$  is the width of the sample and  $t$  is the thickness of the sample)

Any plane perpendicular to current flow direction is an equipotential surface. Therefore, potential difference between front and rear faces is zero. If magnetic field is applied normal to crystal surface and to the current flow, a transverse potential difference is produced between the faces F & F'. It is called Hall voltage  $V_H$ .

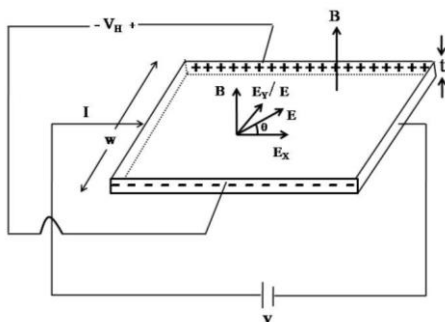


Fig. Hall effect in conductors or n type semiconductors

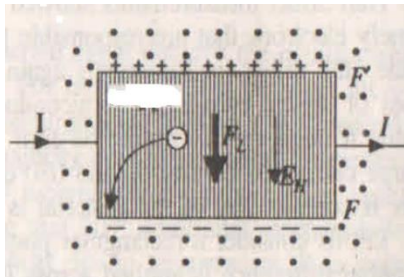


Fig. Direction of magnetic force and Hall field in a conductor

In the absence of magnetic field  $B$ , the charge carriers move in a direction parallel to faces F & F' as shown in the above figure. On the application of magnetic field  $B$ , the Lorentz force comes into existence and this force deflects the electrons sideways due to the magnetic force  $F_L$ . The magnitude of this force is given by.

$$F_L = e B v_d$$

Because of this force, electrons will move towards the front face F and pile up there. Initially the material is electrically neutral everywhere. However, as electrons pile up on the front side, a corresponding equivalent positive charge is left on the rare face F<sup>|</sup>. As a result, an electric field is produced across F & F<sup>|</sup>. The direction of electric field ( $E_H$ ) will be from rare face to front face. A condition of equilibrium is reached when force ( $F_H$ ) due to transverse electric field  $E_H$ , balances the Lorentz force ( $F_L$ ). The transverse electric field  $E_H$  is known as Hall field.

At equilibrium condition

$$F_L = F_H \quad (3)$$

$$F_H = e E_H = e (V_H/w) \quad (4)$$

Substituting for  $F_L$  and  $F_H$  in eqn (3) we get

$$eBv_d = eV_H/w \quad (5)$$

Substituting for  $v_d$  from equation (2) in equation (5)

$$\frac{BI}{nwt e} = \frac{V_H}{w} \quad (6)$$

$$\text{Hall voltage } V_H = \frac{BI}{net} \quad (7)$$

Reciprocal of Carrier charge density is called **Hall co-efficient  $R_H$**

$$R_H = 1/ne$$

Equation (6) can be written as

$$\frac{1}{ne} = \left(\frac{V_H}{B}\right) \frac{t}{I}$$

$$R_H = \frac{V_H t}{BI}$$

The Hall voltage can be measured with a voltmeter with the direction of magnetic field & current depicted in fig, the sign of Hall voltage is negative.

The charge carrier concentration is given by.

$$n = -\frac{1}{R_H e} = -\frac{BI}{V_H t e}$$

The number of charge carriers in metals is of the order of  $10^{28}/\text{m}^3$  and in n or p type semiconductors it ranges from  $10^{19}$ - $10^{23}/\text{m}^3$ .

### HALL EFFECT IN SEMICONDUCTORS:

The Hall effect in semiconductors is similar to that of metals. In case of metals and n -type semiconductors the majority charge carriers are electrons and hence the same derivation holds good for both.

In a p-type semiconductor the only difference is that majority charge carriers are **holes**, with positive charge, hence with slight modifications we can obtain the Hall effect parameters following the method used for metals.

Let us consider a rectangular plate of p-type semiconductor. When potential difference is applied across its ends, a current 'I' flows through it along x direction. If holes are majority charge carriers in p-type semiconductors, then the current is given by

$$I = pAev_d \quad (1)$$

Where p - concentration of holes

A-Area of cross section of end face

e- charge on the hole

$v_d$ - drift velocity of holes

$$\text{therefore } v_d = I/pAe = I/pwte \quad (2)$$

Any plane perpendicular to current flow direction is an equipotential surface. Therefore, potential difference between front and rear faces is zero. If magnetic field is applied normal to crystal surface and also to the current flow, a transverse potential difference is produced between the faces F & F'. It is called Hall voltage  $V_H$ .

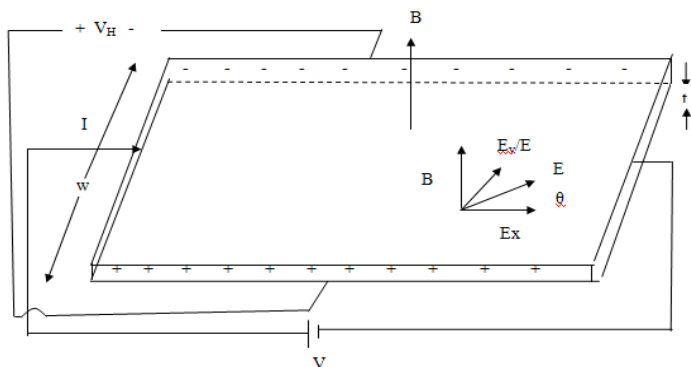


Fig. Hall effect in p type semi-conductor

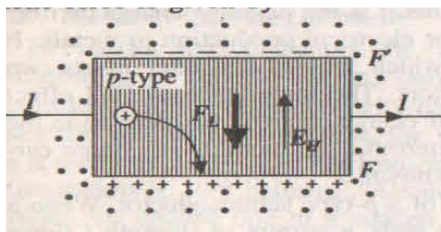


Fig. Direction of magnetic force and Hall field in p-type semiconductor

Before the application of magnetic field  $B$ , the holes move in an orderly way parallel to faces  $F$  &  $F^|$ . On the application of magnetic field  $B$ , the holes experience a sideways deflection due to the Lorentz force  $F_L$ . The magnitude of this force is given by

$$F_L = e B v_d$$

Because of this force, holes are deflected towards the front face  $F$  and pile up there. Initially the material is electrically neutral everywhere. However, as holes pile up on the front side, a corresponding equivalent negative charge is left on the rear face  $F^|$ . As a result an electric field is produced across  $F$  &  $F^|$ . The direction of electric field will be from front face to rear face. It is such that it opposes the further pile up of holes on the front face  $F$ . A condition of equilibrium is reached when  $F_H$  due to transverse electric field  $E_H$  balances the Lorentz force. The transverse electric field  $E_H$  is known as Hall field.

In equilibrium condition  $F_L = F_H$

$$F_H = e E_H = e(V_H/w) \quad (3)$$

Substituting for  $F_L$  and  $F_H$  in eqn (3) we get

$$eBv_d = eV_H/w \quad (5)$$

Substituting for  $v_d$  from equation (2) in equation (5)

$$\frac{BI}{pwte} = \frac{V_H}{w} \quad (6)$$

$$\text{Hall voltage } V_H = \frac{BI}{pet} \quad (7)$$

Reciprocal of Carrier charge density is called **Hall co-efficient  $R_H$**

$$R_H = 1/pe$$

Equation (6) can be written as

$$\frac{1}{pe} = \left(\frac{V_H}{B}\right) \frac{t}{I} \quad R_H = \frac{V_H t}{BI}$$

The Hall voltage is a real voltage & can be measured with a voltmeter with the direction of magnetic field & current depicted in this fig, the sign of Hall voltage is +ve.

For n-type semiconductor Hall voltage will be -ve, when the direction of current is same as in the fig. Therefore, by knowing the sign of Hall voltage the type of semiconductor & the sign of the majority charge carriers will be known.

The carrier concentration of p type semiconductor is given by.

$$p = \frac{1}{R_H e} = \frac{BI}{V_H t e}$$

$$\text{In case of n-type semiconductor } n = -\frac{1}{R_H e} = -\frac{BI}{V_H t e}$$

## Appendix

### Expression for the band gap of a Semiconductor:

The band gap is the energy separation between the conduction band and the valence band of a semiconducting material.

The conductivity of an intrinsic semiconductor is given by

$$\sigma = n_i e \mu_e + n_i e \mu_h$$

$$\sigma = n_i e (\mu_e + \mu_h)$$

Substituting the value of  $n_i$ , we get

$$\sigma = 2 \left[ \frac{2\pi k T m}{h^2} \right]^{\frac{3}{2}} x \left[ \frac{m_e^* m_h^*}{m^2} \right]^{\frac{3}{4}} \exp \left[ \frac{-E_g}{2kT} \right] e (\mu_e + \mu_h)$$

The above equation can be written as  $\sigma = A \exp \left[ \frac{-E_g}{2kT} \right]$

$$\text{Where } A = 2 \left[ \frac{2\pi k T m}{h^2} \right]^{\frac{3}{2}} x \left[ \frac{m_e^* m_h^*}{m^2} \right]^{\frac{3}{4}} e (\mu_e + \mu_h)$$

$$\text{As } \sigma = \frac{1}{\rho} : \rho = B \exp \left[ \frac{E_g}{2kT} \right] \quad \text{We know that } \rho = \frac{RA}{l} \text{ then}$$

$$R = B \frac{l}{A} \exp \left[ \frac{E_g}{2kT} \right]$$

$$R = C \exp \left[ \frac{E_g}{2kT} \right] \quad \text{Where } C = \frac{Bl}{A}$$

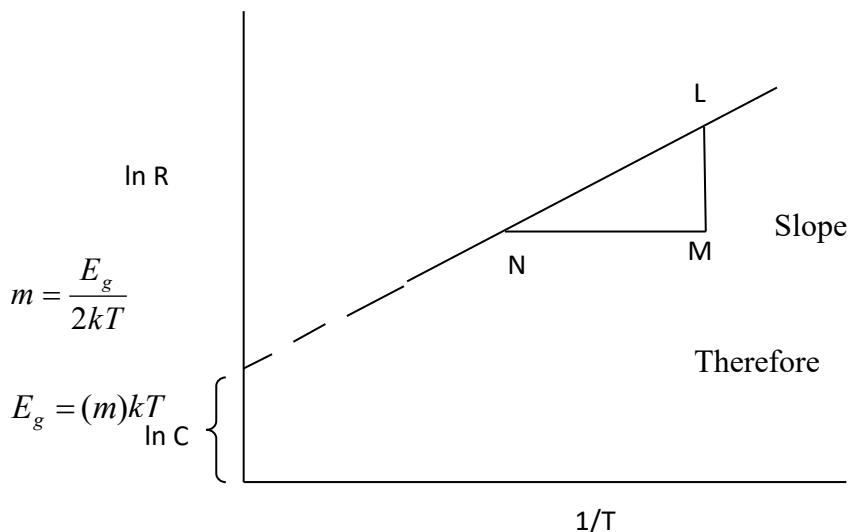
$$\text{Taking log on both sides } \ln R = \ln C + \frac{E_g}{2kT}$$

$$\text{Therefore } \frac{E_g}{2kT} = (\ln R - \ln C)$$

The band gap is given by  $E_g = 2kT(\ln R - \ln C)$



$\ln R = \ln C + \frac{E_g}{2kT}$  is of the form  $y = mx + c$ : By taking  $\ln R$  in the y-axis and  $\frac{1}{T}$  in the x-axis, if a graph is plotted, a straight line is obtained as shown in below figure.



By finding the slope of the straight line, the band gap of the semiconductor is determined using the relation,  $E_g = 2k \times \text{slope of the straight line drawn between } \ln R \text{ and } 1/T$ .

## SOLVED NUMERICALS:

1. What is the probability of a level lying 0.01 eV below the Fermi level not being occupied by electrons at  $T = 300\text{K}$ ?

**Solution:**

$$\begin{aligned}\text{Probability of electrons not being occupied} &= 1 - f(E) \\ &= 1 - (e^{(E-E_F)/k_B T} + 1)^{-1} \\ &= 1 - (e^{0.01/0.026} + 1)^{-1} \\ &= 1 - [1/(1.47 + 1)] = 0.405\end{aligned}$$

2. Find the temperature at which there is 1% occupancy probability of a state 0.5 eV above Fermi energy.

**Solution:**

$$f(E) = 0.01 = 1/[e^{(E-E_F)/k_B T} + 1] \text{ for } E-E_F = 0.5 \text{ eV}$$

$$\text{Solving we get } 0.01 = 1/[e^{5797/T} + 1].$$

$$\text{Thus } e^{5797/T} = 1/0.01 - 1 = 99.$$

$$\text{Taking log we get, } T = 5797/4.595 = 1261.1 \text{ K}$$

3. The effective mass of holes in a material is 4 times that of electrons. At what temperature would the Fermi energy be shifted by 10% from the middle of the forbidden energy gap? Given band gap = 1 eV.

**Solution:**

$$E_F = (E_C + E_V)/2 + (3kT/4) \log(m_h/m_e)$$

$$\text{Fermi level is shifted by } 10\% = 0.1 \text{ eV.}$$

$$\text{Originally Fermi energy was } 0.5 \text{ eV above } E_V.$$

$$\text{Now it is } 0.5 + 0.1 = 0.6 \text{ eV above } E_F.$$

$$(E_V + 0.6) \text{ eV} = (E_C + E_V)/2 + (3kT/4) \log(4) \text{ -----(1)}$$

$$\text{And } (E_V + 0.5) \text{ eV} = (E_C + E_V)/2 \text{ -----(2)}$$

$$\text{Subtracting 2 from 1 we get } 0.1 \text{ eV} = (3kT/4) \log(4)$$

$$0.1602 \times 10^{-19} \text{ J} = (3 \times 1.38 \times 10^{-23} \times T/4) 0.6021.$$

$$T = 1116 \text{ K}$$

4. The Fermi level in silver is 5.5eV at 0K. Calculate the number of free electrons per unit volume and the probability occupation for electrons with energy 5.6eV in silver at the same temperature.

**Solution:**

$$E_{F_0} = \left[ \frac{h^2}{8m} \right] \left[ \frac{3}{\pi} \right]^{2/3} n^{2/3} \quad n = 5.84 \times 10^{28} m^{-3}.$$

5. Calculate the probability of an electron occupying an energy level 0.02eV above the Fermi level at 200K and 400K in a material.

**Solution:**

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

$$f(E) = \frac{1}{1 + e^{\frac{0.02 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 200}}} = 0.24$$

$$f(E) = 0.36 \text{ at } 400K.$$

6. A semiconducting material 12 mm long, 5 mm wide and 1 mm thick has a magnetic flux density of 0.5 Wb/m<sup>2</sup> applied perpendicular to the largest faces. A current of 20 mA flows through the length of the sample, and the corresponding voltage measured across its width is 37μV. Find the Hall coefficient of the semiconductor.

**Solution:**

$$\text{Hall coefficient } R_H = E_y / J_x B_z = -1/ne.$$

$$\text{Since } E_y = V_y / w, R_H = V_y / w J_x B_z$$

$$\text{Thus } R_H = (37 \times 10^{-6} \times 10^{-3}) / (20 \times 10^{-3} \times 0.5) = 3.7 \times 10^{-6} m^3 C^{-1}$$

**UNIT- II: BASICS OF SOLID STATE PHYSICS**  
**CONDENSED MATTER PHYSICS FOR ENGINEERS**  
 Electrical& Electronics Engineering Stream- (EC, EE, EI and ET)

S. No	Sample Questions
1.	Write the assumptions of Quantum free electron theory.
2.	Arrive at an expression for carrier concentration in metals.
3.	Sketch the graph of Fermi factor $f(E)$ verses $E$ for the case $E=E_F$ at $T > 0K$ in metals.
4.	Define density of states in metals.
5.	Write an expression for density of states in metals.
6.	Draw the energy level diagram for an n type semiconductor at 0 kelvin.
7.	Draw the energy level diagram for an n type semiconductor at 0 kelvin.
8.	Derive an expression for electron concentration in the conduction band of an intrinsic semiconductor.
9.	Arrive at an expression for fermi level in an intrinsic semiconductor.
10.	State law of mass action in semiconductors.
11.	Derive an expression for electrical conductivity in a semiconductor.
12.	Define Hall effect. Derive an expression for Hall coefficient in an n type semiconductor.
13.	Define Hall effect. Derive an expression for Hall coefficient in a p type semiconductor.
14.	With an energy level diagram, explain the variation of fermi level with doping concentration in an n type semiconductor.
15.	What is the effect of increase of impurity concentration on band gap in an extrinsic semiconductor?
16.	Electron concentration in a semiconductor is $10^{20} \text{ m}^{-3}$ . Calculate Hall coefficient
17.	In Hall effect experiment, what is the polarity of Hall voltage for an n-type semiconductor?
18.	At 300K, if probability for occupancy of an energy state $E$ by an electron is 0.75, calculate probability for occupancy of the same state by a hole.
19.	Where does the Fermi level lie in case of an n type semiconductor with high impurity concentration?

20.	For silicon semiconductor with band gap 1.12eV, determine the position of the Fermi level at 300K if $m_e^* = 0.12m_0$ and $m_h^* = 0.28m_0$ where $m_0$ is the mass of the electron.
21.	What are Fermions?
22.	Find the temperature at which there is 1% probability that a state with energy 0.5 eV above Fermi energy is occupied.
23.	A sample of silicon is doped with $10^7$ phosphorous atoms/cm <sup>3</sup> . Find the Hall voltage, if the sample is 100μm thick, the current passing through the sample is 1 mA and the applied magnetic field is $10^{-5}$ Wb/m <sup>2</sup> .
24.	Find the probability with which an energy level 0.02 eV below Fermi level will be occupied at 300K.
25.	With the help of a graph, explain the variation of carrier concentration with temperature for an n type semiconductor.
26.	Explain the variation of fermi level with temperature in a p type semi-conductor with the help of energy band diagram.