

## UNIT II: ELECTRICAL CONDUCTIVITY AND METALS

There are three electron theories existing in solid between them

- (1) Quantum Field electron theory
- (2) Classical Field electron theory (1900)
- (3) Zone theory

### CLASSICAL FREE ELECTRON THEORY: (Drude Lorentz theory)

Assumption of CFET:

- (1) A metal is imagined as a three dimensional ordered network of positive ions with the outermost electrons of the metallic atom freely moving about the solid.
  - (2) The free electrons are treated as equivalent to gas molecules and thus assumed to obey the laws of the kinetic theory of gases. They should obey the following formula:
- $$\frac{3}{2} kT = \frac{1}{2} m v^2 \quad \rightarrow \text{thermal velocity of the electrons}$$
- (3) The electric potential due to the ionic core (lattice) is taken to be essentially constant throughout the metal.
  - (4) The attraction b/w free electrons and the lattice ions and the repulsion b/w the electrons are considered insignificant.

### Failures of classical free electron theory:

- (1) The molar specific heat of a gas at constant volume is  $C_v = 3R$ . When we experimentally find it, we get:  $C_v = 10^{-1} R$ , here 3 and  $10^{-1}$  have a difference, and  $T$  is an extra term in the  $C_v$  expression, thus CFET fails to explain the difference.
- (2) The electrical conductivity of a metal is inversely proportional to  $\tau$ . According to CFET, electrical conductivity is inversely proportional to the square root of temperature, i.e.  $\sigma \propto \frac{1}{\sqrt{T}}$

$$\sigma = \frac{n e^2 \tau}{m}$$

$\sqrt{T}$ , mean collision/  
mean relaxation time

(3) Electrical conductivity is given as  $\sigma = ne^2 T$

According to CFET, electrical conductivity  $\sigma$  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 coefficient 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.

### QUANTUM FREE ELECTRON THEORY:

#### Assumptions of QFET:

- (1) The energy values of free electrons are quantised. The allowed energy values are realised in terms of a set of energy levels.
- (2) The distribution of electrons in the various allowed energy levels, follows Pauli Exclusion Principle.
- (3) Distribution of electrons in energy state 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 b/w the free electrons and lattice ions, the repulsion b/w the electrons themselves are ignored.

#### FERMI LEVEL AND FERMI ENERGY:

The highest occupied <sup>energy</sup> level in metals at  $0\text{ Kelvin}$  is called as Fermi Level and the corresponding energy value at that level is called as Fermi Energy ( $E_F$ )

#### FERMI DIRAC STATISTICS:

The distribution of electrons among the energy levels follows statistical rule known as Fermi Dirac Statistics.

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

$$f(E) =$$

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

$k$  (Boltzmann's constant)

$T$  (Absolute temperature)

$E$  (Energy level)

$E_F$  (Fermi Energy level)

Fermi-Dirac statistics is applicable to fermions, fermions are indistinguishable particles with half integral spin, according to Pauli exclusion principle, since electron has half spin they obey Fermi-Dirac statistics and they are called fermions.

### DEPENDENCE OF FERMI FACTOR ON TEMPERATURE:

#### CASE 1:

The probability of occupation for  $E < E_F$  at  $T=0K$

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

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

$f(E) = 1$  indicates that the levels below  $E_F$  are occupied by electron.

#### CASE 2:

The probability of occupation for  $E > E_F$  at  $T=0K$

Substituting the value at  $T=0K$ , for Fermi function, we get

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

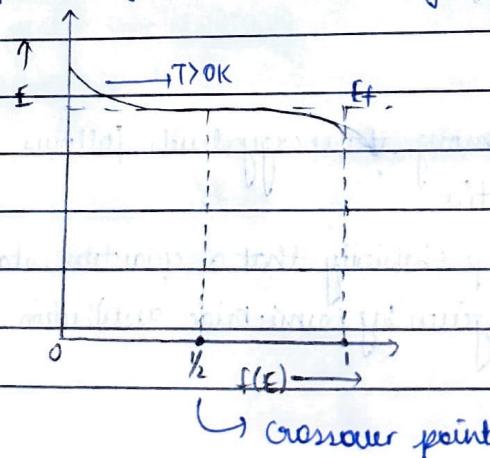
This shows that all the energy levels above  $E_F$  are vacant.

#### CASE 3:

probability of occupation at temperature  $> 0K$

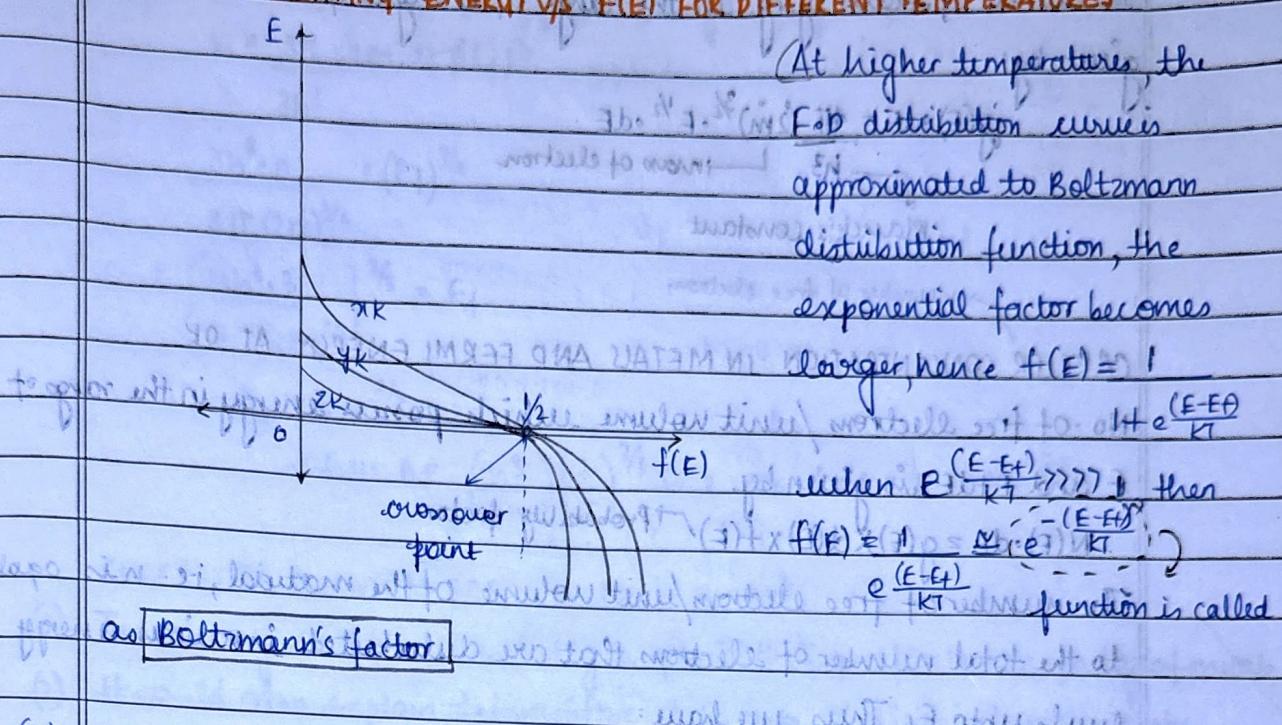
$$E = E_F; f(E) = \frac{1}{1 + e^{\frac{(E - E_F)}{kT}}} = \frac{1}{1 + e^0} = \frac{1}{2}$$

The probability is 50% of finding the  $e^-$  in  $E_F$  fermi energy level.





### GRAPH REPRESENTING ENERGY V/S F(E) FOR DIFFERENT TEMPERATURES



- (Q) Find the probability with which an energy level 0.02eV below Fermi level will be occupied at room temperature (300K).

$$(A) f(E) = \frac{1}{1 + e^{\frac{(E-E_F)}{KT}}} = \frac{1}{1 + e^{\frac{-0.02 \times 1.6 \times 10^{-19}}{300 \times 1.38 \times 10^{-23} \cdot (2) + (2) \cdot 0}}} = 0.681.$$

- (Q) In a solid, consider the energy band lying 0.01eV below the fermi level, what is the probability of this level not being occupied by an electron.

$$(A) f(E) = \frac{1}{1 + e^{\frac{(E-E_F)}{KT}}} = 1 - f(E) = 1 - \frac{1}{1 + e^{\frac{-0.01 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}}} = 1 - 0.595 = 0.405.$$

### DENSITY OF STATES $g(E)$ :

The permitted energy levels for electrons in a solid will be in terms of band, measured in terms of eV. If each energy level consists of two states and each state accommodates one electron each. Therefore, energy level can be occupied by two electrons only, having opposite directions of spin.

Mark definition

Density of state 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 b/w  $E$  and  $E+df$  is given by:

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

mass of electron  
Planck's constant  
number of free electrons

CARRIER CONCENTRATION IN METALS AND FERMI ENERGY AT OK

No. of free electrons/unit volume which possess energy in the range of  $E$  and  $E+df$  is given by

$$N(E) \cdot df = g(E) \times d(E) \times f(E)$$

↑ Probability factor

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:

$$n = \int_{E=0}^{E_f} N(E) \cdot df$$

$$n = \int_{E=0}^{E_f} g(E) \cdot f(E) \cdot df$$

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

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

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

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

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

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

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

Expression for Fermi energy at 0K, is given by  $E_F = \text{constant}$  (2)

$$n = \frac{8\pi}{3} \frac{(2m)^{3/2}}{h^3} (E_F)^{3/2} \quad \text{volume of metal } V \neq 0 \text{ volume.}$$

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

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

$$\Rightarrow E_F = B \cdot n^{2/3}$$

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

### 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.

- (Q) The Fermi level in a material is 2.1 eV, what is the energy for which the probability of occupancy at 300K is 0.99.

$$(A) E_F = 2.1 \text{ eV}; f(E) = 0.99; T = 300 \text{ K}; E = ?$$

$$f(E) = \frac{1}{1 + e^{\frac{(E - E_F)}{kT}}} \Rightarrow 0.99 = \frac{1}{1 + e^{\frac{(E - 2.1 \times 1.6 \times 10^{-19})}{300 \times 1.38 \times 10^{-23}}}}$$

$$0.99 = \frac{e^{\frac{(E - E_F)}{kT}}}{1 + e^{\frac{(E - E_F)}{kT}}} = \frac{1}{1 + e^{\frac{(E - E_F)}{kT}}} = 1 - \frac{1}{1 + e^{\frac{(E - E_F)}{kT}}}$$

$$\frac{1}{1 + e^{\frac{(E - E_F)}{kT}}} = 1 - 0.99 = 0.01$$

$$\Rightarrow E - E_F = \ln \left( \frac{1}{0.99} - 1 \right) \cdot 300 \times 1.38 \times 10^{-23}$$

$$\Rightarrow E = 2.01 \times 10^{-19} \times 1.6 \times \ln \left( \frac{1}{0.99} - 1 \right) \times 300 \times 1.38 \times 10^{-23}$$

$$\Rightarrow E = 1.981 \times 10^{-23} \text{ J} = 1.981 \text{ eV.}$$

(Q) Find the temperature at which there is 1% probability that a state with an energy 0.5 eV above fermi energy is occupied.

$$(A) T = ?; f(E) = 0.01; (E - E_F) = 0.5 \text{ eV}$$

$$f(E) = \frac{1}{1 + e^{\frac{E - E_F}{kT}}} \Rightarrow 0.01 = \frac{1}{1 + e^{\frac{0.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times T}}}$$

$$\frac{1}{0.01} = 1 + e^{\frac{0.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times T}}$$

$$1 - 1 = e^{\frac{0.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times T}}$$

$$\ln\left(\frac{1}{0.01} - 1\right) = \frac{0.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times T}$$

$$\text{down to solving for } T \Rightarrow T = \frac{0.5 \times 1.6 \times 10^{-19}}{0.01 \times 1.38 \times 10^{-23} \times \ln\left(\frac{1}{0.01} - 1\right)} = 126.2 \text{ K}$$

(Q) The fermi level in silver is 5.5 eV at 0K, calculate the no. of free electrons per unit volume.

$$(A) E_F = 5.5 \text{ eV} = 5.5 \times 1.6 \times 10^{-19} \text{ J}; f(E) = 1; T = 0 \text{ K}$$

$$n = \frac{8 \pi (2m)^{3/2} (E_F)^{3/2}}{3h^3} \cdot N_A \text{ (to find no. of free electrons)}$$

$$n = \frac{8 \times 3.14 \times (2 \times 9.1 \times 10^{-31})^{3/2} \times (5.5 \times 1.6 \times 10^{-19})^{3/2}}{3 \times (6.626 \times 10^{-34})^3} \cdot N_A$$

$$n = 5.81 \times 10^{28} \text{ m}^{-3}$$

Hence (Q) Calculate the fermi energy for copper at 0K,  $f(E) = 1$ ; given  $n = 8.4905 \times 10^{28} \text{ m}^{-3}$

$$(A) E_F = B \cdot n^{2/3}$$

$$= 5.85 \times 10^{28} \times (8.4905 \times 10^{28})^{2/3}$$

$$= 1.013 \times 10^{-18} \text{ J}$$

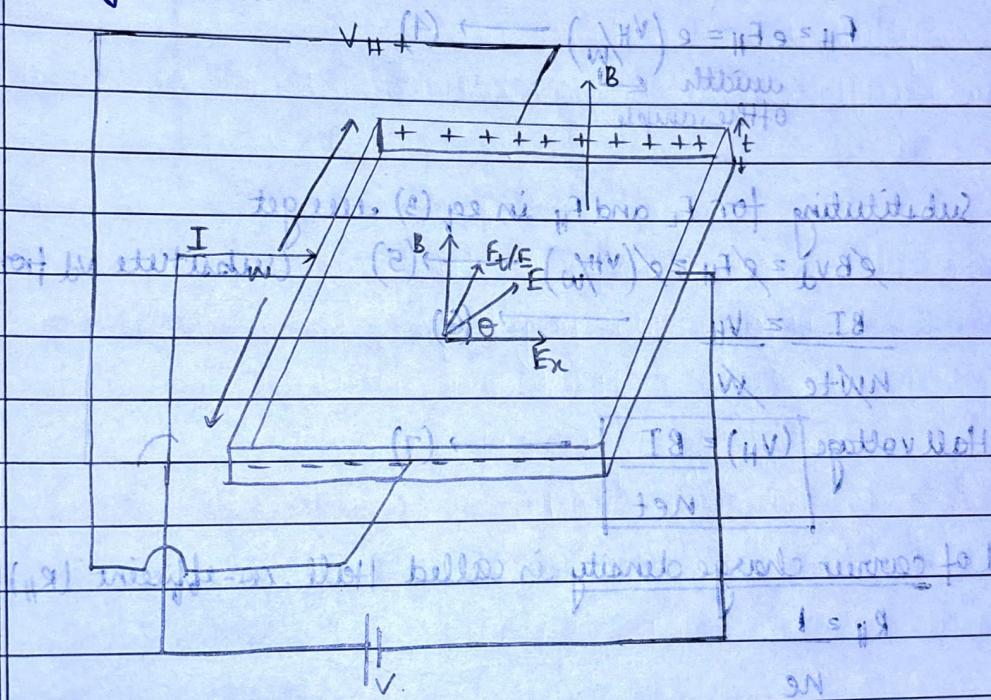
$$= 7.06 \text{ eV} \times \left(1 - \frac{1}{N_A}\right) \text{ m}^{-3} \times 8.4905 \times 10^{28} \text{ m}^{-3}$$

$$= 7.06 \times 10^{18} \text{ eV} \cdot \text{m}^{-3}$$

**HALL EFFECT:**

When a transverse magnetic field ( $B$ ) is applied perpendicular to current carrying conductor, a potential difference is developed across the specimen in a direction perpendicular to both current and the magnetic field. This effect is called Hall effect. The voltage so developed is called Hall voltage. Hall voltage can be positive (or) negative depending on the presence of electron (or) hole.

Hall effect helps to (i) determine the sign of charge carrier in the material (ii) determine the charge carrier concentration (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 exists two types of charge carriers in a semiconductor.



The current passing through the metal by:

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

$n$  no. of concentration carriers  
 $A$  Area of cross section

$$V_d = I / nAe = I / nhv_0 t \quad (2)$$

where  $A = 1 \text{ cm}^2$

$$\frac{t}{V_H} = \frac{1}{Bh} \quad (3)$$

Any plane perpendicular to current flow dir<sup>n</sup> is an equipotential surface

in view of relativity of charge (a), b) Therefore potential difference b/w front and rear faces is 0. If B is applied

drift will drift in downward direction due to current I normal to the crystal and also to the magnetic field. At equilibrium, current flow, a transverse PD b/w the faces F<sub>L</sub> and F', called Hall voltage (V<sub>H</sub>)

$$F_L = eBv_d \quad (\text{Lorentz force})$$

where magnetic field is present

The dir<sup>n</sup> of electric field (F<sub>II</sub>) will be from rear face to front face. A condition of equilibrium is reached when F<sub>II</sub> due to transverse electric field (E<sub>II</sub>), balances the Lorentz force (F<sub>L</sub>).

At equilibrium conditions, width of the sample

$$F_L = F_{II} \longrightarrow (3)$$

$$F_{II} = eE_{II} = e(V_H/w) \longrightarrow (4)$$

width  
of the sample

Substituting for F<sub>L</sub> and F<sub>II</sub> in eq (3) we get

$$eBv_d = eE_{II} = e(V_H/w) \longrightarrow (5)$$

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

note

$$\boxed{\text{Hall voltage } (V_H) = \frac{BI}{w}} \longrightarrow (7)$$

Reciprocal of carrier charge density is called Hall coefficient (R<sub>H</sub>)

$$R_H = \frac{1}{ne}$$

Equation (6) can be written as

$$\frac{1}{ne} = \frac{(V_H) \cdot t}{B \cdot I} \quad (1)$$

$$\boxed{R_H = \frac{V_H \cdot t}{B \cdot I}}$$

$$m = -\frac{1}{R \cdot h \cdot e} = -\frac{B}{V_H}$$

Conclusion → the negative sign tells us that the metal is either a conductor (or) n type semiconductor depending on the number of charge carriers ( $n$ ), we can conclude that the sample is a metal (or) an n type semiconductor.

If the  $V_H$  is positive, the sample is a p type semiconductor.

### SEMICONDUCTORS:

$E$  ↑

$E_g$

CB

VB

$n = \text{no. of electrons}; p = \text{no. of holes}; n_i \rightarrow \text{intrinsic concentration (or) intrinsic density}$

### CARRIER CONCENTRATION IN INTRINSIC SEMICONDUCTOR: (6 marks)

(I) (a) Electron concentration in the conduction band of an intrinsic semiconductor

We know that;

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

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

→ we don't know which levels the  $e^-$  is in

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

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

$m_e^*$  → effective mass of the electron  
↳ influence of other external source

For an intrinsic semiconductor  $g_c(E) = \frac{4\pi}{h^3} (2m_e^*)^{3/2} (E - E_f)^{1/2} \cdot dE$

$$(m) follows \int_{E_f}^{\infty} \frac{4\pi}{h^3} (2m_e^*)^{3/2} (E - E_f)^{1/2} \cdot dE \rightarrow (3)$$

$$\text{As } E > E_f \Rightarrow e^{\frac{E-E_f}{kT}} \gg 1, 1 + e^{\frac{E-E_f}{kT}} \approx e^{-\frac{(E-E_f)}{kT}}$$

Therefore  $\frac{1}{1 + e^{\frac{E-E_f}{kT}}} \approx e^{-\frac{(E-E_f)}{kT}}$

Using this eqn in eqn(3) we get

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

Add and subtract  $E_f$  to the exponential term in the above equation,

$$\text{Therefore } n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{\frac{(E_f-E_f)}{kT}} \int_0^{\infty} x^{1/2} e^{-x} \cdot dx$$

$$\int_0^{\infty} x^{1/2} e^{-x} \cdot dx = \sqrt{\pi} \rightarrow \text{standard integral form where } a = \frac{1}{kT}$$

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

Let  $E = E_f + x$ , then  $dx = dE$

Lower limit when  $E = E_f$ ;  $x = E_f - E_f = 0$

Upper limit when  $E = \infty$ ;  $x = \infty - E_f = \infty$

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{\frac{(E_f-E_f)}{kT}} \left( \frac{\sqrt{\pi}}{2} (kT)^{3/2} \right) \rightarrow (4) \cdot \pi T$$

Rearranging the terms, we get

$$n^2 = 2 \left[ \frac{4\pi m_e^* k T}{h^3} \right]^{3/2} e^{-\frac{(E_f-E_f)}{kT}} \quad (5)$$

$$\text{let } N_c = 2 \left[ \frac{4\pi m_e^* k T}{h^3} \right]^{3/2}$$

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

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

### (b) Hole concentration in the valence band.

$$p = N_v e^{-(E_f - E_v)/kT}$$

$$N_v = 2 \left[ \frac{2\pi m_h^* kT}{h^2} \right]^{3/2}$$

virtual mass.

### FERMI LEVEL IN INTRINSIC SEMICONDUCTOR: (6 marks)

In an intrinsic semiconductor electron and hole concentrations are equal.

Therefore  $n = p$

$$N_c e^{-(E_c - E_f)/kT} = N_v e^{-(E_f - E_v)/kT}$$

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

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

Multiplying by  $kT$  throughout

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

$$2E_f = kT \ln \left( \frac{N_v}{N_c} \right) + E_c + E_v$$

$$E_f = \frac{1}{2} \left[ kT \ln \left( \frac{N_v}{N_c} \right) + E_c + E_v \right]$$

Substitute the values of  $N_v$  and  $N_c$  and after simplification, we get

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

As  $kT$  is small and the effective mass  $m_h^*$  and  $m_e^*$  do not differ much, the 2<sup>nd</sup> term in eq(1) may be ignored. If  $m_e^* = m_h^*$ , then we get

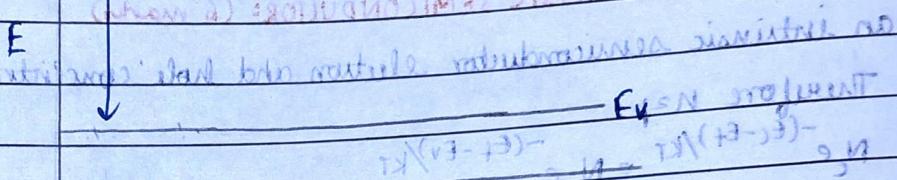
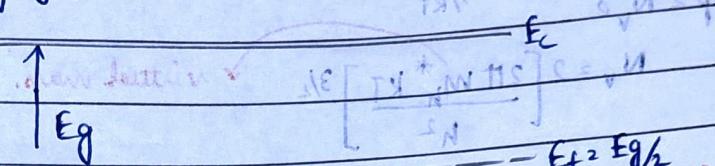
$$E_f = \frac{(E_c + E_v)}{2} \quad (2)$$

We can write eq(2) as  $E_f^2 = \left( \frac{E_c + E_v + E_v - E_v}{2} \right)^2 = \left( \frac{E_c + E_v}{2} \right)^2 + E_v^2$

but  $(E_c - E_v)^2 = E_g$  and  $E_f^2 = E_g + E_v^2$

If top of the valence band ( $E_v$ ) is taken as zero level then  $E_v^2 = 0$

Thus, Fermi level in the intrinsic semiconductor lies at the centre of the energy gap as shown below.



### LAW OF MASS ACTION: (1 mark)

Mathematically  $\rightarrow n_p = N_i^2 = \text{constant}$  current IV and graph given  
 $\downarrow$  intrinsic carrier conc.

### ELECTRICAL CONDUCTIVITY OF SEMICONDUCTOR:

The drift velocity is given by  $v_d = \mu E$

The total current through the semiconductor is given by:

$$I = I_e + I_h = \mu_e N_e v_d + \mu_h N_h v_d$$

The current density due to electrons:

$$J_e = n_e v_d = n_e \mu_e E$$

The current density due to holes:

$$J_h = p_e v_d = p_e \mu_h E$$

i. Total current through the semiconductor:

$$I = I_e + I_h$$

$J = I/A$  (A = cross sectional area of sample)

$$J = J_e + J_h$$

Conductivity is a result of movement of  $e^-$  from valence band to conduction band  
 atoms get ionised and the free electrons move to the CB, in the depletion region the no. of free  $e^-$  produced is reduced, in the intrinsic region the  $e^-$  in the VB move to the CB and the conduction ↑  
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$$\Rightarrow n_e n_e F + p e \mu_H$$

$$\Rightarrow (n_e n_e + p e \mu_H) E$$

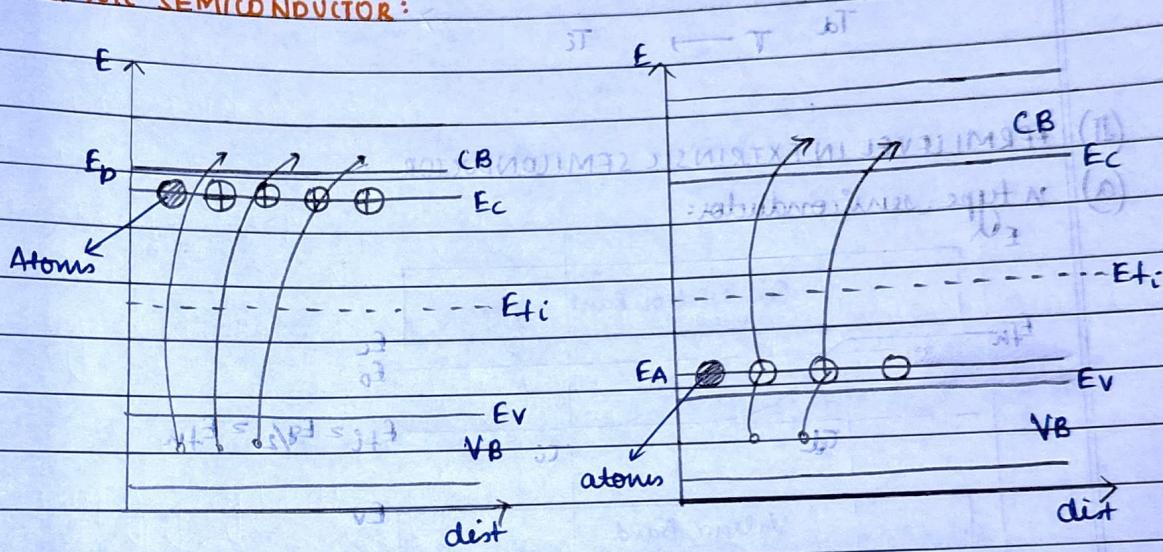
Comparing the above expression with Ohm's law  $I = \sigma E$ , we obtain the expression for conductivity as follows

$$\sigma = n_e n_e + p e \mu_H$$

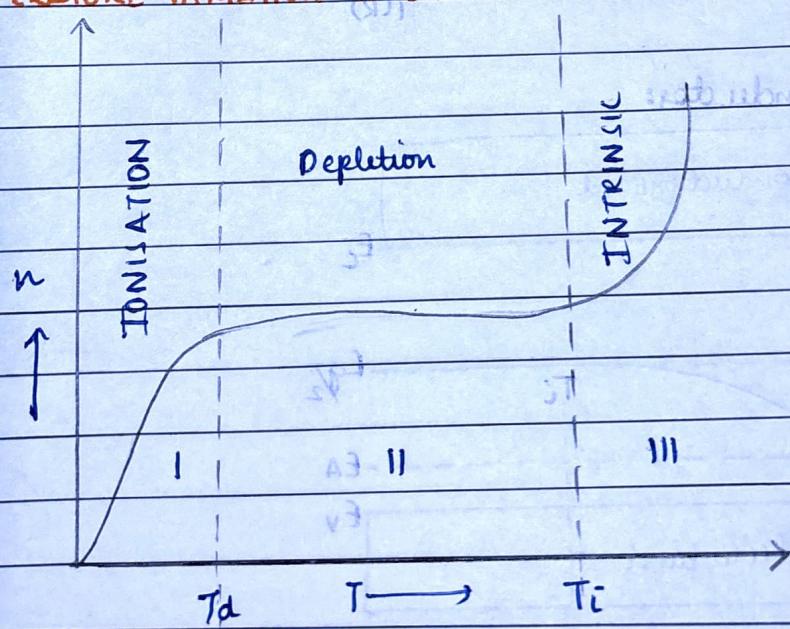
$$n^2 p = n_i$$

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

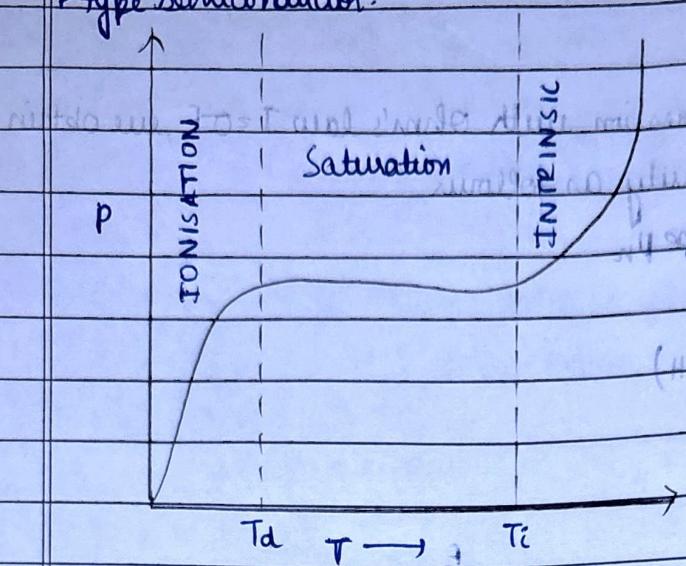
### EXTRINSIC SEMICONDUCTOR:



### TEMPERATURE VARIATION OF CARRIER CONCENTRATION IN EXTRINSIC SEMICONDUCTOR

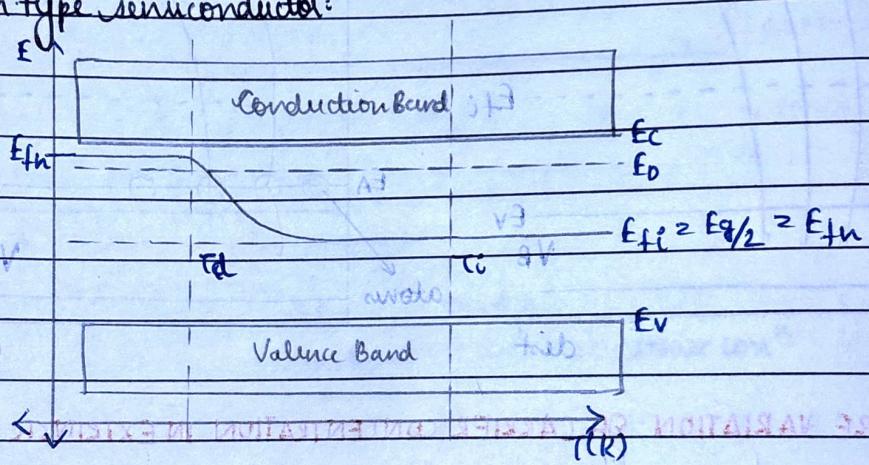


P type semiconductor:

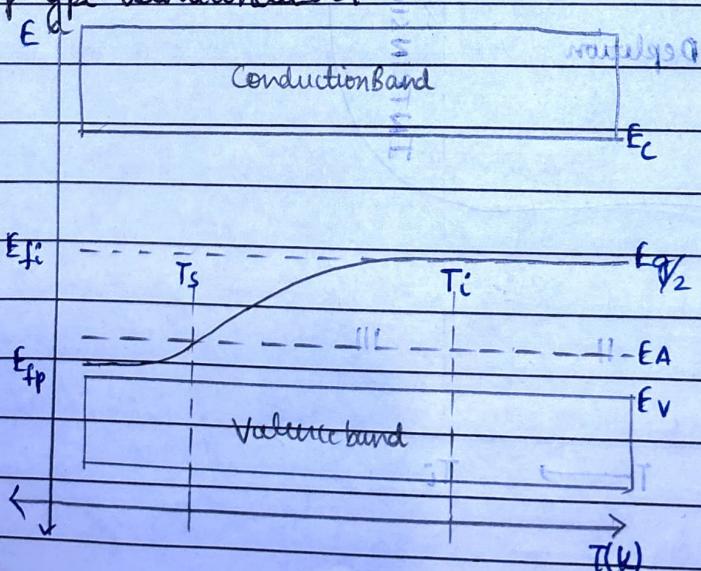


## (ii) FERMI LEVEL IN EXTRINSIC SEMICONDUCTOR

(a) n-type semiconductor:



(b) p-type semiconductor:



$E_g$  is not temperature dependent but varies with dopant concentration.

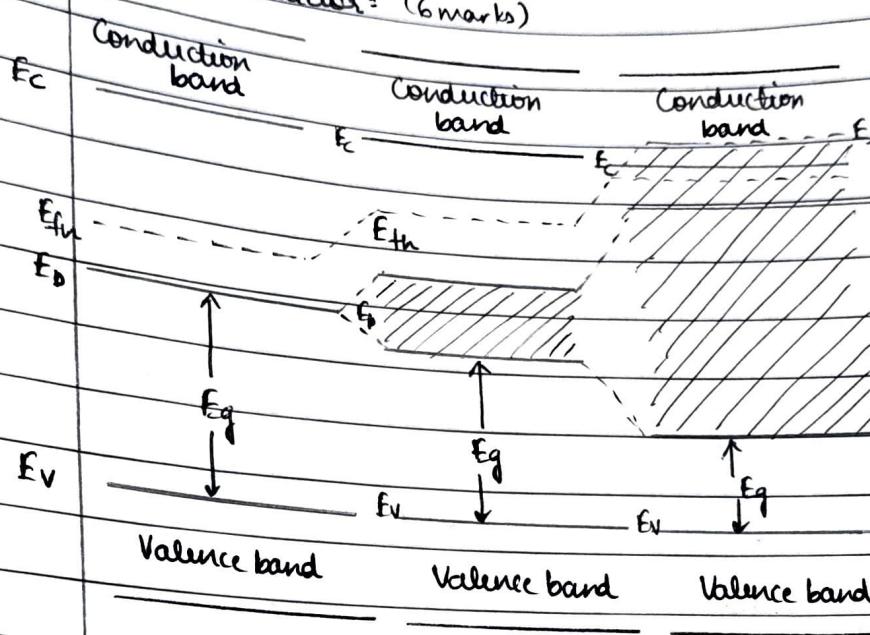
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(III)

(a)

### EFFECT OF VARIATION OF IMPURITY CONCENTRATION ON ENERGY BAND STRUCTURE



(a)  
low doping

(b)  
medium  
doping

(c)  
heavy  
doping

HALL EFFECT IN N TYPE SEMICONDUCTOR: (\*) refer Hall effect in metals

- (1) Illustrate the derivation for hall effect of p type semiconductor
- (2) Doping concentration in p type semiconductor.