Band Theory of Solids

Q. Give quantum numbers of electron in atom.

Ans. Energy levels for the electron are characterised by a set of four quantum numbers.

1. Principal quantum number n
2. Azimuthal or orbital quantum number *l* [0 to (n-1)]
3. Magnetic quantum number m (-*l* to +*l*)
4. Spin quantum number s ($\pm\frac{1}{2}$)

Q. State Pauli's exclusion principle.

Ans. Pauli's exclusion principle statement:

"No two electrons can have all the four quantum number same."

Bohr's theory is true for single electron atom. For higher atoms, inter electron interaction becomes dominant, many lines arise in spectrum. Inter atomic interaction introduce additional energy levels and spectrum is continuous.

Q. Explain Bloch theorem for particle moving in periodic potential.

Bloch Theorem:

According to free electron theory, an electron in crystal lattice, experiences a constant potential V_0. One dimensional Schrodinger equation for this electron is,

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}(E-V_0)\psi=0 \qquad \text{.........................(Eq. 3.1)}$$

Where Ψ is a wave function associated with electron of mass M and total energy E. Solution of equation (3.1) is,

$$\psi(x)=e^{\pm ikx} \qquad \text{.........................(Eq. 3.2)}$$

For one dimensional periodic potential V(x), equation (3.1) can be written as,

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}[E-V(x)]\psi=0 \qquad \text{.........................(Eq. 3.3)}$$

The periodicity of potential is equal to lattice constant a,

$$V(x) = V(x+a)$$

According to Bloch Theorem, solution of equation (3.3) is a plane wave similar to equation (3.2) modulated by the function $u_k(x)$ with periodicity of lattice.

$$\psi(x)=e^{\pm ikx}u_k(x)$$

$$u_k(x) = u_k(x+a) \qquad \text{.........................(Eq. 3.4)}$$

The wave function of type of equation (3.4) is called Bloch function.

Q. Discuss behavior of electron in periodic potential using Kronig Penny model. OR Explain origin of forbidden energy gap in solid using Kronig- Penny model.

Answer- Kronig – Penny Model:

Kronig – Penny model illustrates the beahviour of electron in periodic potential.

Assumption of Kronig – Penny model- Potential near the ion core is zero and in between the cores, it is constant V_0.

The potential of electron in a linear array of positive nuclei has a form of square well of period (a+b).

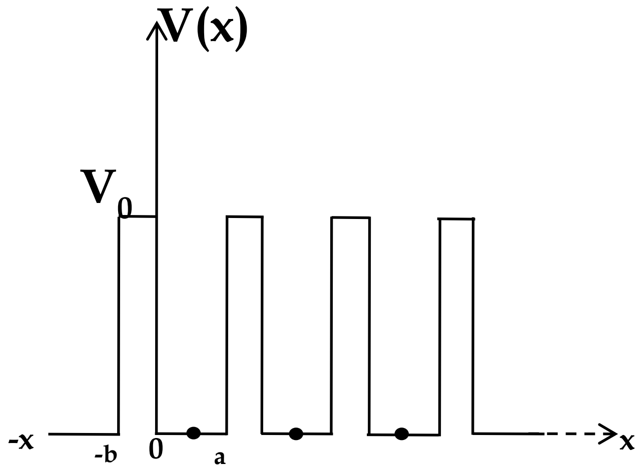


Fig.

For 0 <x<a, electron is close to the nucleus and its potential is zero.

For –b<x<0, potential energy of electron is V_0.

Schrodinger wave equations for these two regions can be written as,

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}E\psi=0, \qquad For\ \ 0<x<a \text{ ....(Eq. 3.5)}$$

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}(E-V_0)\psi=0 \quad For\ -b<x<0 \text{ ....(Eq. 3.6)}$$

According to Bloch theorem, Solutions of these equations have the form of plane wave modulated by periodicity of lattice.

$$\psi(x)=e^{\pm ikx}u_k(x)$$

$u_k(x)$ is periodic function with periodicity (a+b).

Kronig-Penny assumed that energy of electron is less than V_0 and wave functions and their first order derivatives are continuous throughout the crystal. Also, the product of height V_0 and width of Potential barrier b is finite. i.e. when V_0 tends to infinity, b tends to zero. The allowed values for electron energies are given by relation,

$$P\left[\frac{\sin\alpha a}{\alpha a}\right]+\cos\alpha a=\cos Ka \qquad \text{.........................(Eq. 3.7)}$$

Where, $P=\frac{mV_0ab}{\hbar^2}$

and $\alpha^2=\frac{2mE}{\hbar^2}$, m is mass of electron.

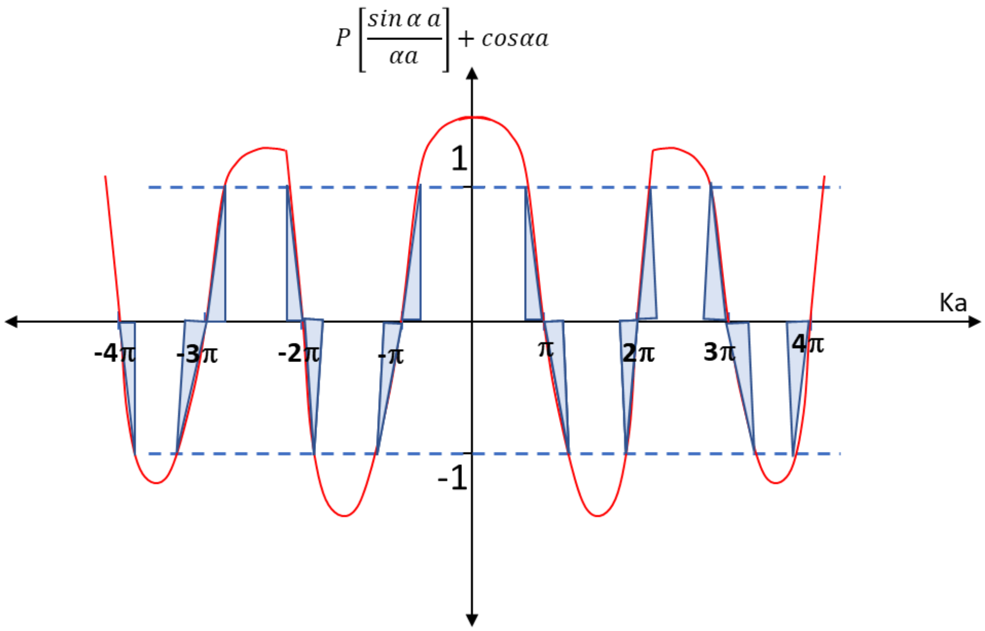
Right hand side of equation (3.7) is cos Ka and its value is between +1 and -1. Hence equation (3.7) is satisfied only for the values of αa that give value of left hand side between +1 and -1. Such values of αa represent allowed solutions while the other values of αa are not allowed, which results in the origin of forbidden gap. Graph of $P\left[\frac{\sin\alpha a}{\alpha a}\right] + \cos\alpha a$ verses Ka is oscillatory in nature as shown in figure.

Physical significance of P – As P increases, area of potential barrier increases and electron is strongly bound to the particular potential well and as P tends to zero, potential barrier becomes weak and electron becomes free.

Thus in the energy spectrum of electron,

- There are alternate allowed and forbidden energy bands
- The width of energy band increases with increase in energy.
- When P tends to infinity, bands are compressed into discrete energy levels.

In the graph of Energy verses K, there are discontinuities for K = nπ/a where n= 0, 1, 2, 3….

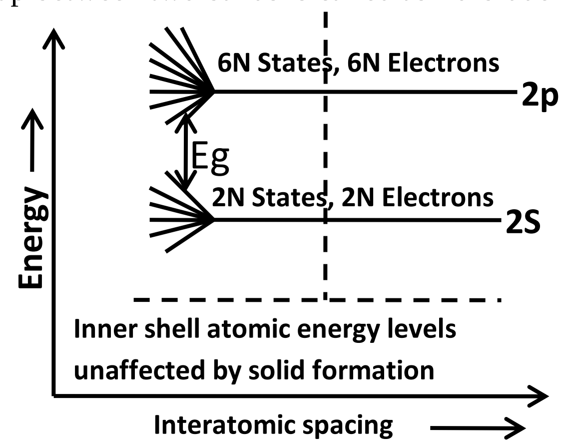


Q. Explain formation of energy bands in solid with one example.

Ans. An isolated atom has discrete energy levels. As the atoms are brought together to form molecule, electrons of one atom are influenced by nucleus of other atom and vice-versa. The electronic energy states gradually change and Pauli's exclusion principle is applied for molecule as whole. Each atomic level consequently splits into multiple molecular levels.

If there are N identical atoms in a molecule, each atomic level splits into N levels as shown in figure. Valence electrons in an atom are loosely bound to the nucleus and mostly affected in the formation of molecule. Atomic wave functions overlap and there is intermixing of electrons. Valence electrons become common to entire solid. Instead of single energy levels associated with single atom, band of energy levels associated with solid as a whole forms. Energy levels are very close to each other and seem to be a continuous band.

The energy gap between two bands is called as Forbidden Energy gap Eg.



The filling of energy band follows a simple rule- States of lower energy are filled first, then the next lowest and so on, till all the available electrons are accommodated.

Fermi level or Fermi energy E_F - Highest filled energy state.

At absolute zero, all states upto E_F are filled and all above are empty. At high temperature, electrons acquire thermal energy and are excited to higher energy states.

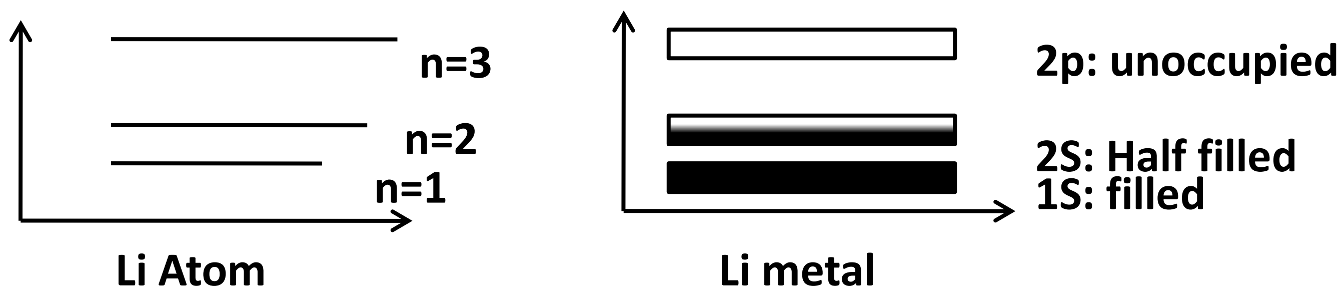
Energy Bands in Lithium:

$_3Li^6$: Electron configuration: $1S^2\ 2S^1$

If there are N Lithium atoms, Electrons will be 3N. Each energy level splits into N levels or 2N states.

1S state has 2N states and 2N electrons- completely filled.

2S state has 2N states and N electrons- half filled

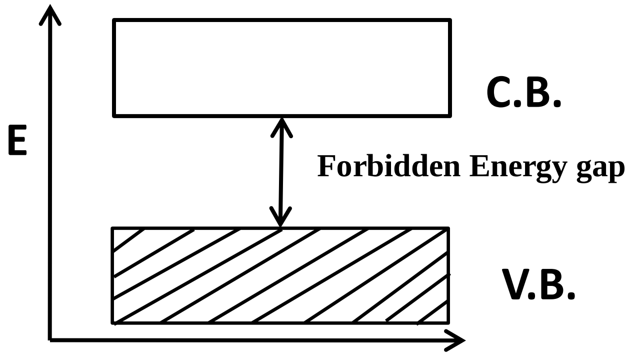


Q. Explain the concept of valence band, conduction band and forbidden gap.

Ans. Valence band: The band containing valence electrons is called valence band. It is completely or half filled.

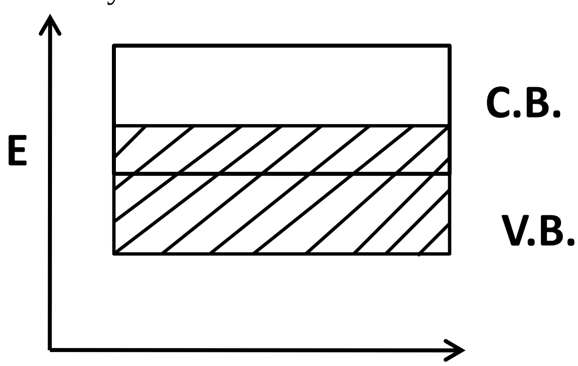
Conduction band: Next higher permitted band to valence band is called conduction band. It may be empty or partially filled. It is lowest unfilled energy band.

Forbidden gap: The difference between valence and conduction band is forbidden gap. It is energy given to valence electrons to excite to conduction band.



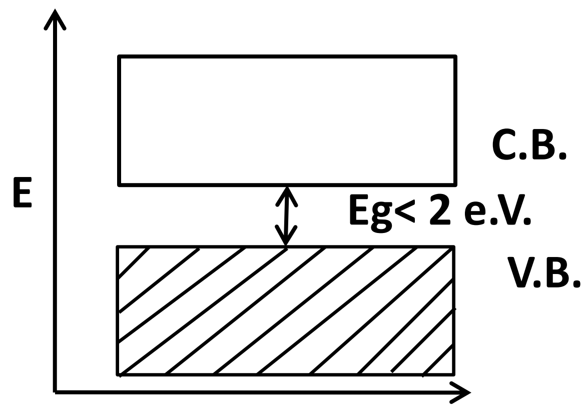
Q. Discus classification of solids on the basis of band theory of solids.
Ans. Electrical conduction is due to electrons in conduction band. Hence Eg is important to determine type of solid.
Conductor: Plenty of free electrons are available for conduction.
In terms of energy bands,

1. Overlapping of valence and conduction band.
2. No physical distinction between V.B. and C.B. Hence large number of conduction electrons is available.
3. No structure to establish holes. Total current is due to electrons.
4. Resistivity is of the order of 10^{-6} Ωcm and increases with temperature.



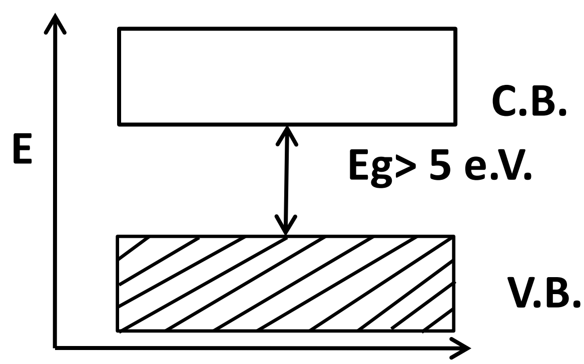
Semiconductor: Electrical conductivity is between conductor and insulator. e.g. silicon, germanium.
In terms of energy bands,

1. Almost empty C.B. and filled V.B. with narrow energy gap.(less than 2 eV)
2. At 0K, no electrons in C.B. and it is insulator.
3. At high temperature, due to small energy gap, there is finite probability for electrons to cross the energy gap and reach C.B. It leaves holes in V.B.
4. Both electrons and holes are responsible for conductivity
5. Resistivity – 10^{-4} to 10^{-6} Ωcm and decrease with temperature.



Insulator: It doesn't conduct electricity.
In terms of energy bands,

1. Completely filled V.B. and Empty C.B.
2. Energy gap 5 – 10 eV.
3. Resistivity – 10^7 to 10^{16} Ωcm and decrease with temperature. At high temperature, it becomes semiconductor.



Q. State and explain law of mass action in solids OR show that product of majority and minority charge carriers is constant in semiconductor.

Ans. In case of intrinsic semiconductor, product of electron and hole concentration at given temperature is constant and given by,

$$np = n_i^2 = N_c N_v e^{-Eg/KT} \text{ -----------------------(1)}$$

where N_c and N_v are constants – effective density of states in C.B. and V.B.

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

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

m_e* and m_h* are effective masses of electron and hole in band model.

Electron and hole concentration in n – type semiconductor are given by,

$$n_n = N_c e^{\left[\left(E_F - E_c\right)/KT\right]} \quad \text{and}$$

$$p_n = N_v e^{\left[\left(E_v - E_F\right)/KT\right]}$$

$$\therefore n_n p_n = N_c N_v e^{\left[\left(E_F - E_c + E_v - E_F\right)/KT\right]}$$

$$= N_c N_v e^{-\left[\left(E_c - E_v\right)/KT\right]}$$

$$= N_c N_v e^{-\left[E_g/KT\right]}$$

$$= n_i^2$$

Similarly for p – type semiconductor,

$$n_p p_p = N_c N_v e^{-\left[E_g/KT\right]} = n_i^2$$

Statement: “The product of majority and minority carrier concentration remains constant in extrinsic semiconductor and is independent of doping concentration.”

Q. Write a note on Fermi level OR define Fermi level and give its significance.

Ans. Fermi level: It is highest occupied energy state at 0 K. It is reference energy level from which all energies are conveniently measured.

Electrons obey Pauli’s exclusion principle and follow Fermi – Dirac distribution.

$$f(E) = \frac{1}{1 + e^{\left(E - E_F\right)/KT}}$$

K – Boltzmann constant and

f(E) – Probability that energy state E is occupied by electron at temperature T.

At T = 0 K, $f(E) = 1$ for $E < E_F$

$= 0$ for $E > E_F$

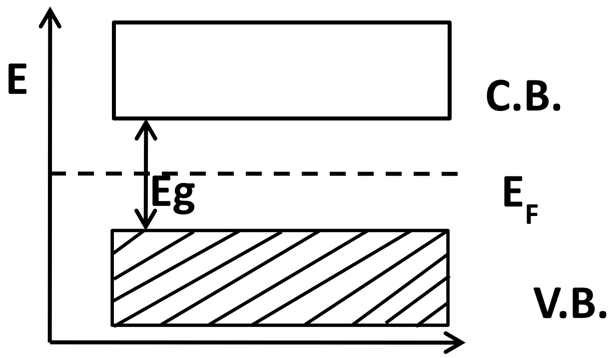
At 0 K, every available energy state upto E_F is filled and all above are empty. At higher temperature, some states above E_F are filled and some probability $[1 – f(E)]$ that some states below E_F are empty.

E_F is symmetrical at all temperatures.

Probability $f(E_F + \Delta E)$ that state ΔE above E_F is occupied is same that $[1- f(E_F - \Delta E)]$, state ΔE below E_F is unoccupied.

Q. Define Fermi level and derive its position in intrinsic semiconductor.

Ans. Fermi level in semiconductor: It is centre of gravity of conduction electrons and holes in valence band weighted according to their energy.
Fermi level in intrinsic semiconductor:
At 0 K, filled V.B. and empty C.B. At room temperature, few electrons in C.B. and equal number of holes in V.B. Hence E_F is midway of forbidden gap.
Let n_c – number of electrons in C.B.
n_v – number of electrons in V.B.



Assumptions –
1. Width of energy band is small as compared to forbidden gap. Hence all levels in band have same energy.
2. Energy of all levels in V.B. is zero and C.B. is E_g

Probability of finding the electron in C.B. = Probability of finding hole in V.B.

$$\therefore f(E_g) = 1 - f(0)$$

$$\frac{1}{1+\exp\left[\frac{(E_g - E_F)}{KT}\right]} = 1 - \frac{1}{1+\exp\left(-\frac{E_F}{KT}\right)}$$

$$= \frac{\exp\left(-\frac{E_F}{KT}\right)}{1+\exp\left(-\frac{E_F}{KT}\right)}$$

$$\therefore 1+\exp\left(-\frac{E_F}{KT}\right) = \exp\left(-\frac{E_F}{KT}\right)\left[1+\left(\exp\frac{(E_g - E_F)}{KT}\right)\right]$$

$$= \exp\left[\frac{(E_g - 2E_F)}{KT}\right] + \exp\left(-\frac{E_F}{KT}\right)$$

$$\therefore \exp\left[\frac{(E_g - 2E_F)}{KT}\right] = 1$$

$$\therefore \frac{E_g - 2E_F}{KT} = 0 \qquad \therefore E_g = 2E_F \qquad E_F = \frac{E_g}{2}$$

Thus in intrinsic semiconductor, Fermi level lies midway between top of V.B. and bottom of C.B.

Q. Derive position of Fermi level in extrinsic semiconductor and explain effect of temperature and doping concentration on it.

Ans. Fermi level in semiconductor: It is centre of gravity of conduction electrons and holes in valence band weighted according to their energy.

n- type semiconductor: Number of electrons in C.B. is greater than number of holes in V.B. Hence centre of gravity moves up. Donors represent separate energy level below C.B. as shown in figure. Hence electrons from donor level can be easily excited to C.B.

Thus Fermi level in n-type semiconductor is given by,

$$\therefore E_{Fn} = \frac{E_d + E_c}{2} + \frac{KT}{2}\log\left[\frac{n_d}{2\left(\frac{2\pi m_e^* KT}{h^2}\right)^{3/2}}\right]$$

At T= 0 K,

$$E_F = \frac{E_d + E_c}{2}$$ lies midway between E_d and E_c.

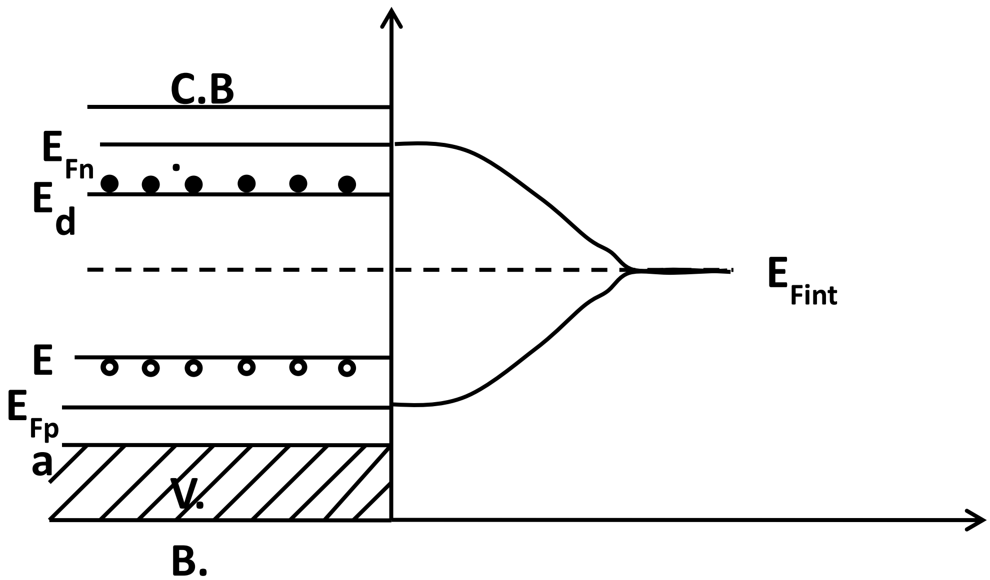
As temperature increases, log factor containing T becomes negative, hence Fermi level drops and falls below donor level and approaches centre of forbidden gap which makes it intrinsic. It also shows that as doping concentration increases, Fermi level rises and approaches conduction band and for heavy doping, enters C.B.

Similarly for p – type,

$$E_{F_p} = \frac{E_a + E_v}{2} + \frac{KT}{2}\log\left[\frac{2\left(\frac{2\pi m_h^* KT}{h^2}\right)^{3/2}}{n_a}\right]$$

At T = 0 K,

$$E_{Fp} = \frac{E_a + E_v}{2}$$ lies midway between E_a and E_v.



As temperature increases, it rises and approaches centre of forbidden gap. Thus it puts limit on operating temperature of extrinsic semiconductor. It also shows that as doping concentration increases, Fermi level drops and approaches valence band and for heavy doping, enters V.B.

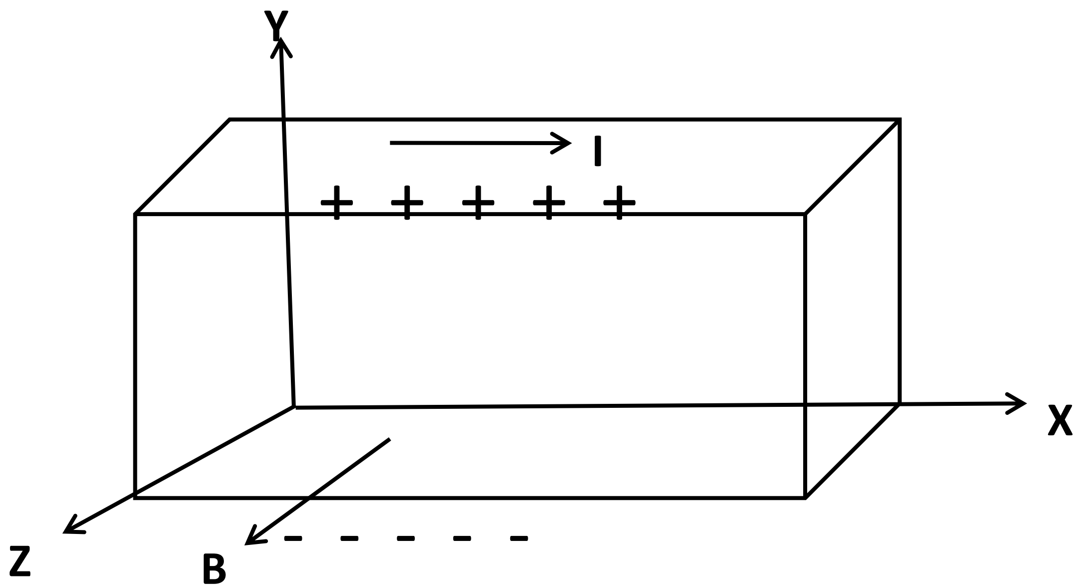
Q. Define Hall effect and derive equation for Hall voltage. Write its significance.

Ans. "When magnetic field is applied perpendicular to current carrying conductor, voltage is developed across the specimen in the direction perpendicular to both current and magnetic field."

Consider a metal slab subjected to electric field E in X- direction and magnetic field I Z - direction as shown in figure. Electrons will experience Lorentz force,

$$F = -e\left[\overline{E} + \bar{v} \times \overline{B}\right]$$

Electrons are deflected towards lower plane (Fleming's left hand rule) and collected at the bottom of slab. Thus positive charge is induced on the top as shown in figure. This produces electric field in Y – direction called Hall field E_y which counteracts the Lorentz force and at equilibrium, electron experience no net force.



Hall voltage in Y – direction,

$V_H = E_y d$ where d is width of slab. ---------------(1)

In equilibrium,

$0 = -e[E_y - v_x B_z]$

$\therefore E_y = v_x B_z$ ------------------------------------(2)

Current density, $I_x = - nev_x$ $\therefore v_x = \frac{-I_x}{ne}$

$$\therefore E_y = -\frac{1}{c}\frac{I_x}{ne}H_z$$

$$\frac{E_y}{I_x H_z} = R_H = \frac{-1}{ne}$$

R_H is Hall coefficient.

From equations (1) and (2),

$$V_H = v_x B_z d$$

$$= \frac{I}{ne} B_z d$$

Thus Hall voltage $V_H \propto \frac{1}{n}$ Hence it is greater for semiconductor than for metal.

$$R_H = \frac{1}{ne} \qquad \sigma = ne\mu_e$$

$$\therefore \mu_e = R_H \sigma$$

Thus using Hall effect number of charge carriers, mobility can be directly measured. Sign of charge carriers can also be determined.

Numerical Problems

1) Compute the probability of exciting the electron in conduction band at 300 K. Energy gap is 0.9 eV. (3.067×10^{-8})

2) Estimate the fraction of electrons in conduction band at room temperature in diamond with Eg = 5.6 eV. (1.7×10^{-47})

3) Compare the number of conduction electrons in silicon at temperatures 27°C and 37°C. Given Eg = 1.1 eV and $m_e^* = m_e$ $\left(\frac{n_2}{n_1} = 2.96\right)$

4) The number of electrons near the top of valence band available for thermal excitation is $5 \times 10^{25}/m^3$ and intrinsic carrier density is $2.5 \times 10^{19}/m^3$ at room temperature. Find the energy gap of germanium. (0.75 eV)

5) A sample of intrinsic germanium has a carrier concentration of $2.4 \times 10^{19}/m^3$ at room temperature. It is doped with antimony at a rate of one atom per million atoms of germanium sample. If the concentration of germanium atoms is $4 \times 10^{28}/m^3$, determine the hole concentration. ($1.4 \times 10^{16}/m^3$)

6) Magnetic field of 0.6 T is applied to semiconducting sample of width 3mm. If current density is 450 A/m^2 and Hall voltage developed across the sample is 0.45 mV, find conductivity of sample. Mobility of electrons is $0.4 m^2/Vs$.

(1.67×10^{-3} mho/m)

7) In n- type germanium, donor density is $10^{21}/m^3$, magnetic field applied is 0.5 T and current density 500 A/m^2. Find Hall coefficient.

($6.25 \times 10^{-3}\ m^3/C$)

8) In n- type germanium, donor density is $10^{21}/m^3$, magnetic field applied is 0.5 T and Hall voltage developed is 4.7 mV. Find current density if the width of sample is 3mm.

(500 A/m^2)