

Material Science & Semiconductor Physics

- **Bonding In Solids**
 - **Covalent Bond**
 - **Metallic Bond**
- **Energy Band in Solids**
 - **Classification of Solids**
- **Intrinsic & Extrinsic Semiconductors**
- **Fermi Dirac Distribution Function**
- **Conductivity in Semiconductors**
- **Hall Effect & its Applications**

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UNIT-5

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* Bonding in Solids:

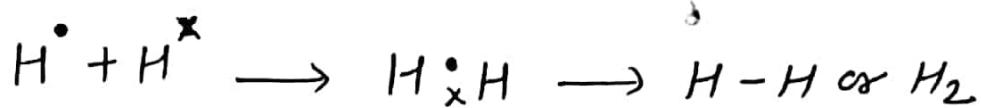
A crystal consists of atoms or molecules bound by interatomic forces or bonds. The interatomic forces are electrostatic in nature. These forces consist of both attractive and repulsive forces. Attraction forces are between negatively and positively charged particles and repulsive forces are between same kinds of particles. The different types of bonds are due to differences in electronic structure of atoms. Depending on the strength and directionality, bonds are divided into two types:

(I) Primary bonds (II) Secondary bonds. Primary bonds are interatomic in nature whereas secondary bonds are intermolecular in nature.

Primary bond is a direct consequence of the transfer or sharing of valence electrons so as to obtain eight [or two] electrons in the outermost ^{shell} for stability. The primary bonds are ionic, covalent and metallic bonds.

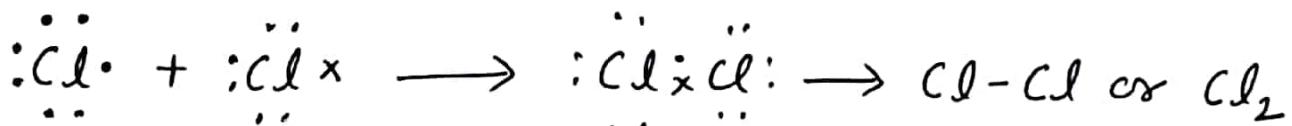
Covalent Bonds: Covalent bonds are formed by sharing pairs of electrons among atoms

Examples, (I) Hydrogen molecule (H_2)



[• electron belongs to left H-atom and \times electron belongs to right H-atom]

(II) Chlorine [Cl_2]



and N_2 , O_2 , CH_4 etc.

Properties of Covalent Compounds:

- (I) Covalent compounds are mostly gases or liquids. Covalent crystal are hard and brittle and incapable of an appreciable bending since the bonds are directional.
- (II) Most of covalent substances are insulators because of non-availability of free electrons and ions.
- (III) They are insoluble in polar solvents like H_2O and soluble in non-polar solvents like benzene, C_6H_6 etc.

* Metallic bond: A collective bond formed between the positive ions and free electrons of a metal is called metallic bond. In metallic bonding, each atom of metal gives one or two valence electrons to the crystal, which hold the atoms together and are not bound to individual atoms but move freely throughout the whole metal. In metal, the ionisation energies are low so that metallic atoms give their valence electrons to the crystal. These valence electrons will form an electron cloud or electron gas, that occupy throughout the metal space. The positive ions are held together by the electrostatic forces due to free electrons. The electrostatic interaction between the positive ions and the electron gas hold the metal together.

Properties of metallic substances:

- (I) The free electrons in metals can easily migrate through large distance in crystal so that metals have high electrical and thermal conductivities
- (II) Metals may deform without fracture.
- (III) Metals are opaque to light, since light energy is absorbed by free electrons.

(IV) Their melting points range from moderate to high
examples: Cu, Na, Ag, Al, Au etc

Energy band in solids

From Bohr's atomic model, we know that the electrons have well defined energy level in an isolated atom. But due to interatomic interactions in a crystal, the electrons of the outer shells are forced to have energies different from those in isolated atoms. Each energy level splits into a number of energy levels forming a continuous band, called energy band.

"An enormously large number of energy levels closely spaced in a very small energy range constitute an energy band".

Consider a small single crystal of Silicon (Si). Suppose it has N atoms. Imagine that these atoms are being brought closer from infinity so as to form a crystal of lattice spacing ' a '. This is shown in fig. 1 in which

the interatomic spacing is plotted along x-axis and the energy along y-axis. $[\text{Si}] : 1s^2, 2s^2 2p^6, 3s^2 3p^2$

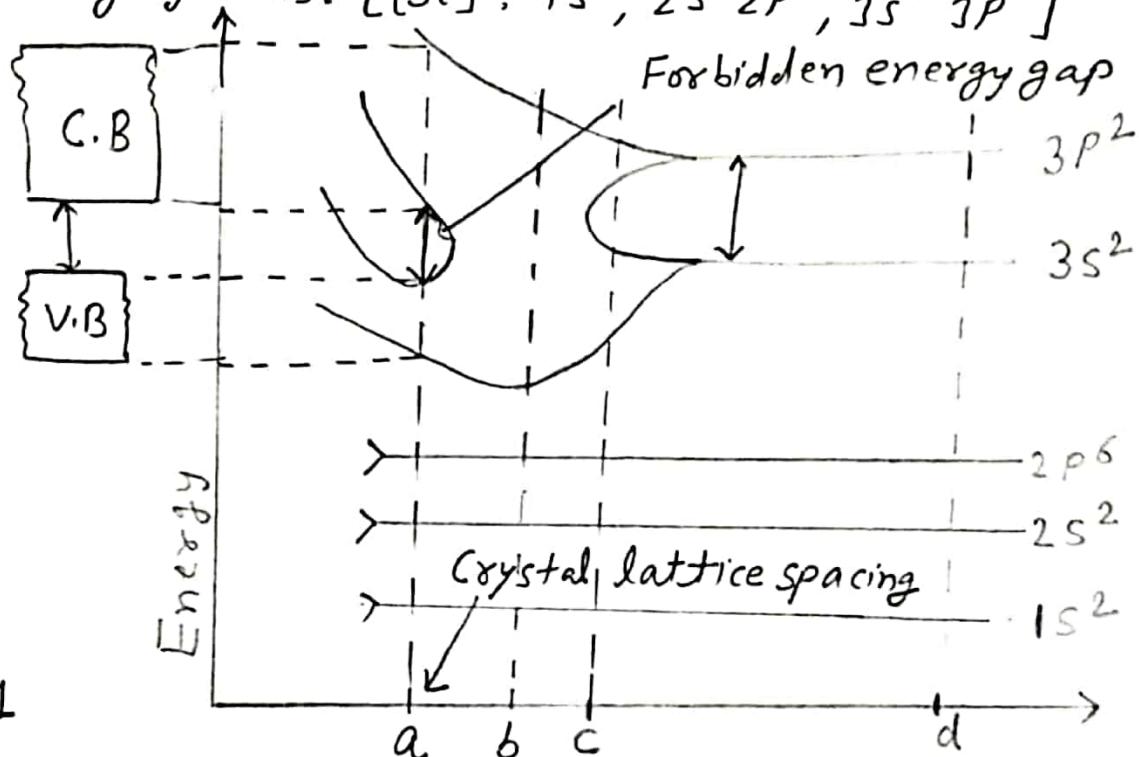


fig. 1

- When $x = d \gg a$, At this large interatomic spacing, there is no interaction between neighbouring atoms. All the N atoms have identical energy levels. In the outer shells, N energy levels associated with $3s$ orbitals are completely filled with $2N$ electrons. Out of $3N$ energy levels associated with $3p$ orbitals, only N energy levels are filled with $2N$ electrons and remaining levels are empty.

2. When $r=c \gg a$, but $c < d$

As interatomic separation decreases, the valence electrons of the neighbouring atoms begin to interact. The energies of 3s and 3p levels of each atom get slightly changed (both increase and decrease). We now have N different energy levels of 3s type and $3N$ different levels of 3p types. The energy gap between 3s and 3p levels decreases. As N is very large ($\approx 10^{23}$ atoms/cm³), we have enormously large number of energy levels (N of 3s type and $3N$ of 3p type) spaced in a very small energy range. Such sets of closely spaced energy levels are called energy bands.

3. When $r=b > a$. As the separation r decrease further, the energy gap between 3s and 3p levels completely disappears and the upper and lower energy band merge with each other. We now have a set of continuously distributed $4N$ energy levels.

4. When $r=a$. At this equilibrium separation, the band of $2N$ filled energy levels gets separated from the band of $2N$ empty energy levels by an energy gap.

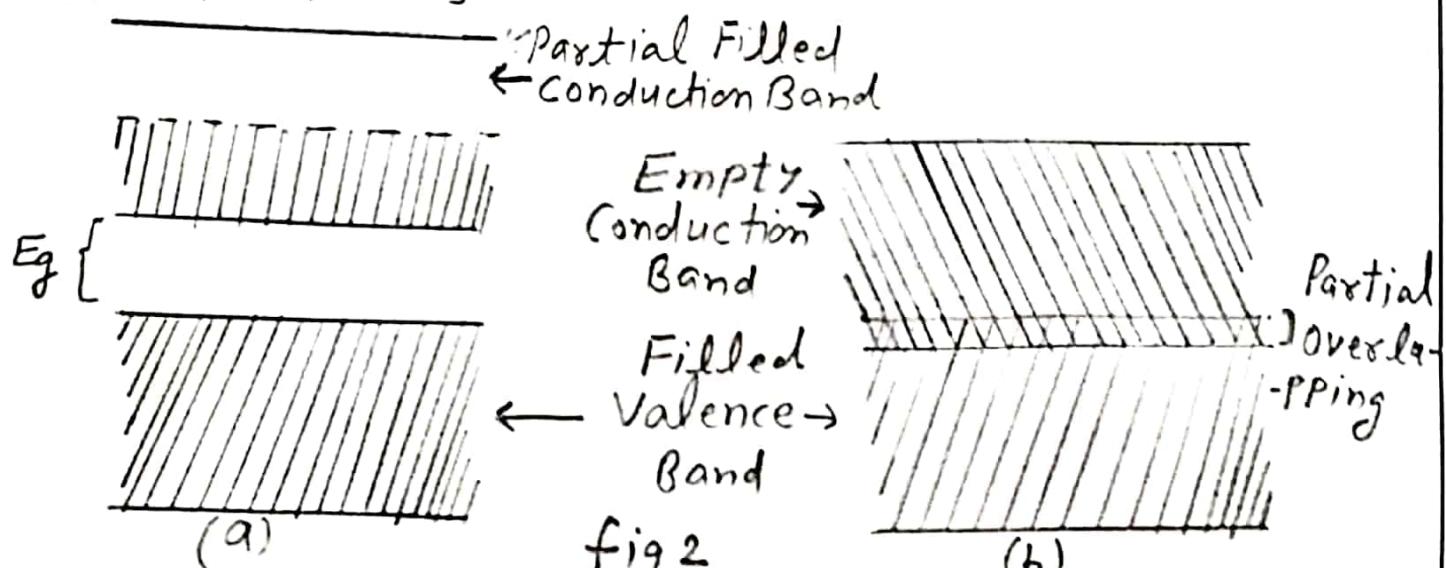
- * The highest energy band filled with valence electrons is called Valence band.
- * The lowest unfilled allowed energy band next to Valence band is called Conduction band.
- * The gap between top of Valence band and bottom of conduction band in which no allowed energy levels for electrons can exist is called energy band gap or energy gap.

Classification of Solids as Insulators, Semiconductors and Conductors

(1) Conductors or Metals: Two types of band structures are found in metals

(a) Either there is energy gap between the completely filled Valence band and the partially filled conduction band. fig. 2(a)

Exp: [Li, Na, K etc.]



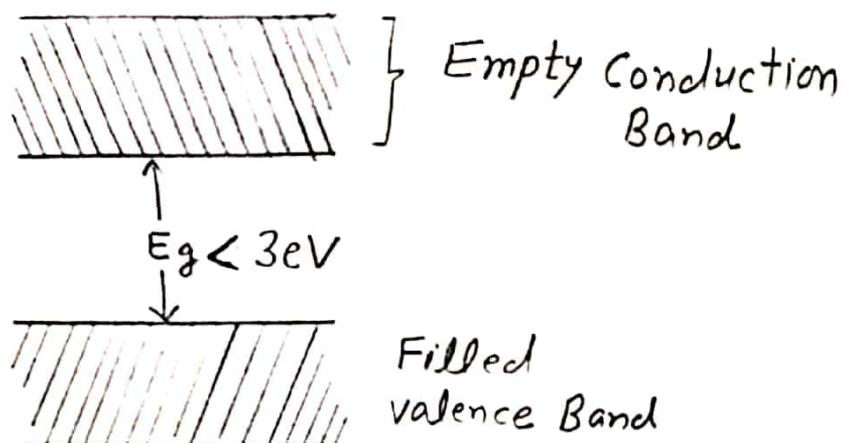
(b) Or the conduction and valence bands partly overlap
As shown in above fig. 2(b)

Exp. [Be ($Z=4: 1s^2, 2s^2$), Mg ($Z=12: 1s^2, 2s^2, 2p^6, 3s^2$)]

Semiconductors: At 0K, the conduction band is empty and the valence band is filled. There is no free electron to conduct electricity at absolute zero so, the material behave as insulator. Energy gap between conduction and valence bands is small [$E_g < 3\text{ eV}$]

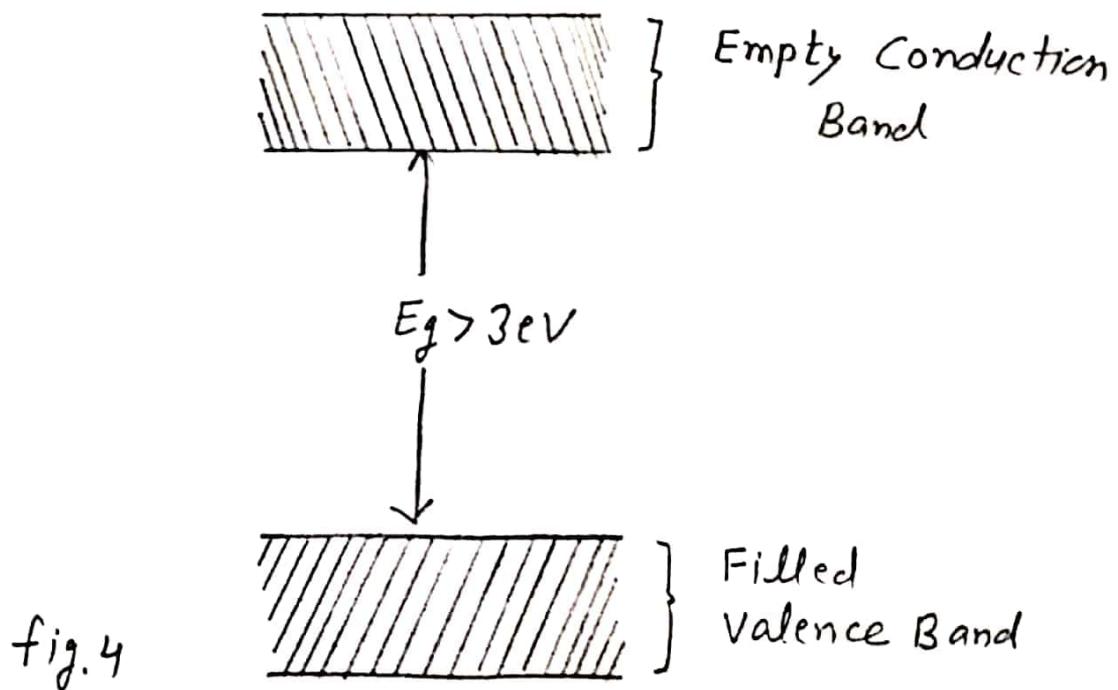
Exp: $E_g = 1.17\text{ eV}$ for Si, $E_g = 0.74\text{ eV}$ for Ge

At room temperature, some valence electrons acquire enough thermal energy and jump to conduction band where they are free to conduct electricity.



3. Insulators. In insulators, the valence band is completely filled while the conduction band is empty. As shown in given fig. 4, there is a large energy gap ($E_g > 3\text{eV}$) between the valence and conduction bands.

Example: $E_g = 6\text{eV}$ for diamond

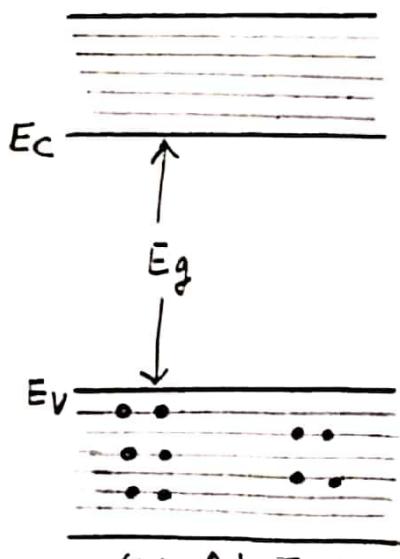


Intrinsic and extrinsic semiconductors

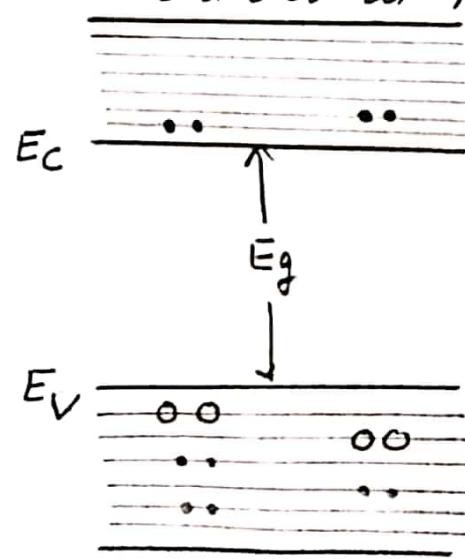
Intrinsic Semiconductors: The pure semiconductors are called intrinsic semiconductor. The presence of mobile charge carriers (electrons and holes) is an intrinsic property of the materials and these charges are obtained as a result of thermal excitation.

Energy band diagram:

At $T=0K$, the valence band of a semiconductor is completely filled with electrons while the conduction band is empty as shown in fig. 5(a). Hence an intrinsic semiconductor behaves like an insulator at $T=0K$.



(a) At $T=0K$



(b) At $T>0K$

fig.5

At higher temperature ($T > 0K$), some electrons of the valence band gain sufficient thermal energy and jump to the conduction band, creating an equal number of holes in the valence band. These thermally excited electrons occupy the lowest possible energy levels in the conduction band. Therefore, the energy band diagram of an intrinsic semiconductor at $T > 0K$ is of type shown in fig. 5(b).

The number of electrons in conduction band is equal to the number of holes in valence band.

Extrinsic Semiconductor: A semiconductor doped with some suitable impurity atoms so as to increase its number of charge carriers is called extrinsic semiconductor.

Extrinsic semiconductors are of two types

- (I) n-type semiconductor
- (II) P-type semiconductor

(I) n-type semiconductor: This semiconductor is obtained by doping the tetravalent semiconductor Si (or Ge) with Pentavalent impurities such as As, P or Sb. of

Group V of periodic table. Such impurity donate one electron to crystal are called donor impurity.

Energy band diagram of n-type semiconductor:

In n-types semiconductors, the extra (fifth) electron is very weakly attracted by the donor impurity. A very small energy ($\approx 0.01\text{eV}$) is required to free this electron from the donor impurity when free, this electron will occupy the lowest possible energy level in the conduction band i.e., the energy of the donor electron is slightly less than E_C . Donor energy level E_D lies just below the bottom of the conduction band as shown in below fig. 6

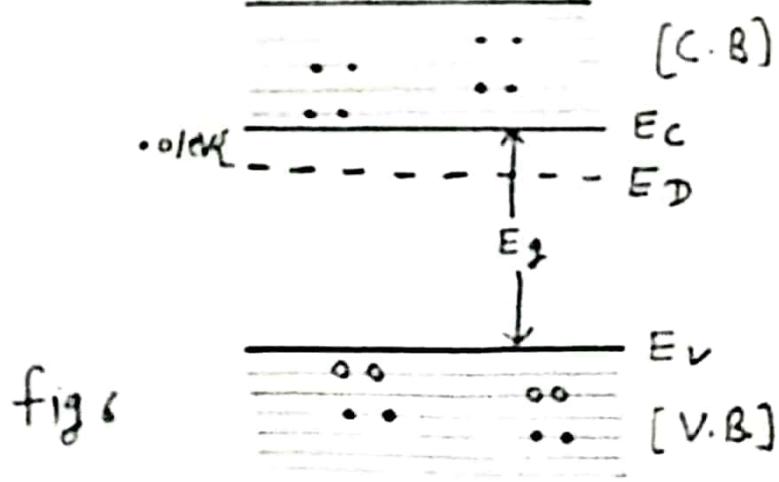


fig 6

At room temperature this small energy gap is easily covered by thermally excited electrons. The conduction band has more electrons (than holes in the Valence band)

(II) P-type Semiconductor: Such a semiconductor is obtained by doping the tetravalent semiconductor Si (or Ge) with trivalent impurities such as In, B, Al or Ga. The trivalent impurity atom is called an acceptor because it creates a hole which can accept an electron from the neighbouring bonds.

Energy band diagram of P-type semiconductor:

In P-type semiconductor, each acceptor impurity creates a hole which can be easily filled by an electron of Si-Si covalent bond i.e., a very small energy ($\approx 0.01 - 0.05 \text{ eV}$) is required by an electron of the valence band to move into this hole. Hence the acceptor energy level E_A lies slightly above the top of the valence band as shown in fig. 7.

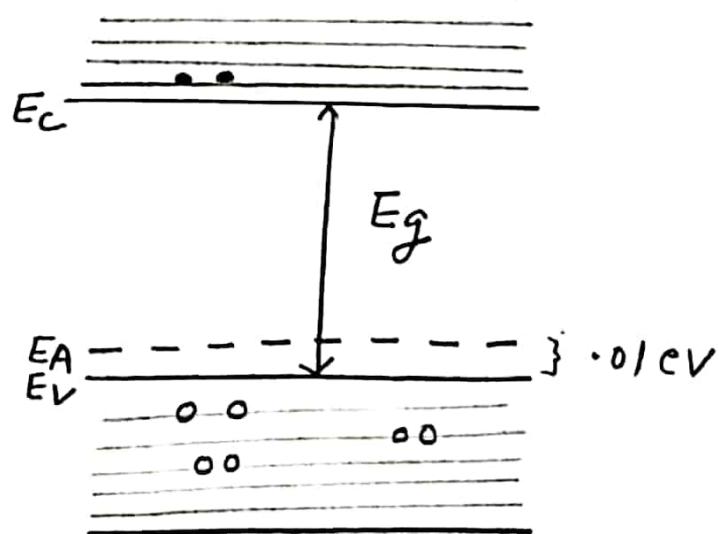


fig. 7

At room temperature, many electrons of the valence band get excited to these acceptor energy levels, leaving behind

equal number of holes in the valence band. These holes can conduct current. Thus the valence band has more holes than electrons in the conduction band.

Fermi - Dirac distribution function

or

Fermi function

Fermi function gives the probability that a given energy state of energy E is occupied by an electron at a given temperature T .

Fermi function is described by

$$f(E) = \frac{1}{1 + \exp\left[\frac{E - E_f}{kT}\right]} = \frac{1}{1 + e^{\frac{(E - E_f)}{kT}}}$$

E = Energy of electron in a given energy state

E_f = Fermi Energy

k = Boltzmann Constant

T = Given temperature

Special Cases :

(Q) At $T=0K$ and $E < E_f$

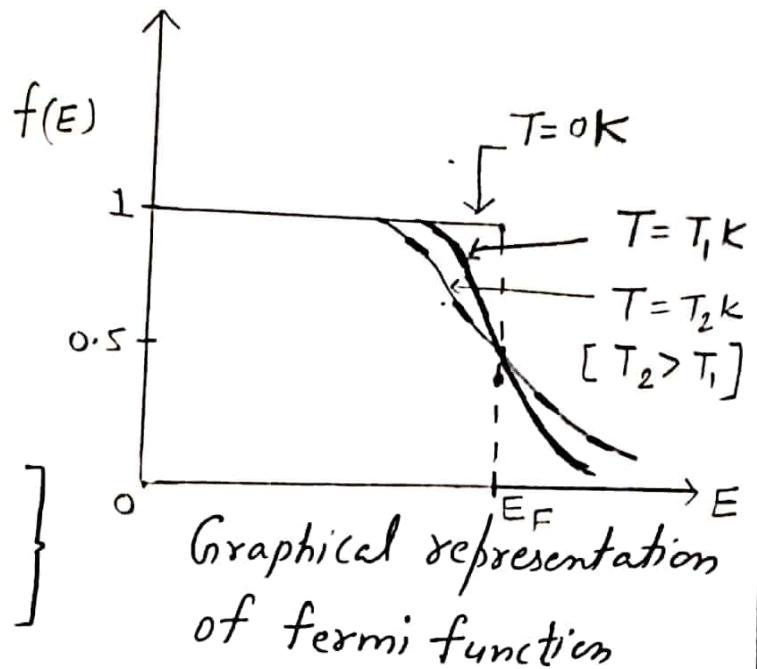
using above expression of $f(E)$

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

$$f(E) = \frac{1}{1 + e^{-\infty}} \quad \left[\begin{array}{l} E - E_f = -ve \\ T = 0K \\ e^{-\infty} = 0 \end{array} \right]$$

$$f(E) = \frac{1}{1+0}$$

$$\boxed{f(E) = 1}$$



All the energy states upto fermi energy are completely filled with electron at absolute zero.

(B) At $T=0K$ and $E > E_f$

$$f(E) = \frac{1}{1 + e^{\infty}} \quad \left[\begin{array}{l} E - E_f = +ve \\ T = 0K \\ e^{\infty} = \infty \end{array} \right]$$

$$f(E) = \frac{1}{1+\infty}$$

$$f(E) = 0$$

All the energy states above fermi Energy are empty at absolute zero.

(C) At $T \neq 0K$ and $E = E_f$

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

$$f(E) = \frac{1}{1+1}$$

$$f(E) = \frac{1}{2}$$

$$f(E) = 0.5 \text{ or } 50\%$$

The probability of an electron lies at fermi level at any non-zero temperature ($T \neq 0K$) is always equal to 0.5 or 50%.

- (d) As temperature increase the electrons lies just below the fermi level absorb thermal energy and jump into the higher energy level.
- (e) $1 - f(E)$ gives the probability that a particular energy state is not occupied by an electron.

Electrical Conductivity of semiconductors

Semiconductors are those material whose electrical conductivity lies between conductors and insulators.

There are two types of charge carriers in semiconductors.

- (i) Free electrons in conduction band
- (ii) Holes in valence band

Let us consider a rod of intrinsic semiconductor [Si or Ge] connected to a battery as shown in fig. Then, electric field exist along x -direction. This field accelerates the free electrons along negative x -direction and holes along positive x -direction. So, the velocity of

electrons along negative x-direction increase and attains some constant resultant velocity called drift velocity (v_d). The total electrical current through the semiconductor is the sum of electron current I_e and hole current I_h .

$$I = I_e + I_h \quad \text{--- (1)}$$

A [area of cross section]

$\circ = \text{hole}$
 $\cdot = \text{electron}$

fig. 8

Let A be the area of cross-section of rod, v_d be the drift velocity of electron and n be the number of free electrons per unit volume of the semiconductor.

The number of free electrons present in a volume AV_{de} will cross an imaginary planes perpendicular to rod in one second
 $= nAV_{de}$

The electron charge which crosses the plane in one second $= neAV_{de}$

This represent electron current I_e :

$$I_e = neAV_{de} \quad \text{--- (2)}$$

The electron current density

$$J_e = \frac{I_e}{A} = n_e V_{de} \quad \text{--- (3)}$$

from ohm's law, the current density (J_e) due to electrons

$$J_e = \sigma_e E \quad \text{--- (4)}$$

σ_e is the electrical conductivity of electrons
from eq.(3) and eq.(4)

$$\sigma_e E = n_e V_{de} \quad \text{--- (5)}$$

As we know $V_{de} = \mu_e E$ [μ_e = mobility of electrons]

$$\sigma_e E = n_e \mu_e E$$

$$\sigma_e = n_e \mu_e \quad \text{--- (6)}$$

eq. (6) represent electrical conductivity due to electrons.
similarly, the electrical conductivity of holes (σ_h) can be obtained.

Let P be the number of holes per unit volume, μ_h mobility of holes and the charge on a hole is e then

$$\sigma_h = P e \mu_h \quad \text{--- (7)}$$

Total Conductivity

$$\sigma = \sigma_e + \sigma_h$$

$$\sigma = n_e \mu_e + P e \mu_h \quad \text{--- (8)}$$

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For an intrinsic semiconductor $n = p = n_i$

where n_i = intrinsic charge carrier density

$$\sigma_i = n_i e (\mu_e + \mu_h) \quad - (9)$$

For n-type semiconductor [Majority charge carriers are electrons]
 $n >> p$

$$\boxed{\sigma = n e \mu_e} \quad - (10)$$

For P-type semiconductor [Majority charge carriers are holes]
 $p >> n$

$$\boxed{\sigma = p e \mu_h} \quad - (11)$$

Hall Effect

Many interesting effects arise when a metal is subjected to a magnetic field. Hall effect is one of them.

This effect was discovered in 1879 by E.H. Hall.

It is used to determine

- (i) Types of charge carrier in a given material
- (ii) Types of semiconductor whether its n-type or p-type
- (iii) Mobility of charge carrier
- (iv) Carrier density (n or p)

Hall Effect: When a current carrying conductor or semiconductor is placed in transverse uniform magnetic field then a potential difference is developed across two end of conductor which is perpendicular to both applied magnetic field and direction of flow of current. This effect is called Hall effect and corresponding potential difference and electric field is called Hall voltage and Hall electric field respectively.

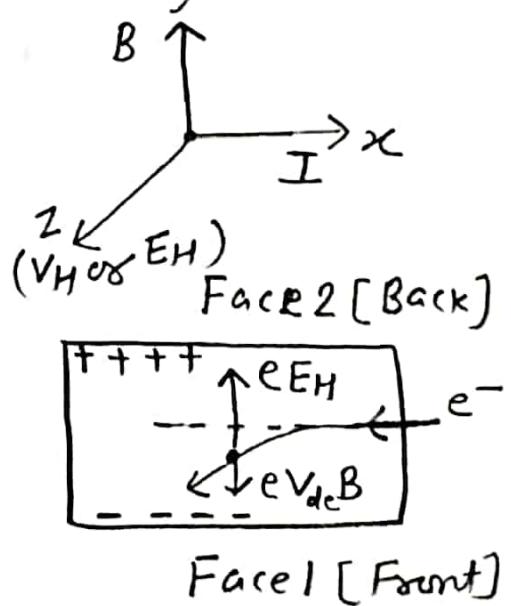
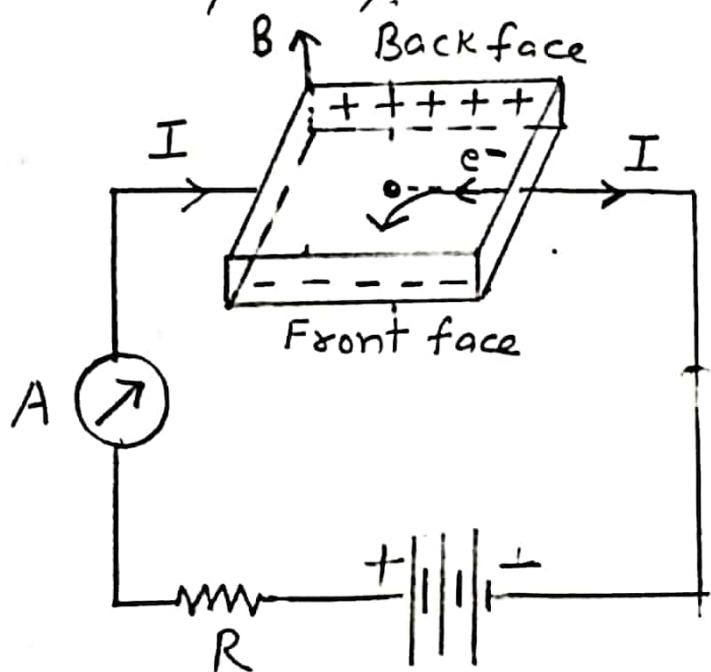


fig.8

Case-1 Conductor or n-type semiconductor:

Consider a current carrying conductor of length 'l'

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width 'b' and thickness 't' is placed in uniform magnetic field as shown in fig. 8.

As current is flowing along $+x$ direction so electrons are moving along $-x$ direction. When a moving electron is placed in uniform magnetic field, It experience a magnetic force

$$\vec{F}_B = q (\vec{V}_{de} \times \vec{B})$$

$q = -e$ [electron has negative charge]

$$\vec{V}_{de} = V_{de} [-\hat{i}] \quad (V_{de} = \text{drift velocity of electrons})$$

$$\vec{B} = B (\hat{j}) \quad [\text{magnetic field } \vec{B} \text{ along } y\text{-direction}]$$

$$\vec{F}_B = -e [-V_{de} (\hat{i}) \times B \hat{j}]$$

$$= e V_{de} B [\hat{i} \times \hat{j}]$$

$$\vec{F}_B = e V_{de} B \hat{k} \quad \text{---(1)}$$

electron experience a magnetic force along z -direction, This cause the electron current to be deflected towards front surface and cause a negative charge to accumulate on the front surface of the slab. A potential difference ~~comes~~ is therefore established from back to front face of specimen with front face negative. This potential

difference cause a field E_H in the positive $-z$ direction, and so there is a force of eE_H acting on electron

$$\vec{F}_E = q \vec{E}_H$$

$$q = -e, \vec{E}_H = E_H \hat{k}$$

$$\vec{F}_E = -eE_H \hat{k} \quad (2)$$

So electron experience ^{electric} force ~~on~~ along $-z$ -direction.

In steady state

$$|\vec{F}_B| = |\vec{F}_E|$$

$$ev_{de}B = eE_H$$

$$v_{de} = \frac{E_H}{B} \quad (3)$$

If J_x is the current density along $+x$ direction

$$J_x = nev_{de} \quad (4)$$

$$v_{de} = \frac{J_x}{ne} \quad (5)$$

using eq.(3) and eq.(5)

$$\frac{E_H}{B} = \frac{J_x}{ne} \Rightarrow E_H = \frac{J_x B}{ne} \quad (6)$$

The Hall effect is described by means of Hall coefficient R_H , defined in terms of current density J_x by the relation

$$E_H = R_H J_x B \quad (7)$$

Now Compare eq. (6) and eq. (7)

$$R_H = \frac{1}{ne} \quad \text{or} \quad R_H = \frac{E_H}{J_x B}$$

In this case $R_H = -\frac{1}{ne}$

For Conductor or n-type semiconductor, Hall Coefficient (R_H) is always negative.

All the three quantities E_H , B and J_x can be measured, and so the Hall Coefficient and carrier density n can be found out.

Fig. 9 shows the condition that exist in a similar P-type specimen when the current is entirely by holes.

$$R_H = \frac{E_H}{B J_x} = \frac{1}{P e}$$

where P is the hole density

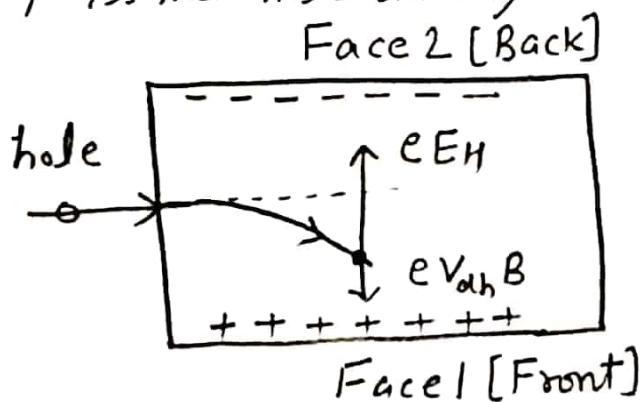


fig.(9)

For P-type semiconductor, Hall Coefficient (R_H) is always positive.

Determination of Hall coefficient

The Hall coefficient is determined by measuring the Hall Voltage that generates the Hall field.

If V_H is the Hall voltage across the sample of width 'b' then

$$V_H = E_H b$$

Current density $J_x = \frac{I_x}{b t}$ [b = width of sample
 t = thickness of sample]

$$R_H = \frac{E_H}{J_x B} = \frac{V_H}{b \times \frac{I_x}{b t} \times B} = \frac{V_H t}{I_x B}$$

* Note that the polarity of V_H will be opposite for n- or p-type semiconductor.

Applications of Hall Effect

(i) Determination of semiconductor type:

For an n-type semiconductor the Hall coefficient is negative whereas for a p-type semiconductor it is positive. Thus, the sign of the Hall coefficient can be used to determine whether a given semiconductor is n- or p-type.

(ii) Calculation of carrier concentration:

The Hall Voltage V_H is measured as usual by placing the

two probes at the center of front and back faces of the sample

$$n = \frac{1}{R_H e}$$

$$\text{Where } R_H = \frac{1}{ne} = \frac{V_H t}{I_x B}$$

(III) Determination of mobility:

If the conduction is due to one type of charge carriers, e.g. electrons,

$$\sigma = n e \mu_n$$

$$\mu_n = \frac{\sigma}{ne} = \sigma R_H$$

(IV) Measurement of magnetic flux density:

Since Hall Voltage V_H is proportional to the magnetic flux density B for a given current I_x through a sample, the Hall effect can be used as the basis for the design of a magnetic flux density meter.