

Chapter-5 Material Science & Semiconductor Physics

Bonding in Solids

What are solids?

The collection of closely packed atoms resulting in the formation of bulk materials called solids. Solids are one among the three fundamental states of matter. In solids, the atoms are tightly packed together and have a definite shape and structure that can't be retained or changed.

Solids are mainly classified into TWO types. They are..

Crystalline Solids: The solids in which the constituent particles of matter are arranged and organized in a specific manner are called Crystalline Solids. Examples-Quartz, Calcite, Sugar, Mica, Diamonds etc.

Amorphous Solids: The solids in which the constituent particles of matter are arranged in a random manner are called amorphous solids. Examples: Plastics, Glass, Rubber, Metallic Glass, Polymers, Gel etc.

What is bonding in solids?

The binding force that exists due to charge distribution in the atoms of the elements is known as Bonding.

Different charge distributions lead to different types of bonding.

Bonding is defined as the binding force (i.e., attractive / repulsive force) that occurs due to charge distribution in the atoms of the elements.

Bonding in solids is broadly classified into FIVE types. They are as follows...

- Ionic Bonding
- Covalent Bonding
- Metallic Bonding
- Hydrogen Bonding
- Vander-Waal's Bonding

Covalent Bond

What is Covalent Bond?

Covalent bond is formed when a pair of valence electrons are mutually shared between the atoms of the element and the stable attractive and repulsive forces existing between these atoms is known as covalent bonding. Here the valence electrons are not transferred between the atoms but are equally shared by both the atoms. Covalent bond is formed only by donating the electrons by each of the participating atoms of the element.

Mutual sharing of pair of valence electrons between the atoms leads to the formation of covalent bond

The covalent bonds are classified into three types based on the number of pair of valence electrons shared by the atoms of the element.

Single Covalent Bond - It is formed when only one pair of electrons are shared between the atoms of the element, example - HCl, H₂.

Double Covalent Bond - It is formed when two pairs of electrons are shared between the atoms of the element, example - O₂.

Triple Covalent Bond - It is formed when three pairs of electrons are shared between the atoms of the element, example - N₂.

Example

Let us consider a molecule of HCl as an example of covalent bond formation. The covalent bond formation in HCl (Hydrogen Chloride) can be understood by Lewis electron-dot structure.

Lewis Electron-dot Structure of HCl

Lewis electron dot structure is based on the concept of number of valence electrons present in the outermost shell of the atom.

The element HCl contains two atoms H and Cl.

H (Hydrogen) Atom

The electronic configuration of H is - $1S^1$

By the above electronic configuration, we can observe that only one valence electron is present in the Hydrogen atom. So the electron dot structure of H atom can be written as



Cl (Chlorine) Atom

The electronic configuration of Cl is - $1S^2 2S^2 2P^6 3S^2 3P^5$

By the above electronic configuration, we can observe that 7 valence electrons are present in the outermost shell of Cl atom. So the electron dot structure of Cl atom can be written as



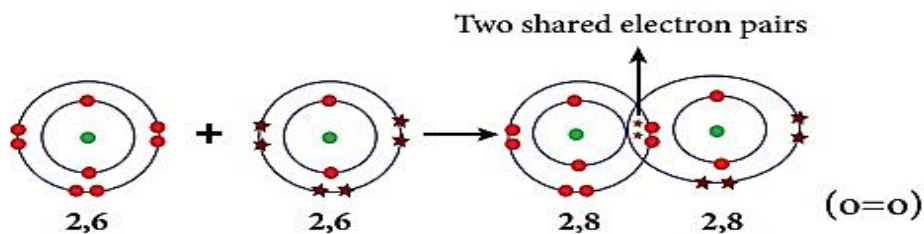
Single Covalent Bond Formation in HCl

The valence electron of H (Hydrogen) atom is shared with the valence electron of Cl (Chlorine) atom to attain stable electronic configuration (Octet configuration). Therefore a single covalent bond is formed between Hydrogen and Chlorine atoms.



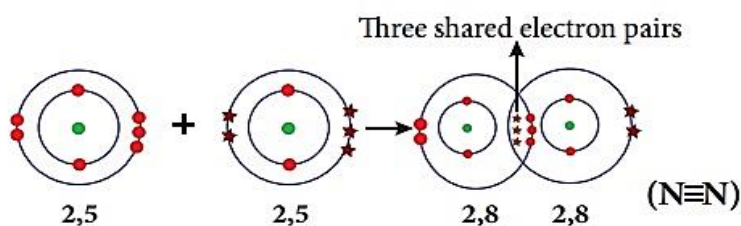
Double covalent bond, Formation of oxygen molecule (O_2)

Oxygen molecule is formed by two oxygen atoms. Each oxygen atom has six valence electrons (2, 6). These two atoms achieve a stable electronic configuration (octet) by sharing two pair of electrons. Hence a double bond is formed in between the two atoms.



Triple covalent bond, Formation of nitrogen molecule (N₂)

Nitrogen molecule is formed by two nitrogen atoms. Each nitrogen atom has five valence electrons (2, 5). These two atoms achieve a stable completely filled electronic configuration (octet) by sharing three pair of electrons. Hence a triple bond is formed in between the two atoms.



Characteristics of Covalent Solids

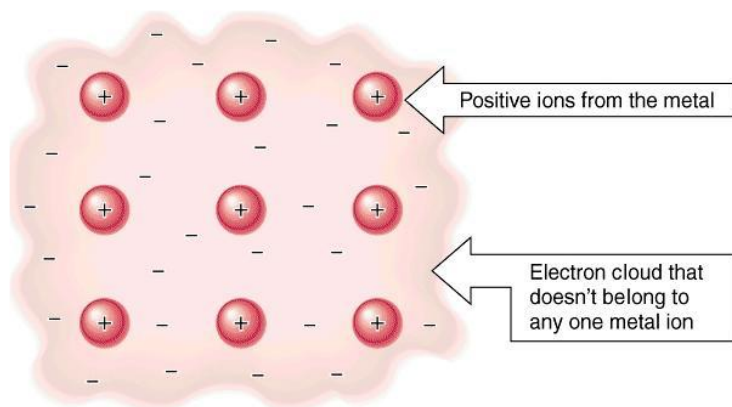
As said earlier, the properties of compounds depend on the nature of bonding between their constituent atoms. So the compounds containing covalent bonds possess different characteristics when compared to ionic compounds.

- a) **Physical state** – Depending on force of attraction between covalent molecule the bond may be weaker or stronger. Thus covalent compounds exist in gaseous, liquid and solid form. Eg. Oxygen-gas; Water-liquid; Diamond-solid.
- b) **Electrical conductivity** – Covalent compounds do not contain charged particles (ions), so they are bad conductors of electricity.
- c) **Melting point** – Except few covalent compounds (Diamond, Silicon carbide), they have relatively low melting points compared to ionic compounds.
- d) **Solubility** – Covalent compounds are readily soluble in non-polar solvents like benzene (C₆H₆), carbon tetra chloride (CCl₄). They are insoluble in polar solvents like water.
- e) **Hardness and brittleness** – Covalent compounds are neither hard nor brittle. But they are soft and waxy.
- f) **Reactions** – Covalent compounds undergo molecular reactions in solutions and these reactions are slow.

Metallic Bonding

The valence electrons from all the atoms belonging to the crystal are free to move throughout the crystal. The crystal may be considered as an array of positive metal ions embedded in a “cloud” or “sea” of free electrons as shown in Fig. This type of bonding is called metallic bonding. A metallic structure is therefore determined largely by the packing of the positive ions alone; the electron cloud is just a sort of negatively charged glue.

1. The metallic bonding is an electrostatic attraction between positive metal ions which are fixed in a metal to the electron cloud which are moving freely in between the metal ions.
2. The bonding in a metal must be considered in terms of all the atoms of the solid taken together. No valence electron is associated with a specific atom. The valence electrons from all the atoms belonging to the crystal are free to move throughout the crystal.



3. Materials bound in this manner are good conductors of electricity and heat. The metallic bonding can be considered as a limiting case of the ionic bonding in which the negative ions are just electrons. For example sodium chloride contains equal number of Na^+ and Cl^- , while metallic sodium contains equal number of Na^+ and e^- .
4. The crucial difference is that the mass of an electron is very small as compared to the mass of Cl^- ions. As a result of this, its zero point motion is large so that it is not localized on a lattice. They are held together by the resulting electrostatic interaction between the positively charged metal ions and the cloud of negative electrons.
5. The unsaturated nature of metallic bonding accounts for the alloying properties of metals. If the atoms have more loosely held valence electrons, the more metallic is the bonding.

For example Sodium, Copper, Silver has high electrical and thermal conductivities because their valence electrons are very mobile. They are opaque because the free electrons absorb energy from light and they have high reflectivity, because these free electrons re-emit this energy as they fall back to lower energy.

Properties of metallic bond materials:-

1. They have high electrical and thermal conductivities
2. The metals are opaque to all electromagnetic radiations
3. The metals have high optical reflection and absorption co-efficient
4. The metallic bond is comparatively weaker than the ionic and covalent bond
5. Metallic solids have crystalline structure
6. Metallic crystals possess a high degree of crystal symmetry due to symmetrical arrangement of positive ions.

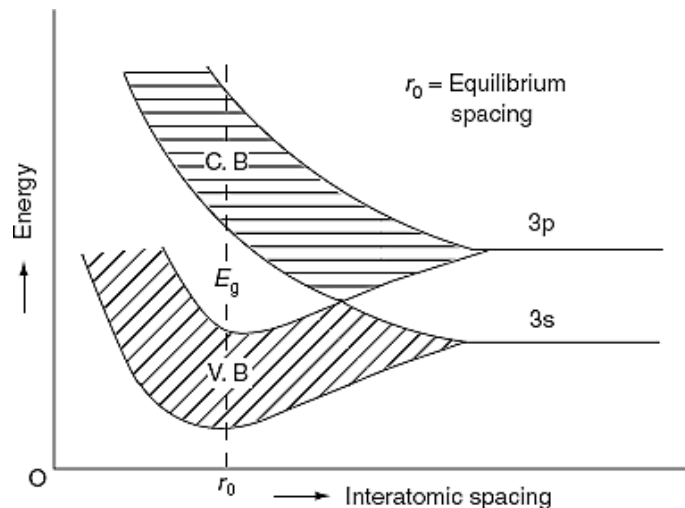
Band Theory in Solids

Origin of energy bands formation in solids

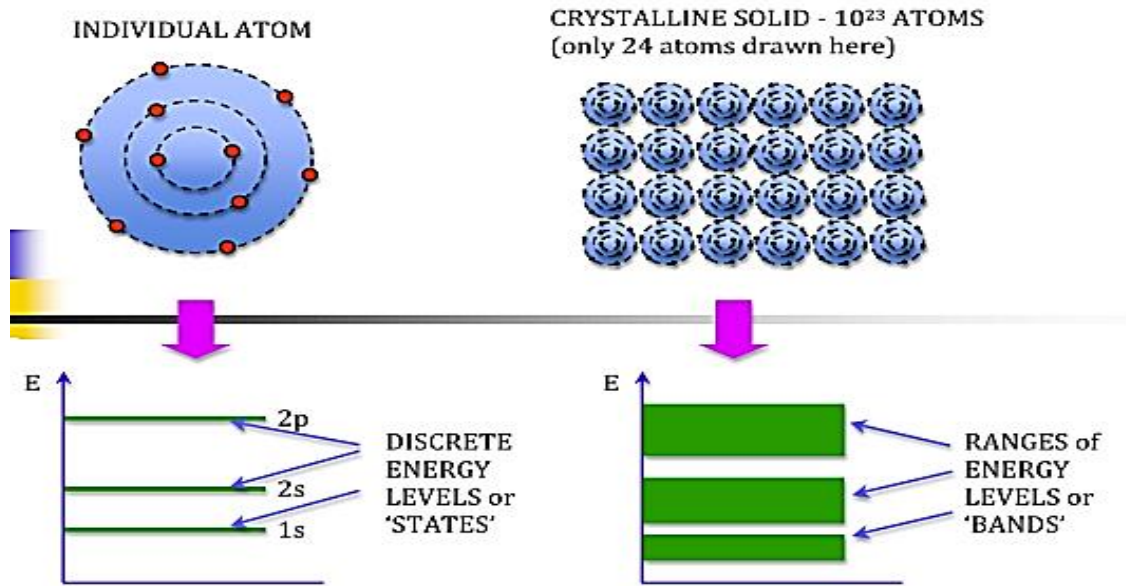
An isolated atom possesses discrete energies of different electrons. Suppose two isolated atoms are brought to very close proximity, then the electrons in the orbits of two atoms interact with each other. So, that in the combined system, the energies of electrons will not be in the same level but changes and the energies will be slightly lower and larger than the original value. So, at the place of each energy level, a closely spaced two energy levels exists. If 'N' number of atoms are brought together to form a solid and if these atoms' electrons interact and give 'N' number of closely spaced energy levels in the place of discrete energy levels, it is known as bands of allowed energies. Between the bands of allowed energies, there are empty energy regions, called forbidden band of energies. Kronig-Penney model supports the existence of these bands of energies (allowed bands and forbidden bands). The mathematical solution for Schrödinger's wave equation is very tedious but it provides a clue in understanding the origin of energy bands.

The formation of energy bands has been explained taking Sodium (Na) metal as an example. When isolated sodium atoms are brought together to form a solid, then the energy levels of the valence electrons spread into bands. The 3S and 3P orbitals electrons energies are shown in fig. These bands are seen to overlap strongly at the interatomic spacing of sodium.

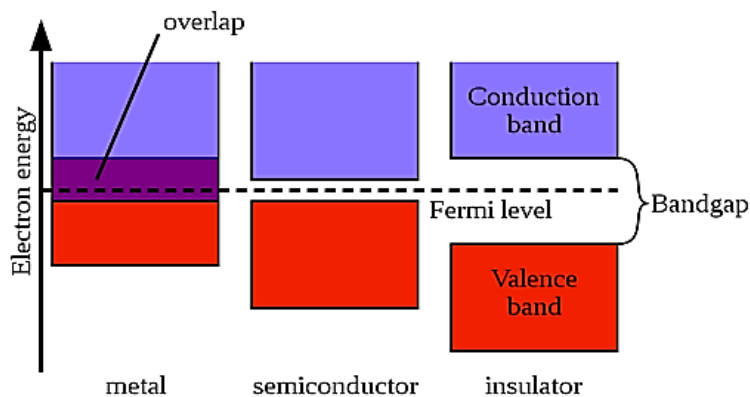
Figure 1 Spreading of energy levels into energy bands in sodium metal



Atoms have been seen to have discrete energy levels. When a huge number of atoms are combined to form a solid however, these discrete energy levels are replaced by discrete ranges of energy, or energy bands, within which there are so many individual allowed energy values that within the bands the distribution can be considered to be continuous. This idea is seen in the following figure:



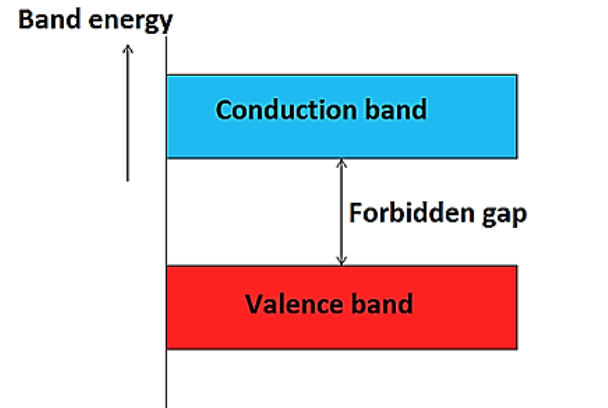
- In between energy bands are ranges of energy which are entirely impossible known as band gaps
- Different substances have different band structures which in many ways dictate the characteristics of that substance in terms of electrical conduction, as there exists an energy band called the conduction band, in which electrons can be propagated as current. The valence band on the other hand is the energy level of valence electrons which are bound into the atomic structure of the substance
- When a substance is placed in an electric field its electrons gain potential energy. For a metal (conductor) the conduction and valence bands overlap, and so the additional energy is enough to free electrons and cause current as there are allowable energy values directly above the initial state. For insulators however, there is often a band gap between the initial energy state and the next possible value, and so a huge amount of energy is required to cause the electron to be freed and accelerated as current. For semiconductors there is still a band gap however it is a lot smaller. This is all seen in the following band diagram:



Important energy bands in solids

There are number of energy bands in solids but three of them are very important. These three energy bands are important to understand the behavior of solids. These energy bands are

- Valence band
- Conduction band
- Forbidden band or forbidden gap



Valence band

The energy band which is formed by grouping the range of energy levels of the [valence electrons](#) or outermost orbit electrons is called as valence band.

Valence band is present below the conduction band as shown in figure. Electrons in the valence band have lower energy than the electrons in conduction band.

The electrons present in the valence band are loosely bound to the nucleus of atom.

Conduction band

The energy band which is formed by grouping the range of energy levels of the [free electrons](#) is called as conduction band. Generally, the conduction band is empty but when external energy is applied the electrons in the valence band jumps in to the conduction band and becomes free electrons. Electrons in the conduction band have higher energy than the electrons in valence band.

The conduction band electrons are not bound to the nucleus of atom.

Forbidden gap

The energy gap which is present between the valence band and conduction band by separating these two energy bands is called as forbidden band or forbidden gap. In solids, electrons cannot stay in forbidden gap because there is no allowed energy state in this region. Forbidden gap is the major factor for determining the electrical conductivity of a solid. The classification of materials as insulators, conductors and semiconductors is mainly depends on forbidden gap.

The energy associated with forbidden band is called energy gap and it is measured in unit electron volt (eV).

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

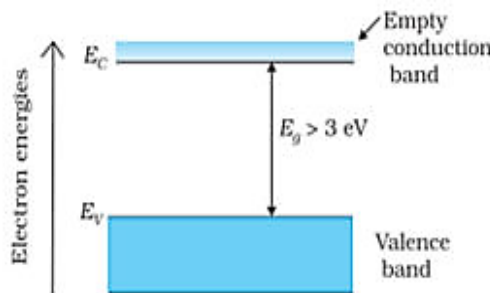
The applied external energy in the form of heat or light must be equal to to the forbidden gap in order to push an electron from valence band to the conduction band.

Distinction between metals, semiconductors and insulators

According to band theory, the electrons in a solid can possess bands of energies called allowed bands of energies and these electrons may not possess some other bands of energies called forbidden bands of energies. The allowed bands of energies and forbidden bands of energies are present alternatively one after another for the electrons of a solid. The top-most band is called Conduction band and the next band below Conduction band is valance band. These two bands are separated by forbidden band. The electrical conduction properties of solids are concerned, only the valance band and conduction band energies of the electron are considered. Completely filled bands and completely empty bands do not contribute to electrical conduction. The electrons in valance band are attached to the lattice and are not free to move If they acquire sufficient energy to cross the forbidden gap E_g , they occupy the conduction band states are available for conduction. On the basis of the band theory, solids are classified into three categories;

1. Insulator
2. Semiconductor
3. Conductor

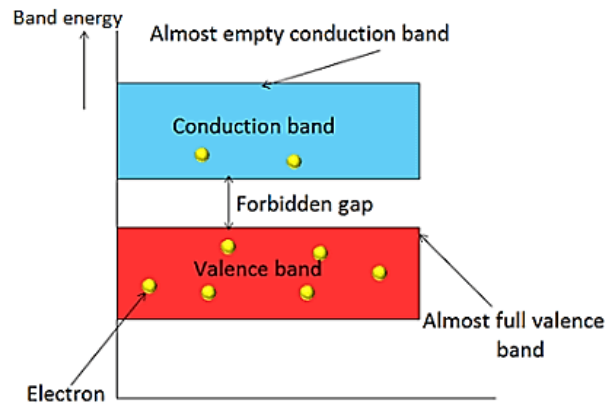
1. **Insulator:** The valence band of those materials remains full of electrons. The conduction band of those materials remains empty. The forbidden energy gap between the conduction band and the valence band is widest. The difference is more than 3 eV. Crossing the forbidden energy gap from valence band to conduction band require large amount of energy. Mica, glass, eboniote etc are the examples of insulators.



Features of Insulators

- A full valance band
 - An empty conduction band
 - A large band gap E_g ; = 3-10 eV
 - Very high resistivity of order of $10^9 \Omega \text{ cm}$
 - Some samples at high temperature and under sufficient electric field, some electrons may move from valance band to conduction band. Hence insulator shows small conductivity at high temperature. e.g. diamond and glass
2. **Semiconductors:** A semiconductor remains partially full valence band and partially full conduction band at the room temperature the energy gap is narrower. The conduction band remains full empty of a semiconductor where the valence band remains full of electrons at absolute zero temperature. The value of $E_g = 1.1 \text{ eV}$ for silicon crystal and $E_g = 0.7 \text{ eV}$ for germanium. It can easily overcome due to thermal

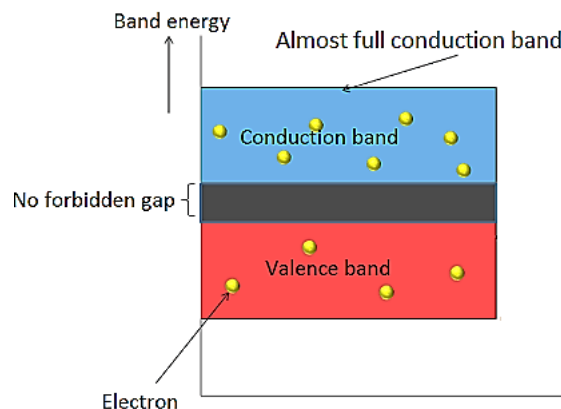
agitation or light. So, silicon and germanium are insulators at absolute zero temperature. On the other hand with the increasing of temperature the electrical conductivity of semiconductors increase.



Features of Semiconductors

- At 0°K , the valance band is completely filled and the conduction band is empty.
- As temperature increases the electron in valance band acquire enough energy to cross the small energy gap and move to CB. Thus the conductivity of semiconductors increases with temperature.
- The electron moving to CB leave behind positive holes in VB . Hence, semiconductor current is the sum of electron and hole current flowing in opposite direction.
- The resistivity varies from 10^{-12} to $10^9 \Omega \text{ cm}$ e.g. $\text{Ge} = E_g = 0.7 \text{ eV}$ and $\text{Si} = E_g = 1.1 \text{ eV}$
- The resistance of semiconductor decreases with increase in temperature.

3. **Conductors:** The valence band and the conduction band overlap each other. There is no forbidden energy gap here so $E_g=0$. At absolute zero temperature large number of electrons remains in the conduction band. The resistance of conductor is very low; large number charge carriers are available here. So, the electricity can pass easily through the conductors. Aluminum, Silver, etc are good conductors



Features of Conductors

- Conductors may be defined as solids characterized by a single energy band called conduction band, which is partially filled at any temperature.

- Alternatively, a conductor as a solid, in which the conduction and valance bands overlap and there is no energy gap between the two bands
- As there is no forbidden gap, there is no structure to establish holes.
- The total current is simply due to the flow of electrons.

Fermi level and Fermi energy

In a solid crystal, the free electrons possess different energies. According to quantum theory, at absolute zero of temperature, the free electrons occupy different energy levels continuously without any vacancy in between filled states. This can be understood by dropping the free electrons of a metal one by one into the potential well. The first electron dropped would occupy the lowest available energy, E_0 (say), and the next electron dropped also occupy the same energy level. The third electron dropped would occupy the next energy level. That is, the third electron dropped would occupy the energy level $E_1 (>E_0)$ and so on because of Pauli's exclusion principle. If the metal contains N (even) number of electrons, they will be distributed in the first $N/2$ energy levels and the higher energy levels will be completely empty as shown in Fig..

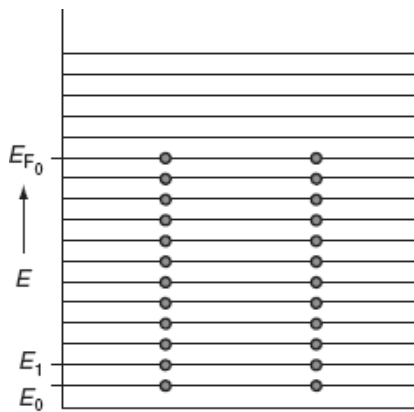


Fig : Distribution of electrons in various energy levels at 0° K.

The highest filled level, which separates the filled and empty levels at 0° K is known as the Fermi level and the energy corresponding to this level is called Fermi energy (E_F). Fermi energy can also be defined as the highest energy possessed by an electron in the material at 0°K. At 0°K, the Fermi energy E_F is represented as E_{F_0} . As the temperature of the metal is increased from 0°K to $T^\circ\text{K}$, then those electrons which are present up to a depth of $K_B T$ from Fermi energy may take thermal energies equal to $K_B T$ and occupy higher energy levels, whereas the electrons present in the lower energy levels i.e., below $K_B T$ from Fermi level, will not take thermal energies because they will not find vacant electron states.

Fermi-Dirac Distribution Function

The probability that a particular quantum state at energy E is filled with an electron is given by Fermi-Dirac distribution function $f(E)$, given by:

$$f(E) = \frac{1}{1 + \exp(E - E_F) / K_B T} \quad \text{where } K_B = \text{Boltzmann constant.}$$

A graph has been plotted between $f(E)$ and E , at different temperatures 0°K , $T_1^\circ\text{K}$, $T_2^\circ\text{K}$, $T_3^\circ\text{K}$ is shown in Fig.

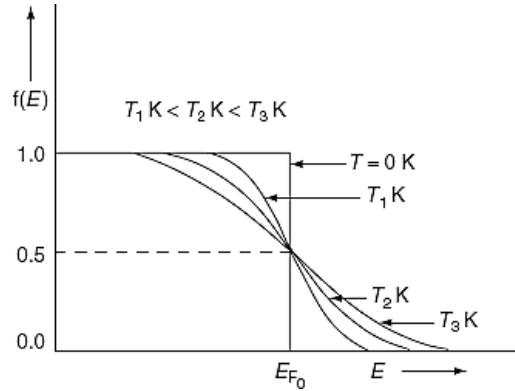


Figure: Graph between $f(E)$ and E

Analytical Treatment at 0°K :

Substitute $T = 0^\circ\text{K}$ in the Fermi-Dirac distribution, we have

$$f(E) = \frac{1}{1 + \exp[(E - E_F)/K_B \times 0]} = 1 \text{ for } E < E_F$$

$$= 0 \text{ for } E > E_F$$

The curve has step-like character with $f(E) = 1$ for energies below E_{F0} and $f(E) = 0$ for energies above E_{F0} . This represents that all the energy states below E_{F0} are filled with electrons and all those above it are empty.

At $T > 0^\circ\text{K}$

$$f(E) = \frac{1}{1 + \exp(E - E_F)/K_B T} < 1 \text{ for } E < E_F$$

$$> 0 \text{ for } E > E_F$$

$$= \frac{1}{2} \text{ for } E = E_F$$

The above condition states that, $T=0^\circ\text{K}$, there is a 50% probability for the electrons to occupy Fermi energy.

The probability function $f(E)$ lies between 0 and 1. Hence there are three possible probabilities namely

$f(E) = 1$ 100% probability to occupy the energy level by electrons.

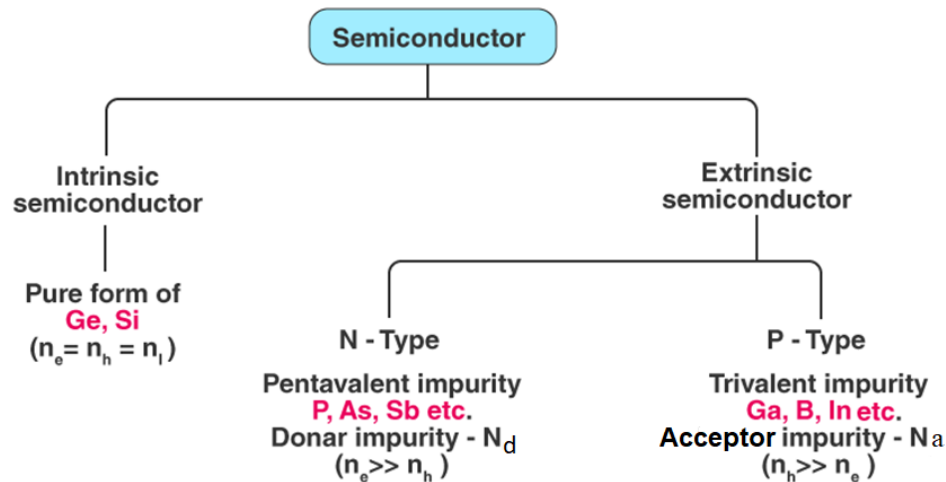
$f(E) = 0$ No probability to occupy the energy levels by electrons and hence, it is empty.

$f(E) = 0.5$ 50% probability of finding the electron in the energy level.

As the temperature is raised from absolute zero to $T_1\text{K}$, the distribution curve begins to depart from step-like function and tails off smoothly to zero. Again with a further increase in temperature to $T_2\text{K}$ and to $T_3\text{K}$, the departure and tailing of the curves increases. This indicates that more and more electrons may occupy higher energy states with an increase of temperature and as a consequence the number of vacancies below the Fermi level increases in the same proportion. At non-zero temperatures, all these curves pass through a point whose $f(E) = 1/2$, at $E = E_F$. So E_F lies half way between the filled and empty states.

Semiconductor

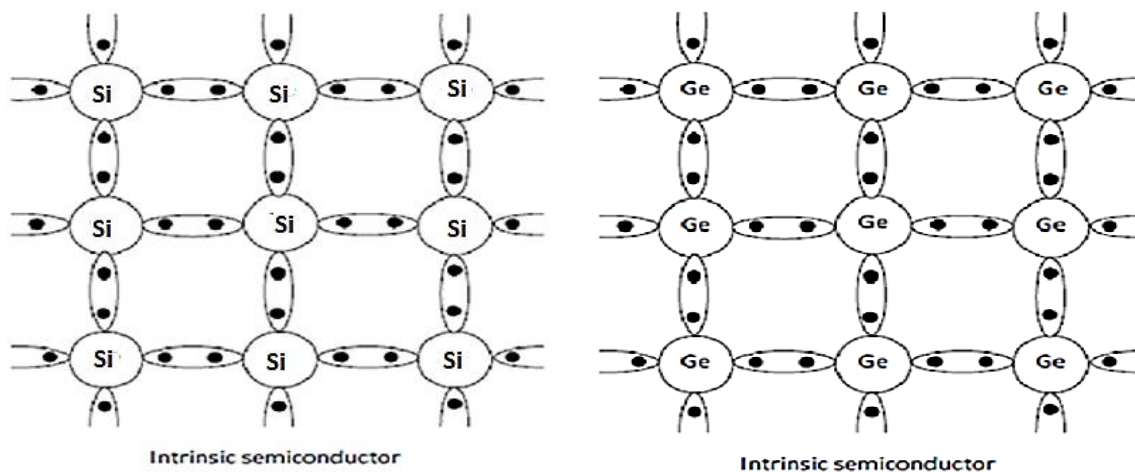
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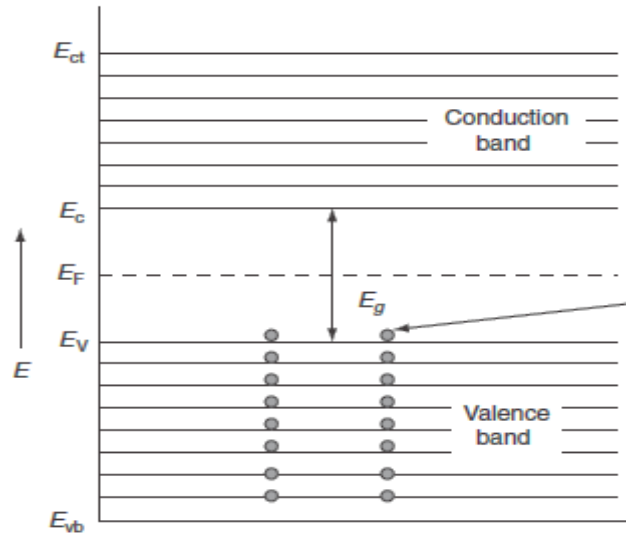


A semiconductor is a material that has a resistivity lies between that of a conductor and an insulator. The conductivity of a semiconductor material can be varied under an external electrical field. Devises made from semiconductor materials are the foundation of modern electronics, including computer, radio, telephones and many other devises. In a metallic conductor, current is carried by the flow of electrons. In semiconductors, current can be carried by either flow of electrons or flow of holes or both. Germanium and Silicon are the best examples for semiconductor materials. Both are tetravalent (i.e. four valence electrons) and both have diamond crystal structure. At $T=0^{\circ}\text{K}$, the semiconductor acts as insulator. Semiconductors are classified into two types, they are- 1. Intrinsic semiconductor 2. Extrinsic semiconductor

Intrinsic semiconductor:

A pure semiconductor is called intrinsic semiconductor. A pure crystal of Germanium and Silicon is an example for intrinsic semiconductor. At $T=0^{\circ}\text{K}$, the semiconductor acts as insulator. Germanium and silicon are tetravalent atoms (i.e. four valence electrons) and both have diamond crystal structure. In order to gain stability each silicon atom makes four covalent bonds with the four surrounding silicon atoms by sharing of their valence electrons as shown in figure.





At 0°K, the semiconductor crystal acts as a perfect insulator since the covalent bonds are strong and no free electrons are available. At room temperature ($T > 0^\circ\text{K}$) the semiconductor gives some conductivity since some of the covalent bonds are broken due to the thermal energy supplied to the crystals. The vacancy of an electron in the covalent is called hole. Thus the valence band has holes and conduction band has electrons. For silicon energy gap is 1.12eV and for germanium energy gap is 0.7eV. In intrinsic semiconductor the electron concentration is equal to the hole concentration. In intrinsic semiconductors Fermi level is always lies between valence band and conduction band.

$$E_F = \frac{E_C + E_V}{2}$$

The law of mass action for intrinsic semiconductors is $np = n_i^2$

In intrinsic semiconductor the carrier concentration of electrons (n) and holes (p) is

$$n = N_c e^{-\frac{(E_C - E_F)}{KT}}$$

$$p = N_v e^{-\frac{(E_F - E_V)}{KT}}$$

Intrinsic carrier concentration:

In intrinsic semiconductor

$$n = p$$

Hence $n = p = n_i$ is called intrinsic carrier concentration

$$n_i^2 = N_c e^{-\frac{(E_C - E_F)}{KT}} \cdot N_v e^{-\frac{(E_F - E_V)}{KT}}$$

$$n_i^2 = N_c \cdot N_v e^{-\frac{(E_C - E_F)}{KT}} \cdot e^{-\frac{(E_F - E_V)}{KT}}$$

$$n_i^2 = N_c \cdot N_v e^{-\frac{(E_C - E_V)}{KT}}$$

Where $E_C - E_V = E_g$ is the forbidden gap.

$$n_i^2 = N_c \cdot N_v e^{-\frac{E_g}{KT}}$$

$$n_i = (N_c \cdot N_v)^{1/2} e^{-\frac{E_g}{2KT}}$$

The above equation shows the intrinsic carrier concentration.

Fermi level in intrinsic semiconductor:

In intrinsic semiconductor $n = p$

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

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

$$\frac{N_v}{N_c} = e^{\frac{2E_F - (E_c + E_v)}{KT}}$$

Taking logarithms on both sides

$$\log_e \frac{N_v}{N_c} = \frac{2E_F - (E_c + E_v)}{KT}$$

$$\because \log_e e^x = x$$

$$KT \log_e \frac{N_v}{N_c} = 2E_F - (E_c + E_v)$$

$$2E_F = (E_c + E_v) + KT \log_e \frac{N_v}{N_c}$$

$$\frac{N_v}{N_c} = \frac{2 \left(\frac{2\pi m_h^* KT}{h^2} \right)^{\frac{3}{2}}}{2 \left(\frac{2\pi m_e^* KT}{h^2} \right)^{\frac{3}{2}}}$$

$$\frac{N_v}{N_c} = \frac{(m_h^*)^{\frac{3}{2}}}{(m_e^*)^{\frac{3}{2}}}$$

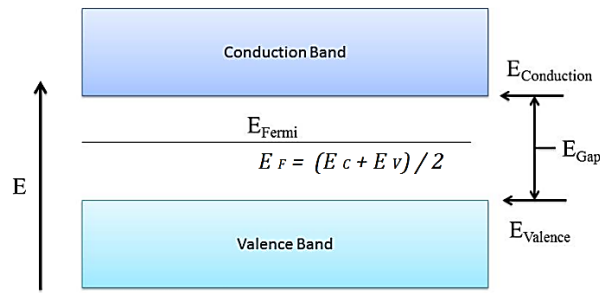
Therefore

$$\frac{2E_F - (E_c + E_v)}{KT} = \log_e \frac{(m_h^*)^{\frac{3}{2}}}{(m_e^*)^{\frac{3}{2}}}$$

Normally m_h^* is greater than m_e^*

Since $\log_e \frac{m_h^*}{m_e^*}$ is very small, so Fermi level is just above the middle of the Energy Band Gap and slightly rises with increase in temperature. In case of Si and Ge, $m_h^* \approx m_e^*$, hence the Fermi level lies at the middle of energy gap.

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



Hence Fermi level lies in middle of Energy band gap.

Extrinsic Semiconductor:

The conductivity of semiconductors can be greatly improved by introducing a small number of suitable replacement atoms called impurities. The process of adding impurity atoms to the pure semiconductor is called doping. Usually, only 1 atom in 10^7 is replaced by a dopant atom in the doped semiconductor.

An extrinsic semiconductor can be further classified into:

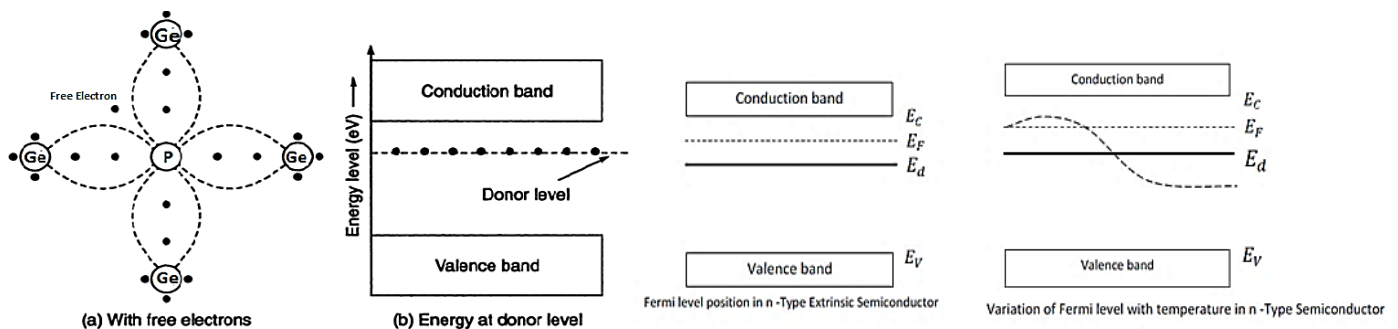
n- Type extrinsic semiconductor

p- Type extrinsic semiconductor

N- Type extrinsic semiconductor:-

Generally pure semiconductors has four valence electrons and can form four covalent bonds. When a pentavalent impurity, like P or Antimony (Sb) ,(which have five valence electrons) is added to any Ge, the four electrons of Ge bond with 4 electrons of 'P' and one extra electron is left out alone. That, it is ready to 'donate' this electron. Such type of semiconductor is called 'N-type semiconductor' or 'DONOR'. These free electrons are responsible for electrical conduction.

In a N - type semiconductor holes are minority current carriers and electrons are majority current carriers. In a N- type semiconductor, the energy level of this donor impurity lies just below the conduction band of the semiconductor. This energy level is called **donor level** and it is represented as E_d .



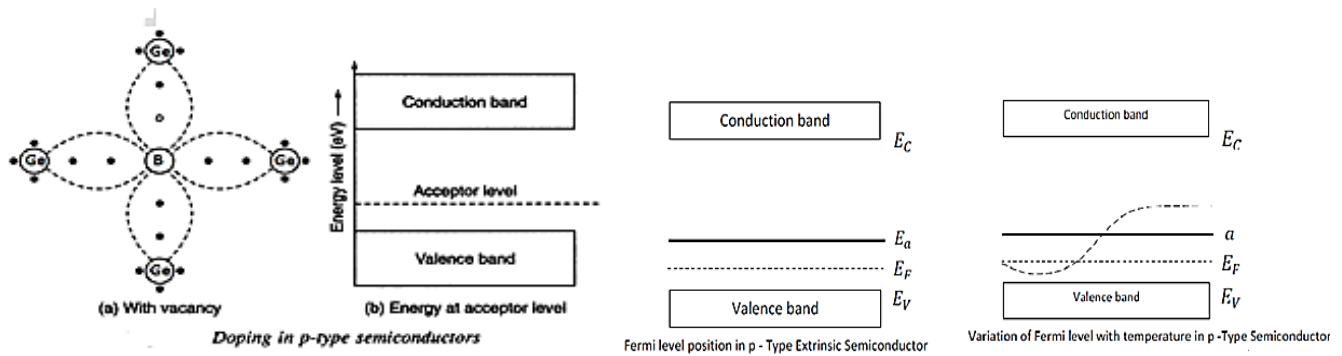
In n-type semiconductors, the Fermi is always lies between conduction level and donor level at lower temperatures but at higher temperatures the Fermi level moves towards the intrinsic Fermi level.

$$E_F = \frac{(E_d + E_c)}{2} - \frac{KT}{2} \log \left(\frac{N_c}{N_d} \right)$$

P – Type Semiconductor:

Generally pure semiconductor has 4 valence electrons and can form four covalent bonds. When a trivalent impure atoms (which have three valence electrons) like Gallium (Ga), Al, In or Boron (B) is added, these three valence electrons form three covalent bonds with, say Ge atom. But the 4th electron doesn't have a pair, so a 'hole' exists. This means that it's ready to 'accept' an electron to fill the hole. Thus a small amount of trivalent impurity creates 'majority of holes', which are positive, and are called as 'p-type semiconductor' or 'Acceptors'. In a P - type semiconductor holes are majority current carriers and electrons are minority current carriers. In a P- type semiconductor, the energy level of this acceptor impurity lies just above the valence band. This energy level is called acceptor level and it is represented as E_a .

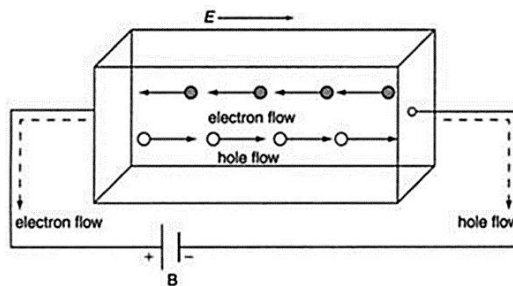
In p-type semiconductor, the Fermi level is always lies between valence level and acceptor level at lower temperatures but at higher temperatures the Fermi level moves towards the intrinsic Fermi level.



$$E_F = \frac{(E_V + E_a)}{2} + \frac{KT}{2} \log \left(\frac{N_V}{N_a} \right)$$

Conductivity of semiconductor:

In semiconductor, the conduction band electron and valence band hole participate in electrical conduction. To obtain expression for electrical conductivity consider an intrinsic semiconductor bar which is connected to external battery as shown in fig.



The electric field exist along x direction. The field accelerate electrons (conduction electrons) along negative X-direction and holes along positive X-direction. They starts moving with a constant velocity called Drift velocity v_d

The total current in the semiconductor (due to both electron and hole)

$$I = I_e + I_h$$

or total current density

$$J = J_e + J_h \dots \dots (1)$$

In order to find the current density of electrons, let the concentration of electrons are 'n', charge is 'e' and drift velocity is 'v_e', Then

$$J_e = nev_e \dots \dots \dots (2)$$

The drift velocity produced per unit electric field is called 'mobility', Thus

$$\mu_e = \frac{v_e}{E} \quad \text{or} \quad \mu_e E = v_e$$

Substituting the value of v_e in eq. 2

$$J_e = ne\mu_e E \dots \dots \dots (3)$$

From Ohms law J = σE Therefore J_e = σ_eE

$$\sigma_e E = ne\mu_e E$$

or

$$\sigma_e = ne\mu_e \dots \dots \dots (4)$$

Similarly current density for holes

$$J_h = \sigma_h E = pe\mu_h E \dots \dots \dots (5)$$

and conductivity of holes

$$\sigma_h = pe\mu_h \dots \dots \dots (6)$$

Substituting value of J_e and J_h from eq. 3 and 5 in eq.1, we get

$$J = (ne\mu_e + pe\mu_h)E$$

and conductivity

$$\sigma = (\sigma_e + \sigma_h) = (ne\mu_e + pe\mu_h) \dots \dots \dots (7)$$

Effect of Temperature on Conductivity

We have

$$n_i = CT^{3/2}e^{-E_g/2KT}$$

$$n_i = (n + p)$$

Therefore

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

$$\sigma = CT^{3/2}e^{-E_g/2KT}e(\mu_e + \mu_h) \dots \dots \dots (8)$$

The mobilities of carrier depend upon temperature as

$$\mu \propto \frac{1}{T^{3/2}}$$

For Electrons $\mu_e \propto \alpha T^{-3/2}$ and for holes $\mu_h \propto \beta T^{-3/2}$

$$(\mu_e + \mu_h) = (\alpha + \beta)T^{-3/2} = \gamma T^{-3/2} \dots \dots (9)$$

Using equation no. 9 in equation no. 8

$$\sigma = CT^{3/2}e^{-E_g/2KT}e\gamma T^{-3/2}$$

$$\sigma = Ce^{-E_g/2KT}e\gamma$$

Let

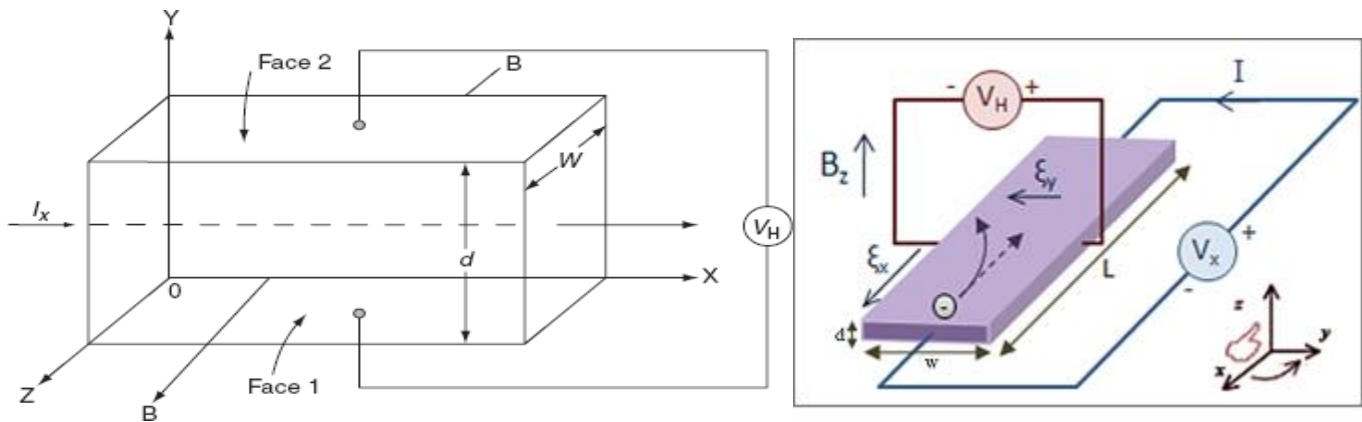
$$B = C e \gamma$$

$$\sigma = B e^{-E_g/2KT}$$

Hall Effect:

When conductor (metal or semiconductor) carrying a current is placed in a transverse magnetic field, an electric field is produced inside the conductor in a direction normal to both the current and the magnetic field. This phenomenon is known as “**Hall effect**” and the generated voltage is called “**Hall voltage**”.

Hall Effect can be explained by considering a rectangular block of an extrinsic semiconductor in which current is flowing along the positive X-direction and magnetic field B is applied along Z-direction as shown in Fig.



Suppose if the semiconductor is n-type, then mostly the carriers are electrons and the electric current is due to the drifting of electrons along negative X-direction or if the semiconductor is p-type, then mostly the carriers are holes and the electric current is due to drifting of the holes along positive X-direction. As these carriers are moving in magnetic field in the semiconductor, they experience Lorentz force (FL) equal to $Bevd$, where v_d is the drift velocity of the carriers.

The direction of this force can be obtained by applying Fleming’s left-hand rule in electromagnetism. [If we stretch the thumb, fore finger and middle finger in three perpendicular directions so that the fore finger is parallel to the magnetic field and the middle finger is parallel to the current direction, then thumb represents the direction of force on the current-carrying carriers]. The Lorentz force is exerted on the carriers in the negative Y-direction. Due to Lorentz force, more and more carriers will be deposited at the bottom face [face 1] of the conductor. The deposition of carriers at the bottom face is continued till the repulsive force due to accumulated charge, balances the Lorentz force. After some time of the applied voltage, both the forces become equal in magnitude and act in opposite direction, then the potential difference between the top and bottom faces is equal to Hall voltage and that can be measured.

At equilibrium, the Lorentz force on a carrier

$$F_L = Bev_d \dots \dots \dots (1)$$

and the Hall force

$$F_H = eE_H \dots \dots \dots (2)$$

where E_H is the Hall electric field due to accumulated charge.

At equilibrium,

$$F_H = FL$$

$$eE_H = Bev_d$$

$$\therefore E_H = Bv_d \dots \dots \dots (3)$$

If 'd' is the distance between the upper and lower surfaces of the slab, then the Hall field

$$E_H = \frac{V_H}{d} \dots \dots \dots (4)$$

In n-type material, $J_x = -nev_d$

$$\text{Or } v_d = -\frac{j_x}{ne} \dots \dots \dots (5)$$

where n is free electron concentration, substituting Equation (5) in (3) gives:

$$E_H = \frac{-Bj_x}{ne} \dots \dots \dots (6)$$

For a given semiconductor, the Hall field E_H is proportional to the current density J_x and the intensity of magnetic field 'B' in the material.

$$\text{i.e. } E_H \propto J_x B$$

or

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

where R_H = Hall coefficient

Equations (6) and (7) are same so, we have:

$$R_H j_x B = \frac{-Bj_x}{ne} \quad (\text{or}) \quad R_H = \frac{-1}{ne} = \frac{-1}{\rho} \dots \dots \dots (8)$$

where ρ is charge density. Similarly for p-type material,

$$R_H = \frac{1}{ne} = \frac{1}{\rho} \dots \dots \dots (9)$$

Using Equations (8) and (9), carrier concentration can be determined.

Thus, the Hall coefficient is negative for n-type material. In n-type material, as more negative charge is deposited at the bottom surface, so the top face acquires positive polarity and the Hall field is along negative Y-direction. The polarity at the top and bottom faces can be measured by applying probes. Similarly, in case of p-type material, more positive charge is deposited at the bottom surface. So, the top face acquires negative polarity and the Hall field is along positive Y-direction. Thus, the sign of Hall coefficient decides the nature of (n-type or p-type) material. The Hall coefficient can be determined experimentally in the following way:

Multiplying Equation (7) with 'd', we have:

$$E_H d = V_H = R_H J_x B d \dots \dots (10)$$

From Fig. 1, we know the current density (J_x)

$$J_x = \frac{I_x}{Wd}$$

Then, Equation (10) becomes:

$$V_H = R_H \frac{I_x}{Wd} B d = R_H \frac{I_x B}{W} \quad (\text{or}) \quad R_H = \frac{V_H W}{I_x B} \dots \dots \dots (11)$$

Substituting the measured values of V_H , I_x , B and W in Equation (11), R_H is obtained. The polarity of V_H will be opposite for n- and p-type semiconductors.

The mobility of charge carriers can be found by using the Hall Effect, for example, the conductivity of electrons is:

$$\sigma_n = ne\mu_n$$

Or

$$\mu_n = \frac{\sigma_n}{ne} = \sigma_n R_H \dots \dots \dots (12)$$

Using Equations (11) and (12), we get:

$$\mu_n = \frac{\sigma_n V_H W}{I_x B}$$

Hall Angle:

$$\text{Hall Angle, } \phi_H = \tan^{-1} \frac{E_H}{E_x}$$

$$\text{From equation (2), } E_H = \frac{V_H}{d}$$

Electric field component in X-direction can be given as:-

$$\begin{aligned} E_x &= \frac{\text{Voltage drop along the length}}{\text{Length of Specimen}} \\ &= \frac{IR}{l} = \frac{I \times \text{resistivity} \times l}{l \times A} = \frac{I}{A} \times \text{resistivity} = J \times \frac{1}{\sigma} \end{aligned}$$

Substituting the values of E_x and E_H in the expression of Hall's Angle we have: -

$$\begin{aligned} \phi_H &= \tan^{-1} \frac{E_H}{E_x} = \tan^{-1} \frac{V_H/d}{J/\sigma} = \tan^{-1} \frac{BI/\rho wd}{J/\sigma} = \tan^{-1} \frac{BJ/\rho}{J/\sigma} = \tan^{-1} \frac{B\sigma}{\rho} \\ &= \tan^{-1} \sigma B R_H = \tan^{-1} \mu B \end{aligned}$$

APPLICATIONS OF HALL EFFECT

1. It is used to determine whether the material is p-type or n-type semiconductor. (ie) if R_H is negative then the material n-type. If the R_H is positive then the material p-type.

2. It is used to find the carrier concentration
3. It is used to find the mobility of charge carriers μ_e , μ_h .
4. It is used to find the sign of the current carrying charges.
5. It is used to design magnetic flux meters and multipliers on the basis of Hall voltage. It is used to find the power flow in an electromagnetic wave.