

## THEORIES OF BONDING IN METALS.

(1)

① What is metallic bonding? write about the free electron theory of metal.

Ans. Metallic bonding: The force that binds a metal ion to the mobile electrons within its sphere of influence is known as metallic bond.

Free electron theory: This theory is also called Drude-Lorentz theory.

According to this theory each atom in a metal crystal loses all its valence electrons. The electrons thus obtained form an electron pool and the resulting positively charged metal ions are believed to be held together by this electron pool. The positively charged metal ions (kernels) do not float randomly in the sea of electrons. They have definite position at measurable distances from each other in the crystal lattice.

The valence electrons are not attached to any individual ion or pairs of ions but belong to the crystal as a whole. They are free to move throughout the lattice as gas molecules move freely throughout their container. Thus metallic solids may be supposed as a collection of positive atomic cores immersed in a sea of mobile electrons.

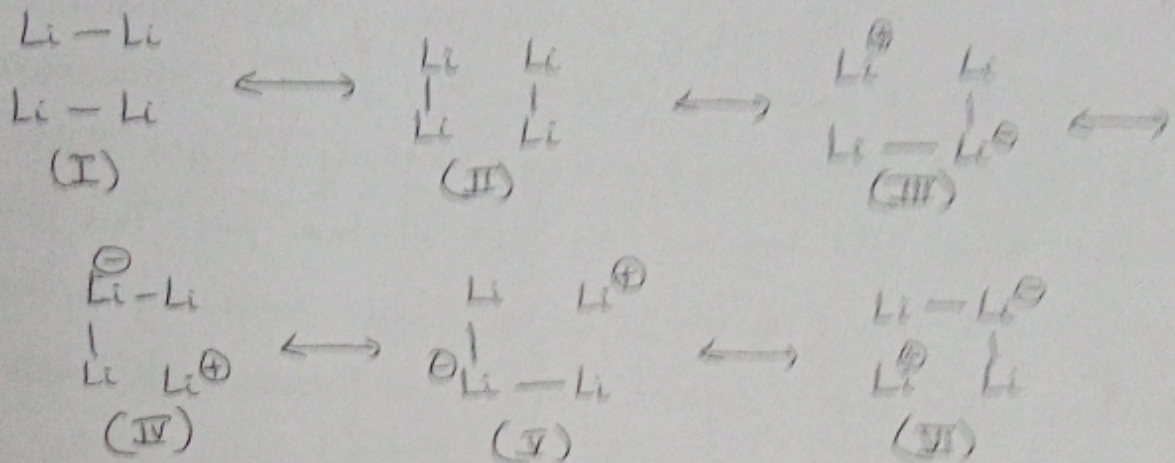
This theory explains qualitatively a number of metallic properties like metallic lustre, thermal conductivity, electrical conductivity, elasticity, malleability and ductility.

② Explain about the valence bond theory of metals. shorter

Ans. Valence bond theory: It was proposed by Pauling. According to it the metallic bonding is essentially covalent in nature and metallic structure involves resonance of electron-pair bonds between each atom and its nearest neighbours.

Consider the case of Lithium metal in which each atom has 8 nearest neighbours shown by X-ray studies. The configuration of Li atom is  $1s^2 2s^1$ . It shows that Li atom has only one valence electron which is insufficient to form bonds between each atom of Li and all its neighbours so it is assumed that resonance takes place throughout the lithium solid.

Although various resonance forms may be drawn as



Although only four atoms have been shown in these forms, the actual bonding includes all the atoms of the crystal and is three dimensional.

Resonance in structures I and II is called synchronised resonance with the shift of two bonds. Resonance in structures III, IV, V and VI is unsynchronised resonance where only one bond is shifted. It results in a single ion forming two bonds.

The electronic configuration of Li atom is  $1s^2 2s^1$ . Since the energy of  $2s$ -orbital is close to that of vacant  $2p$ -orbitals, an electron from  $2s$ -orbital of one lithium atom can be easily transferred to one of the 3 vacant  $2p$ -orbitals of other Li atom and converting it as  $\text{Li}^-$  ion. The Li atom which gives the electron to other atom becomes  $\text{Li}^+$  ion. Now  $2s$  and  $2p_z$ -orbitals of  $\text{Li}^-$  ion hybridise together to form two  $sp^2$ -hybrid orbitals. These hybrid orbitals which are singly filled form two covalent bonds with other two other Li atoms.

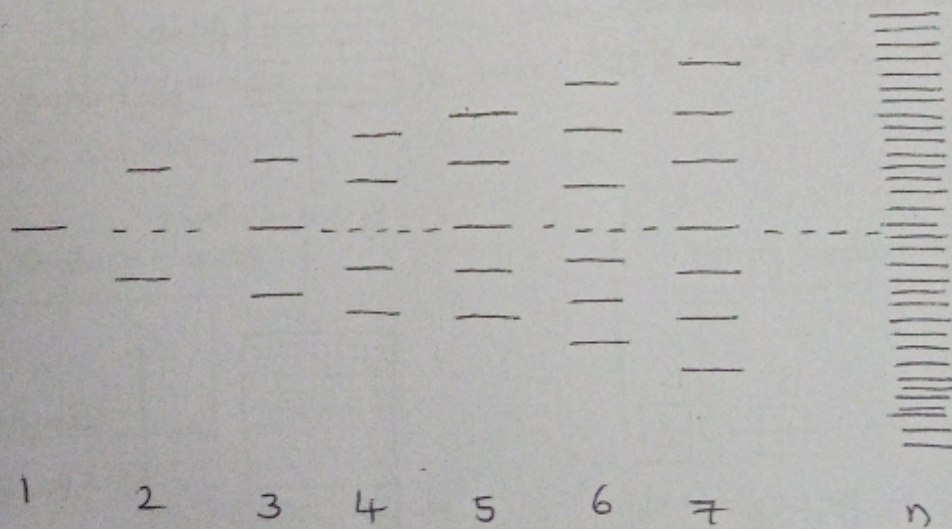
The two vacant  $2p_y$  and  $2p_x$  orbitals on  $\text{Li}^-$  ion can accept the conductivity electrons and thus contribute to metallic conduction. These two vacant  $2p$ -orbitals are called as metallic orbitals.

Q. Explain Band theory. (10 marks)

Ans: Band theory (Molecular orbital theory): According to this theory metallic bonding results from the delocalisation of the free electron orbitals over all the atoms of a metal crystal.

The total number of molecular orbitals formed will be equal to the total number of atomic orbitals involved. When two atomic orbitals combine, two molecular orbitals are obtained. Out of these, one is bonding molecular orbital and other is anti-bonding molecular orbital. When three atomic orbitals combine, three molecular orbitals are obtained i.e. bonding molecular orbital, non-bonding molecular orbital and anti-bonding molecular orbital. Similarly when  $n$  atomic orbitals combine,  $n$  molecular orbitals are formed.

In a metal crystal, a large number of atoms will be present. So large number of molecular orbitals will be formed. The energy difference between these molecular orbitals will be very small and hence will be very close to one another. These closely spaced molecular orbitals are considered as an energy band. Hence the theory is called band theory.



Formation of  $n$  molecular orbitals formed by a combination of  $n$  atomic orbitals

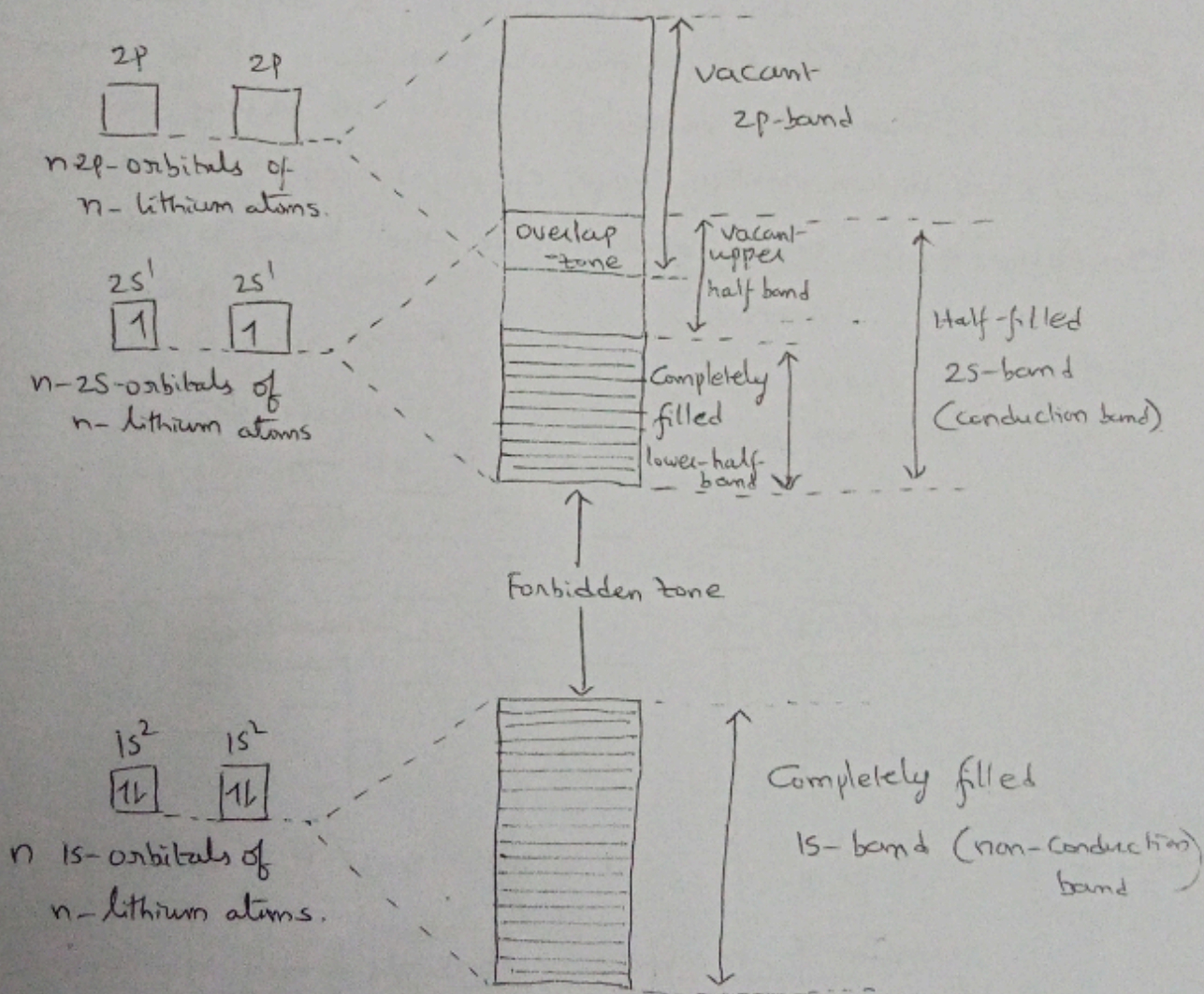
We know that a ~~solid~~ <sup>metal</sup> crystal may be supposed to contain energy bands. (Energy bands formed by the inner energy levels are known as non-conduction bands and are very narrow) The energy bands obtained from the valence levels are quite wide and are known as valence bands.

The valence bands which are completely filled are called non-conduction bands while those which are partially filled are called conduction bands.

The level below which all energy levels are filled is termed Fermi level which may fall within a band or within the gap between the bands.

The energy bands where the electrons can move are called permitted bands (Brillouin zones). The permitted bands are separated from each other by the energy gap <sup>is</sup> ~~are~~ called forbidden zone (or) forbidden energy gap.

Consider the case of lithium crystal. Electronic configuration of Li atom is  $1s^2 2s^1 2p^0$ . If  $n$  atoms of lithium metal are allowed to combine to form lithium crystal, they will form three energy bands.



Q. What are conductors, insulators and semi-conductors? ✓

Ans. Conductors (metals): The materials in which plenty of electrons are available for electric conduction are called conductors.

In terms of energy bands the conduction band of a conductor is partly filled and contains a very large number of electrons. These electrons can be promoted to the nearby vacant levels in the same band by electric or thermal energy. This explains the high electrical and thermal conductivity of metals.

Insulators (non-metals): The materials in which valence electrons are bound tightly to their parent atom are called insulators. Their electrical conductivity is very low.

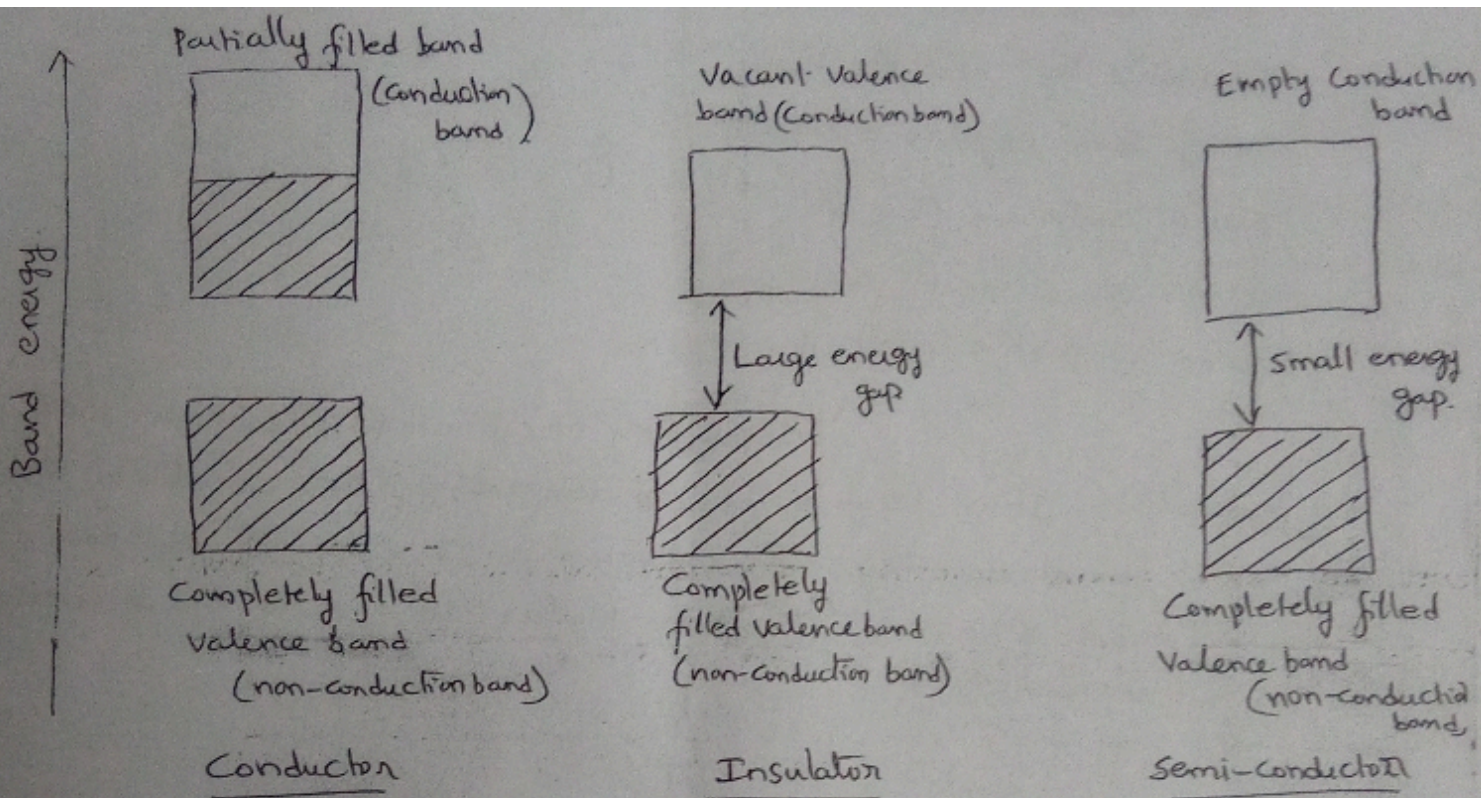
In terms of energy bands, an insulator has empty conduction band. The energy gap between the valence shell band which is completely filled (non-conduction band) and the conduction band is very large. Thus energy required for shifting an electron from the completely filled valence shell band to the empty conduction band is very high and is not normally available. This explains that non-metals are insulators.

Semi-conductors: The materials whose electrical properties lie between those of insulators or conductors are called semi-conductors.

When the semi-conductors are in their pure form, they are called intrinsic semi-conductors.

Ex: Silicon and Germanium are common examples.

When substances (normally insulators) can be made semi-conductors by the addition of impurities, they are called extrinsic semi-conductors. They may be n-type and p-type semiconductors.

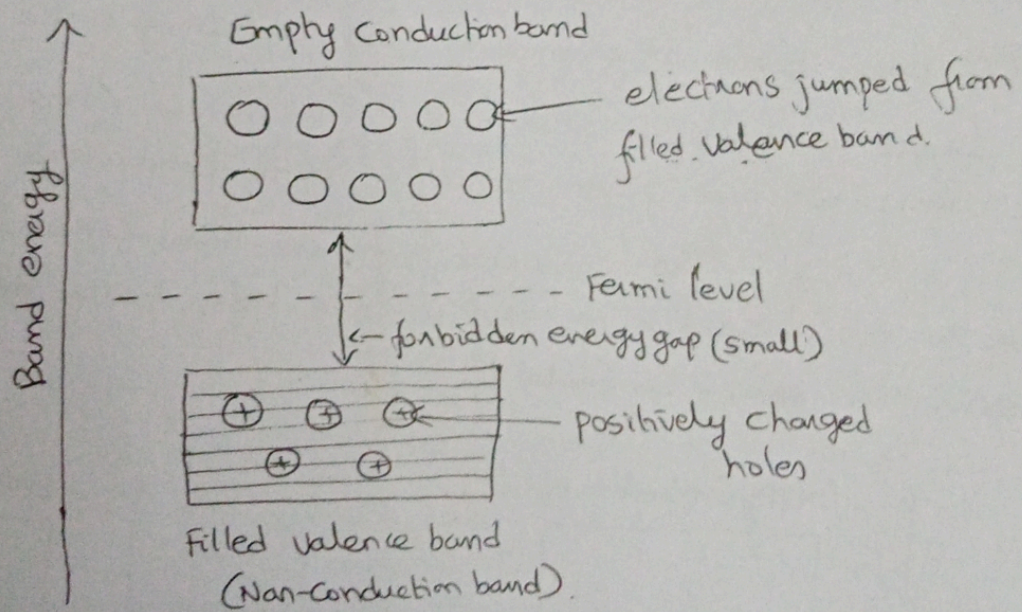


Q. what are intrinsic and extrinsic semiconductors? Explain.

Ans. Intrinsic Semi-Conductors: <sup>When</sup> Semi-Conductors are in their pure form they are called intrinsic semi-conductors.

Silicon and germanium are common examples of it. At absolute zero, these materials are practically insulators.

In terms of energy bands these have filled valence band (non-conduction band) and empty conduction band. The forbidden energy gap between them is so small that even at room temperature, <sup>some</sup> many electrons from the filled valence band jump to the vacant conduction band. This shows low thermal conductivity. As the temperature is ~~raised~~ increased, width of the forbidden energy gap is decreased and hence some more electrons jump to the conduction band. So ~~with~~ the increase in temperature, increases the conductivity.



~~It is~~ In this Fermi level lies exactly in the middle of the energy gap. It is to be noted that for each electron liberated into the conduction band, a positively charged hole is created in the valence band. Number of holes is equal to the number of electrons jumped to the conduction band.

Extrinsic Semi-Conductors: Sometimes substances which are normally insulators can be made semi-conductors when small amounts of impurities are added to them. Such substances are called extrinsic semi-conductors.

Depending on the nature of impurity added, extrinsic

Semi-conductors are of two types.

① n-type extrinsic semi-conductors: These are obtained when an impurity atom to be added has more <sup>Extra</sup> (external) electrons than the parent insulator atom.

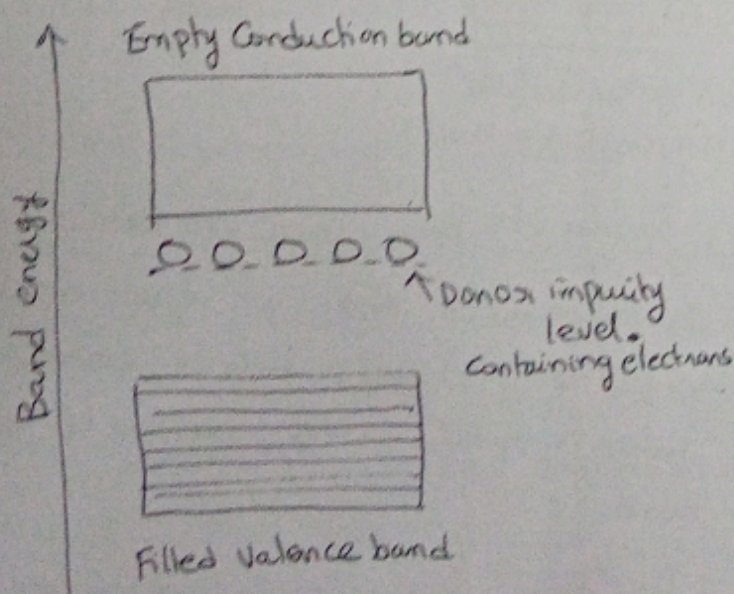
Ex: when phosphorous (or) Arsenic (or) Antimony (all containing five valence electrons) are added to pure silicon or germanium (both containing four valence electrons), we get n-type semi-conductors.

Phosphorous, Arsenic and Antimony are called donor impurities. Crystals of Si or Ge are ~~sem~~ semi-conductors because of the presence of extra electrons in donor impurities, hence the name n-type extrinsic semi-conductors.

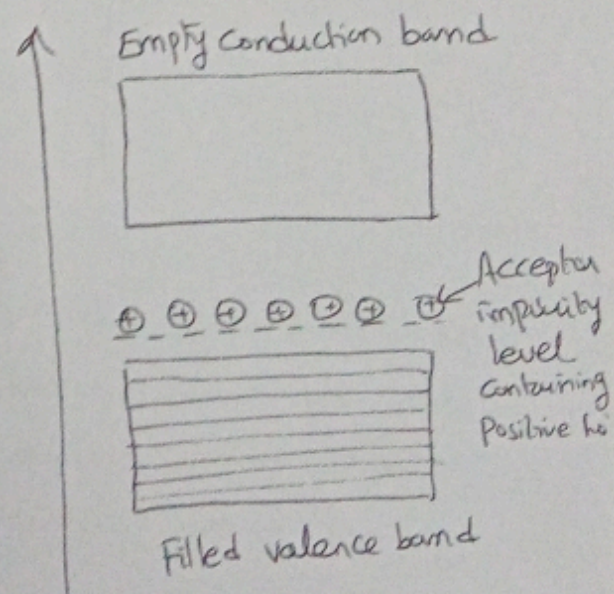
② p-type extrinsic semi-conductors: These are obtained when an impurity atom to be added has fewer (external) <sup>Extra</sup> electrons than the parent insulator atoms.

Ex: when boron or aluminium (both containing three valence electrons) atoms are added to pure silicon or germanium (both containing four valence electrons), we get p-type extrinsic semi-conductors.

The conduction in these semi-conductors can be thought due to the migration of the positive hole, hence the name p-type extrinsic semi-conductors.



n-type extrinsic semi-conductor.



p-type extrinsic semi-conductor.