

## INORGANIC CHEMISTRY

### UNIT III : SOLID STATE III

#### Metallc Crystals:

Metallc crystals consist of an assemblage of positive ions immersed in a sea of mobile electrons. Thus each electron belong to a number of positive ion and each positive ion belong to a number of electrons. The force that binds a metal ion to a number of electrons within its sphere of influence is known as metallc bond. This force of attraction is strong and is thus responsible for a compact solid structure of metals.

#### FREE ELECTRON AND BAND THEORIES:

In the case of a single isolated atom, there are various discrete energy levels. In solids, atoms are arranged in a systematic space lattice and each atom is influenced by neighbouring atoms. The closeness of atoms results in intermixing of electrons of neighbouring atoms. Due to this, number of permissible energy level increases. Hence in the case of solid, instead of permissible single energy level associated with single atom, there will be bands of energy levels. A set of such closely packed energy levels is called an energy band.

The completely filled levels are known as core levels and the electrons filling these levels are known as core electrons. The electrons in the outermost level are called valence electrons. The partially filled outermost level is valence level and the permitted levels which are vacant are known as conduction levels.

In solids, there are a large number of atoms which are very close to each other. The energy of s or p level is of order of eV, therefore the levels are very closely spaced. The first orbit electrons form a band called first energy band. Similarly second orbit electrons form second energy band and so on.

Valence band:

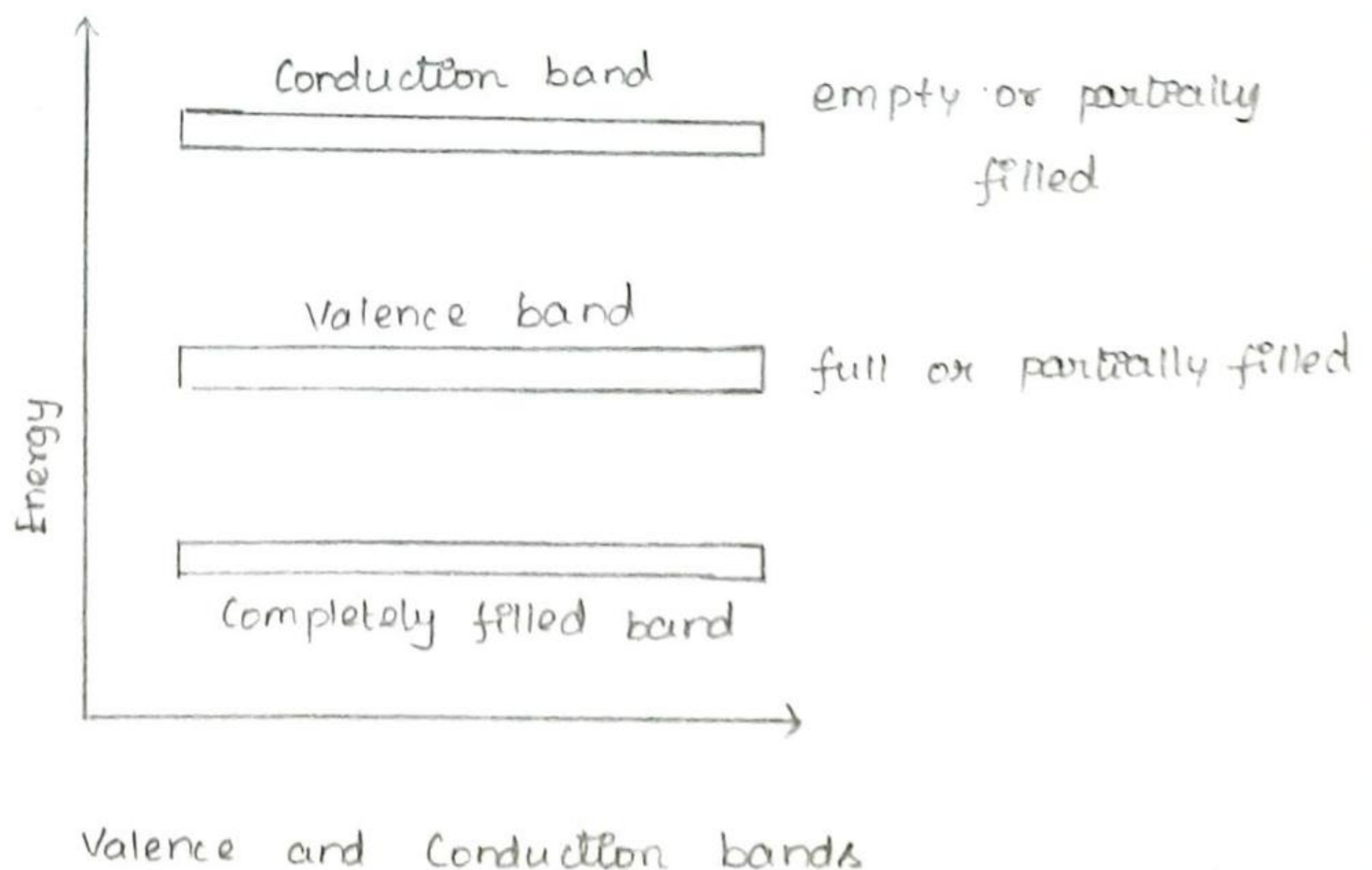
In solids, the electrons revolve around the nucleus in certain permitted energy levels. The electrons in the inner shell are strongly bound to the nucleus. A band which is occupied by valence electrons or a band having highest energy is called as valence band. The valence band may be partially or completely filled. This band can never be empty.

Conduction band:

In some materials, the valence electrons are loosely attached to nucleus. Even at room temperature, some valence electrons can leave the valence band. These are called free electrons. They are responsible for conduction of current in a conductor and henceforth called as conduction electrons. The band occupied by these electrons is called conduction band. This band may be empty or partially filled band.

Forbidden energy gap:

The separation between valence band and conduction band is known as forbidden energy gap. If an electron is to be transferred from valence band to conduction band, external energy is required, which is equal to forbidden energy gap.



### Insulators:

In Insulators, the forbidden energy gap is very large.

The forbidden energy gap is more than 3eV and almost no electrons are available for conduction. Therefore very large amount of energy must be supplied to valence electron to enable it to move to the conduction band.

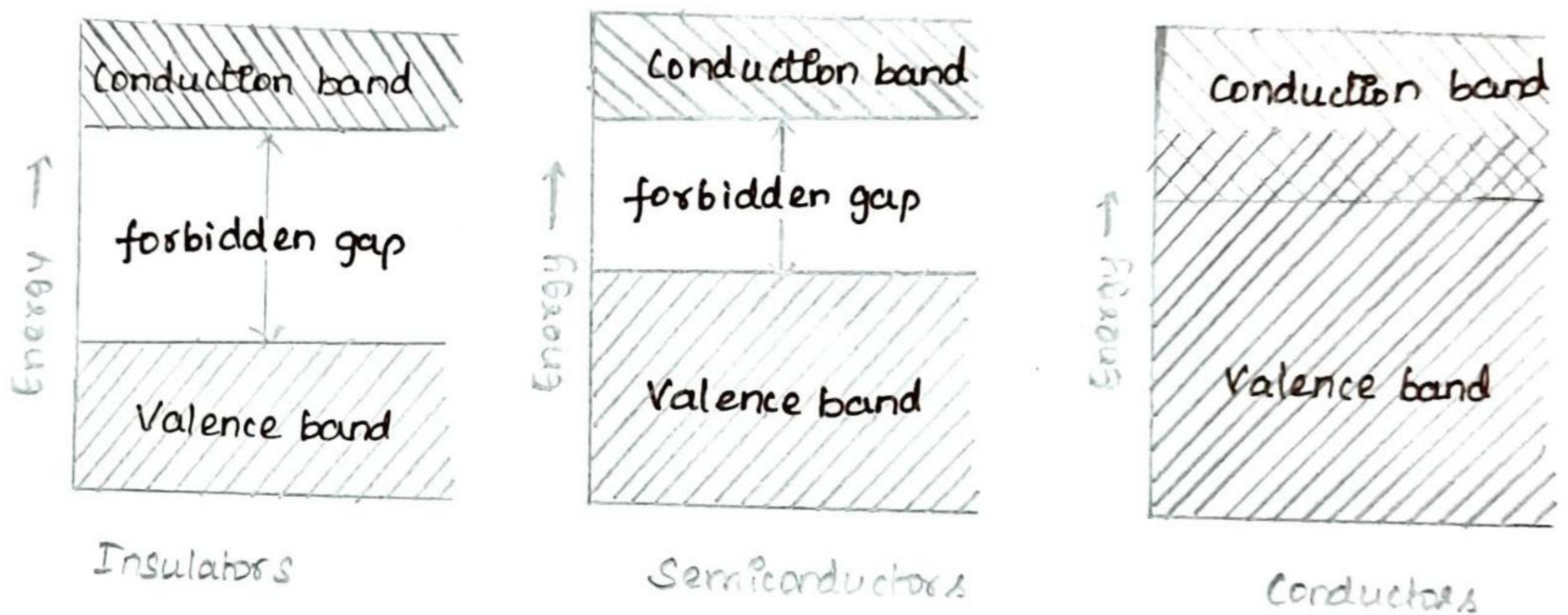
In material like glass, the valence band is completely filled at 0K. The energy gap between valence band and conduction band is of order 10eV. Even in presence of high electric field, the electrons cannot move from valence band to conduction band.

### Semiconductors:

In semiconductors, the forbidden energy gap is very small. Germanium and silicon are examples. The forbidden energy gap is of order 0.7eV for Ge and 1.1eV for Si. There are no free electrons in the conduction band. The valence band is completely filled at 0K. When a small amount of energy is supplied, the electrons can jump easily from valence band to conduction band. The conductivity of semiconductor is of order  $10^2 \text{ mho m}^{-1}$ .

Conductors:

In conductors, there is no forbidden gap available, the valence and conduction band overlap each other. The electrons from valence band freely enter into the conduction band. Due to overlapping of valence and conduction bands, a very low potential difference can cause continuous flow of current.



### NON-STOICHIOMETRY POINT DEFECTS:

If the deviation occurs due to missing atoms, displaced atoms or extra atoms, the imperfection is known as point defect. Such defect arises due to imperfect packing during the original crystallisation or they may arise from thermal vibrations of atoms at elevated temperatures. The most common point defects are Schottky defect and Frenkel defect.

## SCHOTTKY DEFECT:

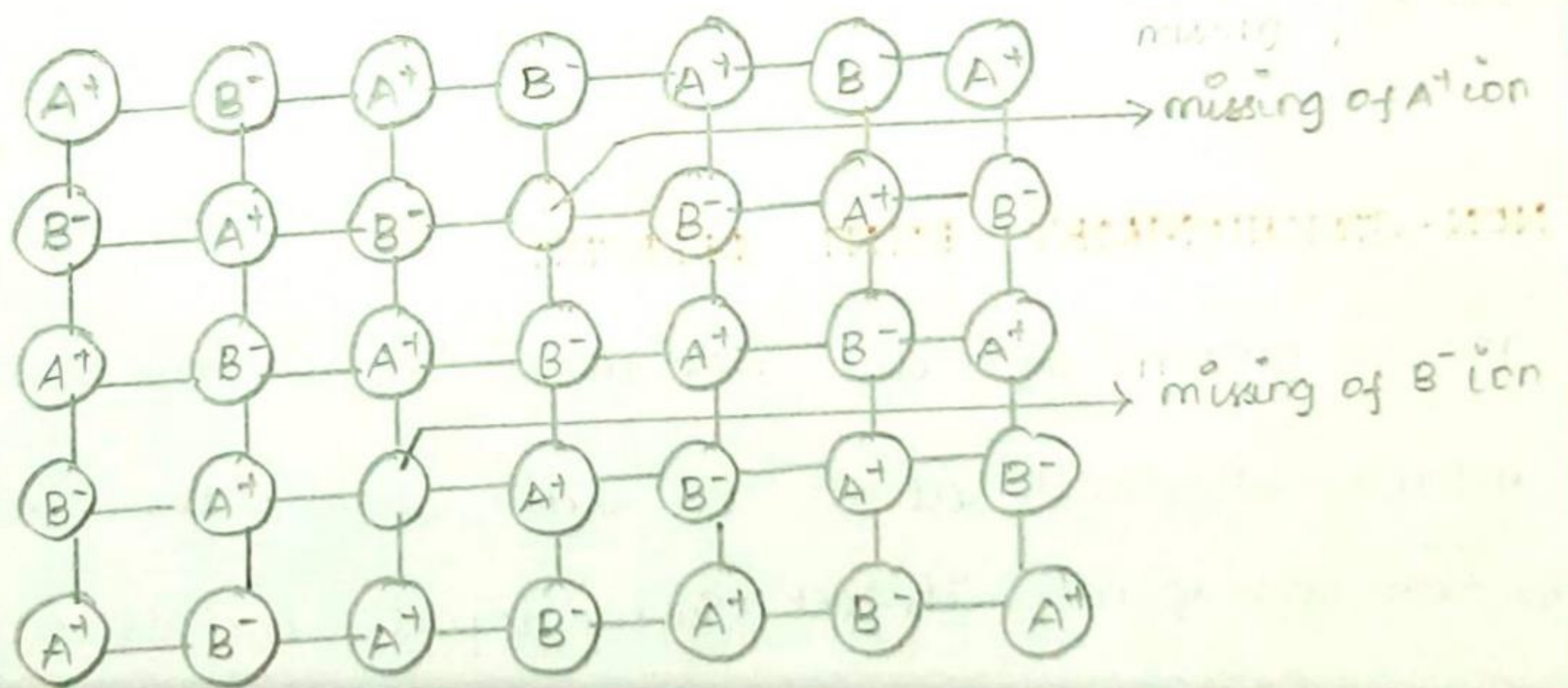
1) This defect arises if some of the lattice points are unoccupied.

2) The points which are unoccupied are called as lattice vacancies or holes.

3) There are two holes, one due to missing of positive ion and the other due to the missing of a negative ion in the crystal lattice.

4) The crystal remains neutral on the whole since the number of missing positive ions and negative ions are same.

5) Schottky defect generally appears in ionic crystals having high coordination number.



Schottky defect in crystal AB

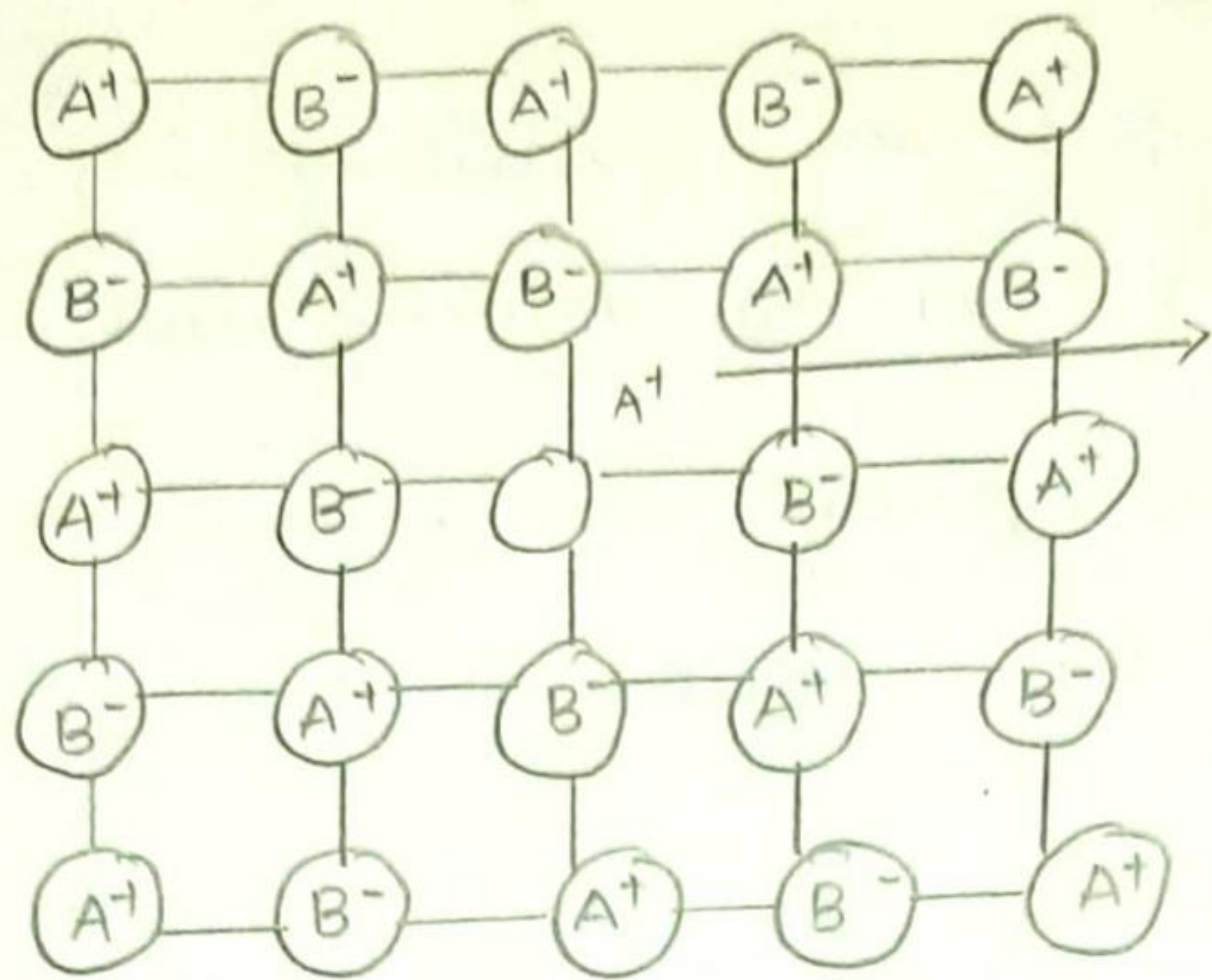
6) Schottky defect appears in crystal where positive and negative ions do not differ much in size.

7) NaCl and CsCl which have coordination number 6 and 8 gives Schottky defect.

8) It is also called as vacancy defect.

## FRENKEL DEFECT:

- 1) Frenkel defect arises when an ion occupies interstitial position between the lattice points.
- 2) One of the positive ion occupies a position in the interstitial space rather than at its own appropriate site in the lattice.
- 3) A hole is created in the lattice.
- 4) The crystal on the whole remains neutral since the number of missing positive ion is equal to that of the negative ion.
- 5) Frenkel defect generally appears in compounds where the negative ion is larger in size than the positive ion.
- 6) Coordination number in such compounds is low.
- 7) AgBr, some of  $\text{Ag}^+$  ions are generally missing from their regular positions and occupy position between other ions in the lattice.
- 8) The presence of  $\text{Ag}^+$  ion in the interstitial space of AgBr is responsible for the formation of photographic image on expose of AgBr crystal to light.
- 9) In ZnS,  $\text{Zn}^{2+}$  ions occupy interstitial space leaving holes in the space.
- 10) It is also called as interstitial defect.



A<sup>+</sup> ion in interstitial position

Frenkel defect in AB crystal

## DISLOCATIONS AND ITS EFFECTS:

Dislocation is another type of defect in crystal. Dislocations are areas where the atoms are out of position in the crystal structure. Dislocations are generated and move when stress is applied. The motion of dislocations allow slip-plastic deformation to occur.

There are two types of dislocations.

- a) Edge dislocation
- b) Screw dislocation

Actually edge and screw dislocations are just extreme forms of the possible dislocations structure that can occur. Most dislocations are probably a hybrid of edge and screw forms.



### Edge dislocation:

Edge dislocation can be easily visualised as an extra half plane of atoms in the lattice. This dislocation is called line defect because the locus of the defective point produced in the lattice by dislocation along a line. This line runs along the top of the extra half plane. The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line.

### Screw dislocations:

The screw dislocation is slightly more difficult to visualize. The motion of screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to the direction of the stress and the atom displacement rather than parallel.

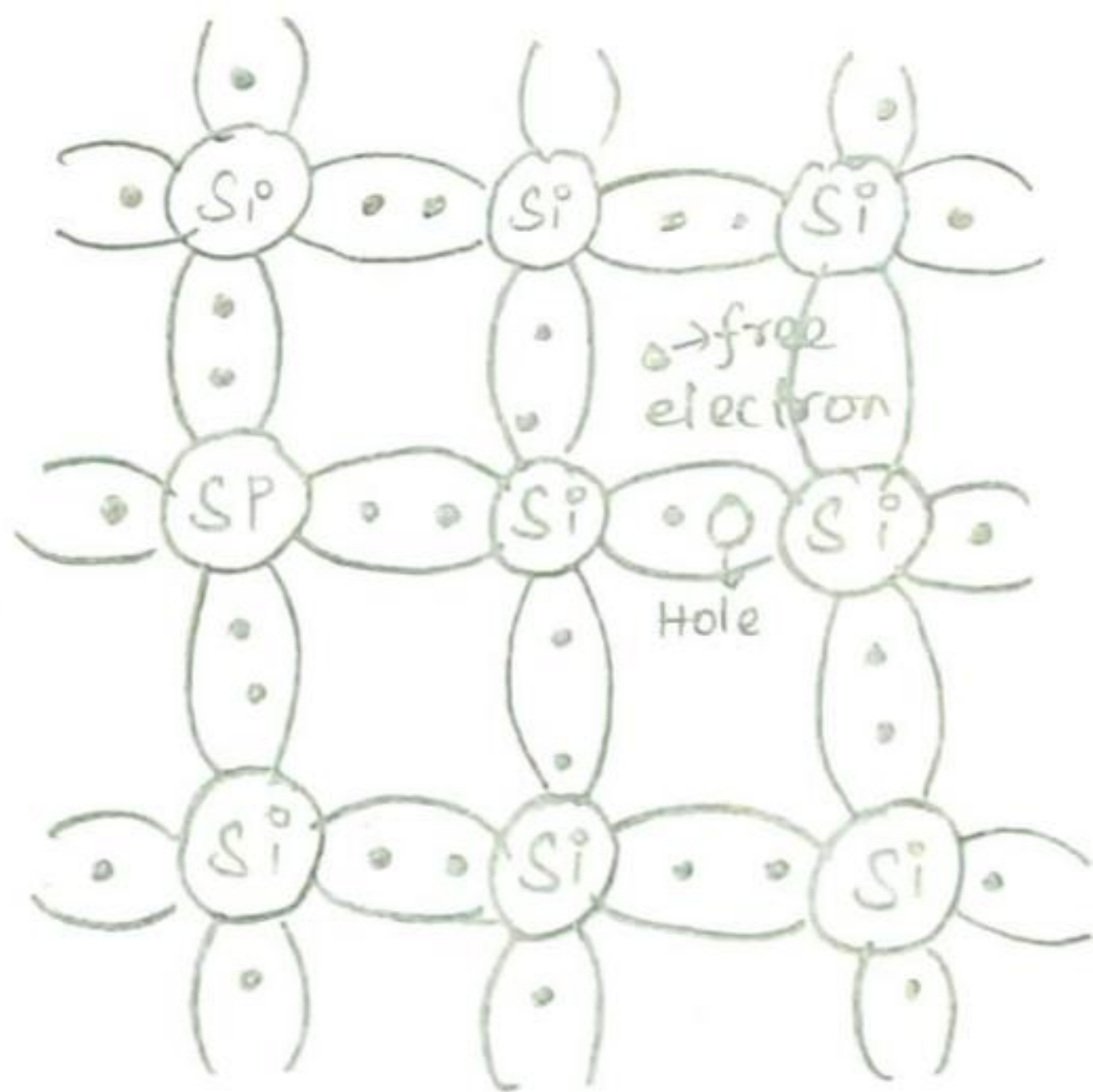
### SEMICONDUCTORS:

The materials which have resistivity between conductors and insulators are known as semiconductors. The resistivity of semiconductors lie approximately between  $10^{-2}$  and  $10^4 \Omega m$  at room temperature. The resistance of semiconductor decreases with increase in temperature over a particular temperature range.

Germanium, Silicon, Indium, Arsenic are examples.

## INTRINSIC SEMICONDUCTOR:

A semiconductor which is pure and contains no impurity is known as intrinsic semiconductor. In intrinsic semiconductor, the number of electrons and holes are equal. Pure germanium and silicon are examples of intrinsic semiconductor.



Intrinsic semiconductor

## EXTRINSIC SEMICONDUCTOR:

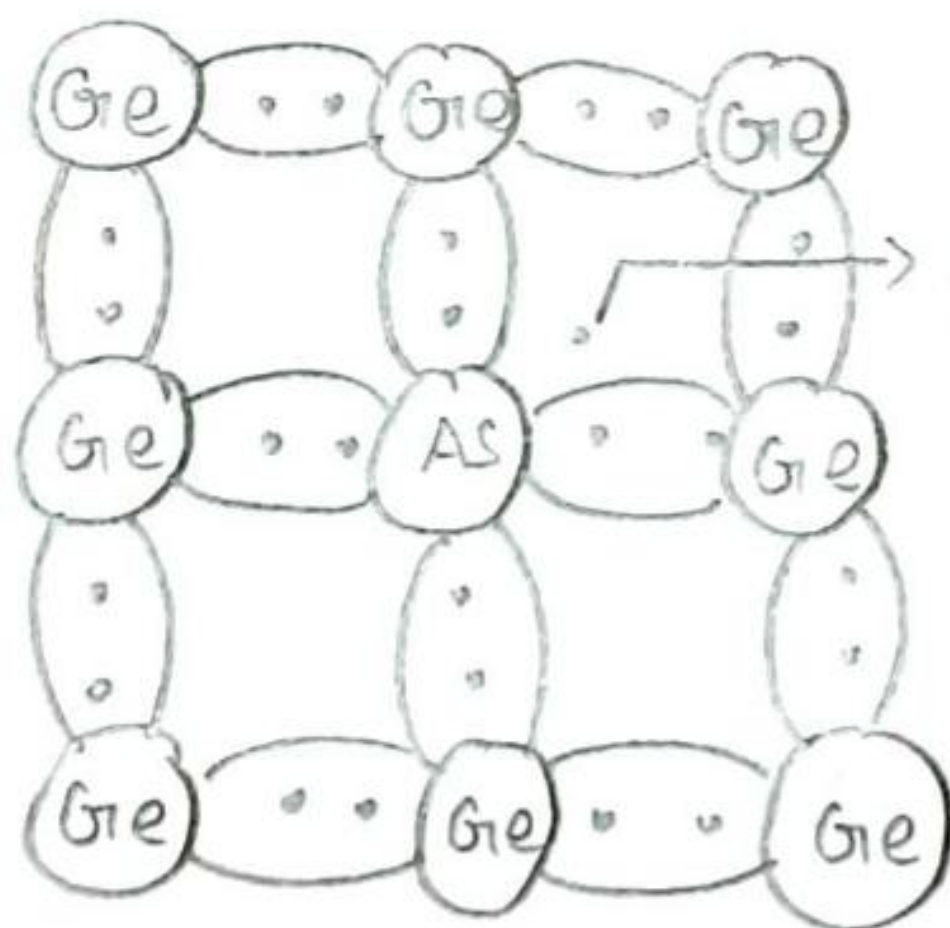
An extrinsic semiconductor is one in which an impurity with valency higher or lower than the valency of pure semiconductor is added, so as to increase the electrical conductivity of the semiconductor.

Depending upon the type of impurity atom added, an extrinsic semiconductor is classified as N type and P-type semiconductor.

## N-type Semiconductor:

When a small amount of pentavalent impurity such as arsenic is added to a pure germanium semiconductor crystal, the resulting crystal is called as N-type semiconductor.

In N-type semiconductor, the number of electron increases compared to the available number of charge carriers in the intrinsic semiconductor. In N-type semiconductors, free electrons are the majority charge carriers and the holes are minority charge carriers.



As - pentavalent impurity atom

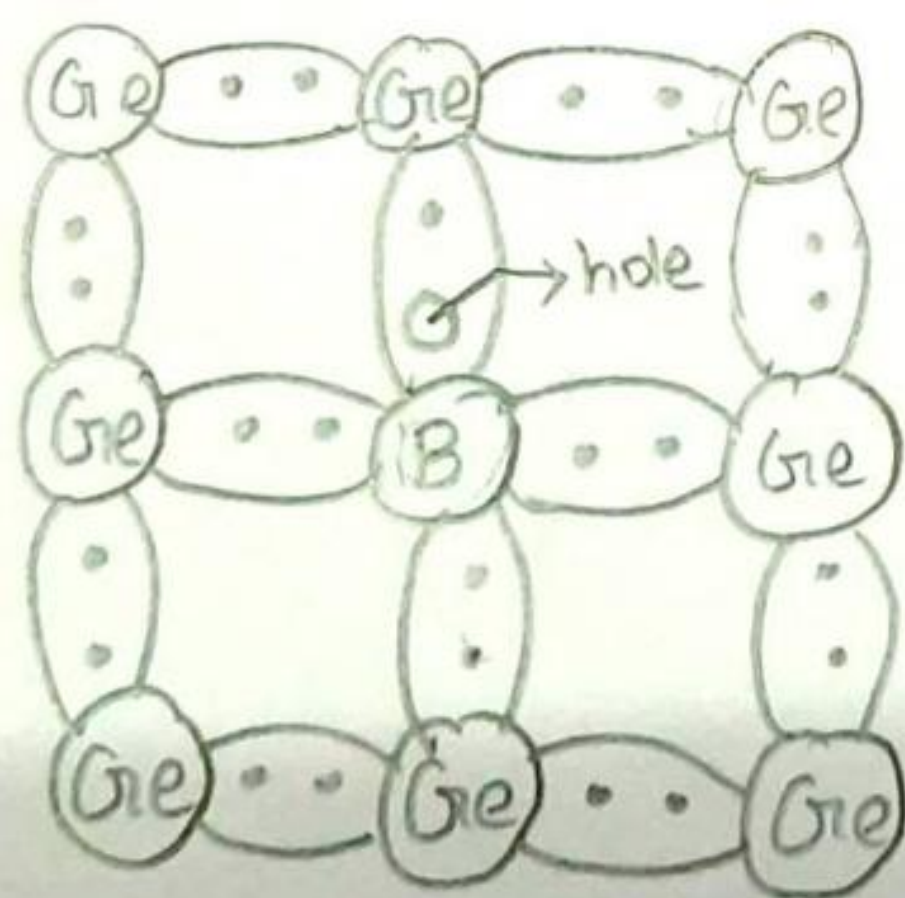
N-type Semiconductor

## P-TYPE SEMICONDUCTOR:

When a small amount of trivalent impurity such as Indium, boron or gallium is added to a pure semiconductor crystal, the resulting crystal is called as P-type semiconductor.

When trivalent boron atom impurity is added with pure germanium crystal, three valence electrons of boron atom forms covalent bond with three neighbourhood germanium atoms. In fourth covalent bond, only one valence electron from germanium atom is available and there is deficiency of one electron which is called as hole. Since the holes accept electron from neighbourhood, the impurity is called acceptor.

In P-type semiconductor, holes are majority carriers and free electrons are minority charge carriers.

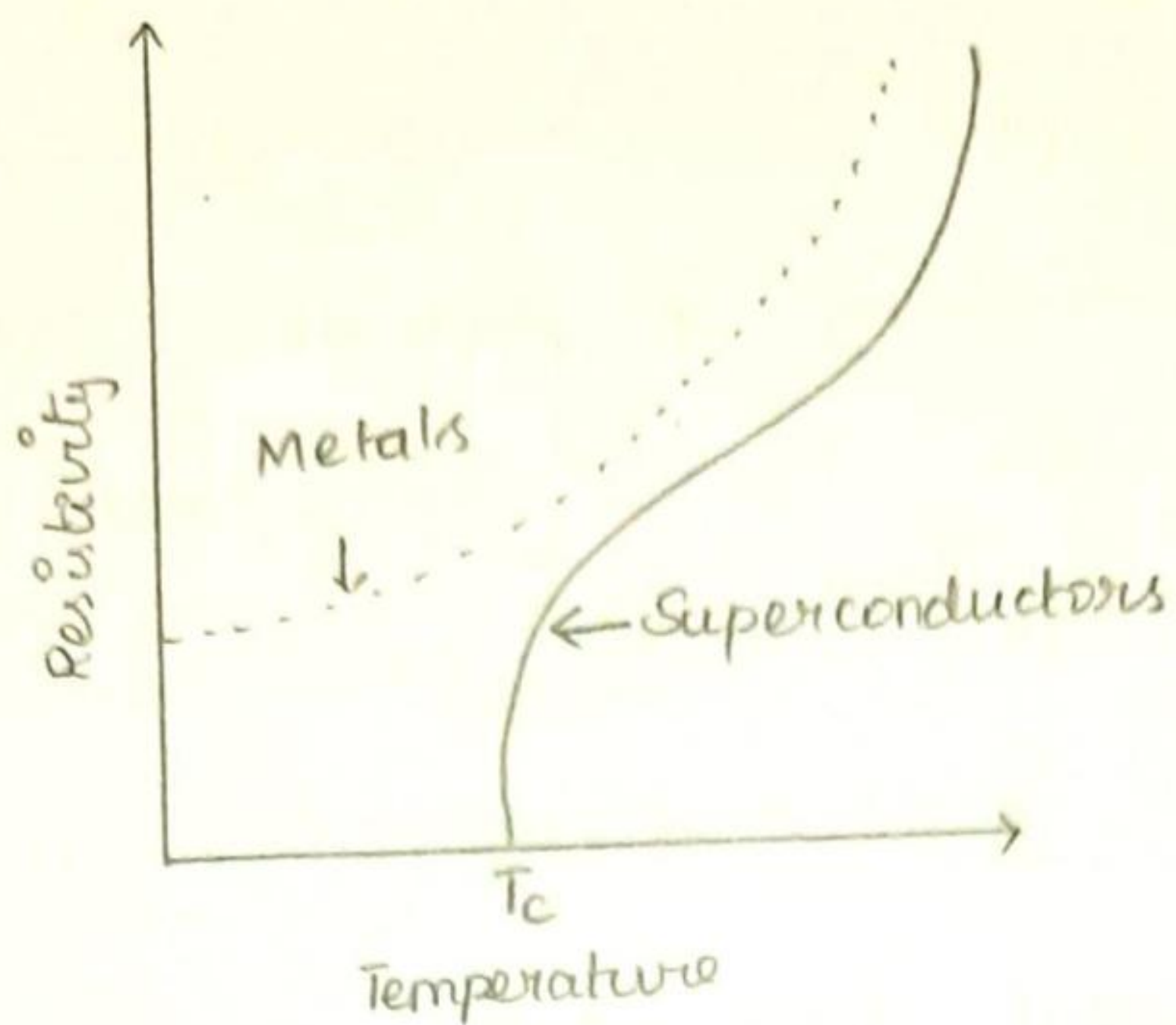


B - trivalent impurity atom

P-type Semiconductor

### SUPERCONDUCTORS:

The ability of certain ultra cold substances to conduct electricity without resistance is called as superconductivity. This superconductivity state is a state in which materials have virtually zero electrical resistance. Substances having this property are called superconductors.



Superconducting transition temperature  $T_c$  of a material is defined as the critical temperature at which the resistivity of the material is suddenly changed to zero. Thus at that temperature a material is changed from normal material to superconductor.

#### APPLICATIONS:

1) Superconducting solenoids are used in Nuclear Magnetic Resonance Imaging equipment which is a whole body scan equipment.

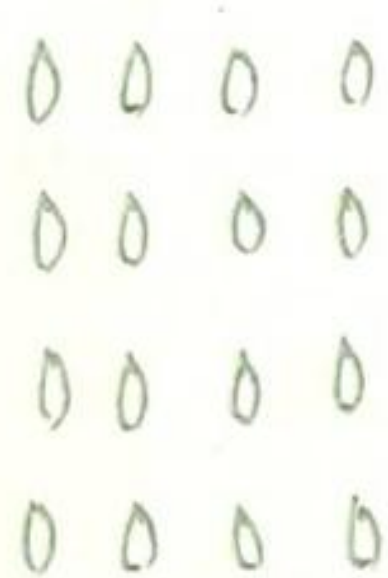
2) High efficiency ore separating machines may be built using superconducting magnets.

3) Superconducting magnets generators are smaller in size and weight than conventional generators. These generators consume very low energy and so we can save more energy. It is the basis of new generation of energy saving power systems.

## LIQUID CRYSTALS:

A liquid crystal is a thermodynamic stable phase characterised by anisotropy of properties without the existence of three-dimensional crystal lattice, generally lying in the temperature range between solid and isotropic liquid phase and hence the term mesophase.

Liquid crystals have general characteristics. Rod-like molecular structure, rigidity of the long axis, strong dipole and easily polarisable substituents.



Solid

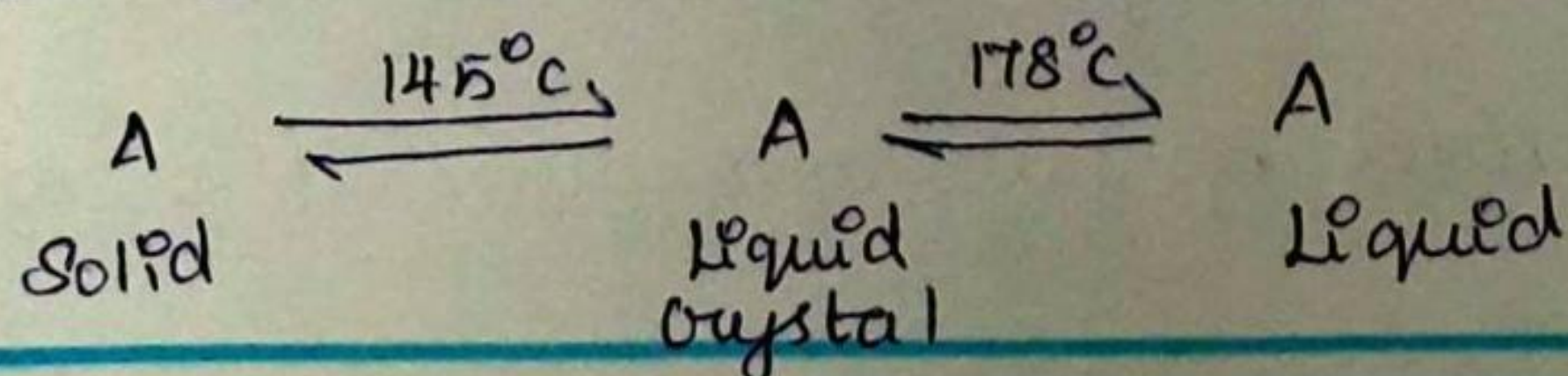


Liquid crystal



Liquid

Cholesteryl benzoate  $C_6H_5COOC_{27}H_{45}$  was the first solid discovered having this peculiar property. It fuses sharply at  $145^\circ C$  to give a turbid liquid which on further heating changes suddenly into clear liquid at  $178^\circ C$ . The above changes are reversed on cooling. The clear liquid when cooled first changes into turbid state at  $178^\circ C$  and then into solid state at  $145^\circ C$ .



A - p-cholesteryl benzoate

Liquid crystals can be classified into two types.

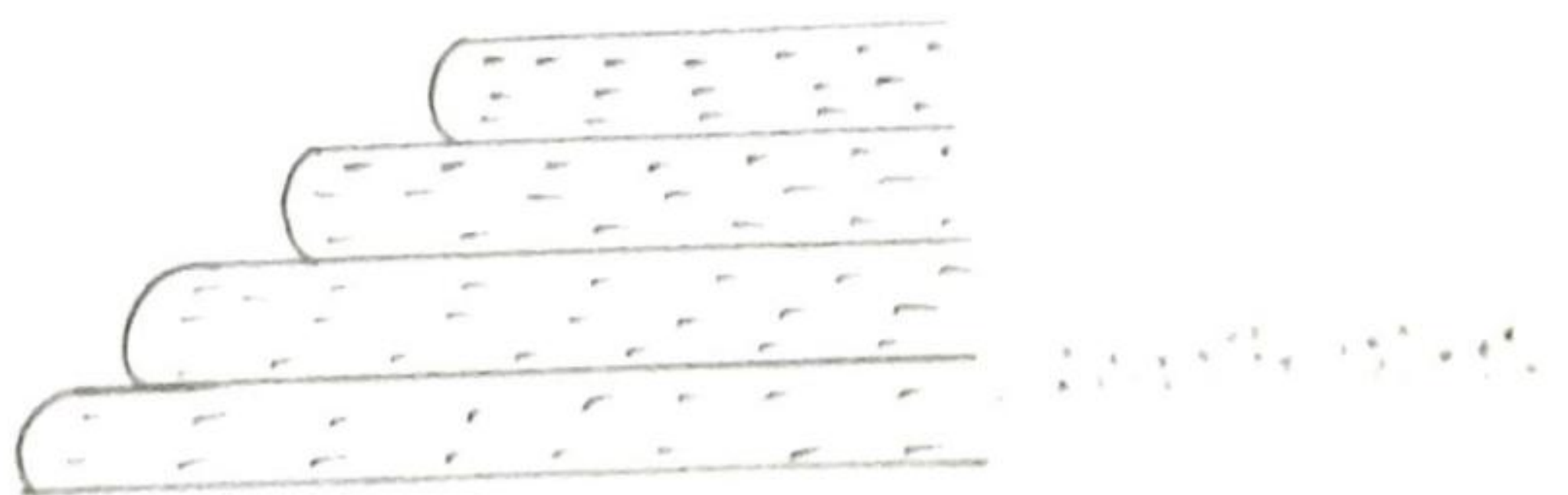
a) Smectic (soap-like) liquid crystal

b) Nematic (thread-like) liquid crystal

### SMECTIC LIQUID CRYSTAL:

Smectic liquid crystal do not move like normal liquids. They have limited mobility. They are layers as if different layers or planes are sheets gliding over one another. The distribution of velocity in different layer is found to be different from that found in true liquid. The concept of viscosity is not applicable to this type. When spread over a clean glass surface, they form series of terraces. Smectic liquid crystal give x-ray diffraction patterns like solid crystals but in one direction only. They have complex internal structures. When viewed in polarised light, smectic phases have fan-like appearance. They are always uniaxial and unaffected by magnetic field.

Eg: ethyl p-oxoxy benzoate, ethyl p-oxoxy cinnamate



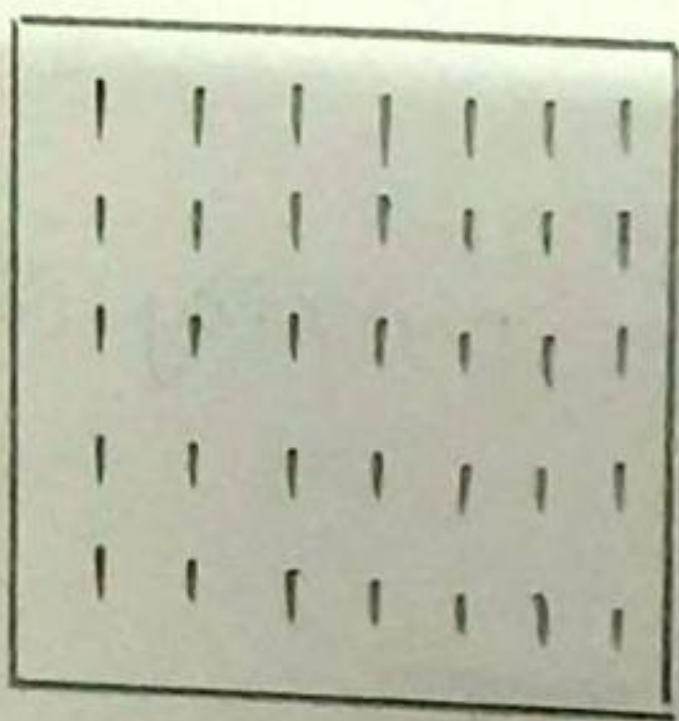
Smectic Liquid Crystal

## NEMATIC LIQUID CRYSTAL:

Nematic liquid crystal show nearly normal flow behaviour of liquids. They flow more readily than smectic liquid crystal. Newtonian and concept of viscosity is applicable. Their viscosity is low than true liquids. They have liquid like character and yet being turbid and anisotropic.

In polarised light, nematic liquid crystals have thread-like appearance. They are uniaxial but affected by magnetic field. In presence of strong magnetic field, they appear clear and in the absence of magnetic field, they appear turbid.

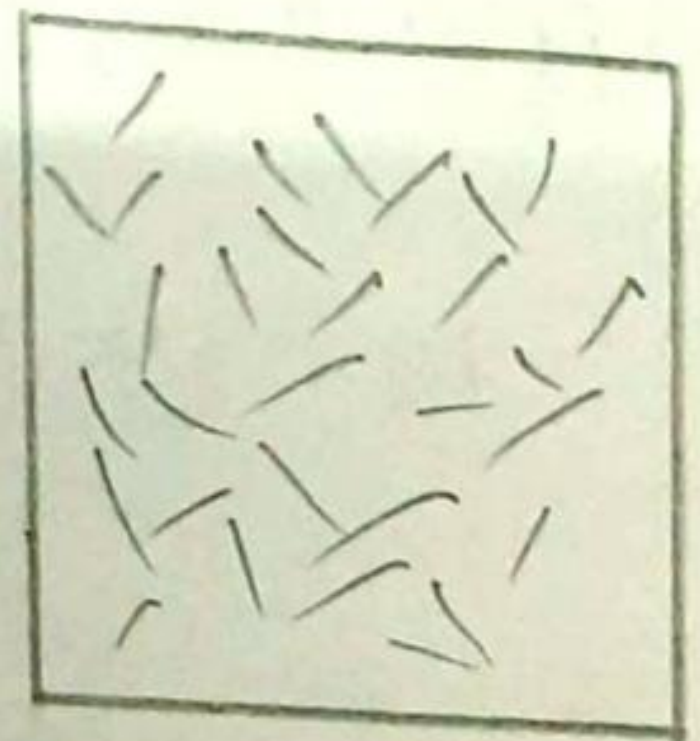
eg: p-azoxy anisole, p-azoxy phenatole, Anisaldazine



Smectic phase



Nematic phase



clear  
liquid

### Applications:

The most common application of liquid crystal is liquid crystals displays (LCD).