CHE-MM: XII

1. SOLID STATE

Solids have definite mass, volume and shape. This is due to the fixed position of their constituent particles, short distances and strong interactions between them.

CLASSIFICATION OF SOLIDS

On the basis of orderly **arrangement of particles**, solids can be classified into two –

Crystalline solids	Amorphous solids
Regarded as **true solids**	Regarded as **pseudo solids** or **super cooled liquids**
The arrangement of particles is well defined (**long range order**)	The arrangement of particles is not well defined (**short range order**).
Have a **characteristic shape**	**Irregular shape**
They possess a **sharp melting point**	Do not have a sharp m.p
Have a **definite heat of fusion**	Do not have definite heat of fusion
Gives a **clean cut** when cut with a sharp edged tool	Gives **irregular cut**
Anisotropic (physical properties like *electrical conductance, refractive index* etc are different in different directions)	**Isotropic** (physical properties are same along any direction)
E.x.: NaCl, quartz	E.x.: Glass, rubber, plastics

On cutting-

Crystalline solids   Amorphous solids
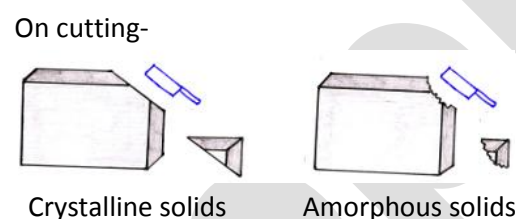
CLASSIFICATION OF CRYSTALLINE SOLIDS

Depending upon the nature of intermolecular forces, solids can be divided into 4 types, namely: **molecular, ionic, metallic** and **covalent solids**. They differ widely in their properties-

Type of Solid	Constituent particles	Bonding / attractive forces	Examples	Physical nature	Electrical conductivity	Melting point
1. Molecular solids i) Non-polar	Molecules	Dispersion / London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
ii) Polar	"	Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
iii) H-bonded	"	H-bonding	H_2O (ice)	Hard	Insulator	Low
2. Ionic solids	Ions	Coulombic / electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulator in solid state but conductor in molten state and in aqueous solution	High
3. Metallic solids	Positive ions in a sea of free e⁻	Metallic bonding	Fe, Cu, Ag, Mg	Hard, malleable & ductile	Conductors in solid state as well as in molten state	Fairly high
4. Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), C (diamond), AIN	Hard	Insulator	Very high
			C (graphite)	Soft (because layers can slide one over the other)	Conductor (due to the presence of free e⁻ between layers)	

CRYSTAL LATTICES AND UNIT CELLS

The 3D arrangements of constituent particles of a crystal in space is called *crystal lattice*.

Unit cell: It is the smallest repeating unit of a crystal lattice which, when repeated in three dimension gives a whole crystal. A unit cell is characterised by its **edge lengths** and **three angles** between these edges.
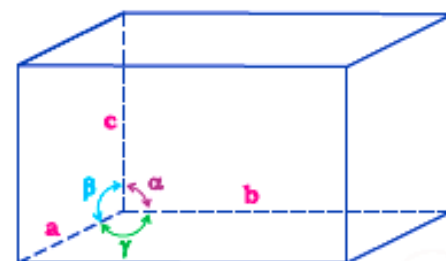
Unit cells can be broadly divided into two -

1. Primitive Unit Cells:

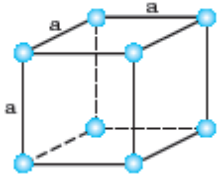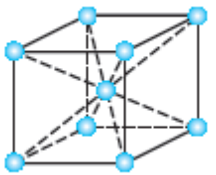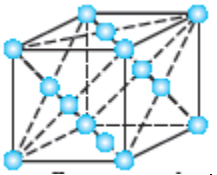Here the constituent particles are present only at the **corners** of the unit cell.
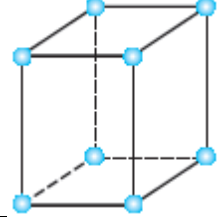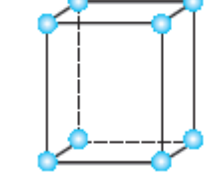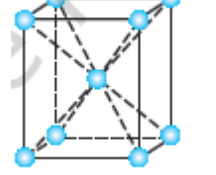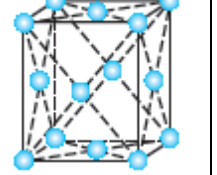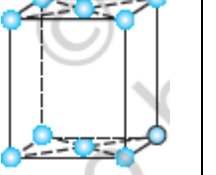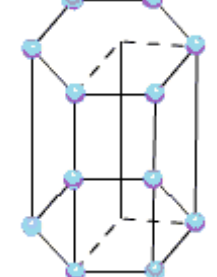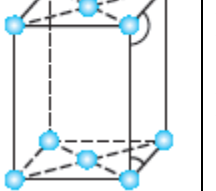
2. Centred Unit Cells:

The constituent particles are present at the **corners** and **other positions** of the unit cell. These are of 3 types:

i. *Body-centred unit cells*: The constituent particles are present at the **body centre** and at the **corners** of the unit cell.

ii. *Face-centred unit cells*: The constituent particles are present at the **centre of each faces** and at the **corners** of the unit cell.
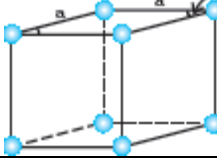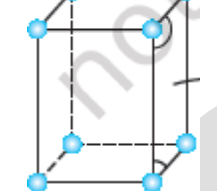
iii. *End-centred unit cells*: The constituent particles are present at the **centre of any two opposite faces** and at the **corners** of the unit cell.

In all, 14 different types of lattices are possible which are called **Bravais lattices**.

Bravais lattices -

	Crystal	Possible variations				Examples
1.	**Cubic** $a = b = c$ $\alpha = \beta = \gamma = 90^0$	Primitive	Body-centered	Face-centered		NaCl, Zinc Blende, Cu
2.	**Tetragonal** $a = b \neq c$ $\alpha = \beta = \gamma = 90^0$	Primitive	Body-centered			White tin, SnO_2, TiO_2, $CaSO_4$
3.	**Orthorhombic** (Rhombic) $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^0$	Primitive	Body-centered	Face-centered	End-centered	Rhombic sulphur, KNO_3, $BaSO_4$
4.	**Hexagonal** $a = b \neq c$ $\alpha = \beta = 90^0, \gamma = 120^0$	Primitive				Graphite, ZnO, CdS
5.	**Rhombohedral / Trigonal** $a = b = c$ $\alpha = \beta = \gamma \neq 90^0$	Primitive				Calcite $(CaCO_3)$, HgS (Cinnabar)
6.	**Monoclinic** $a \neq b \neq c$ $\alpha = \gamma = 90^0, \beta \neq 90^0$	Primitive		End-centered		Monoclinic sulphur, $Na_2SO_4.10\,H_2O$
7.	**Triclinic** $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^0$	Primitive				$K_2Cr_2O_2$, $CuSO_4.5H_2O$, H_3BO_3

Calculation of Number of Atoms in a Unit Cell

1. Primitive cubic unit cell (Simple Cubic):

Here atoms are present only at the corners of the cube. Each corner atom is shared by 8 unit cells.

Therefore, contribution to one unit cell = $^1/_8$

Since each unit cell has 8 atoms at the corners, the total number of atoms in one unit cell = $8 \times ^1/_8 = 1$

So for a primitive (simple cubic) unit cell, Z = 1

2. Body-centred cubic (bcc) unit cell:

Here the particles are present at the corners of the cube and also one atom at the body centre.

The number of atoms at the corner = $8 \times ^1/_8 = 1$

The atom present at the centre of the body is not shared by other atoms. So the number of atoms at the body-centre = 1

Therefore, total number of atoms in the unit cell = 1+1=2

So, for a bcc, Z = 2

3. Face-centred cubic (fcc) unit cell:

Here the atoms are present at the corners and also at the centre of each faces. Each corner atom is shared by 8 unit cells and each face centre atom is shared by 2 unit cells.

Number of corner atoms = $8 \times ^1/_8 = 1$

Number of face-centre atoms = $6 \times ^1/_2 = 3$

Therefore, total number of atoms = 1+3 = 4

So, for an fcc, Z = 4

Packing In Solids

Atoms are space filling entities and structures can be described as resulting from the packing of spheres. The most efficient closest packing can be achieved in two ways, one of which is called **hexagonal close-packing** (hcp) and the other, **cubic close-packed** (ccp)**.**

Place spheres in a row, touching each other (first row). Then spheres of the second row are placed in the depressions of the first row, the spheres of the third row are placed in the depressions of the second row and so on. Thus the *first layer* formed in this manner is in **hexagonal** arrangement.

The *second layer* is placed above the depressions of the first layer. On placing the second layer there arises two types of **voids** (empty spaces) above the second layer – **tetrahedral voids** and **octahedral voids**.

> ➤ **Tetrahedral voids** are holes surrounded by 4 spheres present at the corners of tetrahedron. Number of tetrahedral voids is double the number of spheres (2N)
>
> ➤ **Octahedral voids** are holes surrounded by 6 spheres located on a regular octahedron. Number of octahedral voids is equal to the number of spheres (N)
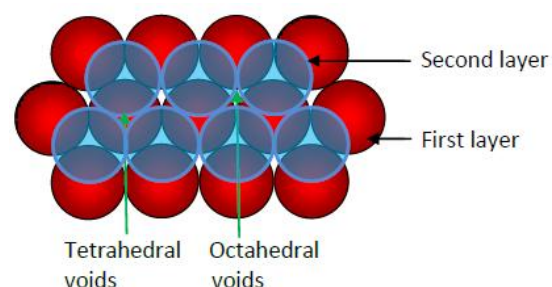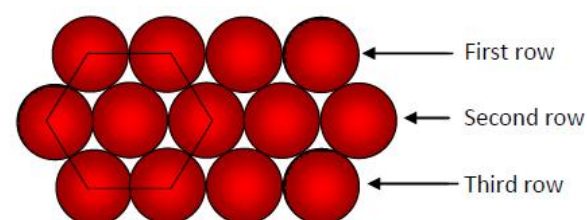
Hexagonal close-packing (hcp)

If the *third layer* is placed above the **tetrahedral voids** of the second layer, the first layer and the third layer are identical. If we call the first layer as 'A' and the second layer as 'B', then the third layer will be 'A', the fourth layer will be 'B' and so on. This will form the pattern ABAB……
This type of close packing is called *Hexagonal close packing (hcp)*.
➜ This type of arrangement is found in metals like **Mg, Zn** etc.
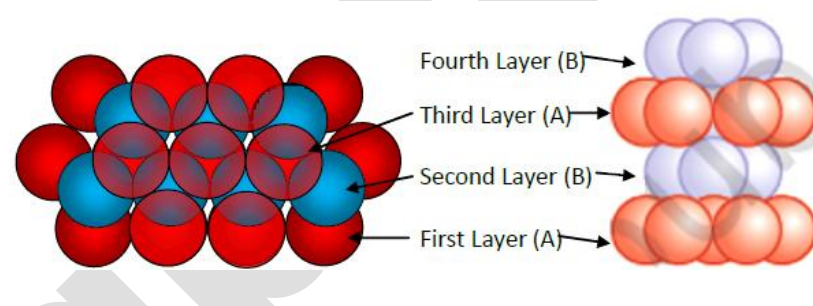
Cubic close-packed (ccp) or Face centred cubic (fcc)

On the other hand, if the *third layer* is placed above the **octahedral voids** of the second layer, the third layer is different from the first or the second layer. If we call this unique, third layer as 'C', it will form the pattern ABCABC…… This type of close packing is called *Cubic close packing (ccp)* or *face-centred cubic(fcc) packing*.
➜ This type of arrangement is found in metals like **Cu, Ag** etc.
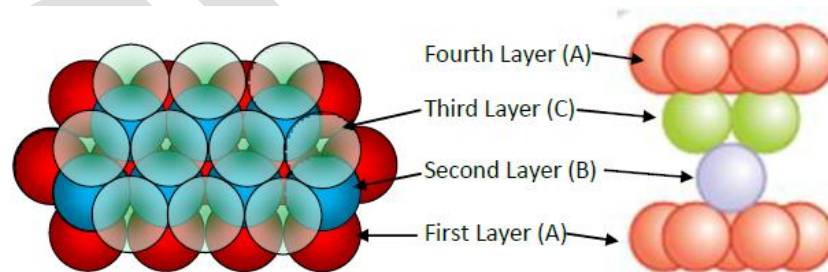
Packing Efficiency

Packing efficiency is the percentage of the total space occupied by spheres (particles).

$$\text{Packing Efficiency} = \frac{\text{Volume occupied by all the spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\%$$

Calculation of Packing Efficiency

1) In hcp and ccp structures

Consider a cube with edge length 'a' and face diagonal 'b'
In ΔABC, $AC^2 = AB^2 + BC^2$
   i.e. $b^2 = a^2 + a^2 = 2a^2$
   or, $b = \sqrt{2}a$
If 'r' is the radius of the sphere, then b = 4r
   $\therefore 4r = \sqrt{2}a$

   Or, $a = \dfrac{4r}{\sqrt{2}} = 2\sqrt{2}r$

We know that, in ccp (fcc) or hcp, there are 4 spheres per unit cell

   $\therefore$ Volume of four spheres = $4 \times (4/3)\pi r^3$
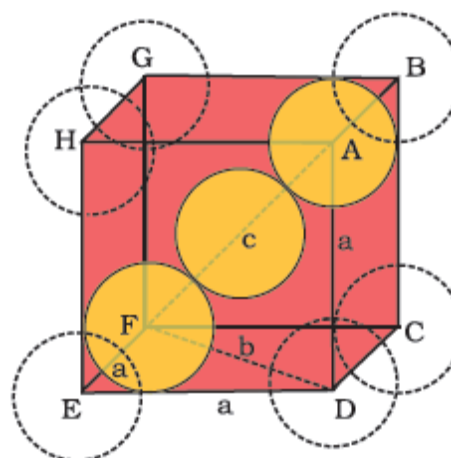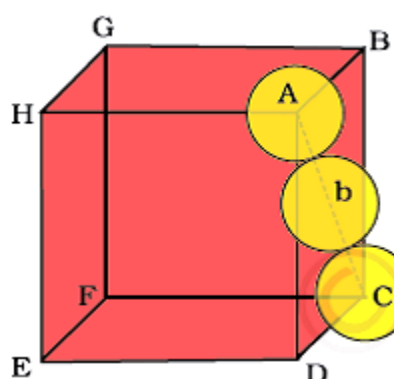
   Volume of the cube = $a^3 = (2\sqrt{2r})^3$

$\therefore$ Packing Efficiency = $\dfrac{\text{Volume occupied by 4 the spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\%$

   $= \dfrac{4 \times (4/3)\pi r^3}{(2\sqrt{2r})^3} \times 100\% = 74\%$

2) In Body-centred cubic (bcc) structures:

Consider a cube with edge length 'a', face diagonal 'b' and body diagonal 'c'. From the figure it is clear that the atom at the centre is in contact with the other two atoms diagonally placed.

In ΔEFD, $FD^2 = EF^2 + ED^2$
   i.e. $b^2 = a^2 + a^2 = 2a^2$
   or, $b = \sqrt{2}a$

In ΔAFD, $AF^2 = AD^2 + FD^2$

       i.e. $c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$

      or, $c = \sqrt{3}a$

We know that, $c = 4r$ (where r is the radius of the particle)

$\therefore \sqrt{3}a = 4r$

  Or, $a = \dfrac{4r}{\sqrt{3}}$

We know that, in a bcc, there are 2 spheres per unit cell

  $\therefore$ Volume of 2 spheres $= 2 \times (4/3)\,\pi r^3$

    Volume of the cube $= a^3 = (4r/\sqrt{3})^3$

  $\therefore$ Packing Efficiency $= \dfrac{\text{Volume occupied by 2 the spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\%$

         $= \dfrac{2 \times (4/3)\,\pi r^3}{(4r/\sqrt{3})^3} \times 100\% \underline{\underline{= 68\%}}$

3) In simple cubic structures:

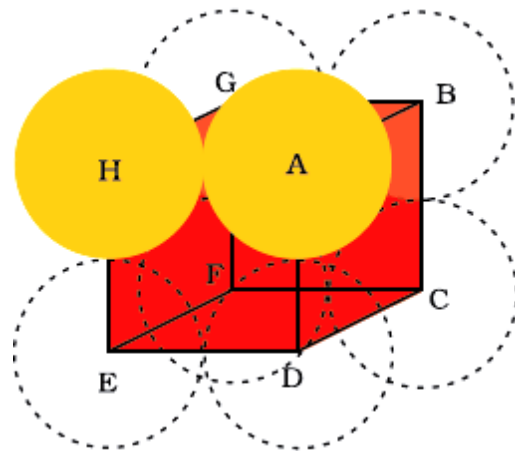Consider a cube with edge length 'a' and the radius of the particle 'r'.

Since particles touch each other along the edge, $a = 2r$

The volume of the cubic unit cell $= a^3 = (2r)^3 = 8r^3$

We know, a simple cubic unit cell contains only one particle.

  $\therefore$ Volume of one sphere $= (4/3)\,\pi r^3$

  $\therefore$ Packing Efficiency $= \dfrac{\text{Volume of 1 sphere in the unit cell}}{\text{Total volume of cubic unit cell}} \times 100\%$

         $= \dfrac{4/3\,\pi r^3}{8r^3} \times 100\% \underline{\underline{= 52.4\%}}$

DENSITY OF A UNIT CELL

Suppose edge length of a cubic unit cell is 'a','d' is the density and 'M' is the molar mass (i.e. mass of Avogadro number of atoms).

Mass of unit cell = Number of atom in unit cell **x** Mass of each atom $= z \times m$

Mass of each atom (m) $= \dfrac{\text{Molar mass (M)}}{\text{Avogadro number } (N_A)}$

$\therefore$ Mass of unit cell $= z \times \dfrac{M}{N_A}$

Volume of the unit cell $= a^3$.

  $\therefore$ Density of the unit cell $= \dfrac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

        $\underline{\underline{d = \dfrac{z \times M}{a^3 \times N_A}}}$

IMPERFECTIONS IN SOLIDS

Solids are not perfect in structure. There are different types of imperfections or defects in them. ***Point defects*** and ***line defects*** are common types of defects.

  I.   **Point defect** - The irregularity or deviation from the ideal arrangement around a point (an atom) in a crystalline substance.

  II. **Line defect** - The irregularity or deviation from the ideal arrangement along a row.

Types of Point defects

Point defects are of 3 types - *stoichiometric defects*, *impurity defects* and *non-stoichiometric defects*.

A. STOICHIOMETRIC DEFECTS:

The point defects which do not disturb the **stoichiometry** (the ratio of positive and negative ions) of the solid. They are also called *intrinsic or thermodynamic defects* (since these defects can also develop when a substance is heated).

In *non-ionic solids,* stoichiometric point defects are present as–

i. Vacancy defect: When some of the **lattice sites are vacant**, the crystal is said to have vacancy defect.

  ✓ This defect decreases the density of the solid.

ii. Interstitial defect: When some constituent **particles occupy an interstitial site**, the crystal is said to have interstitial defect.

  ✓ This defect increases the density of the solid.

Vacancy   Interstitial
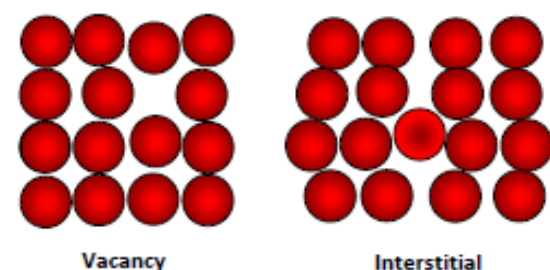
In *ionic solids*, these defects are present as -

iii. **Frenkel defect/** dislocation defect**:** This defect arises when some of the **ions** (generally a cation) **misplacing from the lattice site** to the interstitial site. This type of defect is found in ionic crystals where anion is much larger in size than the cation.
   E.g. ZnS, AgBr, AgI etc.
   ✓ Due to this defect, the density of the solid does not change.
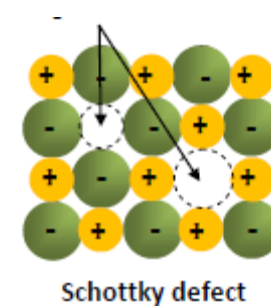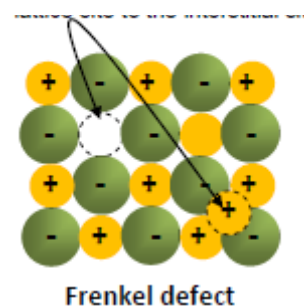
iv. **Schottky defect:** This defect arises due to the **missing of equal number of anions and cations** from the lattice site. It is shown by ionic crystals in which the anionic and cationic sizes are almost equal.
   E.g.: NaCl, KCl, CsCl, etc.
   ✓ Due to this defect the density of the solid decreases.

B. **IMPURITY DEFECTS:**
   Impurity defects are caused by the presence of an impurity (foreign particles) in the crystal. If the ionic impurity has a different valence than the main compound, some vacancies are created.
   E.g.: Sr^{2+} as impurity in NaCl
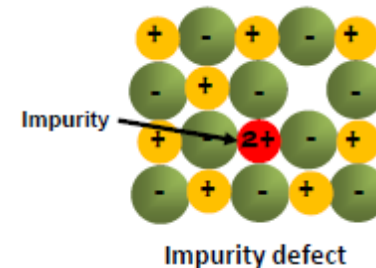
C. **NON-STOICHIOMETRIC DEFECTS*:***
   These are point defects which change the stoichiometry of a solid. These defects are of two types:

i. **Metal excess Defect:** This arises in two ways:
   ❖ *Metal excess defect due to anion vacancies***:** In this defect, some of the anions are missing from the lattice site. The electrical neutrality is maintained by occupying e^- in the anionic sites. These sites are called **f-centres,** where e^- absorb light energy and get excited and thereby give colour to the crystal like *alkali metal halides*.
      E.g.: Excess of Na give **yellow** colour to NaCl crystals
            Excess of Li makes LiCl crystals **pink**
   Excess of K makes KCl crystals **violet**.
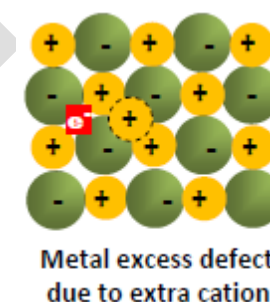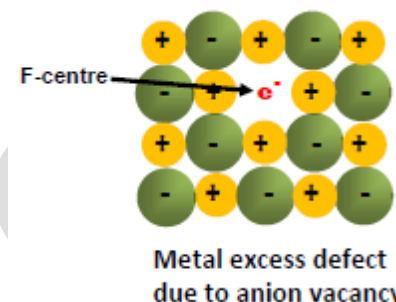
   ❖ *Metal excess defect due to extra cations at interstitial sites:* Here some cations occupy the interstitial sites. The electrical neutrality is maintained by occupying some e^- in adjacent interstitial sites.
      E.g. ZnO crystals (which is white in colour) on heating loses oxygen and becomes yellow-

      $$ZnO \longrightarrow Zn^{2+} + \tfrac{1}{2} O_2 + 2e^-$$
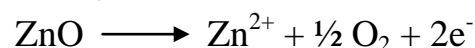
      The Zn ions now move to the interstitial sites and the e^- to neighbouring interstitial sites.
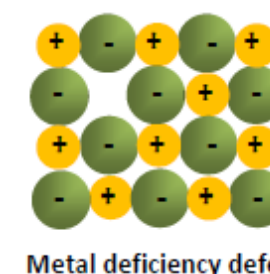
ii. **Metal deficiency Defect:**
   Here the number of cations is smaller than the number of anions. This is mainly arises due to cation vacancies. This type of defect is commonly shown by transition metal compounds. E.g. FeO

Electrical Properties
   Based on the electrical conductivity, solids are classified into 3 types:

(i)**Conductors**: They are solids which allow the passage of electricity through them. These generally include metals. Their conductivity ranges from 10^4 to 10^7 $ohm^{-1}m^{-1}$.
   Reason:-
   A *band* is formed due to closeness of molecular orbitals. This band is *partially filled* or it *overlaps* with a higher energy unoccupied conduction band. If an electric field is applied, the e^- flow and shows conductivity.

(ii) **Insulators**: They are solids which do not allow electricity through them. Their conductivity ranges from 10^{-10} to 10^{-20} $ohm^{-1}m^{-1}$.
   **Reason:-**
   The gap between filled valence band and the unoccupied conduction band is large the e^- cannot jump to it.

(iii) **Semi-conductors**: They are solids which have intermediate conductivity ranging from 10^4 to 10^{-6} $ohm^{-1}m^{-1}$.
   Reason:-
   The gap between the valence band and the conduction band is small. So some e^- may jump from valence band to conduction band and show some conductivity.
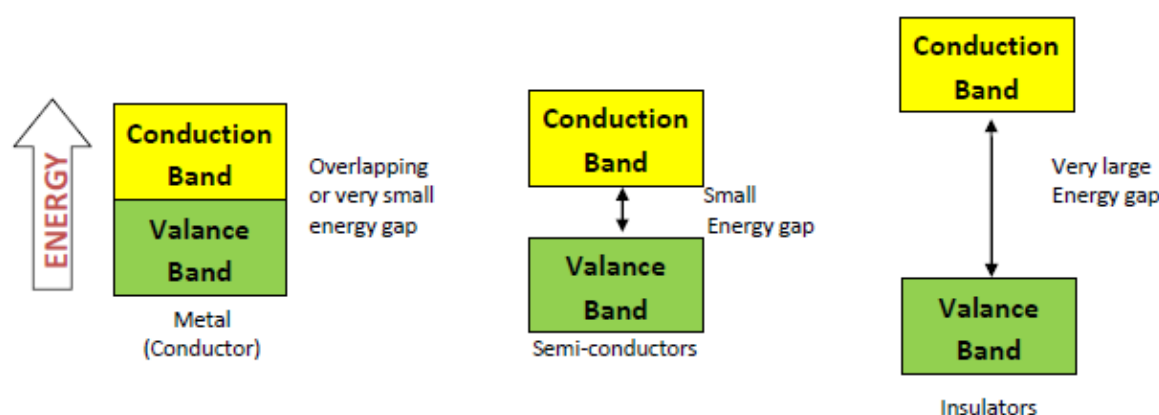
   Their conductivity increases with rise in temperature, since more e^- can jump to the conduction band. Such semiconductors are also called *intrinsic semiconductors*. E.g.: Si, Ge etc.
   Dopping: It is the addition of impurities in semiconductors to enhance their conductivity. It creates electronic defects in them. Such semiconductors are called *extrinsic semiconductors*.

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Types of *extrinsic semiconductors:*

1. *n-type semiconductor*

It is the type obtained by doping of group 14 elements (like Si or Ge) with elements of group 15 (*electron rich,* like P or As). The excess e⁻ in crystals increases the conductivity.
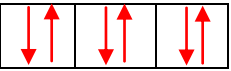
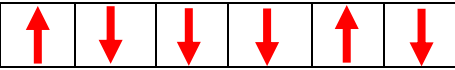**2.** *p-type semiconductors*

It is the type obtained by doping of group 14 elements with elements of group 13 (*electron deficient,* like B, Al or Ga). This creates an e⁻ hole (vacancy). An e⁻ from a neighbouring atom can come and fill the holes. So the position of the hole is moved in the direction opposite to that of the e⁻ has moved. Under the influence of electric field, e⁻ would move towards the positively charged plate through electronic holes. It would appear as if electron holes are positively charged.
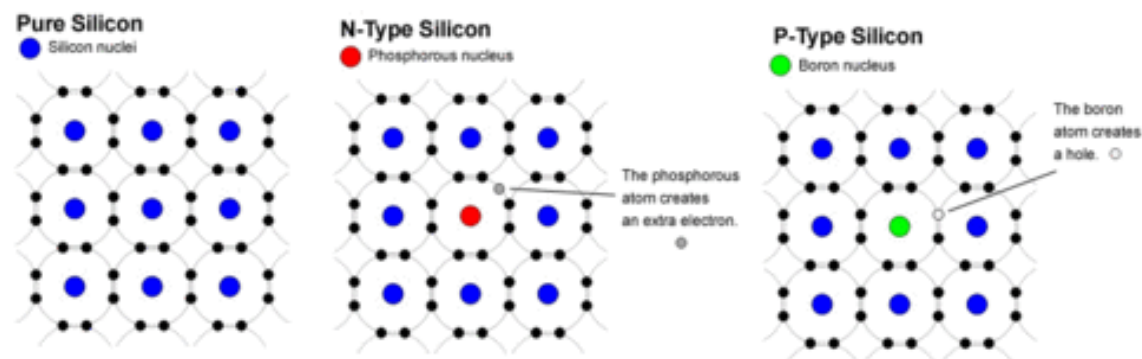
Magnetic Properties

Every solid has some magnetic properties associated with it due to the presence of e⁻. On the basis of magnetic properties, solids can be classified into *five* types-

Properties	Description	Alignment of magnetic dipole	Examples
Diamagnetic	Species **weakly repelled** by an external magnetic field.	Pairing of e⁻ cancels their magnetic moments and so they have no net magnetic moment	H_2O, NaCl, C_6H_6
Paramagnetic	Species **weakly attracted** by an external magnetic field. Temporary magnetism.	Paramagnetism is due to the presence of at least one unpaired e⁻.	O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}
Ferromagnetic	Species **strongly attracted** by a magnetic field. Permanent magnetism.	Ferromagnetism is due to the orientation of all domains in the direction of the magnetic field	Fe, Co, Ni, Gd (Gadolinium), CrO_2
Anti-ferromagnetic	Species having **no net magnetic moment**	This arises when the domains are oppositely oriented and cancel each other.	MnO
Ferrimagnetic	Species having a **small net magnetic moment**	This arises when domains are arranged in opposite directions but in unequal numbers.	Fe_3O_4, $MgFe_2O_4$, $ZnFe_2O_4$

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