

# SOLID STATE

## SOLIDS

- Solids have definite mass, volume and shape.
- They are rigid due to the fixed positions of their constituent particles, short intermolecular distances and strong intermolecular forces between them.
  - Solids can be classified into crystalline and amorphous.
  - On the basis of the nature of order present in the arrangement of their constituent particles.

### → Crystalline Solids.

- They have ordered arrangement of constituent particles with long range order (i.e. the regular pattern of particles arrangement that repeats over the entire crystal).
- They have definite geometrical shape, sharp melting point with definite heat of fusion and are anisotropic in nature.

### → Amorphous Solid

- They consist of particles of irregular shape, are isotropic, have short range order of packing and gradually soften over a range of temperature eg) fused quartz, glass and plastic. Amorphous silicon is used as photovoltaic cell.

**(NOTE)** Glass is considered as supercooled liquid because like liquids, amorphous solids have a tendency to flow though slowly. Glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation.



## → Crystal lattice

A regular three-dimensional arrangement of constituent particles in a crystal in which each particle is depicted as a point is called **Crystal lattice**.

- There are 14 possible three-dimensional lattices.

- These are called **Bravais lattices**.

## → Unit cell

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

1) Unit cell can be broadly divided into two categories, primitive and Centred Unit cells.

In primitive unit cells, constituent particles are particles are present only at the corner positions of unit cell whereas in centred unit cells, one or more constituent particles are present at positions other than corners in addition to those at corners.

Centred unit cell is classified as Body Centred unit cell (BCC), Face Centred cell (FCC)

2) The contribution of particles to a unit cell present at different position in a cubic structure:

Position	No. of pos <sup>n</sup>	Contribution of each part	Total contribution
At corners	8	$\frac{1}{8}$	$8 \times (\frac{1}{8}) = 1$
At each face	6	$\frac{1}{2}$	$6 \times (\frac{1}{2}) = 3$
At Body Centre	1	1	$1 \times 1 = 1$



Number of atoms ( $Z$ ) for different types of unit cell.

Types of unit cell	simple cubic	bcc	FCC
No. of particles ( $Z$ )	$8 \times \frac{1}{8} = 1$	$8 \times \frac{1}{8} + 1 = 2$	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

→ Hexagonal close packed and cubic close packed structures close packing of particles result in two highly efficient lattices, hcp (ABABAB) eg, Mg, Zn, Mo, V, Cd and ccp (ABCABC) eg, Cu, Ag, Au, Ni, Pt. The ccp is similar to FCC packing.

- The remaining space is present in the form of two types of voids - Octahedral voids and tetrahedral voids surrounded by six spheres located on a regular tetrahedron. For  $N$  close packed sphere, there are ' $N$ ' Octahedral voids and  $2N$  tetrahedral voids.

(i) Tetrahedral voids are formed whenever the sphere of the second layer is above the void of first layer. (or vice versa) These are surrounded by four spheres which lie at the vertices of regular tetrahedron.

(ii) Octahedral voids are formed, whenever the triangular voids in the second layer (hcp) are above the triangular voids of the first layer. These are surrounded by six spheres located on a regular octahedron.

→ Coordination Number.

- Coordination Number is the No. of atoms or ions surrounding a particular atom in crystal lattice.



- For NaCl type ionic crystal (NaBr, KBr, CaO, AgCl, CsI, MnO) the coordination No. for each cation and anion is 6:6
- For CsCl type ionic crystal (CsI, CsBr, TlBr, NH<sub>4</sub>Br). The coordination No. for each cation and anion is 8:8
- For ZnS type (CuCl, CuBr, CuI, HgS) it is 4:4.

### → Packing efficiency

- It is the percentage of total space filled by the particles (lattice points) in a unit cell.

$$\text{In general, packing efficiency} = \frac{\text{No. of spheres} \times \text{Vol. of 1 sphere} \times 100}{\text{Total Vol. of unit cell}}$$

- In hcp and ccp (or fcc) structures. Both hcp and ccp are equally efficient

$$\text{Packing efficiency} = \frac{\text{Vol. occupied by 4 spheres} \times 100}{\text{Total volume (a}^3\text{)}}$$

$$= \frac{4 \times \frac{4}{3} \pi r^3 \times 100}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \underline{\underline{74\%}}$$

$$\left(\text{For ccp, } a = \frac{4r}{\sqrt{2}}\right)$$

- In bcc structures.

Here, atom at the centre touches the other two atoms that are diagonally arranged.

$$\text{Packing efficiency} = \frac{\text{Vol. by 2 spheres} \times 100}{\text{Total Vol.}}$$

$$\left(\text{For bcc, } a = \frac{4r}{\sqrt{3}}\right)$$

$$= \frac{2 \times \frac{4}{3} \pi r^3 \times 100}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 68\%$$



### → Simple Cubic lattice

Here, atoms are located only at the corners of the cube  
the atoms touch each other along the edge

$$\begin{aligned}\text{Packing efficiency} &= \frac{\text{Volume of 1 atom} \times 100}{\text{Total Volume}} \\ &= \frac{4/3 \pi r^3 \times 100}{(2r)^3} = 52.4\%\end{aligned}$$

★ Thus, scp structure have maximum packing efficiency.

### → Relation between atomic radii and edge length.

Atomic radii is related to the edge length as

$$\rightarrow r = \frac{a}{2} \text{ (simple)}$$

$$\rightarrow r = \frac{\sqrt{3}a}{4} \text{ (body centred)}$$

$$\rightarrow r = \frac{a}{2\sqrt{2}} \text{ (Face centred)}$$

### → Calculations Involving Unit cell Dimension

$$\text{Density} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\rho = \frac{Zm}{a^3} = \frac{Z \times M}{a^3 \times N_A} \text{ g cm}^{-3}$$

$m$  = mass of single atom

$Z$  = No. of atoms in unit cell, i.e., 1 for simple, 2 (bcc), 4 (Fcc)

$M$  = Molar mass

$a$  = edge length

$N_A$  = Avogadro's Number



## → Radius Ratio Rules.

$$\text{Radius ratio} = \frac{\text{Radius of cation } (r_+)}{\text{Radius of anion } (r_-)}$$

Radius Ratio	Coordination Number	Structure	Structure type	Examples
0.155 - 0.225	3	Planar triangular	-	$B_2O_3$
0.225 - 0.414	4	tetrahedral	spinelite, ZnS	$CuCl, CuBr, CuI, BaS, HgS$
0.414 - 0.732	6	Octahedral	Sodium chloride	$NaBr, KBr, MgO, MnO, CaO$
0.732 - 1	8	Body centred cubic	$CSCl$	$CSI, CsBr, TlBr$

## → Imperfection in Solids

- Any Deviation from the perfectly ordered arrangement of constituent particles

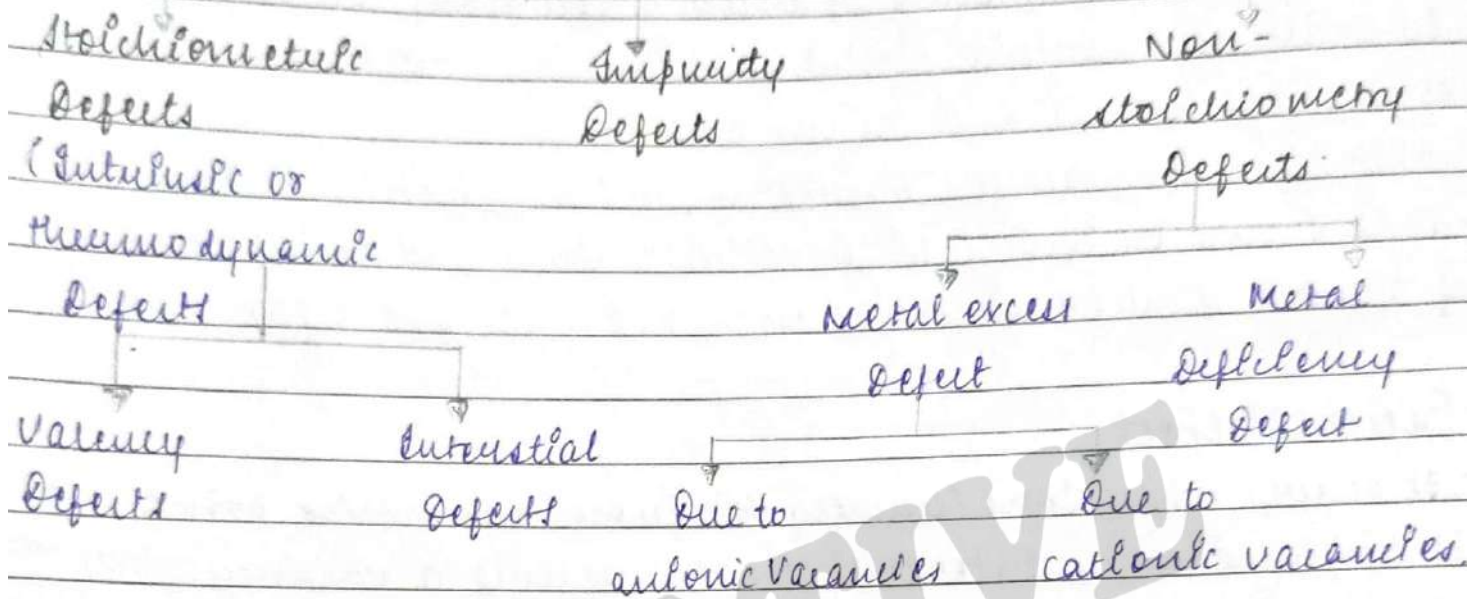
### → Point and Line Defects

- Point Defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline lattice.

- Line Defects are the irregularities or deviations from ideal arrangement in entire row of lattice point. These irregularities are also called as crystal lattice



## Point Defects



### → Stoichiometric Defects.

- These are the point defects that do not disturb the stoichiometry of a solid.

These are of two type:

#### ① Vacancies Defects

- Vacancy defect occurs when positions that should contain atoms or ions are vacant.

- This results in decrease in density of the crystal.

- Vacancy defects are shown by Non-Ionic solid.

#### ② Interstitial Defects.

- Interstitial defects occur when some constituent particles occupy an interstitial site.

- This defect increases the density of the substance.

- These defects are shown in case of covalent or metallic solids.



## - Schottky Defects

- Schottky Defects are basically a vacant defect in ionic solids that occur due to missing of atoms or ion from lattice points.
- In order to maintain electrical neutrality, the Number of missing cations and anions are equal.
- this defect Decrease the Density of the substance.
- It is shown by ionic sub<sup>st</sup> in which cations and anions are of almost similar sizes like NaCl, KCl, CsCl and AgBr.

## - Frenkel Defect

- It occurs when ions (usually  $\text{Ag}^+$ ) from the lattice points is displaced to an interstitial site creating a vacancy at its original site.
- It does not change the Density of the substance.
- It is shown by ionic substance in which there is a large difference in the size of ion eg) ZnS, AgCl, AgBr, AgI due small size of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$  ion.

(\*) AgBr shows Both, Frenkel as well as Schottky Defect.

## → Impurity Defects

these defect arise when some Foreign atoms or ions are present in the lattice site or in the interstitial site  
eg) molten NaCl with little amount of  $\text{SrCl}_2$   
solid solution of  $\text{CdCl}_2$  and AgCl.

## → Non-stoichiometric Defects

- It disturbs the stoichiometry of solids
- It is of two types.



### ① Metal excess defect Due to anionic Vacancies.

- This is shown by alkali halides like NaCl and KCl.
  - In such defects, a negative ion missing from its lattice site leaving a hole which is occupied by an electron to maintain Neutrality.
  - The anionic sites occupied by unpaired  $e^-$  are called F-centres.
  - They impart colour to the alkali halide.
- eg) Excess of Na makes NaCl crystal yellow,  
Excess of  $Li$  makes LiCl crystal pink,  
Excess of K makes KCl crystal violet.

### ② Metal excess defect Due to the presence of cations.

- Extra cations at interstitial sites as shown by ZnO.
  - when it is heated
  - On heating ZnO (white) loses its oxygen and turns yellow.
- $$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + \frac{1}{2} O_2 + 2e^-$$

### ③ Metal Deficiency Defect.

- It is shown by solids which contain less amount of the metal as compared to the stoichiometric proportion.

eg) FeO which is mostly found with a composition of  $Fe_{0.95}O$

### → Magnetic properties of solids.

- These properties arise due to the spinning of  $e^-$  present in the solid. Thus, each  $e^-$  has a permanent spin and an orbital magnetic moment associated with it.
- On the basis of magnetic properties, sub<sup>d</sup> can be classified as paramagnetic, diamagnetic, ferromagnetic, anti-ferromagnetic and ferrimagnetic.



### → Diamagnetic Substances.

- Diamagnetic substances are feebly repelled by magnetic fields. These substances have all paired electrons eg)  $\text{TiO}_2$ , NaCl etc.

### → Paramagnetic Substances.

- Paramagnetic substances are weakly attracted by magnetic field. These substances have at least one unpaired electron eg)  $\text{Cu}^{2+}$ ,  $\text{TiO}$ ,  $\text{Cu}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{O}_2$  etc.

### → Ferromagnetic Substance.

- Ferromagnetic substances are strongly attracted by magnetic field and have permanent magnetism even when magnetic field is removed.
- When Ferromagnetic substance is placed in a magnetic field, dipoles are aligned in the same direction ( $\uparrow\uparrow\uparrow$ ) eg) Fe,  $\text{Ni}$ , Co etc.

NOTE In solid state, metal ions of ferromagnetic sub<sup>st</sup> are grouped together into small regions called domains.

### → Anti-Ferromagnetic Substances.

- They have domain structure similar to ferromagnetic substances but their domains are oppositely oriented ( $\uparrow\downarrow\uparrow\downarrow$ ), therefore these substances have net magnetic moment equal to zero eg)  $\text{MnO}$ ,  $\text{MnO}_2$ .

### → Ferrimagnetic Substances.

- Expected to have large magnetism but they are weakly attracted by magnetic field as compared to ferromagnetic substances.



- These domains are aligned in parallel and anti-parallel directions in unequal numbers ( $\uparrow\downarrow\downarrow\uparrow\uparrow$ ), therefore these substance have some magnetic moment. eg)  $\text{Fe}_3\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ .

NOTE Piezoelectric crystals produce electricity due to mechanical stress.

→ Electrical properties.

The electrical conductivity of solid varies from  $10^{-20}$  to  $10^7 \Omega^{-1}\text{m}^{-1}$ . So, on the basis of electrical conductivity, solids or crystal can be classified as.

### Crystals

#### Conductors

Allow the passage of electric current

conductivity  
 $10^4 - 10^7 \Omega^{-1}\text{m}^{-1}$

#### Semi-conductors

Conducts electricity due to presence of impurities

conductivity  
 $10^{-6}$  to  $10^{24} \Omega^{-1}\text{m}^{-1}$

#### Insulators

Do not allow the passage of electric current

conductivity  
 $10^{-20}$  to  $10^{-10} \Omega^{-1}\text{m}^{-1}$