# THE SOLID STATE

The solid state chemistry covers the latest advances in advanced inorganic materials with applications ranging from energy storage systems, electronic materials and sensors to the more traditional, but increasingly hi-tech materials and industries that include glass, cement and refractories.



MASTERJEE CLASSE

Classification based on Crystal Lattice SOLIDS

Amorphous Solids

Classification based on Magnetic Properties

## Crystalline Solids

- True solids.
- Anisotropic.
- Have definite pattern of arrangements of atoms, ions or molecules.
- Exhibit plane, axis and centre of symmetry.
- Long range order.
- Are categorised according to intermolecular forces into:
  Molecular, ionic, metallic and covalent solids,

- Isotropic.
- Pseudo solids or supercooled liquids.
- Do not have a definite pattern of arrangement.
- Short range order.
- Do not show any symmetry.

#### **Primitive Unit Cells**

- Constituent particles are present only at the corners of the unit cell.
- Consist of 7 types of arrangements with cubic as most symmetric and triclmic as least symmetric.

- Diamagnetic Substances: Substances which are weakly repelled by external magnetic field, e.g., N<sub>2</sub>, NaCl, Zn, TiO<sub>3</sub>, etc.
- Paramagnetic Substances: Substances which are weakly attracted by external magnetic field, e.g., O<sub>2</sub>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, etc.
- Ferromagnetic Substances: Substances which show permanent magnetism even in the absence of external magnetic field, e.g., Ni, Γe, Co, etc.
- Antiferromagnetic Substances: Substances which have zero net dipole moment even though they have large number of unpaired electrons, e.g., MnO.
- Ferrimagnetic Substances: These are the substances which possess very small net magnetic moment even though they have large number of unpaired electrons, e.g., Fe<sub>3</sub>O<sub>4</sub>.

## **Crystal Lattice and Unit Cells**

#### Centred Unit Cells

Constituent particles are present at the corners and at:

- the centre of the unit cell (bcc)
- the centre of each face of the unit cell (fcc)
- the centre of any two opposite faces (End-centred)

# **Cubic System**

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

Type	Simple cubic	bcc	fcc
Z	$8 \times \frac{1}{8} = 1$	$8 \times \frac{1}{8} + 1 \times 1 = 2$	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
C. No.	6	8	12
Relation of r, d & a	$r = \frac{d}{2} = \frac{a}{2}$ since $d = a$	$r - \frac{d}{2} - \frac{a}{2\sqrt{2}}$ since $d = \frac{a}{\sqrt{2}}$	$r = \frac{d}{2} = \frac{\sqrt{3}a}{4}$ since $d = \frac{\sqrt{3}a}{2}$
Packing Efficiency	52.4%	68%	74%

### **Types of Defects**

## Staichiometric Detect (Intrinsic or

Thermodynamic Defect)

Does not disturb the stoichiometry of solid.

# Non-stoichiometric Defect

Arises due to the presence of constituent particles in nonstoichiometric ratio.

#### Frenkel Defect

- It is due to missing of ions (usually cations) from the lattice sites and these occupy interstitial sites.
- It has no effect on the density of crystal.
- This is found in crystal with low coordination no. e.g., AgI, ZnS, etc.

#### Schottky Defect

- It is due to equal no. of cations and anions missing from lattice sites.
- ⇒ It results in decrease in density of crystal.
- This is found in the highly ionic compounds having cation and anion of same size, e.g., NaCl, CsCl, etc.

# Volds

Туре	Size	No. of Voids
Octahedral	0.414 R	N
Tetrahedral	0.225 R	2N

**Metal Excess Defect**: Arises due to anionic vacancies, leaving a hole which is occupied by an electron thus, maintaining electrical balance. The anionic sites, occupied by unpaired electrons, are called *F*-centres and these impart colour to crystals.

**Metal Deficiency Defect**: Arises when metal shows variable valency *i.e.*, in transition metals. The defect occurs due to missing of a cation from its lattice site and the presence of the cation having higher charge in the adjacent lattice site.

