

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.

# CONCEPT

# Classification based on Crystal Lattice

# 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.

#### 1

- Isotropic.
- Pseudo solids or supercooled liquids.

**Amorphous Solids** 

- 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 triclinic as least symmetric.

- Diamagnetic Substances: Substances which are weakly repelled by external magnetic field, e.g., N<sub>2</sub>, NaCl, Zn, TiO<sub>2</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, Fe, 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**

<i>1</i> _	$Z \times M_{\sigma}$	$cm^{-3}$
<i>a</i> =	$\overline{a^3 \times N_A}^{\rm B}$	CIII

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 $d = a$	$r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$	$r = \frac{d}{2} = \frac{\sqrt{3}a}{4}$ since $d = \frac{\sqrt{3}a}{2}$
#3 2	onice or - or	since $d = \frac{a}{\sqrt{2}}$	since $d = \frac{1}{2}$
Packing Efficiency	52.4%	68%	74%

# **Types of Defects**

#### Stoichiometric Defect (Intrinsic or

Thermodynamic Defect)

Does not disturb the stoichiometry of solid.

#### Frenkel Defect Schottl

- ⇒ 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

**Non-stoichiometric Defect** 

Arises due to the

presence of constituent

particles in non-

stoichiometric ratio.

- 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.

#### Voids

Type	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.