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## SOLID STATE

- ⇒ In solid state, the constituent particles are closely packed and the intermolecular forces of attraction are very strong. In solid state, the constituent particles are only able to vibrate about their mean positions.
- ⇒ Characteristics of the solid are :
- (i) Definite shape and definite volume
  - (ii) High rigidity and high density
  - (iii) Low compressibility
  - (iv) Only vibrational motion of the constituent particles.
- ⇒ Types there are two types of solids.
- (i) Crystalline solid, characterized by
    - (i) sharp edges, flat faces
    - (v) definite geometrical shape
    - (ii) sharp melting point
    - (vi) consist of very large number of units called crystals.
    - (iii) presence of long range order (basic unit repeats itself infinitely)
    - (iv) anisotropic in nature
  - (2) Amorphous solids
    - (i) The arrangement of building constituents is not regular but haphazard
    - (ii) Melting points are not sharp
    - (iii) Isotropic in nature
    - (iv) called supercooled liquids.

### Space lattice and unit cell

A regular repeating arrangement of points in space is called space lattice. It is an array of points showing how molecules or atoms or ion are arranged in different sites in three dimensional space.

A unit cell is the smallest, but complete unit in space lattice which when repeated in three dimensional space generates the crystal. A unit cell possesses all the structural properties of the given crystal.

### Types of unit cells

- (1) Primitive : atoms are present only at the corners, not at another position.
- (2) Non-primitive or centered : atoms are present at other positions (centre of face, edge, body) in addition to atoms at the corners.

There are seven primitive unit cells called seven crystal systems :

All crystals do not have simple lattices. There can be 14 different ways in which similar points can be arranged in three dimensional space. These are called 14 Bravais lattices.

System	Axes	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, CsCl, ZnS diamond, alums, $\text{CaF}_2$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{TiO}_2$ (rutile), Sn (White) $\text{ZrSiO}_4$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{CdSO}_4$ , $\text{HgBr}_2$ , $\text{BaSO}_4$ , $\text{KNO}_3$ , S(rhombic)
Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	$\text{CaCO}_3$ (calcite), $\text{NaNO}_3$ , Quartz
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma \neq 90^\circ$	$\text{SiO}_2$ , graphite, $\text{PbI}_2$ , Mg, $\text{ZnO}$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq 90^\circ$ $\neq 90^\circ$	$\text{NaHSO}_3$ , $\text{CuSO}_4$ , $5\text{H}_2\text{O}$ , $\text{K}_2\text{Cr}_2\text{O}_7$

### Types :

Type	Structure	No. of atoms per unit cell	Atomic radius
Simple cubic		$\frac{1}{8} \times 8 = 1$	$r = \frac{a}{2}$
Face centered cubic (fcc)		$\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$ (Corners)(Face)	$r = \frac{\sqrt{2}}{4} a$
Body centered cubic (bcc)		$\frac{1}{8} \times 8 + 1 = 2$ (Corners)	$r = \frac{\sqrt{3}}{4} a$

- ⇒ The structure of solid is determined by X-ray diffraction method. Diffraction is the bending of light and the patterns produced when a light falls on a solid are called diffraction patterns.
- ⇒ Bragg's Law : When X-rays falls on a crystal face, they penetrate into the crystal and strike the atoms in different planes. X-rays are deflected from each of these planes. Bragg gave the relationship between the wavelength of the X-rays and the distance between the planes as

$$2d \sin \theta = n\lambda$$

where  $d$  = interplanar distance

$\lambda$  = wavelength of the X-rays

$\theta$  = reflection angle or glancing angle

$n = 1, 2, \dots$  positive integer, reflects the order of reflection.

### Types of ionic crystals :

- ⇒ Coordination number is the number of nearest neighbours. It is also defined as the number of oppositely charged ions surrounding the central ion.

### Types of ionic crystals :

#### (1) Rock salt type lattice (NaCl type) [AB type]

The cation  $A^+$  are present at the centre of each edge and at the centre of the cube. Anion  $B^-$  present at the corners as well as at the centre of each face.

Coordination number of each ion is 6. The number of formula units per unit cell is 4. The distance between the cation and anion is  $r_A + r_B = \frac{a}{2}$  where  $a$  = cell edge.

Example : KCl, KNO<sub>3</sub>, LiAlH<sub>4</sub>, KCN

#### (2) Cesium chloride type lattice (CsCl) : The cation $A^+$ are present at the centre of the cube, and the anion $B^-$ are present at the corner. The coordination number of each ion is 8. (8 : 8 coordination lattice). The number of

formula units equal to 1. The distance between the cation and anion is  $r_A + r_B = \frac{\sqrt{3}}{2} a$

Example : CsBr, TiCl, TiBr.

#### (3) The sphalerite structure (ZnS) : Zn<sup>2+</sup> ions are present at one fourth of the distance along each body diagonal and sulphide ions are present at the lattice points (at the corners and at the centre of each face). The coordination number of each ion is 4. The number of formula units equal to 4. Example : CuCl, CuBr

- (4) Fluorite type  $\text{AB}_2$  ( $\text{CaF}_2$ ) : This is a 8 : 4 coordination lattice. The cation  $\text{A}^{2+}$  are at the fcc lattice points and the  $\text{B}^-$  occupy all the eight tetrahedral voids. There are 4 formula units per unit cell. Example  $\text{SrF}_2$ ,  $\text{BaF}_2$ ,  $\text{PbF}_2$  and  $\text{BaCl}_2$ .
- (5) Antifluorite Type ( $\text{A}_2\text{B}$ ) : This is a 4 : 8 coordination lattice. There are 4 formula units per unit cell. The cation and anion position as obtained in the fluorite structure gets reversed. Example :  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ ,  $\text{Rb}_2\text{S}$ .

### Density Calculation :

$$\text{The density of solid is defined as } d = \frac{zM}{a^3 N_A}$$

$z$  = number of atoms or formula units per unit cell

$M$  = mole mass of formula mass

$N_A$  = Avogadro's number

$a$  = cell edge

The density of solid generally we express in g per  $\text{cm}^3$ .

⇒ Packing in solids means close-packed arrangement of atoms and the atom is considered as a hard sphere. Crystal can be generated by stacking one layer over another. The external shape of the crystal is related to the shape of the unit cell. There are four types of packing :

- (1) square based packing (also called simple cubic) : The atoms are arranged in such a way that the centres of all the particles in any row are in a straight line. The coordination number within the layer is four.
- (2) Body-centered cubic (bcc) : In this packing, the spheres of the second layers are placed between the vacant space of the first layer. The coordination number is 8.
- (3) Hexagonal close packing (hcp) and cubic close packing (ccp) :
  - (i) In both, the coordination number within a layer is six, but in three dimension, the coordination number is 12.
  - (ii) In hcp, the packing pattern is ABABAB ..... every third layer has same arrangement of atoms as the first.
  - (iii) In ccp, the packing pattern is ABC, ABCABC .....
  - (iv) In both hcp and ccp, the packing fraction is 0.74.
  - (v) Examples of hcp are Mg, Zn and ccp are Cu, Ag, Au.

### Packing Fraction :

- (i) Simple cubic (square based packing) : No. of atoms per unit cell = 1

$$V_{\text{one atom}} = \frac{4}{3}\pi r^3$$

In simple cubic, the atoms are in touch with each other along the cell edge, therefore,  $a = 2r$  and

$$V_{\text{unit cell}} = a^3 = 8r^3$$

$$\text{Hence, packing fraction. } \phi = \frac{1 \times \frac{4}{3}\pi r^3}{8r^3} = \frac{\pi}{6} = 0.52$$

- (ii) Body centered cubic packing : Atoms are in touch with each other along the body diagonal, therefore,

$$4r = \sqrt{3} a \text{ and } a^3 = \frac{64}{3\sqrt{3}}r^3$$

$$\text{Packing fraction } \phi = \frac{2 \times \frac{4}{3}\pi r^3}{\frac{64}{3\sqrt{3}}r^3} = 0.68$$

(iii) Cubic close packing (fcc) :

$$\phi = \frac{4 \times \frac{4}{3} \pi r^3}{a^3} \text{ but } a = \frac{4}{\sqrt{2}} r \text{ (atoms are in touch along the face diagonal).}$$

$$\therefore a^3 = \frac{64}{2\sqrt{2}} r^3 \quad \text{and} \quad \phi = \frac{\frac{4}{3} \pi r^3}{\frac{64}{2\sqrt{2}} r^3} \quad \phi = 0.74$$

### VOIDS :

⇒ The unoccupied space in the lattice is called void or hole or interstices. In a cubic close packed structure, there are two types of voids.

(1) Octahedral void, the coordination number of an atom occupying the void is 6.

(2) Tetrahedral void, the coordination number is 4. Tetrahedral void is smaller in size than octahedral void in cubic close packed structure.

The number of octahedral voids =  $2 \times$  number of atoms in a ccp structure.

### RADIUS RATIO

⇒ For ionic solids, the ratio of the radius of the cation to that of anion is called the radius ratio. The radius ratio for a given coordination number is fixed. radius ratio =  $\frac{r_+}{r_-}$

Radius ratio	Coordination number	Types of lattice	No. of formula units per unit cell	Example
0.155 to 0.225	3	Planar triangle	-	$\text{BO}_3^{3-}$ , solid $\text{SO}_3$
0.225 to 0.414	4	ZnS type	4	$\text{ZnS}$ , $\text{CuCl}$
0.414 to 0.732	6	NaCl type	4	$\text{MaO}$ , $\text{NaBr}$
0.732 to 1.00	8	CsCl type bcc	2 atoms in bcc and 1 formula unit in CsCl	$\text{CsCl}$ , $\text{CsBr}$

⇒ In a ccp structure, the octahedral voids can be located at the centre of each edge and at the body center. Thus, the number of octahedral voids.

$$= 1 + \frac{1}{4} \times 12 = 4$$

⇒ Tetrahedral voids are located at the body diagonal. Each body diagonal has two tetrahedral void.

∴ the number of tetrahedral voids = 8

### CRYSTAL DEFECTS :

⇒ Any deviation from an ordered arrangement in a crystal is called imperfection or defect. Defect due to missing

atoms or ion is called point defect. The point defect propagating along a line is called line defect and propagating along a plane is called plane defect.

A. Point defects are of two types :

- (1) Stoichiometric defect in which the cation to anion ratio is 1 : 1 and
- (2) Non-stoichiometric defect in which the cation to anion ratio is not equal to 1 : 1.

⇒ There are two types of stoichiometric defect.

(1) Schottky defect :

- one pair of ions (one cation and one anion) missing from the lattice position.
- The lattice remains electrically neutral.
- The density of the solid decreases.
- The defect is found only in those solids with high coordination number and high ionic character.
- Examples : NaCl, KNO<sub>3</sub>, KCl

(2) Frenkel defect :

- In this one of the ion (preferably cation) occupies the interstitial sites leaving lattice site vacant.
- The density of the solid remains same.
- The defect is observed in ionic crystals in which anion is much larger in size than the cation, e.g. AgBr, ZnS.

⇒ Silver halides (AgBr) are the solids which shows both Schottky and the Frenkel defect.

The defects in which there is a change in overall chemical combinations are called Non-stoichiometric defects.

B. Non-stoichiometric defects.

Non-stoichiometric defects are of two types

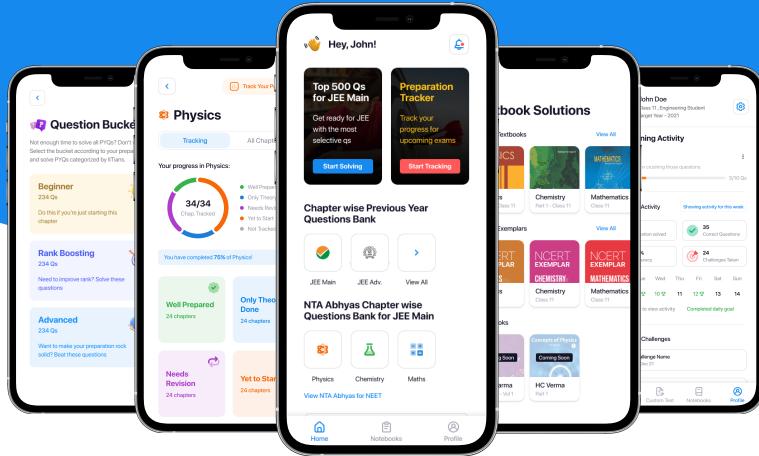
- (1) Metal excess
- (2) Metal deficiency

⇒ Metal excess defects : It can be of two types

- (1) A negative anion is missing from the lattice site which is occupied by an extra electron to make the lattice electrical neutral. The lattice position occupied by electron is called F-centre. The solids with F-centre are paramagnetic and coloured. Example : Alkali metal / alkali metal halide.
  - (2) An extra cation is present in the interstitial position and to maintain electrical neutrality, we also add one electron to the interstitial position. Such crystals are coloured and semiconductor. Example ZnO is a white solid (stoichiometric) at low temperature but yellow (non-stoichiometric) at high temperature.
- Metal deficiency defect : In this one of the cation is missing from the lattice site and the extra negative charge can be neutralized by developing an extra positive charge on the nearby cation. These crystals show semiconduction. Example : NiO, FeO. The defects which arise due to the presence of impurities in the crystal are called impurity defects.



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