

# SOLID STATE

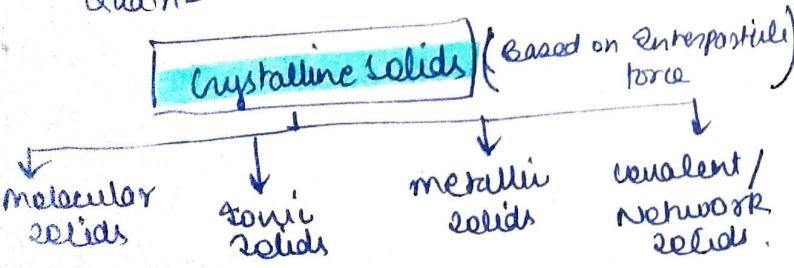
(Rough notes)

- every substance have two forces opposing forces
  - Attractive
  - thermal
- General characteristics of solid state -
  - Def. mass, volume & shape
  - Intermolecular forces are strong.
  - Intermolecular distance are short.
  - The particles only oscillate on their mean position.
  - They are incompressible and rigid.
- there are 2 types of solids -

**Crystalline**      **Amorphous.**

- |  |  |
|--|--|
| ① Have def. <del>regular</del> shape.  | ① irregular shape.                                     |
| ② long range order   | ② short range order                                    |
| ③ True solids  | ③ Pseudo solid or super cooled liquid                  |
| ④ Anisotropic  | ④ Isotropic  |
| ⑤ when cut into pieces the surface of the solid is sharp and plain & smooth. | ⑤ when cut into pieces the surface have irregularities |

eg: NaCl crystal,      eg: Quartz glass.



## 1) Molecular Solids

- ① Non-Polar molecular solids
- either formed by (Ar, He) or molecules formed by non polar covalent bonds ( $H_2, Cl_2$ )
  - Held by weak dispersion forces or London forces.
  - Soft and non conductors of electricity.
  - low melting points
  - usually lig or gaseous at room temp.

## (b) Polar molecular solids -

- ↳ Dipole-dipole interaction
- ↳ soft and non-conductors of electricity
- ↳ melting Points: PMS > NPMs
- ↳ At room temp., most of them are lig or gas.

## (c) Hydrogen Bonded molecular solids -

- ↳ Polar covalent bonds betn H and F, O & N.
- ↳ Strong H-Bonding in ice.
- ↳ Non conductors of electricity
- ↳ At room temp. → volatile, soft solids

## (2) Ionic solids

- ↳ 3 dimensions structure formed by cations and anions bounded by electrostatic forces.
- ↳ Hard and Brittle
- ↳ High m.p. and B.P.
- ↳ In solids, Ions → not free to move. so, they're electrical insulators in solid state.
- ↳ But in molten state / when dissolved in water → conduct electricity.

## (3) Metallic solids

- ↳ metal are +ve ions surrounded a sea of free electrons.
- ↳ metallic bonding
- ↳ Fe, Cu, Ag, mg.
- ↳ melting point → Fairly High
- ↳ Hard, brittle & malleable.

## (4) Covalent or network solids

- ↳ crystalline solids form non-metals result in the formation of covalent bonds betn adjacent atoms.

- ↳ Insulators.
- ↳ melting point → High

↳ eg:  $SiO_2$  (quartz), diamond, graphite

Crystal lattice - A regular 3-D arrangement of constituent in space.

Characteristics of crystal lattice :-

- ① Each point in a crystal lattice  $\rightarrow$  lattice point / lattice site
- ② Each point represents 1 constituent particle
- ③ Lattice points are joined by straight lines.

Unit cell - smallest portion of crystal lattice.

$a, b, c \rightarrow 3 \text{ edges}$   
 $\alpha, \beta, \gamma \rightarrow \text{Angle b/w edges}$  ]  $\rightarrow$  six parameters

Types of unit cells-

(a) Primitive unit cells - only at corners.

(b) Centered unit cells -

- (i) Body centered unit cells  $\rightarrow$  one particle at its body centre.
- (ii) Face centered unit cells  $\rightarrow$  one particle at the centre of each face.
- (iii) End centered  $\rightarrow$  particle is present at the centre of any 2 opp faces.

There are 7 unit cells and 14 possible 3-D lattices  $\rightarrow$  Bravais lattice.

Cubic  $\rightarrow a=b=c, \alpha=\beta=\gamma=90^\circ$

Tetragonal  $\rightarrow a=b \neq c, \alpha=\beta=\gamma=90^\circ$

Orthorhombic  $\rightarrow a \neq b \neq c, \alpha=\beta=\gamma=90^\circ$

Monoclinic  $\rightarrow a \neq b \neq c, \alpha=\beta=90^\circ, \gamma=120^\circ$

Hexagonal  $\rightarrow a=b \neq c, \alpha=\beta=90^\circ, \gamma=120^\circ$

Rhombohedral  $\rightarrow a=b=c, \alpha=\beta=\gamma=120^\circ$

Twinned  $\rightarrow a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$

Number of atoms in a unit cell

(a) Primitive unit cubic cell  $\rightarrow 8 \times \frac{1}{8} = 1$

(b) Body centered cubic [BCC]  $\rightarrow 8 \times \frac{1}{8} + 1 = 2$

(c) Face centered cubic [FCC]  $\rightarrow 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

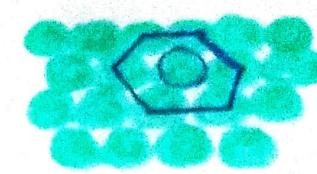
Closely packed structures -

① In 1-D -  $\hookrightarrow CN \rightarrow 2$ .

② In 2-D -  $\hookrightarrow CN \rightarrow 4$  (i) AAA type -  $\hookrightarrow CN=4$ .

(b) ABAB type -

$\hookrightarrow CN \rightarrow 6$ .



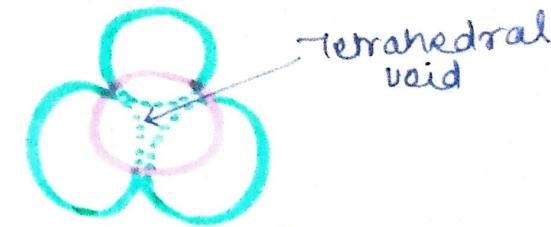
③ In 3-D

(a) 3D close packing from 2D square closed packed layers (AAA... type)

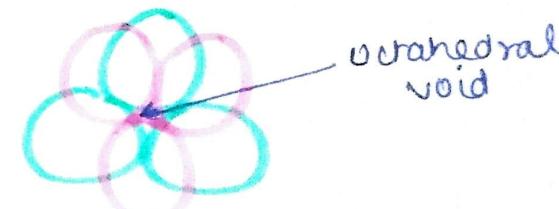
(b) 3D close packing from two dimension hexagonal close packed layers.

(i) Placing second layer over the first layer:

Tetrahedral voids  $\rightarrow$

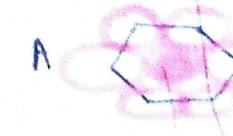
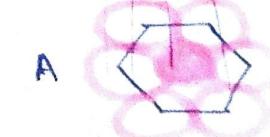


Octahedral voids  $\rightarrow$

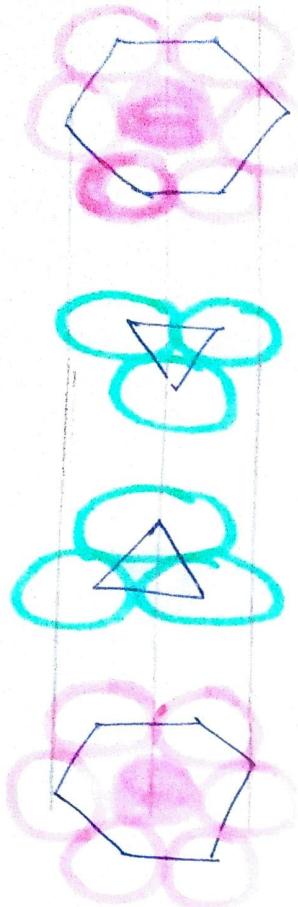


(ii) Placing third layer over the 2nd layer

(a) covering Tetrahedral voids -



(b) Covering octahedral voids  $\rightarrow$



$$8.1 \text{ g Al} = \frac{6.022 \times 10^{23} \times 8.1}{27}$$

No. of atoms in CCP = 4

$$\text{Then no. of unit cell in } 8.1 \text{ g Al} = \frac{6.022 \times 10^{23} \times 8.1}{4 \times 27}$$

$$= [4.52 \times 10^{22}]$$

[CBSE 2017]

Ques. What is the total weight of compound forms CCP structure. What is the total no. of voids in 0.5 mol of it? How many of these are tetrahedral voids? [CBSE 2013]

Ans. No. of atoms in 1 mol CCP lattice =  $6.022 \times 10^{23}$

$$\text{No. of atoms in } 0.5 \text{ mol} = \frac{6.022 \times 10^{23}}{2} = N$$

$$\text{No. of octahedral voids} = N = 3.011 \times 10^{23}$$

$$\text{No. of tetrahedral voids} = 2N = 6.022 \times 10^{23}$$

$$\text{Total voids} \rightarrow [3.011 + 6.022] \times 10^{23}$$

$$= [9.033 \times 10^{23}] \text{ voids}$$

Note :- In CCP / FCC : CN = 12  
[Each sphere is in contact w/ 12 spheres]

Formula making -

Ques. What is the formula of a compound in which the element Y forms CCP lattice and atoms of X element occupy  $\frac{2}{3}$ rd of octahedral void? [CBSE 2015]

Ans.  $X_2Y_3$

Ques. What is the formula of a compound in which the element Y formed CCP lattice and atom of X occupy  $\frac{1}{3}$ rd of tetrahedral void? [Rehni 2015]

Ans.  $X_2Y_3$

Ques. Calculate the no. of unit cells in 8.1 g of aluminium, if it crystallises in a face centered cubic structure. (Atomic mass of Al = 27 g/mol)

Ans. 27 g of Al (1 mol) =  $6.022 \times 10^{23}$  atoms.

Ques. An alloy of gold and cadmium crystallizes with a cubic structure in which gold atoms occupy the corners and cadmium atoms fit into the face centres. Assign formula for this alloy. [CBSE 2011]

Ans. No. of gold atoms in a unit cell = 1

1d at face centre = 3 atoms.

Ratio of no. of atoms = 1 : 3

$\therefore$   $[Au_1 Cd_3]$

## Packing efficiency -

① In HCP and CCP structures -

$$\hookrightarrow r = \frac{a}{2\sqrt{2}}$$

Volume of unit cell =  $[2\sqrt{2}r]^3$

Packing efficiency = 74.1.

② In BCC -

$$\hookrightarrow r = \frac{\sqrt{3}}{4}a$$

Volume of the unit cell =  $\left(\frac{4r}{\sqrt{3}}\right)^3$

Packing efficiency = 68.1.

③ In simple cubic lattice -

$$\hookrightarrow a = 2r$$

$$\hookrightarrow \text{volume} = 8r^3$$

Packing efficiency = 52.41.

Density of a unit cell =  $\frac{zM}{a^3 N_A}$

Ques 1. Aluminium crystallizes in fcc structure. Atomic radius of metal is 125 pm what is the length of the side of unit cell of the metal? [CBSE 2013]

$$\text{Ans. } r = \frac{a}{2\sqrt{2}}$$

$$125 \times 2\sqrt{2} = a$$

$$[a = 353.61 \text{ pm}]$$

Ques 2. An element with density  $11.2 \text{ g cm}^{-3}$  form a fcc lattice with edge length  $4 \times 10^{-8} \text{ cm}$ . calculate the atomic mass of the element.

$$\text{Ans. } d = \frac{zM}{a^3 N_A}$$

$$M = \frac{11.2 \times (4 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{4}$$

$$M = 108 \text{ g mol}^{-1}$$

Question Silver crystallizes in fcc lattice if edge length of unit cell is  $4.077 \times 10^{-8} \text{ cm}$ . Then calculate the radius of silver atom. [CBSE 2015]

Answer

$$a = 4.077 \times 10^{-8} \text{ cm}$$

For FCC,  $Z=4$ ;  $r = \frac{a}{2\sqrt{2}}$

$$\text{then, } r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 4.077 \times 10^{-8}}{4}$$

$$[r = 1.44 \times 10^{-8} \text{ cm}]$$

Ques Tungsten crystallizes in BCC unit cell. If edge length of unit cell is 316.5 pm, what is the radius of tungsten atom?

$$\text{Ans. For BCC } [r = \frac{\sqrt{3}}{4}a] \quad a = 316.5 \text{ pm}$$

$$r = \frac{\sqrt{3}}{4} \times 316.5 = 137.04 \text{ pm.}$$

Ques. The density of copper metal is  $8.95 \text{ g cm}^{-3}$ . If the radius of copper atom is 127.8 pm. Is the copper unit cell in simple cubic, a BCC or FCC structure  
[Atomic mass of Cu =  $63.54 \text{ g mol}^{-1}$ ,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ ]

Ans.

$$\text{Given, } d = 8.95 \text{ g cm}^{-3}$$

$$r = 127.8 \text{ pm}$$

$$\textcircled{a} \text{ simple cubic } \therefore a = 2r = 2 \times 127.8 = 255.6 \text{ pm}$$

$$\text{density, } d = \frac{1 \times 63.5}{255.6 \times 10^{-10} \times 6.02 \times 10^{23}}$$

$$\boxed{d = 6.34 \text{ g cm}^{-3}}$$

[Not simple cubic]

$$\textcircled{b} \text{ BCC: } 4r = \sqrt{3}a$$

$$\text{then } a = \frac{4}{\sqrt{3}} \times 127.8 = 295.15 \text{ pm}$$

$$= 8.21 \text{ g cm}^{-3}$$

$$d = \frac{2 \times 63.5}{(295.15)^3 \times 6.02 \times 10^{23}}$$

[Not FCC]

① FCC :  $\frac{4a}{\sqrt{2}} = 4r$   
 $a = \frac{4}{\sqrt{2}} \times 127.8 = 361.4 \text{ pm}$

density,  $d = \frac{4 \times 63.5}{(361.4 \times 10^{-10})^3 (6.02 \times 10^{23})}$

$d = 8.94 \text{ g cm}^{-3}$

∴ Hence copper unit cell is FCC.

Question: An element has atomic mass 93 g/mol and density 11.5 g/cm<sup>3</sup>. If the edge length of its unit cell is 300 pm, identify the type of unit cell.

Ans.  $m = 93 \text{ g mol}^{-1}$ ,  $d = 11.5 \text{ g cm}^{-3}$   
 $a = 300 \text{ pm}$

$$d = \frac{Zm}{a^3 N_A}$$

$$Z = \frac{da^3 N_A}{M}$$

$$Z = \frac{11.5 \times (300)^3 \times 6.02 \times 10^{23}}{93}$$

$Z = 2$ . → BCC unit cell

Question: Niobium crystallises in BCC structure. If its density is 8.55 g/cm<sup>3</sup> calculate the atomic radius of niobium (Atomic mass 93 u)

Answer  $d = 8.55 \text{ g cm}^{-3}$   
 $m = 93 \text{ g/mol}$

$$d = \frac{Zm}{a^3 N_A}, a = \sqrt[3]{\frac{Zm}{d N_A}}$$

$$a = \sqrt[3]{\frac{2 \times 93}{8.55 \times 6.02 \times 10^{23}}}$$

$$a = 3.3 \times 10^{-8} \text{ cm}$$

For BCC,  $4r = \sqrt{3}a$

$$r = \frac{\sqrt{3} \times 3.3 \times 10^{-8}}{4} = 1.42 \times 10^{-8} \text{ cm}$$

$r = 1.42 \times 10^{-8} \text{ cm}$ .

Ques The well known mineral fluoride is chemically calcium fluoride. It is known that is one unit cell of this mineral, there are 4  $\text{Ca}^{2+}$  ions and of ions and that  $\text{Ca}^{2+}$  ions are arranged in fcc lattice. The  $\text{F}^-$  fill all tetrahedral holes in FCC lattice of  $\text{Ca}^{2+}$  ions. The edge of unit cell is  $5.46 \times 10^{-8} \text{ cm}$  in length. The density of solid is  $3.188 \text{ g cm}^{-3}$ . Use this information to calculate Avogadro No.  
[molar mass of  $\text{CaF}_2$  = 78.08 g/mol]

Ans

$\Rightarrow N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

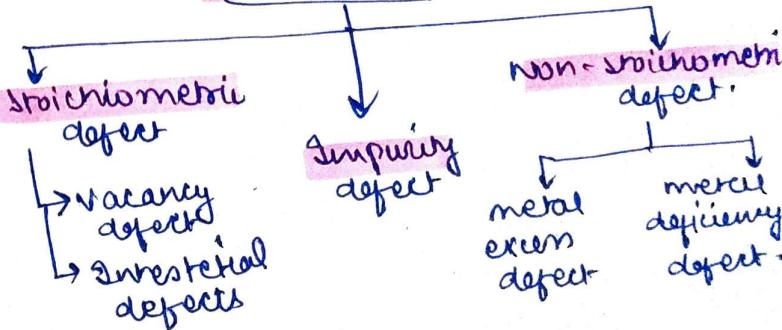
### Impurities in solid

Defects (impurities) in solid  
↳ Deviation from the perfectly ordered arrangement of constituent particle.

Point defects - deviation from ideal arrangement around a point in a crystal substance.

Line defects - deviation from ideal arrangement in entire row of lattice points

### Point defects



### 1. Stoichiometric Defects

↳ do not disturb the stoichiometry of the solid. → intrinsic / thermodynamic defects.

#### ① Vacancy defect.

↳ when some lattice sites are vacant.  
↳ density ↓  
↳ can also be developed when the substance is heated.

## (b) Interstitial defect

↳ when some particle occupy interstitial sites.

↳ Density ↑

## (c) Frenkel Defect

↳ when cations displaces from its normal site to an interstitial site.

↳ distortion defect

↳ does not change the density

e.g.: Ionic solids [ZnS, AgCl, AgBr]

↳ large size difference between cations and anions.

## (d) Schottky defect

↳ Vacancy defect → missing of both cations and anions.

↳ decreases the density of substance.

e.g.: NaCl, KCl, CsCl, AgBr.

↳ AgBr shows both Frenkel & schottky defect [Delhi 2014, 2015]

Note:

- ① Density decreases → schottky/vacancy defect.
- ② Density does not change → Frenkel effect.
- ③ Density increases → interstitial defect

Impurity Defects - If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised.

~~the occupied sites of  $\text{Na}^+$  ion are occupied by  $\text{Sr}^{+2}$~~   
each  $\text{Sr}^{+2}$  replaces two  $\text{Na}^+$  ions.  
occupies the site of one ion and other site remains vacant.

[No. of cationic vacancies = No. of  $\text{Sr}^{+2}$  ions]

## Non-stoichiometric Defect :-

### (i) metal excess defect →

↳ due to anionic vacancies: Alkali halides like NaCl and KCl.

↳ crystals of NaCl is heated in an atmosphere of sodium vapour. Na atoms → deposited on surface of crystals.

↳  $\text{Cl}^-$  ions diffuse to the surface of crystal and combine with Na to form NaCl, this happens w/ a loss of e-. by Na atom to form  $\text{Na}^+$  ion. Crystal now have extra  $\text{Na}^+$  ion.

↳ Anionic sites occupied by  $\text{e}^-$  are known as F-centres.

↳ Due to presence of F-centre in NaCl → crystal turns → yellow colour.

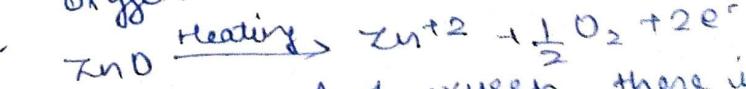
↳ Excess of Li makes LiCl → pink colour.

↳ Excess of K makes KCl → violet colour.

Reason of colour :-  
the colour results by excitation of unpaired electrons - when they absorb energy from the visible light falling on the crystal.

# metal excess defect due to presence of extra cations at interstitial sites.

↳ ZnO is white in colour at room temperature. On heating it loses oxygen and turns yellow.



→ After removal of oxygen, there is excess of zinc in crystals and its formula becomes  $\text{Zn}_{1+x}\text{O}$ .

↳  $\text{Zn}^{+2}$  and electrons move to interstitial sites.

## Metal Deficiency defect.

↳ Solids which contain less amount of metal than the stoichiometric proportion.



↳ Some  $\text{Fe}^{+2}$  cations are missing and less of positive charge is made up by the presence of required no. of  $\text{Fe}^{+3}$  ions.

Ques: - If  $\text{NaCl}$  is doped with  $10^{-3}$  mole present percent  $\text{SrCl}_2$ . What will be the concentration of cationic vacancies?

Ans.

$$\text{Conc}' \text{ of } \text{Sr}^{+2} = 10^{-3} \text{ mol percent} = \frac{10^{-3}}{100} \\ = 10^{-5} \text{ mol}$$

$$1 \text{ mol of } \text{Sr}^{+2} = 6.022 \times 10^{23} \text{ Sr}^{+2} \text{ ions}$$

$$10^{-5} \text{ mol of } \text{Sr}^{+2} = 6.022 \times 10^{23} \times 10^{-5}$$

The conc' of cationic vacancies =

$$6.022 \times 10^{-18}$$

Ques: A metal crystallizes in FCC unit cell with  $a = 0.56 \text{ nm}$ . Calculate the density of metal if it contains 0.1% Schottky defects. [At. mass = 40 g/mol]

Ans. Due to Schottky defect, the vacant space increases resulting in the decrease of no. of atoms per unit cell.

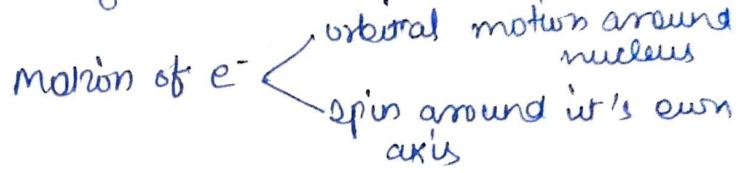
$$Z = 4 - \frac{4 \times 0.1}{100} = 3.996 \text{ atom}$$

$$d = \frac{Z M}{a^3 N_A} = \frac{3.996 \times 40}{(0.56)^3 \times 6.022 \times 10^{23}}$$

$$d = 1.51 \text{ g/cm}^3$$

## Magnetic Properties of solids

$e^-$  motion inside the atom is responsible for magnetic behaviour.

Motion of  $e^-$  

If all the  $e^-$ 's are paired,  
∴ The Net magnetic moment = 0

### • Diamagnetic

↳ weakly repelled by the magnetic field.

↳ Net magnetic moment = 0  
e.g., diamagnetic substances have all  $e^-$  paired.

e.g.:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NaI}$

### • Paramagnetic

↳ weakly attracted by external magnetic field.

↳ Arises due to presence of unpaired  $e^-$ .

↳ temporary magnetised

e.g.:  $\text{U}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Fe}^{+2}$ ,  $\text{O}_2$ ,  $\text{Cr}^{+3}$

### • Ferromagnetic

↳ strongly attracted by the magnetic field

↳ permanently magnetised.

e.g.:  $\text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{CrO}_2$ ,  $\text{Yd}$ .

↳ Parallel alignment of magnetic moments.

### • Antiferromagnetic

↳ unaffected in external magnetic field

↳ magnetic moments are arranged anti-parallel, ∴ Net magnetic moment = 0.

