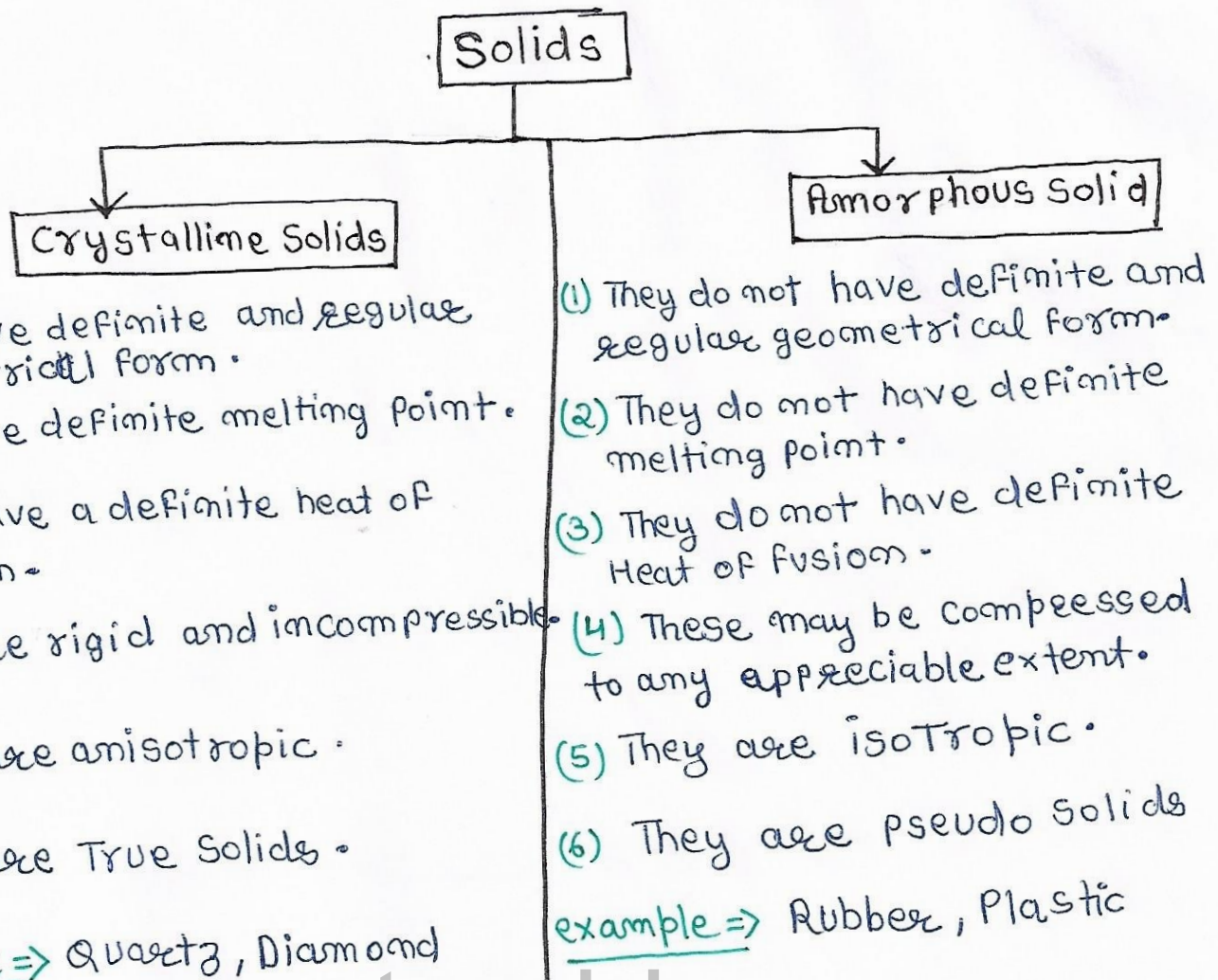


# Solid state

Solids are characterised by the state of matter in which particles are closely packed and held together by strong intermolecular attractive forces.

## Properties of Solids =>

- (1) In Solid state the particles are not able to move randomly.
- (2) They have definite shape and volume.
- (3) Solids have high density.
- (4) Solids have high and sharp melting point which depends on the strength or value of binding energy.
- (5) They are very low compressible.
- (6) They show very slow diffusion.

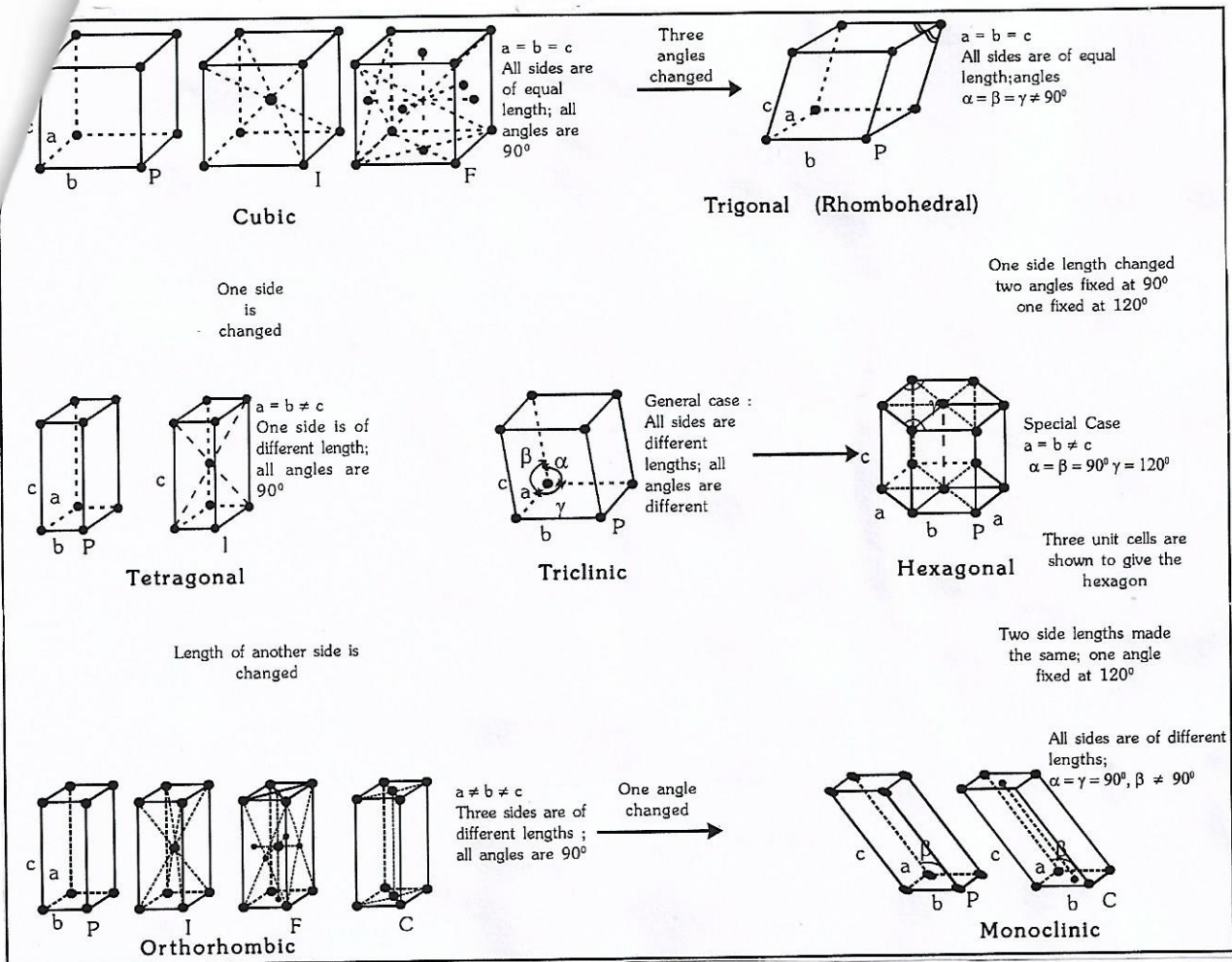


# Classification of Crystalline Solids

[On the basis of intermolecular forces]

Some Important Characteristics of Various types of Crystals

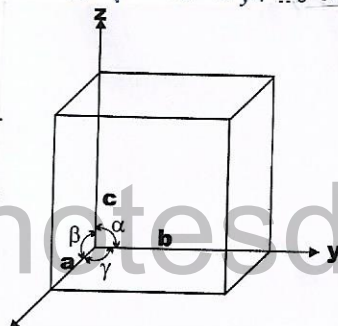
Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
1. Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
2. Binding forces	Electrostatic attraction between ions	Shared electrons	vander Waals or Dipole-dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
3. Hardness	Hard	Very hard Graphite is soft	Soft	Hard or soft
4. Brittleness	Brittle	Intermediate	Low	Low
5. Melting point	High	Very high	Low	Varying from moderate to high
6. Electrical Conduction	Semi conductor due to crystal imperfections, conductor in fused state	Non-conductor Graphite is good conductor	Bad conductor	Good conductors
7. Solubility in Polar solvents	Soluble	Insoluble	Soluble as well as insoluble	Good conductors
8. Heat of Vaporisation (kj mol <sup>-1</sup> )	NaCl(s) 170-75	Graphite 718-43	NH <sub>3</sub> (s) 23.55	Cu(s) 304.59
9. Heat of fusion (kj mol <sup>-1</sup> )	NaCl 28.45	- -	NH <sub>3</sub> (s) 5.65	Cu(s) 13.016
10. Example	NaCl, KNO <sub>3</sub> CsCl, Na <sub>2</sub> SO <sub>4</sub> ZnS	Diamond, graphite, Quartz (SiO <sub>2</sub> ), SiC	H <sub>2</sub> O(s), CO <sub>2</sub> (s), Sulphur, Sugar, Iodine, noble gases	Na, Cu, Ag, Fe, Pt, alloys



\*\* These crystal systems differ in the length of unit cell edges ( $a, b, c$ ) and the angles between the unit cell edges. In cubic and trigonal systems, the three unit edges are of equal length, but for the rest five systems it is not so.

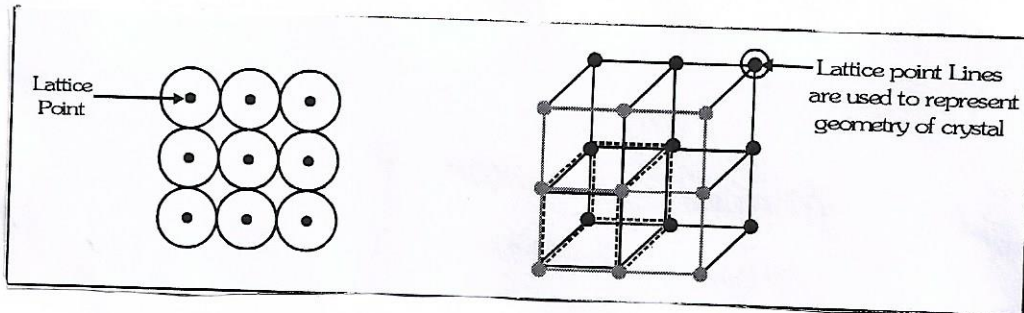
Unit-cell ⇒ Unit cell of the crystalline substance is defined as the smallest repeating unit which shows the complete geometry of the crystalline substance.

\*\* A unit cell is characterized by the edge length  $a, b, c$  along the three edges of the unit cell and the angles  $\alpha, \beta, \gamma$  between the pair of edges  $bc, ca$  and  $ab$  respectively.



# Crystalline Lattice/Space-Lattice/3D-Lattice =>

Space Lattice is a regular arrangement of Lattice points showing how the particles are arranged at different site in 3D-view.



\*\* The three dimensional distribution of component particles in a crystal can be found by X-Ray diffraction of different faces of the crystal

\*\* on the basis of the classification of symmetry, the crystals have been divided into seven systems. These can be grouped into 32 classes which in turn can be regrouped into 7 crystal system.

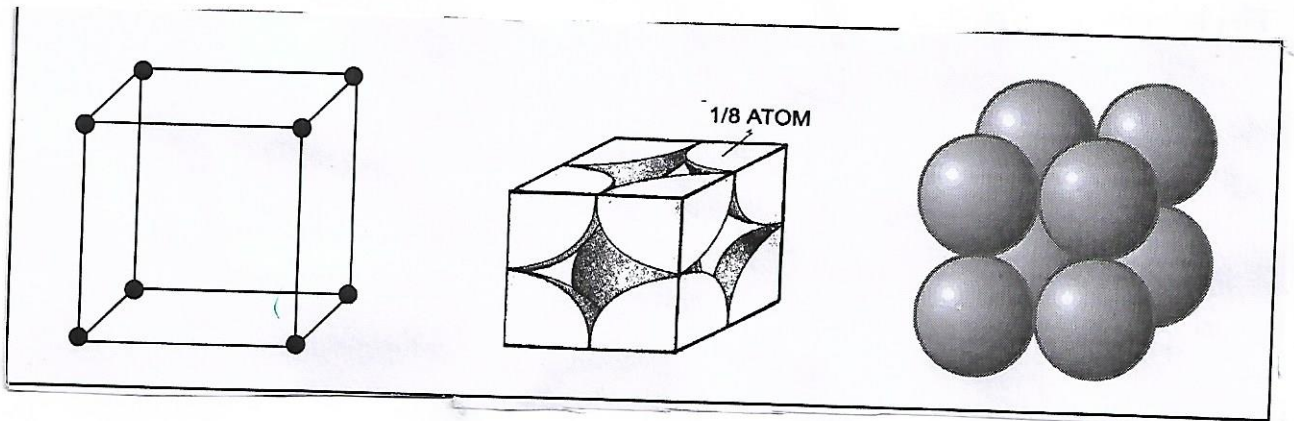
The Seven Crystal Systems

Name of System	Axes	Angles	Bravais Lattices
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred = 3
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Body centred = 2
3. Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive = 1
4. Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred End centred = 4
5. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ;$ $\beta \neq 90^\circ$	Primitive, End - centred = 2
6. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive = 1
7. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Primitive = 1 Total = 14

## Types of unit cell [Bravais-Lattice] =>

### [a] Simple / primitive / Basic unit cell =>

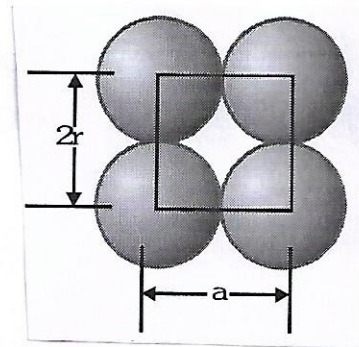
A unit cell having Lattice point only at corners called S.C.C i.e in this case there is one atom at each of the eight corners of the unit cell considering an atom at one corner. ~~as the~~ it will be found that this atom is surrounded by six atoms thus C.N will be Six.



### (i) Relationship between edge length "a" and atomic radius r

$$a = 2r$$

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



### (ii) Number of atoms in unit cell =>

$$\frac{1}{8} \times 8 = 1$$

corners

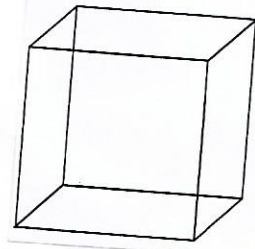
### (iii) Packing efficiency [P.E] =>

$$P.E = \frac{1 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} \left[ r = \frac{a}{2} \text{ and } V = a^3, n = 1 \right]$$

$$= \frac{\pi}{6} = 0.524 \text{ or } 52.4\%$$

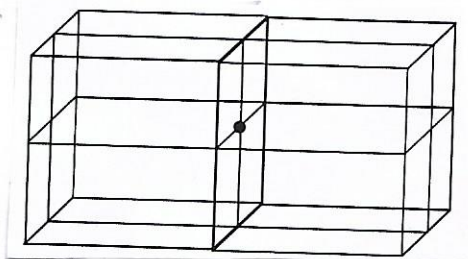
## GEOMETRY of a cube $\Rightarrow$

- \*\* Number of corners = 8
- \*\* Number of faces = 6
- \*\* Number of edges = 12
- \*\* Number of cube centre = 1
- \*\* Number of cube diagonals = 4
- \*\* Number of face diagonals = 12

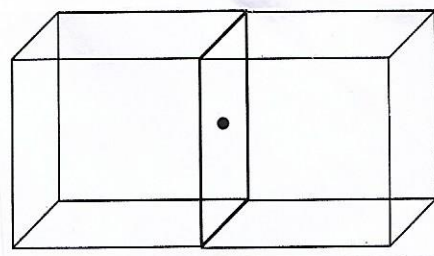


## Contribution of an atom at different sites of cube $\Rightarrow$

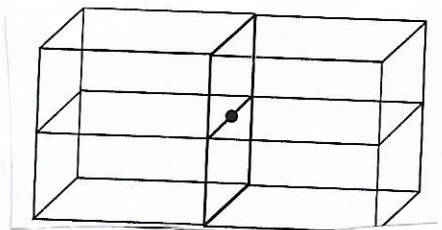
- (a) A corner of a cube is common in 8 cubes. so  $\frac{1}{8}$ <sup>th</sup> part of an atom is present at this corner of cube.
- (b) A face of cube is common in 2 cubes. so  $\frac{1}{2}$ <sup>th</sup> part of an atom is present at the face of a cube.
- (c) An edge of a cube is common in 4 cubes, so  $\frac{1}{4}$ <sup>th</sup> part of the atom is present at the edge of a cube.
- (d) A cube centre is not common in any another cube. so one complete atom is present at the cube centre.



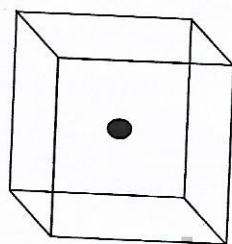
[at corner]



[at face]



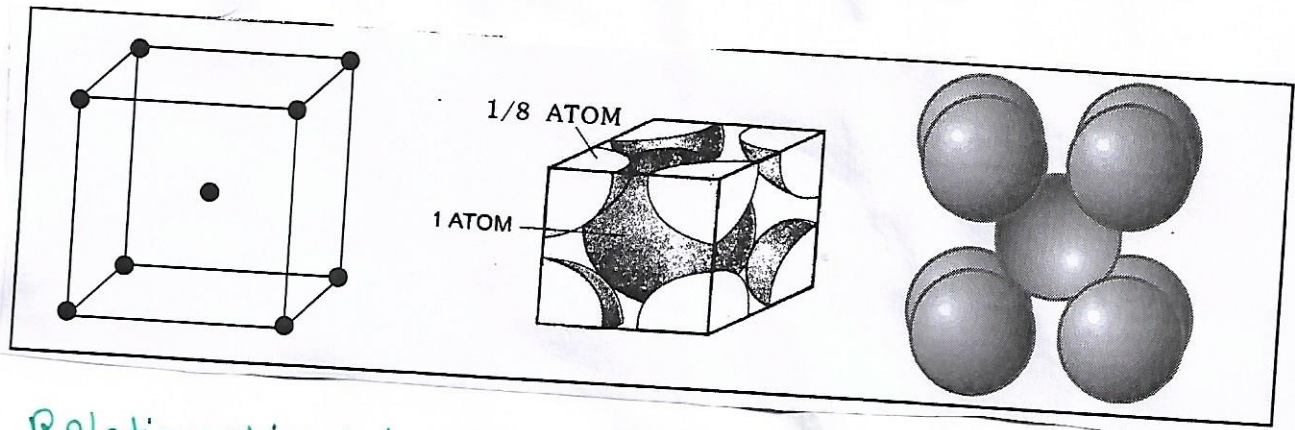
[at edge]



[at cube centre]

## (b) Body-centred cubic cell [b.c.c] $\Rightarrow$

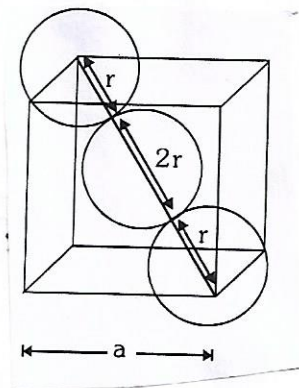
A unit cell having lattice point at the body centre in addition to the lattice corners as body centred unit cell.



(i) Relationship b/w edge length 'a' and 'r'  $\Rightarrow$

cube diagonal  $\leftarrow \sqrt{3} a = 4r$

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



(ii) Number of atom present in unit cell  $\Rightarrow$   
 $\left(\frac{1}{8} \times 8\right) + (1 \times 1) = 2$   
at corner at Body centre

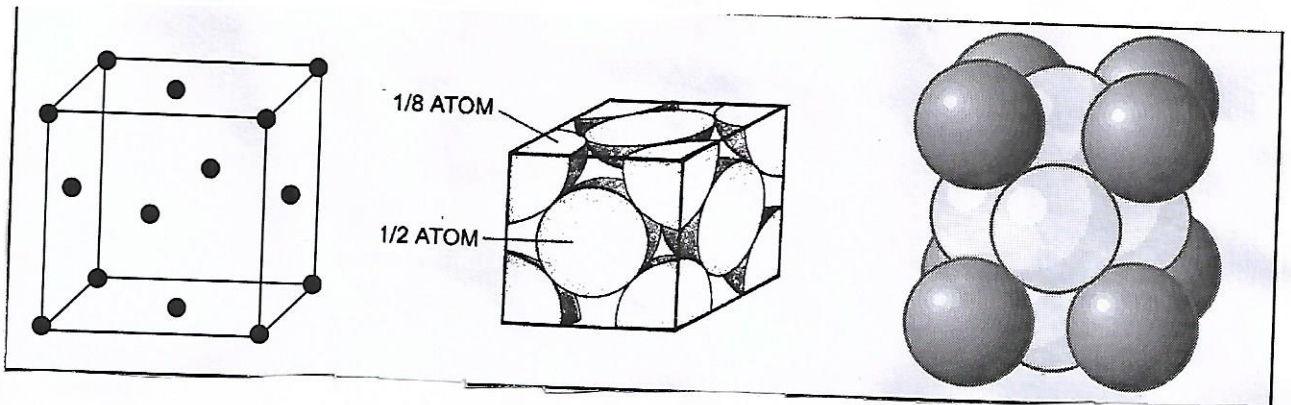
(iii) Packing efficiency  $\Rightarrow$

$$P.E = \frac{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3} a}{4}\right)^3}{a^3} = \frac{\sqrt{3} \pi}{8} = 0.68$$

In B.C.C 68% of Total Volume is occupied by atom.

### (c) Face-centred cubic cell [F.C.C.] =>

A unit cell having Lattice point at every face centre in addition to the Lattice point at every corner called F.C.C.  
For F.C.C.

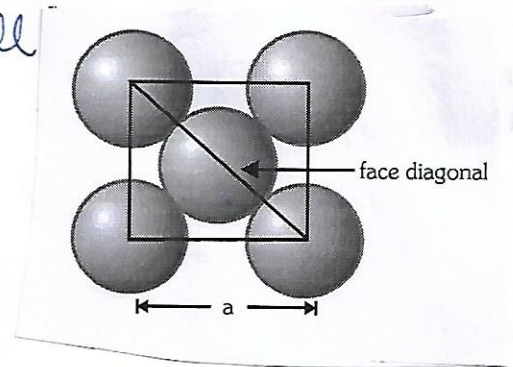


### (i) Relationship b/w 'a' and 'r' =>

In FCC, along the face diagonal all atoms touches each other and the length of face diagonal is  $\sqrt{2}a$

$$4r = \sqrt{2}a$$

$$r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$$



### (ii) Number of atoms per unit cell =>

$$\underbrace{\left(\frac{1}{8} \times 8\right)}_{\text{corners}} + \underbrace{\left(6 \times \frac{1}{2}\right)}_{\text{faces}} = 1 + 3 = 4$$

### (iii) Packing efficiency =>

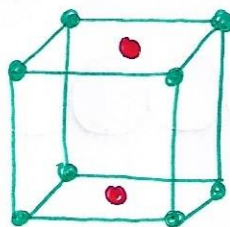
$$\begin{aligned} \text{P.E} &= \frac{n \times \frac{4}{3} \pi r^3}{V} \\ &= \frac{4 \times \frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \end{aligned}$$

In FCC, 74% of total volume is occupied by atoms.



### (d) end centered unit cell =>

A unit cell having lattice point at the centres of only one set of opposite faces in addition to the lattice point at every corner called as end centered unit cell.



### Crystal density of the crystal =>

If the length of edge of the unit cell is known we can calculate the density of the crystal as follows:

Let edge length of a cubic crystal =  $a$  cm

$\therefore$  Volume of unit cell =  $a^3$  cm

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

$$\text{mass of unit cell} = \text{no of atoms in unit cell} \times \text{mass of each atom}$$

$$= Z \times m$$

$$m = \frac{M}{N_A} \rightarrow \text{molar mass}$$

$$\text{SO C.D} = \frac{Z \cdot m}{a^3} = \frac{Z \cdot M}{a^3 N_A}$$

$$\boxed{\text{C.D} = \frac{ZM}{a^3 N_A}}$$

## close packed structure $\Rightarrow$

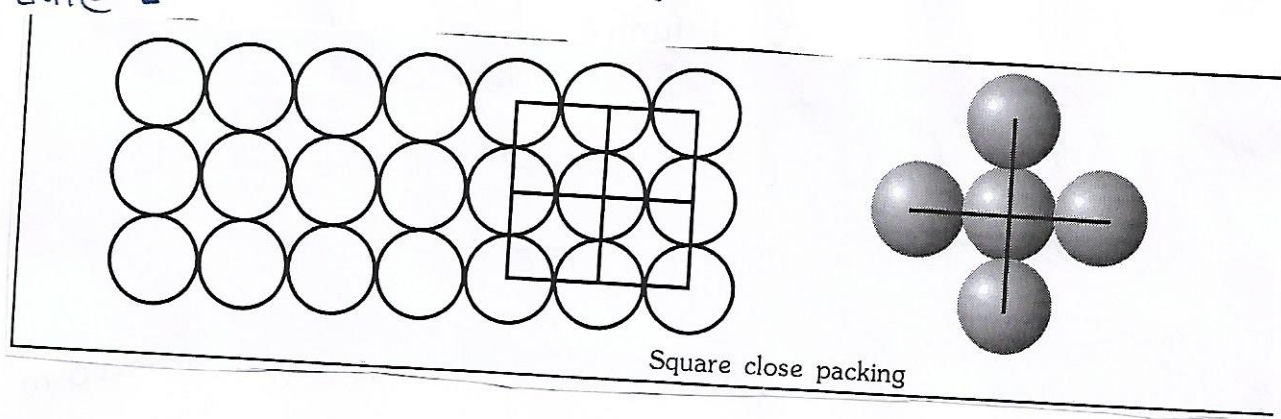
### (a) One-dimension $\Rightarrow$

Arrangement of different atoms in a row touching each other forms one dimension close packing

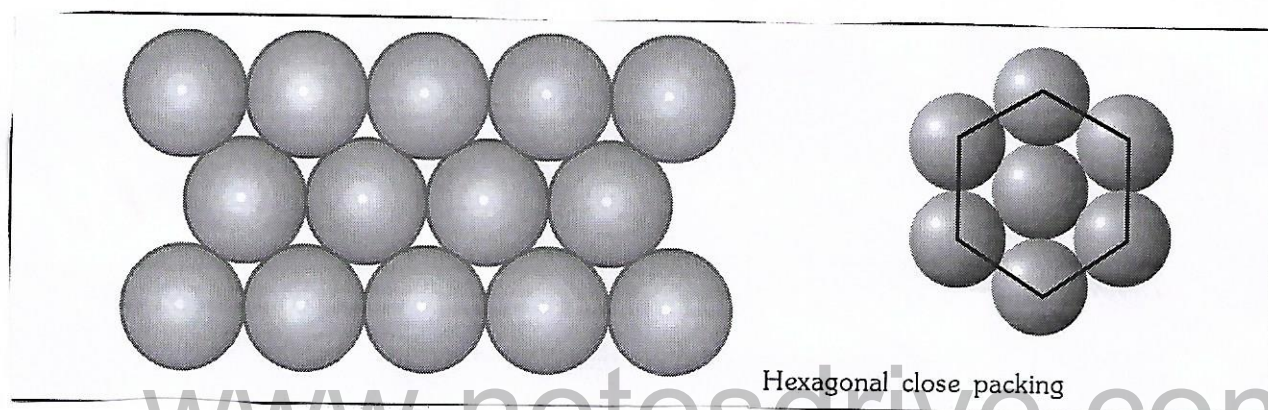


### (b) 2-D - close packing $\Rightarrow$ The row of particle can be stacked in two ways


(i) square - close packing  $\Rightarrow$  Spheres are packed in such a way that they align together vertically as well as horizontally and center of all spheres are in a straight line.

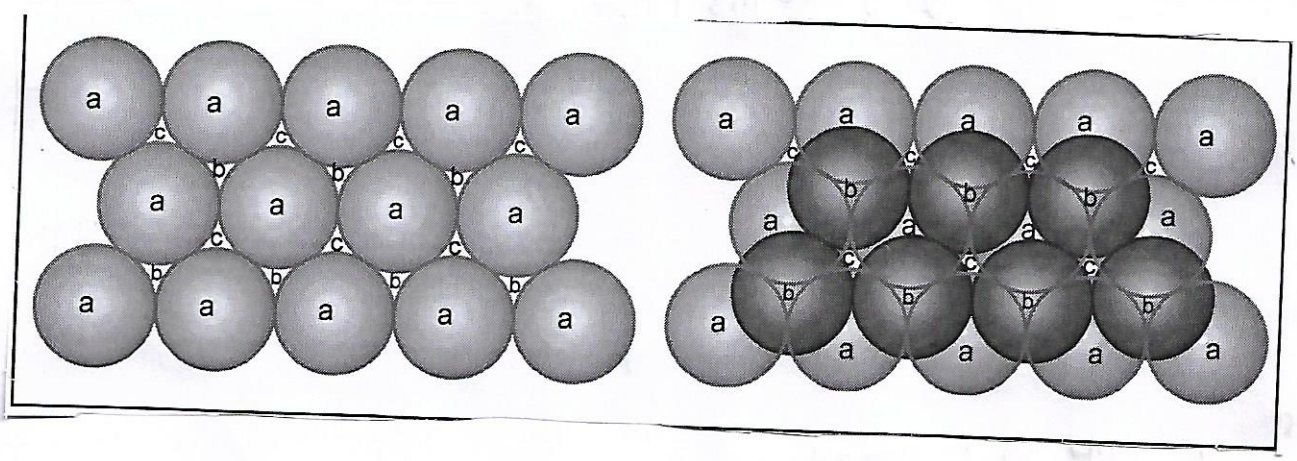


(ii) Hexagonal close packing  $\Rightarrow$  when second row is arranged in the depressions of first row and all atoms diagonally to each other.




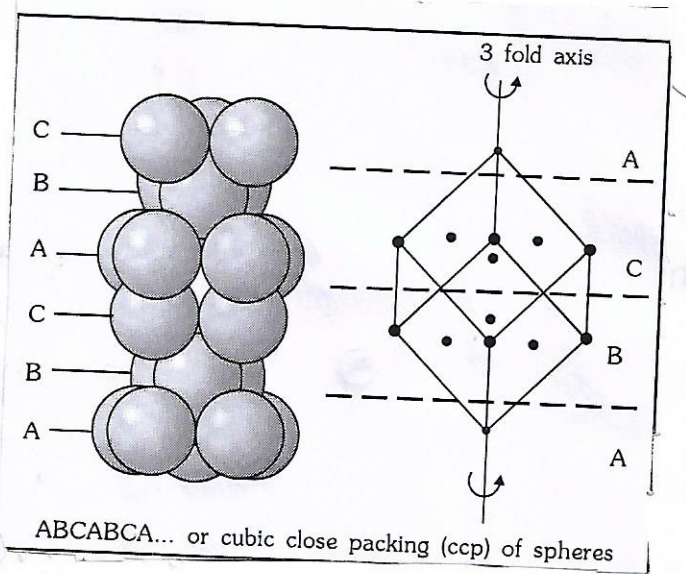
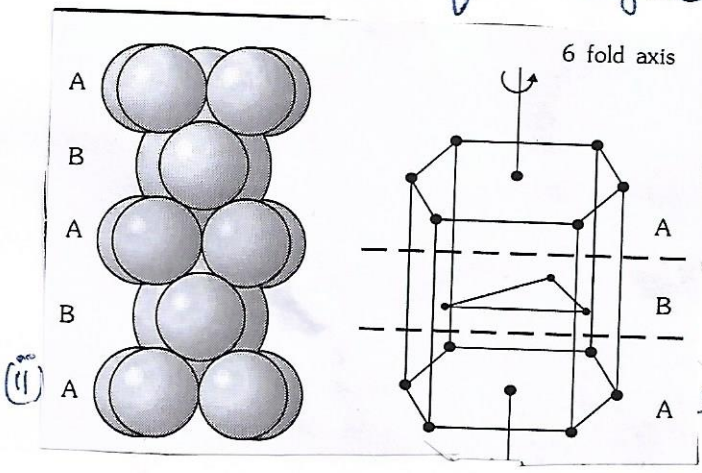
(iii) 3-D close packing  $\Rightarrow$

(i) 3-D close packing from 2-D square close packed layers  $\Rightarrow$   
 It is layer packing in which second layer is placed over first layer in such a way that all the spheres are exactly above each other. This arrangement forms AAA Type of lattice.  forms simple cubic lattice and its unit cell is primitive cubic unit cell.



(ii) 3-D close packing from 2-D hexagonal close packed layers  
 When layers containing hexagonal close packing are arranged over each other, two types of arrangements are feasible.

(i) Arrangement of 2<sup>nd</sup> layer over the first layer 



(ii) Formation of 3<sup>rd</sup> layer over the 2<sup>nd</sup> layer.

Q A unit cell consists of a cube in which x atoms are at the corners and y atoms are at the face centres. If two atoms are missing from two corners of the unit cell, what is the formula of the compound?

Sol<sup>n</sup>

Total contribution of "x" atom from 6 corners

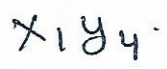
$$= 6 \times \frac{1}{8} = \frac{3}{4}$$

No of y atoms from face centres =  $6 \times \frac{1}{2} = 3$

$$X : Y = \frac{3}{4} : 3$$

$$= 3 : 12$$

$$= 1 : 4$$



Q A compound is formed by two elements X and Y. Atoms X are in CCP arrangement and Y-atom occupy all oh sites and alternative Th formula?

Sol<sup>n</sup>

CCP = FCC

X  $\rightarrow$  4

Th-Void - 8

oh-Void - 4

$$= X_4 Y_8$$

$$= X Y_2$$

Q Three atoms P, Q, R crystallize in a cubic solid lattice having P-atoms at corners, Q-atom at body centre and R-atoms at the face centres. Find formula of compound?

Sol<sup>n</sup>

P  $\rightarrow$  corners

Q  $\rightarrow$  Body centre

R  $\rightarrow$  face centre

$$\left( \frac{8 \times \frac{1}{8}}{8} \right) \cdot Q \cdot \left( \frac{6 \times \frac{1}{2}}{2} \right) \rightarrow P Q R_3$$

Ex. Element A is every element of FCC, atom B is present at every Octahedral void, atom C is present at 25% of Tetrahedral void. Find out the possible molecular formula of the compound ?

Sol. Atom A is every element of FCC = 4 atoms of A

Atom B is present at every octahedral void = 4 atoms of B

Atom C is present at 25% of tetrahedral void =  $8 \times \frac{25}{100} = 2$  atom of C

So, the possible molecular formula is  $A_4 B_4 C_2 = A_2 B_2 C$ .

### 16. LIMITING RADIUS RATIO :

An ionic crystal contains a large number of cations and anions. Generally cations are Smaller in size than that of anions. The cations are surrounded by anions and they touch each other. These ions are arranged in space in such a way to produce maximum stability. The stability of the ionic crystal may be described in terms of radius ratio i.e. the ratio of the radius of cation ( $r$ ) to that of anion ( $R$ ) is ( $r/R$ ). The range of ( $r/R$ ) may be expressed as limiting radius ratio. This value is important to determine the arrangement of the ion in different types of crystals.

Evidently radius ratio ( $r/R$ ) plays a very important role in deciding the stable structure of ionic crystal. Larger cations prefer occupying larger holes (cubic etc.) and smaller cations prefer occupying smaller holes (tetrahedral etc.)

(i) **Triangular** : All anions touches each other and co-ordination number is 3

$$\cos\theta = \frac{r^-}{r^- + r^+}$$

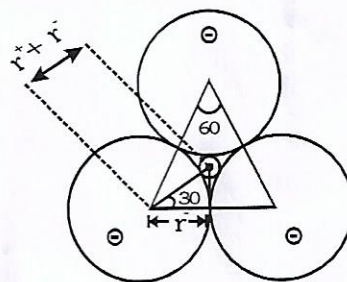
$$\cos 30 = \frac{\sqrt{3}}{2} = \frac{r^-}{r^- + r^+}$$

$$\sqrt{3}r^- + \sqrt{3}r^+ = 2r^-$$

$$\sqrt{3}r^+ = (2 - \sqrt{3})r^-$$

$$\frac{r^+}{r^-} = \frac{2 - \sqrt{3}}{\sqrt{3}} = \frac{2 - 1.73}{1.73} = \frac{0.27}{1.73} = 0.155$$

$$\text{L.R.R.} = 0.155 = \frac{r^+}{r^-} < 1$$



(ii) **Tetrahedral void** : All anions touches each other and co ordination number of cation is 4.

$$\text{Face diagonal } AC = \sqrt{2}a = 2r^-$$

$$r^- = \frac{a}{\sqrt{2}} \text{ or } a = \sqrt{2}r^-$$

Triangle ACD -

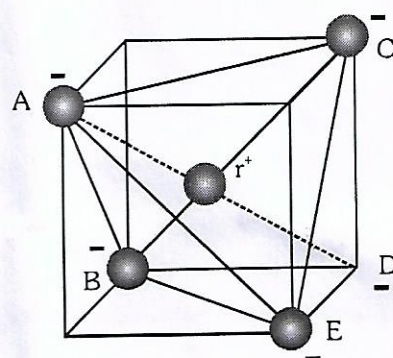
$$AD^2 = AC^2 + CD^2$$

$$AD^2 = (\sqrt{2}a)^2 + (a)^2 = 2a^2 + a^2 = 3a^2$$

$$AD = \sqrt{3} a$$

According to cube diagonal AD

$$\therefore \frac{\sqrt{3}a}{2} = r^+ + r^-$$



$$\therefore \sqrt{3}a = 2r^+ + 2r^- = AD$$

Put the value of  $a = \sqrt{2}r^-$

$$\sqrt{3} \times \sqrt{2} r^- = 2r^+ + 2r^-$$

$$\frac{\sqrt{3} \times \sqrt{2} r^-}{2r^-} = \frac{2r^+ + 2r^-}{2r^-}$$

$$\frac{\sqrt{3}}{\sqrt{2}} = \frac{r^+}{r^-} + 1$$

$$\frac{r^+}{r^-} = \frac{\sqrt{3}}{\sqrt{2}} - 1$$

$$\frac{r^+}{r^-} = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.73 - 1.414}{1.414} = 0.225$$

(iii) **Octahedral void** : All the anions are touch each other and co ordination number is 6.

$$\text{In } \triangle ABC \quad AC^2 = AB^2 + BC^2$$

$$= a^2 + a^2$$

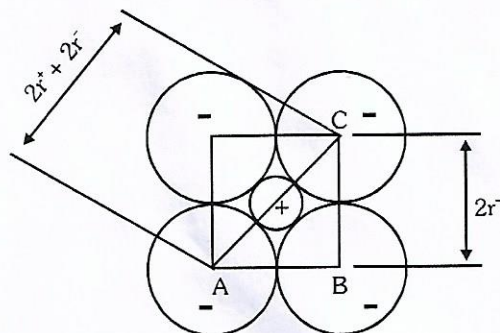
$$AC = \sqrt{2} a$$

$$2r^+ + 2r^- = AC = \sqrt{2} a$$

$$BC = a = 2r^-$$

$$\frac{2r^+ + 2r^-}{2r^-} = \frac{\sqrt{2} \times 2r^-}{2r^-}$$

$$\frac{r^+}{r^-} + 1 = \sqrt{2} \Rightarrow \frac{r^+}{r^-} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$



(iv) **Cubic void** : All the anions are touch each other and co ordination number is 8.

According to cube diagonal

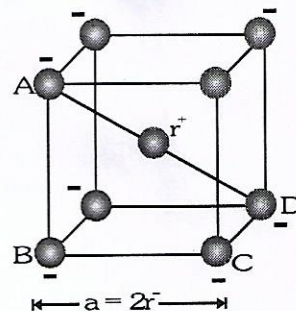
$$AD = \sqrt{3} a = 2r^+ + 2r^-$$

$$(a = 2r^- = BC)$$

$$\sqrt{3} \times 2r^- = 2r^+ + 2r^-$$

Dividing by  $2r^-$  on both sides.

$$\sqrt{3} = \frac{r^+}{r^-} + 1 \Rightarrow \frac{r^+}{r^-} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$$



The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular  $\xrightarrow{0.225}$  Tetrahedral  $\xrightarrow{0.414}$  octahedral  $\xrightarrow{0.732}$  Cubic

#### Limiting radius ratio for various types of sites

Limiting radius ratio = $r/R$	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO <sub>2</sub>
0.414 - 0.732	4	Square planaer	-
0.414 - 0.732	6	Octahedral	NaCl, MgO <sub>2</sub>
0.732 - 1.000	8	Cubic	CsCl

## Defects & Imperfection in Solids =>

The crystal in which all the lattice points are occupied by the component particle or groups of particles is called an ideal crystal. Defect in crystals are produced either due to thermal effects or by adding certain impurities in the pure crystals.

- (1) Stoichiometric - defects
- (2) Non-stoichiometric defects

(1) Defects in stoichiometric defect => Stoichiometric Compounds are those in which the number of positive and negative ions are exactly in the ratio as shown by their chemical formula.

(a) Schottky defect

(b) Frenkel defect

(a) Schottky defect =>

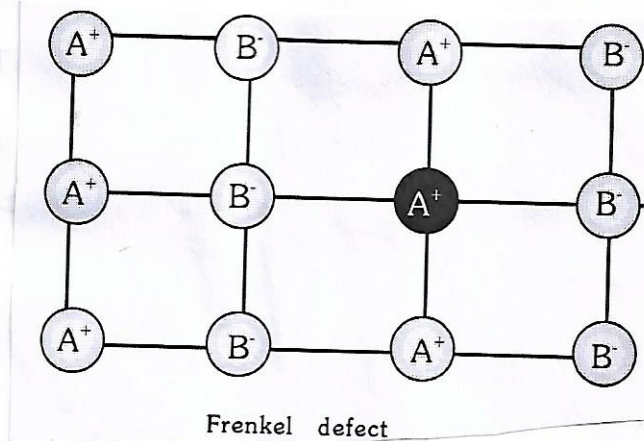
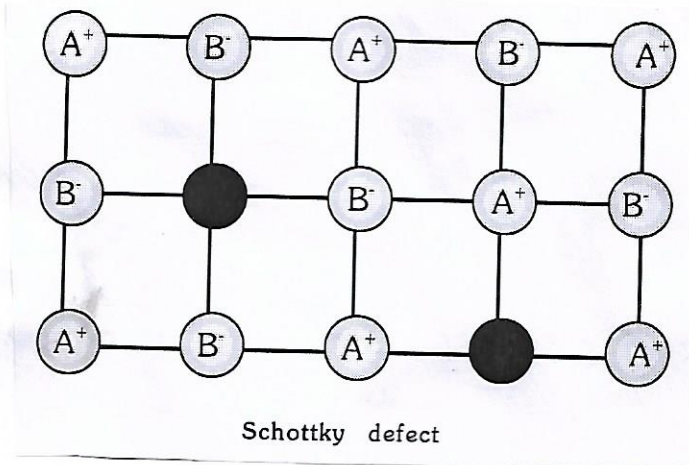
- > Vacancy defect in ionic solids.
- > Equal no. of cations and anions are missing.
- > Density of substance  $\downarrow$  and stability  $\downarrow$
- > The solids have comparable cationic and anionic radii.
- > C.N is High
- > Highly found in - NaCl, KCl, AgBr

(b) Frenkel defect =>

- > Smaller ions usually cations are dissociated from normal site to some interstitial site.
- > Density same but stability  $\downarrow$
- > Large size variation b/w cation and anion
- > C.N Low

ex ZnS, AgCl, AgBr

-> Conductivity  $\uparrow$



(2) Non-stoichiometric defect  $\Rightarrow$  These Types of defects are observed in the compound of transitional element. These defects arise either due to the presence of excess metal ion or excess non-metal ion.

(i) Metal excess defect due to anion vacancies  $\Rightarrow$

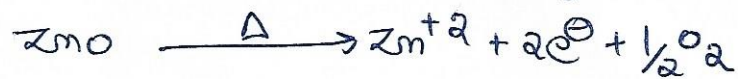
A compound may have excess metal ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron.

When alkali-metal halide are heated in an atmosphere of vapours of the alkali metal, anion vacancies are created. The anions diffuse to the surface of the crystal from their appropriate lattice sites to combine with the newly generated metal cation. The  $e^-$  lost by the metal atom diffuses through the crystal and are known as F-centres. For example, when NaCl crystal is heated in an atmosphere of Na vapours, it becomes yellow.



(ii) presence of extra cation in interstitial sites  $\Rightarrow$

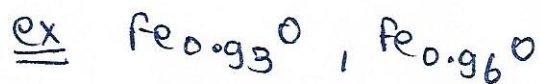
Zinc oxide is white in colour at room temperature on heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes  $\text{Zn}_{1+x}\text{O}$ . The excess  $\text{Zn}^{+2}$  ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(iii) metal-deficiency defects  $\Rightarrow$  it is a common defect in

transition metal compounds in which metal shows variable valency, in fact a few metal cations in lower oxidation state are missing from crystal lattice and their charge is balanced by the other cations of same metal in higher oxidation state. It causes some vacant points or holes and there is a net loss of metal causing metal deficiency.



Q Sodium has a bcc structure with nearest neighbour distance 365.9 pm. calculate its density (Atomic mass of Na = 23)

Sol<sup>n</sup> For bcc structure, nearest neighbour distance ( $2r$ ) is related to edge length ( $a$ ) as

$$2r = \frac{\sqrt{3}}{2} a$$

$$\therefore a = \frac{2}{\sqrt{3}} \times 2r = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

$$M = 23$$

For bcc structure,  $z = 2$

$$d = \frac{z \times M}{a^3 \times N_A} = \frac{2 \times 23}{(422.5 \times 10^{-10})^3 \times 6.023 \times 10^{23}} \\ = 1.51 \text{ gm/cm}^3$$

Q An element crystallizes in face centred cubic lattice with density 5.20 gm/cm<sup>3</sup> and edge length of the side of unit cell as 300 pm. Calculate the mass of the element which contain  $3.01 \times 10^{24}$  atoms

Sol<sup>n</sup> For FCC  $z = 4$

$$d = \frac{z \times M}{a^3 \times N_A}$$

$$5.20 = \frac{4 \times M}{(3 \times 10^{-8})^3 \times 3.01 \times 10^{24}}$$

$$5.20 = \frac{4 \times M}{27 \times 10^{-24} \times 3.01 \times 10^{24}}$$

$$5.20 = \frac{4 \times M}{27 \times 3.01}$$

$$M = 105.65 \text{ gm}$$

THANK YOU  
bachoo !!

(Deewan tiwari)