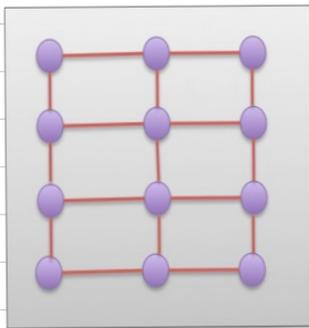


Solid State

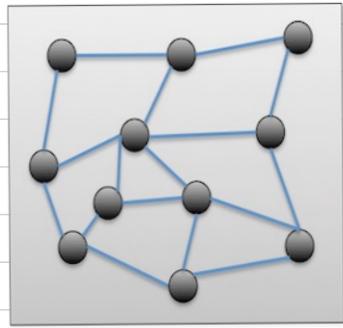
Crystals (True Solids)

- Strong forces which work in long ranges.
- Regular and fixed arrangement of particles.
- Sharp m.p.
- Definite value of enthalpy of fusion.
- Anisotropic in nature.

eg: Ice, Diamond, Graphite, NaCl etc



Crystalline Solid



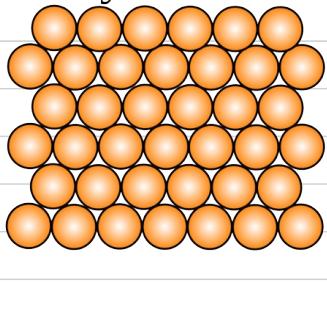
Amorphous Solid

Amorphous Solids

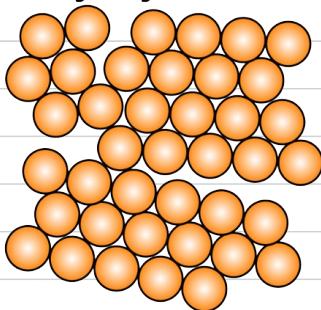
- Weak forces which work in short ranges.
- Random arrangement of particles.
- Melt over a range of temp.
- Enthalpy of fusion is not fixed.
- Isotropic in nature.

eg: glass, rubber, polymers etc

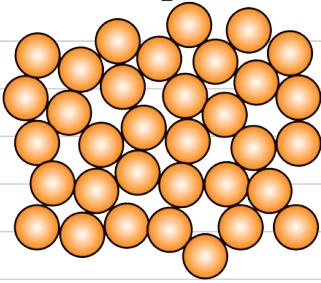
Crystalline



Polycrystalline



Amorphous



Crystalline Solids	Amorphous solids
They have a definite shape and geometrical form.	They do not have a definite geometrical shape.
They have a sharp (definite) melting point.	They melt over a wide range of temperatures.
They are rigid and incompressible.	They too are usually rigid and cannot be compressed to any appreciable extent. However graphite is soft because of its unusual structure.
They give a clean cleavage, i.e, break into pieces with plane surfaces.	They give irregular cleavage.
They have a definite heat of fusion.	They do not have a definite heat of fusion.
Anisotropic, i.e. their mechanical properties and electrical properties depend on the direction along which they are measured.	Isotropic, i.e. they have similar physical properties in all directions because the constituents are arranged in random manner.

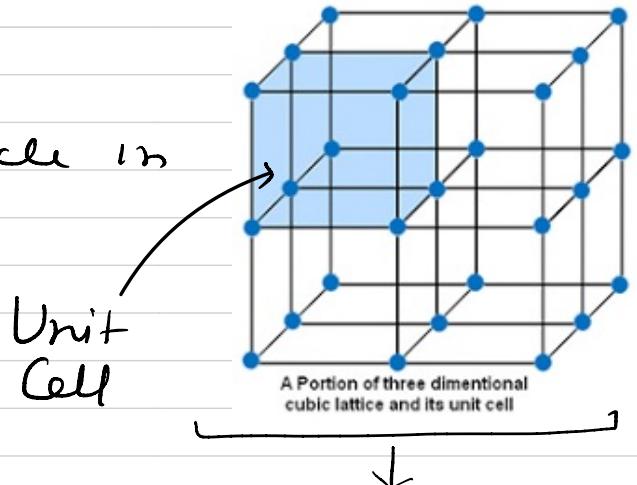
Type of crystals

Type	Structural Particles	Intermolecular Forces	Typical Properties	Examples
① Metallic	Cations and delocalized electrons	Metallic bonds	Hardness varies from soft to very hard; melting point varies from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na, Mg, Al, Fe, Sn, Cu, Ag, W
② Ionic	Cations and anions	Electrostatic attractions	Hard; moderate to very high melting points; nonconductors as solids, but good electric conductors as liquids; many are soluble in polar solvents like water	NaCl, MgO, NaNO ₃
③ Covalent Crystal				
④ Network covalent	Atoms <i>or molecules</i>	Covalent bonds	Most are very hard and either sublime or melt at very high temperatures; most are nonconductors of electricity	C (diamond), C (graphite), SiC, AlN, SiO ₂
⑤ Molecular Nonpolar	Atoms or nonpolar molecules	Dispersion forces	Soft; extremely low to moderate melting points (depending on molar mass); sublime in some cases; soluble in some nonpolar solvents	He, Ar, H ₂ , CO ₂ , CCl ₄ , CH ₄ , I ₂
Polar	Polar molecules	Dispersion forces and dipole-dipole attractions	Low to moderate melting points; soluble in some polar and some nonpolar solvents	(CH ₃) ₂ O, CHCl ₃ , HCl
Hydrogen-Bonded	Molecules with H bonded to N, O, or F	Hydrogen bonds	Low to moderate melting points; soluble in some hydrogen-bonded solvents and some polar solvents	H ₂ O, NH ₃

Terms used in crystals:

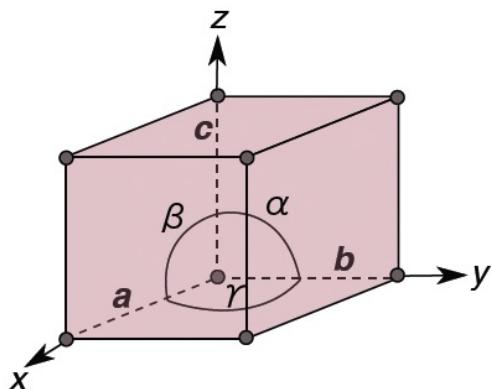
Crystal lattice

3-D arrangement of particle in crystal is called as Crystal lattice.



Crystal Lattice.

Unit cell



where, x, y, z = Crystallographic axis

a, b, c = Dimension of Unit cell

α, β, γ = Crystallographic angle.

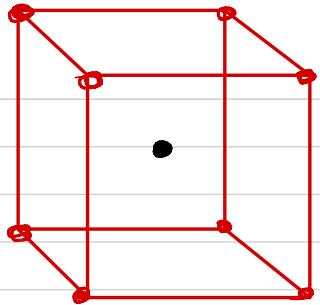
On the basis of position of particle Unit cell is divided in to -

① Primitive : Particles are present only at the corners.

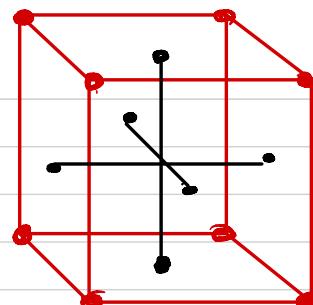
② Centered → ① Body centered : Particles are at the corners and at the body center.

→ ② Face centered : Particles are at the corners and at the center of each face.

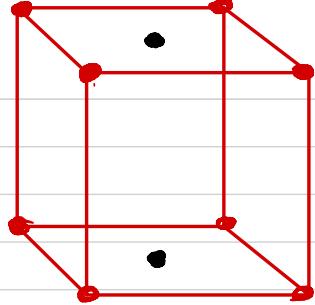
→ ③ End centered : Particles are at the corners and at the center of two opposite faces only.



Body Centered



Face Centered



End Centered

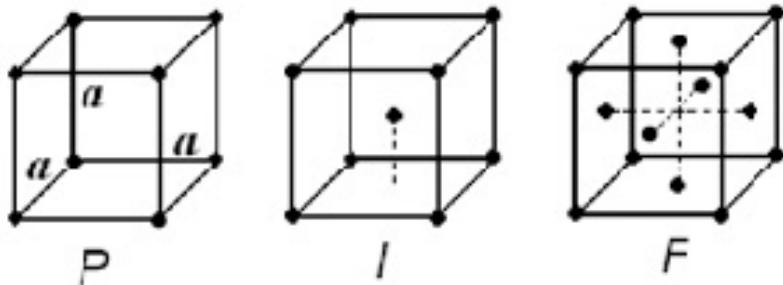
SOLID 1.pdf

On the basis of dimension and crystallographic angle

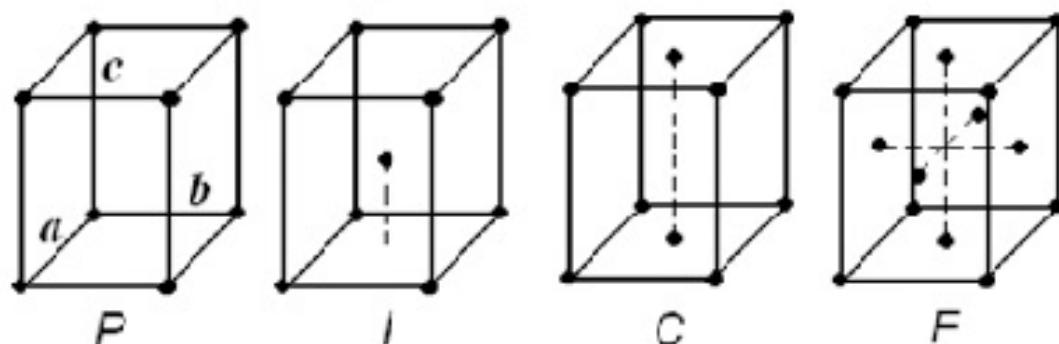
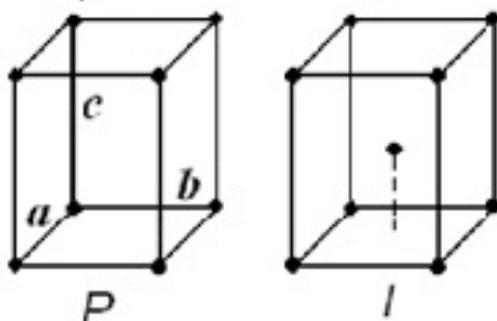
Unit Cell	Dimension	Angle	Lattice
① Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	P + B + F
② Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P + B
③ Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P + B + F + E
④ Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	P + E
⑤ Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	P
⑥ Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	P
⑦ Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	P
<u>Total</u>			<u>14</u>

\Rightarrow Bravais Lattice = 14

cubic system

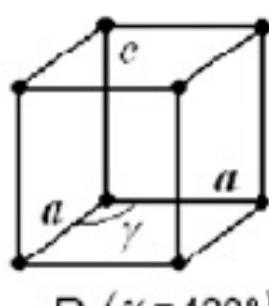


tetragonal system

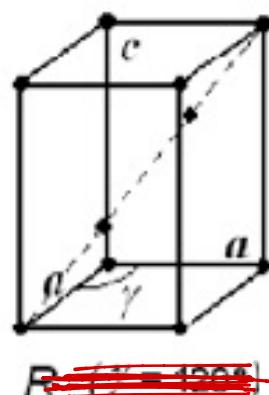


orthorhombic system

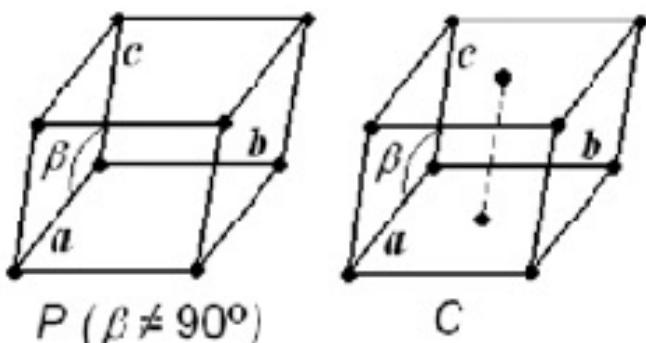
hexagonal & trigonal systems



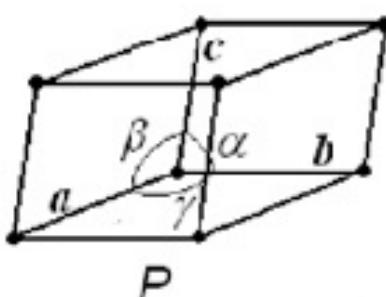
trigonal system



monoclinic system



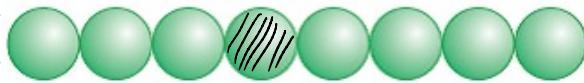
triclinic system



Close packing in crystals:

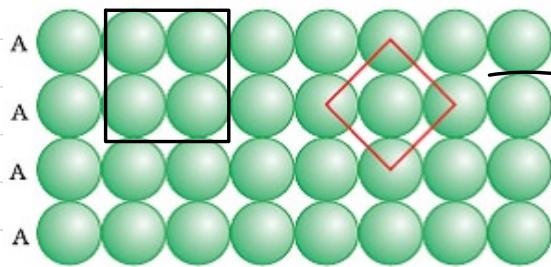
① 1-D Close packing:

$$CN = 2$$



② 2-D Close packing (Close packing of layers)

a) Square close packing :- AAA----- type



$$CN = 4$$

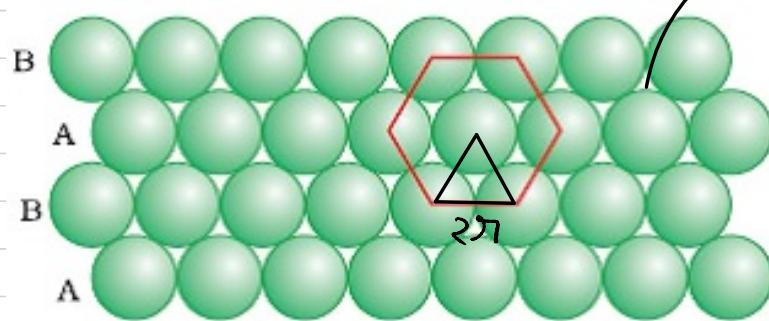
→ Square planar void

PF of Layer

$$= \frac{4 \times \frac{4}{3} \pi r^3}{4r \times 4r \times 2r} = \frac{\pi}{6} = 0.524$$

$$2\text{-D PF} = \frac{4 \times \pi r^2}{4r \times 4r} = \frac{\pi}{4} = 0.785$$

b) Hexagonal Close packing :- CN = 6



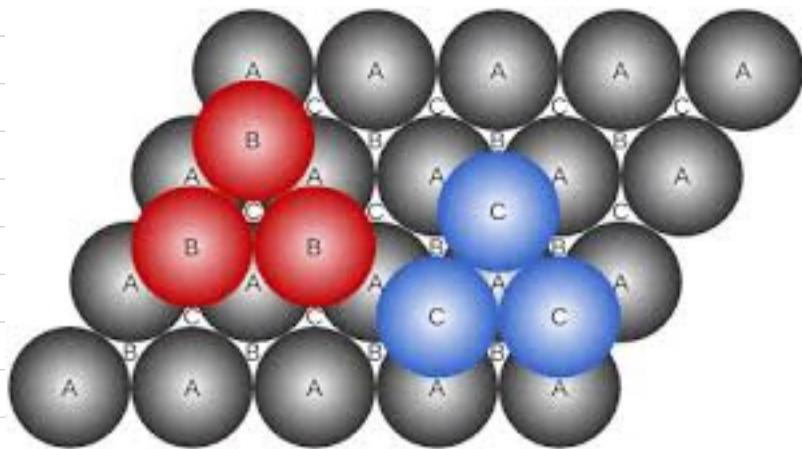
→ Triangular void

$$PF \text{ of Layer} = \frac{3 \times \frac{4}{3} \pi r^3}{(\frac{\sqrt{3}}{4} \times 4r^2) \times 6 \times 2r}$$

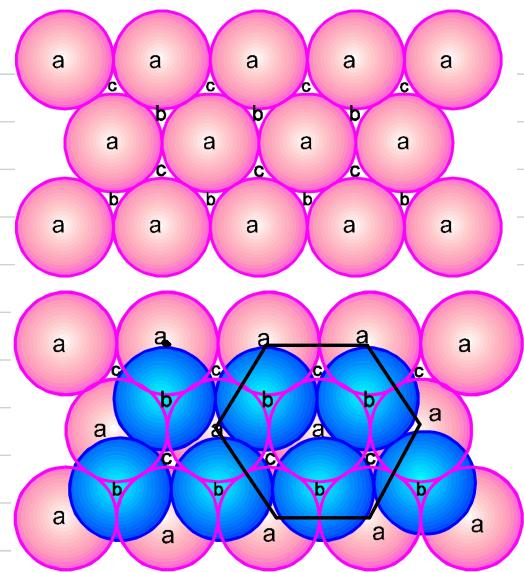
$$= \frac{\pi}{3\sqrt{3}} = 0.604$$

$$2\text{-D PF} = \frac{3 \times \pi r^2}{(\frac{\sqrt{3}}{4} \times 4r^2) \times 6} = \frac{\pi}{2\sqrt{3}} = 0.906$$

Close packing b/w layers (or 3D Close packing)

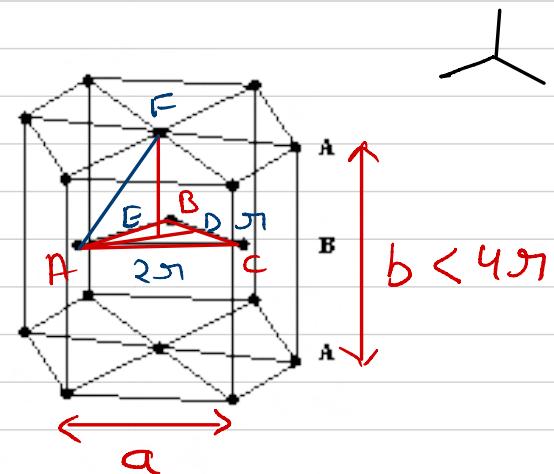
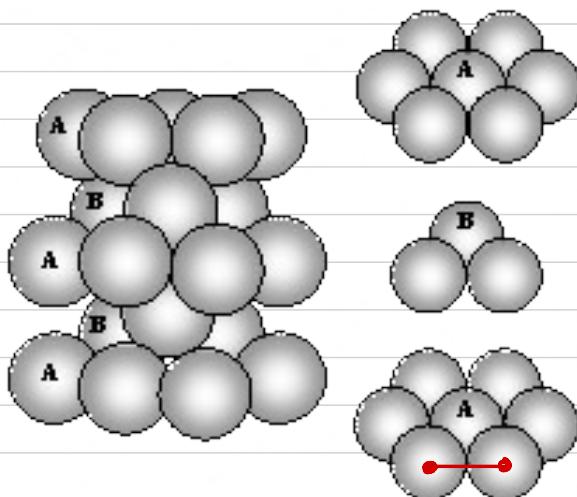


A, B = tetrahedral
C = Octahedral



① ABAB..... type (or hexagonal Close Packing)

h.c.p arrangement of 3-D



$$\textcircled{1} \text{ Effective No. of particle (z)} = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} \\ = 6$$

$$\textcircled{2} \text{ CN} = 3 + 6 + 3 = 12$$

$$\textcircled{3} \text{ } a = 2r$$

$$AF = 2r$$

$$AD = \sqrt{(AC)^2 - (CD)^2} \\ = \sqrt{4r^2 - r^2} = r\sqrt{3}$$

$$AE = \frac{2}{3} AD = \frac{2r}{\sqrt{3}}$$

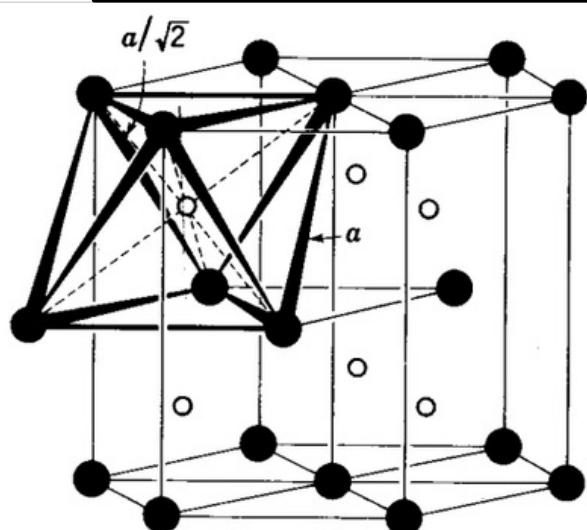
$$(FE) = \sqrt{(AF)^2 - (AE)^2} = \sqrt{4r^2 - \frac{4r^2}{3}} \\ = 2r\sqrt{\frac{2}{3}}$$

$$b = 2(EE) = 49 \sqrt{\frac{2}{3}}$$

$$\text{Effective THV} = 4 + 4 + 2 \times 6 \times \frac{1}{3} = 12$$

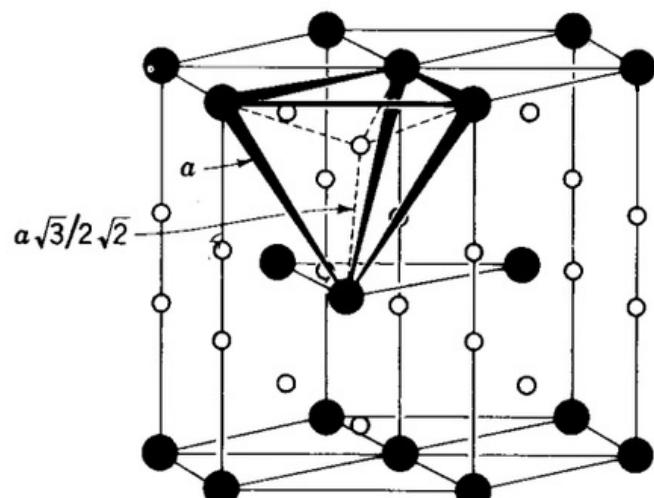
$$\text{Effective OHV} = 3 + 3 = 6$$

Tetrahedral and Octahedral voids:



● Metal atoms
○ Octahedral interstices

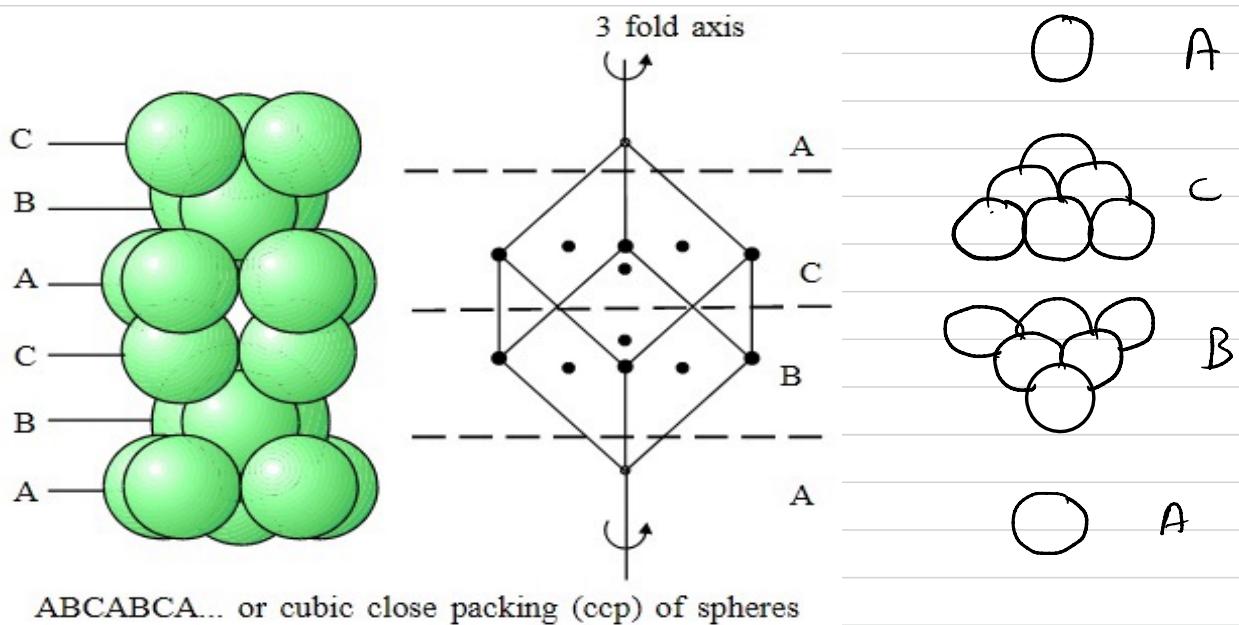
(a)



● Metal atoms
○ Tetrahedral interstices

(b)

② ABCABC----type of packing (or FCC or CCP)



Octahedral void :

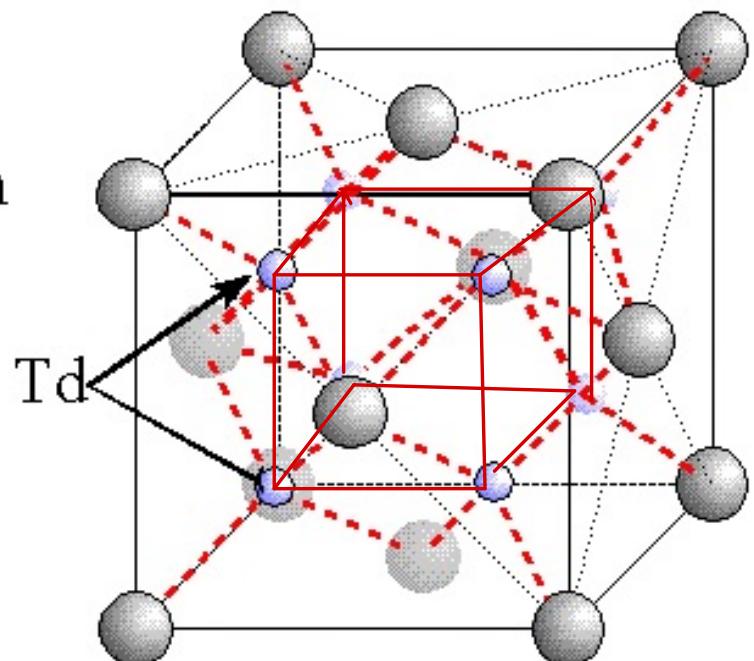
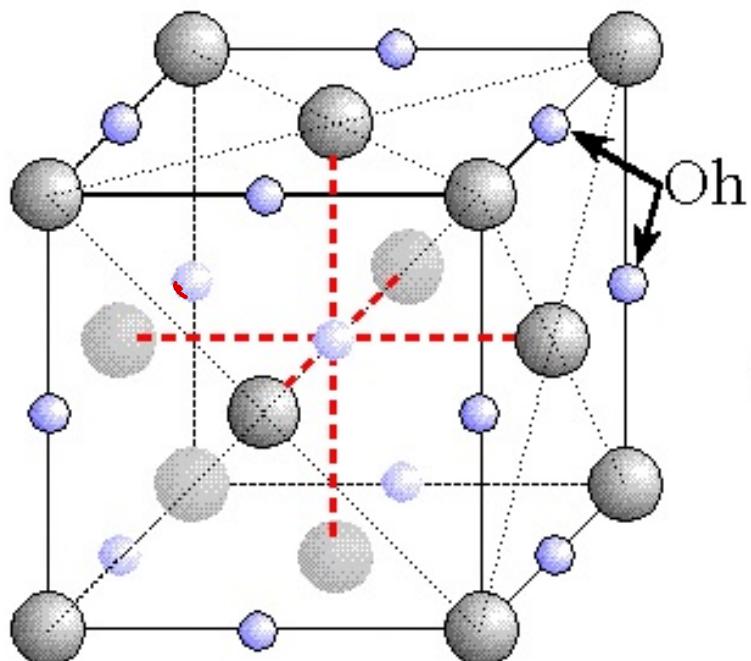
Effective OHV

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

Tetrahedral Void

Effective THV = 8

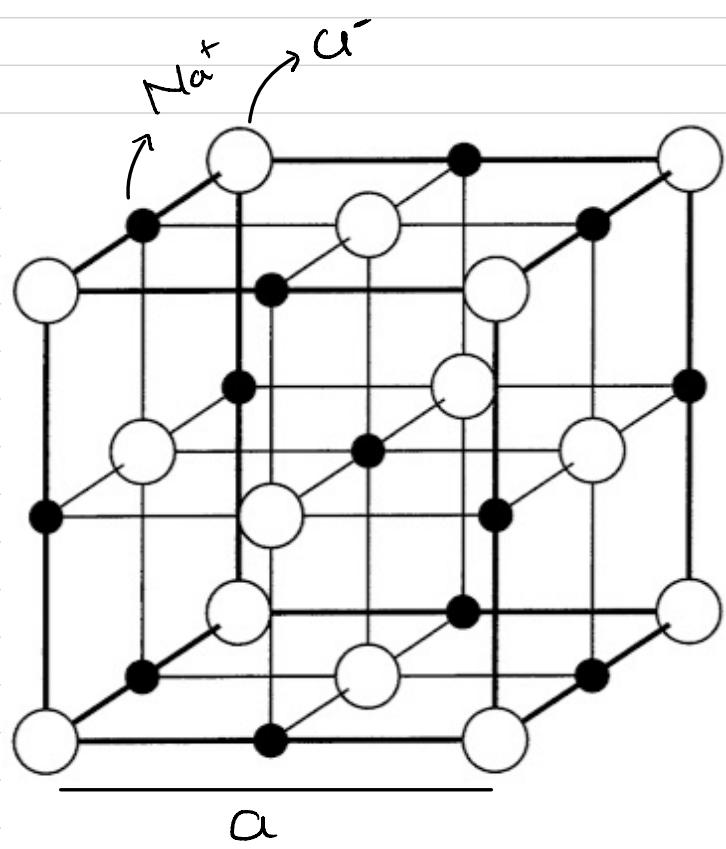
distance of THV from corner = $\frac{a\sqrt{3}}{4}$



Face-Centred Cubic
Octahedral and Tetrahedral 'Holes'

Different type of Ionic crystals

① Rock salt type (or NaCl type):



$\text{Cl}^- = \text{All CCP or FCC lattice Pt}$
 $\text{Na}^+ = \text{All OHV}$

Effective $\text{Cl}^- = 4$
 $\text{Na}^+ = 4$

CN :- $6 : 6$

$$a = 2r_+ + 2r_- \quad \text{--- (I)}$$

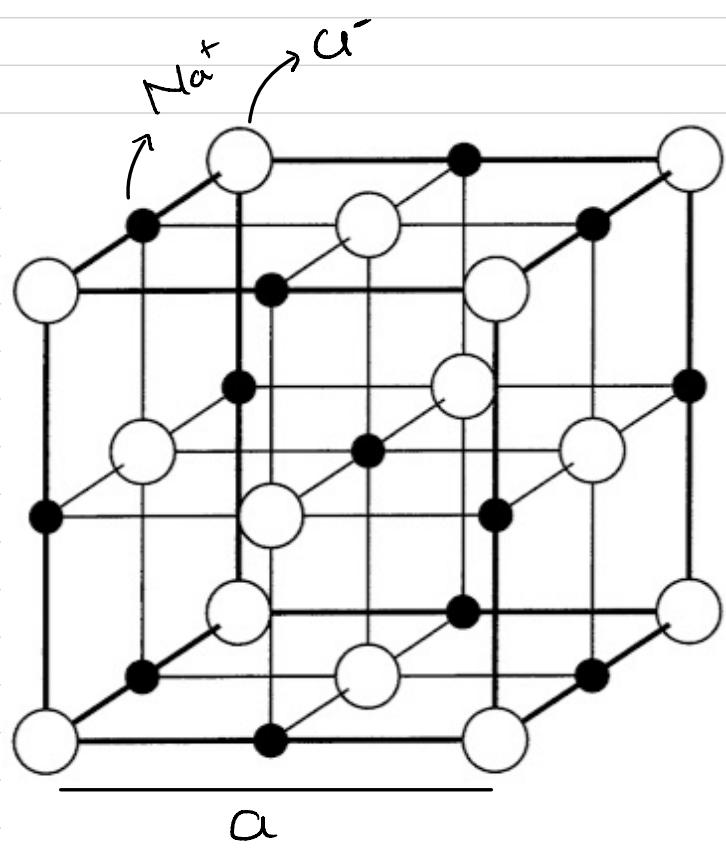
$$\frac{r_+}{r_-} = 0.414 \quad \text{--- (II)}$$

$$2r_- = \frac{a}{\sqrt{2}} \quad \text{--- (III)}$$

Ideal

Different type of Ionic crystals

① Rock salt type (or NaCl type):



$\text{Cl}^- = \text{All CCP or FCC lattice Pt}$
 $\text{Na}^+ = \text{All OHV}$

Effective $\text{Cl}^- = 4$
 $\text{Na}^+ = 4$

CN :- $6 : 6$

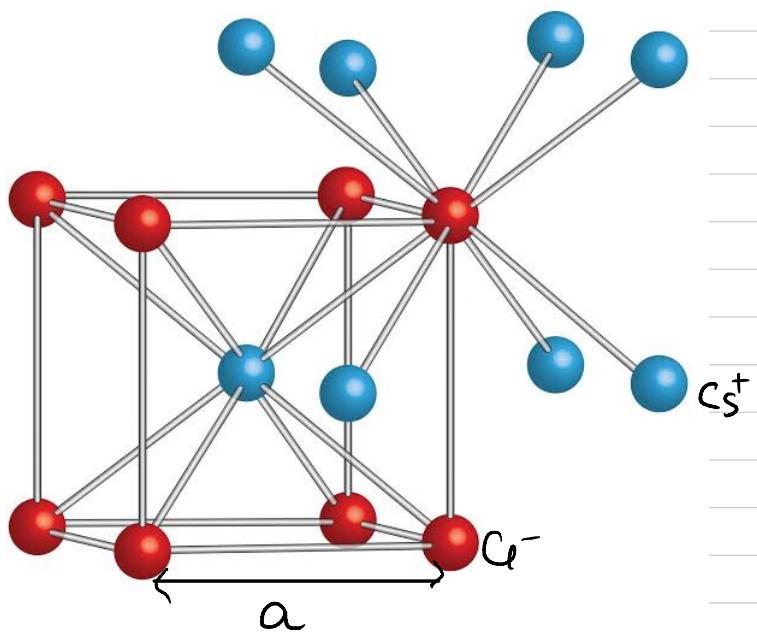
$$a = 2r_+ + 2r_- \quad \text{--- (I)}$$

$$\frac{r_+}{r_-} = 0.414 \quad \text{--- (II)}$$

$$2r_- = \frac{a}{\sqrt{2}} \quad \text{--- (III)}$$

Ideal

CSC type :-



Cs^- = All corners of cube } Info
 Cs^+ = Body centre }

Effective $Cs^- = 1$ }
 $Cs^+ = 1$ }

CsC

CN:

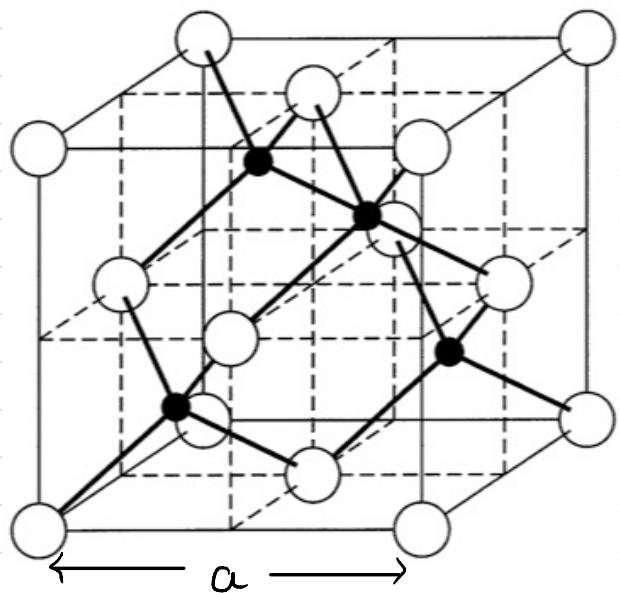
$B : 8$

$$\frac{a\sqrt{3}}{2} = r_+ + r_- \quad \text{--- (I)}$$

$$\frac{r_+}{r_-} = 0.732 \quad \text{--- (II)} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{ Ideal}$$

$$a = 2r_- \quad \text{--- (III)}$$

③ ZnS type (or Zinc blend type or Sphalerite type):



S^{2-} = All FCC lattice Pt }
 Zn^{+2} = Alternate THV } Info
 Effective $S^{2-} = 4$
 $Zn^{+2} = 4$ }

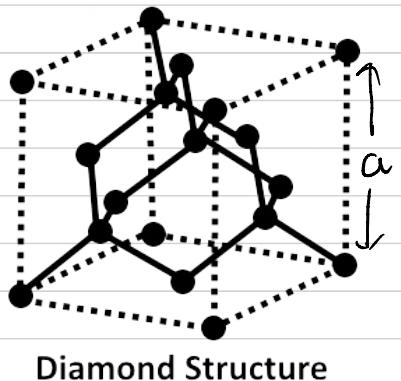
ZnS
 CN:- $4 : 4$

A_xB_y
 CN: $y : 2x$

$$\frac{a\sqrt{3}}{4} = \sigma_+ + \sigma_- \quad \text{--- (I)}$$

$$\begin{aligned} \frac{\sigma_+}{\sigma_-} &= 0.225 \quad \text{--- (II)} \\ 2\sigma_- &= \frac{a}{\sqrt{2}} \quad \text{--- (III)} \end{aligned} \quad \left. \begin{array}{l} \text{Ideal} \\ \text{---} \end{array} \right\}$$

Structure of Diamond:



Similar to ZnS type

C = All FCC lattice Pt +
 Alternate THV

Effective $C = 4 + 4 = 8$

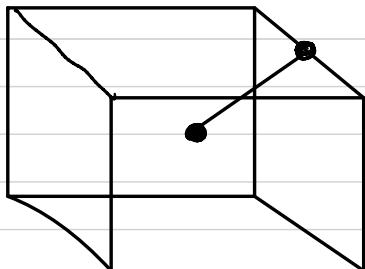
$$\frac{a\sqrt{3}}{4} = 2\sigma_C$$

$$d = \frac{8 \times \frac{12}{N_A}}{\left(\frac{8\sigma_C}{\sqrt{3}}\right)} ; \quad PF = \frac{B \times \frac{4}{3}\pi\sigma_C^3}{\left(\frac{8\sigma_C}{\sqrt{3}}\right)^3} = 0.34$$

Prob: Crystal AB shows NaCl type arrangement.
 Where $\sigma_+ = 2A^\circ$, $\sigma_- = 4A^\circ$, $M_{AB} = 60 \text{ gm/mol}$
 $N_A = 6 \times 10^{23}$

Calculate

- (a) Edge length of Unit cell $a = 2\sigma_+ + 2\sigma_- = 12 A^\circ$
- (b) Nearest No of Cation from a given Cation 12
- (c) No of Unit cell in 1.8 gm Crystal.
- (d) Density of Crystal (gm/cm^3)



$$\left(\frac{1.8}{60}\right)^{\frac{1}{3}} \times N_A \times \frac{1}{4} = \frac{0.3 \times 6 \times 10^{23}}{4 \times 10} \\ = \underline{4.5 \times 10^{21}}$$

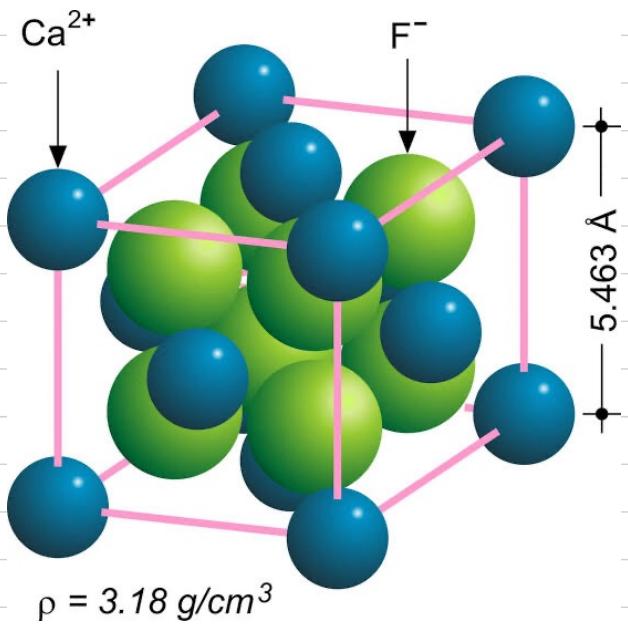
$$d = \frac{4 \times \frac{M_A}{N_A} + 4 \times \frac{M_B}{N_A}}{a^3}$$

$$= \frac{4 \times \frac{60 \times 10}{6 \times 10^{23}}}{(12 \times 10^{-8})^3}$$

$$= \frac{4 \times 10 \times 10}{12 \times 12 \times 12} = 0.23 \text{ gm/cm}^3$$

Fluoride type (CaF_2 type)

F^- = All corners of Cube
 Ca^{+2} = Body centre
 Θ_1



$\text{Ca}^{+2} = \text{All FCC lattice Pt}$ } Info
 $\text{F}^- = \text{All THV}$

Effective $\text{Ca}^{+2} = 4$
 $\text{F}^- = 8$

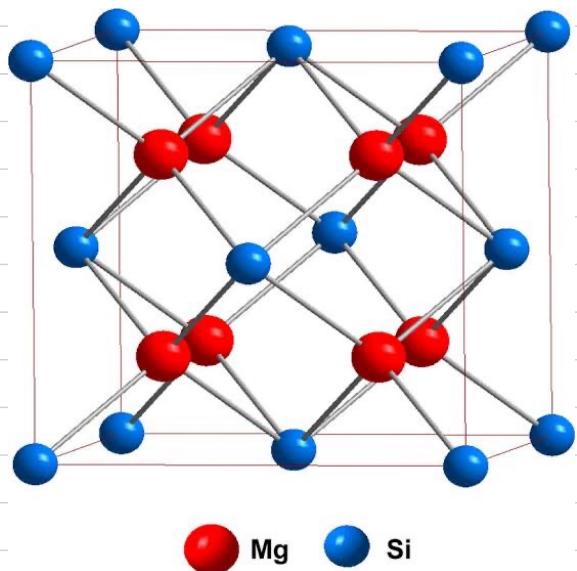
$\text{CN}:-$ CaF_2
 $8:4$

$$\sigma_+ + \sigma_- = \frac{a\sqrt{3}}{4} - ①$$

AntiFluoride type (Na_2O type)

$\text{O}^{-2} = \text{All FCC lattice Pt} = 4$
 $\text{Na}^+ = \text{All THV} = 8$

\downarrow
 Na_2O
 $4:8$



An ionic compound ($A^+ B^-$) crystallizes in rock salt structure. If the ionic radii of A^+ and B^- is 200 pm and 400 pm respectively, then calculate distance between nearest cations in Å.

$$a = 2r_+ + 2r_- \\ = 1200 \text{ pm} = 12 \text{ Å}^\circ$$

$$\frac{a}{\sqrt{2}} = \frac{12}{\sqrt{2}} = 6\sqrt{2} \text{ Å}^\circ$$

In a solid $r_{(+)} = 1.6 \text{ Å}$ and $r_{(-)} = 1.864 \text{ Å}$. Use the radius ratio rule to determine the edge length of the cubic unit cell in Å.

$$\frac{r_+}{r_-} = 0.858 \\ \downarrow (0.732 - 1) \\ CsCl$$

$$r_+ + r_- = \frac{a\sqrt{3}}{2}$$

$$a = 4 \text{ Å}^\circ$$

$$a = 2r_+ + 2r_-$$

Packing fraction of NaCl unit cell [assuming ideal] if ions along one of its body diagonal are absent (Cl^- forms FCC) :

$$(a) \text{ P.F.} = \frac{\frac{4}{3}\pi(r_+^3 + r_-^3)}{16\sqrt{2}r_+^3}$$

$$(b) \text{ P. F.} = \frac{\frac{4}{3}\pi\left(3r_+^3 + \frac{15}{4}r_-^3\right)}{16\sqrt{2}r_-^3}$$

$$(c) \text{ P.F.} = \frac{\frac{4}{3}\pi\left(4r_+^3 + \frac{15}{4}r_-^3\right)}{16\sqrt{2}r_-^3}$$

$$(d) \text{ P.F.} = \frac{\frac{4}{3}\pi(3r_+^3 + 4r_-^3)}{16\sqrt{2}r_-^3}$$

$$\text{Pf} = \frac{\frac{4}{3}\pi\left[3r_+^3 + \frac{15}{4}r_-^3\right]}{16\sqrt{2}r_-^3}$$

$$2r_- = \frac{a}{\sqrt{2}} \Rightarrow a = 2\sqrt{2}r_-$$



Match the columns.

Column I	Column II
(A) Rock salt structure	(P) Coordination number of cation is 4.
(B) Zinc blend structure	(Q) $\frac{\sqrt{3}a}{4} = r^+ + r^-$
(C) Fluorite structure	(R) Coordination number of cation and anion is same.
	(S) Distance between two nearest anion is $\frac{a}{\sqrt{2}}$.

A solid contains A^{n+} and B^{m-} ions. The structure of solid is FCC for B^{m-} ions and A^{n+} ions are present in one-fourth of the tetrahedral voids as well as in one-fourth of octahedral voids. What is the simplest formula of solid?

- (a) A_3B_4 (b) A_4B_3
 (c) AB_2 (d) A_2B

Sodium oxide has anti-fluorite structure. The percentage of the tetrahedral voids occupied by the sodium ions is

- (a) 12% (b) 25%
 (c) 50% (d) 100%

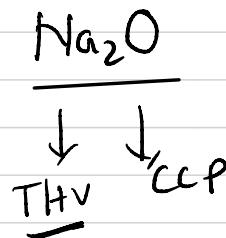
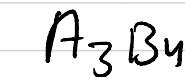
Copper has a FCC lattice with a unit cell edge length of $\frac{0.5}{\sqrt{2}}$ nm.

Q What is the size of the largest atom that could fit into octahedral holes of the lattice without disturbing the lattice?

- (a) $\frac{0.207}{\sqrt{2}}$ nm (b) $\frac{0.366}{\sqrt{2}}$ nm
 (c) 0.092 nm (d) 0.052 nm

$$B = 4$$

$$A = \frac{1}{4} \times 8 + \frac{1}{4} \times 4 = 3$$



$$4r_- = a\sqrt{2} = 0.5$$

$$r_- = 0.5/4$$

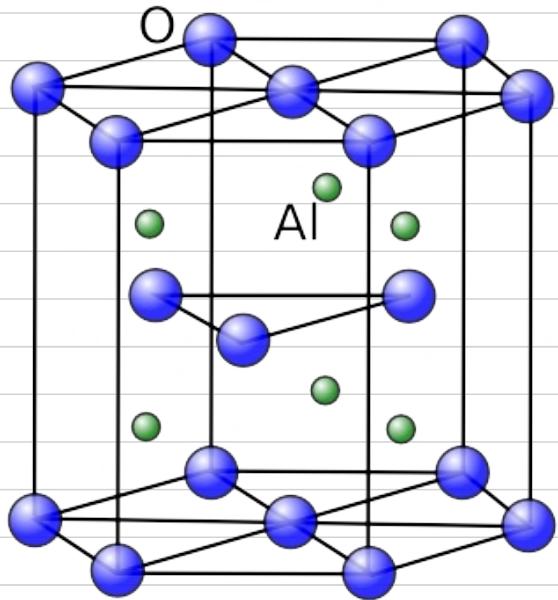
Q What is the size of the largest atom that could fit into tetrahedral holes of the lattice without disturbing the lattice?

- (a) 0.028 nm (b) 0.052 nm
(c) $\frac{0.1125}{\sqrt{2}}$ nm (d) $\frac{0.207}{\sqrt{2}}$ nm

$$\frac{r_+}{r_-} = 0.414 \Rightarrow r_+ = 0.414 \times \frac{0.5}{4} = 0.052$$

$$\frac{r_+}{r_-} = 0.225 \Rightarrow r_+ = 0.225 \times \frac{0.5}{4} = 0.028$$

Corundum type (or Al_2O_3):-



O^{2-} = All hcp lattice pt
 Al^{+3} = $\frac{2}{3} \text{ of OHV}$ } info

Effective O^{2-} = 6

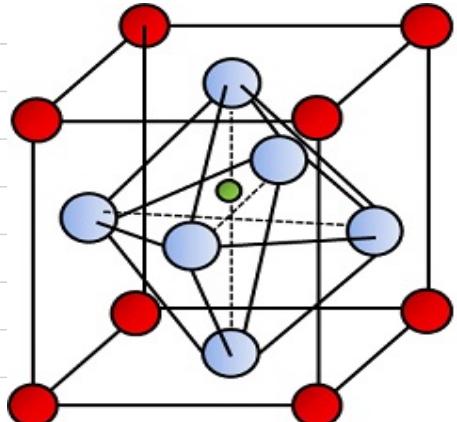
$$\text{Al}^{+3} = \frac{2}{3} \times 6 = 4$$

↓

Al_2O_3

CN: $6 : 4$

Pervoskite type (CaTiO_3):-



Ca^{2+} = All corners of cube

O^{2-} = All Face centre

Ti^{4+} = Body centre

$$\text{Ti}^{+4} \begin{cases} \text{O}^{2-} = 6 \\ \text{Ca}^{+2} = 8 \end{cases}$$

$$\begin{array}{c|c} \text{O}^{2-} & \begin{array}{l} \text{Ca}^{+2} = 4 \\ \text{Ti}^{+4} = 2 \end{array} \\ \hline \text{Ca}^{+2} & \begin{array}{l} \text{O}^{2-} = 12 \\ \text{Ti}^{+4} = 8 \end{array} \end{array}$$

Spinel and Inverse Spinel :- (AB₂O₄) :-

Spinel

$O^{+2} = \text{All CCP lattice Pb} = 4$

$A^{+2} = \frac{1}{8} \text{ th THV} = 1$

$B^{+3} = \frac{1}{2} \text{ OHV} = 2$

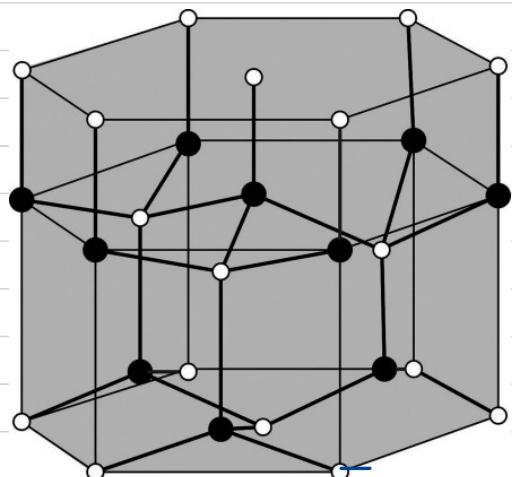
Inverse Spinel

$O^{+2} = \text{All CCP lattice Pb} = 4$

$A^{+2} = \frac{1}{8} \text{ th THV} = 1$

$B^{+3} = \frac{1}{4} \text{ th OHV} + \frac{1}{8} \text{ th THV} = 2$

* Wurtzite (or ZnS) :-



$S^{-2} = \text{All HCP lattice Pt}$

$Zn^{+2} = \text{Alternate THV}$

Defects in crystals

formation of defect is endothermic which increase entropy

$$\Delta G_f = \underbrace{\Delta H}_{+ve} - T \cdot \Delta S_{-ve} = -ve \Rightarrow \text{Spontaneous}$$

$T \uparrow \Rightarrow \text{defect} \uparrow$

If defect is present on a position/point in crystal then it is called point defect.

Types of Point Defects :

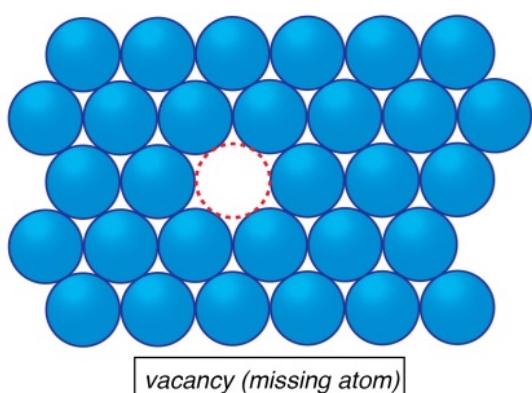
Point defect can be classified into three types:

- (i) Stoichiometric defects
- (ii) Non-stoichiometric defects
- (iii) Impurity added defect

Stoichiometric Defect

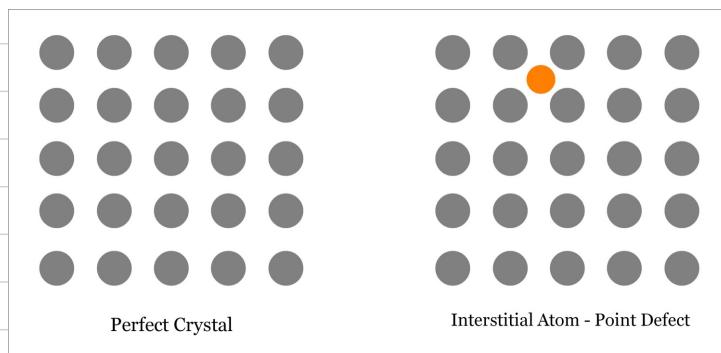
:- If due to defect stoichiometry of crystal is not affected then it is called Stoichiometric defect.

(a) Vacancy Defect :



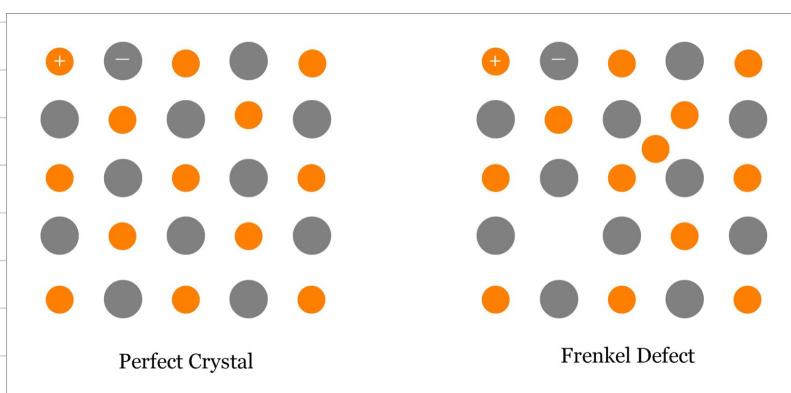
density ↓

(b) Interstitial Defect :



density ↑

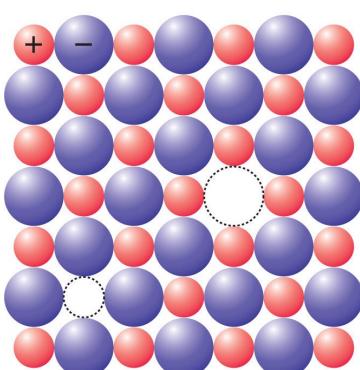
(c) Frenkel Defect :



\Rightarrow density = const
 \Rightarrow Dislocation defect.
 \Rightarrow Conduction ↑
 \Rightarrow Low coordination No compound. where diff in size of cation and anion is large
Dielectric constant example, ZnS, AgCl, AgBr

and AgI due to small size of Zn^{2+} and Ag^+ ions.

(d) Schottky Defect :



A⁺B⁻

density ↓

Conduction ↑

Diff in size of cation and anion is not very large.
High coordination No compound

10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16}

Defects in crystals

formation of defect is endothermic which increase entropy

$$\Delta G_f = \underbrace{\Delta H}_{+ve} - T \cdot \Delta S_{-ve} = -ve \Rightarrow \text{Spontaneous}$$

$T \uparrow \Rightarrow \text{defect} \uparrow$

If defect is present on a position / point in crystal then it is called point defect.

Types of Point Defects :

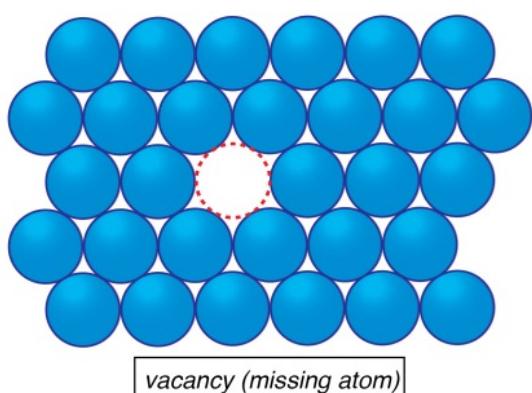
Point defect can be classified into three types:

- (i) Stoichiometric defects
- (ii) Non-stoichiometric defects
- (iii) Impurity added defect

Stoichiometric Defect

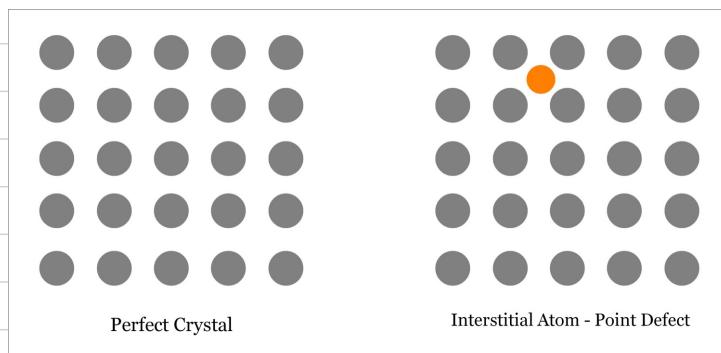
:- If due to defect stoichiometry of crystal is not affected then it is called Stoichiometric defect.

(a) Vacancy Defect :



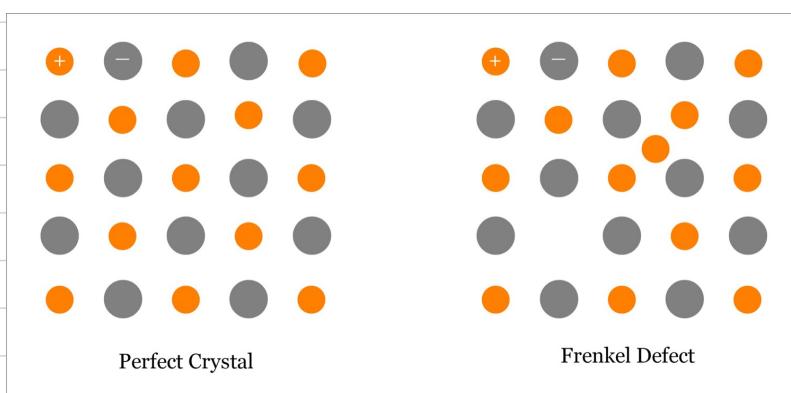
density ↓

(b) Interstitial Defect :



density ↑

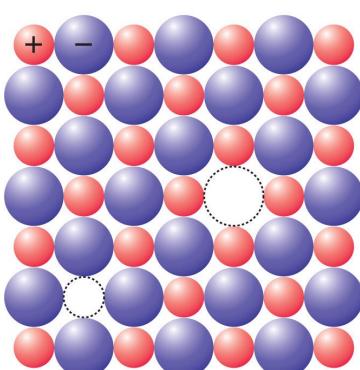
(c) Frenkel Defect :



\Rightarrow density = const
 \Rightarrow Dislocation defect.
 \Rightarrow Conduction ↑
 \Rightarrow Low coordination No compound. where diff in size of cation and anion is large
Dielectric constant example, ZnS, AgCl, AgBr

and AgI due to small size of Zn^{2+} and Ag^+ ions.

(d) Schottky Defect :



A⁺B⁻

density ↓
Conduction ↑
Diff in size of cation and anion is not very large.
High coordination No compound

10^6 Schottky pairs per cm^3 at room temperature. In $1 cm^3$ there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16}

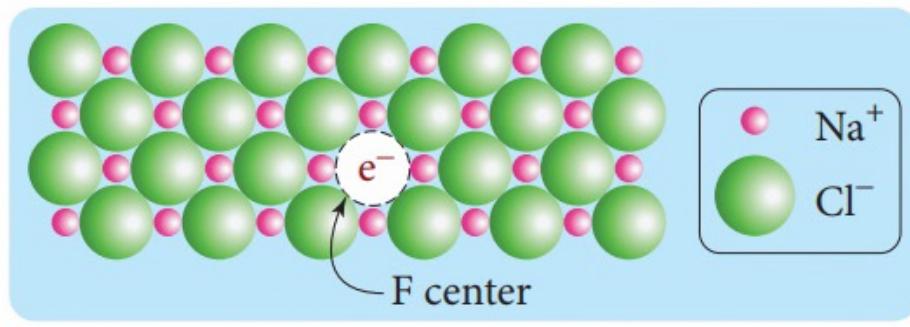
For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

(ii) Non-Stoichiometric Defects:

- (a) Metal excess defect.
- (b) Metal deficiency defect.

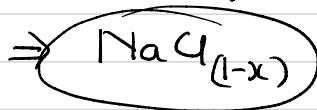
(a) Metal Excess Defect

(I) Metal excess defect due to anionic vacancies :



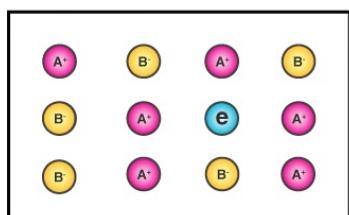
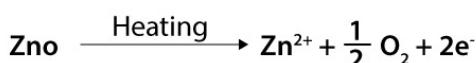
\rightarrow density \downarrow
 \rightarrow Conduction \uparrow
 \rightarrow F-Centre are responsible
 for colour impurities

\rightarrow Schottky defect.

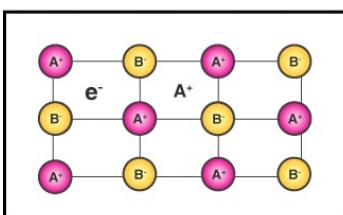


They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

(II) Metal excess defect due to the presence of extra cations at interstitial sites :

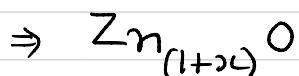


Metal excess defect due to anionic vacancy

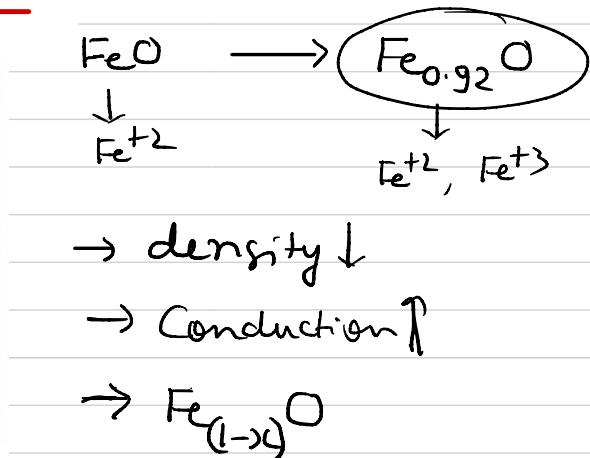
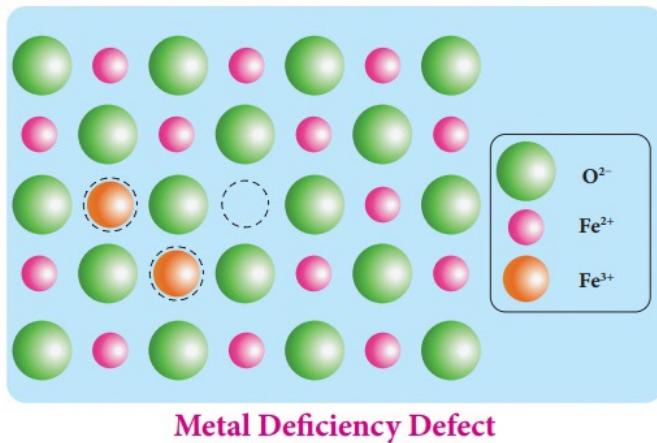


Metal excess defect due to the presence of interstitial cation:

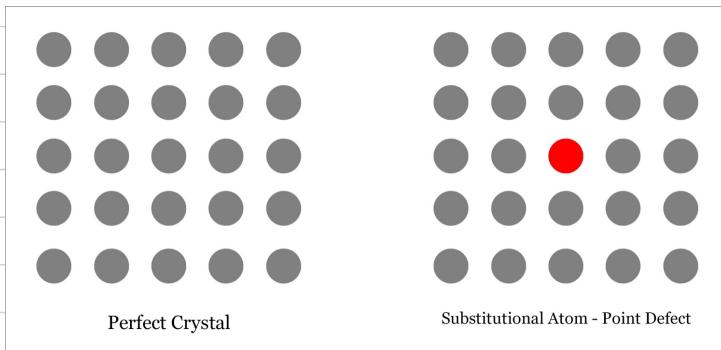
\rightarrow Frenkel defect
 \rightarrow density \uparrow
 \Rightarrow Conduction \uparrow



(b) Metal Deficiency Defect

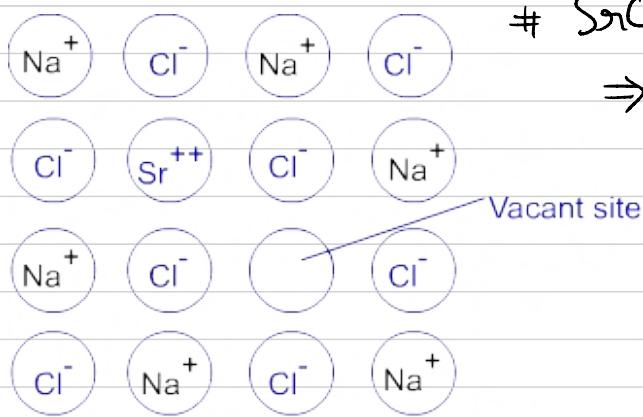


(iii) Impurity Defects



density \uparrow or \downarrow

~~eg:~~



SrCl_2 in NaCl

$\Rightarrow x \text{SrCl}_2 \Rightarrow x$ Cationic Vacancy

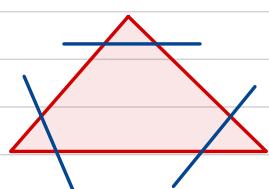
\Rightarrow Conduction \uparrow

Vacancy defect because of Sr^{++} ion

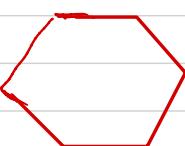
Truncated System:

⇒ Corners cut by a plane

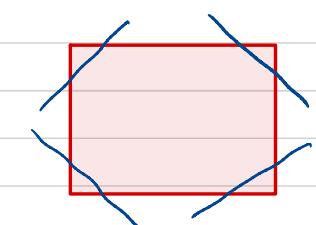
#



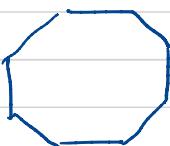
⇒



#



⇒



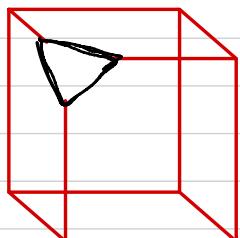
Truncated Cube:

Corners = 24

Sides = 36 = 24 + 12

Triangles = 8

Octagons = 6



Truncated Tetrahedron



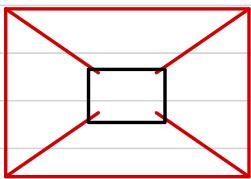
Corners = 12

Sides = 18

Triangle = 4

Hexagons = 4

Truncated Octahedron



Corners = 24

Sides = 36

Square = 6

Hexagons = 8

Radius Ratio rule

Void	r_+/r_-	range	CN (+)
Tetrahedral	0.225	$[0.225, 0.414)$	4
Octahedral	0.414	$[0.414, 0.732)$	6
Cubical	0.732	$[0.732, 1)$	8

$\frac{r_+}{r_-} = 2 \Rightarrow \left(\frac{r_-}{r_+} = 0.5 \right) [0.414 - 0.732]$

Octahedral void

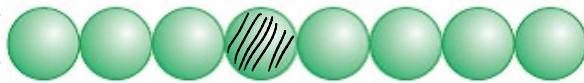
Note:



Close packing in crystals:

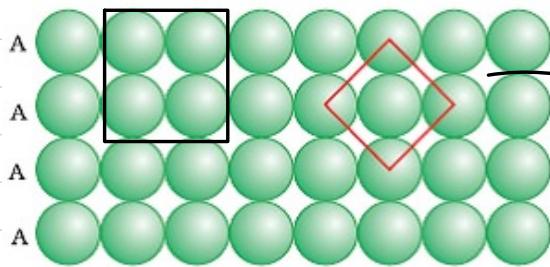
① 1-D Close packing:

$$CN = 2$$



② 2-D Close packing (Close packing of layers)

a) Square close packing :- AAA----- type



$$CN = 4$$

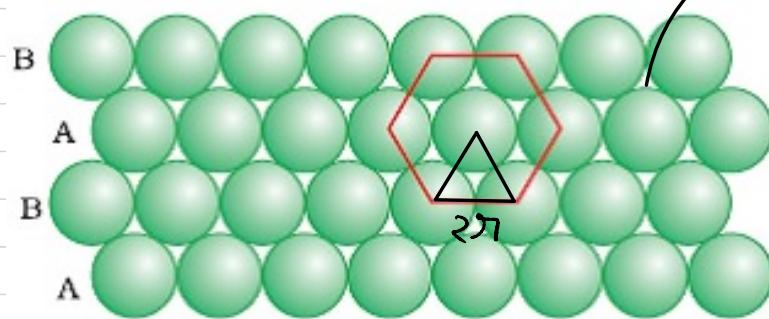
→ Square planar void

PF of Layer

$$= \frac{4 \times \frac{4}{3} \pi r^3}{4r \times 4r \times 2r} = \frac{\pi}{6} = 0.524$$

$$2\text{-D PF} = \frac{4 \times \pi r^2}{4r \times 4r} = \frac{\pi}{4} = 0.785$$

b) Hexagonal Close packing :- CN = 6



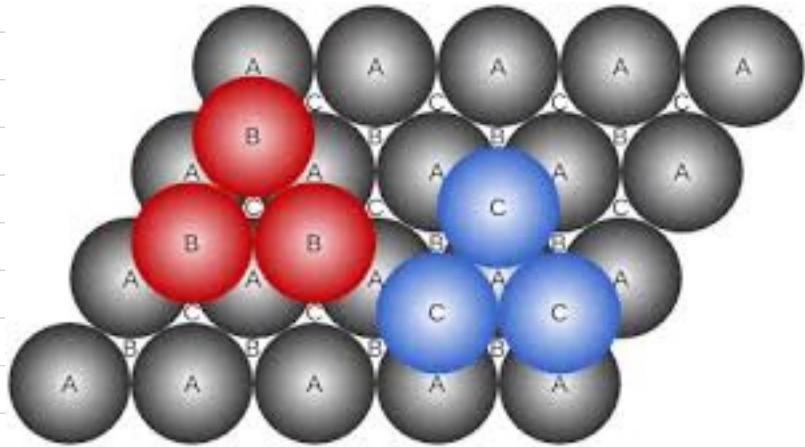
→ Triangular void

$$PF \text{ of Layer} = \frac{3 \times \frac{4}{3} \pi r^3}{(\frac{\sqrt{3}}{4} \times 4r^2) \times 6 \times 2r}$$

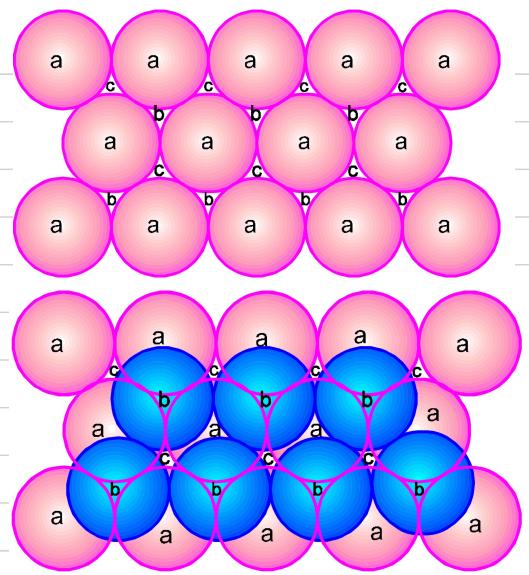
$$= \frac{\pi}{3\sqrt{3}} = 0.604$$

$$2\text{-D PF} = \frac{3 \times \pi r^2}{(\frac{\sqrt{3}}{4} \times 4r^2) \times 6} = \frac{\pi}{2\sqrt{3}} = 0.906$$

Close packing b/w layers (or 3D close packing)

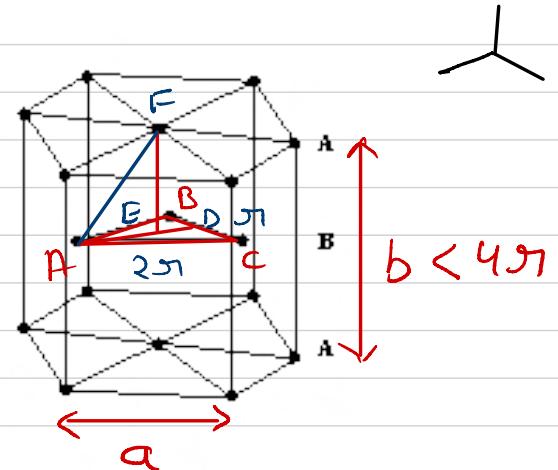
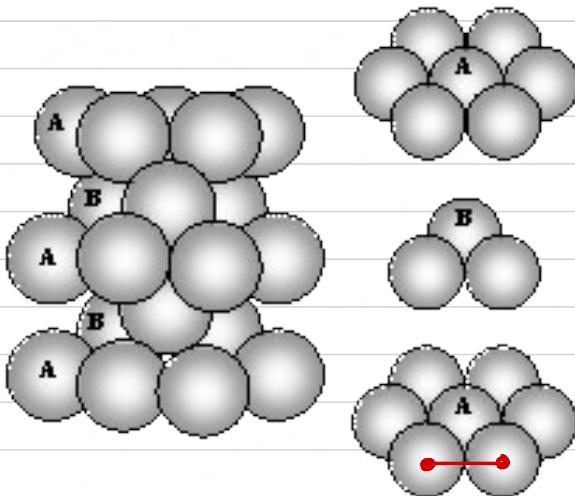


A, B = tetrahedral
C = Octahedral



① ABAB----- type (or hexagonal close packing)

hCP arrangement of 3-D



$$\textcircled{1} \text{ Effective No of particle (z)} = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} \\ = 6$$

$$\textcircled{2} \quad CN = 3 + 6 + 3 = 12$$

$$\textcircled{3} \quad a = 2\pi$$

$$AF = 29$$

$$AD = \sqrt{(AC)^2 - (CD)^2}$$

$$= \sqrt{49\pi^2 - \pi^2} = \pi\sqrt{3}$$

$$AE = \frac{2}{3} AD = \frac{2g_1}{\sqrt{3}}$$

$$(FE) = \sqrt{(AF)^2 - (AE)^2} = \sqrt{4r^2 - \frac{4r^2}{3}} = 2r\sqrt{\frac{2}{3}}$$

LEARN NCERT EXAMPLES OF CRYSTALLINE AND AMORPHOUS