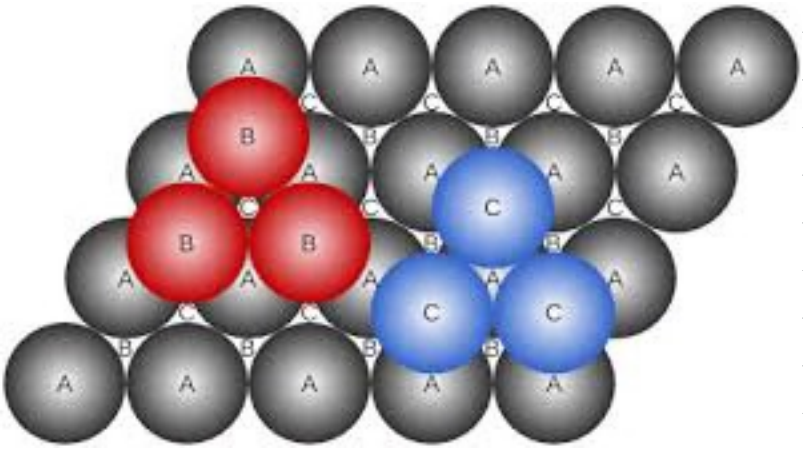
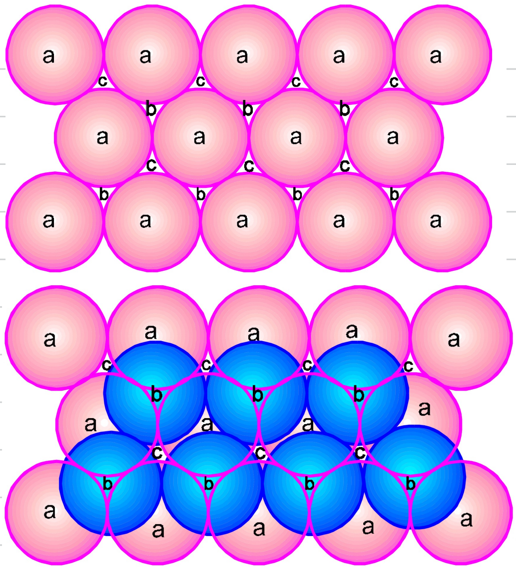
Close packing b/w layers (or 3D Close packing)

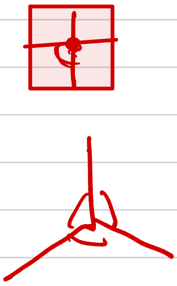


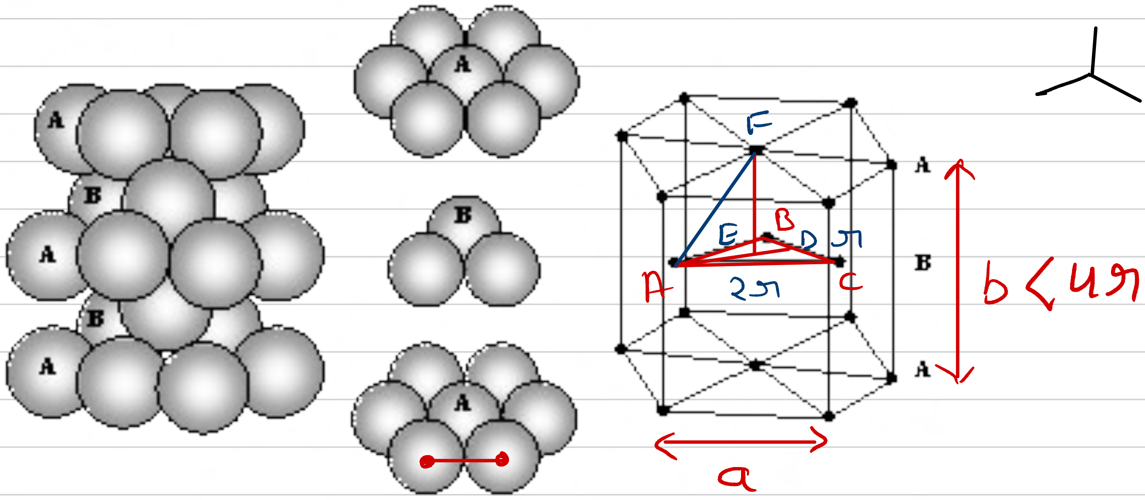


A, B = tetrahedral
C = Octahedral

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

hcP arrangement of 3-D

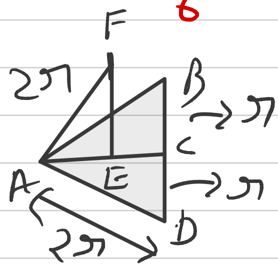




$b < 4r$

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

$= 6$



② CN $= 12$

③ $a = 2r$

$AC = \sqrt{4r^2 - r^2} = r\sqrt{3}$

$AF = 2r$

$AE = \frac{2}{3}\times AC = \frac{2}{\sqrt{3}}r$

$FE = \sqrt{4r^2 - \frac{4r^2}{3}} = 2r\times\sqrt{\frac{2}{3}}$

$$\boxed{b = 2FE = 4r\sqrt{\frac{2}{3}}}$$

(4) $V = \left(\frac{\sqrt{3}}{4} \times a^2 \times 6\right) \times b = \frac{\sqrt{3}}{4} \times 4r^2 \times 6 \times 4r\sqrt{\frac{2}{3}}$

$$V = 24\sqrt{2}\, r^3$$

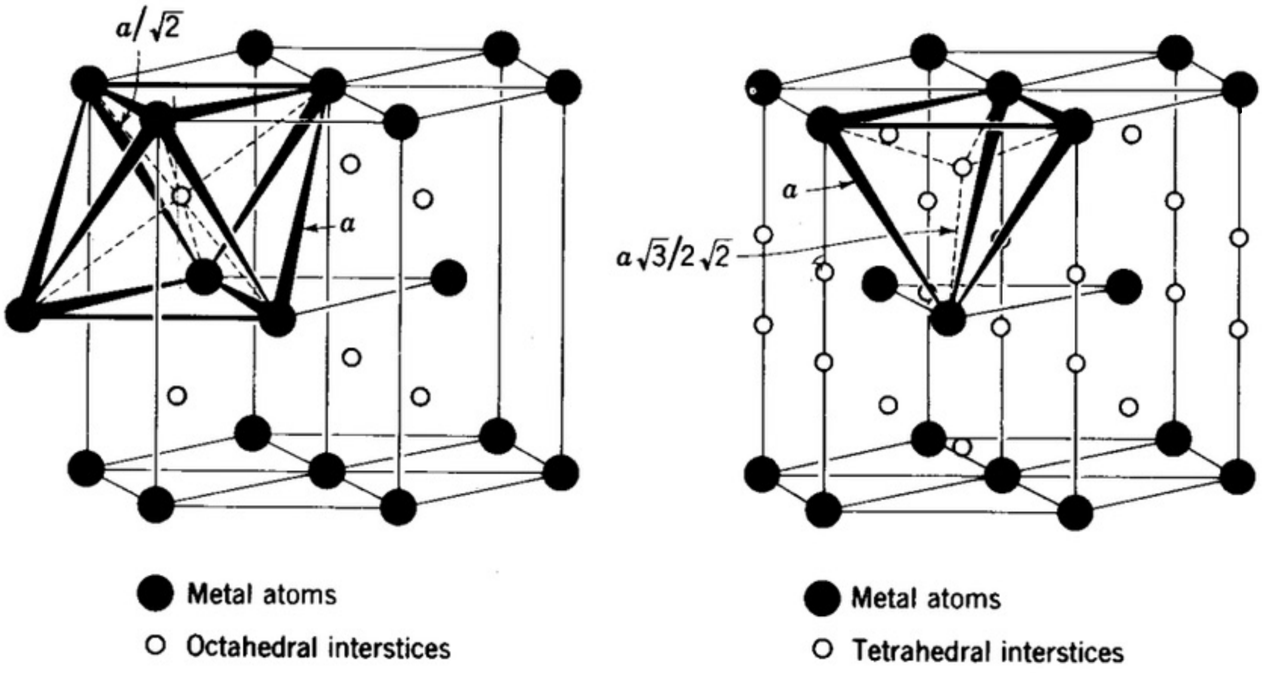
(5) $PF = \dfrac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}\, r^3} = \underline{\underline{0.74}}$

Effective THV $= 4 + 4 + (2 \times 6) \times \frac{1}{3}$

$= 12$

Effective OHV $= 3 + 3 = 6$

Tetrahedral and Octahedral void :



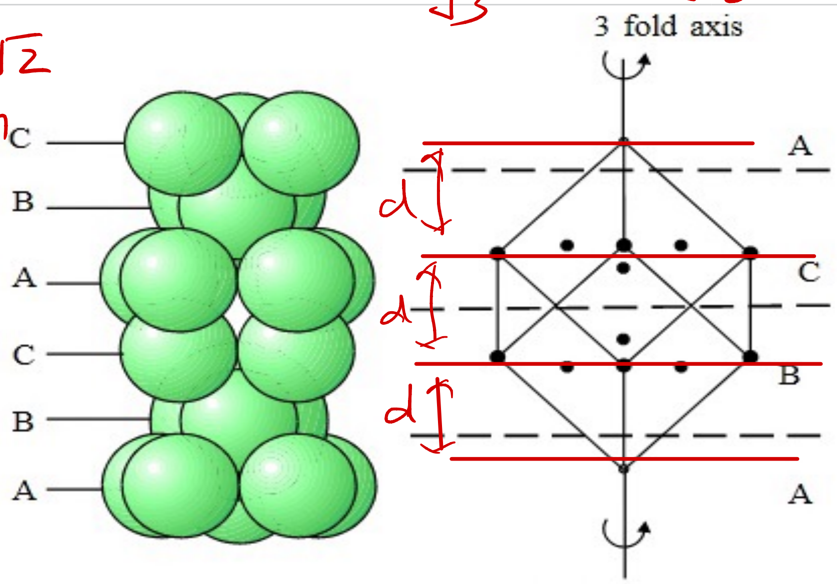
(a) (b)

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

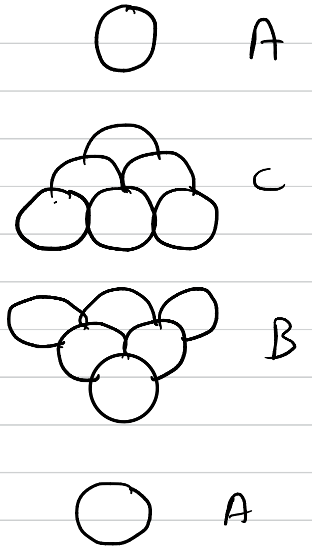
$3d = a\sqrt{3} \Rightarrow d = \frac{a}{\sqrt{3}} = 2\sqrt{\frac{2}{3}}\, r$

$4r = a\sqrt{2}$

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



ABCABCA... or cubic close packing (ccp) of spheres



Octahedral void :

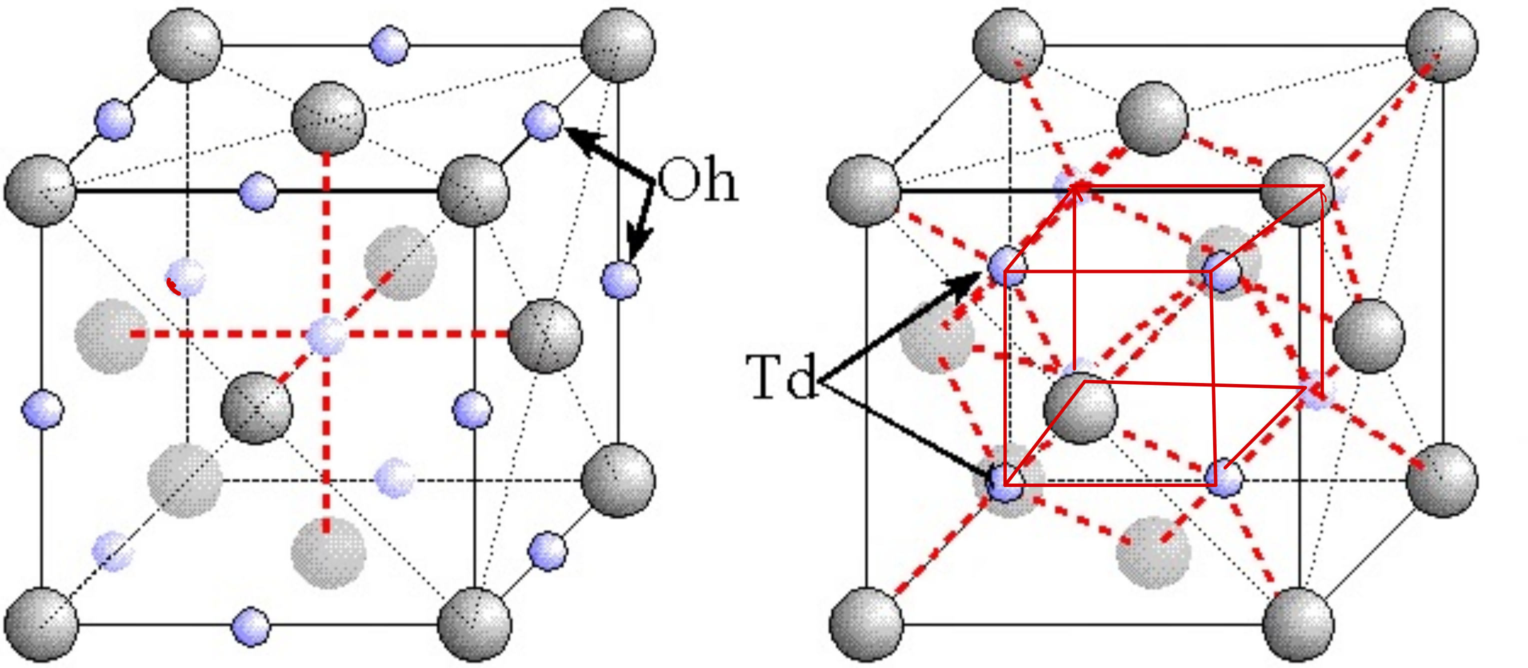
Effective OHV

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

Tetrahedral Void

Effective THV = 8

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



Face-Centered Cubic

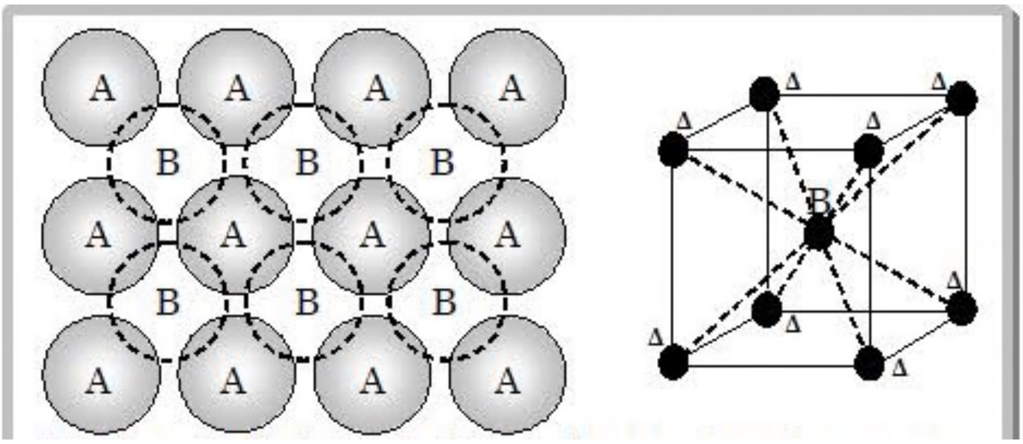
Octahedral and Tetrahedral 'Holes'

All the THV inside create a smaller cube of side $a/2$.

Note :-

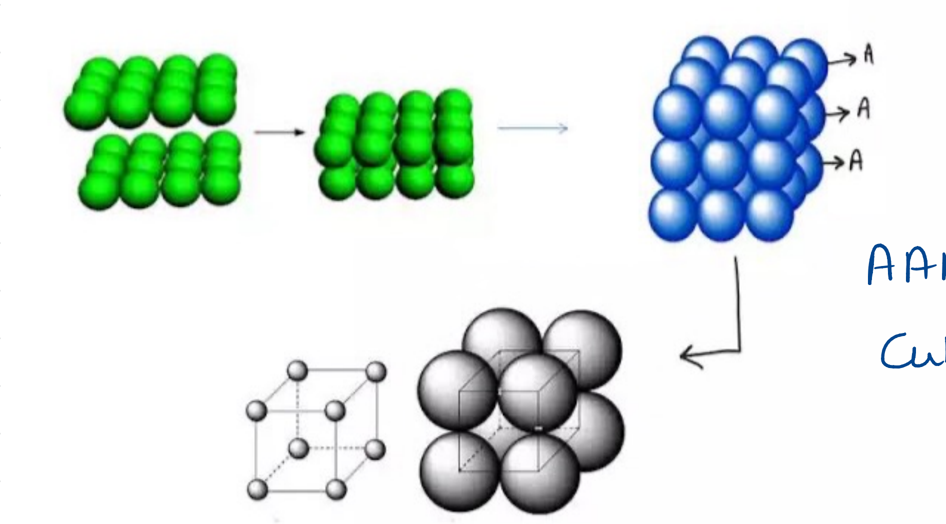
① BCC type arrangement

ABAB - - - type



Close packing ✗

② Simple cubic type :-

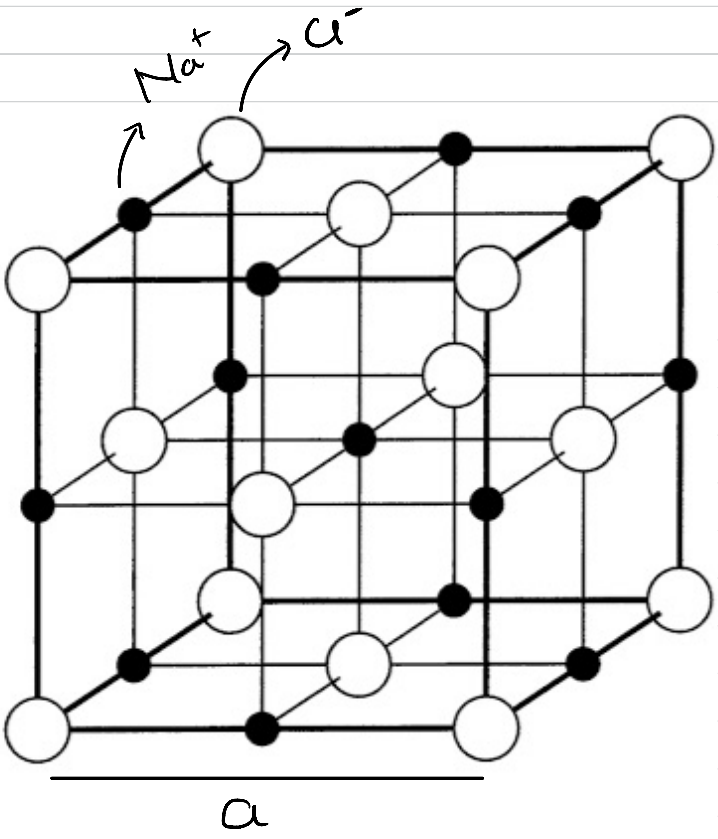


AAA . . . . type

Cubical void

Different type of Ionic crystals

① Rock Salt type (or NaCl type):



$Cl^- =$ All CCP or FCC lattice Pt
$Na^+ =$ All OHV

Effective $Cl^- = 4$
$Na^+ = 4$

$Na^+ Cl^-$

CN :- 6 : 6

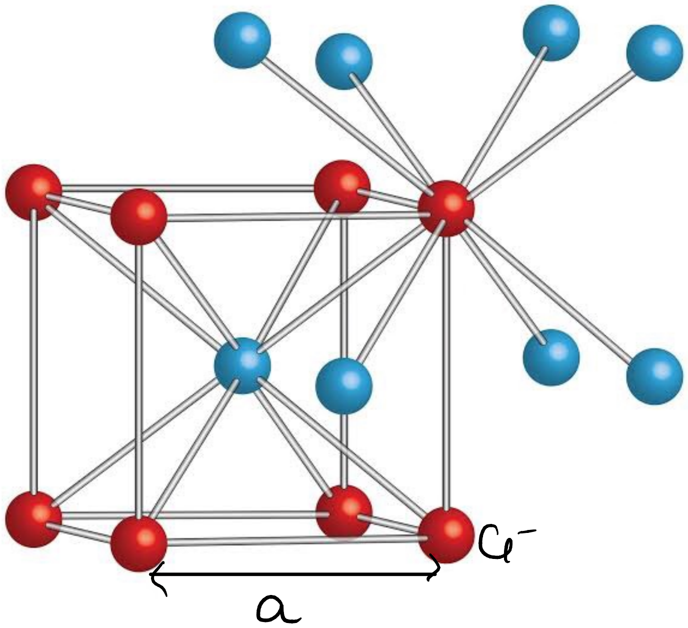
$a = 2r_+ + 2r_-$ — (I)

$\frac{r_+}{r_-} = 0.414$ — (II)

$2r_- = \frac{a}{\sqrt{2}}$ — (III)

Ideal

CsCl type :-



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

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

$\rightarrow$ CsCl

CN: $\boxed{8:8}$

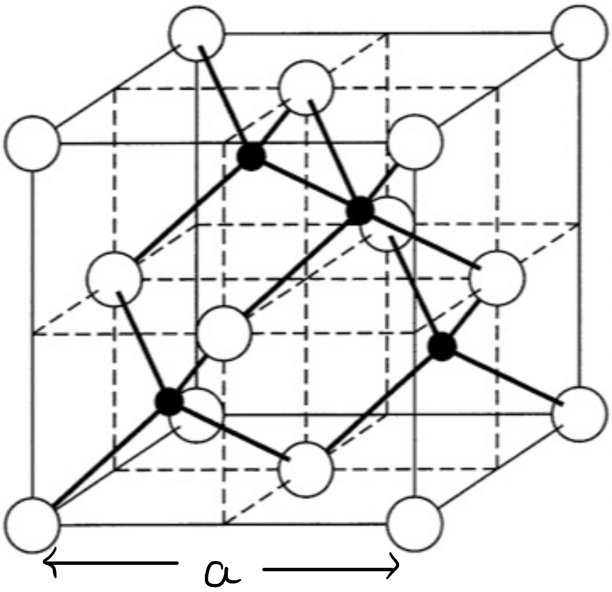
$$\frac{a\sqrt{3}}{2} = r_+ + r_- \quad \text{— (I)}$$

$$\frac{r_+}{r_-} = 0.732 \quad \text{— (II)}$$

$$a = 2r_- \quad \text{— (III)}$$

} Ideal

(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 : $y : x$

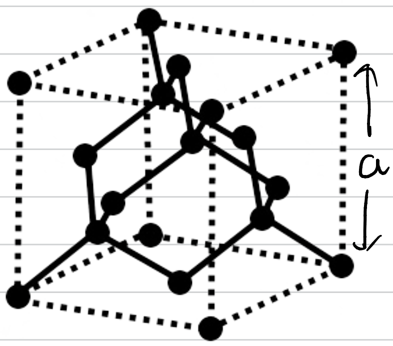
$$\frac{a\sqrt{3}}{4} = r_+ + r_- \quad \text{— (I)}$$

$$\frac{r_+}{r_-} = 0.225 \quad \text{— (II)}$$

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

} Ideal

Structure of Diamond :



Diamond Structure

Similar to ZnS type

C = All FCC lattice Pt + Alternate THV

Effective C = 4 + 4 = 8

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

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

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

Calculate

$a = 2r_+ + 2r_-$
$= 12A^\circ$

(a) Edge length of unit cell

(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)

$$\left(\frac{1.8}{60}\right) N_A \times \frac{1}{4} = \text{No of Unit cell}$$

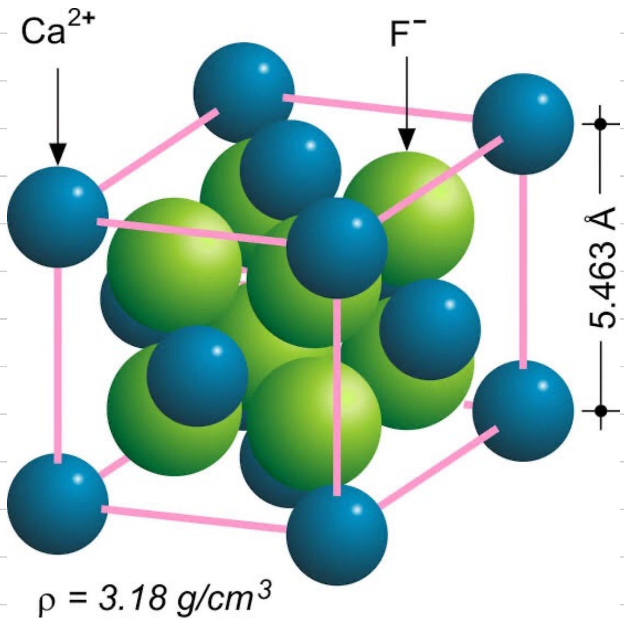
$$= \frac{1.8}{\cancel{60}\ 10} \times \cancel{6} \times 10^{23} \times \frac{1}{4}$$

$$= \underline{4.5 \times 10^{21}}$$

$$d = \frac{4 \times \frac{\cancel{60}\ 10}{\cancel{6} \times 10^{23}}}{(12 \times 10^{-8})^3} = \frac{40 \times 10^{-23} \times 10^{24}}{12 \times 12 \times 12} = \frac{400}{1728} = 0.23 \ \frac{gm}{cm^3}$$

Fluoride type (CaF_2 type)

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



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

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

CaF_2

CN :- 8 : 4

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

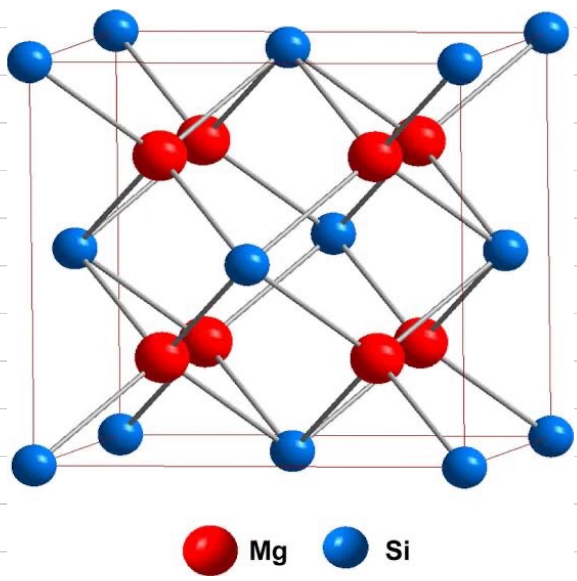
Antifluoride type (Na_2O type)

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

⇓

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.

$a = 2r_+ + 2r_-$

$= 1200$ pm

$\frac{a}{\sqrt{2}} = \frac{1200}{\sqrt{2}} = 600\sqrt{2}$ pm

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

$\frac{r_+}{r_-} = \frac{1.6}{1.864} = 0.858$

$(0.732 - 1)$

$\downarrow$

Cubical void

CsCl

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

$a = \frac{(1.6 + 1.864)2}{\sqrt{3}} = 4$

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

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

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

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

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

$PF = \dfrac{3 \times \frac{4}{3}\pi r_+^3 + \frac{15}{4} \times \frac{4}{3}\pi r_-^3}{a^3}$

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