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SOLID STATE

* **Some common terms ~~voids~~ used :-**

1.) Void :- Space present b/w atoms arranged in a crystal lattice.

→ 2D voids
→ 3D voids

2-D Voids

(i) Triangular Void :-

Geometry formed by joining the centres of the atoms is also the geometry of the void.

Cordination No. = 3.

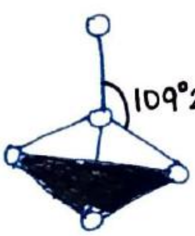
(ii) Square-Planar Void :-

$\boxed{C.N. = 4}$

Coordination no. of void is the no. of atoms forming that void.

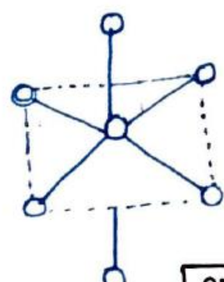
3-D Voids :-

(i) Tetrahedral voids :-



$\boxed{C.N. = 4}$

(ii) Octahedral Void :-



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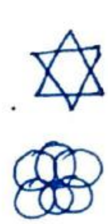
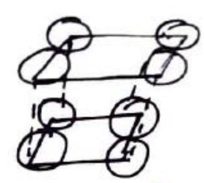


$\boxed{CN = 6}$

(iii) Cubical Void :-



$\boxed{C.N. = 8}$

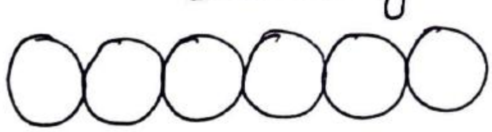
* जो Void का C.N. होता है वही C.N. उसमे present atom या ion का होगा।

* Packings in Solid

There can be 3 types of packing –

(i) One-Dimensional packing
(ii) 2-D packing
(iii) 3-D packing.

1-D Packing

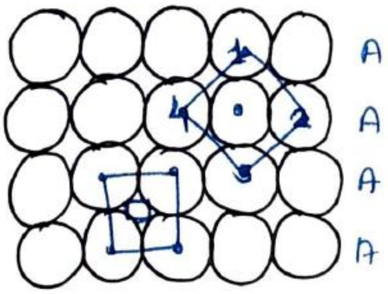


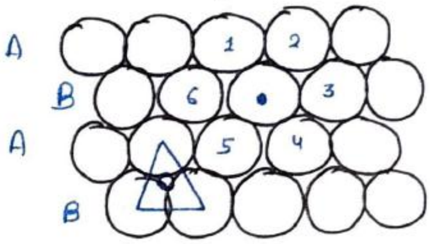
C.N. for 1-D packing = 2.

But for cornermost atom, CN = 1.

2-Dimensional Packing

(scp) (hcp)





- A-A type packing
- Square planar voids are formed
- C.N. for void = 4
- Co.No. for atom in A-A = 4
- Hence also known as square close packing **(scp)**

- A-B A B type packing
- Triangular voids are formed
- C.N. for void = 3
- C.N. for atom in AB = 6.
- Also known as hexagonal closed packing **(hcp)**.

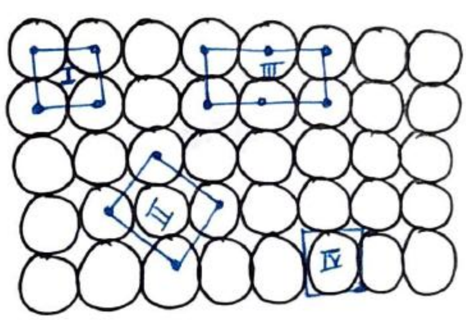
*** Parameter for the stability of solid** :- Packing efficiency ↑ stability ↑ .

Unit cell :- The smallest unit that can generate the whole arrangement by its repitition, in different direction.

In S.C.P., unit cell = square.

Other possible unit cells in scp :- (TJFR)

Hence there can be infinite no. of unit cells in any arrangements, but we have to stick to any one of them to know the concept & solve problems.



Unit cells :-
- Primitive Unit cells ⇒ Only at corners {atoms present}
- Non-Primitive Unit cells ⇒ Corners as well as any other site {atoms present}

Ex ⇒ In above SCP,

II = Non-Primitive

III = Non-Primitive.

I = Primitive.

IV = Can-not be classified {as no atom is present at corner}

*** Packing Efficiency** :-

$$P.E. = \frac{\text{Space occupied by an atoms in unit cell}}{\text{Space occupied by unit cell}} \times 100$$

For this we need a new term,

(Z) = No. of atoms present in a unit cell.

For the values of z, we can use

(i) Angle for 2-D.
(ii) Sharing for 3-D.

Hence for the diagramme drawn behind,

For II, $\angle = 90^\circ$.

Total angle = 360, hence portion of atom in unit cell $= \frac{90}{360} = \frac{1}{4}$..

$Z_{II} = \frac{1}{4} \times 4$ {corners} + 1 (centre)

$\boxed{Z_{II} = 1+1 = 2}$

Now, P.E. of II unit cell:

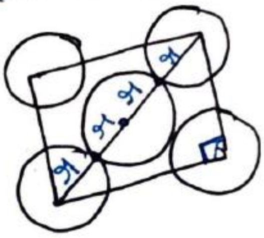
$$P.E._{II} = \frac{Z \times \text{Area of 1 atom}}{\text{Area of unit cell}}$$

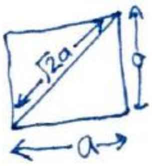
$$P.E._{II} = \frac{2 \times \pi r^2}{a^2}$$ a = edge length.
r = radius of atom.

Rel^n b/w (a & r) वहीं से आयेगा जहाँ atoms एक-दूसरे को Touch करेंगे।

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

$\Rightarrow a = 2\sqrt{2}r$ Now, $a^2 = 8r^2$.

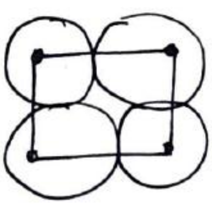




$$P.E._{II} = \frac{2\pi r^2}{8r^2} \times 100 = 78.5\%$$

$\frac{P.E.}{100} = P.F.$ % void = 100 − P.E.

Similarly for I

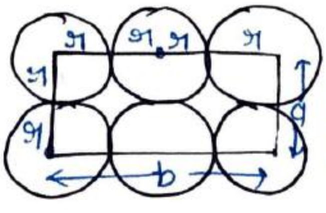


$$P.E. = \frac{Z \times \pi r^2}{a^2}$$

but,
Z = 1
and a = 2r ⇒ PE. = 78.5%

Similarly for III:

$$P.E._{III} = \frac{Z \times \pi r^2}{a \times b} \times 100$$

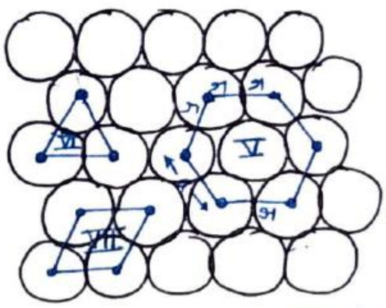


a = 2r
b = 4r

$\Rightarrow a \times b = 2r \times 4r = 8r^2$

$P.E._{III} = 78.5\%$

* In Hexagonal Closed Packing:



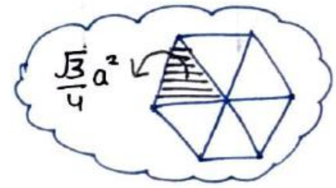
For V^{th}:

$$P.E. = \frac{3 \times \pi r^2}{6 \times \frac{\sqrt{3}}{4} a^2} \times 100$$

$$Z = \frac{1}{3} \times 6 + 1 = 3.$$

$\boxed{a = 2r}$

$\boxed{P.E. = 90.6\%}$



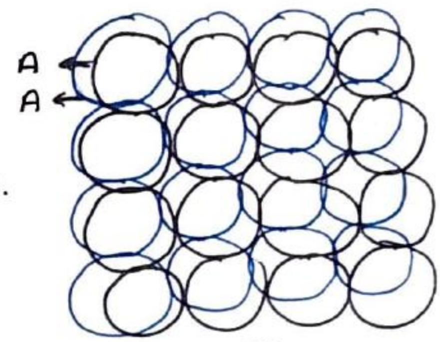
For VI^{th}

$$Z = \frac{1}{6} \times 3 = \frac{1}{2}$$

and $a = 2r$

$$P.E. = \frac{\frac{1}{2} \times \pi r^2}{\frac{\sqrt{3}}{4} \times a^2} \times 100$$

$\boxed{P.E. = 90.6\%}$

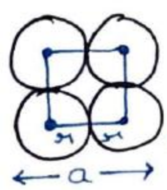


AAA packing.

⇓ unit cell

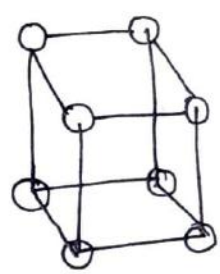
Let's Jump to 3-D:

(scp) ⟶ 3-D

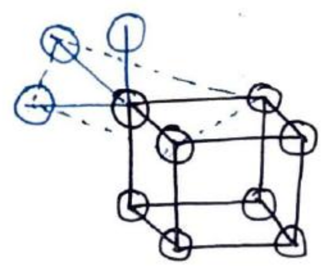


a) $a = 2r$

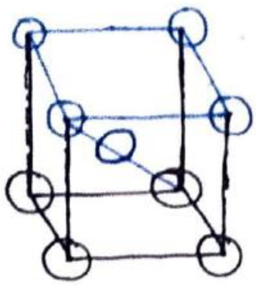
- AAA type packing as $Z = \frac{1}{8} \times 8 = 1.$
- $Z = 1$
- $P.E. = 52.4\%$
- Cubical void is present at the body centre of simple cubic unit cell.
- Co-ordination no. of atom = 6.

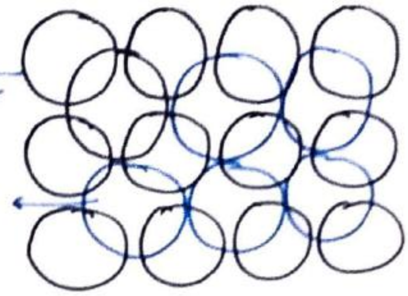


Simple cubic unit cell



*** Second Arrangement :- ABAB.**





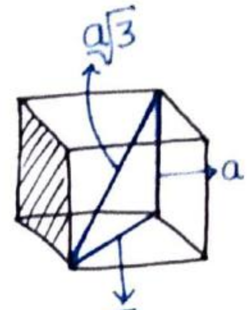
Body centred cubic unit cell
(bcc)

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

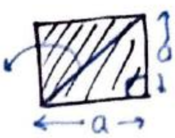
- $\boxed{Z = 2}$
- $\boxed{a = \frac{4}{\sqrt{3}} r}$

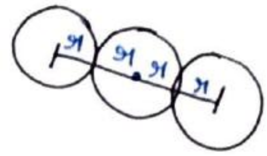
$P.E. = \frac{2 \times \frac{4}{3}\pi r^3 \times 100}{a^3}$

- $\boxed{P.E. = 68\%}$
- C.No. = 8



Diagonals,
- face (12 diag.)
- body (4 diagonals)





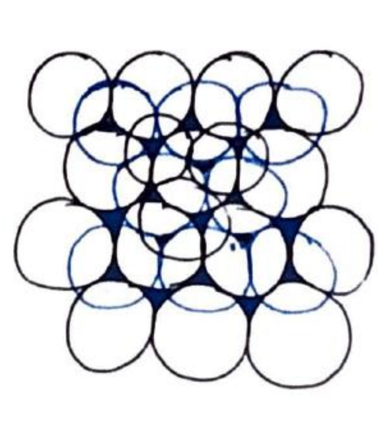
$\Rightarrow a\sqrt{3} = 4r$

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

α-Polonium is the only element to form simple cubic unit cell at high temp.

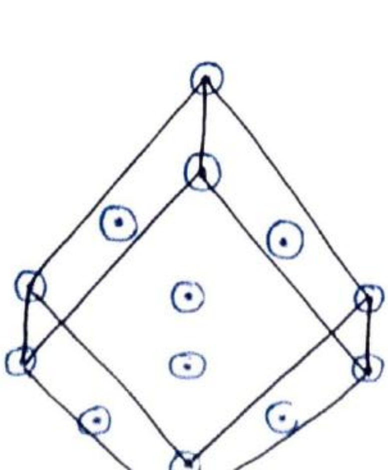
*** HCP(2D) ⟶ (3D)**

ABCABC arrangement.



HCP(2D)
- △ → atoms
  - T.V.(a) (N)
  - T.V.(b) N
  - ↓ ABAB (hcp)
- ▽ → O.V.(a) ↓N ABCABC (ccp).

Unit cell formation :-



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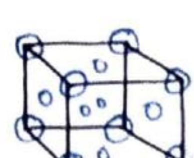
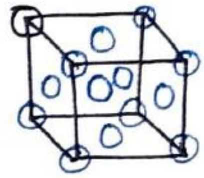
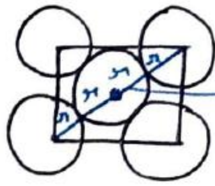


* Cubic Closed Packing :- {fcc} face centred cube.



$$Z = \frac{1}{8}\times 8 + \frac{1}{2}\times 6 = 4 \Rightarrow \boxed{Z=4}$$

* Rel^n b/w 'a' & 'r'.



$a\sqrt{2} = 4r$

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

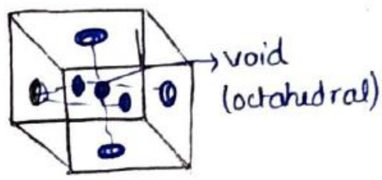
$$* \; P.E. = \frac{4\times\frac{4}{3}\pi r^3\times 100}{a^3}$$

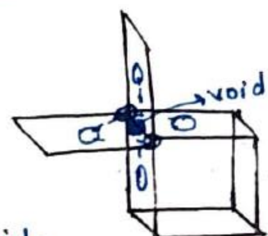
$$= \frac{\frac{16}{3}\pi r^3\times 100}{16\sqrt{2}r^3} = 74\% \Rightarrow P.E. = 74\%$$

* Co-ordination No. of Atom = 12 {3 above the plane, 3 below the plane and 6 in the plane}.

found from original ccp-arrangement.

Voids → Tetrahedral voids.
→ Octahedral voids



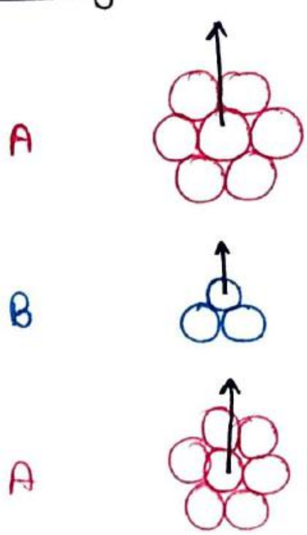


Hence there will be a total of 12 octahedral voids on edges and 1 at the body centre; but the total contribution of octahedral voids is 3 as every edge is connected to 4 unit cells.

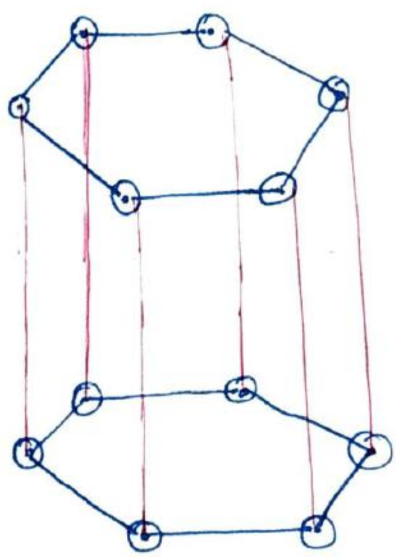
* Total tetrahedral voids in fcc = 8.

2 Td-voids are present in each body diagonal.

* Hexagonal closed packing :-



Unit cell ⇒



Hexagonal unit cell.

Hexagonal;

$a = b \neq c$

$\alpha = \beta = 90°$

$\gamma = 120°$

a b c
α β γ

∠ b/w a & b = γ
b & c = α
c & a = β

$Z = \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3 = 6$

corners   face

$Z = 6$

* Packing efficiency = 74%
* Co-ordination number = 12.
* 6 octahedral and 12 tetrahedral voids are present.

QUICK REVISION

1-D → 2-D

2-D → scp (P.E. = 78.5%) → 3D

2-D → hcp (P.E. = 90.6%) → 3-D

scp → AAAA → simple cubic

scp → ABAB → Body centre cubic

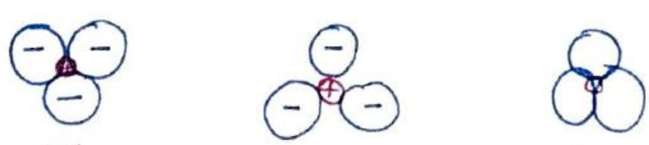
hcp → ABAB (hcp) → Hexagonal

hcp → ABCABC (ccp) → fcc.

	simple cubic	Body centre cubic	Hexagonal	fcc
Z =	1	2	6	4
a/r =	$a = 2r$	$a\sqrt{3} = 4r$	–	$a\sqrt{2} = 4r$
P.E. =	52.4%	68%	74%	74%
C.No. =	6	8	12	12
Void =	Cubical	–	12 Td & 6 Oh	4 Oh & 8 Td.

* IONIC CRYSTALS :-

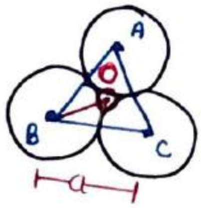
Q Which is most stable lattice among the following.

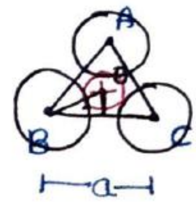


I   II   III

Structure (I) is more stable.

* Study of Structure I and II :-





Let suppose the above diagramme is ideal case.

In Δ OBD

$$\frac{\sqrt{3}}{2} = \cos 30° = \frac{BD}{OB} = \frac{a/2}{r+R}$$

$$\boxed{a = \sqrt{3}(r+R)}$$

Let suppose the above diagramme is real case.

In Δ OBD

$$\frac{\sqrt{3}}{2} = \cos 30° = \frac{BD}{OB} = \frac{a/2}{r+R}$$

$$\boxed{a = \sqrt{3}(r+R)}$$

For Ideal we have;

$$a = 2R$$

for radius ratio we have,

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

On solving, $\boxed{\frac{r}{R} = 0.155}$

r = radius of void
R = Radius of cell

* Radius Ratio Rules :-

$$\boxed{\text{Radius Ratio Rule} = \frac{r}{R}\ \frac{(\text{radius of smaller ion/void})}{(\text{Radius of larger ion/ cell})}}$$

Radius Ratio's	Void	Co-ordination No.
$0 < \frac{r}{R} < 0.155$	Linear	2
$0.155 < \frac{r}{R} \leq 0.225$	Triangular	3
$0.225 < \frac{r}{R} \leq 0.414$	Tetrahedral	4
$0.414 < \frac{r}{R} \leq 0.732$	Octahedral	6
$0.732 < \frac{r}{R} \leq 1$	Cubical/ bcc	8

Don't Do these mistakes :-

(1) Given $\frac{r_{A}^{+}}{r_{B}^{-}} = 1.5$ ∵ Since Ratio is >1, we need to invert it to find correct arrangement & void.

Correct = $\frac{r_{B}^{-}}{r_{A}^{+}} = \frac{1}{1.5} = 0.66$: {Oh. void}

(2) From Table, radius ratio rule increases with ↑ing void size.

(3) Find Co-ordination number for.

$$\frac{A^{+} = 100\,pm}{B^{\ominus} = 200\,pm} = 0.5.$$

~~RN lies~~ Radius ratio lies in octahedral void. Hence Co-ordination number is 6.

* Applications :-

To find the formulae of the compound :-

formulae of the compound is hidden inside the unit cell.

Type-I ; B → present at all corners of the cube.
A → all face centres.

Formulae = Simplest whole no. ratio

$B \rightarrow \frac{1}{8} \times 8 = 1 \Rightarrow B_1$

$A \rightarrow \frac{1}{2} \times 6 = 3 \Rightarrow A_3$

$\boxed{\text{Formulae} = AB_3}$

TIFR :- Which of the following expressions represent correct formulae.

(a) AB_3 (b) A_2B_6 (c) A_3B_9 (d) All of the above

✓ See the def^{n} of formulae.

Example :- Find formulae for;

B → Corner
A → 1 face-centre only.

$B \rightarrow \frac{1}{8} \times 8 = 1 \Rightarrow B_1$

$A \rightarrow \frac{1}{2} \times 1 = \frac{1}{2} \Rightarrow A_{1/2}$

$\Rightarrow$ formulae = $A_{1/2}B \Rightarrow \boxed{AB_2}$

Example :- $X \rightarrow$ 6 corners of cube
$Y \rightarrow$ remaining corners + face centre which are not opposite to each other.
$O \rightarrow$ Remaining face-centre + Body centre.

$X \rightarrow X = \frac{1}{8} \times 6 = \frac{3}{4} \Rightarrow X_{3/4}$

$Y \rightarrow \frac{1}{8} \times 2 + \frac{1}{2} \times 3 \Rightarrow \frac{1}{4} + \frac{3}{2} = \frac{7}{4} \Rightarrow Y_{7/4}$

$O \rightarrow \frac{1}{2} \times 3 + 1 \Rightarrow \frac{3}{2} + 1 = \frac{5}{2} \Rightarrow O_{10/4}$

$\boxed{\text{Formulae} = X_3 Y_7 O_{10}}$

Type-II :- When unit cells are not given :-

For the formulae, we need unit cell & for unit cell find packing.

Example :- B forms c.c.p. & A occupies all oh. voids.

Sol^n $\left\{ \begin{array}{l} B \rightarrow ccp \\ A \rightarrow \text{all o.v.} \end{array} \right\} \xrightarrow{\text{unit cell}}$ FCC

Contribution of B in FCC $= \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$.

$B \Rightarrow B_4$

Now total oh. voids in F.C.C. = 4

$A \Rightarrow A_4$

Formulae $= A_4 B_4 \Rightarrow \boxed{AB}$

Example :- $\left\{ A \rightarrow \frac{1}{8} \times T.V. \; ; \; B \rightarrow \frac{1}{2} \times O.V. \; ; \; O \rightarrow ccp. \right\}$

In c.c.p. packing ;

unit cell = FCC.

$\Rightarrow$ Contribution of $O = O_4$.

Tetrahedral voids = 8.

$\Rightarrow$ Contribution of $A = \frac{1}{8} \times 8 = A_1$

Octahedral voids = 4

$\Rightarrow$ Contribution of $B = \frac{1}{2} \times 4 \Rightarrow B_2$

Formulae $= AB_2O_4$

* Ionic Crystals in Our Course :-

(i) NaCl (Rock-salt)
(ii) CaF_2 (Fluorite)
(iii) Na_2O (Anti-fluorite)
(iv) CsCl (
(v) ZnS.

1.) NaCl :- (Rock salt)

Remember ⇒ $\boxed{\begin{array}{l} Cl^{\ominus} = \text{c.c.p. arrangement} \\ Na^{\oplus} = \text{All octahedral voids} \end{array}}$

For formulae ⇒ find packing / unit cell.

$$Cl^{\ominus} = c.c.p \longrightarrow \boxed{F.C.C} \Rightarrow Cl_4$$
$$\downarrow$$
$$\boxed{4\ O.V} \Rightarrow Na_4$$

Formulae $= Na_4Cl_4 \Rightarrow 4NaCl$, $\boxed{4}\boxed{NaCl}$

Formulae unit (z) ⇑ 4

⇓ NaCl: Formulae of compound

> Formulae unit tells the no. of units of any compound (NaCl, in this case) present inside one unit cell.

Ex: Find mass of 1 unit of NaCl.

Sol^{n} Remember, there are 4 units of NaCl present in 1 unit cell.

⇒ $\boxed{\text{Mass of 1 unit cell} = 4 \times \text{Molecular weight of NaCl}}$

Ex:- No. of ions in 1 unit cell.

Sol^{n}:- Total moles of NaCl in 1 unit cell = 4

Hence we will have $4Na^{\oplus}$

* **Co-ordination Number Ratio** :- Find the atom/ion present in the void.

Here, Na^+ is present in void.

C.N. of $Na^+ = 6$ {as Na^+ occupies Oh. void}

How to find C.N. Ratio :-

	Na	Cl
charge ratio =	1	1
C.N. ratio =	6	6.

2) CsCl

$\boxed{\begin{array}{l} Cl^{\ominus} = \text{simple cubic} \\ Cs^{+} = \text{cubical void.} \end{array}}$

$Cl^{\ominus} = \frac{1}{8} \times 8 = 1 \Rightarrow Cl_1^-$

$Cs^{+} = 1 \Rightarrow Cs_1^+$

$\boxed{\text{Formulae} = CsCl}$

C.No. of Cs^+ = 8 {as Cs^+ occupies cubical void}

	CsCl
charge ratio	1:1
C.N. ratio	8:8

3.) CaF_2 (fluorite):-

$\boxed{\begin{array}{l} Ca^{2+} \rightarrow ccp \\ F^{\ominus} \rightarrow \text{all T.V.} \end{array}}$

$Ca^{2+} = 4$ {ccp}

$F^{\ominus} = 8$ {T.voids}

$\boxed{\text{Formulae} = Ca_4F_8 = 4CaF_2}$

$\boxed{\text{Formulae unit} = 4}$

C.N. of $F^{\ominus} = 4$.

	CaF_2
charge ratio =	2:1
C.N. ratio =	8:4

4.) Na_2O (anti-fluorite):-

$\boxed{\begin{array}{l} O^{2-} = ccp \\ Na^{+} = \text{all Td.Voids} \end{array}}$

$O^{2-} = 4$ {ccp ⇒ fcc}

$Na^{+} = 8$ {8 Td Voids}

$\boxed{\text{Formulae} = Na_8O_4 = 4Na_2O}$

$\boxed{\text{Formulae unit} = 4}$

Cord. No. of $Na^{\oplus} = 4$

	Na_2O
charge ratio =	2:2
C.N. ratio =	4:8

5.) ZnS :- It forms two types of crystals . . .

$$\text{Blende} \leftarrow \boxed{ZnS} \rightarrow \text{Wurtzite}$$

Blende

$\boxed{\begin{array}{l} S^{2-} = ccp \\ Zn^{2+} = \text{Half T.V.} \end{array}}$

Formulae = Zn_4S_4

= $4ZnS$.

C.N. Ratio = 4:4

Wurtzite

$\boxed{\begin{array}{l} S^{2-} = hcp \\ Zn^{2+} = \text{Half T.V.} \end{array}}$

Formulae = Zn_6S_6

$6ZnS$

C.N. Ratio = 4:4.

Example :- TiO_2

where, $\boxed{\begin{array}{l} O^{2-} = hcp \\ Ti^{4+} = \text{half Oh·void} \end{array}}$

$O^{2} \Rightarrow hcp \Rightarrow O_6$

$Ti^{4+} \Rightarrow$ Half Oh·Void $= \frac{1}{2} \times 6 = 3 \Rightarrow Ti_3$

$\boxed{\text{Formulae} = Ti_3O_6 = 3TiO_2}$

C·N· Ratio

TiO_2

charge ratio = **4 : 2**

C·N· ratio = 6 : 3

: COVALENT CRYSTALS :-

1.) Diamond :-

Only C-atoms are present.

* Unit shows similarity with ZnS blende.

$\boxed{\begin{array}{l} C = ccp \\ C = \text{half Td·void} \end{array}}$

$\boxed{\begin{array}{l} S^{2-} = ccp \\ Zn^{2+} = \text{Half Td·Void} \end{array}}$

$C = ccp \xrightarrow{\text{unit cell}} \boxed{FCC}$

FCC → (4 Carbons)

FCC → $\boxed{\text{8 Td Voids}} \xrightarrow{\text{C-atoms}} \boxed{4}$

Total C-atoms = 8 (in 1 unit cell)

Formulae = 8C
↳ Formulae unit

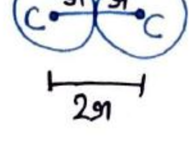
$\boxed{\frac{a}{r} \Rightarrow \frac{a\sqrt{3}}{4} = 2r}$ **

Here $\boxed{a\sqrt{2} \neq 4r}$

* Packing efficiency :- $\frac{8 \times \frac{4}{3}\pi r^3}{a^3} \times 100 = \boxed{34\%}$

* C–C bond length ; Since only C-atoms are present,

$\boxed{\text{C-C bond length} = 2r}$



2.) Carborundum (SiC) :-

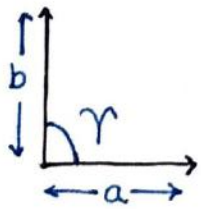
Half of carbon in diamond are replaced by silicon.

C → 4 Si → 4

$\boxed{\text{Formulae} = 4CSi}$
↳ Formulae unit

* Parameters for unit cell :-

2-D



$a = b$, $\gamma = 90°$ ⇒ square unit cell.

$a \neq b$, $\gamma = 90°$ ⇒ rectangle unit cell.

3-D :- 6 Parameters.

3 edge length a, b, c and angle b/w them α, β, γ.

7 types of unit cells are possible.

1.) Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, BCC, FCC
2.) Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, BC
3.) Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, BC, FC, End C.
4.) Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	Primitive
5.) Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive
6.) Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Primitive, End C
7.) Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive.

1.) Cubic	a^3	3
2.) Tetragonal	a^2b	2
3.) Orthorhombic	abc	4
4.) Hexagonal	$\frac{6\sqrt{3}}{4} a^2c$	1
5.) Rhombohedral	a^3	1
6.) Monoclinic	abc	2
7.) Triclinic	abc	1

14 types of lattices are formed known as Bravia's Lattice.

* Density of unit cell :

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

Mass of unit cell = Mass of Z atom = Z × Mass of 1 atom.

↳ formulae unit.

Example :

Molar mass of Na = 23 g/mol.

⇒ 6.023×10^{23} atom of Na = 23 g mol^{-1}

$$1 \text{ Na atom} = \frac{23}{6.023 \times 10^{23}}$$

$$\Rightarrow \boxed{1 \text{ Na atom} = \frac{M_w}{N_A}}$$

M_w = Molecular Weight

N_A = Avogadro Number.

$$\Rightarrow \boxed{\text{Mass of 1 atom} = \frac{M_w}{N_A}}$$

$$\boxed{\text{Mass of 1 unit cell} = \frac{Z \times M_w}{N_A}}$$

For,

SCC	BCC	FCC
Z = 1	Z = 2	Z = 4

$$\boxed{\text{Volume of cube} = a^3}$$

$$\boxed{\text{Density of cubic unit cell } (\rho) = \frac{Z \times M_w}{N_a \times a^3}}$$

Example :- A metal X ⇒ FCC a = 200pm .

200g of metal 'x' contains 24×10^3 atoms . Find density.

Sol^n Since, X ⇒ FCC ⇒ $\boxed{Z = 4}$

Mass = 200gm
Atoms = 24×10^3 . } → M_w.

$$\boxed{\rho = \frac{Z \times M_w}{N_a \times \underbrace{a^3}_{200pm}}}$$

Example :-

$$Ag \rightarrow r = 144 \text{ pm} \qquad \rho = 106 \text{ g/cm}^3 \qquad M = 108 \text{ g/mol}$$

To which cubic crystal do silver belong.

Sol^n: Since silver belongs to cubic crystal ⇒ z may be any number depending upon crystal lattice.

We know that,

$$\rho = \frac{Z \times M}{a^3 \times N_a} \quad \text{—(i)}$$

Since we have two unknown variables i.e. 'Z' and 'a'.
Therefore we will find the value of $\left(\frac{Z}{a^3}\right)$ from (i) and put it in the eq^n of packing efficiency.

$$P.E. = \frac{Z \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

On putting values, we have

$$\boxed{P.E. = 74\%}$$

Hence Ag forms FCC cubic crystals

Possible Outcomes

1.) Simple Cubic
$a = 2r$
2.) BCC ($a\sqrt{3} = 4r$)
3.) FCC ($a\sqrt{2} = 4r$)

पर आगे यहाँ से Help नहीं मिलेगी क्योंकि Type of packing नहीं पता है।

The value of P.E. will give us the idea of unit cell as we know.

SC = 52%
BCC = 68%
FCC = 74%

Example :- A metal 'X' forms a cubic lattice of edge length 2.88 A°. The density of unit cell is 7.20 g/cm³. Find no. of unit cell in 100g of that compound.

Given :- Metal 'X' = Cubic lattice
edge-length (a) = 2.88 A° $\qquad \rho = 7.20 \text{ g/cm}^3 \qquad$ 100g of X ⇒ No. of unit cell.

We know that,

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

$$\boxed{\text{No. of unit cell} = \frac{\text{Given Mass}}{\text{Mass of 1 unit cell}}} \qquad \boxed{\text{No. of unit cell} = \frac{\text{Given Volume}}{\text{Volume of 1 unit cell}}}$$

* Density of Unit Crystal :- {Ionic Crystals}

Type-I :- NaCl type crystals (Rock Salt).

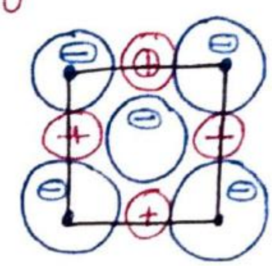
$$\boxed{\text{Density} = \frac{\text{Mass of 1 unit cell}}{\text{Volume of 1 unit cell}}}$$

Mass of 1 unit cell → formulae unit

Volume of 1 unit cell → edge length (a)

$NaCl \Rightarrow Cl^{\ominus} = ccp$

$Na^{\oplus}$ = all oh void ⇒ edge centres + body centre



$Cl^{\ominus} = ccp \rightarrow 4Cl^{\ominus}$

$\rightarrow$ 4 oh Voids = $4Na^{+}$

Formulae = 4NaCl

↳ Formulae unit

Edge length (a) = $2(r_{Na^+} + r_{Cl^\ominus})$

Mass of unit cell = 4 × Mass of 1 NaCl.

Mass of 1 NaCl = Mass of 1 Na + Mass of 1 Cl.

$$\frac{M_w}{N_A} = \frac{23}{6.023 \times 10^{23}} \qquad \frac{M_w}{N_A} = \frac{35.5}{6.023 \times 10^{23}}$$

$$\frac{58.5}{6.023 \times 10^{23}}.$$

$$\boxed{\text{Mass of unit cell} = \frac{4 \times 58.5}{6.023 \times 10^{23}}}$$

$$\boxed{\text{Density}(\rho) = \frac{Z \times M_w}{N_A \times a^3}}$$

Z = Formulae ~~Mass~~ Unit

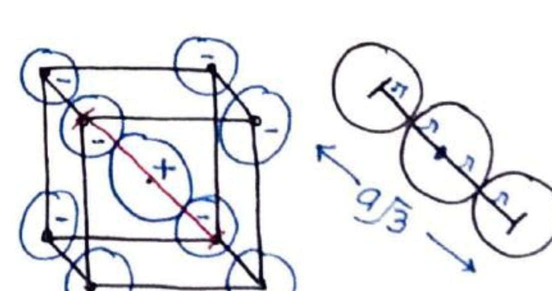
M_w = ~~Mol~~ Formulae Mass

$$\boxed{\underset{\text{(covalent)}}{\text{Molar Mass}} = \underset{\text{(Ionic)}}{\text{Formulae Mass}}}$$

Type-II :- CsCl Type.

Z = 1

$$\boxed{\rho = \frac{Z \times M}{N_A \times a^3}}$$



$$\boxed{a\sqrt{3} = 2(r_{Cs^+} + r_{Cl^-})}$$

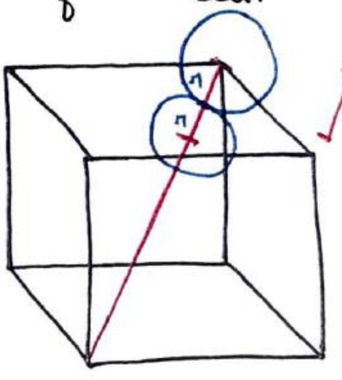
Example :- Density of CaF_2 is 3.18 g/cm³. Find the length of unit cell.

Sol^{n} $CaF_2 \Rightarrow$ $Ca^{2+} = ccp$

$F^{\ominus}$ = all Td·voids (8)

$\Rightarrow \boxed{\dfrac{a\sqrt{3}}{4} = R_{Ca^{2+}} + R_{F^-}}$ formulae unit (z) = 4

$\boxed{\rho = \dfrac{Z \times M}{N_a \times a^3}}$ formulae mass (M) = 78 gm/mol.



$\dfrac{a\sqrt{3}}{4}$

* LATTICE ENERGY *

*** Lattice Energy :-** Minimum energy required to break 1 mole of lattice into constituent ions.

$NaCl\,(s) \longrightarrow Na\,(s) + Cl_2\,(g)$ + Energy ≠ lattice energy as states are different.

*** How to Determine :-**

(1) Born-Haber Cycle

(2) Born-Lande Equation.

*** Born-Haber Cycle :-** This cycle is based on Hess' Law.

$$Na\,(s) + \tfrac{1}{2}Cl_2\,(g) \xrightarrow{\Delta H_f} \overset{+1}{Na}\overset{-1}{Cl}\,(s)$$

$Na\,(s) \xrightarrow{\Delta H_{sub}} Na\,(g) \xrightarrow{I.E.} Na^+\,(g)$

$\tfrac{1}{2}Cl_2\,(g) \xrightarrow{B.D.E. = \frac{1}{2} B.D.E.} Cl\,(g) \xrightarrow{\Delta H_{e^- gain}} Cl^{\ominus}\,(g)$

$Na^+\,(g) + Cl^{\ominus}\,(g) \xrightarrow{\Delta H_{Lattice}} NaCl\,(s)$

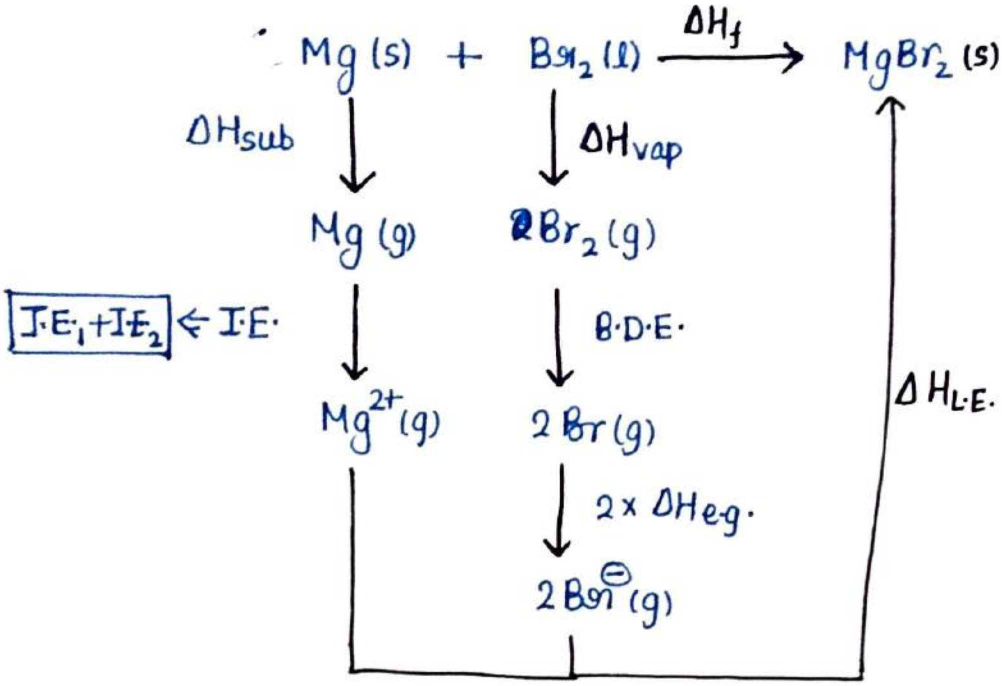
B.D.E. = ½ B.D.E. .... as we need to break only half mole of chlorine.

ΔH_f (enthalpy of formation) — Reactants should be in natural state; Product should be 1 mole.

According to Hess' Law;

$$\boxed{\Delta H_f = \Delta H_{sub} + I.E. + \tfrac{1}{2} B.D.E. + \Delta H_{e^{\ominus} gain} + \Delta H_{L.E.}}$$

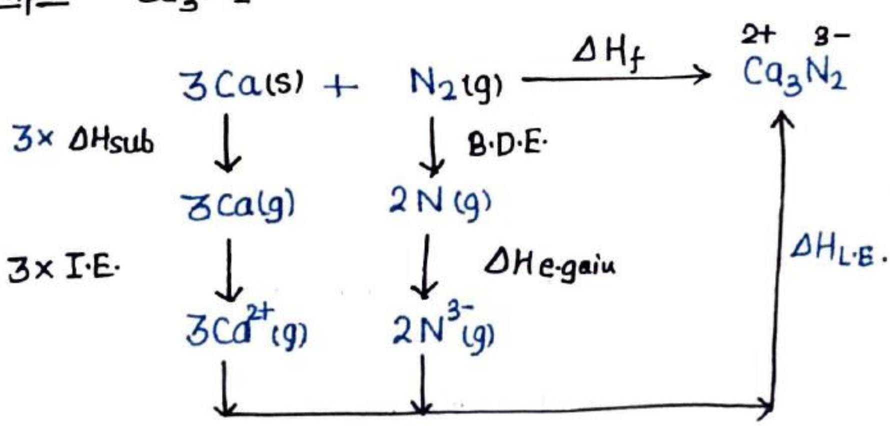
Example :- $MgBr_2$



According to Hess law;

$$\Delta H_f = \Delta H_{sub} + I.E. + \Delta H_{vap} + B.D.E. + 2\Delta H_{eg} + \Delta H_{L.E.}$$

Example :- Ca_3N_2



2.) Born-Lande's Equation :-

$$\boxed{U = \frac{K Z_{\oplus} Z_{\ominus} \cdot e^2 N_A \cdot M}{r}\left(1 - \frac{1}{n}\right)}$$

where;

$K = \frac{1}{4\pi\varepsilon_0} = 9.0 \times 10^9 \ N\text{-}m^2/C^2$

$e^{\ominus}$ = charge on an electron = 1.6×10^{-19} Coulomb.

$Z^{\oplus}$ = positive charge {value with sign}

$Z^{\ominus}$ = negative charge {value with sign}

M = Madulueg's constant

n = Born-exponent

N_A = Avogadro Number

r = Interionic distance. $\boxed{r = r_+ + r_-}$

Ex:- NaCl: $Z_+ = 1$ $Z_- = -1$

$MgCl_2$: $Z_+ = 2$ $Z_- = -1$

CaO: $Z_+ = 2$ $Z_- = -2$.

$\boxed{U = \text{Potential energy} = \text{Lattice Energy.}}$

Note :- Whenever we are calculating L.E. using Born-Lande equ^{n} for two oppositely charged ions, we need to report it (-)ve value.

* Modulueg's Constant :-

→ depends upon geometry of crystal

→ does not depend upon charge on ions and ionic radii.

Ex NaCl has rocksalt structure. For NaCl M = 1.7476.

What will be the value of M for a compound having formulae AB_2 if it has rock salt structure.

Ans M = 1.7476 as it depends upon structure.

Q1) If MgO Possess rock salt structure, find value of M?

Sol^n M = 1.7476.

* Interionic distance :-

Type-I :-

Edge length of NaCl (a) = 200 pm find r = ?

⇒ a = 2r

⇒ r = 100 pm.

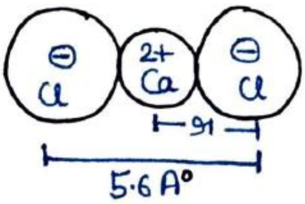
Type-II :-

$r_{Cs^+} = 186$ pm $\quad r_{Cl^-} = 181$ pm.

$$\boxed{r = r_{Cs^+} + r_{Cl^-}}$$

Type-III

Suppose $CaCl_2$ be a linear molecule and distance b/w two chlorine atoms is 5.6 A°



$$r = \frac{5.6}{2} = 2.8\ A^0$$

* Born-Exponent :-

Element	Born Exponent (n)
He	5
Ne	7
Ar	9
Kr	10
Xe	12

* Find value of Born-Exponent(n) for -

1.) Li^+H^-

$Li^+ = n_1 = 5$

$H^\ominus = n_2 = 5$

$$n = \frac{n_1 + n_2}{2} = \frac{5+5}{2} = 5$$

$$\boxed{n=5}$$

2.) NaCl

$Na^+ = n_1 = 7$

$Cl^\ominus = n_2 = 9$

$$n = \frac{n_1 + n_2}{2} = \frac{7+9}{2} = 8$$

$$\boxed{n=8}$$

3.) CsCl

$Cs^+ = n_1 = 12$

$Cl^\ominus = n_2 = 9$

$$n = \frac{n_1 + n_2}{2} = \frac{12+9}{2} = 10.5$$

$$\boxed{n=10.5}$$

Type-I :- Calculate L.E. of NaCl if M= 1.7476 and r = 2.814 A° and n = 8.

Sol^n:- For NaCl,

$Z_{(+)} = +1 \quad Z_{(-)} = -1, \quad e = 1.6\times10^{-19}C \quad r = 2.814\ A^\circ \quad M = 1.7476 \quad n=8$

$$\boxed{L.E. = U = \frac{K Z_{(+)} Z_{(-)} e^2 N_A M}{r}\left(1 - \frac{1}{n}\right)}$$

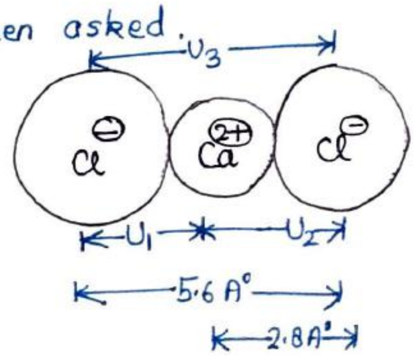
IIT 2015 :- Calculate Lattice Energy for CsCl if $r_{Cs^+} = 181$ pm and $r_{Cl^-} = 167$ pm and $\frac{NMe^2}{4\pi\varepsilon_0} = 2.45\times10^{-4}$ Jmmol^{-1}.

Sol^n:- $r_{Cs^+} = 181$ pm $\quad r_{Cl^-} = 167$ pm $\quad r = (r_{Cs^+} + r_{Cl^-}) = (181\ \text{pm} + 167\ \text{pm})$

$$U = \frac{2.45\times10^{-4} \times 1 \times(-1)}{(181+167)\times10^{-12}}\left(1 - \frac{1}{10.5}\right) \qquad n = 10.5.$$

IIT 2016 :- Formulae for Ionisation energy b/w two ions is given by $U = 1389.4\left[\frac{Z_1 Z_2}{r/A^\circ}\right]$ KJ/mol. Find Potential Energy of $CaCl_2$ $\boxed{\text{molecule}}$ assuming it to be linear.

Sol^n:- Here Potential energy of complete molecule has been asked.



Net Potential Energy (U) = $U_1 + U_2 + U_3$

$U_1 = 1389.4\left[\frac{2\times(-1)}{2.8}\right]$ KJ/mol

$U_2 = 1389.4\left[\frac{2\times(-1)}{2.8}\right]$ KJ/mol

$U_3 = 1389.4\left[\frac{(-1)\times(-1)}{5.6}\right]$ KJ/mol.

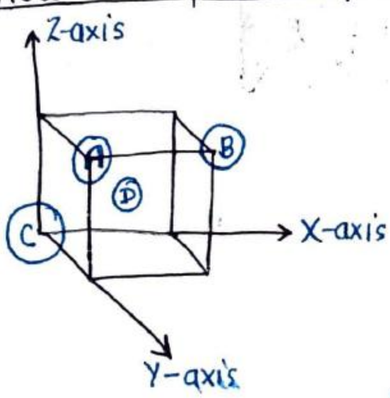
Experimental Part

X Rays :- X-Rays has the energy to excite the core $e^\ominus$.

→ X-Rays can not be used to detect two atoms having almost same no. of $e^\ominus$.

→ Hydrogen atom can not be detected.

* How to represent position of atom in unit cell :



Let, edge length = 1 unit.

Co-ordinates of A = (0, 1, 1)

Co-ordinates of B = (1, 1, 1)

Co-ordinates of C = (0, 0, 0)

Co-ordinates of D = $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

While finding position of other atoms we can fix any one of the atoms as origin.

*** How to represent a plane :-** We identify the plane with intercept axes.

*** Miller Indices :-** Let a plane intercepts

2a → on X-axis   3b → on Y-axis   −c → on z-axis.

Intercepts = $(\underset{x}{2a},\ \underset{y}{3b},\ \underset{z}{-c})$.

How to find Miller Indices :-

Step-I → Find out weiss indices ⇒ Multiples of edge length i.e. (2, 3, −1) or numerical coefficients of intercepts.

Step-II: Take the reciprocal of weiss indices $\left(\frac{1}{2}, \frac{1}{3}, \frac{1}{-1}\right)$

Step-III: Remove the frac^{n} by multiplying with smallest integer, i.e. in our case smallest possible integer is 6.

$$\left(\frac{6}{2}, \frac{6}{3}, \frac{6}{-1}\right) = (3, 2, -6).$$

Step-IV: Representation of Miller Indices (hkl)

$$(3, 2, -6) \xrightarrow{M.I.} (3 2 \bar{6}).$$

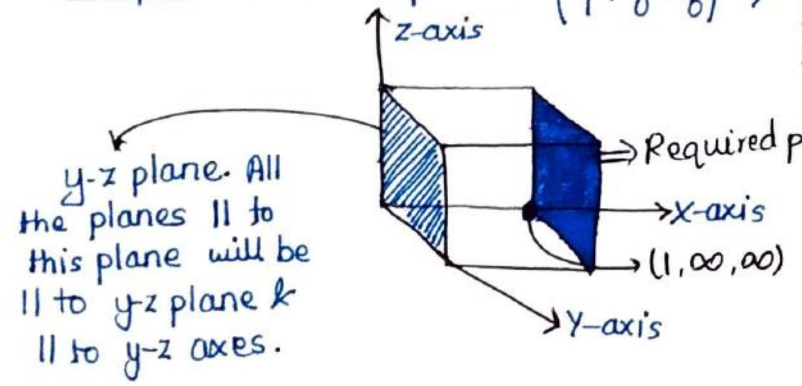
* If Miller Indices are given then how to represent the plane.

Let suppose (100) is the plane. Now we have to find coordinates of the plane.

Step-I: Take reciprocal $\left(\frac{1}{1}, \frac{1}{0}, \frac{1}{0}\right) \Rightarrow (1, \infty, \infty)$

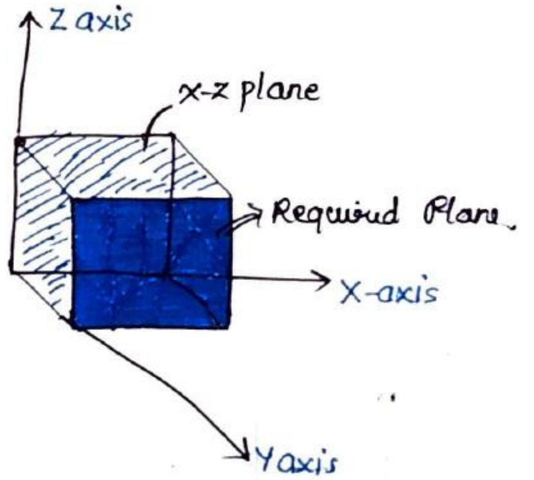
$\uparrow x \quad \uparrow y \quad \uparrow z$ ⇒ plane should be ∥ to z-axis.

↳ plane should be ∥ to y-axis.

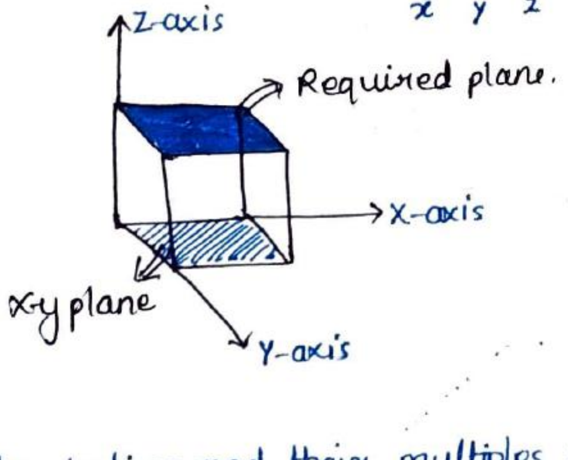


Similarly (0,1,0) plane ⇒ $(\infty, 1, \infty)$
$\uparrow x \quad \uparrow y \quad \uparrow z$

⇒ x-z plane.



Similarity (001) plane ⇒ $(\infty, \infty, 1)$
$\uparrow x \quad \uparrow y \quad \uparrow z$

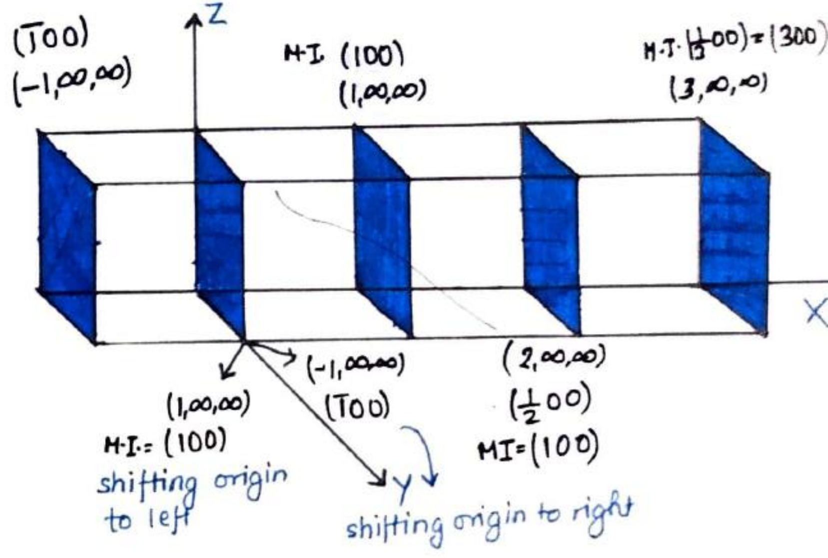


* Miller indices and their multiples represents different planes.
* Miller indices and their (-)ve represent same planes.
* Miller indices can never be infinity it will be zero.
* Intercepts can never be zero, they will be infinity.

* When plane seems to form at origin, then we just simply shift the origin.

Q :-) What are Miller Indices ?

Miller Indices represent a set of ‖ planes one of which passes through origin and rest at equal distances from each other.



***Distance b/w two planes ;**

$$\boxed{\frac{1}{d^2_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

where, a, b, c = intercepts on edge length.

* Valid only for :- Orthorhombic, ~~tetrahedral~~ and cubic system.
(x) Tetrahedral ⟶ Tetragonal (✓).

i.e. valid for only those system who have interaxial angle = 90°.

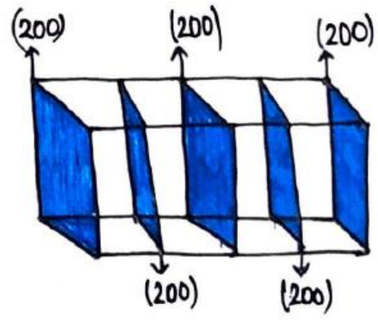
Ex :- For cubic system ;

$$\boxed{\frac{1}{d^2_{hkl}} = \frac{h^2+k^2+l^2}{a^2}} \quad \text{or} \quad \boxed{d^2_{hkl} = \frac{a^2}{h^2+k^2+l^2}}$$

Ex :- Find interplanar distance b/w $\underset{h\,k\,l}{(1\,0\,0)}$

$$d = \frac{a}{\sqrt{1^2+0^2+0^2}} = a$$

$\Rightarrow \boxed{d = a}$



*** Conceptual ; Find (200) plane.**

$\Rightarrow$ (200) plane $\Rightarrow$ $(\frac{1}{2}, \infty, \infty)$
⇑ Coordinates

Now, we will fix one plane as origin and will assume intercept as (200) because from the definition of Miller Indices, the set of parallel planes passes through the origin and all the planes are equidistant from one-another. This time around no plane will be (100) as we have fixed origin with (200)

$$\boxed{d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}} \text{ for cubic,}$$

→ Interplanar distance
→ Perpendicular distance from origin.

* **Angle b/w two planes:-**

$$\boxed{\theta = \cos^{-1}\left(\frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2+k_1^2+l_1^2}\sqrt{h_2^2+k_2^2+l_2^2}}\right)}$$

* **Another variation in density:-**

Ex:- $d_{111} = 108$ pm.

from here we can calculate edge length (a) :

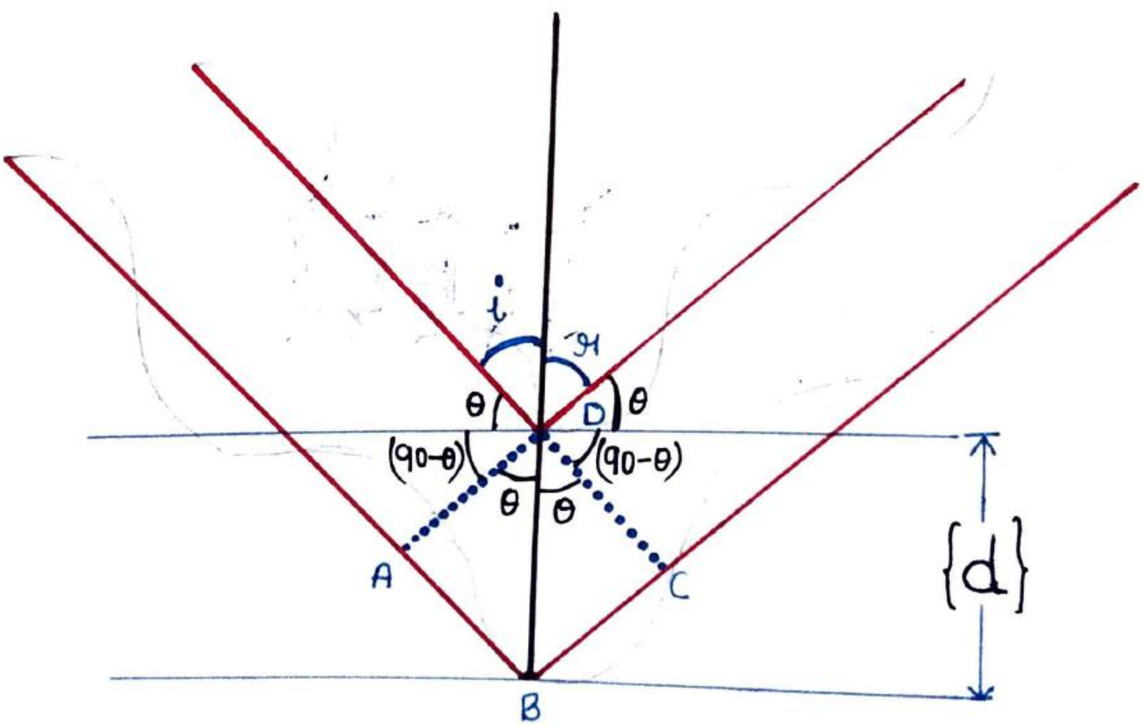
$$\boxed{a = d_{111}\sqrt{h^2+k^2+l^2}}$$

with the help of edge length, we can calculate density.

$$\boxed{\rho = \frac{ZM}{N_A \times a^3}}$$

? From where will this 'd' (interplanar distance) come ?

Ans = Bragg's Law.

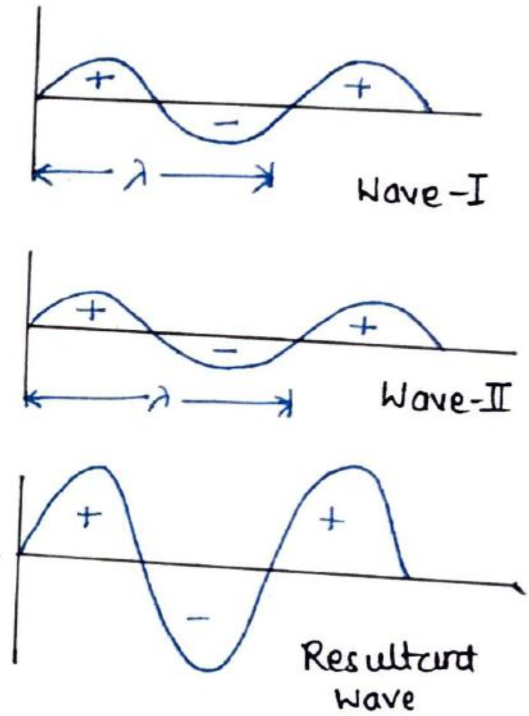


In ΔABD, $\sin\theta = \frac{AB}{BD} \Rightarrow AB = BD\sin\theta \Rightarrow \boxed{AB = d\sin\theta}$ $\because BD = d$.

Similarly in ΔBCD, $\sin\theta = \frac{BC}{BD} \Rightarrow BC = BD\sin\theta \Rightarrow \boxed{BC = d\sin\theta}$ $\because BD = d$.

Path diff:- $AB + BC \Rightarrow d\sin\theta + d\sin\theta \Rightarrow \boxed{2d\sin\theta}$

Hence 2^{nd} ray travels extrapath by $2d\sin\theta$.



Constructive Interference.

*** Conditions for Constructive Interference :-**

If the second wave travels a distance of $(\lambda, 2\lambda, 3\lambda, \ldots\ldots n\lambda)$ in it's path difference, then the wave emerging out will be in same phase.

i.e. $\boxed{2d\sin\theta = n\lambda}$ → order of reflection/diffraction.

for first order, $n=1$
for second ,, , $n=2$
for third ,, , $n=3$

*** For destructive Interference :-**

If the second wave travels a distance of $\left(\lambda/2, 3\lambda/2, 5\lambda/2, \ldots\ldots \frac{(2n-1)\lambda}{2}\right)$ in it's path difference, then the wave emerging out will be in different phase.

$$\boxed{2d\sin\theta = \frac{(2n-1)\lambda}{2}} \quad \text{or} \quad \boxed{n\lambda = 4d\sin\theta}$$

→ $(2n-1)$

*** Extreme peak** ⇒ Constructive Interference.

*** Selection rule** ⇒ Which planes gives reflection and which do not.

Simple cubic ⇒ All planes gives reflection.
BCC ⇒ When $(h+k+l)$ = even. no.
FCC ⇒ Either, h, k, l ⇒ all are odd.
or h, k, l ⇒ all are even.

Ex:-

	(200)	(100)
SCC	✓	✓
BCC	✓	✓
FCC	✓	×

From Bragg's Rule :-

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

and

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \Rightarrow \quad n\lambda = \frac{2a\sin\theta}{\sqrt{h^2+k^2+l^2}} \;;$$

for, n=1

$$\boxed{\sin\theta = \frac{\lambda}{2a}\sqrt{h^2+k^2+l^2}}$$

Now, squaring both sides ;

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2)$$

Let, $\frac{\lambda^2}{4a^2} = K$ (constant)

$$\boxed{\sin^2\theta = (h^2+k^2+l^2)K}$$

$\sin^2\theta$	h	k	l	SC	BCC	FCC
1K	1	0	0	✓	×	×
2K	1	1	0	✓	✓	×
3K	1	1	1	✓	×	✓
4K	2	0	0	✓	✓	✓
5K	2	1	0	✓	×	×
6K	2	1	1	✓	✓	×
7K	—	—	—	—	—	—
8K	2	2	0	✓	✓	✓

$\because \sin^2\theta = (h^2+k^2+l^2)K$,

Now, no such arrangement of h, k, l is possible, so as to produce $\boxed{h^2+k^2+l^2 = 7}$.