

Solid State.

15 July 2019.

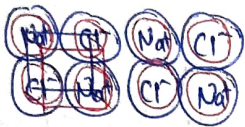
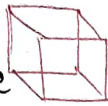
* Solids - definite shape and volume in which constituent particles are arranged in definite manner.

Solids.

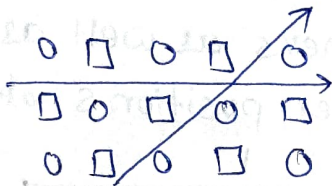
Crystalline.
(True solids.)

ex. NaCl.

cubic shape



Anisotropy nature.



Results of all physical prop. will change if directⁿ of measurement is changed.

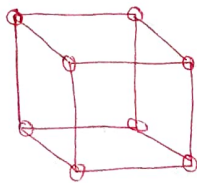
M.P. is sharp.

definite heat of fusion.

⇒ long range order.

(Extends over a large distance).

Simple cube



No. of corners - 8

No. of edges - 12

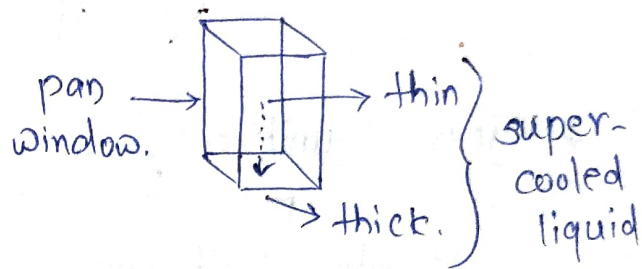
No. of faces - 6

No. of face diagonals - $2 \times 6 = 12$

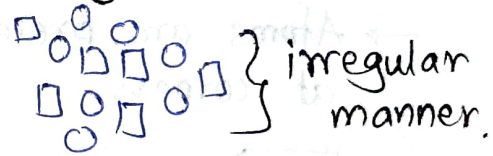
No. of body diagonals - $\frac{8}{2} = 4$.

Amorphous.

(Pseudo solids / Supercooled liquid.)



Isotropy nature.



All physical prop. will remain same in any direction. due to irregular arrangement.

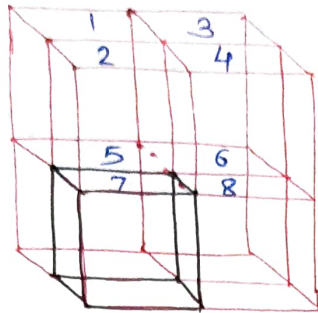
M.P. is not sharp.

do not have definite H. of fusion

(liquids at all temp. ≡ amorphous solids).

* Unit cell & space lattice -

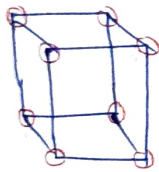
Unit cell - Repeating unit in all possible directions & gives whole lattice on extension.



* Types of unit cells -

Primitive Unit Cell
(Simple cubic.)

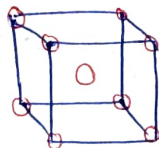
→ Atoms are present only at corners.



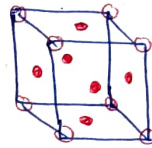
Non primitive Unit cell

→ Atoms are present at corners as well as at other positions also.

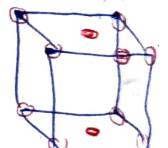
BCC



FCC



End centred (EC)



At any two opp. faces atoms are present.

(2014 TIFR)

Que. Which of the following is/are the unit cell of given space lattice.



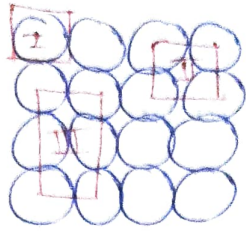
① I

② II

③ III

✓ ④ All.

Que. Classify the types of unit cell. either primitive or non primitive

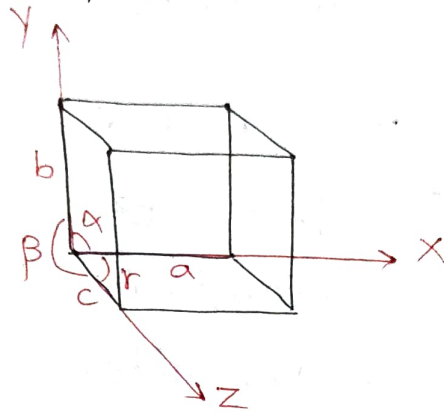


I. neither primitive nor non-primitive

II. primitive.

III. Non-primitive.

* Parameters of cubic unit cell -



a, b, c - lengths.

α, β, γ - interfacial angles.

* Classification of primitive unit cell -
7 crystal systems.

Type of system.	Edge length.	Interfacial angle.	Bravais lattice.	AOS	POS	ex
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC	13	9	NaCl.
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC	5	5	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC, EC	3	3	
Hexagonal.	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	SC	7	7	
Rhombohedral Trigonal.	$a = b = c$	$\alpha = \beta = \gamma, \neq 90^\circ$	SC	7	7	
Monoclinic.	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 120^\circ$	SC, EC.	1	1	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	SC	0	0	

* Most symmetric in nature \rightarrow Cubic.

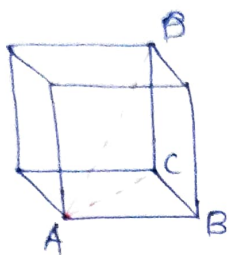
Most asymmetric \rightarrow Triclinic.

Higher Bravais lattice system \rightarrow Orthorhombic.

Total no. of Bravais lattice $\rightarrow 14$.

* How to calculate length ?

→ try to find the 90° angle & then apply pythagoras th^m



length of face diagonal AC -

$$\begin{aligned} AC &= \sqrt{AB^2 + BC^2} \\ &= \sqrt{a^2 + a^2} \\ &= a\sqrt{2} \text{ units.} \end{aligned}$$

length of body diagonal AD -

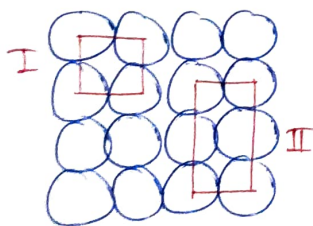
$$\begin{aligned} AD &= \sqrt{AC^2 + CD^2} \\ &= \sqrt{(a\sqrt{2})^2 + a^2} \\ &= a\sqrt{3} \text{ units.} \end{aligned}$$

* How to calculate z. (effective no. of atoms.)

2D

Angle Method.

$$\frac{\theta}{360^\circ} \times n$$



$$\theta = 180 - \frac{360}{n}$$

no. of edges of geometric figure.

$$\textcircled{\text{I}} \rightarrow \frac{90}{360} \times 4 = 1$$

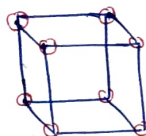
$$\textcircled{\text{II}} \rightarrow \left(\frac{90}{360} \times 4\right) + \left(\frac{180}{360} \times 2\right) = 2$$

$$\left(\frac{180}{360} \times 6\right) + 1 = 2 + 1 = 3$$

+1 centre atom.

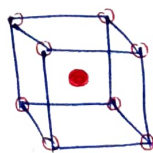
3D

Sharing Method.



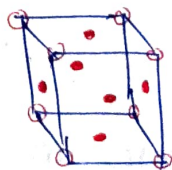
SC

$$\frac{1}{8} \times 8 = 1 \text{ atom.}$$



BCC

$$\left(\frac{1}{8} \times 8\right) + (1) = 2 \text{ atoms}$$



FCC

$$\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right)$$

$$= 4 \text{ atoms.}$$

* How to find formula & formula unit -

(TIFE 2016)

Que. In a face centered arrangement of A & B atoms, where A atoms are at the corners of unit cell & B atoms are at the face centres. For each unit cell one A atom is missing from a corner position & one B atom is missing from one face position. The simplest formula of the resulting compd will be -

- ① $A_{14}B_{40}$ ✓ ② A_7B_{20} ③ $A_{1-x}B_{3-x}$ ④ AB_2

A → Corners. B → Face centres. formula - $A_{7/8}B_{5/2}$

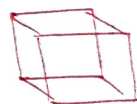
⑦ $\times \frac{1}{8} = \frac{7}{8}$. ⑤ $\times \frac{1}{2} = \frac{5}{2}$. simplest f. - A_7B_{20} .

(NET - Dec. 2013).

Que. A compd. of M & X atoms has a cubic unit cell. M atoms are at corners & body centre position & X atoms are at face centre positions of cube. The molecular formula of compd is -

- ① MX ② MX_2 ③ M_3X_2 ✓ ④ M_2X_3 .

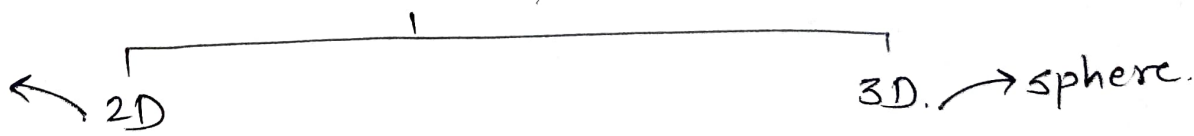
$$M\left(\frac{1}{8} \times 8\right) + 1 \times \left(\frac{1}{2} \times 6\right) = M_2X_3.$$



16 July 2019.

* Voids (Interstitial sites or holes).

assume circle.

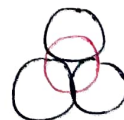


I. triangular void.



C.N. - 3

1. tetrahedral void.



C.N. - 4



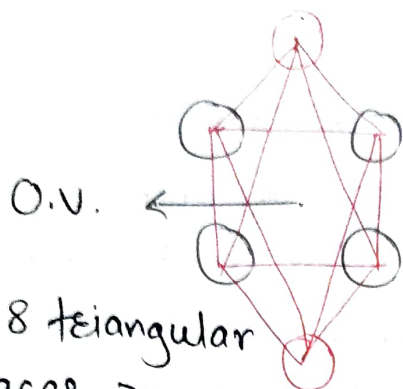
II. Square planar void.



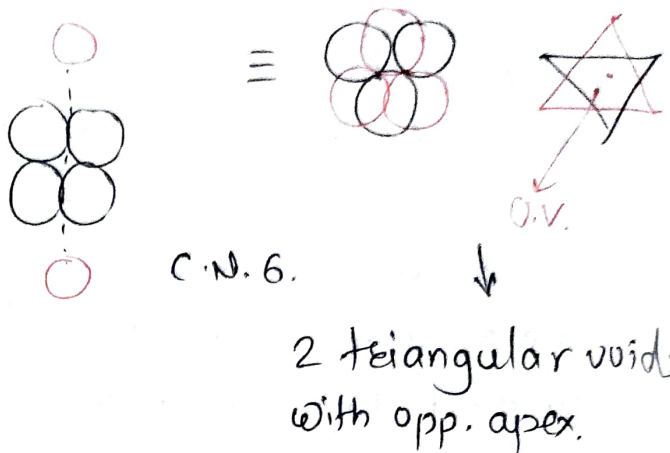
C.N. - 4

2. Octahedral void.

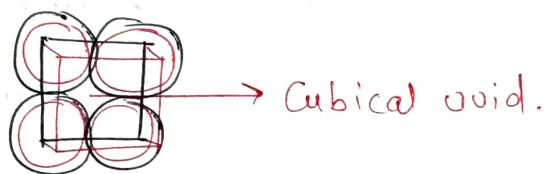
II. Octahedral void.



∴ 8 triangular faces ⇒ name. Octahedral.

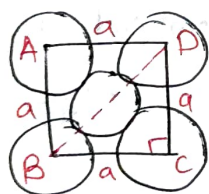


III. Cubical void.



C.N. - 8.

* How to find the relation bet. a & r .

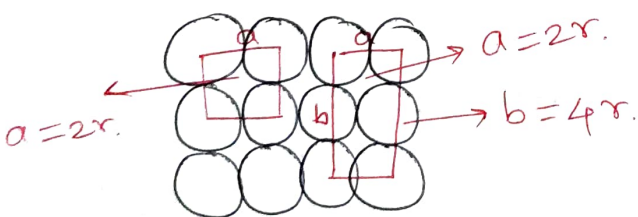


$$BD = 4r.$$

$$BD = \sqrt{a^2 + a^2} = a\sqrt{2}.$$

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

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



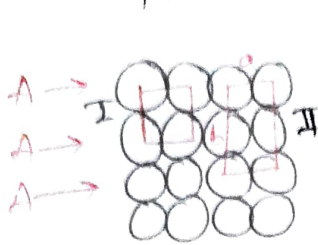
* Packing efficiency -

$$P.E = \frac{\text{Total } \overset{\text{area.}}{\text{space occ. by sphere/circle}} \text{ (in unit cell. (indigram).)} \times 100}{\text{Total } \underset{\text{area.}}{\text{space occ. by unit cell.}}$$

$$\text{Packing fraction.} = \frac{P.E.}{100}$$

$$= \frac{\text{total sp. occ. by sphere}}{\text{total sp. occ. by unit cell.}}$$

* P.E. for SCP (square close packing).



(AAA type) $Z=1$

$$P.E. = \frac{1 \times \pi r^2}{a^2} \times 100 = \frac{\pi r^2}{4r^2} \times 100 = \frac{\pi}{4} \times 100 = 78.5\%$$

area of circle
area of square.
 $a=2r$

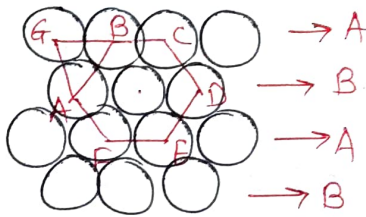
% of void = $100 - 78.5 = 21.5\%$

II. $Z = \left(\frac{90}{360} \times 4\right) + \left(\frac{180}{360} \times 2\right) = 2$

$$P.E. = \frac{2 \times \pi r^2}{a \times b} \times 100 = \frac{2 \pi r^2}{2r \times 4r} \times 100 = \frac{\pi}{4} \times 100 = 78.5\%$$

P.E. remains same for same packing.

* P.E. for hcp (hexagonal close packing.)



ABAB... type layer.

area of eq. $\Delta = \frac{\sqrt{3}}{4} a^2$

here, $Z = \left(\frac{120}{360} \times 6\right) + 1 = 3$

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

$$= \frac{\pi}{2\sqrt{3}} \times 100 = \frac{1.57}{1.7320} \times 100 = 90.64\%$$

% of void = $100 - 90.64 = 9.36\%$

for ABG - $Z = \frac{60}{360} \times 3 = \frac{1}{2}$

$$P.E. = \frac{\frac{1}{2} \times \pi r^2}{\frac{\sqrt{3}}{4} a^2} \times 100 = \frac{\frac{1}{2} \pi r^2}{\frac{\sqrt{3}}{4} 4r^2} = \frac{\pi}{2\sqrt{3}} \times 100 = 90.54\%$$

no. of edges. $\frac{180 - 360}{3} = 120$

Ques. Find the packing eff. of following given arrangement.



Solⁿ - extend the arrangement.



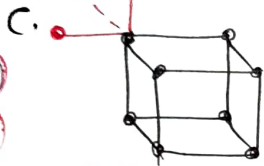
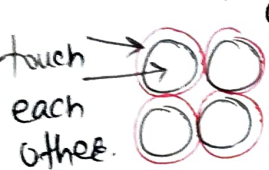
hcp. arrangement.

$$\therefore \underline{\underline{90.64\%}} = \text{P.E.}$$

* Packing efficiency for 3D -

$$a = 2r, \quad z = 1.$$

* Simple cubic. -



$$\text{P.E.} = \frac{\text{Vol. of sphere in u.c.}}{\text{total vol. of u.c.}} \times 100$$

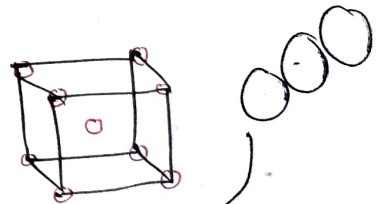
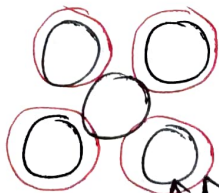
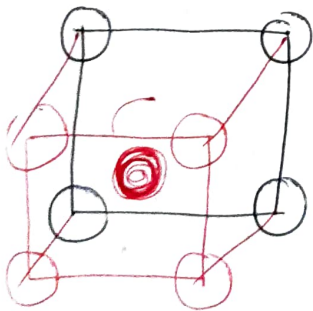
$$\text{P.E.} = \frac{1 \times \frac{4}{3} \pi r^3}{a^3} \times 100 = \frac{\frac{4}{3} \pi r^3}{(2r)^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= \underline{\underline{52.33\%}}$$

$$\% \text{ of void} = 100 - 52.33 = 47.67\%$$

* P.E. of S.C is very low. -

* B.C.C.



$$\sqrt{3} a = 2r, \quad a = \frac{4r}{\sqrt{3}}$$

do not touch each other.

for BCC $\rightarrow z = 2.$

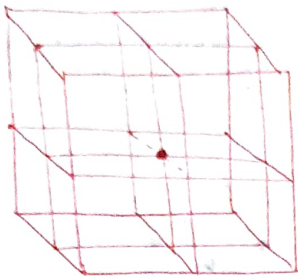
$$\text{P.E.} = \frac{2 \times \frac{4}{3} \pi r^3}{a^3} \times 100 = \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} \times 100 = \frac{8\pi r^3}{8 \times \frac{64r^3}{\sqrt{3}}} \times 100$$

$$= \frac{\pi \cdot \sqrt{3}}{8} \times 100 = 67.98 \approx \underline{\underline{68\%}}$$

For BCC -

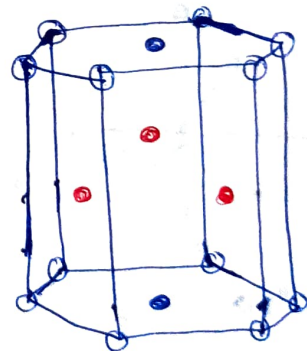
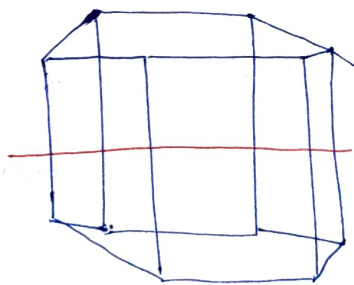
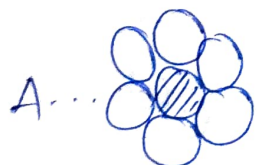
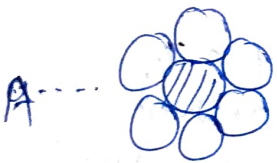
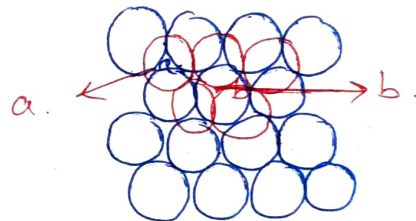
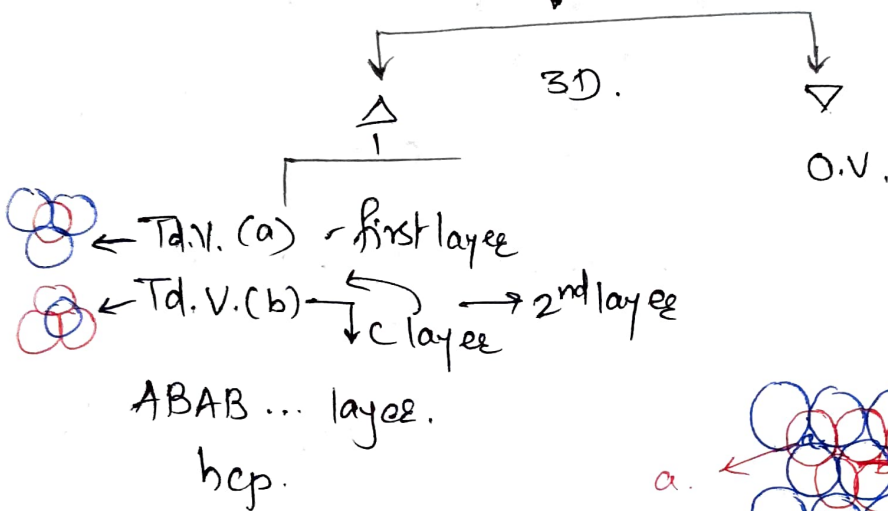
C.N. of body centred atom = 8.

C.N. of corner atom = 8. \rightarrow \because it touches body centred atoms of 8 adjacent unit cells



17 July 2019.

hcp (2D)



C.N. = 12

$$Z = \frac{12 \times \frac{1}{6}}{\text{corner}} + \frac{2 \times \frac{1}{2}}{\text{base}} + \frac{3}{\text{inside}} = \underline{\underline{6}}$$

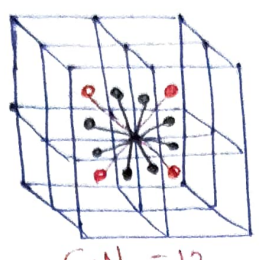
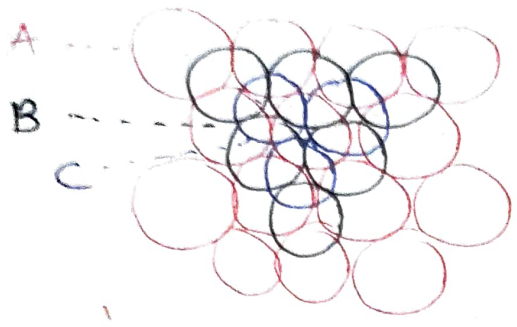
Total no. of T.V. = 12.

Total no. of O.V. = 6.

P.E. = 74%

Δ -
 $\circ \rightarrow$ octah. v.

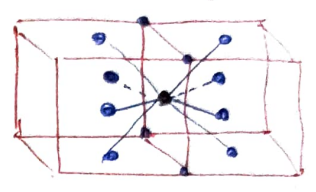
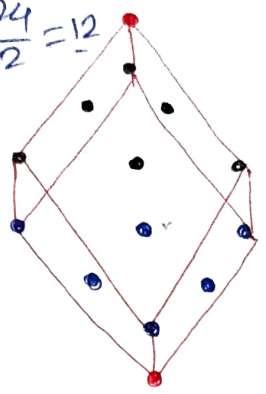
(3D). ∇ hcp (2D)
 \circ hcp (3D)
 \downarrow



Cubic close packing
 CCP
 \downarrow unit cell
 fcc.

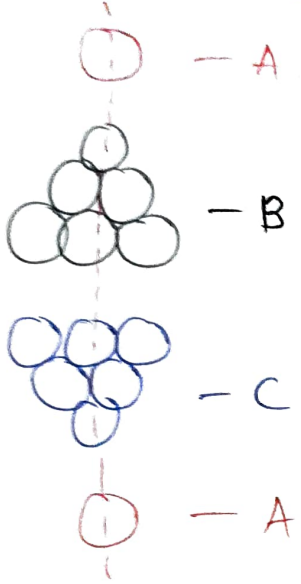
C.N. = 12
 (coord.) =

$$8 \times 3 = \frac{24}{2} = 12$$



C.N. (face centered atom) = 12.

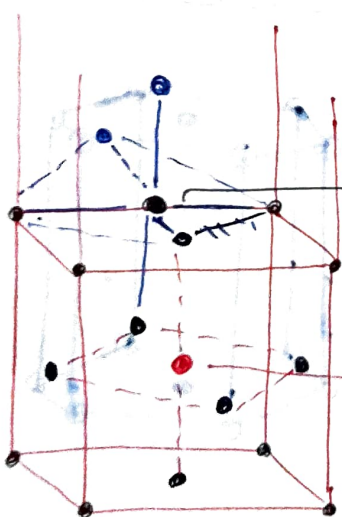
(C.N. same for corner atoms = FCC.)



$$Z = 4$$

No. of Td.v. = 2N & no. of O.v. = N,
 where N - no. of atoms.
 effective

* Location of tetrahedral & Octahedral Void, in ccp. (unit cell - fcc).



O.V. at edge center of

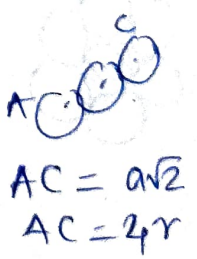
body centered atom.
 C.N. - 6.

$$Z = 4$$

How many o.v. are present in this structure?
 $\Rightarrow 4$.

$$\text{edge center} \rightarrow \text{body center} \\ (12 \times \frac{1}{4}) + 1 = 4$$

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



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

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

$$= \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} \times 100 = \frac{2\sqrt{2} \pi}{\frac{12}{6}} \times 100 = 74.01\%$$

* Order of packing efficiency -

18 July 2019.

FCC > BCC > SC
74% > 68% > 52%

Ques. Which of the foll. order is correct for the foll. system.
PE.

- ✓ (a) FCC > BCC > SC > Diamond. 74% 68% 52% 36%. *though highest hardness. P.E. is low. → hardness is due to covalent strong c-c bond.*
- (b) BCC > FCC > SC > D
- (c) D > SC > FCC > BCC
- (d) None. / D > FCC > BCC > SC.

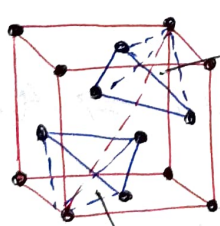
* Relationship bet. a & r in different unit cells -

SC - $a = 2r \Rightarrow r = a/2 \Rightarrow a = d$ (nearest neighboring dist.)

BCC - $a = \frac{4r}{\sqrt{3}} \Rightarrow r = \frac{a\sqrt{3}}{4} \Rightarrow d = \frac{a\sqrt{3}}{2}$

FCC - $a = \frac{4r}{\sqrt{2}} \Rightarrow r = \frac{a}{2\sqrt{2}} \Rightarrow d = a/\sqrt{2}$

* Location of tetrahedral & Octahedral voids in ccp.



O.V. = 4
T.V. = 8.

Total no. of Td. v. = 8.
∵ One body diagonal contains 2 Td. voids.
& there are 4 body diagonals.
∴ 4 × 2 = 8 Td. voids.

* Td. Void is made from 3 face centered atoms & 1 corner

FCC - Z = 4.
T.V = 2N = 8
O.V = N = 4

* How do calculate coordination number.

Co. No. = charge ratio.

Que. - Find the formula unit & C.N. of NaCl when Na^+ are present in all octahedral void & Cl^- are present in ccp lattice.

Solⁿ -

Na^+ - present in all O.V. $\Rightarrow 4 \text{Na}^+$.

Cl^- - in ccp lattice - fcc u.c. $\Rightarrow 4 \text{Cl}^-$.

$\therefore \text{Na}_4\text{Cl}_4$.

$Z \rightarrow \underline{4 \text{NaCl}}$ - simplest form.

C.N. = charge ratio.

	Na^+	Cl^-
	+1	-1
due to present in O.V.	6	6
C.N. of O.V. = 6.		6:6

Que. Find the formula unit & C.N. of CaF_2 (fluorite) when fluorite ion F^- present in all tetra. void & Ca^{2+} are present in ccp lattice.

Solⁿ - F^- - present in T.V. $\Rightarrow 8 \text{F}^-$

Ca^{2+} - present in ccp lattice \Rightarrow fcc u.c. $\Rightarrow 4 \text{Ca}^{2+}$

$\therefore \text{Ca}_4\text{F}_8$.

formula unit = Z. $\leftarrow \therefore \underline{4 \text{CaF}_2}$ - simplest form

C.N. = charge ratio.

	F^-	Ca^{2+}
	-1	+2
$\therefore \text{F}^-$ present in tetrahedral void.	8	4

4:8

Que. Find the formula unit & c.n. of Na_2O when Na^+ are present in all tetra. v. & O^{2-} are present in ccp lattice. (antifluorite).

Soln - Na^+ - t.v. $\Rightarrow 8\text{Na}^+$
 O^{2-} - ccp lattice $\Rightarrow 4\text{O}^{2-}$.



Formula unit $\leftarrow \underline{4} \text{Na}_2\text{O} \rightarrow$ simplest form.

c.n. = charge ratio.

Na^+	O^{2-}
+1	-2

\therefore present in T.V. \hookrightarrow 4 8

4:8

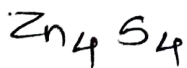
$\frac{\text{Li}_2\text{O}, \text{K}_2\text{O} \text{ etc.}}{\text{antifluorite.}}$

* Zinc blende (Zns)

S^{2-} - ccp \rightarrow fcc $\rightarrow 4\text{S}^{2-}$.

Zn^{2+} - Alternative T.V.

\downarrow
 4Zn^{2+}



$\therefore 4\text{ZnS}$.

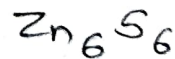
\therefore formula unit = 4

Zinc wurzite (Zns)

S^{2-} - hcp $\rightarrow 6\text{S}^{2-}$

Zn^{2+} - Alternative T.V.

\downarrow
 6Zn^{2+}



$\therefore 6\text{ZnS}$.

formula unit = 6

\therefore Diff. in arrangement of atoms - differs structure formula unit is different.

But. c.n. remains same.

as. c.n. = charge ratio. & charge ratio is same here. i.e. 2

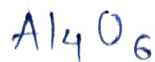
Zn^{2+}	S^{2-}
+2	-2

Que. Find the formula unit & C.N. of each ion in corundum structure.



Soln. O^{2-} - hcp $\rightarrow 6 \text{O}^{2-}$

Al^{3+} - $\frac{2}{3}$ rd of O.V. $\rightarrow 6 \times \frac{2}{3} = 4 \text{Al}^{3+}$.



C.N. = charge ratio.

\therefore occupied.	Al^{3+}	O^{2-}
O.V.	+3	-2
	$\rightarrow 6$	4
	$6:4$	

Que. Titanium dioxide (TiO_2).

$\text{Ti}^{4+} \rightarrow$ half of O.V. $\rightarrow 3 \text{Ti}^{4+}$

$\text{O}^{2-} \rightarrow$ hcp $\rightarrow 6 \text{O}^{2-}$



C.N. = charge ratio.

Ti^{4+}	O^{2-}
+4	-2

C.N. $\Rightarrow \underline{6} \quad \underline{3}$

Que. Cesium Chloride (CsCl).

$\text{Cs}^+ \rightarrow$ present in cubical void $\rightarrow 1 \text{Cs}^+$

$\text{Cl}^- \rightarrow$ in simple cubic arrangement $\rightarrow 1 \text{Cl}^-$



+1 -1

C.P.

$\therefore \underline{8} \quad \underline{8}$

Que. If in NaCl, we interchange the cation (Na⁺) & anion (Cl⁻) position, what effect on crystal.

Solⁿ - Na⁺ - ccp lattice \rightarrow fcc u.c. \rightarrow 4 Na⁺
 Cl⁻ - ^{at all.} oct. voids \rightarrow 4 Cl⁻

$$\therefore \text{Na}_4\text{Cl}_4$$

$$\underline{4 \text{ NaCl}}$$

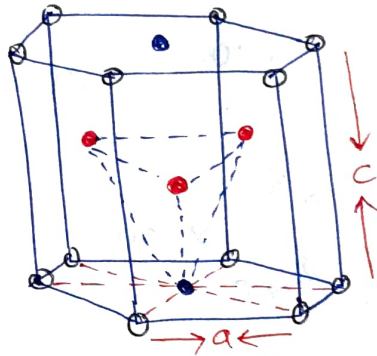
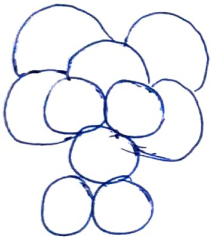
Na ⁺	Cl ⁻
+1	-1

C.N. 6 6 \rightarrow \therefore occupied oct. void.

\therefore No. effect on crystal.

22/07/2019.

* P.E. in hcp. -



3 middle atoms are occupied in alternate equilateral Δ 's. at top & bottom.

tetrahedral voids - 3 at base & 3 at top by corner atoms & middle \bullet atoms } 6.

& 4 by corner atoms with adjacent unit cells.

$$6 + 4 = 12.$$

\therefore contribution of 1 corner atom = $\frac{1}{3}$.

P.E.

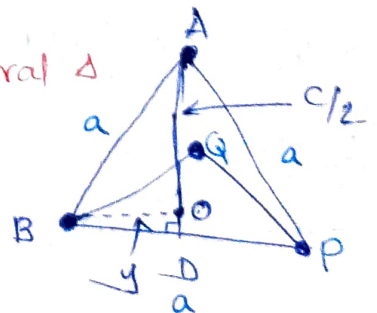
$$\text{Vol. of occupied sphere} = 6 \times \frac{4}{3} \pi r^3$$

$$\text{Vol. of hcp u.c.} = 6 \times \frac{\sqrt{3}}{4} a^2 \times c. \quad \rightarrow \text{height.}$$

area of equilateral Δ

Now, $AB^2 = (AO)^2 + (BO)^2$

$$a^2 = \left(\frac{c}{2}\right)^2 + y^2.$$



In $\Delta BOD \Rightarrow \angle B = 30^\circ$. ($\because \Delta BPQ$ is equilateral Δ
 $\angle B = 60^\circ$.
 \therefore in ΔBOD , $\angle B = 30^\circ$)

$$\therefore \cos 30^\circ = \frac{BD}{y} \rightarrow a/2$$

$$\frac{\sqrt{3}}{2} = \frac{a}{2y} \Rightarrow y = a/\sqrt{3}$$

Now,

$$\therefore (AB)^2 \text{ i.e. } a^2 = \left(\frac{c}{2}\right)^2 + \left(\frac{a}{\sqrt{3}}\right)^2$$

$$a^2 - \frac{a^2}{3} = \frac{c^2}{4}$$

$$\frac{2}{3}a^2 = \frac{c^2}{4}$$

$$\therefore \frac{c}{a} = \frac{2\sqrt{2}}{\sqrt{3}}$$

$$\text{i.e. } \frac{c}{a} = 1.63$$

$$\& \frac{a}{c} = 0.6134$$

$$\therefore \text{P.E.} = \frac{6 \times \frac{4}{3} \times \pi r^3}{6 \times \frac{\sqrt{3}}{4} \times a^2 \times c} \times 100 \quad (r = a/2)$$

$$= \frac{6 \times \frac{4}{3} \times \pi \times a^3}{8 \times \frac{\sqrt{3}}{4} \times a^2 \times c} \times 100$$

$$= \frac{2\pi \cdot a}{3\sqrt{3} \cdot c} \times 100$$

$$= 74\%$$

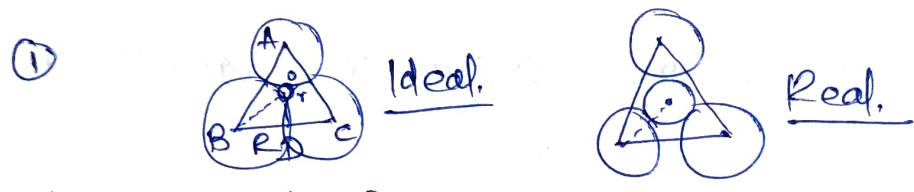
* Radius-Ratio Rule - (r/R)

It is defined as the ratio of smaller ion into the bigger ions.

to determine the most stable arrangement of cations & anions in the crystal lattice.

Always true.	Radius ratio. $= \frac{r_{ct}}{r_a}$	Ideal cond ⁿ A-A } touch. C-A }	Real. A-A } do not touch C-A } touch.	Types of voids	Ex
--------------	---	--	---	----------------	----

$a = \sqrt{3}(r+R)$	0.155-0.225	$0.155 \leq \frac{r}{R}$	< 0.225	triangular.	B_2O_3
$a = \frac{(r+R)4}{\sqrt{3}}$	0.225-0.414	$0.225 \leq \frac{r}{R}$	< 0.414	tetrahedral	ZnS
$a = 2(r+R)$	0.414-0.732	$0.414 \leq \frac{r}{R}$	< 0.732	Octahedral	NaCl
$a\sqrt{3} = 2(r+R)$	0.732-1	$0.732 \leq \frac{r}{R}$	< 1	Cubical	$CaCl_2$



In $\triangle BDO$, at $\angle B$.

$$\cos 30^\circ = \frac{BD}{OB} = \frac{R}{R+r}$$

$$\frac{\sqrt{3}}{2} = \frac{R}{R+r}$$

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

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

$$\rightarrow 2R = \sqrt{3}R + \sqrt{3}r.$$

$$R(2 - 1.732) = \sqrt{3}r.$$

$$\frac{r_{void}}{R_{sphere}} = \frac{1.732}{2 - 1.732 / 1.732}$$

$$= \underline{0.155} \text{ min.}$$

Size of cation \uparrow , C.N. also \uparrow .

* Limitations of radius ratio rule -

1. The ^{c.p. of} lithium salts does not predict by radius ratio rule cause of Fajan's rule.

Acc. to this smaller is the size of cation & larger is the size of anion, it will show more covalent character.

Que. In the closest packing of atoms A (radius: r_a) the radius of atom B that can be fitted into tetrahedral voids is

- ① $0.155 r_a$ ② $0.225 r_a$ ③ $0.414 r_a$ ④ $0.732 r_a$

tetrahedral - $\frac{0.225 - 0.414}{}$ for closest packing.

* Density of Solids - \rightarrow formula unit.

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

\rightarrow molar mass
 \rightarrow Avogadro No. - 6.022×10^{23} molecules.
 \rightarrow vol. for cubic.

Volumes -

Hexagonal - $6 \cdot \frac{\sqrt{3}}{4} a^2 \times c$ - area of base \times height.

Cubic - a^3

Orthorhombic - $a \times b \times c$

Tetragonal - $a^2 b$.

Que. Calculate the no. of unit cell in 58.5 g. of NaCl.

- (a) 6×10^{20} (b) 3×10^{22} (c) 1.5×10^{23} (d) 0.5×10^{24}

Solⁿ - Mol. mass NaCl = $28 + 35.5 = 58.5$ g/mole.

58.5 g. of NaCl contains ionic molecules = 6.022×10^{23} .

$$\therefore 1 \text{ g. of NaCl} \quad " \quad = \frac{6.022 \times 10^{23}}{58.5}$$

$$\therefore 58.5 \text{ g. of NaCl} \quad " \quad = \frac{6.022 \times 10^{23}}{58.5} \times 58.5$$

$$= 6.022 \times 10^{23}$$

\therefore 1 unit cell of NaCl is formed by the contribution of 4 NaCl molecules.

\therefore No. of unit cells present in 6.022×10^{23} molecules of NaCl should be = $\frac{6.022 \times 10^{23}}{4} = 1.505 \times 10^{23}$.

* Concept of nearest neighbouring distance -

Simple cubic.

distance.

No. of atoms.

First neighbour

a

6

Second "

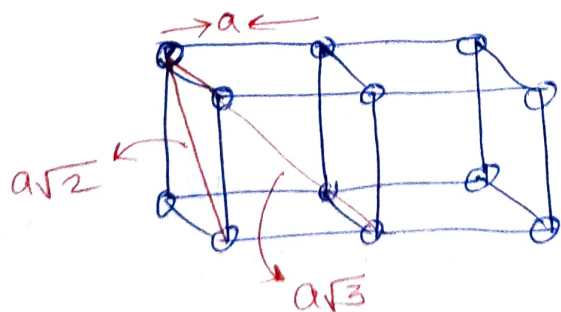
$a\sqrt{2}$

12

Third "

$a\sqrt{3}$

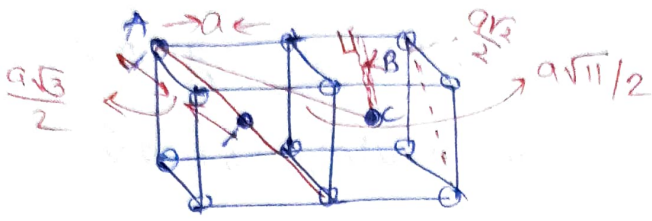
8



BCC structure.

distance

no. of atoms.



$$AC = \sqrt{\left(\frac{3a}{2}\right)^2 + \left(\frac{a\sqrt{2}}{2}\right)^2}$$

$$= \frac{a\sqrt{11}}{2}$$

First neighbour.

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

8.

Second neighbour.

$$a$$

6.

Third "

$$a\sqrt{2}$$

12

Fourth "

$$\frac{a\sqrt{11}}{2}$$

24.

Fifth "

$$a\sqrt{3}$$

8

for FCC structure -

First nearest

$$\frac{a\sqrt{2}}{\sqrt{2}} \text{ i.e. } \frac{a\sqrt{2}}{2}$$

12

Second. "

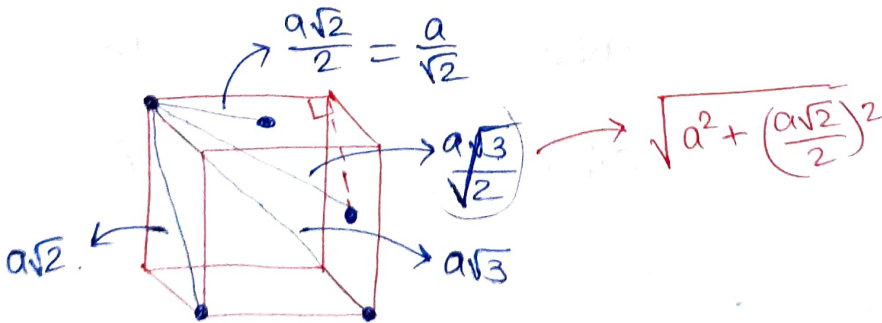
$$a$$

6

Third "

$$a\sqrt{3}/2$$

24



Fourth nearest.

dist.

$$a\sqrt{2}$$

12.

no. of atoms.

6.

12.

8.

* general
 tick: $a, 2a, 3a, \dots$
 $a\sqrt{2}, 2a\sqrt{2}, \frac{a}{\sqrt{2}}$
 $a\sqrt{3}, 2a\sqrt{3}$

Que. An element exist in two crystallographic modification with fcc & bcc structures. The ratio of the densities of the fcc & bcc modifications in terms of the volumes in their unit cells. (M, NA is same. Z is different).

① $V_{bcc} : V_{fcc}$

$n_{fcc} : 2 \text{ bcc}$

✓ ② $2 V_{bcc} : V_{fcc}$

$2 : 4 \quad 4 : 2$

③ $V_{bcc} : 2 V_{fcc}$

$V_{bcc} : 2 \quad 2 : 1$

④ $V_{bcc} : \sqrt{2} V_{fcc}$

$$\frac{d_{fcc}}{d_{bcc}} = \frac{\frac{Z \times M}{V_{fcc} \times N_A}}{\frac{Z \times M}{V_{bcc} \times N_A}} = \frac{A^2}{V_{fcc}} \times \frac{V_{bcc}}{Z}$$

$\Rightarrow V_{fcc} = 2 V_{bcc}$

Que. Metallic gold crystallizes in fcc structure with unit cell dimension of 4.00 \AA . The atomic radius of gold is

- Ⓐ 0.866 \AA ✓ Ⓑ 1.414 \AA Ⓒ 1.732 \AA Ⓓ 2.000 \AA

\Rightarrow for fcc -
Solⁿ - $4r = a\sqrt{2}$

$$a = r = \frac{4.00 \times \sqrt{2}}{4} = \sqrt{2} = 1.414 \text{ \AA}$$

Que. The effective radius of the iron atom is 1.42 \AA . It has fcc structure. Calculate its density (Fe = 56 amu). (56 amu = 56 g.)

Solⁿ - For FCC, $z = 4$. , $a = 4r = 4 \times 1.42 \text{ \AA} = 4 \times 10^{-8} \text{ cm}$

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

$$\Rightarrow a = \frac{4r}{\sqrt{2}} = \frac{4 \times 1.42}{1.414} = 4 \text{ \AA} = 4 \times 10^{-8} \text{ cm}$$

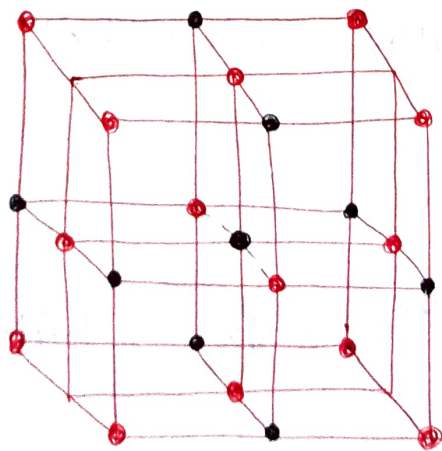
$$d = \frac{z \times M}{a^3 \times N_A} = \frac{4 \times 56 \text{ g}}{(4 \times 10^{-8})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= \frac{56}{16 \times 6.022 \times 10^{-24}}$$

$$= 5.81 \text{ g/cm}^3$$

Que. Find the nearest neighboring atoms present in Na^+ & Cl^- in the ionic crystal of NaCl.

- Na^+ - at all oct. voids.
- Cl^- - ccp lattice.



for Na^+ -

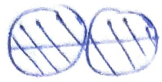
1st nearest	$a/2$	Cl^-	6
2nd "	$a\sqrt{2}$	Na^+	12
3rd "	$a\sqrt{3}$	Cl^-	8

for Cl^- -

1st nearest	$a/2$	Na^+
2nd "	$a\sqrt{2}$	Cl^-
3rd "	$a\sqrt{3}$	Na^+

* Born - Lande Equation -

It is used for the calculation of potential ene. & lattice energy.



For 2D



$1 \times 1.6 \times 10^{-19}$

$\rightarrow r \leftarrow$



$1 \times 1.6 \times 10^{-19} C, -1 \times 1.6 \times 10^{-19} C.$

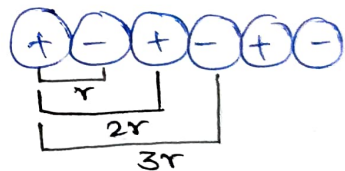
$$E_p = -k \cdot \frac{q_1 \cdot q_2}{r}$$

where, $k = \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$

$\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$

$q_1 = Ze$
for Ca^{2+}
 $Z = 2$
 $\therefore q_1 = 2 \times e$

$$\therefore E_p = \frac{-k \cdot z_+ \cdot z_- \cdot e^2}{r}$$



For 3D

$$E_p = -\frac{k \cdot z_+ z_- e^2}{r} + \frac{k \cdot z_+ z_+ e^2}{2r} - \frac{k \cdot z_+ z_- e^2}{3r} + \dots$$

$$= -\frac{k \cdot z^2 e^2}{r} \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

$$E_p = -\frac{k \cdot z^2 e^2}{r} \cdot M$$

This energy stabilizes (due to neg. sign).
Attraction ene.

M < Only depends on geometrical arrangement.
do not depend upon charge & ionic radii.
(Madelung constant).

A stable lattice can result only if there is also repulsion energy to balance the attractive Coulombic energy. Born suggested the repulsion energy.

$$U_{\text{rep}} = -\frac{B}{r^n}$$

where, B & n are constants.

& depend on the nature of ion.

B is repulsion coefficient & n is called Born exponent.

The net stabilization ene. (lattice energy) gained due the formation of lattice by the combinatⁿ of ions in gaseous state can be represented as the sum of

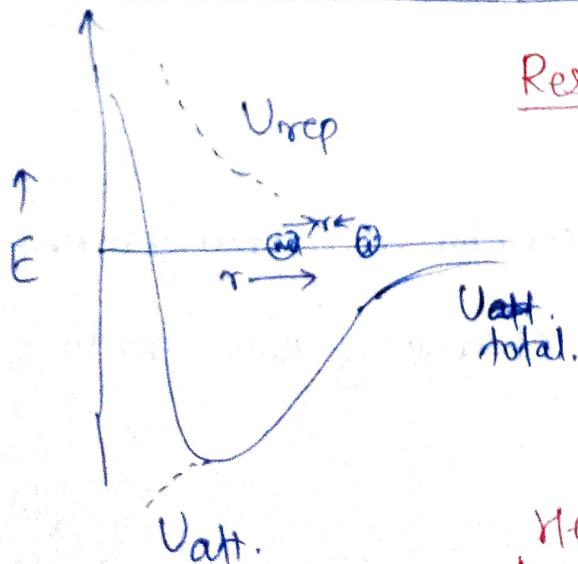
$$U = U_{\text{attr.}} + U_{\text{rep.}}$$

$$= \left(\frac{k \cdot z^+ \cdot z^- \cdot e^2}{r} \cdot M \cdot N_A \right) + \left(\frac{B}{r^n} \cdot N_A \right)$$

$$\frac{dU}{dr} = 0 = U_0 = -\frac{k \cdot z^+ \cdot z^- \cdot e^2 \cdot M \cdot N_A}{r^2} - \frac{n \cdot B \cdot N_A}{r^{n+1}}$$

$$B = -\frac{M \cdot k \cdot z^+ \cdot z^- \cdot e^2 \cdot r_0^{n+1}}{n}$$

$$\therefore U_0 = \frac{M \cdot N_A \cdot k \cdot z^+ \cdot z^- \cdot e^2}{r_0} \left(1 - \frac{1}{n} \right)$$



Result - (1) Lattice ene. is inversely prop. to interionic distance.

\therefore lattice ene. of a system \uparrow as the interionic distance \downarrow .

(2) Lattice ene. is directly prop. to product of ionic charges

Hence, lattice ene \uparrow with the \uparrow in ionic charge product.

For calculation of n (Born Exponent) -

He 2

NaCl.

$\overset{\equiv \text{Ne}}{\text{Li}^+} \overset{\equiv \text{Ne}}{\text{H}^-}$

Ne 5

$\text{Na}^+ \equiv \text{Ne}$ $\text{Cl}^- \equiv \text{Ar}$

$$n = \frac{2+2}{2} = \underline{\underline{2}}$$

Ar 7

Kr 9

$$n = \frac{5+7}{2} = \underline{\underline{6}}$$

$\overset{\equiv \text{Ar}}{\text{K}^+} \overset{\equiv \text{Ar}}{\text{Cl}^-}$

Xe 10

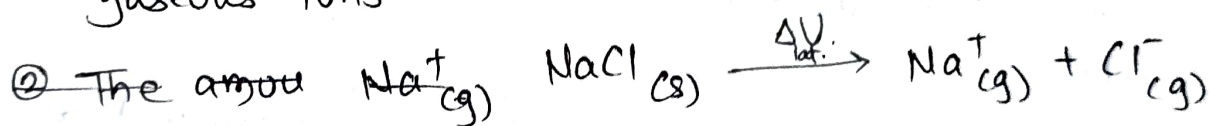
Rn 12

$$n = \frac{7+7}{2} = \underline{\underline{7}}$$

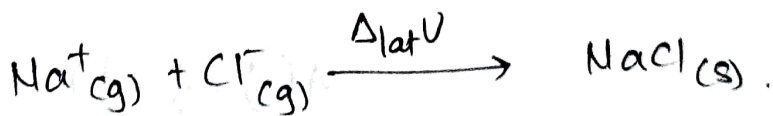
* Born-Haber's Cycle -

Lattice ene. -

① The amount of energy required to break 1 mole of crystals in solid state into their gaseous ions is called lattice energy.



② The amount of ene. evolved when two opposite ions in their gaseous state come together & form 1 mole of solid substance is called lattice enthalpy.



Through experimentally, it is not possible to determine lattice energy. while with the help of Born-Haber's cycle it can be calculated.

Rules for finding Miller Indices -

Step I - Find Intercepts

$$(2, 1, 3)$$

Step II - Find weiss indices.

$$(2, 1, 3)$$

Step III - Reciprocal of weiss indices.

$$\left(\frac{1}{2}, 1, \frac{1}{3}\right)$$

Step IV - Remove fraction by multiplying with smallest integer.

$$(3, 6, 2) \equiv \underline{(3 \ 6 \ 2)}$$

Miller Indices.

Step V - Do not reduce Miller Indices to lowest integers.

$(2 \ 2 \ 2)$ & $(1 \ 1 \ 1)$ these two miller indices represent dif. planes.

Step VI - If negative sign is there it is replaced by bar.

$$(-1 \ 2 \ 3) \equiv (\bar{1} \ 2 \ 3)$$

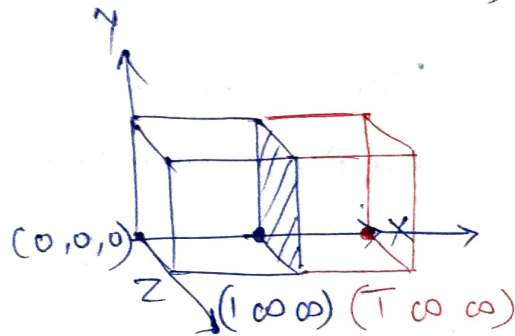
Step VII - Representation by (hkl) .

Que. Find the Miller Indices of a crystal planes which cuts through the crystal axis at
 a. $(6a, 3b, 3c)$ & b. $(2a, -3b, -3c)$.

Solⁿ - $(6a, 3b, 3c)$
 $(6, 3, 3)$
 $(\frac{1}{6}, \frac{1}{3}, \frac{1}{3})$
 $(1 \rightarrow 2 \rightarrow 2)$

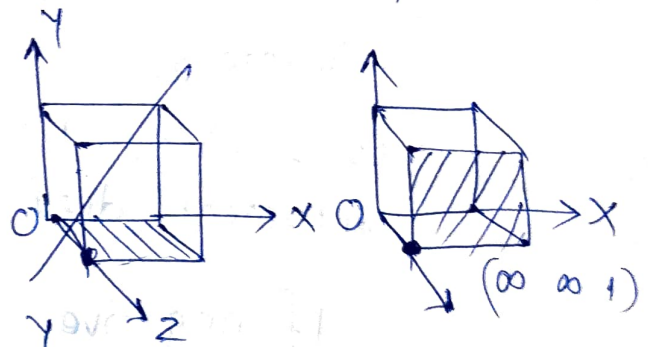
$(2a, -3b, -3c)$
 $(2, -3, -3)$
 $(\frac{1}{2}, -\frac{1}{3}, -\frac{1}{3})$
 $(3 \rightarrow \bar{2} \rightarrow \bar{2})$

* Intercept $(1, 0, 0)$ M.I.
 $(1, \infty, \infty)$

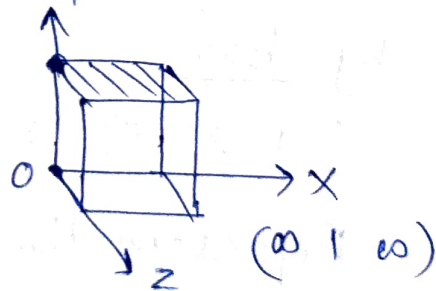


M.I. & their negative represents same plane.*

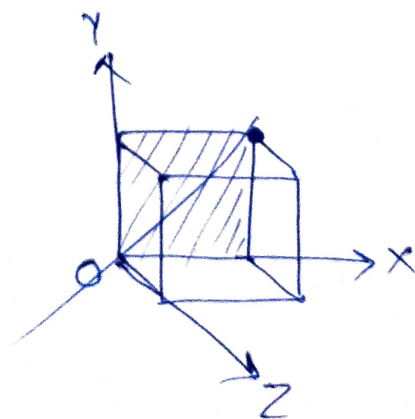
* Intercepts $(0, 0, 1)$ M.I.
 $(\infty, \infty, 1)$



* Intercepts $(0, 1, 0)$ M.I.
 $(\infty, 1, \infty)$

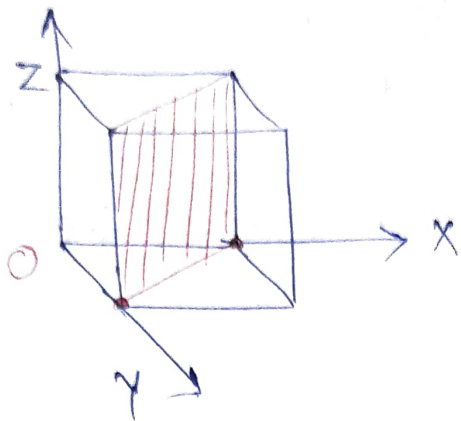


* ~~Intercepts $(1, 1, 0)$~~
~~M.I. $(1, 1, \infty)$~~



M.I.
Weiss Indices $(1, 1, 0)$

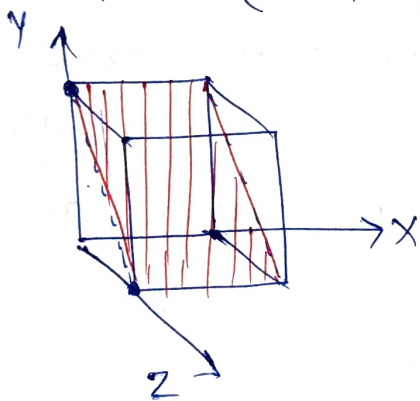
M.I. $\rightarrow (1, 1, \infty)$



* Miller Indices will be 0 (can never be ∞)
for intercept ∞ .

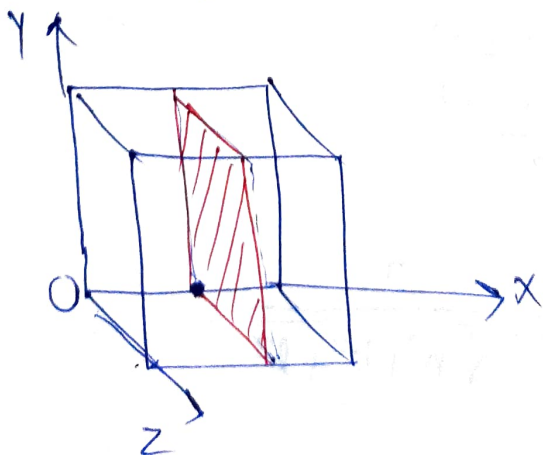
M.I.
* Weiss Indices $(0, 1, 1)$

Intercepts $(\infty, 1, 1)$

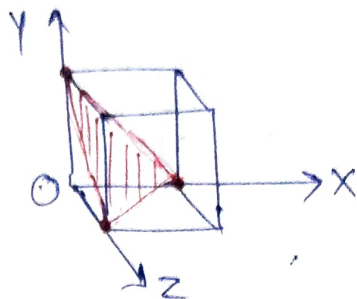


* M.I. $(2, 0, 0)$

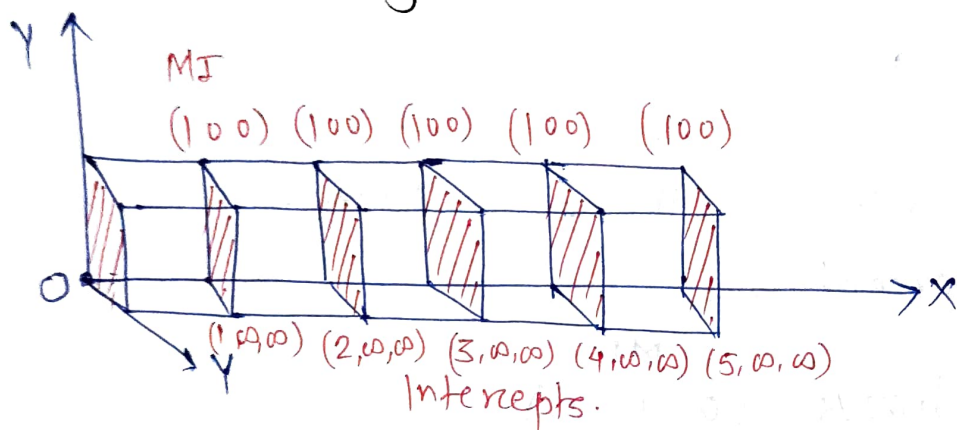
Intercepts $(\frac{1}{2}, \infty, \infty)$



* M.I. (1, 1, 1)
Intercepts (1, 1, 1)



* If the plane pass th. origin (0, 0, 0) the plane shift left or right.



* If we consider the plane passes through origin is (1 0 0) then the plane drawn is respect to origin & if we consider origin plane of (2 0 0) then all the plane drawn above are of (2 0 0).

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

Interplanar distance. Always valid for parallel planes.

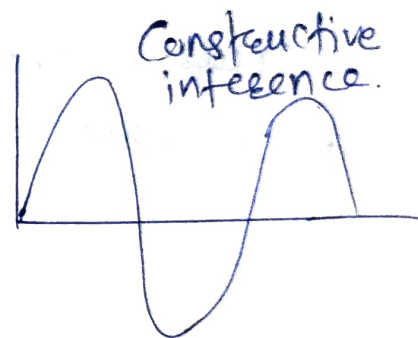
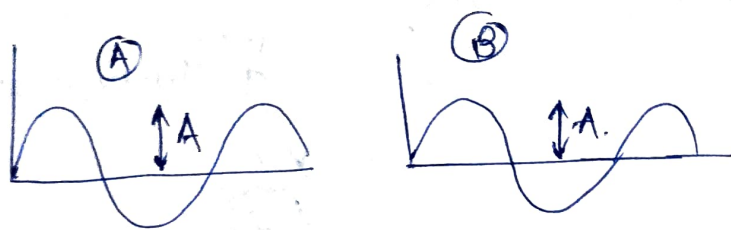
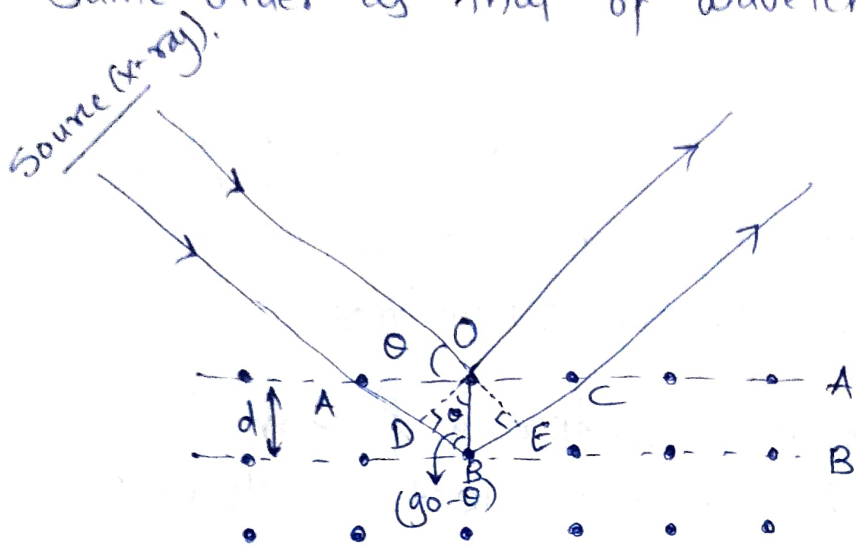
for cubic system - ($a = b = c$).

$$\therefore \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$\therefore d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Bragg's Equation -

The crystals can diffract x-rays 'cause the interplanar spacing in a crystal lattice is of the same order as that of wavelength of x-rays.



$$\text{path diff.} = DBE = 2BD$$

$$\text{Now, } \sin \theta = \frac{BD}{OB}$$

$$\Rightarrow BD = d \cdot \sin \theta$$

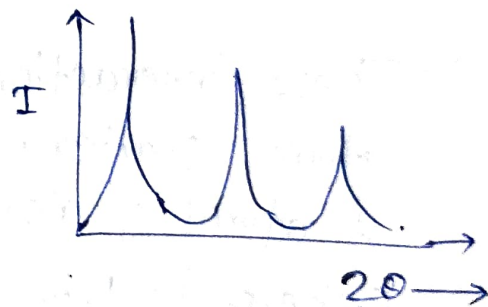
$$\therefore \text{path. difference} = 2d \cdot \sin \theta$$

$$\boxed{\therefore n\lambda = 2d \sin \theta}$$

* where $n = 1, 2, 3, \dots$

when $n=1$, it is called as first order reflection.

when $n=2$, it is called as 2nd order reflection.



* Structure Factor

Structure factor of a Bragg's reflection (which is complete quantity) is defined as

$$F_{hkl} = \sum_{j=1}^N f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

↳ for graphical representation,

x_j, y_j & z_j are the fractional co-ordinates of j^{th} atom & these are quantities

⇒ The value of atomic scattering factor is max. at the center of the electron cloud & decreases exponentially as one moves away from this center.



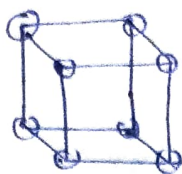
⇒ These interactions depend on the individual atomic scattering factors of different species of atoms & also on their positions. (x_j, y_j, z_j) (where $j = 1, 2, \dots, N$).

$$\Rightarrow I_{hkl} \propto |F_{hkl}|^2$$

$$\text{or } |F_{hkl}| \propto \sqrt{I_{hkl}}$$

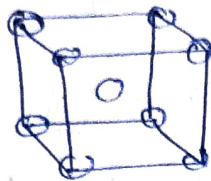
$|F_{hkl}|$ is the structure factor of amplitude of Bragg reflection & is proportional to the square root of the experimentally available Bragg's intensity.

SC.



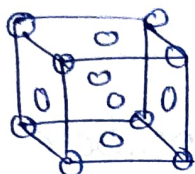
SC \rightarrow $(0, 0, 0)$
for corner atoms.

BCC



BCC \rightarrow $(0, 0, 0)$
for corner atoms.
 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for center atom.

FCC



FCC \rightarrow $(0, 0, 0)$
for corner atoms.
 $(0, \frac{1}{2}, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$
for face centered atoms.

Euler's Theorem -

$$e^{i\theta} = \cos \theta + i \cdot \sin \theta.$$

$$e^{i\pi} = \cos \pi + i \sin \pi.$$

$$e^{i2\pi} = \cos 2\pi + i \sin 2\pi.$$

$$\sin n\pi = 0 \quad (\text{for } n=0, 1, 2, 3, \dots)$$

$$\cos n\pi = +1 \quad (\text{for } n \text{ is even, } n=0, 2, 4, \dots)$$

$$\cos n\pi = -1. \quad (\text{for } n \text{ is odd, } n=1, 3, 5, \dots)$$

$$\therefore e^{i\pi} = \cos \pi + i \cdot \sin \pi = -1 + 0 = -1$$

$$e^{i2\pi} = \cos 2\pi + i \sin 2\pi = +1 + 0 = +1$$

$$\therefore e^{i3\pi} = -1 \quad e^{i9\pi} = -1$$

$$e^{i4\pi} = +1$$

* Atomic Scattering Amplitude (f) -

It describes the scattering power of a single atom in comparison to that of single e^- .

$$f = \frac{\text{Amplitude of radiation scattered by an atom}}{\text{Amplitude of radiation scattered by an electron}}$$

* Total Scattering Amplitude (F) -

It describes scattering power of the complete unit cell in comparison to that of single electron.

$$* F = \frac{\text{Amplitude of radiation scattered by a unit cell}}{\text{Amplitude of radiation scattered by an electron}}$$

Scattering Factor - (S).

The ratio of F & to f is called ~~as~~ S . (scattering factor).

$$S = \frac{F}{f}$$

$$* (Sp)_{\text{atom}} = f \times (Sp)_e$$

$$(Sp)_{\text{electron unit cell}} = F \times (Sp)_e$$

* Significance of S -

⇒ If $S=0$; $f=0$; $F=0$

then $I=0$

forbidden reflection.

⇒ If $S \neq 0$; $f \neq 0$, $F \neq 0$.

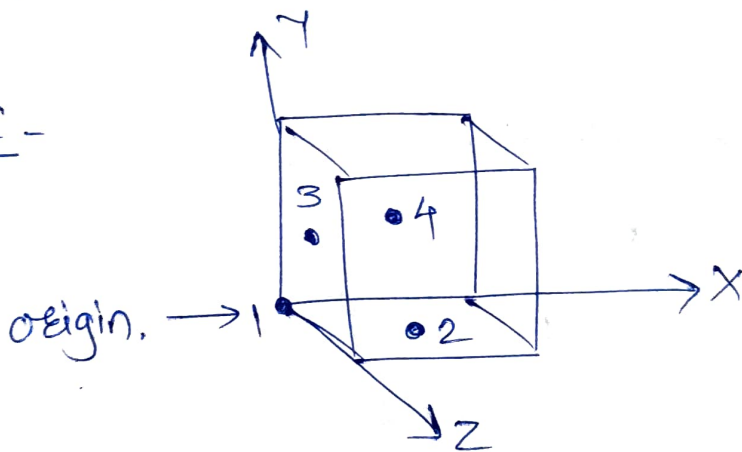
then $I \neq 0$.

∴ Allowed reflections.

* Selection rule for allowed reflections -

⇒ Structure factor must be non-zero.

for FCC -



1 atom $(0, 0, 0)$

2 atom $(\frac{1}{2}, 0, \frac{1}{2})$

3 atom $(0, \frac{1}{2}, \frac{1}{2})$

4 atom $(\frac{1}{2}, \frac{1}{2}, 0)$

$$S = e^{2\pi i (0h + 0k + 0l)} + e^{2\pi i (\frac{1}{2}h + 0k + \frac{1}{2}l)} \\ + e^{2\pi i (0h + \frac{1}{2}k + \frac{1}{2}l)} + e^{2\pi i (\frac{1}{2}h + \frac{1}{2}k + 0l)}$$

$$S = 1 + e^{i(h+l)\pi} + e^{i(k+l)\pi} + e^{i(h+k)\pi}$$

Case I :

When all h, k, l are odd.

let us consider $(h=1, k=3, l=5)$

$$\therefore S = 1 + e^{i6\pi} + e^{i8\pi} + e^{i4\pi}$$

$$= 1 + 1 + 1 + 1$$

$$\boxed{S = 4} \neq 0$$

\therefore Allowed ~~to~~ reflection, Since $S \neq 0$.

Also, $I = |F|^2$

$$S = \frac{F}{f} \Rightarrow F = S \times f \\ = 4f.$$

$$\therefore I = |4f|^2 = 16f^2 \neq 0.$$

$$\boxed{I = 16f^2}$$

Case II :

when all are even.

h	k	l
0	2	4

$$S = 1 + e^{i(4)\pi} + e^{i(6)\pi} + e^{i(2)\pi}$$

$$= 1 + 1 + 1 + 1 = 4 \neq 0.$$

\therefore Allowed reflection, Since $S \neq 0$.

Case III: When h, k, l are even & odd mixed.

$$(h, k, l) \equiv (1, 2, 3)$$

$$S = 1 + e^{i(4)\pi} + e^{i(5)\pi} + e^{i(5)\pi}$$

$$= 1 + 1 - 1 - 1$$

$$= 0$$

$\therefore S = 0 \Rightarrow$ Forbidden reflection.

Selection Rule -

For allowed reflection -

In FCC Miller Indices are either ~~odd~~ all even or all odd.

In BCC.

For BCC - $(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

$$S = e^{2\pi i (0h+0k+0l)} + e^{2\pi i (\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l)}$$

$$= e^0 + e^{i(h+k+l)\pi}$$

$$= 1 + e^{i(h+k+l)\pi}$$

Case I:

If $h+k+l = \text{odd}$.

$$h=1, k=3, l=5$$

$$S = 1 + e^{i(2\pi)}$$

$$= 1 - 1$$

$$= 0$$

$F=0, I=0$, Forbidden reflection

Case II - $h + k + l = \text{even}$.

$$h=1, k=1, l=0.$$

$$S = 1 + e^{i2\pi}$$

$$= 1 + 1$$

$$= 2$$

$S \neq 0$. Allowed reflections.

* Selection Rule for allowed reflection of BCC -
Summation of miller indices must be even.

For FCC - $(0, 0, 0)$.

$$S = e^{2\pi i (0h + 0k + 0l)}$$

$$= e^0 = 1$$

$$F = 1f = f.$$

$$I = |F|^2 = f^2 \neq 0.$$

Allowed reflections always.

Lattice.	Selection Rule for allowed reflections.
Sc	Any h, k, l .
Bcc	$h+k+l = \text{even}$
Fcc	h, k, l either all odd or all even.
Dcc (Diamond)	h, k, l either all even or odd (if even; $h+k+l$ must be divisible by 4).
Triangular lattice.	$l = \text{even}$ $h+2k$ must not be divisible by 8. $l = \text{odd}$. $h+2k$ must be divisible by 3.

Lattice	100	110	111	200
Sc	✓	✓	✓	✓
Bcc	✗	✓	✗	✓
Fcc	✗	✗	✓	✓
Triangular lattice.	✓	⊗	✓	✓

[(* 0 is considered as even here)]

According to Bragg's Equation,

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

For cubic system,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

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

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

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

* 7k, ~~10k~~^{15k, 23k} reflections will not possible in all type of unit cell.

Defects (Imperfections) in solids -

Stoichiometric defects

Non-stoichiometric

* Schottky

* Frenkel

1. Metal Excess defects.
2. Metal deficiency defect.

* Schottky defects -

1. Appear in ionic crystal.
2. Equal no. of positive & negative sites will be vacant.

Conditions -

Positive & negative ions do not differ much in size.

$$n = N \cdot \exp\left(\frac{-E}{2kT}\right)$$

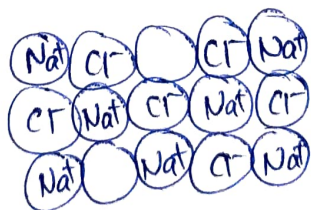
Boltzmann constant.

no. of defects.

total no. of atoms present in crystal.

* Electroneutrality is always maintained in any crystal.

ex. NaCl.



(i.e. if + positive charge is absent then + -ve charge must be absent.)

Consequences & Result -

- ① Due to Schottky defect the density of crystalline solid decreases. Lattice ene. & thermal stability decreases. Entropy dec. increases.

Examples -

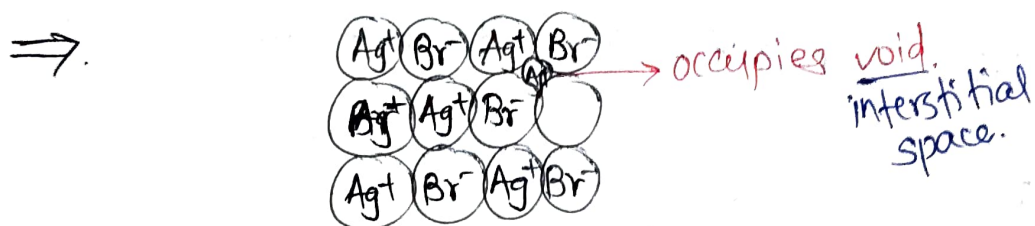
KCl, KBr, AgBr* → shows Frenkel defect also.

Frenkel Defects -

1. Ion occupies position in the interstitial space.
2. When negative ions are much larger than the positive ions.

Example -

AgBr, ZnS, AgCl, AgI etc.



Consequences & result -

1. There is no change in the density of solids.

L.E. ↓

Entropy ↑

(Frenkel defect increases dielectric constant)

Imp
* * In both the defects electroneutrality is maintained.

$$n = (N \cdot N_i)^{1/2} \cdot e^{-E/2kT}$$

no. of atoms in i th level.

* The no. of Schottky & Frenkel defects would increase exponentially with increase in temp.

Temp ↑ ⇒ n ↑

* The presence of Ag⁺ ions in the interstitial space of AgBr crystal is responsible for the formation of photographic image on exposure of AgBr crystal.

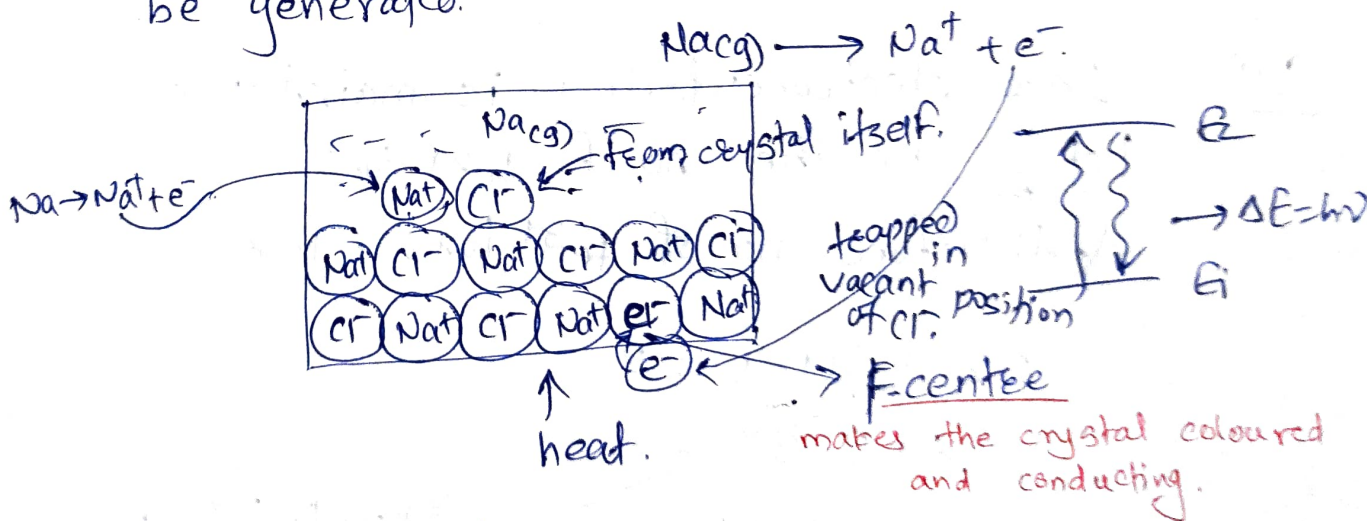
IMP Metal Excess Defect -

⇒ It will observe when crystal of NaCl is heated in sodium vapour, it acquires yellow colour.

In this case, non stoichiometric sodium chloride will be present & is represented



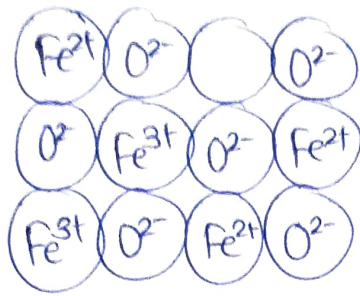
where δ is the excess sodium metal doped in the crystal. In this case, F centres will be generated.



Another example -

* (i) Formation of magenta coloured non-stoichiometric compd. of KCl by exposing the crystal of KCl to K metal vapour.

* Metal Deficiency Defect



} electroneutrality is maintained by Fe³⁺ ions

Another examples -

FeS (Iron sulphide)

Nickel Oxide

Que. The composition of a sample of wuzite is Fe_{0.93}O_{1.00}. What percentage of the iron is present in the form of Fe³⁺?

Solⁿ - Since, electroneutrality is maintained

Let x be the no. of Fe²⁺ ions.

& therefore no. of Fe³⁺ ions = 1-x.

~~$$2x + 3(1-x) = 2$$~~

~~$$2x + 3 - 3x = 2$$~~

~~$$-3 - x = 2$$~~

~~$$2x + 279 - 3x = +200$$~~

~~$$2x + 3(93-x) = 2 \times 100$$~~

~~$$2x + 279 - 3x = 200$$~~

~~$$279 - 200 = x$$~~

$$\Rightarrow x = 79.$$

$$\begin{aligned} \% \text{ of } \text{Fe}^{2+} &= \frac{\text{Atoms of } \text{Fe}^{2+}}{\text{Total Fe.}} \times 100 \\ &= \frac{79}{93} \times 100 \\ &= 84.94\% \end{aligned}$$

$$\begin{aligned} \therefore \% \text{ of } \text{Fe}^{3+} &= 100 - 84.94 \\ &= \underline{\underline{15.06\%}} \end{aligned}$$

* $\text{Fe}_{0.93}\text{O}$.
2nd Method: Conceptual.

Replacement of Fe^{2+} ion by Fe^{3+} ion increases one positive charge. Thus, 14 +ve charges are compensated by the presence of 14 Fe^{3+} ions. Out of it total of 93 iron ions.

$$\begin{aligned} \therefore \% \text{ Fe}^{3+} \text{ ions present} &= \frac{14}{93} \times 100 \\ &= 15.06\% \end{aligned}$$

Que. Analysis shows that Nickel oxide has the formula $\text{Ni}_{0.98}\text{O}$. What fractions of the Nickel exists as Ni^{2+} & Ni^{3+} ions?

Solⁿ - Since electroneutrality is maintained.

Let x be the no. of Ni^{2+} ions.

$$\therefore \text{no. of } \text{Ni}^{3+} \text{ ions} = \underline{\underline{1-x}}$$

$$2x + 3(98-x) = 2 \times 100$$

$$x = 294 - 200$$

$$= \underline{\underline{94}}$$

$$\% \text{ of Ni}^{2+} = \frac{\text{Atoms of Ni}^{2+}}{\text{Total Ni}} \times 100$$

$$= \frac{94}{98} \times 100$$

$$= 95.91\%$$

(0.95)

$$\therefore \% \text{ of Ni}^{3+} = 100 - 95.91$$

$$= \underline{\underline{4.09\%}}$$

(0.04)

2nd method -

$$\frac{4}{98} \times 100$$