

Handwritten Notes on Solid State



Solid State

Characteristics of Solid State :-

1. They have definite mass, Vol^m and shape.
2. Intermolecular distances are short.
3. Intermolecular forces are strong.
4. Their constituent particles (atoms, molecules or ions) have fixed posⁿ and can only oscillate about their mean posⁿs.
5. They are incompressible and rigid.

Type of Solid :-

Property	Crystalline	Amorphous
Shape	Definite geometrical shape	Irregular shape
Melting Point	Melt at sharp temp	Gradually soften over range of temp.
Cleavage Property	When cut with sharp edged tool, they split into 2 pieces with plain and smooth surface	When cut with sharp edged tool, they cut into 2 pieces with irregular surfaces
Heat of fusion	definite	do not have definite
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liq.
Order in arrangement of constituent particles	Long range order	Only short range order

Classification of Crystalline solid :-

Type of Solid	Constituent Particles	Bonding / Attractive Forces	Example	Physical Nature	Electrical Conductivity	Melting Point
Molecular solids	Non-Polar	(i) Dispersion or London forces	Ar, CCl ₄ , H ₂ , I ₂ , CO ₂	Soft	Insulator	very low
		(ii) Dipole-Dipole	HCl, SO ₂	Soft	Insulator	low
	(iii) Hydrogen bond	(iii) Hydrogen bonding	H ₂ O (ice)	Hard	Insulator	low
Ionic solids	Ions	(i) Coulombic or electrostatic	NaCl, MgO, ZnS, CaF ₂	Hard but brittle	Insulator in solid but conductor in molten & aq. soln	High
		(ii) Metallic Bonding	Fe, Cu, Ag, Mg	Hard but malleable & ductile	Conductor in solid as well as in molten state	Fairly high
Covalent network solids	Atoms	(i) Covalent Bonding	SiO ₂ (quartz), SiC, C (diamond)	Hard	Insulator	very high
		(ii) Graphite	AlN, C (graphite) → soft	→ soft	Conductor (exception)	

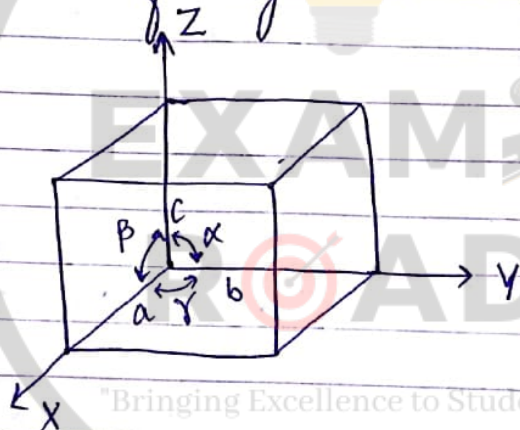
Crystal Lattice / space Lattice / 3-D Lattice :-

3-D arrangement of constituent particle in space is c/a \Rightarrow 3-D Lattice / Crystal Lattice.

Lattice Point :- It is the posⁿ in crystal lattice where constituent particle is located.

Unit Cell :- It is the smallest portion of crystal lattice which generate the entire lattice by repeating in itself in diff. dirⁿs.

- Unit cell is characterised by edge length a, b & c along 3 axis of unit cell at the angles α, β & γ b/w the pairs of edges a, b, c & ab, bc, ca .



Unit Cell

Primitive
When constituent particle are +nt at only corner of cube

Centred unit cell

- B.C.C. \rightarrow Corner of cube & centre of cube
- F.C.C. \rightarrow Corner of cube & face centre
- End centre \rightarrow corner of cube & at any 2 opp. face

Cube :-

Corner $\rightarrow 8$

Face $\rightarrow 6$

Edge $= 12$

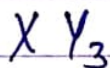
Body Centre $= 1$

Face dia Body Diagonal $= 4$
Face " $= 2 \times 6 = 12$

- \rightarrow There are 8 corners in cube and 1 corner is common in for 8 cube.
- \rightarrow Its contribution in its own cube is $1/8$.
- \rightarrow A cube has 6 faces & one face is common for 2 cube.
- \rightarrow Its contribution in its own cube is $1/2$.
- \rightarrow A cube has 12 edges & one edge is common for 4 cube.
- \rightarrow Its contribution in its own cube is $1/4$.
- \rightarrow Body There is one body centre in cube & no contribution to other cube.

Ques A solid is formed by crystallization of X & Y elements. If X occupies corner of cube & Y occupies face centre of cube then find molecular formula of cube.

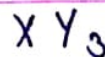
$$\begin{aligned} X &\rightarrow \text{corner} \rightarrow \frac{1}{8} \times 8 = 1 \text{ atom} \\ Y &\rightarrow \text{face centre} \rightarrow \frac{1}{2} \times 6 = 3 \end{aligned}$$



Ques Find molecular formula of solid if X occupies corner of cube & Y occupies edge centre of cube.

$$X \rightarrow \text{corner} \rightarrow \frac{1}{8} \times 8 = 1$$

$$Y \rightarrow \text{edge centre} \rightarrow \frac{1}{4} \times 12 = 3$$



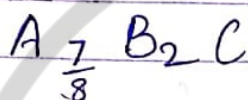
Ques .

A solid is consist of A, B & C type atoms. If A occupy corner of cube but one corner ~~is~~ missing, B occupies face centre but 2 faces are missing & C occupies body centre. Then find mol. formula of solid.

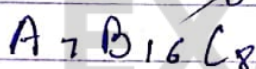
$$A \rightarrow \text{corner} \rightarrow \frac{1}{8} \times 8 = 1 - \frac{1}{8} = \frac{7}{8}$$

$$B \rightarrow \text{face centre} \rightarrow \frac{1}{2} \times 6 = 3 - 1 = 2$$

$$C \rightarrow \text{body centre} \rightarrow 1$$



$$A : B : C = \frac{8 \times 7}{8} : 2 \times 8 : 1 \times 8$$



Ques A solid is consist of A, B & C type ^{elements} atoms. A occupies corner of cube, B occupies face centre & C occupies Body centre. Find mol. formula of solid if -

$$A \rightarrow \text{corner} \rightarrow \frac{1}{8} \times 8 = 1$$

$$B \rightarrow \text{face centre} \rightarrow \frac{1}{2} \times 6 = 3$$

$$C \rightarrow 1$$

① If all atoms along a diagonal Passing through 2 corners

② & face centre are removed

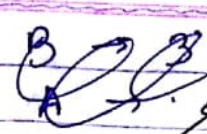
$$B \rightarrow 3 - \frac{1}{2} = \frac{5}{2}$$

$$A \rightarrow 1 - \frac{2}{8} = \frac{6}{8}$$

$$C \rightarrow \frac{1}{2}$$

$$A : B : C = 6 \times 8 : 5 \times 8 : 1 \times 8 \Rightarrow A_6 B_5 C_1$$

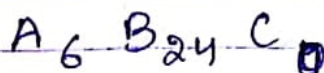


② If  all atoms along one body diagonal removed.

$$B \rightarrow 3$$

$$A \rightarrow \frac{6}{8}$$

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

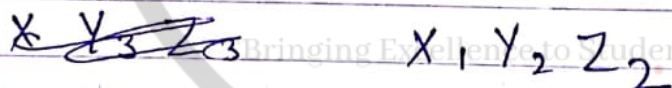


Q.5 A solid is consist of x, y & z type of atoms. If x occupies alternate corners of cube. y " " " " face centre " " z " " " " edge centre " "

$$X \rightarrow \frac{1}{8} \times 4 = \frac{1}{2}$$

$$Y \rightarrow \frac{1}{2} \times 2 = 1$$

$$Z \rightarrow \frac{1}{4} \times 4 = 1$$



Then find mol. formula of solid

Type of Unit Cell :-

① Primitive / simple Cubic Unit cell :-

Lattice Point : at corners of cube

$$Z = \text{no. of eff. particles in unit cell} = 8 \times \frac{1}{8}$$

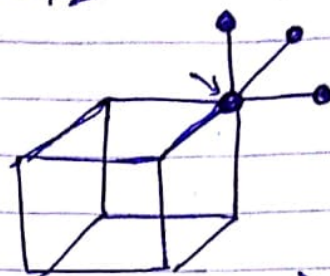
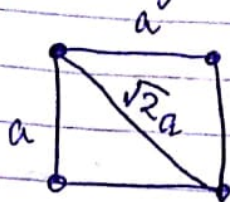
$$Z = 1$$

Coordination No. :- no. of nearest neighbour particles around a specific particle in a crystal lattice c.f. C.N.

$$C.N. \text{ of S.C.C.} = 6$$



next nearest neighbours = $\frac{8 \times 3}{2} = 12$



(distance = $\sqrt{2}a$)

1 Face \rightarrow 3 next nearest

Total cube attached = 8

2 cube share common

(next)² nearest neighbour = $\frac{8 \times 1}{1} = 8$ (distance = $\sqrt{3}a$)

Touching condⁿ

$$a = 2r$$



Packing efficiency = $\frac{\text{Vol. occupied by atoms}}{\text{Vol. of unit cell}}$

$$P.E. = \frac{Z \times \frac{4}{3} \pi r^3}{a^3} = \frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = \frac{\pi}{6} = 0.524 \text{ or } 52.4\%$$

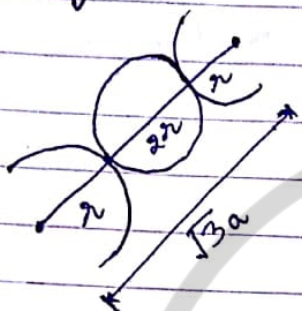
$$\% \text{ void space} = 100 \left(1 - \frac{\pi}{6} \right) \% = 47.6\%$$

$$\text{density} = \frac{\text{mass}}{\text{Vol}^m} = \frac{Z \times M / N_A}{a^3}$$



② Body Centre Cube :-
 Lattice Point :- at corner & Body centre
 $Z = 8 \times \frac{1}{8} + 1 = 2$

Touching condⁿ



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

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

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

C.N. : C.N. of corner atom in its unit cell = 1
 & corner atom is shared in 8 cubes

→ so C.N. of corner atom = 8

→ C.N. of body centre atom = 8

→ next nearest neighbour = 6
 (distance = a)

→ (next)² nearest neighbour

→ corner atom shared in 8 cubes

$$= \frac{8 \times 3}{2} \rightarrow \text{in a unit cell a distance } \sqrt{2}a \text{ (face)}$$

$\rightarrow 1$ face is shared by 2 cubes

$$= 12$$

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

$$= \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4}{\sqrt{3}} r\right)^3}$$

$$= \frac{2 \times \frac{4}{3} \pi r^3}{\frac{64}{3\sqrt{3}} r^3}$$

$$= \frac{\sqrt{3} \pi}{8}$$

$$= 0.68 \text{ or } 68 \%$$

$$\% \text{ void} = \left(1 - \frac{\sqrt{3} \pi}{8}\right) \times 100\% = 32\%$$



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

$$= \frac{2 \times \frac{M}{N_A}}{\left(\frac{4}{\sqrt{3}} r\right)^3}$$

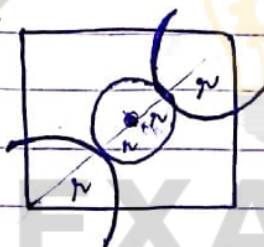
3.) F.C.C. :-

Lattice Point :- at corner & face centre

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

Touching Condⁿ :

Face



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

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

In F.C.C. corner ^{atom} ~~do~~ not touch each other

C.N. :

$$\text{C.N. w.r.t. to corner atom} = \frac{8 \times 3}{2} = 12$$

$$\text{C.N. w.r.t. to face centred atom} = 12$$

↑

(4 corner + 8 face centre)

$$\text{Nearest Neighbours} = 12 \quad \left(\text{distance} = \frac{\sqrt{2} a}{2} = \frac{a}{\sqrt{2}} \right)$$

$$\text{next nearest neighbour} = 6 \quad (\text{distance} = a)$$

$$(\text{next})^2 \quad " \quad " = \frac{8 \times 3}{1} \quad \left(" = \sqrt{\frac{3}{2}} a \right)$$

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

$$= \frac{4 \times \frac{4}{3} \pi r^3}{(2\sqrt{2} r)^3}$$

$$= \frac{4 \times \frac{4}{3} \pi r^3}{16\sqrt{2} r^3}$$



$$P.E. = \frac{\pi}{3\sqrt{2}}$$

$$P.E. = 0.74 \text{ or } 74\%$$

$$\% \text{ Void} = \left(1 - \frac{\pi}{3\sqrt{2}}\right) 100 = 26\%$$

$$\text{density} = \frac{Z \times M / N_A}{a^3}$$

Ex-2(A)
Ex 21

F.C.C.

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

$$\sqrt{2} \times 408 = 4r$$

204

$$r = 204 \times 1.4 =$$

288

Q.26

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

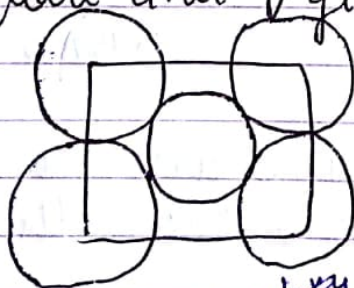
$$\sqrt{2} \times 404 = 4r$$

101 Giving Excellence to Students

$$\text{Density} = 4 \times \frac{M}{N_A a^3}$$

$$\frac{2.72 \times a^3 \times N_A}{4} = M$$

Ques find Packing efficiency of 2-dimensional square unit give below



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

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

$$2 \times \frac{1}{2} \times \pi r^2 = \frac{\pi}{2} r^2$$

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

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

1x1



- ① 54.2% ② 68.4% ③ 74.03% ④ 78.04%

$$Z = 2$$

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

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

$$P.E. = \frac{Z \times \text{area of one square}}{\text{area of Unit Cell}}$$

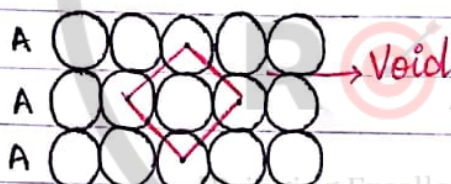
$$= \frac{2 \times \pi r^2}{a^2} = \frac{2 \pi r^2}{(2\sqrt{2}r)^2}$$

Closed Packed structure :-

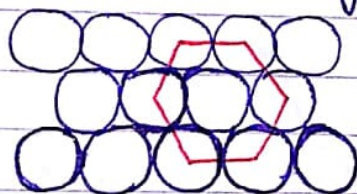
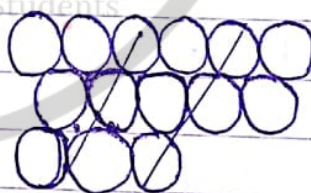
1. Closed Packed in 1-D :-



2. Closed Packed in 2-D :-



Square close Packing
AA - - - type



Hexagonal Close
Packing
ABAB - - - type.

3. Closed Packing in 3D :-

(i) 3-D Close Packing from 2-D Square close Packing :-
2-D square unit one over each other
form SCC



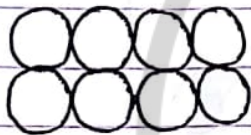
3-D Close Packing from 2-D hexagonal close packing :-

If no. of atom in unit cell = N
(Closed Packed Sphere)

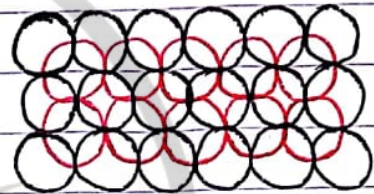
Tetrahedral = $2N$

Octahedral = N

Square layer over each other

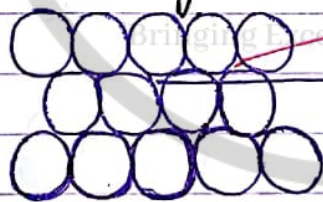


SCC

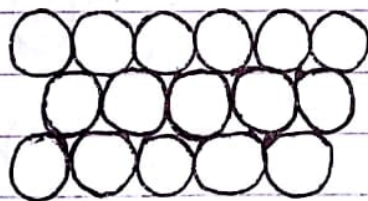


B.C.C.

© 3-D Close Packing in multi layer



C type void
→ B type void



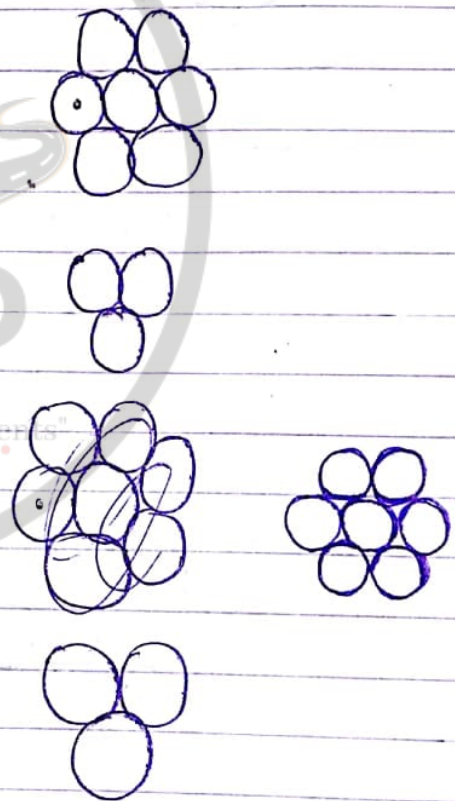
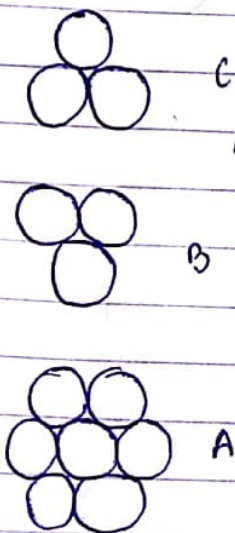
Third layer can be placed in 2 ways

C type voids can be covered by a different 'C' type layer giving ABC... type arrangement

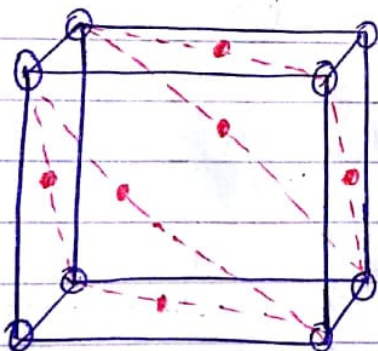
it represent cubic closed Packed [CCP] arrangement
or FCC arrangement

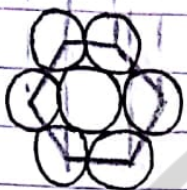
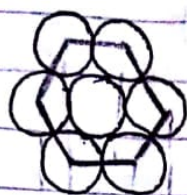
Void created in B layer can be covered by a layer which have same arrangement of A type layer giving ABAB... type arrangement

Hexagonal close close Packing [HCP]



CCP or FCC





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

$$C.N. = \underline{12}$$

Touching Condⁿ :- $a = 2r$

$$d = \frac{Z \times M}{N_A \times \text{Vol. of unit cell}}$$

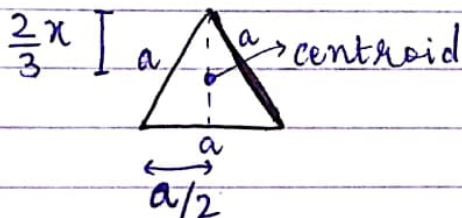
Vol. of unit cell = $H \times \text{area of base}$



$$\frac{\sqrt{3}}{4} a^2$$

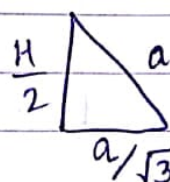
$$\text{Area of base} = 6 \times \frac{\sqrt{3}}{4} a^2$$

$$= 6 \times \frac{\sqrt{3}}{4} (2r)^2$$



$$\frac{2}{3} H = \frac{2}{3} \times \frac{\sqrt{3}}{2} a = \frac{a}{\sqrt{3}}$$

$$H = \sqrt{a^2 - \left(\frac{a}{2}\right)^2} = \frac{\sqrt{3}}{2} a$$



$$\frac{H}{2} = \sqrt{a^2 - \left(\frac{a}{\sqrt{3}}\right)^2} = \frac{\sqrt{2}}{2} a$$

$$H = 2 \sqrt{\frac{2}{3}} a = 2 \sqrt{\frac{2}{3}} (2r)$$

$$H = 4 \sqrt{\frac{2}{3}} r$$

$$\text{Vol}^m \text{ of unit cell} = H \times \text{area of base} \\ = 4 \sqrt{\frac{2}{3}} r \times \frac{6\sqrt{3}}{4} (2r)^2$$

$$\text{Vol. of unit cell} = \boxed{24\sqrt{2} r^3}$$

$$\begin{aligned} \text{P.E.} &= \frac{Z \times \frac{4}{3} \pi r^3}{\text{Vol. of unit cell}} \\ &= \frac{6 \times \frac{4}{3} \pi r^3}{24\sqrt{2} r^3} \\ &= \frac{\pi}{3\sqrt{2}} \end{aligned}$$

$$0.74 \text{ or } 74 \%$$

$$\% \text{ Void} = \boxed{26} \% \text{ IIT-2008}$$

Type of Voids :-

Tetrahedral Voids :-

→ It is triangular void surrounded by 4 spheres.

→ Hence its C.N. is 4



Posⁿ of tetrahedral void in F.C.C. :-

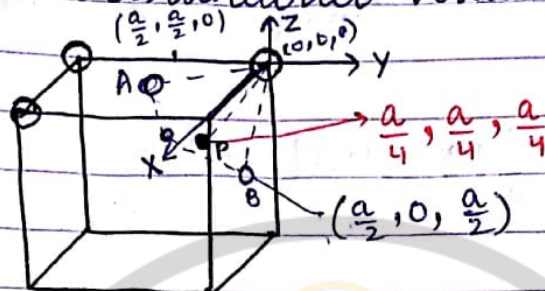
In F.C.C., one corner atom & 3 face centre atoms formed a tetrahedral void so 2 tetrahedral voids are formed are body diagonal of FCC

There are 4 body diagonal in cube hence there are 8-tetrahedral voids in FCC

OR

Total no. of atoms in fcc = $N = 4$

" " " tetrahedral voids in FCC = $2N = 8$

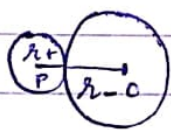


Let consider origin at any corner atom = $(0, 0, 0)$
 then coordinates of
 face central atom
 A $(a/2, a/2, 0)$
 B $(a/2, 0, a/2)$
 C $(0, a/2, a/2)$

Void P $(\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$

$$\text{distance } OP = \sqrt{\left(\frac{a}{4} - 0\right)^2 + \left(\frac{a}{4} - 0\right)^2 + \left(\frac{a}{4} - 0\right)^2}$$

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



anion at corner
cation at voids

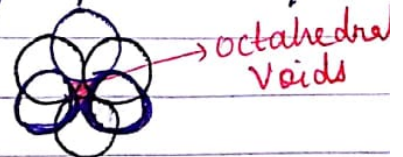
$$r_+ + r_- = \frac{\sqrt{3}}{4} a$$

Octahedral Voids :-

The vacant space b/w 6 touching sphere is c/a Octahedral Voids.

C.N. $\rightarrow 6$

Posⁿ of Octahedral Voids in FCC Lattice :-



Body centre & edge centre

$$\text{No. of octahedral void in fcc} = 1 + 12 \times \frac{1}{4}$$

$$= 1 + 3 = 4$$

Body centre edge centre

or

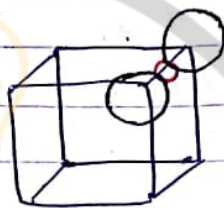
$$\text{No. of atoms in fcc unit cell} = N = 4$$

$$\text{No. of octahedral voids} = N = 4$$

Touching Condⁿ

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

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

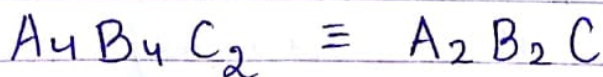


Ques Atom A is + every element of FCC, atom B is +nt at every octahedral void, atom C is +nt at 25% of Tetrahedral void. Find out the M.F.

$$\text{Atom A} \rightarrow \text{FCC} \rightarrow \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4 \text{ atoms}$$

$$\text{Atom B} \rightarrow \text{Octahedral Void} = 4 \text{ atoms}$$

$$\begin{aligned} \text{Atom C} \rightarrow 25\% \text{ of Tetrahedral Void} &= \frac{25}{100} \times 8 \\ &= 2 \text{ atoms of C} \end{aligned}$$



Limiting Radius Ratio :-

- It tells the stability of ionic crystal
- tells about coordination no.
- tells about geometry of void.

$$\boxed{C.N. = 3}$$

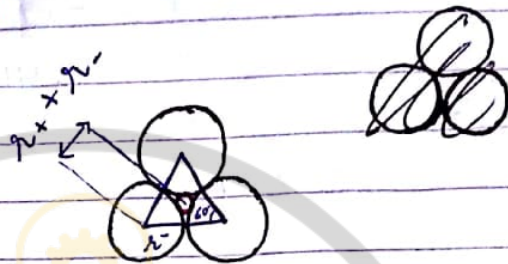
Triangular Void

$$\cos 30^\circ = \frac{r_-}{r_+ + r_-}$$

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

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

$$\frac{r_+}{r_-} = \frac{2 - \sqrt{3}}{\sqrt{3}} = \frac{2 - 1.73}{1.73} = 0.155$$



Range of triangular void

$$0.155 \leq \frac{r_+}{r_-} < 0.225$$

C.N. = 4 — Tetrahedral
— Square

Tetrahedral : Anion - F.C.C.

$$4 r_- = \sqrt{3} a \quad \text{--- (1)}$$

cation → Tetrahedral void

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

$$4 r_+ + 4 r_- = \sqrt{3} a \quad \text{--- (2)}$$

$$\frac{4 r_+ + 4 r_-}{4 r_-} = \frac{\sqrt{3}}{\sqrt{2}}$$

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

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

$$r_+ < 0.225 r_-$$



Range for tetrahedral Void
 $0.225 \leq \frac{r_+}{r_-} < 0.414$

Square :-

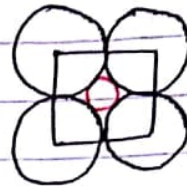
$$2r_- = a \quad \text{--- (1)}$$

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

$$\frac{2r_+ + 2r_-}{2r_-} = \frac{\sqrt{2}}{1} = 1.414$$

$$\frac{r_+}{r_-} = 1.414 - 1$$

$$\frac{r_+}{r_-} = 0.414$$



Octahedral Void : — C.N. = 6 at edge centre
 — C.N. = 8

Octahedral Void at edge centre C.N. = 6

$$4r_- = \sqrt{2}a \rightarrow \text{(1) at FCC}$$

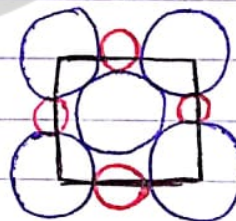
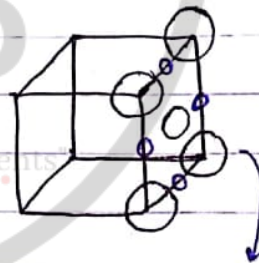
$$2r_+ + 2r_- = a \quad \text{--- (2)}$$

$$\frac{(2) \times 2}{(1)}$$

$$\frac{4r_+ + 4r_-}{4r_-} = \frac{2a}{\sqrt{2}a} = \frac{\sqrt{2}}{1}$$

$$\frac{r_+}{r_-} = \sqrt{2} - 1$$

$$\frac{r_+}{r_-} = 0.414$$



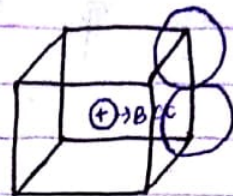
Range for Octahedral Void at edge centre
 $0.414 \leq \frac{r_+}{r_-} < 0.732$

Octahedral Void at B.C. C.N. = 8

$$2r_- = a \quad \text{--- (1) at s.c.c.}$$

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

$$\textcircled{2}/\textcircled{1} \quad \frac{2r_+ + 2r_-}{2r_-} = \frac{\sqrt{3}}{1} = 1.732$$



$$\& \quad \frac{r_+}{r_-} = 1.732 - 1$$

$$\frac{r_+}{r_-} = 0.732$$

Range for octahedral Void at BCC C.N. = 8

$$0.732 \leq \frac{r_+}{r_-} < 1$$

	C.N.	Void	Range	Example
1.	3	Triangular	$0.155 \leq \frac{r_+}{r_-} < 0.225$	B_2O_3
2.	4	Tetrahedral	$0.225 \leq \frac{r_+}{r_-} < 0.414$	ZnS, SiO_2, CaF_2
3.	4	Square	$0.414 \leq \frac{r_+}{r_-} < 0.732$	
3.	6	Octahedral	$0.414 \leq \frac{r_+}{r_-} < 0.732$	$NaCl, MgO, KCl$
4.	8	Octahedral	$0.732 \leq \frac{r_+}{r_-} < 1$	$CsCl$

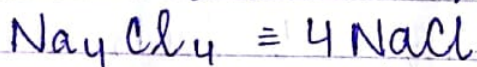
Type of Ionic Crystal :-

Rock Salt str. (NaCl type)

anions \rightarrow FCC arrangement

cations \rightarrow Octahedral voids

In a unit cell there are 4 anions & 4 cations

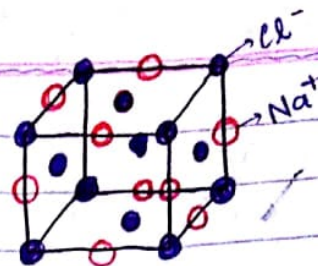


There are 4 formula units in a unit cell, i.e. $Z = 4$



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

$$d = \frac{4 \times M_{NaCl}}{N_A \times a^3}$$



C.N. of cation = 6

C.N. of anion = 6

Touching condⁿ : $2r_{Na^+} + 2r_{Cl^-} = a$

$$r_{Na^+} + r_{Cl^-} = \frac{a}{2}$$

Packing efficiency :-

$$P.E. = \frac{Z_+ \times \frac{4}{3} \pi r_+^3 + Z_- \times \frac{4}{3} \pi r_-^3}{a^3} \times 100$$

$$Z_+ = Z_- = 4$$

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

$$= \frac{4 \times \frac{4}{3} \pi}{3} \left[\frac{r_+^3 + r_-^3}{a^3} \right] \times 100$$

$$= \frac{4 \times \frac{4}{3} \pi r_-^3}{a^3} \times 100 \left[\left(\frac{r_+}{r_-} \right)^3 + 1 \right]$$

$$= 74 \times \left[(0.414)^3 + 1 \right]$$

$$P.E. = 79.25 \%$$

eg halides of Li, Na, K, Rb.

Oxides & Sulphides of alkaline earth metal.

Sphalerite Type (ZnS type)

$S^{2-} \rightarrow$ at CP&P arrangement i.e. FCC

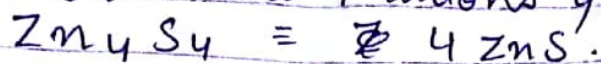
$Zn^{2+} \rightarrow$ at alternate Tetrahedral Voids

or

50% of Tetrahedral Void



There are 4 anions & 4 cations in unit cell.



There are 4 formula units in a unit cell i.e. Z=4

$$d = \frac{4 \times M}{N_A \times a^3}$$

C.N. of cation = 4

C.N. of anion = 4

Touching condⁿ $r_+ + r_- = \frac{\sqrt{3}a}{4}$

$$\text{P.E.} = \frac{4 \times \frac{4}{3} \pi r_+^3 + 4 \times \frac{4}{3} \pi r_-^3}{a^3} \times 100$$

$$= \frac{4 \times \frac{4}{3} \pi r_-^3}{a^3} \times 100 \left[\left(\frac{r_+}{r_-} \right)^3 + 1 \right]$$

$$\text{P.E.} = 74 \times \left[(0.225)^3 + 1 \right]$$

$$\text{P.E.} = \text{74.84\%}$$

P.E. of anion = 74%

P.E. of cation = 0.84%

eg BeO, BeS, CaO, AgI, CuCl, CuBr, CuI.

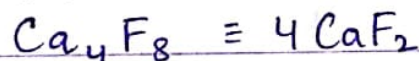
Fluorite Type CaF_2 :-

Size of cation is greater than size of anion.

Cations \rightarrow CCP arrangement i.e. FCC

anion \rightarrow THV

* There are 4 cations & 8 anions in one unit cell.



There are 4 formula unit in a unit cell
 $Z=4$

$$d = \frac{4 \times M}{N_A \times a^3}$$

C.N. of cation = 8

C.N. of anion = 8 ~~2~~ 4

Touching condⁿ $\Rightarrow r_+ + r_- = \frac{\sqrt{3}a}{4}$



$$P.E. = \frac{4 \times \frac{4}{3} \pi r_+^3 + 8 \times \frac{4}{3} \pi r_-^3}{a^3} \times 100$$

$$P.E. = \frac{4 \times \frac{4}{3} \pi r_+^3}{a^3} \left[1 + 2 \left(\frac{r_-}{r_+} \right)^3 \right]$$

$$P.E. = 74\% \times [1 + 2(0.225)^3]$$

$$P.E. = 75.68\%$$

CaF_2 , CaCl_2

SrF_2 , SrCl_2

BaF_2 , BaCl_2

Antifluorite Type Na_2O

anion \rightarrow CCP i.e. FCC

cation \rightarrow THV

There are 8 cations & 4 anions in a unit cell



There are 4 formula units per unit cell i.e. $Z=4$

$$d = \frac{4 \times M}{N_A \times a^3}$$

C.N. of cation = 4

C.N. of anion = 8

Touching condⁿ $r_+ + r_- = \frac{\sqrt{3}a}{4}$

$$P.E. = \frac{8 \times \frac{4}{3} \pi r_+^3 + 4 \times \frac{4}{3} \pi r_-^3}{a^3} \times 100$$

$$= \frac{4 \times \frac{4}{3} \pi r_-^3 \times 100}{a^3} \left[2 \left(\frac{r_+}{r_-} \right)^3 + 1 \right]$$

$$= 74 \times [2(0.225)^3 + 1]$$

$$P.E. = 75.68\%$$

$$\text{Anion} = 74\%$$

$$\text{Cation} = 1.68\%$$

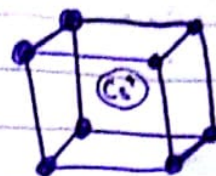


CsCl type $\therefore 1:1$ -type

$\text{Cs}^+ \rightarrow \text{B.C.}$

$\text{Cl}^- \rightarrow \text{SCC}$

There are 1 cation & 1 anion per unit cell. CsCl



There is only 1 formula unit in unit cell $z=1$

$$d = \frac{1 \times M}{N_A \times a^3}$$

$$N_A \times a^3$$

$$\text{C.N. of } \text{Cs}^+ = 8$$

$$\text{C.N. of } \text{Cl}^- = 8$$

Touching condition

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

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

$$\text{P.E.} = 1 \times \frac{4}{3} \pi r_+^3 + 1 \times \frac{4}{3} \pi r_-^3 \times 100$$

$$= \frac{\frac{4}{3} \pi r_-^3 \left[\left(\frac{r_+}{r_-} \right)^3 + 1 \right] \times 100}{a^3}$$

$$= \frac{\frac{4}{3} \pi r_-^3}{a^3} \times 100 \left[(0.732)^3 + 1 \right]$$

\downarrow
52.4

$$\text{P.E.} = 72.95 \%$$

Defect in Crystals \therefore

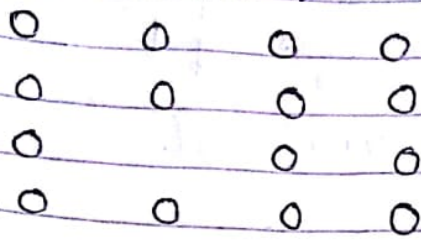
Defect in Ionic Crystal are arisen due to missing ions or in lattices or dislocation of ions in lattices.

Reasons:

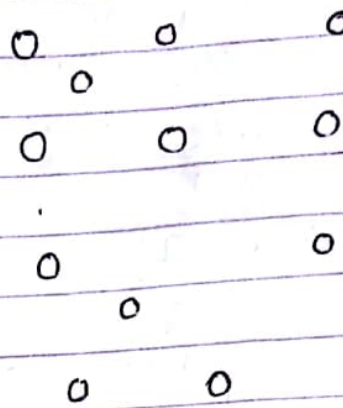
1. Vibration in solid
2. Increase in temp.



Missing of ions generate vacancy defect.
 Dislocation of ions generate interstitial defect.

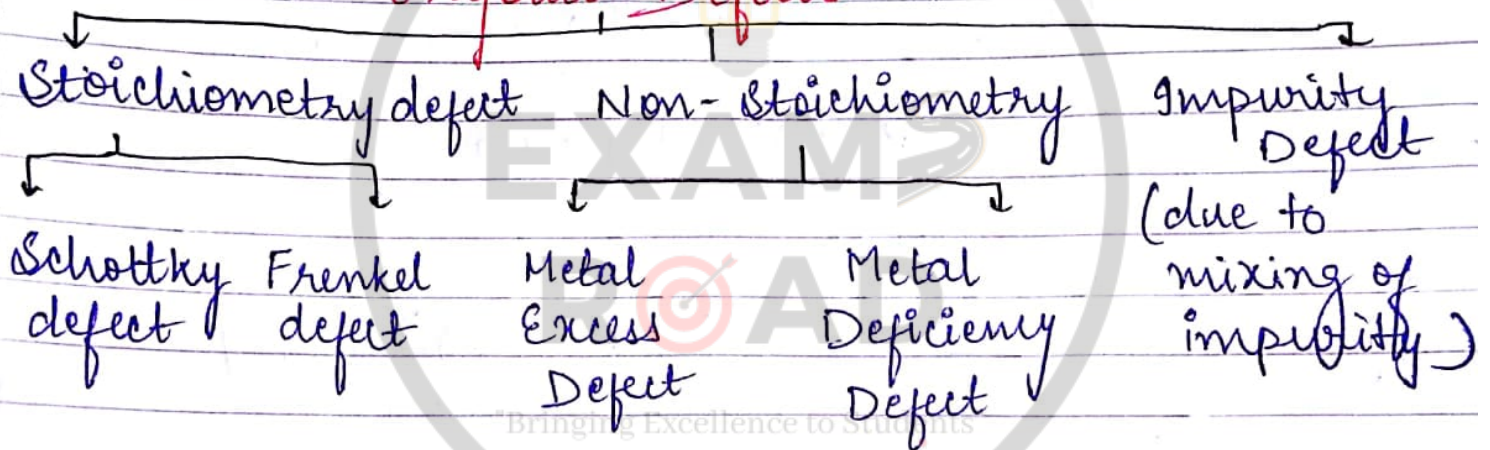


Vacancy defect



Interstitial Defect

Crystal Defects



Stoichiometry Defect: In this defect, stoichiometry of crystal remains same.

Schottky Defect: Found in crystals in which have

1. ~~big~~ C.N. is high.
2. Difference in size of cation or anion is not large.

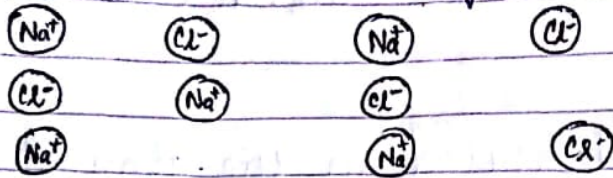
Example \rightarrow NaCl, CsCl, KCl, AgBr.

\rightarrow Schottky defect is observed when equal no. of cation & anion leave the crystal lattices.



Result :-

- Solid/crystal remains electrically Neutral
 - Density of solid \downarrow i.e.
- It is kind of vacancy defect.



Frenkel Defect :- Found in solids in which

- C.N. is low.
 - Difference in size of cation & anion is large.
- Example ZnS, AgBr, AgI, AgCl

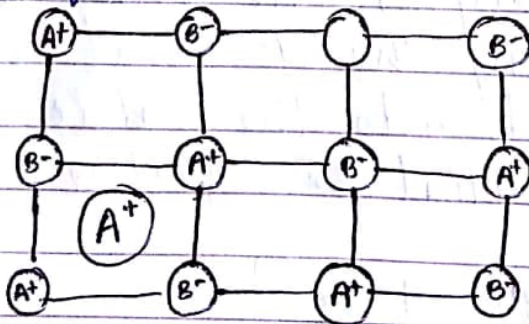
Note AgBr shows both defect Schottky & Frenkel defect.

Result :- In this type of defect, ^{ion} (mainly cation) leaves its actual site & occupies interstitial sites of lattice.

Result :-

- Solid Remains electrically Neutral
- Density remains same.

It is kind of interstitial defect or dislocation effect



Non-stoichiometry Defect :-

In which stoichiometry of crystal change.
There are 2 types of non-stoichiometry defect.

Metal Excess Defect :- due to anionic vacancy.
eg NaCl, KCl.

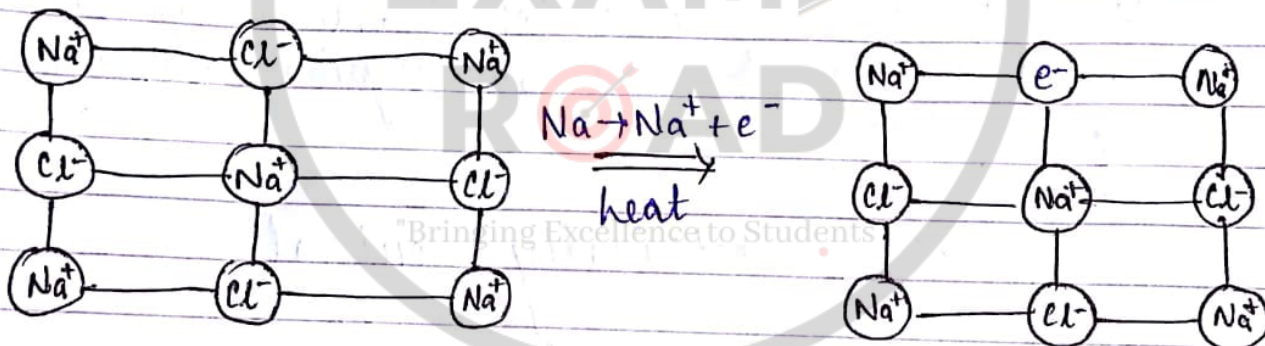
When NaCl_{solid} is heated in the atmosphere of Na then some Cl⁻ leaves the lattices & for maintaining the electrical neutrality hole is occupied by e⁻ & this is c/a F-centre.

F-Centre \Rightarrow Farbenzenter
↳ color

NaCl \rightarrow Yellow

KCl \rightarrow Violet

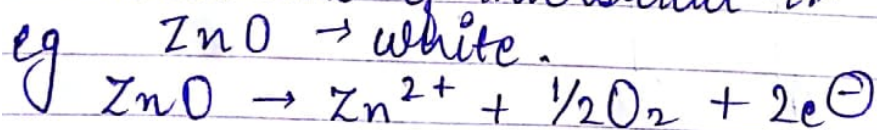
LiCl \rightarrow Pink



Metal excess defect due to interstitial cations :-

~~In this~~ In this defects, cations are doped into the lattice & it occupies the interstitial sites of lattice for maintaining the electrical neutrality. e⁻ are also doped into the lattice and it occupies other site of interstitial to lattice.

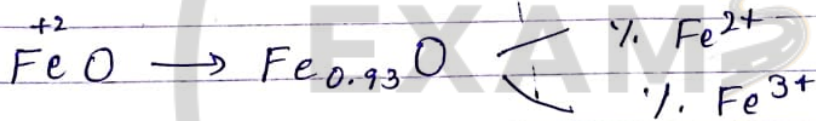
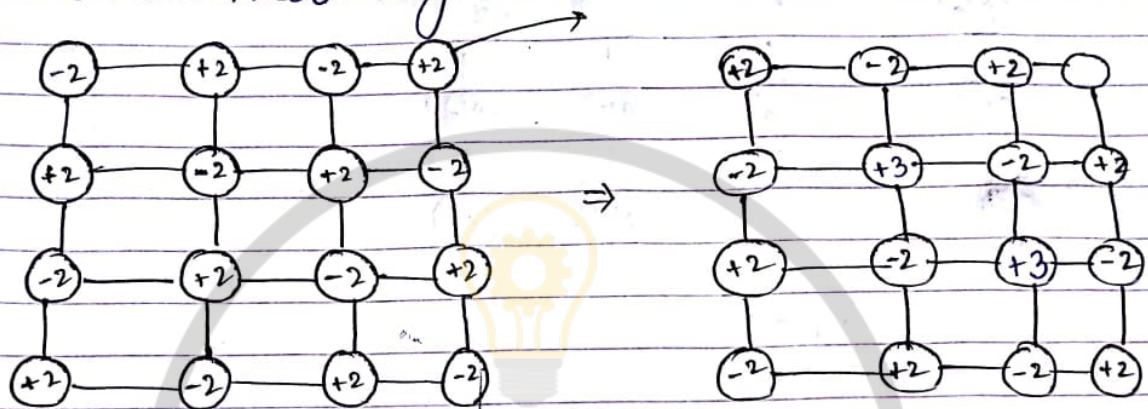
eg ZnO \rightarrow white.



Metal Deficiency Defect: Found in transition metal compd.

- In this type of defect, some metal of lower oxidation state leaves the site for maintaining the electrical neutrality.

Metal ion of lower ~~or~~ Oxidation State is converted into Higher O.S.



0.07 Fe^{2+} leaves site

Loss of 1 Fe^{2+} ion generate \Rightarrow 2 Fe^{3+} ions

So 0.07 Fe^{2+} will generate $= 2 \times 0.07 = 0.14 Fe^{3+}$ ions

$$\% Fe^{3+} = \frac{0.14}{0.93} \times 100$$

$$\% Fe^{2+} = 100 - \% of Fe^{3+}$$

or

$$Fe^{3+} \rightarrow x$$

$$Fe^{2+} \rightarrow 0.93 - x$$

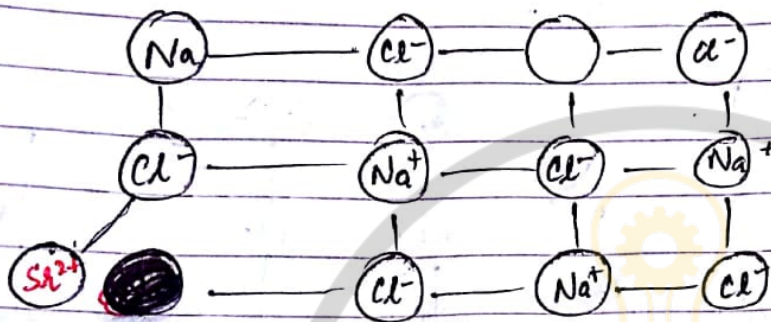
$$3x + 2(0.93 - x) - 2 = 0$$

$$x = 0.14$$

Impurity Defect:-

When small amt. of SrCl_2 is +nt in NaCl
impurity

2 Na^+ ions leaves site
1 Sr^{2+} occupy one site of Na^+ while other remains
vacant, it is k/n as impurity defect.



density ↓ bc.

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