

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 Nature	Anisotropic in nature True solids	Isotropic in nature. 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
1. Molecular solids	Molecules	(i) Dispersion or London forces (ii) Dipole-Dipole (iii) Hydrogen bonding (iv) Coulombic or electrostatic	Air, CCl ₄ , H ₂ , I ₂ , CO ₂ HCl, SO ₂ H ₂ O (ice) NaCl, MgO, ZnS, CaF ₂	Soft Soft Hard Hard but brittle	Insulator Insulator Insulator Insulator in solid but conductor in molten & aq. soln	very low low low High
2. Ionic solids	Ions					
3. Metallic Solid	+ve ions in a sea of delocalised e ⁻	Metallic Bonding	Fe, Cu, Ag, Mg	Hard but malleable & ductile	Conductor in solid as well as in molten state	Fairly high
4. Covalent or network Solids	Atoms	Covalent Bonding	SiO ₂ (quartz), SiC, C (diamond), AlN, C (graphite) → soft	Hard	Insulator Conductor (exception)	very high

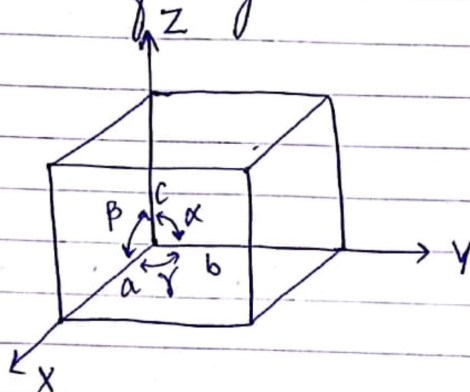
Crystal Lattice / space Lattice / 3-D Lattice :-

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 & bc, ca & ab .



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.

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

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

XY_3

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

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

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

XY_3

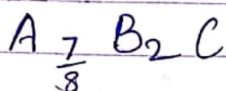
Ques .

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.

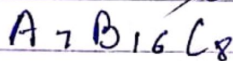
$$A \rightarrow \text{corner} \rightarrow \frac{1}{8} \times 8 = 1 - \frac{1}{8} = \frac{7}{8}$$

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

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



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



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

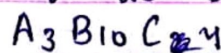
of face centre are removed

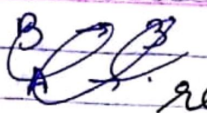
$$B \rightarrow 3 - \frac{1}{2} = \frac{5}{2}$$

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

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

$$A : B : C = \frac{6 \times 8}{8} : \frac{5 \times 8}{2} : \frac{1 \times 8}{2} \Rightarrow A_6 B_{20} C_4$$

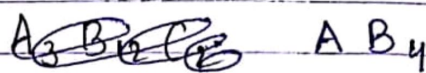
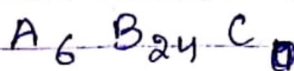


② If  all atoms along one body diagonal are removed.

$$B \rightarrow 3$$

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

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

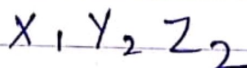


Q.5 A solid consists of X, Y & Z type of atoms. If X occupies alternate corners of cube. Y " " " face centre " " Z " " " edge centre " "

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

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

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



Then find mol. formula of solid

Type of Unit Cell :-

① Primitive / simple Cubic Unit cell :-

Lattice Point : at corners of cube

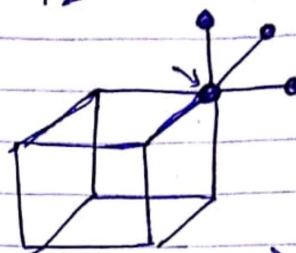
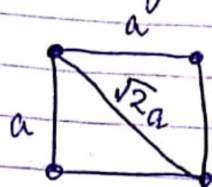
$$Z = \text{no. of eff. particles in unit cell} \\ = 8 \times \frac{1}{8}$$

$$Z = 1$$

Coordination No. : no. of nearest neighbour particles around a specific particle in a crystal lattice i.e. C.N.

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

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

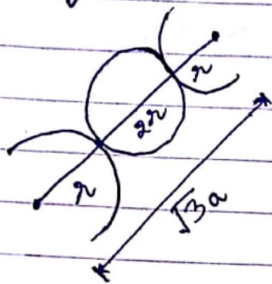
$$P.E. = \frac{Z \times \frac{4}{3} \pi r^3}{a^3} = \frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = \frac{\pi}{6} = 0.524 \text{ or } 52.4\%$$

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

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

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

Touching condⁿ



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

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

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

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

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

→ 1 face is shared by 2 cubes

$$= 12$$

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

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

$$= \frac{2 \times \frac{4}{3} \pi r^3}{\frac{64}{3\sqrt{3}} r^3} = \frac{\sqrt{3} \pi}{8}$$

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

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

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

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

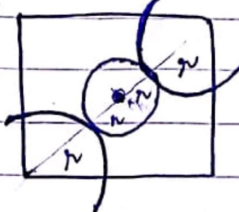
3.) F.C.C. :-

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. :

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

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

$$\text{Nearest Neighbours} = 12 \quad \left(\begin{array}{l} \text{4 corner + 8 face centre} \\ \text{distance} = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}} \end{array} \right)$$

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

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

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

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

AIPMT 2015

NCERT 4.3, 4.4, 4.5
1.18, 1.16.

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

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

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

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

Ex. 2(A)

ex 21

F.C.C.

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

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

$$r = 204 \times 1.4 =$$

$$288$$

Q. 26

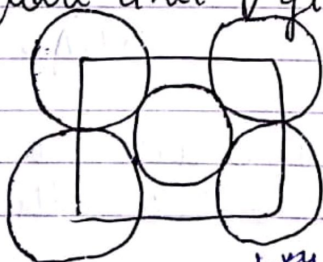
$$\sqrt{2}a = 4r$$

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

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

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

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



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

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

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

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

- ① 54.2% ② 68.4% ③ 74.03% ④ 78.04%

$$Z = 2$$

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

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

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

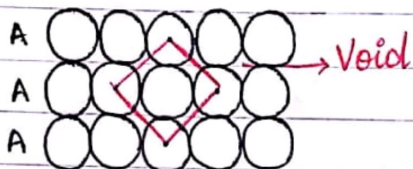
$$= \frac{2 \times \pi r^2}{a^2} = \frac{2 \pi r^2}{(2\sqrt{2}r)^2}$$

Closed Packed structure :-

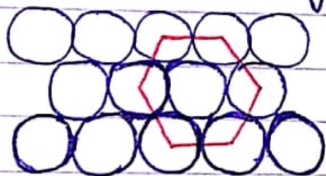
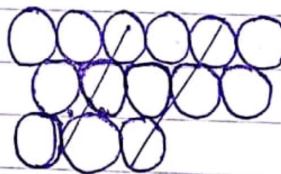
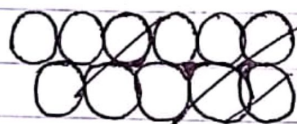
1. Closed Packed in 1-D :-



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 2D Square close Packing :-
2-D square unit one over each other
↓
form SCC

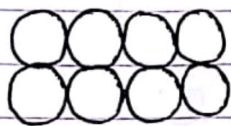
3-D Close Packing from 2-D hexagonal close packing :-

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

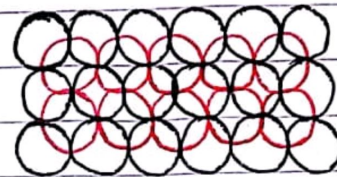
Tetrahedral = $2N$

Octahedral = N

Square layer over each other

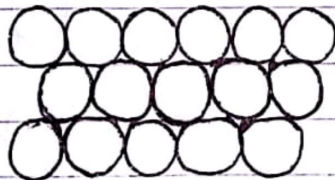
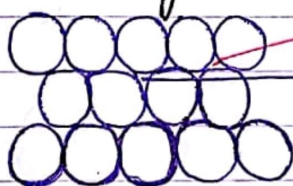


scc



B.C.C.

© 3-D Close Packing in multi layer



Third layer can be placed in 2 ways

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

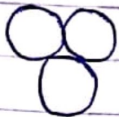
it represent cubic closed Packed [CCP] arrangement
or FCC arrangement

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

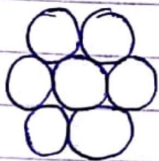
Hexagonal close Packing [HCP]



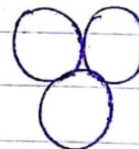
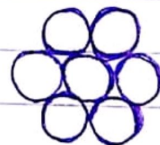
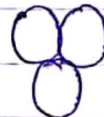
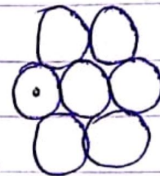
C



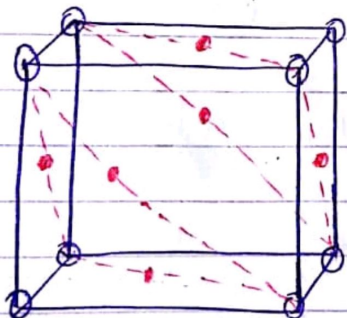
B

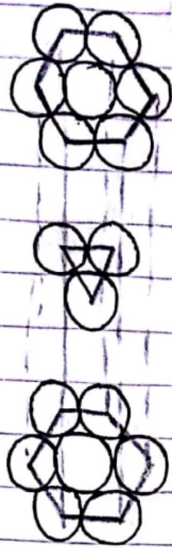


A



CCP or FCC





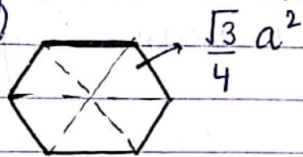
$$Z = 12 \times \frac{1}{6} + 3 + 2 \times \frac{1}{2} = \underline{6}$$

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

Touching condⁿ :- $a = 2r$

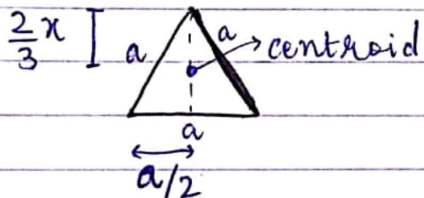
$$d = \frac{Z \times M}{N_A \times \text{Vol. of unit cell}}$$

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



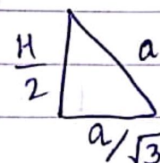
$$\text{Area of base} = 6 \times \frac{\sqrt{3}}{4} a^2$$

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



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

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



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

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

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

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

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

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

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

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

Type of Voids :-

Tetrahedral Voids :-

→ It is triangular void surrounded by 4 spheres.

→ Hence its C.N. is 4



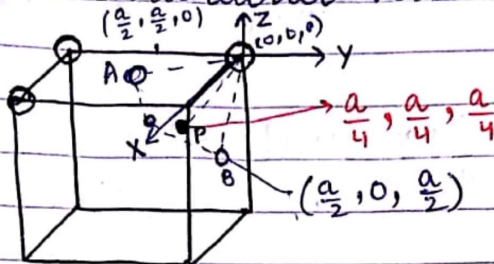
Posⁿ of tetrahedral void in F.C.C. :-

In F.C.C., one corner atom & 3 face centre atom formed a tetrahedral void. so 2 tetrahedral voids are formed are of 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 A $(a/2, a/2, 0)$

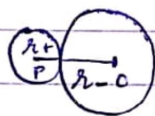
face central atom B $(a/2, 0, a/2)$

C $(0, a/2, a/2)$

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

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

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



anion at corner
cation at voids

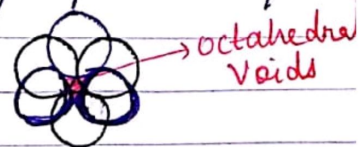
$$r_+ + r_- = \frac{\sqrt{3} a}{4}$$

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

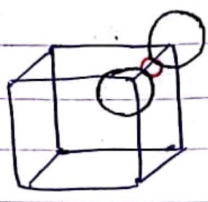
$$\text{No. of atoms in fcc unit cell} = N = 4$$

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

Touching Condⁿ

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

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



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

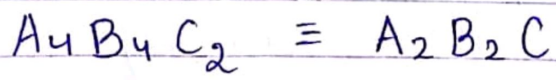
$$\text{Atom A} \rightarrow \text{FCC} \rightarrow \frac{1}{8} \times 8 + \frac{1}{2} \times 6$$

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

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

$$\text{Atom C} \rightarrow 25\% \text{ of Tetrahedral Void} = \frac{25}{100} \times 8 \times 2$$

$$= 2 \text{ atoms of C}$$



Limiting Radius Ratio :-

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

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

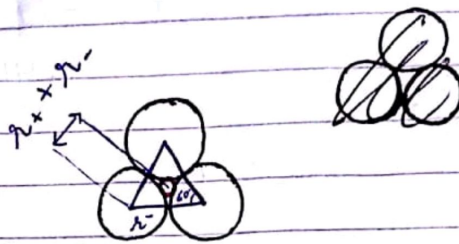
Triangular Void

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

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

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

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



Range of triangular void

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

C.N. = 4 — Tetrahedral
Square

Tetrahedral : Anion - F.C.C.

$$4r_- = \sqrt{3} \sqrt{2} a \quad \text{--- (1)}$$

cation → Tetrahedral void

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

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

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

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

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

$$\frac{r^+}{r_-} = 0.225$$

Range for tetrahedral void

$$0.225 \leq \frac{r_+}{r_-} < 0.414$$

Square :-

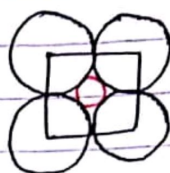
$$2r_- = a \quad \text{--- (1)}$$

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

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

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

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



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

Octahedral void at edge centre C.N. = 6

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

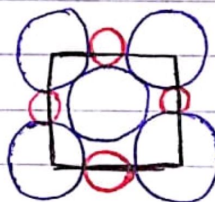
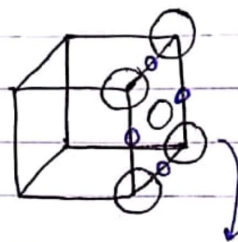
$$2r_+ + 2r_- = a \quad \text{--- (2)}$$

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

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

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

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



Range for Octahedral void at edge centre

$$0.414 \leq \frac{r_+}{r_-} < 0.732$$

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

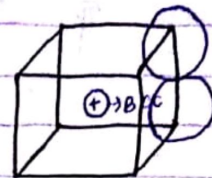
$$2r_- = a \quad \text{--- (1) at s.c.c.}$$

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

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

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

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



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

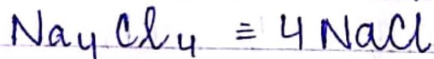
Type of Ionic Crystal :-

Rock Salt Str. (NaCl type)

anions \rightarrow FCC arrangement

cations \rightarrow Octahedral voids

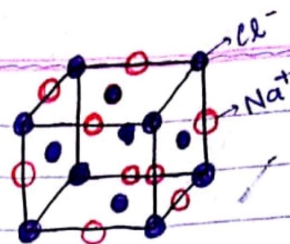
In a unit cell there are 4 anions & 4 cations



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

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

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



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

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

$$\text{Touching cond}^n : 2r_{Na^+} + 2r_{Cl^-} = a$$

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

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.
 $Zn_4S_4 \equiv 4 ZnS$.

There are **4** formula units in a unit cells 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 $r_+ + r_- = \frac{\sqrt{3}a}{4}$

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

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

$$P.E. = 74 \times \left[(0.2225)^3 + 1 \right]$$

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

P.E. of anion = 74%

P.E. of cation = 0.84%

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

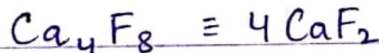
Fluorite Type CaF_2 :-

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~~ 4

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

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

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

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

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

CaF₂, CaCl₂

SrF₂, SrCl₂

BaF₂, BaCl₂

Antifluorite Type Na₂O

anion → CCP i.e. FCC

cation → THV

There are 8 cations & 4 anions in a unit cell
Na₈O₄ = 4Na₂O

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

$$\# \text{ Touching cond}^n \quad r_+ + r_- = \frac{\sqrt{3}a}{4}$$

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

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

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

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

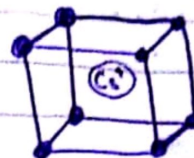
Anion = 74%
Cation = 1.68%

CsCl type \therefore 1:1 type

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

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

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 condⁿ $2r_+ + 2r_- = \sqrt{3}a$

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

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

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

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

$\rightarrow 52.4$

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

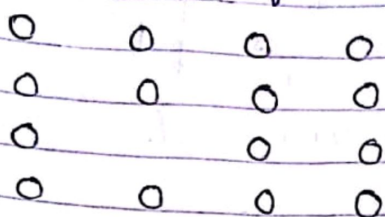
Defect in Crystals \therefore

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

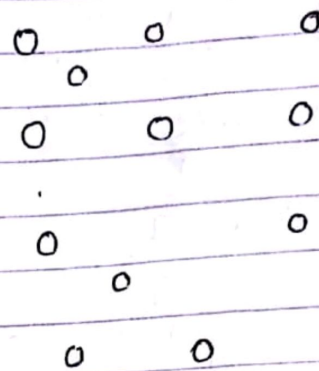
Reasons:

1. Vibration in solid
2. Increase in temp.

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

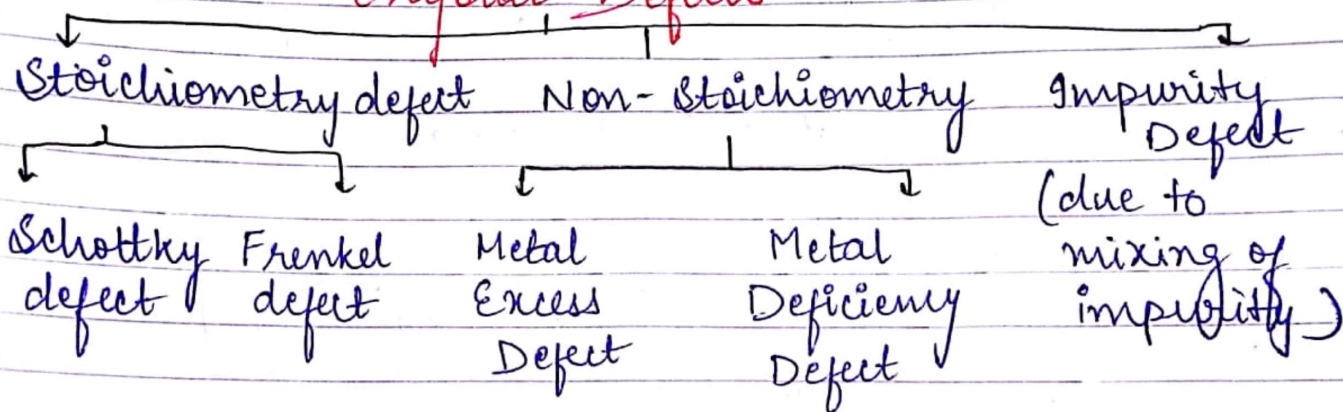


Vacancy defect



Interstitial Defect

Crystal Defects



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

Schottky Defect: Found in crystals ⁱⁿ which have

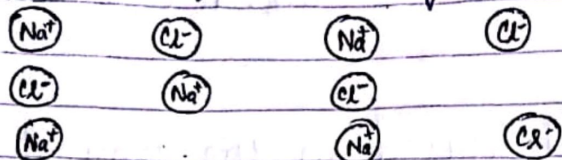
1. ~~big~~ C.N. is high.
2. Difference in size of cation or anion is not large.

Example \rightarrow NaCl, CsCl, KCl, AgBr.

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

Result :-

- Solid/crystal remains electrically Neutral
 - Density of solid ↓ 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

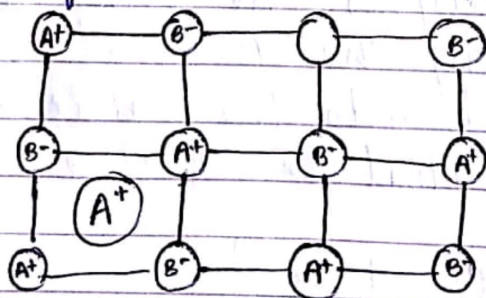
Note AgBr shows both defect Schottky & Frenkel defect.

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.

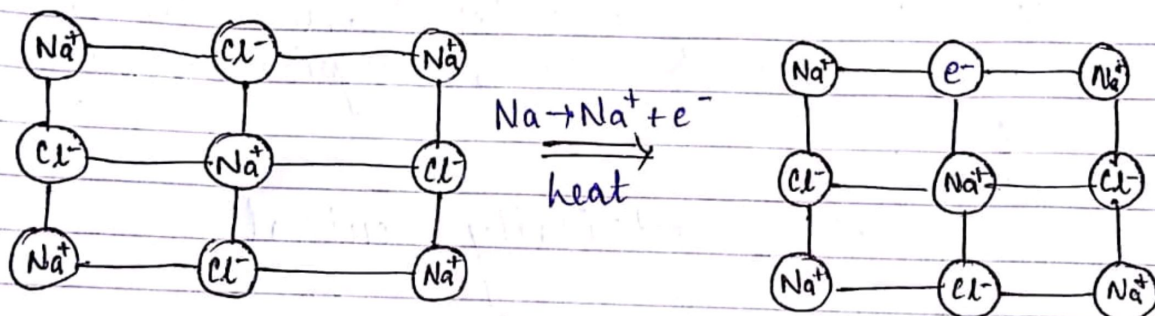
When NaCl_s is ^{solid} heated in the atmosphere of Na then some Cl⁻ leaves the lattices & for maintaining the electrical neutrality hole is occupied by e⁻ & this is c/a F-centre.

F-Centre \Rightarrow Farbenzenter
 \hookrightarrow color

NaCl \rightarrow Yellow

KCl \rightarrow Violet

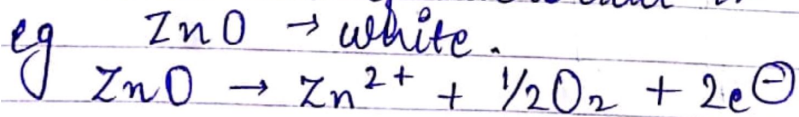
LiCl \rightarrow Pink



Metal excess defect due to interstitial cations :-

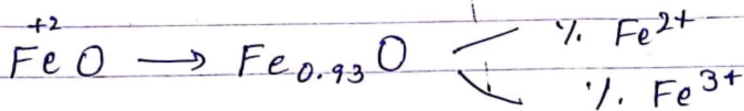
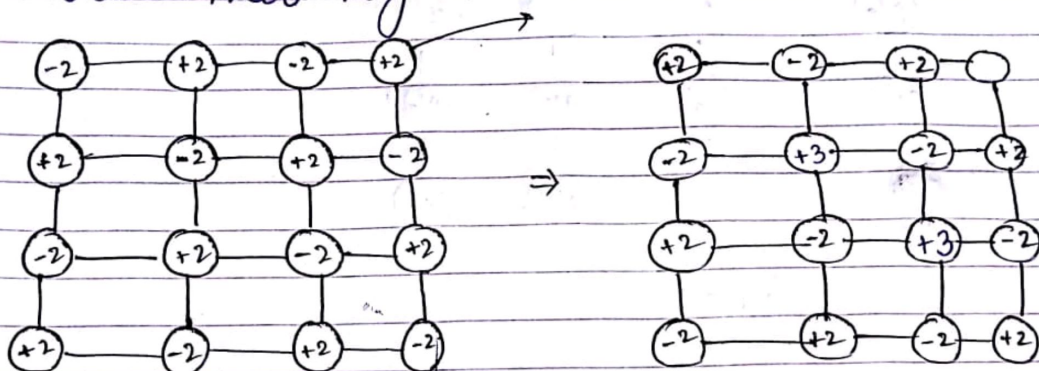
~~In this~~ In this defects, cations are doped into the lattice & it occupies the interstitial sites of lattice for maintaining the electrical neutrality. e⁻ are also doped into the lattice and it occupies other site of interstitial to lattice.

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 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

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

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

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

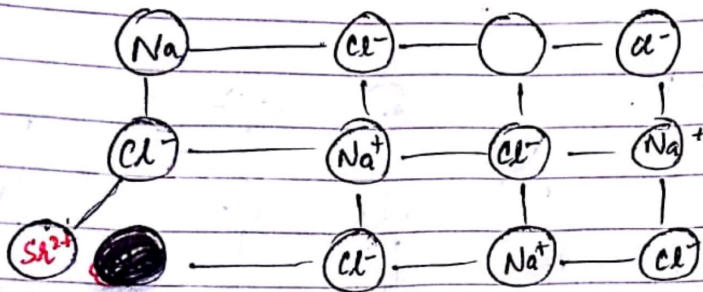
$$x = 0.14$$

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 \downarrow bc.