Solid State

Characterstics 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 pos^{n} and can only oscillate about their mean pos^{n}s.
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
Anisotrophy	Anisotropic in nature	Isotropic in nature.
Nature	True solids	Pseudo solids or super cooled liq.
Order in arrangement of constituent particles	Longe range order	Only short range order

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Classification of Crystalline solid :-

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Example	Physical Nature	Electrical Conductivity	Melting Point
1. Molecular solids (i) Non-Polar	Molecules	(i) Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	very low
(ii) Polar		(ii) Dipole-Dipole	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bond		(iii) Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
2. Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulator in solid but conductor in molten & aq. soln	High
3. Metallic Solid	+ve ions in a sea of delocalised $e^{\ominus}$	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,	Hard	Insulator	Very high
			C (graphite) → soft		Conductor (exception)	

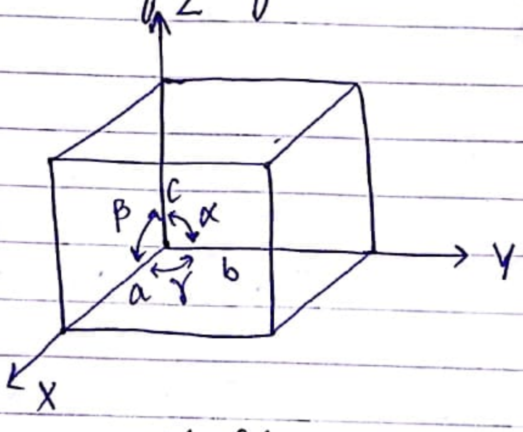
Crystal Lattice / Space Lattice / 3-D Lattice :-

3-D arrangement of constituent particle in space is c/a 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 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 bc, ca & ab.



Unit Cell

- Primitive: When constituent particle are +nt at only corner of cube
- Centred unit cell
  - B.C. → Corner of cube & centre of cube
  - F.C.: corner of cube & face centre
  - End centre: corner of cube & at any 2 opp. face

Cube :-

Corner → 8
Face → 6
Edge = 12
Body Centre = 1
~~Face dia~~ Body Diagonal = 4
Face " = ~~6~~ 2 × 6 = 12

→ There are 8 corners in cube and 1 corner is common ~~in~~ for 8 cube.
→ Its contribution in its own cube is 1/8.
→ A cube has 6 faces & one face is common for 2 cube.
• Its contribution in its own cube is 1/2.
→ A cube has 12 edges & one edge is common for 4 cube
• Its contribution in its own cube is 1/4.

→ ~~Body~~ There is one body centre in cube & no contribution to other cube

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

X → ~~atom~~ corner → $\frac{1}{8} \times 8 = 1$ atom
Y → face centre → $\frac{1}{2} \times 6 = 3$

XY_3

Ques find molecular formular of solid If X occupies corner of cube & Y occupies edge centre of cube.

X → corner → $\frac{1}{8} \times 8 = 1$
Y → edger centre → $\frac{1}{4} \times 12 = 3$

XY_3

Qus .

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

A → Corner → $\frac{1}{8} \times 8 = 1 - \frac{1}{8} = \frac{7}{8}$

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

C → body centre → 1

$A_{\frac{7}{8}} B_2 C$

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

$A_7 B_{16} C_8$

Qus A solid is consist of A, B & C type ~~atom~~ elements. A occupies corner of cube, B occupies face centre & C occupies Body centre. Find mol. formula of solid if –

A → corner → $\frac{1}{8} \times 8 = 1$

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

C → 1

(1) If all atoms along a diagonal passing through 2 corners & face centre are removed

B → $3 - \frac{1}{2} = \frac{5}{2}$

A → $1 - \frac{2}{8} = \frac{6}{8}$

C → 1

A : B : C = $\frac{6 \times 8}{8}$: $\frac{5 \times 8}{2}$: 1×8 ⇒ $A_6 B_{20} C_8$

$A_3 B_{10} C_4$

(2) If ~~B~~ ~~C~~ all atoms along one body diagonal removed.

B → 3

A → $\frac{6}{8}$ $\qquad A_6 B_{24} C_0$

C → ~~2~~ 0 $\qquad$ ~~$A_3B_{12}C_2$~~ $\; AB_4$

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 " "
Then find mol. formula of solid

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

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

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

~~$X Y_3 Z_3$~~ $\quad X_1 Y_2 Z_2$

Type of Unit Cell :-

(1) Primitive / simple Cubic Unit cell :-

Lattice Point : at corners of cube

Z = no. of eff. particles in unit cell

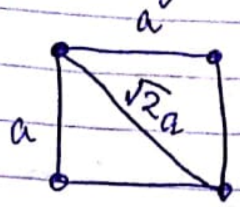
$= 8 \times \frac{1}{8}$

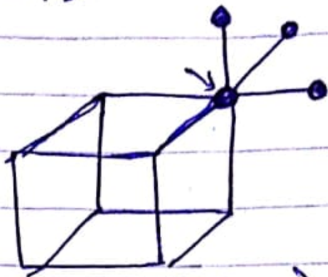
$Z = 1$

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

C.N. of S.C.C. = 6

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



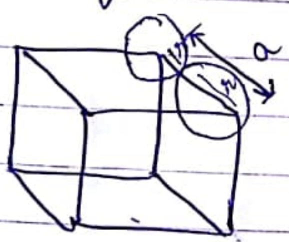


(distance = $\sqrt{2}\,a$)
1 Face → 3 next nearest
Total cube attached = 8
2 cube share common face

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

Touching cond^n

$a = 2r$



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

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

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

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

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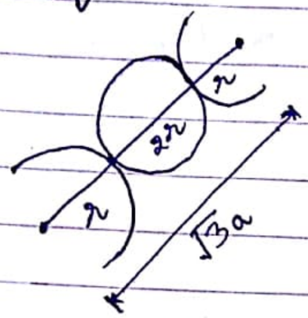
② Body Centre Cube :-

Lattice Point :- at corner & Body centre

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

Touching cond^n



$a = 2r$ ✗

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

$\sqrt{3}a = 4r$

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

$= \frac{8 \times 3}{2}$ — corner atom shared in 8 cubes; 3 → in a unit cell a distance $\sqrt{2}a$ (face); 2 → 1 face is shared by 2 cubes

$= 12$

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

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

$= 0.68$ or 68%

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

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

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

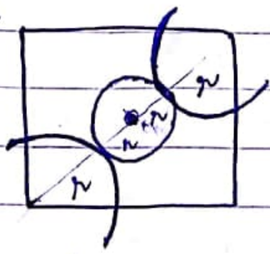
3.) F.C.C. :-

Lattice Point :- at corner & face centre

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

Touching Cond^n :

Face



$\sqrt{2} a = 4r$

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

In F.C.C. corner atom does not touch each other

C.N. :

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

C.N. w.r.t. to face centred atom $= 12$ ↑

(4 corner + 8 face centre)

Nearest Neighbours $= 12$ (distance $= \frac{\sqrt{2} a}{2} = \frac{a}{\sqrt{2}}$)

next nearest neighbour $= 6$ (distance $= a$)

$(next)^2$ " " $= \frac{8 \times 3}{1}$ (" $= \sqrt{\frac{3}{2}}\, a$)

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

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

AIPMT 2015 NCERT 4.3, 4.4, 4.5
1.18, ~~1.16~~.

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

$P.E. = 0.74$ or 74%

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

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

Ex. 2(A)
ex 21 F.C.C.

$\sqrt{2}a = 4r$

$\sqrt{2} \times \frac{408}{204} = 4r$

$r = 204 \times 1.4 =$

$2r$

Q.26

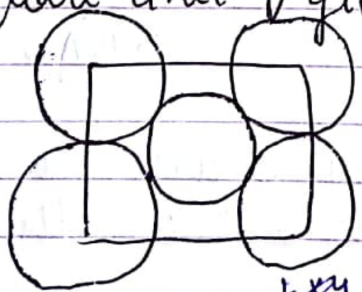
$\sqrt{2}a = 4r$

$\sqrt{2} \times \frac{404}{101} = 4r$

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

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

Q.28 Ques find Packing efficiency of 2-dimensional square unit give below



1×1

$4r = \sqrt{2}a$

$a = 2\sqrt{2}r$

~~$\frac{2 \times \frac{4}{3} \pi r^3}{4 \times 2 r^3} = \frac{\pi}{6}$~~

~~$\frac{1}{8} \times 4 = \frac{1}{2}$~~

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① 54.2 % ② 68.4 % ③ 74.03 % ④ 78.04 %

$Z = 2$

$\sqrt{2}a = 4r$

$a = 2\sqrt{2}r$

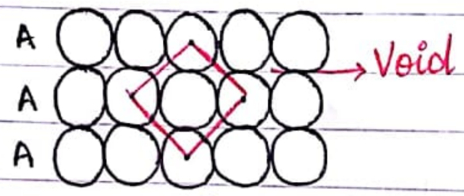
$$P.E. = \frac{Z \times \text{area of one square}}{\text{area of Unit Cell}}$$

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

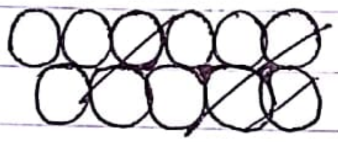
Closed Packed structure :-

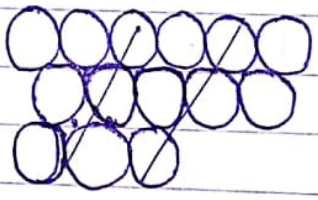
1. Closed Packed in 1-D :-

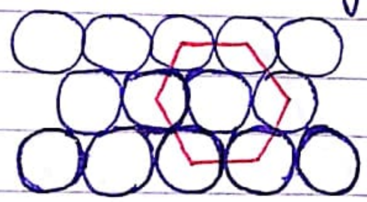
2. Closed Packed in 2-D :-



Square close Packing
AA - - - type







Hexagonal Close Packing
ABAB - - - type.

3. Closed Packing in 3D :-

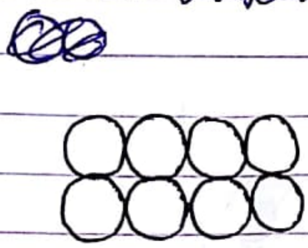
(i) 3-D close Packing from 2D square close Packing :-

2-D square Unit one over each other form SCC

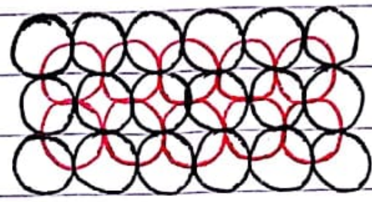
3-D Close Packing from 2-D hexagonal close packing :-

If no. of atom in unit cell = N
(Closed Packed Sphere)
Tetrahedral = 2N
Octahederal = N

Square layer over each other

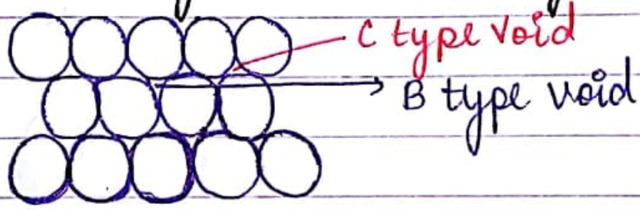


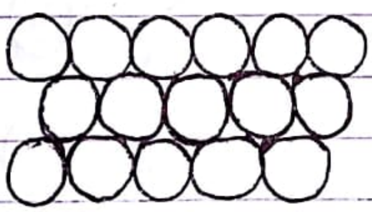
SCC



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

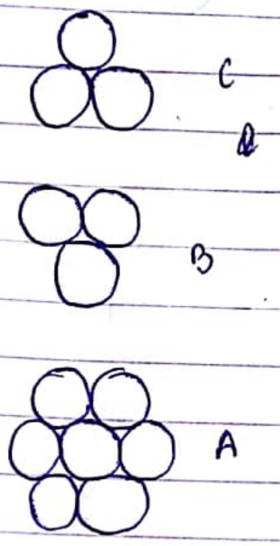
⇓

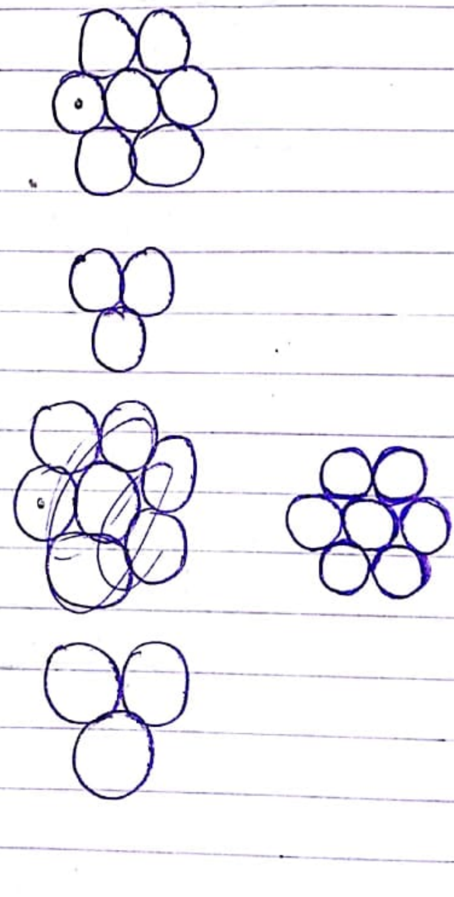
or FCC arrangement

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

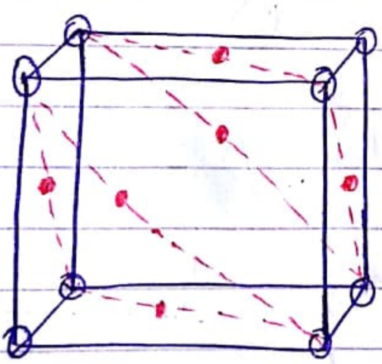
↓

Hexagonal close Packing [HCP]





CCP or FCC



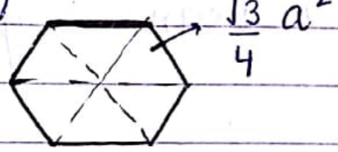
$$Z = 12 \times \frac{1}{6} + 3 + 2 \times \frac{1}{2} = 6$$

C.N. = 12

Touching Cond^n :- $a = 2r$

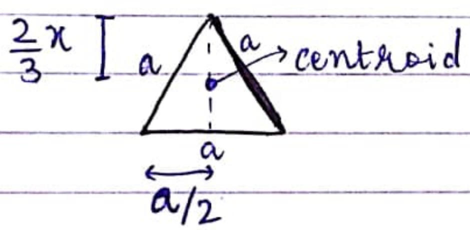
$$d = \frac{Z \times M/N_A}{\text{Vol. of unit cell}}$$

Vol. of unit cell = H × area of base



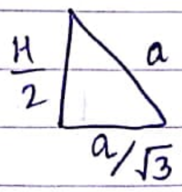
Area of base $= 6 \times \frac{\sqrt{3}}{4} a^2$

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



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

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



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

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

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

Vol[m] of unit cell = H × area of base

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

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

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

$$= \frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}\,r^3}$$

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

0.74 or 74 %

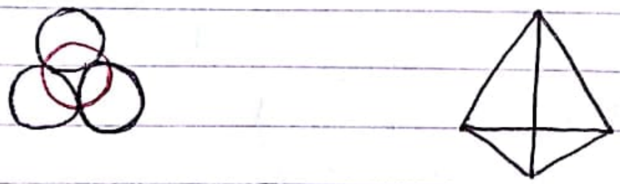
∴ % Void = 26 %. IIT-2008

Type of Voids :-

Tetrahedral Voids :-

→ It is triangular ~~op~~ void surrounded by 4 spheres.

→ Hence its C.N. is 4



Pos[n] of tetrahedral void in F.C.C. :-

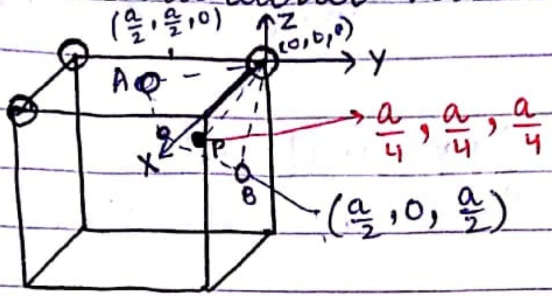
In F.C.C., one corner atom & 3 face centre atom formed a tetrahedral void so 2 tetrahedral voids are formed, are at body diagonal of FCC

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 $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$

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

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

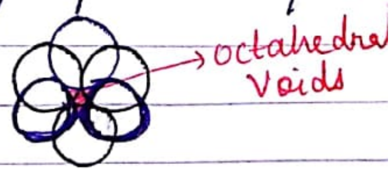
anion at corner
cation at voids

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

Octahedral Voids :-

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

C.N. → 6



Posn of Octahedral Voids in FCC Lattice :-

Body centre & edge centre

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

$= 1 + 3 = 4$

↑ Body centre ↑ edge centre

or

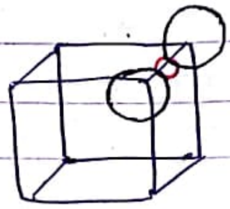
No. of atoms in fcc unit cell $= N = 4$

No. of octahedral voids $= N = 4$

Touching Condn

$2r_+ + 2r_- = a$

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



Ques Atom A is present 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.

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

$= 4$ atoms.

Atom B → Octahedral Void $= 4$ atoms

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

$= 2$ atoms of C

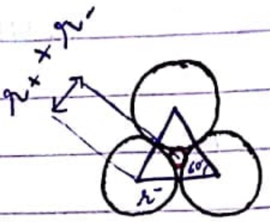
$A_4B_4C_2 \equiv A_2B_2C$

Limiting Radius Ratio :-

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

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.

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

cation → Tetrahedral void

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

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

2/1
$$\frac{4r_+ + 4r_-}{4r_-} = \frac{\sqrt{3}}{\sqrt{2}}$$

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

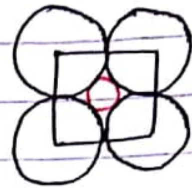
$$\frac{r_+}{r_-} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}}$$

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

Range for tetrahedral Void

$$0.225 \leq \frac{r^+}{r^-} < 0.414$$

Square :-



$$2r_- = a \quad — (1)$$

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

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

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

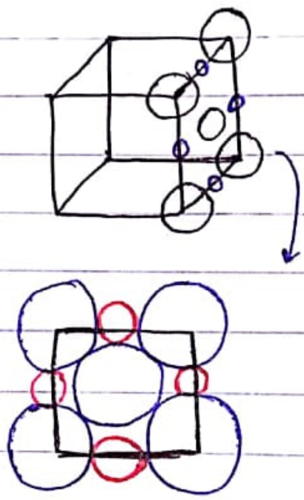
$$\frac{r_+}{r_-} = 0.414$$

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

Octahedral Void at edge centre C.N. = 6

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

$2r_+ + 2r_- = a \quad — (2)$



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

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

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

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

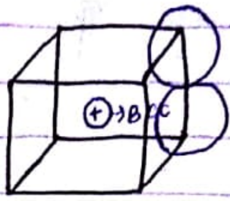
Range for Octahedral Void at edge centre

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

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

$2r_- = a$ —① at S.C.C.

$2r_+ + 2r_- = \sqrt{3}a$ —② at BCC



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

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

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

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 ~~0.732~~ $\leq \frac{r_+}{r_-} < 0.732$	NaCl, MgO, KCl
4.	8	Octahedral	$0.732 \leq \frac{r_+}{r_-} < 1$	CsCl

Type of Ionic Crystal :-

Rock Salt Str. (NaCl type)

anions → FCC arrangement

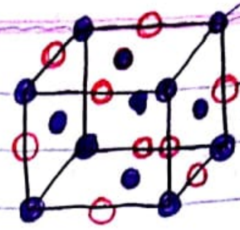
cations → Octahedral voids

- In a unit cell there are 4 anions & 4 cations

$Na_4Cl_4 = 4NaCl$

↓

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

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

$$Z_+ = Z_- = 4$$

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

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

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

$\rightarrow$ FCC

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

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

eg Halides of Li, Na, K, Rb.

Oxides & Sulphides of alkaline earth metal.

Sphalerite Type (ZnS type)

S^{-2} → at CCP arrangement i.e. FCC

Zn^{2+} → at alternate Tetrahedral Voids

or

50 % of Tetrahedral Void

There are 4 anions & 4 cations in unit cell.
$Zn_4S_4 = 4\ ZnS$.
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 $r_+ + r_- = \frac{\sqrt{3}a}{4}$

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

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

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

$$P.E. = 74.84\%$$

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 → CCP arrangement i.e. FCC
anion → THV
* There are 4 cations & 8 anions in one unit cell.
$Ca_4F_8 \equiv 4CaF_2$
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 = 4
Touching condⁿ ⇒ $r_+ + r_- = \frac{\sqrt{3}a}{4}$

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

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

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

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

CaF_2 , $CaCl_2$

SrF_2 , $SrCl_2$

BaF_2 , $BaCl_2$

Antifluorite Type Na_2O

anion → CCP i.e. FCC

cation → THV

There are 8 cations & 4 anions in a unit cell

$Na_8O_4 = 4Na_2O$

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

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

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

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

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

anion = 74 %

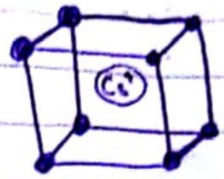
Cation = 1.68 %

CsCl type : 1:1 type

$Cs^+ \rightarrow$ B.C.

$Cl^- \rightarrow$ SCC

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



There is only 1 formula unit in unit cell Z = 1

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

C.N. of $Cs^+ = 8$

C.N. of $Cl^- = 8$

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

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

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

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

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

$\rightarrow 52.4$

P.E. = 72.95 %

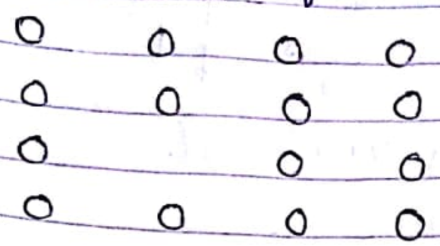
Defect in Crystals :

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



Vacany defect

Interstitial Defect

Crystal Defects

- Stoichiometry defect
  - Schottky defect
  - Frenkel defect
- Non-Stoichiometry
  - Metal Excess Defect
  - Metal Deficiency Defect
- Impurity Defect (due to mixing of impurity)

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

Schottky Defect: Found in crystals in which ~~have~~

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

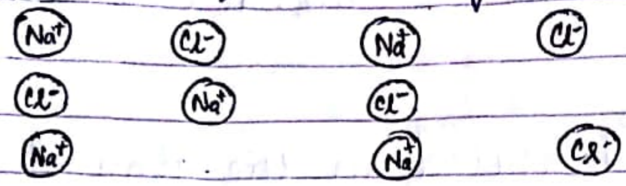
Example → NaCl, CsCl, KCl, AgBr.

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

Result :-

- Solid/Crystal remains electrically Neutral
- Density of solid ↓se.

It is kind of vaccancy defect.



Frenkel Defect :- Found in solids in which

- C.N. is low.
- Difference in size of cation & anion is large.

<u>Example</u> ZnS, AgBr, AgI, AgCl

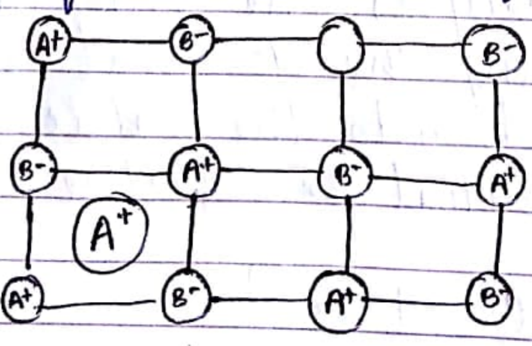
<u>Note</u> AgBr shows both defect Schottky & Frenkel defect.

~~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 :-

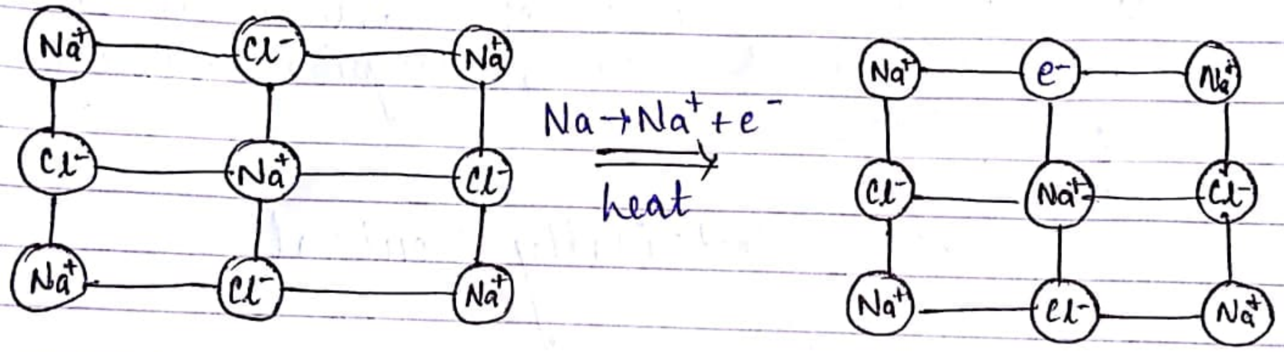
In which stiochiometry of crystal change.
There are 2 types of non-stiochiometry defect.

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

When NaCl solid is ~~needed~~ heated in the atmosphere of Na then some Cl^- leaves the lattices & for maintaing the electrical neutrality hole is occupied by $e^{\ominus}$ & this is c/a F-centre.

F-Centre ⇒ Farbenzenter (↳ color)

NaCl → Yellow
KCl → Violet
LiCl → 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 maintaing the electrical neutrality. $E^{\ominus}$ are also doped into the Lattice and it occupies other site of interstitial ~~to~~ lattice.

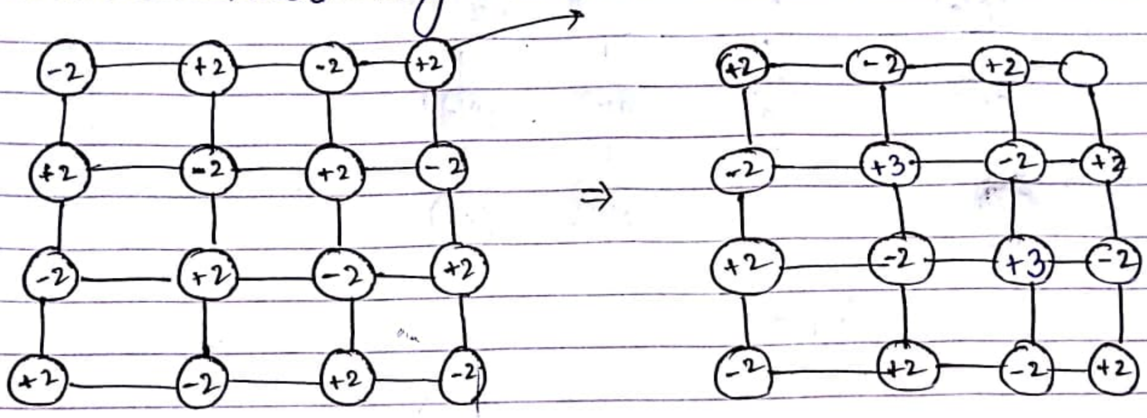
eg ZnO → white.

$ZnO \rightarrow Zn^{2+} + \frac{1}{2}O_2 + 2e^{\ominus}$

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 ~~OS~~ Oxidation State is converted into Higher O.S.



$\overset{+2}{Fe}O \longrightarrow Fe_{0.93}O$ — % Fe^{2+} / % Fe^{3+}

0.07 Fe^{2+} leaves site

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

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

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

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

or

$Fe^{3+} \to x$

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

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

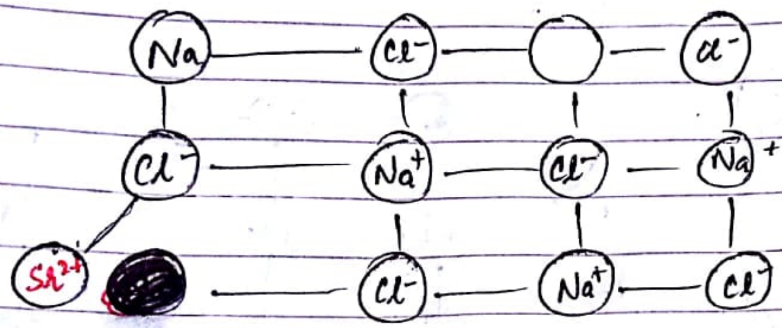
$$x = 0.14$$

Impurity Defect:-

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

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 ↓se.