rigid sp.. Not chan

08/05/17

Solid state.

Solid state

1. Crystaline Solid	2. Amorphous Solid.
1) Constituent particles are arranged in long definate pattern.	1) Not arrange in a long definate pattern. or Arrange in a short pattern.
2. On clevage Provide smooth surface	2) On Clevage provide Rough surface.
3) True solid	3) Pseudo solid
4) ΔH fussion and melting point have a sharp value	4) ΔH fussion and Melting Point exist in a range
5) an Isotropic in nature	5) Isotropic in nature.

Isotropic:

If some physical properties like refraction of light depend on direction of substance then this type of Substance is called an isotropy in nature.

* Glass, Plastic, rubber etc are example of Amorphous Solid.

* **Types of Crystilline Solid:** On the basic of attraction force b/w constituent particles.

2

* Type of Solid.

type of solid	Constituent Particles	types of attraction force	example
1) Ionic solid	ion	ionic bond	NaCl, KCl, $CaCl_2$ etc
2) Metallic solid	Cation in sea of electron (+)	Metallic bond	Zn, Cu, Na, K
3) covalent solid or Network solid	atoms	covalent bond	diamond, SiO_2 graphite, AlN SiC.
4) Molecular Solid	Molecules	H-bonding, London force, dipole-dipole	H_2O, SO_2, HCl, SO_2

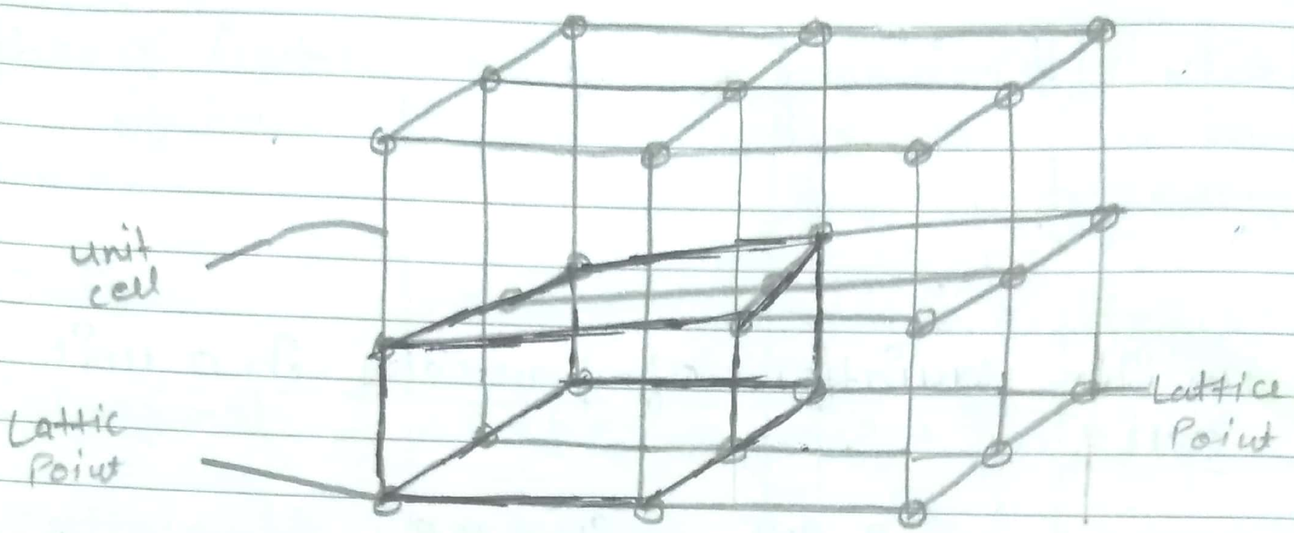
Generally substance found in gasous and liquid form will be example of Molecular solid if there will be converted in solid state. by decreasing of temperature.

P_4, S_8, C_{60} are example of Molecular solid.

* Some defination related to Crystilline Solid :-

1) Crystallin latice :- Part of Crystilline solid in which constituent Particles are arrange in a long definate Pattern will be called Crystall lattice

* 2) Space lattice :



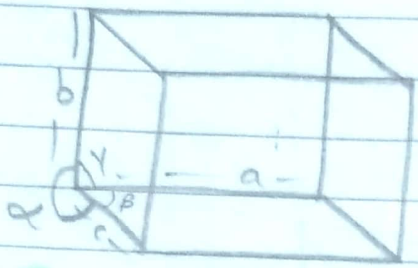
If centre of constituent particle is replaced by dots then resultant geometry will be called space ~~ta~~ lattice.

* Unit cell :

Most symmetrical minimum 3 dimensional unit by repeating this. we can completely construct lattice structure called unit cell.

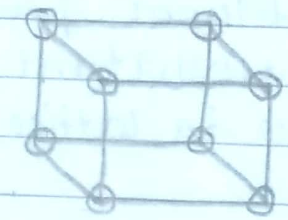
Six parameters are required to construct the unit cell.

Three dimensional a, b, c originating from a corner and three angles α (b & c) β (a & c) γ (a & b) between three sides.

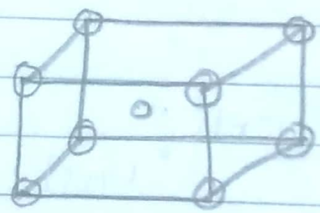


* Possible variations of particles in a unit cell :

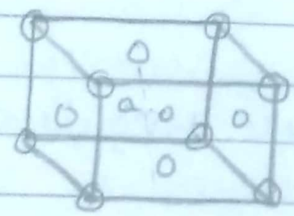
1) Simple / Primitive unit cell :



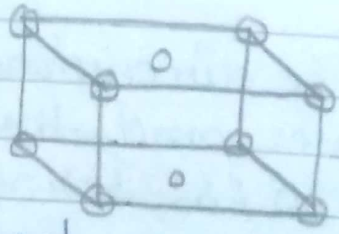
2.) Body centred unit cell :



3.) face Centred unit cell :



4) End Centred unit cell :



Constituent particles are found on alternate face centred along with corner.

* Seven Crystall latice system :

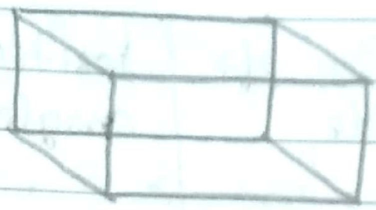
Types of Crystall system	Position of side	Position of angle	Possible type of particle arrangement
1) Cubic	$a = b = c$	$\alpha \neq \beta \neq \gamma = 90°$	P, BC, FC
2) tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	P, BC
3) Orthorombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	P, BC, FC, EC
4) Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90$	P
5) Hexagonal	$a = b \neq c$	~~$\alpha = \beta \neq \gamma \neq 90$~~ $\alpha = \beta = 90°$ $\gamma = 120$	P
6) Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	P
7) Monoclinic	$a \neq b \neq c$	~~$\alpha = \beta = 90°, \gamma \neq 90°$~~ $\alpha = \gamma = 90°, \beta \neq 90°$	P, EC.
			14.

⇒ Over all 14 different type of lattice structure are present possible in solid state

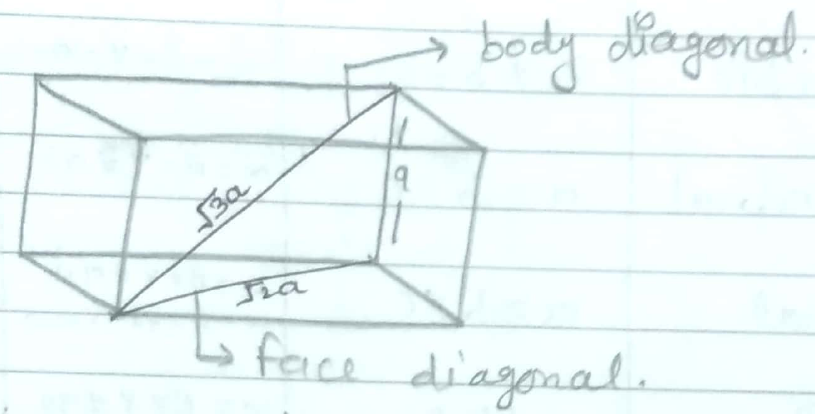
⇒ Orthorombic is only unit cell which have all four type of particle variations.

⇒ Triclinic is most symettric unit cell.

* Cubic :



In a cubical lattice system i cube, 6 side and 12 face of different unit cell join at a corner.



* Analysis of Cubical lattice system :

1). Coordination no. :

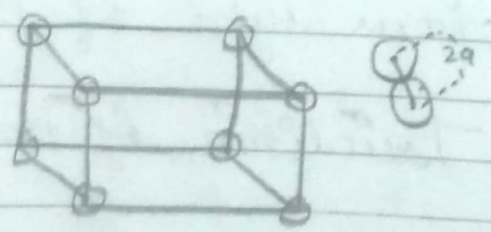
Nearest Neighbour of a particle in complete lattice structure will be coordination no. of that particle.

In solid state nearest neighbour will be always touch one another.

i) Simple Cube :

Coordination no. - 6

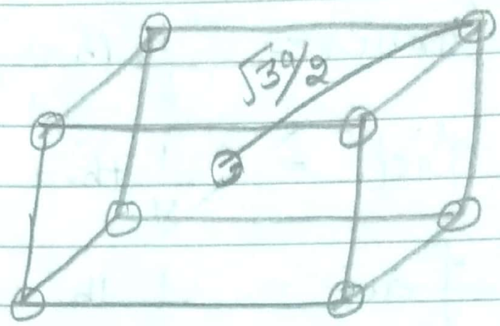
$d = a = 2r$



(ii) Body Centred Cube (B.C.C):

Co-ordination no.- 8

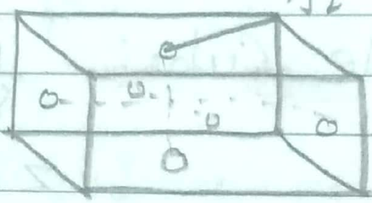
$d = \frac{\sqrt{3}a}{2} = 2r$



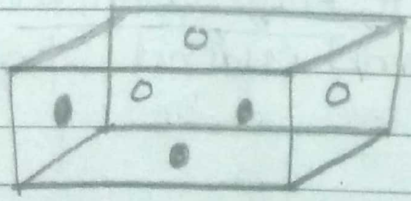
iii) face centred Cube (f.c.c):

Co-ordination no : 12

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



	Ist nearest or nearest neighbour (d, C.N)	2nd nearest or next nearest.	Third nearest next to next nearest
S.C	a, 6	$\sqrt{2}a$, 12	$\sqrt{3}a$, 8
B.C.C	$\frac{\sqrt{3}a}{2}$, 8	a, 6	$\sqrt{2}a$ 12
f.C.C	$\frac{a}{\sqrt{2}}$, 12	a, 6	$\frac{\sqrt{3}}{2}a$, 24.



* Rank of unit cell :

Corner = $\frac{1}{8}$ th

Side = $\frac{1}{4}$ th

Face = $\frac{1}{2}$ th

Body Centred = 1

* Simple Cube : $\frac{1}{8} \times 8 = 1$

$z = 1$

* Body Centred Cube :

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

* Face Centred Cube :

$z = \left(8 \times \frac{1}{8}\right) + 6 \times \frac{1}{2} = 4$

Que: In a Cubical lattice system atom A is present on all the Corner of the unit cell atom B is present at 50%. face Centred of unit cell and atom c is present on alternate edge Centre. then what will be empherical formula of compound.

Ans: $A \rightarrow \frac{1}{8} \times 8 = 1$

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

$C = 4 \times \frac{1}{4} = 1$

$= 1 : \frac{3}{2} : 1$

$= 2 : 3 : 2$ Ans

Date: 12/05/17

* **Packing efficiency (P.E):**

1) $P.E \Rightarrow \frac{\text{volume of sphere in lattice}}{\text{volume of lattice}} \times 100$

$P.E \Rightarrow \frac{\text{Volume of spheres in a unit cell}}{\text{Vol. of unit cell}} \times 100$

$P.E \Rightarrow \frac{z(4/3 \pi r^3)}{V} \times 100$ If unit cell is cube $\Rightarrow$ $V = a^3$.

z = effective no. of particle of unit cell.

If more than one types of Particles are present in unit cell.

$P.E = \frac{z_1(\frac{4}{3}\pi r_1^3) + z_2(4/3 \pi r_2^3) + \cdots}{V}$

Amu = $\frac{1}{Na}$ 1ml = 1cm³

1Å =

1nano

* Density of Solid / Lattice :

$$D = \frac{\text{mass of lattice}}{\text{Vol. of lattice}}$$

$$d = \frac{\text{mass of one unit cell}}{\text{Vol. of unit cell.}}$$

where m is mass of one particle in unit cell

$$d = \frac{Zm}{V}$$

*→ generally mass of 1 constituent particle will be in a.m.u per particle. for converting it in gram we have to divided by N_A.

$$d = \frac{Z\left(\frac{M}{N_A}\right)}{V}$$ Imp

$$d = \frac{ZM}{V \times N_a}$$

where $V = a^3$

*

1ml =	$1cm^3$
1A° =	10^{-8} c.m
1nm =	10^{-9} meter = 10^{-7} cm.
1Pm =	10^{-12} meter = 10^{-10} cm.

Que! In a Cubical lattice system Particle A is formed on 6 corners, Particle B is found on remaining corners and face centers which are not opposite to one another.

$A_3B_7C_{10}$

Particle c is found on remaning face centres and Body centre of unit cell then calculate simplest formula of compound and also calculate density of compound in Amu/A°^{3}

Ans:- Given

Side length of unit cell = 2A°
Molar mass of A = 40g/mol
molar mass of B = 60g/mol
molar mass of C = 80g/mol

$$P.E = \frac{Z_1 m_1 + Z_2 m_2 + Z_3 m_3}{V}$$

$$A = 6 \times \frac{1}{8} = \frac{6}{8} = \frac{3}{4}$$

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

$$C = 3 \times \frac{1}{2} = \frac{3}{2} + \frac{1}{1} = \frac{5}{2}$$

$$A = 6 \times \frac{1}{8} = \frac{6}{8} = \frac{3}{4}$$

$$B \rightarrow 2 \times \frac{1}{8} + 3 \times \frac{1}{2} = \frac{7}{4}$$

$$C \rightarrow 3 \times \frac{1}{2} + 1 \times 1 = \frac{5}{2}$$

$$A_3 B_7 C_{10}$$

$$P.E = \frac{\frac{3}{4} \times (40) + \frac{7}{4}(60) + \frac{5}{2}(80)}{2^3} \text{ A.M.U/A°}^3$$

$$\frac{30 + 105 + 200}{8} = \frac{335}{8}$$

Que: Potassium crystallising B.C.C structure if radius of Pottassium atom is 1 A° then calculate Density of pottasium in gram/ml.

Ans:

$K = 19 = 39.$

$d = \frac{2 \times 39}{1 A^\circ} = \frac{78}{1 cm^3}$

$= \frac{78}{1 cm^3}$

$\left[\frac{\frac{z(m)}{Na}}{V} \right]$

$d = \frac{2 \times \left(\frac{39}{Na}\right)}{V}$

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

$a = \frac{4}{\sqrt{3}} A^\circ$

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

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

$= \frac{2\left(\frac{39}{Na}\right)}{\left(\frac{4}{\sqrt{3}} \times 10^{-8}\right)^3}$

* Packing efficiency in different unit cell:

1) Simple cube:

$P.E = \frac{1 \times (4/3 \pi r^3)}{a^3}$

Simple cube $[a = 2r]$

$= \frac{4/3 \pi r^3}{8 r^3} = \frac{\pi}{6} = 52.4$

2) For B.C.C:

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

$\left[\frac{\sqrt{3}a}{2} = 2r\right]$

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

$= 0.68$

68%.

3) face :-

$$P = \frac{4 \times \frac{4}{3}\pi r^3}{a^3} \qquad \left[\frac{a}{\sqrt{2}} = 2r\right]$$

$$= \frac{\frac{16}{3}\pi r^3}{\left(\frac{a}{\sqrt{2}}\right)^3} \qquad a = 2\sqrt{2}r$$

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

Que: Potassium crystilised in B.B.C St. then calculate no. of unit cells in 78 g sample ~~central~~ of Potassium.

Ans: (A) ✓ N_A (B) $N_A/2$ (C) $2N_A$ (d) none.

d = ~~2×39~~

Mole of K = $\frac{78}{39}$ g/mol = 2 mol.

No. of K particles = $2N_a$.

No. of unit cell = $\frac{2N_a}{2}$ = N_a

M 3.464

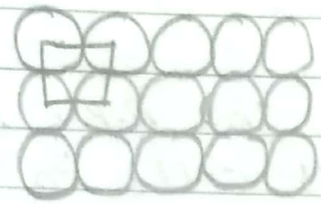
* Packings of solid :

1) One Dimensional packing of solids :

C.N = 2

2) Two - D packing of solids :

i) Square 2-D packing :



$z = 4 \times \frac{1}{4} = 1$

$a = 2r$

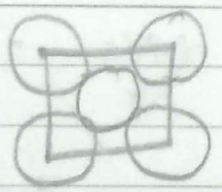
C.N = 4

$$P.E = \frac{\text{Area of circle in a unit cell}}{\text{area of unit cell}}$$

$$= \frac{(1)\pi r^2}{a^2} = \frac{\pi r^2}{4r^2}$$

$$P.E = \frac{\pi}{4} = \frac{\pi}{4}$$

* Que : Calculate



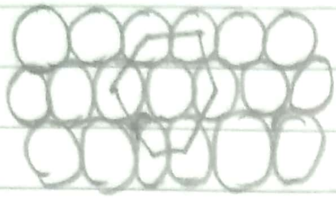
$z = 2$

$$P.E \Rightarrow \frac{2(\pi r^2)}{a^2} \Rightarrow \qquad \left[\frac{a}{\sqrt{2}} = 2r\right]$$

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

Area of Regular hexagonal → $6 \cdot \frac{\sqrt{3}}{4} a^2$

2) Hexagonal 2D Packing:



$z = 1 + 6 \times \frac{1}{3} = 3$

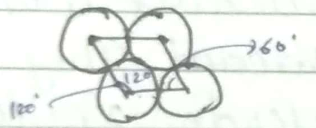
$a = 2r$

C.N = 6.

$P.E \Rightarrow \frac{\text{Area of circle in a unit cell}}{\text{area of unit cell.}}$

$= \frac{3(\pi r^2)}{6 \cdot \frac{\sqrt{3}}{4} a^2} = \frac{3\pi r^2}{2r} = \frac{\pi}{2\sqrt{3}}$ Ans

Que:



Ans: $z = \frac{1}{6} + \frac{1}{3} + \frac{1}{6} + \frac{1}{3} = 1$

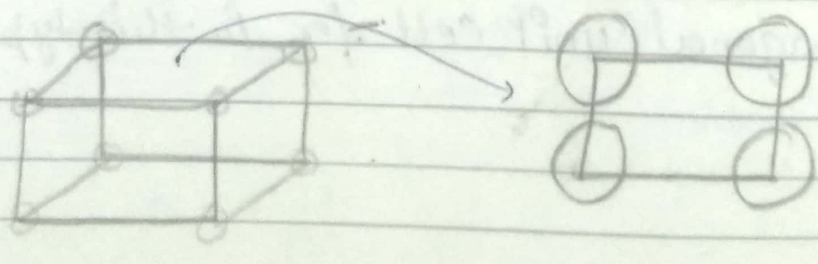
Area πgram $= |ab \sin\theta|$

$z = 1$

$P.E = \frac{(1)\pi r^2}{2r \times 2r \times \frac{\sqrt{3}}{2}}$

Que: Calculate Packing effeciency of edge & face of B.C.C unit cell

Ans:



$\frac{1}{4} + \frac{1}{4}$

face of BCC unit cell -

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

$$P.E = \frac{2r}{a}$$

Edge of BCC unit cell

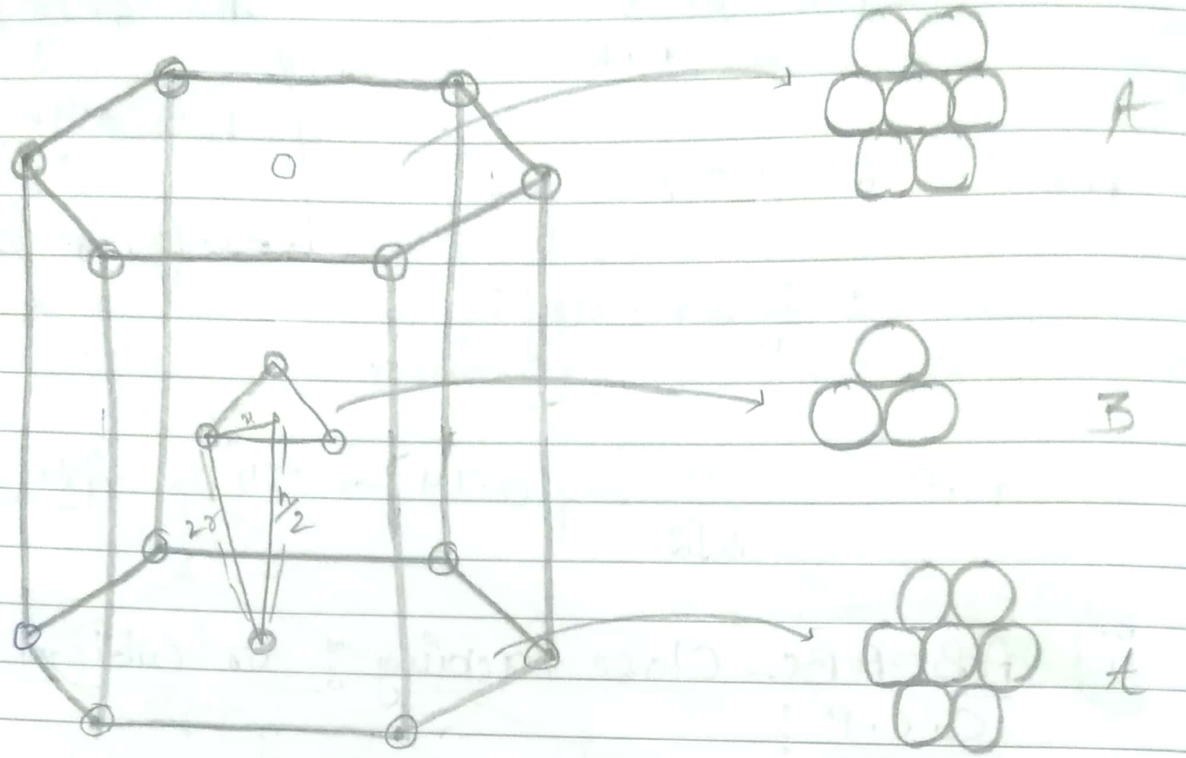
P.E =

* 3 - 3D Packing of Solids :-
14 differen type of structure are possible in 3D but we will stude only close pack St. in 3D.
Close Packed St. are structure which have minimum void space or vacant. They can be octend by extende 2D Hexagonal.

Date: 15/05/17

Two type of close packed structure are possible in 3D.

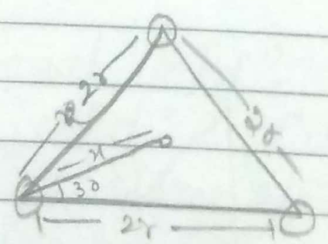
1) ABAB close Packing. or Hexagonal Packing
Hexagonal unit cell for this type of packing



HCP unit cell.

* Coordination No. ⇒ 12
* $z = 3 + \left(2 \times \frac{1}{2}\right) + 12 \times \frac{1}{6} = 6$
* Height of HCP unit cell ⇒

$2L = h/2 \quad \frac{2r}{2\sqrt{3}}$



$$\frac{h}{2} = \sqrt{(2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2}$$

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

$x \cos 30 = r$

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

Distance b/w 2 consecutive layer in a hcp unit cell will be equal to $2r\sqrt{2/3}$

$\left[6 \cdot \frac{\sqrt{3}}{4} a^2\right]$

$$P.E = \frac{6 \times \frac{4}{3}\pi r^3}{A \cdot h}$$

$A = 6 \cdot \frac{\sqrt{3}}{4} a^2$

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

$\rightarrow = 6 \cdot \frac{\sqrt{3}}{4} \cdot 4r^2 \{a = 2r\}$

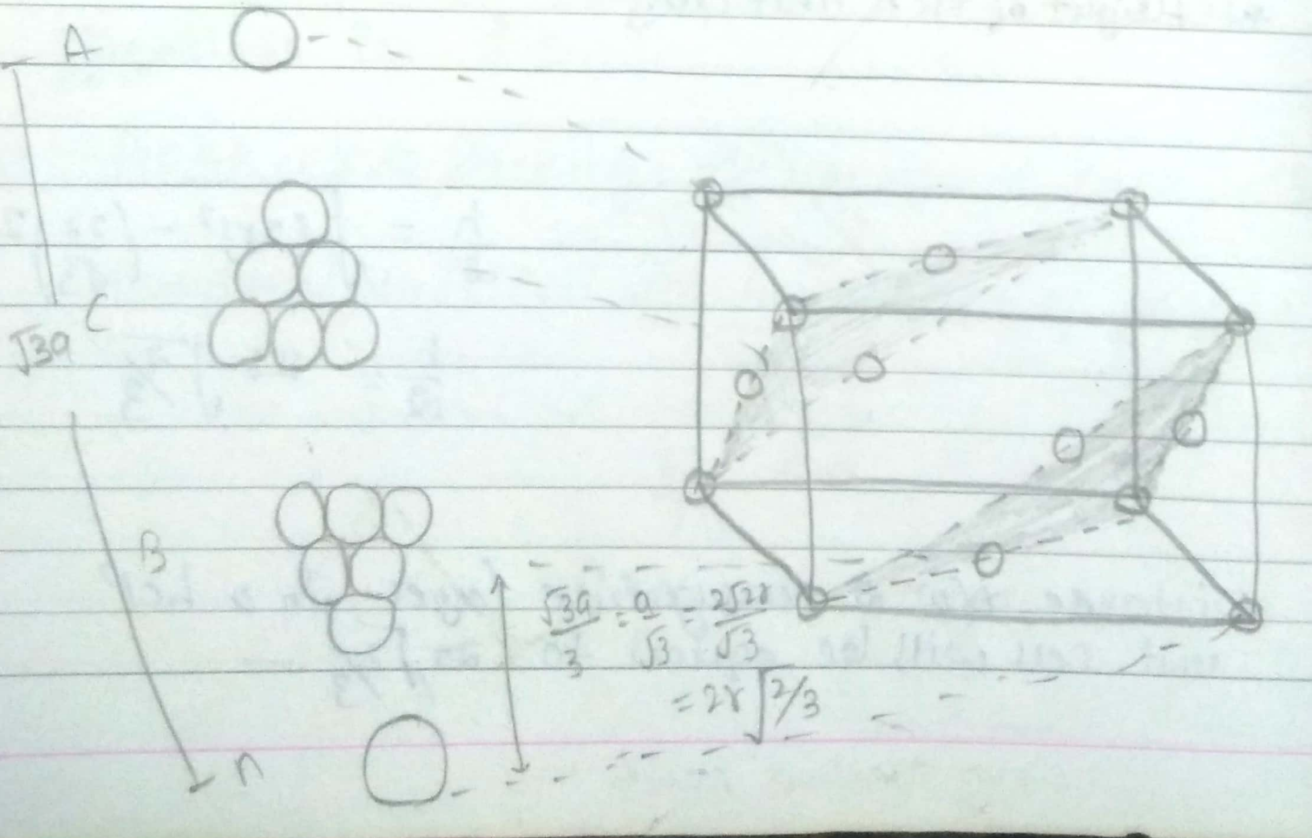
$$P.E = \frac{6 \times \frac{4}{3}\pi r^3}{6 \cdot \frac{\sqrt{3}}{4} \cdot 4r^2 \cdot 4r\sqrt{\frac{2}{3}}}$$

$$P.E = \frac{\pi}{3\sqrt{2}} \simeq 0.74 \rightarrow 74\% \text{ Ans}$$

ii) ABCABC.. Close Packing : or Cubical close Packing : C.C.P :

C.C.P = FCC

FCC unit cell will form in ABCABC--- Close Packing FCC unit cell is a part of Cubical lattice system that's why it is also called cubical close packing.



* C.N = 12
* Z = 4
* P.E = 74%.

Note: Coordination no., Packing effeciency, density and distance between two consecutive layer ($2r\sqrt{2/3}$) will be equal in HCP and CCP unit cell.

Cubic
- S.C — AAA-- Square Packing
- B.C.C — ABAB Square Packing
- FCC (CCP) — ABCABC. Close Packing

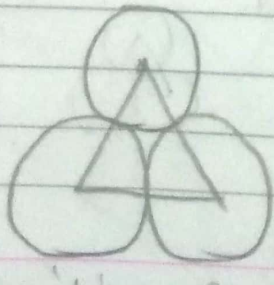
HCP
→ ABAB - Close Packing.

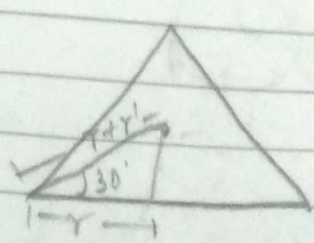
⇒

Date: 17/05/17

* Void of solid:

a) Two dimensional Void:
i) Triangular void: [C.N = 3]
Name of Void is given according to mathematically geometry that will form on joining centre of spheres that are formene void.





Limiting Radius Ratio

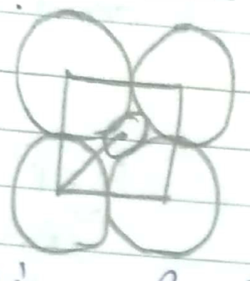
{Concentration term - 2 complete
Q.no 18}

$$(r+r')\cos 30^\circ = r$$
$$r+r' = \frac{2r}{\sqrt{3}}$$
$$1+\frac{r'}{r} = \frac{2}{\sqrt{3}}$$

$$\boxed{\frac{r'}{r} = 0.155}$$ fuk

ii) Square planar void:

[C.N=4]



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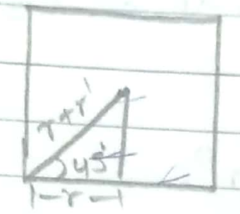


Limiting radius ratio:

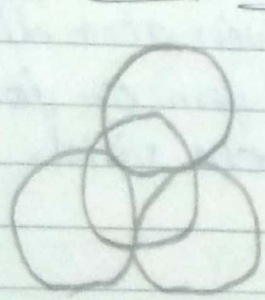
$$(r+r')\cos 45^\circ = r$$

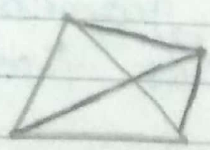
$$r+r' = \sqrt{2}r$$
$$1+\frac{r'}{r} = \sqrt{2}$$

$$\boxed{\frac{r'}{r} = 0.414}$$

* Three dimensional Void:

i) Tetra hedral void: [C.N = 4]





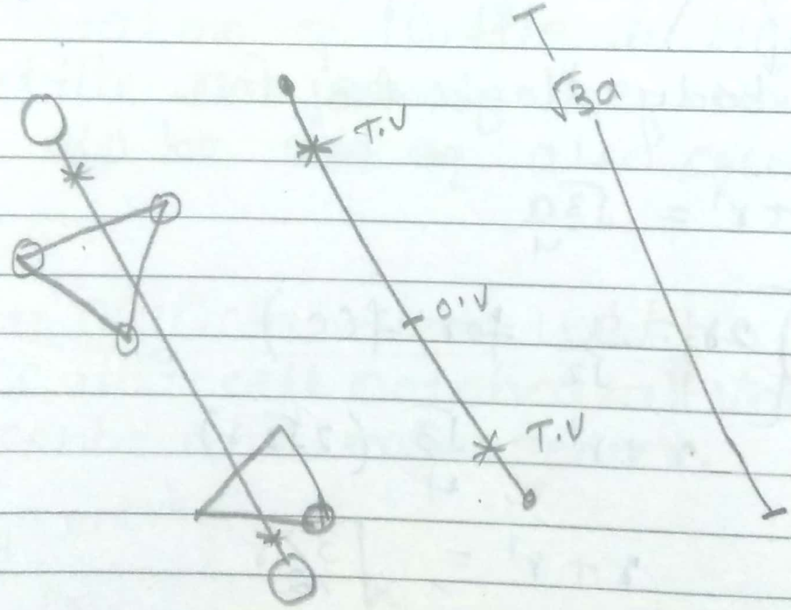
Important

Note! Tetrahedral void formed both fcc and hcp unit cell.

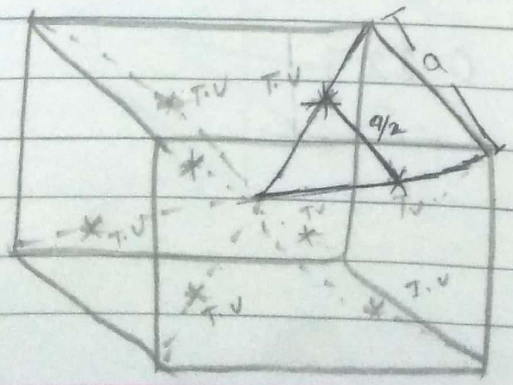
* If N Particle are present in HCP or fcc lattice then total no. of tetrahedral void will be equals to 2N.

* Location of tetrahedral void in fcc unit cell.

In fcc unit cell centre of tetrahedral void exist at a distance of $\frac{\sqrt{3}a}{4}$ on body diagonal from corner of fcc unit cell.



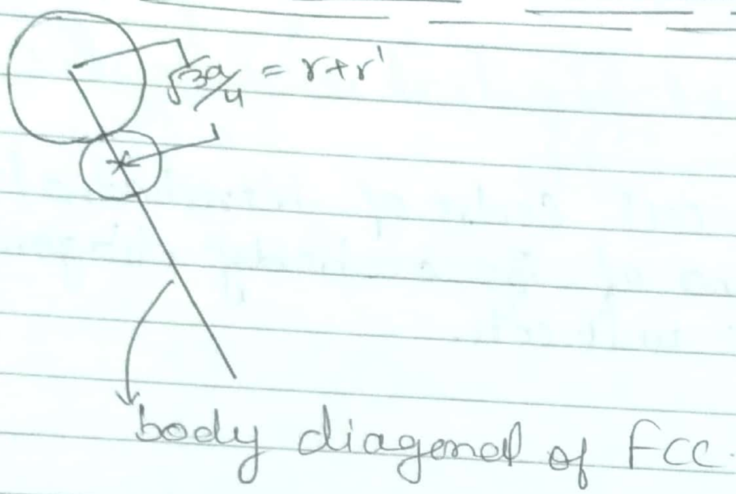
Body diagonal of fcc unit cell



F.CC unit cell.

* Minimum distance b/w two T.V in a fcc unit cell $= a/2$
* Maximum distance b/w two T.V in a fcc unit cell $= \frac{\sqrt{3}a}{2}$

Limiting radius Ratio for tetrahedral Void:



$$r + r' = \frac{\sqrt{3}a}{4}$$

$$\left\{ 2r = \frac{a}{\sqrt{2}} \text{ for fcc} \right)$$

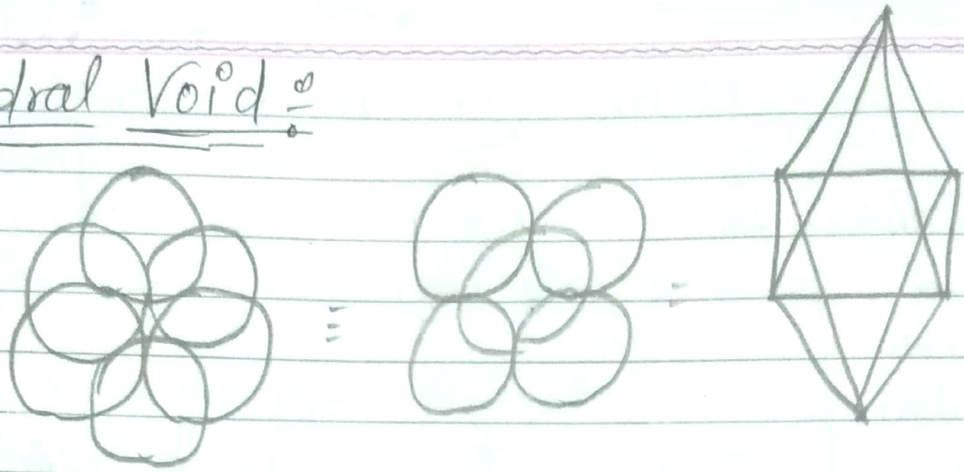
$$r + r' = \frac{\sqrt{3}}{4}(2\sqrt{2}r)$$

$$r + r' = \sqrt{3/2}\,r$$

$$1 + \frac{r'}{r} = \sqrt{\frac{3}{2}}$$

$$\boxed{\frac{r'}{r} = 0.225}$$

2) Octahedral Void :-



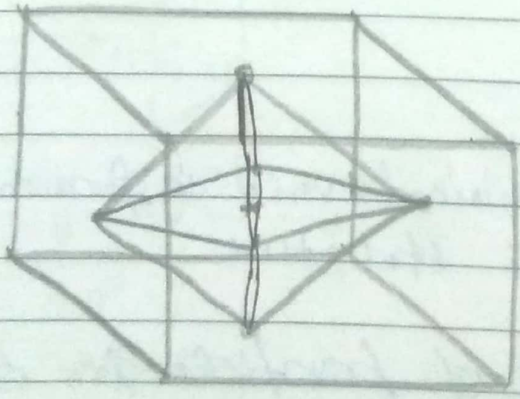
Imp

* Octahedral Void form in HCP and FCC unit cell

= If Total no. of Particle in HCP and FCC lattice are ~~an~~ N then No. of octahedral void will be ~~also eq~~ also equal to N.

* Location of Octahedral void in fcc unit cell:-
In fcc unit cell octahedral void found on body centre and edge centre.

Body centre



JIA ⇒ 6, 8, 9, 10, 11

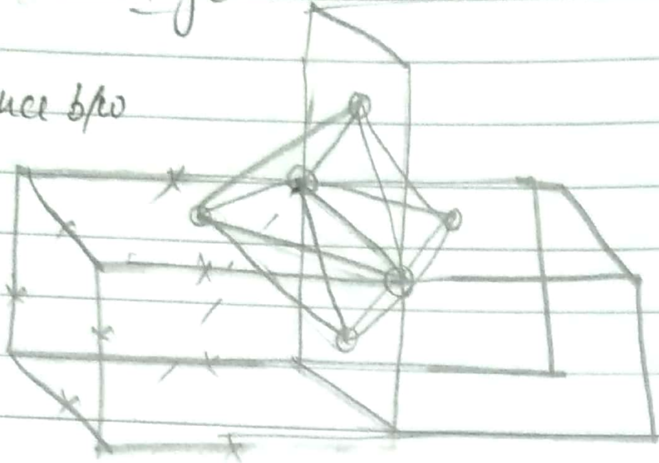
fcc { TV ⇒ $\frac{\sqrt{3}a}{4} = r + r'$; OV ⇒ $r + r' = \frac{a}{2}$ }

Edge Centre

[maximum distance $\sqrt{2}a$]

minimum distance b/w two O.V in a fcc unit cell

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



Body centre ↑, face diagonal ↑

$1 + 12 \times \frac{1}{4} = 4$

* Effective no. of octahedral void in fcc unit cell. 4.

* Limiting Radius Ratio :

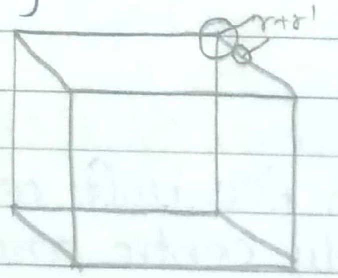
$$r + r' = \frac{a}{2}$$

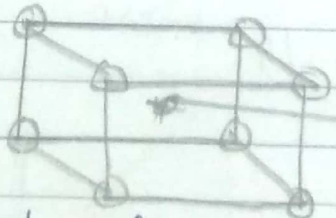
$$\left\{ \text{for f.c.c} \quad \frac{a}{\sqrt{2}} = 2r \right\}$$

$$r + r' = \frac{2\sqrt{2}r}{2}$$

$$1 + \frac{r'}{r} = \sqrt{2}$$

$$\frac{r'}{r} = 0.414.$$





* Cubical Void :

Cubical void is formed in simple cubic lattice structure

* If effective no. of particle in simple cubic lattice structure are N. then total no. of cubical void will be equals to N.

fcc effective 8
av = 8

octa 3 jump
tetra

amu = 1 × gram × NA = gram

Limiting Radius Ratio :-

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

{for simple cube $a = 2r$}

$r + r' = \sqrt{3}r$

$1 + \frac{r'}{r} = \sqrt{3}$

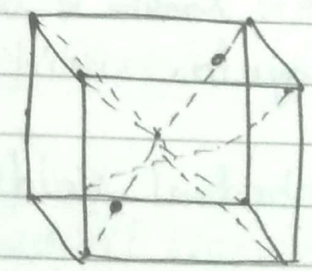
$\boxed{\frac{r'}{r} = 0.732}$

(Two T.V = neighbor distance = $\frac{a}{2}$)

Que: Particle A formed fcc unit cell and Partical B is Present in Alternate T.V then Calculate Simplest formula of Compound. If edge length of unit cell is 2Å then also Calculate Packing Afficency.

[If Particle Present in the void do not distub lattice structure]

Ans: Particle A = 4
Particle B =
Alternate T.V = 4
1 : 1
AB.



Packing efficiency: $\frac{4 \times \frac{4}{3}r_A^3 + 4 \times \frac{4}{3}r_B^3}{a^3}$

$a = 2Å$

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

$\Rightarrow \frac{r'}{r} = \frac{r_B}{r_A} = 0.225$

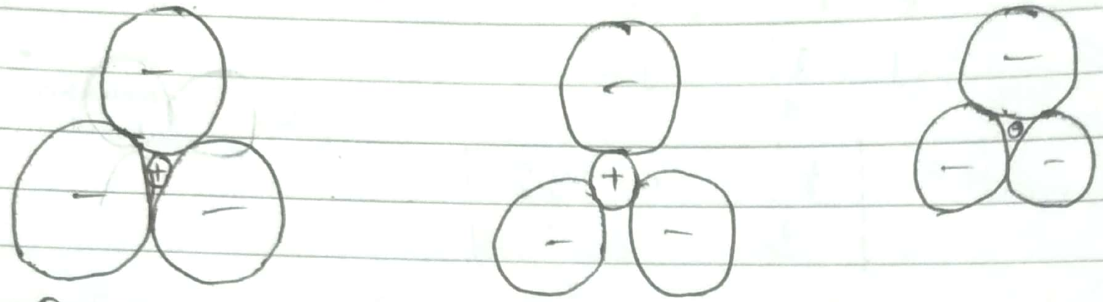
$= r' + r = \frac{\sqrt{3}a}{4}$

cation present in void

Important

Ionic Solid :-

In Ionic solid bigger sized Ion (generally anion ~~from~~ formed lattice structure and smaller size ion (generally Cation). occupy void location



Perfect void — imperfect — unstable st.

$\frac{r^+}{r^-} = 0.155$ — $\frac{r^+}{r^-} > 0.155$

* Both Cation-Cation and anion-anion will exist
  - R ⇒ Radius of Bigger size ion
  - R' ⇒ Radius of Smaller size ion
* Cation-anion contact will exist but anion-anion contact will not exist.

Tringular void — $\frac{r'}{r} = 0.155$ —— < 0.225

tetrahedral void — $\frac{r'}{r} \geq 0.225$ —— < 0.414

O.V / Square plannar — $\frac{r'}{r} \geq 0.414$ —— < 0.732

$\frac{r'}{r}$ — $\frac{r'}{r} \geq 0.732$ —— < 1

Que:- In a Compound A_2B_3 Radius of cation A is 3 A° and Radius of anion B^- is ~~7~~ 7 A° then calculate Courdination no. of anion and Cation. in this lattice Structure.

$\frac{\sqrt{3}a}{4}$ = T.V 27

2

T.V = 4
Cubic =

Ans: $\frac{r'}{r} = \frac{3}{7} = 0.42$

r' will be in O.V.

Coordination no. of Cation = 6.

* A_2B_3

C.N (A^{+3}) : C.N (B^{-2})

6 : 4 T.V

A_xB_y

C.N(A^{+y}) $\propto y$

C.N (B^{-x}) $\propto x$

$\frac{C.N(A^{+y})}{C.N(B^{-x})} = \frac{y}{x}$

* Different types of Ionic solid Structures:-

i) NaCl Structure or Rock Salt Structure:

i) $Cl^{\ominus}$ will form f.c.c unit cell &
$Na^{\oplus}$ will occupy all octahedral void.

2) effective no. of cation and anion in a unit cell.

⇒ Na_4Cl_4

iii) Relation b/w $r^{\ominus}$ and $r^{\oplus}$:

$\Rightarrow r^{\ominus} + r^{\oplus} = \frac{a}{2}$ [always valid]

$\Rightarrow \frac{r^{\oplus}}{r^{\ominus}} = 0.414$ [Perfect]

$= \frac{a}{\sqrt{2}} = 2r^{\ominus}$ [Perfect void].

(iv) $P.E = \frac{4\left(\frac{4}{3}\pi r^{+3}\right) + 4\left(\frac{4}{3}\pi r^{\ominus 3}\right)}{a^3}$

(v) $\text{density} = \frac{4\left(\frac{M_{Na^+}}{N_A}\right) + 4\left(\frac{M_{Cl^{\ominus}}}{N_A}\right)}{a^3}$

$= \frac{4(M_{Na^+} + M_{Cl^{\ominus}})}{N_A a^3}$

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

(vi) C.N (Na^+) : C.N $(Cl^{\ominus})$

6 : 6

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Na^+ = All O.V
Cl^- ⇒ f.c.c.

→ f.c.c

C.N. (Na^+) : C.N (Cl^-)
6 : 6
f.c.c → ⌐ O.V

* In ionic solid coordination no. for cation
Cation : ~~neig~~ nearest no. of anion.

for anion : nearest no. of cation.

* **ZnS structure or zinc blend structure :**

1) S^{-2} ⇒ fcc Zn^{+2} ⇒ Alternate t.v
2) formula of unit cell or effective no. of anion and cation in unit cell. = Zn_4S_4.
3) relation b/w r^+ and r^-
   i) $r^- + r^+ = \frac{\sqrt{3}a}{4}$ (always aplicable).
   ii) $\frac{r^+}{r^-} = 0.225$ [Perfect Void]
   iii) $\frac{a}{\sqrt{2}} = 2r^-$ [Perfect Void]
4) $P.E = \frac{4\left(\frac{4}{3}\pi r^{+3}\right) + 4\left(\frac{4}{3}\pi r^{-3}\right)}{a^3}$
5) $d = \frac{4\left(\frac{M_{Zn^{+2}}}{N_A}\right) + 4\left(\frac{M_{S^{-2}}}{N_A}\right)}{a^3}$

T = 4
O.V = 6
C =

T.V → fcc, HCP

Na_2 → T.V. = 4

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

T.V = made by 4

6) C.N (Zn^{+2}) : C.N (S^{-2}) → f.c.c

4 → f.c.c ; 4 → Alternate T.V

Zn^{+2} → 4 ; S^{-2} → 8

3) Na_2O structure or antifluorite structure :

1) O^{-2} ⇒ f.c.c

2) formula of unit cell = Na_8O_4

3) relation b/w r^+ & r^-

i) $r^- + r^+ = \frac{\sqrt{3}a}{4}$ [always]

ii) $\frac{r^+}{r^-} = 0.225$ [Perfect void]

iii) $\frac{a}{\sqrt{2}} = 2r^-$ [Perfect void]

4) $P.E = \frac{8\left(\frac{4}{3}\pi r^{+3}\right) + 4\left(\frac{4}{3}\pi r^{-3}\right)}{a^3}$

5) $T = 8\left(\frac{M_{Na^+}}{N_A}\right) + 4\left(\frac{M_{O^{-2}}}{N_A}\right)$

$$d = \frac{\frac{4}{N_a}\left(2 M_{na^+} + M_{o^{-2}}\right)}{a^3}$$

$$d = \frac{4 M_{Na_2O}}{N_A a^3}$$

All t.v ← → f.c.c

6) C.N (Na^+) : C.N (O^{-2})

4 : 8

Simple cube ↓ ↳ Alternate cubical Void.

* CaF_2 structure of fluorite structure:

1) Ca^{+2} ⇒ f.c.c $F^{\ominus}$ ⇒ All t.v

2) formula of unit cell : Ca_4F_8

3) Relation b/w r^+ and $r^{\ominus}$

i) $r^{\ominus} + r^{\oplus} = \frac{\sqrt{3}a}{4}$ [always]

ii) $\frac{r^{\ominus}}{r^+} = 0.225$ (Perfect void]

(iii) $\frac{a}{\sqrt{2}} = 2r^{\oplus}$ [Perfect void]

4) $$P.E = \frac{4\left(\frac{4}{3}\pi r^{+3}\right) + 8\left(\frac{4}{3}\pi r^{-3}\right)}{a^3}$$

5) $d = \dfrac{4 \cdot \left[\frac{4}{3}\pi r^{3}\right) + 8\left(\frac{M_{F^-}}{N_A}\right)}{a^3}$

$d = \dfrac{\frac{4}{N_A}\left(M_{Ca^{+2}} + 2M_{F^-}\right)}{a^3}$

$d = \dfrac{4\,M_{CaF_2}}{N_A a^3}$

f.c.c → T.V

6) C.N (Ca^{+2}) : C.N ($F^{\ominus}$)

↓ Alternate cubical void

↓ Simple Cube

* **CsCl like b.c.c Structure:**

1) $Cl^{\ominus}$ ⇒ Simple Cube Cs^{+} ⇒ Cubical void.

2) effective no. of anion and Cation in a unit cell. CsCl.

3) i) $r^- + r^+ = \frac{\sqrt{3}a}{2}$ [always.]

ii) $\frac{r^+}{r^-} = 0.732$ [Perfect Void]

iii) $a = 2r^-$ [Perfect void]

Structure: 1 NaCl, 2 CsCl, 3 ZnS } Imp

4) $P.E = \frac{\left(\frac{4}{3}\pi r^{+3}\right) + \left(\frac{4}{3}\pi r^{-3}\right)}{a^3}$

5] $d = \frac{\left(\frac{M_{Cs^+}}{N_A}\right) + \left(\frac{M_{Cl^\ominus}}{N_A}\right)}{a^3}$

$d = \frac{1}{N_A}\frac{(M_{Cs^+} + M_{Cl^-})}{a^3}$

$d = \frac{M_{CsCl}}{N_A a^3}$

6) C.N (Cs^+) : C.N ($Cl^\ominus$)

cubical → simple cube; simple cube → cubical.

Que: Calculate No. of NaCl unit cells in one gram NaCl.

Ans: Na_4Cl_4

Z = 4

Mole of NaCl = $\frac{1}{58.5}$ mol.

No. of NaCl molecules = $\frac{1}{58.5} \times N_A$

No. of unit cells = $\frac{\frac{1}{58.5} \times N_A}{4}$ Ans

3) F.C.C ⇒ C.N = 12
BCC ⇒ 8 C.N
SCC ⇒ 6 ⇒ C.N

$\left[\frac{a}{\sqrt{2}}\right]$

H.W = S-1 complete
Q-1, Q-18

Que! In NaCl structure fill the table.

	coordination No. or nearest no. of Ion.	Second nearest
$Cl^{\ominus}$	6	12
$Na^{\oplus}$	6	12
Zn^{+2}	4	12
S^{-2} F.C.C	4	12

✱ Imperfuction in solid or defects in solids!

Due to defects in solid Conductance and entropy of solid will increases. defects can be of three types.
1) Stochimetric defect.
2) Non - Stochimetric defect.
3) Impurity deffect.

1) Stochimetric defect:-
formula of Compound is remain unchanged

2) Non - Stochimetric defect!
formula of compound is Changed.

Date: 24/05/17

1) Stochimetric defect:
A) Vacancy defect: generate in metallic solids and density will decrease.
~~it Ind~~ ~~in side~~

B) Interstitial defect:
generate in metallic Solid and density will increase.

x Ionic Solid
(C) Frankel defect:
i) generate in ionic solid
ii) also called dislocation defect
(iii) density will remain unchanged.
(iv) Generate in Ionic solid which have smaller size cation as compared to anion.

Example: ZnS, AgCl, AgI, AgBr

D) ~~Sho~~ Schottky defect:
Generate in Ionic solid
ii) Density will decrease

$$\%\text{ of schottky defect} = \frac{\partial_{Th} - \partial_{Practical}}{\partial_{Th}} \times 100$$
% of vacancy

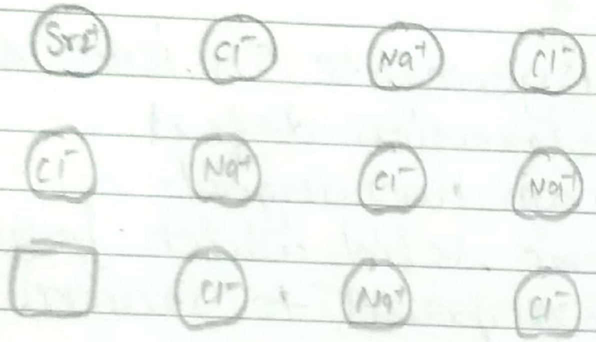
iii) Generate in Ionic solid which have Comparable size of anion and cation.

example: NaCl, CsCl, KCl, (AgBr represent Schottky and frenkle defect.)

2) Impurity defect:

If NaCl lattice is dropped by $SrCl_2$ then one Sr^{+2} will replace $2Na^+$ and will create one vacancy.

In Impurity defect density may increase, decrease or remain unchanged



doped by $SrCl_2$

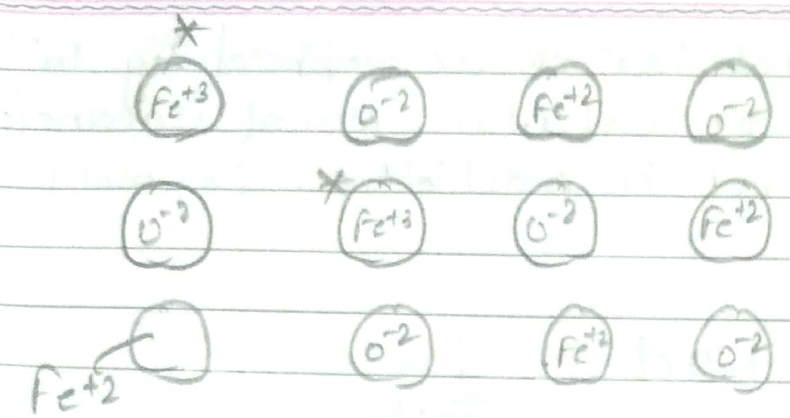
3) Non-stochiometric defect:

i) Metal deficiency defect:

Generate in compound which have metel of variable oxidation state

Ex: In FeO lattice, Some Fe^{+2} ion convert in Fe^{+3} so mentain electrical neutrity of lattice some Fe^{+2} ions come out from lattice. and Metal becomes deficient in the lattice.

By this defect density of compound will decrease.



Eg ⇒ $Fe_{0.96}O$

100 molecules

Fe — 96 ; O — 100

96 → +3 : y ; +2 : $(96-y)$

$3y + 2(96-y) = 200$

$y = 8$

% of Fe^{+3} w.r.t total Fe $= \frac{8}{96} \times 100$.

Que: Copper found in oxidation of +1 & +2 then in a non-stoichometric compound $Cu_{1.5}S$ find % of Cu^{+1} with respect to total copper.

Ans $Cu_{1.5}S$

Cu — 150 ; S — 100

150 → +1 : y ; +2 : $(150-y)$

$y + 2(150-y) = +200$

$y + 300 - 2y = 200$

$-y = 200 - 300$

$y = 100$

% of $Cu^{+1} = \frac{100}{150} \times 100$

Que: One gram NaCl lattice is dopped by 10^{-5} % $SrCl_2$ then calculate No. of vacancies that will creat in NaCl lattice. (by mol.)

Ans:

Sr

Mole of NaCl $= \frac{1}{58.5}$

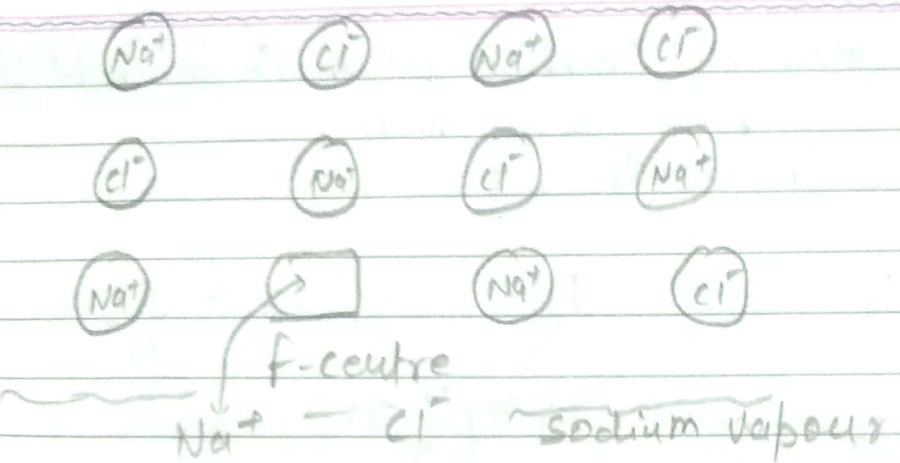
mol of $SrCl_2 = \frac{1}{58.5} \times \frac{10^{-5}}{100}$

No. of $SrCl_2$ molecules $= \frac{1}{58.5} \times \frac{10^{-5}}{100} \cdot N_A$

No. of $Sr^{+2} = \frac{1}{58.5} \times \frac{10^{-5}}{100} \cdot N_A$

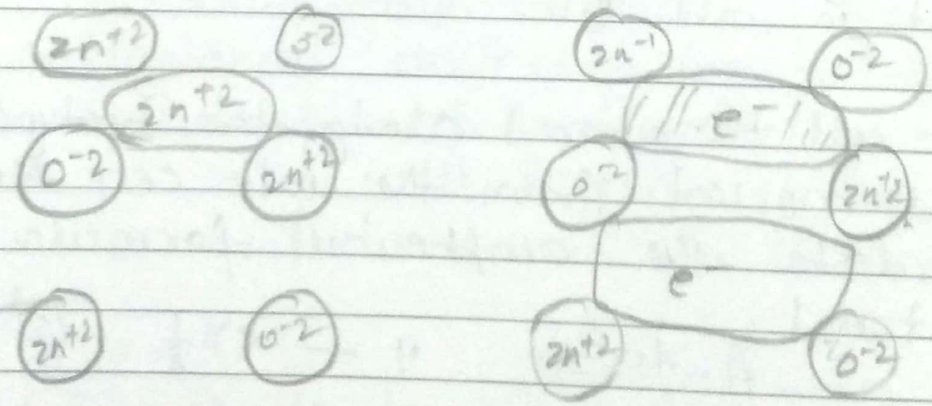
(ii) Metel Excess defect:

If NaCl lattice is heated in presence of sodium vapour, sodium atom will attached to NaCl lattice for gained stability newly attached sodium atom & stard defusing anion from inside lattice, so vacancy will create at place of anion. This vacancy is further occupied by electron i.e released by sodium atom. This type of anionic vacany occupied by e^- called F-centre. This will be responsible for colour impording finomina of lattice



* density of lattice will decrease.

* On Heating ZnO lattice Zn^{+2} will come in exess amount due to libration of O_2. In this Process ZnO lattice restructured itself by placing extra Zn^{+2} and electron in interstitial side. As a resullt density of lattice will be increase and colour of ZnO will be turn from white to Yellow



* Structure of Diamond :

In Diamond structure carbon atom will form FCC and Carbon atom itself will be present in alternate tetrahedral void.

1 Body diagonal : 2

OV = C

* effective no. of Carbon atom in a unit cell :

$$Z = \underset{f.c.c}{4} + \underset{\text{Alternate}}{4} = 8$$

$\Rightarrow \quad r' + r = \frac{\sqrt{3}a}{4} \Rightarrow 2r = \frac{\sqrt{3}}{4}$

Packing efficiency : $\frac{8 \times \left(\frac{4}{3}\pi r^3\right)}{a^3} \approx 34\%$

$$\text{density} = \frac{8 \times \left(\frac{12}{N_A}\right)}{a^3}$$

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Que: In a structure A form f.c.c unit cell St. B exist in all t.v and C exist in all O.V.

Now all the atoms along one body diagonal are removed from the unit cell then calculate the empherical formula of resultant.

Ans ⇒ A – fcc ⇒ $4 - 2 \times \frac{1}{8} = \frac{15}{4}$

B – t.V ⇒ 8 – 2 = 6

C – O.V ⇒ 4 – 1 = 3

$\frac{15}{4} : 6 : 7$

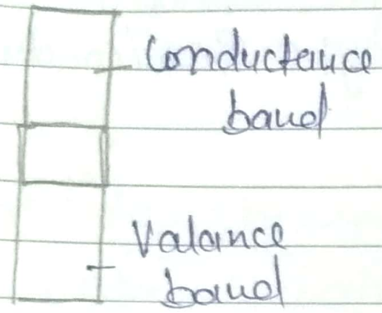
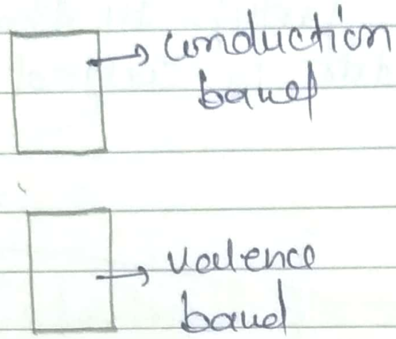
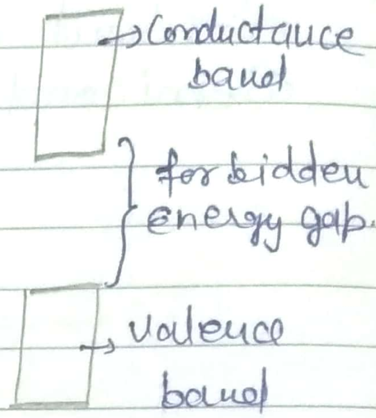
$\frac{5}{4} : 2 : 1$

5 : 8 : 4

$c \propto \frac{1}{R}$

* Electrical properties of Solid :

* Types of Solid on the Basis of Conductance :

Conductor	Semiconductor	insulater
		
Conductance will exist in * 10^4 to 10^7 Ω^{-1}	Conductance will exist in * 10^{-6} to 10^4 Ω^{-1}	Conductionce will * exist in * 10^{-20} to 10^{-10} Ω^{-1}
* ON increasing temp conductance Conductance will decrease	~~temp. Conduct~~ on increasing temp conductance will increase	No significance change will be observe on increasing temp. ~~* By dop~~

* By doping Conductance of these material can be increases.

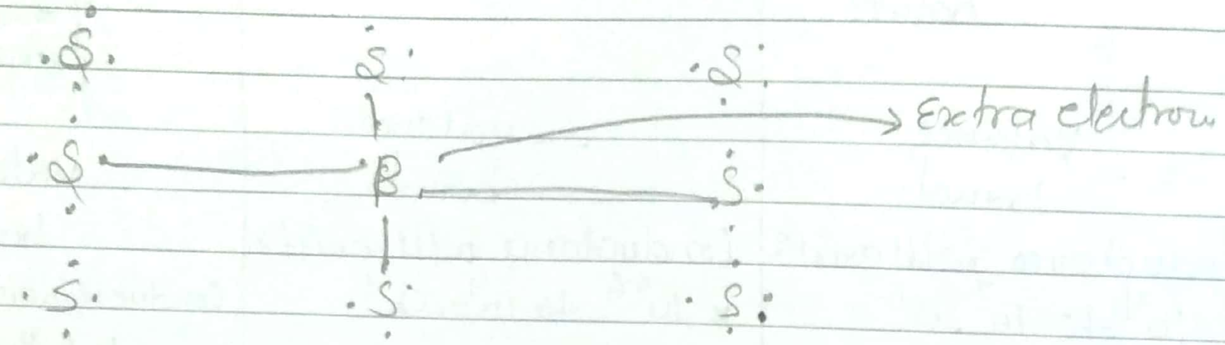
* Example of semiconductor :- Si, Ge, etc

* Doping of Semiconductors :-

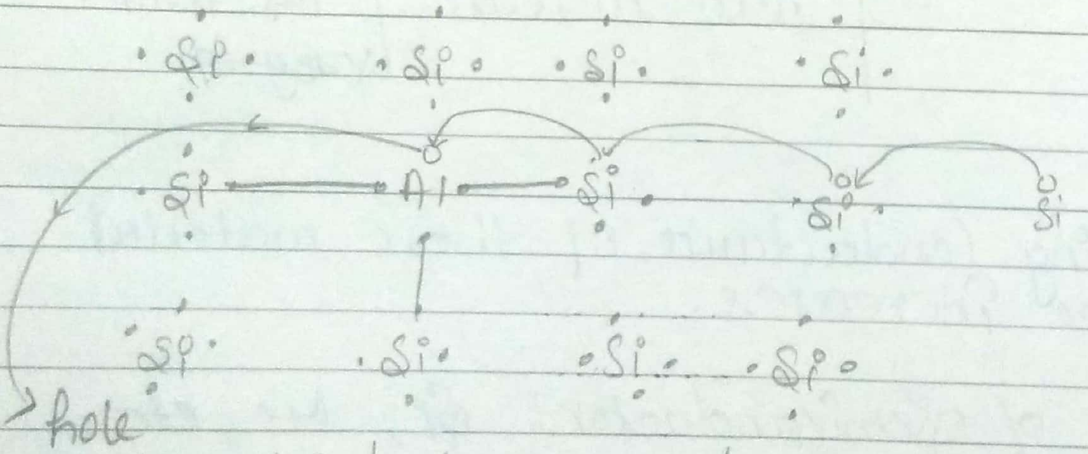
more then

(i) By electron rich impurity : or n-type Semiconductor :-

If elements of group 15 are mixed him element of group 14 then resultant semiconductor is called n-type semiconductor.



(ii) By mixing electron deficient impurity or P-type semiconductor :- If element of group 13 or 12 are mixed him element of group 14 resultant semiconductor is called P type semiconductor.



(It will behave just like a positive charge)

* Magnetic properties of Substance :

1) Solids in which unpaired electron exist.

2) Solids in which all the electron are in Paired form.

* Solids which have unpaired electron :-

i) ferromagnetic Substance

i) All the unpaired electrons will be aline in parallel direction

ii) These Substances are strongly attracted by external magnetic field.

Ex :- Fe, Co, Ni, CrO_2.   ↑↑↑↑↑↑↑↑↑↑

* After removing external field magnetic moment of ferromagnetic substance will not change.

2) ferrimagnetic Substance :

↑↑↑↓↓↑↑

* Unequal no. of electron will exist in Parallel and antiparallel direction.

* These types of Substances are weakly attracted by external magnetic field.

Ex! Fe_2O_3, Fe_3O_4 $ZnFe_2O_4$

3) **Antiferromagnetic Substance!**

↑↓↑↓↑↓↑

* equal no. of electron will be in parallel and antiparallel direction
* Idealy their must not be any impact of external magnetic field.

Ex! ~~Mn_3~~ Mn_3O_4, MnO_2

4) **Para magnetic Substance !**

↗↑↗↗↖ → ↗ ↑ ↓

↓↑↓↑ ↑↓↑ (after magnetic field).

* Magnetic moment of unpair electrons will be in random direction before applying external magnetic field.
  But after applying extranal ~~E~~ magnetic field. electron will arrange in Parallel and Anti parallel direction of magnetic.
  As a result finally they are weakly attract by extranal Magnetic field.

Ex! TiO_2, VO, VO_2, $FeSO_4$, CuO.

* ON Removing External Magnetic field e's in Paramagnetic substance will again Randomise.
* But in ferromagnetic, ferimagnetic and anti ferromagnetic on removing external magnetic field unpaired electrons will not again Randomise
* on increasing temperature ferromagnetic, ferrimagnetic and antiferromagnetic substance convert in paramagnetic substance.

(5) Substance which have all the electron are in paired form

Diamagnetic Substance :
External magnetic field try to Reduce stability of diamagnitic substance. So, these substances are repailed by external magnetic field.
Ex : Zn^{+2}, Sc^{+3}, H_2O.