∵ Rank of atom = Z_{eff}

Solid

Crystalline Solid (Real Solid)

→ Regular arrangement of particles
→ eg :- NaCl, Quartz

Amorphous Solid (Pseudo solid)

→ Irregular arrangement of particles
→ eg :- Quartz Glass, Glass, rubber, plastics

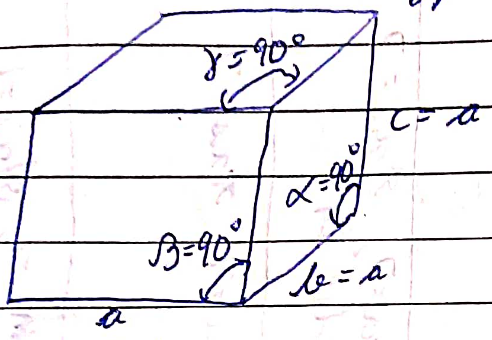
(Continuation of table ahead)

Property	Crystalline Solid	Amorphous Solid
Shape ~~melting pt.~~	Definite characteristic shape	Irregular shape
Melting pt.	Melt at sharp & characteristic temperature	Gradually soften over a range of temperature
Cleavage Property	When cut with a sharp edged tool, they split into two pieces & the newly generated surfaces are plain & smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have definite & characteristic heat of fusion	They do not have definite heat of fusion
Anisotrophy	Anisotropic in nature	Isotropic in nature
Nature	True Solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order

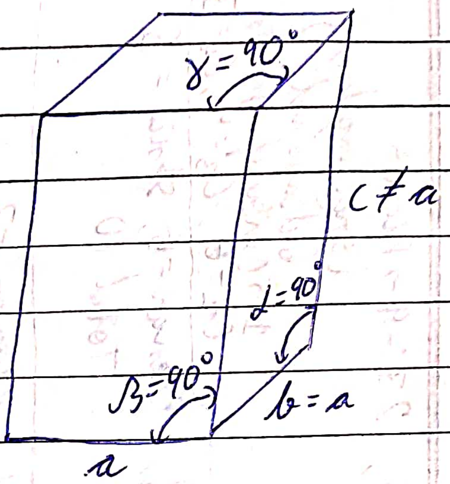
S.No.	Type of Solid	Constituent Particles	Bonding / Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting pt
1)	Molecular Solids (i) Non Polar	Molecules	Dispersion or London Forces	Cl_2, C_6H_6 Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very Low
	(ii) Polar		Dipole - Dipole interactions	HCl, SO_2/ Urea, (Solid)$_2$ Solid NH_3	Soft	Insulator	Low
	(iii) Hydrogen Bonded		Hydrogen Bonding	H_2O (ice)	Hard	Insulator	Low
2)	Ionic Solids	Ions	Coulombic or Electrostatic	$NaCl$, MgO, ZnS, CaF_2, K_2SO_4, $(NH_4)_3PO_4$, $LiBr$	Hard but brittle	Insulator in solid state Conductor in molten state & in aqueous solutions	High
3)	Metallic Solids	Positive ions in a sea of delocalised electrons	Metallic Bonding	Fe, Cu, Ag, Mg, Tin (Sn) Rubidium, Brass	Hard but malleable & ductile	Conductors in solid state as well as in molten state	Fairly High
4)	Covalent or Network Solids	Atoms	Covalent Bonding	SiO_2 (Quartz), SiC, C (Diamond)'	Hard	Insulators	Very High
				C Graphite	Soft	Conductor (exception)	

Unit Cells

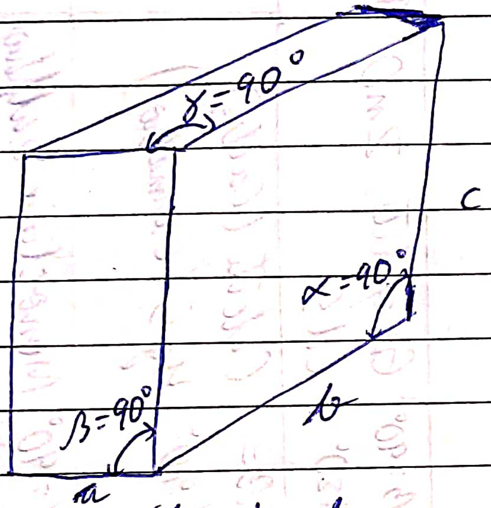
There are seven types of unit cells :-



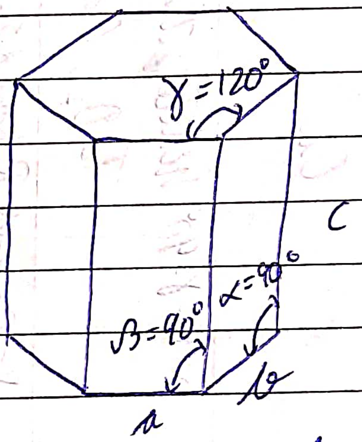
Cubic



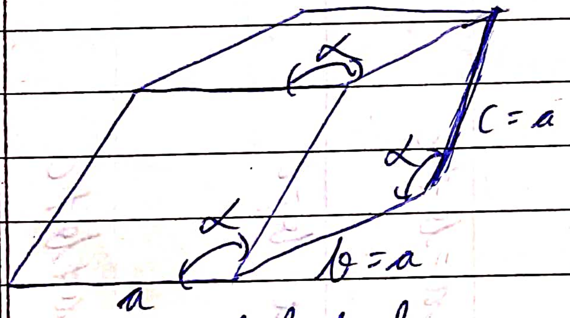
Tetragonal



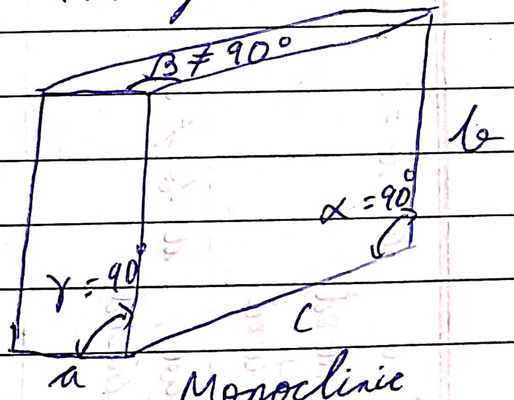
Orthorhombic



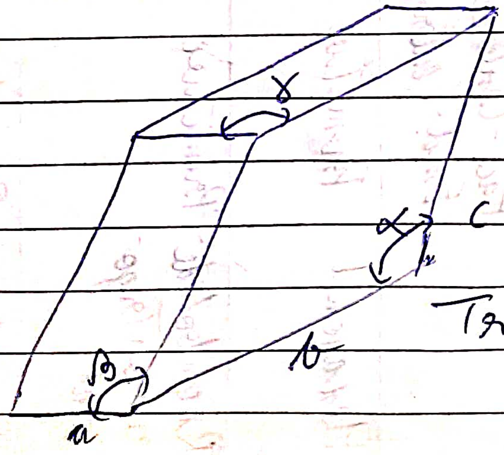
Hexagonal



Rhombohedral



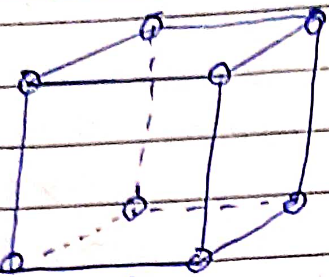
Monoclinic

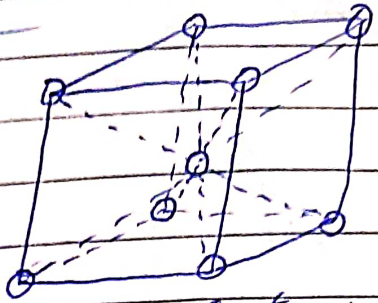


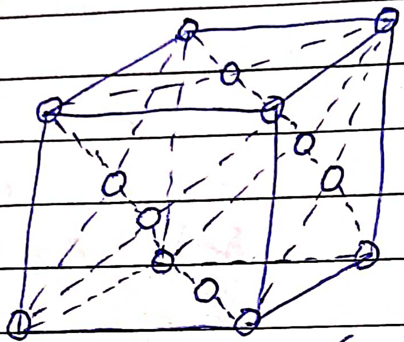
Triclinic

Crystal System	Possible Variations	Axial Distances or edge lengths	Axial Angles	Examples	Max. Symmetry
Cubic	Primitive, Body-Centered, Face-Centered	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc Blende, Cu	23 :- 9 → Planar (3 rectangular, 6 diagonal) 1 → Centre of symmetry $C_2 = 6$, $C_3 = 4$, $C_4 = 3$
Tetragonal	Primitive, Body-Centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2, TiO_2, $CaSO_4$	Planar = 5, Axis = 5 Total 10
Orthorhombic	Primitive, Body-Centered, Face-Centered, End-Centered	$a \neq b \neq c$	$\gamma = \beta = \alpha = 90^\circ$	Rhombic Sulphur, KNO_3, $BaSO_4$	Planar = 3, Axis = 3 Total 6
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Graphite, ZnO, CdS	Planar = 7, Axis = 7 Total 14
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta =$ $\gamma \neq 90^\circ$	Calcite ($CaCO_3$) HgS (Cinnabar)	Plane = 7, Axis = 7
Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Monoclinic Sulphur, $Na_2SO_4 . 10H_2O$	Plane = 1, Axis = 1
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90$	$K_2Cr_2O_7$, $CuSO_4 . 5H_2O$ H_3BO_3	No symmetry

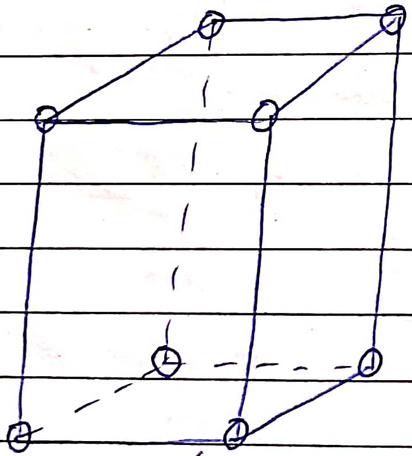
14 Bravais Lattices

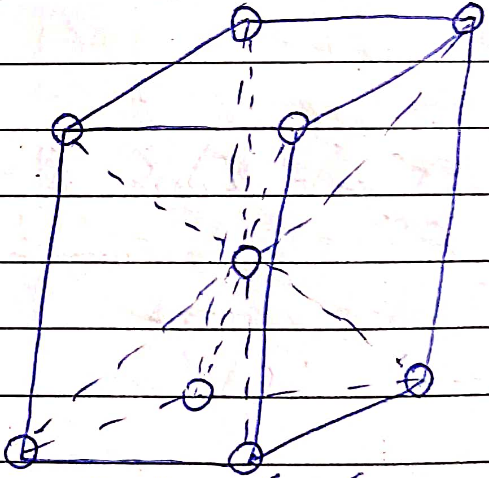

Primitive (or simple)


Body-Centered


Face-Centered

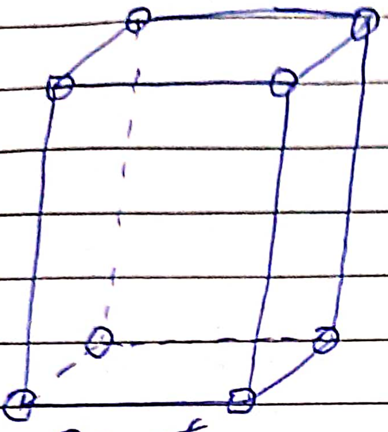
Cubic


Primitive

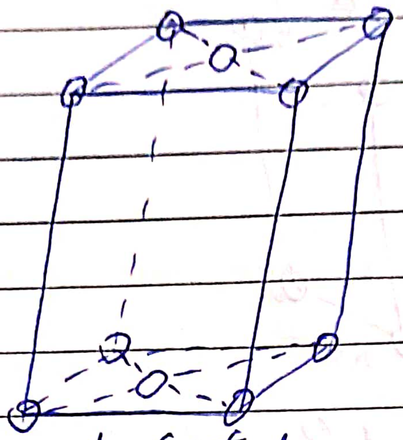

Body-Centered

Tetragonal

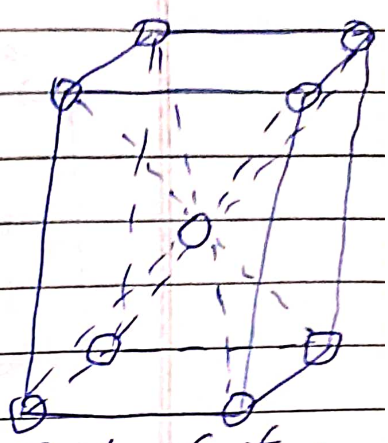
Orthorhombic



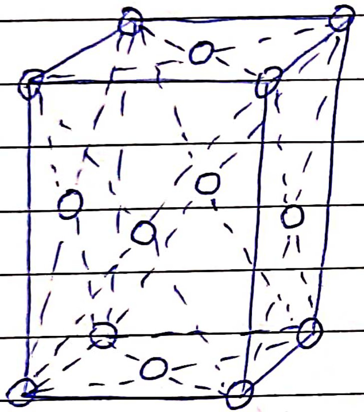
Primitive



End-Centred

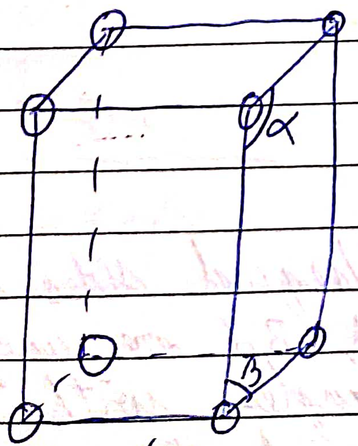


Body-Centred



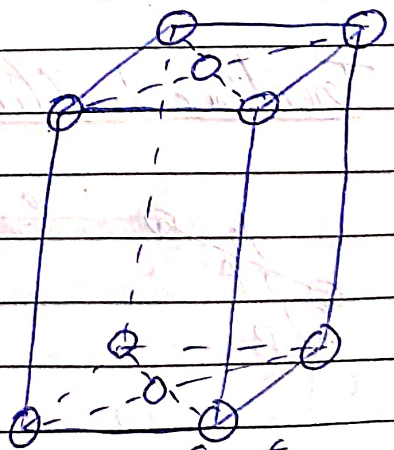
Face-Centred

Monoclinic



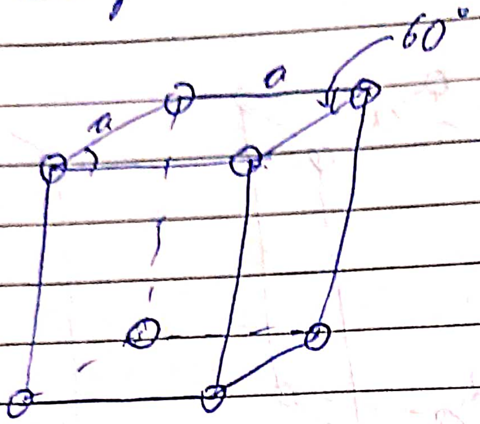
$\alpha > 90^\circ$
$\beta < 90^\circ$

Primitive



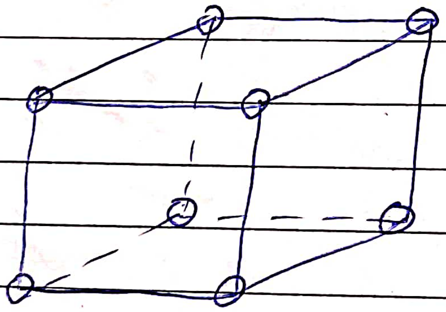
End Centred

Hexagonal



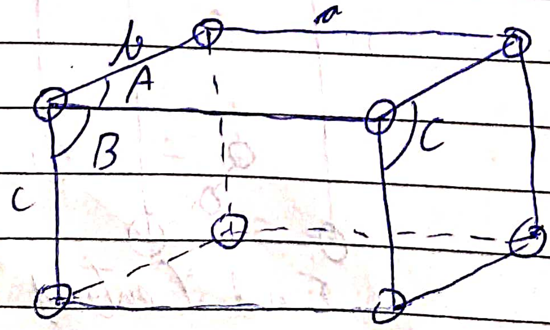
One side different in length to the other two, marked angles on two faces are 60°

Rhombohedral



All sides of equal length angles on two faces are less than 90°

Triclinic Lattice



Unequal sides a, b, c, A, B, C are unequal angles with none equal to 90°

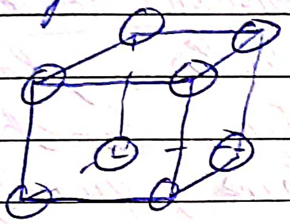
* Five Fold (C_9) axis of symmetry does not exist in any crystal

Unit Cells

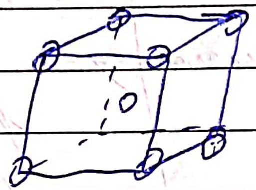
On the basis of Arrangement of Particles

- Primitive
  - Particles present only at corners
- Non Primitive
  - Body Centered
  - Face Centered
  - End Centred

eg:-

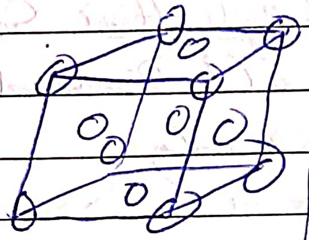


Body Centered



~~All fa~~ corners + Centre

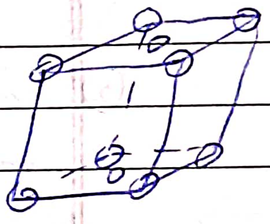
Face Centered



~~All faces~~ + Corners

End Centred

Corners + Opposite faces



Contribution of Particles:-

Cube:- Corner = $\frac{1}{8}$ Edge = $\frac{1}{4}$

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

In a Cube, total 23 symmetry
9 plane of symmetry
1 centre of symmetry
13 axis of symmetry
2 fold (C_2) :- 6
3 fold (C_3) :- 4
4 fold (C_4) :- 3

: Silicon :- best photo

Q:- Why NH_3 does not exist as hydrogen bonding solid?=
→

	Crystalline Solid	Amorphous Solid
①	eg:- NaCl, Diamond, Sucrose, Quartz	eg:- Rubber, glass, plastic, starch, proteins, quartz glass
②	There is a regularity in external form	There is no regularity in external form
③	They are rigid & not distorted by mild forces	Not very rigid, can be distorted by mild forces like bending
④	Physical property like refractive index, Thermal expansion, conductivity is diff. along diff. directions due to diff. arrangement of atom diff directions	Physical properties same
⑤	~~Cryst~~	
eg:-	Benzoic Acid, Cu	Polyurethane, teflon, celloph PVC, fibre glass

Page No. ______
Date

Crystallites :- In some cases amorphous solids contain small region of orderly arrangment. These small parts of these amorphous solids are called Crystallites.

Unit Cell :- Smallest repeating unit in a ~~cry~~ crystalline structure is called unit cell.

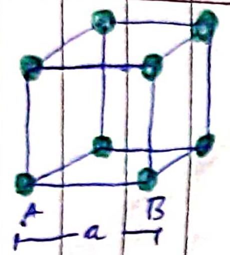
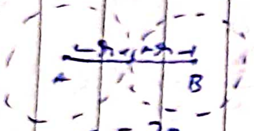
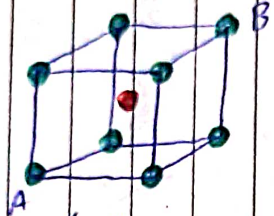
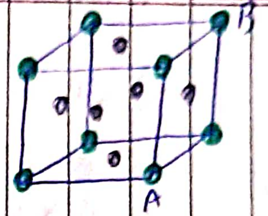
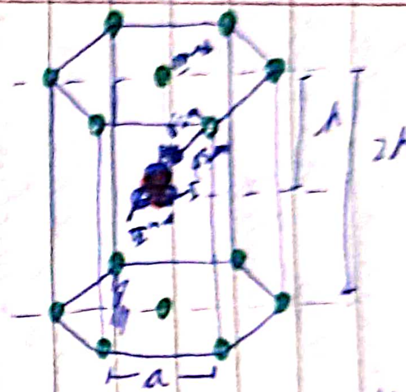
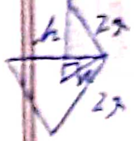
Lattice pt :- Particle which make up a unit cell. They may be atom, molecules, ion etc.

Lattice Space :- Space in which lattice pts are present

Primitive Unit Cells :- Particles are present only on the corner

On heating, amorphous solids become crystalline at some temperature. Some glass objects are found to become milky in appearance because of some crystallisation.

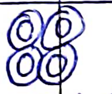
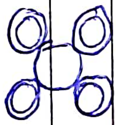
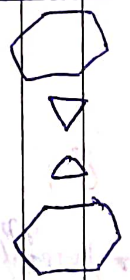
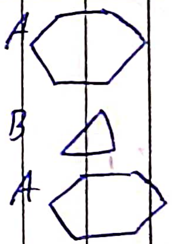
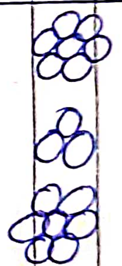
" Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity

	Simple Cubic Structure	Body Centre Cubic	Face Centred Cubic (CCP)	Hexagonal Closed Packing
① Structure	  $\underline{a = 2r}$	 $a \neq 2r$  $AB = 4r \Rightarrow \underline{4r = \sqrt{3}a}$	 $AB = 4r$ $\underline{4r = \sqrt{2}a}$	 $\underline{a = 2r}$  $x = \frac{2r}{\sqrt{3}}$ $4r^2 = h^2 + x^2$ $h = 2\sqrt{\frac{2}{3}}\,r$
② Effective No. of Atoms	$z = 8 \times \frac{1}{8} = \underline{1}$	$z = 8 \times \frac{1}{8} + 1\times 1$ $= \underline{2}$	$Z = 8\times\frac{1}{8} + 6\times\frac{1}{2} = 1+3$ $= \underline{4}$	$Z = 6\times\frac{1}{6} + 1\times\frac{1}{2} + 3\times 1 + 1\times\frac{1}{2} + 6\times\frac{1}{6}$ $= \underline{6}$
③ Volume	$V = a^3 = (2r)^3$	$V = \left(\frac{4r}{\sqrt{3}}\right)^3$	$V = \left(\frac{4r}{\sqrt{2}}\right)^3$	$V = \cancel{6}^{3} \times \frac{\sqrt{3}}{\cancel{4}} \times (2r)^2 \times 2h$ $= 3\sqrt{3} \times 4r^2 \times 2\frac{\sqrt{2}}{\sqrt{3}}r$ $\underline{V = 24\sqrt{2}\,r^3}$
④ Density $N_A \to M$ $1 \to \frac{M}{N_A}$ $Z \to \frac{MZ}{N_A}$	$d = \frac{1\times M}{N_A V}$	$d = \frac{2\times M}{N_A V}$	$d = \frac{4\times M}{N_A V}$	$d = \frac{6\times M}{N_A V}$

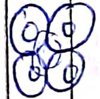
1 → $\frac{M}{N_A}$

2 → $\frac{Mz}{N_A}$

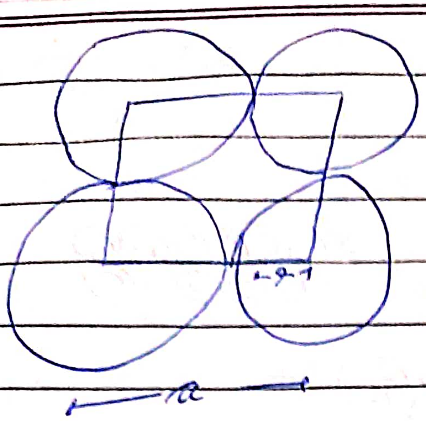
$d = \frac{Mz}{N_A V}$

Packing Fraction $P_f = \frac{2\times\frac{4}{3}\pi r^3}{V}$ Packing efficiency $= 100P_f$	$P_f = \frac{1\times\frac{4}{3}\pi r^3}{\cancel{8}(2r)^3}$ $= \underline{0.5236}$ $\underline{52.36\%}$	$P_f = \frac{2\times\frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3}$ $= \underline{0.68}$ $\underline{68\%}$	$P_f = \frac{4\times\frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3}$ $= \underline{0.74}$ $\underline{74\%}$	$P_f = \frac{6\times\frac{4}{3}\pi r^3}{24\sqrt{2}\, r^3}$ $= \underline{0.74}$ $\underline{74\%}$
Void Space $= 1 - P_f$	V.S $= 1 - 0.52$	V.S $= 1 - 0.68$	V.S $= 1 - 0.74$	V.S $= 1 - 0.74$
Layer View	A A  A-A distance $= 2r$	 A B A	 A C B A	A B A  
Layer Distance	A-A distance $= 2r$		A-A distance $= \sqrt{3}\,a$ A-B " $=$ B-C distance $=$ C-A distance $= \frac{a}{\sqrt{3}}$	
Coordination No.	6	8	12	12

⑩ Types of Voids	Simple Cubic Structure	Body Center Cubic	Face Centred Cubic	Hexagonal Closed Packing
	Cube Voids	Linear Void & Octahederal Void	Octahederal, Tetrahederal	Octahederal, Tetrahederal
⑪ Effective No. of Voids	1	Linear Void = $12 \times \frac{1}{4}$ $= 3$ Octahederal Voids $= 6 \times \frac{1}{2}$ $= 3$ Total = 6	No. of Octahederal Voids = 4 (1 is inside) (12 at edges $\Rightarrow 12 \times \frac{1}{4}$) Tetrahederal voids = 8 (All present at corners inside)	No. of effective octahederal voids = 6 No. " " tetrahederal voids = 12
⑫ First Nearest Neighbour	6	8	12	12
⑬ 2nd Nearest Neighbour	12	6	6	6
⑭ 3rd Nearest Neighbour	8	12	24	~~6~~ 2
⑮ Distance of 1st Nearest Neighbour	$a = 2r$	$\frac{a\sqrt{3}}{2}$	$\frac{a}{\sqrt{2}}$	$2r$

(16) Distance of 2nd Nearest Neighbours	$\sqrt{2}a = 2\sqrt{2}r$	a	a	$2\sqrt{2}r$
(17) Distance of 3rd Nearest Neighbours	$\sqrt{3}a = 2\sqrt{3}r$	$\sqrt{2}a$	$\cancel{2}\sqrt{\frac{3}{2}}a$	$2h = 4\sqrt{\frac{2}{3}}r$
(18) Coordination No. of Voids	8 (Formed by touching 8 atoms) 	Linear Void = 2 Octahedral Void = 6	Octahedral = 6 Tetrahedral = 4	Octahedral 6 Tetrahedral 4

Q:-

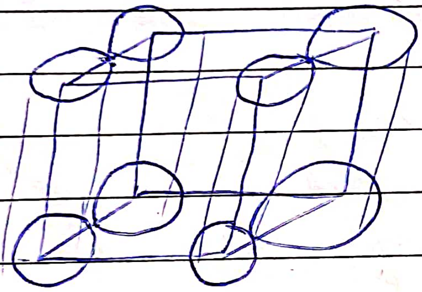


Find ~~V_f~~ P_f

→ $a = 2r$ $\quad P_f = \frac{\pi r^2}{a^2} = \frac{\pi}{4}$

Since fig. is 2D

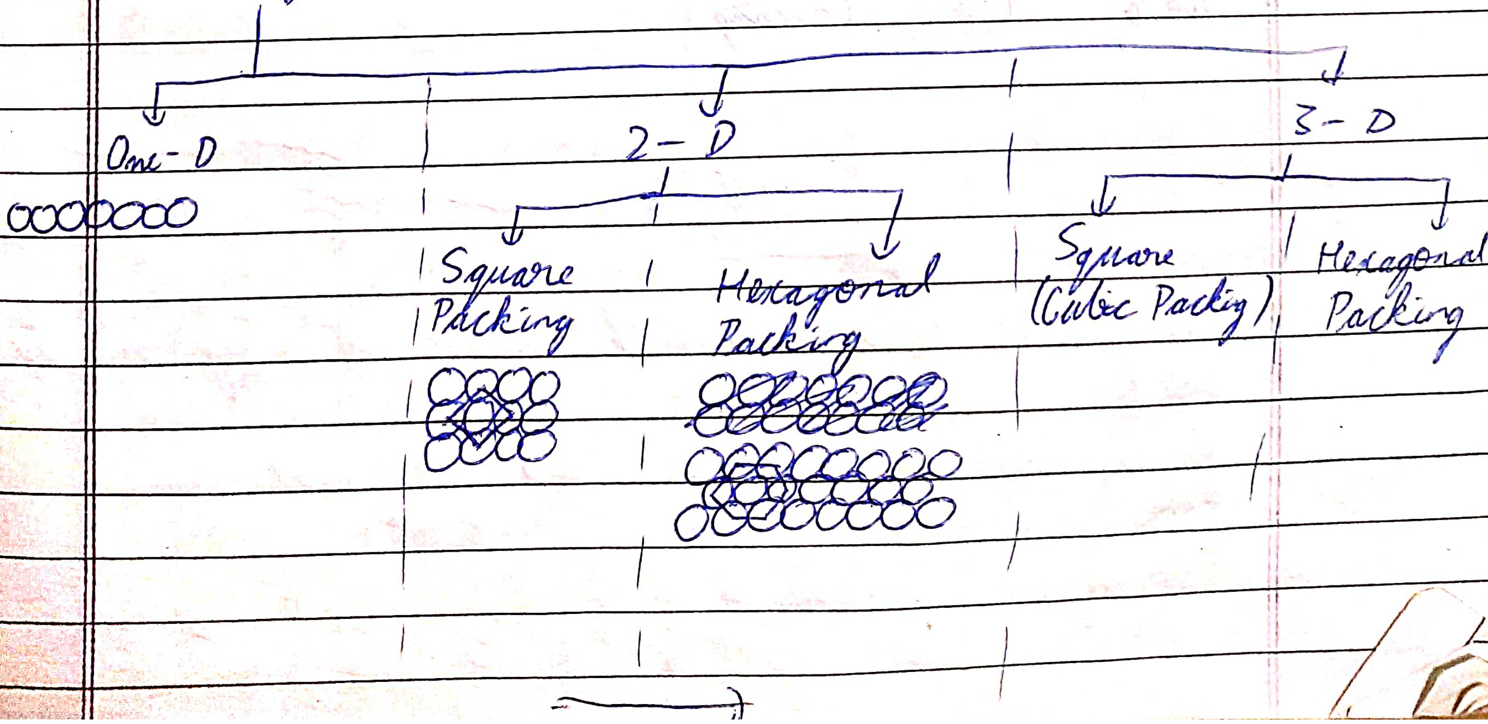
Q:-



All particles touching each other
Find P_f

→ $P_f = \frac{\pi r^2 \cdot a}{a^3} = \frac{\pi}{4}$

Packing



Metallic Solids

(1) Free & mobile e^- responsible for high electrical & thermal conductivity.

(2) Highly Malleable & Ductile

(3) When heat is supplied to one portion of a metal, the thermal energy is uniformly ~~dis~~ spread throughout by free e^-.

Covalent or Network Solids

(1) Also called giant molecules.

(2) Covalent bonds are stong & directional in nature, thus atoms held very strongly at their positions.

(3) Extremely high melting pts & may even decomplose before melting.

Imperfection In Solids

A solid consists of an aggregate of large no. of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rates.

Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects.

Types of Defects:-

1) Point Defects:- Irregularities or deviations from ideal arrangement around a pt or an atom in an crystalline substance

2) Line Defects:- Deviation from ideal arrangement in entire rows of lattice pts

These irregularities are called crystal defects.

Point Defects

I Stoichiometric Defects

① Do not disturb the stoichiometry of the solid.

② Also called intrinsic or thermodynamic defects.

③ Two types → Vacancy Defects
→ Interstitial defects

Vacancy Defects

① When some of the lattice sites are vacant, the crystal is said to have vacancy defect.

② Results in decrease in density

③ Can develop when a substance is heated.

Interstitial Defect

① When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect.

② Increases the density of the substance.

Vacancy & interstitial defects can be ~~see~~ shown by non-ionic solids (Ionic solids must always maintain electrical neutrality)

Ionic solids show these defects as Frenkel & Schottky Defects

→

∴ AgBr shows both as they have same size but have low coordination no.

Frenkel Defects

① The smaller ion (usually cation) is dislocated from its normal site to an interstitial site. It creates a vacancy defect at its original site & an interstitial defect at its new location. Shown by those which have low Coordination No.

② Also called Dislocation defect

③ Does not change density of the solid. Dielectric Constant increases

④ Shown by ionic substances in which there is a large difference in the size of ions.
eg:- ZnS, AgCl, AgBr, AgI due to small size of Zn^{2+} & Ag^{+} ions.

⑤ Conduction of electricity also there

Schottky Defect

① A vacancy defect in ionic solids.

② To maintain electrical neutrality, no. of missing cations & anions are equal.

③ Decreases density of the substance.

④ No. of such defects in ionic solids is quite significant.
eg:- In NaCl, there are approx. 10^{6} Schottky pairs per ~~10^6~~ cm^3.

** Energy reqd to create a Frenkel defect is less than that reqd to create a Schottky defect

⑤ Schottky defect is shown by ionic substances in which the cation & anion are of almost similar sizes.
eg:- $NaCl$, KCl, $CsCl$, $AgBr$

⑥ Conduction of electricity due to holes

* $AgBr$ shows both, Frenkel & Schottky defects.

⑦ Shown by those which have high Coordination no.

II Impurity Defects

If molten $NaCl$ containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion & the other site remains vacant. The cationic ~~valancies~~ vacancies thus produced are equal in no. to that of Sr^{2+} ions.
Another similar example is the solid solⁿ of $CdCl_2$ & $AgCl$.

III Non-Stoichiometric Defects

A large no. of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures

Two types → Metal excess defect
→ Metal Deficiency Defect

- Increases thermal & electric conductance (n-type semiconductor)
- Increases paramagnetism.

Metal Excess Defect

(i) Due to Anionic Vacancies :-

① Alkali halides like NaCl & KCl show this type of defect.

② When crystals of NaCl are heated in an atmosphere of sodium vapour, the Na atoms are deposited on the surface of the crystal. ~~& combine with Na atoms to give NaCl.~~
The Cl^- ions diffuse to the surface of the crystal & combine with Na atoms to give NaCl. The happens by loss of e^- by Na atom.
The released e^- diffuse into the crystal & occupy anionic sites.
Now crystal has an excess of Na.
The anionic sides occupied by unpaired e^- are called F-Centres.
Net formula $Na_{(1+x)}Cl$,
They impart yellow colour to the crystals of NaCl.

③ The colour results by ~~exc~~ excitation of these e^- when they absorb energy from the visible light falling on the crystals.

④ ~~Lim~~ Similarly, excess of Li makes LiCl crystals pink, excess of K makes KCl crystal violet (or lilac)

(ii) Due to presence of extra cations at interstitial sites

① Zinc oxide is white in colour at room temp. On heating it loses oxygen & turns yellow.

$$ZnO \xrightarrow{heating} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of Zn in the crystals & its formula become $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites & the e^- to neighbouring interstitial sites.

Metal Deficiency Defect

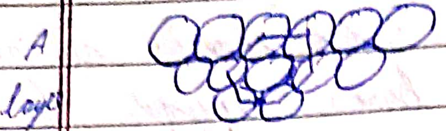
① Contain less amount of the metal as compared the stoichiometric properties

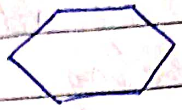
② eg:- FeO is most found as $Fe_{0.95}O$.
It can range from $Fe_{0.93}O$ to $Fe_{0.96}O$.
In crystals some Fe^{2+} cations are missing & the loss of +ve charge is made up by the presence of reqd. no. of Fe^{3+} ions.

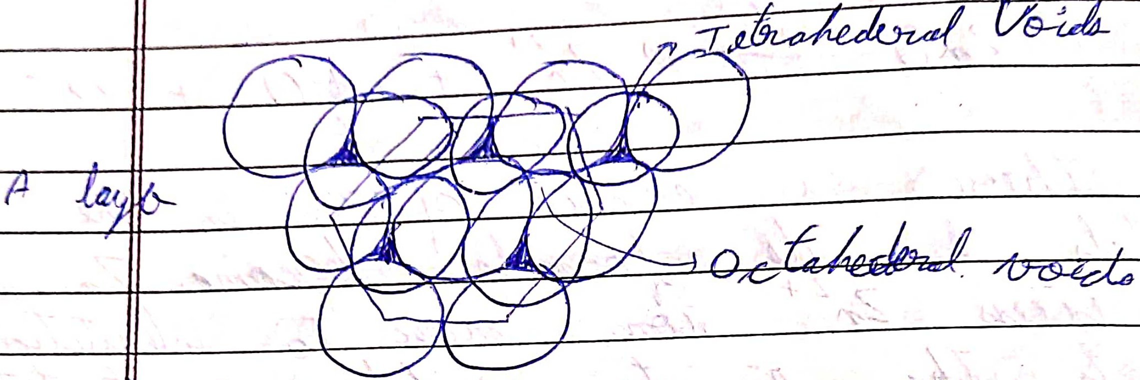
③ Increases electrical conductance increases (p-Type semiconducto

Electrical Properties

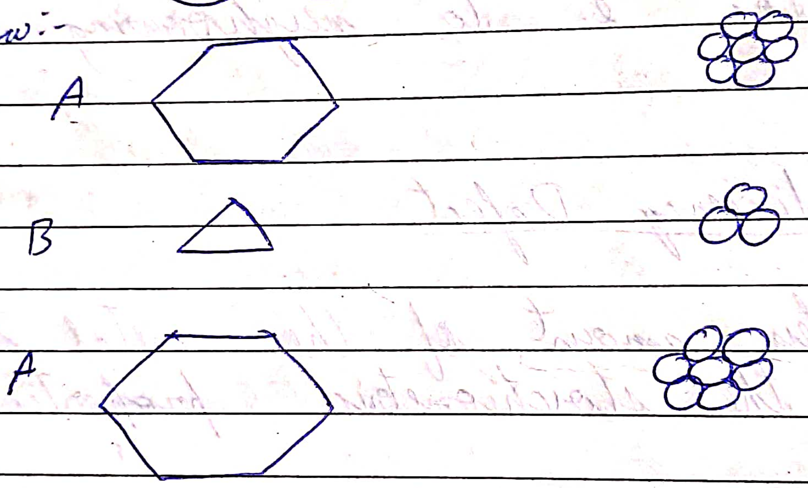
Hexagonal closed Packing







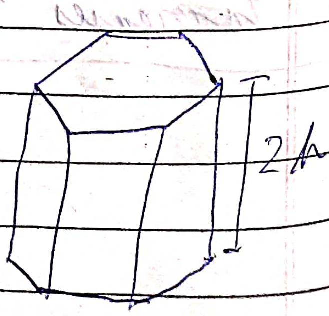
Layer View:-



In HCP:-

- Z_{eff} Tetrahedral voids = 12
  8 voids inside
  voids present at:-
  3 at $h/4$
  3 at $\frac{7h}{4}$
  1 at $\frac{5h}{4}$
  1 at $\frac{3h}{4}$

(If ht of packing is 2h)



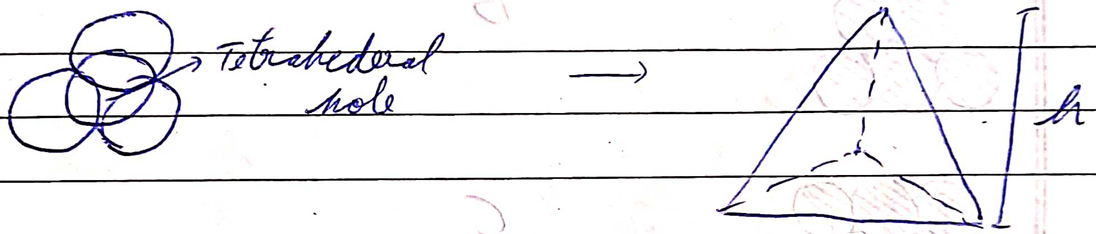
& remaining 12 at edges

∴ Contribution of each = $\frac{1}{3}$

∴ 4 partially outside

1 out of 12 , 6 at $\frac{3h}{4}$, 6 at $\frac{5h}{4}$)

- All 6 octahedral voids inside
  3 at $\frac{h}{2}$, 3 at $\frac{3h}{2}$



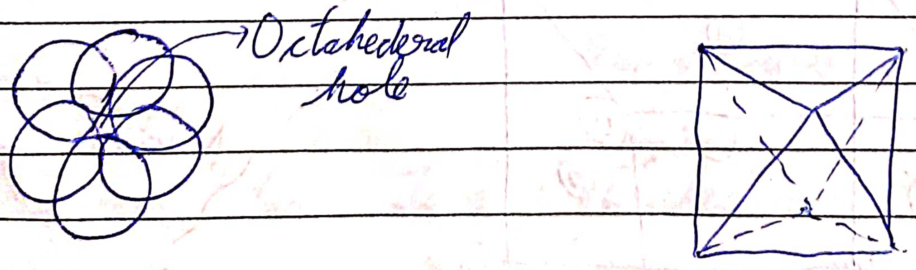
Tetrahederon

ht = h

∴ Centre of this will lie ht
∴ at $\frac{h}{4}$

∴ 3 at $\frac{h}{4}$ & 3 at $\frac{2h}{4}$

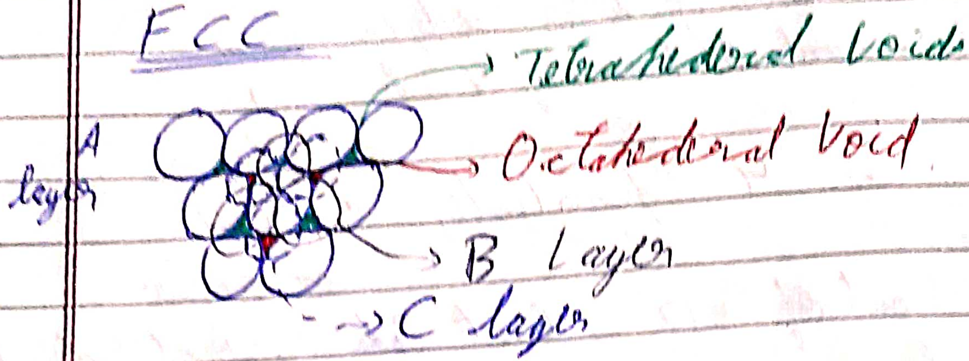
1 will lie at $\frac{3h}{4}$ (forms inverted tetrahederon)

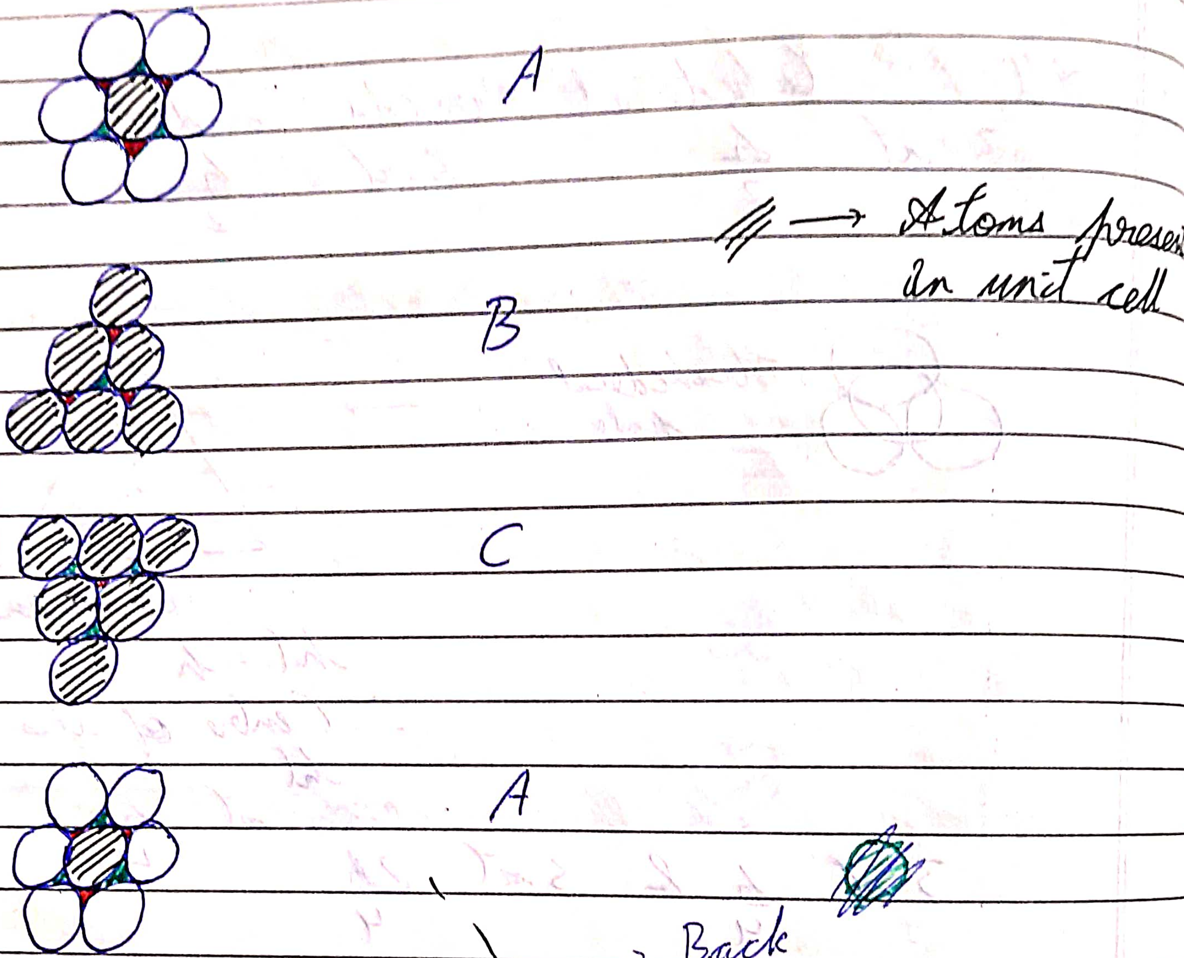


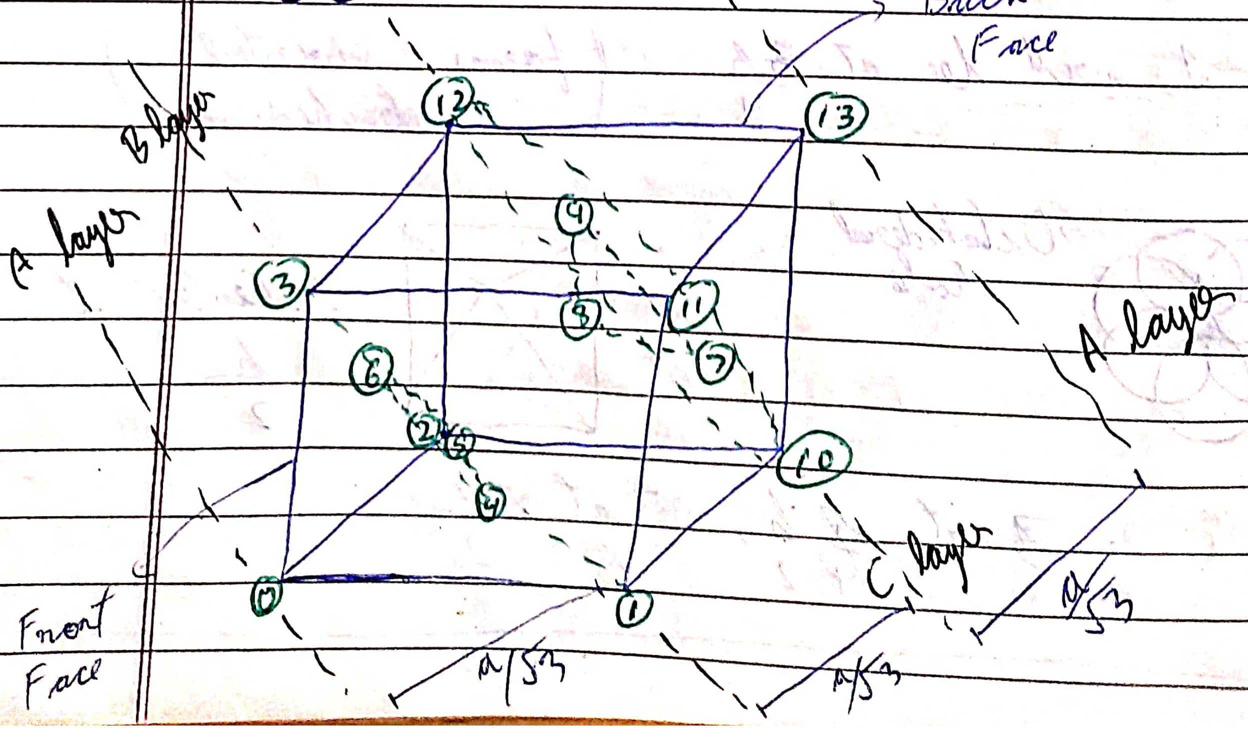
∴ Centre at $\frac{h}{2}$

∴ 3 at $\frac{h}{2}$, 3 at $\frac{3h}{2}$

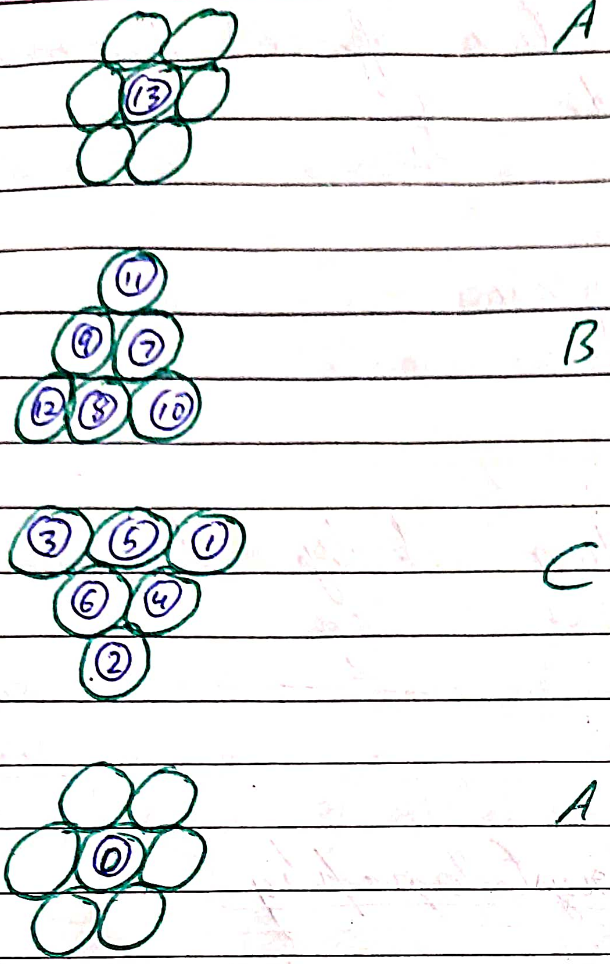
FCC


A layer
Tetrahedral Voids
Octahedral Void
B layer
C layer


A
B
C
A
→ Atoms present in unit cell


Back Face
B layer
A layer
A layer
C layer
Front Face
12
13
3
4
8
11
7
6
2
5
4
10
0
1
a/√3
a/√3
a/√3

Corresponding atoms

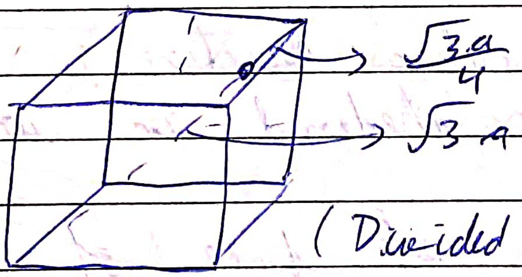


a → edge length

- Distance b/w any 2 consecutive layers = $\frac{a}{\sqrt{3}}$

If Edge length is = a

- Distance b/w ~~two~~ ~~adjacent~~ a tetrahedral void and a vertex = $\frac{\sqrt{3}.a}{4}$

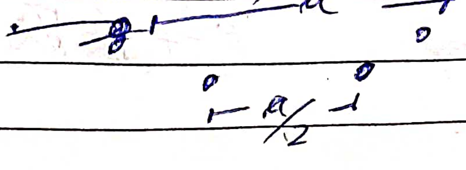


For symmetry

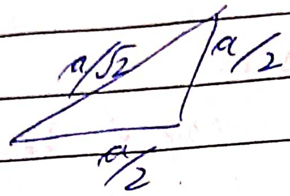
(Divided cube into 8 cubes)

- Distance b/w Two tetrahedral voids = $\frac{a}{2}$

(Divided cube into 8 cubes)



- Distance b/w two face diagonal tetrahedral voids $= \frac{a}{\sqrt{2}}$



- Distance b/w two body diagonal tetrahedral voids $= \frac{\sqrt{3}a}{2}$

First Law of Crystallography

In general, shape of crystalline solid depends on:-

a) Temperature
b) Rate of growth
c) Extent of impurity

eg:- NaCl → cubic structure in aqueous solⁿ
→ octahederal in urea

Angle b/w ~~a~~ face of crystals of same substance, whatever conditions be, is constant.

F → Faces   E → Edges   V → Vertices

~~F + E V~~

F + ~~E~~ V = ~~E~~ + 2

$F + V = E + 2$

Volume of 6 sided face 3d structure

$$V = abc\left(1 - \cos^2\alpha \cancel{+} - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta + 2\cos\beta\cos\gamma + 2\cos\alpha\cos\gamma\right)^{1/2}$$

Electrical Properties

Solids exhibit electrical conductivities ranging from orders 10^{-20} to $10^{7}\ ohm^{-1} m^{-1}$.

Classification of solids on the basis of conductivities :-

1) Conductors :- • Conductivities ranging b/w 10^{4} to $10^{7}\ ohm^{-1} m^{-1}$
• Metals have that in order of $10^{7}\ ohm^{-1} m^{-1}$ & are good conductor.

2) Insulators :- • Conductivities ranging b/w 10^{-20} to $10^{-10}\ ohm^{-1} m^{-1}$

3) Semiconductors :- • Range :- 10^{-6} to $10^{4}\ ohm^{-1} m^{-1}$

Conduction of Electricity in Metals

- Conductor may conduct electricity through movement of electrons or ions.
- Metallic conductors → through e^-
  Electrolytes → through ions.
- Metals conduct electricity in solid as well as molten state

- Conductivity of metals depend upon the number of valence e⁻ available per atom.

- The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a band.
If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field & metal shows conductivity

- If the gap b/w valence band & the conduction band is large, e⁻ can't jump to it & such a substance has very small conductivity & it behaves as an insulator.

Conduction of Electricity in Semi Conductors

- The gap b/w valence band & conduction band is small. Thus, some e⁻ may jump to conduction band & show some conductivity.

- For semiconductors, conductivity increases with rise in temperature, since more e⁻ can jump to the conduction band.

- Silicon & Germanium show this type of behaviour & are called intrinsic semiconductors.

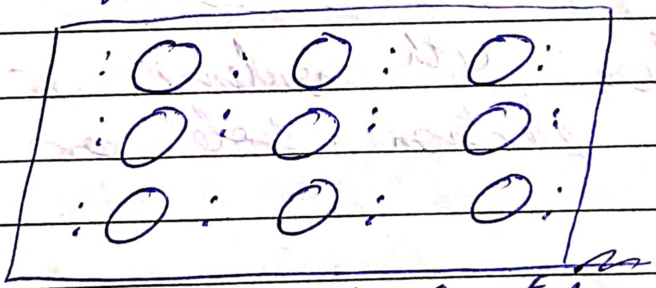
- The conductivity of these intrinsic semiconductors is too low.

- To increase their conductivity, an appropriate ~~t~~ amount of suitable impurity is added. This process is called doping. Doping can be done with an impurity which is e^- rich or e^- deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce electronic defects.

a) Electron-rich impurities

- Silicon & germanium belong to gp 14, thus 4 valence e^-.

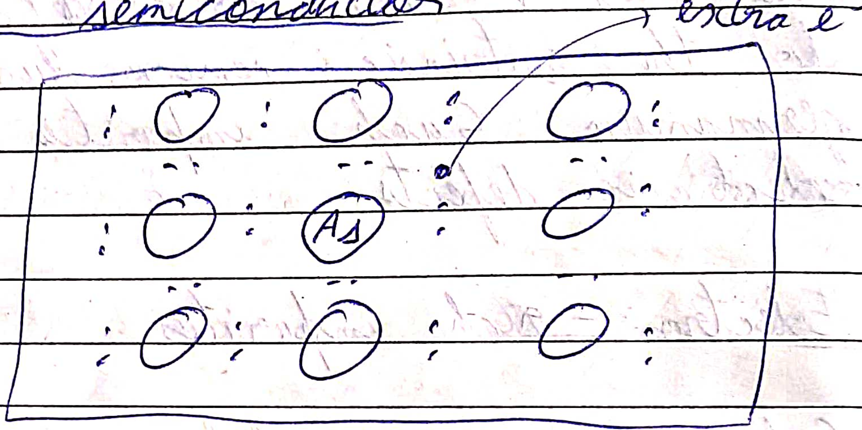
- In crystal, each atom forms 4 covalent bonds with its neighbours



Perfect Crystal

- When a gp 15 element like P or As (5 valence e^-) is doped in it, they occupy some of the lattice sites in silicon or germanium crystals.

- 4 out 5 e^- used in formation of covalent bonds.
- 5th extra e^- becomes delocalised & increases conductivity of doped silicon or germanium.
- Conductivity increased due to negatively charged e^-, hence these are called n-type semiconductor



b) Electron-Deficit Impurities

- Gp 13 elements like B, Al or Ga used (3 valence e^-).
- Place where 4th valence e^- is missing is called electron hole or electron vacancy.
- An e^- from a neighbouring atom can come & fill the e^- hole, but in doing so it would leave an e^- hole at its original position
- It would appear as if the e^- hole has

moved in the direction opposite to that of the e⁻ that filled it.

- ~~Unde~~ Under electric field, e⁻ would move towards the positively charged plate through electronic holes, but it would appear as if e⁻ holes are +ve charged & are moving towards -ve charged plate.

- This type of semi conductors are called p-type semiconductors.

Applications of n-type & p-type semiconductors

- Various combinations of n-type & p-type semiconductors used for making electronic ~~con~~ components.

- eg:- Diode → used as a rectifier

- Transistors → • sandwiching a layer of one type of semiconductor b/w 2 layers of other "
  - npn & pnp type
  - Used to detect or amplify radio or audio signals

- Solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

- Large variety of solid state materials have been prepared by combination of gp 13 & 15 or 12 & 16 to simulate average valence of 4 as in Ge or Si.

- ~~Th~~ Typical compounds of gp 13-15 are InSb, AlP, GaAs.
- Gallium arsenide (GaAs) → • very fast respon
  • revolutionarised design of semiconductor devices
- ZnS, CdS, CdSe & HgTe are examples of gps 12-16 compounds.
- In these, bonds are not ~~fe~~ perfectly covalent & the ionic character depends on the electronegativities of the two elements
- Transition metal oxides show marked differences in electrical properties.
- TiO, CrO_2, ReO_3 → behave like metals.

Rhenium Oxide, ReO_3 → like metallic copper in its conductivity & appearance.

VO, VO_2, VO_3, TiO_3 → show metallic or insulating properties depending on temp.

Date

Magnetic Properties

- Origin of magnetic properties lies in the e^-. Each e^- behaves like a tiny magnet in an atom.

- Its magnetic moment originates from :-
  - Orbital motion around nucleus
  - Spin around its own axis

- e^- ~~can be~~ undergoing these motions can be considered as a small current loop which posses a magnetic moment.

- This magnetic moment is very small & is measured in the unit called Bohr Magnetron, μ_B. $\underline{\mu_B = 9.27 \times 10^{-24} \, Am^2}$

On the basis of magnetic properties, substances are classified as :-

1) Paramagnetism :-
   - Weakly attracted by a magnetic field
   - Magnetised in a magnetic field in same direction
   - This is due to presence of one or more ~~unpf~~ unpaired e^- which are attracted by the magnetic field.
   - eg :- O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}.

2) Diamagnetism:-

- Weakly repelled by a magnetic field
- Weakly magnetised in magnetic field in opposite direction.
- All e^- are paired & no unpaired e^-.
- Pairing of e^- cancels magnetic ~~moments~~ moments & they lose their magnetic character.
- eg:- H_2O, $NaCl$, C_6H_6

3) Ferromagnetism:-

- Attracted very strongly by a magnetic field.
- Can be permanently magnetised
- In solid state, metal ions are grouped together into small regions called domain.
- Each domain acts as a tiny magnet.
- Initially they are randomly oriented, when magnetic field is applied, they get oriented & it persist even after field is removed & form permanent magnets.

- eg:- Iron, Cobalt, Nickel, Gadolinium, CrO_2

4) Antiferromagnetism:-

- Domains are oppositely oriented & cancel each other's magnetic moment.

- eg:- MnO, MnO_2

5) Ferrimagnetism:-

- Domains aligns in parallel & anti-parallel directions in unequal numbers.

- Weakly attracted by magnetic field as compared to ferromagnetic substances.

- These lose ferrimagnetism on heating & become paramagnetic

- eg:- Fe_3O_4 (Magnetite), ferrites like $MgFe_2O_4$ & $ZnFe_2O_4$

Radius Ratio (used for

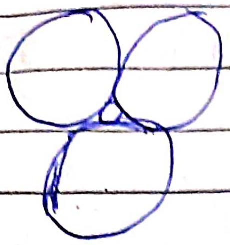
$$\frac{\text{Radius of cation } (r_+)}{\text{Radius of anion } (r_-)}$$

Generally $r_+ < r_-$

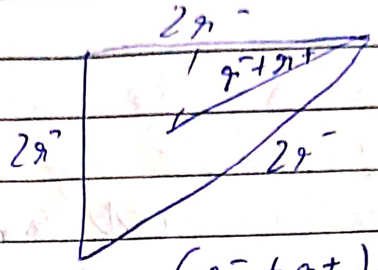
Radius ratio represent ionic environment of cation & anion, how anion are arranged abt cation. They give information abt. the shape.

$r_+ \to$ Void $r_- \to$ Lattice Pt	C.N of Voids	Example	Shape
< 0.155	2	BeF_2	Linear
0.155-0.225	3		Planar
0.225-0.414	4	CuCl, CuBr, CuI, BaS, MgS ZnS	Tetrahedron
0.414-0.732 ~~0.732-0.999~~	4	$PtCl_4^-$	Square Planar
0.414-0.732	6	MgO, NaBr, CaS, CaO, MnO, KBr, NaCl	Octahedral
0.732-0.999	8	NH_4Br, CsBr, CsCl	Body Centred

C·N = 3



Limiting radius ratio

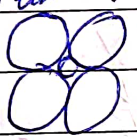


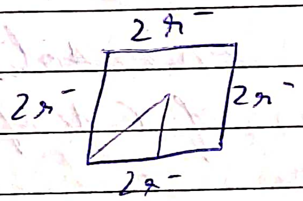
$(r^- + r^+)\cos 30° = r^-$

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

C·N = 4

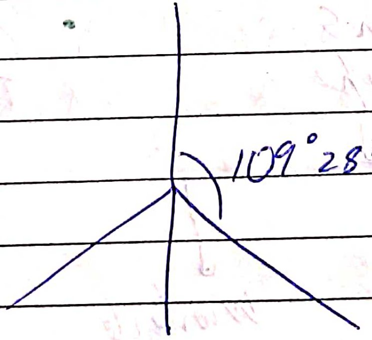
Square Planar :-

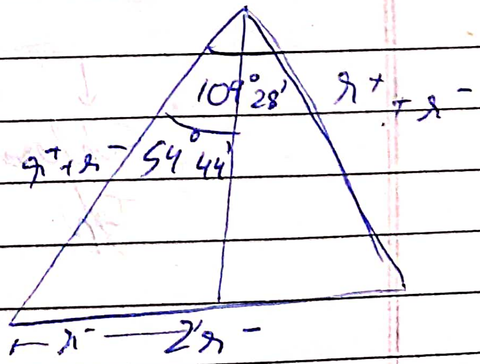




$(r^+ + r^-)\frac{1}{\sqrt{2}} = r^-$ $\frac{r^+}{r^-} = 0.414$

Tetrahedral :-





$\frac{r^-}{r^+ + r^-} = \sin 54°44'$

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

Classification of Ionic Solid

- AB Type
- A_2B Type
- AB_2 Type

Ionic Solid

C.N ratio

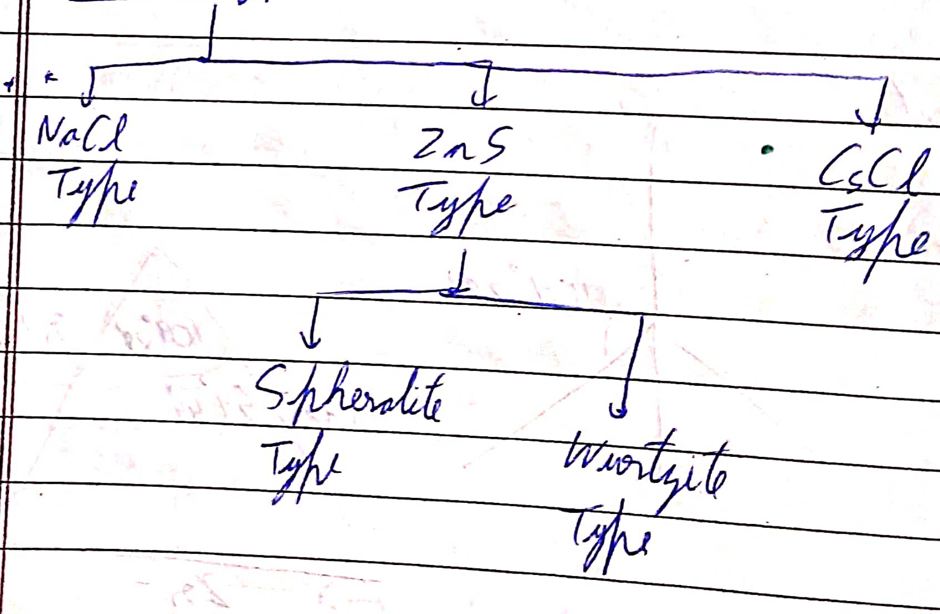
$A^+ : B^- = y : x$

Comp. Mol. formula

A_xB_y

For any ionic solid of formula A_xB_y, the ratio of C.N of $A : B$ is $y : x$

AB Type



NaCl Type

NaCl : F.CC / C.C.P

Na^+ ↓ void Cl^- ↓ Lattice

$$\frac{r_{Na^+}}{r_{Cl^-}} = \frac{95}{181} = 0.524$$

~~But it has FCC / HCCP structure~~

∴ ~~Thus~~ C.N of voids = 6 (Octahedral Voids)

Na^+ is present in octahedral voids, tetrahedral voids are empty

$Z_{eff}\ Cl^- = 4$ $Z_{eff}\ Na^+ = 4$

1 unit cell = 4 NaCl molecules

$$r_{Na^+} + r_{Cl^-} = \frac{a}{2} \quad -①$$

$$4r_{Cl^-} = \sqrt{2}\,a \quad -②$$

$$P.f = \frac{4 \times \frac{4}{3}\pi r_{Na^+}^3 + 4 \times \frac{4}{3}\pi r_{Cl^-}^3}{a^3}$$

$$= \frac{4 \times \frac{4}{3} \times \pi\, r_{Na^+}^3 + 4 \times \frac{4}{3}\pi r_{Cl^-}^3}{\left(\frac{4r_{Cl^-}}{\sqrt{2}}\right)^3}$$

$$= \frac{4 \times \frac{4}{3} \times \pi \left(\frac{r_{Na^+}}{r_{Cl^-}}\right)^3 + 4 \times \frac{4}{3}\pi}{\left(\frac{4}{\sqrt{2}}\right)^3} = 0.793$$

Here we use value 0.414 for $\frac{r_{Na^+}}{r_{Cl^-}}$ in all numericals not the actual value

Most of the halides of alkali metals oxides & sulphides of alkaline earth metals have this type of structure. Some of the common examples are NaI, KCl, RbI, RbF, NH_4Cl, NH_4Br, $AgCl$, $AgBr$, AgI, MgO,

Ferrous oxide also has sodium chloride types of structure in which O^{2-} ions are arranged in ccp & Fe^{2+} ions ~~are~~ occupy octahedral voids. However this oxide is always non-stoichiometric & has the composition $Fe_{0.95}O$. It can be explained on the assumption that some of the Fe^{2+} ion are replaced by 2/3rd as many Fe^{+3} ions in the ~~oct~~ octahedral void. This structure is called ~~blax~~ Wustite structure

ZnS Type

1) ZnS (Zinc Blende) ⇒ Spherolite structure

$$ZnS \rightarrow F.C.C / C.C.P$$

Zn^{+2} ↓ Voids ↓ Half of Tetrahederal Voids (Alternate)

S^{2-} ↓ Lattice pts

$$\frac{r_{Zn^{+2}}}{r_{S^{2-}}} = \frac{74}{184} = 0.4$$

$$Z_{eff}\ S^{2-} = 4 \qquad Z_{eff}\ Zn^{+2} = 4$$

1 unit cell = 4 ZnS molecules

For limiting ratio $\frac{r_{Zn^{+2}}}{r_{S^{-2}}} = 0.225$ (Assumed this in numericals)

C.N

$Zn^{+2} = 4$

$S^{2-} = 4$

ratio = 4 : 4

AB type

$$P_f = \frac{4 \times \frac{4}{3} \times \pi r^3_{Zn^{+2}} + 4 \times \frac{4}{3} \pi r^3_{S^{2-}}}{\left(\frac{4 r_{S^{2-}}}{\sqrt{2}}\right)^3}$$

$= ~~0.7489~~ \; 0.75734$

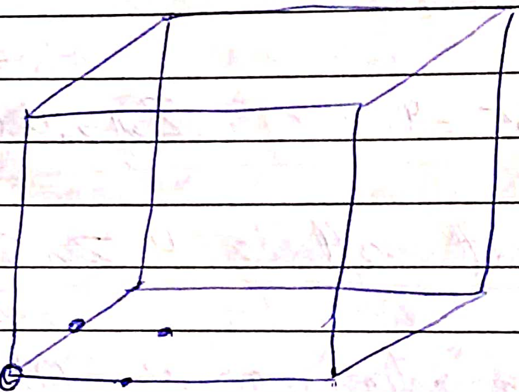
Examples of ionic solids having Zinc Blende structures are CuCl, Cu Br, Cu I, Ag I, Beryllium Sulphide, Mg S, Diamond (Packing Fraction efficiency = 0.34), Ge, Si, Grey Tin

same structure as diamo

Diamond:- Carbon are present at lattice pt & carbon are present at half of tetrahedral voids (alternate)
(FCC)

Q. Calculate the P_f of diamond

→



min. distance b/w 2 carbon atom

$$2r = \min\left\{\frac{\sqrt{3}a}{4}, \frac{a}{\sqrt{2}}, \frac{a}{2}\right\}$$

$$r = \frac{\sqrt{3}a}{8}$$

$$P_f = \frac{8 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{3}a}{8}\right)^3}{a^3} = 0.34$$

∴ For diamond, $P_f = 0.34$. not 0.74

Wurtzite Structure

$ZnS \rightarrow$ H.C.P

Zn^{+2}

- Alternate T.V
- ~~CN~~ $Z_{eff}\,Zn^{+2} = 6$

S^{-2}

- Lattice Pf
- $Zn\,S^{2-} = 6$

1 unit cell = 6 ZnS molecules

C.N

$Zn^{+2} = 4$

$S^{2-} = 4$

ratio = 1:1 ∴ AB Type

$$P_f = \frac{6 \times \frac{4}{3}\pi (r_{Zn^{+2}})^3 + 6 \times \frac{4}{3}\pi (r_{S^{-2}})^3}{24\sqrt{2}\, r_{S^{2-}}^3}$$

$$= 0.7930$$

eg:- ZnO, CdS, BeO

→

CsCl :-

CsCl :- Simple Cubic

Cs^+
- Void Cubic (C.N = 8)
- $Z_{Cs^+} = 1$

Cl^-
- Lattice Pt
- $Z_{Cl^-} = 1$

1 unit cell = 1 CsCl molecule

$$2r_{Cl^-} = a \quad -①$$

$$2r_{Cl^-} + 2r_{Cs^+} = \sqrt{3}a \quad -②$$

$$P_f = \frac{\frac{4}{3} \times \pi \times (r_{Cl^-})^3 + \frac{4}{3} \times \pi \times (r_{Cs^+})^3}{2(r_{Cl^-})^3}$$

$$= 0.7289$$

Effect of Temperature on Crystal Structure

Increase of temperature decreases the coordination no., eg:- upon heating to 760 K, the CsCl type crystal structure having coordination 8:8 changed to NaCl type crystal structures having coordinaton 6:6

CsCl type crystal $\xrightarrow[\text{Temp.}]{\text{High}}$ NaCl type crys

Effect of Pressure on Crystal Structure

Increase of pressure increases the coordination no. during crystallization.
eg:- by applying pressure, NaCl type crystal having coordination 6:6 changes to CsCl type crystal having coordination 8:8

$$\text{NaCl Type Crystal} \xrightarrow[\text{Pressure}]{\text{High}} \text{CsCl Type crystal}$$

Ionic Compound of type AB_2

Calcium Fluoride (Fluorite) structure

① The Ca^{+2} ions arranged in ccp arrangement.

② F^- occupy all the tetrahederal holes.

③ Since there are 2 tetrahederal holes for each Ca^{+2} ion & F^- ions occupy all the tetrahederal holes, there will be two F^- ions for each Ca^{+2} ions, thus the stoichiometry of the compound is 1:2

④ Each Ca^{+2} ion surrounded by 8F^- ions & each F^- ions surrounded by 4Ca^{+2} ions. This type of coordination is called 8:4 coordination.

⑤ Each unit cell has 4 Ca^{+2} ions &

$8F^-$ ions
Thus, no. CaF_2 units per unit cell → 4

Other examples of this structure are SrF_2, $BaCl_2$, BaF_2, PbF_2, CdF_2, HgF_2, CuF_2, $SrCl_2$

Ionic Compound of A_2B type

The compound having A_2B formula are compounds having anti fluorite structure.

Anti Fluorite structure is having arrangement of cations & anions opposite to the fluorite structure
Li_2O has an anti fluorite structure

① In the crystal structure of Li_2O, the O^{2-} ions constitute a cubic close packed lattice (fcc structure) & the Li^+ ions occupy all the tetrahedral voids.

② Each oxide ion, O^{2-} ion is in contact with $8Li^+$ ions & each Li^+ ions having contact with 4 oxide ion.
Thus, Li_2O has 4:8 coordination.

eg:- Na_2O, K_2O, K_2S, Na_2S, Rb_2O, Rb_2S, H_2

Normal Spinel Structure

Spinel is a mineral $MgAl_2O_4$. In it oxide ions are arranged in ccp with Mg^{+2} ions occupying tetrahedral voids & Al^{+3} ions in a set of octahedral voids. Many ferrites (such as $ZnFe_2O_4$) also possess spinel structure. These are very important magnetic materials & are used in telephone & memory loops in computers.

General formula :- AB_2O_4 (A^{2+}, B^{3+}, O^{2-})

- O^{2-} form fcc packing
- $\frac{1}{8}$th of Tetrahedral voids occupied by A^{2+}
- half of octahedral voids occupied by B^{3+}
- Ratio of T.V / O.V occupied in spinel structure

  No. of T.V occupied = 1
  No. of O.V " = 2
  ∴ Ratio = $\frac{1}{2}$ = 1 : 2

- Ratio of T.V / O.V unoccupied in spinel structure

  No. of T.V unoccupied = 8 − 1 = 7
  No. of O.V " = 4 − 2 = 2
  ∴ ~~The~~ Ratio = $\frac{7}{2}$ = 7 : 2

eg:- $ZnAl_2O_4$, $MgAl_2O_4$, $ZnFe_2O_4$

Inverse Spinel Structure

General formula :- AB_2O_4 A^{+2}, B^{+3}, O^{2-}

- O^{2-} form fcc packing
- $\frac{1}{8}$th of T.V occupied by A^{2+}
- B^{3+} are present in $\frac{1}{8}$th of T.V + $\frac{1}{4}$th of O.V
- Ratio TV / OV occupied in inverse spinel structure

No. of TV occupied = 1 + 1 = 2
" " O.V " = 1
Ratio = $\frac{2}{1}$ = 2 : 1

This ratio is inverse of spinel structure. Hence, the name inverse spinel structure.

- Ratio of TV / OV unoccupied

No. of TVs unoccupied = 8 − 2 = 6
" " OVs " = 4 − 1 = 3
Ratio = $\frac{6}{3}$ = 2 : 1

eg :- Fe_3O_4, $MgFe_2O_4$

In Fe_3O_4, Fe^{+2} & F^{+3} ions are present. It may be considered as $FeO \cdot Fe_2O_3$. In Fe_3O_4, Oxide arranged in ccp, Fe^{+2} occupy T.V & Fe^{+3} in O.V & T.V.

$MgFe_2O_4$ also has same structure. In this Mg^{+2} ions are present in place of Fe^{+2} ion in Fe_3O_4.

Mn crystallises as Simple Cubic (Only element in periodic table to do so).

Corundum Structure

Al_2O_3

Follow HCP structure

$O^{2-} \rightarrow$ lattice pts

$Al^{+3} \rightarrow 2/3^{rd}$ of O.V

(T.V empty)

Rutile Structure

TiO_2

HCP structure

$O^{2-} \rightarrow$ lattice pts

$Ti^{+4} \rightarrow$ ions occupy $(1/2)$ of O.V

~~Perost~~ Perwoskytes Structure

$CaTiO_3$ F.C.C Structure

$Ca^{+2} \rightarrow$ At corners

$O^{2-} \rightarrow$ Face centres

$Ti^{+} \rightarrow$ At Centre of Cube (1 O.V)

Defects :-

- At absolute 0 Kelvin, no. of defects is min.
- As temp. increases, no. of defects increases exponentially.
- For defect formation :-

  $\Delta H > 0 \quad \Delta S > 0$

  ⇒ More spontaneous at higher temp.
- No matter how many imperfections are present in a crystal, it is always electrically neutral.

Isomorphism

- The occurance of a given substance in more than one solid crystalline forms have different physical properties is polymorphism. This property when exist in elements is called allotropy.
- We sometimes come across examples of chemically different solids ~~crystalline~~ having same crystalline structure are called ~~isop~~ isomorphous

Their chemical constituents are very similar & in some ~~ones~~ cases crystals ~~are~~ of one substance continue to grow in saturated sol^n of other.

eg:- Potash alum & chrome alum & can be grown in each other

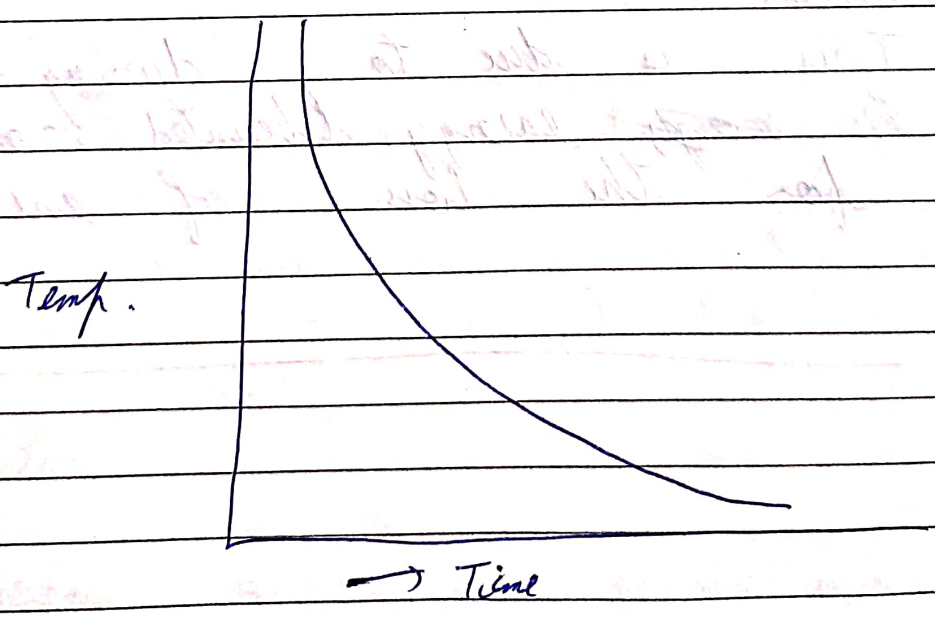
Isomorphous have similar chemical structure

eg :- · Phosphate & Arsenate,

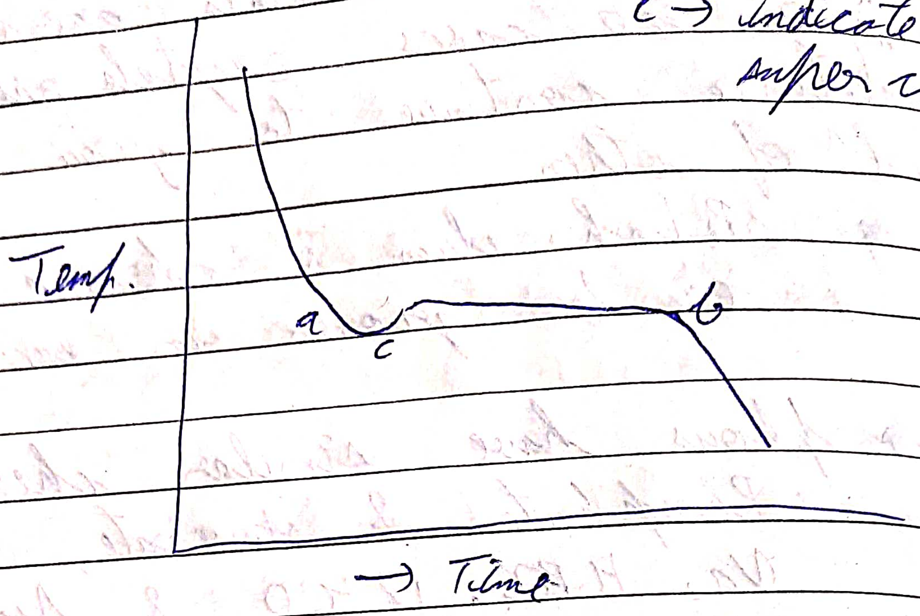
$Na_2HPO_4 . 12H_2O$ & $Na_3AsO_4 . 12H_2O$

- K_2CrO_4 & K_2SO_4
- $ZnSO_4 . 7H_2O$, $MgSO_4 . 7H_2O$, $FeSO_4 . 7H_2O$
- $KMnO_4$, $KClO_4$
- $K_2SO_4 . Al_2(OH)_3 . 24H_2O$, $K_2SO_4 . Cr(OH)_3 . 24H_2O$

Cooling Curve



Cooling curve of an amorphous solid



c → Indicate super cooled

Cooling curve of crystalline solids

In crystalline solids, 2 break pts 'a' & 'b' appear.

These pts ~~be~~ indicate the beginning (a) & end (b) of crystallisation.

In this time interval, temp. remain constant.

This is due to :- during crystallisation Th ~~energy~~ energy liberated compensates for the loss of energy.

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Date

Structure Determination by X-Ray (Not in IIT)

Bragg's Eqⁿ

Nowadays protein & nucleic acids are determined by this.

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

$\lambda \rightarrow$ wavelength of light
$\theta \rightarrow$ angle b/w incident ray & plane of crystal
The diffracted beam makes an angle of 2θ

$d \rightarrow$ distance b/w plane of constituent particles in crystals
$n \rightarrow$ integer represent order

---

2 D lattice

5 types :-

1) Hexagonal
2) Square
3) Rectangular
4) Rhombic
5) Parallelogram

Allotropy :-

3. Types -

1) Enantiotropy:- One form is interconvertible to another at a fixed temp & pressure. Rmax

2) Monotropy

3) Dyanamic allotropy

Monotropy :-

One form is unstable at all temperatures & is converted to stable form. eg:- ~~Red P to~~ white ~~yellow P~~, ~~O_2 to O_3~~

eg:- $O_2 \rightarrow O_3$, red P_4 → yellow P_4

Dyanamic Allotropy :-

Both form exist side by side in eqlb at all temp.

eg:- λ_m & μ Sulphur.

Enantiotropy:- One form is interconvertible to another at a fixed transition temp. under specified pressure.

eg:- ~~#~~96.6°C, rhombic S to monoclinic S & vice versa

Dielectric & Electric Property of Polar Crystals

1) Piezoelectricity

When mechanical stress applied on polar crystals, electricity produced due to ~~movement of ions~~ displacement of ions. eg:- $PbZrO_3$, $NH_4H_2PO_4$, quartz

2) Pyroelectricity

Electricity produced on heating a polar crystals

3) Ferroelectricity

These crystals remain permanently polarized even in the absence of electric field.

eg:- $BaTiO_3$, Rochelle salt, KH_2PO_4

→

4) **Antiferroelectricity**

Crystals have net dipole moment 0 as they have equal no. of opposite dipoles

eg:- $PbZrO_3$

* All ferroelectric crystals are piezoelectric but reverse is not true.

5) **SuperConductivity**

When the electrical resistance of a ~~conductor~~ substance become almost zero, it is called superconductor.

eg:- Hg becomes superconductor at 4K, $YBa_2Cu_3O_7$ at 90 K

Masses:-

Li :- 7
Na :- 23
K :- 40
Cs :- 132
F :- 19
Cl :- 35.5
Br :- 80
I :- 127

Zn :- 65
Pb :- 207
Cr :- 52
Fe :- 56
Cu :- 63.5
Ag :- 107