

CHAPTER - 1THE SOLID STATE

Solid State :- it is a state of Matter which has definite shape & volume & also has a greater Vanderwall force of attraction.

Classification :-① Crystalline

- Systematically Arranged

- Long Range order

- fixed Density

- Sharp Melting point

- True Solids

- clean cleavage

- Definite heat of fusion

- Anisotropic

- Ex- NaCl, diamond

- ZnS, CaF₂, Na₂F, SiO₂ etc.

② Amorphous

- Randomly Arranged

- Short Range order

- Density not fixed

- Low M.P.

- Super Cooled or Pseudo Solids.

- Irregular Cut

- Not fixed heat of fusion

- Isotropic

- Rubber, plastic, salt

- PVC etc.

Types of Crystalline Solid :- 4 types① Non-polar

① Molecular Solid - Molecules are the Constituent particles of Molecular Solids.

3 types -

① Non-Polar Molecular Solid \rightarrow Dispersive (weak) force present.

\rightarrow Soft

\rightarrow Low Melting & boiling point

\rightarrow Insulators

Ex- O_2 , N_2 , Cl_2 , CH_4 , CCl_4 , He , Xe etc.

② Polar M.s. \rightarrow Dipole-Dipole force present.

\rightarrow Soft

\rightarrow High Melting point than non-polar M.s.

\rightarrow Insulators

Ex- CO_2 , H_2S etc.

③ H-Bonded M.s. \rightarrow H-Bonding present

\rightarrow Soft

\rightarrow Insulators

\rightarrow High M.p. & B.p. than Polar & Non-Polar M.s.

④ Covalent Solid \rightarrow Covalent Bond present

\rightarrow Hard & Brittle

\rightarrow High Melting point

\rightarrow Non-conductors

Ex- Diamond, SiO_2 , etc.

⑤ Ionic Solid \rightarrow electrostatic force of attraction b/w cation and anion.

\rightarrow High Melting point

\rightarrow They are Insulators in Solid State but conductors in Molten State.

Ex- $NaCl$, KCl etc.

④ Metallic Solids \rightarrow electrostatic force of attraction b/w kernels & free electrons

$$\text{Na} \rightarrow \text{Na}^{+} + e^{-}$$

10^{23} 10^{19}

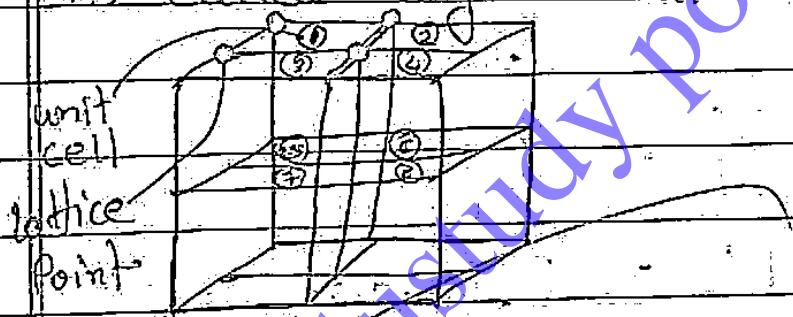
Kernels	Valence
cell	cell

\rightarrow Hard

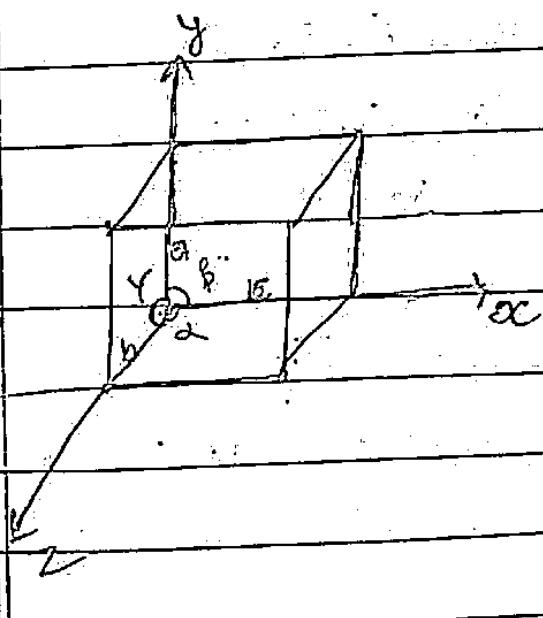
\rightarrow Conductors (High Thermal & electrical conductivity)

\rightarrow Very High Melting point

Crystal lattice \triangleq An ordered Arrangement of Constituents particle in 3D space
is called crystal lattice

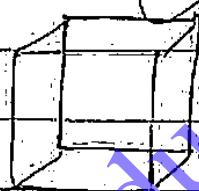


Unit Cell \Rightarrow it is the Smallest portion of Crystal lattice which Repeated in all direction.



Crystal System	Axial length	Axial angle	Examples
① Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl
② Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{PbSO}_4, \text{SnO}_2$
③ orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombohedral $\text{KNO}_3, \text{K}_2\text{SO}_4$
④ Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$	$\text{ZnO}, \text{Al}_2\text{O}_3$
⑤ Rhombohedral or Trigonal	$a = b = c$	$\gamma = 120^\circ$ $\alpha = \beta = \gamma \neq 90^\circ$	$\text{CaCO}_3, \text{K}_2\text{S}$
⑥ Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
⑦ Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7, \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Unit cell -



corners = 8

faces = 6

Edges = 12

Body diagonal = 4

Face diagonal = 12

Contribution -

① Body centre = 1 = 100%

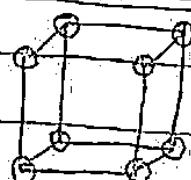
② face centre = $1/2 = 50\%$

③ Edge centre = $1/4 = 25\%$

④ Corner = $1/8 = 12.5\%$

Classification of unit cell :-

① Primitive / Simple unit cell - unit cell at the corner



SCC - Simple cubic crystal

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

② Non-primitive / centred unit cells -

a- Body centred unit cell - BCC.

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

b- face centred unit cell - FCC.

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

c- End-centred unit cell - FCC

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

Closed Packed Unit Cell :-

④ 1D close packed unit cell -

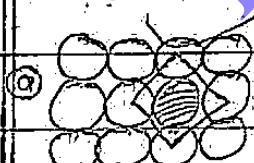
coordination Number



$$(CN) = 2$$

Linear close packing.

⑤ 2D close packed structure -



$$CN = 4$$

Square close packing.

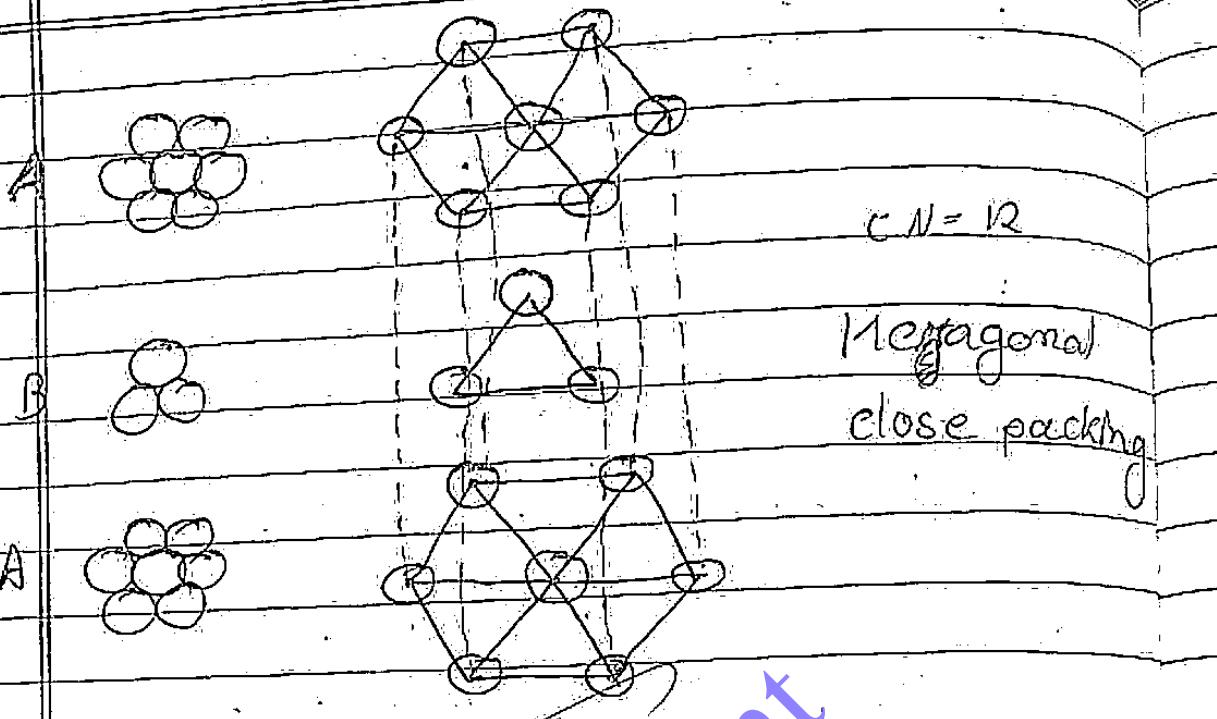


$$CN = 6$$

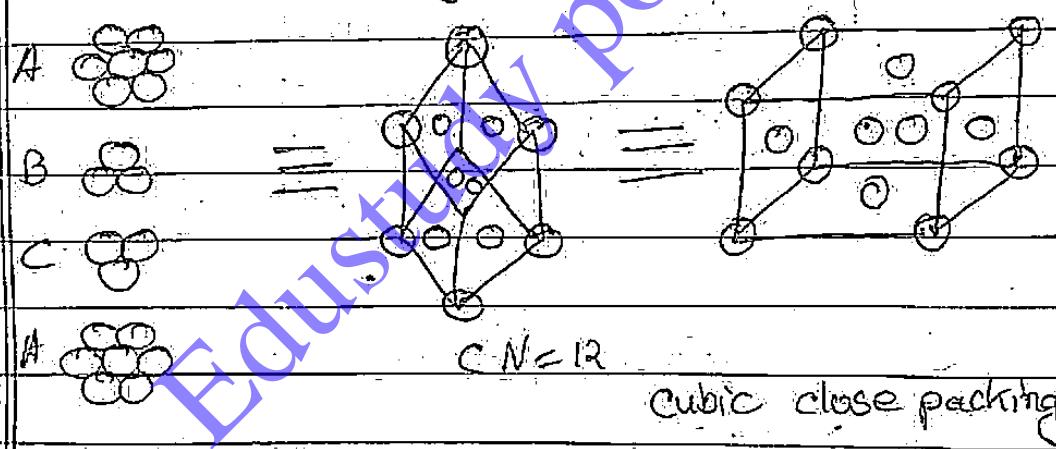
Hexagonal close packing.

⑥ 3D close packed structure -

ABABAB --- type.



(b) ABC ABC... type



Void :- The Space present in Constituent two particles is called Void.

① Octahedral Void -

$$CN = 6$$

effective no. of octahedral voids

$$= 1 \times 1 + 12 \times 4 = 48$$

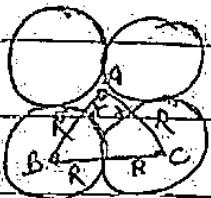
Size of Octahedral Void -

Radius of Octahedral void (r) = $\frac{C + 4R}{6}$

Radius of void

Radius of atom

Relation b/w r & R in Octahedral Void.



In $\triangle ABC$

$$BC^2 = AB^2 + AC^2$$

$$(QR)^2 = (R+r)^2 + (R+r)^2$$

$$4R^2 = 2(R+r)^2$$

$$\sqrt{2}R = R+r$$

$$r = \sqrt{2}R - R$$

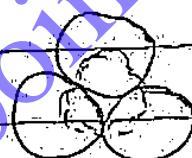
~~$$r = R(\sqrt{2}-1)$$~~

~~$$r = R(1.414 - 1)$$~~

~~$$r = R(0.414)$$~~

② Tetrahedral Void -

$$CN = 4$$



Effective no. of tetrahedral void = 8

Packing Efficiency : the percentage of

PE = Volume occupied by all atom
in one unit cell

- Volume of unit cell

if all atoms are identicals

PE = Effective no. of atom in \times volume
of atom unit cell
Volume of unit cell

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

$$\% PE = Z \times \frac{4}{3} \pi \left(\frac{r}{a}\right)^3 \times 100$$

QF 9. Coordination No. & Radius

	PE (%)	CN	Radius
SCC	52%	6	$r_1 = \frac{9}{2}$
BCC	68%	8	$r_2 = \frac{\sqrt{3}}{4} a$
FCC	74%	12	$r_3 = \frac{9}{2\sqrt{2}}$

Density of unit cell

$$\rho = \frac{\text{Mass of all atom in one unit cell}}{\text{Vol. of unit cell}}$$

\Rightarrow if all atoms are identical

$$\rho = \frac{\text{Mass of Atom} \times \text{Effective no. of atom in unit cell}}{\text{Vol. of unit cell}}$$

$$\rho = \frac{m \times Z}{V}$$

$$\therefore \text{Mass of atom} = \frac{\text{Molar Mass}}{\text{Avogadro's No.}} = \frac{m}{N_A}$$

$$\rho = \frac{Z M}{N_A \cdot a^3}$$

Radius Ratio -

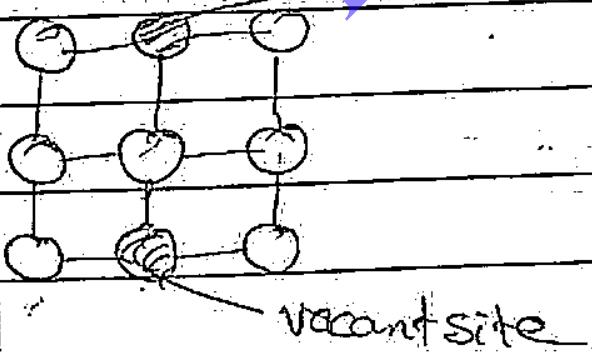
$$R.R. = \frac{r_1}{r_2}$$

R.R.	C.N.	geometry	Ex
$0.155 - 0.225$	3	Trigonal planar	B_2O_3
$0.225 - 0.414$	4	Tetrahedral	ZnS
$0.414 - 0.732$	6	Octahedral	MgCl_2
$0.732 - 1.00$	8	BCC	CsCl

Defects: Any Departure from perfectly ordered crystal of constituent particle is known as defect.

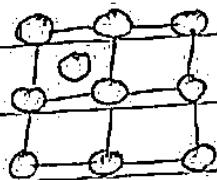
(1) Stoichiometric Defect :- This defect occurs due to the Ratio of cation and Anion Remain Same.

(2) Vacancy Defect :-



→ density decrease

→ It occurs in non-ionic compound.

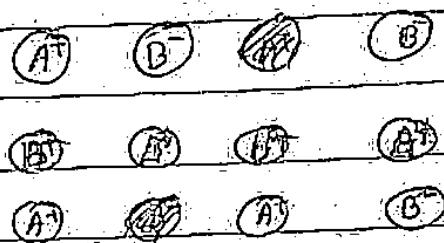
(b) Interstitial defects

→ density increase.

→ it also occurs in non-ionic compound

(c) Schottley defect

→ equal no. of cation and



Anion one missing from

their position

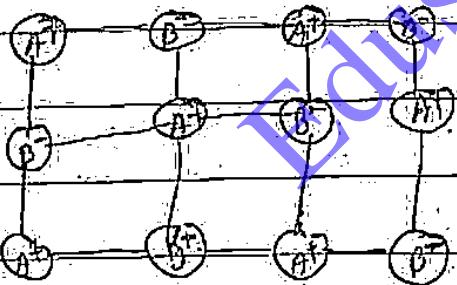
→ Electrical neutrality

Maintain

density Decrease

Ex - NaCl, KCl, KBr, etc.

AgBr, CsCl

(d) Frankel defect→ Cation one missing from
their position and occupy
at interstitial site→ It maintains electrical
neutrality & stoichiometry

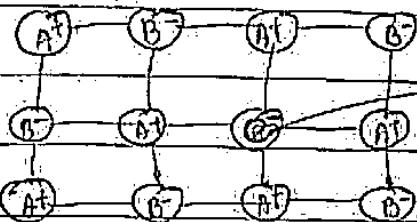
→ No effect on density

Ex: AgBr, AgI, ZnS

II

The Nonstoichiometric defect - Defects arise due to the ratio of cation and Anion become different.1. Metal excess defect -

(a) by Anionic Vacancy -



F-centre (Ferbe) which
Impart colour

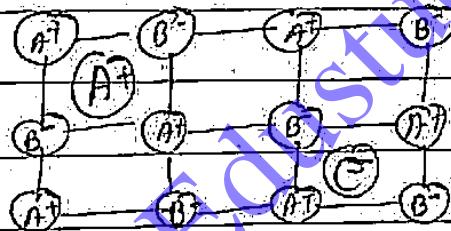
→ Anion are missing from their position,
they create a hole.

→ Electrical neutrality maintain due to
presence of electron-

→ No effect on density

Ex- NaCl, KCl, LiCl

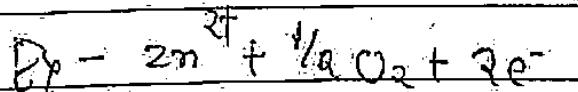
(b) By presence of extra cations



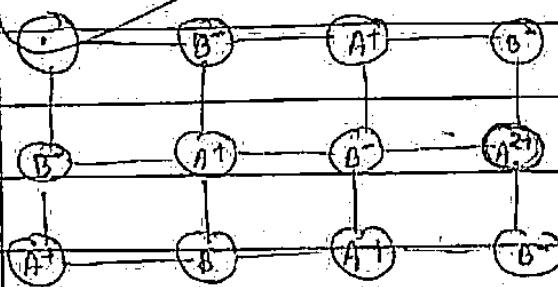
→ Extra cation occupy at
interstitial site

→ Electrical neutrality
Maintain

→ density increase



2. Metal deficiency defect



→ This defect arise
due to metal show
when
Variable Valency

Ex- FeO, FeS, NiO

→ Electrical neutrality maintained

→ No effect on density