

SOLID STATE →

General Characteristics of Solid state →

- Definite mass, Volume, shape.
- Intermolecular particles are at small distances
- Intermolecular forces are strong.
- Constituent particles have fixed position, can oscillate only about mean position
- Incompressible and rigid.

On basis of arrangement of particle

	Crystalline	Amorphous
Shape	definite geometrical shape.	Irregular Shape
Cleavage	split in plain, smooth surface	split in 2 pieces with irregular shape.
Heat of fusion	Definite HOF	Do not have definite HOF.
Melting point	melt at sharp temp.	soften over a range of temperature
Arrangement of particle	Long range order	Short range order
Nature	True Solid	Pseudo/super cooled liquid (tendency to flow)
	Anisotropic ✓ diff. physical property in diff. direction eg- Refractive index, electrical resistance	Isotropic physical properties same along all directions

Solid

Crystalline

Amorphous

Molecular Solid
Non polar
polar
H-Bonded

Ionic Solid

Metallic Solid

Covalent Network Solid

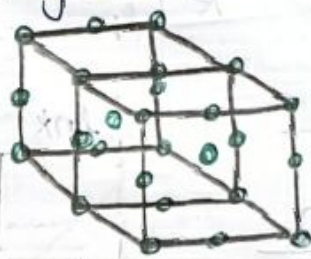
Crystal Lattice and Unit Cell →

Crystal Lattice →

Regular 3D arrangement of particle in space (atom/ion/molecules)

Unit Cell →

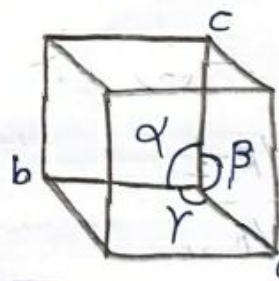
Small portion of crystal lattice, when repeated in different direction generated entire lattice.



Lattice point

Characterised by 6 parameters →

a, b, c edge length
 α, β, γ angles
may/maynot be perpendicular



Unit Cell

Unit Cell →

primitive unit cell

particles present only at corner of unit cell

Centered unit cell

particles on corner as well as other positions

Body CC
Face CC
End CC
centered

7 primitive unit cell

Cubic

Tetragonal

Orthorhombic / Trigonal

Hexagonal

Monoclinic

Triclinic

Type of Solid	Constituent particle	Bonding / attractive forces	Physical property	Electrical conductance	Melting point	Examples
Molecular solid						
Non-polar	Molecule	Dispersion / London forces	Soft	Insulator	Very low	$\text{CH}_4, \text{CCl}_4, \text{CS}_2, \text{H}_2$
polar	Molecule	Dipole-dipole interac.	Soft	Insulator	Low	$\text{HCl}, \text{dry SO}_2$
H-Bonded	Molecule	H-Bond	Hard	Insulator	Low	$\text{H}_2\text{O}, \text{ice}$
Ionic Solid	Ions	Electrostatic / Coulombic F.O.A.	Hard, Brittle	Insulator (solid state) Conductor (molten / aqueous state)	High	$\text{NaCl}, \text{MgO}, \text{ZnS}, \text{CaF}_2$
Metallic Solid	\oplus ions in sea of delocalised e^-	Metallic bonding	Hard, malleable, ductile.	Conductor	V. High	$\text{Fe}, \text{Cu}, \text{Ag}, \text{Mg}$
Covalent / network solid	atom	Covalent bond	Hard graphite soft	Insulator	V. High	SiO_2 (quartz) SiC, C (diamond) AlN

✓ (14) Bravais Lattice (7 primitive + 7 body centered) 7 Crystal System

	No. of Unit Cell.	Edge \checkmark_{imp}	Angles \checkmark_{imp}
Cubic	(3) Primitive Body Centred Face Centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	(2) Primitive Body Centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	(4) Primitive Body centred Face Centred End Centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Rhombohedral	(1) primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	(1) primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ \gamma = 120^\circ$
Monoclinic	(2) primitive edge centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \beta = 120^\circ$
Triclinic	(1) primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
(14) \rightarrow Total			

No. of atoms in Unit Cell —

① Primitive Cubic Unit Cell.



8 atoms on corner, contribute $\frac{1}{8}$

$$\text{No. of atom (Z)} = 8 \times \frac{1}{8} = 1$$

CN=6

② Body Centered Unit Cell —



$$\text{No. of atom (Z)} = \frac{1}{8} \times 8 + 1 = 2$$

CN=8

③ Face Centered Unit Cell —



$$\text{No. of atom} = \frac{1}{8} \times 8 + \frac{1}{2} \times 6$$

$$(Z) = 1 + 3 = 4$$

CN=12

④ Edge Centered Unit Cell —

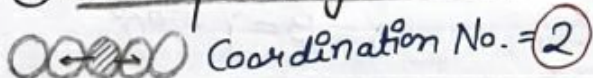


$$\text{No. of atom} = \frac{1}{8} \times 8 + \frac{1}{4} \times 12$$

$$(Z) = 1 + 3 = 4$$

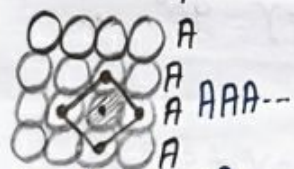
Close Packed Structures —

① Close packing in 1-D —



Coordination No. = 2

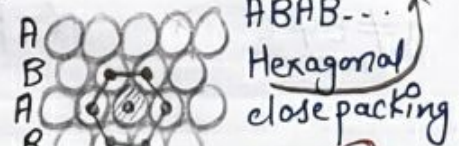
② Close packing in 2-D —



Sq. close packing

C.N. = 4

$$Z = 1, PF = 78.5\%$$



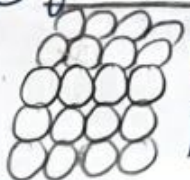
ABAB... Hexagonal close packing

C.N. = 6

2 triangular voids
apex downward: $Z = 3$
apex upward: $Z = 3$

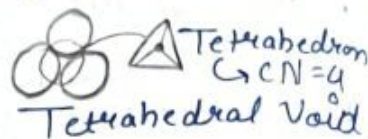
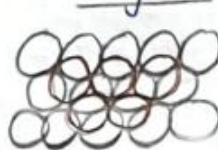
③ Close packing in 3-D —

① from 2-D sq. close packed layers.



AAA type
primitive cubic unit cell
generated

② placing 2nd layer over 1st — Tetrahedral Void generated from 2-D Hexagonal Close pack layers —



Tetrahedron
CN=4
Tetrahedral Void

Octahedral Void.



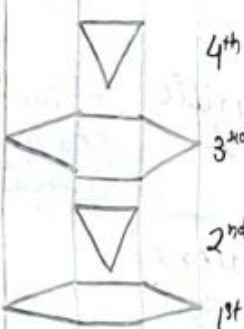
→ CN=6

→ placing 3rd layer over 2nd —

① Covering tetrahedral voids —

ABAB type str.

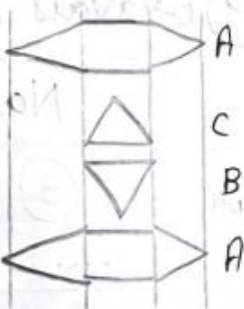
Hexagonal Close packing
eg - Mg, Zn



② Covering Octahedral Void —

ABCABC...

Cubic close packing /
face centered
eg - Cu, Ag



No. of close packed sphere = N

Octahedral Void = N

Tetrahedral Void = 2N

Imp. Results —

Crystal System	Rank atom / Unit Cell	Relation b/w a and b
Simple Cubic Unit Cell	1	$a = 2r$ $r = \frac{a}{2}$
Face Centered	4	$a = \frac{4r}{\sqrt{2}}$ $r = \frac{\sqrt{2}a}{4}$
Body Centered	2	$a = \frac{4r}{\sqrt{3}}$ $r = \frac{\sqrt{3}a}{4}$

Packing Efficiency →
% of total space filled by particles.

$$PE = \frac{\text{Vol occupied by atoms}}{\text{Total vol. of unit cells}} \times 100\%$$

① PE for Simple Cubic Unit Cell →
edge length = a , Volume = a^3 , $a = 2r$

$Z=1$

$$PE = \frac{\text{Vol of atom}}{\text{Vol of cubic unit}} \times 100$$

CN=6

$$= \frac{\frac{4}{3} \pi r^3}{a^3} \times 100 \rightarrow \frac{\frac{4}{3} \pi r^3}{(2r)^3} \times 100$$

$$= 52.4\%$$

② PE for Body Centered Cubic Unit Cell →

Volume = a^3
cubic unit

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

$$PE = \frac{\frac{4}{3} \pi r^3 \times 2}{\left(\frac{4r}{\sqrt{3}}\right)^3} \times 100 = 68\%$$

CN=12

③ PE for face Centered Cubic Unit Cell →

Cubic Unit Vol = a^3 , $Z=4$, $a = \frac{4r}{\sqrt{2}}$

$$PE = \frac{\frac{4}{3} \pi r^3 \times 4}{\left(\frac{4r}{\sqrt{2}}\right)^3} \times 100$$

$$= 74\%$$

Imp Table →

	% P.E.	% Void
Simple Cubic	52.4%	47.6%
Face Centred	74%	26%
Body Centred	68%	32%

Density of Unit Cell →

$$\text{Density of Unit Cell} = \frac{\text{Mass of Unit Cell}}{\text{Vol. of Unit Cell}}$$

$$\rho = \frac{\text{No. of atom of unit cell} \times \text{Mass of atom}}{a^3}$$

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

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

$$N_A = 6.023 \times 10^{23}$$

Que) Li crystallize in BCC unit cell
 $a = 346 \text{ pm}$. Radius = ?

Sol. →

(BCC)

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

$$346 = \frac{4r}{\sqrt{3}} \Rightarrow 346 = \frac{4r}{1.732}$$

$$r \approx 150 \text{ pm}$$

Radius Ratio → Only for Ionic Compounds
NaCl, KCl, ZnS, CaF₂

$$R_{\text{ratio}} = \frac{R_{\text{cation}}}{R_{\text{anion}}}$$

$R_{\text{cation}} \uparrow \uparrow$, Compound stability $\uparrow \uparrow$.

$R_{\text{c}} / R_{\text{a}} \uparrow \uparrow \rightarrow \text{C.N.} \uparrow \uparrow$.

→ Cation, anion assumed spherical and touching each other

→ Anion generally will not touch other anion

→ Cation must be surrounded with max anion

→ Anion - packing - fix size

→ Cation - fill voids - vary in size

Anion to Cation	'R _x ' Range
Linear	$0 \leq R_x \leq 0.155$
Triangular	$0.155 \leq R_x < 0.225$
Tetrahedral	$0.225 \leq R_x < 0.414$
Octahedral	$0.414 \leq R_x < 0.732$
Bcc	$0.732 \leq R_x < 1$

Ionic Crystal System - ⑤

Defects in Solid
 missing / lacking / misalignment in lattice.

point / Atomic Defect

Impurity Defect

→ Vacancy defect
 → Interstitial defect
 → Schottky defect
 → Frenkel defect

Stoichiometric Defect

→ Metal Excess Defect

Non-Stoichiometric defect

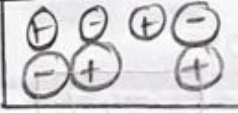
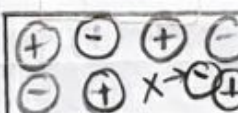
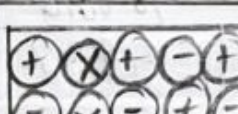
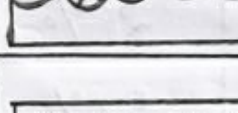
→ Metal excess
 → Metal deficiency

	Geometry	Ratio, C:A
NaCl type 1:1 type Rock salt type	CCP Na ⁺ - at OHV Cl ⁻ - at every element of CCP	6:6
CsCl type 1:1 type	BCC Cs ⁺ - at body centre of cubic void Cl ⁻ - at every corner	8:8
ZnS type 1:1 type Zinc blende	CCP Zn ²⁺ - 50% of THV S ²⁻ - every element of CCP	4:4
CaF ₂ type 1:2 type Fluorite type	CCP Ca ²⁺ every element of CCP F ⁻ - at every THV	8:4
Na ₂ O 2:1 antifluorite	CCP Na ⁺ at every THV O ²⁻ at every element of CCP	4:8

Metal Excess Defect
 a) Due to anion vacancy
 → NaCl is observed in presence of Na vapours.
 $\text{NaCl} \xrightarrow{\Delta} \text{Na}^+ + \text{Cl}^-$
 $\text{Na} \xrightarrow{\Delta} \text{Na}^+ + e^-$
 anionic sites are occupied by unpaired e⁻, called F-centres
 → Consequence = Colour due to F-centre.

Intensity ∝ no. of F centres of colour

Stoichiometric Defect →

Defect	Defination	Solid	Density	Crystal str.
Vacancy defect	Some lattice site vacant	Non-Ionic	Decrease	
Interstitial effect	Some constituent atoms occupy interstitial sites	Non-Ionic	Remain same	
Schottky effect	Equal no. of cation, anion removed vacancy defect. (NaCl, KCl, AgBr)	Ionic Solid	Decrease	
Frenkel effect	One cation/anion occupy interstitial site. Dislocation defect (ZnS, AgCl, AgI, AgBr)	Ionic Solid	Remain same	

LiCl → pink
 NaCl → yellow
 KCl → violet

b) Due to extra interstitial cation
 → excess ⊕ ion is located in interstitial site.

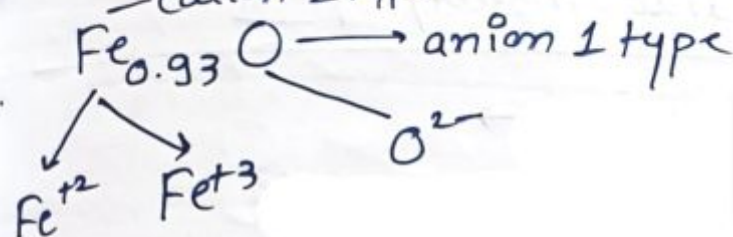
$\text{ZnO} \rightarrow \text{Zn}^{2+} + \text{O}^{2-}$
 electrical neutrality maintained.

→ Yellow colour of ZnO when heat is due to trapped e⁻.

Metal deficiency effect
found in d-block metal oxides,
because they show multiple
oxidation state.

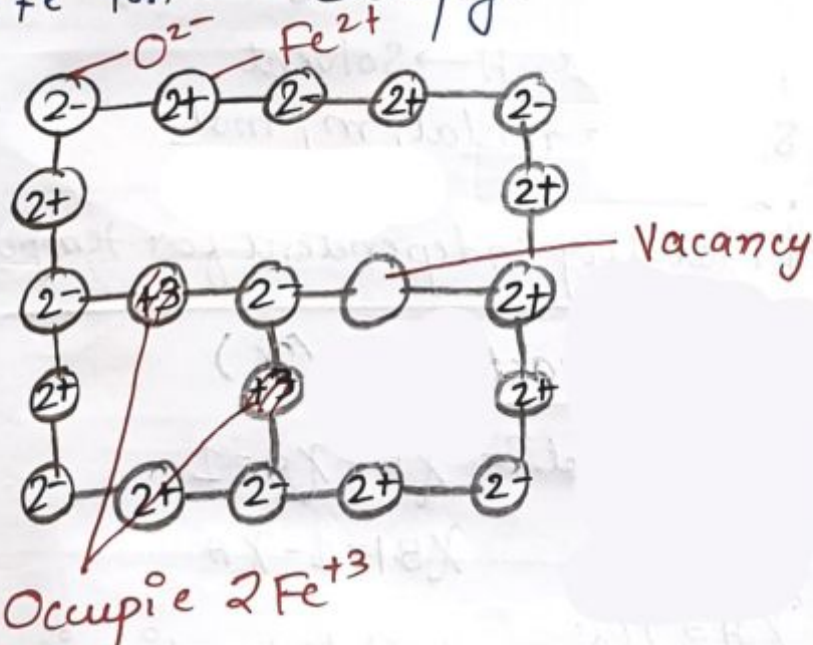
eg- $\text{Fe}_{0.93}\text{O}$, $\text{Mn}_{0.98}\text{O}$, $\text{Ni}_{0.98}\text{O}$

— cation 2 type



$3\text{Fe}^{+2}\text{ion} \rightarrow \text{Vacant}$
 \downarrow

$2\text{Fe}^{+3}\text{ion} \rightarrow \text{Occupy}$



**NEET
SLAYER.**

Impurity Defect

If molten NaCl containing little
amount of SrCl_2 is crystallised,
Some site of Na^+ ions are occupied
by Sr^{2+} .

Each Sr^{2+} replaces 2Na^+ ions

Cationic Vacancy.

eg- NaCl , CdCl_2 , AgCl .