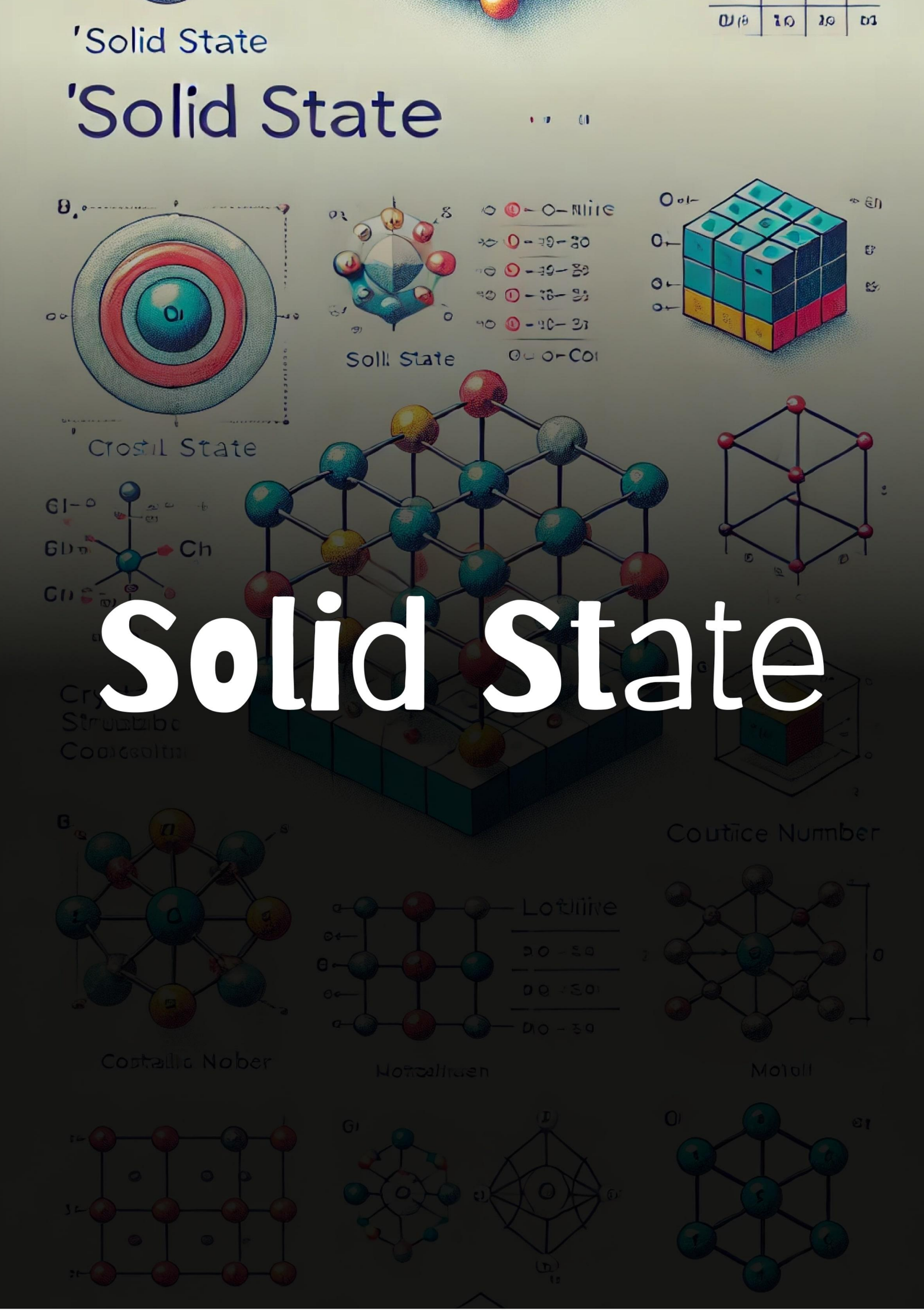
Solid State



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- IMF —— Vanderwaal's attraction Forces

① London Forces or Dispersion Forces $\propto$ surface area $\propto \frac{1}{r^6}$

② Dipole - Dipole $\propto \frac{1}{r^3}$ (stationary) $\propto \frac{1}{r^6}$ (Rotating)

③ Dipole - Induced Dipole $\propto \frac{1}{r^6}$

④ H-Bonding —— D-D —— N, O, F } H

- K.E $\propto$ T.E

T.E $\propto$ T

① IM - very strong, T.E - low } solid state

② IMF - very weak, T.E - very high } Gaseous state

③ IMF, T.E } Liquid state

-	Crystalline solids	Amorphous solids
	① Systematic geometric pattern	① Random arrangement
	② Long Range order	② Short Range Order
	③ Smooth surface	③ Rough surface
	④ Sharp M.P	④ No sharp M.P
	⑤ Definite Heat of Fusion	⑤ No definite Heat of Fusio
	⑥ Symmetry elements	⑥ No symmetry
	⑦ Anisotropic Nature	⑦ Isotropic nature.

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	Molecular Solids	C·P	attraction Forces	Examples	physical nature	Electrical Conduct	M·P
①	Non polar		London	H_2 Cl_2 Ar CO_2	Soft	Insulators	
②	Polar	Molecules	D-D	HCl, HBr, SO_2	Soft		Very
③	H-bonded		H-Bonding	H_2O	Hard		low
④	Ionic Solids	Ions	Ionic Bond	NaCl, CsCl KCl, MgO, ZnS	Hard Brittle	Insulators Solid state Conductors in molten/aq soln	High
⑤	Metallic Solids	Metal ions in the sea of $e^{\ominus}$s (Kernels)	Metallic bonding	Cu, Ag, Au Pt, Na, K etc.	Hard Malleable Ductile	Conductors	Fairly High
⑥	Covalent Solids	Atoms	Covalent Bond sp^2 — C (diamond) Td C (Graphite) — Soft — Conductor sp^2 linear	SiC, AlN, SiO_2	Hard	Insulators	Very High

- Amorphous silicon — Used as photovoltaic material
  - converts light ⟶ Electrical energy

- Poly crystalline solids ⟶ overall amorphous - isotropic
  single crystalline - anisotropic
- Crystal lattice: 3D arrangement of C·P
  - lattice points / lattice sites
- Unit cell : smallest part of crystal by which we can explain all the properties of crystal is called Unit cell.

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1) - Based on Dimension (Interfacial angles and edge lengths) are of unit cell are classified into 7 types → crystal systems

①	Cubic	$a=b=c$	$\alpha=\beta=\lambda=90^\circ$	S FC BC
②	tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^\circ$	S BC
③	Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^\circ$	S FC BC EC
④	Monoclinic	$a\neq b\neq c$	$\alpha=\lambda=90^\circ$ $\beta\neq 90^\circ$	S EC
⑤	Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90^\circ$	S
⑥	Hexagonal	$a=b\neq c$	$\alpha=\beta=90^\circ$ $\gamma=120^\circ$	S
⑦	Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90^\circ$	S

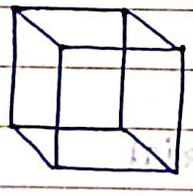
Unit Cell → simple / Primitive — CP are present only corners

↓

Centred → Face centred — corners + Face centers

→ Body centered — corners + Body centre

→ Edge centred — corners + alternate Face centres (any two opp. Faces)



8 - corners (8C)

12 - edges (4C) $a=b=c=a$

6 - Faces (2C) $\alpha=\beta=\gamma=90^\circ$

		location	Zeff	Rel	C.N	P.F	V.F
①	Simple Cubic	Corners	$8\times\frac{1}{8}=1$	$a=2r$	6	52%	48%
						0.52	0.48
②	Face centred (FCC/CCP)	Corners + Face Centres	$8\times 1/8+6\times 1/2=4$	$a=2\sqrt{2}r$	12	74%	26%
						0.74	0.26
③	Body Centred (BCC)	Corners + Body Centres	$8\times 1/8+1=2$	$a=\frac{4r}{\sqrt{3}}$	8	68%	32%
						0.68	0.32

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- Density: $d = \frac{Zeff \times M}{a^3 \times N_A}$ M – Molar mass, N_A – Avagadro number
- Close packing in crystals:

① 1D — C.NO – 2 — Linear

② 2D — ① Square closepacking — C.NO – 4 — AAA

② Hexagonal closepacking (HCP) — C.NO – 6 — ABAB

③ 3D

From HCP in 2D

① HCP → ABABAB — TV — CN – 4, OC — CN – 16

② FCC/CCP → ABCABC — Cubic close packaging arrangement

- In HCP Unit Cell
  - Zeff = 6
  - PF = 74%
  - VF = 26%
  - C.N = 12
  - each Body Diagonal has 2 TV $= \frac{\sqrt{3}}{4} a$
- No. of Voids in a unit cell
  - O.V = Zeff
  - TV = 2 × Zeff
  - Total voids = 3 × Zeff

① In FCC: T.V = 8, O.V = 4, Total = 12

② In HCP: T.V = 12, O.V = 6, Total = 18

1 at Body centre (6 Face centres) + 3 at edge centre (2 centre + 4 Face centres)

- Ionic crystals:
  - C.P = Ions
  - C.N of C^+ = no. of anions surrounding
  - C.N of A^- = no. of cations surrounding

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① If the charges of C^+ and A^- are same then C.No are also same.

② Higher the charge higher will be C.No.

③ The Ratio of C.No always equal to the inverse ratio of their numbers

		C.N	Geometry
• $\frac{r^+}{r^-}$ values → Radius Ratio (w.r.t c^+)	— < 0.155	2	linear
	0.155 - 0.225	3	TGP
	0.225 - 0.414	4	Tetrahedral
	0.414 - 0.732	6	Octahedral
	0.732 - 0.999	8	BCC

① Rock salt (NaCl)

$Cl^{\ominus}$ = FCC = 4

$Na^{\oplus}$ = all OVS = 4

each unit cell has 4 NaCl formula units

C.NO $Na^+ = 6$

C.NO $Cl^- = 6$

$r^+ + r^- = \frac{a}{2}$

② Zinc Blende (ZnS)

S^{2-} = FCC = 4

Zn^{2+} = alternate TVS = 4

each unit cell has 4 ZnS Units

C.No $Zn^{2+} = 4$

C.No $S^{-2} = 4$

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

③ CsCl

Cl^- = simple cube = 1

Cs^+ = at Body centre = 1 (cubic void)

each unit cell has 1 CsCl Formula units.

C.N of $Cs^+ = 8$

C.N of $Cl^- = 8$

$r^+ + r^- = \frac{\sqrt{3}\,a}{2}$

④ Fluorite (CaF_2)

Ca^{+2} = FCC = 4

F^- = all TVS = 8

each unit cell has 4 CaF_2 Formula units

C.N of $Ca^{2+} = 8$

C.N of $F^- = 4$

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

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⑤ Anti Fluorite (Na_2O)

O_2^- = FCC = 4

Na^+ = all TVS = 8

each unit cell has 4 Na_2O molecules

C·No of $Na^+ = 4$

C·No of $O_2^{-2} = 8$

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

- Imperfections / defects in solids:

Deviation From Ideal arrangement.

Defects

Point Defects — Line Defects

- Point Defects
  - ① Stiochiometric Defects — Formula does not change.
  - ② Impurity — Si → P → n-type; Si → Al → p-type
  - ③ Non-stiochemetric Defects — Formula will change

- Vacancy defect — Density decreases.
  Interstitial defect — Density increases.

- Ionic solids (stiochiometric defects)

Schottky:

- same no. of c^+ and A^- are missing.
- Maintain electrical neutrality
- density decreases
- Ionic crystals having High C·N.
- In which c^+ and A^- having almost same size.
- Vacancy defect.

Frenkel:

- Generally c^+ missing its position and occupies same interstitial void
- Maintain electrical neutrality
- No change in density
- Ionic crystals having low CN.
- c^+ is much smaller than A^-
- Interstitial defect.

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- Impurity defects : P-type — Si $\xrightarrow{Al}$
  n-type — Si $\xrightarrow{P}$

$NaCl \xrightarrow{SrCl_2} Na^+$

electrical neutrality should be maintained

each Sr^{2+} ion make 1 cation vacancy on doping NaCl

- Non stiochiometric defects : —— ① Metal excess — Anion vacancy — extra metal ion
  ② Metal deficiency — Schottky defect — Frenkel defect

$FeO + Fe^{+2} \; Fe^{+3}$

$Fe_{0.94}O$

$Ni_{0.96}O$

NaCl - Yellow, KCl - Lilac — F-centre

ZnO - Yellow white

- Magnetic properties :

① Paramagnetic :- Weakly attracted in magnetic field unpaired $e^{\ominus}$ are present.

② Diamagnetic :- Weakly repelled in magnetic field due to absence of unpaired $e^{\ominus}$s.

③ Ferro-magnetic - Fe, Co, Ni, Gd and CrO_2 ⇑⇑⇑⇑

④ Anti - Ferromagnetic - MnO ⇑⇓⇑⇓⇑

- unpaired $e^{\ominus}$ present But diamagnetic

⑤ Ferri - magnetic - Fe_3O_4 ⇑⇑⇑⇑⇓

$MgFe_2O_4$

$ZnFe_2O_4$

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