Solid state

Solid state

- They have definite mass, volume and shape.
- Intermolecular distance are short
- Intermolecular Forces are very strong
- Particles have fixed positions
- They are almost incompressible and rigid

CRYSTALLINE	AMORPHOUS
• Regular shape	• Irregular shape
• Have sharp melting Point	• Have range of melting Point
• Anisotropic in nature	• Isotropic in nature
• Long range order	• Short range order
• True solids	• Pseudo solids or supercooled liquids
eg. KNO_3, NaCl, Cu, SiO_2	eg. Rubber, plastic, glass, Quartz glass

TYPES OF CRYSTALLINE SOLIDS

1) **Molecular Solid** (Low Melting point)

* constituent particles → molecules

a) Non Polar Molecular Solid — $\mu = 0$

eg. H_2 (H-H, $\mu = 0$), CCl_4 ($\mu = 0$)

b) Polar Molecular Solid — $\mu \neq 0$ eg. HCl

c) H-Bonding Molecular Solid — H-F/O/N

H-F ..... H-F (↳ H-Bonding)

Order of M.P :- Non Polar < Polar < H-Bonding

2) **Ionic Solids** (High Melting point)

Constituent Particles : Ions → Cations and Anion

Forces → Electrostatic Forces → STRONG IONIC BOND

eg. NaCl, KNO_3, ZnO

NOTE: On increasing T → Conductance increases

∵ No of ions ↑

3) **Metallic Solid** (High Melting Point)

Constituent Particles → metals → Kernels + Outer e^-

eg. Na, Cu, Ag, Au, Al

NOTE : For metallic solid,

T ↑ → Conductance ↑ → ∵ Resistance ↑

4) **Covalent or Network Solid** (Very Very High M.P)

eg. Si, SiO_2 (quartz), AlN, Graphite, Diamond, SiC

NOTE : Network solid have highest M.P

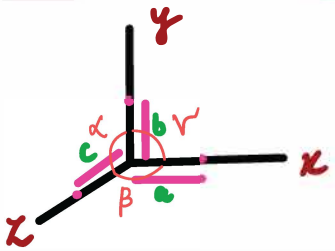
UNIT CELL

→ Smallest unit which can repeat itself over again and again to form crystal lattice.

a) Primitive → Simple cubic

b) Non-Primitive → BCC, FCC

CRYSTAL LATTICE



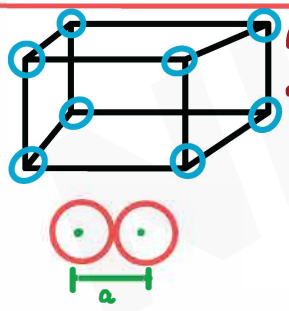
Parameters — Distance → a, b, c
Angle → α, β, γ

CRYSTAL SYSTEM

→ 7 Crystal System
→ 14 Bravias lattice

Crystal System	Axial Distance	Axial Angle	Unit Cell [Bravias lattice]
Cubic	a=b=c	α=β=γ=90	③ SC, FCC, BCC
Rhombhedral	a=b=c	α=β=γ≠90°	① SC
Tetragonal	a=b≠c	α=β=γ=90°	② SC, BCC
Hexagonal	a=b≠c	α=β=90° γ=120°	① SC
OrthoRhombic	a≠b≠c	α=β=γ=90°	④ SC, BCC, FCC, EC
Monoclinic	a≠b≠c	α=γ=90° β≠90°	② SC, EC
Triclinic	a≠b≠c	α≠β≠γ≠90°	① SC

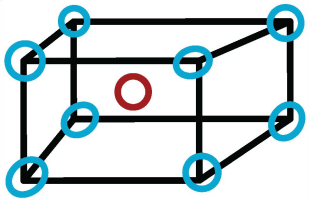
SIMPLE CUBIC



a = cube length
r = radius of atom

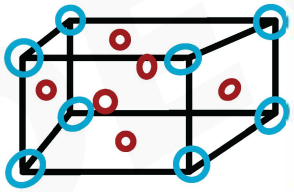
- 8 atoms in 8 corners
- Sharing of corners = 1/8
- $Z_{eff} = 8 \times \frac{1}{8} = 1$
- Coordination Number = 6
- Relation b/w a and r
  - $2r = a$

BODY CENTERED CUBIC CELL (BCC)



- 8 atoms in 8 corners + 1 atom at body center
- Sharing of Corners = 1/8
- Sharing of Body Center = 1
- $Z_{eff} = 8 \times \frac{1}{8} + 1 \times 1 = 2$
- Coordination Number = 8
- Relation b/w a and r
  - $4r = \sqrt{3}\,a$

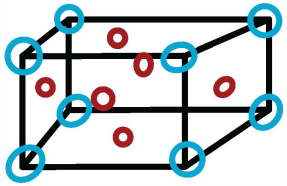
FACE CENTERED CUBIC CELL (FCC)



- Relation b/w a and r
  - $4r = \sqrt{2}\,a$

- 8 atoms in 8 corners
- 6 atoms at face centers
- Sharing of corners = 1/8
- Sharing of face centers = 1/2
- $Z_{eff} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
- Coordination Number = 12

FACE CENTERED CUBIC CELL (FCC)



- Relation b/w a and r
  - $4r = \sqrt{2}\,a$

- 8 atoms in 8 corners
- 6 atoms at face centers
- Sharing of corners = 1/8
- Sharing of face centers = 1/2
- $Z_{eff} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
- Coordination Number = 12

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Packing Fraction

2D → Area $\%\ PF = \frac{Z_{eff} \times A_{atom}}{A_{unitcell}} \times 100$

3D → Volume $\%\ PF = \frac{Z_{eff} \times V_{atom}}{V_{unit\ cell}} \times 100$

$V_{unit\ cell} = a^3$

Unit Cell	Packing Efficiency	% Void
Simple Cubic	52.4 %	47.6 %
BCC	68%	32 %
FCC	74 %	26 %

DENSITY

$d = \frac{MM\ (Molar\ Mass) \times Z_{eff}}{N_A \times a^3}$

SC → $Z_{eff} = 1$

BCC → $Z_{eff} = 2$

FCC → $Z_{eff} = 4$

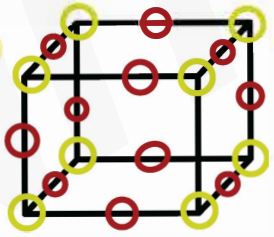
VOIDS → Vacant Spaces

$\%\ Void = 100 - \%\ PF$

OCTAHEDRAL VOID (OHV)

Location: 1) Body Center 2) Edge Center

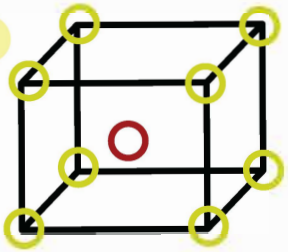
Edge Center:



OHV at edge center:

$12 \times \frac{1}{4} = 3$

Body Center:



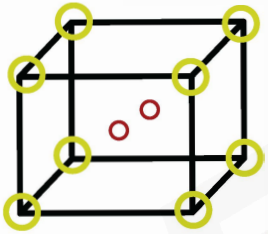
OHV at Body center

$1 \times 1 = 1$

Total OHV = 3+1 = 4

TETRAHEDRAL VOID (THV)

Location: At Body diagonal



1 Body Diagonal → 2 THV

4 Body Diagonal → 8 THV

∴ THV = 8

NOTE: Valid only for FCC, HCP

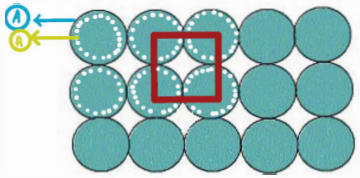
∴ atoms = z

OHV = z

THV = 2z

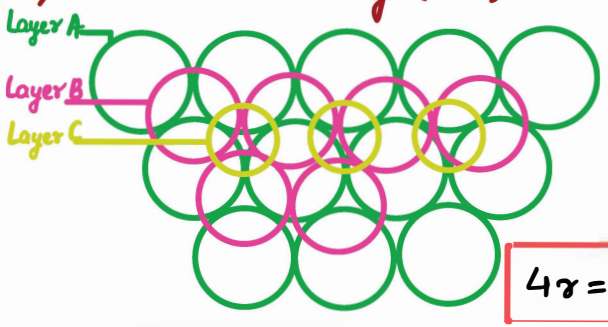
CLOSED PACKING

a) Square closed packing (SCP)



- AA layer Type
- unit cell → simple cubic
- $Z_{eff} \rightarrow 1$
- PF → 52.4%
- CN = 6
- $a = 2r$

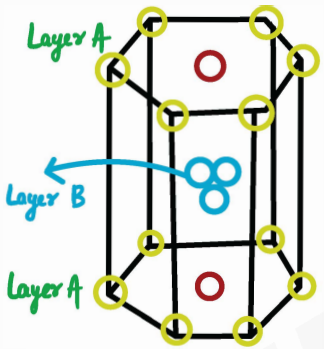
b) Cubic closed Packing (CCP):-



$4r = \sqrt{2}\,a$

i) ABC type layer
ii) unit cell → FCC
iii) Z_{eff} → 4
iv) CN → 12
v) PF → 74%.

c) Hexagonal closed Packing (HCP) unit cell :



i) AB layer type

ii) $Z_{eff} = 3\times1 + 2\times\frac{1}{2} + 12\times\frac{1}{6}$

$= 6$

Body center | Face center | Corner

iii) CN = 12

6 Corners | 3 Body center | 3 Body center of another unit cell.

iv) Packing Fraction

PF = 74% , void = 26%

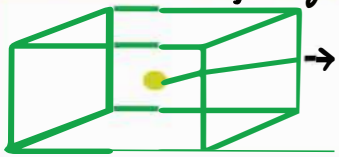
Relation b/w a and r

$a = 2r$

ELEMENT OF SYMMETRY

1) Centre of Symmetry

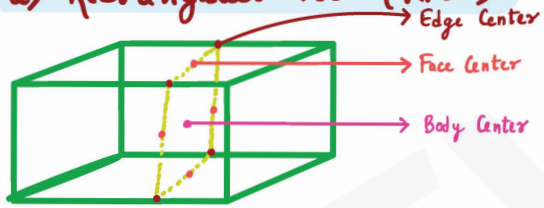
COS = 1



→ COS (Body center)

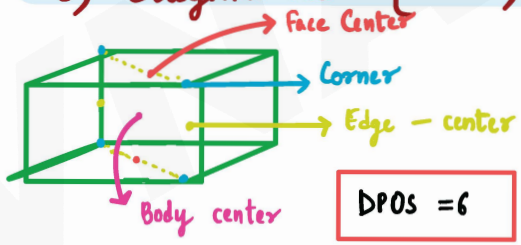
2) PLANE OF SYMMETRY (POS)

a) Rectangular POS (RPOS)



RPOS = 3

b) Diagonal POS (DPOS)

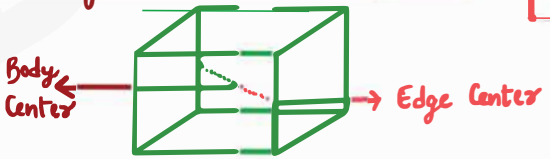


DPOS = 6

3) Axis of Symmetry

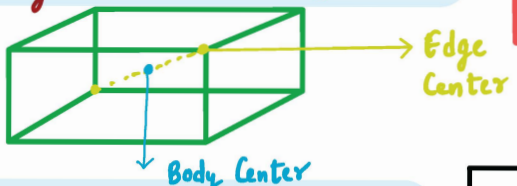
a) Edge center OR C_2-AOS

AOS = 6

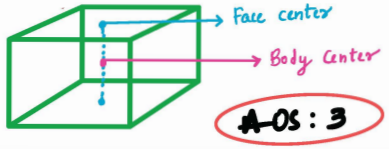


b) Body Diagonal AOS or C_3-AOS

AOS = 4



c) C_4-AOS or Face Center AOS



AOS : 3

NOTE:

Total Element of Symmetry : 23

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RADIUS RATIO

$\frac{\text{Rcation}}{\text{Ranion}}$

Radius Ratio	COORDINATION NUMBER	GEOMETRY	Example
$0.155 \leq RR < 0.225$	3	Triangular	B_2O_3
$0.225 \leq RR < 0.414$	4	Tetrahedral	ZnS
$0.414 \leq RR < 0.732$	6	Octahedral	NaCl
$0.732 \leq RR < 1$	8	Cubic	CsCl

ZnS (Zinc Blende)

(4) ← S^{-2} → FCC

(4) ← Zn^{+2} → 50% THV

$4\,Zn^{+2} + 4\,S^{-2} \rightarrow 4\,ZnS$

Formula Unit : 4

Coordination Number C : A = 4 : 4

ZnS (Wurtzite Structure)

S^{-2} → HCP → 6

Zn^{+2} → 50% THV → $\frac{1}{2} \times 12 = 6$

$6\,Zn^{+2} + 6\,S^{-2} \rightarrow 6\,ZnS$

Formula unit = 6

Coordination Number C : A = 8 : 4

NaCl Type Structure

Rock salt Type of structure

OHV = 4 THV = 8

(4) ← Cl^- → CCP Lattice → FCC

(4) ← Na^+ → 100% OHV

$4\,Na^+ + 4\,Cl^- \rightarrow 4\,NaCl$

Formula unit : 4

Coordination Number C : A = 6 : 6

CaF_2 (Fluorite Structure)

Ca^{+2} → FCC → 4

F^{-1} → 100% THV → 8

$4\,Ca^{+2} + 8\,F^{-1} \rightarrow 4\,CaF_2$

Formula unit : 4

Coordination Number C : A = 8 : 4

CsCl

(1) ← Cl^- → Simple Cubic (SCC)

(1) ← Cs^+ → Cubic void (Body center)

$1\,Cs^+ + 1\,Cl^- \rightarrow 1\,CsCl$

Formula Unit : 1

Coordination Number C : A = 8 : 8

DIAMOND

C → 50% THV → $\frac{1}{2} \times 8 \rightarrow 4$

C → FCC → 4

Total Zeff = 8

PF = 34%

DEFECTS

- NON STOICHIOMETRIC
  - * METAL EXCESS
    - ↳ Anion Vacancy
  - * METAL EXCESS
    - ↳ Extra Cation
  - * METAL DEFIENCY DEFECT
- STOICHIOMETRIC
  - * SCHOTKY
  - * FRENKEL

SCHOTTKEY DEFECT

* Equal number of cations and anions are missing from crystal lattice.
* Density decrease
* High Coordination number — CN = 6,8

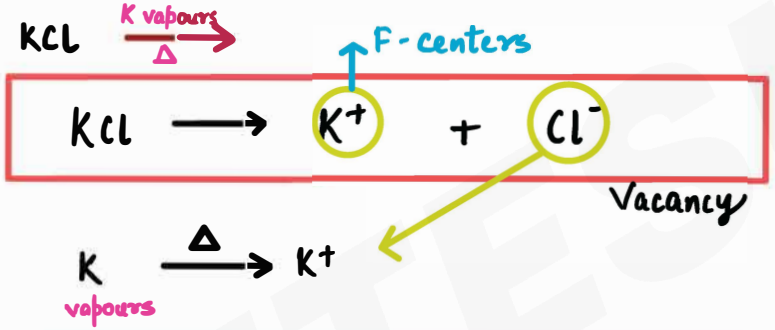
eg. NaCl, CsCl, CsBr, KBr, AgBr

FRENKEL DEFECT

* One of the ion is dislocated from lattice point to interstial site
* No effect on density
* Low Concentration Number — CN = 3,4

eg. ZnS, AgCl, AgI, AgBr

METAL EXCESS - ANION VACANCY



LiCl	NaCl	KCl
Pink	yellow	violet

→ F-center

METAL EXCESS - EXTRA CATION

$ZnO \rightarrow Zn^{+2} + O^{2-}$

$ZnO \rightarrow Zn^{+2} + \frac{1}{2}O_2\uparrow$ (gas)

EXTRA CATION

ZnO → white when cold

ZnO → yellow when hot

METAL DEFICIENCY DEFECT

* d-Block

$Fe_{0.98}O$

$Ni_{0.96}O$

NON - STOCHIOMETRIC

NITESH DEVNANI