➩ SOLIDS :- • well ordered, Packed.
• Strong Cohesive forces.

Amorphous: not 3-D (not sharp m & B. Points) (no definite heat of fusion)

crystalline: 3-D (crystalline → Amorphous → Heating → Rapid cooling)

crystallites: Crystalline Part of Amorphous solid.

➩ PROPERTIES OF CRYSTALLINE SOLIDS:

- **Geometric Shape:** [Faces angles etc remains same even in powdered form.]
- **M. Points:** [Sharp]
- **Cleavage Plane:** [Broken along definite plane]
- **Anisotropy:** [Variation in physical properties (ie refractive index, coefficient of Thermal Expansion, conductance etc) depends on Direction.
(Graphide in Parallel direction → conductor)

(360°) • **SYMMETRY:** (identical Positions; Indistinguishable form)

(i) Center of Symmetry:

(ii) Plane of Symmetry: Two halfs are mirror images.

(iii) Rotation Axis of Symmetry: Same apperance more than one.

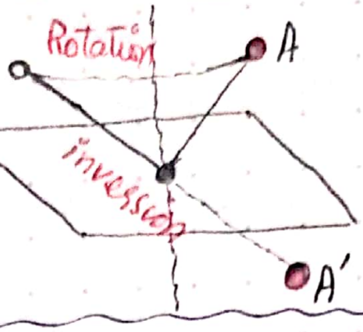
360° = 180°, 240°, 360°
2-folds, 4-folds, 6-folds

(iv) **AXIS OF ROTATION:** n-folds rotation → Same Reflection

---

(v) **Inversion Axis:**

$\bar{n}=2$ means 180°



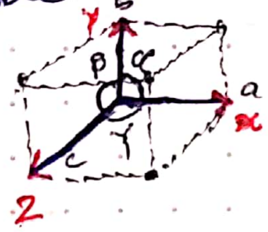
- **HABIT OF CRYSTALS:** (Usually Grow). Crystals are always same. Same conditions → Same shape
  - NaCl → needle like by 10% urea impurity.

- **UNIT CELL:** "The smallest part of Crystal lattice having all the characteristic structures of entire crystal is called unit cell"

Crystallographic elements

x-axis	a → α
y-axis	b → β
z-axis	c → γ

These are unit cell dimensions



θ b/w ab is α

θ b/w bc is β

θ b/w ca is γ.

⇒ **TYPES:**

(i) SIMPLE

(ii) FACE CENTERED

(iii) End Face Centered

(iv) Body Centered

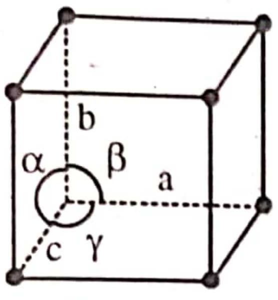
⇒ CLASSIFICATIONS OF UNIT CELL:

(i) 7-Basic Shapes (ii) 14- BRAVIS LATTICE

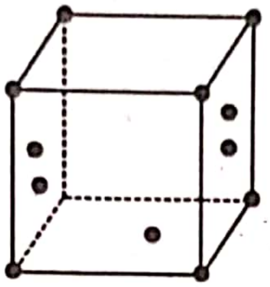
(PICS INSERTED)

CRYSTAL SYSTEMS

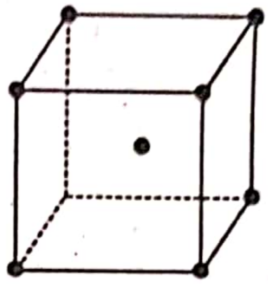
(1) Cubic:



Simple



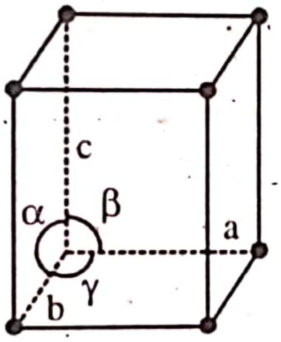
Face-centred



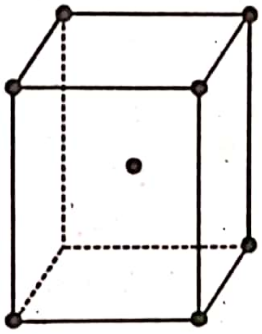
Body-centred

a = b = c
$\alpha = \beta = \gamma = 90^\circ$

(2) Tetragonal:



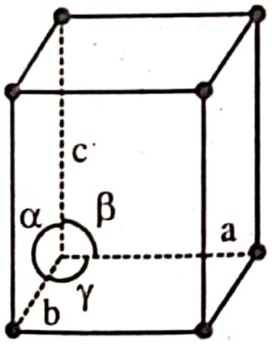
Simple



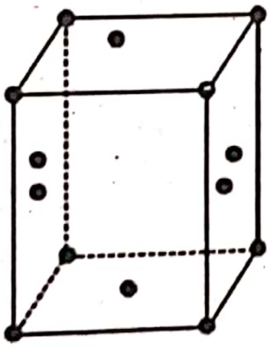
Body-centred

$a = b \neq c$
$\alpha = \beta = \gamma = 90^\circ$

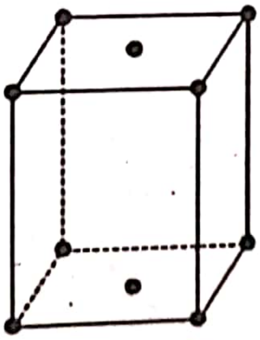
(3) Orthorhombic:



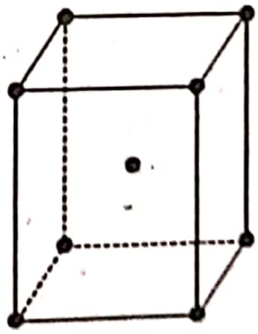
Simple



Face-centred



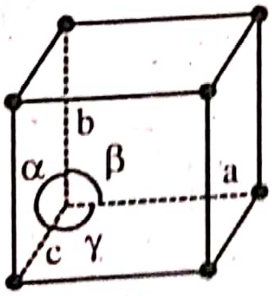
End-centred



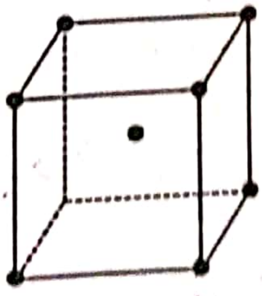
Body-centred

$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$

(4) Monoclinic:



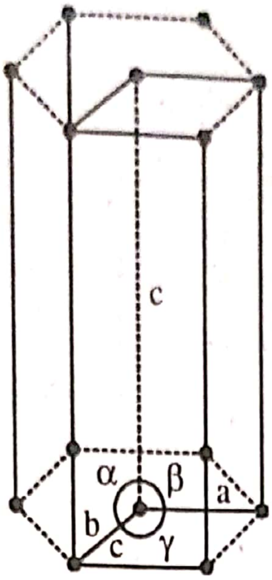
Simple



Body-centred

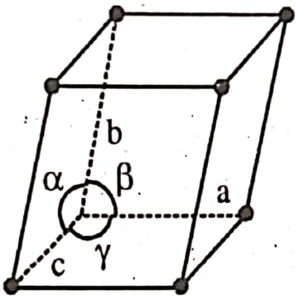
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$

(5) Hexagonal:



$a = b \neq c$
$\alpha = \beta = 90^\circ$
$\gamma = 120^\circ$

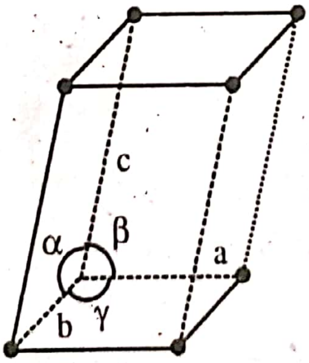
(6) Rhombohedral (Trigonal):



Simple

$a = b = c$
$\alpha = \gamma = 90^\circ$
$\beta = 90^\circ$

(7) Triclinic:



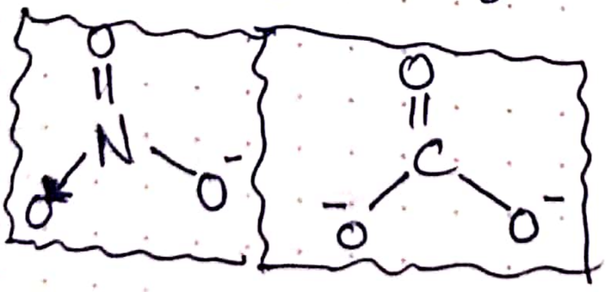
Simple

$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^\circ$

(iso → same) (morphus → form)

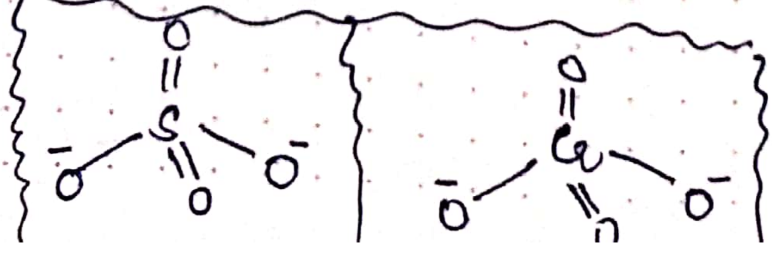
ISOMORPHISM : (Two Substance, Same form)

- Crystalline form is independent of chemical nature. & depends on ways of combination.
- Chemical formulas must be analogous.
- Size of ions must not be very different.
- Polarization must not be very different.
- Must have same no of (+ve) & (-ve) ions in simillar geometrical positions.
- Same Atomic Ratio.
- Molecular volume must be nearly equal.
- Physical & Chemical properties are quite different from each other.
- Isomorphic substances crystallize together in all proportions in homogeneous mixture.
- Structures of $NO_3^{\ominus}$ & CO_3^{2-} are same



Trigonal Planar (sp^2)

- Shapes of SO_4^{2-} & CrO_4^{2-} are same



Tetrahedral (sp^3)

IIC PART 1 BOOK

Isomorphs	Crystalline form	Atomic ratio
$NaNO_3$, KNO_3	rhombohedral	1:1:3
K_2SO_4, K_2CrO_4	orthorhombic	2:1:4
$ZnSO_4$, $NiSO_4$	- do -	1:1:4
NaF, MgO	cubic	1:1
Cu, Ag	cubic	1:1
Zn, Cd	hexagonal	1:1

(Poly → many) (morphus → form)

- **POLYMORPHISM** : (Same Substance → Two forms)
- compound exists in more than one crystalline form
- Same chemical properties, different in Physical

$AgNO_3$ → Rhombohedral, Orthorhombic

$CaCO_3$ → Trigonal, Orthorhombic

TYPES:

(i) Enantiotropic : one change into other by varying temp & Pressure i.e S

(ii) Monotropic : change b/w two ~~layers~~ forms is irreversible e.g Glyceryl stearates.

- Optical crystallography is used for identification of polymorphs.

- **ALLOTROPY** :
- Element exist in more than one crystalline form

S → Rhombic, Monoclinic

Plastic Sulphur is amorphous

C → Cubic (Diamond), hexagonal (graphite)

Tin (Sn) → Grey tin (cubic), White tin (tetragonal)

⇒ TRANSITION TEMP.:

- Two crystalline form of same substance co-exist in Equilibrium.
- At Tran. temp; one crystalline form → other.
- Above trans. temp, only one form exists.
- Transition temp of elements is always less than its melting Point.

(PICTURE PART I)

iven below

(I) Grey tin (cubic) $\xrightleftharpoons{13.2^\circ C}$ White tin (Tetragonal)

(ii) Sulphur S_8 (rhombic) $\xrightleftharpoons{95.5^\circ C}$ Sulphur S_8 (monoclinic)

(iii) KNO_3 (orthorhombic) $\xrightleftharpoons{128^\circ C}$ KNO_3 (rhombohedral)

(iv) Na_2SO_4-$10H_2O$ (hydrated form) $\xrightleftharpoons{32.38^\circ C}$ Na_2SO_4 (anhydrous from) + 10 H_2O

(v) Na_2CO_3- 10 H_2O (higher hydrated form) $\xrightleftharpoons{32.92^\circ C}$ Na_2CO_3-$7H_2O$ (lower hydrated form) + $3H_2O$

CLASSIFICATION OF SOLIDS:

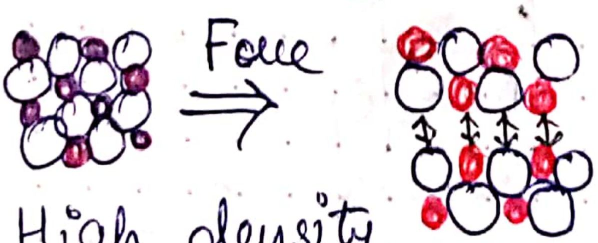
FOUR TYPES:

(1) IONIC SOLIDS:

- By +ve & -ve charges. (electrostatic force) (ionic Bond)
- Solid at Room temp. High m.Point.
- Very stable, Low volatility, very hard.
- Do not exist as individual neutral molecule.
- Non-directional forces

ionic bond is non directional

- Arrange in symmetric fashion.
- Structure of ionic crystal depends upon ratio of cation and anion. ie NaCl & CsF have same structure → same radius ratio.
- Formula mass is used for ionic compounds.
- Insulator in solid form.
- Highly Brittle external force → layers Slide



Same ions of layers repel each other

- High density.
- Polar solvent is used for reaction.
- Having isomorphism & polymorphism.

STRUCTURE OF NaCl: (Face Centered Cubic)

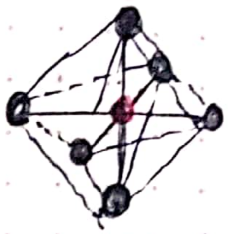
- Radius of Na = $R_1 = 0.95\,\text{Å}$
- Radius of Cl = $R_2 = 1.81\,\text{Å}$

$$\boxed{\frac{R_1}{R_2} = 0.526}$$

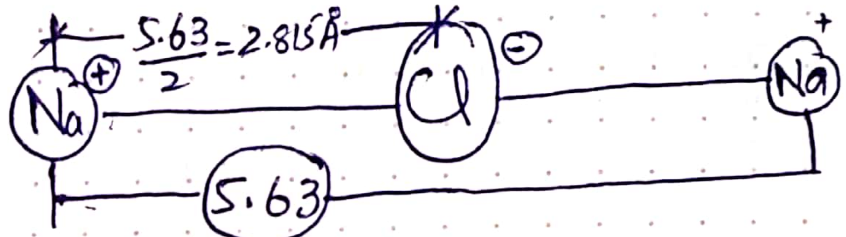
$\Downarrow$

Co. No = 6

Radius Ratio	Co. No	
0.155 – 0.225	3	→ Trigonal
0.225 – 0.414	4	→ Tetrahedral
0.414 – 0.732	6	→ Octahedral
0.732 – 1.000	8	→ Cubic

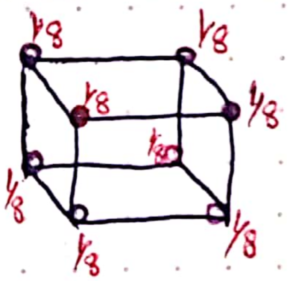


Octahedral



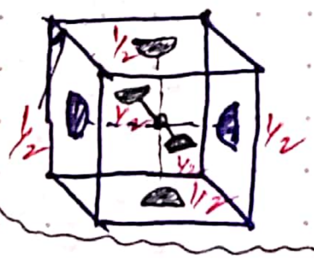
- Each $Na^{\oplus}$ by $6\,Cl^{\ominus}$ and vice versa.
- 8 corners.

(8-parts)



$8 \times \frac{1}{8} = ①$

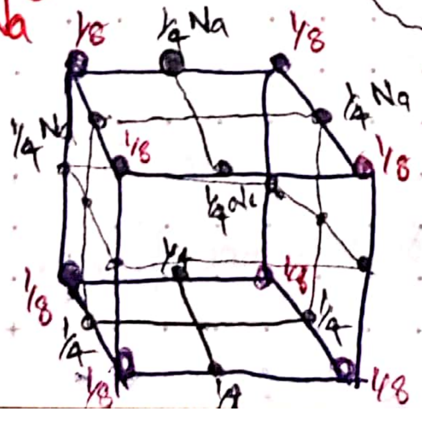
- 6-sides.



$6 \times \frac{1}{2} = ③$

$$\boxed{\text{Total} = 3 + 1 = 4\,Cl^{\ominus}}$$

For $Na^{\oplus}$



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

$1\,Na^{\oplus} = 1$

Total = 4.

Video Demonstration

⇒ LATTICE ENERGY :-

- Energy released when one mole of ionic crystal is formed from the gaseous ion. (vice versa)

$$Na^{\oplus} + Cl^{\ominus} \longrightarrow NaCl \qquad \Delta H_l = -787\ kjmol^{-1}$$

$\Delta H_l =$

$LiCl \rightarrow -833$

$NaCl \rightarrow -787$

$KCl \rightarrow -690$

kj/mol

ΔH_l decrease By Radius of (+ve) increase

$NaF \rightarrow -895$

$NaCl \rightarrow -787$

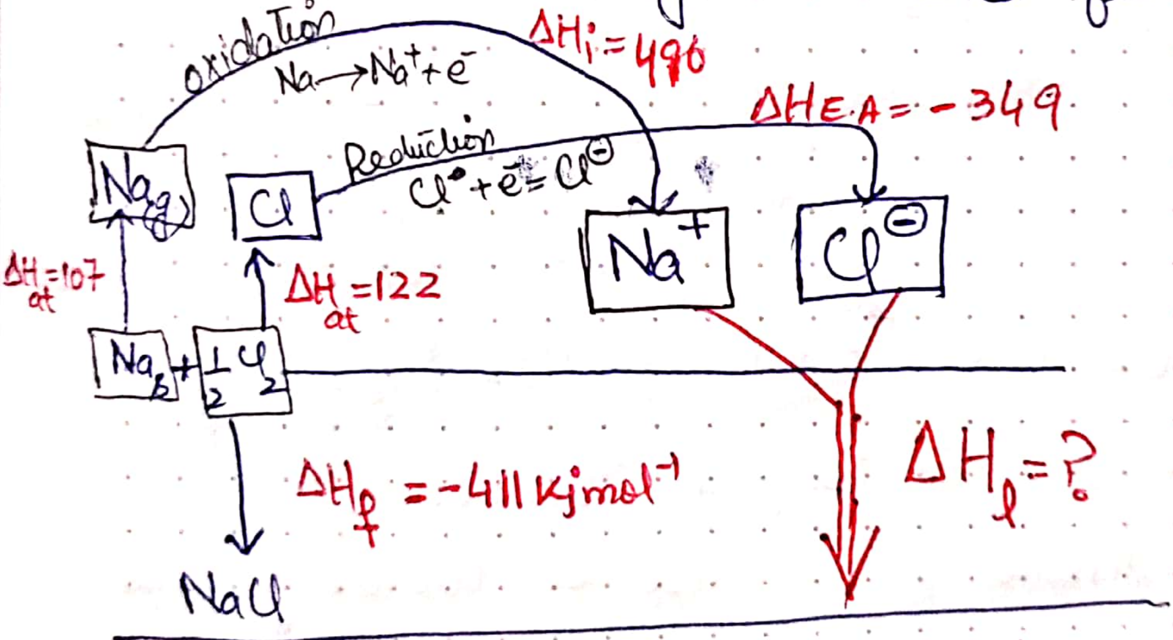
$NaBr \rightarrow -728$

$NaI \rightarrow -690$

decrease by size of anion increase

→ CALCULATION OF LATTICE Energy

- We can't find lattice Energy directly.
- BORN-HABER cycle is used for this purpose



Total Energy = Sum of all the energies.

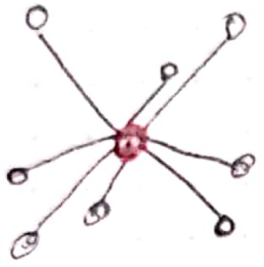
$$\Delta H_f = \Delta H_{at\,Na} + \Delta H_{i\,Na} + \Delta H_{(cl)\,at} + \Delta H_{E.A\,cl} + \Delta H_l$$

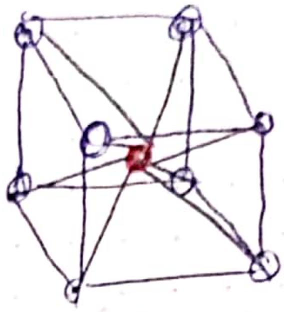
$$-411 = 107 + 496 + 122 - 349 + \Delta H_l$$

$$\boxed{\Delta H_l = -787}$$

STRUCTURE OF CsCl: . Body centered Cubic.

- Coordination no 8.





STRUCTURE OF Zinc Blende :(ZnS)

- Face Centered Cubic.
- Coordination no = 4

STRUCTURE OF CaF_2:

- Cubic (simple), tetrahedral geometry.

HEAT CAPACITY OF SOLIDS.

- Metals = 26 $J K^{-1} mol^{-1}$
- C_V is measured

ie $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

$\boxed{C_V = 3R}$

$E = 3RT$

$\frac{E}{T} = 3R$

$C_V = 3 \times 8.314\ J K^{-1} mol^{-1}$

$= 25\ J K^{-1} mol^{-1}$

$C_V = 0$ at 0K.

C_V increase with T

→ EFFECT OF TEMP & PRESSURE ON Crystal

- Change with Temp & Pressure.
- Coordination no increase by Pressure increase.
- Coordination no decrease by Temp increase.

- High Pressure converts NaCl into body centered cubic structure (co. No = 8).
- If CsCl is heated to 760K then its structure will become NaCl like ie (co. no = 6)

→ XRD:
- used for structural determination.
- Bragg's Equation $\{n\lambda = 2d\sin\theta\}$

(d) = interplane distance.

(n) = Path difference (integral multiple)

(λ) = wavelength

(θ) = Angle of reflection.

{for known λ
d can be measu
and vice versa

{FOR NaCl analysis}

$\theta = 5.9 \quad n = 1 \quad \Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{1\times\lambda}{2\times\sin 5.9}$

$\boxed{d = 4.85\lambda}$

{by putting λ, d is calculated
& vice versa}

→ POWDER METHOD:
- Diffraction of x-rays from cover of powder.
- Random orientation.
- Scattered x-rays are detected by X-ray Film.
- Bright spot gives the position of reflection.
- Glancing angle $2\theta = \frac{S}{R}$ — S: radius of Powder rin / R: radius of camera

(PICTURE)

→ Laue's Method:
- Crystal is Placed in the path of x-rays.
- X-rays impression is obtained.
- Scattering beams are arranged to get shape.

(2) COVALENT CRYSTALS:

- Directional nature
- Very hard. » High M.P, Low Volatility
- Bad conductors. (Graphite → Semi Conductor)
- Dissolved in non-polar solvents.
- Slow covalent reactions.

⇒ STRUCTURE OF DIAMOND: 4C → sp^3-sp^3

- Tetrahedral  109.5° C—C = 154 pm.
- Macro-Molecule.

(3) MOLECULAR SOLIDS:

Intermolecular forces.
(i) Dipole - Dipole
(ii) Van der Waals forces

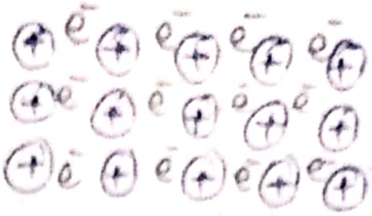
- Solidified noble gases
- Non-polar compounds
- Weaker than crystalline solids.
- Ice, Sugar, I_2, S, P, CO_2.
- Polar molecules having high M & B points as compare to non-polar.
- Soft & easily compressible.
- Volatile in nature (Low M.& B. Points)
- Low density, transparent to light.
- Solubility → "Like dissolves like"

IODINE:

- Face Centred Cubic

I—I solid = 271.5 pm
I—I gas = 266.6 pm.
} Poor Conductor

(4) METALLIC SOLIDS:



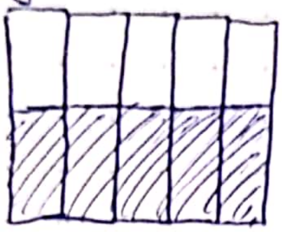
(o) +ve centres

(o) Freely moving electrons.

(o) L. Pauling ⟶ delocalized valance Bonds

(o) M.O.T ⟶ completely filled orbitals ⟶ Localized.
⟶ Valance $\bar{e}$ Partially filled ⟶ delocalized.
⟶ Closely spaced states.

Bands of Energy



Band Theory

Properties:

(o) Good Conductors (decrease with temp increase)

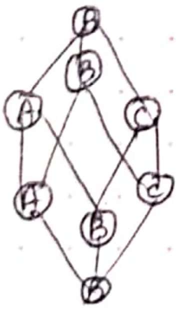
(o) Metallic Luster. (excited electrons)

(o) Malleable and Ductile.

⇒ STRUCTURE OF METALS.

(1) CUBIC (Face Centered)

ABC... ABC



(2) Hexagonal.

AB... AB...