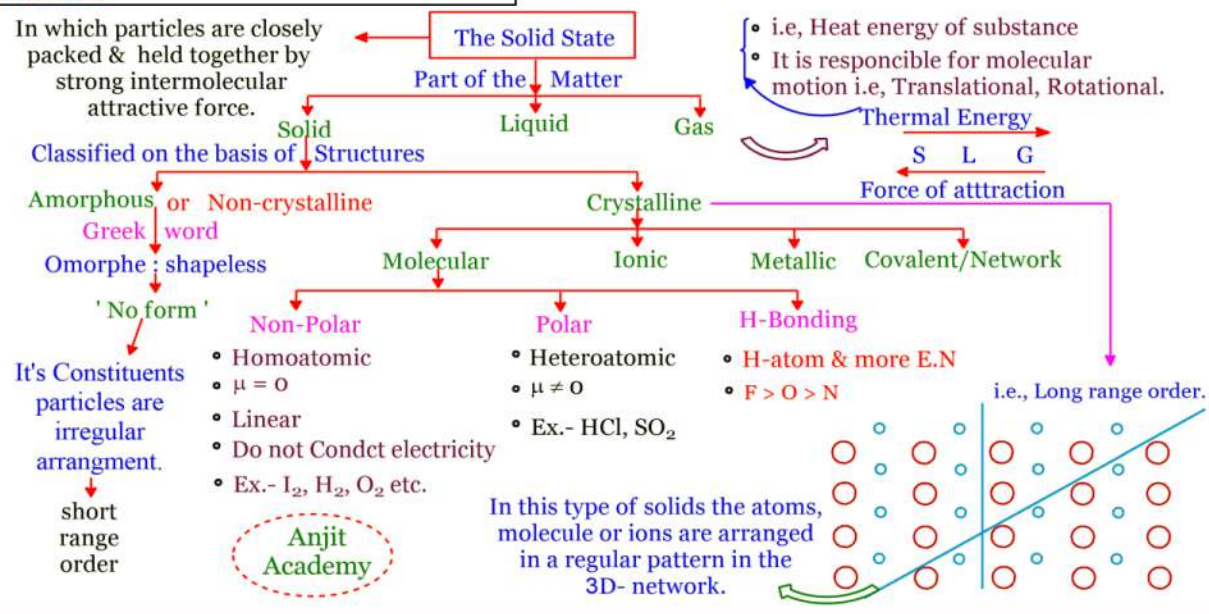
*Super Short Tricky Chemistry By*
**Er. Jitendra Gupta Sir**

Conceptual Notes for NEET/JEE/Boards

**Table of Contents:**



## 1. Introduction



### 1.1 Properties of solids:

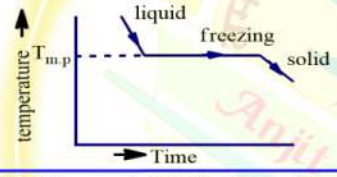
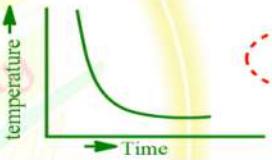
(a) In solid state the particles are not able to move randomly.
(b) They have definite shape and volume.
(c) Solids have high density.
(d) Solids have high and sharp melting point which depends on the strength or value of binding energy.
(e) They are very low compressible.
(f) They show very slow diffusion.

**Note:**

1. **Meting Point:** is the temp. at which solid melts at 1 atm. Pr. Is M.P of the solid.
2. **Molecular Motion:** Ocellate about the mean position (centre of mass)

### 1.2 Difference b/w Crystalline & Amorphous Solids :

**Anisotropy:** Crystalline solids are anisotropic in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions.

| Property | Crystalline solids | Amorphous solids |
|---|---|---|
| Shape | Definite characteristic geometrical shape | Irregular shape |
| Melting point | Melt a sharp and characteristic temperature | Gradually soften over a range of temperature |
| Cleavage property | When cut with a sharp edged tool, they split into two pieces are plain and smooth | When cut with a sharp edged tool, they cut into two pieces with irregular surfaces |
| Heat of fusion | They have definite and characteristic value | They do not have definite value |
| Anisotropy | Anisotropic in nature except cubic crystals | Isotropic in nature |
| Nature | True solids | Pseudo solids or super cooled liquids |
| Order in arrangement of consitituent particles | Long range order | Only short range order |
| Law of Crystallography | Follows | Does not follow |
| X-ray diffraction | Forms | Does not form |
| Cooling curve | Cooling curve is not smooth   | Cooling curve is smooth    |
| Examples | NaCl, Diamond, MgO, $CaF_2$, Quartz, Red P. | Glass, Rubber, Plastic, Quartz glass |

**Note :**

1. Glass are supercooled Liquid (due to viscosity)
2. Ionic compound generally forms solid. (KCl)
3. NaCl (Rock Salt) do not conduct electricity, It conduct electricity only in molten or aqueous stage.

### 1.3 Classification of Crystalline Solids:

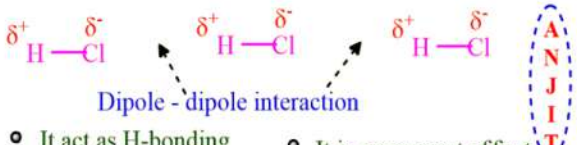
| SN | Type of Crystal | Constituents Unit | Attractive Force | Example | M.P (K) | Physical Properties | Electrical Conductivity |
|---|---|---|---|---|---|---|---|
| 1. | Molecular Solid<br>▪ Non-Polar<br>▪ Polar<br>▪ H-Bonding | Contains Molecules | London Force | $H_2$ | Low | soft | Bad conductor |
| | | | Dipole-Dipole Interaction | HCl | Low | soft | Insulator |
| | | | H-bonding | $H_2O$ (ice) | Low | hard | Insulator |
| 2. | Ionic Solid | Ions ( +ve & -ve ) | Electrostatic force of attraction 'or' Coulombic force | NaCl<br>KCl | high | hard | NaCl (molten stage) |
| 3. | Covalent 'or' Network solid | Atom | Covalent bonding | Diamond | 4000 K | Hard | Insulator |
| | | | | Graphite | soft | soft | Conductor |
| 4. | Metallic Solid | Atom (kernel: +ve charge are held together by free e- charge) | Metallic force | Cu<br>Fe<br>Ag | Fairly high 4800K | soft | Conduction |

**Note : 01. London Force/ Dispersion Force :**

- Frizz London in 1930, developed a force b/w two Non-polar molecules like- $N_2$, $O_2$, $H_2$ or monoatomic gases like- He, Ne, Ar etc. Due to momentary dipole and Induced dipole.
- These force only suitable for short distance.
- Their energies are in range 1-10 kJ/mol

**Example :** Dispersion force Order : $C_4H_{10} > C_3H_8 > C_2H_6 > CH_4$
b/coz bigger molecules easily polarised.

**02. Dipole-Dipole Interaction or Keesom Forces :**



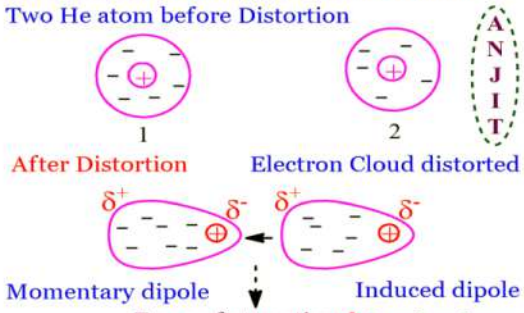

- It act as H-bonding
- It is permanent effect

ANJIT

Relative strength of four intermolecular forces is:

Ionic > H-Bond > Dipole-dipole > Vander waaals forces

- The forces develop b/w polar mol. like-HCl, $NO_2$, $SO_2$ etc
- Compound having difference E.N act as polar.




⇨ It depends on Two factors :

1. Molecular Size :

Dispersion force ∝ Mol. mass ∝ B.P

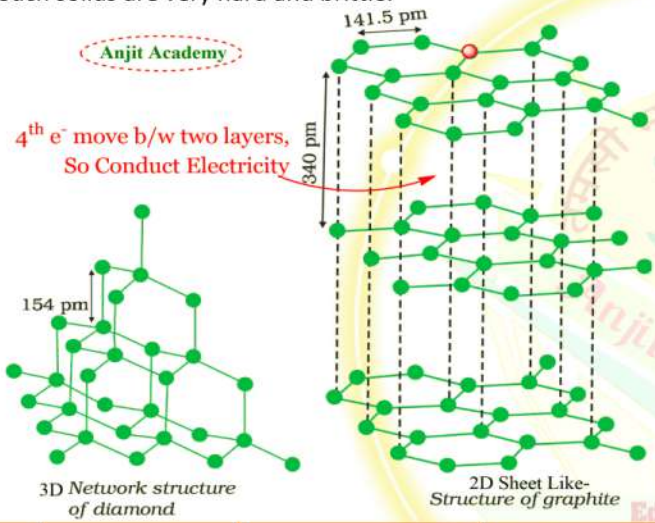
2. Molecular Geometry :

Dispersion force ∝ straight chain ∝ B.P

so, n- > iso- > neo-

### 1.4 Covalent or Network Solids:

Covalent bonds are strong and directional in nature; therefore, atoms are held very strongly at their positions. Such solids are very hard and brittle.




| SN | Properties | Diamond | Graphite |
|---|---|---|---|
| 1. | Force / Nature | Strong Covalent Bond (Hard). Mohs scale = 10 rating. (to check hardness of diamond) | Weak wander Waal force of attraction (soft). Mohs scale = 1-2 rating. |
| 2. | B.L | 154 pm | 141.5 pm |
| 3. | Hybridisation | $Sp^3$ | $Sp^2$ |
| 4. | Transparency | High refractive index (2.417). So, transparent. | It is black in colour & posses metallic lustures |
| 5. | Crystal System | Octahedral | Hexagonal |
| 6. | Z (Effective Nuclear charge) | 8 (4 = FCC + 4 = alternate *Tetrahedron* | 4 |
| 7. | Density | 3.5 g/cm3 | 2.3 g/cm3 |
| 8. | r (refractive index) | 2.414 | - |
| 9. | Lattice Structure | FCC | Hexagonal |
| 10. | C.N | 4 | 3 |
| 11. | Uses | Jewellery, Cutting | Pencil, Lubricant EMF of cell. |

## 2. Crystal Lattice & Unit Cell

### 2.1 Crystal Lattice / Space lattice :

The arrangement of constituents atom, ions and molecules in different sites in three dimensional space, with a long range order is called space lattice.

**The following are characteristics of a crystal lattice**:

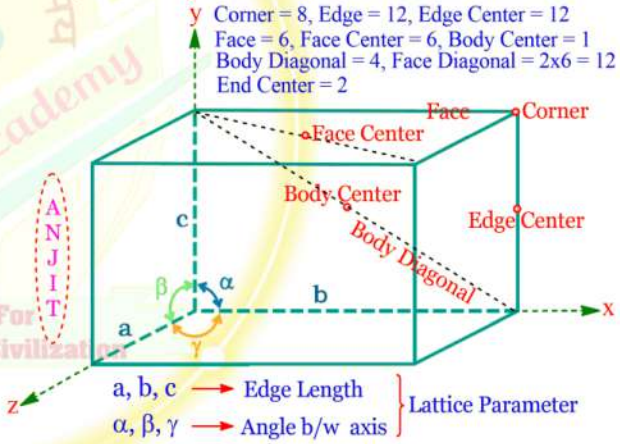
(a) Each point in a lattice is called lattice point or lattice site

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

### 2.2 Geometry of Cube :

⇨ Geometry of Cube :




**Note : Interfacial angles :** Angle b/w the perpendiculars two intersecting faces called interfacial angles.

### 2.3 Type of Unit Cell :

**Unit Cell** → The smallest repeating unit in space lattice, which repeated again and again in different direction called unit cell.

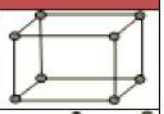
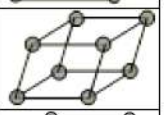
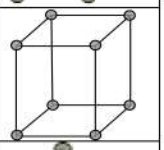
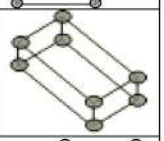
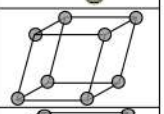
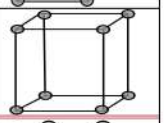
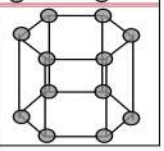
- Primitive/Simple unit cells (SC)
- Centred unit cells
  - Body-centred unit cells (BCC)
  - Face-centred unit cells (FCC)
  - End-centred unit cells (EC)

| | Primitive/Simple unit cells (SC) | Body-centred unit cells (BCC) | Face-centred unit cells (FCC) | End-centred unit cells (EC) |
|---|---|---|---|---|
| | Constituent particles are present Only on the corner positions of a unit cell | Constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners. | Constituent particle present at the centre of each face, besides the ones that are at its corners. | at the centre of any two opposite faces besides the ones present at its corners. |
| No. of Lattice : | 8 | 8+1 | 8+6 | 8+2 |
| Contribution of atom : | 1/8 = 25% | 1 = 100% | 1/2 = 50% | 1/2 = 50% |
| C.N (Coordination Number) : | 6 | 8 | 12 | 4 |
| Z ( Effective no. of Atoms) or No. of atom per unit cell : | 1/8 x 8 = 1 | 1/8 x 8 + 1x1 = 2 | 1/8 x 8 + 6 x 1/2 = 4 | 1/8 x 8 + 2 x 1/2 = 2 |

C.N (Coordination Number) → is the number of nearest atoms (or ions) surrounding an atom (or iron) in a crystal lattice.

## 3. Crystal System & Bravais Lattice System

These 14 Bravais lattices & 7 crystal system based on unit cell symmetry .

| SN | Crystal systems | No. of B.L | Bravais lattices | Example | Unit cell parameters | | Unit Cell |
|---|---|---|---|---|---|---|---|
| | | | | | Edge Length | Edge/Crystal angles | |
| 1. | Cubic | 3 | SC, FCC, BCC | NaCl, KCl, Diamond, Cu, Ag, Au (G-11) | a = b = c | $\alpha = \beta = \gamma = 90^0$ |  |
| 2. | Rhombohedral Or Trigonal | 1 | Primitive (SC) | Calcite, Haematite ($Fe_2O_3$), Quartz, As, Sb, Bi (G-15) | a = b = c | $\alpha = \beta = \gamma \neq 90^0$ |  |
| 3. | Orthorhombic Or Rhombic | 4 | SC, FCC , BCC, End centre | $BaSO_4$, $MgSO_4$, $I_2$, S. | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^0$ |  |
| 4. | Triclinic | 1 | Primitive | $H_3BO_3$, $Na_2B_4O_7$ | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^0$ |  |
| 5. | Monoclinic | 2 | Primitive , End centred | $Na_2SO_4.10H_2O$ $CaSO_4.2H_2O$ | $a \neq b \neq c$ | $\alpha = \beta = 90^0 \neq \gamma$ |  |
| 6. | Tetragonal | 2 | SC, BCC | $SnO_2$, $TiO_2$ | a = b ≠ c | $\alpha = \beta = \gamma = 90^0$ |  |
| 7. | Hexagonal | 1 | Primitive (SC) | Graphite, ZnO, ZnS | a = b ≠ c | $\alpha = \beta = 90^0, \gamma = 120^0$ |  |

⇨ Super Short Trick, How to learn Crystal Lattice :

ANJIT Academy

C – Cubic (3): a = b = c, $\alpha = \beta = \gamma = 90^0$, NaCl, KCl, Diamond, G-11

R – Rhombohedral (1): a = b = c, $\alpha = \beta = \gamma \neq 90^0$, Calcite, Haemetite, G-15

O – Orthorhombic (4): $BaSO_4$, $MgSO_4$, $I_2$, S; $\alpha = \beta = \gamma = 90^0$, $a \neq b \neq c$

M – Monoclinic (2): $Na_2SO_4.10H_2O$, $CaSO_4.2H_2O$; $\alpha = \gamma = 90^0 \neq \beta$, $a \neq b \neq c$

T – Tetragonal (2): a = b ≠ c, $\alpha = \beta = \gamma = 90^0$, $SnO_2$, $TiO_2$

H – Hexagonal (1): a = b ≠ c, $\alpha = \beta = 90^0, \gamma \neq 120^0$, Graphite, ZnO, ZnS

T – Triclinic (1): $Na_2B_4O_7$, $H_3BO_3$; $\alpha \neq \beta \neq \gamma \neq 90^0$, $a \neq b \neq c$

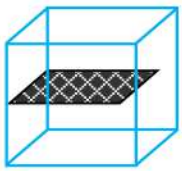
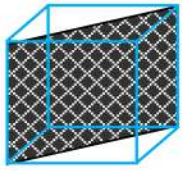
- Match box has orthorhombic geometry
- Ice may give hexagonal or trigonal crystals
- Quartz may give hexagonal or trigonal crystals

## 4. Laws of Crystallography

### 4.1 Law of constancy of Symmetry :

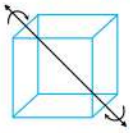
A crystal possess following three types of symmetry -

1. **Plane of symmetry :** It is an imaginary plane which passes through the centre of a crystal and can divide it into two equal portions which are exactly the mirror images to each other. So, Total = 3 + 6 = 9

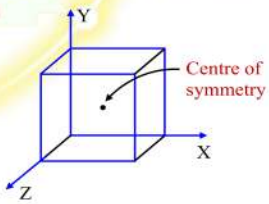
Face of cube / 2 = 3 Opposite edge / 2 = 6

2. **Axis of symmetry :**



∴ Faces/2 + Coroners/2 + Edges /2 = 3 + 6 + 4 = 13

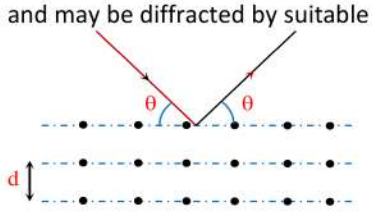
3. **Centre of symmetry :** It is a point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side. Hence, equal to = 1




A cubic crystal possesses total = 9 + 13 + 1 = 23 symmetry

### 4.2 X-ray study of the crystal : Bragg's Law :

X - rays are electromagnetic waves of short wavelength and may be diffracted by suitable diffracting centres.




$2dsin\theta = n\lambda$

$d$ ⇢ distance b/w two parallel ($d_{hkl}$) surface

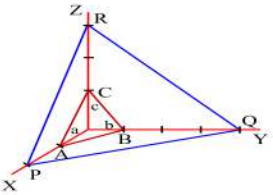
$\lambda$ ⟶ wavelength, $\theta$ ⟶ Angle of deflection

$n$ ⟶ no. of reflection 'or' order of reflection

### 4.3 Miller Indices ( Plane & Direction ) :

- It is used to calculate direction & plane of the crystal system by using h, k, l integer.
- $h = \frac{a}{Intercept\ on\ the\ x-axies}$, $k = \frac{b}{Intercept\ on\ the\ y-axies}$

$l = \frac{c}{Intercept\ on\ the\ z-axies}$

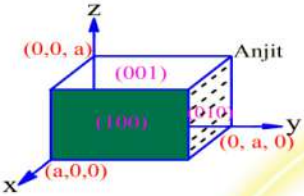



- The distance between the parallel planes in a crystal are designated as $d_{hkl}$ for different cubic lattices these interplanar spacings are given by the following general formula as -

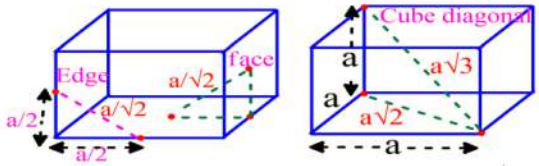
$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

where, a = length of the cube side & h,k,l = Miller indices of the plane

- Direction of miller indices ⟶ [ hkl ]
  Complete family ⟶ < hkl > & Value ⟶ ( hkl )
- **Procedure :**
  1. Intercept on the axis = x, y , z
  2. Axis is parallel = ∞
  3. take the reciprocal of fractional intercepts of its face on the various axes.




### 4.4 Length of Face diagonal & Cube diagonal :

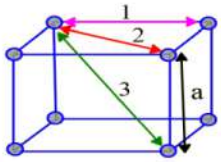



- Distance b/w two adjacent Face centre = $a/\sqrt{2}$
- Distance b/w two adjacent edge centre = $a/\sqrt{2}$
- Length of face diagonal = $a\sqrt{2}$
- Length of cube diagonal = $a\sqrt{3}$

Anjit

### 4.5 First three nearest neighbour distance for primitive cubic unit cell will be : Nearest distance d = 2r

**1st nearest distance :** SC ( a ), BCC ( $\frac{a\sqrt{3}}{2}$ ) , FCC ( $\frac{a}{\sqrt{2}}$ )




ANJIT

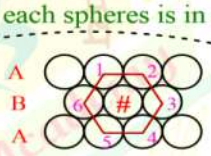
- 1st nearest neighbour distance = a
- 2nd nearest neighbour distance = $a\sqrt{2}$
- 3rd nearest neighbour distance = $a\sqrt{3}$

## 5. Cubic Closed Packing on Crystal

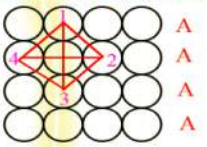
- In crystal, the constituents' particles (sphere) are arranged, In such a way that arrangement have minimum energy & max Stability.
- For max. stability the constituent particle are surrounded by max. no of neighbour particles.

### Packing of Constituents in Crystals

- 1 D - Close packing: are placed side by side in a row. Sphere are arranged in horizontal rows Only.
  ○①#②○○ C.N = 2 In this arrangment, each spheres is in contact with two of its neighbours.
- 2 D - Close packing: ---- 1 D + 1 D
  - can be arranged in two different way to build crystal plane.
  - sphere are arranged Horizontal & Vertical alignment and so on.
  - In Hexagonal close packing arrangment is more dense (Stable ) than square close packing (2D).



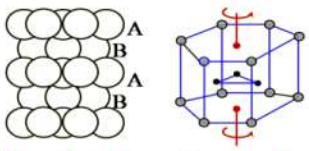

C.N = 6
Hexagonal close packing
- Stacking Pattern : ABABAB.....type arrangment
- In which the spheres in every second row are seated in the depression between the spheres of first row.
- In hexagonal close packing about 60.4% of available space is occupied by spheres



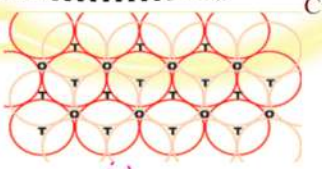

C.N = 4
Square close packing
Stacking Pattern : AAA.....type
Each sphere in this arrangement is in contact with four other spheres.
Occupies only 52.4% of the space by spheres.

- 3 D - Close packing:
  1 D + 2 D
  is obtained by stacking 2D layers one above the other.

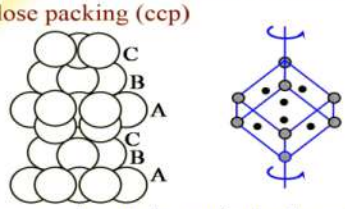
Hexagonal close packing (hcp)




When the spheres in every layer is placed above only one type of voids (B or C) of previous layer, the spheres of every third layer lie strictly above the spheres of first layer. This arrangement if continued infinitely in the same sequence is represented as AB AB AB ..... .



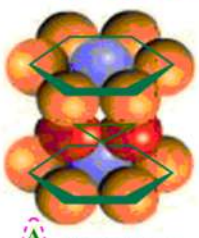
Cubic close packing (ccp)

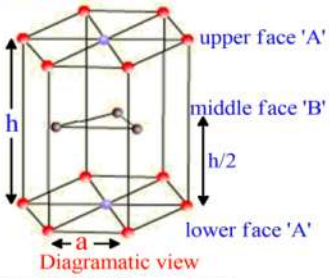



When the spheres are placed alternatively above the voids B and C type, then the spheres of every fourth layer lie strictly above the spheres of first layer. This arrangement, If continued infinitely in the same sequence, is represented as ABC ABC ABC.....
This arrangement is exactly same as fcc.

ANJIT Academy

⇨ HCP (Hexagonal Cubic Packed):






Normal view Diagramatic view

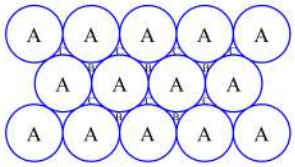
ANJIT

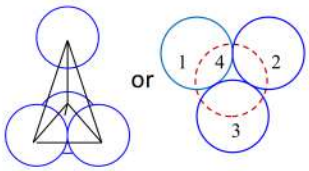
- Stacking Pattern : ABABAB--------type
- CN : 3 + 6 + 3 = 12
- Z = 6 x 1/6 + 6 x 1/6 + 3 x 1 + 2 x 1/2 = 6
- h/a = 2√2 / √3 = 1.633

### 5.1 Tetrahedral void :

(i) This type of void is formed when a triangular void of a hexagonal closed plane is covered by an atom of another atomic layer.

(ii) In any closed packed structure each atom has two tetrahedral void.



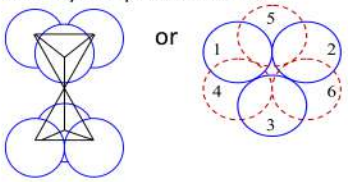




### 5.2 Octahedral void :

(i) The unoccupied space surrounded by six atoms or ions is called octahedral void.

(ii) In any closed packed structure each atom has one octahedral void.

(iii) This type of void is obtained when triangular void of another layer of HCP layer is placed over it.




### 5.3 Location of void :

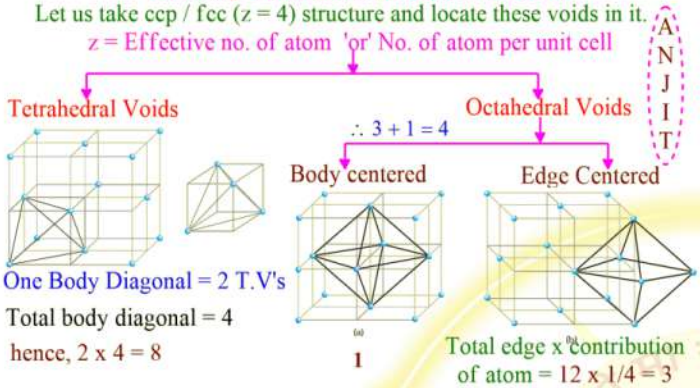
- If constituents Particles = N then, Octahedral Voids = N

And, No. of Tetrahedral Voids = 2N (Twice)

Locating Tetrahedral and Octahedral Voids

Let us take ccp / fcc (z = 4) structure and locate these voids in it.

z = Effective no. of atom 'or' No. of atom per unit cell

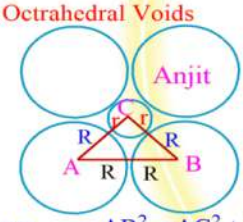



### 5.4 Relation b/w Void radius & Sphere radius:

**1. Octahedral Voids :**

- Two equilateral triangle is formed b/w Six Sphere.
- r/R = 0.414

⇨ Octrahedral Voids




ΔABC, ∴ $AB^2 = AC^2 + BC^2$

$\Rightarrow (2R)^2 = (r + R)^2 + (r + R)^2$

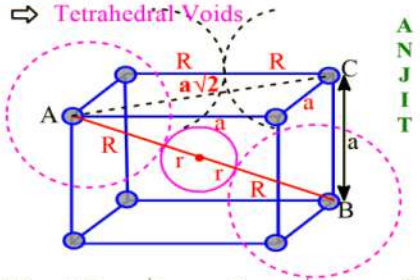
$\Rightarrow 2R = 2\sqrt{}(r + R) \Rightarrow \sqrt{2} = r/R + 1$

$\Rightarrow r/R = 1 - 1.414 = 0.414$

**2. Octahedral Voids :**

- One equilateral triangle is formed b/w four Sphere.
- r/R = 0.225

⇨ Tetrahedral Voids




$2R = AC = a\sqrt{2} \Rightarrow R = a/\sqrt{2}$ --------(i)

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

$\Rightarrow (2r + 2R)^2 = (a\sqrt{2})^2 + a^2$

$\Rightarrow 2(r + R) = 3a^2 \Rightarrow r + R = \sqrt{3}\, a$ ---(ii)

from, eqⁿ i & ii, $r/R + 1 = (a\sqrt{3}) / (a\sqrt{2})$

$\Rightarrow r/R = (\sqrt{3} - 1) / \sqrt{2} = 0.225$

## 6. Mathematics Analysis of Cubic Crystal

### 6.1 Packing fraction (P.F.) & Packing Efficiency (P.E):

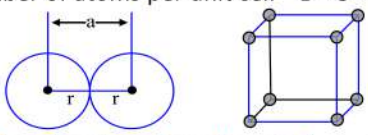
It is defined as ratio of the volume of the unit cell that is occupied by spheres of the unit cell to the total volume of the unit cell.

$$P.E = \frac{Volume\ occupied\ by\ total\ no.of\ sphere}{Vol.\ of\ Unit\ Cell} \times 100$$

$$\Rightarrow PE = \frac{z \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

**(a) Simple cubic unit cell :**

Number of atoms per unit cell z = 8 × 1/8 = 1




And, " Atom touches along the axis." r = a/2 ⇒ a = 2r

$\therefore$ P.F = $\frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} = 0.52 = \frac{\pi}{6}$ So, % P.F = 52.4 %

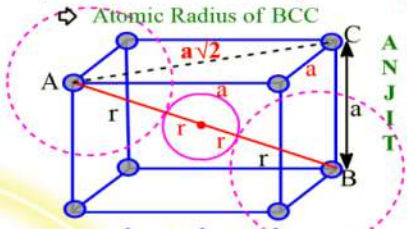
% of void 'or' Empty space = 100 – 52 = 47.6 %

**(b) Body cantered cubic unit cell :**

Number of atoms per unit cell z = 8 × 1/8 + 1 = 2

And, "Atom touches along the body centre."

⇨ Atomic Radius of BCC




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

$\Rightarrow (4r)^2 = (a\sqrt{2})^2 + a^2$

$\Rightarrow 4r = 3a^2 \Rightarrow r = \sqrt{3}\, a / 4 \Rightarrow a = \frac{4r}{\sqrt{3}}$

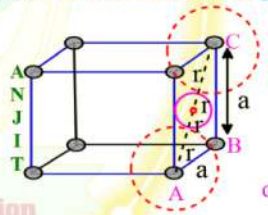
$\therefore$ P.F = $\frac{2 \times \frac{4}{3}\pi r^3}{(4r/\sqrt{3})^3} = \frac{\pi\sqrt{3}}{6}$ = 0.68 so, P.E = 68 %

% of void 'or' Empty space = 100 – 68 = 32 %

**(c) Face centered cubic unit cell :**

Number of atoms per unit cell z = 4

And, "Atom touches along the face centre."




⇒Δ ABC,

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

$\Rightarrow r = a / 2\sqrt{2}$

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

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

$\therefore$ P.F = $\frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \frac{\pi\sqrt{2}}{6}$ = 0.74 'or' % P.F.= 74 %

% of void 'or' empty space = 100 – 74 = 26 %

**Note:** Any Metal crystal in FCC/BCC/Sc arrange & surface *adjacent atom* along the edge of unit cell 'or' Interfacial separation (*distance*) b/w he atoms at the edge = **a – 2r**

### 6.2 Density of Cubic Crystal :

It is defined as the ratio of mass of unit cell to the total volume of unit cell.

$$d = \frac{m}{v} = \frac{mass\ per\ unit\ cell}{Volume\ of\ unit\ cell} = \frac{Z \times Mol.\ mass}{N_A \times volume\ of\ unit\ cell}$$

$$\therefore\ d = \frac{z \times M}{a^3 \times N_A}\ g/cm^3 \quad or \quad Kg/m^3$$

Where, Z → is the number of atoms per unit cell

$N_A$ → is the Avogadro number.

a → edge length / distance / unit cell length

### 6.3 Calculation of Ionic Radii or relation b/w r & a :

(a) NaCl Crystal = FCC Lattice :

$a = 2\,(r_{Na^+} + r_{Cl^-})$ or $r_c + r_a = \frac{a}{2}\ (no.of\ nearest\ distance)$

(b) CsCl Crystal = BCC Lattice :

$a\sqrt{3} = 2\,(r_{Cs^+} + r_{Cl^-})$ or $r_c + r_a = \frac{a\sqrt{3}}{2}$

### 6.4 Limiting Radius Ratios ( R.R ) & Structure :

| R.R = $(r^+)/(r^-)$ | C.N | Shape | Crystal | Ex. |
|---|---|---|---|---|
| < 0.155 | 2 | Linear | - | - |
| 0.155 – 0.225 | 3 | Trigonal | - | $B_2O_3$ |
| 0.225 – 0.414 | 4 | Tetrahedral | FCC/CCP | ZnS |
| 0.414 – 0.732 | 6 | Octahedral | FCC | NaCl |
| 0.732 – 1 | 8 | *Cubic* | *BCC* | *CsCl* |

## 7. Imperfection/Defects in Solid

Imperfection in a crystal is the departure of constituent particles of the system from its regular position in the lattice.

**Imperfection / Defects** i.e. irregularities in crystal

Point defect arises due to irregularties from ideal arrangement around a point in a crystalline substance.

Line defects are the deviations in entire rows of lattice points.

Anjit Aacdemy

**Point defects**

**Intrinsic defect**

**Stoichiometric Defects** Based on

- **Non-ionic Solid**
  - **Vaccancy defects**
    - Vacant Lattice Space
    - This type of defects arises due to missing of some vacant space.
    - Density (↓)
  - **Interstitial defect**
    - Extra at interstitial site
    - Density (↑)
- **Ionic Solid**
  - **Schottky defect** (ion-pair missing)
    - Same no. of cation & anion missing from their reglar normal lattice site.
    - $r^+ = r^-$
    - C.N high (b/coz same no. of cation & anion are missing)
    - Entropy (↑)
    - Density (↓)
    - Electrically neutral
    - NaCl, KCl, AgBr
  - **Frenkel Defect** (Dislocation of ion)
    - In this defect missing of cation from their normal lattice site & occupy interstitial site.
    - $r^- > r^+$
    - C.N decrease (due to holes)
    - Entropy (↑)
    - No effect on Density
    - Electrically neutral
    - Zns, AgBr

$SrCl_2 \Rightarrow Sr^{2+} + 2Cl^-$ / $2Na^+$

In NaCl powder containing $SrCl_2$ as Impurities is allowed to cool.

ANJIT Academy

**Non Stoichiometric Defect**

- **Metal excess defects**
  - an Extra cation Occuping the interstial site
  - F-centre
  - F = Farbenzenter Colour Centre
  - The free e- traped in the anionic vacancy is called F-centre.
  - LiCl = Pink
    NaCl = Yellow
    KCl = Violet
- **Metal deficiency defects**
  - caused by a missing of negative ions

**Impurity Defects**

- In ionic solid
- In covalent solid

**Line defects**

**Note :** **AgBr Show Schottky & Frankel defects both, Why ?**

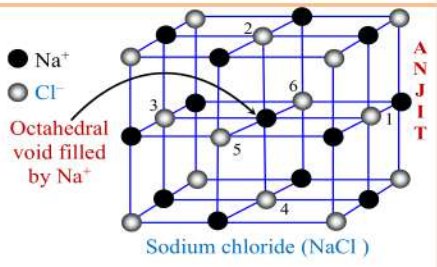
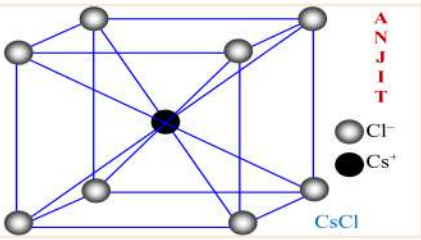
- Schottky defect is observed in crystal High C.N and cation & anion have similar size.
- Frekel defect is observed in those crystal whose there is large difference in size of cation & anion.

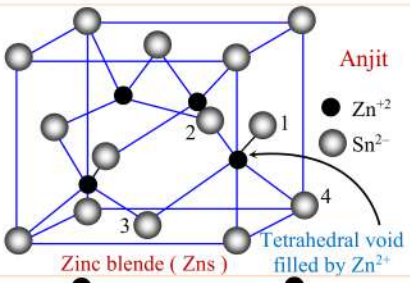
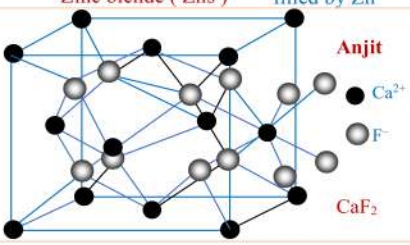
As, $Ag^+$ is small in size & $Cl^-$ is large in size which result in large difference in size of ions & also highly ionic.

## 7. Packing in ionic solids

Ionic crystal

- AB type
  - NaCl type
  - ZnS type
  - CsCl type
- $AB_2$ type
  - $CaF_2$ type
  - $TiO_2$ type
  - $SiO_2$ type
- $A_2B$ type
  - $Na_2O$ type

| Crystal Structure | Description 'or' Arrangement of ions | C.N | Z | |
|---|---|---|---|---|
| **1. Rock Salt (NaCl - type)** | CCP : $Cl^-$ ions in C.C.P, $Na^+$ ions occupy edge centre + body centre *( all the octahedral voids.)* | $Na^+ - 6$<br>$Cl^- - 6$<br>∴ C. N Ratio 6 : 6 | 4 |  Sodium chloride (NaCl ) |
| **2.Casium Chloride (CsCl – type)** | BCC : $Cl^-$ ions bcc arrangement the corner of a cube and $Cs^+$ ions in the body centre 'or' Vice versa. | $Cs^+ - 8$<br>$Cl^- - 8$<br>∴ C. N Ratio 8 : 8 | 1 |  |

| | | | | |
|---|---|---|---|---|
| **3. Zinc. Blende (ZnS)** | CCP : $S^{2-}$ ccp arrangement & $Zn^{+2}$ ions occupy *alternate tetrahedral voids* i.e. only half of the total number of tetrahedral voids are occupied | $Zn^{+2} - 4$<br>$S^{-2} - 4$<br>∴ C. N Ratio<br>4 : 4 | 4 |  |
| **4. Fluorite Struct. ($CaF_2$ – type)** | CCP : $Ca^{+2}$ ions (+ve ions) in C.C.P. & $F^-$ ions (-ve ions) in *all the tetrahedral voids.* | $Ca^{+2} - 8$<br>$F^- - 4$<br>∴ C. N Ratio<br>8 : 4 | 4 |  |
| **5. Anti-flurote Structure** | CCP : $B^{2-}$ Negative ions in CCP & Positive ions $A^+$ in *half tetrahedral voids.* | $Na^+ - 4$<br>$O^{-2} - 8$<br>∴ C. N Ratio<br>4 : 8 | 4 | **Note : Rutile Structure ($TiO_2$) :**<br>$O^{2-}$ : Forming HCP<br>$Ti^{4+}$ : ½ of Octahedral voids |

| Compound Prop. | HCP | CCP/FCC | BCC |
|---|---|---|---|
| Arrangment of packing | Close packed | Close | Not close packed |
| Type of packing | ABAB..... | ABCABC..... | ABAB..... |
| Space occupied | 74% | 74% | 68% |
| C.N | 12 | 12 | 8 |
| Effective no. of atoms (z) | 6 | 4 | 2 |
| Example | G-3, 4, 12 & Be, Mg | G-9,10,11 & Inert gas (Except He, Al) | G-1, 5, 6 & Ba, Fe |

ANJIT

**Effect of Temprature & Pressure on C.N. :** Anjit Academy

Pressure (↑) ⟶ C.N (↑) & Temprature (↑) ⟶ C.N (↓)

NaCl C.N = 6 : 6 ⇌ (Pr.(↑), T (↑)) CsCl C.N = 8 : 8

## 8. Properties of solids

### 8.1 Magnetic properties:

**(a) Diamagnetic Material :**

(i) Materials which are *weakly* repelled by magnetic fields.
(ii) They contains paired electrons .
(iii) Even no. of e- Except : 10 & 16e-.
(iv) Examples of D.M are - $C_6H_6$, NaCl, S, ZnO, $V_2O_5$, $TiO_2$ etc.

**(b) Paramagnetic material :**

(i) Materials which are attracted by the magnetic field.
(ii) They always contain unpaired electrons.
(iii) In this material magnetic dipole tend to orient themselves parallel to the direction of the field and thus produce magnetization in the substance.
(iv) Odd no. of e- with 10 & 16 e-.
(v) Examples : $O_2$, $Cu^{++}$, $Fe^{+2}$, $Fe^{+3}$, $Cr^{+3}$ , CuO, NiO, $Ti_2O_3$ etc

**(c) Ferromagnetic material :**

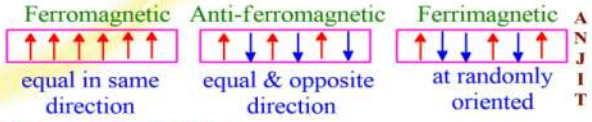
(i) Which are *strongly attracted* by magnetic lines of forces so, net magnetic moment *not equal to zero.*
(ii) Ferromagnetism is due to *spontaneous* alignment of the magnetic dipole in the *same direction.*
(iii) Each ferromagnetic material losses its magnetic character above a critical temp. This temp is called the **curie temperature.**
(iv) They contain a *number* of unpaired electrons
(v) Examples of these materials are Fe, Co, Ni etc.

**(d) Anti-ferromagnetic materials :**

(i) These are the materials, in which alignment of the dipole equal & opposite direction so as to give *zero net dipole* moment.
(ii) MnO, FeO is the example of antiferromagnetic material.

(d) **Ferrimagnetic materials :** These are the material in which dipoles are oriented in parallel and antiparallel direction in unequal numbers, so that there is a net magnetic moment. **Ex.-** $Fe_3O_4$, $MgFe_2O_4$, $NiFe_2O_4$ etc.

- $AB_2O_4$ Type : ------ ferrite.




- ANJIT

### 8.2 Dielectric Properties :

**(1) Piezo electricity :**

(i) When a polar crystal is subjected to a mechanical stress, electricity is produced. The electricity so produced is called piezo electricity.
(ii) If an electric field is applied to a crystal, a mechanical stress is developed in the crystal. Thus, a piezo electric crystal acts as a mechanical-electrical transducer.
Example: Lead Zirconate ($PbZrO_3$)

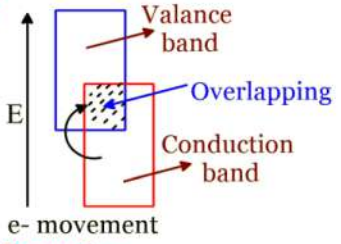
**(2) Pyro electricity :** Those materials which can produce small electric current. This phenomenon is termed as pyro electric effect. The electricity so produced is termed a pyro electricity.

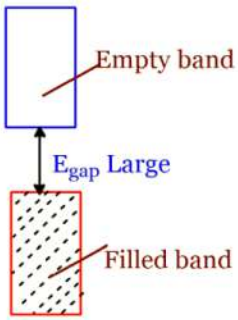
### 8.3 Electrical Properties :

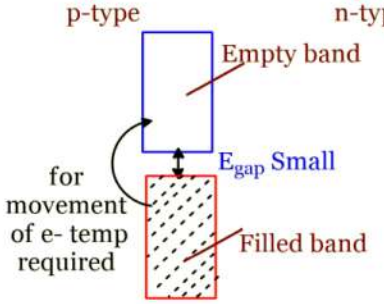
# Electrical Properties

- Conductor
  - Metallic Conductor
  - Electrolytic Conductor
- Insulator/Non-Conductor
- Semi-Conductor
  - Intrinsic Semi-Conductor (Pure semi-conductor)
  - Extrinsic Semi-Conductor (Impure Semi-conductor)
    - p-type
    - n-type

ANJIT



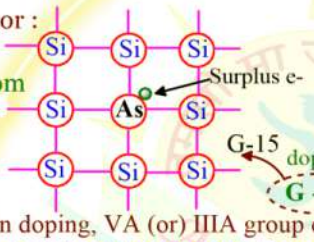



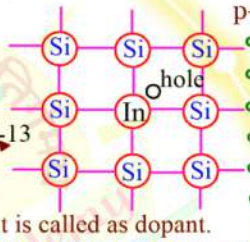

⇨ Properties :

| | Metallic Conductor | Intrinsic Semi-Conductor | Extrinsic Semi-Conductor |
|---|---|---|---|
| Electrical conductivity : | $10^4 - 10^7\ \Omega^{-1}m^{-1}$ | $10^{-20} - 10^{-10}\ \Omega^{-1}m^{-1}$ | $10^{-6} - 10^4\ \Omega^{-1}m^{-1}$ |
| Motion/Movement: | Electron only | e- 'or' holes 'or' both | holes & electron |
| Energy gap : | $E_g$ = 0 ev | > 10 ev | $E_g$ for Si = 1.1 ev , Ge = 0.7 ev |
| Example: | Al, Cu, Fe | Wood, Plastic | Si, Ge (G-14) |

**Extrinsic Semi-Conductor :**
- Their conductivity is due to presence of impurity.
- Some impurity introduced in a pure semi-conductor (G-14) is called Doping.

⇨ n -Type Semi-conductor :
- n-stands for negative.
- penta-valent impurity atom
- e- rich impurities
- e- donor
- Lewis base



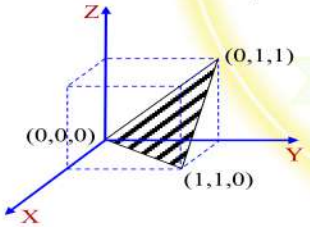

p-Type Semi-conductor :
- p - stands for positive.
- Tri-valent impurity atom
- e- defficient impurities
- e- acceptor
- Lewis acid
- One more e- is required, it is left as a vacant place on the atom.

In doping, VA (or) IIIA group element is called as dopant.

Applications: n - type & p - type semi conductors both are used as- Diode, pnp or npn transistors.

## ➢ Solved Important Questions

**Ex.1** Determine the Miller indices of the shaded plane. Coordinate of the corners of the plane are shown -




**Sol.** A plane parallel to the plane between (0,0,0), (1,1,0) & (0, 1, 1) will intersect the axes at, x= a, y = –b & z = c

| a | b | c | |
|---|---|---|---|
| 1 | –1 | 1 | intercepts |
| 1 | –1 | 1 | reciprocals |

Thus, the Miller indices are $(1, \bar{1}, 1)$ or $(\bar{1}, 1, \bar{1})$.

**Ex.2** What is the simplest formula of a solid whose cubic unit cell has the atom A at each corner, the atom B at each face centre and a C atom at the body centre –
(A) $AB_2C$ (B) $A_2BC$ (C) $AB_3C$ (D) $ABC_3$

**Sol.** number of corner atom (A) per unit cell = 8 ×1/8 = 1.
number of face-centered atoms (B) per unit cell = 6 ×1/2= 3
∴ no. of atoms (C) at the body centre per unit cell = 1.
Hence, the formula of the solid is $AB_3C$.

**Ex.3** Select the correct statement (s) -
(a) The C.N. of cation occupying a tetrahedral hole is 4
(b) The C.N. of cation occupying a octahedral hole is 6
(c) In schottky defects, density of the lattice decreases
(A) a, b (B) b, c (C) a, b, c (D) a, c

**Sol.** [C]

**Ex.4** The unit cell of a metallic element of atomic mass $10^8$ and density 10.5 g/cm$^2$ is a cube with edge length of 409 PM. The structure of the crystal lattice is –
(A) 0.128 (B) 1.42 (C) 3.22 (D) 4.22

**Sol.** For a face-centred cube, we have,

radius = $\frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 0.361}{4}$ nm **= 0.128.**

**Ex.5** Copper metal has a face-centred cubic structure with the unit cell length equal to 0.361 nm. Picturing copper ions in contact along the face diagonal, The apparent radius of a copper ion is–
(A) fcc (B) bcc (C) hcp (D) None

**Sol.** $\rho = \frac{Z \times M}{N \times a^3}$ Here, M = 108 $N_A = 6.023 \times 10^{23}$

Put on these values and solving we get -

a = 409 PM = $4.09 \times 10^{-8}$ cm

∴ Z = 4 = number of atoms per unit cell

So, The structure of the crystal lattice is fcc.

**Ex.6** A solid contains $A^+$ and $B^-$ ions. The structure of solid is fcc for $B^-$ ions and $A^+$ ions are present in one fourth of tetrahedral voids as well as in one fourth of octahedral voids. What is the simplest formula of solid ?

**Sol.** The structure is fcc for $B^-$ and hence

$Z_B = 8 \times 1/8 + 6 \times 1/2 = 4$

fcc contains 8 tetrahedral voids and four octahedral voids per unit cell and hence,

$Z_A = 8 \times 1/4 + 4 \times 1/4 = 3$

∴ formula of solid = $A_3B_4$.

## Multiple Choice Questions

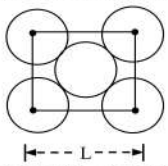
**Q.7** In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is –
(A) $AB_2$ (B) $A_2B$ (C) $A_4B_3$ (D) $A_3B_4$

**Q.8** A substance $A_xB_y$ crystallizes in a face centered cubic (FCC) lattice in which atoms 'A' occupy each corner of the cube and atoms 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance $A_xB_y$
(A) $AB_3$ (B) $A_4B_3$ (C) $A_3B$
(D) Composition can't be specified

**Q.9** Alternate tetrahedral void in *FCC* are occupied in
(A) NaCl (B) ZnS (C) $CaF_2$ (D) $Na_2O$

**Q.10** The correct statement(s) regarding defects in solids is(are) -
(A) Frenkel defect is usually favoured by a very small difference in the size of cation and anion
(B) Frenkel defect is a dislocation defect
(C) Trapping of an electron in the lattice leads to the formation of F-center
(D) Schottky defects have no effect on the physical properties of solids

**Q.11** The packing efficiency of the two-dimensional square unit cell shown below is -




(A) 39.27 % (B) 68.02% (C) 74.05% (D) 78.54%

**Q.12** For an element of *FCC* crystal lattice having edge length 400 pm, calculate the maximum diameter of an atom which can be placed in interstitial site so that the structure remain same.

**Q.13** For a cubical system the following information are available. Edge length = 5Å; density = 2 gm/cm$^3$, Atomic wt. = 75
Determine the radius of the atom in pm ?

**Q.14** Match the crystal system/unit cells mentioned in Column-I with their characteristic feature mentioned in Column-II.

| Column-I | | Column-II |
|---|---|---|
| (A) simple cubic and face centred cubic | (P) | have these cell parameters $a = b = c$ & $\alpha = \beta = \gamma$ |
| (B) cubic and rhombohedral | (Q) | are two crystal systems |
| (C) cubic and tetragonal | (R) | have only two crystallographic angles of 90° |
| (D) hexagonal and monoclinic | (S) | belong to same crystal system |

**Q. 15** CsBr has cubic structure with edge length 4.3. The shortest inter ionic distance in between $Cs^+$ & $Br^-$ is
(A) 3.72 (B) 1.86 (C) 7.44 (D) 4.3

**Q.16** In the sodium chloride structure, each $Na^+$ ion is surrounded by six $Cl^-$ ions nearest neighbours and ..... $Na^+$ ion next nearest neighbours –
(A) 4 (B) 8 (C) 6 (D) 12

**Q.17** The coordination number of a metal crystallized in a hexagonal close packed structure is
(A) 12 (B) 4 (C) 8 (D) 6

**Q.18** A metallic element crystallizes into a lattice containing sequence of layers of ABABAB..... This packing of sphere leaves out voids in the lattice. What percentage by volume of this space is empty space ?

**Q.19** Chromium metal crystallizes with a body centered cubic lattice. The length of the unit cell is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm$^3$ ?

**Q.20** A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?

**Q.21** A metal crystallizes into two cubic phases, face centered cubic (*fcc*) and body centered cubic (*bcc*), whose unit cell length are 3.5 and 3.0 Å, respectively. Calculate the ratio of density of fcc and bcc.

**Q.22** If an element (at. wt. = 50) crystallizes in fcc lattice, with a = 0.50 nm. What is the density of unit cell if it contains 0.25% schottky defects (use $N_A = 6 \times 10^{23}$)
(A) 2.0 g/cc (B) 2.66 g/cc
(C) 3.06 g/cc (D) none of these

**Q.23**

| Column-I | Column-II |
|---|---|
| (A) Spinel structure | (i) $ZnAl_2O_4$ |
| (B) Glass | (ii) Pseudo solid |
| (C) 6 : 6 Co-ordination | (iii) NaCl type structure |
| (D) Plastics | (iv) Super cooled liquid |

**Q.24** In *fcc* lattice, A, B, C, D atoms are arranged at corner, face centre, octahedral void and tetrahedral void respectively, then the body diagonal contains :
(A) 2A, C, 2D (B) 2A, 2B, 2C
(C) 2A, 2B, D (D) 2A, 2D

**Q.25** The radius of $Ag^+$ ion is 126 pm while that of $I^-$ ion is 216 pm. The co-ordination number of Ag in AgI is –
(A) 2 (B) 4 (C) 6 (D) 8

❖❖❖

| | | | | | | |
|---|---|---|---|---|---|---|
| 7. D | 8. A | 9. B | 10. B,C | 11 . D | 12. 117.1 Pm | 13. 217 Pm |
| 14. | A → (P, S), B → (P, Q), C → (Q), D → (Q, R) | | | | | 15. A |
| 16. D | 17. A | 18. 25.6% | 19. 7.3 g/cm$^3$ | 20. 2.16 g/cm$^3$ | 21. 1.259 | 22. B |
| 23. | A → (i); B → (ii), (iv); C → (iii); D → (ii),(iv) | | | | 24. A | 25. C |

❑ ❑ ❑

☎ आपका परिश्रम + हमारा मार्गदर्शन = निश्चित सफलता ☎

❑ ❑ ❑