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UNIT – I

BONDING IN SOLIDS &

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURES

Question and Answers

1. **What are the different types of bonds in solids? (or)**

Explain various types of bonding in solids with suitable examples.

Ans: Broadly there are two types of bonds.

1.   Primary bonds also known as interatomic bonds

2.   Secondary bonds also known as inter molecular bonds

Primary bonds are strong bonds which hold the atoms together. There are three types of primary bonds: Ionic bonds, covalent bonds and metallic bonds. Secondary bonds are weaker than primary bonds. Examples for secondary bonds are hydrogen bonds and vanderwaal bonds.

Bonds which are localized and occur in fixed angles with respect to each other are directional bonds. Covalent and hydrogen bonds are directional bonds.

In non – directional bonds, bonding is equal at all angles. The bond is not localized to specific direction. Ionic, metallic and vanderwaals bonds are non directional.

Ionic Bonds: By transferring elections from one atom to another, electron shells are filled. The donor atom will take a positive charge and the acceptor will have a negative charge. The charged atoms or ionic will be attracted to each other and form bonds. NaCl is the most common example. When sodium and chlorine atoms are placed together, there is a transfer of electrons from the sodium to the chlorine atoms, resulting in a strong electronics attraction between the positive sodium ions and the negative chlorine ions. Ions crystals are usually insulators transparent, soluble in polar solvents like water and insoluble in non polar solvents like benzene.

Covalent Bonds:

1
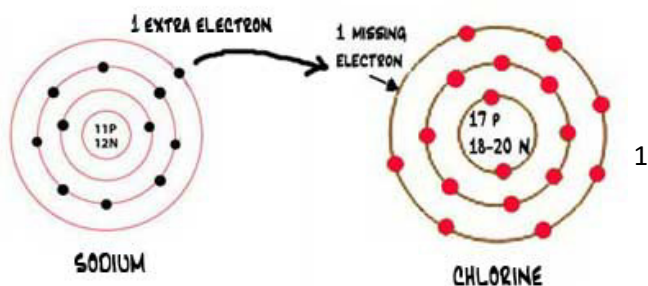
some atoms share the electrons in their outermost shell.

Example: Diamond, O-O, H2 etc. Covalent bonds are very strong directional bonds. Crystal with covalent bonds are hard and brittle and do not conduct electricity because of non availability of free electrons. A single covalent bond occurs in the hydrogen molecule.
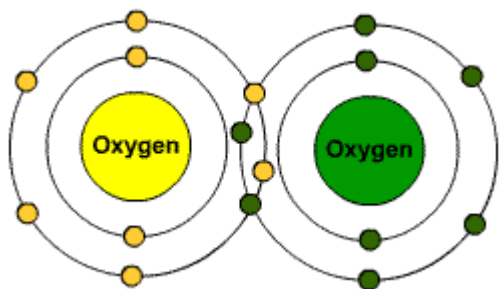
Binding energy is high so that their melting point and boiling points are high. Covalent substance are insoluble in water.

Metallic Bonds: In metallic bonds the outermost electrons of metals are shared among all the atoms in the solid. Each atom gives up its outer electrons and becomes slightly positively charges. The valence electrons form a negative electron cloud. These electrons are not associated with a particular ion but are free to move within the surface of the metal.
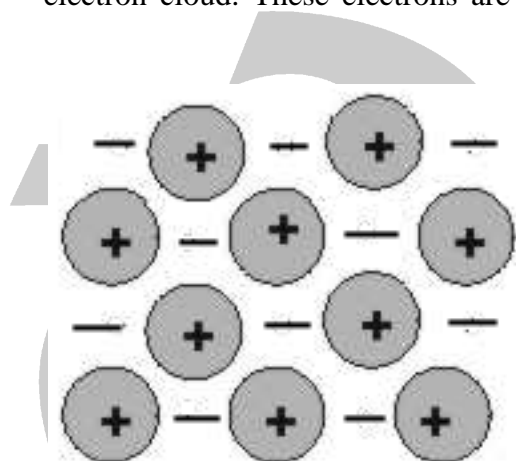
Metals are opaque , ductile, malleable. These have low melting points, high density and have good thermal and have good thermal and electrical conductivity.

Vanderwaals Bonds: Mutual polarization of atoms due to each other takes place.

Hydrogen Bond: The electrostatic force of attraction between a partially positively charged hydrogen atom of a polar molecule and a highly electron negative atom is known as hydrogen bond. In Hydrogen bond lowering of kinetic energy of proton by the arrangement O-H-O takes place.

2

	Ionic	covalent	metallic	vanderwaal	Hydrogen
Principle cause of binding	Transfer of electrons between atoms and electrostatic attraction between them.	Mutual sharing of Valence electrons between atoms	The attraction between the lattice of ion cores and the free electron gas.	Mutual polarisation of atoms due to each other	Lowering of K.E of proton by the arrangement O-H-O.
properties	Very strong binding	Strong binding	Moderate strong binding	Weak binding	Weak binding
	Poor electrical and thermal conductors	Conductivities over a wide range	High electrical and thermal conductivities	Poor electrical conductors	Low electrical and thermal conductivities.
	Transparent over a wide range of frequencies Closed packed structure.	Transparent to long wave length radiation but opaque to shorter wavelength.Loose packed structure.	Opaque to all electromagnetic radiations from very low frequency to middle ultraviolet where they become transparent.Closed Packed structure.	Transparent to electromagnetic radiation. Closed packed structure	Transparent Loose structure
	Non directional bond	Strongly directional bond	Non directional bond	Non directional bond	Peculiar directional properties
Examples	NaCl,KCl,NaBr,KBr,MgO,MgCl	CH,Cl,H,Si,Ge.	Na,K,Mg,Al,Pb.	Na,N,He,Ar,Kr,Xe	Ice,KH,PO

2. Derive the expression for the equilibrium spacing for two atoms for which the potential energy is minimum and hence obtain the dissociation energy? (or) Derive an expression for cohesive energy?   OR

Plot and explain the variation of

    1) **Attraction potential energy   2) Repulsive potential energy and**

    3) **Resultant potential energy with inter-atomic distance, when two atoms are bought nearer.**

Ans: Cohesive energy is defined as the minimum energy required to dissociate a solid into individual atoms, cohesive energy is also called binding energy. The potential energy is due to interaction between the two atoms and it depends upon interatomic spacing. The potential energy is given as

$$U = -\frac{A}{r^m} + \frac{B}{r^n}$$

Where,

U attractive $\alpha \dfrac{A}{r^m}$

U attractive $= -\dfrac{A}{r^m}$

U repulsive $\alpha \dfrac{1}{r^n}$

U repulsive $= \dfrac{B}{r^n}$

Work of attraction is done by the system; hence the attractive energy is negative.

$U = \frac{-A}{r^m} + \frac{B}{r^n}$

Where,
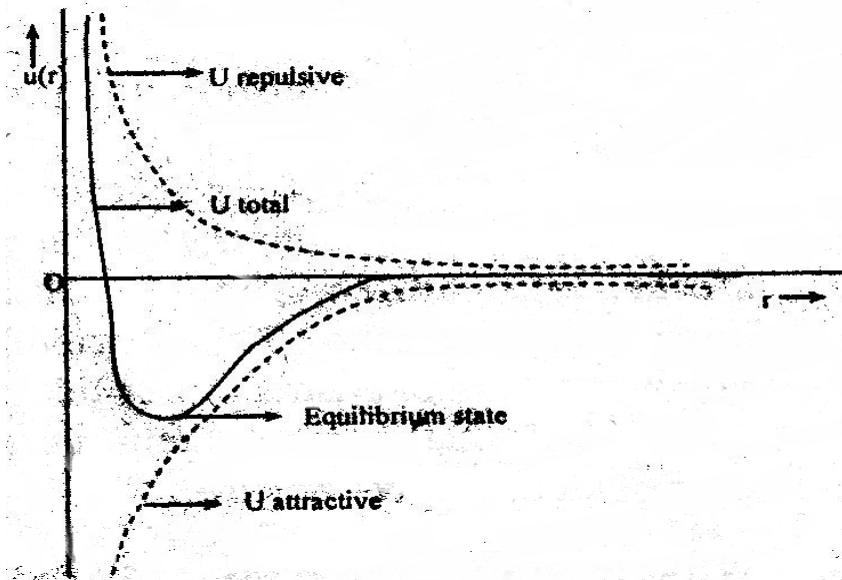
A is the attraction constant

B is the repulsive constant

m is the attraction exponent

n is the repulsive exponent

4

At equilibrium distance (r) the potential energy should be minimum, mathematically it is represented as.

$\left[\frac{dU}{dr}\right]_{r=r_0} = 0$

The variation of u(r) with r is shown in the graph

The distance where the energy the is minimum r is called equilibrium separation and the minimum energy = U_0

U_0 is called the cohesive energy or binding energy

Now

$$U_0 = -\frac{A}{r_0^m} + \frac{B}{r_0^n} \text{------ (1)}$$

On differentiating U_0 with respect to 'r'

$$\frac{\partial U_0}{\partial r} = \frac{mA}{r_o^{m+1}} - \frac{nB}{r_o^{n+1}} = 0$$

$$\frac{mA}{r_o^{m+1}} = \frac{nB}{r_o^{n+1}}$$

$$\frac{mA}{nB} = r_0^{m-n} \quad \text{--------- (2)}$$

$$r_0 = \left[\frac{mA}{nB}\right]^{\frac{1}{m-n}}$$

Where r is the equilibrium separation

We can re write equation (2) as

5

$$\frac{1}{r_0^m} = \frac{mA}{nB*r_{0m}} \quad \text{--------} \quad (3)$$

Substituting equation (3) in equation (1) we get

$$U_0 = -\frac{A}{r_0^m} + \frac{B*mA}{nB*r_0^m}$$

$$U_0 = -\frac{A}{r_0^m} + \frac{mA}{nr_0^m}$$

$$U_0 = -\frac{A}{r_0^m}\left[1 - \frac{m}{n}\right]$$

Where U_0 is the cohesive energy or binding energy.

Hence, the forces repulsion are, due to interpenetration of electronic shells between atoms, ions, and molecules when they approach each other. Therefore all stable arrangements of atoms in a solid are such that the potential energy is minimum where U_0 is of an attractive nature.

3.   What is Madelung constant? Explain.

Ans   The cohesive energy of ionic solids is given by

$$U(r) = \frac{B}{r^n} - \frac{Ae^2}{4\Pi\Sigma_0 r}$$

$\frac{B}{r^n}$ is repulsion energy (short range)

And 'A' is the Madelung Constant.

Which explains the nearest contribution of attractive & repulsive potential energies to the cohesive energy of ionic solids. It depends on the structure of the ionic crystal. The value of madelung constant is of central importance in the theory of ionic crystal. The madelung constant for one-dimensional solid is given by

$$A = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + ...\right]$$

It can be written as A = 2 log 2.

The madelung constant for same ionic solids is listed below

NaCl   1.7475

CsCl   1.7626

ZnS   1.6381

4. **Calculate the bond energy of NaCl molecule. Given Ionization energy is 5.1 eV, Electron affinity is 3.6 eV and r_o is 0.24 nm .**
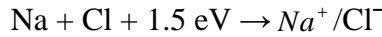
Ans. Ionization energy is energy required to remove the outer electron from Na atom.

$$Na + 5.1 \text{ eV} \rightarrow Na^+ + e^-$$
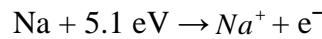
Electron affinity is energy released when electron is added to Cl atom

$$Cl + e^- \rightarrow Cl^- + 3.6 \text{ eV}$$

Net energy spend is creating Na and Cl at infinity is 5.1 - 3.6 = 1.5 eV

$$Na + Cl + 1.5 \text{ eV} \rightarrow Na^+/Cl^-$$

At equilibrium position

i.e., when r_o =0.24nm, the P.E is minimum and energy released in the formation of NaCl is called Bond energy.

$$V = -\frac{Ae^2}{4\Pi\Sigma_0 r_o}$$

$$= -\frac{1(1.602*10^{-19})^2}{4\Pi(8.85*10^{-12})(2.4*10^{-10})} \text{ Joules}$$

$$= -\frac{1(1.602*10^{-19})}{4\Pi(8.85*10^{-12})(2.4*10^{-10})(1.602*10^{-19})} eV$$

$$= - 6 \text{ eV}$$

∴ Energy released during formation of Nacl is = 1.5 – 6 = - 4.5 eV

Bon energyof Nacl is 4.5 eV

5. **Explain the forces between the two interacting atoms when they are brought nearest to a molecule.**

Sol. There are two kinds of forces between the atoms in a solid.

(1) Attractive force

(2) Repulsive force

Attractive force (F) exists between oppositely charged particles is negative and inversely proportional to power of distance between the atoms(r).   1

i.e., $F_a \alpha - \dfrac{1}{r^m}$

$\therefore F_a = -\dfrac{a}{r^m}$

Repulsive force (F_r)

$$F_r \alpha \frac{1}{r^n}$$

$$\therefore F_r = -\frac{b}{r^n}$$

Where b is the proportional constant and n the repulsive constant.

The total force (F) is the sum of the attractive and repulsive forces.

i.e., $$\therefore F = -\frac{a}{r^m} + \frac{b}{r^n}$$

when $r = r_o$, $F = 0$

$$\therefore -\frac{a}{r_0^m} + \frac{b}{r_0^n} = 0$$

$$r_0^{n-m} = \frac{b}{a}$$

$$r_0 = \left(\frac{b}{a}\right)^{\frac{1}{n-m}}$$

r_0 is the equilibrium separation.

What are Bravais Lattice? (or) Write a short note on Bravais lattice.

Ans: There are 14 bravais lattices in three dimensions. Each of these 14 bravais lattices belong to one of the seven crystal systems which are characterized by the group of symmetry elements associated with lattice points. The fourteen bravais lattices in three dimensions are shown below.

6. What are Bravais Lattice? (or) Write a short note on Bravais lattice.

Ans: There are 14 bravais lattices in three dimensions. Each of these 14 bravais lattices belong to one of the seven crystal systems which are characterized by the group of symmetry elements associated with lattice points. The fourteen bravais lattices in three dimensions are shown below.

$\alpha, \beta, \gamma \neq 90°$

1. Triclinic

2. Monocllinic

$\alpha \neq 90°$
$\beta, \gamma = 90°$

$\alpha \neq 90°$
$\beta, \gamma = 90°$
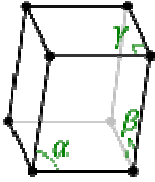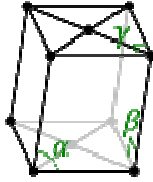
Simple   Base-centered

3.   Orthorhombic:

$a \neq b \neq c$ $a \neq b \neq c$ $a \neq b \neq c$ $a \neq b \neq c$
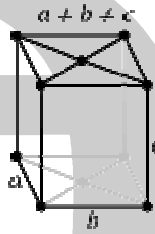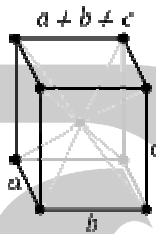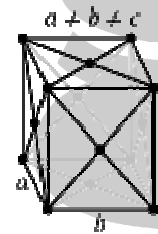
Simple   base-centered   body-centered   face-centered
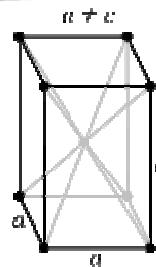
4. Rhombohedral   5. Terragonal

$\alpha = \beta = \gamma \neq 90°$

$a \neq c$ $a \neq c$
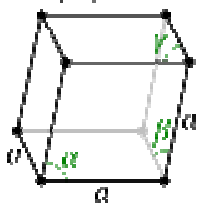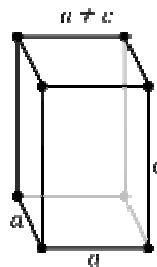
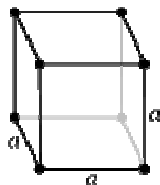Simple   Body-centered

Hexagonal-6   8- Cubic

7. Find the distance between successive planes in a simple cube. (or) Derive an expression for the interplanar spacing in the case of a cubic structure.

Ans: A crystal is made up of a large number of parallel equidistant planesnpassing through the lattice planes can be chosen in various number of ways. The perpendicular distance between adjacent planes is called interplanar spacing. The set of planes are represented by certain numbers called Miller indices.

The distance between the parallel planes whose miller indices are same is called as interplanar distance 'd'.

Consider a cubic crystal:

Let ON be the perpendicular drawn from origin to planes (h k l)

$OA = a/h, \quad OB = a/k, \quad OC = a/l$

$ON^2 = x^2 + y^2 + z^2$

$ON^2 = ON^2 \cos^2 \alpha + ON^2 \cos^2 \beta + ON^2 \cos^2 \gamma$

$1 = \cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma$

$1 = \dfrac{ON^2}{OA^2} + \dfrac{ON^2}{OB^2} + \dfrac{ON^2}{OB^2}$

$\Rightarrow ON^2 \left[\dfrac{h^2}{a^2}\right] + ON^2 \left[\dfrac{k^2}{a^2}\right] + ON^2 \left[\dfrac{l^2}{a^2}\right] = 1$

$ON^2 = \dfrac{a^2}{h^2 + k^2 + l^2}$

$ON = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

Similarly

$OM = \dfrac{2a}{\sqrt{h^2 + k^2 + l^2}}$

Since the primitive for plane 2 is "2a",

$d = OM - ON$

$d = \dfrac{2a}{\sqrt{h^2 + k^2 + l^2}} - \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

d= $\dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

distance between (1 0 0) planes in simple cube is

$d_{100} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

Here h= 1, k= 0, l= 0

$d_{100} = \dfrac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a$

$d_{100} = 1$

∴ distance between (1 1 0) planes in simple cube is $d_{100} \neq \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

Here h= 1, k = 1, l = 0

$d_{100} \neq \dfrac{a}{\sqrt{1^2 + 1^2 + 0^2}}$

$d_{100} \neq \dfrac{a}{\sqrt{2}}$

Distance between (1 1 1) planes in simple cube

$d_{hk} \neq \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

Here h = 1, k = 1, l = 1

$d_{hkl} \neq \dfrac{a}{\sqrt{1^2 + 1^2 + 1^2}}$

$d_{hkl} = \dfrac{a}{\sqrt{3}}$

For a simple cube $d_{100} : d_{110} : d_{111} = 1 : \dfrac{1}{\sqrt{2}} : \dfrac{1}{\sqrt{3}}$

8. Draw a neat diagram to indicate miller Indices of Important planes in a cubic crystal.

Ans. Important planes in a crystal are :

(1 0 0), (1 1 0), (1 1 1).

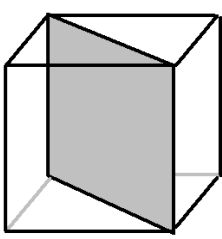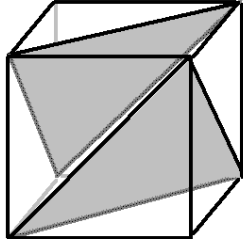(1 0 0) for a simple cubic crystal.
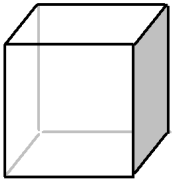
(100)

The above figure represent (1 0 0) plane. The plane is indicated in the following way.

The intercepts and miller indices are reciprocals to each other.

If intercepts of a plane are $(1 \infty \infty)$ then the miller indices are given byb (1 0 0).

(110) $(\bar{1}11)$

Similarly the above figures representing the (1 1 0) and (1 1 1) planes respectively.

Therefore (1 1 1) plane is represented by ABC. The intercepts of the plane are (1 1 1).

9. What is the coordination number ? Give coordination number for SC< BCC< FCC ?. (or)

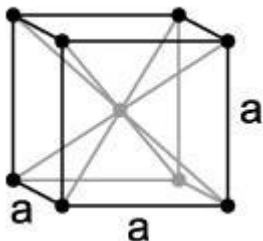**Define coordination number and packing factor of a crystal.**

Sol.   The coordination number is defined as the number of nearest neighbours around any lattice point in the crystal lattic.
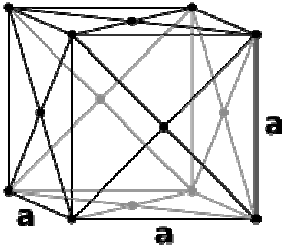
i). Simple Cubic Lattic:
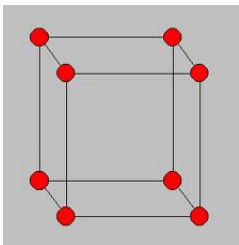
Each atom is surrounded by 6 nearest atoms, so that its coordination number is 6.

ii). Body – Centered Cubic lattice:

The atom at the body center is surrounded by 8 nearest atom. So its coordination number is 8.

iii). Face – Centered Cubic Lattice:

The atom at the face center is surrounded by 12 nearest atoms , so its coordination number is 12.

**10. What is packing fraction ? Find the packing fraction for SC, FCC, BCC? (or)**

Consider a body centered cubic lattice of identical atoms having radius R. Compute i). The number of atoms per unit cell ii). The coordination number and iii) The packing fraction.

Ans. Packing fraction:

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

PF = Volume of the unit cell / Total volume of the unit cell

i). Simple Cube:
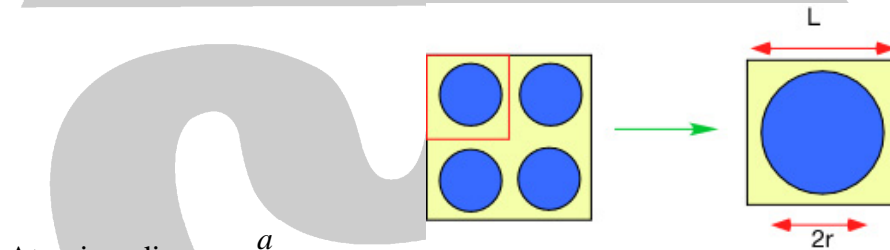
Atomic radius, r = $\dfrac{a}{2}$

Volume of unit cell $= a^3$

Volume of the one atom $= \dfrac{4}{3}\Pi r^3$

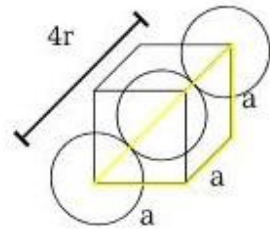$$= \dfrac{4}{3}\Pi \left(\dfrac{a}{2}\right)^3$$

$$= \dfrac{1}{6}\Pi a^3$$

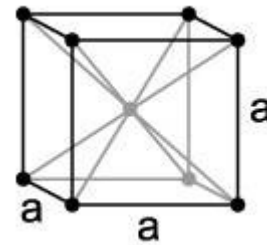$$= \dfrac{\dfrac{1}{6}\Pi a^3}{a^3}$$

$$= \dfrac{1}{6}\Pi$$

$$= 0.52$$

Ex: Polonium

ii) Body- Centred Cubic Lattice:

Body Centered Cube
Atomic arrangement along a body diagonal of a unit cell

Total number of lattice points in any

One cell= $\left(\frac{1}{8} \times 8\right)+1=2$

No of atoms in unit cell=2

Atomic radius r = $\frac{\sqrt{3}}{4} \times a$

Volume of one atom = $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3$

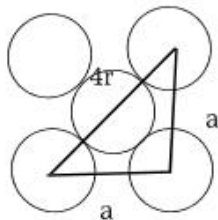= $\frac{\pi a^3 \sqrt{3}}{16}$

P.F =$2 \times \frac{\pi a^3 \sqrt{3}}{16a^3}$

= $\frac{\sqrt{3}}{8}$ = 0.68

Ex: - Na, Fe, etc.

iii) Face Centered Cubic Lattice:

Face Centered Cube
Atomic arrangement on a face of a unit cell

Total no of lattices points belonging to any one cell is $\left(\frac{1}{8}\times 8\right)+\left(\frac{1}{2}\times 6\right)=4$

∴. Numbers of atoms in unit cell = 4

Atomic radius, $r = \dfrac{a}{2\sqrt{2}}$

Volume of 4 atoms $= 4 \times \dfrac{4}{3}\pi \left(\dfrac{a}{2\sqrt{2}}\right)^{3}$

$= \dfrac{\pi a^{3}}{3\sqrt{2}}$

$PF = \dfrac{\dfrac{\pi a^{3}}{3\sqrt{2}}}{2a^{3}} = \dfrac{\pi}{3\sqrt{2}}$

$= 0.74$

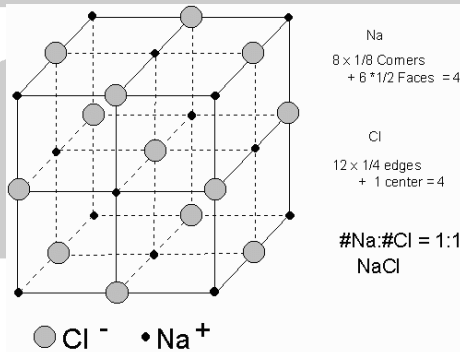Thus the PF of FCC is the highest.

Ex: - Cu, Al, Ag, etc.

11. Describe the structure of NaCl, CsCl, Zincblend and Diamond . (or)

**Explain the bonding in   a) NaCl   b) CsCl   c) Diamond   d) ZnS.**

Sol.

a) **NaCl structure :**

The NaCl crystal is a system of Na^{+} and Cl^{-} ions arranged alternatively in a cubic patterns in space so that the electrostatic attraction between the nearest neighbors is maximum. A cell has 8 corners and 6 faces, so the total number of lattices points in any cell is $\left(\dfrac{1}{8} \times 8\right)+\left(\dfrac{1}{2} \times 6\right) = 4$ ions. Na^{+} Ion has 6 Cl^{-}ion as nearest neighbors and similarly each Cl^{-} ion has 6 Na^{+}ion. Hence the coordination number is 6

b) **CsCl structure**
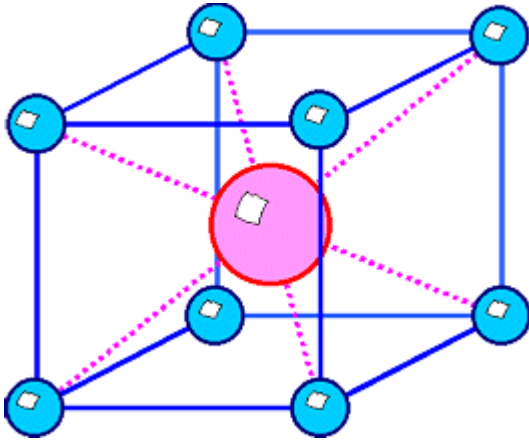
Cesium chloride is considered as the combination of two simple cubic sub-lattices one of Cs^+ ions and another of Cl^- ions. There is one molecule per primitive cell having ions at the corners and the body center positions. The coordination number of CsCl is 8.

c)Diamond structures:

Diamond exhibits both cubic and hexagonal type structures. The diamond lattice is composed of two interleaved f.c.c. sub-lattices, one of which is shifted relative to the other by one-fourth of a body diagonal. The length of each bond is 1.53A°. The coordination number of diamond crystal is 4. The number of atoms per unit cell is 8.Silicon, Germanium and gray tin crystalline in the diamond structure.
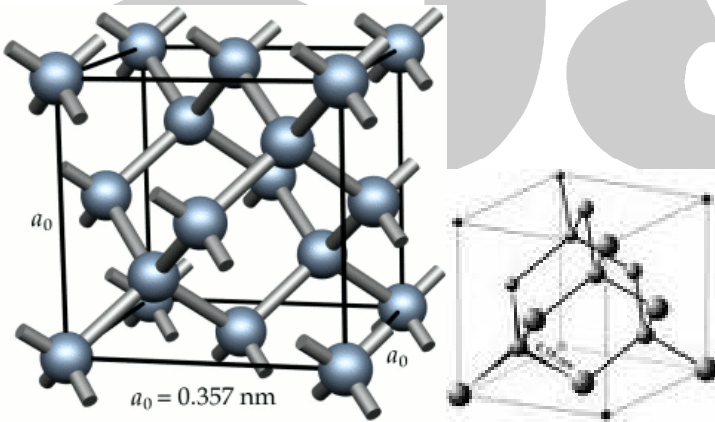
d) Zinc Blend Structure:

The zinc blend structure is similar to the dc structure except that the two penetrating FCC structure are of the different atoms and displaced from each other by one-quarter of the body diagonal. The conventional patterns of this structure are a cube.

ZnS
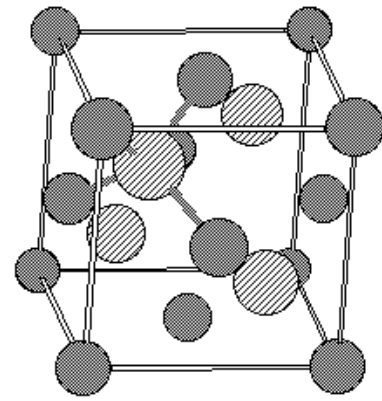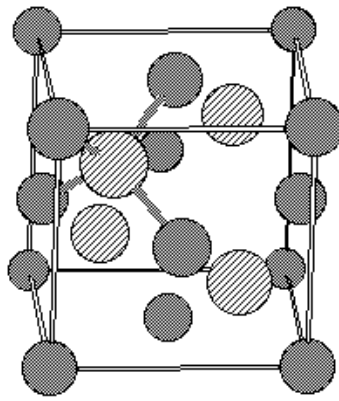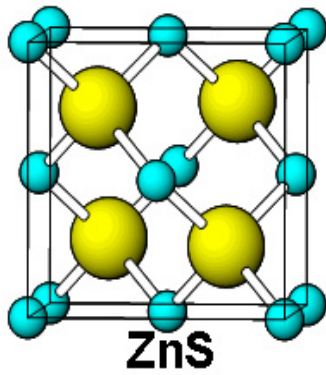
12. a) Define the terms : 1) Atomic   2) Co-ordination numbers

3) Effective number of atoms   4) Atomic packing factor

b) Show that the atomic packing fraction of HCP unit cell is 74%.

Ans. 1) **Atomic radius:** Half of the distance between two neighbouring atom called atomic radius

2) **Co-ordination number:** the number of nearest neighbouring atoms equidistance is called

co-ordination number.

3) **Effective number atoms**: It is the sum of the atoms Of effective contribution of all atoms to the **unit cell**

4) **Atomic Packing Factor (APF):** The fractional Volume occupied by the atom in the unit cell is

Called APF

$$APF = \frac{Effective \ number \ of \ atoms \times volume \ of \ atoms}{Volume \ of \ unit \ cell}$$

It is expressed in terms of percentage(%)

$$Atomic \ Packing \ Fraction = \frac{Number \ of \ atoms \ in \ unit \ cell \times Volume \ of \ atom}{Volume \ of \ unit \ cell}$$

For HCP

(1)Number of atoms:6
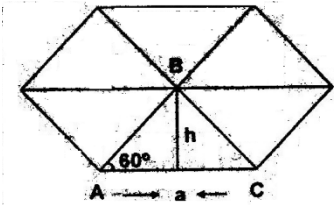
(2) a = 2r

(3) volume of unit cell = V

$$\therefore \ APF = \frac{6 \times \frac{4}{3}\pi r^3}{V}$$

Volume of HCP:

V=area of Hexagon × height

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A→a←c
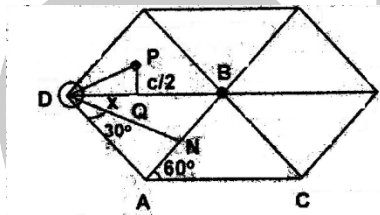
1) *Area of Hexagon:*

$= 6 \times$ Area of (ABC)

$= 6 \times \frac{1}{2} a \times a \times \sin 60°; \quad \left(\frac{h}{a} = \sin 60°\right)$

Area$= \frac{3\sqrt{3}}{2} a^2$

2) **Height of Hexagon:** In HCP there are three body atoms lie in horizontal planes at a height of c/2 from the ortho-centers of equilateral triangles

From figures $DP^2 = QP^2 + DQ^2$

$= \left(\frac{C}{2}\right)^2 + x^2$

From geometry of HCP, we can write

$x = \frac{2}{3} DN = \frac{2}{3} \times \frac{\sqrt{3}a}{2} \qquad \left(DN = \frac{\sqrt{3}}{2} a\right)$

$x = \frac{a}{\sqrt{3}}$

$\therefore DP^2 = \frac{C^2}{4} + \frac{a^2}{3}$

$a^2 - \frac{a^2}{3} = \frac{c^2}{4} \qquad\qquad (DP = a = 2r)$

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$$\frac{2a^2}{3} = \frac{c^2}{4} \Rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} \times a$$

V = Area X height

$$\Rightarrow V = \frac{3\sqrt{3}}{2}a^2 \times c$$

$$= \frac{3\sqrt{3}}{2}a^2 \times \sqrt{\frac{8}{3}} \times a$$

$$\therefore V = 3\sqrt{2}a^3$$

Now ARF $= \dfrac{6 \times \frac{4}{3}\pi r^3}{3\sqrt{2}a^3}$

ARF $= \dfrac{6 \times \frac{4}{3}\pi r^3}{3\sqrt{2}(2r)^3}$ ('.' a=2r)

$\therefore$ APF $= \dfrac{\pi}{3\sqrt{2}} = 0.74 = 74\%$

13. what are miller indices ?how are they obtained?

Ans. Miller indices are three integers designated for a set of equidistant parallel plates.

Miller evolved a method to designate smallest integers denoted by (h k l) for parallel planes.

Method to obtain Miller indices:

1. Find the intercepts of the plane pa, qb, cr

2. Divide by primitive vectors $\dfrac{a}{p}, \dfrac{b}{q}, \dfrac{r}{c}$.

3. Take the reciprocals $\dfrac{a}{p}, \dfrac{b}{q}, \dfrac{r}{c}$.

4. Multiply by LCM to get smallest whole numbers.

5. These are the Miller Indices (h, k, l)

Example: if the intercepts of a plane are 1,2,3 on the x, y and z axis respectively.

Reciprocal are 1, $\dfrac{\frac{1}{2,1}}{3}$.

Multiplying by LCM (6)

(h k l) = (6 3 2)

14. a) Define lattice parameters and What is a primitive cell and how does it differ from unit cell?

Ans: **Lattice parameters**: the lattices parameters completely define the size of the unit cell. There are six lattices parameters. Three axial lengths a, b, c and three inter facial angles , α, β, γ .

The parameters that define the dimensions of an unit cell are called its primitives. The unit cell with sides a, b, and c and with lattice points only at the corners is called a primitives cell. Simple cubic crystal has eight lattice points at the eight corners and hence is a primitive's cell. Unit cell is the smallest volume that repeats itself in a solid but may have lattice points at the body centre and face centers in addition to corners.

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