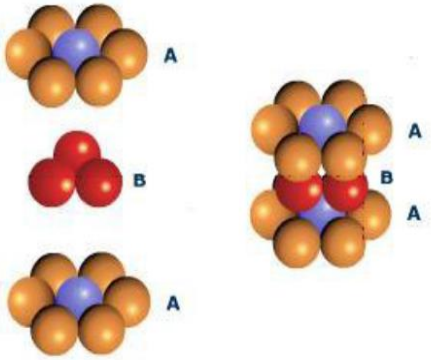
UNIT -IV CRYSTAL PHYSICS

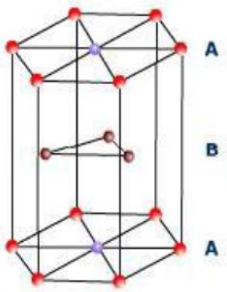
TOPIC – VI CN AND PF FOR HCP STRUCTURE

1.15 HEXAGONAL CLOSELY PACKED STRUCTURE (HCP)

The unit cell of HCP system has 12 corner atoms, one at each and every corner of the hexagon with two base centered atoms, one at the top face of the hexagon and another at the bottom face of the hexagon as shown in figure 1.25. In addition to the corner and base atoms, there are three symmetrically arranged atoms in between the top and bottom face of the hexagon. Three additional atoms are located between top and bottom planes, which are illustrated in hard sphere model as shown in figure 1.25(a).



1.25 (a) Hard sphere model



1.25 (b) Lattice point representation

Number of atoms per unit cell:

The unit of HCP structure is shown in fig 1.26. In HCP, there are three types of atoms viz., (i) corner atoms (ii) base center atoms and (iii) middle layer atoms.

(i) Number of corner atoms per unit cell:

Each corner atom is shared by six surrounding hexagon unit cell. Similarly we have 12 corner atoms in a unit cell.

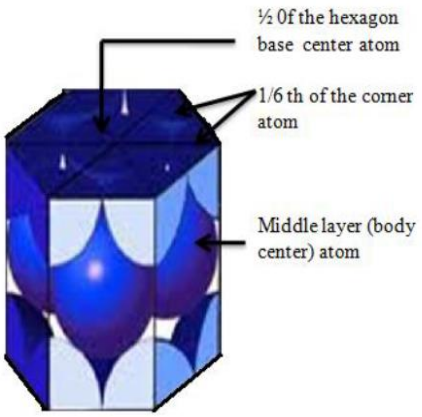


Fig 1.26

Therefore,

The number of corner atoms per unit cell

$$= \frac{1}{6} \times 12 = 2 \text{ atoms.}$$

(ii) Number of base centered atoms per unit cell:

Each base atom is shared by two unit cells. Similarly we have two base centered atoms in a unit cell. Therefore, the number of base centered atoms per unit cell $= \frac{1}{2} \times 2 = 1$ atom.

(iii) Number of middle layer atoms per unit cell:

The 3 atoms situated at the middle layer, within the body of the unit cell are fully contributing to that of the unit cell alone i.e., they are not shared by any other unit cells.

Therefore,

The number of middle layer atoms per unit cell = 3

Therefore,

$$\begin{pmatrix}\text{The total number}\\ \text{of atoms per unit cell}\\ \text{in HCP structure}\end{pmatrix} = \begin{pmatrix}\text{Number of}\\ \text{corner atoms}\\ \text{per unit cell}\end{pmatrix} + \begin{pmatrix}\text{Number of}\\ \text{base atoms}\\ \text{per unit cell}\end{pmatrix} + \begin{pmatrix}\text{Number of}\\ \text{middle atoms}\\ \text{per unit cell}\end{pmatrix}$$

$$= \quad 2 \quad + \quad 1 \quad + \quad 3$$

$$= \quad 6 \text{ atoms}$$

Co-ordination number:

The HCP structure consists of three layer viz., top layer, bottom layer and middle layer as shown in fig 1.27. In the top and bottom layer, the base centered atom is surrounded by six corner atoms.

In the middle layer we have 3 atoms stacked inside the unit cell as shown in fig 1.27.Let us consider two unit cells as shown in fig 1.23. Let 'X' be the reference atom taken in the bottom layer of unit cell-1.

This atom has 6 neighbouring atom in its own plane. Further at a distance of c/2 it has 3 atoms in the middle layer of unit cell-1 and 3 more atoms in the middle layer of unit cell-2. Therefore, the total number of neighbouring atoms are 6 + 3 + 3 = 12.

Thus, the co-ordination number is 12.

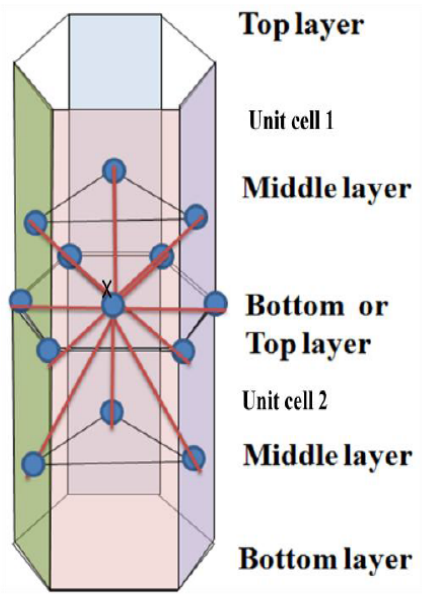


Fig 1.27

Atomic radius:

To find the atomic radius of the HCP structure, consider any two corner atoms. It has to be noted that, each and every corner atoms touches each other, therefore they are the nearest neighbours.

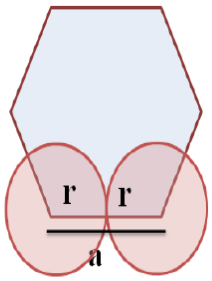


Fig 1.28

From fig 1.28, we can write, a = 2r

i.e., the atomic radius is r = $\frac{a}{2}$

Relation between 'c' and 'a' [c/a ratio]:

To calculate c/a ratio, the triangle in the bottom layer of the HCP unit cell. Let 'c' be the height of the unit cell and 'a' be the distance between two nearest neighboring atoms.Consider the triangle AOC which is shown in the figure. Here, A, O and C are the atoms of the bottom layer and y is the next layer atom which lies exactly above this plane at a distance c/2.

From triangle ABC, $\cos 30^\circ = \frac{AB}{AC}$

$$AB = AC \cos 30^\circ$$

From the fig 1.29, AC = a

Substituting AC and cos 30° values, we get

$$AB = a\frac{\sqrt{3}}{2}$$

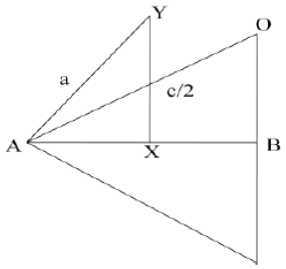


Fig 1.29(a)

But, from the fig 1.29 (b), AX = (2/3) AB

Substituting for AB, we get

$$AX = \frac{2}{3} \times \frac{a\sqrt{3}}{2} = \frac{a\sqrt{3}}{3} = \frac{a\sqrt{3}}{\sqrt{3}\sqrt{3}} = \frac{a}{\sqrt{3}}$$

In the triangle AXY, $AC^2 = AX^2 + XY^2$

Substituting for AX and AC & XY from fig 1.25(a), we get

$$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = (a^2/3) + (c^2/4)$$

$$\frac{c^2}{4} = a^2 - \frac{a^2}{3}$$

$$\frac{c^2}{4} = \frac{3a^2 - a^2}{3} = \frac{2a^2}{3}$$

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

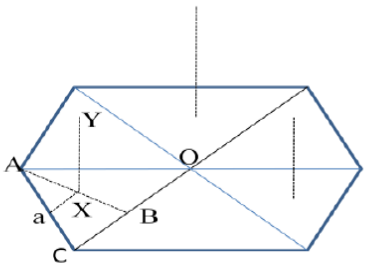


Fig 1.29(b)

Taking square root on both sides,

$$\frac{c}{a} = 1.633$$

Atomic packing factor:

To find Volume of all atoms in a unit cell (v):

Number of atoms per unit cell = 6

Volume of 6 atoms, $v = 6\times\frac{4}{3}\pi r^3 = \frac{24}{3}\pi r^3 = 8\pi r^3$

Where r is the atomic radius

Atomic radius, $r = \frac{a}{2}$

Substituting 'r' values, we get

Volume of 6 atoms (v) $= 8\pi(a/2)^3 = 8\pi a^3/8$

$v = \pi a^3$

Volume of the unit cell (V):

$$\text{Volume of a HCP unit cell} = \begin{pmatrix}\text{Area of}\\ \text{hexagonal face}\end{pmatrix} \times \begin{pmatrix}\text{height of the}\\ \text{hexagon}\end{pmatrix}$$

To find area of hexagon:

Area of the base = 6 × area of triangle ABC

Area of triangle ABC $= \frac{1}{2} \times AB \times BO$

Substituting for BO = a and AB = $a\frac{\sqrt{3}}{2}$,

$$\text{Area of triangle ABC} = \frac{1}{2} \times a \times a\frac{\sqrt{3}}{2}$$

$$= \frac{\sqrt{3}a^2}{4}$$

$$\therefore \text{Area of the base} = 6 \times \frac{\sqrt{3}a^2}{4} = \frac{3\sqrt{3}a^2}{2}$$

Therefore, Volume of a HCP unit cell $= \frac{3\sqrt{3a}^2}{2} \times c$

We know that,

$$\text{Packing factor} = \frac{v}{V}$$

Substituting the values of v and V in above equation we get,

$$PF = \frac{\pi a^3}{\frac{3\sqrt{3a}^2}{2}\times c}$$

$$PF = \frac{\pi}{3\sqrt{3}} \times \frac{a}{c}$$

$$= \frac{\pi}{3\sqrt{3}} \times \frac{1}{1.633}$$

$$= 0.7402$$

$$PF = 74\ \%$$

Therefore, we can say that 74% volume of the unit cell of HCP is occupied by atoms and remaining 26% volume is vacant which implies that HCP structure can be termed as tightly or closely packed structure.

Examples: Zinc, Titanium, and cobalt