UNIT I CRYSTAL PHYSICS

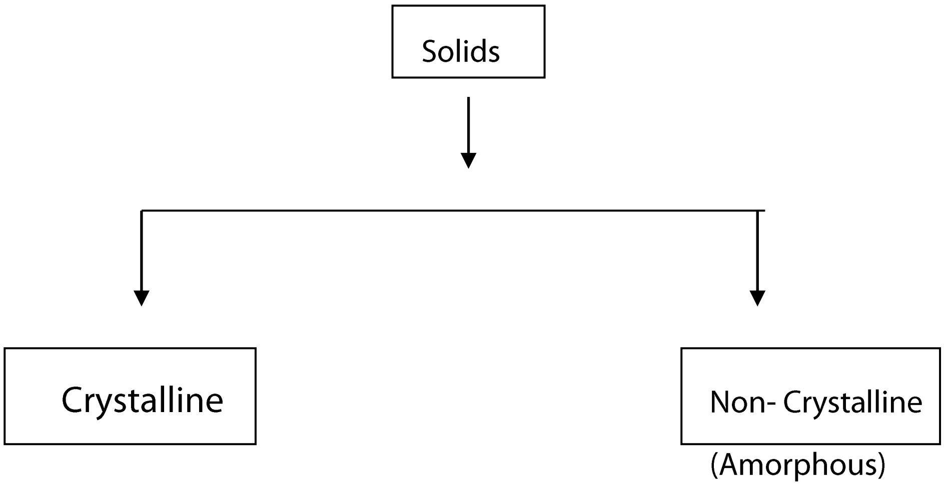
OBJECTIVES

1) To develop the knowledge of Crystal structure and their properties.
2) To explain the fundamental terms of Crystallography.
3) To discuss the various crystal systems according to Bravais lattices.
4) To discuss Miller Indices in crystal plane and their applications
5) To discuss the importance of packing factor in crystal structure
6) To study the different types of crystal imperfections
7) To study the importance of crystal imperfections in crystal structure.
8) To study the crystal growth techniques through melt and solutions

1.1 Crystallography

Solids are of classified into two categories based on the arrangement of atoms or molecules.

- Crystalline Solids
- Non-Crystalline Solids or Amorphous Solids



A substance is said to be crystalline when the arrangement of the units of the matter inside it is regular or periodic or in an orderly fashion.

The crystalline solids may be classified into two types based on the arrangements of the crystal in the structure.

- **Single Crystal:** the entire solid consists of only one crystal.
- **Poly Crystal:** It has an aggregate of many small crystals that are separated by well-defined boundaries.

In amorphous solids, there is no order in the arrangement of their constituent particles.

S.No	Crystalline Material	Non- Crystalline Material
1	They have a definite and regular geometrical shapes which extend	They do not have definite geometrical shape.

	throughout the crystal	
2	They are anisotropic.	They are isotropic.
3	They have sharp melting point.	They do not have sharp melting point.
4	They are most stable.	They are less stable.
5	Examples: Diamond, NaCl, KCl, Copper, Iron, etc.	Examples: Glasses, Plastics, Rubber etc.

Crystal is a regular polyhedral form bounded by smooth surfaces, which is formed by chemical compound under the action of its interatomic forces, when passing from the state of the liquid (or) gas to that of a solid, under suitable conditions.

The phase change from liquid (or) gas to solid is called Crystallization.

The crystal structure gives the arrangement of the atoms with in a crystal.

1.1.1 Fundamental Crystallographic terms

L***attice*** is defined as an array of points which are imaginarily kept to represent the position of atoms in the crystal such that every lattice point has got the same environment as that of the other and hence one lattice point cannot be distinguished from the other lattice point.

Space Lattice or Crystal Lattice is a three dimensional collection of points in space. The environment about any particular point is in everyway the same.

The regular pattern of points which describe the three dimensional arrangement of particles in a crystal structure is called the Crystal Lattice or Space lattice.

Basis is formed by associating with every lattice point a unit of assembly of atoms or molecules identical in composition. This unit assembly is called **Basis.**

The Crystal Structure is formed by the addition of a basis to every lattice point.

Space Lattice + Basis = Crystal Structure

Unit Cell is defined as the smallest geometric figure or pattern, the repetition of which gives the actual crystal structure. This is also defined as fundamental elementary pattern of minimum of atoms or molecules or groups of molecules, which represents total characteristic of the material or the crystal.

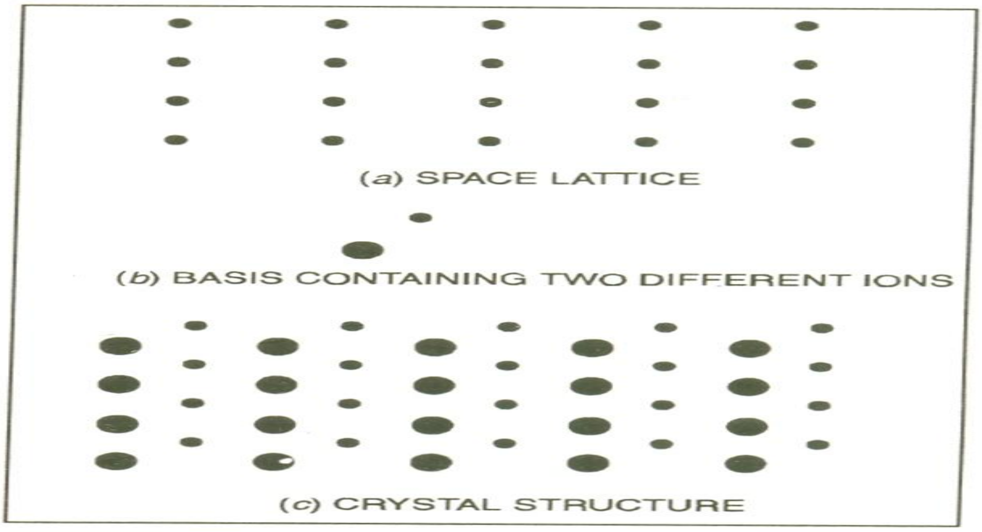


Figure1.1.1 Unit Cell

1.1.2 Lattice Parameters or Unit Cell Parameters

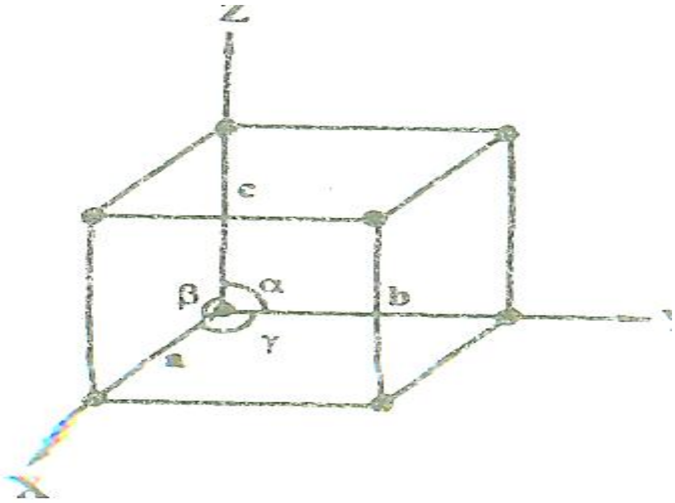


Figure1.1.2

The lines drawn parallel to the lines of intersection of any three faces of the Unit Cell which do not lie in the same plane are called ***Crystallographic Axes.***

The intercepts a, b, c (i.e., the distance between the two lattice points) are nothing but the edges of the unit cell, which defines the dimensions of a unit cell. These intercepts are known as its **primitives or characteristic intercepts** on the axes.

These three quantities a, b, c is also called the fundamental translational vectors or axial lengths. The angles (a, b), (b, c) and (c, a) are denoted by γ, α, β respectively. These three angles (α, β, γ) are called ***Interfacial angle.***

Both the intercepts (a, b, c) and the interfacial angle (α,β,γ) constitutes the lattice parameters or cell parameters of the unit cell.

The actual size of the unit cell can be determined by knowing the values of intercepts and interfacial angles.

Primitive Cells.

A ***Primitive Cell*** is the simplest type of the unit cell, which contains only one lattice point per unit cell. (Contains lattice points at its corner only)

Example: Simple Cubic

Non- Primitive Cell

A ***Non-Primitive Cell*** is one, which contains more than one lattice point per unit cell.

Example: BCC and FCC contain more than one unit cell.

If the number of lattice points per unit cell is two (BCC), three and four (FCC), then the unit cell is called ***doubly primitive, triply primitive and Quadruple primitive*** respectively.

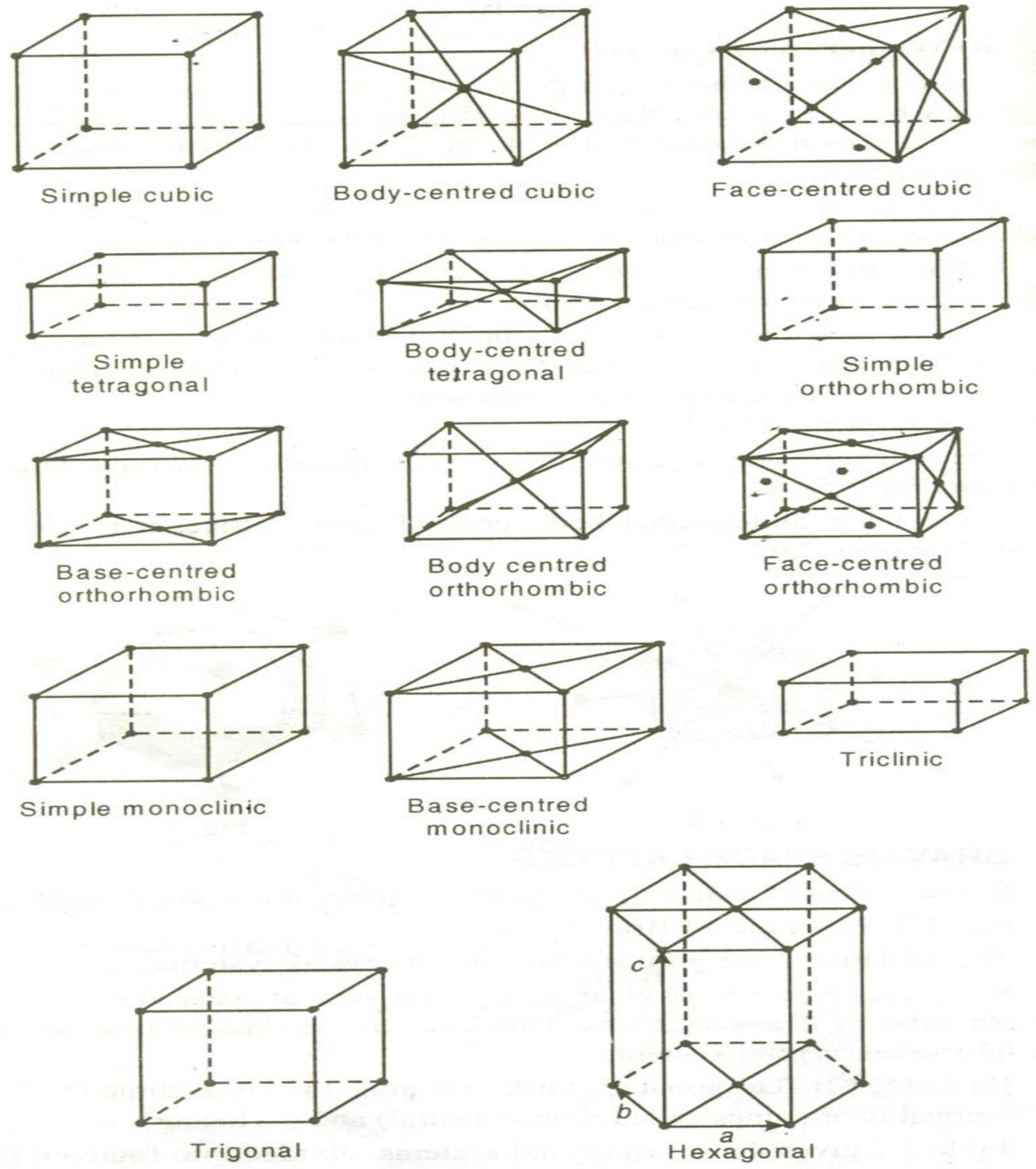
1.1.3 Bravais Space Lattice

Bravais showed that only 14 types of space lattice are possible.

Figure shows the 14 Bravais lattices.

The 14 lattices are grouped into seven crystal systems.

From the figure it is clear that seven sets of axes are sufficient to construct the 14 Bravais lattices. This leads to classification of all crystals into seven crystal systems.



1) Cubic 2) Tetragonal 3) Ortho-Rhombic 4) Monoclinic 5) Triclinic 6) Trigonal (Sometimes called Rhombohedral) and 7) Hexagonal. Table 3.3.1 gives the seven crystal systems, divided into fourteen Bravais Lattices. Note that a simple lattice has points only at the corners, a body – centered lattice has only one additional point at the center of the cell, and a face-centered lattice has six additional points, one on each face.

Table 1.1.3

The Seven Crystal Systems divided into Fourteen Bravais Lattices

System	Bravais Lattice	Unit Cell Characteristics	Characteristic Symmetry elements	Examples
Cubic	Simple Body-Centered Face Centered	$a = b = c$ $\alpha = \beta = \gamma = 90^o$	Four 3 fold rotation axes (along cube diagonal)	NaCl, CaF_2, $NaClO_3$
Tetragonal	Simple Body-Centered	$a = b \neq c$ $\alpha = \beta = \gamma = 90^o$	One 4-fold rotation axis	$NiSO_4$, SnO_2, Indium, White, Tin
Orthorhombic	Simple Base Centered Body-Centered Face Centered	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$	Three mutually orthogonal 2 – fold rotation axes.	KNO_3, $BaSO_4$,$MgSO_4$, Sulphur, Topaz
Monoclinic	Simple Base Centered	$a \neq b \neq c$ $\alpha = \beta = 90^o \neq \gamma$	One 2- fold rotation axis	Na_2SO_4, $FeSO_4$, NO_2SO_3
Triclinic	Simple	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^o$	None	$CuSO_4$, $K_2Cr_2O_7$
Trigonal (Rhombohedral)	Simple	$a = b = c$ $\alpha = \beta = \gamma \neq 90^o$	One – fold rotation axis	$CaSO_4$, Bi, Sb, Calcite
Hexagonal	Simple	$a = b \neq c$ $\alpha = \beta = 90^o$ $\gamma = 120^o$	One – fold rotation axis	Tourmaline, Quartz.

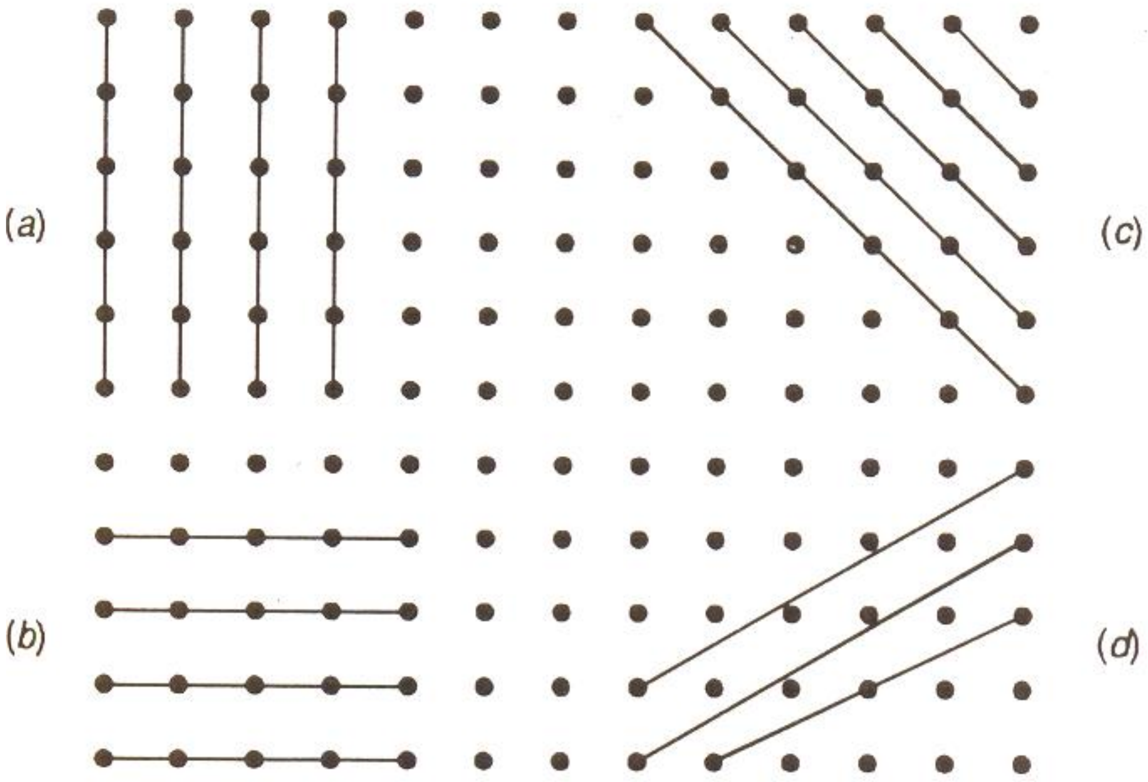
1.1.4 Lattice Planes

A crystal lattice may be considered as an aggregate of a set of parallel equi-distant planes passing through the lattice points. These are called ***Lattice Planes***.

A crystal can be easily split or cleaved along these lattice planes particularly the planes of high density of lattice points. Hence lattice planes are also called Cleavage Points.

For a given lattice, the lattice planes can be chosen in a different number of ways, for example (a), (b), (c), and (d) as shown in the **figure 1.1.4**

The problem is that how to designate a plane in the crystal. Miller evolved a method to designate a plane in a crystal by three numbers (h, k, l) known as ***Miller indices.***



Lattice Planes fig 1.1.4

1.1.5Miller Indices

Miller introduced a system to designate a plane in a crystal. He introduced a set of three numbers to specify a plane in a crystal. This set of three numbers is known as Miller Indices of the concerned plane.

Procedure for finding Miller Indices.

- Determine the intercepts of the plane along the axes X, Y and Z in terms of the Lattice Constant a, b, c.
- Determine the reciprocals of these numbers.

- Find the least common denominator (LCD) and multiply each by this lcd. The result is written in the form (hkl) and is called the Miller Indices of the plane.

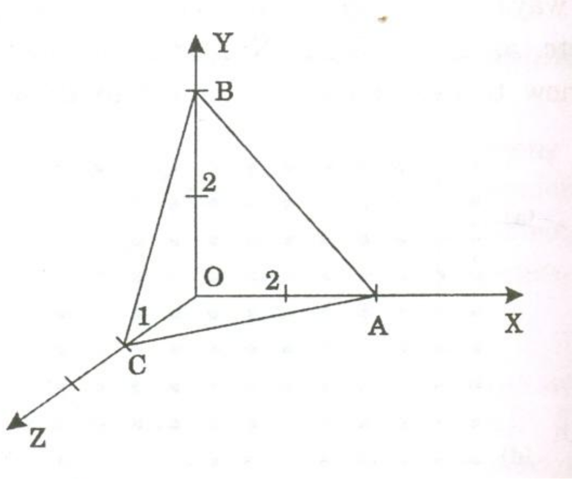


Figure 1.1.5

Example.

Let the plane have intercepts 4,1 and 2 on the three axes. The reciprocals are ¼,1 and ½. Multiplying each by 4, we get 1, 4 and 2. Hence (142) are the Miller Indices of the plane.

Plane ABC (**figure 1.1.5)** has intercepts of 2 axial units on X- axis, 2 axial units on Y-axis and 1 axial unit on Z-axis.

The reciprocals are ½, ½, and 1. The LCM is 2.

Multiplying each by 2, we get 1, 1, 2. Hence the Miller Indices of the plane are (112)

1.1.5.1 Important Features of Miller Indices.

- When a plane is parallel to any axis, the intercept of the plane on that axis is infinity. Hence the Miller Indices for that axis is zero.
- If a plane cuts an axis on the negative side of the origin, corresponding index is negative.
- The indices (hkl) do not define a particular plane but a set of parallel planes. Thus the planes whose intercepts are 1, 1, 1; 2, 2; -3, -3,-3 etc. are all represented by the same set of Miller Indices.

1.1.5.1 (a) Points to ponder

- The Miller Indices should be enclosed only in this bracket.

- There should not be any commas in between the numbers.
- If the Miller Indices is say (2 6 3) means it should be read as two six three, and not as two hundred and sixty three.
- The direction of plane can be represented by enclosing the Miller Indices in a square bracket. For example [2 6 3]
- To represent the family of planes we can use this bracket i.e.→
- Putting a bar over the numbers can represent negative Miller Indices For an example (2 6 3) represents the plane with intercepts on negative axis, positive Y-axis and negative Z-axis.

1.1.6 Separation between Lattice Planes in a cubic Crystal

Consider a cubic crystal with cube edge a. let (h, k, l) be the Miller Indices of the plane ABC.

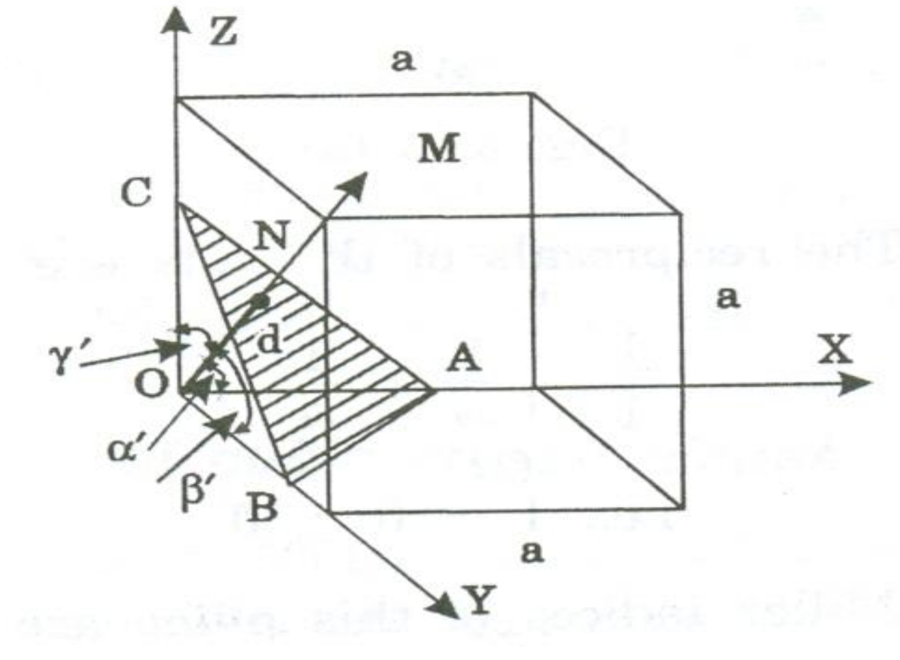


Fig: 1.1.6 Separation between Lattice Planes in a cubic Crystal

Let ON = d be a normal to the plane passing through the Origin O. ON makes angles α', β', γ' with x, y and Z-axes respectively. The direction cosines, $\cos\alpha'$, $\cos\beta'$ and $\cos\gamma'$ are written as

$$\cos\alpha = \frac{ON}{OA} = \frac{d_1}{a/h} = \frac{d_1 h}{a}$$

$$\cos\beta = \frac{ON}{OB} = \frac{d_1}{a/k} = \frac{d_1 k}{a}$$

$$\cos\gamma = \frac{ON}{OC} = \frac{d_1}{a/l} = \frac{d_1 l}{a}$$

$$\therefore \cos\alpha : \cos\beta : \cos\gamma = \frac{d_1 h}{a} : \frac{d_1 k}{a} : \frac{d_1 l}{a}$$

From the law of directions of cosines we can write $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

$$\therefore \left(\frac{d_1 h}{a}\right)^2 + \left(\frac{d_1 k}{a}\right)^2 + \left(\frac{d_1 l}{a}\right)^2 = 1$$

Or $$\frac{d_1}{a^2}\left(h^2 + k^2 + l^2\right) = 1$$

Therefore, $d_1^2 = \frac{a^2}{h^2 + k^2 + l^2}$

$$d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Let the next plane parallel to ABC be at a distance OM from the Origin. Then its intercepts are $OA' : OB' : OC' = \frac{2a}{h} : \frac{2a}{k} : \frac{2a}{l}$

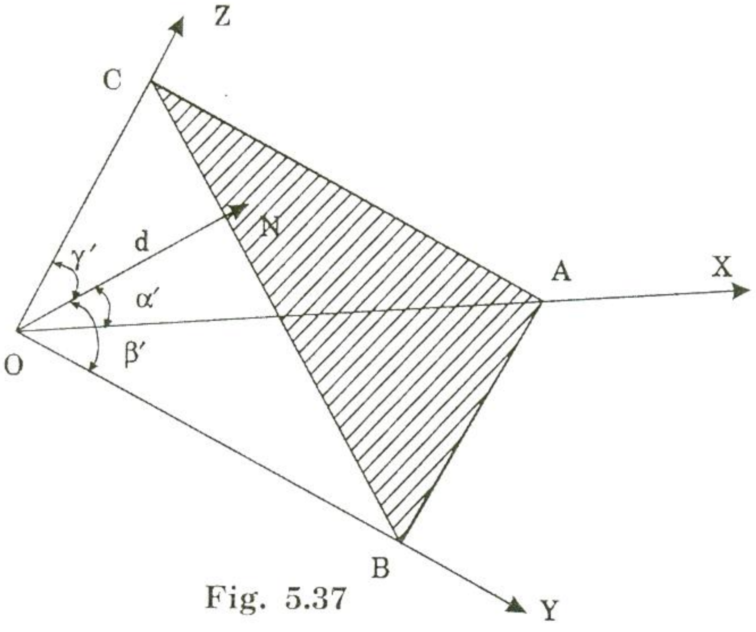


Fig. 5.37

$$\cos\alpha' = \frac{OM}{OA'} = \frac{d_2}{2a/h} = \frac{d_2 h}{2a}$$

$$\cos\beta' = \frac{OM}{OB} = \frac{d_2}{2a/k} = \frac{d_2 k}{2a}$$

$$\cos\gamma' = \frac{OM}{OC} = \frac{d_2}{2a/l} = \frac{d_2 l}{2a}$$

$$\therefore \cos\alpha' : \cos\beta' : \cos\gamma' = \frac{d_2 h}{2a} : \frac{d_2 k}{2a} : \frac{d_2 l}{2a}$$

$$\therefore \left(\frac{d_2 h}{2a}\right)^2 + \left(\frac{d_2 k}{2a}\right)^2 + \left(\frac{d_2 l}{2a}\right)^2 = 1$$

$$\frac{d_2^2 h^2}{4a^2} + \frac{d_2^2 k^2}{4a^2} + \frac{d_2^2 l^2}{4a^2} = 1$$

$$\frac{d_2^2}{4a^2}\left(h^2 + k^2 + l^2\right) = 1$$

$$d_2^2 = \frac{4a^2}{\left(h^2 + k^2 + l^2\right)}$$

$$d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}}$$

Interplanar distance d:

We know interplanar distance is the distance between two successive planes. since'd' is the distance between the two planes ABC and $A'B'C'$, we can write the interplanar distance 'd' as

$$d = d_2 - d_1$$

Interplanar distance

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

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

1.1.7 Characteristics of the Unit Cell

In this section, we discuss some of the important parameters, which are used to describe the crystal structure of the material. A unit cell is characterized by the following parameters.

- Number of atoms per unit cell.
- Coordination number
- Atomic Radius
- Packing factor (or) packing density

No of atoms per unit cell:

The number of atoms possessed by a unit cell is known as number of atoms per unit cell. The distribution of atoms is different for different lattice structure. This can be determined if the arrangement of atoms inside the unit cell is known.

Coordination Number

The coordination number of an atom in a crystal is the number of nearest atoms directly surrounding with that atom. If the coordination number is high, then the structure will be more closely packed. It signifies the tightness of packing of atoms in the crystal.

Atomic radius

Atomic radius is defined as half of the distance between any two nearest neighboring atoms, which have direct contact with each other, in a crystal of a pure element. It is usually expressed in terms of cube edge 'a' (lattice parameter).

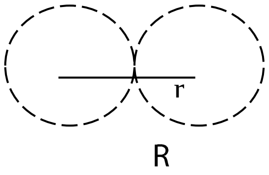


Figure 1.1.7.1

Packing Factor

The packing density is the ratio between the total volume occupied by the atoms or the molecules in an unit cell and the volume of the unit cell.

$$\text{i.e., Packing Density} = \frac{\text{Total Volume of the atoms in a Unit cell}}{\text{Volume of the Unit cell}}$$

$$= \frac{\text{No of the atoms present in Unit cell} \times \text{Volume of an atom}}{\text{Volume of the Unit cell}}$$

Note: Refer the below diagram to calculate coordination no

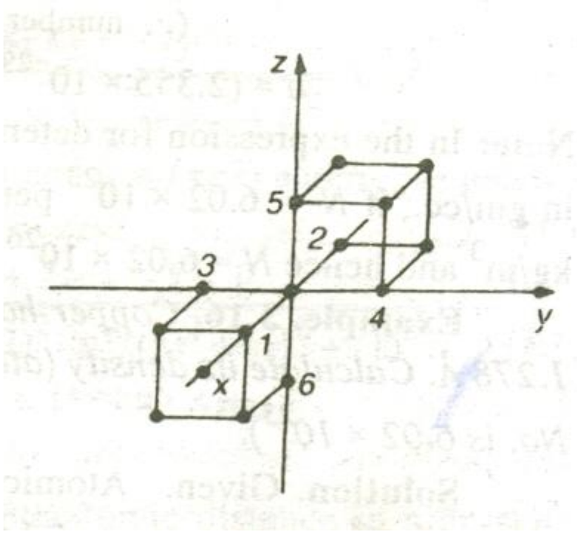
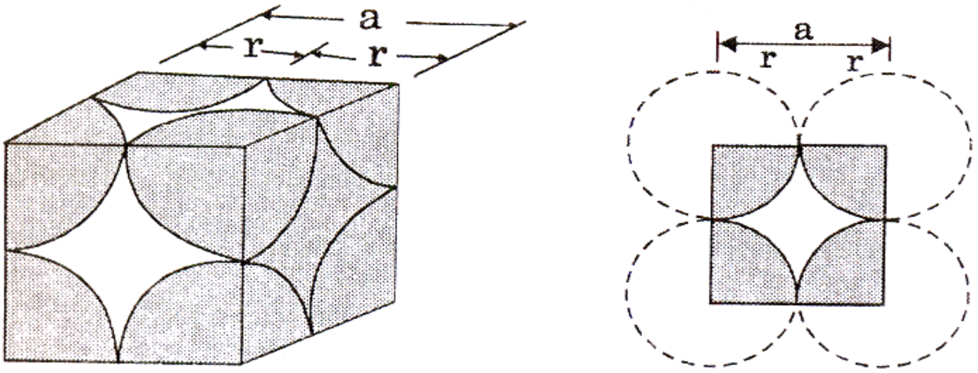


Figure 1.1.7.2



Calculation of Atomic Radius - SC

Figure 1.1.7.2(a)

A simple cubic (SC) unit cell consists of eight corner atoms as shown in the figure

(i) Number of atoms per unit cell

In actual crystal, each and every corner atoms is shared by eight adjacent unit cells. Therefore, each and every corner atoms contribute 1/8 of its part to one unit cell. Hence, the total number of atoms present in the unit cell is $\frac{1}{8}\times 8 = 1$ atom.

(ii) Coordination number

The coordination number of a simple cubic unit can be calculated as follows.

Let us consider any corner atom; there are four nearest neighbors in its own plane. There is another nearest neighbour in a plane, which lies just above this atom, and another just below this atom. Therefore, the total number of nearest neighbors is six and hence the coordination number is 6.

(iii) Atomic radius

For a simple cubic unit cell, the atomic radius is given by, $r = \frac{a}{2}$, where 'a' is the side of the unit cell and is equal to the distance between centers of the two nearest atoms.

(iv) Packing factor

Number of the atoms per unit cell = 1

Volume of one atom $v = \frac{4}{3}\pi r^3$

Where r is the atomic radius

Side of the unit cell, a =2r

$\because atomic\ radius\ r = \frac{a}{2}$

Total volume of the unit cell $V = a^3$

We know the packing factor = $\frac{v}{V}$

Substituting for v and V, we have

$$PF = \frac{\frac{4}{3}\pi r^3}{a^3}$$

Substituting a = 2r, we get

$$\frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\frac{4}{3}\pi r^3}{2^3 r^3} = \frac{\frac{4}{3}\pi r^3}{8\ r^3} = \frac{\pi}{6} = \frac{3.14}{6} = 0.5236$$

Thus 52% of the volume of the simple cubic unit cell is occupied by atoms and the remaining 48% of volume of the unit cell is Vacant.

Thus the packing density is* 52%.** Since the packing density is very low, ***SC has loosely packed structure.

1.1.7.4 Body centered cubic (BCC) Structure

In body centered cubic structure, the unit cell has one atom at each corner of the cube and one at body center of the cube. **Figure 3.8 shows** the arrangement of the atoms in a bcc cell.

(i) Number of atoms per unit cell

In a body centered crystal structure, the atoms touch along the diagonal of the body. Each and every corner atoms are shared by eight adjacent unit cells. Therefore, the total number of atoms contributed by the corner atoms is 1/8×8 = 1 atom.

One full atom at the center of the unit cell = 1 atom

Therefore, total number of atoms present in the bcc unit cell = 1+ 1 = 2 atoms.

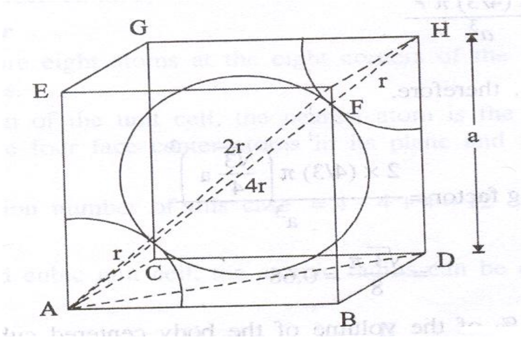
(ii) Coordination Number

The coordination number of the body centered cubic unit cell is calculated as follows.

Let us consider a body-centered atom. The nearest neighbour for a bcc atom is the corner atom. A body-centered atom is surrounded by 8 corner atoms. Therefore, the coordination number of a bcc unit cell is 8.

Atomic radius

For a body centered unit cell, the atomic radius can be calculated as follows from **figure** as follows. From figure, AH = 4r and DH = a



From the triangle AHD,

$AH^2 = AD^2 + DH^2 \longrightarrow$ (1)

From the triangle ABD,

$AD^2 = AB^2 + BD^2$

$AD^2 = a^2 + a^2 \longrightarrow$ (2)

Substituting (2) in (1)

$AH^2 = 2a^2 + a^2$

$AH^2 = 3a^2$

$(4r)^2 = 3a^2$

$16r^2 = 3a^2$

$$r^2 = \frac{3a^2}{16}$$

$$r = \frac{\sqrt{3}}{4}a$$

(iii) Packing Factor

The number of atoms present in a unit cell = 2 atoms

$$\text{Packing Factor} = \frac{\text{Number of atoms present per unit cell} \times \text{Volume of atom}}{\text{Volume of the Unit Cell}}$$

Number of atoms per unit cell = 2

Volume of 2 atoms $v = 2 \times \frac{4}{3}\pi r^3$

Side of the unit cell, $a = \frac{4r}{\sqrt{3}}$

$$\left(\because atomicradius, r = \frac{\sqrt{3}}{4}a\right)$$

Volume of the unit cell $V = a^3$

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

Substituting for v and V, we have

$$\text{PF} = \frac{2\times\frac{4}{3}\pi r^3}{a^3}$$

Substituting for a

$$PF = \frac{2\times\frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\frac{8}{3}\pi r^3}{\frac{4^3 r^3}{\left(\sqrt{3}\right)^3}} = \frac{\frac{8}{3}\pi r^3}{\frac{64r^3}{3\sqrt{3}}} = \frac{8}{3}\pi r^3 \times \frac{3\sqrt{3}}{64r^3} =$$

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

Therefore, we can say that 68% volume of the unit cell of BCC is occupied by atoms and remaining 32% volume is vacant.

Thus the Packing Density is 68%.

Since the packing density is greater than simple cubic, it has tightly packed structure, when compared to SC.

1.1.7.5 Face Centered Cubic

a face centered cubic cell consists of eight corner atoms and six face centered atoms. The arrangement of atoms in face centered cubic unit cell is as shown in **figure**

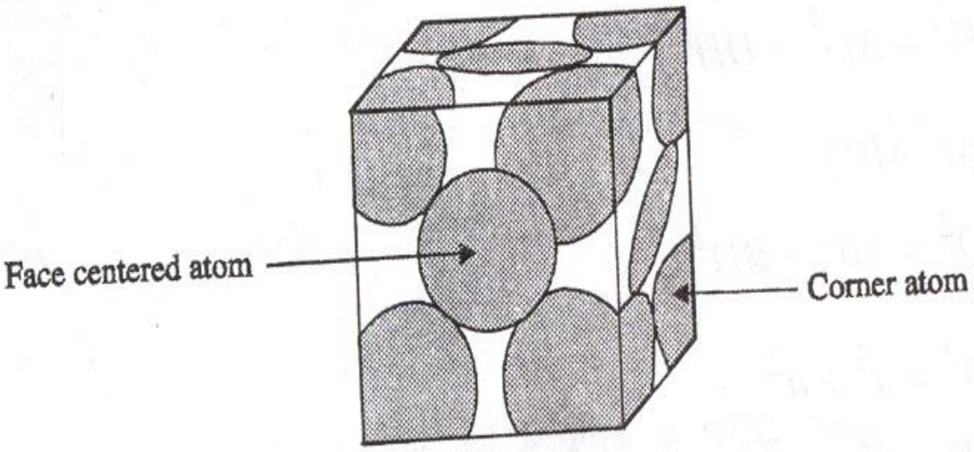


Figure1.1.7.5

(i) Number of atoms per unit cell

An FCC unit cell consists of eight corner atoms and each and every corner atoms is shared by eight adjacent unit cell. Therefore, each and every corner atom contributes 1/8 of its part to one unit cell. The total number of atoms by corner atom = $1/8 \times 8 = 1$ atom.

In addition, there are 6 atoms at the face centers of the cube. Each face-centered atom is shared by two surround unit cells. Hence, the number of face centered atoms in unit cell,

$= ½ \times 6 = 3$ atoms.

Therefore, total number of atoms in one unit cell = 1 + 3 = 4 atoms.

(ii) Coordination Number

In this case, there are eight atoms at the eight corners of the unit cell and 6 atoms at the center of the six faces.

For any corner atom of the unit cell, the nearest atom is face-centered atom. For any corner atom, there are four face-centered atoms in its plane and four above its plane and four below its plane.

Thus, the coordination number in this case = 4 + 4 + 4 = 12

(iii) Atomic Radius

For a body centered cubic unit cell, the atomic radius can be calculated from **figure** as follows.

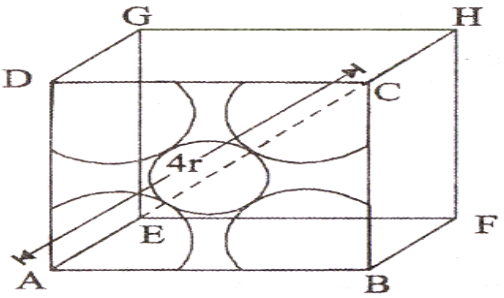


Figure 1.1.7.5(a)

Consider the triangle ABC,

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

$(4r)^2 = a^2 + a^2$

$16 r^2 = 2a^2$

$$r^2 = \frac{2a^2}{16}$$

Taking square root on both sides, we have

$$\sqrt{r^2} = \frac{\sqrt{2a^2}}{\sqrt{16}}$$

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

(iv) Packing Factor

The number of atoms present in an FCC unit cell is four. Therefore, the packing factor of the FCC unit cell be written as

Number of atoms per unit cell = 4

Volume of 4 atoms, $4 \times \frac{4}{3}\pi r^3$

Side of the unit cell, $a = \frac{4r}{\sqrt{2}}$

$$\left(\because atomicradius, r = \frac{\sqrt{2}}{4}a\right)$$

Volume of the unit cell V = $a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3$

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

Substituting for v and V, we have

$$\text{PF} = \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \frac{\frac{16}{3}\pi r^3}{\frac{4^3 r^3}{\sqrt{(\sqrt{2})^3}}} = \frac{\frac{16}{3}\pi r^3}{\frac{64 r^3}{\sqrt{2}\sqrt{2}\sqrt{2}}} = \frac{\frac{16}{3}\pi r^3}{\frac{64 r^3}{2\sqrt{2}}}$$

$$\text{PF} = \frac{16}{3}\pi r^3 \times \frac{2\sqrt{2}}{64 r^3}$$

$$\frac{\pi\sqrt{2}}{6} = 0.74$$

This shows that 74% of the volume of an FCC unit cell is occupied by atoms and the remaining 26% volume of the unit cell is Vacant.

Thus the packing density is 74%.

Since the packing density is very high, the FCC structure has closely (or) tightly packed structure.

1.1.8 Hexagonal Closely Packed Structure (HCP)

The hexagonal closely packed (hcp) is shown in the **figure 1.1.8.** In the hcp structure of an unit cell contains three types of atoms as three layers.

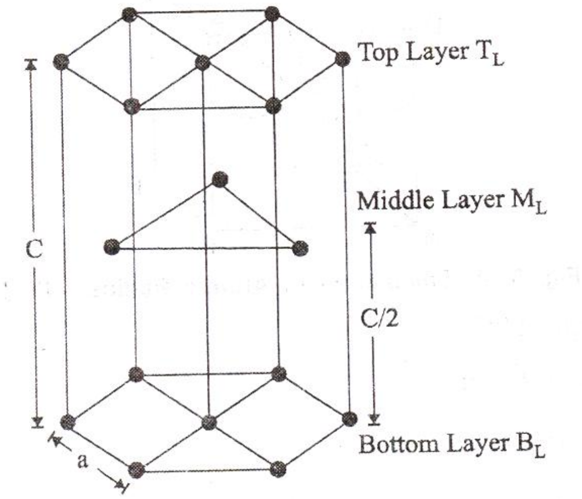


Figure 1.1.8

- 12 corner atoms, one at each and every corner of the Hexagon.
- 2 base centered atoms, one at the top face of the hexagon and another at the bottom face of the hexagon.
- In addition to corner and base atoms, 3 atoms are situated in between the top and bottom face of the hexagon, in alternate vertical faces. Also note that these atoms are situated inside the face so that they can't be shared by other cells as shown in the figure 5.1.10

(i) Number of atoms per unit cell

To calculate the number of atoms per unit cell, first consider the bottom layer. The bottom layer consists of six corner atoms and one face centered atom. Each and every corner atom contributes 1/6 of its part to one unit cell. The total number atoms contributed by the corner atoms is 1/6 × 6 = 1. The face-centered atom contributes ½ of its part to one unit cell. Therefore, the total number of atoms contributes ½ of its part to one unit cell. Therefore, total number of atoms present in the case of the bottom layer is 1 + ½ = 3/2

Similarly, the number of atoms present in the upper layer is 1 + ½ = 3/2

The number of the atoms present in the middle layer = 1 × 3 = 3.

∴ The total number of atoms present in the unit cell = 3/2 +3/2 + 3 = 6 atoms.

(ii) 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 atom touches with each other, therefore they are nearest neighbor.

From figure 1.1.8.1 we can write

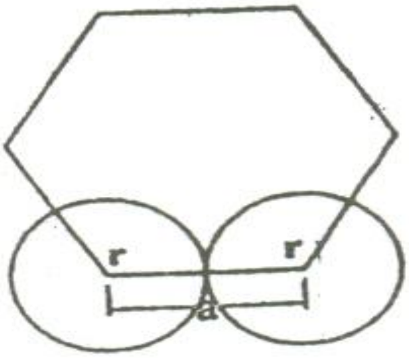


Figure 1.1.8.1

Atomic Radius - HCP Structure

(iii) Coordination Number

The coordination number of the hcp structure can be calculated as follows.

Let us consider two unit cells as shown in the **figure 1.1.8.2**

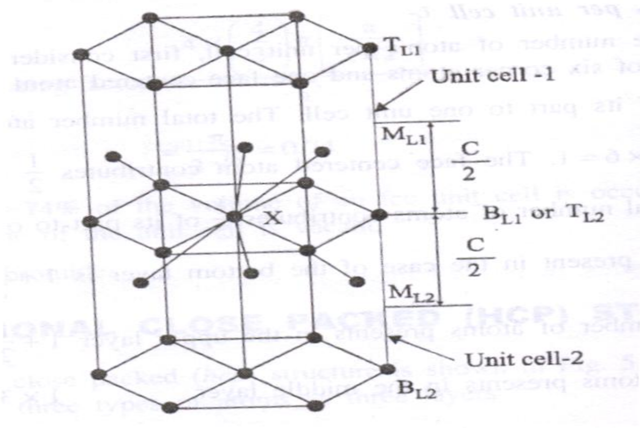


Figure 1.1.8.2

The hcp structure is considered to have three layers viz, 1) Bottom Layer [B_L], 2) Top Layer [T_L] and 3) Middle Layer [M_L] as shown.

In the top and bottom layers, 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.Let us consider two unit cells .let 'X' be the reference atom taken in the bottom layer BL_1 of unit cell 1(or top layer [TL_2] of unit cell 2). This atom has 6 neighboring atom in its own plane. Further at a distance of c/2 it has 3 atoms in the middle layer (ML_1) of unit cell –1 and 3 more atoms in the middle layer (ML_2) of unit cell – 2. Therefore, the total number of neighboring atoms is 6 + 3 +3 = 12.

Thus the coordination number is 12.

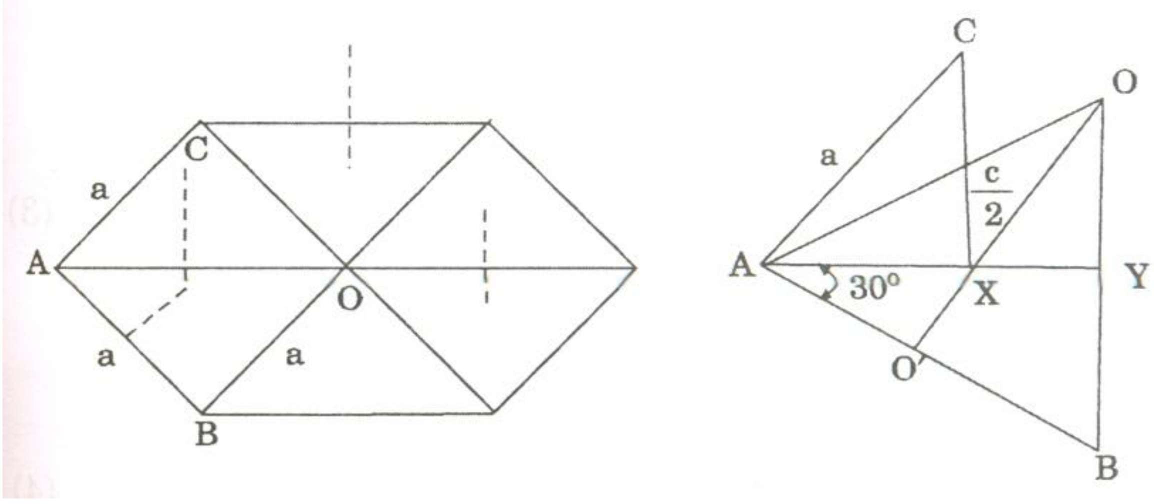


Figure 1.1.8.3

We know that ‘c’ is the height of the unit cell of HCP structure and ‘a’ is the distance between two neighboring atoms. Now consider a triangle ABO in the bottom layer.

Here A, B, and O are the lattice points and exactly above these atoms at a perpendicular distance ’c’/2 the next layer atom lies at C.

In $\Delta ABY, Cos30^0 = \frac{AY}{AB}$

$$AY = AB\cos 30^0 = \frac{a\times\sqrt{3}}{2}$$

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

$$\left(\because AB = a, \cos 30^0 = \frac{\sqrt{3}}{2}\right)$$

But from figure $AX = \frac{2}{3}AY$

Substituting for AY, we get

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

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

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

In ΔAXC,

$$AC^2 = AX^2 + CX^2$$

Substituting the values for

AC = a, $AX = \frac{a}{\sqrt{3}}$ and $CX = \frac{c}{2}$, we get

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

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

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

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

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

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

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

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

Taking square root both sides

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

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

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

(iv) Atomic Packing factor

Volume of all atoms in a unit cell (v)

Nearest neighboring distance, 2r = a

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

No of atoms per unit cell, n= 6

Volume of all the six atoms in the unit cell

$$v = 6 \times \frac{4}{3} \pi r^3$$

Substituting for $r = \frac{a}{2}$,we have

$$v = \frac{24}{3}\pi\left[\frac{a}{2}\right]^3$$

$$v = \frac{24\pi}{3}\frac{a^3}{2^3} = \frac{24}{3}\frac{\pi a^3}{8}$$

$$v = \pi a^3$$

Volume of the Unit Cell V

Area of base = 6 × area of triangle AOB

Area of triangle AOB = $\frac{1}{2} \times (BO) \times (AY)$

Substituting for BO = a and $AY = \frac{a\sqrt{3}}{2}$ we have

$$\frac{1}{2} \times a \times \frac{a\sqrt{3}}{2}$$

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

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

The volume of the unit cell of the HCP = base area × height

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

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

Substituting for v and V, we have

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

$$PF = \frac{2\pi}{3\sqrt{3}}\left(\frac{a}{c}\right)$$

$$PF = \frac{2\pi}{3\sqrt{3}}\left(\frac{3}{8}\right)^{1/2}$$

$$PF = \frac{2\pi}{3\sqrt{3}}\frac{3^{1/2}}{8^{1/2}} = \frac{2\pi}{3\sqrt{3}}\frac{\sqrt{3}}{\sqrt{8}} = \frac{2\pi}{3\sqrt{4\times 2}} = \frac{2\pi}{3\times 2\sqrt{2}}$$

$$PF = \frac{\pi}{3\sqrt{2}} = \frac{3.14}{3\sqrt{2}} = 0.74 = 74\%$$

Thus the packing density is 74% and hence, it is a closed packed structure.

Examples. Zinc, Beryellium and Magnesium

1.1.11 Properties of some Crystal Structure

S.No	Properties	Simple Cubic	Body Centered Cubic	Face Centered Cubic	Hexagonal Close Packed
1	Unit Cell Volume	a^3	a^3	a^3	$3/2\sqrt{3}\, a^2 c$
2.	Number of atoms per unit cell	1	2	4	6
3.	Coordination Number	6	8	12	12
4.	Atomic Radius	$\frac{a}{2}$	$\left(r = \frac{\sqrt{3}}{4}a\right)$	$\left(r = \frac{\sqrt{2}}{4}a\right)$	$\frac{a}{2}$
5.	Packing Factor	0.52	0.68	0.74	0.74
6.	Examples	Polonium	Iron, Barium, Chromium	Aluminum, Copper, Gold	Beryellium, Cadmium

RELATION BETWEEN LATTICE CONSTANT (a) AND DENSITY (ρ)

Consider a cubic crystal of lattice constant a

Density of the crystal = ρ

Volume of the unit cell = a^3

$\therefore$ Mass of the unit cell = $\rho\, a^3$

$$\left(\because density = \frac{mass}{volume}\right)$$

Number of atoms per unit cell = n

Atomic weight of the material = M

Avogadro's number = N

Avogadro's number is the number of atoms per kg mole of the substance.

$$\text{Mass of each atom} = \frac{M}{N}$$

Mass of the unit cell = mass of the each atom in unit cell × number of atoms per unit cell

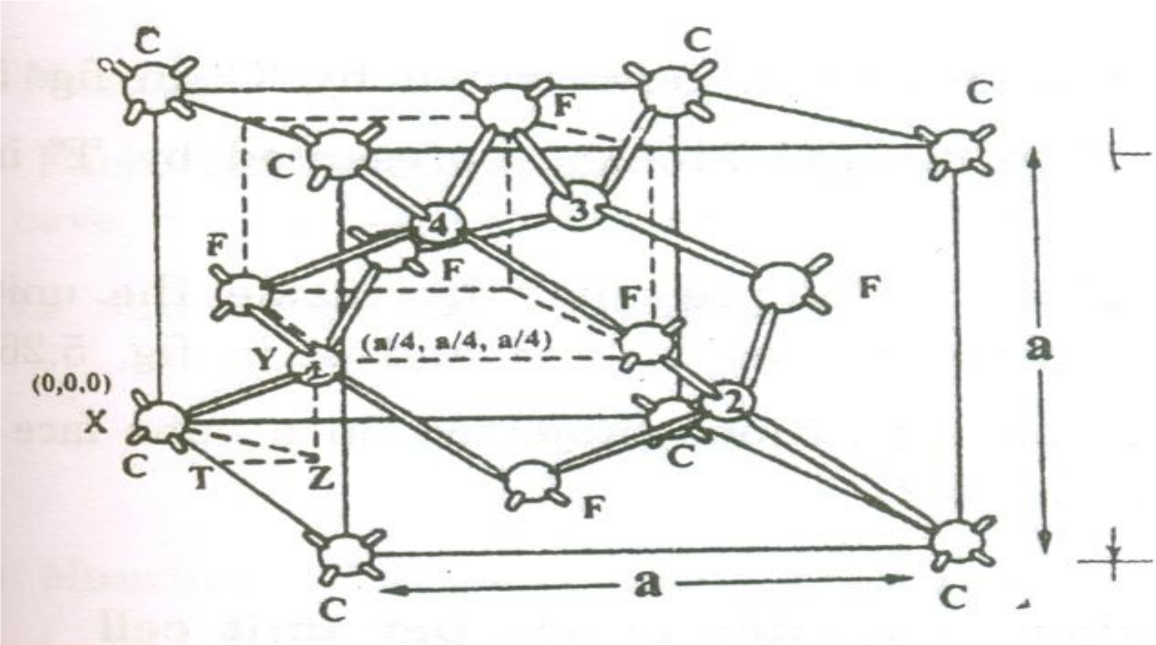
$$\text{Mass of each atom} = \frac{M}{N} \times n \text{ (for n atoms per unit cell)}$$

$$\rho \, a^3 = \frac{M}{N} \times n$$

$$\rho = \frac{nM}{Na^3}.$$

Diamond cubic structure:

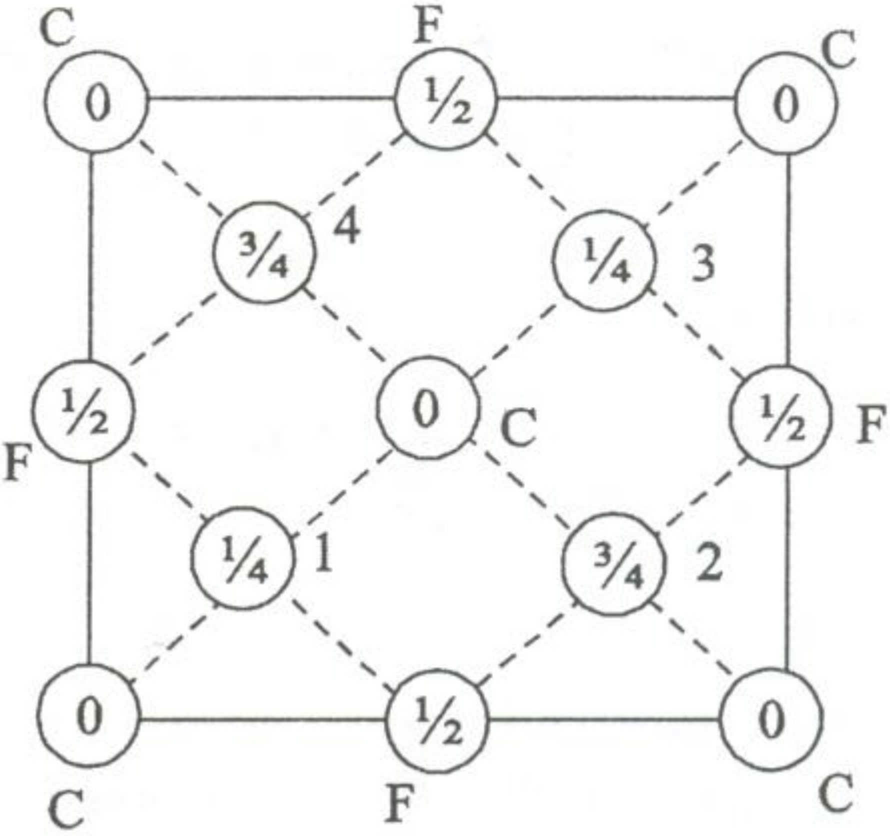
Diamond has face centered structure (FCC) with the basis of two carbon atoms viz., 'X' and 'Y'. The 'X' atom is located with an origin (0, 0, 0) and the Y atom is located with an origin of $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$(i.e) one quarter of the way along the body diagonal as shown in the figure



Thus from the figure we can see that the diamond structure is formed due to the combination of two interpenetrating FCC sub lattices, having the origin (0,0,0) and $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$ along the body diagonal.

Let us now discuss some of the important parameters of the diamond

1. Number of atoms per unit cell
   - i. Corner atoms , represented by 'C' in figure
   - ii. Face centered atoms , represented by 'F' as shown in the figure
   - iii. Four atoms present inside the unit cell an s represented as 1, 2.3,4 as shown in the figure.
   - iv. The three types of atoms positions projected on a cube face is as shown



i. Number of atoms per unit cell:

Each corner atom is shared by 8 unit cells. Similarly we have 8 corner atoms in an unit cell.

$\therefore$ The number of corner atoms per unit cell is $\frac{1}{8}\times 8 = 1 atom$

ii. Number of face centered atoms per unit cell

Each face centered atom is shared by 2 unit cells. Similarly, we have 6 face centered atoms.

$\therefore$ The number of face centered atom per unit cell = $\frac{1}{2} \times 6 = 3 atoms$

iii. Number of atoms inside the unit cell

Inside the unit cell we have 4 atoms, represented by 1,2,3,4 in the figure which is shared by that particular unit cell alone.

$\therefore$ Total number of atoms per unit cell = 1+3+4 = 8

2. Atomic radius

We know atomic radius is defined as half the distance between any two nearest neighbor atoms, which have direct contact with each other.

Here, the corner atoms do not have contact with each other and the face centered atoms also do not have contact with the corner atoms. But both the face centered atoms and the corner atoms have contact with the 4 atoms (1, 2, 3, 4)

From figure, we can see that the nearest two neighbors which have direct contact (shown by double line) are atoms 'X' and 'Y'.

Let us draw perpendicular to the Y atom, which meets the unit cell at a point 'Z' as shown in the figure , which is at a distance of a/4.

$\therefore$ From figure $(XY)^2 = (XZ)^2 + (ZY)^2$

$$= [(XT)^2 + (TZ)^2] + (ZY)^2$$

$$= \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2$$

$$= \frac{a^2}{16} + \frac{a^2}{16} + \frac{a^2}{16}$$

$$\therefore (XY)^2 = \frac{3a^2}{16}$$

Since XY = 2r, we can write

$$(2r)^2 = \frac{3a^2}{16}$$

$$4r^2 = \frac{3a^2}{16}$$

$$r^2 = \frac{3a^2}{16}$$

$\therefore$ Atomic radius r = $\frac{a\sqrt{3}}{8}$

$\therefore$ The lattice constant a $\frac{8r}{\sqrt{3}}$

3. Coordination number:

   We know that the coordination number is the nearest neighboring atoms to a particular atom.

   From figure the number of the nearest atoms (shown by double line) for Y atom is 4. Therefore the coordination number of diamond is 4

4. Atomic packing factor:

   We know

   Atomic packing factor (APF) =

Volume occupied by the atoms per unit cell (v)/ volume of the unit cell (V) $\longrightarrow$ (1)

Volume occupied by 1 atom (Spherical) = $\frac{4}{3}\pi r^3$

In diamond we have 8 atoms per unit cell

$\therefore$ Volume occupied by all the '8' atoms per unit cell (v) = $8 \times \frac{4}{3}\pi r^3$

We know atomic radius for diamond structure $r = \frac{a\sqrt{3}}{8}$

$\therefore$ Volume occupied by the atoms per unit cell (v) = $8 \times \frac{4}{3}\pi \times \left(\frac{a\sqrt{3}}{8}\right)^3$

$\therefore$ Volume occupied by the atoms per unit cell $v = \frac{\pi a^3\sqrt{3}}{16}$ $\longrightarrow$ (2)

Since diamond has cubic structure, the volume of the unit cell (V) = a^3 $\longrightarrow$ (3)

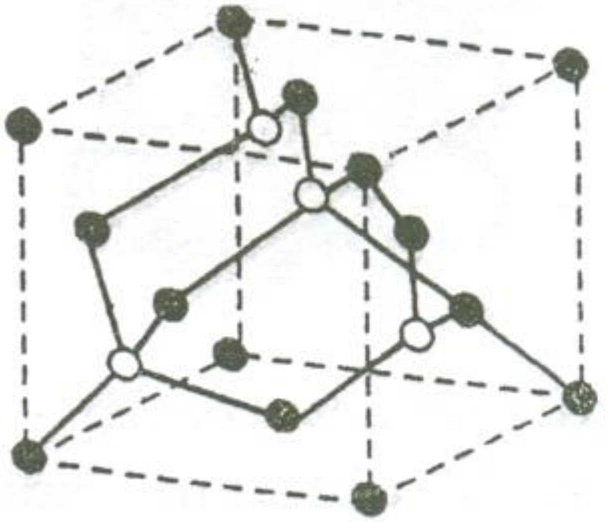
Substituting equations (2) and (3) in (1) we get

$$APF = \frac{\pi a^3 \sqrt{3}}{16 a^3} = \frac{\pi \sqrt{3}}{16} = 0.34$$

$\therefore$ Packing density = 34%

Thus we can say that 34% volume of the unit cell in diamond cubic structure is occupied by the atoms and the remaining 66% volume is vacant.

Since the packing density is very low, it is termed as very loosely packed structure.



○ - S ions
● - Zn ions

SODIUM CHLORIDE STRUCTURE:

Ionic solids are made up of cat ion (+ion) and anions (- ion). Generally, the cations (+ ve) are smaller in size to anions.

Sodium chloride and many other ionic crystals crystalline in rock slat structure which is also known as sodium chloride structure.

Structure composition:

NaCl crystal has FCC structure with Na^+ ion and Cl^- ion as shown in the figure.

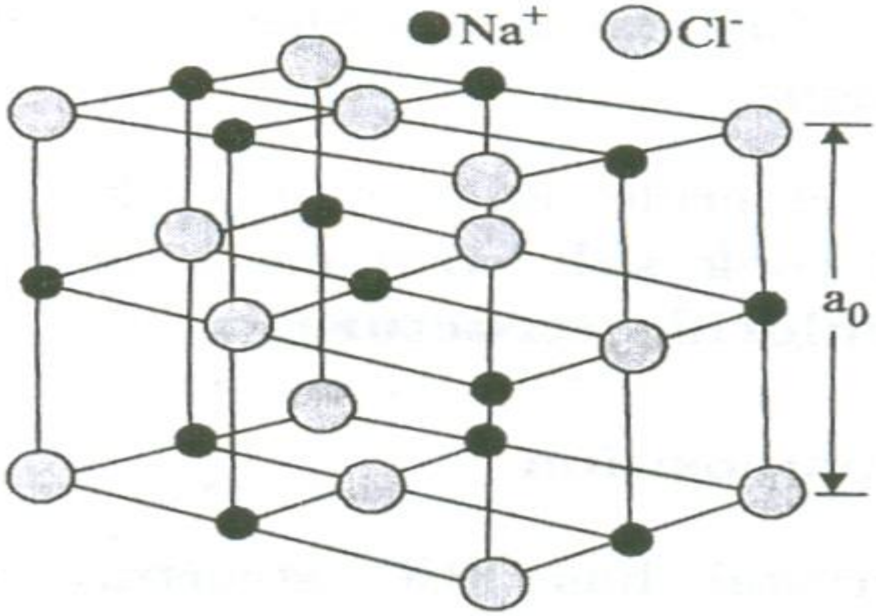
The Cl^- ions are situated at the corners as well as at the centers of the faces of the cube. Na^+ ions are situated exactly at the middle of the axial length of the unit cell along each axis.

Thus NaCl crystal can be thought of as a compound of two FCC Na^+ and

Cl^- sub lattices

When one of the Cl^- ions has the origin at (0,0,0) then one of the nearest

Na^+ ion has the origin at $\left(\frac{1}{2},0,0\right)$



Let us discuss the important parameters of the NaCl crystal.

In NaCl structure, it has two types of ions namely, Na^+ and Cl^- . Let us find the number of sodium ions separately.

a. Number of Na^+ ions per unit cell

   Na^+ ion is located at the midpoint of the axial length. There are 12 such mid points Na^+ ions. Each sodium ion is shared by 4 adjacent unit cells.

   $\therefore$ share of one unit cell

   Number of mid point Na^+ ions per unit cell

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

One sodium ion is located at the center of the unit cell.

Therefore, the number of sodium ions per unit cell = 3+1=4 ions

b. Number of Cl^- ions per unit cell

Here, there are two types of Cl^- ion namely Corner Cl ions and Face centered Cl ions as shown in the figure.

There are 8 chlorine atoms in the corners and they are shared by 8 adjacent unit cells.

$\therefore$ number of corner Cl^- ions per unit cell

$$= \frac{1}{8}\times 8 = 1 \text{ ion.}$$

Each face centered Cl^- ion is shared by 2 adjoining unit cell. There are 6 face centered Cl^- ions.

$\therefore$ Number of face centered Cl^- ions per unit cell

$$= \frac{1}{2}\times 6 = 3 \text{ ions.}$$

Therefore total number of chlorine ions per unit cell = 1+ 3 = 4 ions.

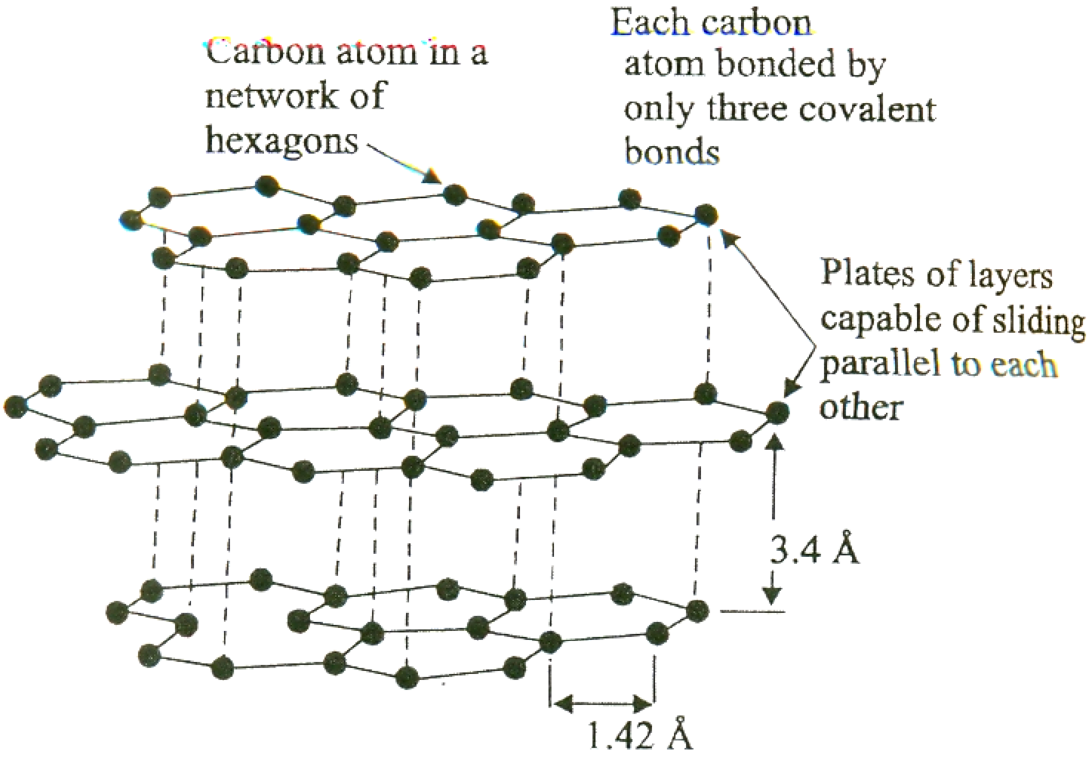
Thus , there are 4 Na^+ and 4Cl^- ions per unit cell. That is total number of sodium and chlorine ions per unit cell are 8.

2. coordination number:

Each Na^+ and 6 Cl^- ions as nearest neighbors and similarly each Cl^- ion has 6 Na^+ ions has nearest neighbours. Hence, the coordination number of NaCl for opposite kind of ions is 6.

3. nearest neighbours distance

The nearest neighbor distance is $\frac{a}{2}$



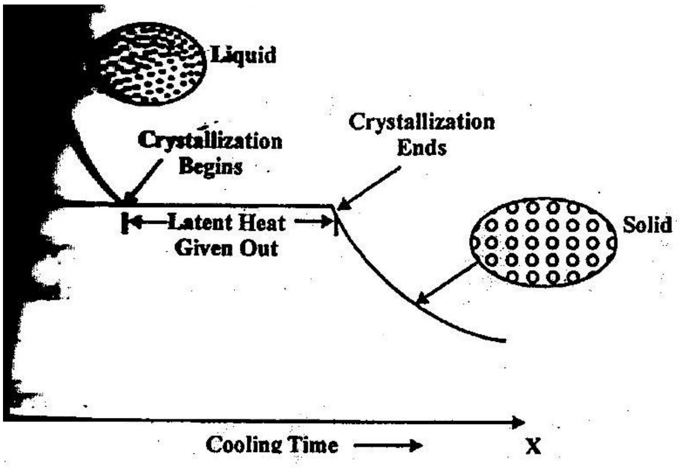
.

Crystal growth

Solidification and Crystallization

In order to understand the crystalline state and its difference from the amorphous state, it is important to consider the process of Solidification.

Solidification is the transformation of material from liquid to the solid state on cooling.



When the liquid solidifies, the energy of each atom is reduced. This energy is given out as latent heat during the solidification process, which for a pure metal occurs at a fixed temperature T_s as shown in figure

During solidification, the disordered structure of the liquid (constituents of material in liquid state have more velocity, more collisions and hence have random position) transforms to the orderly arrangement depending upon the time of solidification.
Crystal growth techniques.
The crystal growth technique is classified into six categories namely

i. Melt growth
ii. Low temperature solution growth
iii. High temperature solution growth
iv. Hydrothermal growth
v. Gel growth
vi. Epitaxial growth

Melt growth:

Melt growth is the process of crystallization by fusion and re solidification of the starting materials
The growth from melt is further sub- grouped into various techniques. The main techniques are

a) Czochralski technique
b) Bridgman Technique
c) Verneuil method
d) Zone melting technique

The major practical factors is to be considered during growth crystals from melt are

1) Volatiltiy
2) Chemical resistivity
3) Melting point

Czochralski technique

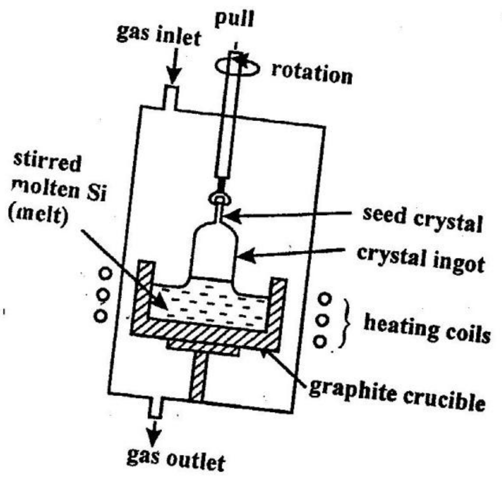
The czochralski method is crystal pulling technique from the melt. The process is based on a liquid – solid phase transition driven by a seed crystal in contact with the melt.

Basically, the seed is to be considered as a heat sink, by which the latent heat of solidification escapes and as a nucleation center; the solidified fraction at the surface of the seed will reproduce its single – crystal structure.

By raising the seed slowly, a crystal is "pulled" from the melt. Decreasing the melt temperature makes the crystal diameter increasing and vice versa.

Description and working

Large single crystals of Si (for IC fabrication) are grown by the Czochralski method. It involves growing a single - crystal ingot from the melt, using solidification on a seed crystal as illustrated in the figure.



Molten Si is held in a quartz (Crystalline SiO_2) crucible in a graphite susceptor. It is heated by radio frequency induction coil (RF heating).

A small dislocation – free crystal called a seed is moved down to touch the melt and then slowly pulled out of melt.

A crystal grows by solidifying on the seed crystal. The seed is rotated during the pulling stage , to obtain a cylindrical ingot.

ADVANTAGES

- Growth from free surface
- Growth of large oriented crystals
- Convenient chemical composition
- Control of atmosphere

Limitations

- High vapor pressure materials

- Liquid phase encapsulation
- Possible contamination of the melt by the crucible
- No reproductivety of the crystal shape

BRIDGEMAN TECHNIQUE

A common technique of growing single crystals. It involves selective cooling of the molten material, so that solidification occurs along a particular crystal direction.

In this technique, the melt in a sealed crucible is progressively frozen from one end. This can be achieved by

- Moving the crucible down the temperature gradient
- Moving the furnace over the crucible
- By keeping both the furnace and the crucible stationery and cooling the furnace so that freezing isotherm moves steadily through the originally molten charge.

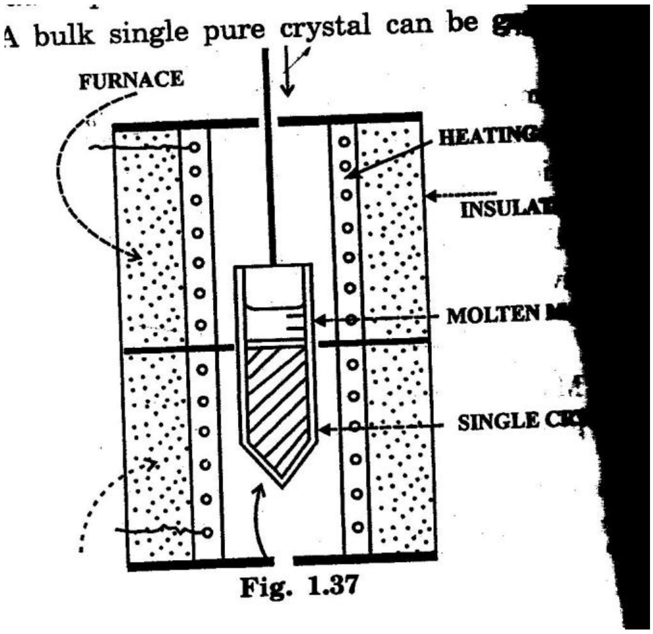


Fig. 1.37

GROWTN PROCESS

Figure shows a platinum crucible filled with high quality nature grown material, to which the desired impurities may be added. The crucible is fixed in the upper furnace until the contents are completely melted. It is then lowered from upper furnace into the lower furnace with the help of electric motor and reduction gearing. Since the potential tip enters the lower furnace first, the grown material starts to crystalline over there.

As the crucible continues to be lowered crystallization proceeds until all the melts become solid crystal. A bulk single crystal can be grown in the crucible at steady rate and keeping the temperature constant.

Sodium chloride : NaCl

Potassium Chloride : KCl

Calcium fluoride : CaF_2

Silver Bromide : AgBr

Examples

Advantages

- Simple technique
- Control over vapour pressure
- Containers can be evacuated and sealed
- Control of shape and size of growing crystals
- Stabilization of thermal gradients.

Limitations

- Confinement of crystals
- Crystal perfection is not better than that of the seed
- No visibility

SOLUTION GROWTH

Low temperature solution growth

The low temperature solution growth is suitable for materials which decompose at high temperature and undergo phase transformation below the melting point.

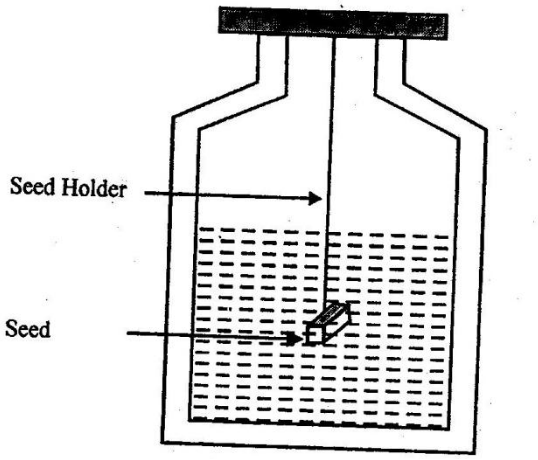
There are two methods of low temperature solution growth. They are

i. Slow cooling method
ii. Slow evaporation method

SLOW COOLING METHOD

Slow cooling is the easiest method to grow bulk single crystals from solution. This technique needs only a vessel for the solution, in which the crystals grow.

The temperature at which crystallization begin is in the range of 45^{0}C to 75^0 C and the lower limit of the cooling is the room temperature.



SLOW EVAPORATION METHOD

In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. The basic apparatus (Manson Jar crystallizer) used for the solution growth technique is shown in the figure

Typical growth conditions involve temperature stabilization at about 0.05^{0}C and rate of evaporation of a few mm^3/h.

ADVANTAGES

i. This is a simple and convenient method of growing single crystals of large size.
ii. Growth of strain and dislocation free crystals.
iii. Permits the growth of prismatic crystals by varying the growth conditions.
iv. Only method which can be used for substances that undergo decomposition before melting.

DISADVANTAGES

i. The growth substance should not react with the solvent
ii. This method is applicable from substances fairly soluble in solvent
iii. Small crystals are also formed on the walls of the vessel near the surface of the liquid. These tiny crystals fall in the solution and hinder the growth of the crystal
iv. A variable rate of evaporation may affect the quality of the crystal

EPITAXIAL GROWTH

The process of growing an oriented single crystal layer on substrate wafer is called Epitaxial growth.

The term “epitaxy” is derived from greek word “epi” literally means “arranged upon”.

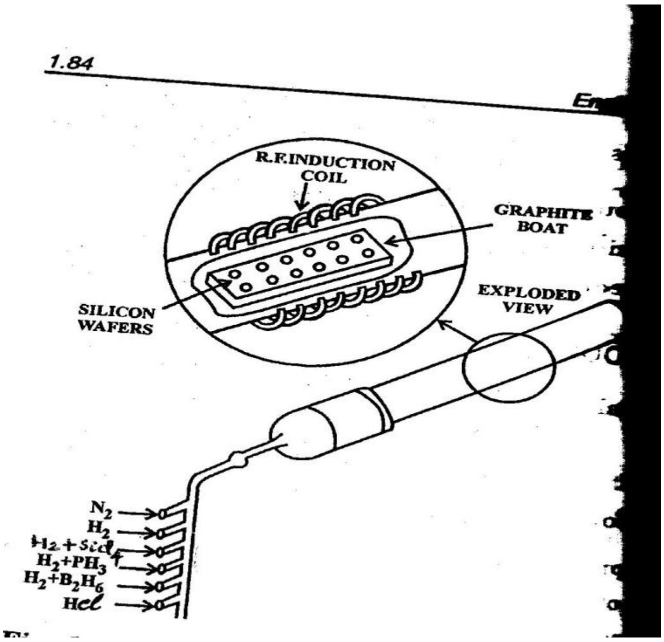
In this method, a thin layer of single crystal (typically a few nanometers to few microns) is grown on the existing crystalline substance such that film has the same lattice structure as the substrate.

Epitaxy is further divided into

i. Vapor Phase Epitaxy
ii. Liquid Phase Epitaxy
iii. Molecular Beam Epitaxy

VAPOUR PHASE EPITAXY (VPE)

Epitaxial growth of Silicon is exclusively carried out by VPE.



Construction:

The process is carried out in reaction chamber consisting of along cylindrical quartz tube encircled by radio frequency induction coil as shown in the figure.

The silicon wafers are placed on a rectangular graphite rod called Boat. This boat is placed in the reaction chamber and heated inductively to a temperature of 1200^{0}C.

The various gases required for the growth of desired epitaxial layers are introduced into the system through a control device.

The reaction is surface analyzed and silicon is deposited on the wafer surface. However, the decomposition temperature is very high. Also, as the reaction is reversible and can proceed in both directions.

Growth process:

Mostly epitaxial films with specific impurity concentration (P- type or N-type) are required. This is accomplished by introducing Phosphine (PH_3) for n- type doping and Biborane (B_2H_6) for P- Type doping.

There is a control console which permits only the required gases at suitable pressure so that it is possible to form an almost step p- n junction layer by the process.

Vapour Phase Epitaxy(VPE) of compound semiconductor , for example, GaAs performed using Gallium(Ga) and Arsenic chloride($AaCl_3$) as source materials.

Advantages:

- Halogen based VPE produces high pure single crystal layers with limited defects.
- Hydride VPE allows proper control over the ratio of group III to group V vapour phase species.

Disadvantages:

- Higher growth temperature results in higher impurity diffusion. So uniform distribution of impurities cannot be obtained.

Applications

- This method is mainly used in the manufacture of LED's and detectors.