

UNIT – V CRYSTAL PHYSICS

Materials differ in their properties due to its crystal structure, based on which solids are classified in to two types.

- i. **Crystalline materials** – Arrangement of atoms in periodic manner; Examples: Copper, Silver
- ii. **Amorphous materials** – Arrangement of atoms in an irregular fashion; Examples: Glass, rubber

Crystallographic terms

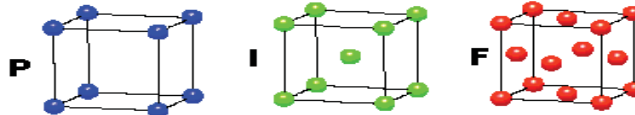
- i. **Crystal** – Three dimensional solid which consists of a periodic arrangement of atoms
- ii. **Space lattice** – Space lattice is an infinite arrangement of points in three dimensions in which every point has an identical surrounding
- iii. **Basis** – The crystal structure is obtained by adding a unit assembly of atoms to each lattice point. This unit assembly is called as basis.
- iv. **Unit cell** – A unit cell is the smallest unit which, when repeated in space indefinitely, will generate the space lattice.
- v. **Lattice parameters** - The intercepts a , b , c of a unit cell and the interfacial angles α , β and γ along the three axes are called the lattice parameters.

SEVEN CRYSTAL SYSTEMS

CUBIC

$$a = b = c$$

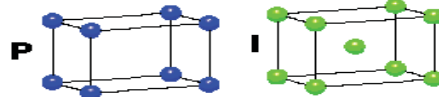
$$\alpha = \beta = \gamma = 90^\circ$$



TETRAGONAL

$$a = b \neq c$$

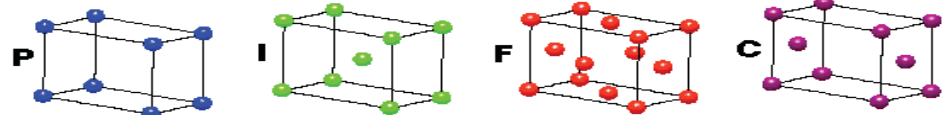
$$\alpha = \beta = \gamma = 90^\circ$$



ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

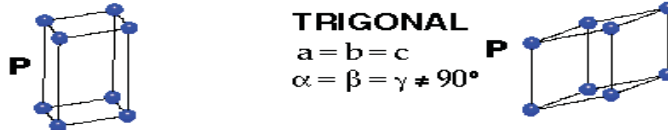


HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

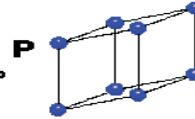
$$\gamma = 120^\circ$$



TRIGONAL

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

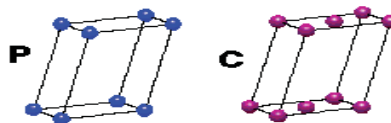


MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

$$\beta \neq 120^\circ$$



TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

→ 14 Bravais Lattices

Bravais lattice – According to Bravais, there are 14 possible types of space lattices out of seven crystal systems. These 14 space lattices are called Bravais lattices.

Characteristics of unit cell

- i) **No of atoms per unit cell** – Number of atoms possessed by a unit cell
- ii) **Coordination number** – Number of nearest atoms directly surrounding a particular atom in a crystal.
- iii) **Nearest neighbor distance (a)** – Distance between the centers of two nearest neighbouring atoms (2r).
- iv) **Atomic radius (r)** – Half of the nearest neighbouring distance in a crystal.
- v) **Atomic packing factor** – Ratio of the volume of atoms in the unit cell to the volume of the unit cell. There is no unit for it since it is a ratio.

Simple Cubic structure: SC

Number of atoms per unit cell

The total number of atoms present or shared by a unit cell is known as number of atoms per unit cell. This number depends on the number of corner atoms; body centered and face centered atoms, which vary from structure to structure. It is evaluated as follows,

The Simple Cubic system (SC) consists of one lattice point on each corner of the cube. Each atom at a lattice point is then shared equally between eight adjacent cubes, and the unit cell therefore contains in total one atom ($\frac{1}{8} \times 8$)=1.

Atomic radius

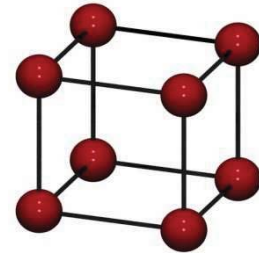
In a Simple Cubic structure the corner atoms touch each other along the edges as shown in fig. Let us consider one face (front face) of the structure

Here the nearest neighbour distance is the lattice constant $a = 2r$

$$\therefore r = a/2$$

Co-ordination number

Is the number of nearest neighbouring atoms to a particular atom. Each corner atom is in contact with six other corner atoms. Hence the coordination number is 6.



Packing factor

Let 'a' be the edge length of the unit cell and r be the radius of sphere.

As the atoms are touching each other

$$a = 2r$$

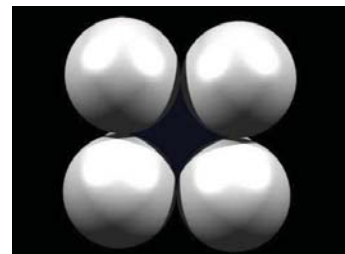
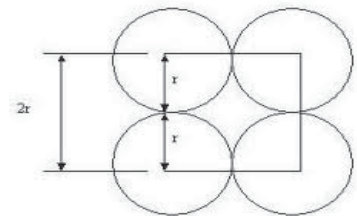
$$\text{No. of atoms per unit cell} = \frac{1}{8} \times 8 = 1$$

$$\text{Volume of the sphere} = \frac{4}{3} \pi r^3$$

$$\text{Volume of the cube} = a^3 = (2r)^3 = 8r^3$$

$$\therefore \text{Fraction of the space occupied} = \frac{1/3 \pi r^3}{8r^3} = 0.524$$

$$\therefore \% \text{ occupied} = 52.4 \%$$



Body Centered Cubic System: BCC

Number of atoms per unit cell

The **body-centered cubic** system (BCC) has one lattice point in the center of the unit cell in addition to the eight corner points. It has a net total of 2 lattice points per unit cell ($\frac{1}{8} \times 8 + 1$) = 1 + 1 = 2.

Atomic radius

In BCC, the corner atoms do not touch each other. But each corner atom touches the body centered atom along the body diagonal as shown. From the geometry of the fig, we can write

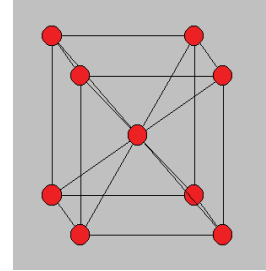
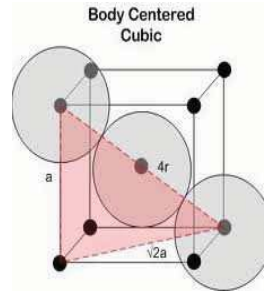
$$\begin{aligned}(AD)^2 &= (AC)^2 + (CD)^2 \\ &= (AB)^2 + (BC)^2 + (CD)^2 \\ &= a^2 + a^2 + a^2 = 3a^2\end{aligned}$$

$$AD = a\sqrt{3}$$

The diagonal of the cube = AD = 4r

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

$$\therefore r = a\sqrt{3}/4$$



Coordination number

In BCC there will be one body centered atom at the center of the unit cell and eight corner atoms. The corner atoms do not touch each other, but the corner atoms touch the body centered atom along the body diagonal, thus there are 8 nearest atoms. Hence the co-ordination number is 8.

Packing Factor

The ratio between the volume of the atoms in the unit cell and the total volume of the unit cell is called packing factor.

Packing factor for BCC

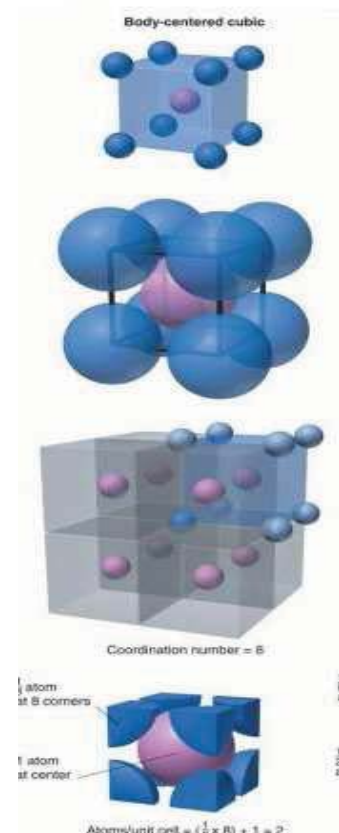
$$\text{A.P.F} = \frac{2 \times \frac{4}{3}\pi r^3}{a^3}$$

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

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

$$\text{A.P.F} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3}$$

$$\text{A.P.F} = \frac{\sqrt{3}\pi}{8} = 0.68$$



Face centered cubic structure: FCC

The face centered cubic structure consists of six face centered atoms in addition to the eight corner atoms.

No of atoms per unit cell

Each corner atom is shared by 8 adjacent unit cells; therefore the contribution of the corner atoms is 1. ($8 \times 1/8 = 1$)

The contribution of each face centered atom to the unit cell is $1/2$. Therefore there are totally 3 face centered atoms in each unit cell.

Hence, the total number of atoms in the unit cell is $3 + 1 = 4$

Coordination number

In FCC each face centered atom is in contact with 4 corner atoms in the same plane, 4 face centered atoms in the plane above and 4 face centered atoms in the plane below.

The totals nearest neighbouring atoms are 12.

Atomic radius

Three atoms are in contact along the face diagonal. Therefore,

$$r + 2r + r = 4r$$

From geometry of the unit cell, the face diagonal of a cube of side 'a' is $a\sqrt{2}$.

$$\text{Equating, } 4r = a\sqrt{2}$$

$$\text{Atomic radius } r = a\sqrt{2}/4.$$

Packing factor for FCC

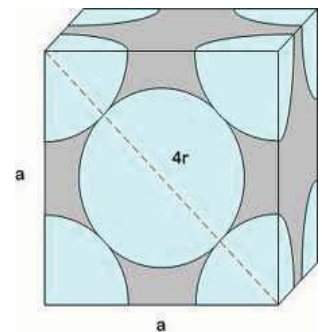
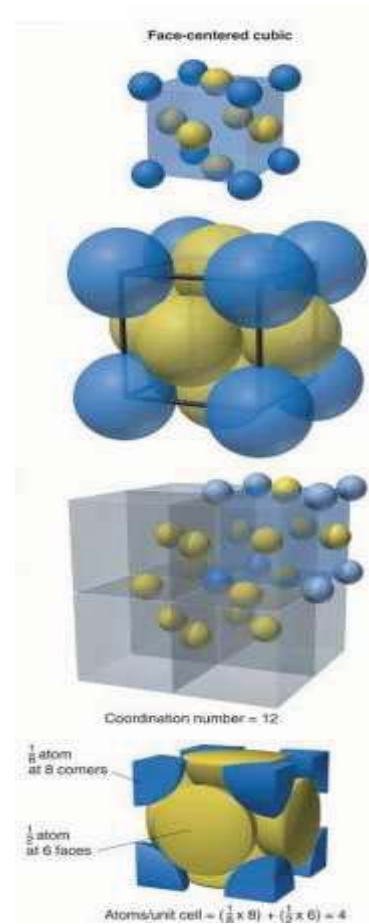
$$\text{A.P.F} = \frac{4 \times \frac{4}{3}\pi r^3}{a^3}$$

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

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

$$\text{A.P.F} = \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3}$$

$$\text{A.P.F} = \frac{\sqrt{2}\pi}{6} = 0.74$$



Hexagonal Close packed structure

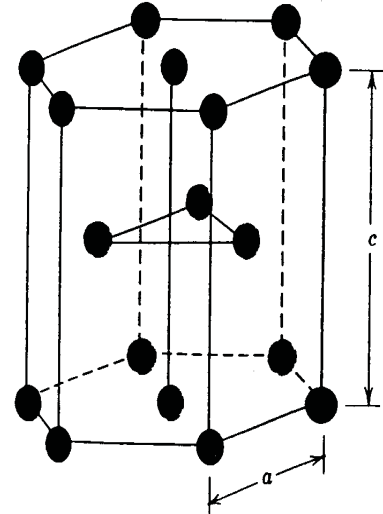
The HCP unit cell consists of three types of atoms

- 12 corner atoms, one at each corner of the hexagon
- 2 base centered atoms, one at the top face and another at the bottom face of the hexagon
- 3 atoms are situated in-between the top and bottom face of the hexagon, in alternate vertical faces, at a distance $c/2$ from the bottom face.

No of atoms per unit cell

- No of corner atoms = 12
Contribution of each corner atom = $1/6$
Effective no of corner atoms = $12 \times 1/6 = 2$
- No of base centered atoms = 2
Contribution of each base centered atom = $1/2$
Effective no of base centered atoms = $2 \times 1/2 = 1$
- Three body centered atoms in the middle layer belong solely to the unit cell. Therefore effective number is $3 \times 1 = 3$

Therefore, total number of atoms per unit cell = $2 + 1 + 3 = 6$

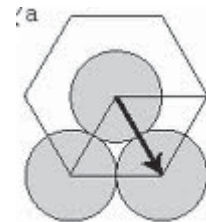


HCP

Atomic radius:

All corner atoms are in contact with each other, hence

$$r = a/2$$



Coordination number:

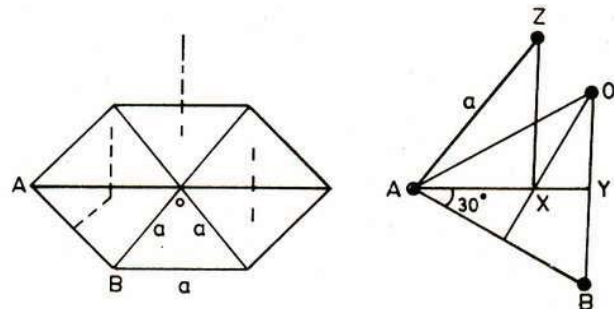
The base centered atom is in contact with 6 corner atoms in the same plane, 3 central atoms in a plane $c/2$ above it and 3 more central atoms in a plane $c/2$ below. The coordination number becomes,

$$6 + 3 + 3 = 12.$$

c/a ratio:

Let c be the height of the unit cell and a the distance between two neighbouring atoms. In the diagram, $\cos 30^\circ = AY/AB$

$$AY = AB \cos 30^\circ = a\sqrt{3}/2$$



$$\text{But } AX = \frac{2}{3}AY$$

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

$$\text{In triangle } AXZ, AZ^2 = AX^2 + ZX^2.$$

$$a^2 = (a/\sqrt{3})^2 + (c/2)^2$$

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

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

Packing factor

$$\text{Volume of all six atoms in the unit cell, } v = 6 \times \frac{4}{3}\pi r^3$$

$$\text{Atomic radius } r = a/2$$

$$v = \pi a^3$$

$$\text{Volume of the unit cell, } V = \frac{3\sqrt{3}a^2c}{2}$$

$$\text{A.P.F} = v/V$$

$$= \frac{\pi}{3\sqrt{2}} = 0.74$$

Miller Indices

Miller indices are defined as the three smallest possible integers which have the same ratio as the reciprocals of the intercepts of the plane concerned along the three axes.

Steps to determine the Miller indices

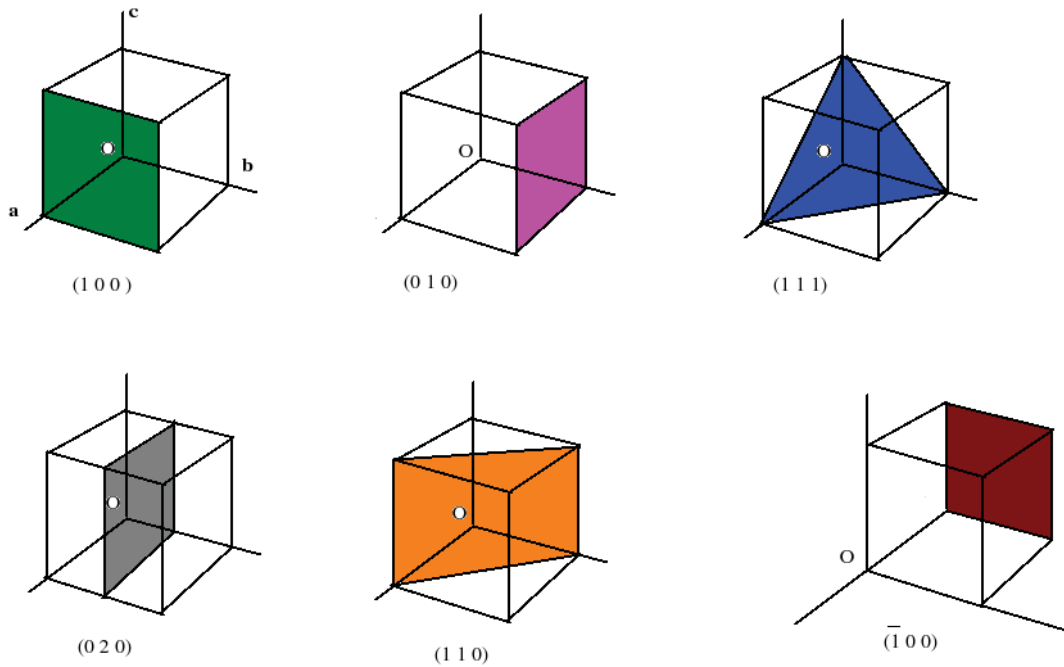
(i) Find the intercepts on the axes along the basis vector a , b , c in terms of the lattice constants a , b and c . The axes may be those of a primitive or nonprimitive cell.

Let these intercepts be x , y , z . We form the fractional triplet $\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right)$

(ii) Take the reciprocals of these numbers.

(iii) Reduce the numbers to three smallest integers by multiplying the numbers with the same integral multipliers.

This last set is enclosed in parentheses ($h\ k\ l$), is called the index of the plane or Miller Indices. The Miller indices specify not just one plane but an infinite set of equivalent planes. Note that for cubic crystals the direction $[hkl]$ is perpendicular to a plane (hkl) having the same indices, but this is not generally true for other crystal systems



Significance of Miller indices:

- Parallel planes have the same Miller indices.
- If a plane is parallel to any one of the coordinate axis, then its intercept will be at infinity and the Miller index for that particular axis is zero
- The plane passing through the origin has non-zero intercepts.
- If a plane cuts the axis on the negative side of the origin, then the corresponding Miller index will be negative.

Relation between interplanar spacing (d) and interatomic distance (a)

Let us consider a cubic crystal with a as length of the cube edge and a plane ABC as shown in figure. Let this plane belong to a family of planes whose Miller indices are (hkl) . The perpendicular OD from the origin of the cube to the plane ABC represents interplanar spacing (d).

The plane ABC makes OA, OB and OC as intercepts on the reference axes, OX, OY and OZ respectively. α , β , and γ are the angles between reference axes OX, OY, OZ and OD.

Miller indices are the smallest integers of the reciprocals of the intercepts. Therefore intercepts are

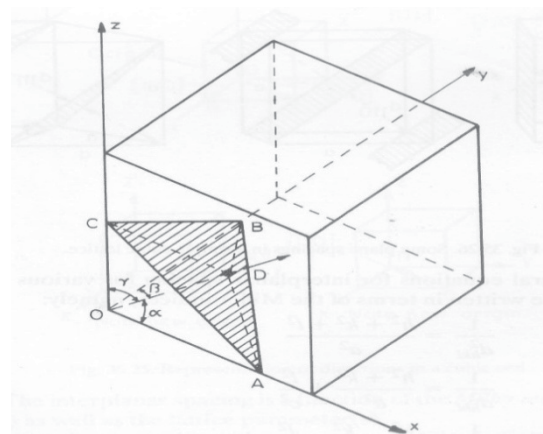


Fig. 35.27. Interplanar spacing in a cubic crystal.

expressed as Miller indices.

$$OA : OB : OC = 1/h : 1/k : 1/l = a/h : a/k : a/l$$

Therefore, $OA = a/h$; $OB = a/k$ and $OC = a/l$

From the geometry of right angles, OAD, OBD and OCD, we have

$$\cos \alpha = OD/OA = d/(a/h) = dh/a$$

Similarly,

$$\cos \beta = OD/OB = dk/a \text{ and } \cos \gamma = OD/OC = dl/a$$

According to the law of direction cosines

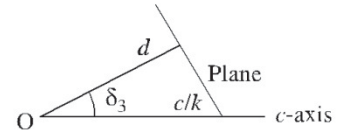
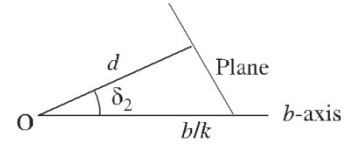
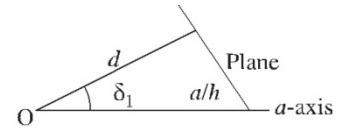
$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

Substituting the values, $(dh/a)^2 + (dk/a)^2 + (dl/a)^2 = 1$

$$d^2(h^2 + k^2 + l^2) = a^2$$

or

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



Diamond structure

Diamond structure is exhibited by carbon, Silicon and Germanium. It consists of two interpenetrating FCC lattices, displaced along the body diagonal of the cubic cell by $\frac{1}{4}$ th of the length of the diagonal. It is also regarded as an FCC lattice with two atoms per lattice site, one centered on the lattice site and the other at a distance of $a/4$ along all axes.

No of atoms per unit cell

Each corner atom is shared by 8 adjacent unit cells, therefore the contribution of the corner atoms is 1. ($8 \times 1/8 = 1$)

The contribution of each face centered atom to the unit cell is $\frac{1}{2}$. Therefore there are totally 3 face centered atoms in each unit cell.

Four atoms are present inside the unit cells which are shared by the particular unit cell alone.

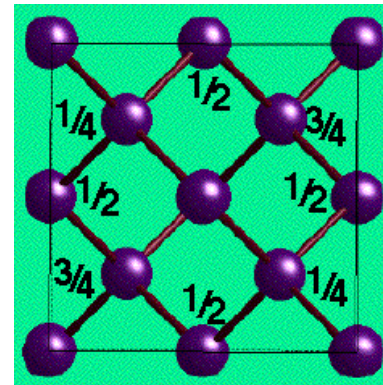
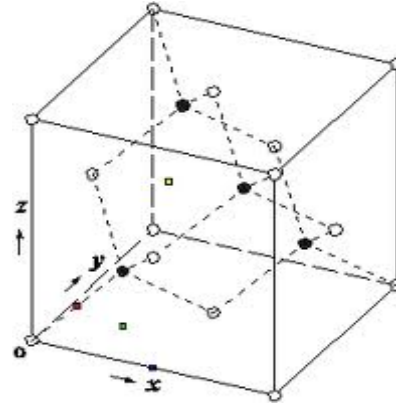
Hence the total number of atoms in the unit cell is $3 + 1 + 4 = 8$

Atomic radius

Both the face centered atoms and the corner atoms are in contact with the four central atoms. From figure, the nearest neighbours in direct contact are X and Y.

$$\begin{aligned}(XY)^2 &= (XZ)^2 + (ZY)^2 \\(XY)^2 &= [(XT)^2 + (TZ)^2] + (ZY)^2 \\&= [(a/4)^2 + (a/4)^2] + (a/4)^2 \\&= 3a^2/16 = 4r^2\end{aligned}$$

Atomic radius, $r = a\sqrt{3}/8$



Coordination number

The number of nearest atoms for the central atom is 4. Therefore, the coordination number for diamond is 4.

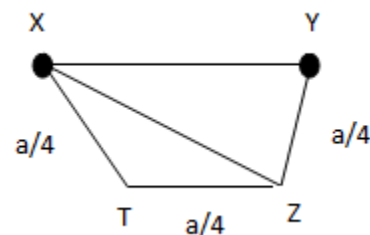
Atomic packing factor

APF = Volume occupied by the atoms per unit cell (v) / Volume of the unit cell (V)

$$\text{A.P.F} = \frac{8 \times \frac{4}{3} \pi r^3}{a^3}$$

$$r = a\sqrt{3}/8$$

$$a = 8r/\sqrt{3}$$



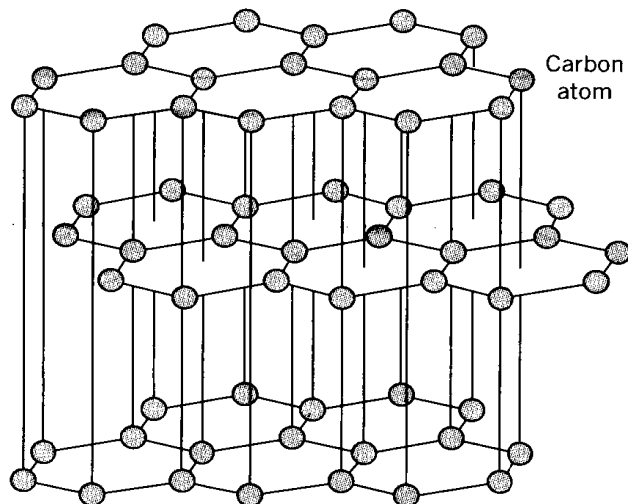
$$\text{A.P.F} = \frac{8 \times \frac{4}{3} \pi r^3}{\left(\frac{8\sqrt{3}}{\sqrt{2}}\right)^3}$$

$$\text{A.P.F} = \frac{\sqrt{3}\pi}{16} = 0.34$$

Structure of graphite

In graphite each carbon atom is covalently bonded to three carbon atoms to give trigonal geometry. Bond angle in graphite is 120° . Each carbon atom in graphite is sp^2 hybridized. Three out of four valence electrons of each carbon atom are used in bond formation with three other carbon atoms while the fourth electron is free to move in the structure of graphite.

Basic trigonal units unite together to give basic hexagonal ring. In hexagonal ring C-C bond length is 1.42\AA . In graphite these rings form flat layers. These layers are arranged in parallel, one above the other. These layers are 3.35\AA apart and are held together by weak vanderwaals forces only. These layers can slide over one another. Thus it is very soft.



Various crystal growing techniques

- Melt growth
- Low temperature solution growth
- High temperature solution growth (Flux growth)
- Epitaxial growth

Melt growth

Melt growth is a process of crystallization by fusion and resolidification of the starting materials.

Major practical factors to be considered during the growth of crystals from melt

- Volatility
- Chemical reactivity and
- Melting point

a) Czochralski method

The Czochralski method is a crystal pulling technique from the on a liquid-solid phase transition drive by a seed crystal in contact with the melt.

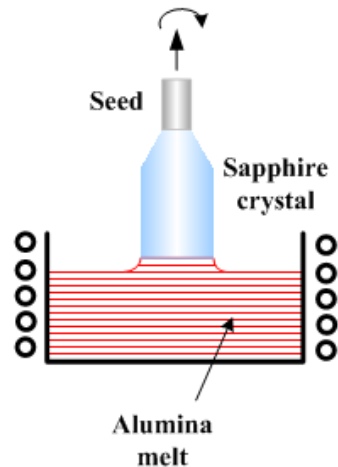
Czochralski method

Advantages of Czochralski method

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

Limitations of Czochralski method

- High vapor pressure materials
- Liquid phase encapsulation.
- Possible contamination of the melt by the crucible.
- No reproductivity of the crystal shape.



b) Bridgman technique

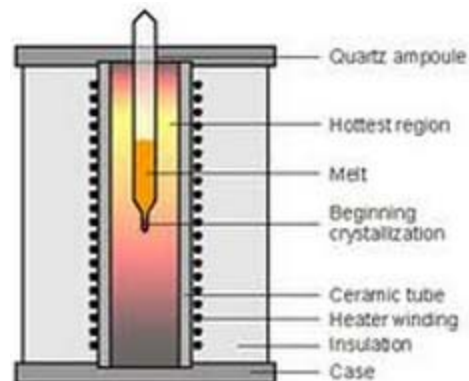
A common technique of growing single crystals involves selective cooling from the molten materials, so that solidification occurs along the crystal direction. In this technique, the melt in a sealed crucible is progressively frozen from one end.

Advantages of Bridgman technique

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

Limitations of Bridgman technique

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



Solution growth – Slow evaporation method

In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. This is simple and convenient method of growing single crystals of large size.

- Growth of strain and dislocation free crystals.
- Permits the growth of prismatic crystals by varying the growth conditions.

- Only method which can be used for substances that undergo decomposition before melting.
- A variable rate of evaporation may affect the quality of the crystal.

Epitaxial growth

The process of growing an oriented single crystal layer on a substrate wafer is called epitaxial growth. This method is mainly used in the manufacture of LED's and detectors.

Different types of epitaxial growth

- Vapour Phase Epitaxy (VPE)
- Liquid Phase Epitaxy (LPE)
- Molecular Beam Epitaxy (MBE)

Vapour phase epitaxy

In this method, material is grown in the form of thin crystalline layer by sublimation process, followed by condensation. The material is taken to the vapour state and then allowed to impinge on the substrate (by using suitable carrier gas) maintained at relatively lower temperature.