

# 2

## Crystal Geometry

---

### Contents

2.1	Introduction .....	2.2
2.2	Unit Cell and its Lattice Parameters .....	2.2
2.3	Bravais Lattices .....	2.3
2.4	Coordination Number .....	2.6
2.5	Crystal Structure of Metals.....	2.7
2.6	Crystallography Planes and Directions (Miller Indices) .....	2.10
2.7	Polymorphism and Allotropy .....	2.13
2.8	Diffusion in Solids .....	2.14
2.9	Crystallization.....	2.15
2.10	Mechanism of Crystallization.....	2.15
2.11	Nucleation .....	2.16
2.12	Crystal Growth .....	2.16
2.13	Imperfection in Crystals .....	2.17
2.14	References .....	2.17

## 2.1 Introduction

- ▶ Crystallography is the study of the crystal formation of solids, including:
    - X-ray determination of lattice structures, Crystal habit, (i.e. the form of a crystal), The shape and defects of crystals. When applied to metals, this science is called metallography.
  - ▶ Crystallography is that branch of science in which the internal structure of crystals, their properties, external or internal symmetries of crystals are studied.
  - ▶ Crystalline materials consist of atoms or molecules arranged in a regular and orderly manner in a three-dimensional pattern.
  - ▶ The various terms associated with crystallography are:
    1. Crystal
    2. Structure
    3. Space lattice
    4. Unit cell
    5. Crystallographic planes
    6. Lattice parameter
    7. Miller indices
    8. Atomic packing factor
    9. Coordinate number, etc.
1. A Crystal is a solid whose constituent atoms or molecules are arranged in a systematic geometric pattern.
  2. The structure implies the arrangement and disposition of the atoms within a crystal.
  3. The atoms arrange themselves in distinct pattern in space called a space lattice.
  4. The unit cell is the smallest group of atoms possessing the symmetry of the crystal.
  5. The layers of atoms or the planes along which atoms are arranged are known as atomic or crystallographic planes.
  6. Characteristic intercepts and interfacial angles of a crystal constitute the lattice parameters of a cell.
  7. Miller Indices is a system of notation for designating crystallographic planes and directions of crystals.
  8. Atomic packing factor is the ratio of the volume of the atoms per unit cell to the total volume occupied by the unit cell.
  9. Coordinate number is the number of nearest atoms directly surrounding a given atom in a crystal i.e., nearest neighbours to an atom in crystal.

## 2.2 Unit Cell and its Lattice Parameters

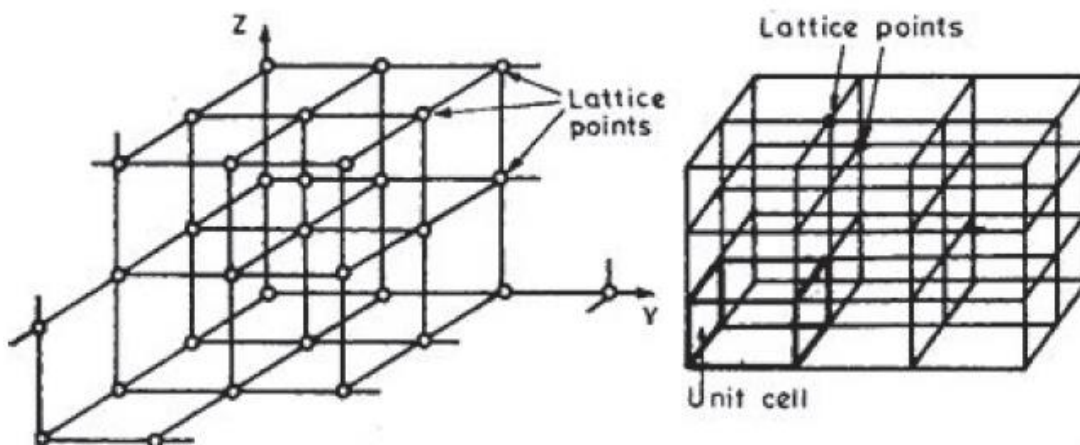


Fig.2.1 – Unit cell and lattice parameter

- ▶ Lattice is the regular geometrical arrangement of points in crystalspace.
- ▶ The atoms arrange themselves in distinct pattern; in space, called a space lattice.
- ▶ Space lattice is the three dimensional network of imaginary lines connecting the atoms.

- ▶ A Space lattice can be considered as an infinite array of points in space, so arranged that it divides space into equal volumes with no space excluded.
- ▶ An important characteristic of a space lattice is that every point has identical surroundings.
- ▶ Space lattice or crystal lattice is the arrangement of atoms in a crystal.
- ▶ As already explained above, a space lattice can be considered as an infinite array of points in space, so arranged that it divides space into equal volumes with no space excluded. Every point, which is called a lattice point, has identical surroundings with every other point.
- ▶ The smallest volume that contains the full pattern of repetition is called a unit cell.
- ▶ Identical unit cells must completely fill the space when they are packed face to face, thus generating a space lattice. If a unit cell is so chosen that it contains lattice points only at its corners, it is called a primitive unit cell or simple unit cell.
- ▶ A primitive unit cell contains only one lattice point because each point at eight corners is shared equally with eight adjacent unit cells. The edge length of the unit cell, called a lattice constant or a lattice parameter, is a lattice translation in a given direction. Simple monoclinic, Triclinic, simple cubic are known as primitive cells. Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces.
- ▶ Fig. shows the unit cell geometry, which is, the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell.
- ▶ Within this framework, an x, y, z coordinate system is established with its origin at one of the unit cell corners; each of the x, y, and z axis coincide with one of the three parallelepiped edges that extend from this corner, as illustrated in Fig.

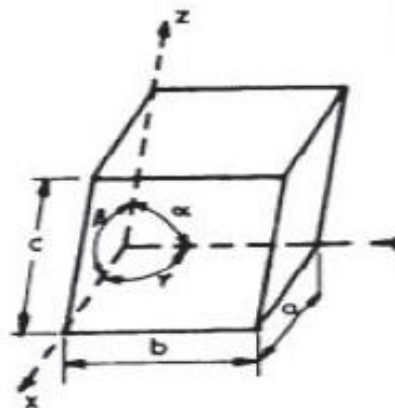


Fig.2.2 – Description A unit cell with x, y and z coordinate axis, showing axial lengths (a, b, and c) and  $\alpha, \beta$  and  $\gamma$

- ▶ The unit cell geometry is completely defined in terms of six parameters: the three edge length a, b, and c and three interaxial angles  $\alpha, \beta$  and  $\gamma$ . These are indicated in Fig. and are sometimes termed the Lattice Parameters of a crystal structure.
- ▶ On this basis, there are found crystals having seven different possible combinations of a, b, and  $\alpha, \beta$  and  $\gamma$ . Each of which represents a distinct function of crystal system.

## 2.3 Bravais Lattices

- ▶ Bravais lattices are the fourteen basic crystal lattices.
- ▶ Bravais showed that there are only fourteen possible different networks of lattice points

- ▶ Therefore, there are only 14 standard space lattices (Fig. 35.9) that are needed to describe all possible arrangements of points in space consistent with translational periodicity. Every crystal structure is based on one of the possible space lattices.
- ▶ There are only 14 independent ways of arranging points in three dimensions in a crystal.
- ▶ Bravais lattices named after their originator Mr. Bravais, are the 14 distinguishable three-dimensional space lattices that can be generated by repeated translation of three non-coplanar vectors  $a$ ,  $b$ , and  $c$  of a unit cell in three-dimensional space.
- ▶ Seven sets of the axis, are needed to construct the fourteen Bravais lattice. Accordingly, all crystalline solids can be classified into 7 crystal systems.
- ▶ The fourteen Bravais lattices continue in three dimensions. Each indicated point has identical surroundings.
- ▶ The fourteen Bravais lattices are explained below:

### 1. Simple Monoclinic Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a \neq b \neq c$  and interaxial angle  $\alpha = \gamma = 90 \neq \beta$

### 2. End Centered Monoclinic Lattice

- ▶ It has lattice points at the eight corners and at two face centers, opposite to each other. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = 90 \neq \gamma$ .

### 3. Triclinic Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha \neq \beta \neq 90 \neq \gamma$ .

### 4. Hexagonal Lattice

- ▶ It has pointed at the twelve corners of the hexagonal prism and at the centers of the two hexagonal faces of the unit cell. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = 90$  and  $\gamma = 120$ .

### 5. Rhombohedral Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a = b = c$  and an interaxial angle.  $\alpha = \beta = \gamma \neq 90$

### 6. Simple Orthorhombic Lattice

- ▶ It has lattice points at the eight corners of the unit. Cell. It has vectors  $a \neq b \neq c$  and interaxial angle  $\alpha = \beta = \gamma = 90$

### 7. Body-Centered Orthorhombic Lattice

- ▶ It has lattice points at the eight corners and at the body center. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90$ .

### 8. End-Centered Orthorhombic Lattice

- ▶ It has lattice points at the eight corners and at two face centers opposite to each other. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90$ .

## 9. Face Centered Orthorhombic Lattice

- ▶ It has lattice points at the eight corners and at the six face centers of the unit cell. It has vectors  $a \neq b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 10. Simple Cubic Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a = b = c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 11. Body-Centered Cubic Lattice

- ▶ It has lattice points at the eight corners and at the body center. It has vectors  $a = b = c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 12. Face Centered Cubic Lattice

- ▶ It has lattice points at the eight corners and at the face centers of the unit cell. It has vectors  $a = b = c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 13. Simple Tetragonal Lattice

- ▶ It has lattice points at the eight corners of the unit cell. It has vectors  $a = b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

## 14. Body-Centered Tetragonal Lattice

- ▶ It has lattice points at the eight corners and at the body center. It has vectors  $a = b \neq c$  and an interaxial angle  $\alpha = \beta = \gamma = 90^\circ$ .

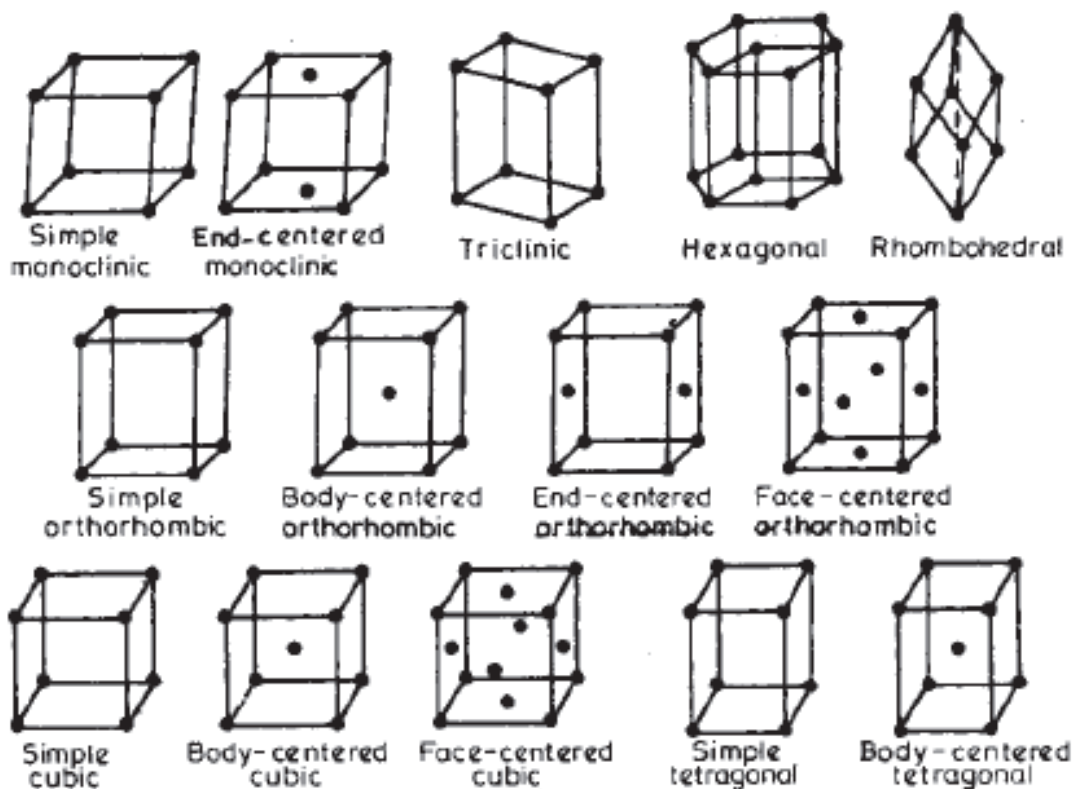


Fig.2.3 - Bravais Lattice

## 2.4 Coordination Number

- ▶ Every atom in a crystal is surrounded by other atoms. By the term coordination number, we mean the number of nearest atoms that are directly surrounding a given atom.
- ▶ The coordination number may also be defined as the nearest neighbors to an atom in a crystal.
- ▶ Fig 2.3 shows that the coordination number of carbon atom is four because it has four hydrogen atoms around it.
- ▶ When the coordination number is larger, the structure is more closely packed.
- ▶ Coordination numbers for a simple cubic, BCC and FCC lattice have been discussed below:

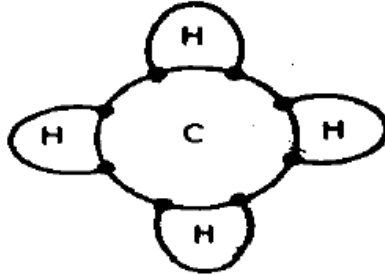


Fig.2.4 - Coordination number

### 1. Simple Cubic Structure

- ▶ There is one atom at each of the (eight) corners of the cube. Any corner atom has four nearest-neighbor atoms in the same plane and two nearest neighbors (one exactly above and other exactly below) in a vertical plane.
- ▶ Hence coordination number for simple cubic structure is  $4 + 2 = 6$ .

### 2. Body-Centered Cubic (B.C.C.) Structure

- ▶ In the B.C.C. structure, there is one atom at each corner of the cube and one atom at the center of the cube. For any corner atom of the unit cell, the nearest atoms are the atoms that are at the centers of unit cells.
- ▶ As such a corner atom is surrounded by eight unit cells having eight body-centered atoms, hence the coordination number is 8.
- ▶ Similarly, by considering the central atom of each unit cell, we can say that the coordination number is 8 because every centered atom is surrounded by eight equidistant neighbors.
- ▶ Hence, the coordination number for the B.C.C. structure is 8.

### 3. Face-centred Cubic (F.C.C.) Structure

- ▶ In the F.C.C. structure, there is one atom at each corner of the cube and one atom at the center of each face of the cube.
- ▶ For any corner atom of the unit cell, the nearest is the face-centered atoms.
- ▶ For any corner atom, there will be 4 face-centered atoms of the surrounding unit cells in its own plane, 4 face-centered atoms below this plane and 4 face-centered atoms above this plane.
- ▶ Hence the coordination number for this case is  $4 + 4 + 4 = 12$

## 2.5 Crystal Structure of Metals

### 1. Body-Centered Cubic (B.C.C.)

If the atoms are represented as spheres, the center atom touches each corner atom but they do not touch each other. Since each corner atom is shared by eight adjoining cubes and the atom in the center cannot be shared by any other cubes.

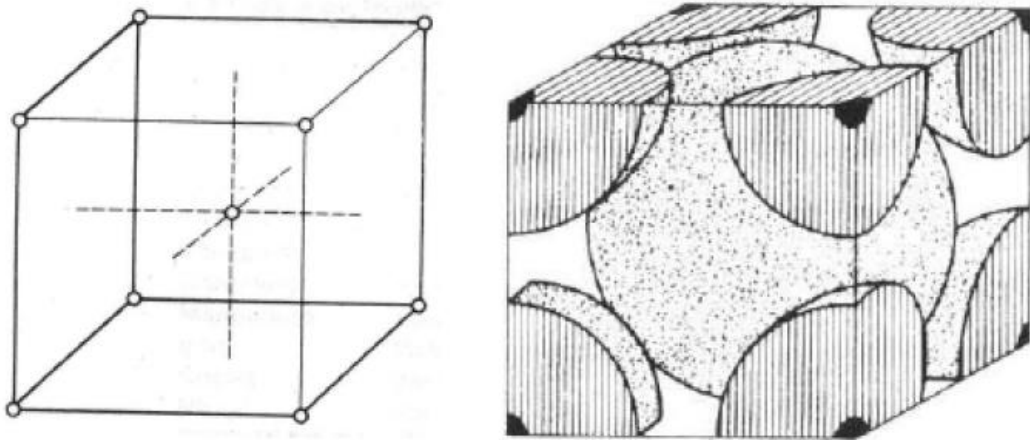


Fig.2.5 –Unit Cell Of B.C.C. Structure

The unit cell of the B.C.C. structure contains.

$$8 \text{ atom at the corner} \times \frac{1}{8} = 1 \text{ Atom}$$

$$1 \text{ center atom} = 1 \text{ Atom}$$

$$\text{Total} = 2 \text{ Atom}$$

### 2. Face Centered Cubic (F.C.C.)

In addition to an atom at each corner of the cube, there is one in the center of each face but none in the center of the cube. Each face atom touches its nearest corner atom. Since each corner atom is shared by eight adjoining cubes and each face is shared by only one adjacent cube.

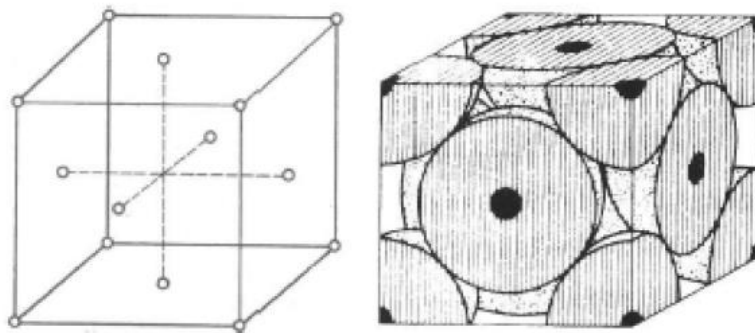


Fig.2.6 –Unit cell of F.C.C. structure

$$8 \text{ atom at the corner} \times \frac{1}{8} = 1 \text{ Atom}$$

$$6 \text{ Face-centered Atom} \times \frac{1}{2} = 3 \text{ Atom}$$

$$\text{Total} = 4 \text{ Atom}$$

This indicates that the F.C.C. structure is more densely packed than the B.C.C. structure.

Example: Aluminum, Nikle, Copper, Gold, Silver, Lead, Platinum, Gamma Iron

### 3. Close Packed Hexagonal (H.C.P.)

C.P.H. shows two based planes in the form of regular hexagons with atoms at each corner of the hexagon and one atom at the center. In addition, there are three atoms in the term of a triangle midway between the two based plane. If the based plane is divided into six equilateral triangles, the additional 3 atoms are nested in the center of an alternate equilateral triangle.

Unit cell of BCC & FCC can be specified by the lattice parameter 'a'. The hexagonal unit cell required with

hexagonal 'a' and distance between base plane 'c'. this determines the axial ratio cross-section  $\left(\frac{c}{a}\right)$ . The axial

ratio varies from 1.58 for beryllium to 1.88 cadmium.

The atomic packing factor is 0.74.

Example: Zinc, Cadmium, Beryllium, magnesium.

No. of atoms in H.C.P.

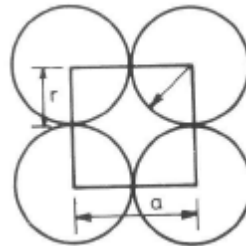
$$\begin{aligned} N &= \frac{N_c}{6} + \frac{N_F}{2} + \frac{N_i}{1} = \frac{12}{6} + \frac{2}{2} + \frac{3}{1} \\ &= 2 + 1 + 3 \\ &= 6 \end{aligned}$$

### Atomic Radius

Assume that atoms are spherical in space and are in contact in a crystal. Atomic radius can be designed as half the distance between the centers of two neighboring atoms.

The atomic radius of simple cubic structure 'a' is the lattice parameter

$$\text{Here, } a = 2r \quad r = \frac{a}{2}$$



### 1. Atomic Radius of F.C.C. Structure

Here a = Lattice parameter

r = Atomic radius

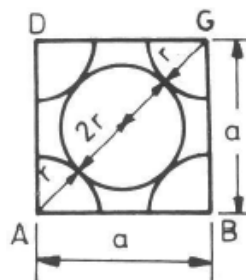
$$AC^2 = AB^2 = BC^2$$

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

$$16r^2 = 2a^2$$

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

□



### 2. Atomic Radius of B.C.C. Structure

Let a = Lattice parameter

r = Atomic Radius



Let, Here

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

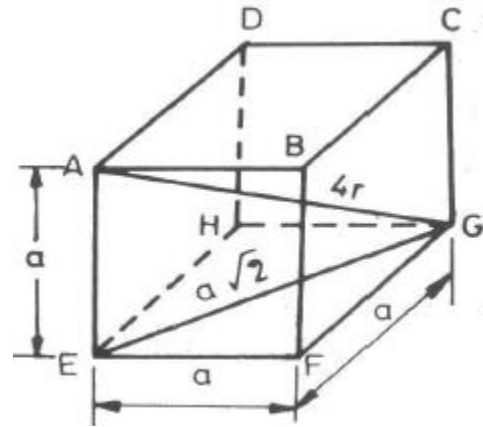
$$\text{Let } EG^2 = a^2 + a^2 = 2a^2$$

$$AG^2 = AE^2 + EG^2$$

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

$$16r^2 = 3a^2$$

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



## Atomic Packing Factor (APF)

### 1. APF For The Simple Cubic Structure

$$APF = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \text{or } a = 2r$$

$$APF = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{8a^3} \right) = 0.52$$

$$APF = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \text{or } a = 2r$$

$$APF = 1 \times \left( \frac{\frac{4}{3} \pi r^3}{8a^3} \right) = 0.52$$

### 2. APF For F.C.C. Structure

$$APF = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 4 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \frac{a\sqrt{2}}{4}$$

$$APF = 4 \times \left( \frac{\frac{4}{3} \pi \left( \frac{a\sqrt{2}}{4} \right)^3}{a^3} \right)$$

$$APF = 4 \times \left( \frac{\frac{4}{3} \pi a^3 \times 2\sqrt{2}}{a^3 \times 64} \right)$$

$$= 0.74$$

### 3. APF For B.C.C. Structure

$$\text{APF} = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 2 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \frac{a\sqrt{3}}{4}$$

$$\text{APF} = 2 \times \left( \frac{\frac{4}{3} \pi \left( \frac{a\sqrt{3}}{4} \right)^3}{a^3} \right)$$

$$\text{APF} = 2 \times \left( \frac{\frac{4}{3} \pi a^3 \times 3\sqrt{3}}{a^3 \times 64} \right)$$

$$= 0.74$$

$$\text{APF} = \frac{V_{\text{atom}}}{V_{\text{cell}}} = 2 \times \left( \frac{\frac{4}{3} \pi r^3}{a^3} \right) \quad \text{Put } r = \frac{a\sqrt{3}}{4}$$

$$\text{APF} = 2 \times \left( \frac{\frac{4}{3} \pi \left( \frac{a\sqrt{3}}{4} \right)^3}{a^3} \right)$$

$$\text{APF} = 2 \times \left( \frac{\frac{4}{3} \pi a^3 \times 3\sqrt{3}}{a^3 \times 64} \right)$$

$$= 0.74$$

## 2.6 Crystallography Planes and Directions (Miller Indices)

- ▶ The layers of atoms or the planes along which atoms are arranged are known as atomic or crystallographic planes.
- ▶ As one becomes more and more involved in the study of crystals, the need for symbols to describe the orientation in space, of important crystallographic planes and directions becomes evident.
- ▶ The Miller system of designating indices for crystallographic planes and directions is universally accepted for the purpose.
- ▶ Miller index is a system of notation that denotes the orientation of the faces of a crystal and the planes and directions of atoms within that crystal.

### Miller Indices for Planes

- ▶ One corner of the unit cell is assumed to be the origin (O) of the space coordinates, then find the intercepts on the three-axis in multiples or fractions of the unit distances on each axis (if a plane is parallel to, an axis it intersects it at infinity).
- ▶ For example, consider a plane ABC. It intersects .Y-axis at 1 unit, Y-axis at 3 units and Z-axis at 2 units from origin O.
- ▶ With this fill in the first (i) line of Table (ii) Take the reciprocal of these numbers; see (ii) line of Table

	X	Y	Z	
Intersection	1	3	2	...(i)
Reciprocal	$\frac{1}{1}$	$\frac{1}{3}$	$\frac{1}{2}$	...(ii)
		(3 × 2 = 6)		
	$\frac{1}{1} \times 6$	$\frac{1}{3} \times 6$	$\frac{1}{2} \times 6$	
Miller indices	6	2	3	...(iii)
	(623)			

Fig.2.7 – Miller indices of a plane

- ▶ (ii) Take the reciprocal of these numbers; see (ii) line of Table (iii) Change these reciprocals to the smallest integers having the same ratio, i.e., by multiplying each reciprocal (or fraction) by the same number such as the common denominator. Refer line (III) of Table (iv) Enclose the values in parenthesis Figs. (b), (c), (d) and (e) show a number of crystallographic planes and their miller indices in a cubic lattice.
- ▶ If a plane cuts any axis on the negative side of the origin, the index will be negative and is indicated by placing a minus sign above the index, as For example, the miller indices of plane ODEF which goes through the origin (O) cannot be determined without changing the location of the origin. Change the origin from point O to point P. The plane ODEF intersects X-axis and Z-axis at infinity but intersects Y-axis at -1. The plane has, therefore, miller indices at (010).

### Miller Indices for Directions

- ▶ The crystallographic direction can be defined as a line joining any two points of the lattice. For example, in Fig. 2.7 (a) OQ OD and OE are all crystallographic directions. Direction indices are simply the vector components of the directions resolved along each of the axes.
- ▶ Consider direction OE The point E lies in the plane OEFG. OE is 1 unit along X-axis, it neither intercepts Y-axis nor Z-axis. Thus the coordinates of point E and the miller indices of direction OE is [100] (x = 1, y = 0, z = 0).
- ▶ Similarly line OC, passes through the origin and the point C having coordinates x = 0, y = 0, z = 1; and thus the miller indices are [011]. Based on the same reasoning, the indices of OD is [111]. A general rule for finding the Miller indices of a crystallographic direction is:
- ▶ Draw a vector from origin parallel to the direction whose indices are desired. For example, if indices of AE are desired, draw a line OH parallel to AE through origin O. Draw CE in the downward direction (dotted), let it cut OH at I and then draw IJ parallel to X-axis to cut Z-axis.
- ▶ Now OI is the line that passes through the origin and is parallel to EA whose indices are to be determined. The point I have coordinates x =1, y =0,z = -1 and thus the indices of line EA is [101] (Parallel lines have the same indices)

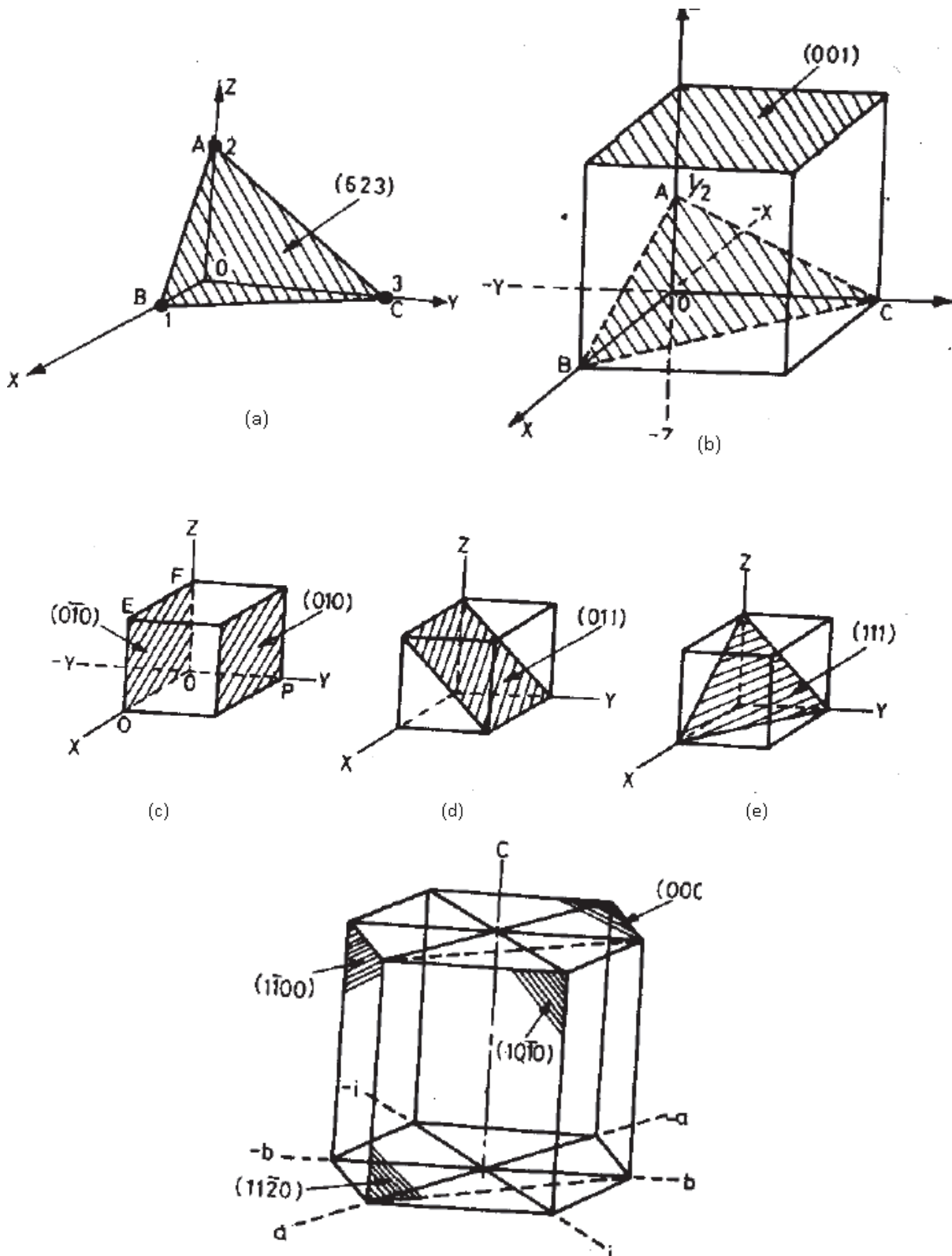


Fig.2.8 – (a) Miller Indices

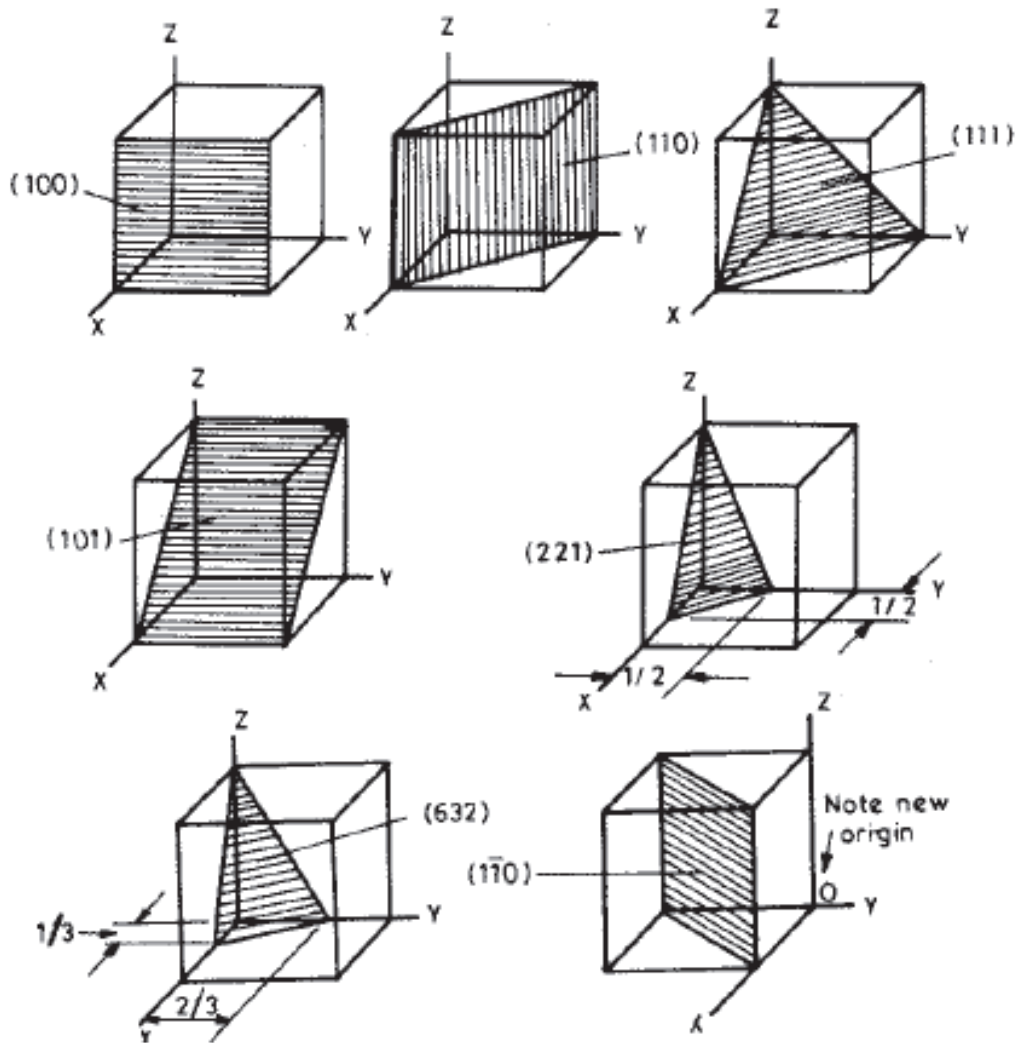


Fig.2.9 – (b) Miller Indices

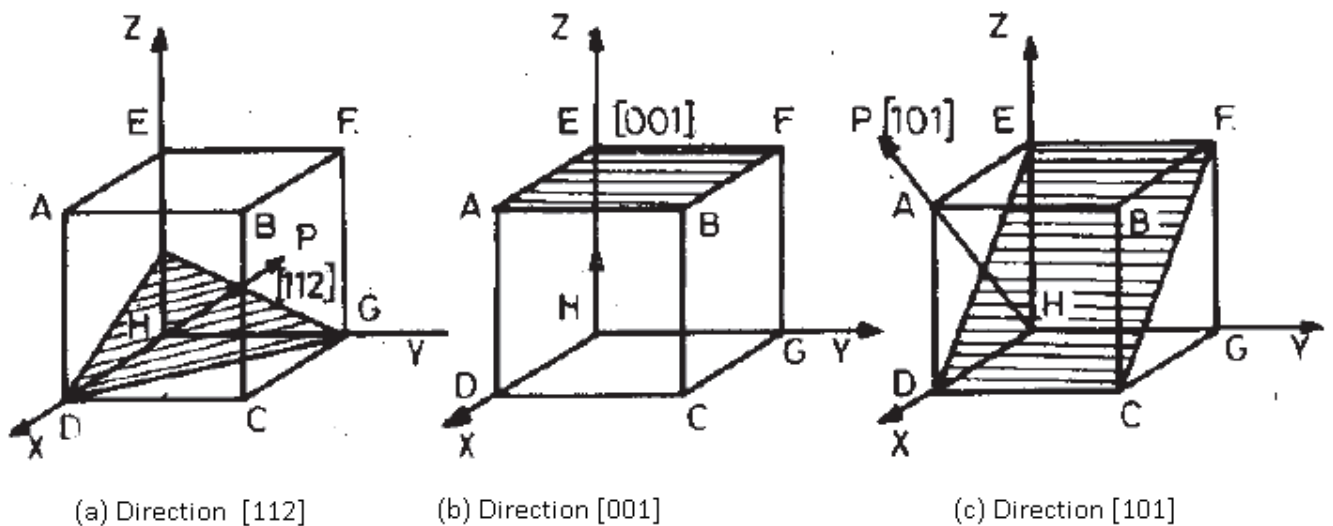


Fig.2.10 – (c) Miller Indices

## 2.7 Polymorphism and Allotropy

- The ability of the material to have more than one structure is called polymorphism.

- ▶ It is the behavior of material to show different crystal structures at a certain temperature or within a temperature range.
- ▶ The atomic arrangement may change according to change in temperature such a change in the crystal structure is called polymorphic change.
- ▶ If the change in the crystal structure is reversible then polymorphic change is known as allotropy.
- ▶ For example, iron ( $\alpha$ -Fe) is BCC at room temperature but it becomes FCC ( $\gamma$ -Fe) when heated to above 910°C.
- ▶ On further heating, to above 1400°C it revered to BCC ( $\delta$ -Fe)
- ▶ These changes are reversed on cooling hence iron changes its structure by allotropic change.

## 2.8 Diffusion in Solids

---

- ▶ Diffusion refers to the transport of atoms through a crystalline or glassy solid. Many processes occurring in metals and alloys, especially at elevated temperatures, are associated with self-diffusion or diffusion.
- ▶ Diffusion processes play a crucial role in many solid-state phenomena and in the kinetics of microstructural changes during metallurgical processing and applications; typical examples include phase transformations, nucleation, recrystallization, oxidation, creep, sintering, ionic conductivity, and intermixing in thin-film devices.
- ▶ Direct technological uses of diffusion include solid electrolytes for advanced battery and fuel cell applications, the semiconductor chip and microcircuit fabrication and surface hardening of steels through carburization. The knowledge of the diffusion phenomenon is essential for the introduction of a very small concentration of an impurity in a solid-state device.

### Types of Diffusion

- i. Self Diffusion: It is the transition of a thermally excited atom from a site of the crystal lattice to an adjacent site or interstice.
- ii. Inter Diffusion: This is observed in binary metal alloys such as the Cu-Ni system.
- iii. Volume Diffusion: This type of diffusion is caused due to atomic movement in bulk in materials.
- iv. Grain Boundary Diffusion: This type of diffusion is caused due to atomic movement along the grain boundaries alone.
- v. Surface Diffusion: This type of diffusion is caused due to atomic movement along the surface of a phase.

### Diffusion Mechanism

- ▶ Diffusion is the transfer of unlike atoms which is accompanied by a change of concentration of the components in certain zones of an alloy. Various mechanisms have been proposed to explain the processes of diffusion. Almost all of these mechanisms are based on the vibrational energy of atoms in a solid.
- ▶ Direct interchange, cyclic, interstitial, vacancy, etc. are the common diffusion mechanisms. Actually, however, the most probable mechanism of diffusion is that in which the magnitude of energy barrier (activation energy) to be overcome by moving atoms is the lowest.
- ▶ Activation energy depends on the forces of interatomic bonds and crystal lattice defects which facilitate diffusion transfer (the activation energy at grain boundaries is only one half of that in the bulk of a grain). For metal atoms, the vacancy mechanism of diffusion is the most probable and for elements with a small atomic radius (H, N, and C), the interstitial mechanism. Now, we will study these mechanisms.
- ▶ Vacancy Mechanism: This mechanism is a very dominant process for diffusion in FCC, BCC and HCP metals and solid solution alloy. The activation energy for this process comprises the energy required to create a vacancy and that required to move it. In a pure solid, the diffusion by this mechanism is shown.
- ▶ Diffusion by the vacancy mechanism can occur by atoms moving into adjacent sites that are vacant. In a pure solid, during diffusion by this mechanism, the atoms surrounding the vacant site shift their

equilibrium positions to adjust for the change in a binding that accompanies the removal of a metal ion and its valency electron.

- ▶ We can assume that the vacancies move through the lattice and produce random shifts of atoms from one lattice position to another as a result of atom jumping. Concentration changes take place due to diffusion over a period of time. We must note that vacancies are continually being created and destroyed at the surface, grain boundaries and suitable interior positions, e.g. dislocations. Obviously, the rate of diffusion increases rapidly with increasing temperature.
- ▶ If a solid is composed of a single element, i.e. pure metal, the movement of a thermally excited atom from a site of the crystal lattice to an adjacent site or interstice is called self-diffusion because the moving atom and the solid are the same chemical-element.
- ▶ The self-diffusion in metals in which atoms of the metal itself migrate in a random fashion throughout the lattice occurs mainly through this mechanism. We know that copper and nickel are mutually soluble in all proportions in solid-state and form substitutional solid solutions, e.g., plating of nickel on copper excited atom from a site of the crystal lattice to an adjacent site or interstice is called self-diffusion because the moving atom and the solid are the same chemical-element. The self-diffusion in metals in which atoms of the metal itself migrate in a random fashion throughout the lattice occurs mainly through this mechanism.

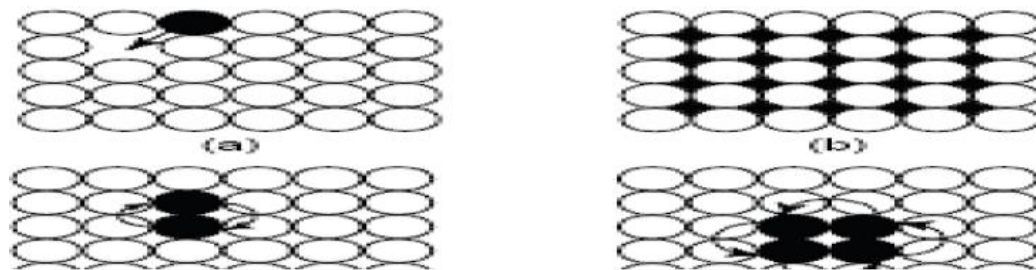


Fig.2.11 – Diffusion

## 2.9 Crystallization

- ▶ Crystallization is the (natural or artificial) process of formation of which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. In chemical engineering, crystallization occurs in a crystallizer. Crystallization is, therefore, an aspect of precipitation, obtained through a variation of the solubility conditions of the solute in the solvent, as compared to precipitation due to chemical reaction.

## 2.10 Mechanism of Crystallization

- ▶ The crystallization process consists of two major events, nucleation and crystal growth. Nucleation is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (elevating solute concentration in a small region), that become stable under the current operating conditions.
- ▶ These stable clusters constitute the nuclei. However, when the clusters are not stable, they dissolve. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Such critical size is dictated by the operating conditions (temperature, supersaturation, etc.). It is at the stage of nucleation that the atoms arranged in a defined and periodic manner that defines the crystal structure □ note that "crystal structure" is a special term that refers to the relative arrangement of the atoms, not the macroscopic properties of the crystal (size and shape), although those are a result of the internal crystal structure.
- ▶ The crystal growth is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while the supersaturation exists.

- ▶ Supersaturation is the driving force of the crystallization, hence the rate of nucleation and growth is driven by the existing supersaturation in the solution. Depending upon the conditions, either nucleation or growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained (control of crystal size and shape constitutes one of the main challenges in industrial manufacturing, such as for pharmaceuticals).
- ▶ Once the supersaturation is exhausted, the solid-liquid system reaches equilibrium and the crystallization is complete unless the operating conditions are modified from equilibrium so as to supersaturate the solution again.
- ▶ Many compounds have the ability to crystallize with different crystal structures, a phenomenon called polymorphism. Each polymorph is, in fact, a different thermodynamic solid state and crystal polymorphs of the same compound exhibit different physical properties, such as dissolution rate, shape (angles between facets and facet growth rates), melting point, etc. For this reason, polymorphism is of major importance in the industrial manufacture of crystalline products.

## 2.11 Nucleation

---

- ▶ It is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organization. Nucleation is typically defined to be the process that determines how long we have to wait before the new phase or self-organized structure, appears.
- ▶ Nucleation is often found to be very sensitive to impurities in the system. Because of this, it is often important to distinguish between heterogeneous nucleation and homogeneous nucleation. Heterogeneous nucleation occurs at nucleation sites on surfaces in the system. Homogeneous nucleation occurs away from a surface.
- ▶ Nucleation the initial process that occurs in the formation of a crystal from a solution, a liquid, or a vapor, in which a small number of ions, atoms, or molecules become arranged in a pattern characteristic of a crystalline solid, forming a site upon which additional particles are deposited as the crystal grows.
- ▶ Nucleation processes are classed as heterogeneous or homogeneous. In the former, the surface of some different substance, such as a dust particle or the wall of the container, acts as the center upon which the first atoms, ions, or molecules of the crystal become properly oriented; in the latter, a few particles come into correct position in the course of their random movement through the bulk of the medium.
- ▶ Heterogeneous nucleation is more common, but the homogeneous mechanism becomes more likely as the degree of supersaturation or supercooling increases. Substances differ widely in the likelihood that they will crystallize under conditions in which the crystalline state is the inherently stable one; glycerol is a well-known example of a compound prone to supercooling.

## 2.12 Crystal Growth

---

- ▶ Once the first small crystal, the nucleus, forms acts as a convergence point (if unstable due to supersaturation) for molecules of solute touching or adjacent to the crystal so that it increases its own dimension in successive layers.
- ▶ The pattern of growth resembles the rings of an onion, as shown in the picture, where each color indicates the same mass of solute; this mass creates increasingly thin layers due to the increased surface area of the growing crystal.
- ▶ The supersaturated solute mass the original nucleus may capture in a time unit is called the growth rate and is a constant specific to the process. The growth rate is influenced by several physical factors, such as surface tension of the solution, pressure, temperature, relative crystal velocity in the solution, Reynolds number, and so forth.



### **The main values to control are, therefore**

- ▶ Supersaturation value, as an index of the quantity of solute available for the growth of the crystal.
- ▶ Total crystal surface in-unit fluid mass, as an index of the capability of the solute to fix onto the crystal.
- ▶ Retention time, as an index of the probability of a molecule of solute to come into contact with an existing crystal.
- ▶ Flow pattern, again as an index of the probability of a molecule of solute to come into contact with an existing crystal (higher in laminar flow, lower in turbulent flow, but the reverse applies to the probability of contact).
- ▶ The first value is a consequence of the physical characteristics of the solution, while the other define a difference between a well and poorly designed crystallizer.

## **2.13 Imperfection in Crystals**

---

- ▶ For a crystalline solid we have tacitly assumed that perfect order exists throughout the material on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various defects or imperfections.
- ▶ As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection; the influence is not always adverse, and often specific characteristics are deliberately fashioned by the introduction of meant a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to geometry or dimensionality of the defect.

### **Point Defects In Metals**

- ▶ The simplest of the point defects is a vacancy, or vacant lattice site, one normally occupied from which an atom is missing. All crystalline solids contain vacancies and, in fact, it is not possible to create such a material that is free of these defects.
- ▶ The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal.

## **2.14 References**

---

Sidney H Avner ” Introduction to Physical metallurgy 2<sup>nd</sup> Edition 2011 Tata Mc Graw- Hill Publication.

O. P. Khanna “Material Science and Metallurgy” Dhanpat Rai Publications.