

Unit I Crystal Physics

Introduction

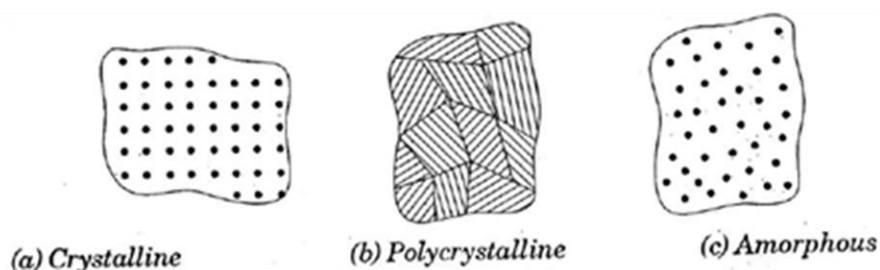
The matter is usually regarded to exist in solid state or fluid state. All the materials are composed of atoms and molecules. A solid is an essentially an ordered array of atoms, bound together by electric forces to form a very large molecule. There are three different types of solids. Crystalline, poly crystalline and amorphous.

In a crystal, atoms are arranged into a regular periodically repeated structure that extends throughout the whole sample. The atoms are said to have long range order. Poly crystalline material is composed of many small crystals or grains of somewhat irregular size. In an amorphous solid a long range order is absent. (i.e.,) they have short range order. There is no periodicity in which atoms are arranged in space. They are also regarded as super cooled liquids.

Examples : metallic crystals : copper, silver, aluminum etc.,

Non metallic crystals: Germanium, silicon

Amorphous or non crystalline materials: glass, rubber, plastic



Difference between crystalline and amorphous material.

S.No	Crystalline	Amorphous
1	Regular arrangement of atoms gives definite and geometric shape.	Random arrangement of atoms does not give definite and Geometrical shape.
2	They are anisotropic	They are isotropic
3	They have sharp Melting Point	They do not have sharp Melting Point
4	They possess internal symmetry	They do not possess internal symmetry

Crystal Physics or **Crystallography** is a branch of physics that deals with the study of all possible types of crystals and the physical properties of crystalline solids by the determination of their actual structure by using X-rays, neutron beams and electron beams.

CLASSIFICATION OF SOLIDS

Solids can broadly be classified into two types based on the arrangement of units of matter.

The units of matter may be atoms, molecules or ions.

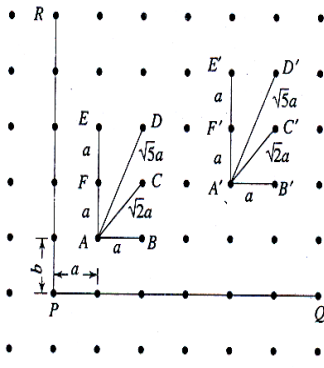
They are,

- Crystalline solids and

- Non-crystalline (or) Amorphous solids

CRYSTALLINE SOLIDS

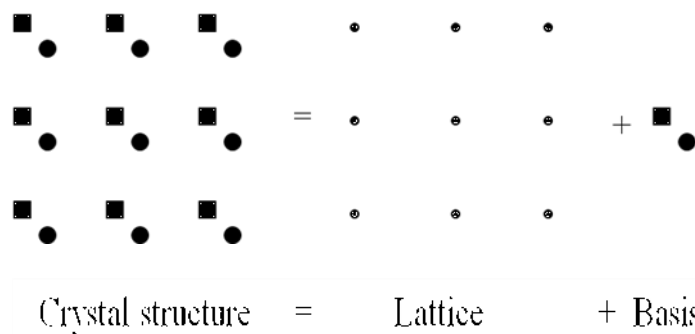
- A substance is said to be crystalline when the arrangement of units of matter is regular and periodic.
- A crystalline material has directional properties and therefore called as anisotropic substance.
- A crystal has a sharp melting point.
- It possesses a regular shape and if it is broken, all broken pieces have the same regular shape.
- A crystalline material can either be a single (mono) crystal or a polycrystal.
- A single crystal consists of only one crystal, whereas the polycrystalline material consists of many crystals separated by well-defined boundaries.
 - Examples
 - Metallic crystals – Cu, Ag, Al, Mg etc,
 - Non-metallic crystals – Carbon, Silicon, Germanium,
- In amorphous solids, the constituent particles are arranged in an orderly manner. They are randomly distributed.
- They do not have directional properties and so they are called as 'isotropic' substances.
- They have wide range of melting point and do not possess a regular shape.
 - Examples: Glass, Plastics, Rubber etc.,
 - **SPACE LATTICE**
- A lattice is a regular and periodic arrangement of points in three dimensions.
- It is defined as an infinite array of points in three dimensions in which every point has surroundings identical to that of every other point in the array.
- The Space lattice is otherwise called the Crystal lattice



- Consider the points P, Q and R.
- Let us join the points P and Q by a straight line, and the point P and R by another straight line.
- The line PQ is taken as X-axis and the line PR is taken as Y-axis.
- The distance between any two successive lattice points in the X-direction is taken as 'a'.
- Similarly, the distance between any two successive lattice points along the Y-direction is taken as 'b'.
- Here a and b are said to be lattice translational vectors. Consider a square lattice in which a=b.
- Consider two sets of points A, B, C, D, E, F and A', B', C', D', E', F'.

- In these two sets, the surrounding environment looks symmetrical; i.e. the distances AB and A'B', AC and A'C', AD and A'D', AE and A'E' and AF and A'F' are equal.
- Therefore, in the arrangement of points, if the surrounding environment looks the same when the arrangement is viewed from different lattice points, then that arrangement is said to be a space lattice.
 - **BASIS:**
- A crystal structure is formed by associating every lattice point with an unit assembly of atoms or molecules identical in composition, arrangement and orientation. This unit assembly is called the '*basis*'.
- ✚ When the basis is repeated with correct periodicity in all directions, it gives the actual crystal structure. The crystal structure is real, while the lattice is imaginary.

CRYSTAL STRUCTURE

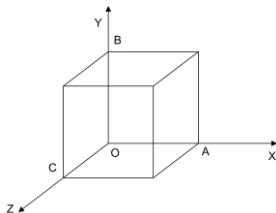


UNIT CELL:

- ✚ A unit cell is defined as a fundamental building block of a crystal structure, which can generate the complete crystal by repeating its own dimensions in various directions.

CRYSTALLOGRAPHIC AXES:

- ✚ Consider a unit cell consisting of three mutually perpendicular edges OA, OB and OC as shown in figure.
- ✚ Draw parallel lines along the three edges.
- ✚ These lines are taken as crystallographic axes and they are denoted as X, Y and Z axes.



LATTICE PARAMETERS

- ✚ Consider the unit cell as shown in figure. Let OA, OB and OC are the intercepts made by the unit cell along X, Y and Z axes respectively.
- ✚ These intercepts are known as *primitives*. In crystallography the intercepts OA, OB and OC are represented as \vec{a} , \vec{b} and \vec{c} .
- ✚ The angle between X and Y axes is represented as γ .

✚ Similarly the angles between Y and Z and Z and X axes are denoted by ' α ' and ' β ' respectively as shown in the above figure. These angles α , β and γ are called as interaxial **angles or interfacial angles**.

✚ To represent a lattice, the three interfacial angles and their corresponding intercepts are essential. These six parameters are said to be **lattice parameters**.

PRIMITIVE CELL:

✚ It is the smallest unit cell in volume constructed by primitives. It consists of only one full atom

A primitive cell is one, which has got the points or atoms only at the corners of the unit cell.

If a unit cell consists of more than one atom, then it is not a primitive cell.

Example for primitive cell: Simple Cubic unit cell.

Examples for non-primitive cell: BCC and FCC unit cell.

CRYSTALS SYSTEMS:

✚ A three dimensional space lattice is generated by repeated translation of three translational vectors a, b and c.

✚ Crystals are grouped under seven systems on the basis of the shape of the unit cell.

✚ The seven crystal systems are distinguished from one another by their lattice parameters.

The seven systems are,

1. Cubic
2. Tetragonal
3. Orthorhombic
4. Trigonal (rhombohedral)
5. Hexagonal
6. Monoclinic
7. Triclinic

The space lattices formed by unit cells are marked by the following symbols.

✚ Primitive lattice: P \rightarrow having lattice points only at the corners of the unit cell.

✚ Body centred lattice: I \rightarrow having lattice points at the corners as well as at the body centre of the unit cell.

✚ Face centred lattice: F \rightarrow having lattice points at the corners as well as at the face centres of the unit cell.

✚ Base centred lattice: C \rightarrow having lattice points at the corners as well as at the top and bottom base centres of the unit cell.

BRAVAIS LATTICES

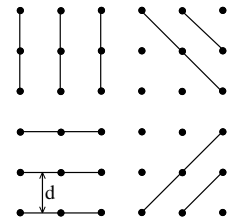
✚ Bravais in 1848 showed that 14 types of unit cells under seven crystal systems are possible. They are commonly called as '**Bravais lattices**'.

S.No.	Crystal system	Axial length	Interfacial angles	Example
1.	Cubic	$a=b=c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, CaF ₂ , Au, Cu
2.	Tetragonal	$a=b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Ordinary white, tin, Indium, SnO ₂
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Sulphur, Topaz, BaSO ₄ , KNO ₃
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ; \gamma \neq 90^\circ$	Na ₂ SO ₄ , FeSO ₄ , Gypsum

5.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	CuSo ₄ , K ₂ Cr ₂ O ₇
6.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite, Sb, Bi.
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ;$ $\gamma = 120^\circ$	Quartz, Zn, Mg.

MILLER INDICES: The crystal lattice may be regarded as made up of an infinite set of parallel equidistant planes passing through the lattice points which are known as lattice planes. Miller indices are defined as the reciprocals of the intercepts made by the plane on the three crystallographic axes. In simple terms, the planes passing through lattice points are called '*lattice planes*'.

- For a given lattice, the lattice planes can be chosen in a different number of ways.
- The orientation of planes or faces in a crystal can be described in terms of their intercepts on the three axes. 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.
- Miller indices are set of three possible integers represented as (h, k, l) which is used to designate plane in the crystal, is the reciprocal of the intercept made by the planes on the crystallographic axes.



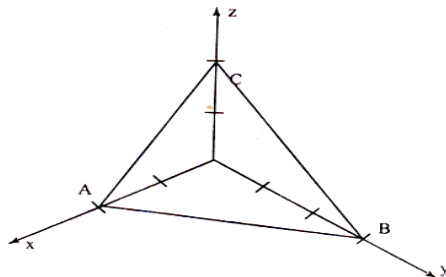
Procedure for finding Miller Indices

Step 1: Determine the intercepts of the plane along the axes X, Y and Z in terms of the lattice constants a, b and c.

Step 2: Determine the reciprocals of these numbers.

Step 3: Find the least common denominator (*lcd*) and multiply each by this *lcd*.

Step 4: The result is written in parenthesis. This is called the 'Miller Indices' of the plane in the form (h k l). This is called the 'Miller Indices' of the plane in the form (h k l).



✚ Plane ABC has intercepts of 2 units along X-axis, 3 units along Y-axis and 2 units along Z-axis.

DETERMINATION OF 'MILLER INDICES'

Step 1: The intercepts are 2, 3 and 2 on the three axes.

Step 2: The reciprocals are $1/2$, $1/3$ and $1/2$.

Step 3: The least common denominator is '6'. Multiplying each reciprocal by lcd, we get 3, 2 and 3.

Step 4: Hence Miller indices for the plane ABC is (3 2 3)

IMPORTANT FEATURES OF MILLER INDICES

For the cubic crystal especially, the important features of Miller indices are,

- A plane which is parallel to any one of the co-ordinate axes has an intercept of infinity (∞). Therefore the Miller index for that axis is zero; i.e. for an intercept at infinity, the corresponding index is zero.

EXAMPLE (1 0 0) plane (Plane parallel to Y and Z axes)



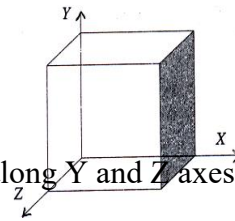
- In the above plane, the intercept along X axis is 1 unit.

- The plane is parallel to Y and Z axes. So, the intercepts along Y and Z axes are ' ∞ '.

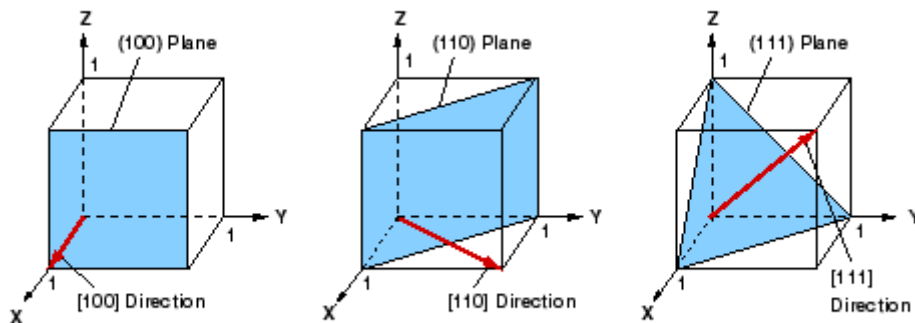
- Now the intercepts are 1, ∞ and ∞ .

- The reciprocals of the intercepts are = $1/1$, $1/\infty$ and $1/\infty$.

- Therefore the Miller indices for the above plane is (1 0 0).



MILLER INDICES OF SOME IMPORTANT PLANES

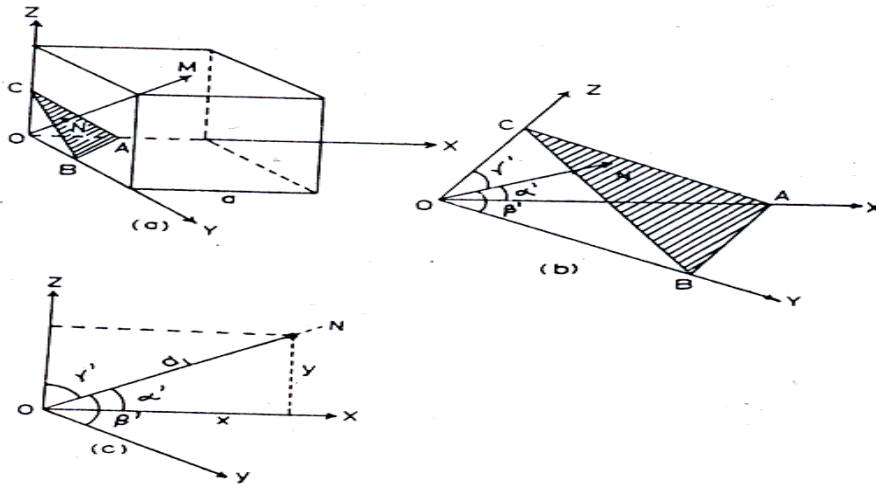


SEPARATION BETWEEN LATTICE PLANES

- Consider a cubic crystal of side 'a', and a plane ABC.

- This plane belongs to a family of planes whose Miller indices are (h k l) because Miller indices represent a set of planes.

- Let $ON = d$, be the perpendicular distance of the plane A B C from the origin.



✚ Let α_1 , β_1 and γ_1 (different from the interfacial angles α , β and γ) be the angles between co-ordinate axes X, Y, Z and ON respectively.

✚ The intercepts of the plane on the three axes are,

$$OA = \frac{a}{h}, \quad OB = \frac{a}{k} \quad \text{and} \quad OC = \frac{a}{l} \longrightarrow (1)$$

From the figure, we have,

$$(2) \quad \cos \alpha_1 = \frac{d_1}{OA}, \quad \cos \beta_1 = \frac{d_1}{OB} \quad \text{and} \quad \cos \gamma_1 = \frac{d_1}{OC} \longrightarrow$$

From the property of direction of cosines,

$$\cos^2 \alpha_1 + \cos^2 \beta_1 + \cos^2 \gamma_1 = 1 \longrightarrow (3)$$

Using equation 1 in 2, we get,

$$\cos \alpha_1 = \frac{d_1 h}{a}, \quad \cos \beta_1 = \frac{d_1 k}{a}, \quad \text{and} \quad \cos \gamma_1 = \frac{d_1 l}{a} \longrightarrow (4)$$

Substituting equation (4) in (3), we get,

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

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

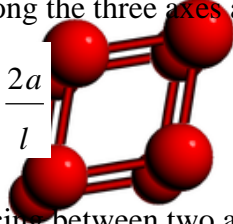
$$d_1^2 = \frac{a^2}{(h^2 + k^2 + l^2)} \quad d_1 = ON = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \longrightarrow (5)$$

i.e. the perpendicular distance between the origin and the 1st plane ABC is,

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

- Now, let us consider the next parallel plane.
- Let $OM=d_2$ be the perpendicular distance of this plane from the origin.
- The intercepts of this plane along the three axes are

- $OA' = \frac{2a}{h}, OB' = \frac{2a}{k}, OC' = \frac{2a}{l}$



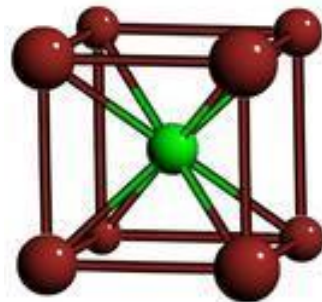
$$OM = d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}}$$

- Therefore, the interplanar spacing between two adjacent parallel planes of Miller indices $(h\ k\ l)$ is given by, $NM = OM - ON$ i.e. interplanar spacing

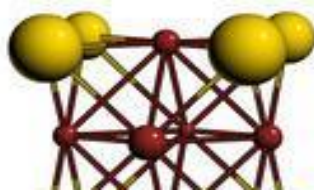
$$\frac{d}{2} - d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

1. Simple cubic structure (SC):

2. Body centered cubic structure (BCC):



3. Face centered cubic structure (FCC):



Properties of the Unitcell (Cubic)

1. Volume of a unit cell:

The general expression for finding the volume a unit cell is

$$V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

Where a,b,c,α,β and γ are called lattice parameters.

For cubic system a=b=c and α=β=γ=90°.

Therefore $V = a^3$.

2. Co-ordination number:

It is the number of nearest neighbors directly surrounding a given atom well within a crystal.

The co-ordination number for an atom in simple cubic structure is = 6

The co-ordination number for an atom in body centered cubic structure is = 8

The co-ordination number for an atom in face centered cubic structure is = 12

3. Number of atoms per unit cell:

In a unit cell atoms are at the corners, at the center of the faces and at the center of the body.

An atom situated at the corner share $1/8^{\text{th}}$ part to a unit cell.

An atom situated at the face share $1/2$ part to a unit cell.

An atom situated at the center of the body share one full part to a unit cell.

1. In a simple cubic structure there are 8 corner atoms.

$$\therefore \text{Total share of all the corner atoms/unit cell} = (1/8) \times 8 = 1$$

$$\therefore \text{The number of atoms/unit cell in simple cube} = 1$$

2. In a body centered cubic structure there are 8 corner atoms and an atom at the center of the unit cell.

$$\therefore \text{Total share of all the corner atoms per unit cell} = (1/8) \times 8 = 1$$

The share of an atom at the center of the body = 1

$$\therefore \text{The number of atoms per unit cell in body centered cube} = 1 + 1 = 2$$

3. In a face centered cubic structure there are 8 corner atoms and 6 face centered atoms in a unit cell.

$$\therefore \text{total share of atoms at the corner/unit cell} = (1/8) \times 8 = 1$$

$$\text{Total share of atoms at all the faces/unit cell} = (1/2) \times 6 = 3$$

$$\therefore \text{The number of atoms/unit cell in face centered cube} = 1 + 3 = 4$$

4. Atomic packing factor (APF)

The fraction of the space occupied by atoms in a unit cell is known as atomic packing factor. It is the ratio of the total volume occupied by the atoms in the unit cell to the total available volume of the unit cell.

1. Simple cubic structure (SC):

There is only one lattice point at each of the eight corners of the unit cell. In a simple cubic structure an atom is surrounded by six equidistant neighbours. Hence the co-ordination number is 6. Since each atom in the corner is shared by 8 unit cells, the total number of atoms in one unit cell is $(1/8) \times 8 = 1$

The nearest neighbour distance '2r' is the distance between the centers of two nearest neighbouring atoms.

The nearest neighbour distance $2r = a$

The number of lattice points per unit cell = 1

Volume of all the atoms in a unit cell $v = \frac{4}{3}\pi r^3$

Volume of unit cell = $V = a^3 = (2r)^3$
 $v \quad 4\pi r \quad \pi$

Packing factor is $P.F = \frac{v}{V} = \frac{4\pi r^3}{3 \times 8r^3} = \frac{\pi}{6} = 0.52 = 52\%$

2. Body centered cubic structure (BCC): In a BCC structure eight atoms are present at eight corners and one atom is at the center. The co-ordination number is 8. The number of atoms per unit cell is $= [(1/8) \times 8] + 1 = 2$

The lattice constant is

$$(AB)^2 = a^2 + a^2 = 2a^2$$

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

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

$$\text{Lattice constant } a = \frac{4r}{\sqrt{3}}$$

Volume of all the atoms per unit cell $v = 2 \times \left(\frac{4}{3}\pi r^3 \right)$

Volume of the unit cell $V = a^3 = \frac{64r^3}{3\sqrt{3}}$

Atomic packing factor = $\frac{v}{V} = \frac{8\pi r^3 \times 3\sqrt{3}}{3 \times 64r^3} = \frac{3\pi}{8} = 0.68 = 68\%$

3. Face centered cubic structure (FCC):

In a FCC structure eight atoms are at the corners of the unit cell and six atoms are present at the center of the six faces. The center atom is surrounded by 12 points. The co-ordination number is 12. Each corner atom is shared by 8 unit cells and the face centered atom is shared by 2 surrounding unit cells.

$$\therefore \text{The number of atoms per unit cell is} = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} = 4$$

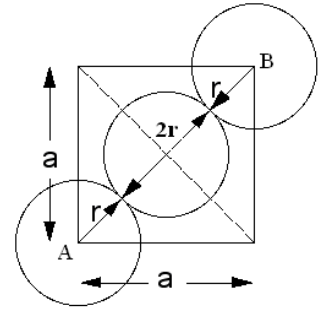
Atomic radius of face centered cube

$$AB = 4r$$

$$(AB)^2 = a^2 + a^2$$

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

$$\text{Lattice Constant } a = \frac{4r}{\sqrt{2}}$$



$$\text{Nearest neighbor distance } 2r = \frac{a\sqrt{2}}{2}$$

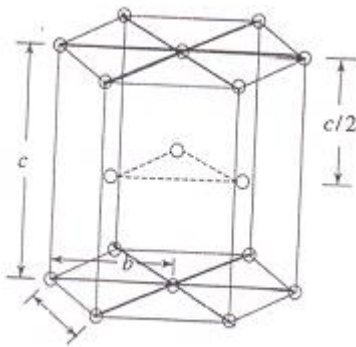
$$\text{Volume of all the atoms in unit cell } v = 4 * (4/3) \pi r^3$$

$$\text{Volume of unit cell } V = a^3 = 64 r^3 / 2\sqrt{2}$$

$$\therefore \text{The packing factor} = v/V = \sqrt{2}\pi/6 = 74\%$$

Parameters	SC	BCC	FCC
Co-ordination number	6	8	12
Atomic Radius (r)	$a/2$	$\sqrt{3}a/4$	$\sqrt{2}a/4$
Atoms per unit cell	1	2	4
Atomic packing factor	$\pi/6$	$3\pi/8$	$2\pi/6$

HEXAGONAL CLOSED PACKED STRUCTURE



- It consists of three layers of atoms.
- The bottom layer has six corner atoms and one face centred atom.
- The middle layer has three full atoms.
- The upper layer has six corner atoms and one face centred atom.
- Each and every corner atom contributes 1/6 of its part to one unit cell.
- The number of total atoms contributed by the corner atoms of both top and bottom layers is $1/6 \times 12 = 2$.
- The face centred atom contributes 1/2 of its part to one unit cell.
- Since there are 2 face centred atoms, one in the top and the other in the bottom layers, the number of atoms contributed by face centred atoms is $1/2 \times 2 = 1$.
- Besides these atoms, there are 3 full atoms in the middle layer.
- Total number of atoms present in an HCP unit cell is $2+1+3 = 6$.

CO-ORDINATION NUMBER (CN)

- The face centered atom touches 6 corner atoms in its plane.
- The middle layer has 3 atoms.

- There are three more atoms, which are in the middle layer of the unit cell.
- Therefore the total number of nearest neighbours is $6+3+3=12$.

ATOMIC RADIUS (R)

- Consider any two corner atoms.
- Each and every corner atom touches each other. Therefore $a = 2r$.

i.e., The atomic radius, $r = a/2$

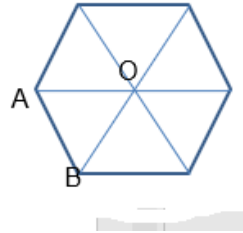
ATOMIC PACKING FACTOR (APF)

$$\text{APF} = v/V$$

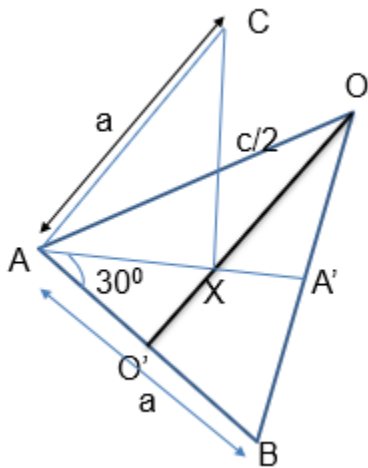
$$v = 6 \times \frac{4}{3} \pi r^3$$

Substitute $r = a/2$

$$v = 6 \times \frac{4}{3} \pi \frac{a^3}{8}$$



$$v = \pi a^3$$



$AB = AC = BO = 'a'$. $CX = c/2$ where $c \rightarrow$ height of the hcp unit cell.

Area of the base = $6 \times$ area of the triangle $ABO = 6 \times \frac{1}{2} \times AB \times OO'$

Area of the base = $6 \times \frac{1}{2} \times a \times OO'$

In triangle $O'OB$

$\angle O'OB = 30^\circ$

$$\cos 30^\circ = \frac{OO'}{BO} = \frac{OO'}{a}$$

$$\therefore OO' = a \cos 30^\circ = a \frac{\sqrt{3}}{2}$$

Now, substituting the value of OO' ,

$$\text{Area of the base} = 6 \times \frac{1}{2} \times a \times \frac{\sqrt{3}}{2} a = \frac{3\sqrt{3}a^2}{2}$$

$V =$ Area of the base \times height

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

$$\therefore \text{APF} = \frac{v}{V} = \frac{\pi a^3}{\frac{3\sqrt{3} a^2 c}{2}}$$

$$\therefore \text{APF} = \frac{2\pi a^3}{3\sqrt{3}a^2 c} = \frac{2\pi}{3\sqrt{3}} \frac{a}{c}$$

Determination of c/a ratio:

In the triangle ABA',

$$\cos 30^\circ = \frac{AA'}{AB} = \cos 30^\circ$$

$$\therefore AA' = AB \cos 30^\circ = a\sqrt{3}/2$$

$$\text{But } AX = 2/3 AA' = \frac{2}{3} a \frac{\sqrt{3}}{2}$$

$$\text{i.e. } AX = \frac{a}{\sqrt{3}}$$

In the triangle AXC,

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

Substituting the values of AC, AX and CX,

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

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

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

$$\frac{c^2}{4} = a^2 \left(1 - \frac{1}{3}\right)$$

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

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

Now substituting the value of c/a to calculate APF of an hcp unit cell,

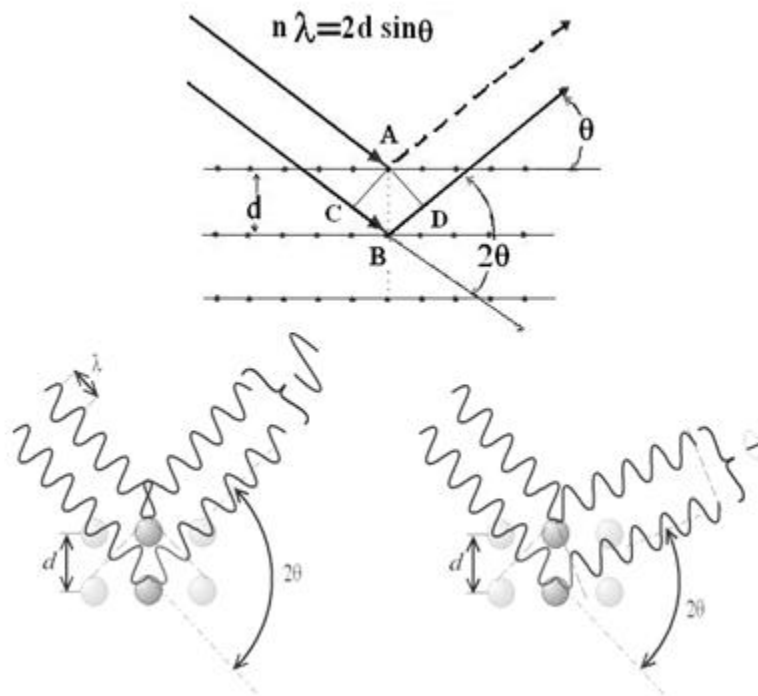
$$\begin{aligned} \text{APF} &= \frac{2\pi}{3\sqrt{3}} \sqrt{\frac{3}{8}} \\ &= \frac{2\pi}{3\sqrt{3}} \frac{\sqrt{3}}{2\sqrt{2}} \end{aligned}$$

$$\therefore \text{APF} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Bragg's Law:

Consider a set of parallel planes called Bragg's planes. Each atom is acting as a scattering center. The intensity of the reflected beam at certain angles will be

maximum when the path difference between two reflected waves from two adjacent planes is an integral multiple of λ .



Let 'd' be the distance between two adjacent planes, ' λ ' be the wavelength of the incident x-ray, ' θ ' be the glancing angle. The path difference between the rays reflected at A & B is given by

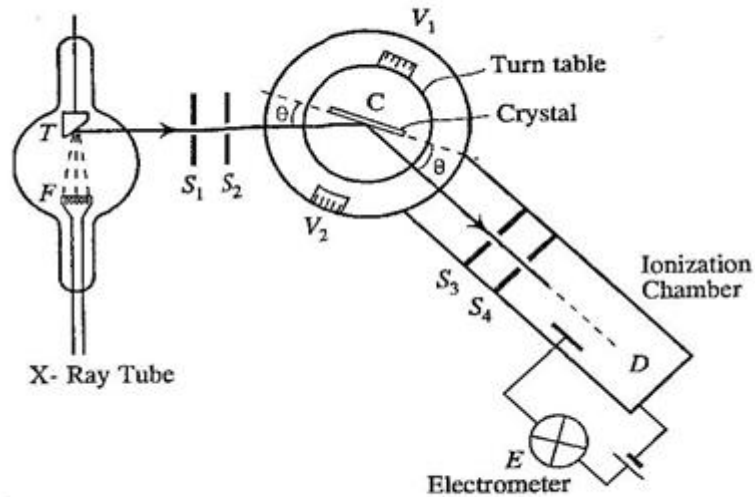
$$= CB + BD$$

$$= d \sin\theta + d \sin\theta = 2d\sin\theta$$

For the reflected light intensity to be maximum, the path difference $2d\sin\theta = n\lambda$, where 'n' is the order of scattering. This is called Bragg's law.

Bragg's x-ray spectrometer:

The schematic diagram of Bragg's x-ray spectrometer is shown in fig. It is used to determine lattice constant and inter-planar distance 'd'. It has 1) x-ray source 2) A Crystal fixed on a circular table provided with scale and vernier. 3) Ionization chamber.

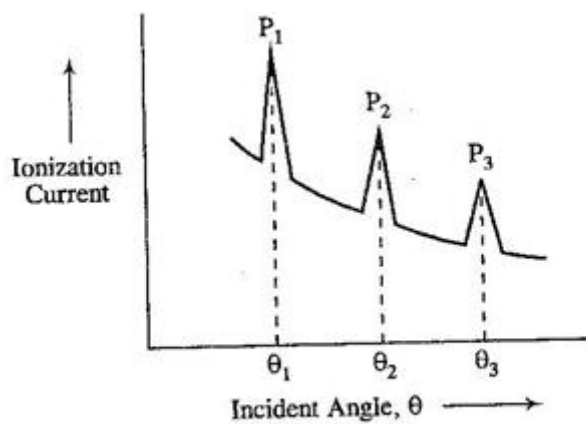


BRAGG'S X-RAY SPECTROMETER

A collimated beam of x-rays after passing the slits S_1 and S_2 is allowed to fall on a crystal C mounted on a circular table. The table can be rotated about vertical axis. Its position can be measured by vernier V_1 . An ionization chamber is fixed to the longer arm attached to the table. The position of which is measured by vernier v_2 . An electrometer is connected to the ionization chamber to measure the ionization current produced by diffracted x-rays from the crystal. S_3 and S_4 are the lead slits to limit the width of the diffracted beam. Here we can measure the intensity of the diffracted beam.

If x-rays incident at an angle ' θ ' on the crystal, then reflected beam makes an angle 2θ with the incident beam. Hence the ionization chamber can be adjusted to get the reflected beam till the ionization current becomes maximum.

A plot of ionization current for different incident angles to study the x-ray diffraction spectrum is shown in fig.



VARIATION OF IONIZATION CURRENT

The rise in Ionization current for different values of 'θ' shows that Bragg's law is satisfied for various values of 'n'. i.e. $2d\sin\theta = \lambda$ or 2λ or 3λ etc. Peaks are observed at $\theta_1, \theta_2, \theta_3$ etc. with intensities of P_1, P_2, P_3 etc.

$$\text{i.e. } 2d\sin\theta_1 : 2d\sin\theta_2 : 2d\sin\theta_3 = \lambda : 2\lambda : 3\lambda$$

The crystal inter-planer spacing 'd' can be measured using $2d\sin\theta = n\lambda$

If d_1, d_2, d_3 be the inter-planer spacing for the planes (100), (110) & (111) respectively.

It can be shown -

For cubic crystal: $d_1:d_2:d_3 = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$

For FCC : $d_1:d_2:d_3 = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

For BCC : $d_1:d_2:d_3 = 1 : \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}}$

Allotropy and Polymorphism

The property possessed by certain elements to exist in two or more distinct forms that are chemically identical but have different physical properties is called allotropy.

- Two or more distinct crystal structures for the same material (allotropy/polymorphism).
- **Allotropy** (Gr. *allos*, other, and *tropos*, manner) or **allotropism** is a behavior exhibited by certain chemical elements that can exist in two or more different forms, known as *allotropes* of that element.
- In each allotrope, the element's atoms are bonded together in a different manner.
- Note that allotropy refers only to different forms of an element within the same phase or state of matter (i.e. different solid, liquid or gas forms) - the changes of state between solid, liquid and gas in themselves are not considered allotropy.

In each different allotrope, the element's atoms are bonded together in a different manner. For example, the element carbon has two common allotropes: Diamond, in which the carbon atoms are bonded together in a tetrahedral lattice arrangement, and graphite, in which the carbon atoms are bonded together in sheets of a hexagonal lattice.

Diamond

- An extremely hard, transparent crystal with
 - tetrahedral bonding of carbon
 - very high thermal conductivity
 - very low electric conductivity.
- The large single crystals are typically used as gem stones
- The small crystals are used to grind/cut other materials
- diamond thin films
 - hard surface coatings – used for cutting tools, medical devices.

Graphite

- a soft, black, flaky solid, with a layered structure – parallel hexagonal arrays of carbon atoms
- weak van der Waal's forces between layers
- planes slide easily over one another

The change between different allotropic forms of an element is often triggered by pressure and temperature, and many allotropes are only stable in the correct conditions. For instance, iron only changes from ferrite to austenite above 1,333°F (723°C), and tin undergoes a process known as tin pest at 56°F (13.2°C) and below.

Other examples of allotropes include:

Phosphorus:

- Red Phosphorus—polymeric solid
- White Phosphorus—crystalline solid
- Black Phosphorus—semiconductor, analogous to graphite

Oxygen:

- dioxygen, O₂—
colourless
- ozone, O₃—
blue
- tetraoxygen, O₄—red

Polymorphism is the phenomenon where a compound can exist or precipitate to form numerous crystal structures. The different crystalline structures each have different physical properties, which can change the use of the chemical. The physical properties that may differ from one polymorphism to another include: solubility, density, melting point and even color. One of the variables that affect the crystallization process is the solvent that is used in the precipitation. Different polymorphisms can also be formed by manipulating the solute

concentrations, flows rates, and equipment configurations. Crystals are used in many areas of science, pharmaceuticals, and materials engineering. Crystals differ from many other organic and inorganic materials because of their ability to form polymorphisms. There are many physical and chemical properties that can be affected by a change in the polymorph.

When a crystal transforms from one of its polymorphs to another, both the chemical and physical properties of the substance are altered. For example, solubility, hardness, shape, melting point, dissolution rate, density, optical and electrical properties, and electromagnetic spectra are some properties that are affected by a change in the crystal structure. In the case of iron the crystal structure has one form at room temperature and another at high temperature. When heated above 910°C the atomic structure changes from body centered cubic to face centered cubic but reverts again when cooled. The allotropy of iron modifies the solubility of carbon, and it is because of this that steel can be hardened.