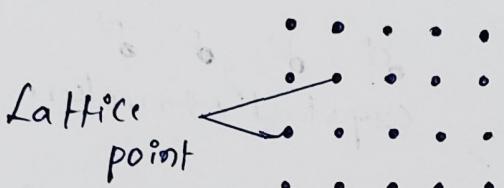


Q. Crystallography & X-ray Diffraction

Lattice points :- The points which have a regular periodic arrangement and have identical environment with respect to other points, are called lattice points.



Lattice :- The regular orderly arrangement of atoms or molecules in 3 dimensional pattern is called Lattice.



* * * * There are 2 types of Lattice. They are
 * * * * ① 2D - Space Lattice ② 3D - Space Lattice.

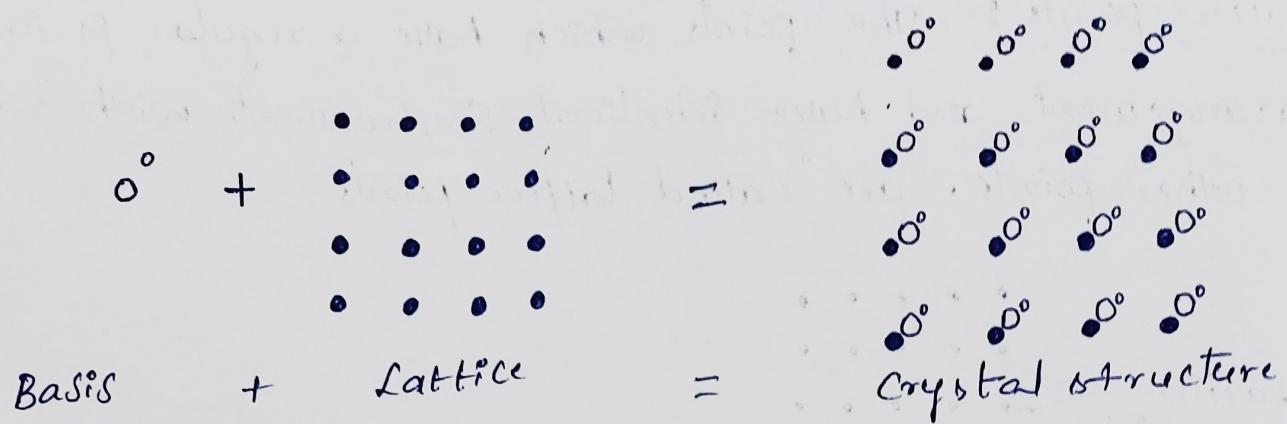
2D - Space Lattice :- An infinite array of points in 2 dimensional space in which every point has same environment with respect to all other points.

3D - Space Lattice :- An infinite array of points in 3 dimensional space in which every point has same environment with respect to all other points.

Basis :- Certain atoms or molecules are attached to each lattice point in a crystal structure. These atoms or molecules attached to any lattice point identical in composition, arrangement and orientation, form the basis of a crystal lattice.

$$\text{Crystal Structure} = \text{Basis} + \text{Crystal lattice.}$$

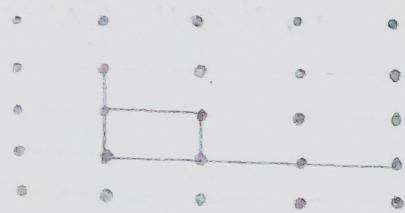
Space Lattice :- An array of points in space such that the environment about each point is same.



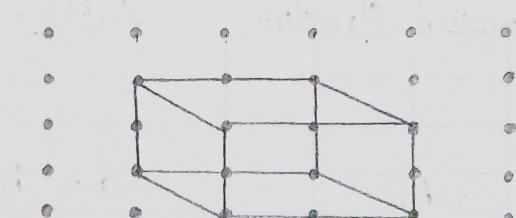
Difference between crystalline solids and Amorphous solids.

| Crystalline Solids | Amorphous Solids. |
|---|---|
| ① Atoms (or) molecules have regular periodic arrangements. | ① Atoms (or) molecules are n't arranged in a regular periodic manner. |
| ② They exhibit different magnitudes of physical properties in different directions. | ② They exhibit same magnitudes of physical properties in different directions. |
| ③ They are anisotropic in nature. | ③ They are isotropic in nature. |
| ④ They exhibit directional properties. | ④ They do not exhibit directional properties. |
| ⑤ They have sharp melting points | ⑤ They don't possess sharp melting points. |
| ⑥ These break along regular crystal planes and hence the crystal pieces have regular shape. Ex:- copper, Silver etc | ⑥ Amorphous solids break into irregular shape due to lack of crystal plane. Ex:- Glass, plastic etc. |

Unit Cell :- The smallest block (or) geometrical figure from which the crystal is build up by repetition in 3 dimensional is called unit cell.



(2-Dimensional unit cell)



(3-Dimensional unit cell).

(or)

The fundamental grouping of particles which are repeating entities is called unit cell.

Crystallographic axes :- The intersection of any three faces of the unit cell, which do not lie in the same plane (ox, oy, oz)

Primitives :- The three sides of unit cell are called primitives. They are denoted by a, b, c . They are also known as lattice constants.

Interfacial angles :- The angle between 3 crystallographic axes of the unit cell are called interfacial angles.

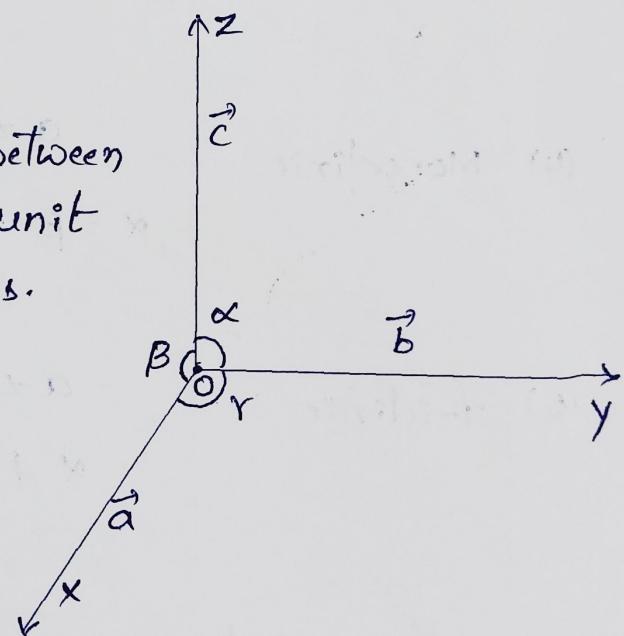
Here a, b, c are primitives.

$\alpha, \beta \& \gamma$ are interfacial angles.

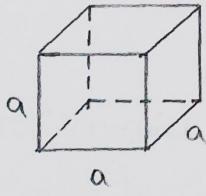
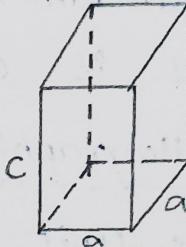
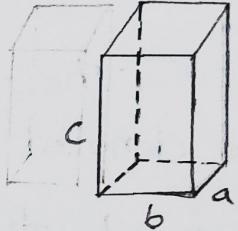
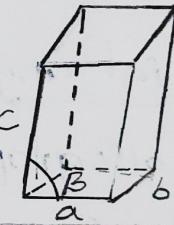
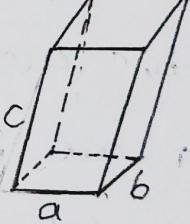
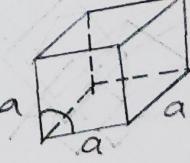
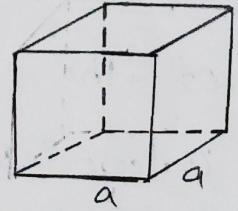
The angle between $y \& z$ axis is α

$z \& x$ axis is β

$x \& y$ axis is γ



Crystal Systems :- On the basis of lattice parameters or shape of the unit cell, crystal systems are classified into seven categories.

| S.NO | Crystal Structure | Lattice parameters | unit cell Geometry |
|------|----------------------------|--|---|
| (1) | Cubic | $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$ |  |
| (2) | Tetragonal | $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$ |  |
| (3) | Orthorhombic | $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$ |  |
| (4) | Monoclinic | $a \neq b \neq c$, $\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$ |  |
| (5) | Triclinic | $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$ |  |
| (6) | Rhombohedral (Trigonal) | $a = b = c$, $\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$ |  |
| (7) | hexagonal | $a = b \neq c$, $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ |  |

Bravais Lattices :-

Bravais showed that there are 14 different types of unit cells under the seven crystal systems. They are commonly called Bravais lattices.

The classification of Bravais lattice is based on the following Crystal lattices.

(1) Primitive Lattice :- (P)

In this lattice, the unit cell consists of Eight corner atoms and all these corner atoms contribute only one effective atom for the lattice.

(2) Body Centred Lattice :- (I)

In addition to the Eight corner atoms, it consists of one complete atom at the centre.

(3) Face Centred Lattice :- (F)

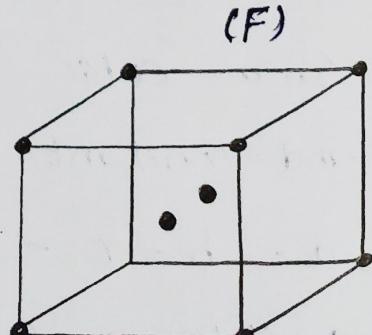
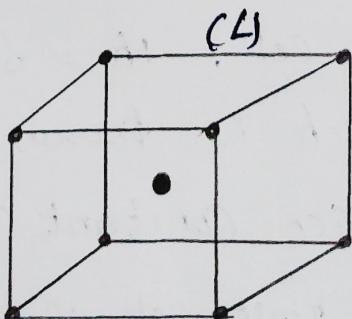
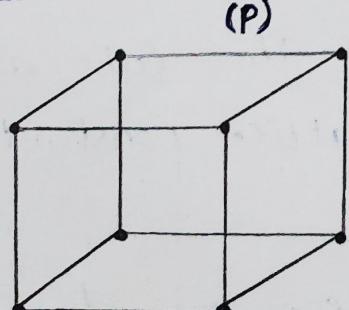
Along with the corner atoms, each face will have one centre atom.

(4) Base Centred Lattice :- (C)

The base and opposite face will have centre atoms along with the corner atoms.

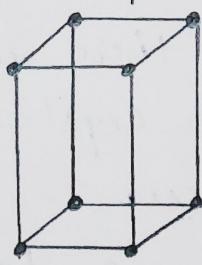
Bravais Lattices :-

(1) Cubic :-

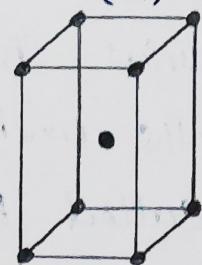


② Tetragonal :-

(P)

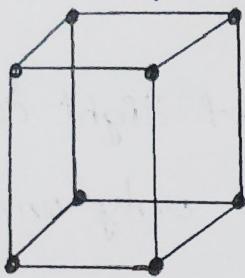


(L)

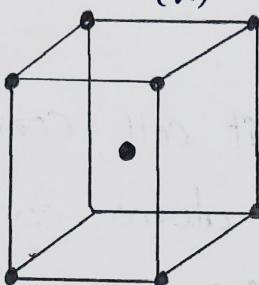


③ Orthorhombic :-

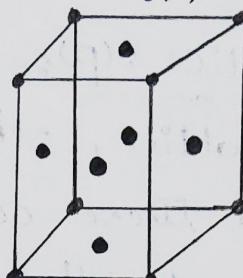
(P)



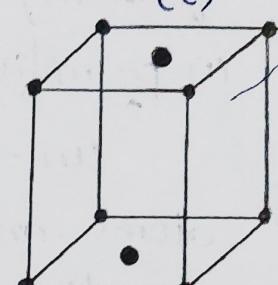
(L)



(F)

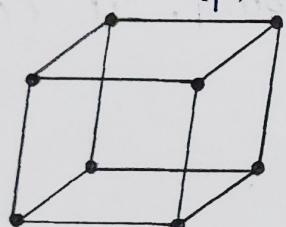


(C)

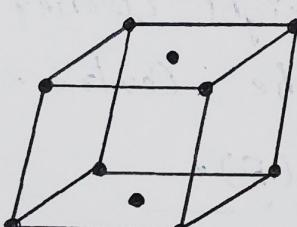


④ Monoclinic :-

(P)

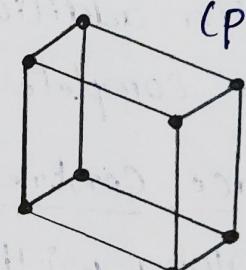


(C)



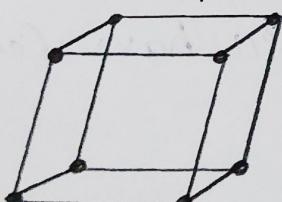
⑤ Triclinic :-

(P)

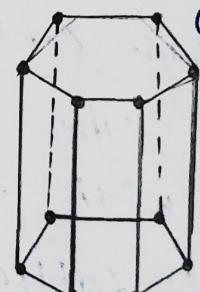


⑥ Rhombohedral (Trigonal) :-

(P)



(P)



⑦ Hexagonal :-

Expression for Lattice Constant :-

In a cubic unit cell, the sides of the cube are Equal and constant, which is known as lattice Constant.

$$a = b = c = \text{lattice Constant } (a)$$

Consider a cubic unit cell with lattice parameters.

$$a = b = c \text{ and } \alpha = \beta = \gamma = 90^\circ$$

Let ρ be the density of the cell.

Volume of the cubic unit cell = a^3

Mass of the cubic unit cell = $a^3 \rho \rightarrow ①$

Let, M be the molecular weight of the cell.

and N_A be the Avagadro's number

Mass of each atom in unit cell = $\frac{M}{N_A}$

If there are ' n ' number of atoms in a unit cell, then

Mass of the cubic unit cell = $\frac{nM}{N_A} \rightarrow ②$

From Eq ① & ②, we have

$$a^3 \rho = \frac{nM}{N_A}$$

$$a^3 = \frac{nM}{\rho N_A}$$

$$a = \left[\frac{nM}{\rho N_A} \right]^{1/3}$$

The above expression represents the Expression for lattice constant

Crystal Structure of Materials :-

Some imp definitions :-

* Atomic radius (r) :-

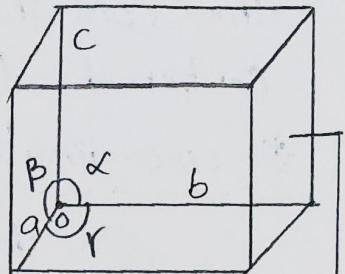
The half of the distance between any two successive atoms in a crystal lattice.

* Nearest Neighbour Distance ($2r$) :-

The distance between two nearest neighbouring atoms in a crystal lattice.

* Effective number of atoms per unit Cell :-

The total number of atoms in a unit cell by Considering



Density (ρ)

the contribution of corner atoms, centre atoms and face centered atoms.

* Co-ordination Number (N) :-

The number of equidistant neighbours that an atom has in a crystal lattice.

* Atomic packing factor :- The ratio between the total volume occupied by the atoms in a unit cell to the volume of the unit cell.

i.e., atomic packing factor = $\frac{\text{Total volume occupied by atoms in a unit cell}}{\text{volume of the unit cell}}$.

= Number of atoms present in a unit cell \times volume of the one atom.

volume of the unit cell.

* Interstitial Space (or) void Space :-

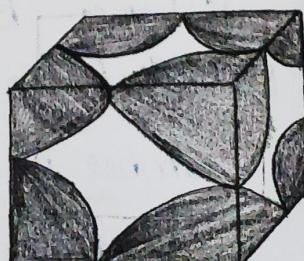
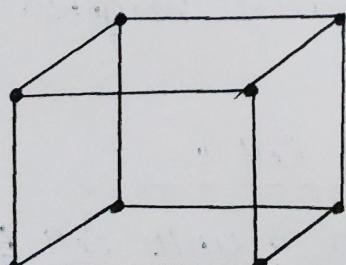
The empty space available in a crystal lattice with atoms occupying their respective positions is the interstitial or void space.

* Density :-

Density of Crystal lattice = $\rho = \frac{nM}{a^3 N_A}$

* Simple cubic crystal structure (SCC) :-

It consists of eight corner atoms. It is a primitive cell.



Lattice parameters :- $a = b = c$ = lattice constant
 $\alpha = \beta = \gamma = 90^\circ$

Effective number of atoms in unit cell :-

In FCC unit cell, each and every corner atom is shared by eight adjacent unit cells. Total number of atoms contributed by corner atoms. $\frac{1}{8} \times 8 = 1$

The effective number of atoms present in FCC unit cell = 1

Coordination Number :- For the corner atom, there are four nearest neighbours in its own plane. There is another nearest neighbour in a plane which lie just above this atom and yet another nearest neighbour in another plane which lies just below this atom. Therefore, the total number of nearest neighbours is six, and hence the coordination number is 6.

Nearest neighbour distance :-

$$2r = a$$

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

Atomic packing factor :

For FCC the total number of atoms present in one:

$$\text{volume of one atom} = \frac{4}{3} \pi r^3$$

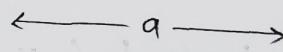
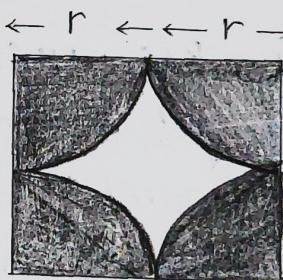
$$\text{volume of unit cell} = a^3$$

Number of atoms present in unit cell = 1

$$\text{A.P.F} = \frac{1 \times \frac{4}{3} \pi r^3}{a^3}$$

Substituting $r = \frac{a}{2}$ in the above relation

$$\text{A.P.F} = \frac{1 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3}$$



atomic packing factor = $\frac{\pi}{6} = 0.52$.

Thus 52% of the volume of sc unit cell is occupied by atoms.

Interstitial Space :- The empty space available = 47%.

Density :- As $n=1$ for sc,

$$\rho = \frac{M}{a^3 N_A}$$
 Ex:- potassium crystal.

* Body centred cubic Structure (Bcc) :-

A body centred cubic structure consists of eight corner atoms and one body centered atom. It is not a primitive cell.

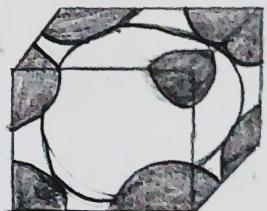
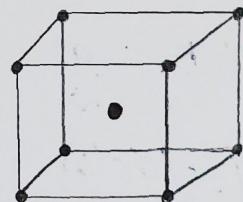
Lattice parameters : $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$

Effective Number of atoms in unit cell :-

In Bcc unit cell, each and every corner atom is shared by eight adjacent unit cells.

Total number of atoms contributed by corner atoms = $\frac{1}{8} \times 8 = 1$

Bcc has 1 full atom at the center of the unit cell.



The effective number of atoms present in bcc unit cell is $= 1 + 1 = 2$

Coordination Number :-

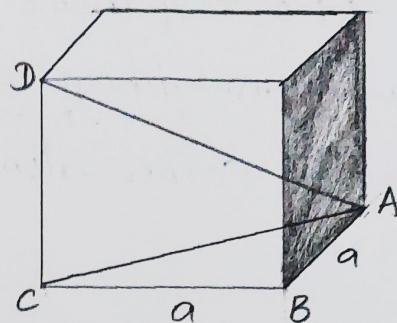
The nearest neighbour for a body centered atom is a corner atom. A body centered atom is surrounded by eight corner atoms. Therefore the coordination number of bcc unit cell is 8.

Atomic radius :- For Bcc the atoms touch along the body diagonal. The diagonal length = $4r$.

$$\text{From } \triangle ABC, AC^2 = AB^2 + BC^2 \\ = a^2 + a^2 = 2a^2$$

$$AC = \sqrt{2}a.$$

$$\text{From } \triangle ACD, AD^2 = AC^2 + CD^2 \\ = 2a^2 + a^2 \\ = 3a^2 \\ AD = \sqrt{3}a.$$



$$\text{Therefore, } \sqrt{3}a = 4r$$

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

Packing factor: $A.P.F \Rightarrow \frac{2 \times \frac{4}{3} \pi r^3}{a^3}$

$$\Rightarrow \frac{2 \times \frac{4}{3} \pi \left[\frac{\sqrt{3}}{4}a \right]^3}{a^3} = \frac{\sqrt{3} \pi}{8} = 0.68$$

The atoms in BCC occupy 68% of the space and the rest is empty.

The void space or interstitial space is 32%.

Density: AS $n=2$ for BCC

$$\rho = \frac{\alpha M}{a^3 N_A}$$

Ex:- sodium, potassium, chromium etc.

* Face centred cubic Structure (Fcc) :-

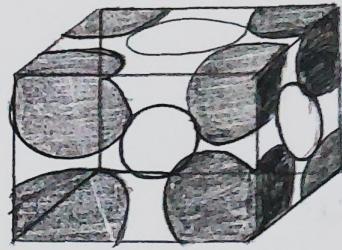
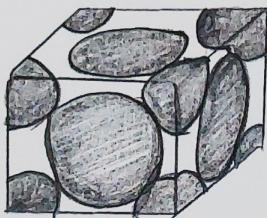
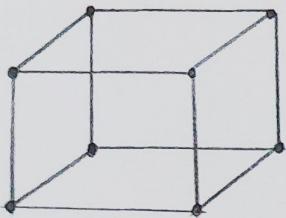
Fcc consists of atoms at Eight corners and each face has a centre atom.

Lattice parameters :- $a=b=c$ and $\alpha=\beta=\gamma=90^\circ$

Effective number of atoms in unit cell:

Each unit cell contains $(\frac{1}{8} \times 8 \text{ corner atoms}) + (\frac{1}{2} \times 6 \text{ face atoms})$
 $= 1 + 3 = 4 \text{ atoms.}$

Nearest neighbour distance :- Let r be the radius of spherical corner atoms. Then the nearest neighbour distance = $2r = a.$



coordination number :- for corner atoms, there are four face centered atoms. These face centered atoms are its nearest neighbours. In a plane just above this corner atom, it has four more face centered atoms. In a plane which lies just below this corner it has yet four more face centered atoms.

Therefore the coordination number of atoms is 12.

Atomic radius :

Consider the $\triangle ABC$

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

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

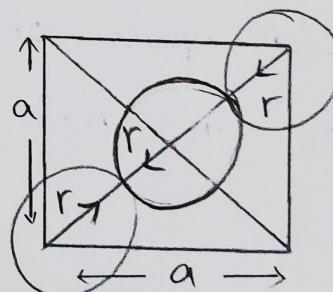
$$16r^2 = 2a^2$$

The atomic radius $r = \frac{a}{2\sqrt{2}}$

Nearest neighbour distance ($2r$)

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

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



Atomic packing factor :-

The Number of atoms present in fcc unit cell is 4.

$$A.P.F = \frac{4\left(\frac{4}{3}\right)\pi r^3}{a^3}$$

Substitute $r = \frac{a}{2\sqrt{2}}$ in above value

$$A.P.F = \frac{4\left(\frac{4}{3}\right)\pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

74% of the volume of an fcc unit cell is occupied by atoms. It is a very closely packed structure than the fcc and bcc.

Interstitial Space: 26%.

Density $n = 4$

$$\rho = \frac{4M}{a^3 N_A}$$

Ex: Cu, Ag, Al etc.

Miller Indices - Crystal planes :-

Miller Indices are three, smallest integers which have the same ratio as the reciprocals of the intercept of the crystal plane with the coordinate axes.

They are a set of three integers used to describe the orientation of crystal planes.

Procedure to find Miller Indices :-

- (1) The intercepts made by the Crystal plane along x, y and z axis in terms of lattice parameters a, b, c are noted.
- (2) Express the intercepts as multiples of a, b, c.
- (3) The reciprocals of the intercepts are taken.
- (4) The reciprocal are converted into integers by multiplying each of them with their L.C.M.
- (5) The integers are enclosed in small parentheses, which represents the miller indices of the crystal planes.

For Eg :-

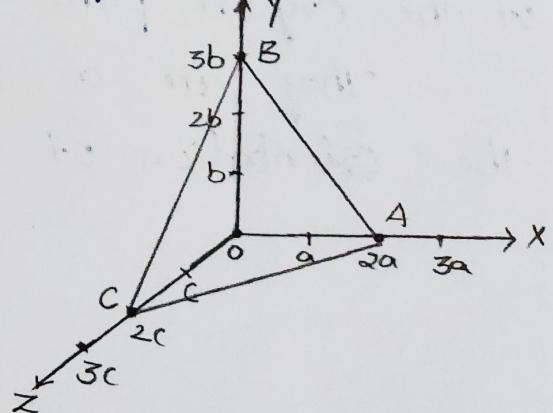
ABC is the crystal plane which makes the intercepts $a/2$, $3b$ and $2c$ along the x, y & z axes. where a, b, c are lattice parameters.

The intercepts as the multiples of a, b, c are $2, 3, 2$. Reciprocals of the intercepts are $1/2, 1/3, 1/2$. Their LCM is 6. Multiply the reciprocal by 6, so that they become integers $(3, 2, 3)$.

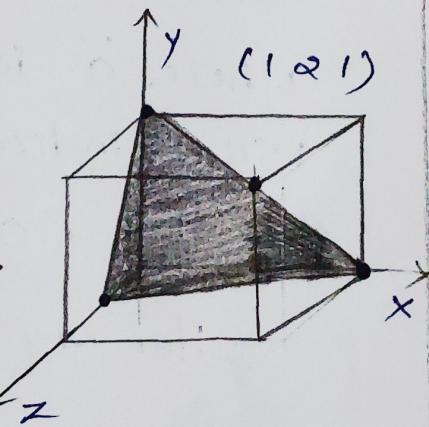
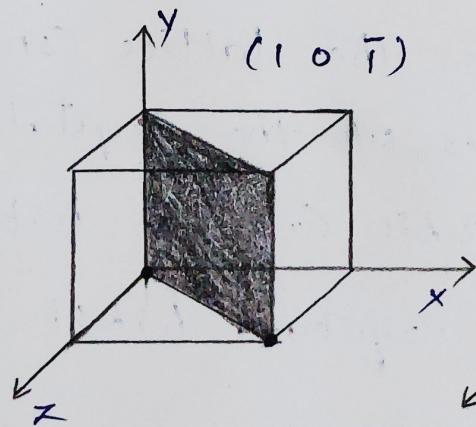
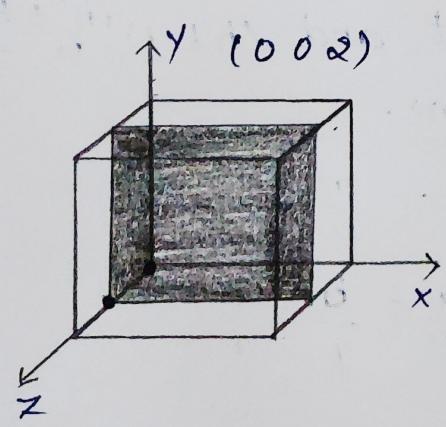
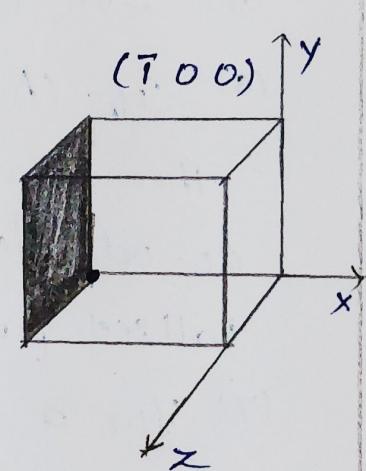
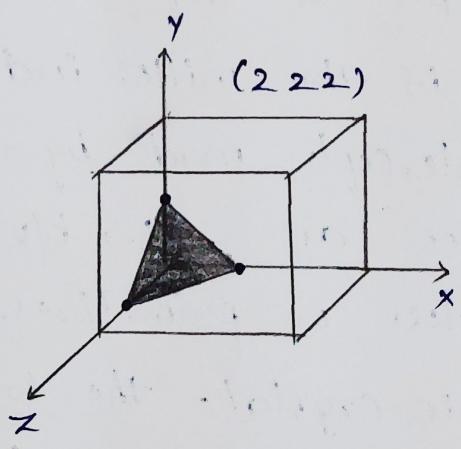
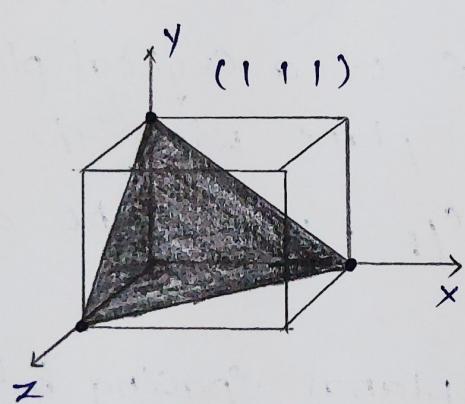
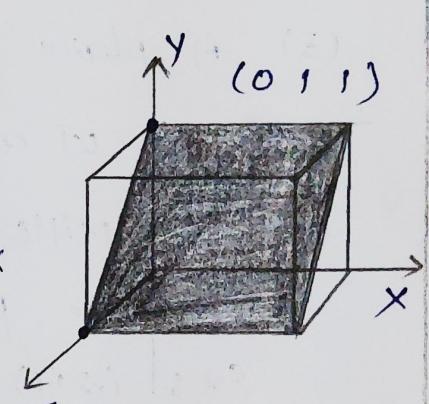
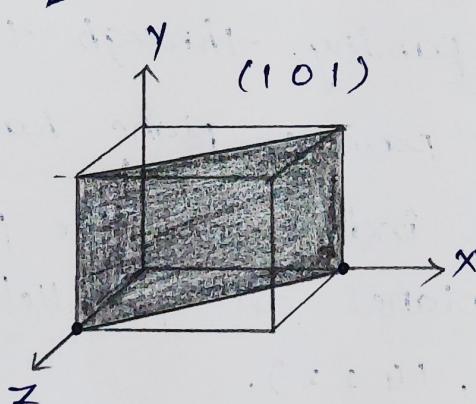
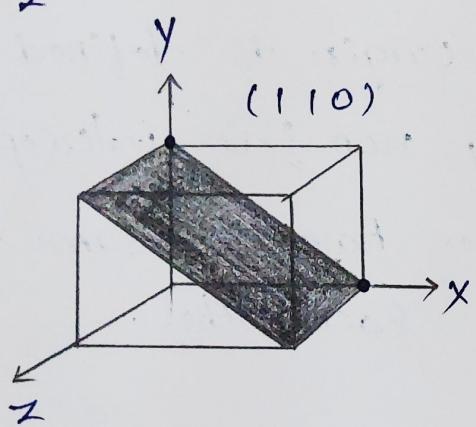
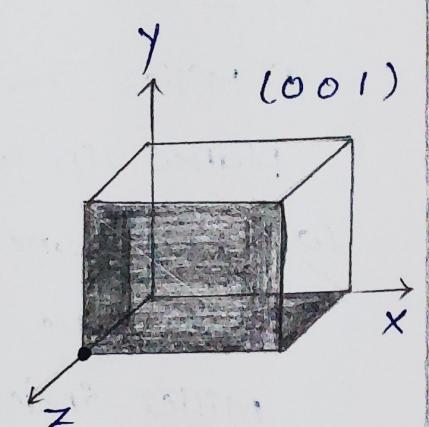
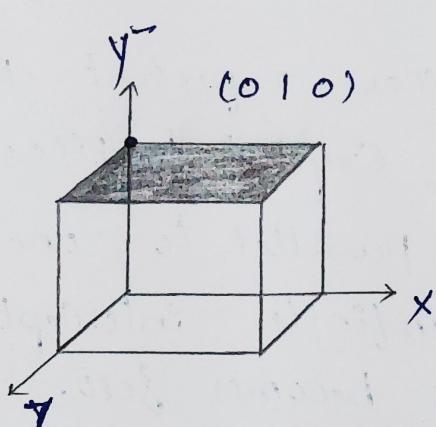
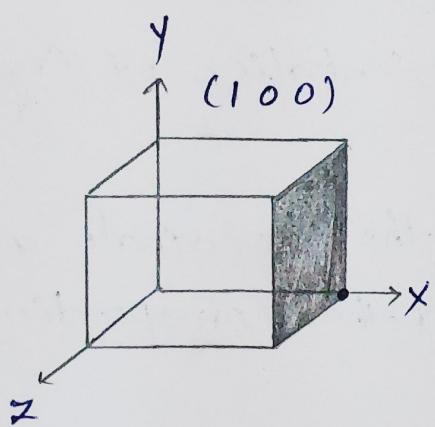
The integers are written with in parentheses without any dot or comma as (323) . (323) represents the Miller indices of the crystal plane ABC.

Note: The +ve x-axis is represented as (100) , y-axis as (010) , z-axis as (001) .

The -ve x-axis is represented as (-100) , y-axis as $(0-10)$, z-axis as $(00-1)$ (or) -ve can be written as $(00\bar{1})$



Miller Indices of the Crystal planes in a unit cubic cell:



Important features of Miller Indices of Crystal planes :-

- (1) Miller Indices represent the orientation of Crystal planes in a crystal lattice.
- (2) Any plane parallel to one of the coordinate axes will have infinite intercept, and the corresponding Miller index becomes zero.
- (3) A plane passing through the origin is defined in terms of a parallel plane having non zero intercepts.
- (4) If Miller indices of the planes have the same ratio then the planes are parallel to each other.
Ex: (211), (422).
- (5) -ve intercepts are represented as bar i.e (100).
- (6) If (hkl) is the miller indices of a crystal plane, then the intercepts made by the plane with the coordinate axes are a/h , b/k , c/l , where a, b, c are the lattice parameters or primitives.
- (7) For a cubic crystal, the interplanar spacing between the adjacent parallel plane is given by $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ where a is the lattice constant and (hkl) is the Miller indices of the crystal plane.
- (8) For a cubic Crystal, $h:k:l = \frac{a}{P} : \frac{a}{Q} : \frac{a}{R}$
For any crystal, $h:k:l = \frac{a}{P} : \frac{b}{Q} : \frac{c}{R}$

(9)

Separation between successive (hkl) planes :-

Let OA, OB, OC be the orthogonal axes. Consider a plane ABC with (h k l) passing through origin 'O'. Let the normal to the plane ABC, ON = d is the interplanar spacing for another plane (xyz).
Let (xyz) makes intercepts $(\frac{a}{h}, \frac{b}{k}, \frac{c}{l})$ along three axes.

$$\cos\alpha = \frac{d}{OA} = \frac{d}{(a/h)} = \frac{dh}{a}$$

$$\cos\beta = \frac{d}{OB} = \frac{d}{(b/k)} = \frac{dk}{b}$$

$$\cos\gamma = \frac{d}{OC} = \frac{d}{(c/l)} = \frac{dl}{c}$$

From the law of direction cosines,

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

$$\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{b}\right)^2 + \left(\frac{dl}{c}\right)^2 = 1 \quad \text{where } a = b = c$$

$$d^2 \left(\frac{h}{a} \right)^2 + d^2 \left(\frac{k}{b} \right)^2 + d^2 \left(\frac{l}{c} \right)^2 = 1$$

$$d^2 \left[\left(\frac{h}{a} \right)^2 + \left(\frac{k}{b} \right)^2 + \left(\frac{l}{c} \right)^2 \right] = 1$$

For cubic lattice $a = b = c$,

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

$$\frac{d}{a} = \left[\frac{1}{h^2 + k^2 + l^2} \right]^{1/2}$$

$$d = \frac{a}{[h^2 + k^2 + l^2]^{1/2}} \Rightarrow$$

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

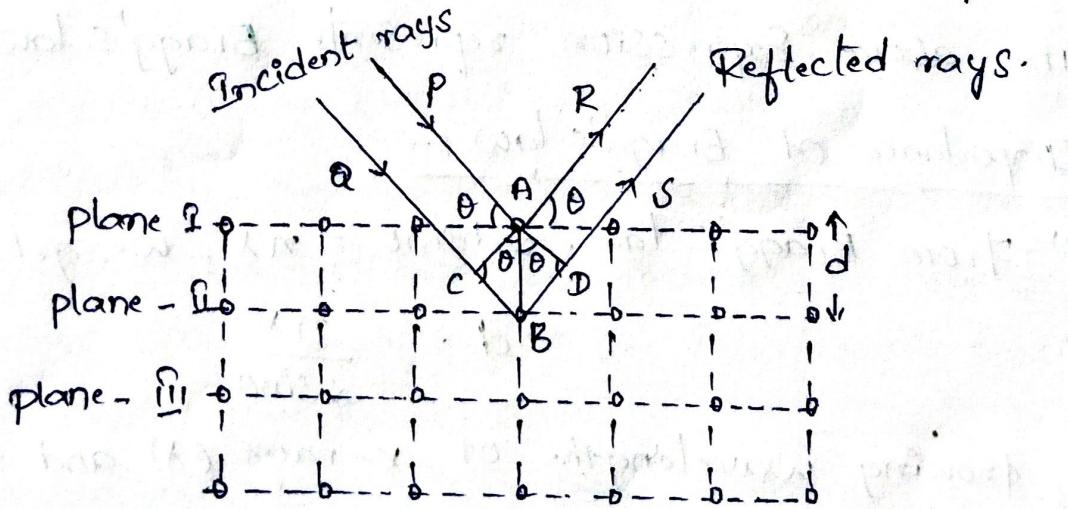
X-ray diffraction

X-ray diffraction by crystal planes :-

- (1) As the wavelength of X-rays is very small (0.1 nm) grating cannot be used to X-ray diffraction studies as the spacing cannot be comparable to wavelength of X-rays.
- (2) Laue suggested that a crystal which consists of three dimensional array of regularly spaced atoms will be produced observable diffraction effects for X-rays.
- (3) The diffraction pattern consists of a central spot and series of spots arranged in a definite pattern around the central spot. This pattern is known as Laue's pattern.

* Bragg's Law :-

Consider a crystal which consists of equidistant parallel planes with the interplanar spacing ' d ' as shown in fig. When the X-rays of wavelength (λ) fall on these crystal planes, the atoms in the planes reflect the X-rays in all directions.



Let the X-ray PA incident at an angle ' θ ' with the plane I be reflected at atom A in the direction AR and another X-ray QB reflected at atom 'B' in the direction BS. These diffracted X-rays will interfere constructively or

or destructively depending on the path difference between the x-rays. To calculate the path difference, two normals AC and AD are drawn from A to QB and BS.

$$\text{path difference} = CB + BD$$

$$\text{From } \triangle ABC, \sin\theta = \frac{CB}{AB}$$

From $\triangle ACB$

$$CB = AB \sin\theta \\ = d \sin\theta$$

Similarly from $\triangle ADB$,

$$BD = d \sin\theta$$

$$\begin{aligned} \text{Path difference} &= CB + BD \\ &= d \sin\theta + d \sin\theta = 2d \sin\theta. \end{aligned}$$

To get maximum intensity, path difference should be equal to integral multiple of λ .

$$\text{So, path difference} = n\lambda$$

$$2d \sin\theta = n\lambda, \text{ where } n = 1, 2, 3, \dots$$

The above expression represents Bragg's law.

Importance of Bragg's law :-

(1) From Bragg's law, $2d \sin\theta = n\lambda$, we get

$$d = \frac{n\lambda}{2 \sin\theta}$$

By knowing wavelengths of x-rays (λ) and the glancing angle θ , 'd' can be calculated.

(2) Knowing 'd' the lattice constant ' a ' of the cubic crystal can be known.

(3) Knowing 'a', P (density) and M (molecular weight) of the crystal, the number of atoms in the unit cell can be calculated.

(4) For a cubic crystal,

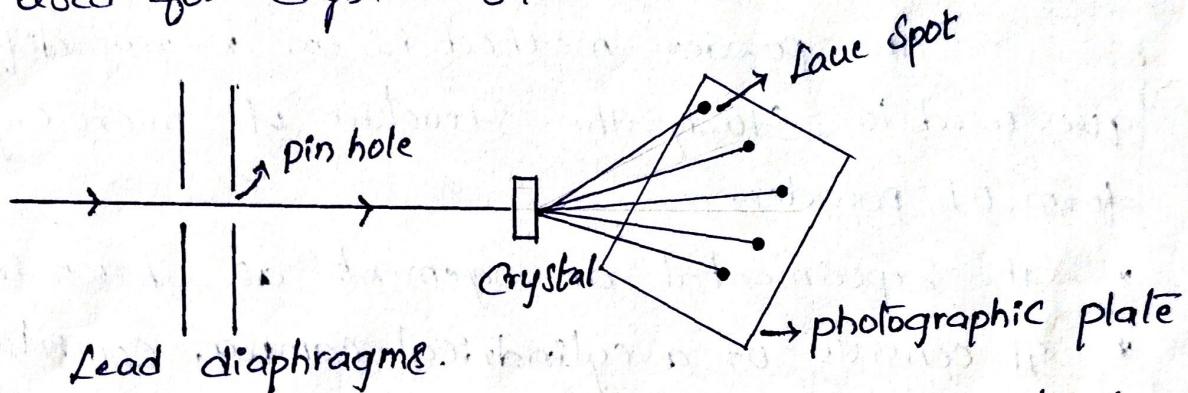
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

knowing d and a, the value of $h^2 + k^2 + l^2$ can be calculated.

(5) Depending on the values of $h^2 + k^2 + l^2$, we can classify the crystals as BCC, FCC, Simple cubic etc.

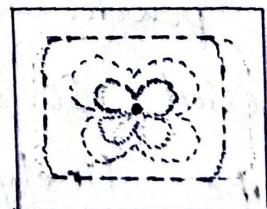
* Lauze Method :-

The Lauze method is one of the X-ray diffraction techniques used for Crystal structure studies.



The crystal whose structure has to be studied, is held stationary in a continuous X-ray beam. After passing through the pin holes of lead diaphragms, we obtain a fine beam of X-rays. These X-rays are allowed to fall on the crystal. The crystal diffract the X-rays satisfying Bragg's law.

The diffracted X-rays are allowed to fall on a photographic plate. The diffraction pattern consists of a series of bright spots corresponding to interference maximum for a set of crystal planes satisfying the Bragg's Equation $2d \sin \theta = n\lambda$ for a particular wavelength of the incident beam.



The distribution of spots depends on the symmetry of the crystal and its orientation with respect to X-ray beam. For a simple cubic crystal, the Laue photograph is shown in above fig.

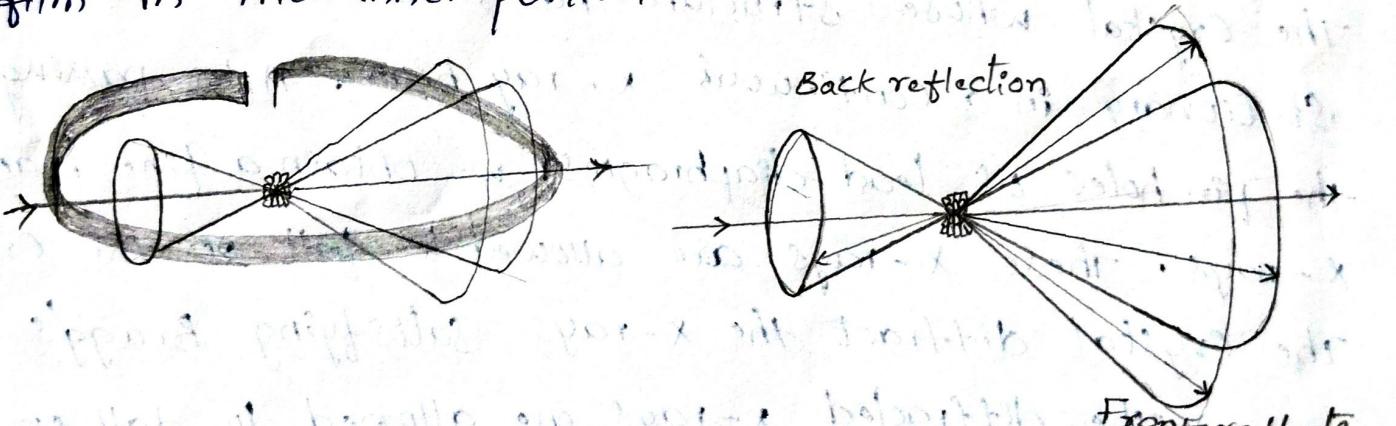
Merits and Demerits :-

- * This method is used for determination of crystal orientation and symmetry.
- * It is also used to study Crystalline Imperfections.
- * As several wavelengths diffract from the same plane, it is not convenient.

* Powder Method (Debye - Scherrer Method) :-

The powder method is an x-ray diffraction technique used to study the structure of micro crystals in the form of powder.

- * The experimental arrangement as shown in fig.
- * It consists of a cylindrical camera, consisting of a thin film in the inner portion.



The powder is prepared by crushing the polycrystalline material. So that it consists of crystallites.

- * The finely powdered crystal is filled in a capillary tube and held stationary.
- * Around the powder specimen a photograph film is set circularly so as to record the diffraction at any possible

angle θ .

procedure :-

- * A fine beam of monochromatic x-rays are send through the powdered Crystal.
- * The x-rays are diffracted from individual micro crystals which orient with planes making Bragg's angle θ with the beam for different values of θ and d .
- * The diffracted ray corresponding to fixed values of θ and d , lie on the surface of a cone with its apex at the tube P and the semi vertical angle 2θ .
- * Different cones are observed for different sets of θ and d , for a particular order of n .
- * The diffracted x-ray cones make impressions on the film in the form of arcs on either side of the exit and entry holes, with centers coinciding with the hole.
- * The angle θ corresponding to a particular pair of arcs is related to the distance 's' between the arcs as

$$4\theta \text{ (rad)} = s/R \quad \{ \text{angle} = \text{arc/radius} \}$$

where 'R' is the radius of the camera

$$\begin{aligned} 4\theta \text{ (deg)} &= [s/R] \times [180/\pi] \\ &= (57.296) s/R. \end{aligned}$$

From the above Expression θ can be calculated
The inter planar Spacing for first order diffraction is

$$d = \frac{n\lambda}{2\sin\theta} = \frac{\lambda}{2\sin\theta}$$

Merits :-

- * using filter, we get monochromatic x-rays (λ remains constant).
- * All Crystallites are Exposed to x-rays and diffractions take place with all available planes.
- * knowing all parameters, crystal structure can be studied completely.