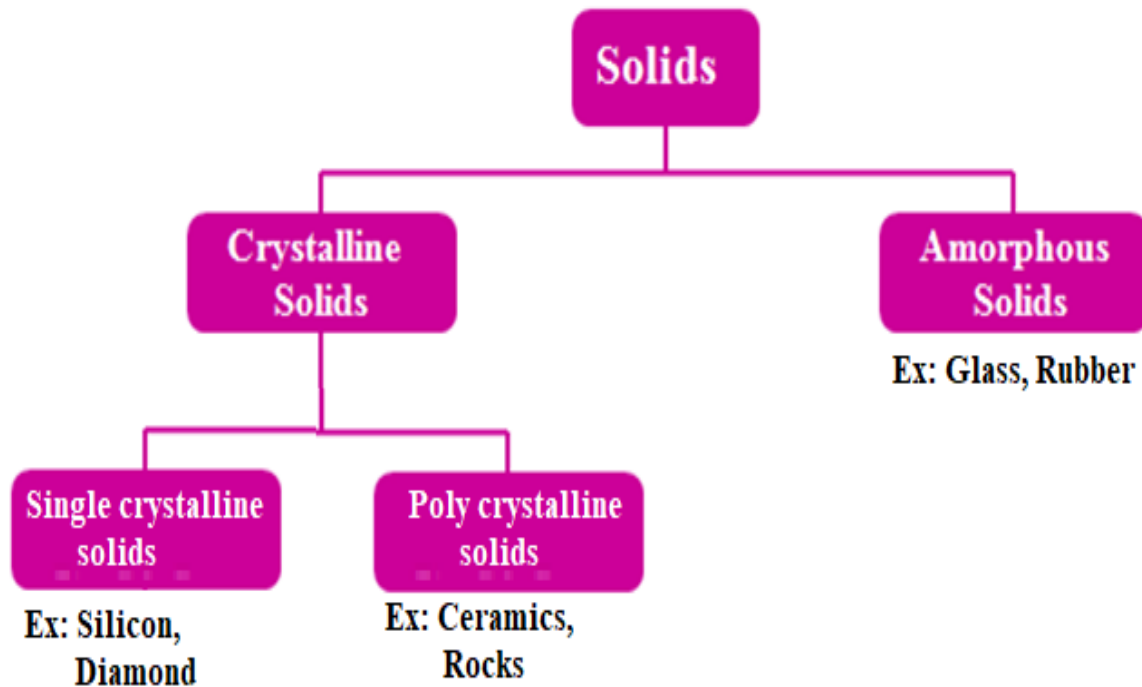# UNIT-II: CRYSTALLOGRAPHY & X-RAY DIFFRACTION

2.1: Crystallography

2.1. Crystalline and amorphous solid:

Based on atomic arrangement, solids are classified as follows.

```
                          Solids
                            |
          ┌─────────────────┴─────────────────┐
     Crystalline                           Amorphous
       Solids                                Solids
          |                             Ex: Glass, Rubber
     ┌────┴────┐
Single crystalline   Poly crystalline
   solids               solids
Ex: Silicon,         Ex: Ceramics,
   Diamond              Rocks
```

1. **Crystalline Materials:** The materials in which the atoms are arranged in an orderly fashion in three-dimensional pattern are known as crystalline materials. Examples are NaCl, Diamond etc.

2. **Amorphous Materials:** The materials in which the atoms are arranged randomly in three-dimensional pattern are known as amorphous materials. Examples are Glass, Rubber etc.

3. **Anisotropic Materials:** If the properties of materials, like Young's modulus, vary with different crystallographic axes, such materials are known as anisotropic materials. Examples are crystalline materials

4. **Isotropic Materials:** If the properties of materials are same in all crystallographic axes, such materials are known as isotropic materials. Example: Amorphous materials

2.2. Difference between crystalline and amorphous solids:

| Crystalline solids	Amorphous solids
• They have periodic arrangement of atoms.	• They have incomplete periodicity of atoms.
• They have regular internal arrangement of atoms.	• They have irregular internal arrangement of atoms.
• They have definite shape and structure.	• They do not have definite shape and structure.
• They have Sharp melting point.	• They have broad melting point.
• They show anisotropic in nature.	• They show isotropic in nature.
• They have long range ordered.	• They have short range ordered.

2.3. Lattice/Space Lattice:

Statement: The symmetrical three-dimensional structural arrangement of atoms or ions or molecules inside a crystal structure is called the lattice of a crystal (OR) A regular arrangement of points extended repeatedly in space is known as space lattice.

- Each point is surrounded by the neighbouring points in an identical way and has an identical environment w.r.t. other points.

- Let us consider a two dimensional square array of atoms along X- and Y- directions as shown in **Fig.**

- The line joining the any two points (a or b) is known as translational vector.

- These vectors are also known as unit cell primitives.

- Consider a lattice point as origin at an arbitrary point 'O' as shown in **Fig.**

- Let 'P' be a lattice point at a distance 'r' from the origin.

- The position vector of the point 'P' can be represented by translational vector as

$$\overrightarrow{OP} = \vec{r} = n_1 \vec{a} + n_2 \vec{b}$$

where n_1 and n_2 are integers and their values depend on the position of the lattice point under consideration w.r.t. the origin. Therefore, $\vec{r} = 2\vec{a} + 1\vec{b}$
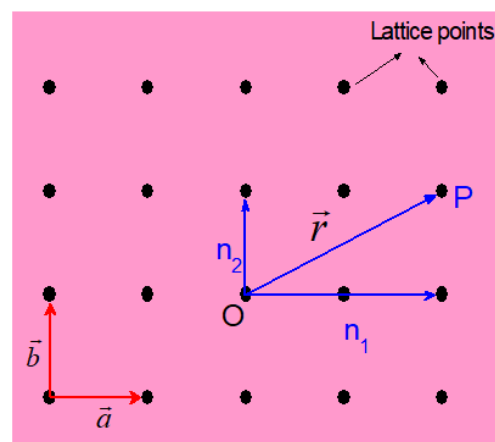
2.4. Basis:

Statement: A unit assembly of atoms identical in composition is known as **basis**.

- In case of the simplest crystals such as copper, silver etc., there is a single atom at each lattice point.

- In other case, there is a group of several atoms at each lattice point. This group is called basis.

- So, each basis is identical in composition, arrangement and orientation with other basis.

- When the basis is represented with correct periodicity in all directions, then it gives the actual structure of crystal.

    $\therefore Crystal\ structure = Spacelattice + Basis$

- A two-dimensional crystal structure which contains two different atoms (for example, CsCl) is shown in Figure.

Basis

- Lattice point
- Cs ion
- Cl ion

2D space lattice of CsCl
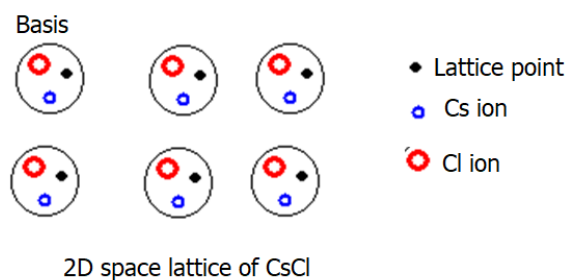
2.5. Unit Cell:

Statement: The smallest possible geometrical figure which when repeated regularly in space gives the actual crystal structure is known as unit cell.

- The simplest form of 3-D unit cell is shown in figure.

- So, unit cell is the smallest group of atoms which has overall symmetry of a crystal.

- It represents the smallest group of atoms from which the entire lattice can be built by repetition in three dimensions.

- The choice of unit cell is not unique but it can be constructed in a number of ways.

- Let us consider a two dimensional crystal with periodic array of atoms as shown in Figure.

- This figure shows the different ways of representing unit cell in two-dimensional crystal.
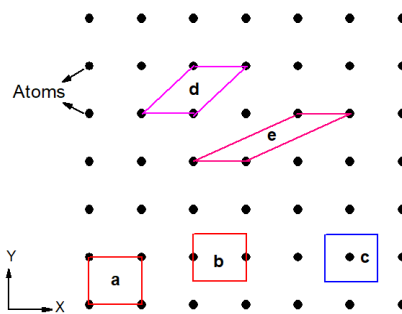
2.6. Primitive and Non-Primitive Unit Cells

If the total number of points in a unit cell is unity, then it is known as **primitive unit cell**.

If the total number of points in a unit cell is more than unity, then it is known as **non-primitive unit cell**.
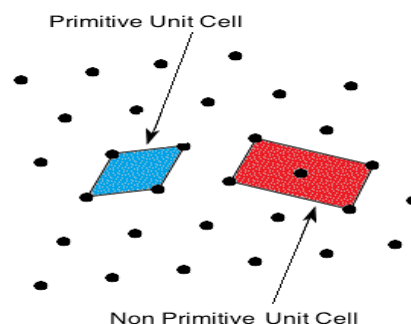
2.7. Classification of crystals (or) Common types of crystals)

Depending on the nature of bonding between the atoms or ions or molecules, the crystals are classified in to five different categories.

(i) **Covalent crystals:** In these crystals, the electron is shared by the neighboring atoms. Examples are Diamond, Si, Ge, etc.

(ii) **Ionic crystals:** In these crystals, the electron is transferred from the cation to anion site. Examples are NaCl, NaF, KCl, KBr, CsCl, etc.

(iii) **Metallic crystals:** In these crystals, the electrons are loosely bound to the corresponding nuclei by metallic bonds. Examples are Fe, Co, Al, Cu, etc.

(iv) **Molecular (or Inert-gas) crystals:** In these crystals, the molecules are bound by weak Van der Waal's forces. They are electrically insulators. Examples are Wax crystals, Sucrose, etc.

(v) **Hydrogen bonded crystals:** In these crystals, the atoms or molecules are bound by hydrogen bonds. Examples are H_2O (Ice), HF, etc.

2.8. Lattice parameters of crystal structures

Definition: The parameters that represent the size and shape of a unit cell are known as lattice parameters.

The three primitives (a, b and c) and three interfacial angles (α, β and γ) together known as lattice parameters.

Let us consider a cubic unit cell with crystallographic axes OX, OY and OZ as shown in figure.
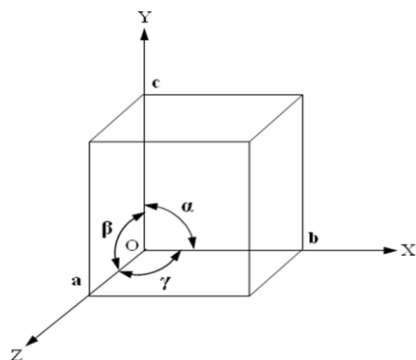
Let a, b and c are the intercepts made by the unit cell along the axes OX, OY and OZ, respectively. These intercepts define the dimensions of unit cell and they are known as primitives.

The angles (α, β and γ) between the three primitives are known as interfacial angles.

Here,   α is the angle between b and c

β is the angle between a and c and

γ is the angle between a and b.

In order to determine the actual size and shape of the unit cell, the six parameters: a, b, c and α, β, γ are essential. These are known as lattice parameters.

2.9. Expression for Lattice constant of a cubic unit cell

(OR) Relation between lattice constant and the density of cubic unit cell

Let us consider a cubic unit cell with lattice parameters as shown in figure.
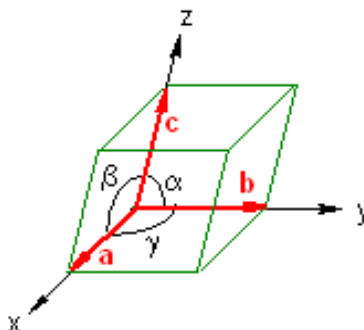
The lattice parameters are $a = b = c$ & $\alpha = \beta = \gamma = 90°$

Volume of unit cell, $V = a^3$ (since, $a = b = c$)

Mass of the unit cell, $M_{UC} = \rho.a^3$ ----------- (1)

where ρ be the density of the material of unit cell.

If M is the molecular weight of the crystal, then

Mass of the unit cell, $M_{UC} = \dfrac{N.M}{N_A}$ ----------- (2)

where N is the number of atoms per unit cell and N_A is Avagadro's number and its value is 6.02×10^{26} mol^{-1} in SI system.
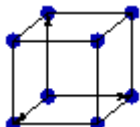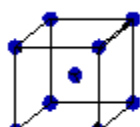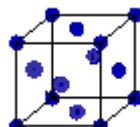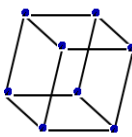
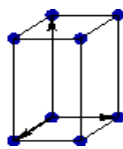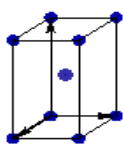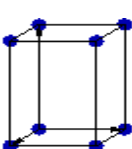From Eqs. (1) & (2), we obtain
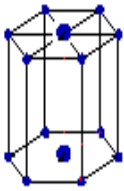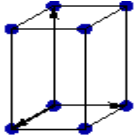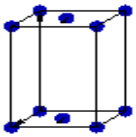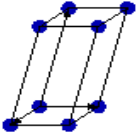
$$\rho.a^3 = \frac{N.M}{N_A}$$

$$a = \left(\frac{N.M}{\rho.N_A} \right)^{1/3} \qquad \text{----------- (3)}$$

2.10. Seven crystal systems with fourteen Bravais lattices

Based on the shape of the unit cell or lattice parameter, the crystals are categorized into seven systems. Bravais stated that fourteen lattices are enough to represent all the materials with seven crystal structures.

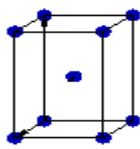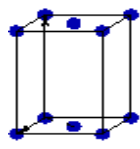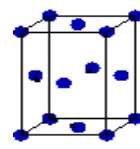| S. No.	Crystal system	Lattice parameters	Bravais lattices			
			Simple (P)	Body centered (I)	Base centered (C)	Face centered (F)
1	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^o$				
		Examples:	Polonium (Po)	Iron (Fe)		Lead (Pb)
2	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^o$				
		Examples:	SnO$_2$	BaTiO$_3$		
3	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$				
		Examples:	Neptunium (Np)	Uranium (U)	Gallium (Ga)	Iron carbide (Fe$_3$C)
4	Trigonal (Rhombohedral)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^o$				
		Examples:	Calcite (CaCO$_3$)			

5	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^o; \gamma = 120^o$				
		Examples:	ZnO			
6	Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90^o ; \gamma \neq 90^o$				
		Examples:	Gypsum (CaSO$_4$.2 H$_2$O)		Merciterite K$_2$Fe(SO$_4$)$_2$.4 H$_2$O	
7	Triclinic (Anorthic)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^o$				
		Examples:	H$_3$BO$_3$			

S. No.	Crystal system	Lattice parameters		Bravais lattices
		Primitives	Interfacial angles	
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	3 (SC, BCC, FCC)
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	2 (Simple, Body-centered)
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	4
4	Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$	1 (Simple)
5	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^o; \gamma = 120^o$	1 (Simple)
6	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^o ; \gamma \neq 90^o$	2 (Simple, Base-centered)
7	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	1 (Simple)

2.11. Important definitions:

(a) Atomic Radius (r): In a crystal lattice, half of the distance between any two successive atoms is known as atomic radius.

(b) Nearest-neighbor Distance (2r): The distance between the centers of two nearest neighboring atoms in a crystal lattice is called nearest neighbor distance. If 'r' is the radius of an atom, the nearest neighbor distance becomes '2r'.

(c) Number of atoms per unit cell (n): The total number of atoms per unit cell is given by

$$n = N_i + \frac{N_f}{2} + \frac{N_C}{8} \ ,$$

where N_i represents the no. of interior or body centered atoms, N_f represents the no. of face-centered atoms and N_C represents the no. of corner atoms.

(d) Coordination number (CN): The number of equidistant nearest neighbours that an atom has in a crystal lattice in known as coordination number. A more closely packed structure has greater coordination number.

Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or coordination number. It is a property of the lattice.

(e) Atomic Packing Factor (APF): The ratio of total volume occupied by the atoms present in a unit cell (v) to the volume of the unit cell (V) is called atomic packing factor. It is also known as atomic packing fraction.

$$APF = \frac{Volume\ of\ atoms\ in\ unit\ cell}{Volume\ of\ unit\ cell} = \frac{v}{V}$$

$$(or)\ APG = \frac{n.v}{V}$$

where n is the no. of atoms present in unit cell, v is the volume of an atom and V is the actual volume of unit cell

Note: **1) APF depends purely on no. of atoms per unit cell bur not on coordination number.**

2) APF helps to know the compactness of the unit cell. So, higher the APF more will be compactness of unit cell.

(f) Interstitial Space or Void Space (VS): The empty space present in a crystal lattice with atoms occupying their respective positions is called interstitial space or void space. [$\therefore$ VS = (1 – APF)]

2.12. Simple Cubic [SC] structure:

A simple cubic (SC) unit cell contains eight corner atoms.

The lattice parameters are a = b = c and $\alpha = \beta = \gamma = 90^\circ$

I. **Number atoms per unit cell (n):**

$$n = N_i + \frac{N_f}{2} + \frac{N_C}{8}$$

For SC, $N_i = 0$, $N_f = 0$ and $N_c = 8$

Therefore, $n = 0 + 0 + \dfrac{8}{8}$ ⟹ n = 1 ----------------------- (1)

II. **Coordination number (CN):**

In case of SC unit cell, each corner atom touches four atoms in its horizontal plane and two atoms in vertical plane (i.e., one is at top and the other is at below). It means that each atom is surrounded by six equidistant nearest neighbours.

Thus for SC, the coordination number, CN = 6 ---------------- (2)

III. **Atomic radius (r):**

In case of SC, the atoms are in contact along the cube edges as shown in Figure.

Lattice constant, a = 2r

Therefore, Atomic radius, $r = \dfrac{a}{2}$ ---------------------------------- (3)
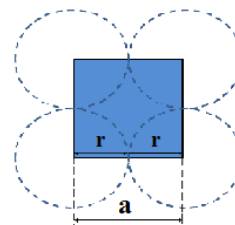
IV. **Atomic packing factor (APF):**

We know that $APF = \dfrac{n.v}{V}$

Number of atoms per unit cell, n = 1

Volume of an atom, $v = \dfrac{4}{3}\pi r^3$

Volume of unit cell, $V = a^3 = (2r)^3$

Therefore, $APF = \dfrac{1 \times \dfrac{4}{3}\pi r^3}{(2r)^3} = \dfrac{\pi}{6} = 0.52\,(or)\,52\%$ ------------------- (4)

V. **Void Space (VS):**

We know that VS = (1 – APF)

Therefore, VS = (1 – 0.52) = 0.48 (or) 48% ----------------------------- (5)

Hence, SC structure is a loosely packed structure.

NOTE: The element like Polonium (Po) possesses SC structure.

2.13. Body Centered Cubic [BCC] structure

A body-centered cubic (BCC) unit cell contains one interior atom along with eight corner atoms.
The lattice parameters are a = b = c and α = β = γ = 90º

I. **Number atoms per unit cell (n):**

$$n = N_i + \frac{N_f}{2} + \frac{N_C}{8}$$

For BCC, $N_i = 1$, $N_f = 0$ and $N_c = 8$

Therefore, n = 1 + 0 + $\frac{8}{8}$ $\Rightarrow$ n = 2 ------------------------- (1)

II. **Coordination number (CN):**

In case of BCC unit cell, the interior or body-centered atom is surrounded by eight corner atoms.
Thus for BCC, the coordination number, CN = 8 ----------------- (2)

III. **Atomic radius (r):**

In case of BCC, the atoms are in contact along the body diagonal as shown in Figure.
The length of diagonal AH is equal to 4r.

In ΔADH, $AH^2 = AD^2 + DH^2$

$$= (AB^2 + BD^2) + DH^2$$

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

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

∴ Atomic radius, $r = \frac{\sqrt{3}}{4}a$ ----------------------------------- (3)

Lattice constant, $a = 4r/\sqrt{3}$ ----------------------------------- (4)
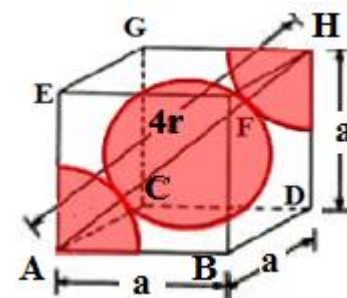
IV. **Atomic packing factor (APF):**

We know that APF = $\frac{n.v}{V}$

Number of atoms per unit cell, n = 2

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

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

Therefore, $APF = \frac{1 \times \frac{4}{3}\pi r^3}{\left(4r/\sqrt{3}\right)^3} = \frac{\sqrt{3}}{8}\pi = 0.68 \ (or) \ 68\%$ ------------------- (4)

V. Void Space (VS):

We know that VS = (1 – APF)
Therefore, VS = (1 – 0.68) = 0.32 (or) 32% -------------------------------- (5)

Hence, the BCC unit cell is closely packed structure compared to SC structure.

NOTE: The elements such as Sodium (Na), Iron (Fe), Tungsten (W), etc., possess BCC structure.

2.14. Face Centered Cubic [FCC] structure

A face-centered cubic (FCC) unit cell contains six face-centered atoms along with eight corner atoms.

The lattice parameters are a = b = c and $\alpha = \beta = \gamma = 90^\circ$

I. Number atoms per unit cell (n): $n = N_i + \dfrac{N_f}{2} + \dfrac{N_C}{8}$

For FCC, $N_i = 0$, $N_f = 6$ and $N_c = 8$

Therefore, $n = 0 + \dfrac{6}{2} + \dfrac{8}{8} = 0 + 3 + 1 \Rightarrow n = 4$ ------------------------ (1)

II. Coordination number (CN):

In case of FCC unit cell, each centre atom has four face-centered atoms in its horizontal plane and four face centered atoms in each of two planes on either side of its plane.

Thus for FCC, the coordination number, CN = 12 ----------------- (2)

III. Atomic radius (r):

In case of FCC, the atoms are in contact along the face diagonal as shown in Figure.

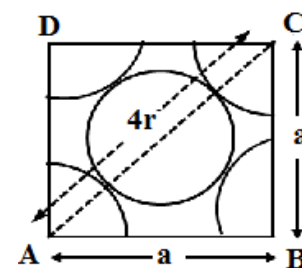The length of diagonal AC is equal to 4r.
In ΔABC,

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

$$\Rightarrow (4r)^2 = a^2 + a^2 = 2a^2 \qquad \Rightarrow 4r = \sqrt{2}\, a$$

$\therefore$ Atomic radius, $r = \dfrac{a}{2\sqrt{2}}$ ----------------------------------- (3)

Lattice constant, $a = 2\sqrt{2}\, r$ ----------------------------------- (4)

IV. Atomic packing factor (APF):

We know that APF $= \dfrac{n.v}{V}$

Number of atoms per unit cell, n = 4

Volume of an atom, $v = \dfrac{4}{3}\pi r^3$

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

Therefore, $APF = \dfrac{1 \times \dfrac{4}{3}\pi r^3}{\left(2\sqrt{2}\, r\right)^3} = \dfrac{\pi}{3\sqrt{2}} = 0.74 \ (or) \ 74\%$ ------------------- (4)

Note: Compared to SC, BCC, the FCC unit cell has high APF due to large no. of atoms per unit cell.

V. Void Space (VS):

We know that VS = (1 – APF)
Therefore, VS = (1 – 0.74) = 0.26 (or) 26% --------------------------------- (5)

Hence, the FCC unit cell is a very closely packed structure compared to SC and BCC structures.

NOTE: The elements such as copper (Cu), aluminium (AL), silver (Ag), lead (Pb), etc., possess FCC structure.

2.15. To show that FCC is more closely packed than Sc and BCC.

We know that the atomic packing fraction, $APF = \dfrac{N.v}{V}$

where $N \rightarrow$ Number atoms per unit cell, $v \rightarrow$ Volume of an atom & $V \rightarrow$ Volume of unit cell

Parameter		Unit Cell		
		SC	BCC	FCC
No. of atoms per unit cell	N	1	2	4
Volume of an atom	v	$\dfrac{4}{3}\pi r^3$	$\dfrac{4}{3}\pi r^3$	$\dfrac{4}{3}\pi r^3$
Atomic radius	r	$\dfrac{a}{2}$	$\dfrac{\sqrt{3}}{4}a$	$\dfrac{a}{2\sqrt{2}}$
Volume of unit cell	$V = a^3$	$(2r)^3$	$\left(4r/\sqrt{3}\right)^3$	$\left(2\sqrt{2}\, r\right)^3$
Atomic packing factor	APF	$\dfrac{1 \times \dfrac{4}{3}\pi r^3}{(2r)^3}$ $\dfrac{\pi}{6} = 0.52$	$\dfrac{2 \times \dfrac{4}{3}\pi r^3}{\left(4r/\sqrt{3}\right)^3}$ $\dfrac{\sqrt{3}}{8}\pi = 0.68$	$\dfrac{4 \times \dfrac{4}{3}\pi r^3}{\left(2\sqrt{2}\, r\right)^3}$ $\dfrac{\pi}{3\sqrt{2}} = 0.74$

From the above discussion, we have $SC_{[APF]} < BCC_{[APF]} < FCC_{[APF]}$
Therefore, FCC is more closely packed than Sc and BCC.

2.17. Miller indices of crystal planes

Lattice/crystal plane is a plane whose intersections with the lattice are periodic. They can be identified by Miller indices.

Definition: *"Millar indices are three smallest integers which have the same ratio as the reciprocals of the intercepts of the crystal plane with the crystallographic axes".*

Procedure to Find the Miller indices

1. Find the intercepts of the desired plane on the three crystallographic axes (X-, Y-, and Z-), respectively. Let these be (pa, qb, rc), where a, b and c are the lattice constants and p, q and r are the corresponding multiples.

2. Take the ratio of reciprocals of the multiples of intercepts i.e., $\dfrac{1}{p}:\dfrac{1}{q}:\dfrac{1}{r}$

3. Convert the reciprocals into integers by multiplying each one of them with their LCM to get smallest integers. Let these be h, k and l.

4. Enclose these integers in small parenthesis as (h k l), which represent the Miller indices.

For example, consider a crystal plane makes intercepts 2a, 3b and 2c along the coordinate axes X-, Y- and Z-, respectively. First of all, the given crystal plane ABC can be represented as shown in figure.

The intercepts as the multiples of a, b and c are 2, 3 and 2, respectively.
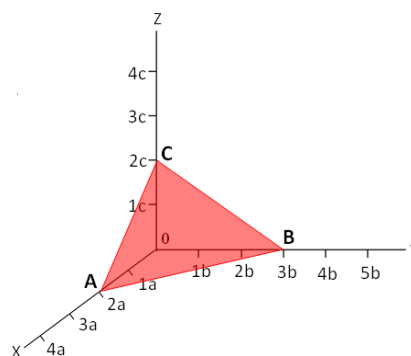
Ratio of reciprocals is $\dfrac{1}{2}:\dfrac{1}{3}:\dfrac{1}{2}$

LCM of the reciprocals is 6

On multiplying each reciprocal with the LCM we get,

$\dfrac{1}{2}\times 6:\dfrac{1}{3}\times 6:\dfrac{1}{2}\times 6 \;\Rightarrow\; 3:2:3$

∴ The Miller indices of the given crystal plane are (3 2 3).

**NOTE: Important features of Miller indices**

- Miller indices represent the orientation of an atomic plane in a crystal lattice.
- They are used to identify the direction of a crystal plane.
- They are used to identify the family of equivalent crystal planes.

2.18. Procedure for drawing the crystal planes for the given miller indices (h k l):

1. With given lattice constants, the unit cell is drawn with the axes X-, Y- and Z- marked. If the lattice constants are not given then unit cubic cell can be taken

2. The reciprocals of the indices are to be taken: $\frac{1}{h}, \frac{1}{k}$ and $\frac{1}{l}$. These reciprocals give the intercepts of the desired plane on the axes X-, Y- and Z-, respectively.

3. The intercepts are marked in the unit cell and plane is drawn.

4. If the intercept value is infinity on any axis, then the plane is drawn parallel to that axis.

Example 1: Sketch the (0 0 1) plane of a cubic unit cell.

Axes	X-	Y-	Z-
Miller plane (h k l)	0	0	1
Reciprocals	$\frac{1}{0}$	$\frac{1}{0}$	$\frac{1}{1}$
Intercepts	∞	∞	1
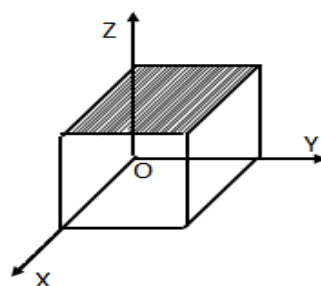
Example-2: Draw the [1 0 0] direction of a simple cubic crystal

Solution: Along the X-, Y- and Z- axes, the unit 1, 0 and 0 are moved to reach the point 'P'. The line joining the origin 'O' and the point 'P' represents the [1 0 0] direction.
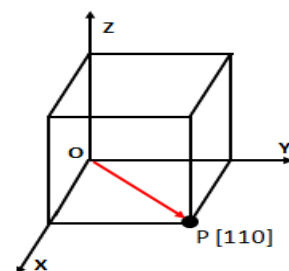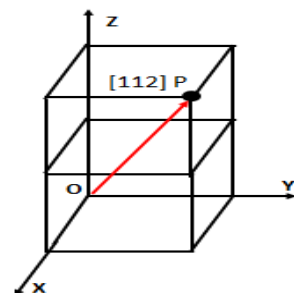
Example-3: Draw the [1 1 2] direction of a simple cubic crystal

Solution: Along the X-, Y- and Z- axes, the unit 1, 1 and 2 are moved to reach the point 'P'. The line joining the origin 'O' and the point 'P' represents the [1 1 2] direction.

2.19. Separation between successive (h k l) planes:

Consider a rectangular coordinate system with origin at 'O' i.e., at one of the lattice point. Assume a plane ABC with Miller indices (h k l). Let this plane makes intercepts OA, OB and OC on X-, Y- and Z- axes, respectively.

These intercepts are OA = $\dfrac{a}{h}$, OB = $\dfrac{b}{k}$ and OC = $\dfrac{c}{l}$,

where a, b and c are the unit cell edge lengths. Let the normal to the plane from the origin intercept the plane at 'N'. The distance (d) of the normal from the origin is called interplanar spacing i.e., ON = d.

Let α, β and γ are the angles made by ON with X-, Y- and Z- axes, respectively.

In ΔONA, $Cos\,\alpha = \dfrac{ON}{OA} = \dfrac{d}{a/h} = \dfrac{d\,h}{a}$

In ΔONB, $Cos\,\beta = \dfrac{ON}{OB} = \dfrac{d}{b/k} = \dfrac{d\,k}{b}$

In ΔONC, $Cos\,\gamma = \dfrac{ON}{OC} = \dfrac{d}{c/l} = \dfrac{d\,l}{c}$

From the law of direction Cosines, we know that

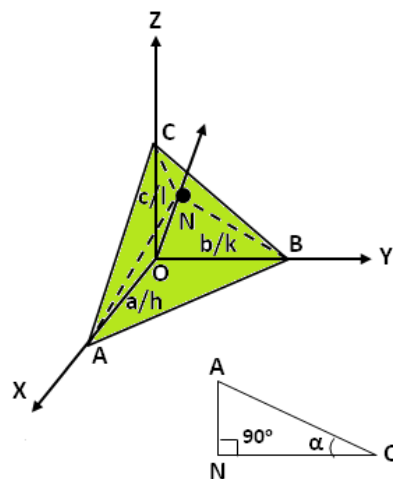$Cos^2\,\alpha + Cos^2\,\beta + Cos^2\,\gamma = 1$

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

$\therefore \; d = \dfrac{1}{\sqrt{\left(\dfrac{h^2}{a^2}\right) + \left(\dfrac{k^2}{b^2}\right) + \left(\dfrac{l^2}{c^2}\right)}}$ ------------------ (1)

This is the general expression for interplanar spacing for any set of planes.

For a cubic system, we know that a = b = c.

$\therefore \; d = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$ ------------------ (2)

2.2 . X-RAY DIFFRACTION

For diffraction to occur, the size of the obstacle must be comparable with wavelength of the incident light ways. Generally, diffraction grating is used for diffraction studies. The grating consists of a large number of closely spaced ruled lines so that the spacing between the lines may be order wavelength of light.

For a smaller wavelength of X-rays (0.1 nm to 10nm) or (1A° to 100 A°) grating cannot be used for X-ray diffraction studies as the spacing cannot be comparable to wave length X-rays. Laue suggested that a crystal which consists of a three-dimensional array of regularly spaced atoms will produce observable diffraction effects for X-rays. So crystal will act as a diffraction grating. Laue Associates with Friedrich and Knipping , succeeded in diffracting X-rays passing through a thin crystal of (ZnS) zinc blend.

Bragg's law for X-ray diffraction:

Principle: The X-rays reflected from various parallel planes of a crystal interfere constructively when the path difference is equal to integral multiple of wavelength of incident X-rays.

Consider a crystal containing equidistant parallel planes of atoms with interplanar spacing d.
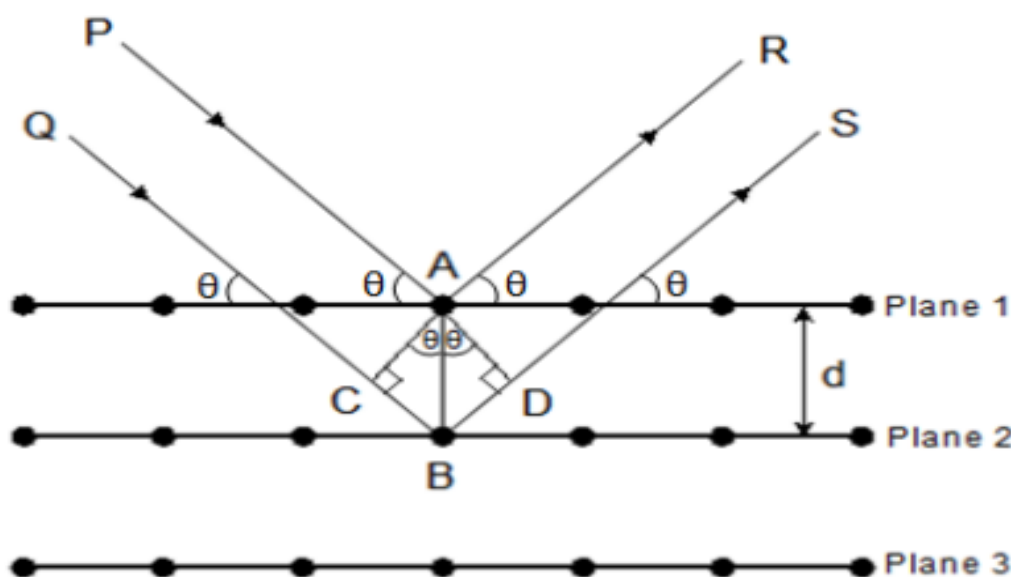
Let the X-rays of wavelength λ fall at an angle θ, called the glancing angle as shown in figure. Each atom in the crystal scatters the X-rays in all directions.

Consider a ray PA reflected at atom A in the direction AR from plane-1 and another ray QB reflected at atom B in the direction BS from plane-2. The path difference between the two reflected rays is (CB+BD). These two reflected rays will interfere constructively or destructively depending on the path difference between them. When the path difference is equal to integral multiple of wavelength of incident X-rays, then the two reflected rays will

interfere constructively and produce an intense spot. To calculate the path difference, normal AC and AD are drawn from the atom A on to QB and BS rays, respectively. According to Bragg, the condition for constructive interference is given as

CB + BD = nλ ……………. (1)

where n = 1, 2, 3 …. Corresponds to 1st, 2nd , 3rd …. diffraction maxima, respectively.

In Δ^{le} ABC, $Sin\,\theta = \dfrac{CB}{AB} \Rightarrow CB = AB\sin\theta$

(or) $CB = d\sin\theta$ ----------------------- (2)

Similarly, Δ^{le} ADB $BD = d\sin\theta$ -------------------------- (3)

From the equation 1 we get $d\sin\theta + d\sin\theta = n\lambda$

$2d\sin\theta = n\lambda$ ------------------- (4)

This is known as Bragg's law.

Limitation of Bragg's condition:

We know that the maximum possible value of glancing angle is 90°.Sin θmax = Sin 90° =1.

From Eq. (4), we get,

n λ = 2 d (or) λ ≤ 2d --------------- (5)

Therefore, the wavelength of X-rays should not exceed twice the interplanar spacing for diffraction to occur.

Significance of Bragg's law:

1. Knowing the value of interplanar spacing, the lattice constant of the cubic crystal can be determined.

2. Knowing the values of glancing angle ratio, the ratio of interplanar spacing and hence the type of crystal i.e., SC, BCC, FCC can be identified.

X-RAY DIFFRACTOMETER:

There are three main X-ray diffraction methods by which the crystal structure can be analyzed.

1. The Laue method [for single crystals]

2. The Powder method [Poly crystalline powders]

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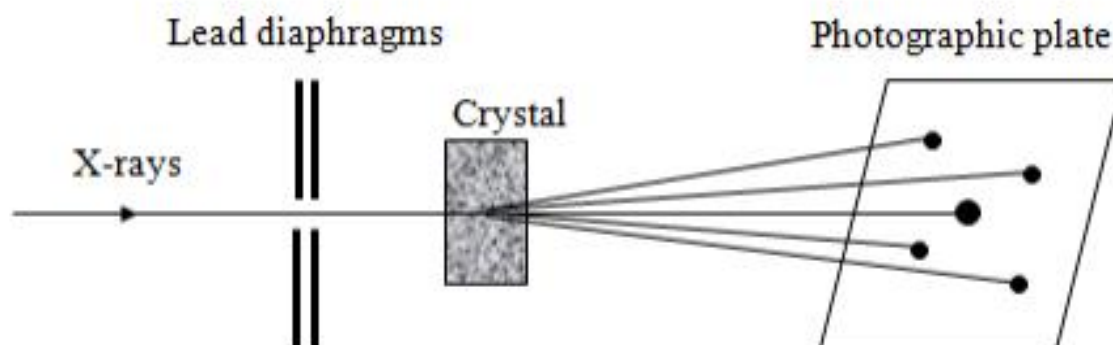
Laue Method:

The Laue method is one of the X-ray diffraction technique used for crystal structure studies. The crystal whose structure has to be studied, is held stationary in continuous X-ray beam. After passing through the pin holes of lead diaphrams, we obtain a fine beam of X-rays. These x-rays are allowed to fall on the crystal. The diffracted rays through the crystal are made to fall on a photographic plate. The resultant diffraction pattern contains a series of spots, called the Laue pattern.

In Laue pattern, each spot corresponds to interference maximum for a set of crystal planes satisfying the Bragg's equation, $2d \sin \theta = n\lambda$ for a particular wavelength of incident X-ray beam. The distribution of spots in the Laue pattern depends on the symmetry of the crystal and its orientation with respect to the X-ray beam.

The atomic arrangement in the crystal can be determined from a study of the position and intensities of the Laue spots. For a simple cubic crystal, the Laue photograph is shown in figure
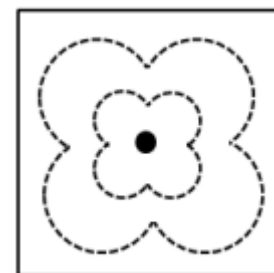
Applications

1. Laue method is convenient for the rapid determination of crystal orientation and symmetry.

2. Laue method is also used to study the crystalline imperfections (defects) under mechanical and thermal treatment. The presence of imperfections forms streaks instead of spots in Laue photograph.

Limitations

1. Laue method failed in determining the unit cell parameters of a crystal because the values of 'λ' for different reflections are not known.

2. Laue method is not convenient for actual crystal structure determination because several wavelengths of X-rays diffract in different order from the same plane and they superimpose on a single spot.

Powder method:

Powder method is an x-ray diffraction technique used to study the structure of micro crystals
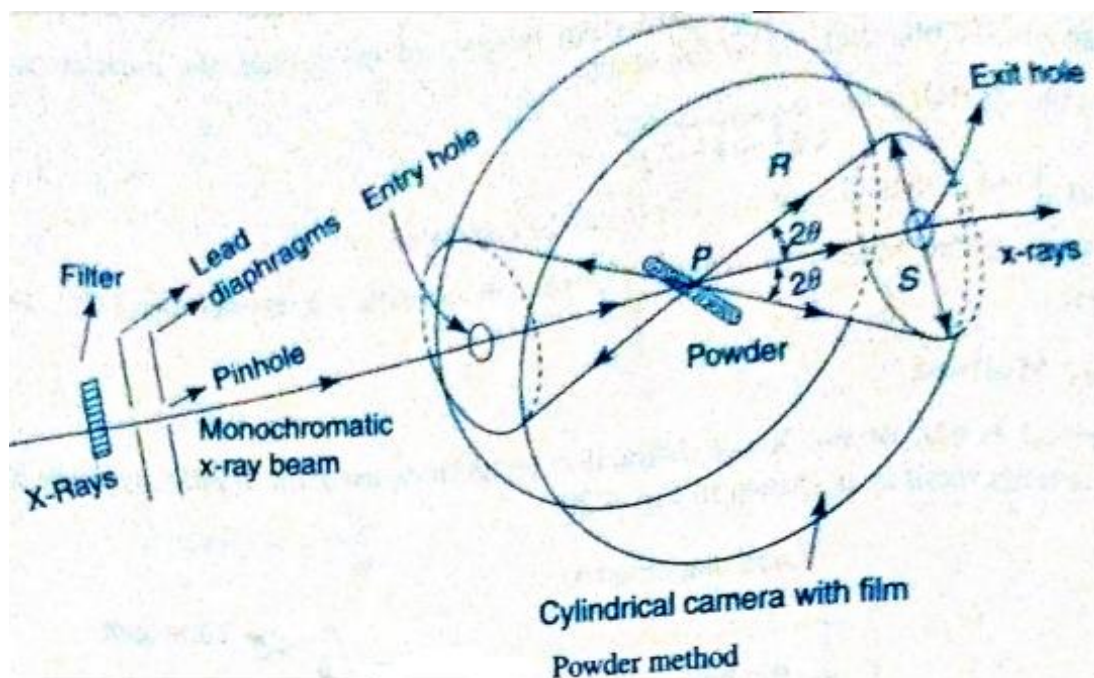
Powder method

(tiny crystallites) in the form of powder. This method gives the information regarding the size and orientations of the crystallites in the powder.

The powder is prepared by crushing the polycrystalline material so that it consists of crystallites. These crystallites are all randomly oriented so that they make all possible angles with the incidence X-rays. Thus all orders of reflections from all possible atomic planes are re-ordered at the same time.

The experimental arrangement consists of a cylindrical camera, called the Debye-Scherrer camera consisting of a film in inner portion. The finally powdered sample is filled in a thin capillary tube made on non-diffracting material. When a beam of monochromatic X-rays is allowed to incident on the powder specimen, then a part of X-rays diffracted by the powder and the remaining part comes out through the exit hole.

As the powder contains randomly oriented crystallites, all possible values of 'θ' and 'd' are available for diffraction satisfying the Bragg's law, $2d\,\sin\theta = n\lambda$. For a particular value of 'θ', various orientations of particular set of planes are possible. The diffracted rays corresponding to fixed values of 'θ' and 'd' will form a cone whose axis lies along the direction of the incident beam. The semi-vertical angle of each cone is equal to 2θ.

Different cones are observed for different sets of 'd' and 'θ' for a particular value of 'n'. Similarly, different cones are observed for different combinations of 'θ' and 'n' for a particular value of 'd'. Thus, for each set of planes and for each diffraction order, there will be a cone of reflected X-rays which form of arcs on either side of the entry and exit holes as shown in figure.

"Since the minute crystals in the powder have completely random orientations, all possible diffraction planes are available for Bragg's reflection to take place and such reflections take place from many sets of parallel planes lying at different angles to the incident X-rays".a

Entry hole   Exit hole
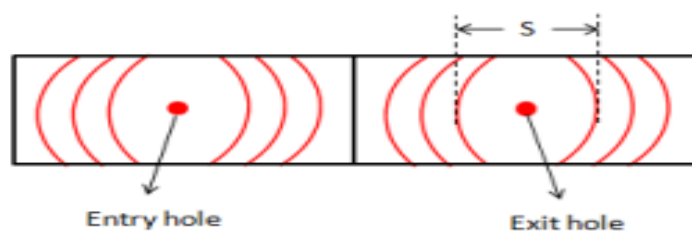
The angle θ corresponding to a particular pair of arcs is related to the distance '**S**' between the arc as

$$4\theta(radius) = \frac{s}{R}\left[\because angle = \frac{arc}{radius}\right]$$

Where R is the radius of the camera

$$4\theta(radius) = \frac{s}{R}\left[\frac{180}{\pi}\right]$$

$$= \frac{57.296S}{R}$$

From the above expression, θ can be calculated. Then the interplanar spacing for first-order diffraction is $\qquad d = \frac{\lambda}{2\sin\theta}$

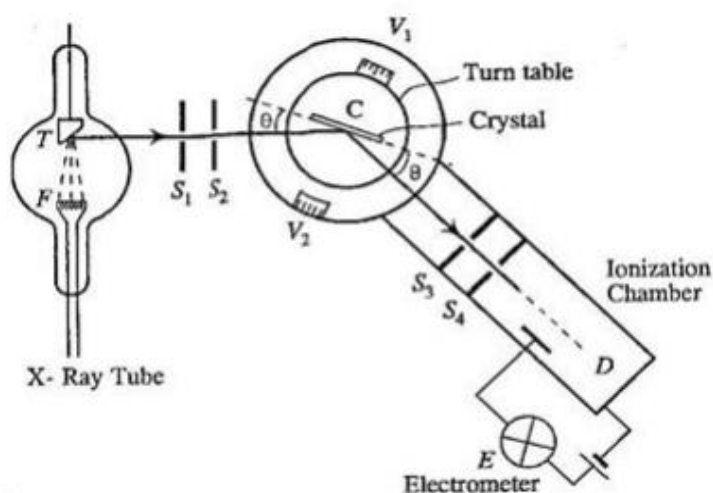Knowing all the parameters, the crystal structure can be studied.

Merits:

1. Using filters, we get monochromatic X-rays (λ remains constant)

2. All crystallites are exposed to X-rays and diffractions take place with all available planes.

3. Knowing all parameters, crystal structure can be studied completely.

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

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A collimated beam of x-rays after passing the slits S1 and S2 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 V1. An ionization chamber is fixed to the longer arm attached to the table. The position of which is measured by vernier v2. An electrometer is connected to the ionization chamber to measure the ionization current produced by diffracted x-rays from the crystal. S3 and S4 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

BRAGG'S X–RAY SPECTROMETER

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 P1, P2,P3 etc. 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 d1, d2, d3 be the inter-planar spacing for the planes (100), (110) & (111) respectively. It can be shown –

For a cubic crystal: $d1:d2:d3 = 1 : \dfrac{1}{\sqrt{2}} : \dfrac{1}{\sqrt{3}}$

For BCC crystal: $d1:d2:d3 = 1 : \dfrac{2}{\sqrt{2}} : \dfrac{1}{\sqrt{3}}$

For Fcc crystal: $d1:d2:d3 = 1 : \dfrac{1}{\sqrt{2}} : \dfrac{2}{\sqrt{3}}$

VARIATION OF IONIZATION CURRENT

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