UNIT-2 CRYSTALLOGRAPHYS & X-RAY DIFFRACTION

1) Show that FCC is more closely packed than BCC & SCC

A) **Face Centered:**

In FCC there are 8 atoms at 8 corners of the unit cell and 6 faces. considering the atoms at the faces center as origin, it can be observed that this face is common to 2 unit cells and there are 12 pts surrounding it situated at a distance equal to half the face diagonal of the unit cell.

Co-ordinate number $N = 12$

Number of atoms in unit cell $= 8 \times 1/8 + 6 \times 1/2 = 4$

Lattice constant $= a = 2r = (\sqrt{2}a/2)$

Volume of the unit cell $= V = a^3 = (4r/\sqrt{2})^3$

Volume of all atoms in unit cell $= V = 4 \times (4/3)\pi r^3$

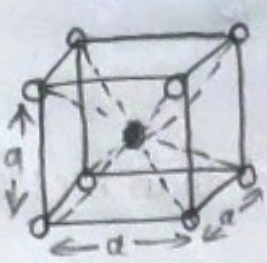
Atomic packing factor $= v/V = \frac{4 \times (4/3)\pi r^3}{(4r/\sqrt{2})^3} = 0.74 = 74\%$.

Ex: Cu, Al, Pb, Ag.

By the above values of Atomic packing factors we can say the FCC is the closed packed structures of all the three cubic structures.

Body Centered:

In a unit cell there are 8 atoms at 8 corners and another 1 at the body center. The 8 corner atoms are shared by 8 unit cells, and as the centre atoms is entirely within the unit cell, it is not shared by any surrounding unit cell.



Co-ordination number = 8

Nearest neighbour distance = $\frac{a\sqrt{3}}{2}$

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

Number of atoms per unit cell = 1+1=2

Volume of all atoms in unit cell = $V = 2 \times (4/3)\pi r^3$

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

Atomic packing factor is $\frac{2 \times (4/3)\pi r^3}{(4r/\sqrt{3})^3} = 0.68 = 68\%$.

Simple Cube:

There are 8 atoms at 8 corners of the cube. The corner atoms touch with each other. If we take a corner atoms as a reference, this atom is surrounded by 6 equidistant nearest neighbour

Co-ordination number(N) = 6 - is defined as number of equidistant nearest neighbours that an atom has given structure.

Total number of atoms (n) = 1 - each corner atoms is share by 8 unit cell, the share of each corner atom is unit cell is 1/8 th of an atom ($8 \times 1/8 = 1$)

Nearest neighbour distance ($2r$) = the distance b/t centers of the nearest neighbour atoms will be $2r$ if 'r' is the radius of the atoms.

Atomic radius (r) : $2r$ - is defined as the distance b/t nearest neighbour in a crystal. Lattice constant - $a = 2r$

Atomic Packing factor (APF) = $\frac{\text{volume of all atoms in unit cell}}{\text{total volume of the unit cell}} = 52\%$

$1/(4/3)\pi r^3 / a^3 = 52$

8) Derive an equation for the interplanar spacing between successive planes of cubic and orthorhombic lattice.

A) Separation between successive planes:

→ Consider a crystal in which the three axes are are orthogonal and the intercepts are same. Take 'o' as origin, and the reference plane passes through the origin i.e, entirely lies on the axis.

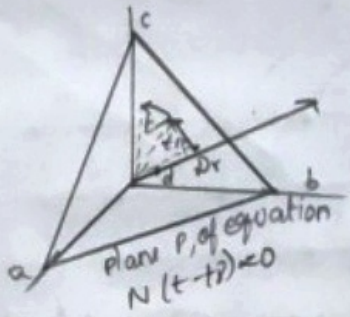
→ The next plane ABC is to be compared with the reference plane which make the intercepts a/h, a/k, a/l on x, y, z axes respectively.

→ Let (hkl) be the miller indices.

→ Let ON = d be a normal drawn to the plane ABC from origin 'o' which gives the distance of separation between adjacent planes.

→ Let the normal ON makes an angle α, β, γ with x, y, z.

Angle α = NOA, angle β = NOB, angle C = NOC



→ Then form ΔNOA, $\cos\alpha = \frac{ON}{OA} = \frac{d}{a/h} = \frac{dh}{a}$

→ Similarly, $\cos\beta = \frac{ON}{OB} = \frac{d}{b/k} = \frac{dk}{b}$

→ $\cos\gamma = \frac{ON}{OC} = \frac{d}{c/l} = \frac{dl}{c}$

→ According to cosine law of direction,

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

→ Therefore $\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{b}\right)^2 + \left(\frac{dx}{c}\right)$

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

→ In a cubic crystal $a = b = c$

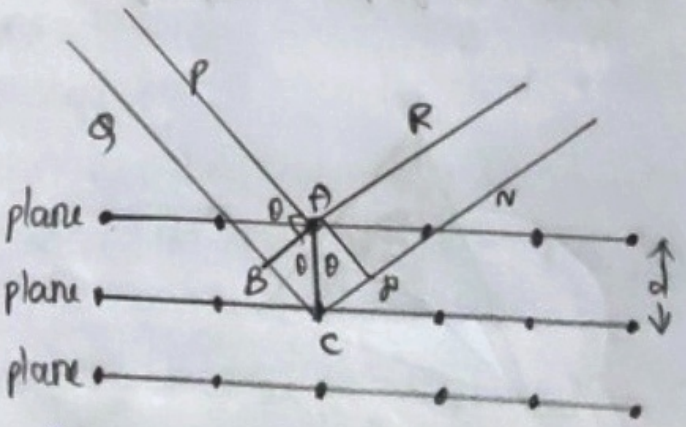
→ Therefore $d^2\left[\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}\right] = 1$

→ Therefore $d^2 = \frac{a^2}{h^2+k^2+l^2}$ i.e; $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$

9) State and explain Braggs law.

Ans. Bragg's law:

Let us consider a set of planes in a crystal spaced by inter planar distance d. Consider a narrow monochromatic x-ray beam of wavelength λ, incident on the first plane, at a glancing angle θ as shown in fig. the incident beam undergoes multiple reflection between the parallel planes of the crystal.



Consider a ray PA, incident on the first plane and it reflected in the direction AR from that plane by the atom A. Let the incident beam PA making glancing angle θ to the first plane. Similarly. consider a parallele ray QC is reflected in the direction CR by another atom C, in the second plane.

To determine the path difference between the two rays PAR and QCS, draw normals from the point A to the line QC and CS. Let the normals AB and AD. Therefore, the path difference;

In the ΔACB $\sin\theta = \frac{BC}{AC}$

Therefore $BC = AC\sin\theta = d\sin\theta$

Similarly, $CD = d\sin\theta$

Therefore, the path difference is given as

$\bar{V} = BC + CD = d\sin\theta + d\sin\theta = 2d\sin\theta$ —①

The two rays AR and CS interfere constructively and produce a maximum intensity, the path difference is $n\lambda$ $\bar{V} = n\lambda$ —②

From eq① and ② $2d\sin\theta = n\lambda$ $(n = 1,2,3,\cdots etc)$

This is known as Bragg's law.

8) Describe the construction and working of a powder method to determine the interplanar distance.

A) Powder Method:

→ In powder method, a specimen is finely powdered and taken in a thin walled capillary tube.

→ The specimen consists of tiny crystals or crystalline which are oriented randomly.

→ When a narrow beam of X-ray incident on the specimen, it comes across few crystallites with planes at glancing angle θ so as the satisfy Bragg's law.

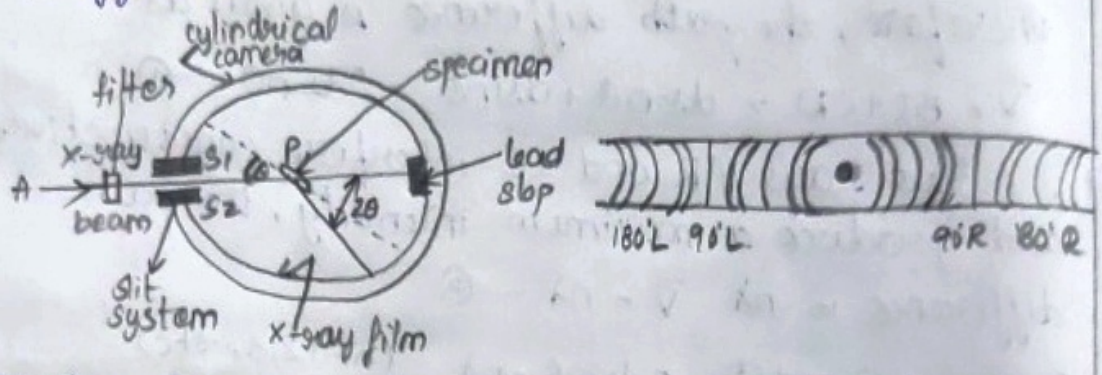
→ Since, all the orientations are equally likely, the diffracted rays will form a cone with the line of incident beam as the axis and the semi angle θ.

→ These diffracted beams are detected by placing a photographic film along the circumference of the circle with specimen at the center.

→ If "L" is the circumferential distance from the two extreme edges of cone formed by the diffracted X-rays and "R" is the radius of the circle along with film was placed, then;

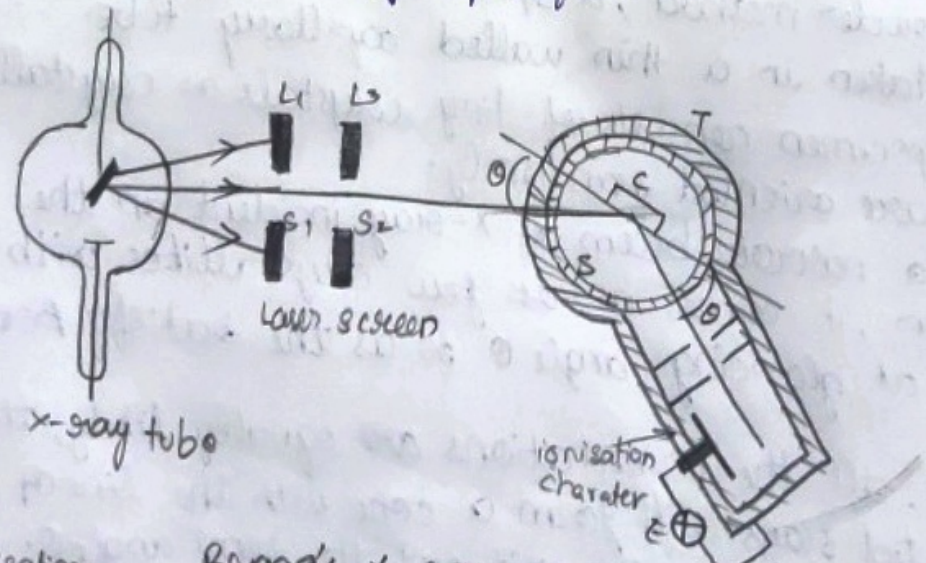
$$\frac{L}{2\pi R} = \frac{4\theta}{360} \Rightarrow \therefore \theta = \frac{45L}{\pi R}$$

→ Using θ, we can find the inter-planar spacing using Bragg's law.

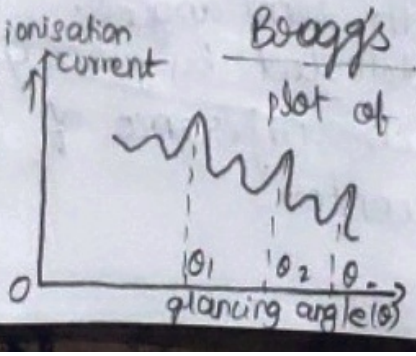


Construction:

X-ray spectrometer consists of a turn table on which a crystal is mounted. It is capable of rotating through any desired position by a vertical axis. It also consisting of ionization chamber to collect the intensity of reflect beam.



Bragg's X-ray spectrometer



Working:

X-ray from x-ray tobe passes through two narrow slits S1 and S2 and strikes the singles crystal mounted on the turntable. The intensity of reflected beam is measured at different angle using ionisation chamber. The Bragg angle i.e; the angle at which reflection is maximum is deduced from this. The glancing angle is varied and the corresponding values of the intensity of the reflected beam are noted. A graph is drawn between the glancing angle and intensity as shown in fig. The graph is known as the x-ray spectrum. The angle corresponding to the prominent peaks and third order respectively of the same wavelength.

Using Bragg's equation $2d\sin\theta = n\lambda$ Inter planar spacing and lattice constant can be calculated.

$$d \propto \frac{\lambda}{\sin\theta} \qquad d_{100} : d_{110} : d_{111} = \frac{1}{\sin\theta_1} : \frac{1}{\sin\theta_2} : \frac{1}{\sin\theta_3}$$

From the Bragg angle it is possible to determine the interplanar spacing of a crystal from which crystal type can be deduced.