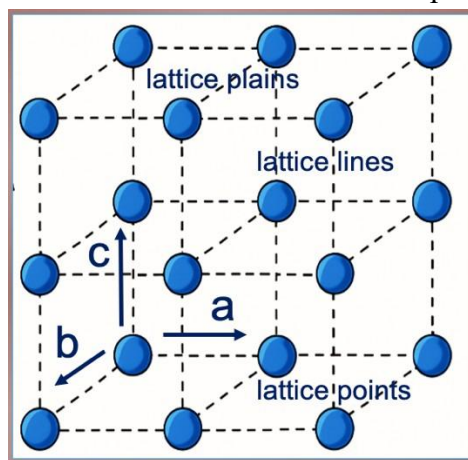


Advanced Engineering Physics
UNIT – II
Crystallography and Materials Characterization

Syllabus:

Introduction, space lattice, unit cell, basis, lattice parameters; crystal structures, Bravais lattices, packing factor: SC, BCC, FCC; Miller indices, inter-planar distance; defects in crystals (Qualitative): point defects, line defects, surface defects and volume defects. Concept of nanomaterials: surface to volume ratio, X-ray diffraction: Bragg's law, powder method, calculation of average crystallite size using Debye Scherrer's formula, scanning electron microscopy (SEM): block diagram, working principle.

Space Lattice (Crystal Lattice): A space lattice is a three-dimensional, periodic arrangement of imaginary points in space, where each point represents the identical environment of atoms, ions, or molecules in a crystal. The lattice points indicate the positions around which the constituent particles are arranged.



Basis: Basis is a structural unit, which is an atom or group of atoms associated with each lattice point in a space lattice.

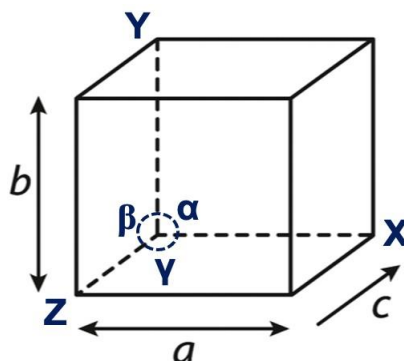
Basis is repeated at every lattice point to get the crystal structure

The crystal structure = Space Lattice + Basis.

Basis is real. The basis specifies what atoms are placed at each lattice point.

Unit Cell: The unit cell is the smallest geometric figure of a crystal which, when repeated in space in all directions, generates the entire crystal structure. It represents the crystal's symmetry and arrangement of atoms.

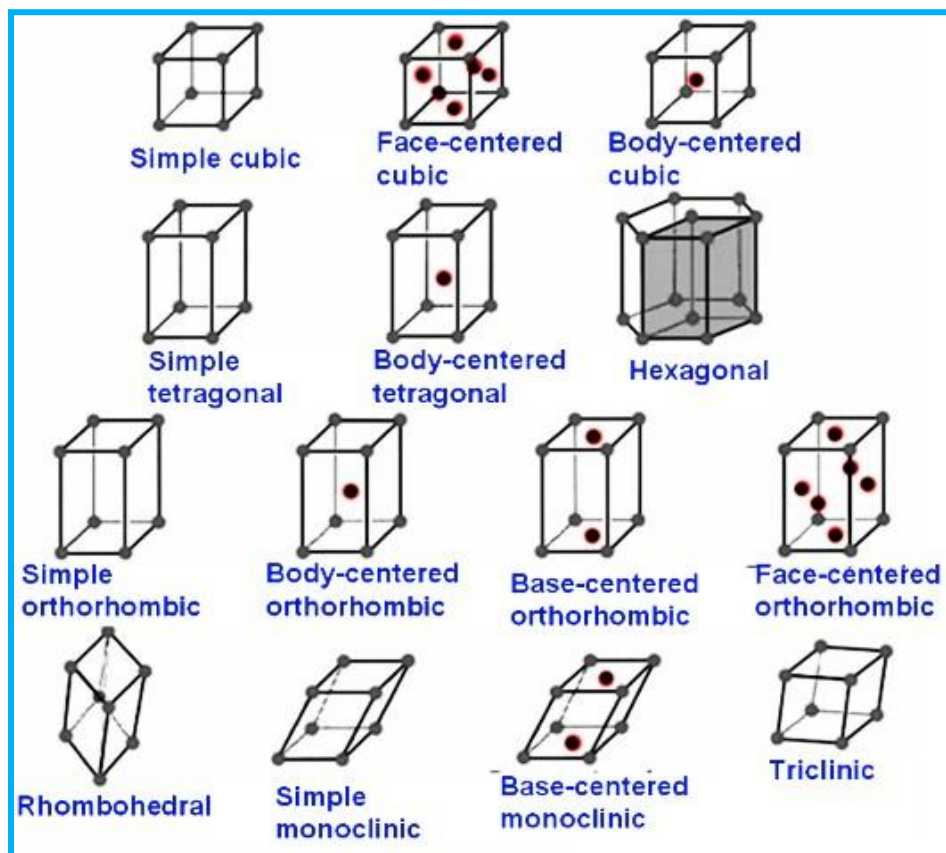
Lattice Parameters (or Lattice Constants): Lattice parameters are the geometric constants that define the dimensions of a unit cell. They include: The lengths of the three edges: a , b , c . The angles between them: α (between b and c), β (between a and c), γ (between a and b). Together, these six parameters uniquely describe the size and shape of the unit cell.



Bravais Lattices

As per Bravais there are totally 14 distinguishable ways of arranging points in three-dimensional space about seven crystal system, which are given in following table.

Crystal System	Lattice Parameters	Bravais Lattices
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90^\circ$	1. Simple Cubic (SC) 2. Body-Centered Cubic (BCC) 3. Face-Centered Cubic (FCC)
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$	1. Simple Tetragonal 2. Body-Centered Tetragonal
Orthorhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$	1. Simple Orthorhombic 2. Body-Centered Orthorhombic 3. Face-Centered Orthorhombic 4. Base-Centered Orthorhombic
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	1. Simple Hexagonal
Trigonal (Rhombohedral)	$a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$	1. Simple Rhombohedral
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	1. Simple Monoclinic 2. Base-Centered Monoclinic
Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$	1. Simple Triclinic



Simple Cubic (SC), Body-Centered Cubic (BCC) & Face-Centered Cubic (FCC) Structures

SCC

In a simple cubic lattice, there is one lattice point at each of eight corners of the unit cell. If we take an atom at one corner as the centre, it is observed that this atom is surrounded by six equidistant nearest neighbours and hence the coordination number of a simple cubic lattice is six.

The total number of atoms in one unit cell will be $(1/8) \times 8 = 1$ atom.

Simple cubic is a primitive cell, so in this structure, the atoms touch each other along the edges.

So the nearest neighbour distance, $2r = a$, where 'a' is a lattice constant.

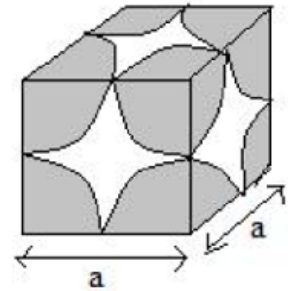
Number of atoms per unit cell, $n = 1$.

Volume of all atoms in a unit cell $= 1 \times \left(\frac{4}{3}\right) \pi r^3$

Volume of unit cell whose lattice constant 'a' is $= a^3$

The atomic packing factor (APF) $= \frac{\text{Volume of all atoms in the unit cell}}{\text{Volume of the unit cell}}$

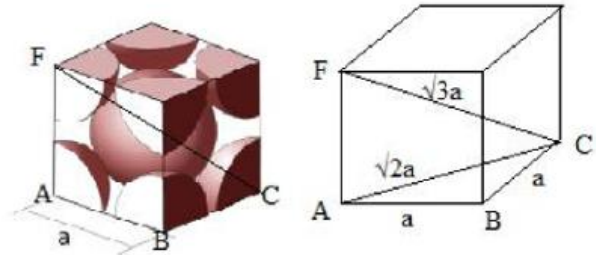
$$\begin{aligned} \text{APF} &= \frac{1 \times \frac{4}{3} \pi r^3}{a^3} && \text{since } 2r=a \quad \text{and} \quad r=a/2 \\ &= \frac{4}{3} \frac{\pi}{8} \frac{r^3}{a^3} = \frac{\pi}{6} && = 0.52 = 52\% \end{aligned}$$



BCC:

In this structure, in a unit cell, there are 8 atoms at the eight corners and another atom at the body centre. The number of atoms per unit cell in BCC is $8 \times (1/8) + 1 = 2$.

The corner atoms do not touch each other, but each corner atom touches the body centre along the body diagonal.



Hence the coordination number for BCC structure is 8.

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

From triangle ACF,

$$\begin{aligned} CF^2 &= AC^2 + AF^2 \\ &= 2a^2 + a^2 \end{aligned}$$

$$CF^2 = 3a^2$$

$$4r = \sqrt{3} a \quad \text{or} \quad a = \frac{4}{\sqrt{3}} r$$

Nearest neighbour

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

Number of atoms per unit cell, $n = 2$.

$$\text{APF} = \frac{\text{Volume of all atoms in the unit cell}}{\text{Volume of unit cell}}$$

$$\text{APF} = \frac{2 \times \frac{4}{3} \pi r^3}{a^3}$$

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

$$\frac{\sqrt{3}}{8} \pi = 0.68 = 68\%$$

$$\text{distance, } 2r = \frac{\sqrt{3}}{2} a$$

FCC:

In FCC lattice, there are eight atoms at eight corners of the unit cell and six atoms at the centres of six faces and each face is common for two unit cells. There are twelve points surrounding it situated at a distance equal to half the face diagonal of the unit cell. Each corner atom is shared by 8 surrounding unit cells.

Total number of atoms in the unit cell, $n = 8 \times \left(\frac{1}{8}\right) + 6 \times \left(\frac{1}{2}\right) = 4$.

Coordination number, $N = 12$.

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

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

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

Volume of unit cell whose lattice constant 'a' is a^3 .

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

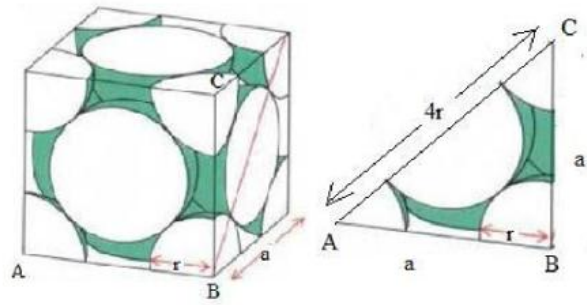
Atomic Packing Factor = $\frac{\text{Volume of all atoms in the unit cell}}{\text{volume of the unit cell}}$

$$\text{APF} = \frac{4 \times \frac{4}{3} \pi r^3}{a^3} \quad \text{Since } r = a \frac{\sqrt{2}}{4}$$

$$= \frac{\pi}{3\sqrt{2}} = 0.74$$

APF for FCC = 0.74. or 74%

Void space = 100% - 74% = 26%.



Miller indices and the procedure for identifying crystal planes.

Miller indices are a set of three integers (h k l) used to denote the orientation of crystal planes in a crystal lattice. They are derived from the intercepts of the plane with the crystallographic axes.

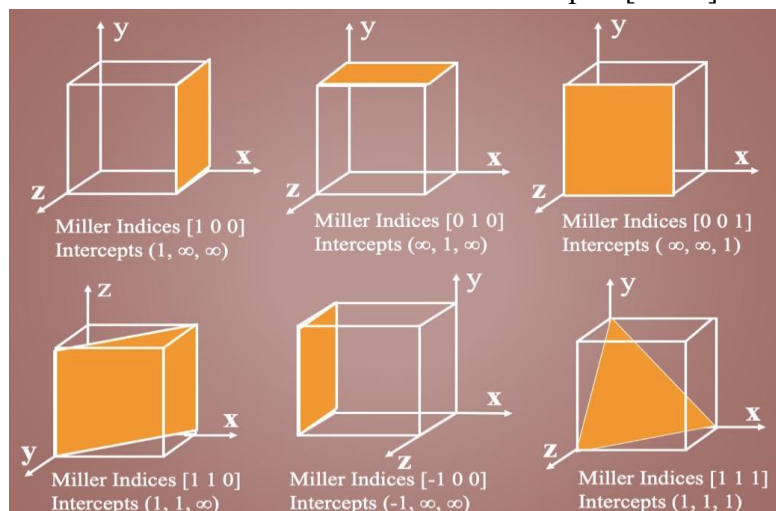
Procedure to Determine Miller Indices:

1. Identify the intercepts of the plane with the crystallographic axes (x, y, z) in terms of lattice parameters a, b, c. Example: A plane cuts the axes at 1a, 2b, and 3c.
2. Take the multiples of intercepts made by the plane. For the above: (1, 2, 3).
3. Take the reciprocals of multiples of intercepts made by the plane: (1, 1/2, 1/3).
4. Convert the reciprocal into smallest set of integers by multiplying with their LCM.

Multiply by 6 $\rightarrow$ (6 3 2).

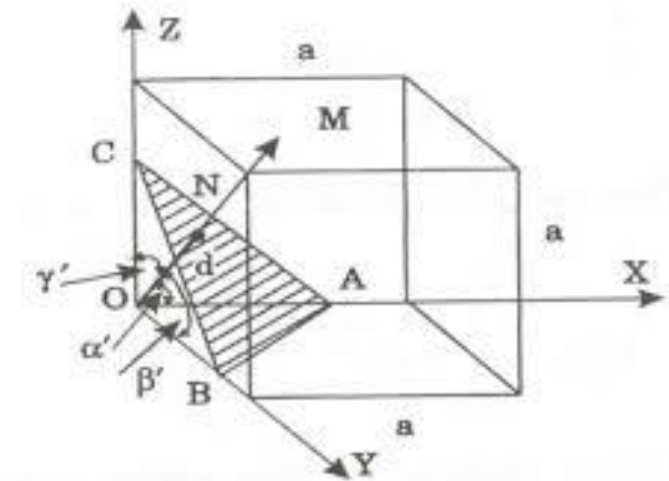
If a plane is parallel to an axis, the intercept is taken as ∞ , and reciprocal is 0.

Negative intercepts are denoted with a bar over the index. Example: $[1\bar{0}1]$.



5. Derive the expression for interplanar spacing in an orthogonal crystal system.

Answer:



Let $(h \ k \ l)$ be the miller indices of the plane ABC.

The intercepts of this plane with the $(x, y, \text{ and } z)$ axes are $a/h, b/k$ and c/l respectively.

Let $ON = d$ be a normal to the plane passing through the origin 'O'.

Let this ON make angles α, β and γ with x, y and z axes respectively (α, β and γ are not interfacial angles).

The cosines of these angles are related to the intercepts and the spacing (d):

$$\cos \alpha = d/(a/h) = dh/a$$

$$\cos \beta = d/(b/k) = dk/b$$

$$\cos \gamma = d/(c/l) = dl/c$$

For any three-dimensional rectangular coordinate system, the sum of the squares of the direction cosines is equal to 1

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

$$(dh/a)^2 + (dk/b)^2 + (dl/c)^2 = 1$$

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

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

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

$$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

In a cubic crystal, the lattice parameters are equal, so $a=b=c$

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

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

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

Concept of nanomaterials.

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where their properties differ significantly from those at a larger scale.

Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometre scale (at least one dimension sized from 1 to 100 nanometres).

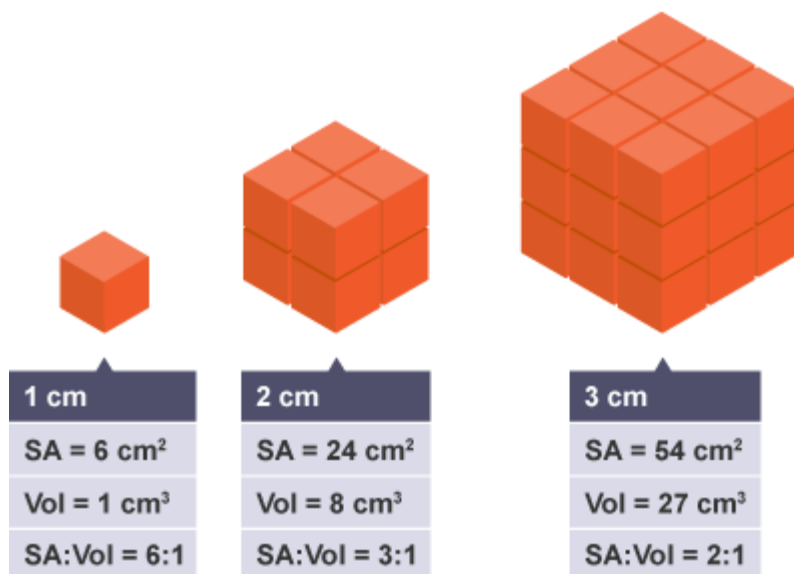
Nanomaterials are materials with at least one dimension (length, width, or thickness) in the nanometre range, typically between 1 and 100 nanometres (nm).

At this scale, materials often exhibit unique physical, chemical, optical, electrical, and mechanical properties that differ significantly from those of the same material in bulk form.

Surface to Volume ratio

The surface to volume ratio, or S/V ratio, refers to the amount of surface a structure has relative to its size. To calculate the S/V ratio, simply divide the surface area by the volume.

For a cube, as cube edge decreases its surface area to volume ratio increases as follows.



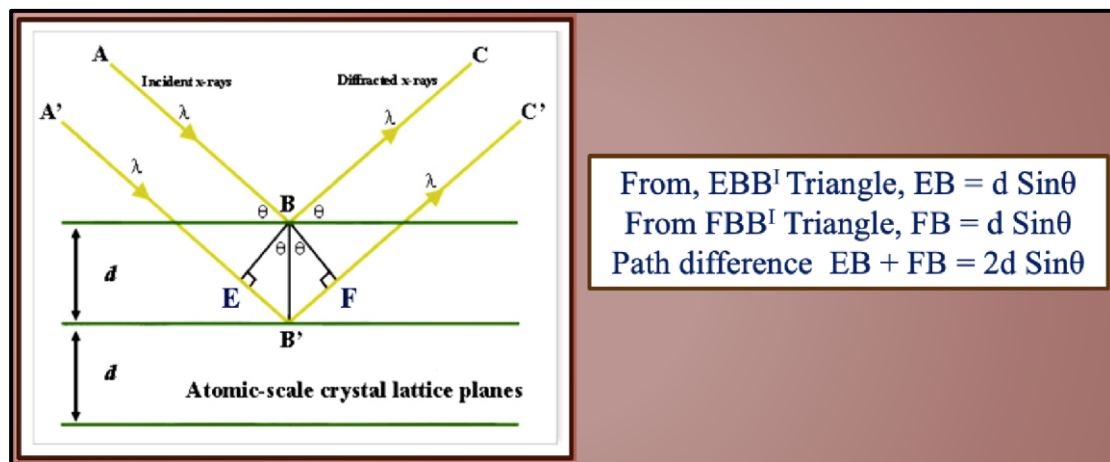
For a sphere, the surface area to the volume ratio of radius (r) will be $\frac{4\pi r^2}{\frac{4}{3}(\pi r^3)} = \frac{3}{r}$. It means that the surface area to volume ratio increases with the decrease in radius of the sphere and vice versa. It can also be concluded that when given volume is divided into smaller pieces, the surface area increases.

Significance of Surface-to-Volume Ratio in Nanomaterials

- High surface area to volume ratio: In nanoparticles, a larger fraction of atoms resides on the surface compared to bulk materials. As particle size decreases, the surface area relative to volume increases dramatically.
- Impact of high surface area: More surface atoms are available for chemical reactions (e.g., catalysis, sensors). Altered mechanical properties: Nanomaterials typically exhibit increased strength and hardness. Surface atoms influence energy levels, leading to phenomena such as quantum confinement.

Bragg's law of X-ray diffraction.

Bragg's Law: When X-rays are incident on a crystalline solid, they are scattered by the regularly spaced lattice planes. Constructive interference occurs when the path difference between the reflected X-rays from successive planes equals an integer multiple of the wavelength.



The condition is expressed as: $n\lambda = 2d \sin\theta$.

Where: n = order of reflection (integer: 1, 2, 3, ...)

- λ = wavelength of incident X-rays
- d = interplanar spacing between crystal planes
- θ = angle of incidence (Bragg angle)

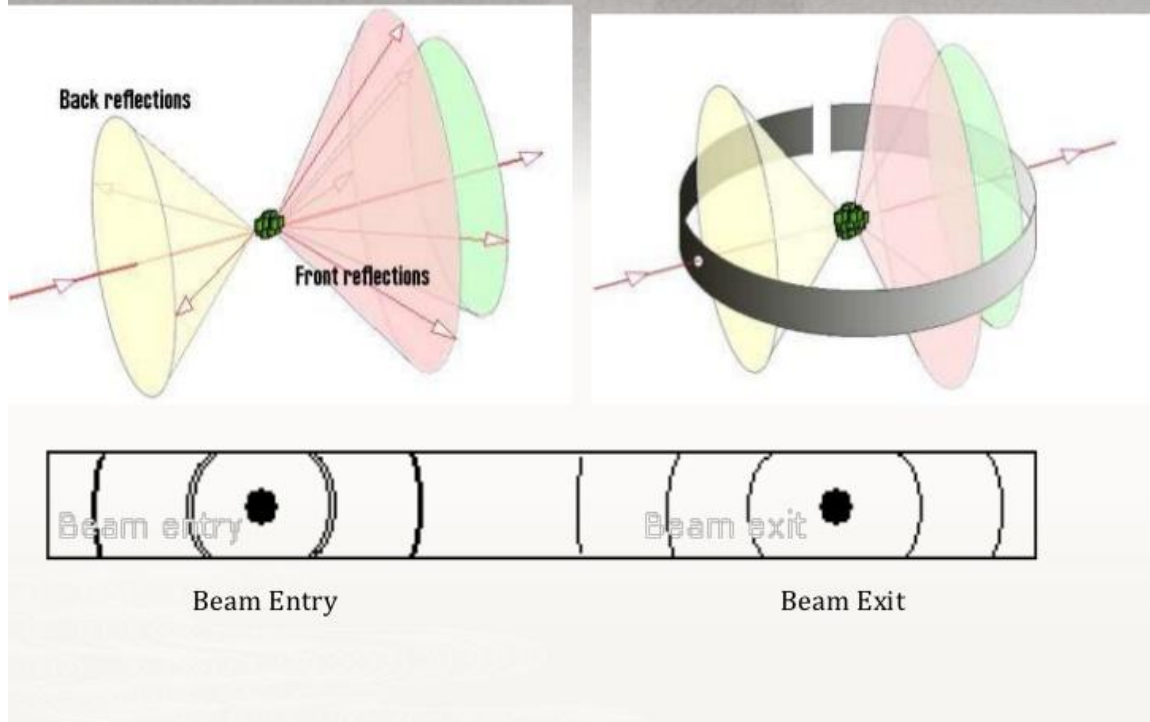
Power method of X-ray diffraction (Debye-Scherrer Method)

The term "powder method" most commonly refers to X-ray Powder Diffraction (PXRD), a technique used to determine the crystal structure of polycrystalline materials by bombarding a fine powder sample with X-rays and analysing the resulting diffraction pattern of Debye-Scherrer rings.

Bragg's Law: Formulae, $2d \sin\theta = n\lambda$

- Debye-Scherrer Method is a method for studying the structure of crystalline solid in powder form using X-ray Diffraction (powdered-crystal method).
- This method is mostly useful for samples that are difficult to obtain in single crystal form.
- It was named after P. Debye and the German physicist P. Scherrer, who proposed this method in 1916.
- Debye-Scherrer camera is a cylindrical camera whose width is smaller as compared to its diameter.
- Material to be studied is taken in the form of fine powder in a small capillary tube and is placed at the centre of drum.
- A narrow parallel beam of monochromatic X rays, upon falling onto a polycrystalline sample and being reflected by the crystallites that make up the sample, produces a number of coaxial (i.e. having one common axis) diffraction cones.

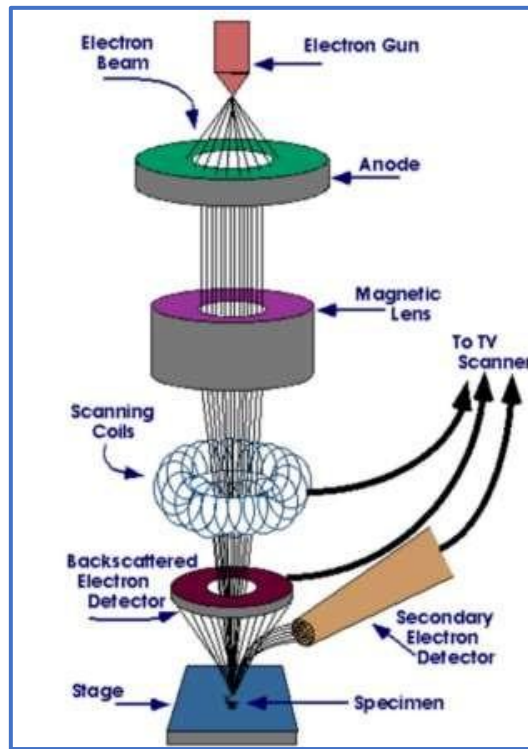
Diffraction cones and the Debye-Scherrer geometry



- This method is used to determine the accurate value of lattice parameters (a, b and c).
- For every set of crystal planes, one or more crystals will be in such orientation to satisfy the Bragg's condition and hence capable of diffraction.
- The powder diffracts the X-rays in accordance with Bragg's law to produce cones of diffracted beams. These cones intersect the photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.
- When film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams.
- If x is the distance at which diffracted beam strikes the film from centre 'O'
then $2\theta = \frac{180^\circ x}{\pi R}$
- Where R is radius of the drum.
or $\theta = \frac{90^\circ x}{\pi R}$
- Let x₁, x₂, x₃..... be the distances between symmetrical arcs on the stretched photographic film. Then,
 $\theta_1 = \frac{90^\circ x_1}{\pi R}$, $\theta_2 = \frac{90^\circ x_2}{\pi R}$, $\theta_3 = \frac{90^\circ x_3}{\pi R}$
- Using these values of θ in Bragg's equation, the interplanar spacing (d) can be calculated.

Scanning Electron Microscope (SEM)

The first scanning electron microscope (SEM) was manufactured in 1942. Then in 1965, Cambridge Scientific Instruments commercialized it for the first time. Its later development was due to an electron beam that involved electrons "scanning" the entire sample. In the characterization of solid materials, scanning electron microscopy (SEM) is extensively used to study surface morphology, structure, and crystallite size. SEM-EDX can be used to determine the distribution of elements. Below figure shows the basic construction of SEM.



SEM consists of an electron gun to produce an electron beam, Lens, a sample holder to place the sample, a secondary-electron detector (SED) to collect secondary electrons, and a visual display unit (VDU).

- **Electron Gun:** The electron beam is generated by heating the tungsten filament and then focused by the magnetic beam with extraneous particles in the atmosphere. Therefore, the electrons emitted as an electron beam flows into the metal plate, the anode, keeping it at a positive potential. The electron beam passes through a hole formed in the centre of the anode. The current of the electron beam can be adjusted by placing the electrode between the anode and the cathode and maintaining it at a negative potential. The electrons from this finely focused beam scans the entire surface of the sample in a series of lines and frames called a raster.
- **Lens: (i) Magnetic lens-**This type of lens is specially manufactured by passing a direct current through a coil winding to form a rotationally symmetric magnetic field. Therefore, a lens effect is generated on the electron beam. The main feature of this lens is that it can change the current flowing through the coil and change the strength of the lens. Optical lenses cannot achieve this. **(ii) Condenser lens and Objective lens-**the condenser lens is located under the electron gun, so the diameter of the electron beam can be adjusted. The objective lens is placed under the condenser lens to generate a thin electron beam.
- **Sample holder:** A sample holder that moves horizontally (x, y) and vertically (z) smoothly to support the sample, i.e., the sample should not fall due to tilting or rotating the sample holder. The x and y movements select the field of view, and the z movement changes the image resolution. Usually, the specimen is observed at high magnification.
- **Secondary Electron Detector (SED):** According to the energy of the emitted electrons, it separates the secondary electrons (less than 50eV) and backscattered electrons (more than 50eV). The detector for each type of electron is placed in the appropriate position in the microscope to collect them. The fluorescent substance is coated on the tip of the SED, and a voltage of about 10-20 kV is applied according to the material being analyzed. The secondary electrons from the sample are attracted to the applied voltage and generate light. Therefore, the light is then amplified and converted into electrical signals. The number of secondary electrons can be easily controlled by changing the voltage.

- **Visual display unit (VDU):** The amplified output signal from the secondary electron detector hits the VDU screen (CRT-cathode ray tube, LED-light emitting diode, LCDliquid crystal display, etc.) that forms the SEM image. For backscattered electrons, the atomic number of the element in the sample is used to determine the contrast in the resulting image. The distribution of different chemical phases in the sample can also be known through these images. The resolution in the image is not as good as the secondary electrons because these electrons are emitted from a certain depth of the sample. The brightness of the image formed by backscattered electrons increases as the atomic number of the element increases. This means that the area of the sample composed of light elements (low atomic number) appears dark on the screen, and heavy elements appear bright. Therefore, to describe the crystallographic structure of the sample, backscattered electrons are used. X-rays in SEM are helpful for energy dispersive X-ray analysis (EDX or EDS) and can analyse the sample's chemical composition.
- **Magnification:** While changing the width of the electron beam, when the SEM image appears on the VDU, the image magnification will change at the same time. Since the size of the monitor remains the same, the magnification can be increased or decreased accordingly by changing the scan width.
-

Limitations:

- SEM analysis is limited to surface images because they only represent the surface.
- The sample must be conductive, so non-conductive materials are coated with carbon or gold-palladium.
- SEM cannot detect materials with a smaller number of molecules than carbon.
- Therefore, a scanning electron microscope (SEM) is used to study the surface morphology.