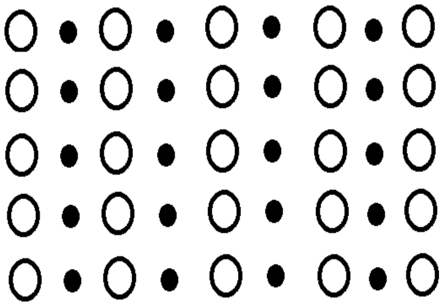
Crystallography

"Crystallography" is the branch of science which deals with the study of geometric form and other physical properties of crystalline solids by using x-rays, electron beams and neutron beams.

Solid: A Solid consists of a large number of closely packed atoms or molecules. Solids are classified into two categories based on the arrangement of atoms. They are

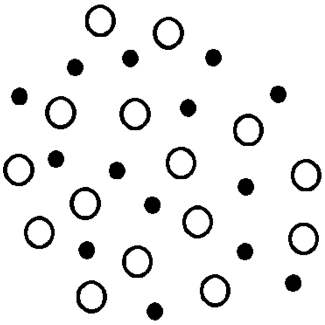
1. Crystalline Solids
2. Amorphous solids

Crystalline Solids



1. In Crystalline Solids atoms or molecules are periodic in space.
2. Some crystalline solids are anisotropic. i.e., the magnitudes of physical properties such as refractive index, electrical conductivity, and Thermal conductivity are different along different directions. Hence the Crystalline Solids have directional property
3. Crystalline solids have sharp melting points.
4. Crystal breaks along certain crystallographic planes.
5. Examples: Rock Salt, Calcite, Sugar etc.

Amorphous solids



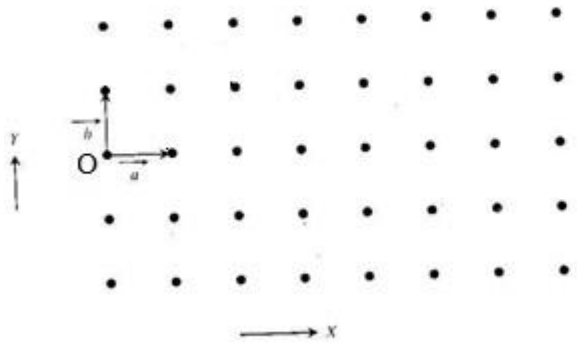
1. In Amorphous solids atoms or molecules are not periodic in space.
2. Amorphous solids are isotropic. i.e., the physical properties are same in all directions.
3. Amorphous solids do not possess sharp melting points.
4. The broken surface is irregular because it has no crystallographic planes.
5. Examples: Glass, Rubber etc.

1. Space lattice (Crystal lattice)

"**Lattice point"** is defined as an imaginary point in space at an atomic or molecules site of the actual crystal

"**Space lattice"** is defined as (the regular and periodic) array of lattice points in space such that the environment of each lattice point is same

In solid crystalline materials, the atoms or molecules are arranged regularly and periodically in three dimensions .To explain crystal symmetries, it is convenient to represent atoms or molecules by a point in space and that point is called lattice point. And the array of these imaginary points in space is called space lattice or crystal lattice. This is not actual crystal structure.



Two dimensional lattice array

Where $\vec{a}$ and $\vec{b}$ are called translational vectors or basis vectors along X and Y directions respectively. They are also called translational primitives.

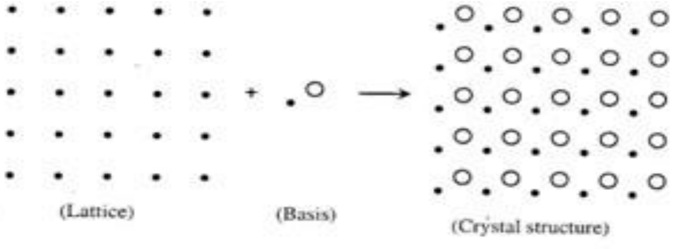
2. The Basis and Crystal structure

The atoms or molecules or ions, which are identical in composition, arrangement and orientation, associating to every lattice point to get the actual crystal structure is called " **basis or Pattern** "

In copper and sodium crystals the basis is a single atom. In Nacl, the basis is diatonic and in CaF_2 the basis is tri-atomic.

The atomic arrangement in a crystal is called crystal structure. If the basis is substituted for all lattice points in a space lattice then the resulting structure is called "**crystal structure**". Thus we can write the following equation

Lattice +Basis=Crystal structure



Generation of crystal structure from lattice and basis

3. Unit cell

A unit cell is the basic structural unit or building block of actual crystal structure. We get an actual crystal structure (entire crystal structure) by repeating the unit cells in three dimensional space. Unit cells for most of the crystals are parallelepiped or cubes having three sets of parallel faces.

A unit cell is defined as the smallest parallelepiped volume or smallest building block by repeating it along the crystallographic axes gives the actual crystal structure. The choice of the unit cell is not unique but it can be constructed in a number of ways.

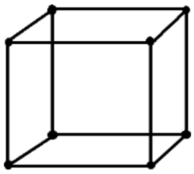
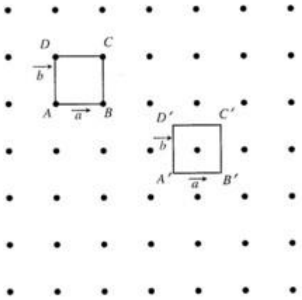


Figure: unit cell in three dimensions

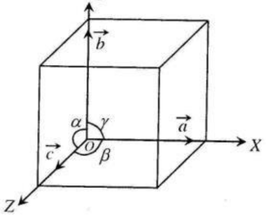
The following figure shows different ways of representing unit cells in a two dimensional lattice.

A unit cell can be represented as ABCD or $A'B'C'D'$etc.



Lattice arrangement along with unit cells

4. Lattice parameters



Cubic

Fig. Lattice parameters of a unit cell

To define the lattice parameters, first we have to define the crystallographic axes. These axes are obtained by intersection of the three non-coplanar faces of the unit cell. The angles between these faces or crystallographic axes are called interfacial or inter axial angles.

The angle between Y and Z axes is a

The angle between Z and X axes is β

The angle between X and Y axes is γ

The translational vectors or primitives a, b, c of unit cell along x, y, z axes and the inter facial anglesα,β, γ are called lattice parameters or unit cell parameters.

The cell parameters determine the actual size and shape of the unit cell. The unit cell formed by primitives and contains only one lattice point per unit cell is called primitive unit cell. If a unit cell contains more than one lattice point, then it is called non-primitive unit cell or multiple cells.

Simple cubic unit cell is primitive unit cell. Body centered cubic and Face centered cubic unit cells are examples for non-primitive unit cells.

5. Crystal Systems and Bravais lattice

For representing the type of distribution of lattice point in space, seven different coordinate systems are required. These coordinate systems are called crystal systems. The crystal systems are named on the basis of geometrical shape and symmetry. The seven crystal systems are 1) cubic 2) Tetragonal 3) orthorhombic 4) monoclinic 5) Triclinic 6) Rhombohedron or Trigonal 7) Hexagonal

Space lattices are classified according to their symmetry. In 1948, Bravais showed that 14 lattices are sufficient to describe all crystals. These 14 lattices are called Bravais lattices and are classified into 7 crystal systems based on unit cell parameters. The Bravais lattices are categorized as primitive lattice (P), body centered lattice (I), face central lattice (F) and base centered lattice (C).

These seven Crystal systems and Bravais lattices are described below.

Primitive unit cell or Simple cell: (P): The primitive cell is defined as a unit cell which contains lattice points at corners only. Such cell contains effectively one lattice point per cell i.e. one lattice point is associated with each primitive cell.

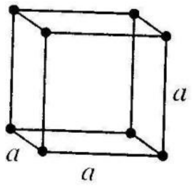
Non-primitive unit cell: - If a unit cell contains more than one lattice point then it is called Non-primitive cell (or) multiple cell. They are

Body centered (I): atoms present at corners and center of unit cell.

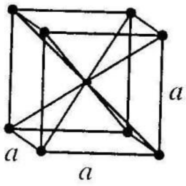
Face centered (F) unit cell: atoms presented at corners and at centers of 6 faces of unit cell.

Base Centered Lattice (C): Along with corner atoms, Base and opposite face will have center atom.

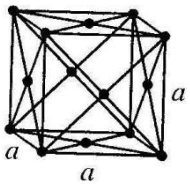
1. Cubic Crystal System: In this Crystal system all the unit cell edge lengths are equal and are at right angles to one another i.e., a =b=c and $\alpha=\beta=\gamma=90^0$. In cubic system, there are three Bravais lattices they are simple, body centered and face centered. Examples for cubic systems are Au, Cu, Ag, Nacl, diamond etc.



Cubic-P



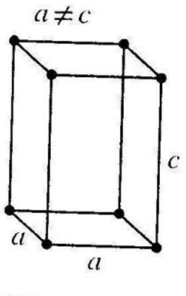
Cubic-I



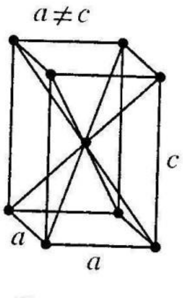
Cubic-F

2. Tetragonal Crystal System: In this Crystal system two lengths of the unit cell edges are equal whereas the third length is different. The three edges are perpendicular to one another i.e, a =b≠c and $\alpha=\beta=\gamma=90^0$

In tetragonal system, these are two Bravais lattices. They are simple and body centered. Examples for tetragonal crystal systems are TiO_2 and SnO_2 etc.

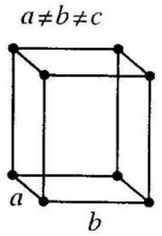


Tetragonal-P

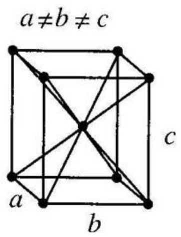


Tetragonal-I

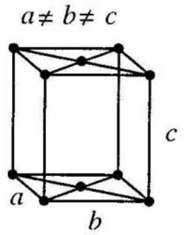
3. Orthorhombic Crystal: In this crystal system, unit cell edge lengths are different and they are perpendicular to one another. i.e, $a \neq$ b≠ c and $\alpha=\beta=\gamma=90^{0\cdot}$ There are four Bravais lattices in this system. They are simple, face centered, body centered and base centered. Examples for Orthorhombic crystal system are $BaSO_4$, K_2SO_4, $SnSO_4$ etc.



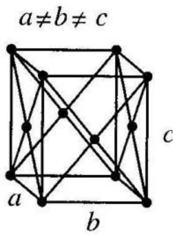
Orthorhombic-P



Orthorhombic-I

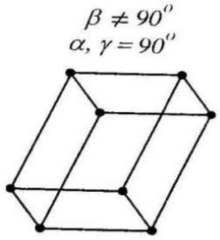


Orthorhombic-C

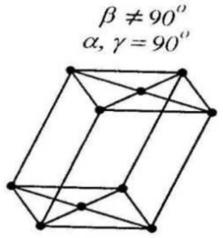


Orthorhombic-F

4. Monoclinic Crystal System: In this crystal system, the unit cell edge lengths are different, two unit cell edges are not perpendicular, but they are perpendicular to third edge. i.e., $a \neq b \neq c$ and $\alpha = \gamma = 90^0 \neq \beta$. This crystal system has two Bravais lattices they are simple and base centers. Examples are $CaSO_4.ZH_2O$(gypsum) and Na_3AlF_6 (cryolite) etc.

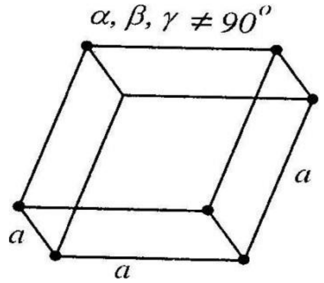


Monoclinic-P



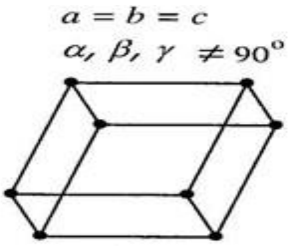
Monoclinic-C

5. Triclinic Crystal System: In this crystal system, the unit cell edge lengths are different, and are not perpendicular. i.e., $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^0$ and all the angles are different. This crystal system exists primitive cell only. Example: $K_2C_2O_7$, $CuSO_45H_2O$ etc.



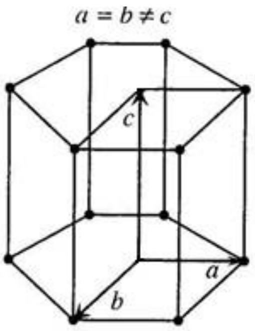
Triclinic

6.RhombohedraCrystal System (Trigonal Crystal): In this crystal system, all the lengths of unit cell edges are equal. The angles between the axes are equal but other than 90^0. i.e., $a = b = c$ and $\alpha = \beta = \gamma \neq 90^0$. The Bravais lattice is only simple lattice. Example are As, Bi, Sb.



Terigonal

7. Hexagonal Crystal System: In this crystal system two sides of the unit cell edge lengths are equal and the angle between these edges is 120^0. These two edges are perpendicular third edge and not equal in length. i.e., $a = b \neq c$ and $\alpha = \beta = 90^0, \gamma = 120^0$. The Bravais lattice is primitive only which is shown below.



Hexagonal

14 Bravais lattices of 7 Crystal systems are given below

S.No.	Crystal System	Type of Bravais Lattice	No.of Bravais lattices	Relation between The lattice parameters
1.	Cubic	P,I,F	3	a =b=c and $\alpha=\beta=\gamma=90^0$
2.	Tetragonal	P,I	2	a =b≠c and $\alpha=\beta=\gamma=90^0$
3.	Orthorhombic	P,I,F,C	4	a ≠b≠c and $\alpha=\beta=\gamma=90^0$
4.	Monoclinic	P,C	2	a ≠b≠c and $\alpha=\gamma=90^0\neq\beta$
5.	Triclinic	P	1	a ≠b≠c and $\alpha\neq\beta\neq\gamma\neq90^0$
6.	Rhombohedra (Trigonal)	P	1	a =b=c and $\alpha=\beta=\gamma\neq90^0$
7.	Hexagonal	P	1	a =b≠c and$\alpha=\beta=90^0\gamma= 120^0$

6. Crystal Structures

To study the Crystal Structures, we require some important parameters. They are

1. **Effective number of atoms per unit cell (or) Number of atoms present in a unit cell:**

   The sum of shares of all atoms in a unit cell gives effective number of atoms per unit cell.

2. **Nearest neighboring distance(2r):**

   The distance between two nearest neighboring atoms is known as nearest neighboring distance.

3. **Atomic Radius (r):**

   Atomic Radius is the half of the distance between nearest neighboring atoms.

4. **Coordination Number(N):**

   The number of nearest equidistant neighboring atoms to an atom in crystal is called Coordination Number.

5. Atomic packing fraction (PF)

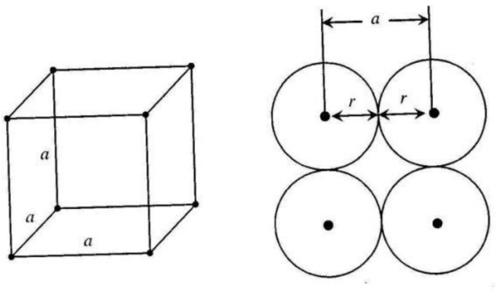
Atomic packing fraction is defined as the ratio of volume of atoms in the unit cell and volume of unit cell.

$$\text{Atomic packing fraction (PF)} = \frac{\text{Volume of atoms in unit cell}}{volume\ of\ unit\ cell(V)}$$

$$\frac{v}{V} = \frac{\text{No.of atoms present in a unit cell X volume of one atom}}{\text{volume of the unit cell}}$$

7. Structure and packing fraction of Simple Cubic (SC) structure

1. The unit cell edge lengths of their structure along the crystallographic axes and inter axial angles are equal. i.e., a=b=c and $\alpha=\beta=\gamma=90^{0.}$
2. Atoms are present only at corners of this unit cell.
3. This unit cell has eight corners, The corner atom is shared by eight unit cells so that the contribution of a corner atom to a unit cell is $\frac{1}{8}$. Hence the contribution of eight corner atoms to a unit cell or the number of atoms per unit cell = $\frac{1}{8} \times 8 = 1$.
4. Coordination number is 6.
5. Let r be the radius of an atom. The surface of the atoms touch along the cube edges. So, the distance between the centers of two neighboring atoms or nearest neighboring distance (2r) is equal to lattice constant „a ‟.



Unit cell of a simple cubic structure

Packing faction:

Lattice constant, a =2r

Number of atoms in the Unit Cell = 1

The volume occupied by atom in the unit call P = $1\times\frac{4}{3}\pi r^3 = \frac{4}{3}\pi r^3$

The volume of unit cell v = a^3

Packing fraction (or) density of packing of simple

Cubic unit cell (PF) = $\frac{volume\ ocupied\ by\ atoms(v)}{volume\ of unit\ cell(V)}$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{4\pi r^3}{3(2r)^3} = \frac{\pi}{6} = 0.52 = 52\%$$

The example for simple cubic structure is polonium.

8. Structure and packing fraction of Body CenteredCubic structure (BCC)

1. For this unit cell atoms are present at the corners of the unit cell and one atom is completely present at the center of the unit cell

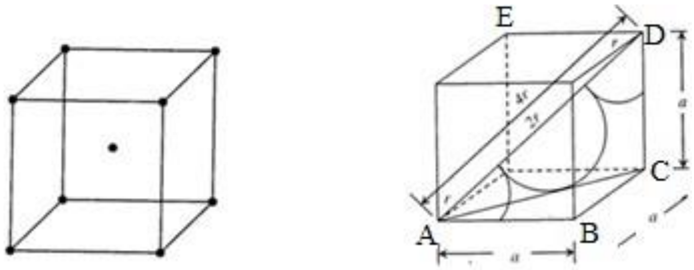
In this structure a =b=c and $\alpha = \beta = \gamma = 90^0$

2. The center of the unit cell is defined as the intersecting point of two body diagonals.

3. A corner atom is shared by eight unit cell so that the contribution of a corner atom to unit cell is $\frac{1}{8}$. There fore the number of atoms per unit cell is $8\times\frac{1}{8}+1=2$.

4. Coordination number is 8.

5. One corner atom do not touch the another side by corner atom but all the corner atoms touch the body centered atom. The surfaces of the atoms are in contact along body diagonal of the unit cell.



Unit Cell of a Body centered cubic structure

Packing fraction:

Length of the body diagonal AD= 4r

$\therefore AD^2 = AC^2 + CD^2$

$AD^2 = AB^2 + BC^2 + CD^2$

$AD^2 = a^2 + a^2 + a^2$

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

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

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

Number of atoms in the Unit Cell = 2

Volume occupied by the atoms in unit cell is $P = 2 \times \frac{4}{3}\pi r^3$

Volume of unit cell $= a^3$

$$\text{Atomic packing fraction} = \frac{\text{volume occupied by atoms}}{\text{Volume of unit cell}}$$

$$= \frac{2 \times \frac{4}{3}\ r^3}{a^3} = \frac{2 \times 4 \times \pi r^3}{3 \times (\frac{4}{\sqrt{3}}r)^3} = \frac{2 \times 4 \times\ r^3 \times 3 \cdot \sqrt{3}}{3 \times 4 \times 4 \times 4 \times r^3}$$

$$= \frac{\sqrt{3}\pi}{8} = 0 \cdot 68 = 68\%$$

Elements like tungsten, chromium, sodium, potassium, etc possess BCC structure.

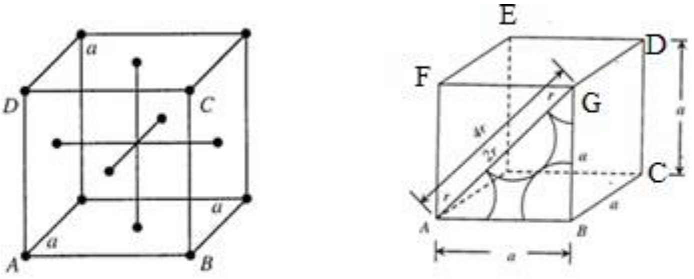
9. Structure and packing fractions of Face Centered Cubic (FCC) structure

1. Atoms are present at the corners and at the face centers of this cubic structure. The intersection of face diagonals represent face center
2. Corner atom is shared by eight unit cells and face centered atom is shared by two unit cells. The cube has eight corner atom and 6 face centered atoms. Hence the no of atoms per FCC unit cell = $8 \times \frac{1}{8} + 6 \times \frac{1}{2}$ = 1+3 = 4.

3. Coordination number is 12.

4. The atoms don‟t touches along the unit cell edge. But the atoms touch along the face diagonally.

Packing faction:



Unit Cell of a Face centered cubic structure

Volume occupied by the atoms in FCC unit cell is $P = 4 \times \frac{4}{3}\pi r^3$

Volume of unit cell=a^3

From Fig,

$$AG = 4r$$

$$AG^2 = AB^2 + BG^2$$

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

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

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

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

Lattice constant$a = 2\sqrt{2}\ r$

Number of atoms in the Unit Cell = 4

Volume occupied by atoms in unit cell $P = 4 \times \frac{4}{3}\pi r^3$

Volume of unit cell V=a^3

$$\text{Atomic packing fraction} = \frac{\text{volume occupied by atoms}}{\text{Volume of unit cell}}$$

$$= \frac{4 \text{ x } \frac{4}{3}\pi r^3}{a^3} = \frac{4 \times 4 \times \pi r^3}{3 \times (2\sqrt{2}\ r)^3} = \frac{4 \times 4 \times \pi r^3}{3 \times 8 \times 2\sqrt{2} \times r^3} = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$$

Atomic packing fraction of FCC structure = 74%

Examples for this structure are Cu, Ag, Al, etc

X- Ray Diffraction:

There are three main diffraction methods by which the crystal structures can be analyzed.

a. Laue method : applicable to single crystals
b. Powder method : applicable to finely divided crystalline or Polycrystalline specimen powder
c. Rotating crystal method : applicable to single crystals.

13. Bragg's law

Statement

Bragg's law states that the path difference between the two reflected X-rays by the crystal planes should be an integral multiple of wave length of incident X-rays for producing maximum or constructive interference.

Path difference = n λ

Let us consider a set of parallel lattice planes of a crystal separated by a distance d apart. Suppose a narrow beam of X-rays of wave length λ be incident upon these planes at an angle θ as shown in the figure. Consider a ray PA reflected at the atom A in the direction AR from plane 1and another ray QB reflected at another atom B in the direction of BS. The path difference between the two rays is (CB+BD). When the path difference between the two rays is an integral multiple of X-rays wavelength, the constructive interference phenomenon will occur.

Thus the condition for constructive interference is

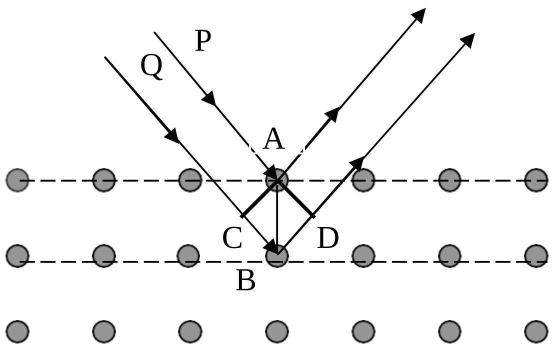
$$(CB+BD)=n\lambda$$

From ΔABC $\sin\theta = \frac{CB}{AB} = \frac{CB}{d}$

$$CB = d\sin\theta$$

From ΔABD $\sin\theta = \frac{BD}{AB} = \frac{BD}{d}$

$$BD = d\sin\theta$$



$$(CB+BD)=2d\sin\theta$$

$$2d\sin\theta = n\lambda$$

Where $n=1,2,3$............etc for first order, second order, third order........................etc maxima respectively.

For first maxima $\sin\theta_1 = \frac{\lambda}{2d}$

For second maxima $\sin\theta_2 = \frac{2\lambda}{2d}$

For third maxima $\sin\theta_3 = \frac{3\lambda}{2d}$

14. Powder method

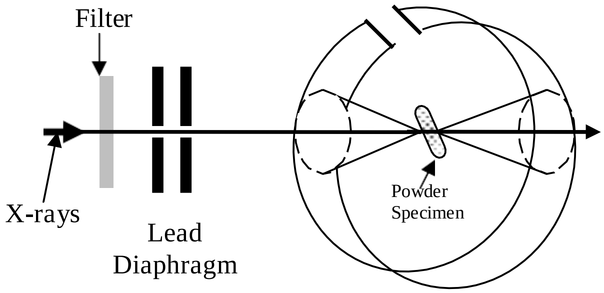
The powder method was developed by Debye and Sherrer in Germany and by hill in America simultaneously. This method is used to study the structure of crystals which cannot be obtained in the form of perfect crystals of appreciable size. This method can be used for pure metals, compounds and alloys.

Basic Principle

The basic principle underlying this powder technique is that, the specimen contains a large number of micro crystals (~10^{12} in $1mm^3$ of powder sample) with random orientations, almost all the possible θ and d values are available. The diffraction takes place for these values of θ and d which satisfy Bragg's condition, i.e., $2d\ \sin\theta = n\lambda$.

Experimental arrangement:-

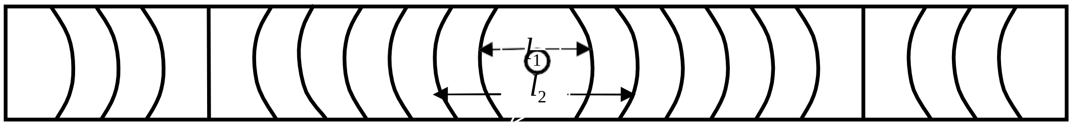
The experimental arrangement is shown in figure. The finely powdered sample is filled in a thin capillary tube and mounted at the center of the drum shaped cassette with photographic film at the inner circumference. Collect the X-rays (non monochromatic or heterogeneous or white or continuous) from the X-ray tube. Heterogeneous can be converted into monochromatic X-Rays by passing through the filter. This monochromatic (or homogenous) x-rays can be converted into fine pencil beam by passing through the lead sheet. The pencil beam of X-rays is allowed to fall on the powder specimen (sample).



Theory

The basic principle underlying this powder technique is that, the specimen contains a large number of micro crystals (~10^{12} in $1mm^3$ of powder sample) with random orientations, almost all the possible θ and d values are available. The diffraction takes place for these values of θ and d which satisfy Bragg's condition, i.e., $2d\ \sin\theta = n\lambda$. Reflection takes place at the lattice planes, which satisfy the Bragg's condition. For the value ofθ , the beam appears at the corresponding 2θ deviation.

The pattern recorded on the photographic film is shown in the figure when the film is laid flat. Due to the narrow width of the film, only parts of circular rings are register on it. The curvature of arcs reverses when the angle of diffraction exceeds 90^0 .



Knowing the distances between the pair of arcs, various diffraction angles $\theta's$ can be calculated by using the formula.

$$\theta = \frac{90^0}{\pi\ D} l$$

Where D, is the diameter of the cylindrical film.

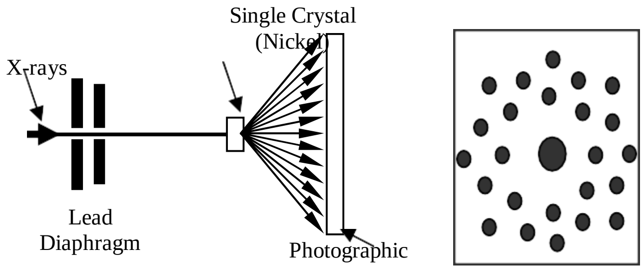
15. Laue method

Basic principle

The basic Principe underlying this Laue technique is that, each reflecting plane selects a wave length according with the Bragg's relation, i.e., $2d \sin\theta = n\lambda$. The resulting diffraction is recorded on the photographic plate.

Experimental arrangement

The experimental arrangement of the Laue technique is shown in the figure.



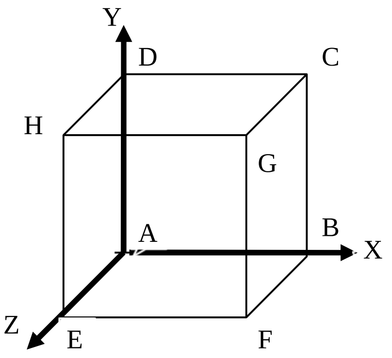
Laue Method

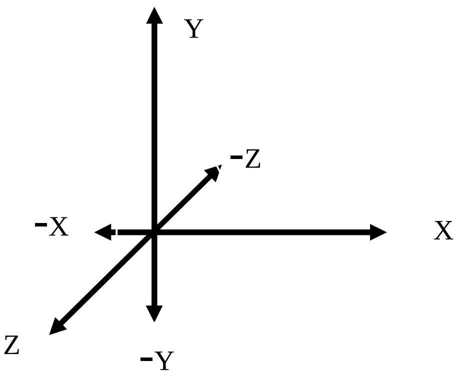
Collect the X-rays of wavelength 0.2 A^0 to 2.0 A^0 from X-ray tube. Collected X-rays are converting in to fine pencil beam by passing through the pin-hole arrangements in lead diaphragms. The size of pin hole should be kept very small to get sharp interference pattern. The smaller is the pinhole diameter, sharper is the interference pattern.

Theory

The fine pencil beam of X-rays is allowed to fall on the single crystal; the X-rays are diffracted and recorded on the photographic plate. The diffraction pattern consists of a bright central spot and a set of spots arranged in a definite pattern about the central spot. The symmetrical pattern caused by X-rays by crystal planes is called the Laue pattern. Each spot in the Laue pattern corresponding to an interference maximum for a set of planes satisfying the Bragg's relation $2d \sin\theta = n\lambda$.

16. Planes in crystals



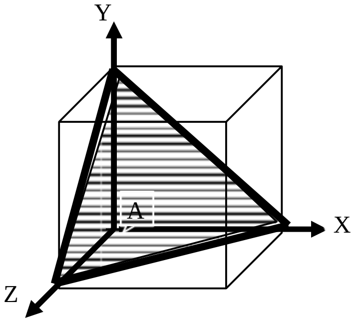


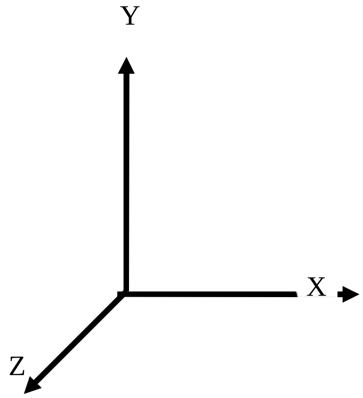
If we consider the origin at position A if all the miller indices are positive. (+++),

B (- + +) , C (- - +), D (+ - +), E (+ + -) F (- + -), G (- - -), H (+ - -)

Miller indices (1 1 1)

Intercepts $\frac{1}{1}, \frac{1}{1}, \frac{1}{1}$ = 1, 1, 1



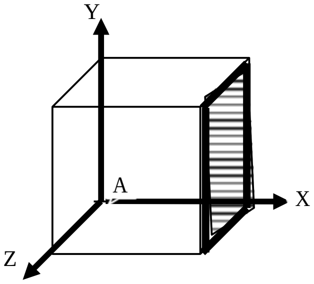


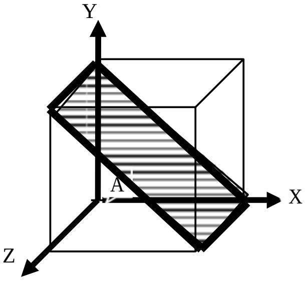
Miller indices (100)

Intercepts $\frac{1}{1}, \frac{1}{0}, \frac{1}{0}$ = 1, ∞ ,∞

Miller indices (110)

Intercepts $\frac{1}{1}, \frac{1}{1}, \frac{1}{0}$ = 1, 1, ∞



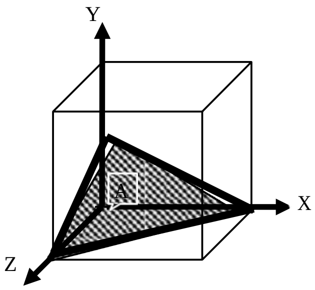


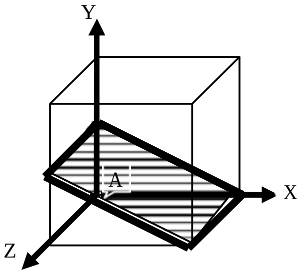
Miller indices (121)

Intercepts $\frac{1}{1}, \frac{1}{2}, \frac{1}{1}$ = 1, $\frac{1}{2}$, 1

Miller indices (120)

Intercepts $\frac{1}{1}, \frac{1}{2}, \frac{1}{0}$ = 1 , $\frac{1}{2}$, ∞



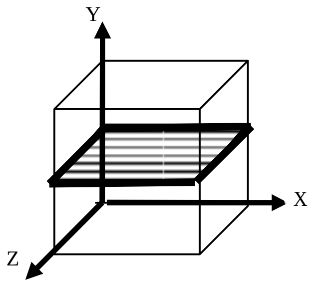


Miller indices (0 2 0)

Intercepts $\frac{1}{0}, \frac{1}{2}, \frac{1}{0}$ = ∞ $\frac{1}{2}$ ∞

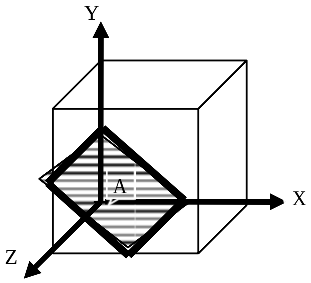
Miller indices (220)

Intercepts $\frac{1}{2}, \frac{1}{2}, \frac{1}{0}$ = $\frac{1}{2}$, $\frac{1}{2}$,∞



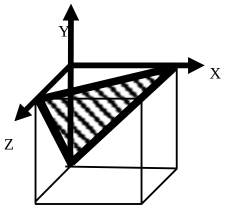
Miller indices $(1\bar{1}1)$

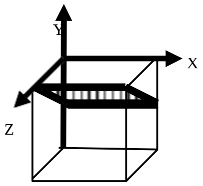
Intercepts = $\frac{1}{1}, -\frac{1}{1}, \frac{1}{1}$ = 1 ,-1, 1



Miller indices $(0\bar{2}1)$

Intercepts $\frac{1}{0}, \frac{-1}{2}, \frac{1}{1} = \infty, \frac{-1}{2}$, 1





Miller indices $(\bar{1}1\bar{1})$

Intercepts $\frac{1}{-1}, \frac{1}{-1}, \frac{1}{-1}$ = -1, -1, -1