SOLID STATE

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INTRODUCTION

Crystallography is science of crystal which is devoted to the study of their development and growth, their external form, Internal Structure, and physical properties.

NATURE OF THE SOLID STATE

- Solid are characterised by High density, Low compressibility, rigidity, mechanical strength and definite shape and volume. This indicates that the molecules, atoms or ions that make up a solid are closely packed. They are held together by strong cohesive forces and cannot move at random. Thus, In Solid well ordered molecules, atomic or ionic arrangement.

- e.g. – Sodium chloride (Nacl), sulphur (S) and Sugar ($C_{12}H_{22}O_{11}$) being in compressible, rigid and characteristic geometrical form.

CLASSIFICATION OF SOLID

Solid are classified on the basis of various properties. They are two type -

1. Crystalline Solid
2. Amorphous Solid

1. Crystalline Solid :

A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules or atom in three dimensional Space. It has a sharp melting point i.e. it changes abruptly into liquid state. Crystalline solid are anisotropic

2. Amorphous Solid :

Amorphous solid does not have any pattern of arrangement of molecules or atoms and does not have any definite geometrical shape. Thus unlike crystalline solids, amorphous solid do not have a long range order.

Different between crystalline an amorphous

| SL. NO.	Properties	Crystalline	Amorphous Solid
1	Arrangement	They have not arranged in a regular way	They have not arranged in any regular way
2	Shape	They have long range order	They have short range order
3	Melting Point	They have sharp melting Point	They melt over a range of range of temperature
4	Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion
5	Compressibility	They are rigid and incompressible	They may be compressed to some extent

6	Cutting with a sharp edged tool	They are given cleavage i.e. they break into two pieces with plane surface.	They give irregular cleavage i.e. they break into two pieces with irregular surface.
7	Symmetry	They possess symmetry	They do not possess any symmetry
8	Isotropy and Anisotropy	They are anisotropic i.e. their physical properties (mechanical, optical and electrical) are different direction	They are isotropic i.e. their physical properties are same in all direction
9	Volume change	There is a sudden change in volume when they melt	There is no sudden change in volume on melting
10	Interfacial angles	They possess interfacial angles	They do not possess interfacial angles

The Space Lattice & Unit Cell

"The <u>3D arrangement</u> of points in space is called <u>space lattice</u>".
"The <u>smallest repeat unit</u> of a crystal structure, in 3D, which <u>shows the full symmetry</u> of the structure" Repetition of unit cell generates entire crystal.

The unit cell is a box with:

- **3 sides - a, b, c**

- **3 angles - α, β, γ**
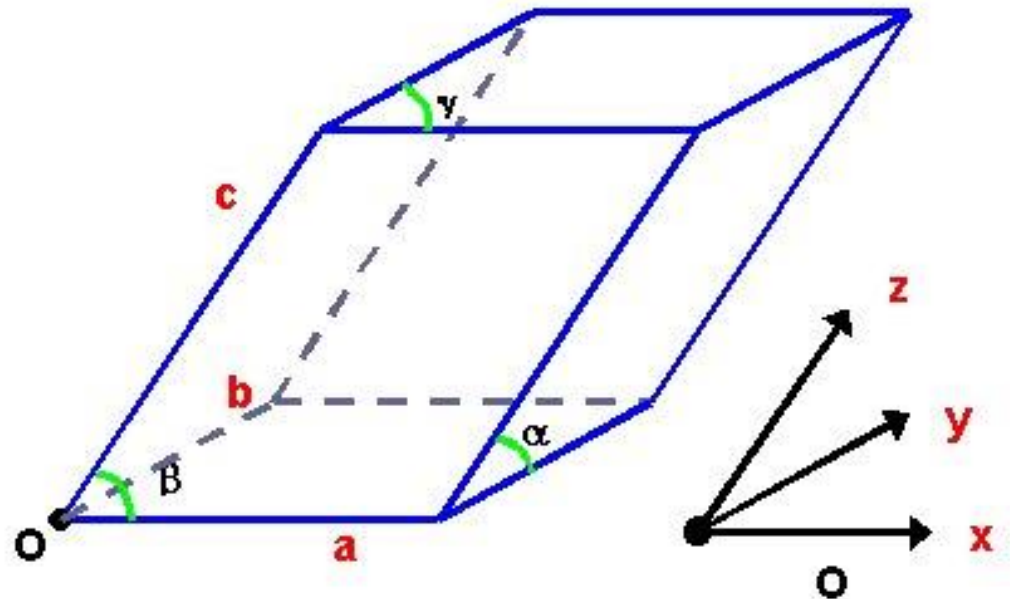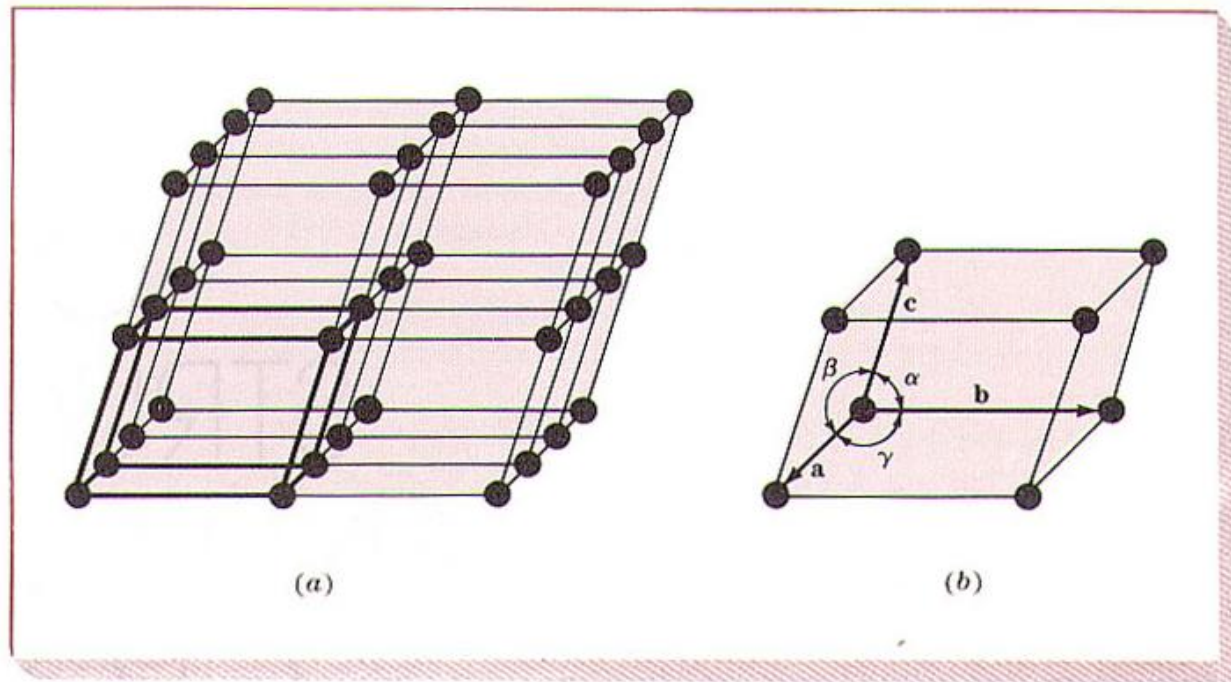
Space lattice and unit cell

Figure: (a) Space lattice of crystalline solid (b) Unit cell

$\Rightarrow$ Three types of unit cell

➢ **Face centered cubic (FCC)**
➢ **Body centered cubic (BCC)**
➢ **Hexagonal closed packed (HCP)**

$\Rightarrow$ Seven unit cell shapes

- **Cubic** $a=b=c$ $\alpha=\beta=\gamma=90°$
- **Tetragonal** $a=b\neq c$ $\alpha=\beta=\gamma=90°$
- **Orthorhombic** $a\neq b\neq c$ $\alpha=\beta=\gamma=90°$
- **Monoclinic** $a\neq b\neq c$ $\alpha=\gamma=90°, \beta\neq 90°$
- **Triclinic** $a\neq b\neq c$ $\alpha\neq\beta\neq\gamma\neq 90°$
- **Hexagonal** $a=b\neq c$ $\alpha=\beta=90°, \gamma=120°$
- **Rhombohedral** $a=b=c$ $\alpha=\beta=\gamma\neq 90°$

Laws of Crystallography

Crystallography is based on three fundamental laws.

(i) Law of constancy of interfacial angles.

➢ This law states that angle between adjacent corresponding faces is inter facial angles of the crystal of a particular substance is always constant inspite of different shapes and sizes and mode of growth of crystal.

➢ The size and shape of crystal depend upon the conditions of crystallisation. This law is also known as Steno's Law.
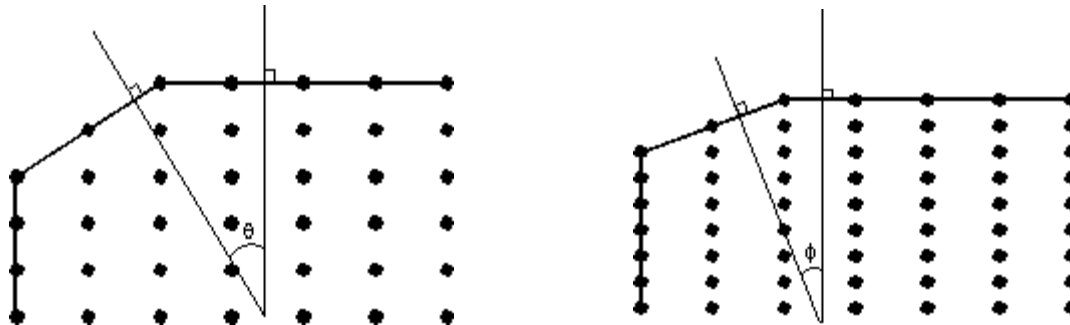
Laws of Crystallography

(ii) Law of rational indices

This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) a, b, c or some simple whole number multiples of them e.g., na, n' b, n''c, where n, n' and n'' are simple whole numbers. The whole numbers n, n' and n'' are called Weiss indices. This law was given by Hauy.

(iii) Law of constancy of symmetry

According to this law, all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and centre of symmetry.

X-Ray Analysis
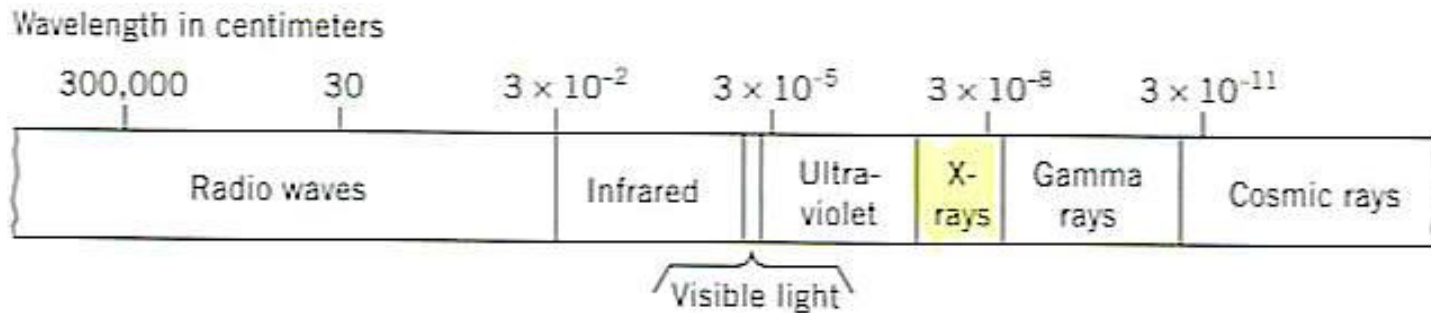
- X-rays discovered in 1895

- Fundamental to understanding of crystal structure and symmetry

- Powder diffraction analyses are a simple and inexpensive method for identifying minerals, especially fine-grained minerals

X-Ray Diffraction

- For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength

- In crystals the typical interatomic spacing ~ 2-3 Å so the suitable radiation is X-rays

- Hence, X-rays can be used for the study of crystal structures
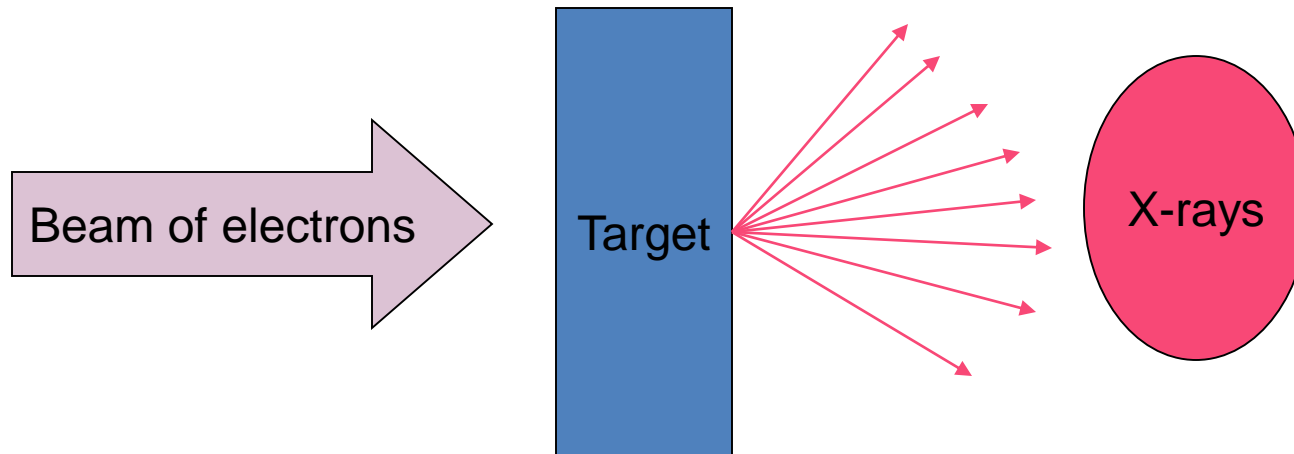
A accelerating charge radiates electromagnetic radiation

Bragg Diffraction

- Diffraction from a three dimensional periodic structure such as atoms in a crystal is called Bragg Diffraction.

- Similar to diffraction though grating.

- Consequence of interference between waves reflecting from different crystal planes.

- Constructive interference is given by *Bragg's law*:

- Where λ is the wavelength, *d* is the distance between crystal planes, θ is the angle of the diffracted wave. and *n* is an integer known as the *order* of the diffracted beam.

Following Bragg's law, each dot (or *reflection*), in this diffraction pattern forms from the constructive interference of X-rays passing through a crystal. The data can be used to determine the crystal's atomic structure.
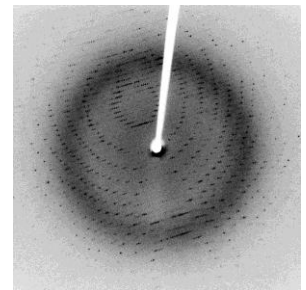
Bragg's law

Sir William Henry Bragg:

➢ William Henry and William Lawrence Bragg (father and son) found a simple interpretation of von Laue's experiment.

➢ They assume that each crystal plane reflects **radiation as a mirror and** analyze this situation for cases of constructive and destructive interference.
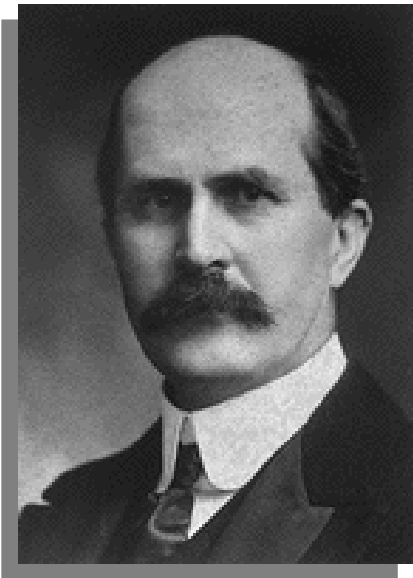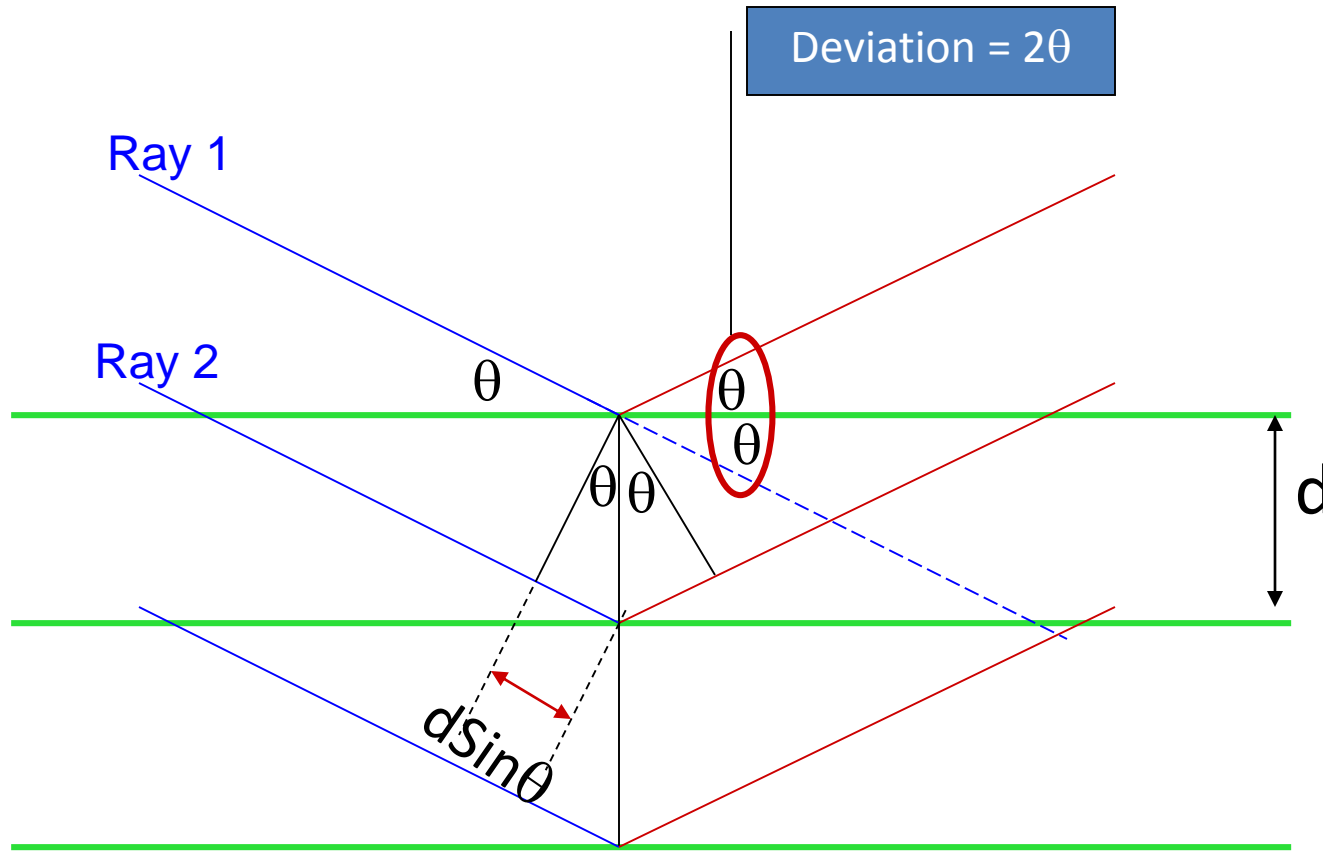
Noble prize 1915

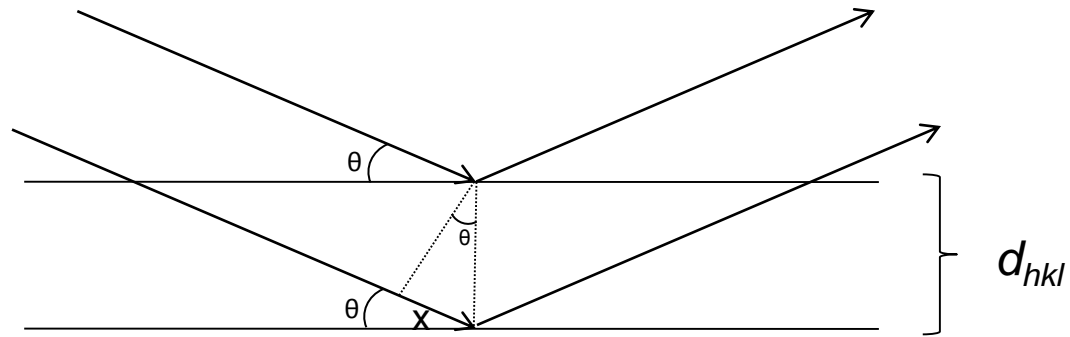$$2d \sin \theta = n\lambda$$

Bragg's equation

Deviation = 2θ

Ray 1

Ray 2

θ θ θ

θ θ

d
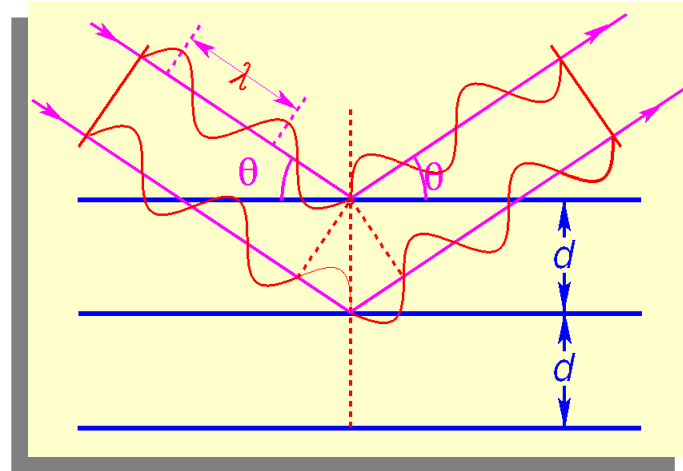
$dSin\theta$

- The path difference between ray 1 and ray 2 = $2d \, Sin\theta$

- For constructive interference: $n\lambda = 2d \, Sin\theta$

Derivation of Bragg's law

$$\sin(\theta) = \frac{x}{d_{hkl}}$$

$$\Rightarrow x = d_{hkl}\sin(\theta)$$

d_{hkl}

Path difference Δ= 2x => phase shift
Constructive interference if Δ=nλ
This gives the criterion for constructive interference:

$$\Rightarrow \Delta = 2d_{hkl}\sin(\theta) = n\lambda$$

Bragg's law tells you at which angle θ_B to expect maximum diffracted intensity for a particular family of crystal planes. For large crystals, all other angles give zero intensity.
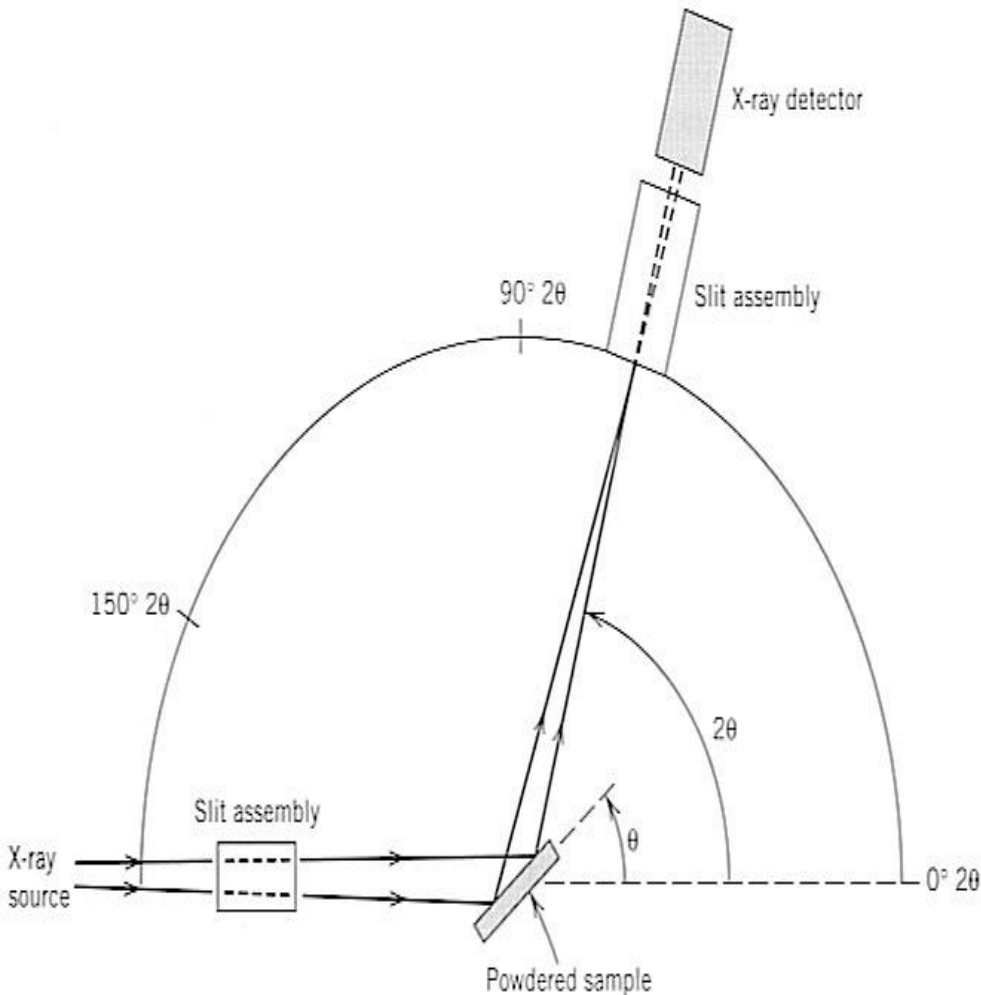
X-ray Crystallography Methods

Single-Crystal: **Laue Method**

➢ **Several directions simultaneously fulfill Bragg equations**

➢ **Good for symmetry, but poor for analysis because distorted**
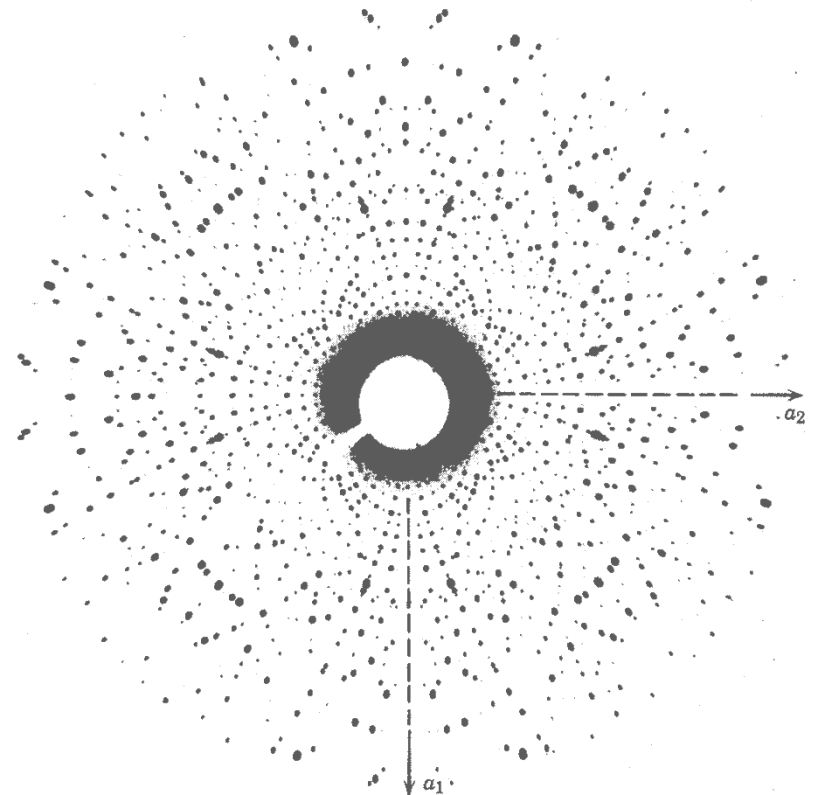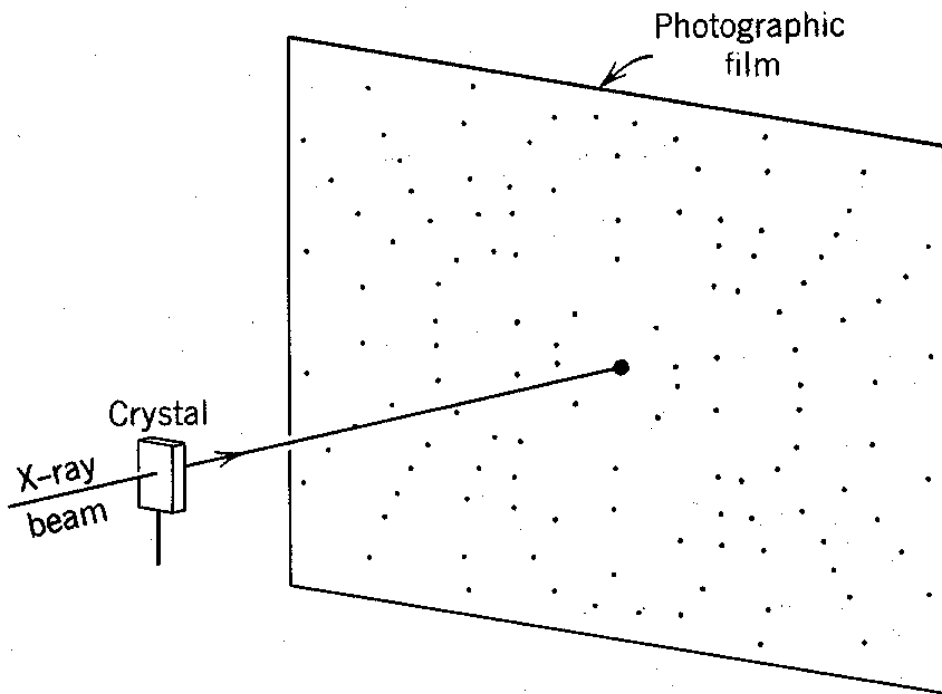
Powder Diffraction Method

- Infinite orientations at once, so only need to vary q, the angle of the incident beam of x-ray light.
- Requires random orientation of very fine crystals
- Incident beam of a certain X-ray wavelength will diffract from atomic planes oriented at the appropriate ϑ angles for the characteristic d spacing
- Random orientation of crystals will produce more intense diffraction peaks for particular angles that correspond to characteristic atomic planes.

FACE CENTERED CUBIC (FCC) CRYSTAL STRUCTURE: NaCl and KCl
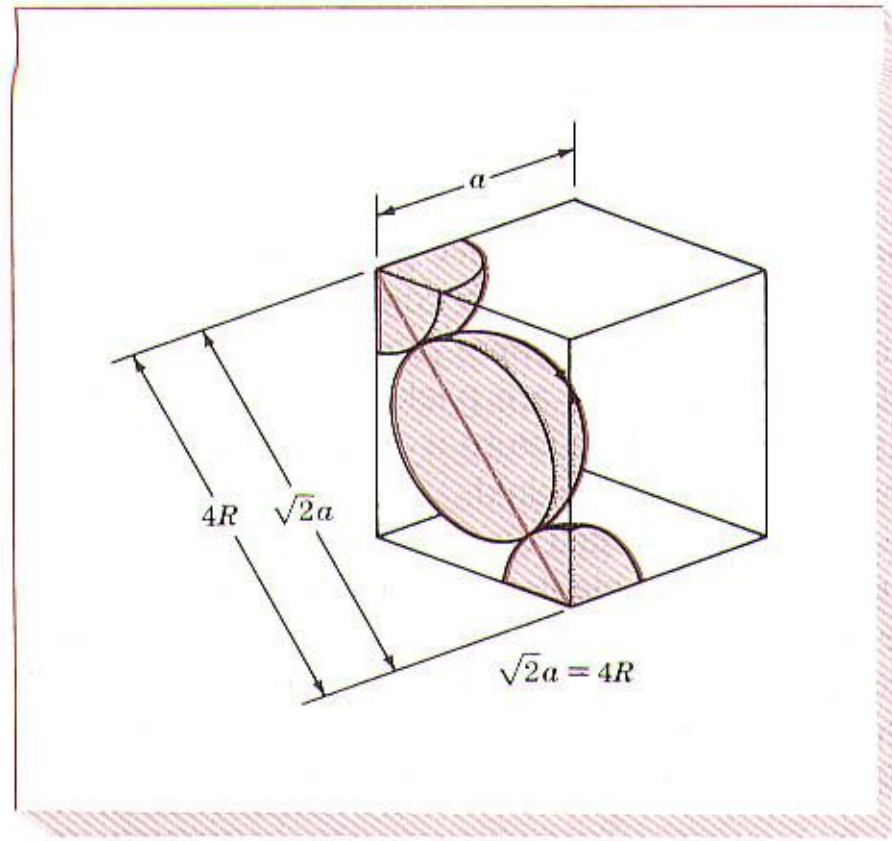
Figure: FCC unit cell showing relationship between the lattice constant a and atomic radius R. Since the atoms touch across the face diagonals $\sqrt{2}a = 4R$
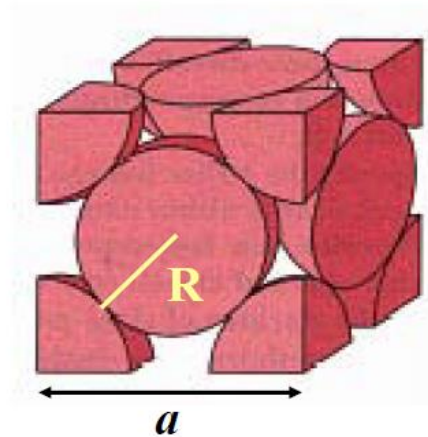
FACE CENTERED CUBIC CRYSTAL STRUCTURE
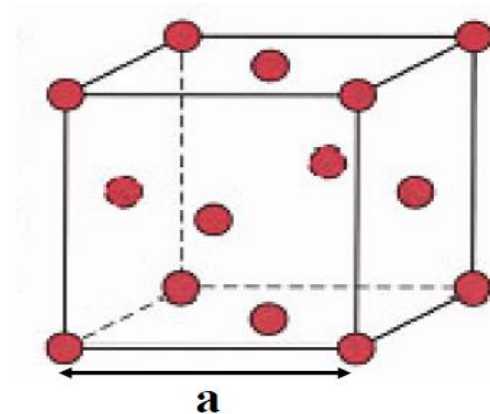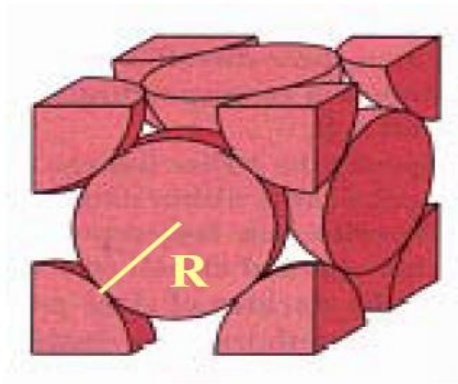
➤ The hard spheres touch one another across a face diagonal ⇒ the cube edge length, **a= 2R√2**

➤ **The coordination number, CN** = the number of closest neighbors to which an atom is bonded = number of touching atoms, **CN = 12**

➤ **Number of atoms per unit cell, n = 4**. (For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, 1/m). In FCC unit cell we have:

  6 face atoms shared by two cells: 6×1/2 = 3
  8 corner atoms shared by eight cells: 8×1/8 = 1

➤ **Atomic packing factor, APF** = fraction of volume occupied by hard spheres = (Sum of atomic volumes)/(Volume of cell) **= 0.74** (maximum possible)

FACE CENTERED CUBIC CRYSTAL STRUCTURE

Let's calculate the **atomic packing factor** for FCC crystal

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

APF = (Sum of atomic volumes)/(Volume of unit cell)

Volume of 4 hard spheres in the unit cell: $4 \times \dfrac{4}{3}\pi R^3$

Volume of the unit cell: $a^3 = 16R^3\sqrt{2}$

$$APF = \frac{16}{3}\pi R^3 \Big/ 16R^3\sqrt{2} = \pi/3\sqrt{2} = 0.74$$
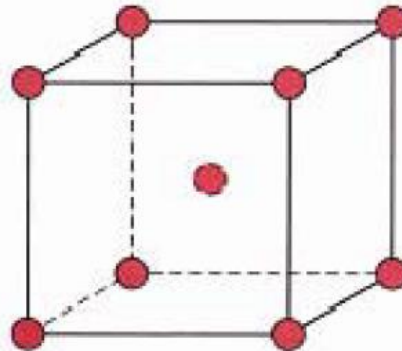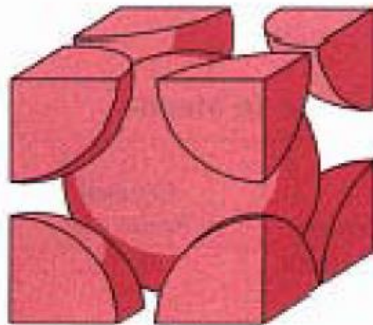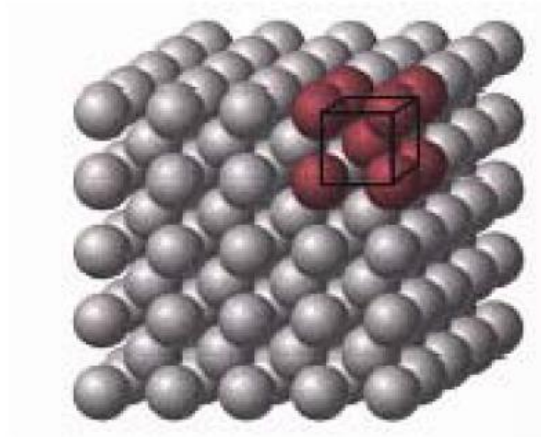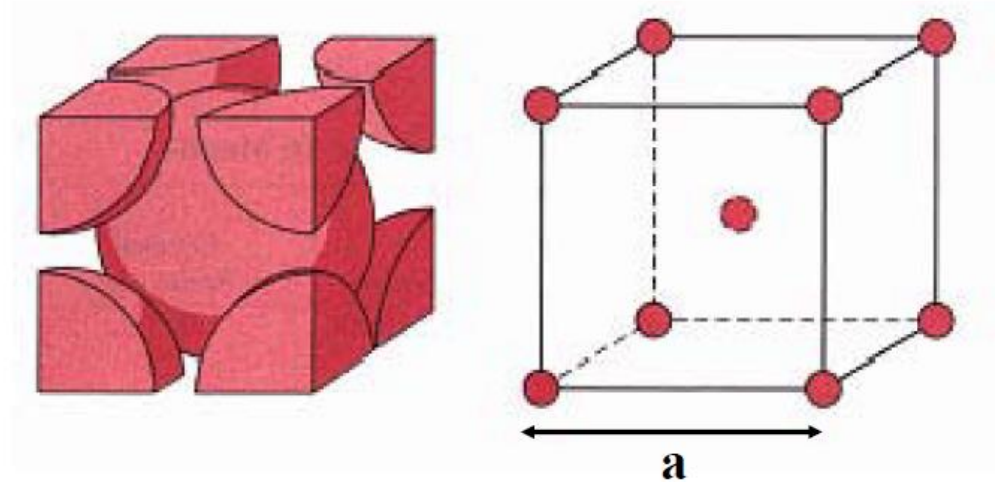
maximum possible packing of hard spheres

BODY CENTERED CUBIC CRYSTAL STRUCTURE: CsCl

Atom at each corner and at center of cubic unit cell

Cr, α-Fe, Mo have this crystal structure

BODY CENTERED CUBIC CRYSTAL STRUCTURE

➢ The hard spheres touch one another along cube diagonal
  ⇒ the cube edge length, **a= 4R/√3**

➢ **The coordination number, CN = 8**

➢ **Number of atoms per unit cell, n = 2**
  Center atom (1) shared by no other cells: 1 x 1 = 1
  8 corner atoms shared by eight cells: 8 x 1/8 = 1

➢ **Atomic packing factor, APF = 0.68**

➢ Corner and center atoms are equivalent