

# PH 113 S2: Physics of Materials and Nuclei

## Unit 1: Crystallography

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# Crystallography

- Crystalline and amorphous solids
- Lattice and unit cell
- Seven crystal system and Bravais lattices
- Symmetry operation
- Miller indices
- Atomic radius, Coordination number, Packing factor calculation for SC, BCC, FCC,
- Bragg's law of X-ray diffraction,
- Laue Method,
- Powder crystal method.

# What are Crystals?

When we hear the word "crystals," we usually think of coloured minerals. But those are not the only types of crystals.

Graphite in pencils, table salt, and snow are crystals, too.

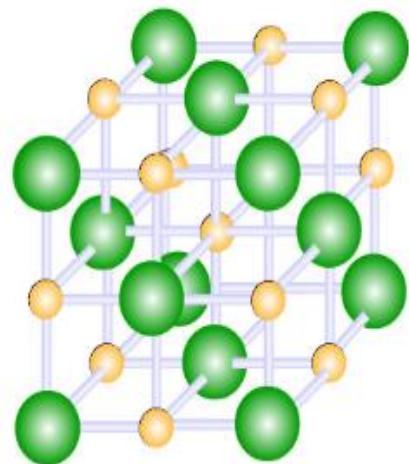
❖ A **crystal** is a solid whose molecules (or atoms) are arranged in a repeating pattern.

❖ For example, in the case of table salt ( $\text{NaCl}$ ), the crystals are made up of cubes of sodium ( $\text{Na}$ ) ions and chlorine ( $\text{Cl}$ ) ions. Each sodium ion is surrounded by six chlorine ions.

Each chlorine ion is surrounded by six sodium ions. It's very repetitive, which is exactly what makes it a crystal!

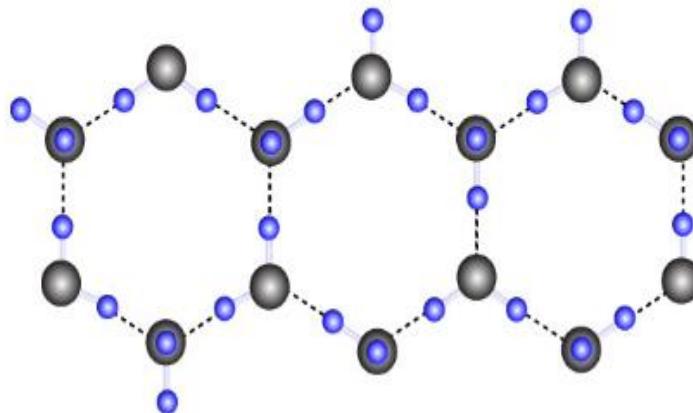
# Salt Crystal

- Chlorine ( $\text{Cl}^-$ )
- Sodium ( $\text{Na}^+$ )



# Ice crystal

- Oxygen
- Hydrogen



Crystals are also called crystalline solids because most crystals are solid. However, liquid crystals also exist.

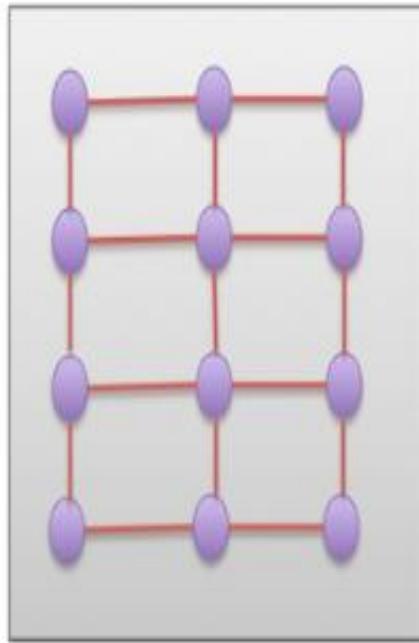
The word “crystal” comes from the Greek word *krustallos*, which means both “rock crystal” and “ice.”

The study of crystals is named crystallography.

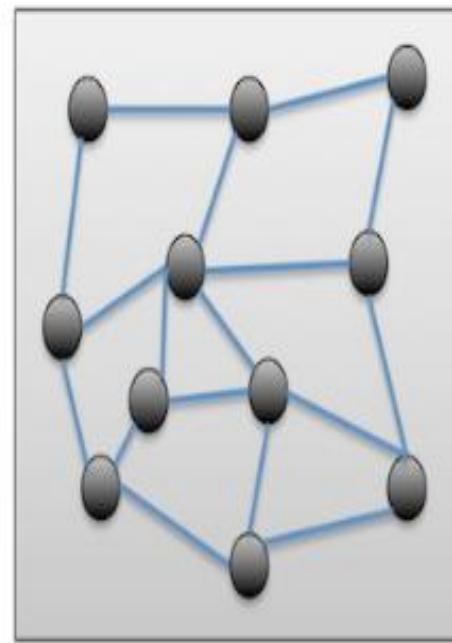
# Types of Solids

On the basis of the arrangement of constituent particles, the solids are classified into two categories, namely:

- Amorphous Solids
- Crystalline Solids



**Crystalline Solid**

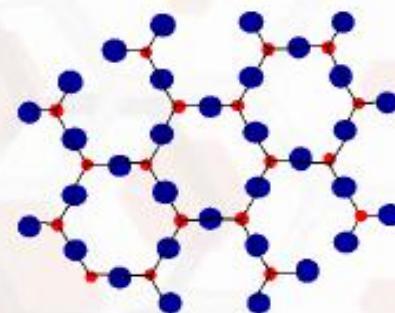


**Amorphous Solid**

# MATERIALS AND PACKING

## Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of:
  - metals
  - many ceramics
  - some polymers



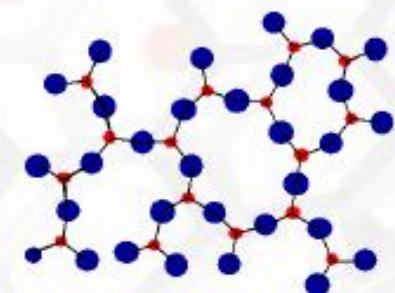
crystalline  $\text{SiO}_2$

## Non-crystalline materials...

- atoms have no periodic packing
- occurs for:
  - complex structures
  - rapid cooling

"Amorphous" = Non-crystalline

• Si      • Oxygen



Non-crystalline  $\text{SiO}_2$

## Characteristics of Amorphous Solids

- The constituent particles inside solid are arranged in a random manner.
- Amorphous Solids don't have definite shape or geometry due to random arrangement of atoms and molecules inside the solid lattice.
- Short-range order is found in amorphous solids
- Amorphous Solids are also called **Pseudo-solids** or **Supercooled Liquids** because they don't form crystalline structure and has the ability to flow
- Amorphous solids don't show sharp melting point, this is because of irregular packing of amorphous solids
- Amorphous solids are unsymmetrical in nature, due to irregular packing of atoms and molecules inside the solid lattice

**Examples:** Plastics, Glass, Rubber, Metallic Glass, Polymers, Gel etc.

## Uses of Amorphous Solids

There are many applications of amorphous solids, some of them are:

- The glass is widely used in packaging (food jars, cosmetics box, and soft-drink bottles), making tableware (utensils), in the construction of buildings (windows, lighting, and shelves) etc.
- Rubber is mainly used in manufacturing of tires, footwear, ropes, camp cloth and as a raw material for several industries
- Use of polymer can be seen in manufacturing of pipes, medicines and as a raw ingredient for many factories
- Amorphous silicon is considered as the best photovoltaic material to convert sunlight into electricity

## **Characteristics of Crystalline Solids**

The main characteristics of crystalline solids are mentioned as below:

- Crystalline solids show regular structure and have definite geometrical shape
- The sharp freezing point is found in crystalline solids. This is because the distance between same atoms/molecules or ions is same and remains constant, unlikely from amorphous solids
- When we cut a crystal solids with a knife, we obtain a flat and smooth surface
- Crystalline solids depict both long range and short range order.

**Examples:** Quartz, Calcite, Sugar, Mica, Diamonds etc.

# Uses of Crystalline Solids

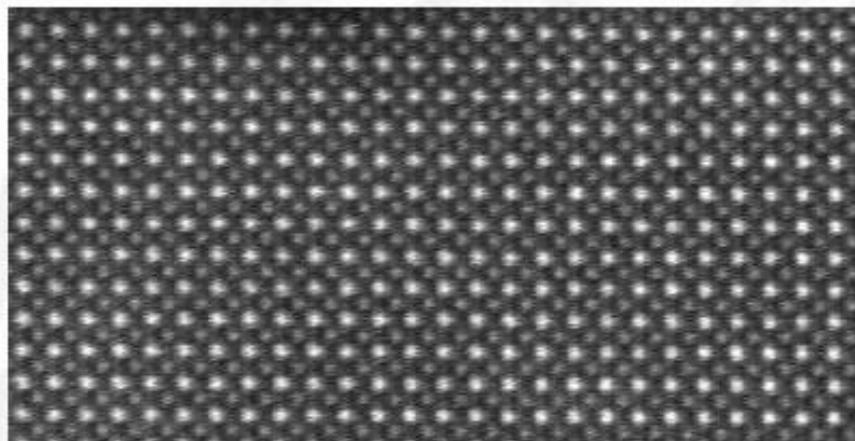
There are many applications of crystalline solids, some are:

- Diamond is the most decent example of crystalline solids and is widely used in making beautiful jewelry items
- Quartz is extensively used in manufacturing of watches and clocks
- Many crystalline solids are used as a raw material in many industries.

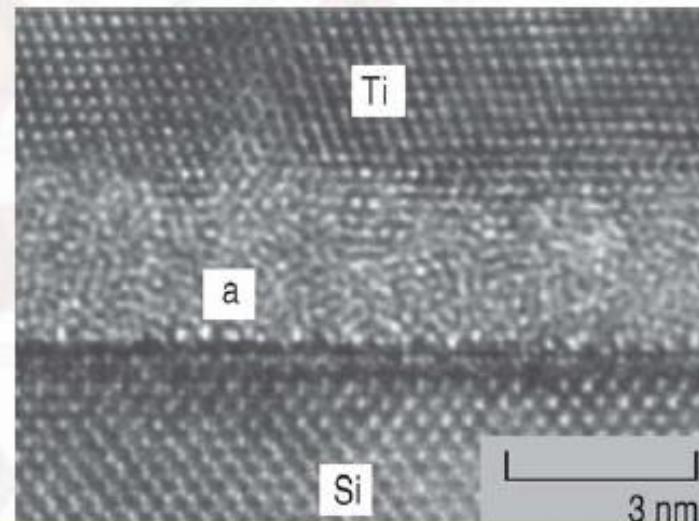
## Difference between Crystalline and Amorphous Solids

CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS
Atoms are arranged in regular 3 dimension	They do not have regular arrangement
Sharp melting point	No particular melting point
Symmetrical	Unsymmetrical
More rigid	Less rigid
Long range order	Short range order
Example: Potassium nitrate, copper	Example: Cellophane, polyvinyl chloride

**Crystallography** is the experimental science of the arrangement of atoms in solids. The word "crystallography" derives from the Greek words *crystallon* = cold drop / frozen drop, with its meaning extending to all solids with some degree of transparency, and *grapho* = write.



A **crystalline solid**: HRTEM image of strontium titanate. Brighter atoms are Sr and darker are Ti.

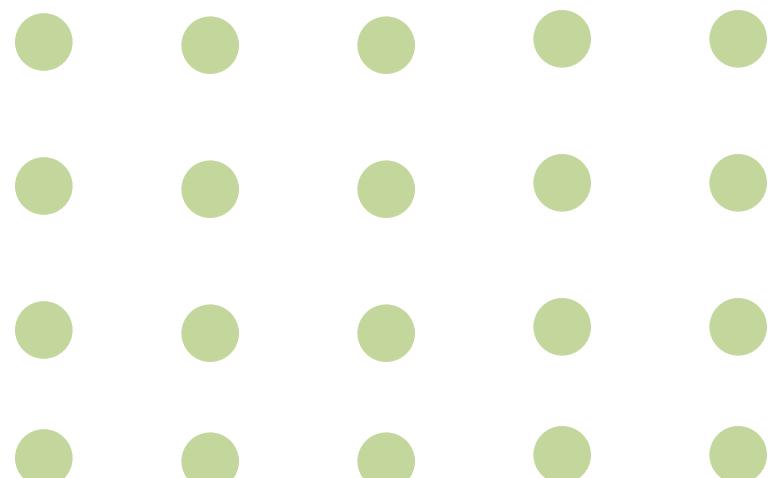


A TEM image of **amorphous interlayer** at the Ti/(001)Si interface in an as-deposited sample.

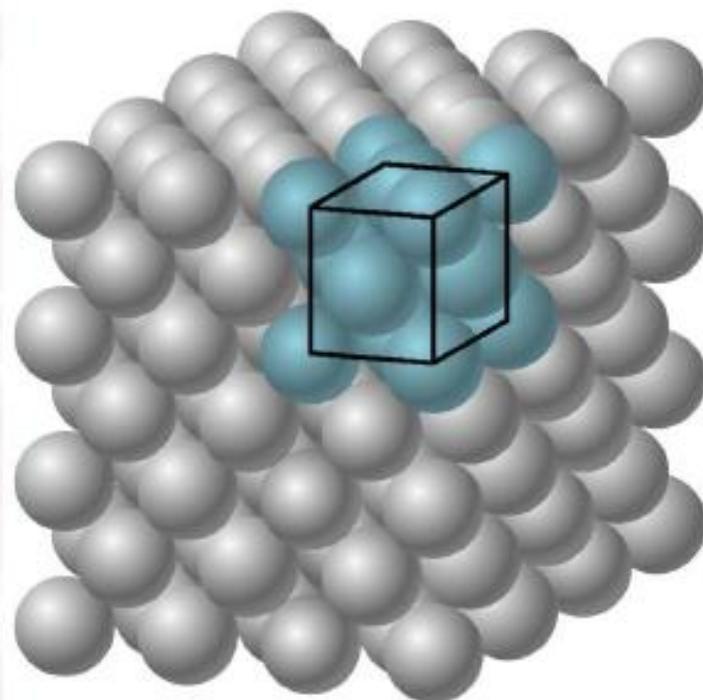
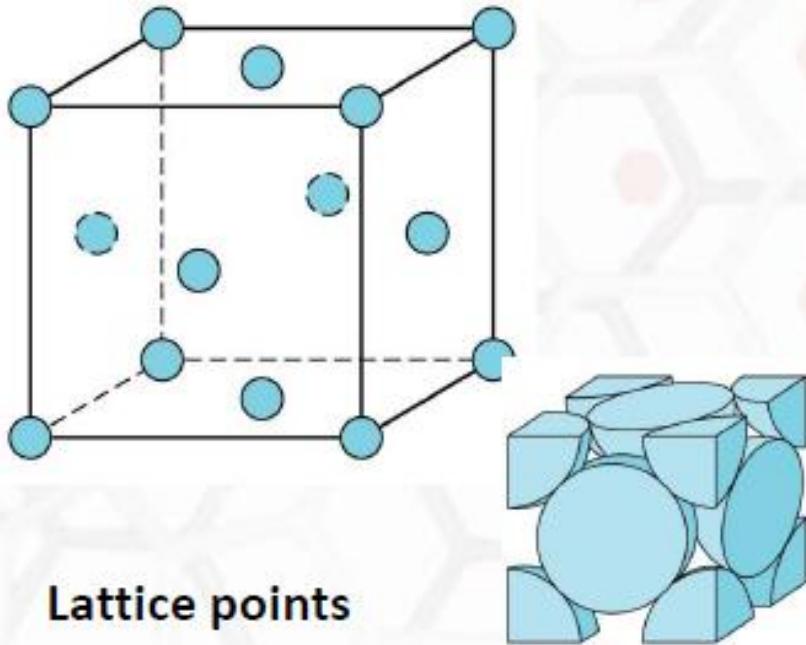
# Lattice

Consider an array of points in such a way that the environment around any one point is identical with the environment about any other point. Such an array of points in 2 Dimensions is called as lattice point. If this array of points is extended in three dimensions then the array of points is called space lattice.

A **Lattice** is defined as parallel net like arrangement of points provided the environment about any point is identical with environment about any other point.



# Unit Cell



- Unit cell is the *smallest* unit of volume that permits **identical** cells to be stacked together *to fill all space*.
- By *repeating* the pattern of the unit cell over and over in all directions, the entire **crystal** lattice can be constructed.

**Crystal structure = Lattice + Basis**

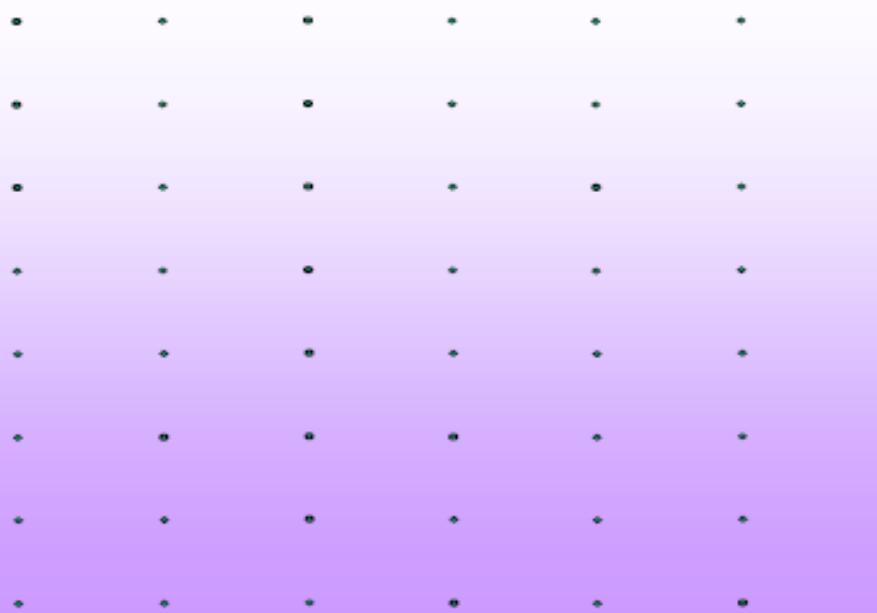
# Basic Of Crystal Structure

## ➤ Lattice:-

"An infinite periodic array of points in a space "

-The arrangement of points defines the lattice symmetry

-A lattice may be one, two or three dimensional



# Cont...

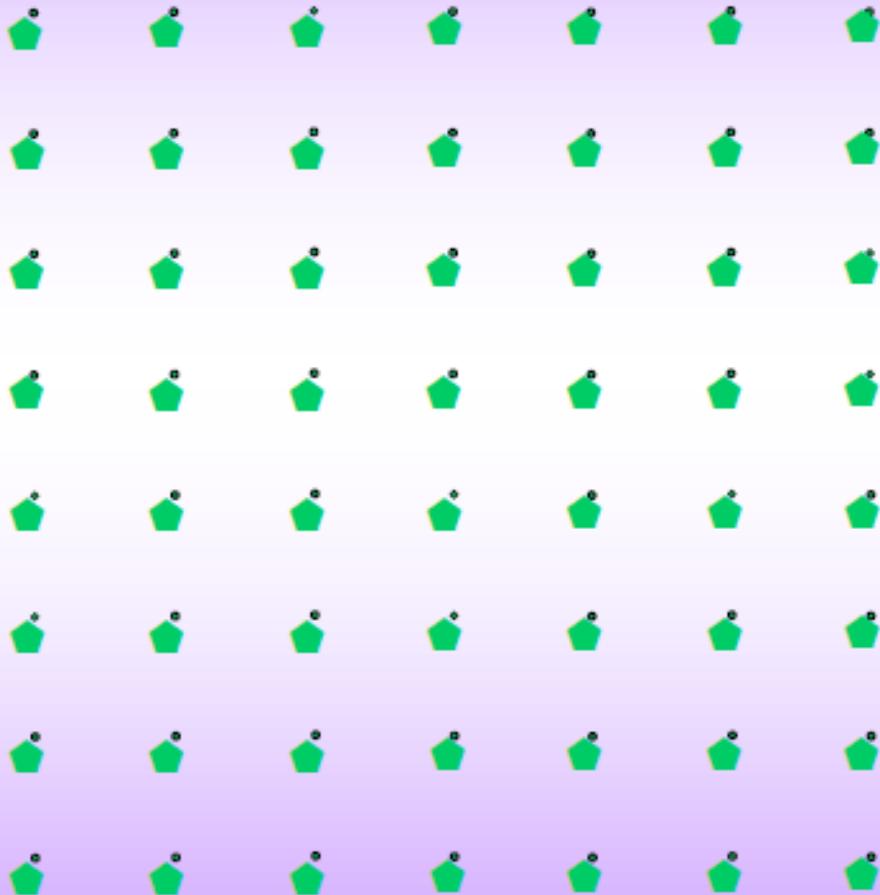
Basis(Motif):-

A group of one or more atoms, located in a particular way with respect to each other and associated with each point, is known as the Motif or Basis.

Motif



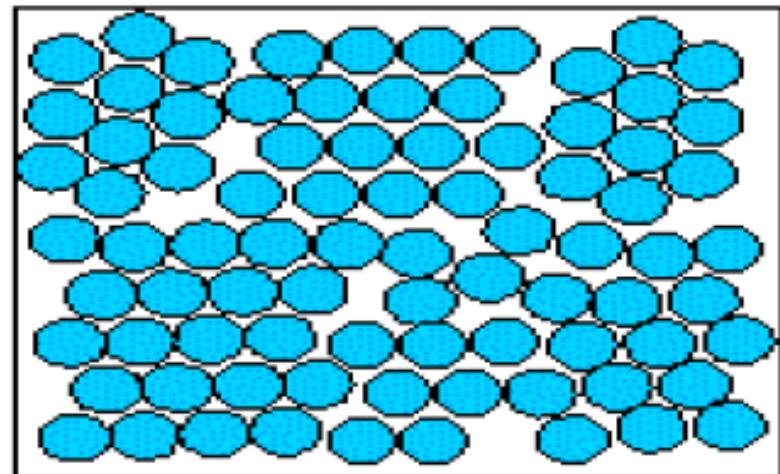
# Crystal structure



- so we obtain a crystal structure by adding the lattice and basis

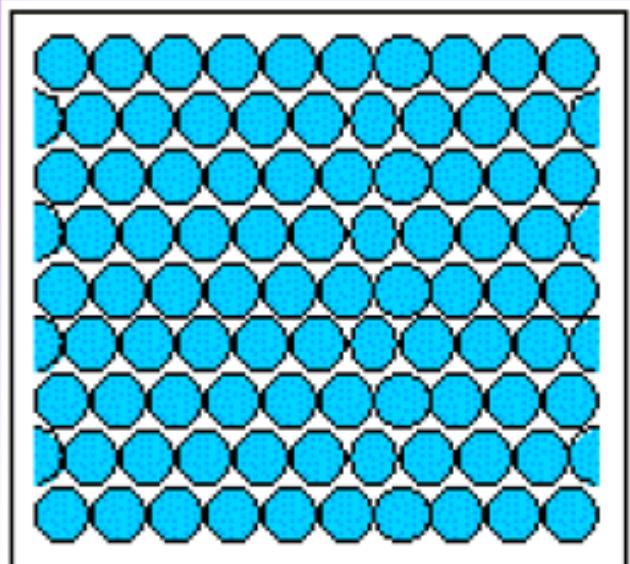
- So we can say that, When an atom or identical group of atoms is attached to every lattice point, we obtain a crystal structure.

- Crystals are classified into two types
  1. Poly crystal
  2. Single crystal
- Poly crystal: In this type of crystal periodicity is not maintained throughout the body.



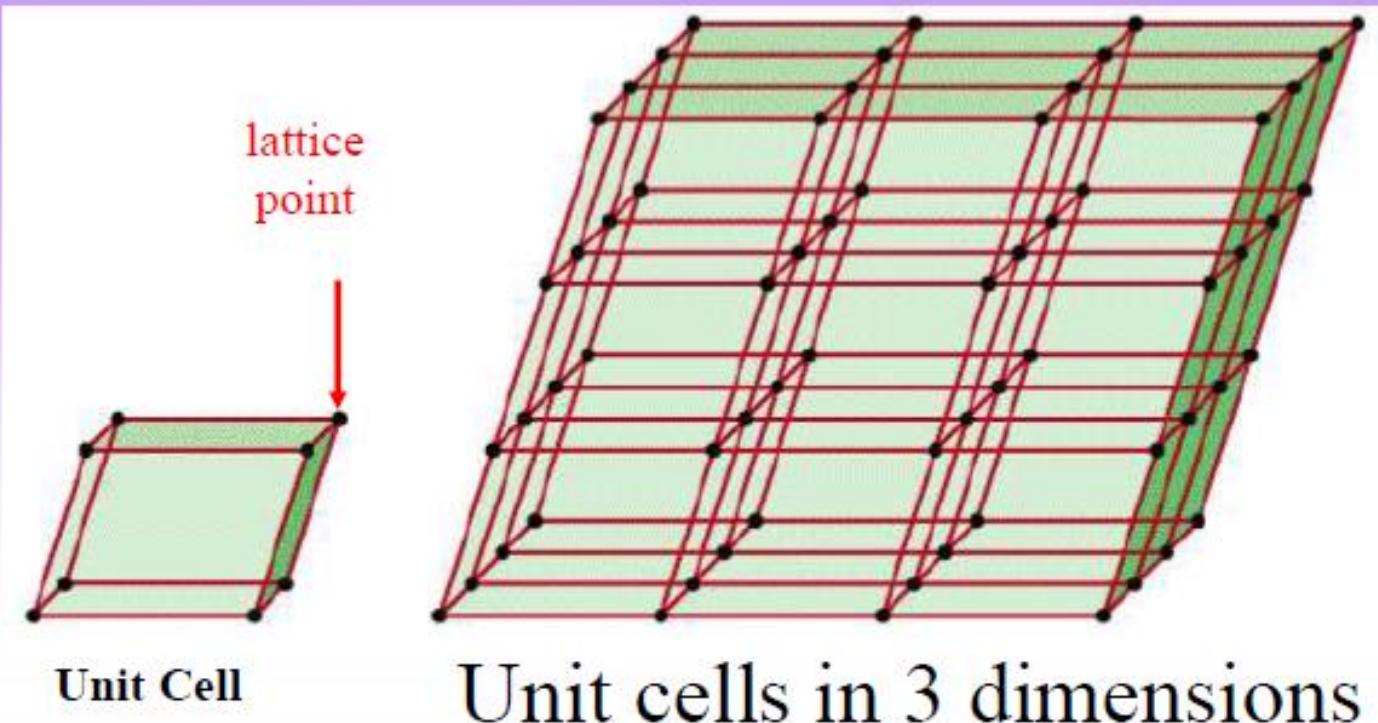
Polycrystal

- Single crystal: In this type of crystal periodicity is maintained throughout the body.



Single crystal

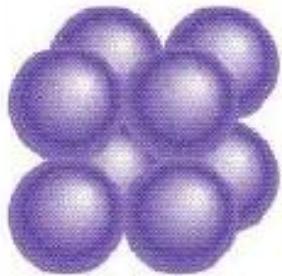
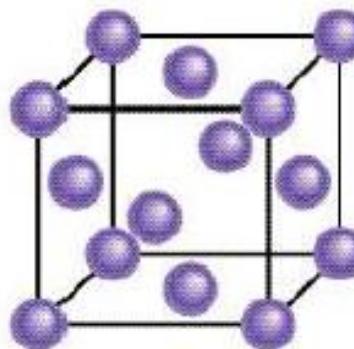
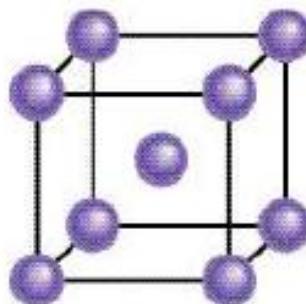
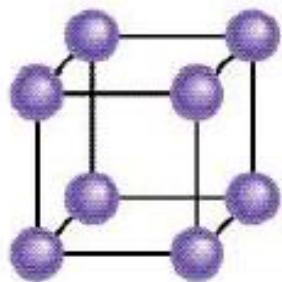
Unit cell:- " Atoms or group of atoms forming a building block of the smallest acceptable size of the whole volume of a crystal is defined as a unit cell ".



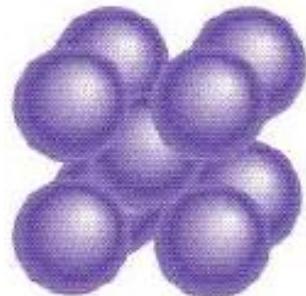
- By stacking identical unit cells, the entire lattice can be constructed.
- Lattice points are located at the corner of the unit cell and in some cases, at either faces or the centre of the unit cell.

- Here for the cubic crystal system we have Simple cubic (SC), Face-centred cubic (FCC),and Body-centred cubic(BCC).

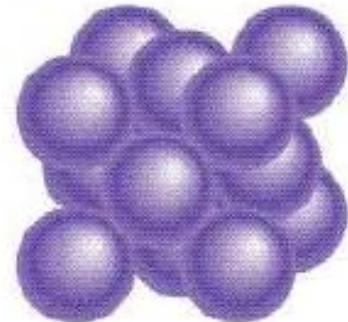
## Three Types of Cubic Cells



Simple cubic

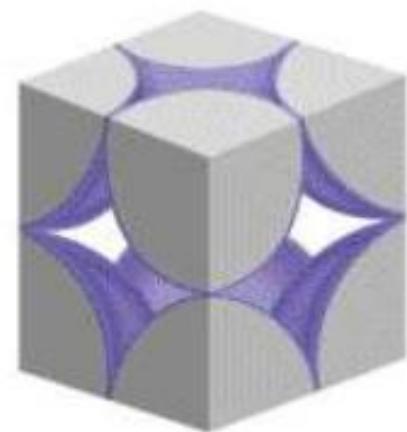
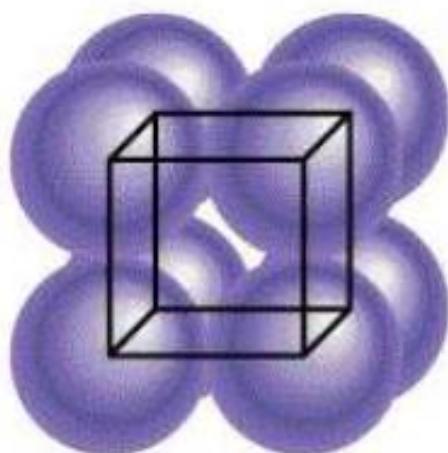
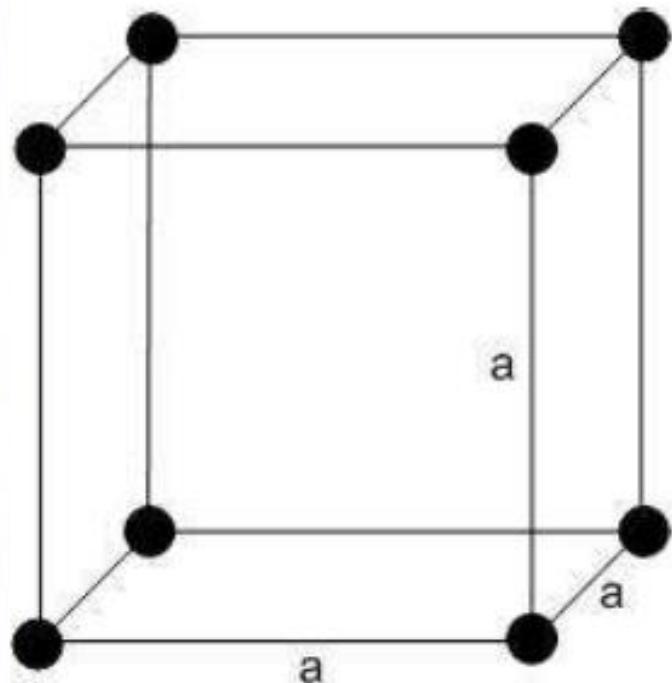


Body-centered cubic



Face-centered cubic

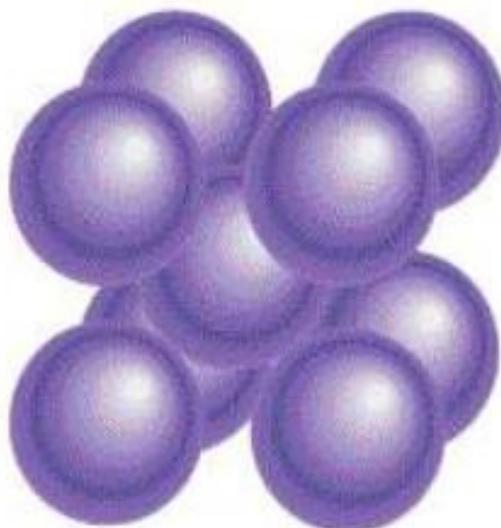
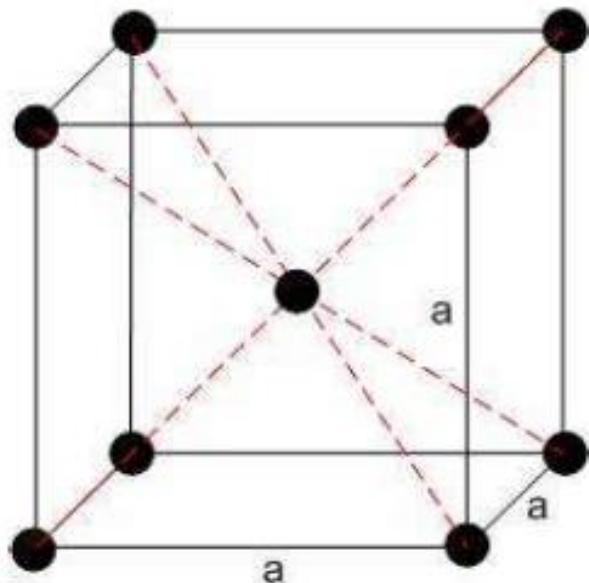
# Arrangement of Identical Spheres in a simple Cubic Cell



Total no. of atom per simple cubic cell is  
 $8(1/8) = 1$  atom

# Arrangement of Identical Spheres in a Body-Centered Cube

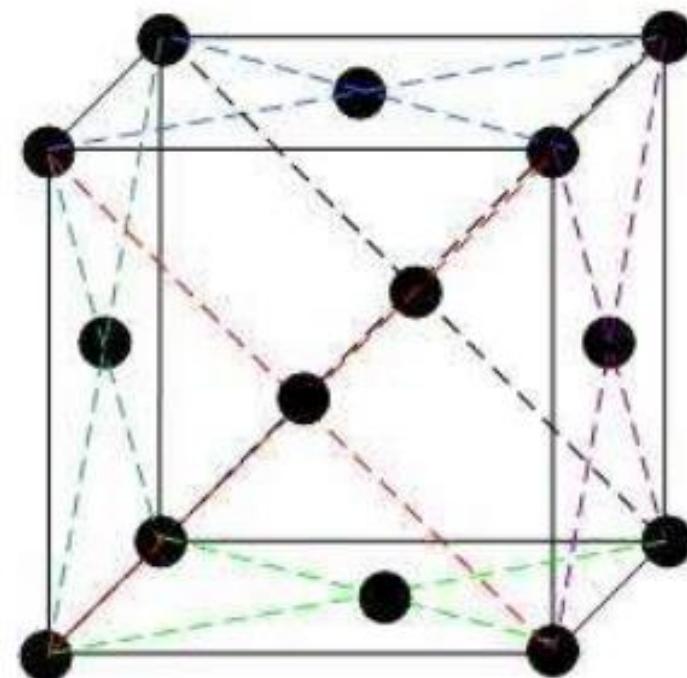
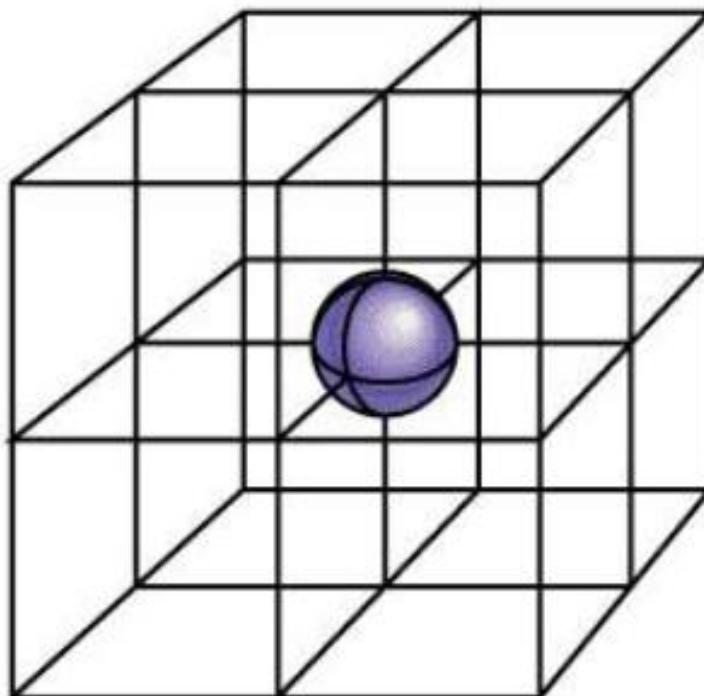
Body Centered Cubic



Total no. of atom per BCC unit cell is  
 $8(1/8)+1 = 2$  atom

# A Corner Atom and a Face-Centered Atom

Face Centered Cubic

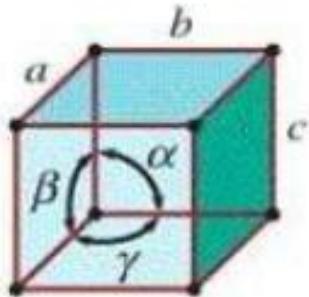


Shared by 8  
unit cells

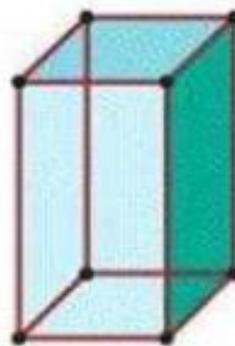
Total no. of atom per FCC unit cell is

$$8(1/8) + 6(1/2) = 4 \text{ atom}$$

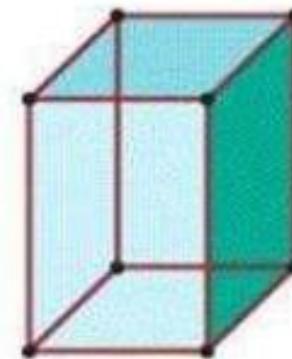
- There are seven unique arrangements, known as crystal systems, which fill in a three dimensional space.



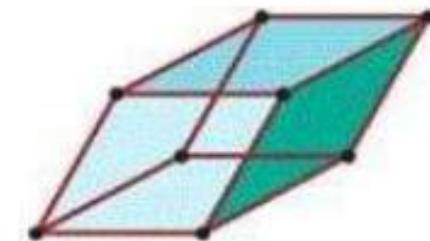
**Simple cubic**  
 $a = b = c$   
 $\alpha = \beta = \gamma = 90^\circ$



**Tetragonal**  
 $a = b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



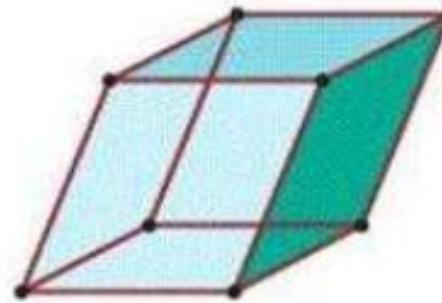
**Orthorhombic**  
 $a \neq b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



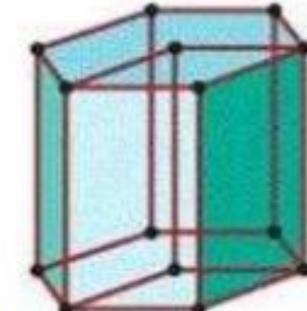
**Rhombohedral**  
 $a = b = c$   
 $\alpha = \beta = \gamma \neq 90^\circ$



**Monoclinic**  
 $a \neq b \neq c$   
 $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$



**Triclinic**  
 $a \neq b \neq c$   
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



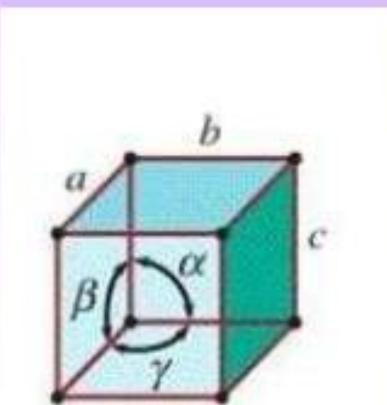
**Hexagonal**  
 $a = b \neq c$   
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

# THE 7 CRYSTAL SYSTEMS

## 1. Cubic Crystals

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$



**Simple cubic**  
 $a = b = c$   
 $\alpha = \beta = \gamma = 90^\circ$



**Fluorite**  
*Octahedron*

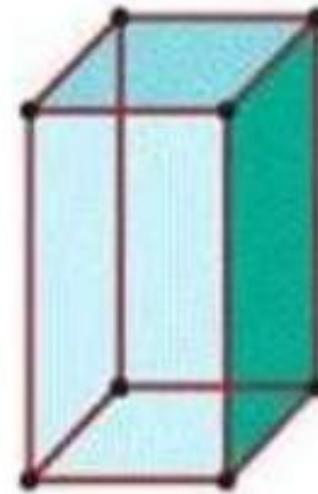


**Pyrite**  
*Cube*

## 2. Tetragonal Crystals

$a = b \neq c$

$\alpha = \beta = \gamma = 90^\circ$



**Tetragonal**

$a = b \neq c$

$\alpha = \beta = \gamma = 90^\circ$

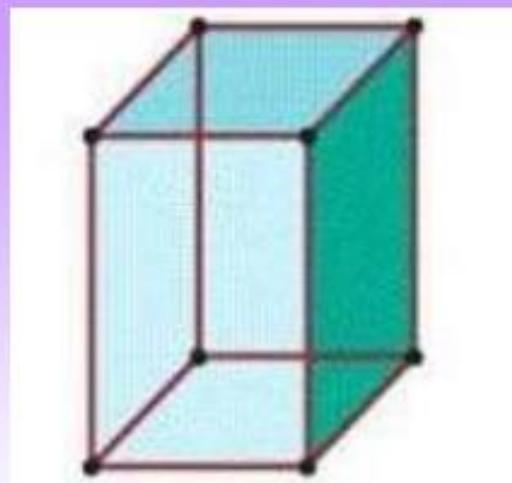
**Zircon**



### 3. Orthorhombic Crystals

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^\circ$



**Orthorhombic**  
 $a \neq b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$

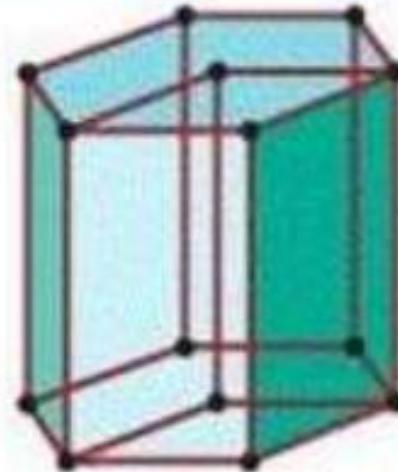
### Topaz



## 4. Hexagonal Crystals

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ \quad \gamma = 120^\circ$$



**Hexagonal**

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$

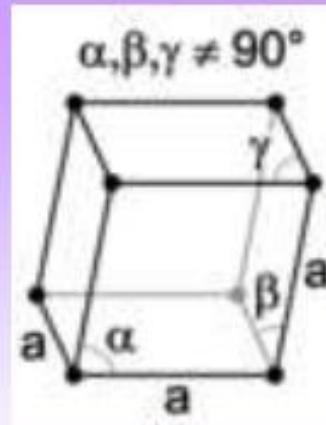


**Corundum**

## 5. Rhombohedral Crystals

$a = b = c$

$\alpha, \beta, \gamma \neq 90^\circ$

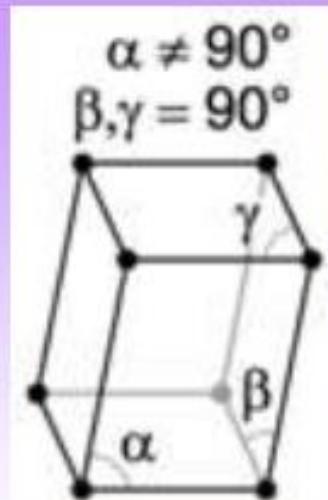


Tourmaline

## 6. Monoclinic Crystals

$a \neq b \neq c$

$\alpha \neq 90^\circ, \beta, \gamma = 90^\circ$



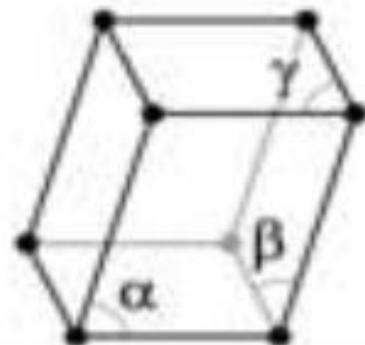
Kunzite

## 7. Triclinic Crystals

$a \neq b \neq c$

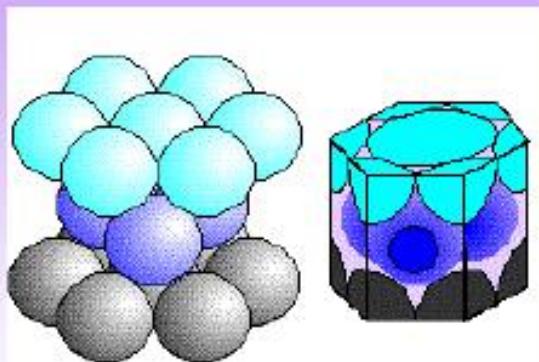
$\alpha \neq \gamma \neq \beta$

$\alpha, \beta, \gamma \neq 90^\circ$



**Amazonite**

# Hexagonal structure



**Hexagonal Structure**



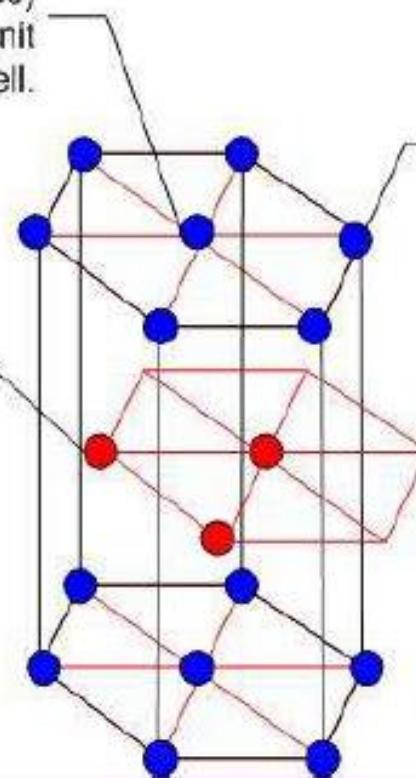
Quartz is the example of hexagonal close pack solid

## Hexagonal Close Pack Unit Cell

The two center atoms (top and bottom faces) are half inside the unit cell.

These atoms (center layer) are entirely inside the unit cell.

The twelve corner atoms are one sixth of inside the unit cell.



This means that a total of  $12(1/6) + 2(1/2) + 3 = 6$  atoms are inside the unit cell

# 7 CRYSTAL LATTICE

- We know that a three dimensional space lattice is generated by repeated translation of three non-coplanar vectors  $a$ ,  $b$ ,  $c$ . Based on the lattice parameters we can have 7 popular crystal systems.

# PRIMITIVE AND CENTRED UNIT CELLS

Unit cells can be broadly divided into two categories , **primitive** and **centred unit cells**.

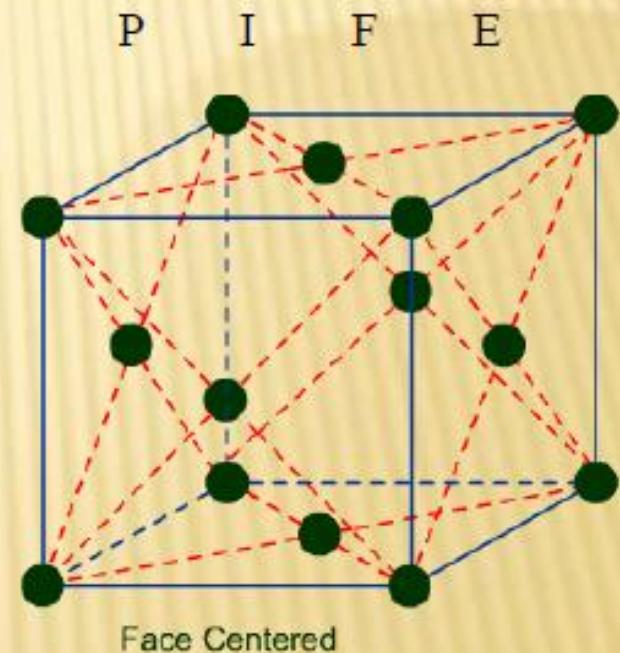
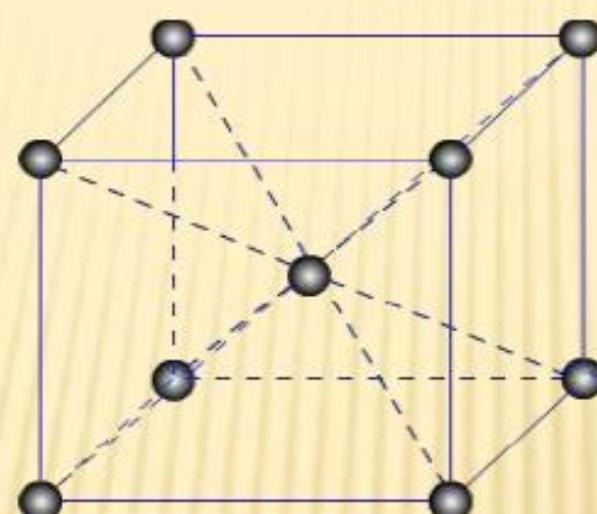
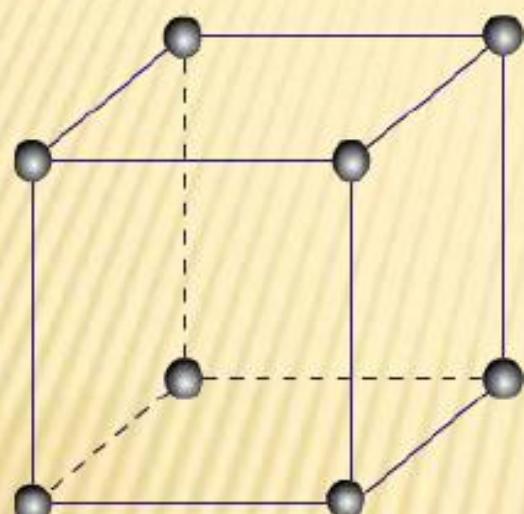
- ✖ When constituent particles are present only on the corner positions of a unit cell. It is called as **Primitive unit cell**.
- ✖ When a unit cell contains one or more constituent particles present at the positions other than corners in addition to those at corners, it is called a **centred unit cell**.

# Bravais Lattice

Bravais Lattice refers to the *14 different 3-dimensional configurations into which atoms can be arranged in crystals.*

# FOURTEEN BRAVAIS LATTICES

1	Cubic	Cube	✓	✓	✓	
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Primitive or Simple

Body Centred

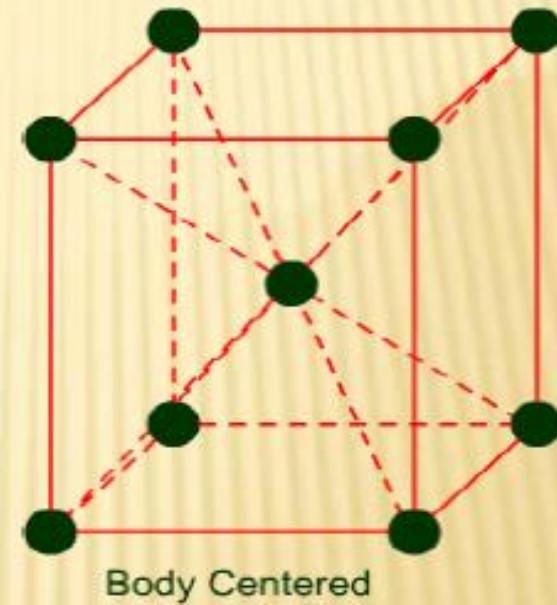
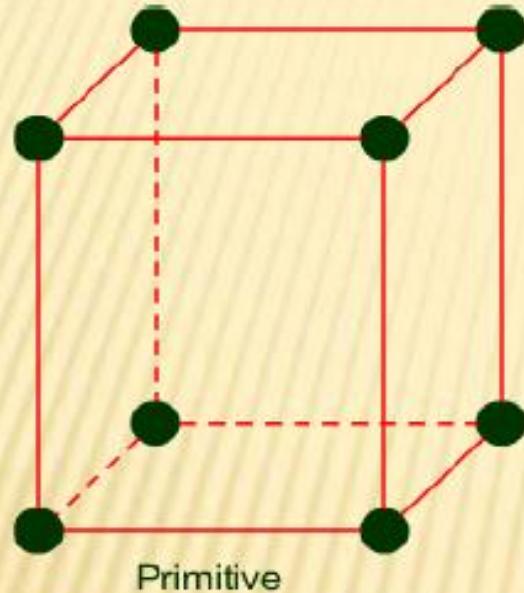
Face Centered

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

Corresponding Examples  
NaCl, Zinc Blende, Cu

			P	I	F	E
2	Tetragonal	Square Prism (general height)	✓	✓		



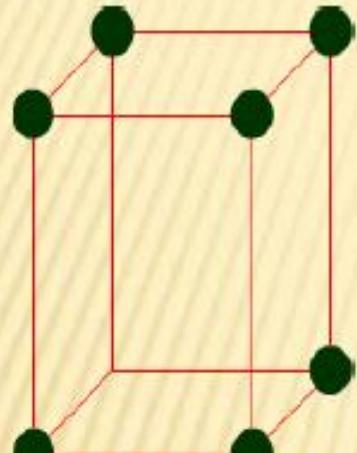
$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

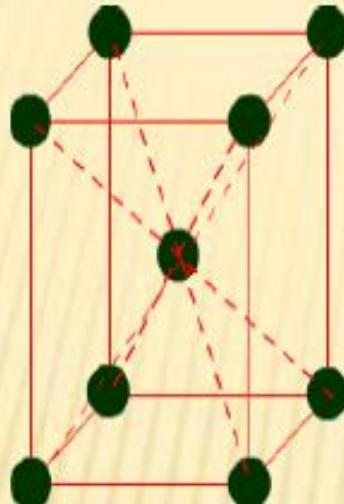
White tin, SnO<sub>2</sub>, TiO<sub>2</sub>, CaSO<sub>4</sub>

P I F E

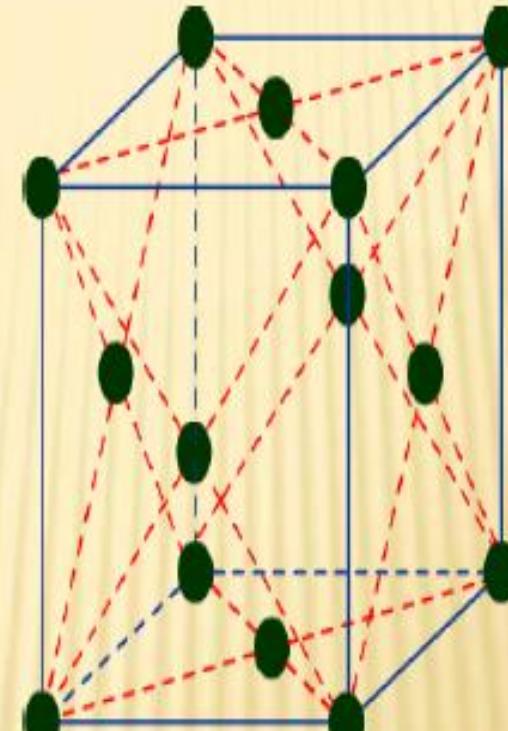
3	Orthorhombic	Rectangular Prism (general height)	✓	✓	✓	✓
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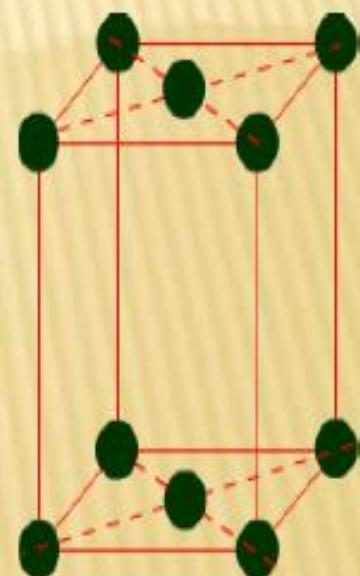
Primitive



Body Centered



Face Centered



End Centered

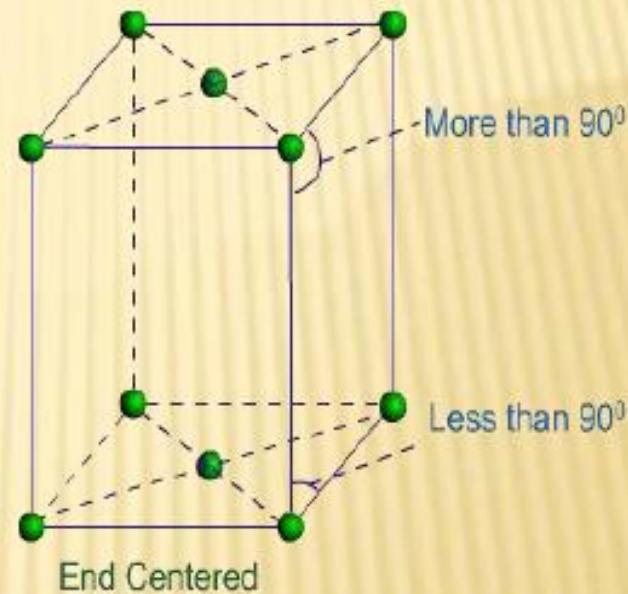
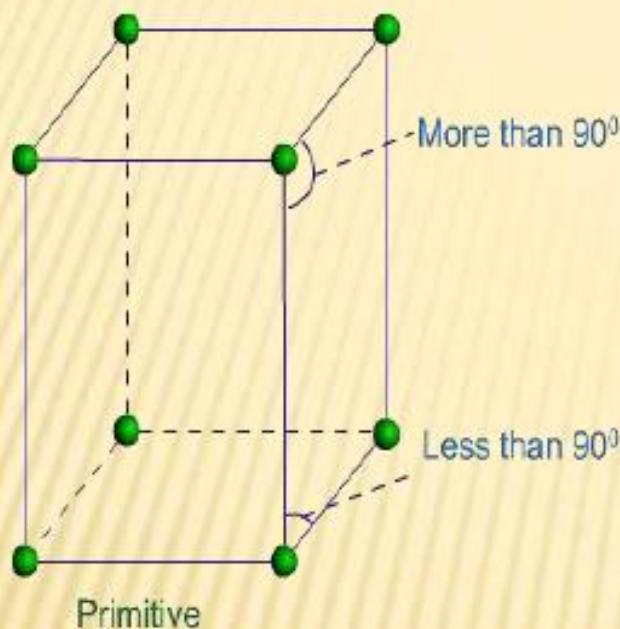
$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

Rhombic sulfur,  $\text{KNO}_3$ ,  $\text{BaSO}_4$

P I F E

4	Monoclinic	Parallogramic Prism	✓				✓
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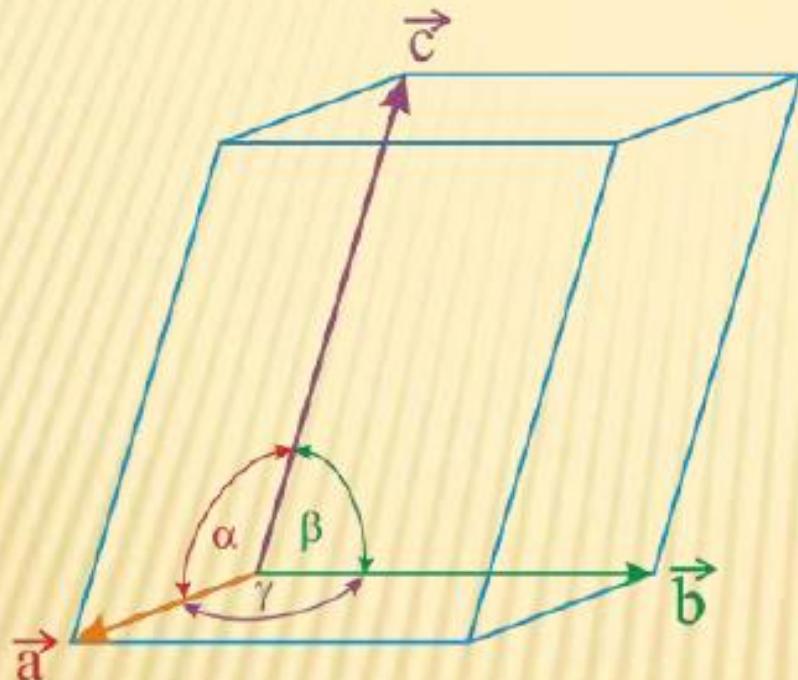


$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ \neq \beta$$

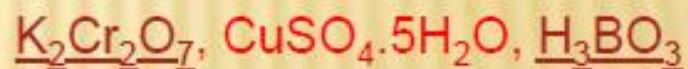
Monoclinic sulfur,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

5	Triclinic	Parallelepiped (general)	✓			
---	-----------	--------------------------	---	--	--	--

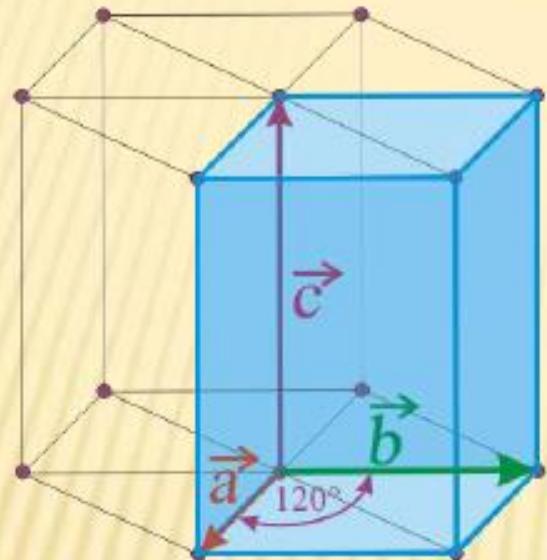


$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma$$



6	Hexagonal	120° Rhombic Prism	✓			
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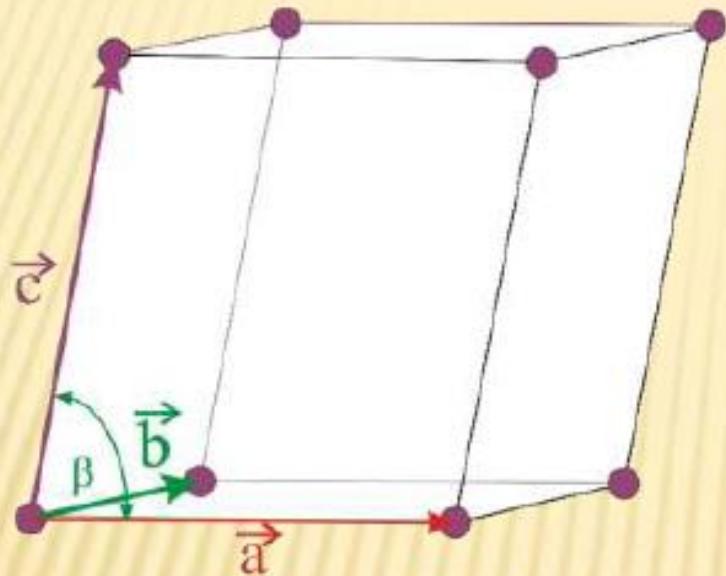


$$a = b \neq c$$

$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$

Graphite, ZnO, CdS

7	Rhombohedral	Parallelepiped (Equilateral, Equiangular)	✓			
---	--------------	---	---	--	--	--



$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

Calcite ( $\text{CaCO}_3$ ), Cinnabar ( $\text{HgS}$ )

## 14 Bravais Lattices divided into 7 Crystal Systems

	Crystal System	Shape of UC	Bravais Lattices			
			P	I	F	C
1	Cubic	Cube	✓	✓	✓	
2	Tetragonal	Square Prism (general height)	✓	✓		
3	Orthorhombic	Rectangular Prism (general height)	✓	✓	✓	✓
4	Hexagonal	120° Rhombic Prism	✓			
5	Trigonal	Paralloped (Equilateral, Equiangular)	✓			
6	Monoclinic	Parallogramic Prism	✓			✓
7	Triclinic	Parallelepiped (general)	✓			

P	Simple*
I	Body Centred
F	Face Centred
C	A/B/C- Centred

\* Not to be confused with Primitive (in spite of a P). Primitive is a type of unit cell (with one lattice point per cell)

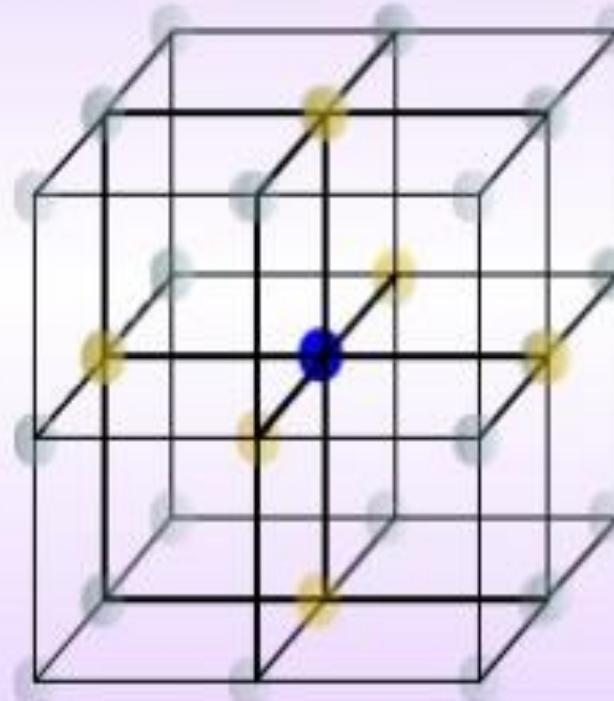
# Coordination Number

- It is the number of nearest equidistant neighbours of an atom in the lattice

Consider a simple cubic structure.

Six yellow atoms are touching the blue atom.

Hence, the blue atom is having six nearest neighbors.



Therefore, for a Simple cubic lattice: coordination number, CN = 6

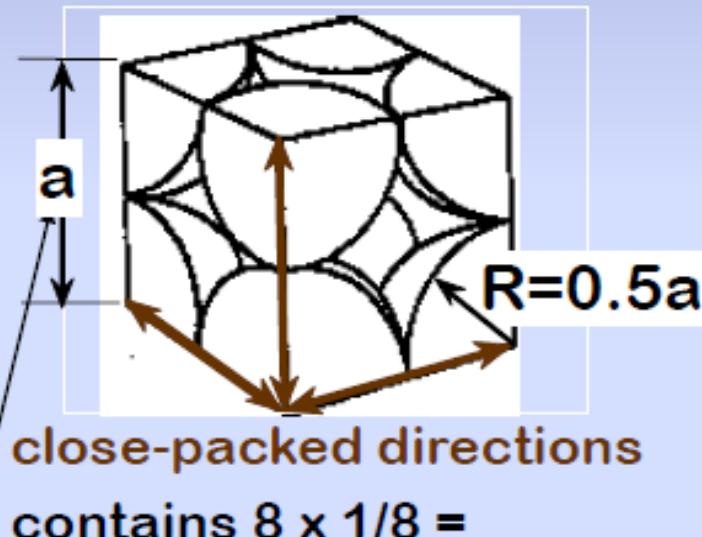
# Atomic Packing Factor

- Atomic Packing Factor is the fraction of volume occupied by atoms in a unit cell.

# SIMPLE CUBIC STRUCTURE

$$APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

\*assume hard spheres



Adapted from Fig. 3.19,  
*Callister 6e.*

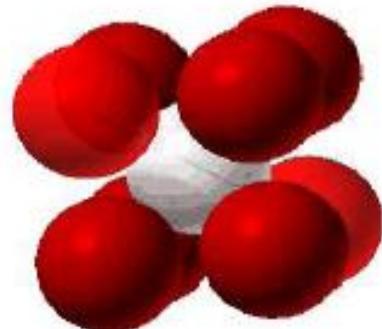
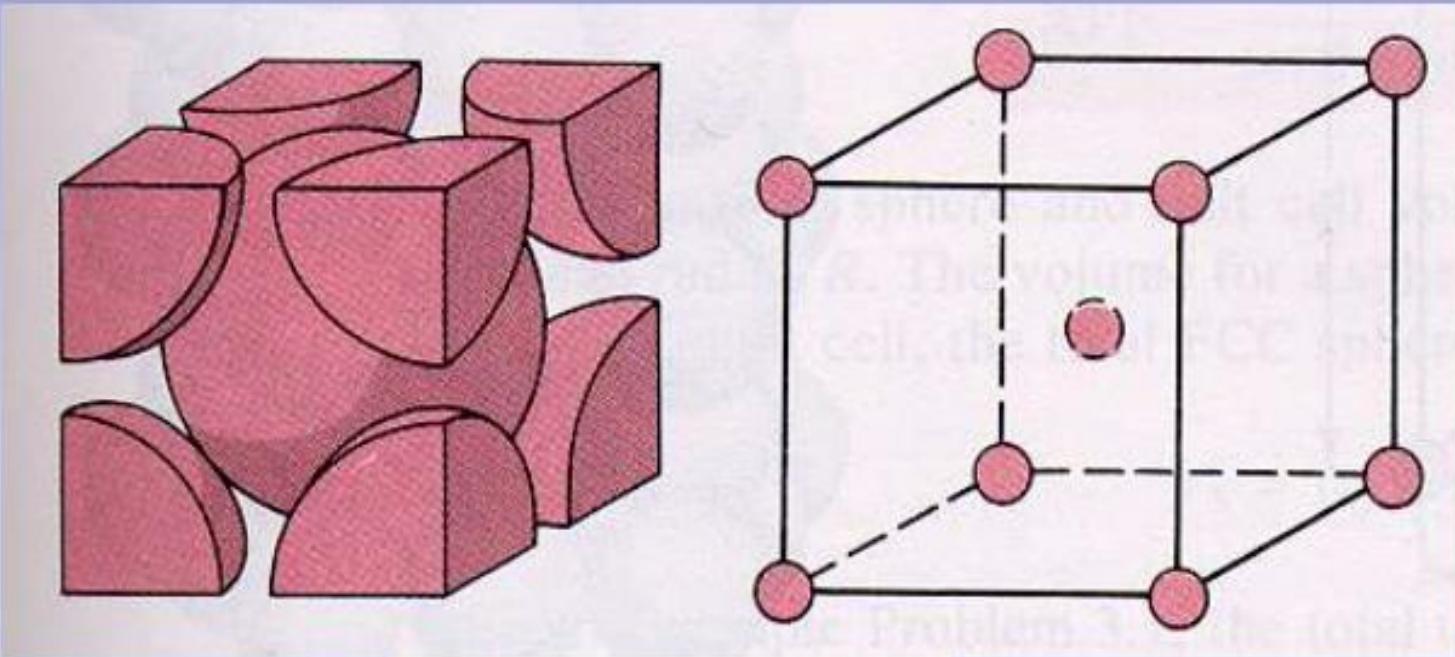
$$APF = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot \frac{4}{3} \pi (0.5a)^3}{a^3}$$

volume  
atom  
volume  
unit cell

Lattice constant

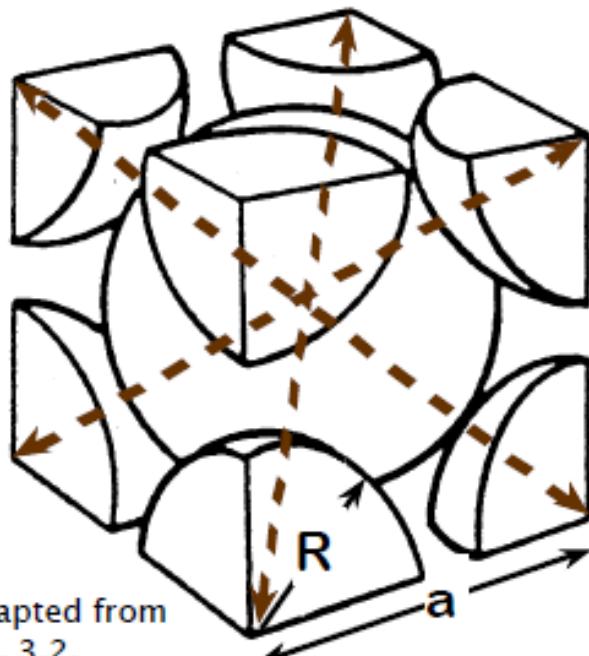
• APF for a simple cubic structure = **0.52**

# BODY CENTERED CUBIC STRUCTURE



- Coordination No. = 8  
(# nearest neighbors)

# ATOMIC PACKING FACTOR: BCC



Close-packed directions:

$$\text{length} = 4R \\ = \sqrt{3}a$$

Unit cell contains:

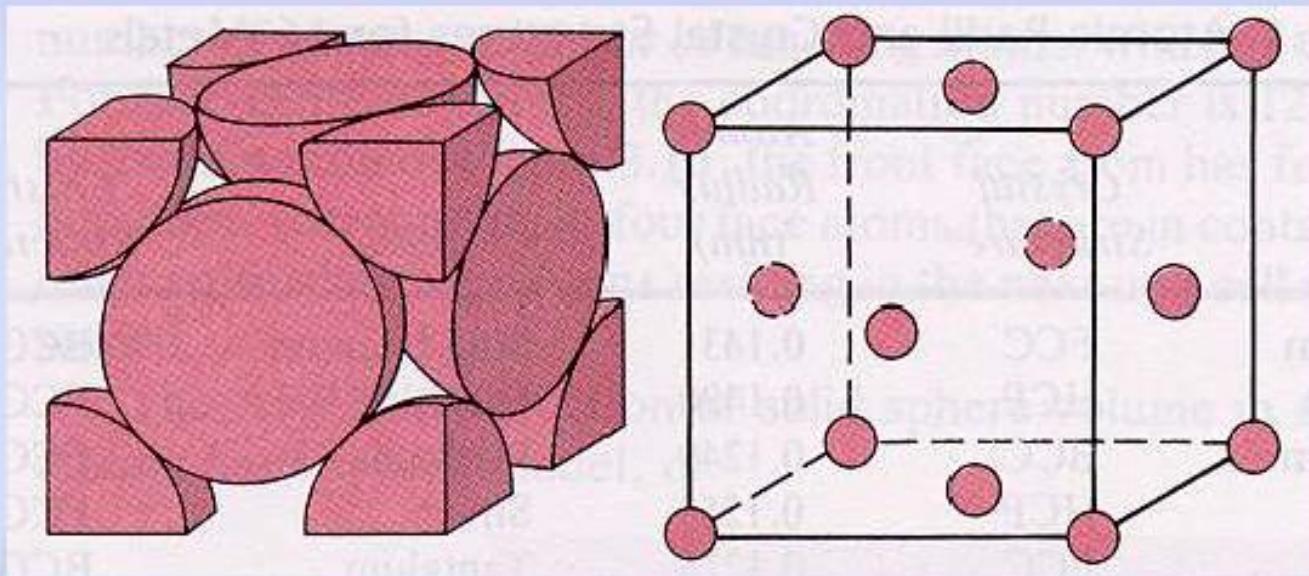
$$1 + 8 \times 1/8 \\ = 2 \text{ atoms/unit cell}$$

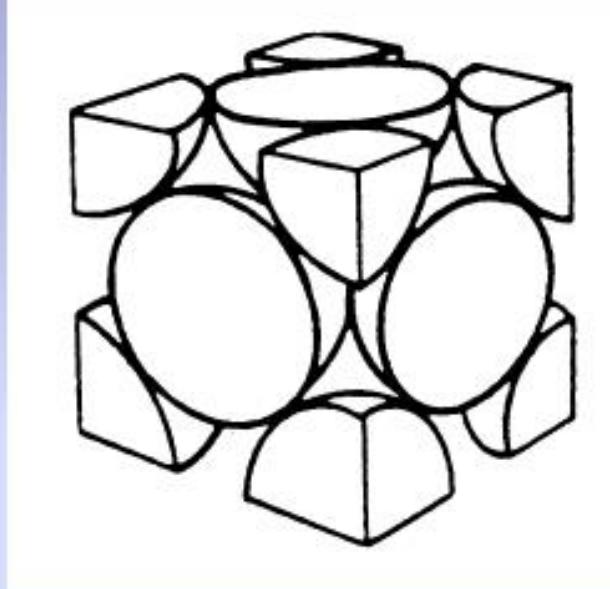
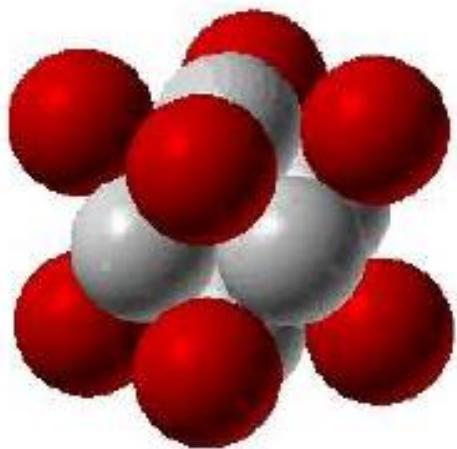
$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{2 \cdot \frac{4}{3} \pi (\sqrt{3}a/4)^3}{a^3}$$

- APF for a body-centered cubic structure =  $\pi\sqrt{3}/8 = 0.68$

## FACE CENTERED CUBIC STRUCTURE

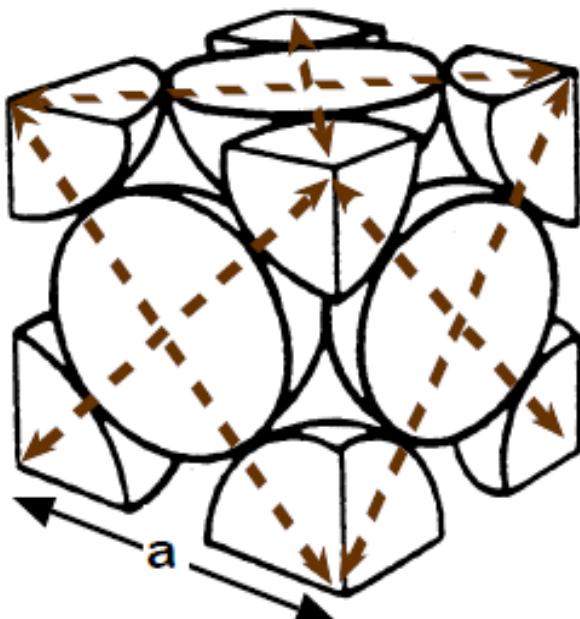
- ▶ Atoms are arranged at the corners and center of each cube face of the cell.
  - Atoms are assumed to touch along face diagonals





- **Coordination No. = 12**  
(# nearest neighbors)

# ATOMIC PACKING FACTOR: FCC



Close-packed directions:

$$\begin{aligned}\text{length} &= 4R \\ &= \sqrt{2}a\end{aligned}$$

Unit cell contains:

$$\begin{aligned}6 \times 1/2 + 8 \times 1/8 \\ = 4 \text{ atoms/unit cell}\end{aligned}$$

$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{4 \frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3}$$

APF for a body-centered cubic structure =  $\pi/(3\sqrt{2}) = 0.74$

## Important Properties of unit cell

	<b>SC</b>	<b>BCC</b>	<b>FCC</b>	<b>HCP</b>
Relation between atomic radius (r) and lattice parameter (a)	$a = 2r$	$\sqrt{3}a = 4r$	$\sqrt{2}a = 4r$	$a = 2r$
Effective Number of atoms per unit cell	1	2	4	6
Coordination Number (No. of nearest equidistant neighbours)	6	8	12	12
Packing Factor	0.52	0.68	0.74	0.74

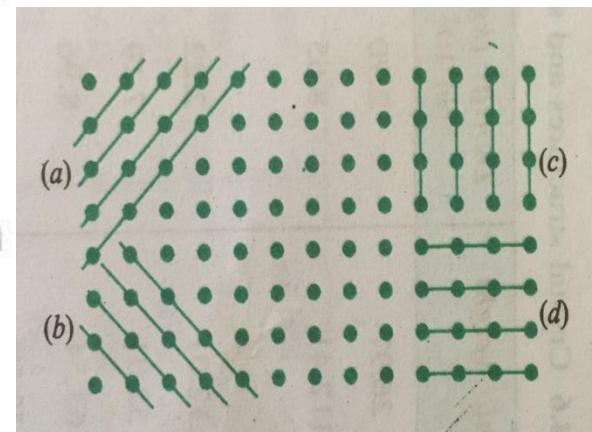
# Miller Indices

## INTRODUCTION

The crystal lattice may be regarded as made up of an infinite set of parallel equidistant planes passing through the lattice points which are known as lattice planes.

In simple terms, the planes passing through lattice points are called '*lattice planes*'.

For a given lattice, the lattice planes can be chosen in a different number of ways.

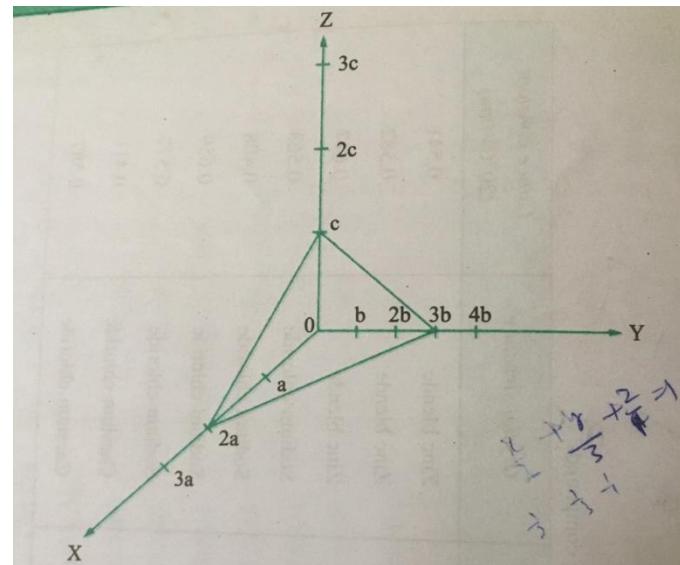


- Miller indices were introduced in 1839 by the British mineralogist William Hallowes Miller. The method was also historically known as the Millerian system, and the indices as Millerian.
- The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid.
- The application of a set of rules leads to the assignment of the Miller Indices,  $(hkl)$ ; a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.
- To determine the crystallography planes we take a unit cell with three axes coordinate system.

## •General Principles:

- i. If a Miller index is zero, the plane is parallel to that axis.
- ii. The smaller a Miller index, the more nearly parallel the plane is to the axis.
- iii. The larger a Miller index, the more nearly perpendicular a plane is to that axis.
- iv. Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane
- v. When the integers used in the Miller indices contain more than one digit, the indices must be separated by commas. E.g.: (3,10,13)
- vi. By changing the signs of all the indices of a plane, we obtain a plane located at the same distance on the other side of the origin.

- The steps to determine Miller indices of a set of parallel planes are as follows :
- (i) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes ( $x, y, z$ ).



<b>x</b>	<b>y</b>	<b>z</b>
2a	3b	c
pa	qb	rc

$$P=2, q=3 \text{ and } r=1$$

(ii) Express the intercepts as multiple of the unit cell dimensions, or lattice parameters along the axes.

$$\frac{2a}{a} \quad \frac{3b}{b} \quad \frac{c}{c}$$

i.e.      2      3      1

(iii) Determine the reciprocals of these numbers:

$$1/2 \quad 1/3 \quad 1/1$$

(iv) Reduce these reciprocals to the smallest set of integral numbers and enclose them in brackets:

$$\begin{matrix} 6 \times 1/2 & 6 \times 1/3 & 6 \times 1 \\ (3 & 2 & 6) \end{matrix}$$

In general it is denoted by (h k l).

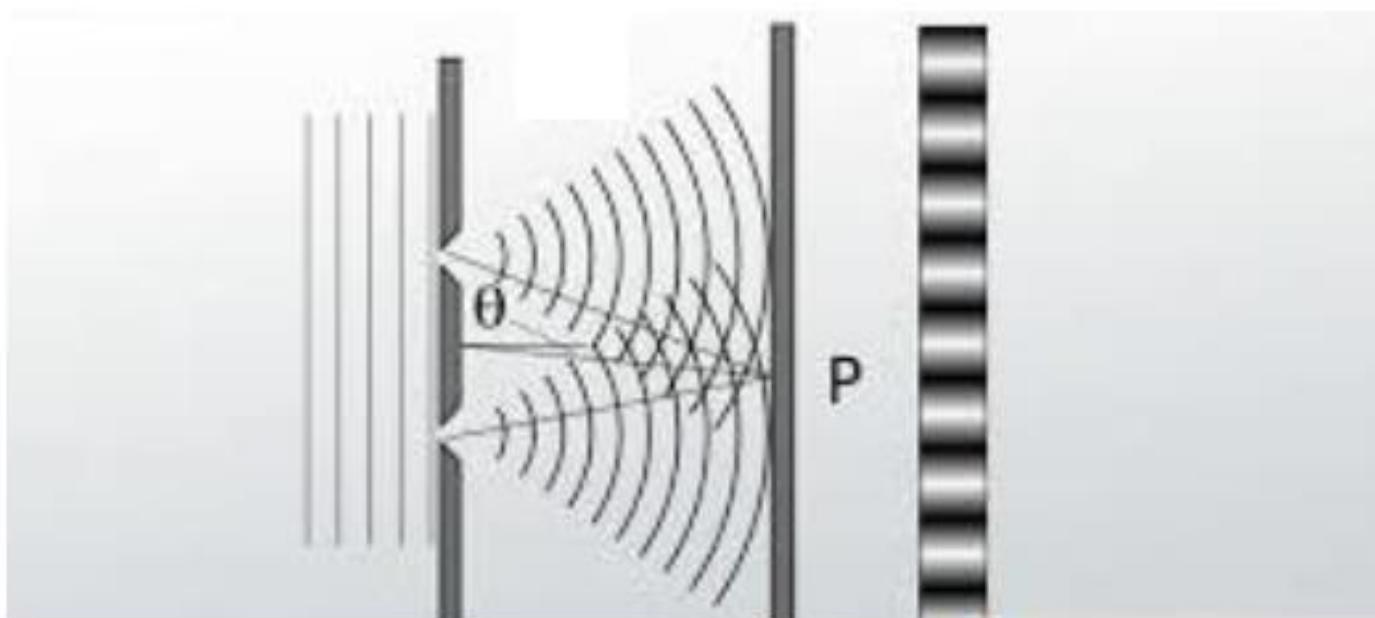
Or  $1/p : 1/q : 1/r = h : k : l$

$$1/2 : 1/3 : 1/1 = 3 : 2 : 6$$

Thus, Miller indices may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest number.

# X- Ray Diffraction

Diffraction



## INTRODUCTION:

X-rays were discovered by Wilhelm Roentgen who called them x-rays because the nature at first was unknown so, x-rays

are also called Roentgen rays. X-ray diffraction in crystals was discovered by Max von Laue. The wavelength range is  $10^{-7}$  to about  $10^{-15}$  m.



Max Von  
Laue

The penetrating power of x-rays depends on energy also, there are two types of x-rays.

- i) **Hard x-rays:** which have high frequency and have more energy.
- ii) **soft x-rays:** which have less penetrating and have low energy

X-Rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen and were called “X-Rays” because their nature was unknown at the time. He was awarded the Physics Nobel Prize in 1901.



Wilhelm Conrad  
Röntgen  
(1845-1923)





## The Nobel Prize in Physics 1915

For their services in the analysis of crystal structure by means of X-rays.



Sir William Henry Bragg

1/2 of the prize

United Kingdom

London University  
London, United Kingdom

b. 1862  
d. 1942



William Lawrence Bragg

1/2 of the prize

United Kingdom

Victoria University  
Manchester, United Kingdom  
b. 1890  
(in Adelaide, Australia)  
d. 1971

# Bragg's Law

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

**The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond.**

Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

# X-RAYS

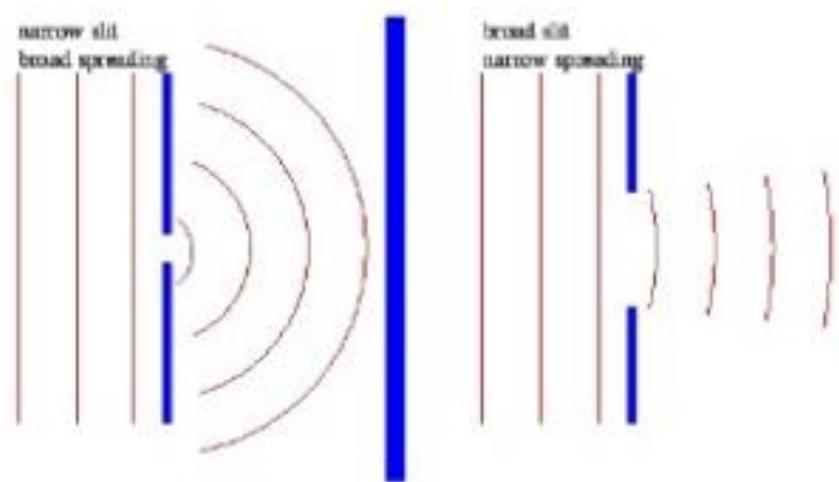
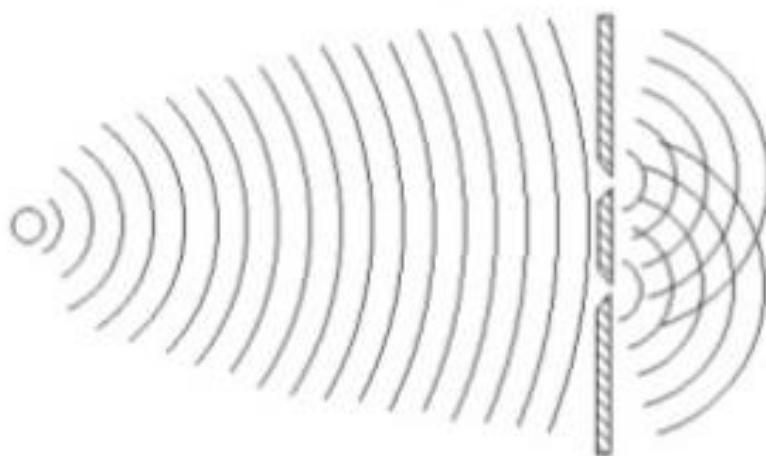
- 1.X-rays are short wave length electromagnetic radiations produced by the deceleration of high energy electrons or by electronic transitions of electrons in the inner orbital of atoms
- 2.X-ray region 0.1to100 Å°
- 3.Analytical purpose 0.7 to 2 Å°

Wavelength = 0.01 to 10 nm

Energy= 100eV to 100 keV

# Diffraction

The process by which a beam of light or other system of waves is spread out as a result of passing through a narrow aperture or across an edge, typically accompanied by interference between the wave forms produced.



# X Ray Diffraction

A technique used to determine the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions.

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction.

A stream of X-rays directed at a crystal diffract and scatter as they encounter atoms. The scattered rays interfere with each other and produce spots of different intensities that can be recorded on film.

# Bragg's Law

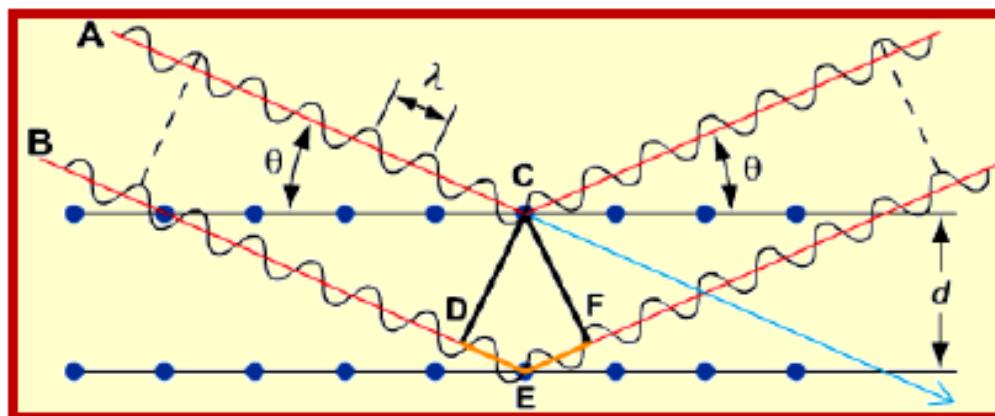
- See Figure. The length DE is the same as EF, so the total distance traveled by the bottom wave is expressed by:
- Constructive interference of the radiation from successive planes occurs when the path difference is an integral number of wavelengths. Note that line  $CE = d$  = distance between the 2 layers

$$EF = d \sin \theta$$

$$DE = d \sin \theta$$

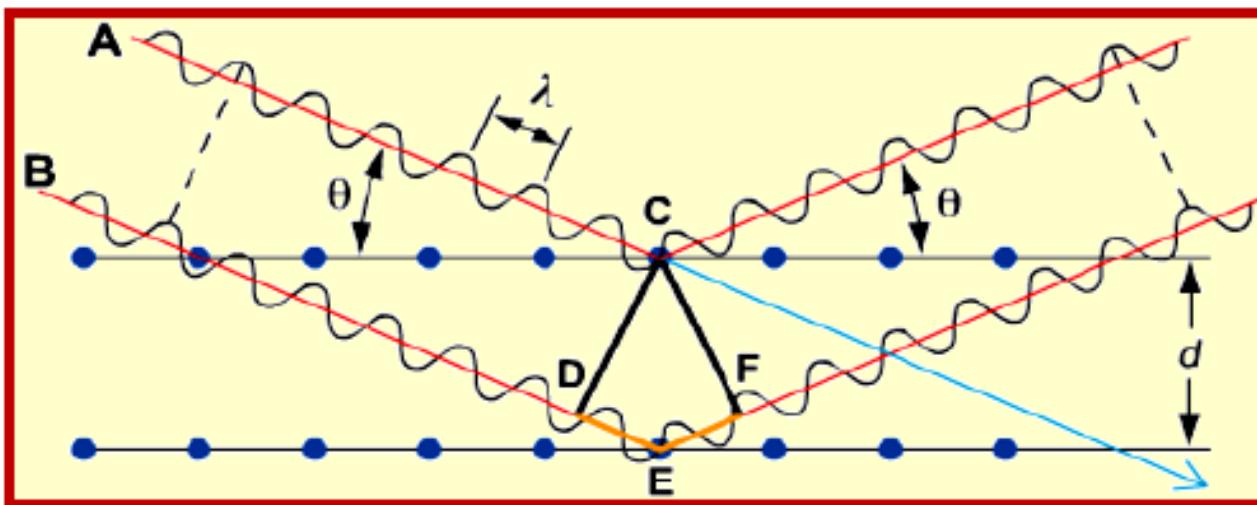
$$DE + EF = 2d \sin \theta$$

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



This is called the  
**Bragg Law**

- Consider crystals as made up of parallel planes of atoms. Incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane reflecting only a very small fraction of the radiation, like a lightly silvered mirror.
- In mirrorlike reflection, the angle of incidence is equal to the angle of reflection.



**Incident Angle  $\equiv \theta$**   
**Reflected angle  $\equiv \theta$**   
**X-ray**  
**Wavelength  $\equiv \lambda$**   
**Total Diffracted Angle  $\equiv 2\theta$**

## Bragg Law (Bragg Equation)

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

d = Spacing of the Planes, n = Order of Diffraction.

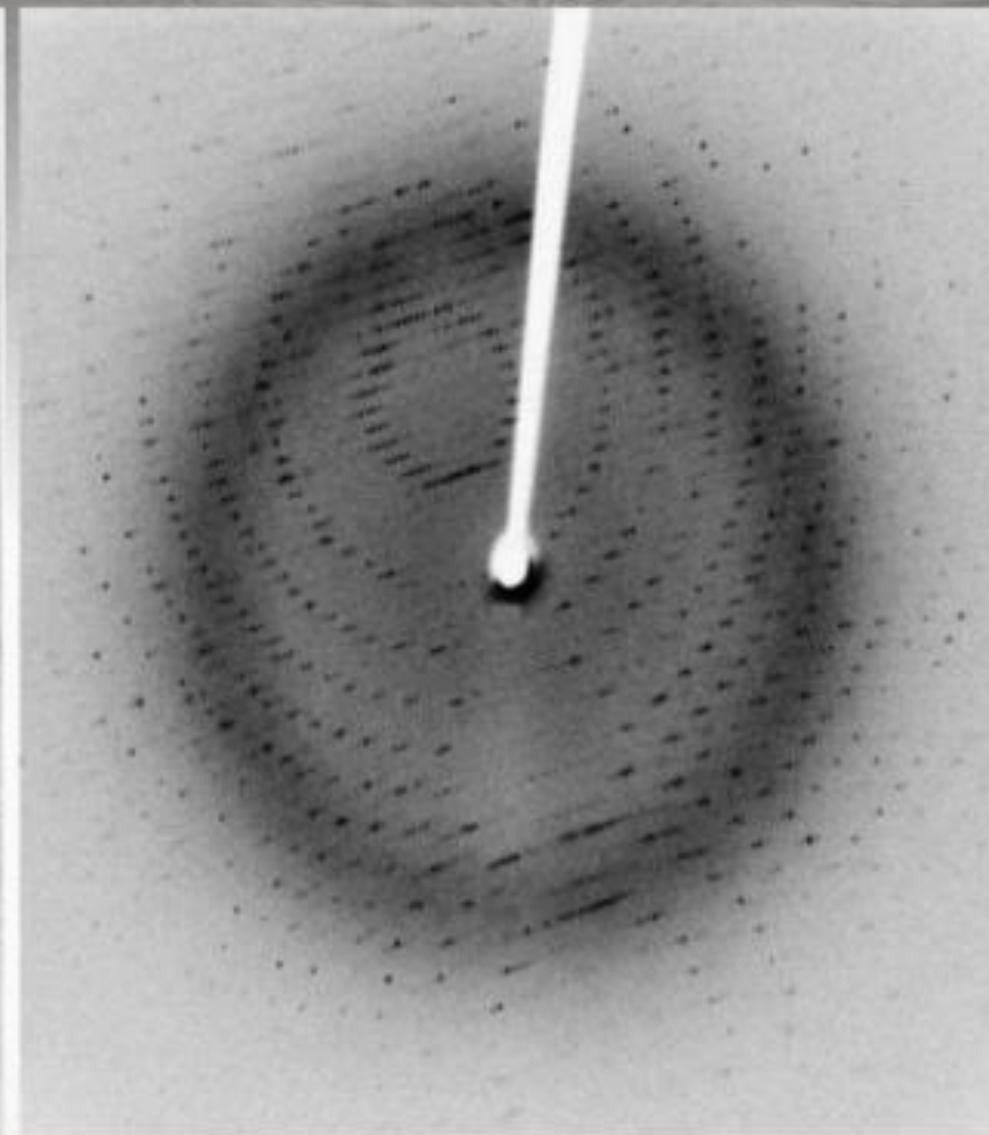
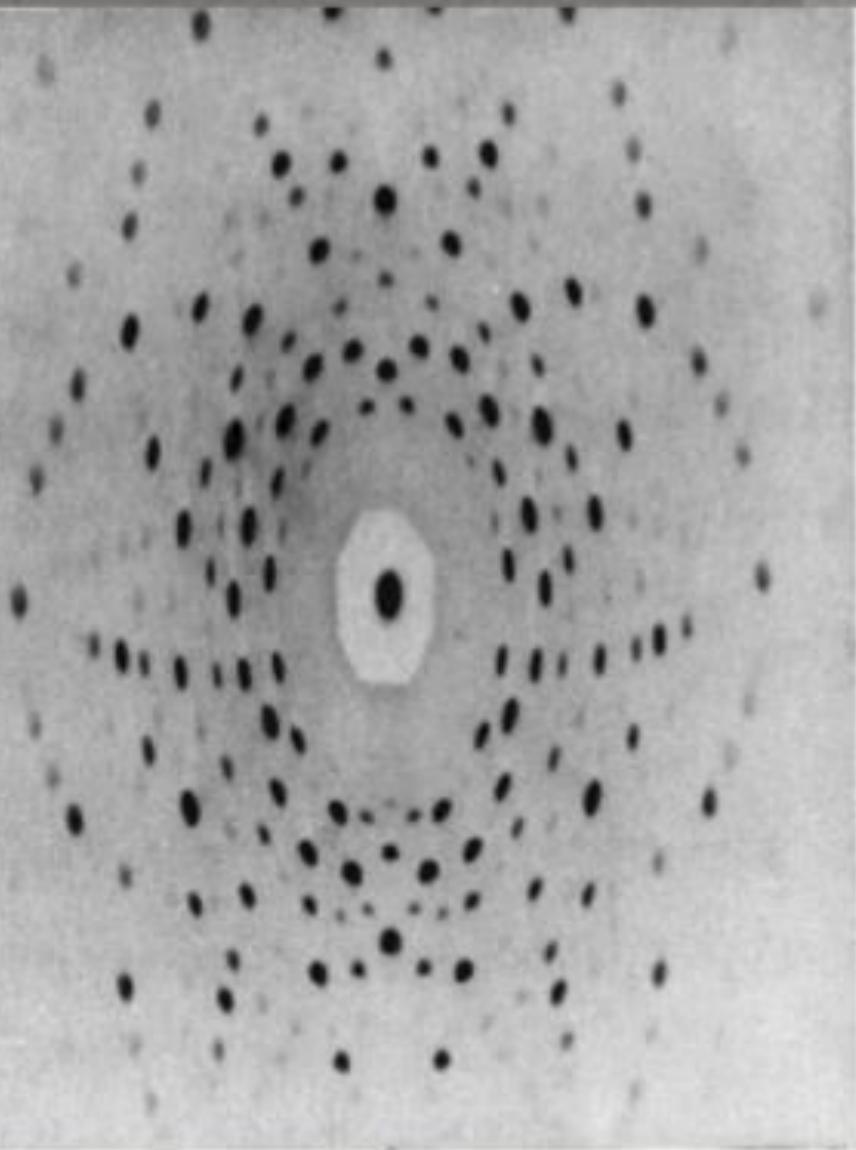
- Because  $\sin \theta \leq 1$ ,

*Bragg reflection can only occur for wavelengths satisfying:*  $n\lambda \leq 2d$

- This is why visible light can't be used. No diffraction occurs when this condition is not satisfied.
- The diffracted beams (reflections) from any set of lattice planes can only occur at particular angles predicted by **Bragg's Law**.

# FUNDAMENTAL PRINCIPLES OF X-RAY POWDER DIFFRACTION (XRD)

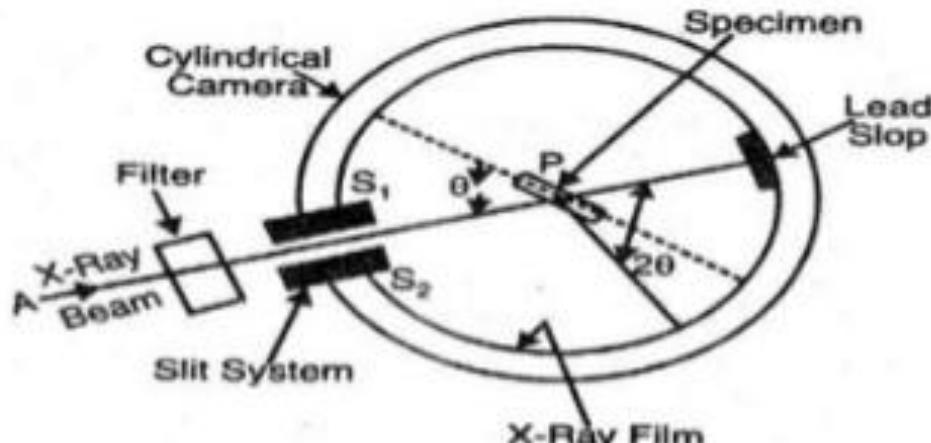
- X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample.
- These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.
- For every set of crystal planes , ***one or more crystals*** will be in the ***correct orientation*** to give the correct Bragg angle to satisfy **Bragg's equation**.
- Each diffraction line is made up of a large number of small spots, each from a separate crystal.
- Each spot is so small as to give the appearance of a continuous line.
- Every crystal plane is thus capable of diffraction.



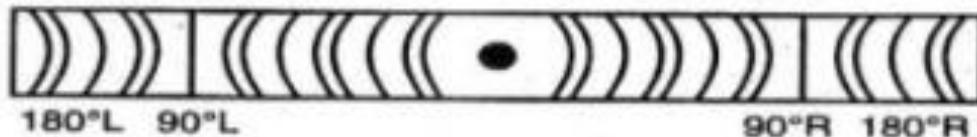
X-ray diffraction pattern



# X-RAY POWDER DIFFRACTION (XRD) INSTRUMENTATION - HOW DOES IT WORK?



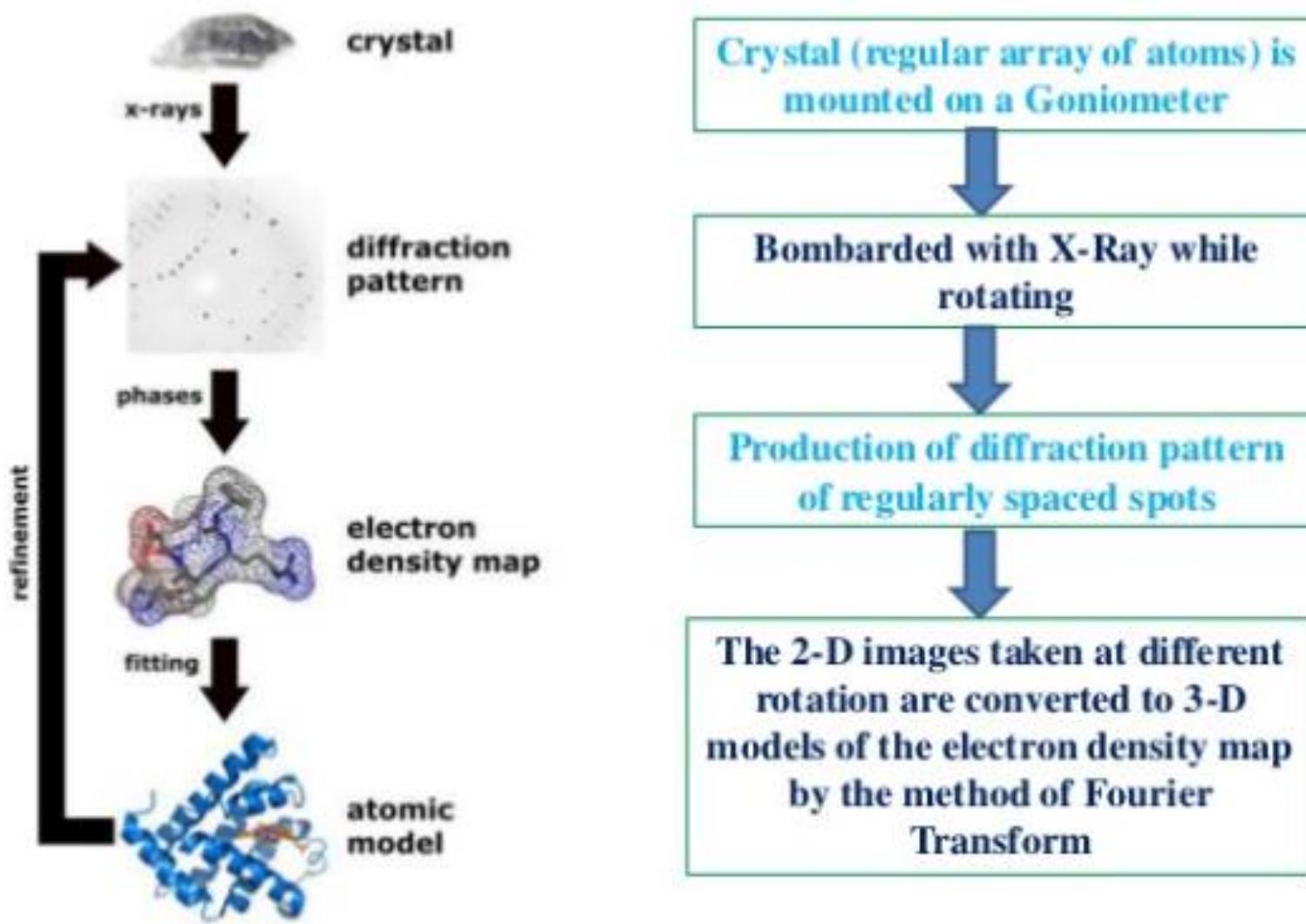
Powder crystal method.



Arrangement of line in a powder photograph.

Figure 1.

# How Does It Work



- The experimental arrangement of powder crystal method is shown in fig.1. its main feature are outlined as below:
  - A is a source of X-rays which can be made monochromatic by a filter
  - Allow the X-ray beam to fall on the powdered specimen P through the slits S1 and S2. The function of these slits is to get a narrow pencil of X-rays.
  - Fine powder, P, struck on a hair by means of gum is suspended vertically in the axis of a cylindrical camera. This enables sharp lines to be obtained on the photographic film which is surrounding the powder crystal in the form of a circular arc.

- The X-rays after falling on the powder passes out of the camera through a cut in the film so as to minimize the fogging produced by the scattering of the direct beam.
- As the sample and detector are rotated, the intensity of the reflected X-rays is recorded.
- When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs.
- A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

# APPLICATIONS

- Identification : The most common use of powder (polycrystalline) diffraction is chemical analysis.
  - This can include phase identification (search/match)
- X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).
- Other applications include :
  - identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically.

- determination of unit cell dimensions.
- measurement of sample purity .
- Most useful for cubic crystal.
- Used for determining the complex structure of metals and alloys.
- Useful to make distinction between the allotropic modifications of the same substance.

# **STRENGTHS AND LIMITATIONS OF X-RAY POWDER DIFFRACTION (XRD)?**

## **□ Strengths :-**

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral.
- In most cases, it provides a clear structural determination.
- XRD units are widely available.
- Data interpretation is relatively straight forward .

## ■ Limitations:-

- Homogeneous and single phase material is best for identification of an unknown.
- Requires tenths of a gram of material which must be ground into a powder.
- For mixed materials, detection limit is ~ 2% of sample.
- Peak overlay may occur and worsens for high angle 'reflections'.
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated .

# What Information Do We Get or Can We Get From Powder X-ray Diffraction

- \* Lattice parameters
- \* Phase identity
- \* Phase purity
- \* Crystallinity
- \* Crystal structure
- \* Percent phase composition

# Summary

**X-rays are electromagnetic radiation of wavelength about 1 Å ( $10^{-10}$  m), which is about the same size as an atom.**

The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science.

We can determine the size and the shape of the unit cell for any compound most easily using X-ray diffraction.

# Laue Method

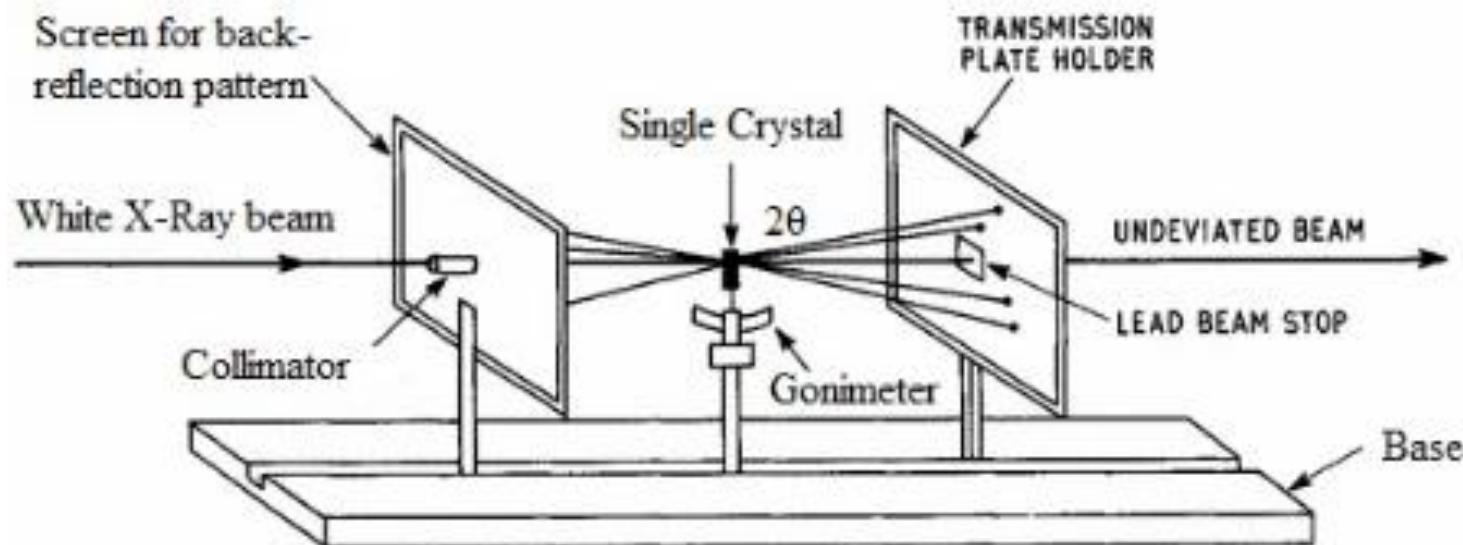
The Laue method is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal.

The diffracted beams form arrays of spots, that lie on curves on the film. The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of  $d$  and  $\theta$  involved. Each curve therefore corresponds to a different wavelength. The spots lying on any one curve are reflections from planes belonging to one zone. Laue reflections from planes of the same zone all lie on the surface of an imaginary cone whose axis is the zone axis.

# Experimental Arrangement

It consists of

- (i) A continuous X- rays beam, well collimated by a pin hole
- (ii) A single crystal held stationary at proper orientation relative to incident X ray beam
- (iii)A flat film to receive the transmitted (or reflected) diffraction beam.



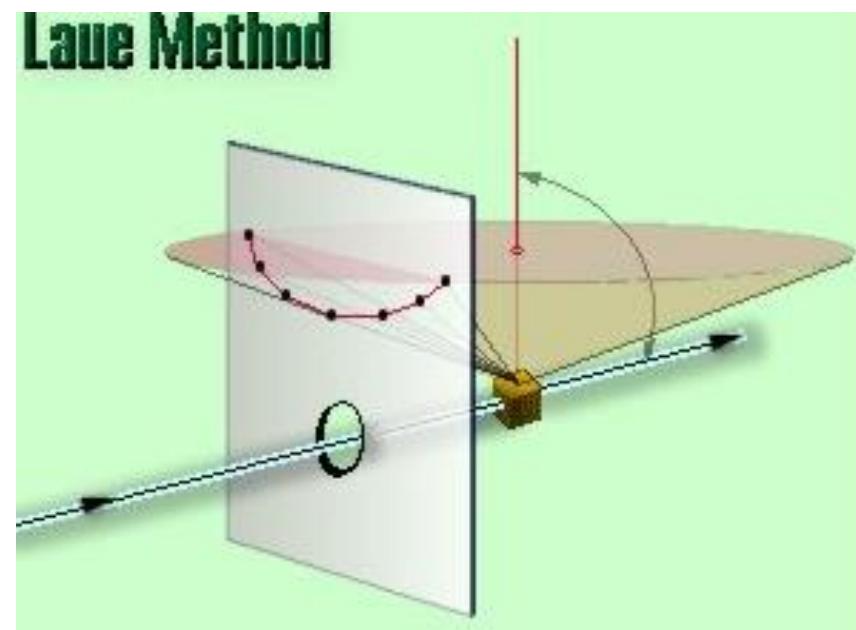
# Working Principle

When X ray beam falls on the crystal, the beam is diffracted. The transmitted beam forms a series of spots on the film called Laue spots which are characteristics of crystal structure.

## Back-reflection Laue

In the back-reflection method, the film is placed between the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

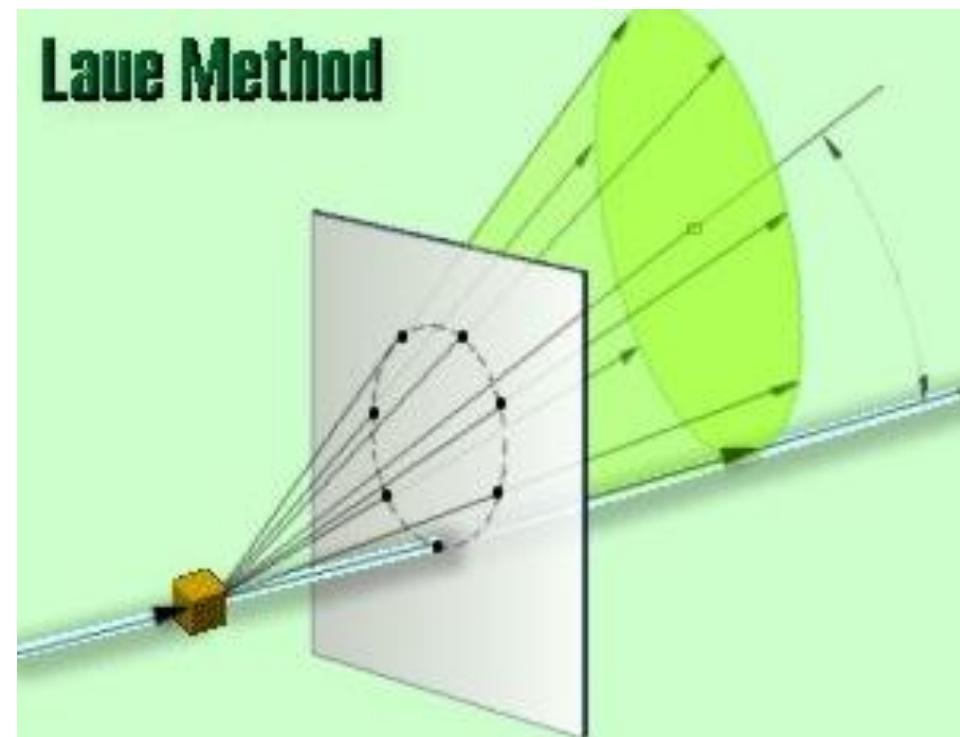
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



## Transmission Laue

In the transmission Laue method, the film is placed behind the crystal to record beams which are transmitted through the crystal.

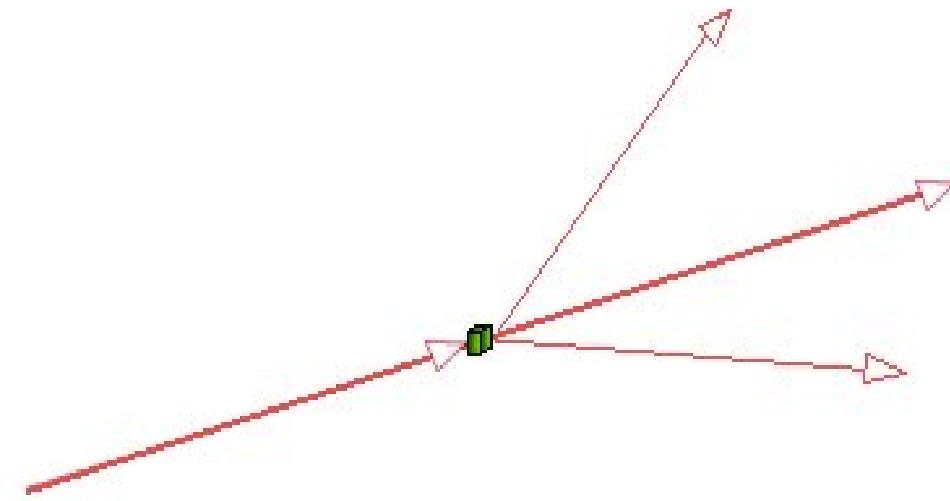
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.



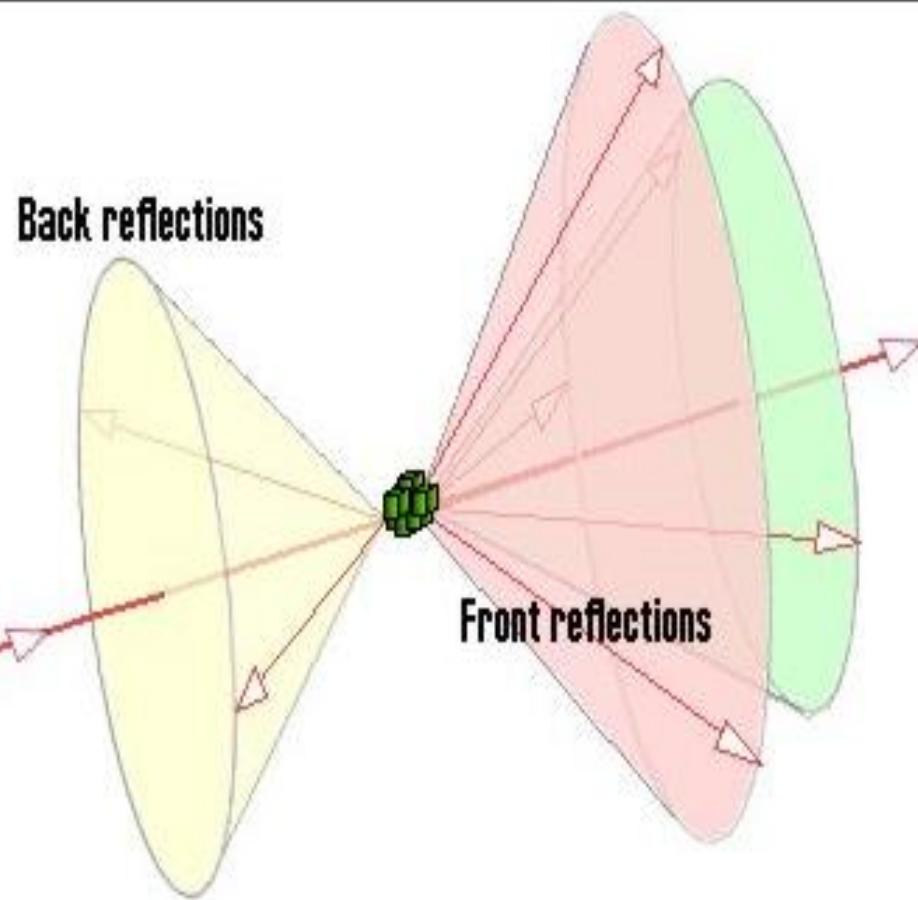
# The Powder Method (Debye and Scherrer Method)

The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors  $a$ ,  $b$  and  $c$  which define the unit cell for the crystal.

If a monochromatic x-ray beam is directed at a single crystal, then only one or two diffracted beams may result.

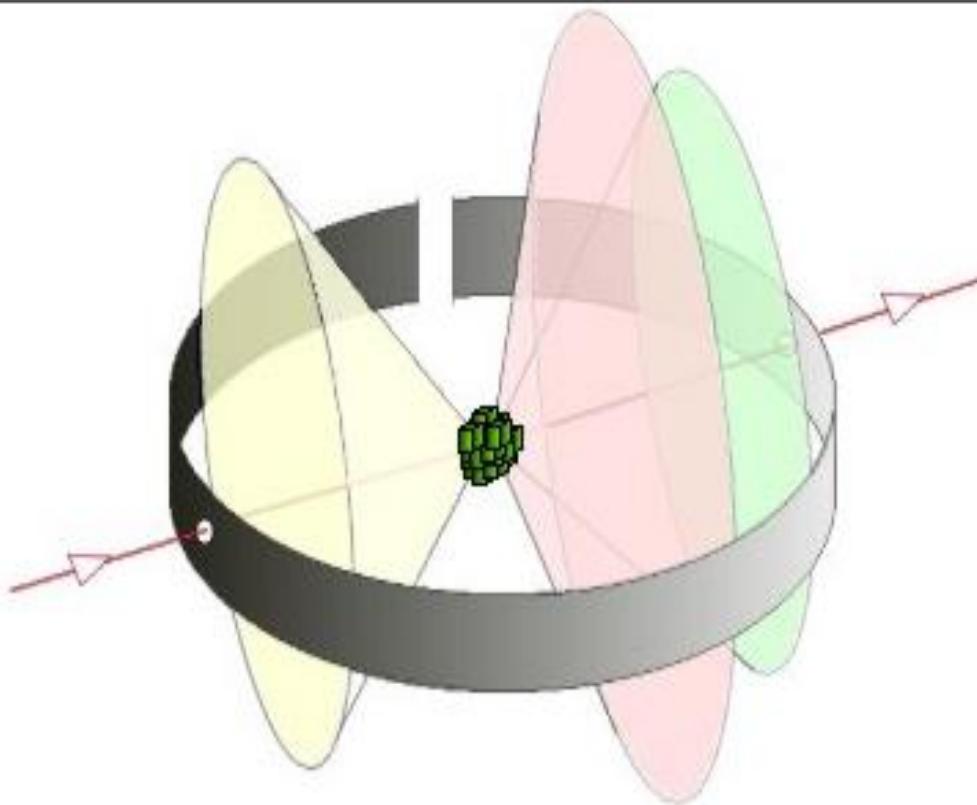


If the sample consists of some tens of randomly orientated single crystals, the diffracted beams are seen to lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards.

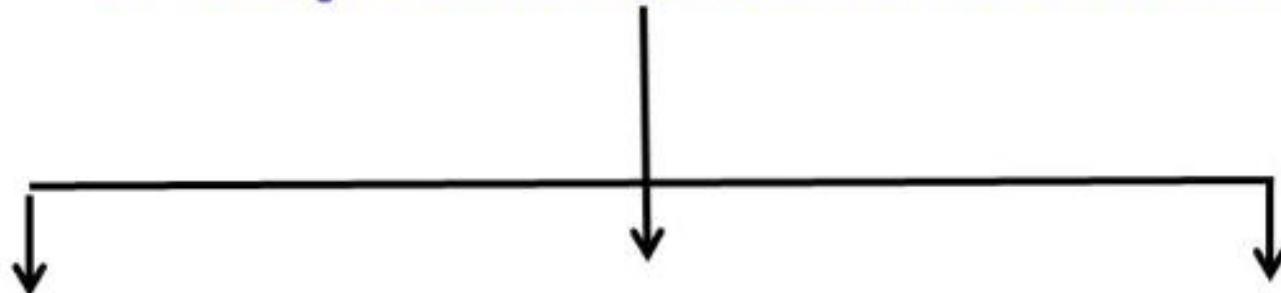


A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones.

A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.



# X-Ray Diffraction Methods



## Von Laue

Orientation  
Single Crystal  
Polychromatic  
Beam, Fixed Angle single  $\theta$

## Rotating Crystal

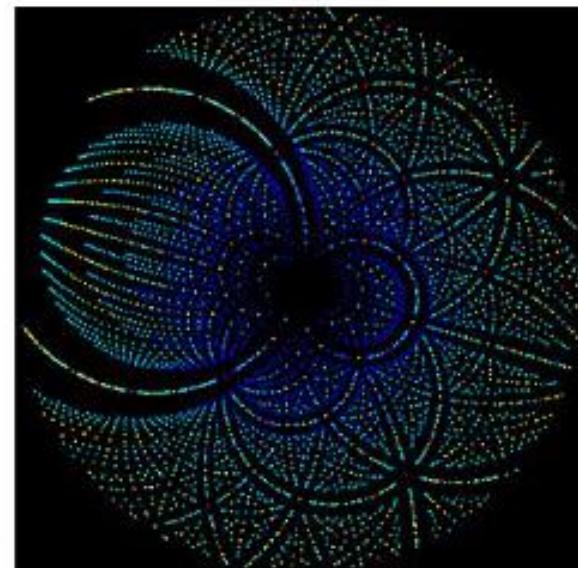
Lattice constant  
Single Crystal  
Monochromatic  
Beam, Variable Angle  $\theta$   
Varied by rotation

## Powder

Lattice Parameters  
Poly Crystal  
Monochromatic Beam, Variable Angle Many  $\theta$ s (orientations)

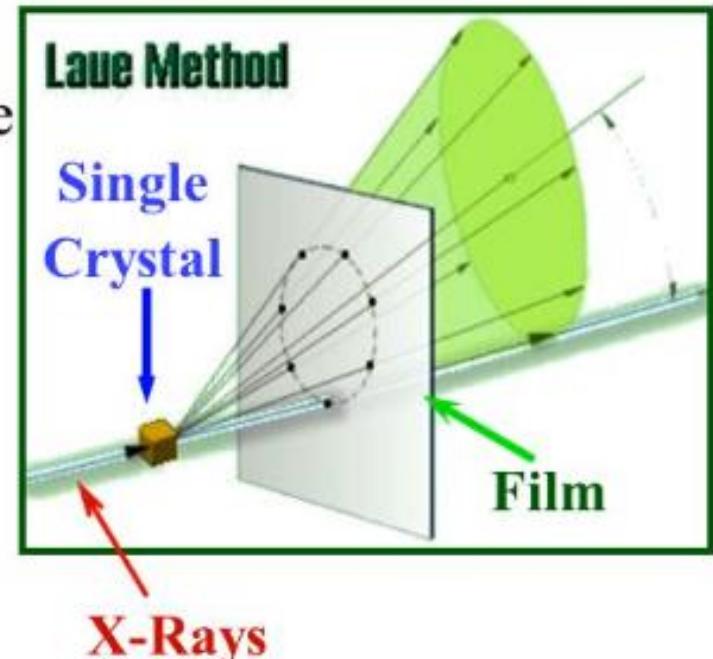
# Laue Method

- The Laue method is mainly used **to determine the orientation of large single crystals** while radiation is reflected from, or transmitted through a **fixed crystal**.
- The diffracted beams form arrays of spots, that lie on curves on the film.
- **The Bragg angle is fixed** for every set of planes in the crystal. Each set of planes picks out & diffracts the particular wavelength from the white radiation that **satisfies the Bragg law for the values of  $d$  &  $\theta$**  involved.



# Transmission Laue Method

- In the transmission Laue method, *the film is placed behind the crystal to record beams* which are transmitted through the crystal.
- In the transmission Laue method, *the film is placed behind the crystal to record beams* which are transmitted through the crystal.
- One side of the cone of Laue reflections is defined by the transmitted beam.
- The film intersects the cone, with the diffraction spots generally lying on an ellipse.

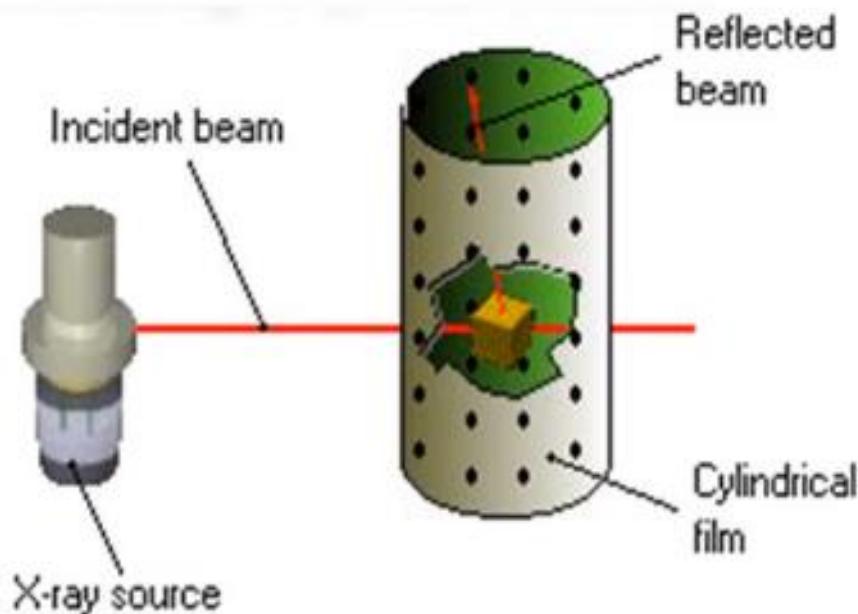


# Crystal Structure Determination by Laue Method

- The Laue method is mainly used to determine the **crystal orientation.**
- Although the Laue method can also be used to determine the crystal structure, **several wavelengths can reflect in different orders from the same set of planes**, with the different order reflections superimposed on the same spot in the film. This makes crystal structure determination by spot intensity **difficult.**
- The rotating crystal method overcomes this problem.

# Rotating Crystal Method

- In the rotating crystal method, a single crystal is mounted with an axis normal to a **monochromatic x-ray beam**. A cylindrical film is placed around it & the **crystal is rotated about the chosen axis**.



- As the crystal rotates, Sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, & at that point a diffracted beam will be formed.

# Rotating Crystal Method

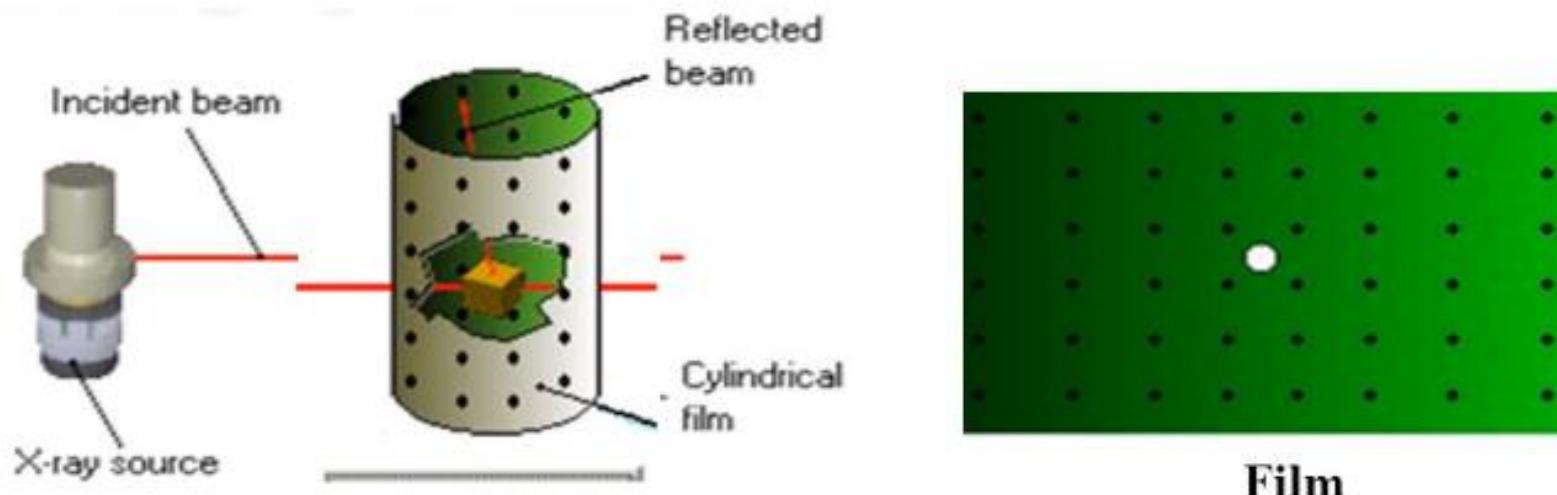
The **Lattice constant** of the crystal can be determined with this method. For a given wavelength  $\lambda$  if the angle  $\theta$  at which a reflection occurs is known,  $d$  can be determined by using **Bragg's Law**.

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

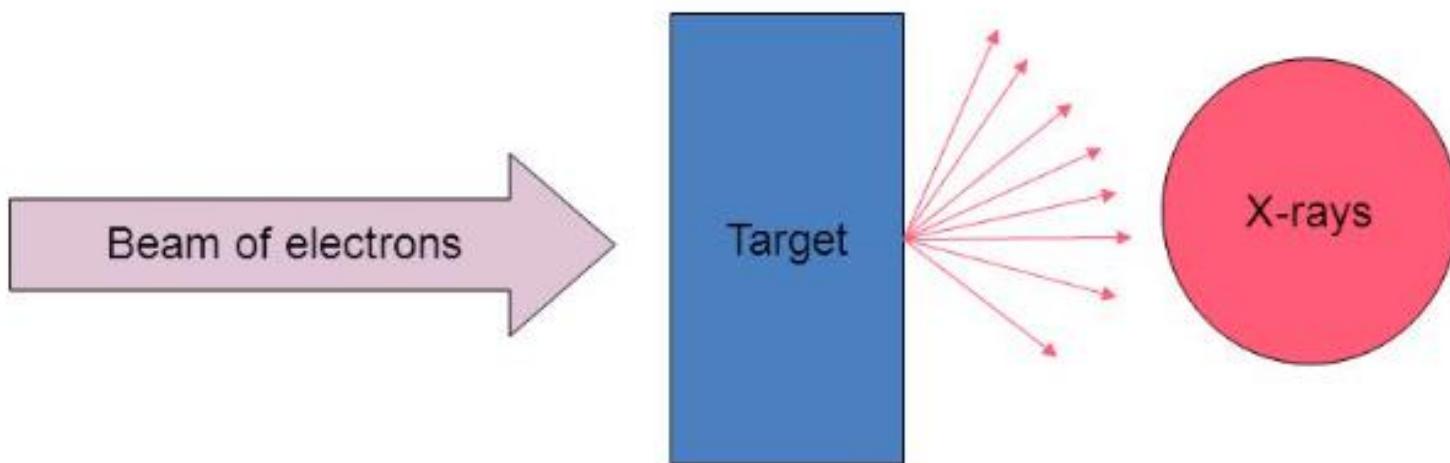
$$2d \sin \theta = n\lambda$$

# Rotating Crystal Method

The reflected beams are located on the surfaces of imaginary cones. By recording the diffraction patterns (both angles & intensities) for various crystal orientations, one can determine the **shape & size of unit cell** as well as the **arrangement of atoms** inside the cell.



- 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  $\sim 2\text{-}3 \text{ \AA}$  so the suitable radiation is X-rays
- Hence, X-rays can be used for the study of crystal structures



An accelerating (/decelerating) charge radiates electromagnetic radiation

# Powder Method

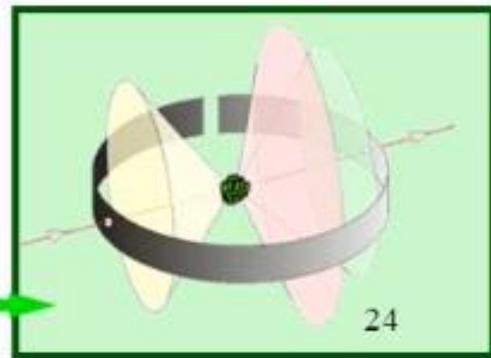
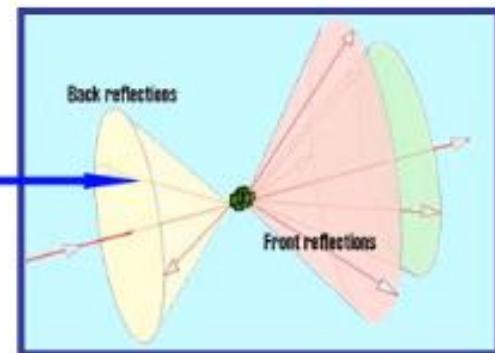
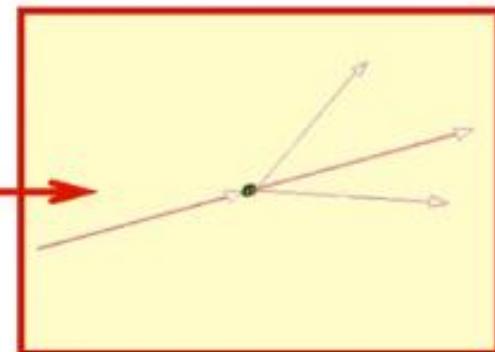
- If a **powdered crystal** is used **instead of a single crystal**, then there is ***no need to rotate*** it, because there will always be some small crystals at an orientation for which diffraction is permitted.  
Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.
- Useful for samples that are difficult to obtain in single crystal form.
- The powder method is used to determine the **lattice parameters** accurately. Lattice parameters are the magnitudes of the primitive vectors **a, b and c** which define the unit cell for the crystal.,,

# The Powder Method

- For every set of crystal planes, by chance, *one or more crystals* will be in the *correct orientation* to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction.
- Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

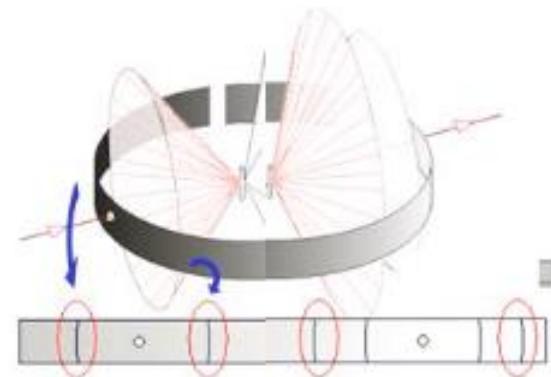
# The Powder Method

- If a monochromatic X-ray beam is directed at a single crystal, then only one or two diffracted beams may result. **See figure**
- For a sample of several randomly orientated single crystals, the diffracted beams will lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards. **See figure**
- For a sample of hundreds of crystals (powdered sample), the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film. **See figure**



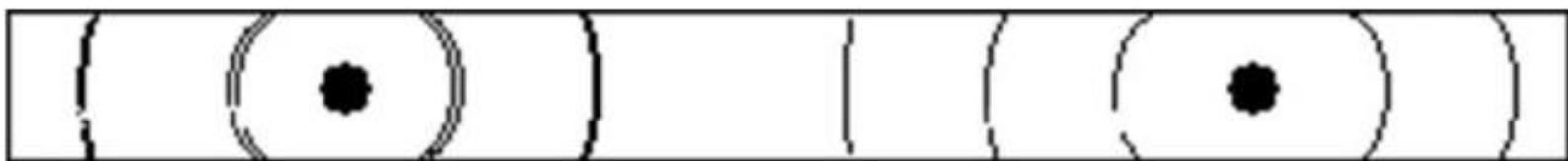
# Debye Scherrer Camera

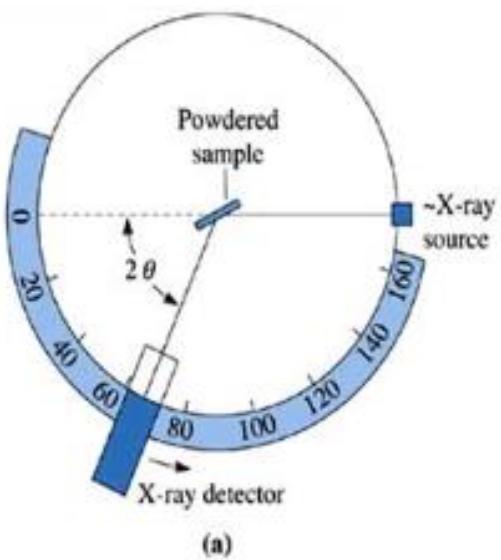
- A small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract **X-Rays**.
- The sample is placed in the **Debye Scherrer** camera and is accurately aligned to be in the center of the camera. **X-Rays** enter the camera through a collimator.
- The powder diffracts the **X-Rays** in accordance with Braggs Law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.



# Powder Diffraction Method

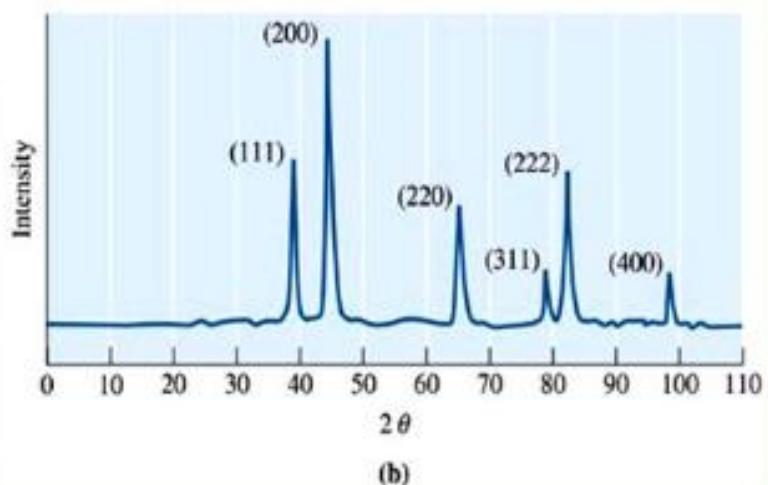
- When the film is removed from the camera, flattened & processed, it shows the diffraction lines & the holes for the incident & transmitted beams.





**(a) Diagram of a diffractometer**

showing a powdered sample, incident & diffracted beams.



**(b) Diffraction Pattern**  
from a sample of gold powder.