# X-Ray Diffraction

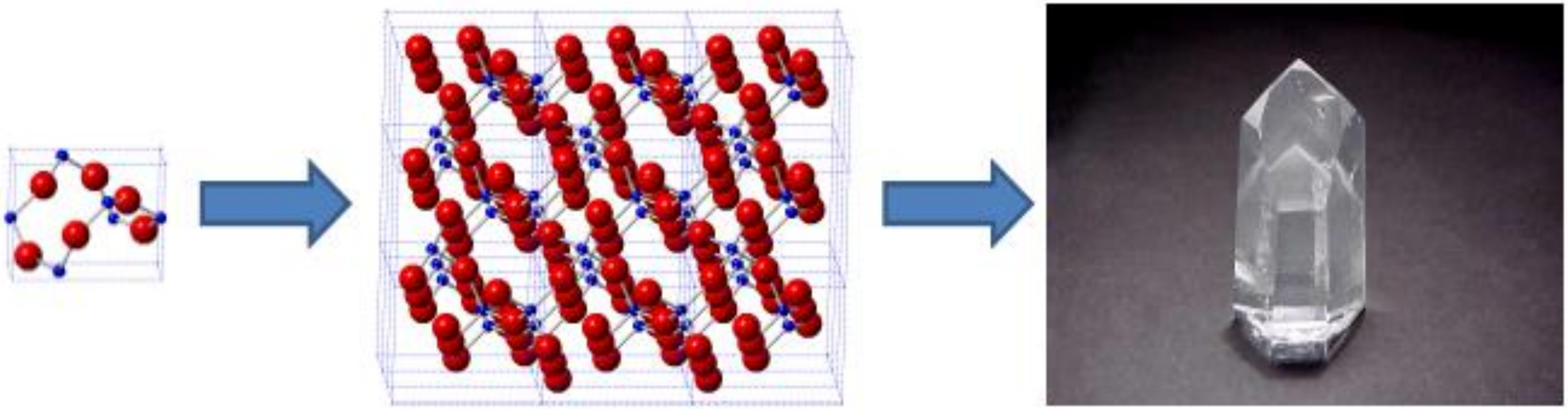
Nazia Tarannum

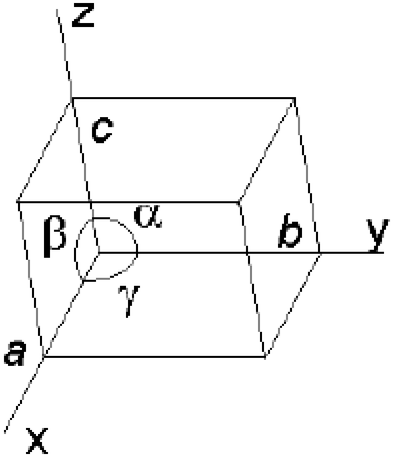
# Crystalline materials are characterized by the long-range orderly periodic arrangements of atoms.

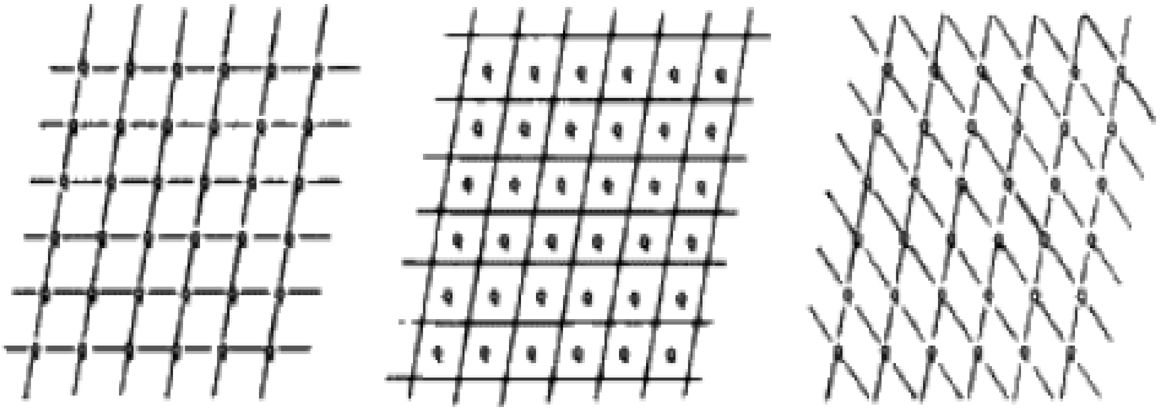
- The unit cell is the basic repeating unit that defines the crystal structure.
  - The unit cell contains the maximum symmetry that uniquely defines the crystal structure.
  - The unit cell might contain more than one molecule:
    - for example, the quartz unit cell contains 3 complete molecules of $SiO_2$.

- The crystal system describes the shape of the unit cell
- The lattice parameters describe the size of the unit cell
- The unit cell repeats in all dimensions to fill space and produce the macroscopic grains or crystals of the material

Crystal System: hexagonal
Lattice Parameters:
4.9134 x 4.9134 x 5.4052 Å
(90 x 90 x 120°)




z
c
α
β
b
y
γ
a
x

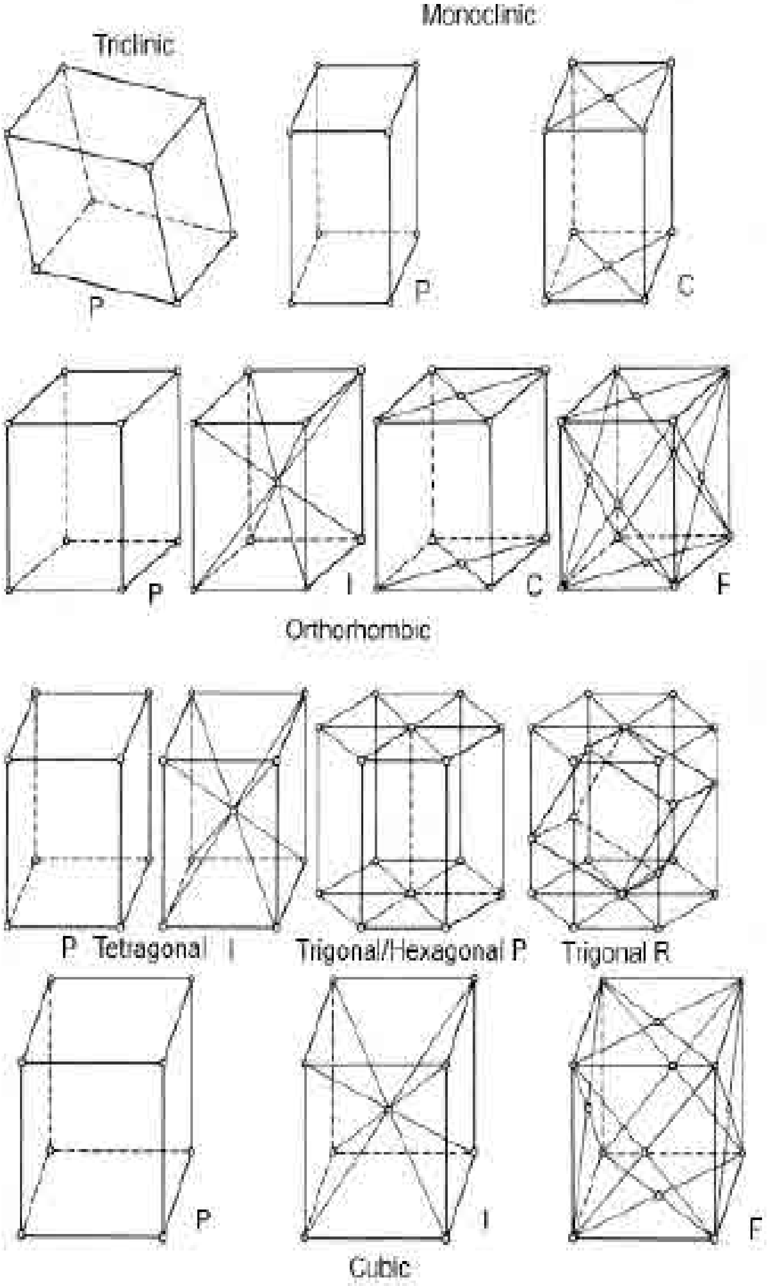


- Arrangement of asymmetric unit in a lattice defines the crystal symmetry.

- The allowed symmetries are 2-, 3, 4, 6-fold rotational, mirror(m), and inversion (i) symmetry (+/-) translation.

- Rotation + translation = screw

- Rotation + mirror = glide



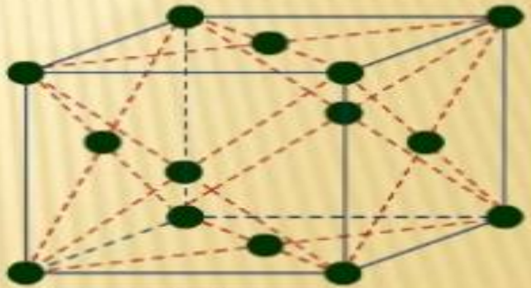
➔ 230 space groups, 32 point groups, 14 Bravais lattice, and 7 crystal systems

# FOURTEEN BRAVAIS LATTICES

| | | | P | I | F | E |
|---|---|---|---|---|---|---|
| 1 | Cubic | Cube | ✓ | ✓ | ✓ | |

Primitive or Simple

Body Centred



Face Centered

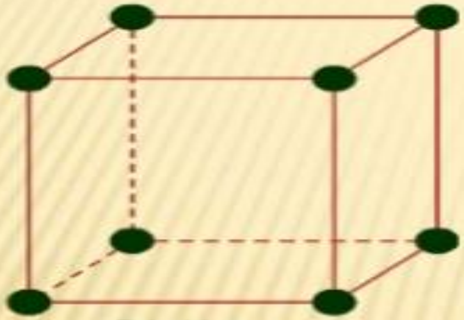
$\boxed{a=b=c}$ $\boxed{\alpha=\beta=\gamma=90^\circ}$

**Corresponding Examples**

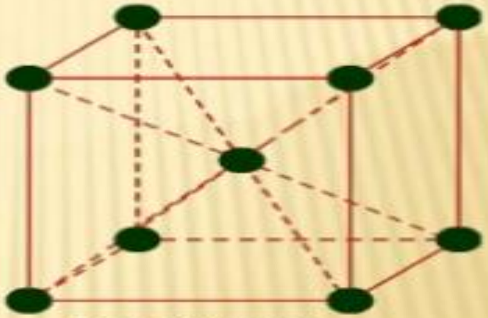
NaCl, Zinc Blende, Cu

---

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



Primitive



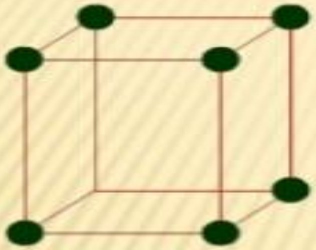
Body Centered

$\boxed{a=b\neq c}$

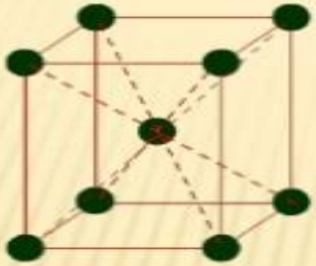
$\boxed{\alpha=\beta=\gamma=90^\circ}$

White tin, $SnO_2$, $TiO_2$, $CaSO_4$

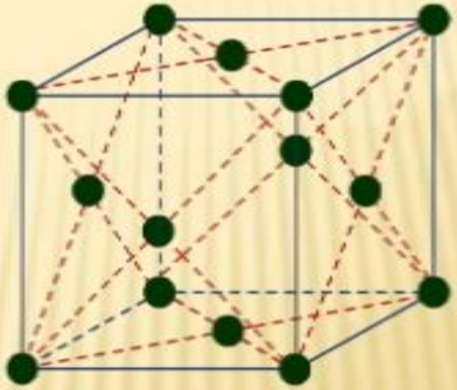
|  |  |  | P | I | F | E |
|---|---|---|---|---|---|---|
| 3 | Orthorhombic | Rectangular Prism (general height) | ✓ | ✓ | ✓ | ✓ |



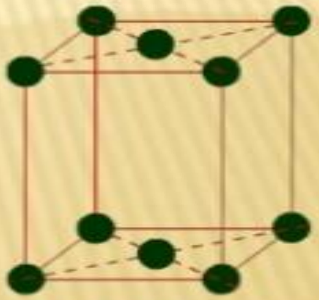
Primitive



Body Centered



Face Centered



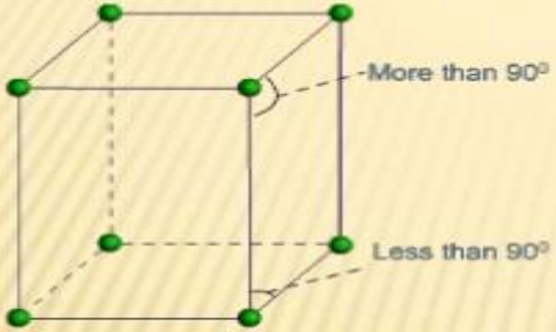
End Centered

$$\boxed{a \neq b \neq c}$$

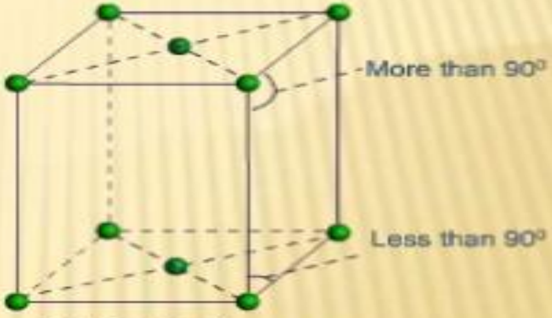
$$\boxed{\alpha = \beta = \gamma = 90^\circ}$$

Rhombic sulfur, $KNO_3$, $BaSO_4$

|  |  |  | P | I | F | E |
|---|---|---|---|---|---|---|
| 4 | Monoclinic | Parallogramic Prism | ✓ |  |  | ✓ |



Primitive



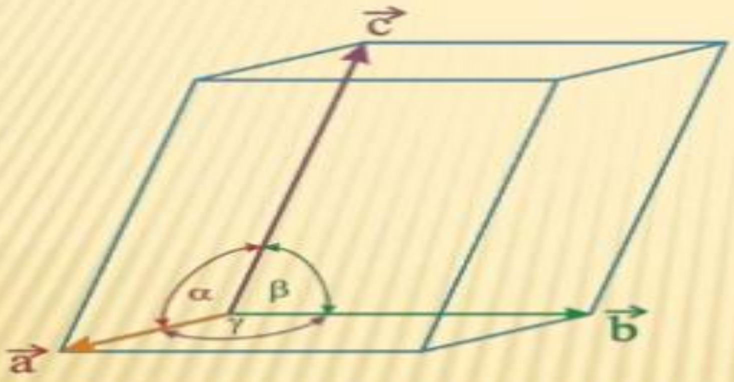
End Centered

$$\boxed{a \neq b \neq c}$$

$$\boxed{\alpha = \gamma = 90^\circ \neq \beta}$$

Monoclinic sulfur, $Na_2SO_4.10H_2O$

| | | | P | I | F | E |
|---|---|---|---|---|---|---|
| 5 | Triclinic | Parallelepiped (general) | ✓ | | | |



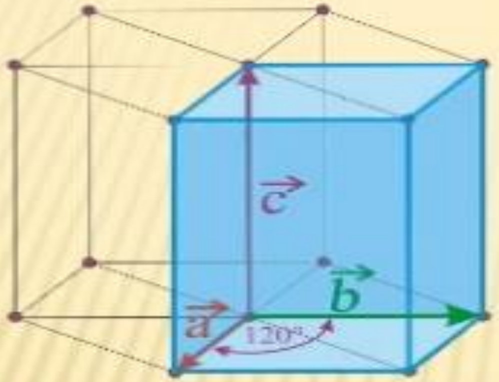
$$\boxed{a \neq b \neq c}$$

$$\boxed{\alpha \neq \beta \neq \gamma}$$

$K_2Cr_2O_7$, $CuSO_4.5H_2O$, $H_3BO_3$

---

| | | | P | I | F | E |
|---|---|---|---|---|---|---|
| 6 | Hexagonal | 120° Rhombic Prism | ✓ | | | |

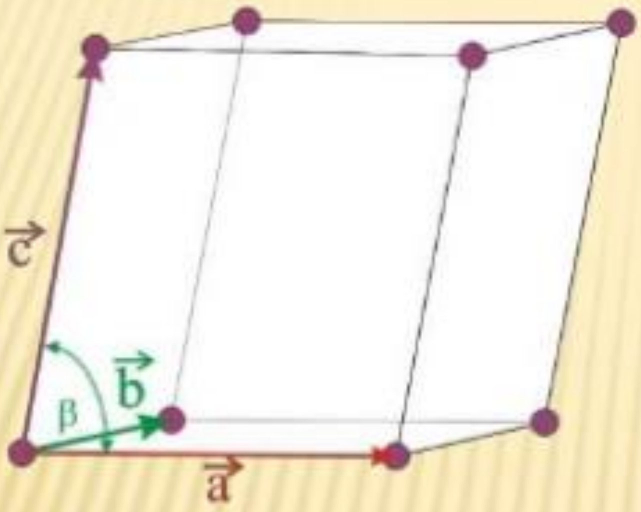


$$\boxed{a = b \neq c}$$

$$\boxed{\alpha = \beta = 90°, \gamma = 120°}$$

Graphite, ZnO, CdS

|  |  |  | P | I | F | E |
|---|---|---|---|---|---|---|
| 7 | Rhombohedral | Parallelepiped (Equilateral, Equiangular) | ✓ |  |  |  |



$$\boxed{a = b = c}$$

$$\boxed{\alpha = \beta = \gamma \neq 90^\circ}$$

Calcite ($CaCO_3$), Cinnabar ($HgS$)

# Crystal structures focus on symmetry elements to define the atomic arrangement

- Symmetry in crystal structures is a product of energy minimization in the atomic arrangement
- Symmetry in the crystal structure often produces symmetry in material properties and behavior

Quartz

Crystal System: hexagonal

Bravais Lattice: primitive

Space Group: $P3_221$

Lattice Parameters: 4.9134 x 4.9134 x 5.4052 Å
(90 x 90 x 120°)

Atom Positions:

|  | x | y | z |
|---|---|---|---|
| Si | 0.47 | 0 | 0.667 |
| O | 0.414 | 0.268 | 0.786 |

Primitive Bravais Lattice

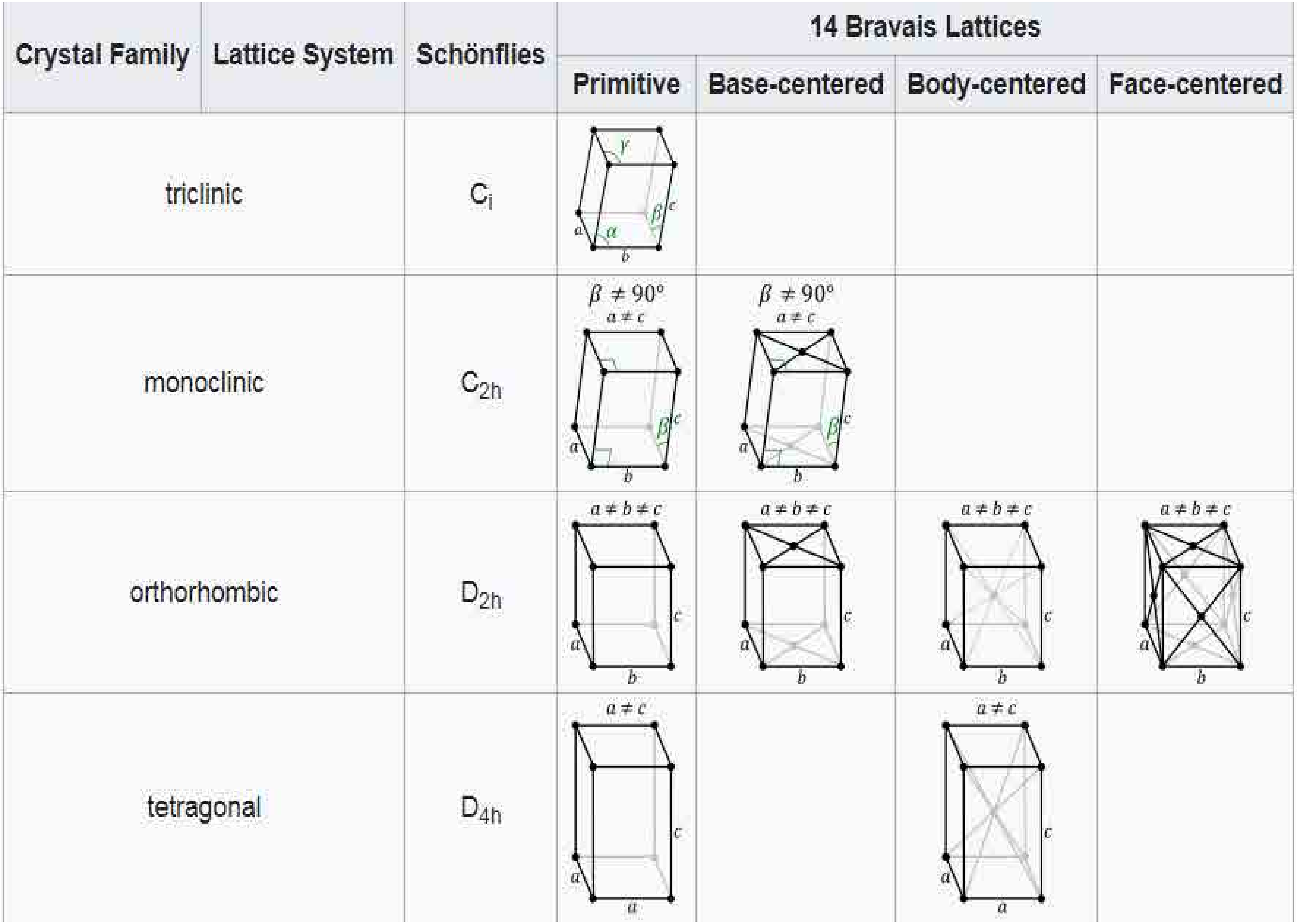
$3_2$ screw axis

2-fold rotational axis

# Symmetry elements are used to define seven different crystal systems

| Crystal System | Bravais Lattices | Symmetry | Axis System |
|---|---|---|---|
| Cubic | P, I, F | m3m | $a=b=c, \alpha=\beta=\gamma=90$ |
| Tetragonal | P, I | 4/mmm | $a=b\neq c, \alpha=\beta=\gamma=90$ |
| Hexagonal | P, R | 6/mmm | $a=b\neq c, \alpha=\beta=90\ \gamma=120$ |
| Rhombohedral* | R | 3m | $a=b=c, \alpha=\beta=\gamma\neq 90$ |
| Orthorhombic | P, C, I, F | mmm | $a\neq b\neq c, \alpha=\beta=\gamma=90$ |
| Monoclinic | P, C | 2/m | $a\neq b\neq c, \alpha=\gamma=90\ \beta\neq 90$ |
| Triclinic | P | 1 | $a\neq b\neq c, \alpha\neq\beta\neq\gamma\neq 90$ |

Quartz
Crystal System: hexagonal
Bravais Lattice: primitive
Space Group: $P322_1$
Lattice Parameters: 4.9134 x 4.9134 x 5.4052 Å
(90 x 90 x 120°)

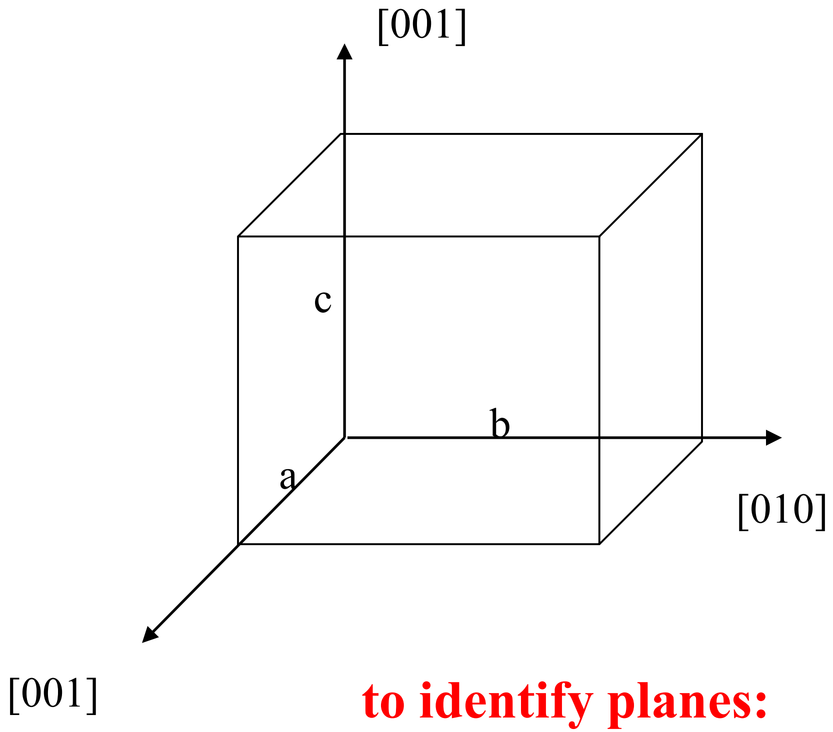


| Crystal Family | Lattice System | Schönflies | 14 Bravais Lattices | | | |
|---|---|---|---|---|---|---|
| | | | Primitive | Base-centered | Body-centered | Face-centered |
| triclinic | | $C_i$ | | | | |
| monoclinic | | $C_{2h}$ | $\beta \neq 90^\circ$<br>$a \neq c$ | $\beta \neq 90^\circ$<br>$a \neq c$ | | |
| orthorhombic | | $D_{2h}$ | $a \neq b \neq c$ | $a \neq b \neq c$ | $a \neq b \neq c$ | $a \neq b \neq c$ |
| tetragonal | | $D_{4h}$ | $a \neq c$ | | $a \neq c$ | |

# Miller Indices

describe which plane of atom is interacting with the x-rays

# How to Identify Miller indices (hkl)?

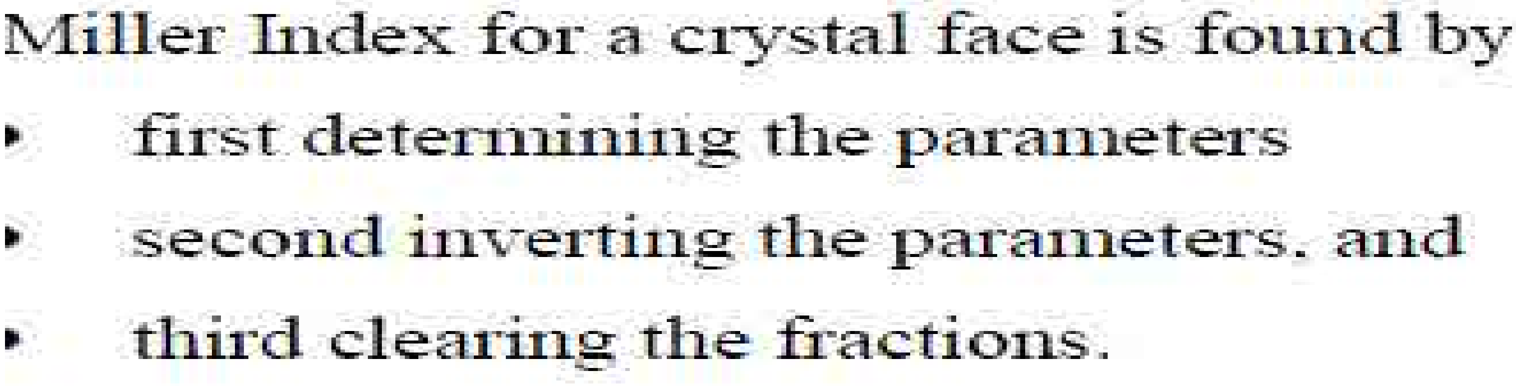


**direction: [hkl]**
**family of directions: <hkl>**
**planes: (hkl)**
**family of planes: {hkl}**

**to identify planes:**

**Step 1 : Identify the intercepts on the x- , y- and z- axes.**
**Step 2 : Specify the intercepts in fractional coordinates**
**Step 3 : Take the reciprocals of the fractional intercepts**

# Calculation of Miller Indices



Miller Index for a crystal face is found by

- first determining the parameters
- second inverting the parameters. and
- third clearing the fractions.

# Miller indices (hkl)

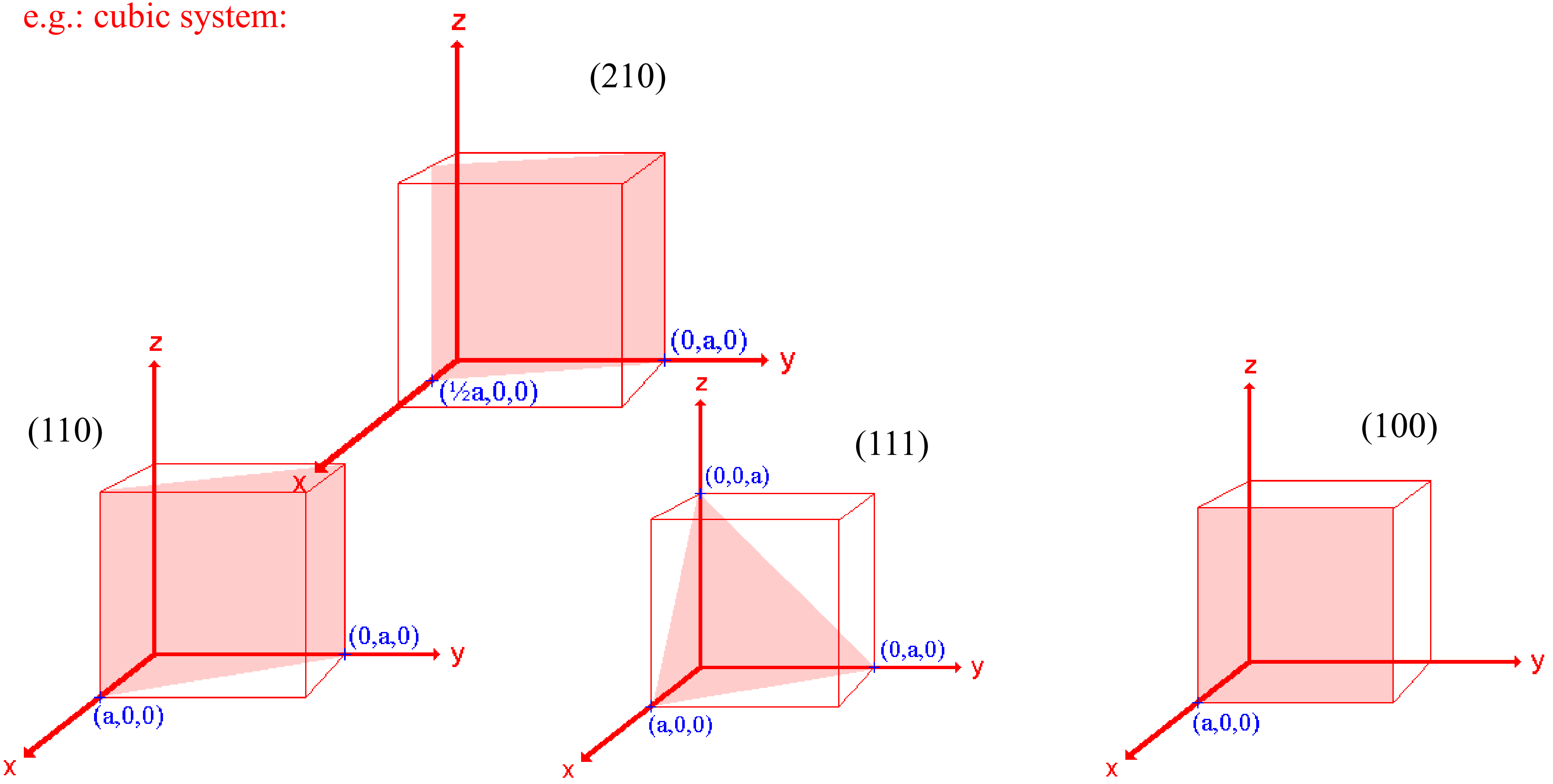
**to identify planes:**

**Step 1 : Identify the intercepts on the x- , y- and z- axes (a/2, ∞, ∞)**

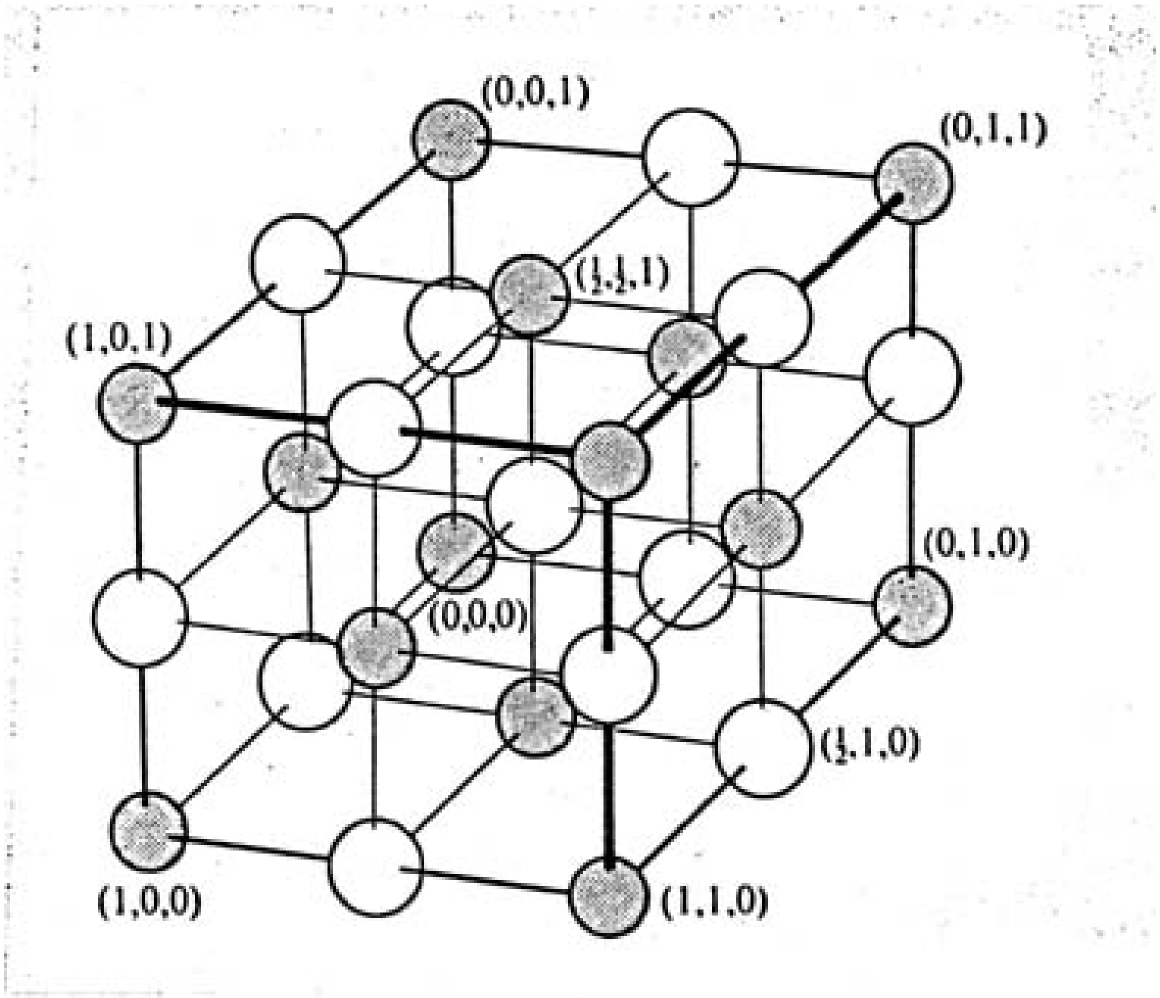
**Step 2 : Specify the intercepts in fractional co-ordinates (a/2a, ∞, ∞) = (1/2,0,0)**

**Step 3 : Take the reciprocals of the fractional intercepts (2, 0, 0)**

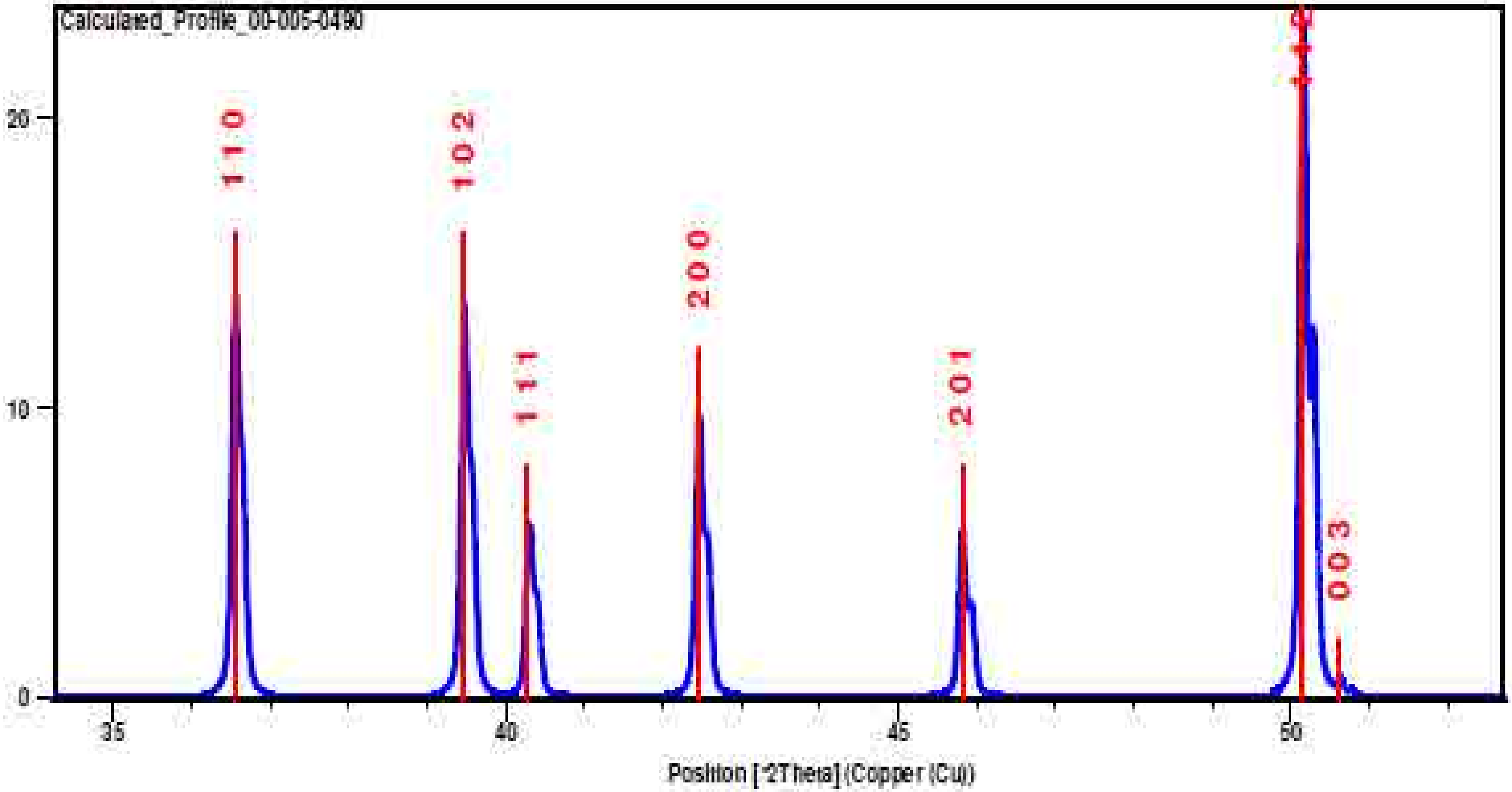
e.g.: cubic system:



# Miller Indices



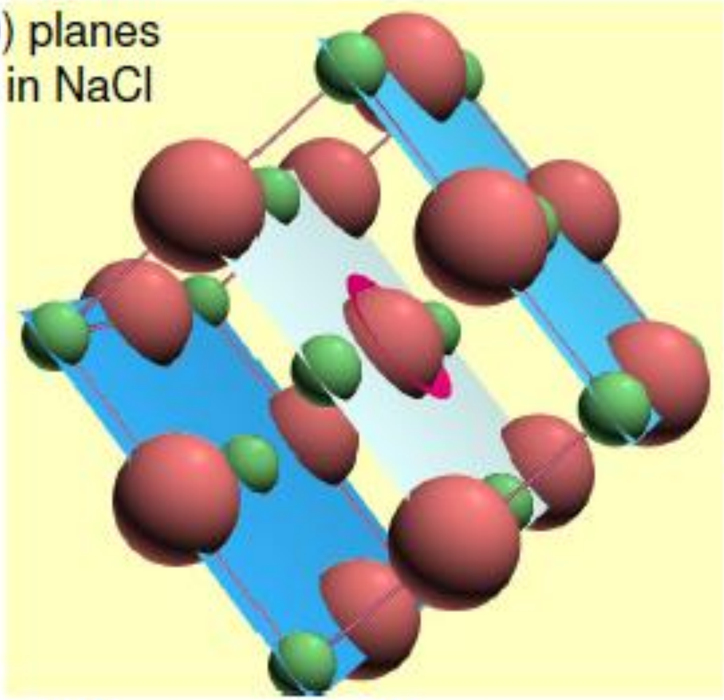
# Diffraction peaks are associated with planes of atoms

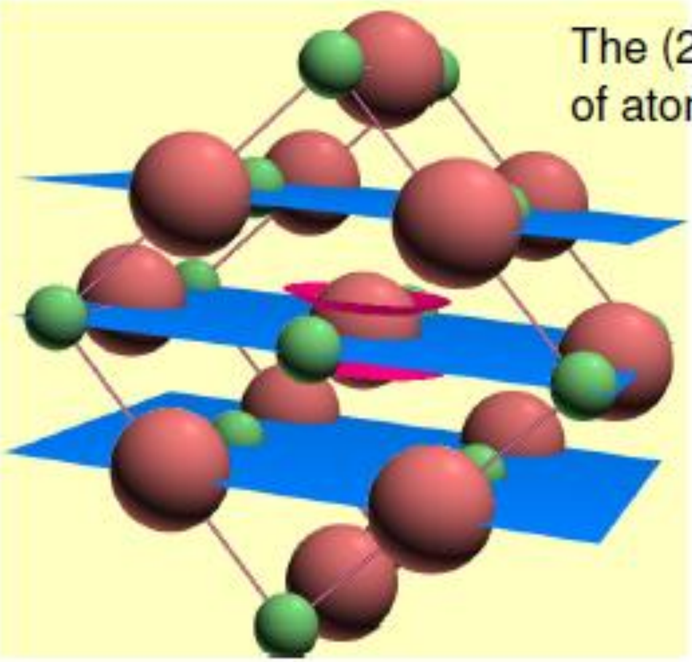


- Miller indices (hkl) are used to identify different planes of atoms
- Observed diffraction peaks can be related to planes of atoms to assist in analyzing the atomic structure and microstructure of a sample

# Parallel **planes of atoms** intersecting the unit cell define directions and distances in the crystal.

The (200) planes of atoms in NaCl



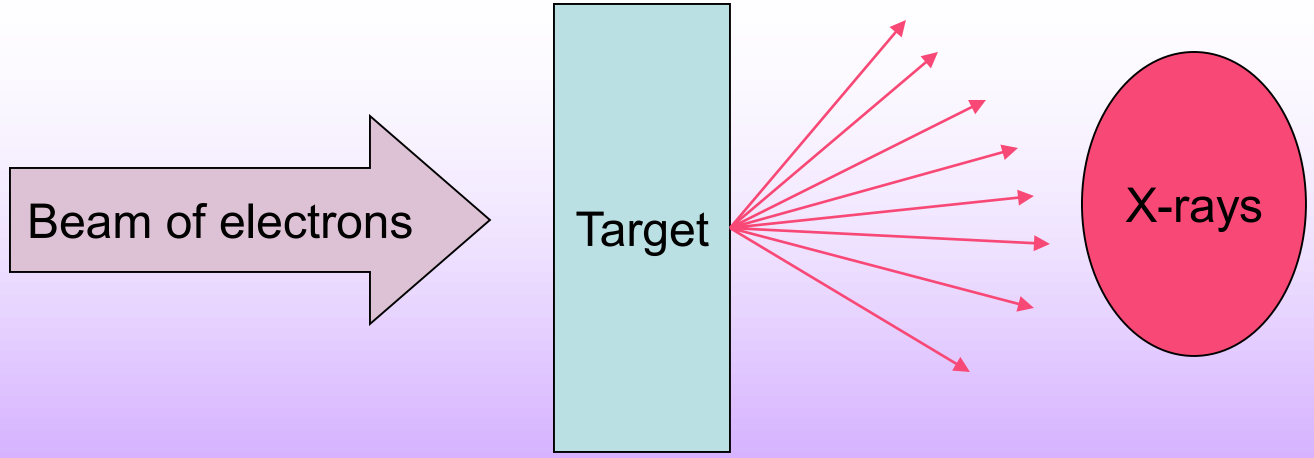


The (220) planes of atoms in NaCl

- The Miller indices (hkl) define the reciprocal of the axial intercepts
- The crystallographic direction, [hkl], is the vector normal to (hkl)
- $d_{hkl}$ is the vector extending from the origin to the plane (hkl) and is normal to (hkl)
- The vector $d_{hkl}$ is used in Bragg's law to determine where diffraction peaks will be observed

# Generation of X-rays

- X-rays can be generated by decelerating electrons.
- Hence, X-rays are generated by bombarding a target (say Cu) with an electron beam.
- The resultant spectrum of X-rays generated (i.e. $\lambda_{\text{X-rays}}$ versus Intensity plot) is shown in the next slide. The pattern shows intense peaks on a 'broad' background.
- The intense peaks can be 'thought of' as monochromatic radiation and be used for X-ray diffraction studies.



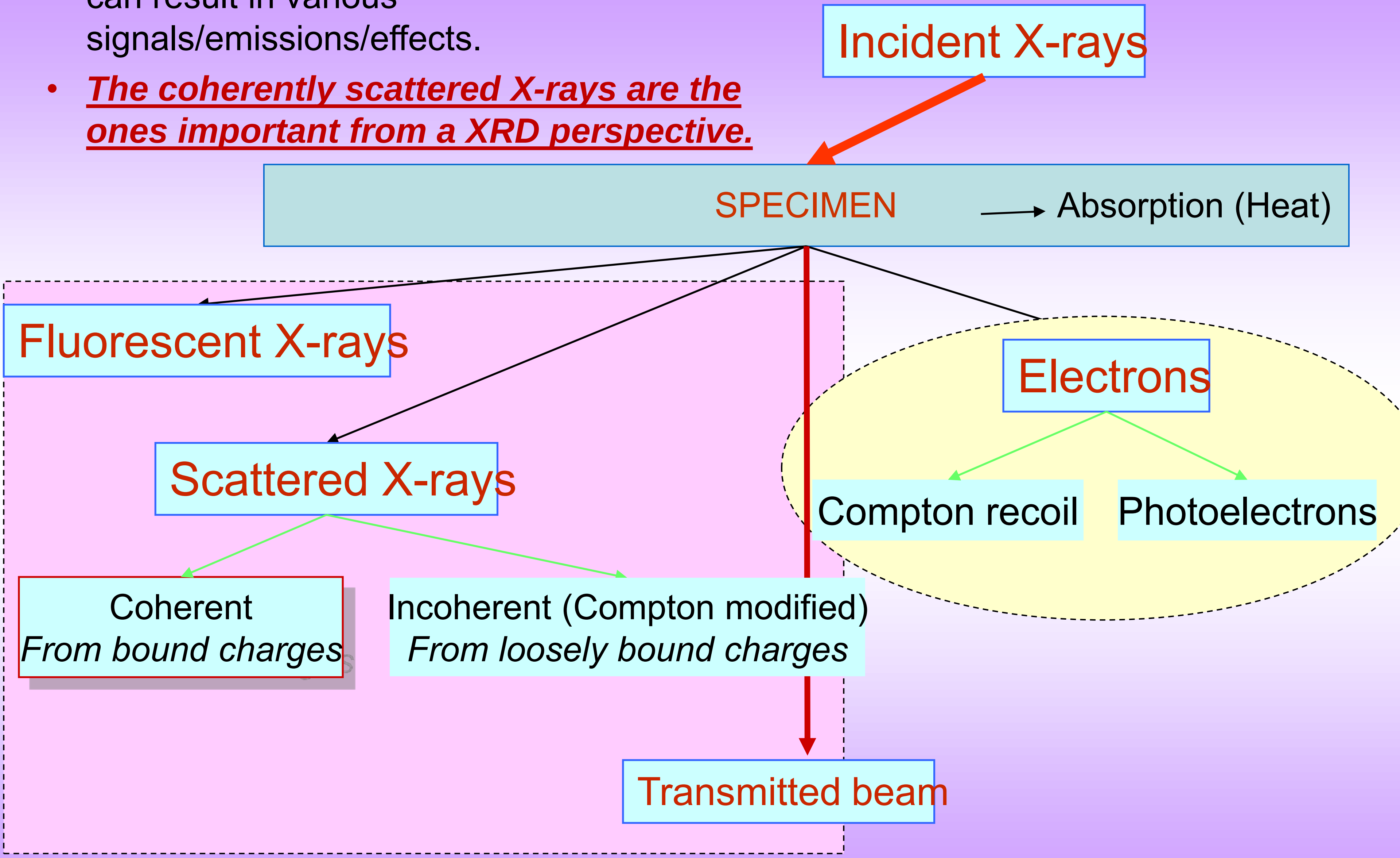
An accelerating (or decelerating) charge radiates electromagnetic radiation

# X-ray sources with different λ for doing XRD studies

| Elements | (KV) | λ Of $K_{\alpha1}$ radiation (Å) | λ Of $K_{\alpha2}$ radiation (Å) | λ Of $K_{\beta}$ radiation (Å) | $K_{\beta}$-Filter (mm) |
|---|---|---|---|---|---|
| **Ag** | 25.52 | 0.55941 | 0.5638 | 0.49707 | Pd<br>0.0461 |
| **Mo** | 20 | 0.7093 | 0.71359 | 0.63229 | Zr<br>0.0678 |
| **Cu** | 8.98 | 1.540598 | 1.54439 | 1.39222 | Ni<br>0.017 |
| **Ni** | 8.33 | 1.65791 | 1.66175 | 1.50014 | Co<br>0.0158 |
| **Co** | 7.71 | 1.78897 | 1.79285 | 1.62079 | Fe<br>0.0166 |
| **Fe** | 7.11 | 1.93604 | 1.93998 | 1.75661 | Mn<br>0.0168 |
| **Cr** | 5.99 | 2.2897 | 2.29361 | 2.08487 | V<br>0.169 |

*C.Gordon Darwin, Grandson of C. Robert Darwin developed the dynamic theory of scattering of x-rays (a tough theory!) in 1912*

- When X-rays hit a specimen, the interaction can result in various signals/emissions/effects.
- ***The coherently scattered X-rays are the ones important from a XRD perspective.***



Incident X-rays

SPECIMEN

Absorption (Heat)

Fluorescent X-rays

Scattered X-rays

Coherent
*From bound charges*

Incoherent (Compton modified)
*From loosely bound charges*

Electrons

Compton recoil

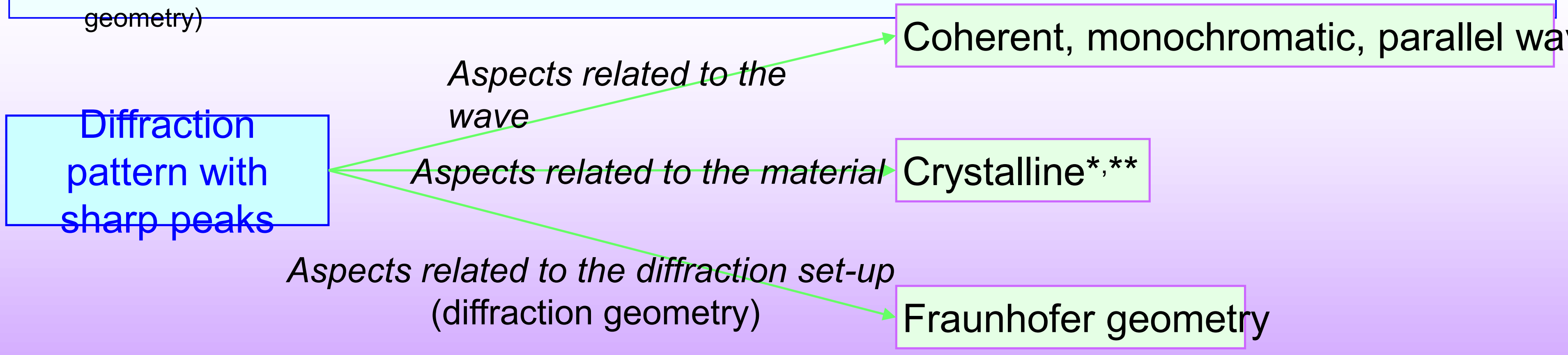
Photoelectrons

Transmitted beam

*X-rays can also be refracted (refractive index slightly less than 1) and reflected (at very small a*

# Diffraction

- Now we shall consider the important topic as to how X-rays interact with a crystalline array (of atoms, ions etc.) to give rise to the phenomenon known as X-ray diffraction (XRD).
- Let us consider a special case of diffraction → a case where we get '*sharp*[1] *diffraction peaks*'.
- Diffraction (*with sharp peaks*) (with XRD being a specific case) requires three important conditions to be satisfied:
  - Radiation related ➢ Coherent, monochromatic, parallel waves& (with wavelength $\lambda$).
  - Sample related ➢ Crystalline array of scatterers* with spacing of the order of (~) $\lambda$.
  - Diffraction geometry related ➢ Fraunhofer diffraction geometry (& this is actually part of the Fraunhofer geometry)



Diffraction pattern with sharp peaks

*Aspects related to the wave*

Coherent, monochromatic, parallel wa

*Aspects related to the material*

Crystalline*,**

*Aspects related to the diffraction set-up* (diffraction geometry)

Fraunhofer geometry

---

*[1] The intensity-$\theta$ plot looks like a '$\delta$' function (in an ideal situation).*

** A quasicrystalline array will also lead to diffraction with sharp peaks (which we shall not consider in this text).*

*** Amorphous material will give broadened (diffuse) peak (additional factors related to the sample can also give a*

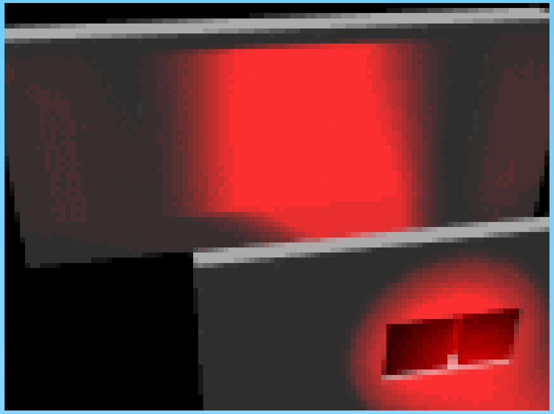
- ❑ The waves could be:
  - ➢ electromagnetic waves (light, X-rays…),
  - ➢ matter waves** (electrons, neutrons…) or
  - ➢ mechanical waves (sound, waves on water surface…).
- ❑ Not all objects act like scatterers for all kinds of radiation.
- ❑ If wavelength is not of the order of the spacing of the scatterers, then the number of peaks obtained may be highly restricted (i.e. we may even not even get a single diffraction peak!).
- ❑ In short diffraction is coherent reinforced scattering (or reinforced scattering of coherent waves).
- ❑ In a sense diffraction is nothing but a special case of constructive (& destructive) interference.

  To give an analogy → the results of Young's double slit experiment is interpreted as interference, while the result of multiple slits (large number) is categorized under diffraction.
- ❑ Fraunhofer diffraction geometry implies that parallel waves are impinging on the scatteres (the object), and the screen (to capture the diffraction pattern) is placed far away from the object.

** With a de Broglie wavelength

# DIFFRACTION

- Diffraction is a wave phenomenon in which the apparent bending and spreading of waves when they meet an obstruction.
- Diffraction occurs with electromagnetic waves, such as light and radio waves, and also in sound waves and water waves.
- The most conceptually simple example of diffraction is double-slit diffraction, that’s why firstly we remember light diffraction.



Width b Variable (500-1500 nm)

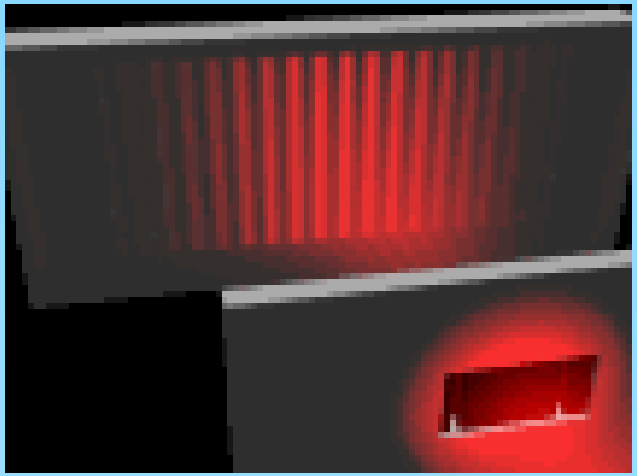
Wavelength Constant (600 nm)

Distance d = Constant

# LIGHT DIFFRACTION

- Light diffraction is caused by light bending around the edge of an object. The interference pattern of bright and dark lines from the diffraction experiment can only be explained by the additive nature of waves; wave peaks can add together to make a brighter light, or a peak and a through will cancel each other out and result in darkness.

**Thus Young's light interference experiment proves that light has wave like properties.**



# Diffraction of Waves by Crystals

- The diffraction depends on the crystal structure and on the wavelength.
- At optical wavelengths such as 5000 angstroms the superposition of the waves scattered elastically by the individual atoms of a crystal results in ordinary optical refraction.
- When the wavelength of the radiation is comparable with or smaller than the lattice constant, one can find diffracted beams in directions quite different from the incident radiation.

# Diffraction of Waves by Crystals

- ***The structure of a crystal*** can be determined by studying the ***diffraction pattern of a*** beam of radiation incident on the crystal.

- Beam diffraction takes place ***only in certain specific directions***, much as light is diffracted by a grating.

- By measuring the ***directions of the diffraction*** and the ***corresponding intensities***, one obtains information concerning the ***crystal structure*** responsible for diffraction.

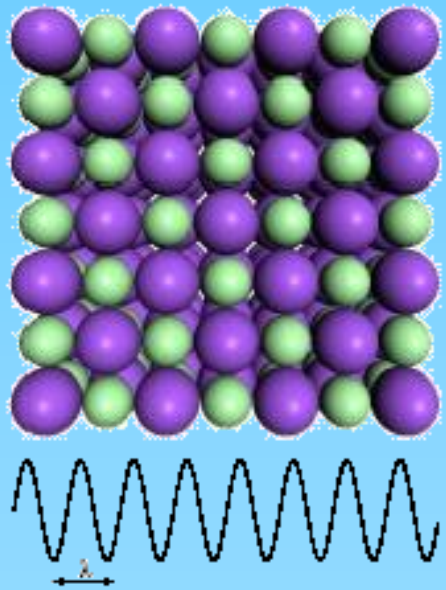
# X-RAY CRYSTALLOGRAPHY

- **X-ray crystallography** is a technique in crystallography in which the pattern produced by the diffraction of x-rays through the closely spaced lattice of atoms in a crystal is recorded and then analyzed to reveal the nature of that lattice.

- X-ray diffraction = (XRD)

# X-Ray Crystallography

- The wavelength of X-rays is typically 1 A°, comparable to the interatomic spacing (distances between atoms or ions) in solids.



- We need X-rays:

$$E_{x-ray} = \hbar\omega = h\upsilon = \frac{hc}{\lambda} = \frac{hc}{1x10^{-10}m} = 12.3x10^{3}eV$$

# Crystal Structure Determination

A crystal behaves as a 3-D diffraction grating for x-rays

- In a diffraction experiment, the spacing of lines on the grating can be deduced from the separation of the diffraction maxima Information about the structure of the lines on the grating can be obtained by measuring the relative intensities of different orders
- Similarly, measurement of the separation of the X-ray diffraction maxima from a crystal allows us to determine the size of the unit cell and from the intensities of diffracted beams one can obtain information about the arrangement of atoms within the cell.

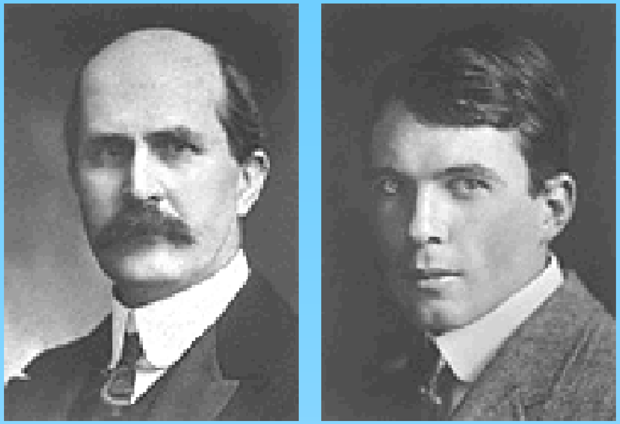
# X-Ray Diffraction

W. L. Bragg presented a simple explanation of the diffracted beams from a crystal.

The Bragg derivation is simple but is convincing only since it reproduces the correct result.

# X-Ray Diffraction & Bragg Equation

- English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ).This observation is an example of X-ray **wave interference**.



***Sir William Henry Bragg (1862-1942), William Lawrence Bragg (1890-1971)***

- 1915, the father and son were awarded the Nobel prize for physics *"for their services in the analysis of crystal structure by means of Xrays".*

# Crystal structure determination

Monochromatic X-rays

Many θs (orientations)
Powder specimen

POWDER METHOD

**Pan**chromatic X-rays

Single θ

LAUE TECHNIQUE

Monochromatic X-rays

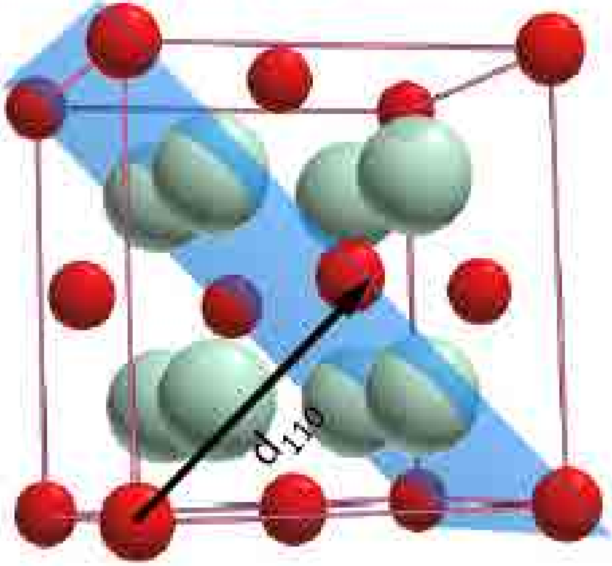
θ Varied by rotation

ROTATING CRYSTAL METHOD

# The position of the diffraction peaks are determined by the distance between parallel planes of atoms.

**Bragg's Law**

$$\lambda = 2d_{hkl} \sin\theta$$



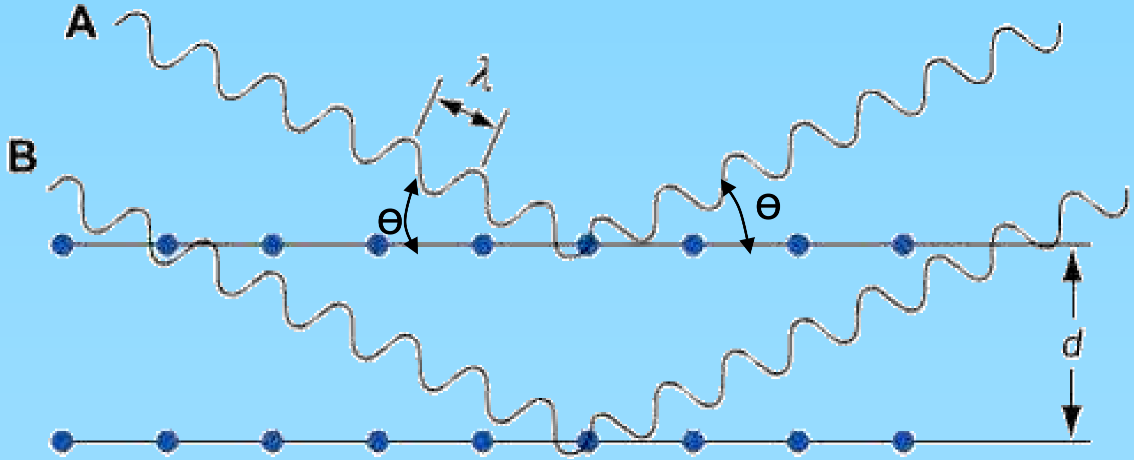
- Bragg's law calculates the angle where constructive interference from X-rays scattered by parallel planes of atoms will produce a diffraction peak.
  - In most diffractometers, the X-ray wavelength $\lambda$ is fixed.
  - Consequently, a family of planes produces a diffraction peak only at a specific angle $2\theta$.
- $\mathbf{d_{hkl}}$ is the vector drawn from the origin of the unit cell to intersect the crystallographic plane (hkl) at a 90° angle.
  - $d_{hkl}$, the vector magnitude, is the distance between parallel planes of atoms in the family (hkl)
  - $d_{hkl}$ is a geometric function of the size and shape of the unit cell

# Bragg Equation

- Bragg law identifies the angles of the incident radiation relative to the lattice planes for which diffraction peaks occurs.
- Bragg derived the condition for constructive interference of the X-rays scattered from a set of parallel lattice planes.

# BRAGG EQUATION

- W.L. Bragg considered crystals to be made up of parallel planes of atoms. Incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane is 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.

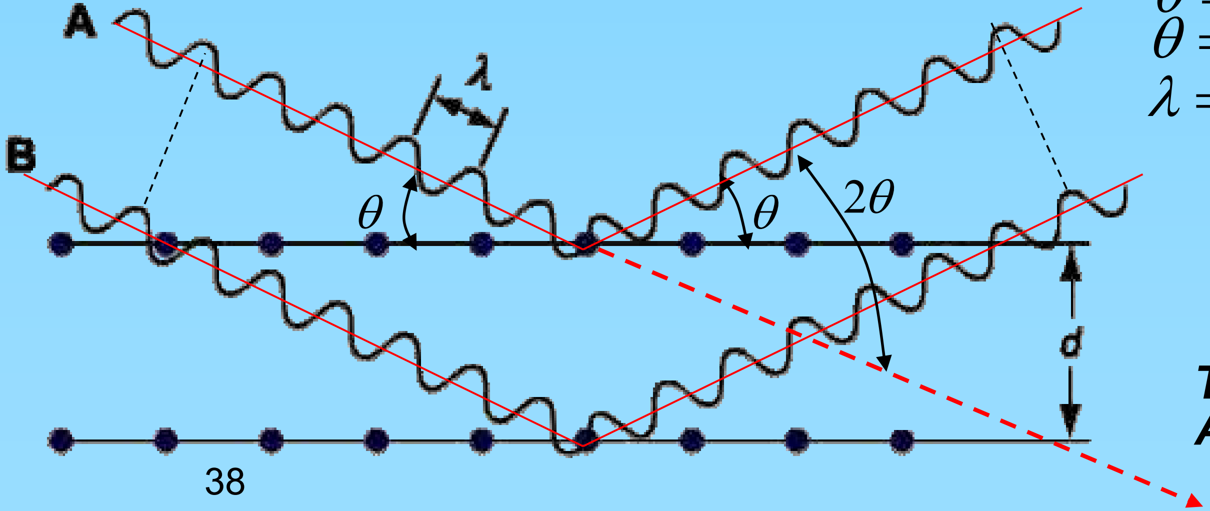


# Diffraction Condition

- The diffracted beams are found to occur when the reflections from planes of atoms interfere constructively.
- We treat elastic scattering, in which the energy of X-ray is not changed on reflection.

# Bragg Equation

- When the X-rays strike a layer of a crystal, some of them will be reflected. We are interested in X-rays that are in-phase with one another. X-rays that add together constructively in x-ray diffraction analysis in-phase before they are reflected and after they reflected.

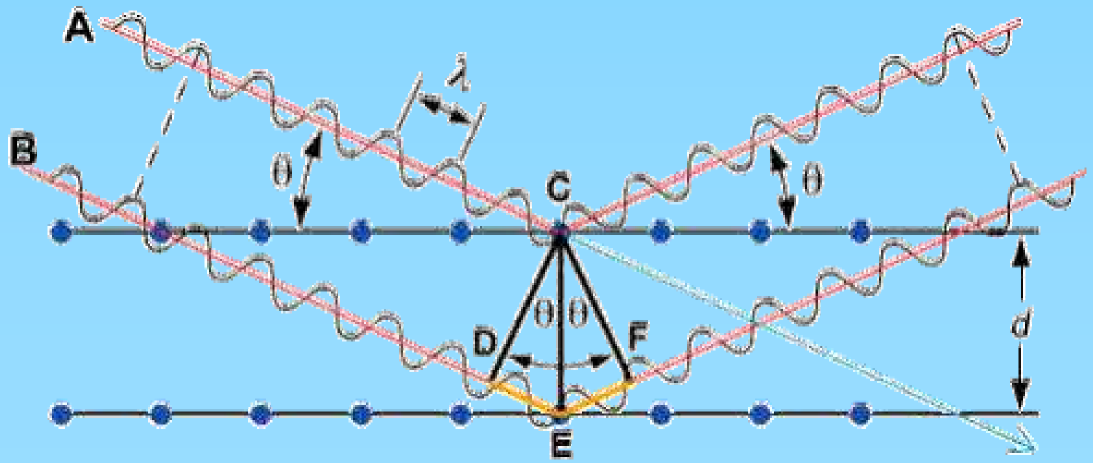


$\theta =$ ***Incident angle***
$\theta =$ ***Reflected angle***
$\lambda =$ ***Wavelength of X-ray***

***Total Diffracted Angle*** $= 2\theta$

# Bragg Equation

- These two x-ray beams travel slightly different distances. The difference in the distances traveled is related to the distance between the adjacent layers.
- Connecting the two beams with perpendicular lines shows the difference between the top and the bottom beams.

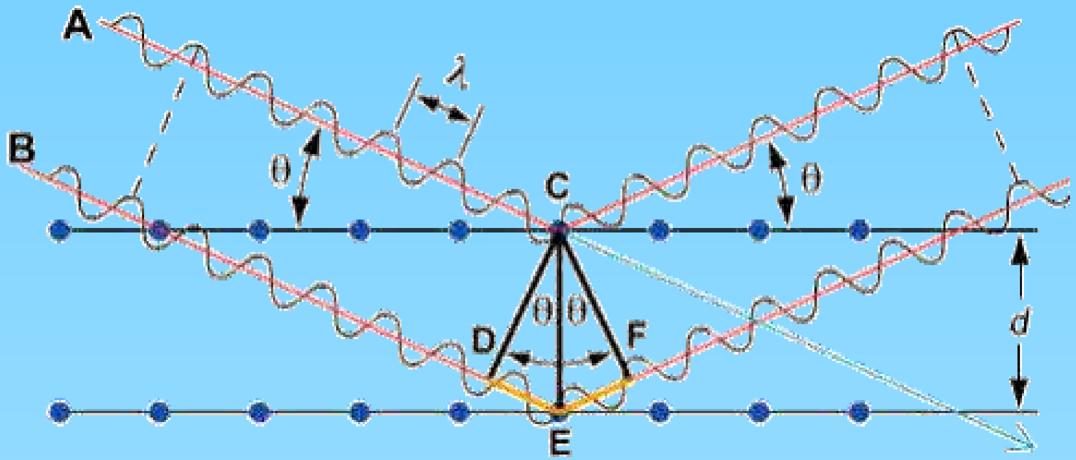


**The line CE is equivalent to the distance between the two layers (d)**

$$DE = d \sin \theta$$

# Bragg Law

- The length DE is the same as EF, so the total distance traveled by the bottom wave is expressed by:



$$EF = d\sin\theta$$

$$DE = d\sin\theta$$

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

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

- Constructive interference of the radiation from successive planes occurs when the path difference is an integral number of wavelenghts. This is the **Bragg Law.**

# Bragg Equation

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

where, d is the spacing of the planes and n is the order of diffraction.

- Bragg reflection can only occur for wavelength

$$n\lambda \leq 2d$$

- This is why we cannot use visible light. No diffraction occurs when the above condition is not satisfied.
- The diffracted beams (reflections) from any set of lattice planes can only occur at particular angles pradicted by the Bragg law.

# Labelling the reflection planes

- To label the reflections, Miller indices of the planes can be used.
- A beam corresponding to a value of n>1 could be identified by a statement such as ‘the nth-order reflections from the (hkl) planes’.
- (nh nk nl) reflection

Third-order reflection from (111) plane

↓

(333) reflection

# Bragg Equation

Since Bragg's Law applies to all sets of crystal planes, the lattice can be deduced from the diffraction pattern, making use of general expressions for the spacing of the planes in terms of their Miller indices. For cubic structures

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

Note that the smaller the spacing the higher the angle of diffraction, *i.e.* the spacing of peaks in the diffraction pattern is inversely proportional to the spacing of the planes in the lattice. The diffraction pattern will reflect the symmetry properties of the lattice.

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

# *Experimental arrangements for x-ray diffraction*

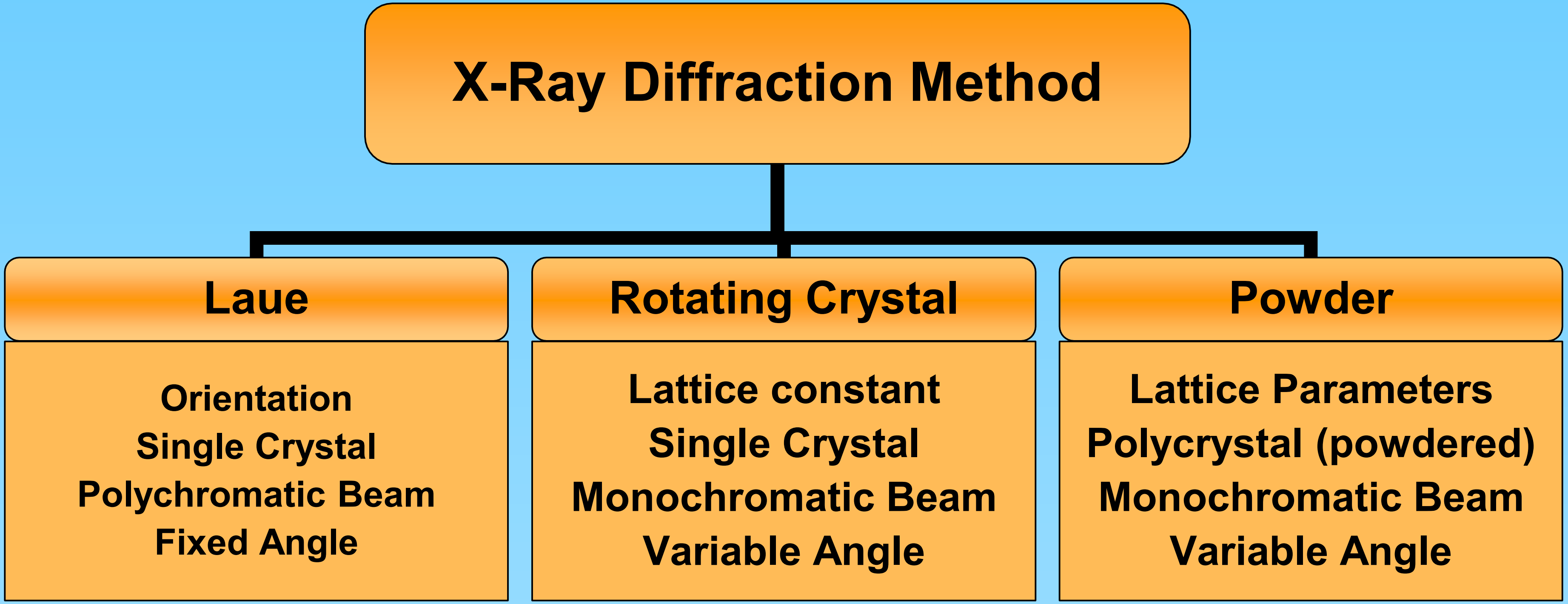
- Since the pioneering work of Bragg, x-ray diffraction has become into a routine technique for the determination of crsytal structure.

# Types of X-ray camera

There are many types of X-ray camera to sort out reflections from different crystal planes. We will study only three types of X-ray photograph that are widely used for the simple structures.

1. Laue photograph
2. Rotating crystal method
3. Powder photograph

# X-RAY DIFFRACTION METHODS



**X-Ray Diffraction Method**

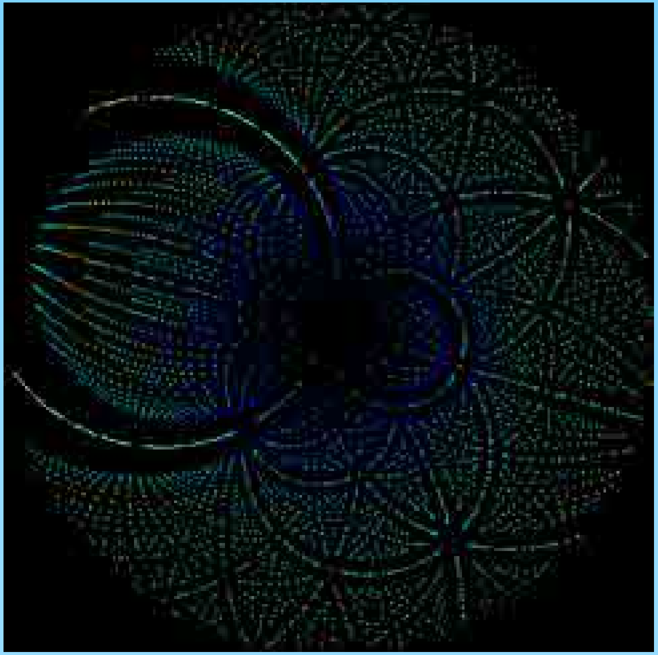
| Laue | Rotating Crystal | Powder |
|---|---|---|
| Orientation<br>Single Crystal<br>Polychromatic Beam<br>Fixed Angle | Lattice constant<br>Single Crystal<br>Monochromatic Beam<br>Variable Angle | Lattice Parameters<br>Polycrystal (powdered)<br>Monochromatic Beam<br>Variable Angle |

# Diffraction Methods

| Method | Wavelength | Angle | Specimen |
|---|---|---|---|
| Laue | Variable | Fixed | Single Crystal |
| Rotating Crystal | Fixed | Variable (in part) | Single Crystal |
| Powder | Fixed | Variable | Powder |

# 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.



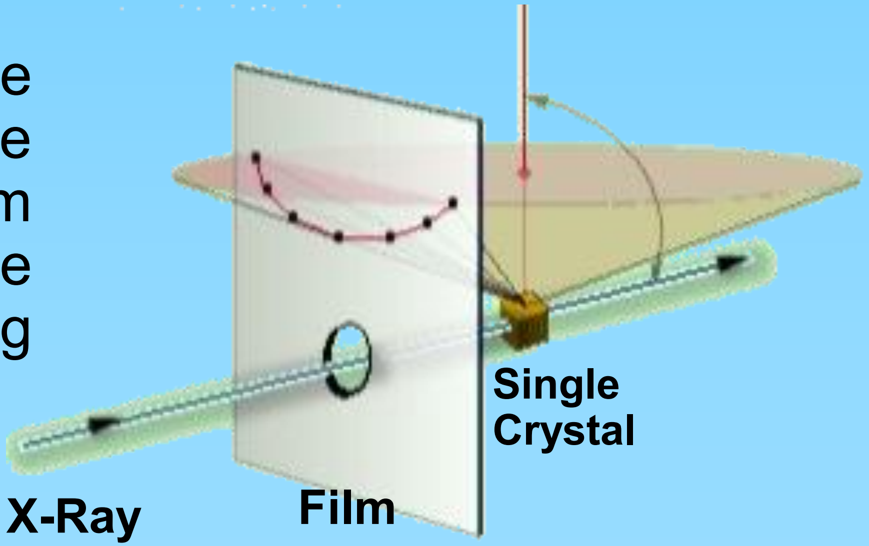
- The diffracted beams form arrays of spots, that lie on curves on the film.

- The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of *d* and θ involved.

# Back-reflection Laue Method

- 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.

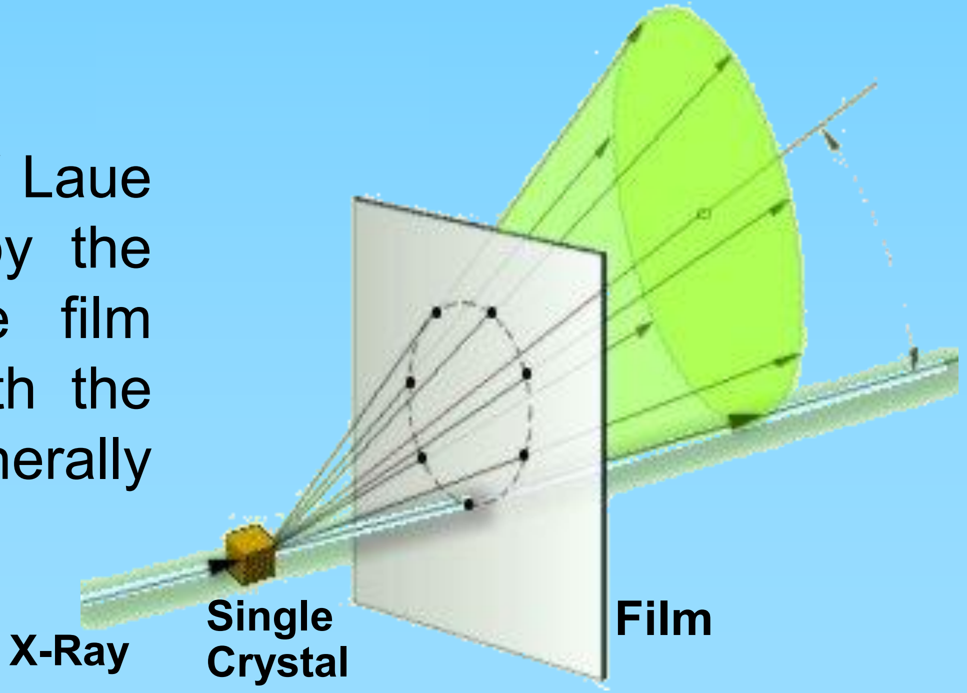
- One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



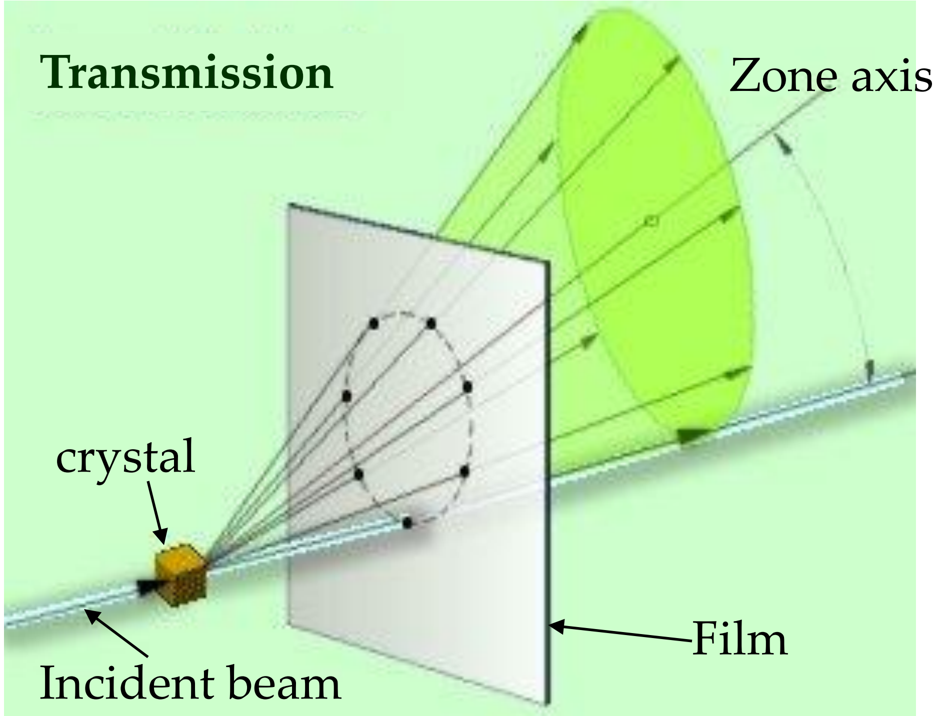
# Transmission Laue Method

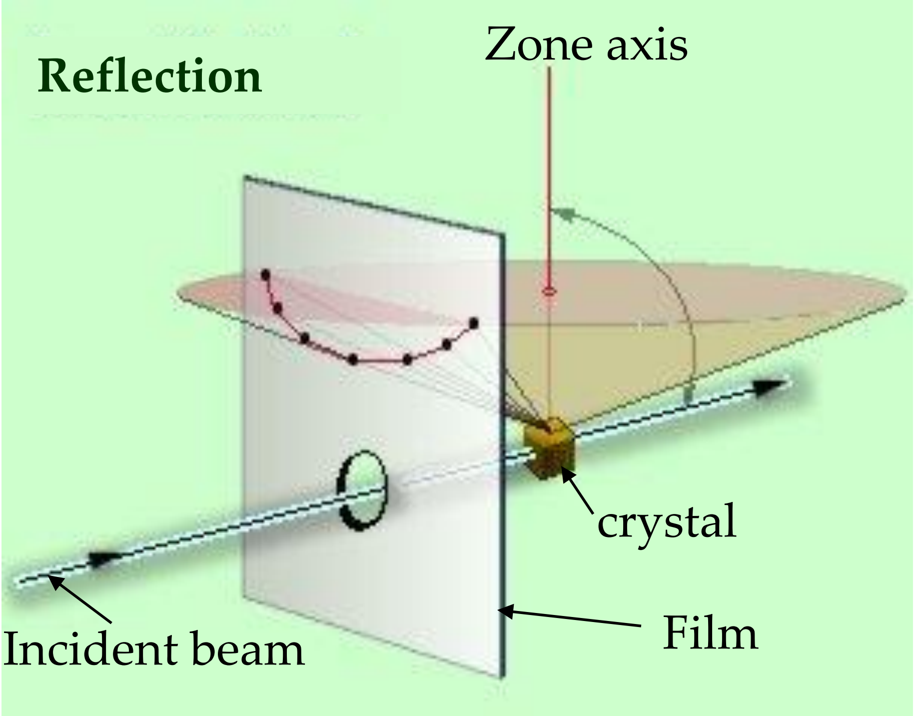
- In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.

- 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.



# Laue Method





- Uses Single crystal
- Uses White Radiation
- Used for determining crystal orientation and quality

# Laue Pattern

***The symmetry of the spot pattern reflects the symmetry of the crystal when viewed along the direction of the incident beam. Laue method is often used to determine the orientation of single crystals by means of illuminating the crystal with a continuos spectrum of X-rays;***

- ☑ ***Single crystal***
- ☑ ***Continous spectrum of x-rays***
- ☑ ***Symmetry of the crystal; orientation***

# Crystal structure determination by Laue method

- Therefore, 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 diffucult.
- Rotating crystal method overcomes this problem. How?

## Laue versus Bragg

- In Laue's picture constructive and destructive interference at various points in space is computed using path differences (and hence phase differences)– given a crystalline array of scatterers.
- Bragg simplified this picture by considering this process as 'reflections from atomic planes'.

---

## Reflection versus Diffraction

- Though diffraction (according to Bragg's picture) has been visualized as a reflection from a set of planes with interplanar spacing 'd' → diffraction should not be confused with reflection (specular reflection).

| Reflection | Diffraction |
|---|---|
| Occurs from surface | Occurs throughout the bulk<br>*(though often the penetration of x-rays in only of the order of 10s of microns in a material)* |
| Takes place at any angle | Takes place only at Bragg angles |
| ~100 % of the intensity may be reflected | Small fraction of intensity is diffracted |

*Note: X-rays can ALSO be reflected at very small angles of incidence*

# Crystal structure determination

- As diffraction occurs only at specific Bragg angles, the chance that a reflection is observed when a crystal is irradiated with monochromatic X-rays at a particular angle is small *(added to this the diffracted intensity is a small fraction of the beam used for irradiation).*
- The probability to get a diffracted beam (with sufficient intensity) is increased by either varying the wavelength ($\lambda$) or having many orientations (rotating the crystal or having multiple crystallites in many orientations).
- The three methods used to achieve high probability of diffraction are shown below.

| | | | |
|---|---|---|---|
| Monochromatic X-rays | Powder specimen | POWDER METHOD | $\theta \rightarrow$ variable |
| **Panchromatic X-rays** | Single $\theta$ | LAUE TECHNIQUE | $\lambda \rightarrow$ variable<br>$\theta \rightarrow$ fixed |
| Monochromatic X-rays | $\theta$ Varied by rotation | ROTATING CRYSTAL METHOD | $\lambda \rightarrow$ fixed<br>$\theta \rightarrow$ rotated |

*Only the powder method (which is commonly used in materials science) will be considered in this te*

# THE POWDER METHOD

- In the powder method the specimen has crystallites (or grains) in many orientations (usually random).
- Monochromatic* X-rays are irradiated on the specimen and the intensity of the diffracted beams is measured as a function of the diffracted angle.
- In this elementary text we shall consider cubic crystals.

$$\lambda = 2d\,Sin\theta$$ (1)

Cubic crystal $$d_{hkl\ Cubic} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$ (2)

(2) in (1)

$$\lambda^2 = \frac{4a^2\sin^2\theta}{h^2+k^2+l^2} \quad \Rightarrow \quad (h^2+k^2+l^2) = \frac{4a^2}{\lambda^2}\sin^2\theta$$

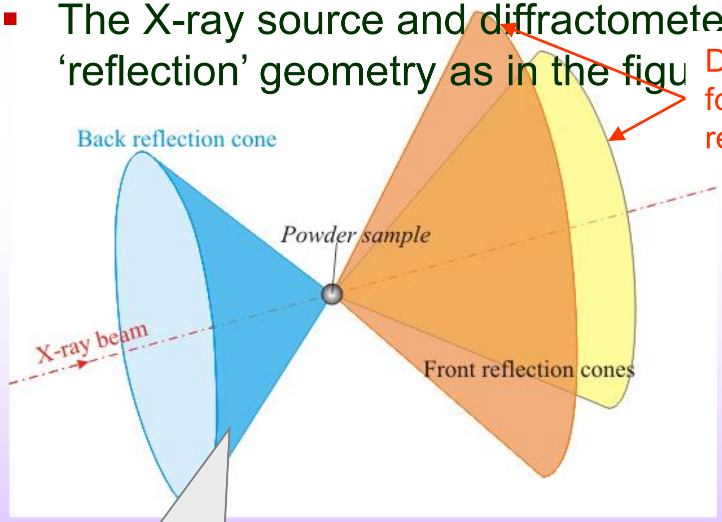
$$a^2 = \frac{\lambda^2}{4\sin^2\theta}(h^2+k^2+l^2) \quad \Rightarrow \quad \boxed{(h^2+k^2+l^2) \propto \sin^2\theta}$$

---

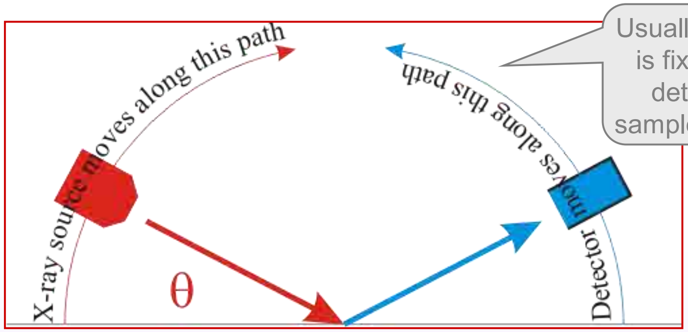
* *In reality this is true only to an extent*

# POWDER METHOD

- In the powder sample there are crystallites in different 'random' orientations (a polycrystalline sample too has grains in different orientations)
- The coherent x-ray beam is diffracted by these crystallites at various angles to the incident direction
- All the diffracted beams (called 'reflections') from a single plane, but from different crystallites lie on a cone.
- Depending on the angle there are forward and back reflection cones.
- A diffractometer can record the angle of these reflections along with the intensities of the reflection
- The X-ray source and diffractometer move in arcs
'reflection' geometry as in the figu

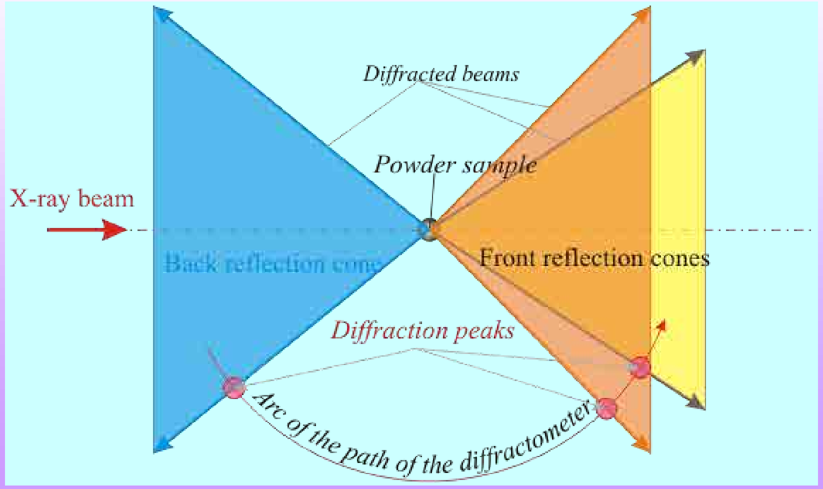


Different cones for different reflections



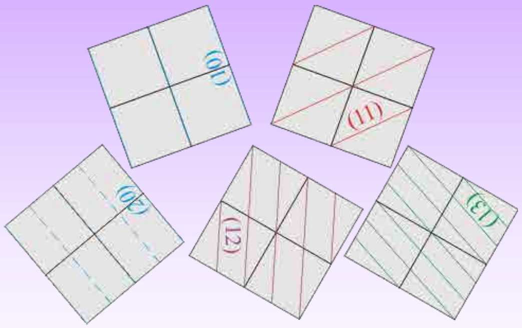
Usually the source is fixed and the detector and sample are rotated

Also called Debye ring



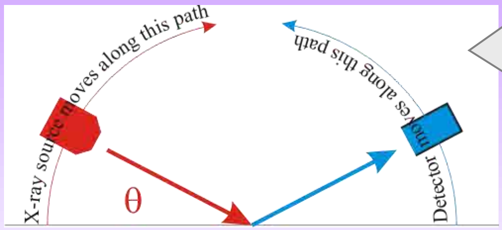
# How to visualize the occurrence of peaks at various angles

*It is 'somewhat difficult' to actually visualize a random assembly of crystallites giving peaks at various angels in a XRD scan. The figures below are expected to give a 'visual feel' for the same. [Hypothetical crystal with a = 4Å is assumed with $\lambda$=1.54Å. Only planes of the type xx0 (like (100,110)are considered].*



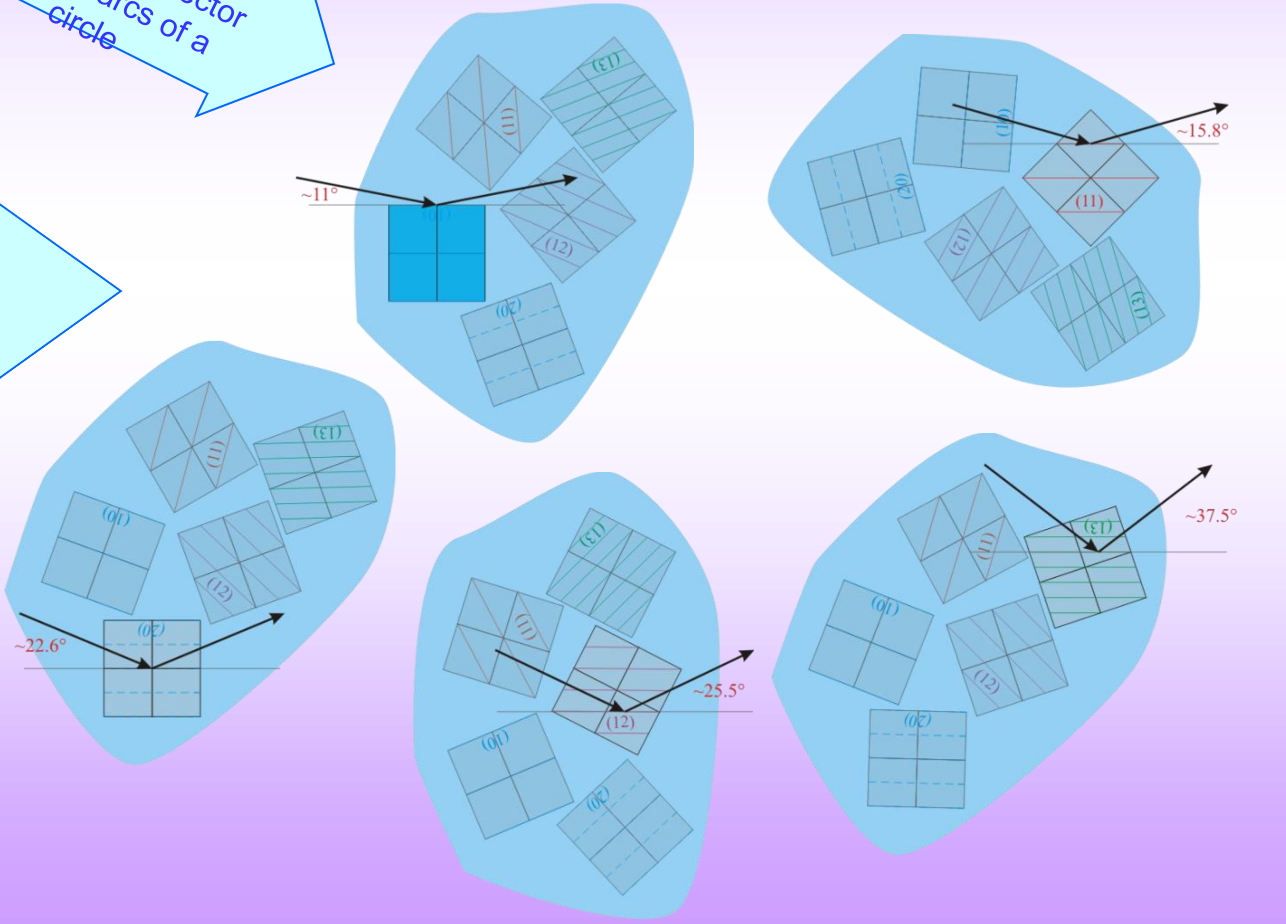
*Random assemblage of crystallites in a material*

The sample is not rotating only the source and detector move in arcs of a circle



For convenience the source may be stationary (and the sample and detector may rotate– but the effect is equivalent)

As the scan takes place at increasing angles, planes with suitable 'd', which diffract are 'picked out' from favourably oriented crystallites

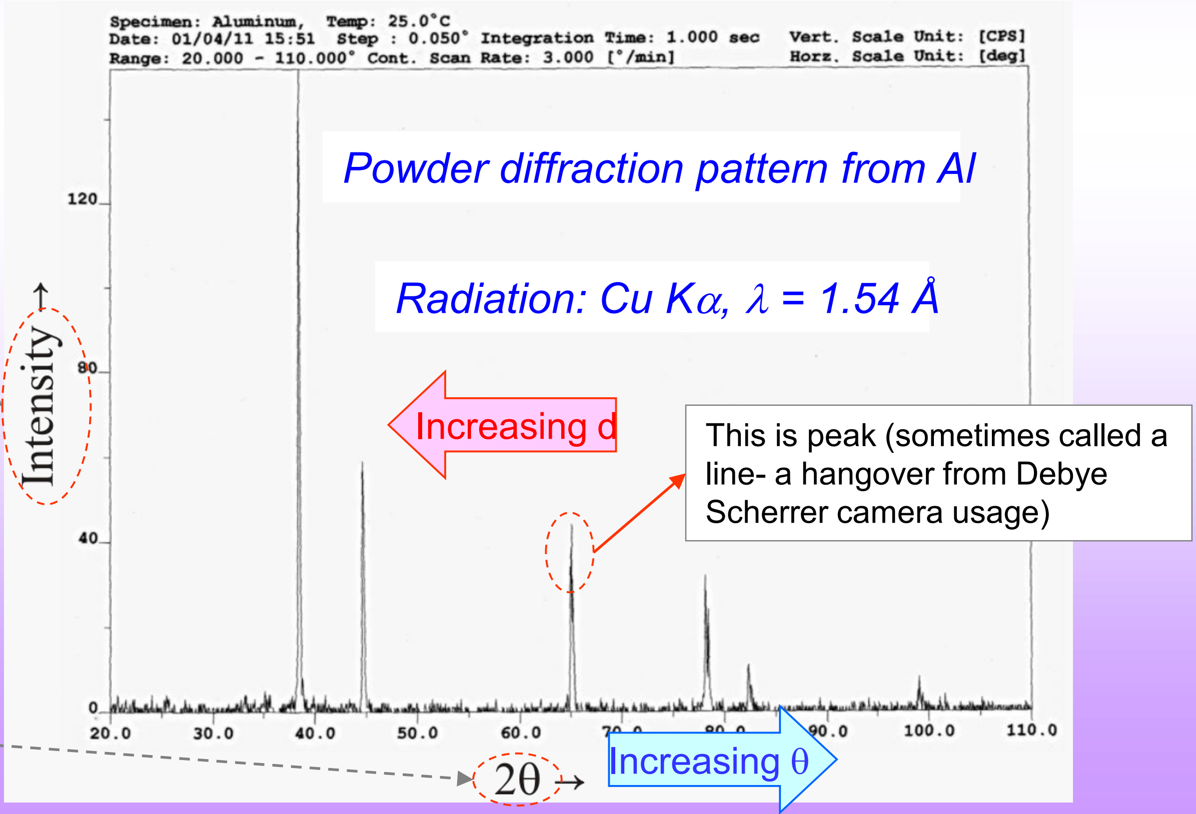


| Σh$^2$ | hkl | d | Sin(θ) | θ |
|---|---|---|---|---|
| 1 | 100 | 4.00 | 0.19 | 11.10 |
| 2 | 110 | 2.83 | 0.27 | 15.80 |
| 3 | 111 | 2.31 | 0.33 | 19.48 |
| 4 | 200 | 2.00 | 0.39 | 22.64 |
| 5 | 210 | 1.79 | 0.43 | 25.50 |
| 6 | 211 | 1.63 | 0.47 | 28.13 |
| 8 | 220 | 1.41 | 0.54 | 32.99 |
| 9 | 300 | 1.33 | 0.58 | 35.27 |
| 10 | 310 | 1.26 | 0.61 | 37.50 |

# Determination of Crystal Structure from 2θ versus Intensity Data in Powder Method

- ❑ In the power diffraction method a 2θ versus intensity (I) plot is obtained from the diffractometer (and associated instrumentation).
- ❑ The 'intensity' is the area under the peak in such a plot (*NOT the height of the peak*).
  - ➢ *I* is really diffracted energy (as Intensity is *Energy/area/time*).

Intensity (I) has units of [Energy/area/time] → but here it is plotted as *arbitrary units*.



```
Specimen: Aluminum,  Temp: 25.0°C
Date: 01/04/11 15:51  Step : 0.050° Integration Time: 1.000 sec   Vert. Scale Unit: [CPS]
Range: 20.000 - 110.000° Cont. Scan Rate: 3.000 [°/min]           Horz. Scale Unit: [deg]
```

*Powder diffraction pattern from Al*

*Radiation: Cu Kα, $\lambda$ = 1.54 Å*

Increasing d

This is peak (sometimes called a line- a hangover from Debye Scherrer camera usage)

Increasing θ

Usually in degrees (°)

# THE POWDER METHOD

If a powdered specimen is used, instead of a single crystal, then there is ***no need to rotate*** the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.

This method is useful for samples that are difficult to obtain in single crystal form.

# THE POWDER METHOD

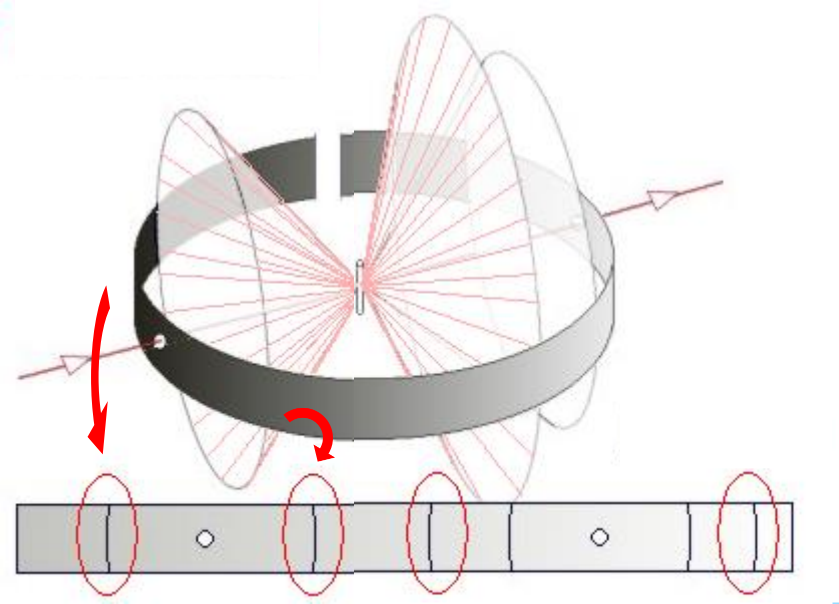
The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors **a**, **b** and **c** which define the unit cell for the crystal.

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.

# Debye Scherrer Camera

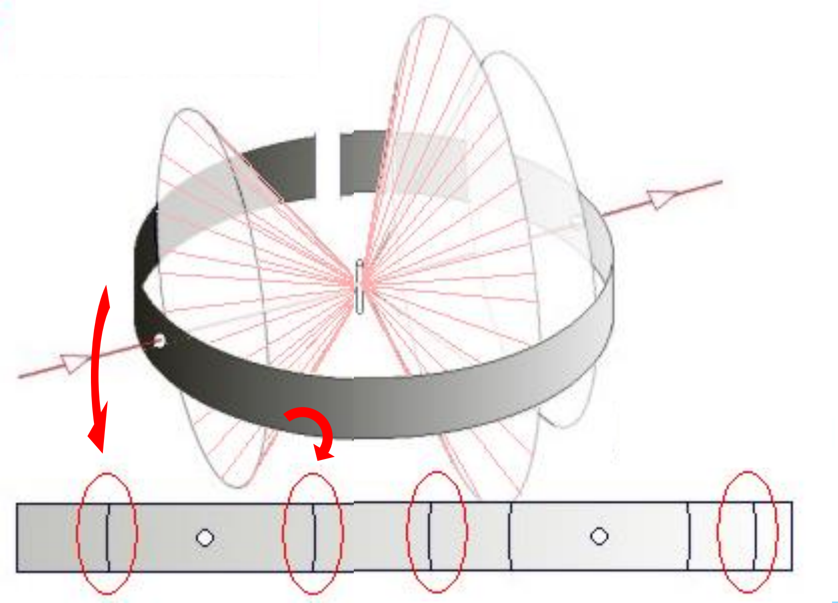
A very small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract x-rays.

The specimen is placed in the **Debye Scherrer** camera and is accurately aligned to be in the centre of the camera. X-rays enter the camera through a collimator.



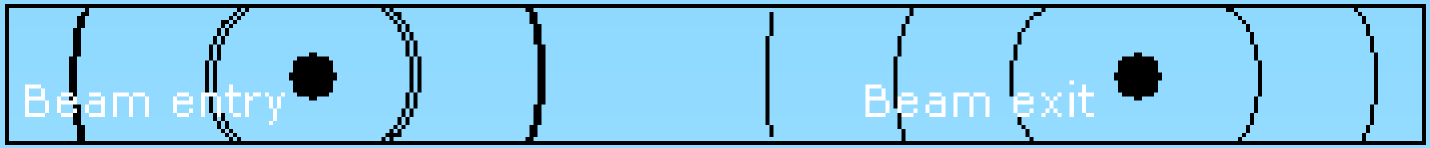
# Debye Scherrer Camera

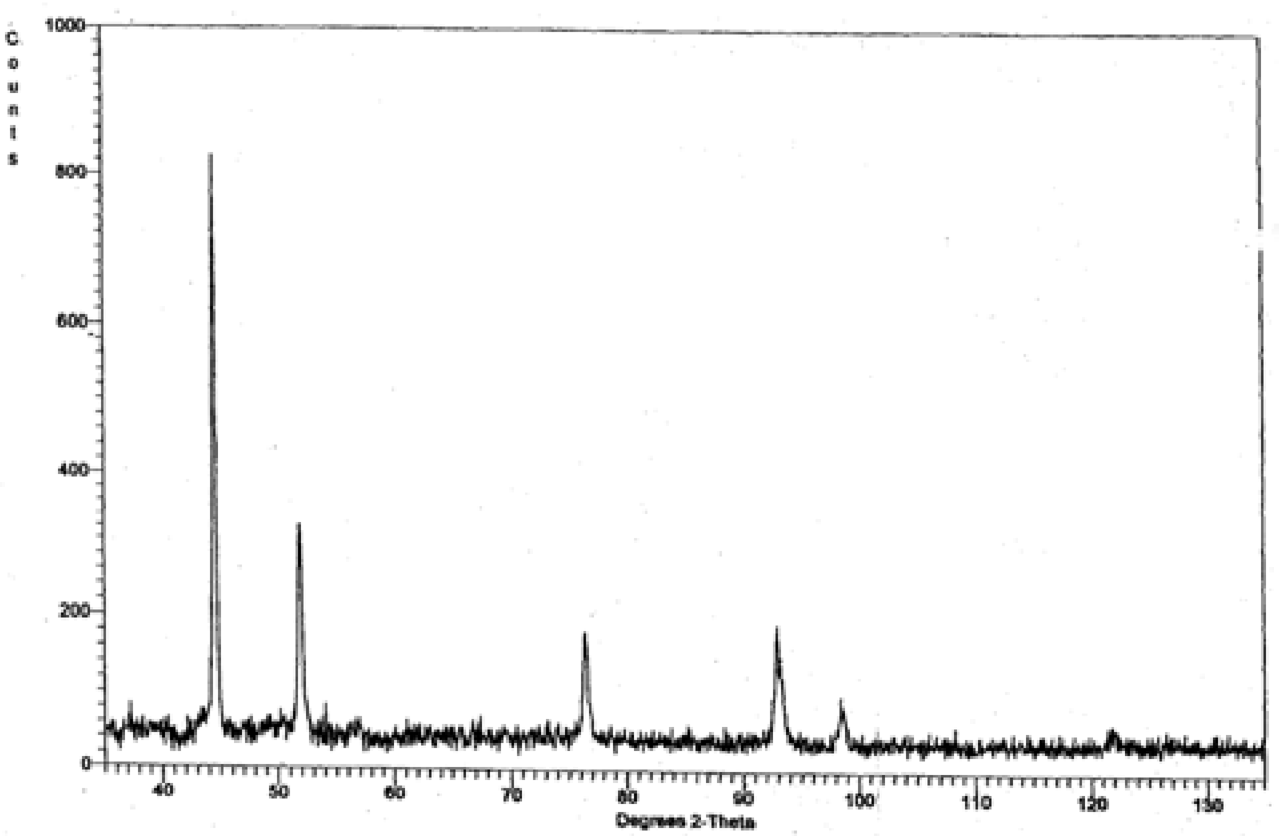
The powder diffracts the x-rays in accordance with Braggs law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.



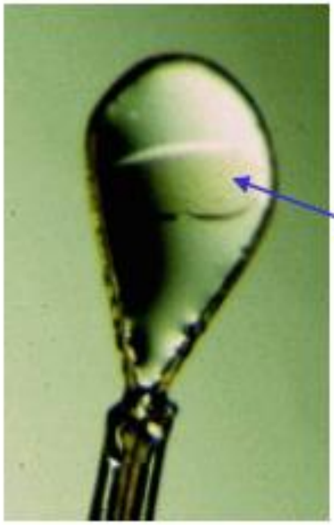
# Powder diffraction film

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

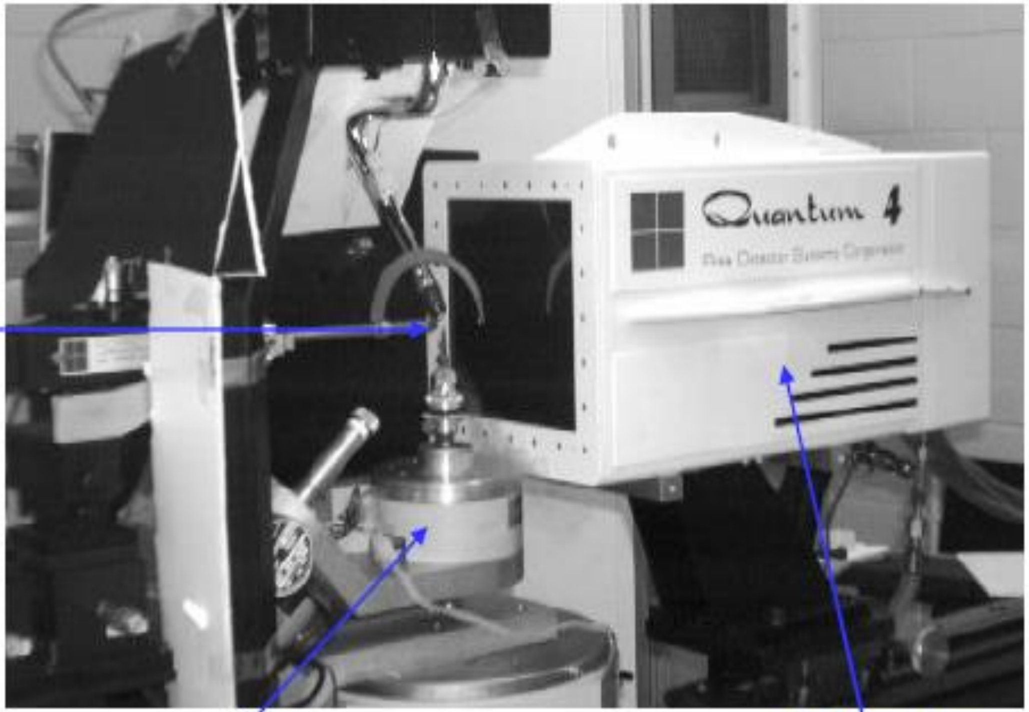



Counts
1000
800
600
400
200
0
40
50
60
70
80
90
100
110
120
130
Degrees 2-Theta

Cryo-loop

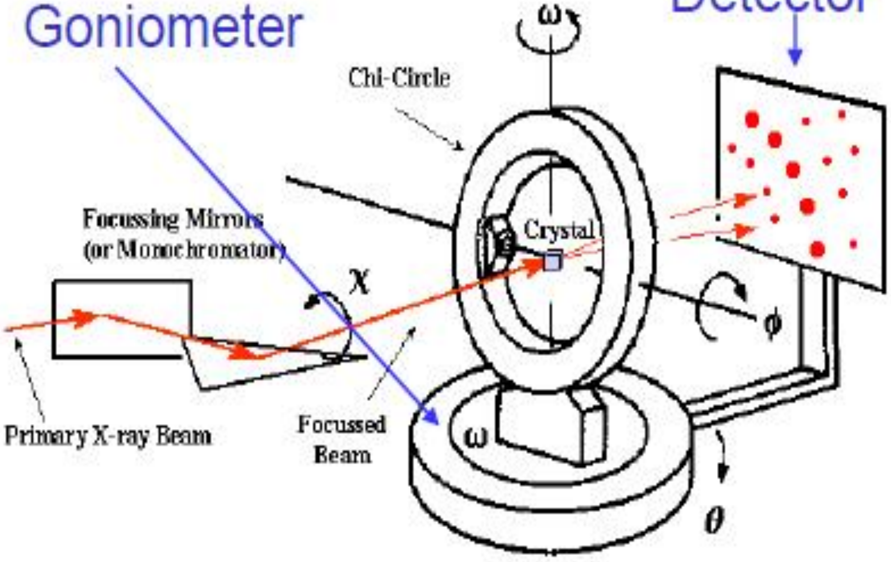


Crystal



Goniometer

Detector

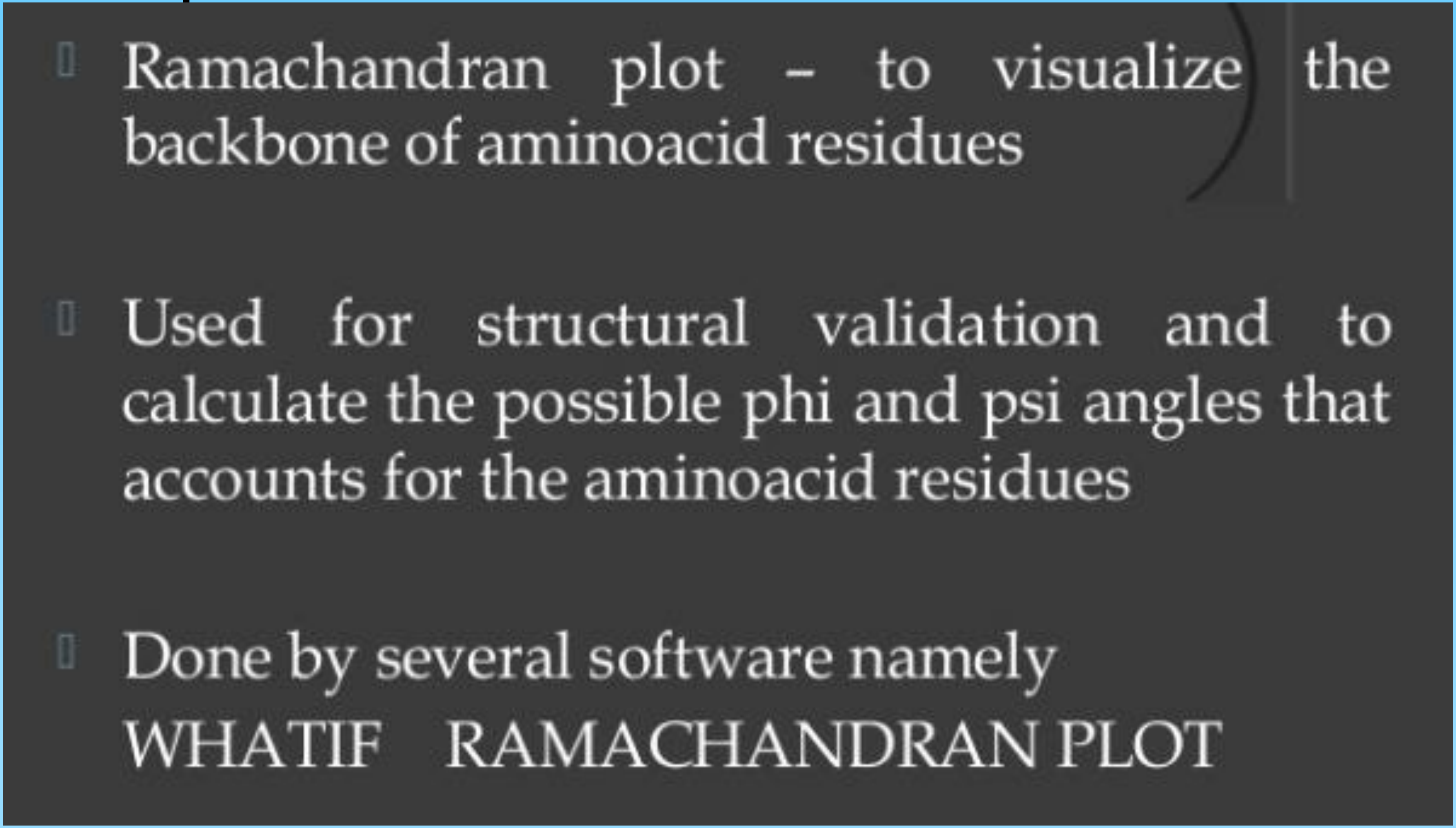


# Application of XRD

XRD is a nondestructive technique. Some of the uses of x-ray diffraction are;

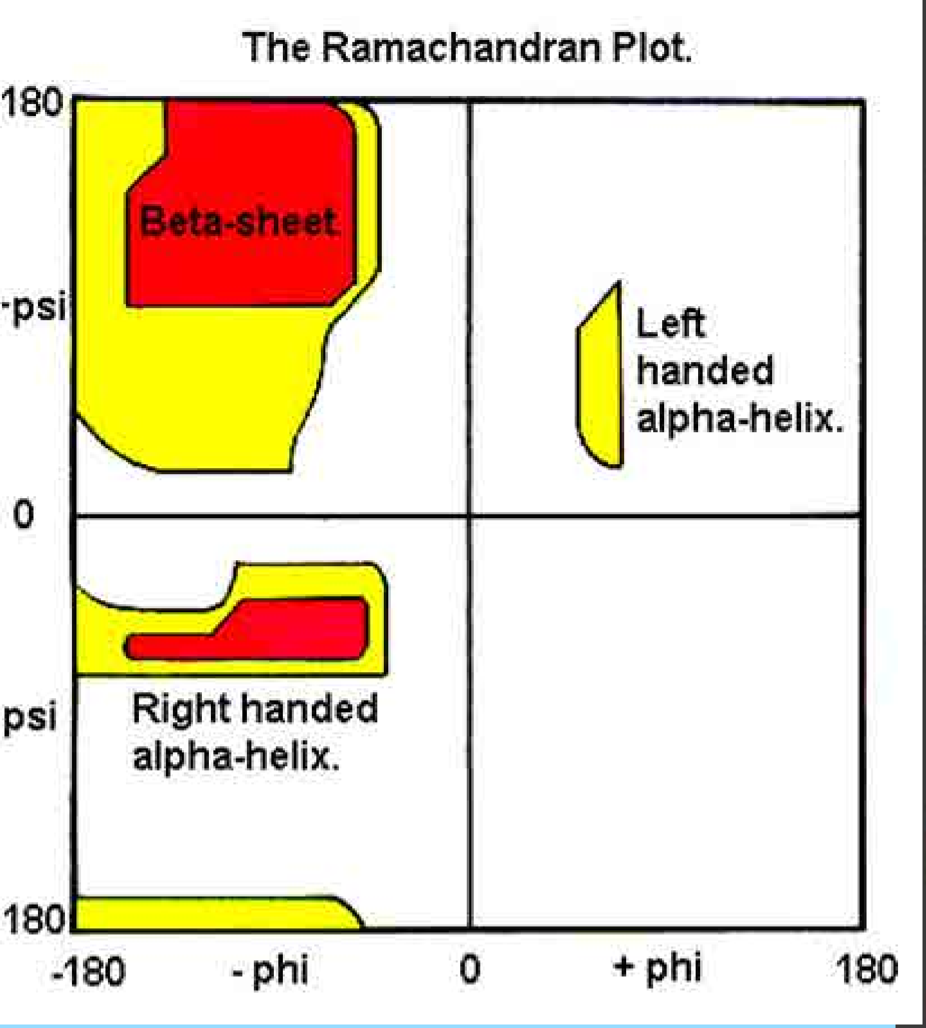
1. Differentiation between crystalline and amorphous materials;
2. Determination of the structure of crystalline materials;
3. Determination of electron distribution within the atoms, and throughout the unit cell;
4. Determination of the orientation of single crystals;
5. Determination of the texture of polygrained materials;
6. Measurement of strain and small grain size…..etc

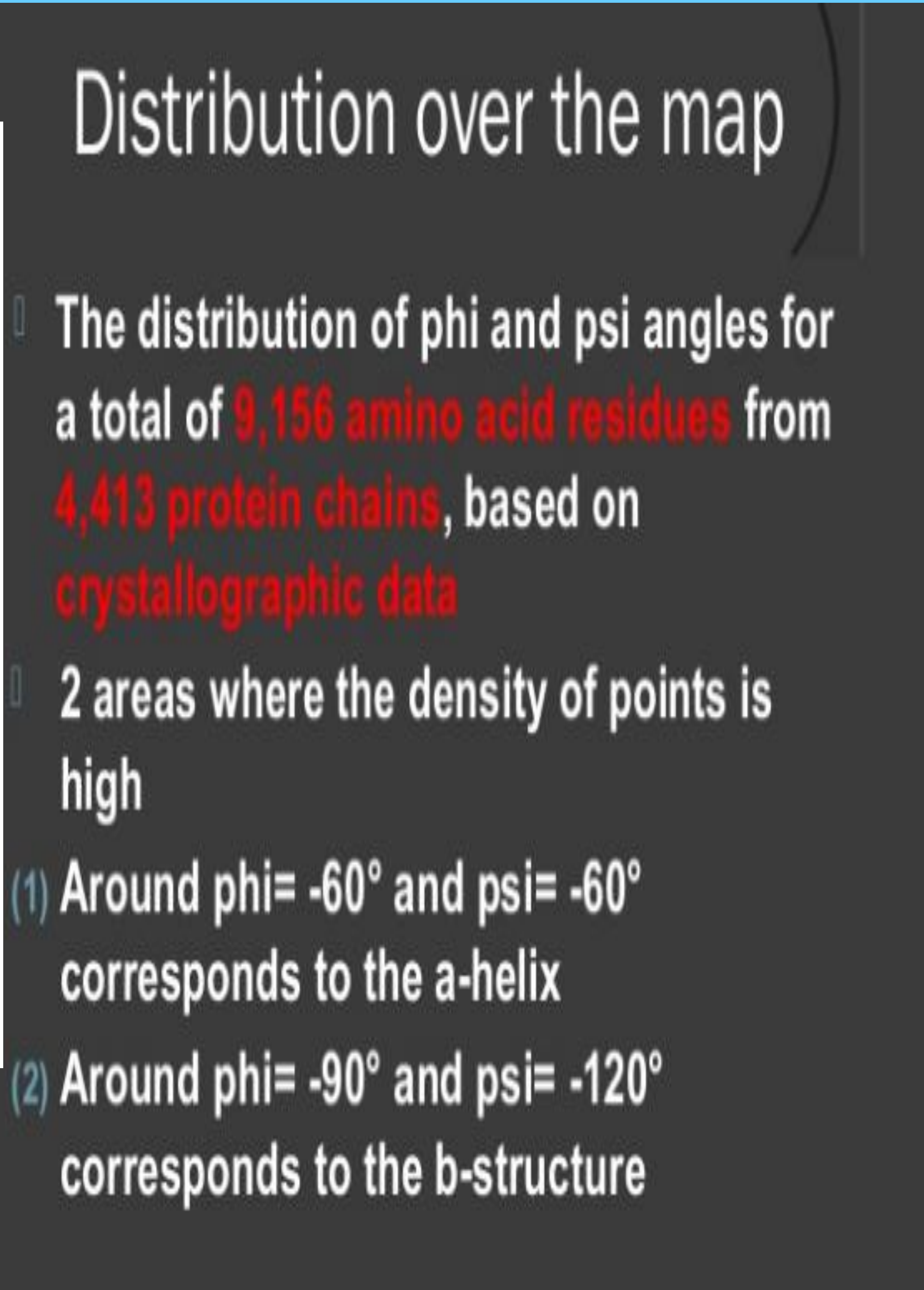
# Ramachandran Plot



- Ramachandran plot – to visualize the backbone of aminoacid residues
- Used for structural validation and to calculate the possible phi and psi angles that accounts for the aminoacid residues
- Done by several software namely

WHATIF RAMACHANDRAN PLOT





# Distribution over the map

- The distribution of phi and psi angles for a total of 9,156 amino acid residues from 4,413 protein chains, based on crystallographic data
- 2 areas where the density of points is high

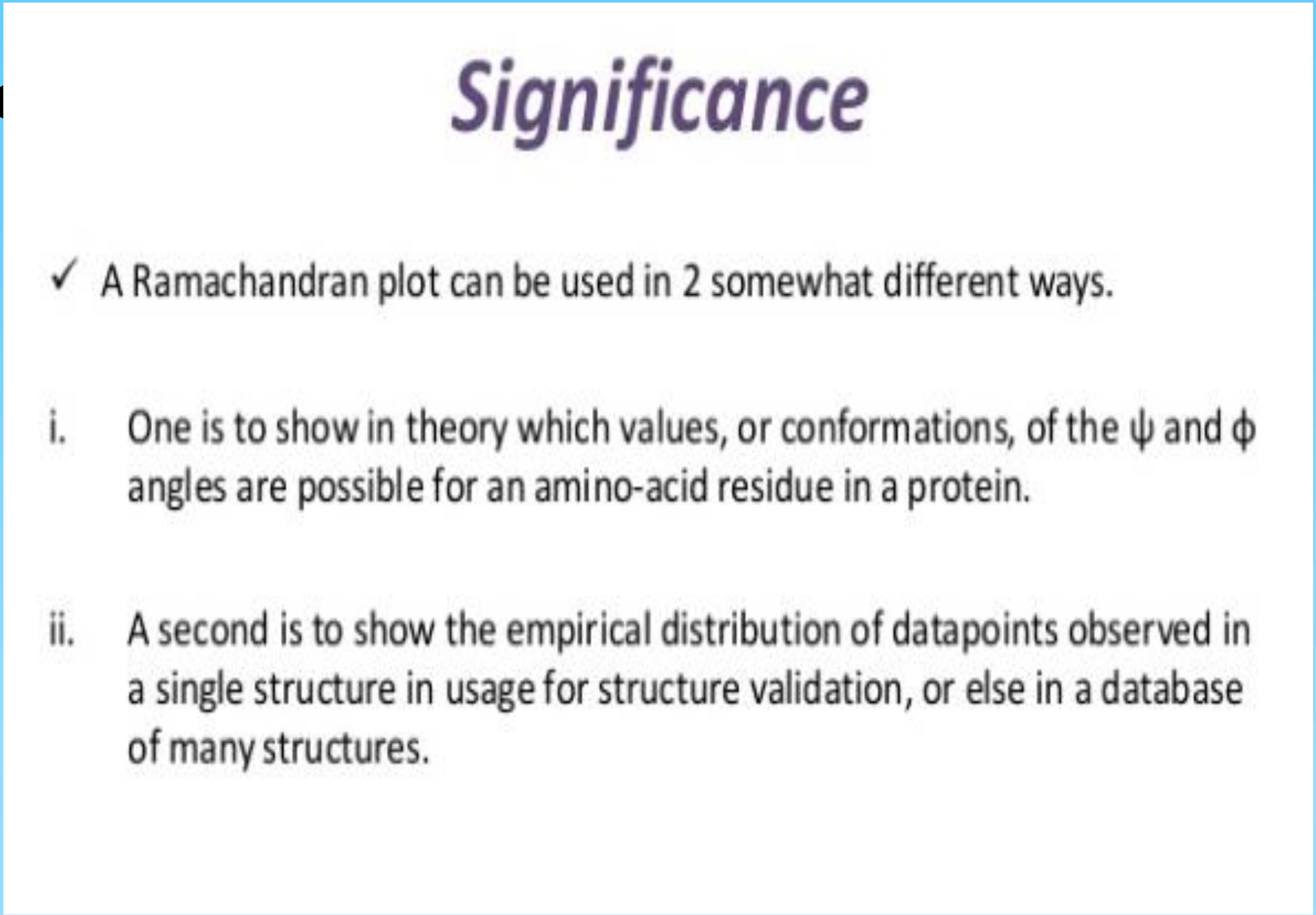
(1) Around phi= -60° and psi= -60° corresponds to the a-helix

(2) Around phi= -90° and psi= -120° corresponds to the b-structure

# Work of Ramachandran

A Ramachandran plot (also known as a Ramachandran diagram or a [φ,ψ] plot), originally developed in 1963 by G. N. Ramachandran, C. Ramakrishnan, and V. Sasisekharan

Initially proposed a modelled structure on collagen as a two bonded system based on the formation of two inter hydrogen bonds between their structures



# Significance

✓ A Ramachandran plot can be used in 2 somewhat different ways.

i. One is to show in theory which values, or conformations, of the ψ and ϕ angles are possible for an amino-acid residue in a protein.

ii. A second is to show the empirical distribution of datapoints observed in a single structure in usage for structure validation, or else in a database of many structures.