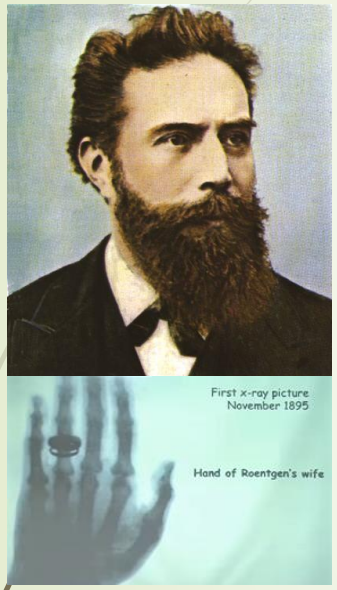
CHAPTER 4- X-RAYS DIFFERACTION

- Dr. Amita Chaudhary



First Nobel Prize in Physics was awarded in 1901 to Wilhelm Conrad Röntgen for the accidental discovery of X-rays in 1895.

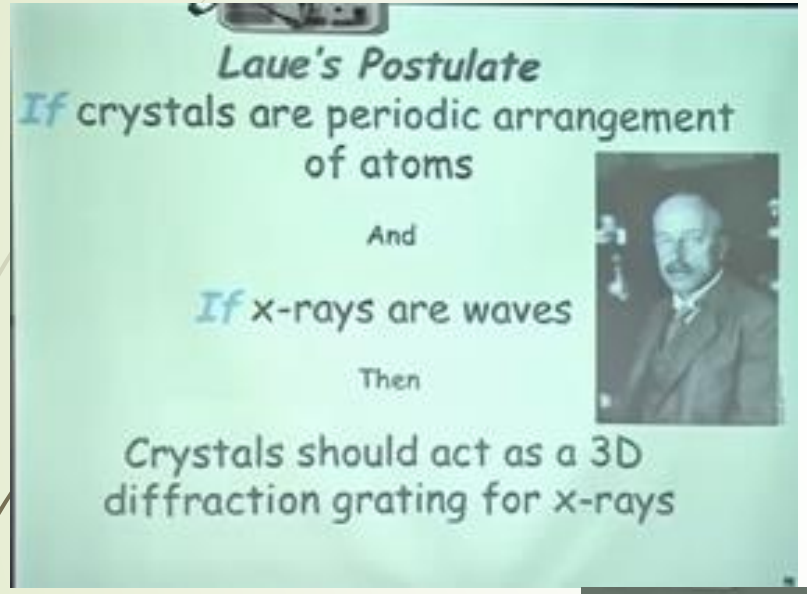
Max Theodor Felix von Laue received the Nobel Prize for Physics for 1914, was his discovery of the diffraction of X-rays on crystals.

The Nobel Prize in Physics 1915 was awarded jointly to Sir William Henry Bragg and William Lawrence Bragg "for their services in the analysis of crystal structure by means of X-rays

Bragg law $n\lambda = 2d \sin\theta$ *Essential condition for diffraction*

Some Aspects of X-Rays

X-rays are electromagnetic radiation of wavelength in the range of 0.5 to 2.5 Å.



Max Theodor Felix von Laue

Dual nature as any other electro-magnetic radiation

Wave nature $\lambda = \frac{c}{\nu}$ → Velocity of light = 3.00×10^8 m/sec

Particle nature $E = h\nu$

https://www.youtube.com/watch?v=QHMzFUo0NL8&feature=youtu.be

X-ray Diffraction

Similarity - from prior knowledge

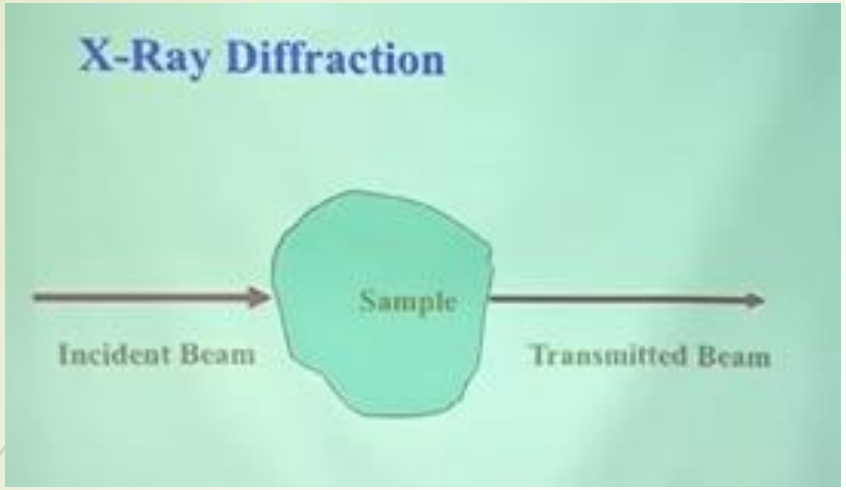
Diffraction – of visible light by a ruled grating

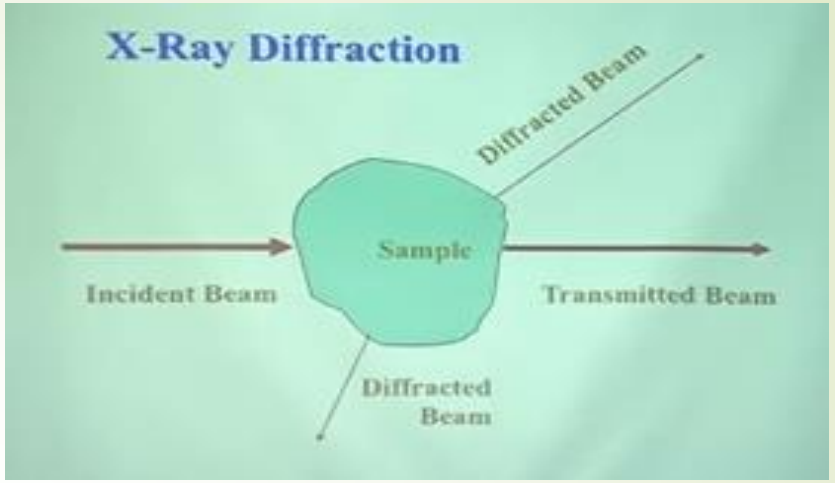
- Wave encounters set of regularly spaced scattering objects
- Wavelength of wave in question has same order of magnitude as of spacing between scattering centers

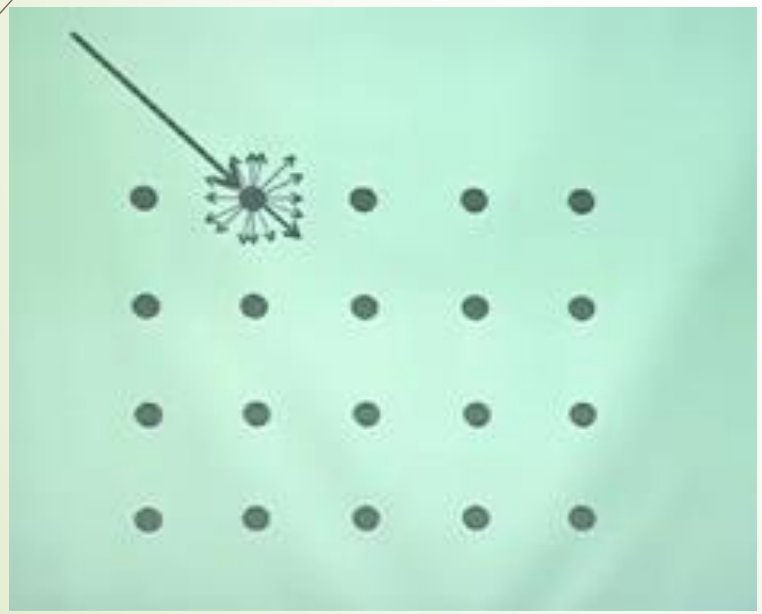
German physicist von Laue reasoned

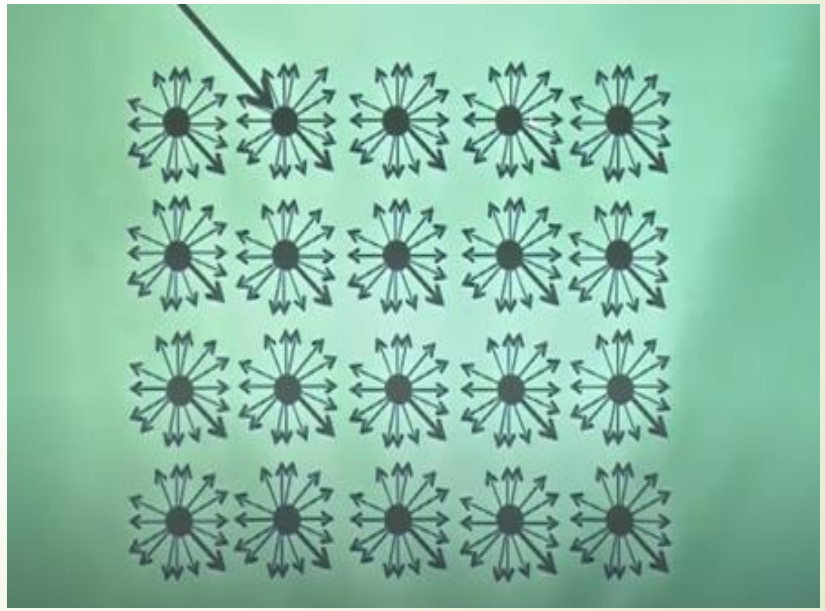
- If crystals are composed of regularly spaced atoms - can act as scattering centers for x-rays
- If x-rays have wavelength about equal to interatomic distance in crystal

It should be possible to diffract x-rays by means of crystals

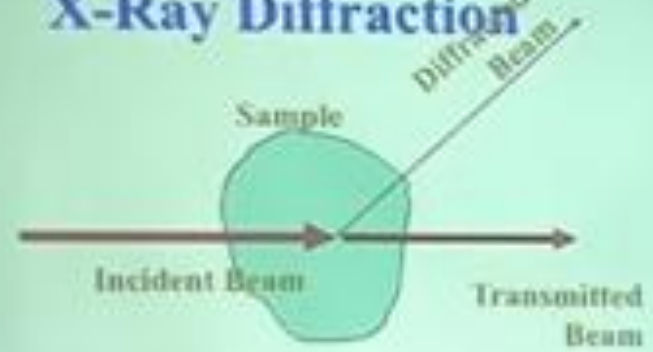

X-Ray Diffraction
Sample
Incident Beam
Transmitted Beam


X-Ray Diffraction
Diffracted Beam
Sample
Incident Beam
Transmitted Beam
Diffracted Beam





X-Ray Diffraction



Braggs Law (Part 1): For every diffracted beam there exists a set of crystal lattice planes such that the diffracted beam appears to be specularly reflected from this set of planes.

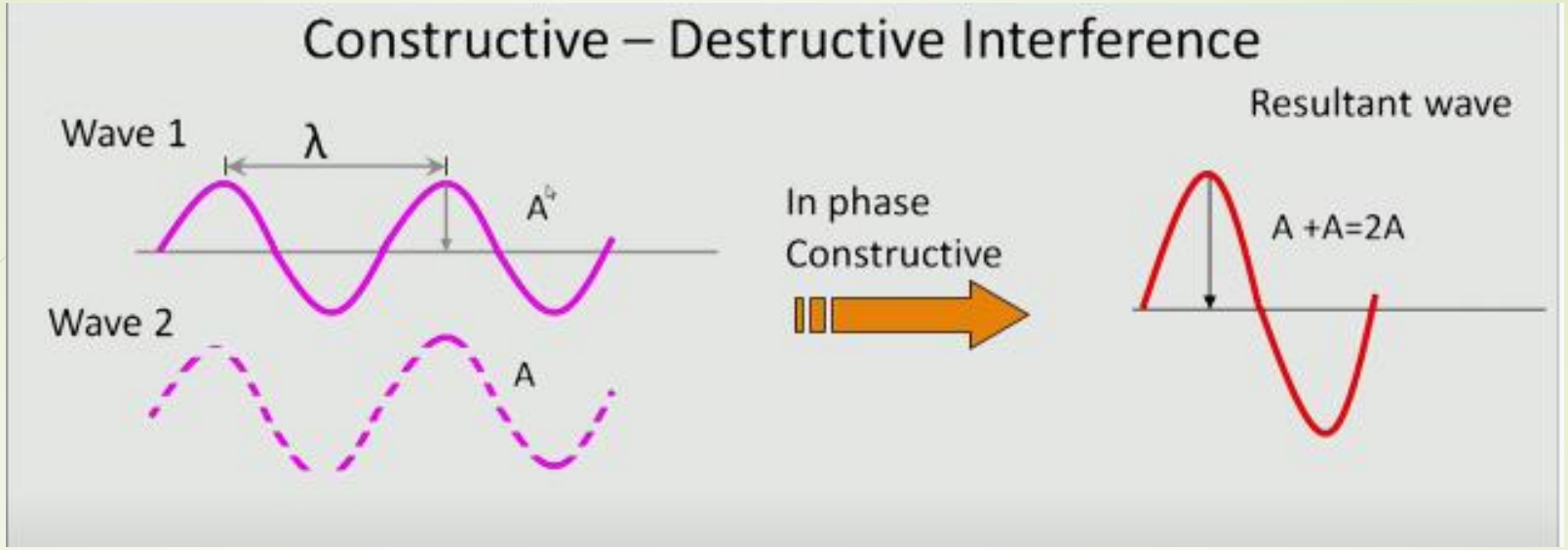
X-Ray Diffraction

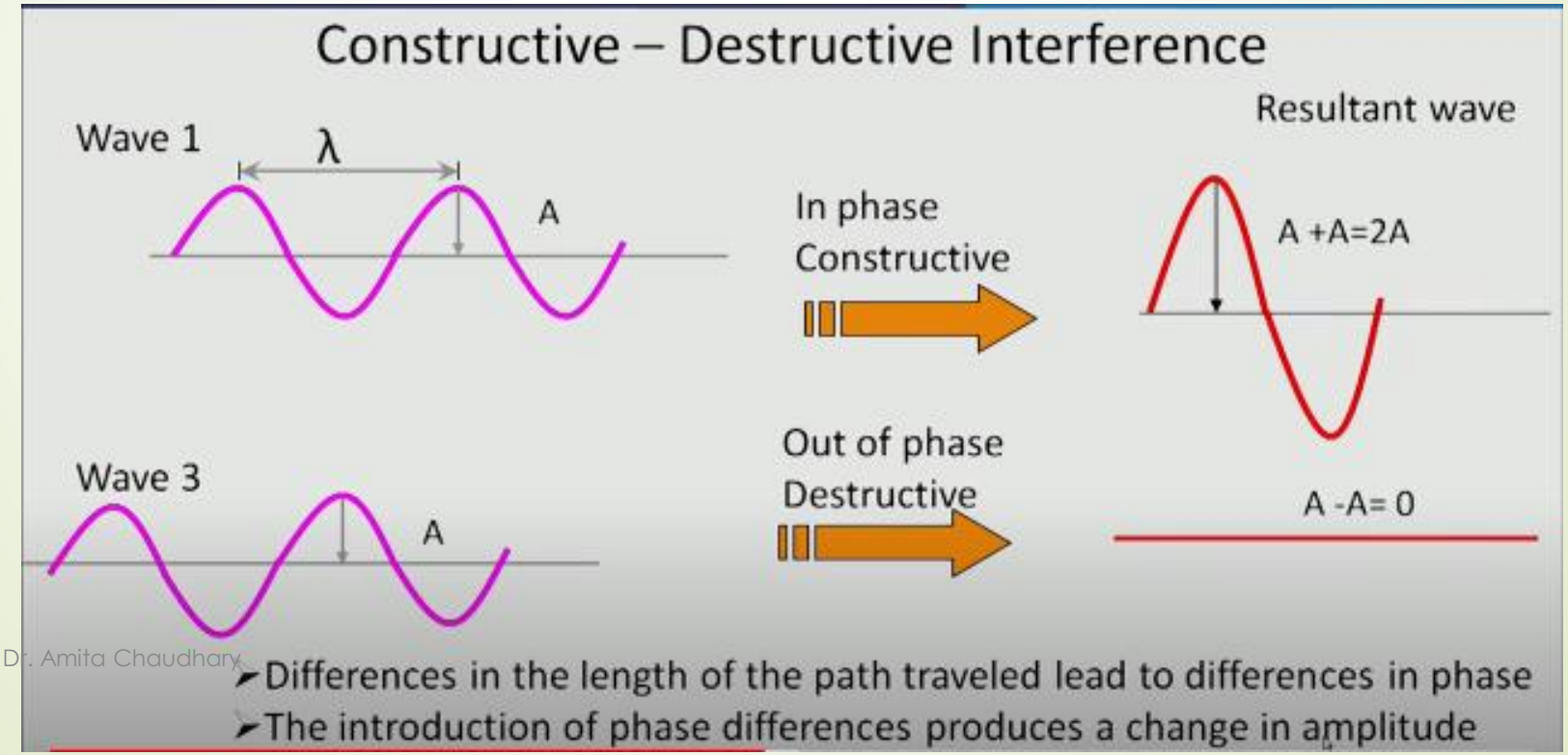
Braggs' recipe for Nobel prize?

Call the diffraction a reflection!!!

"The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them".

W.L. Bragg

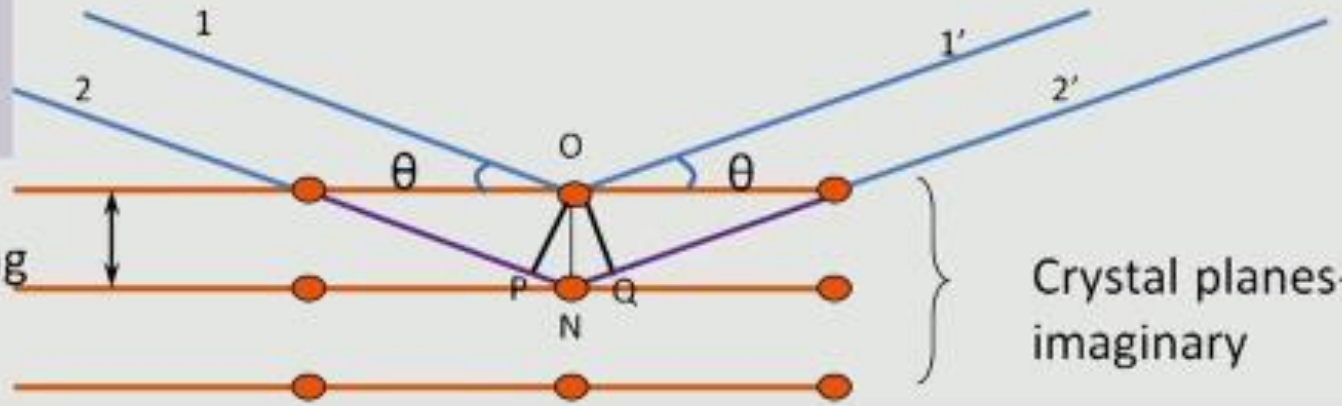




Diffraction

Simplified geometry given by W. H. Bragg and W. L. Bragg

Two parallel rays 1 and 2 making angle θ with the crystal planes

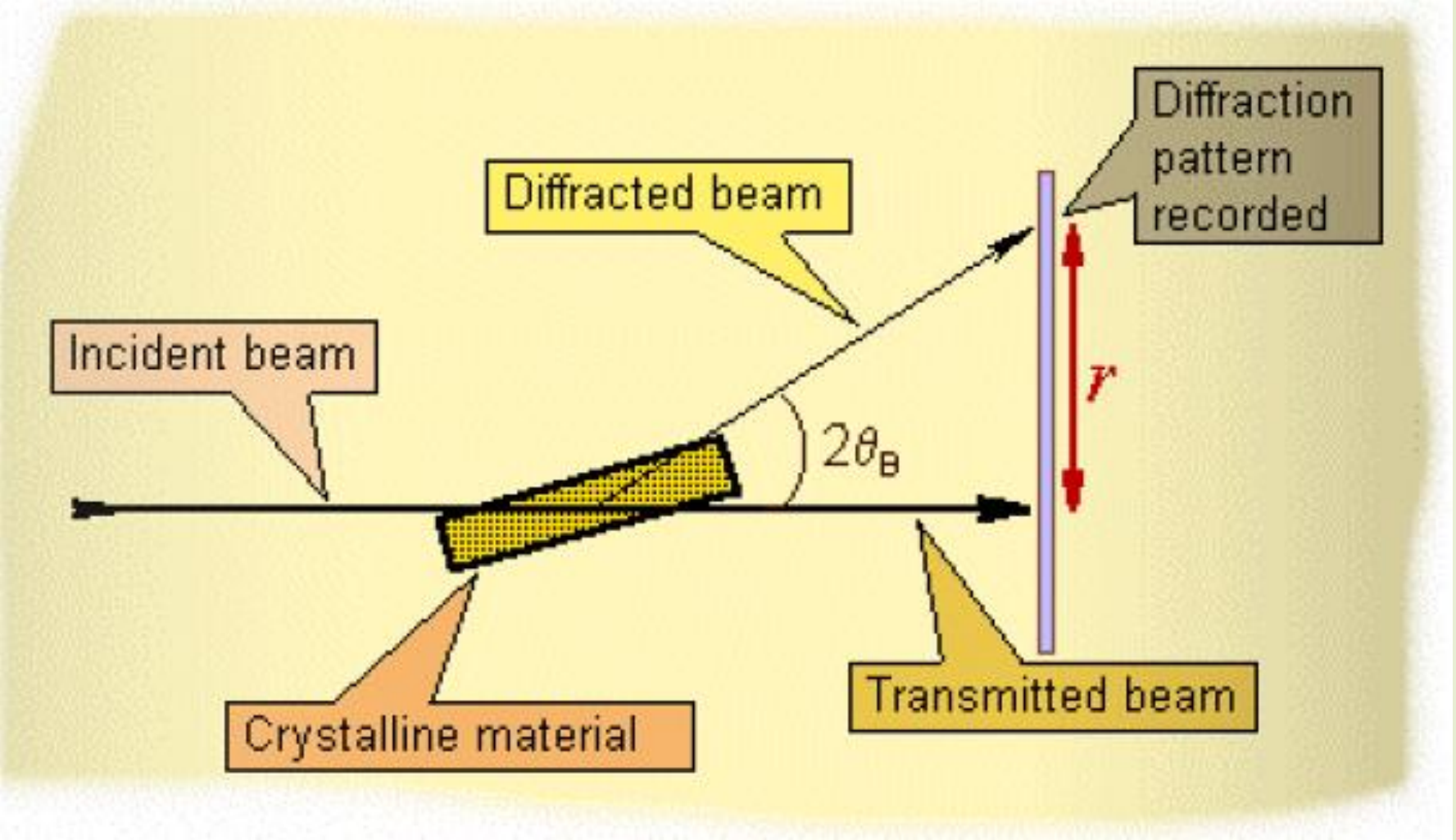


d = interplanar spacing

Crystal planes- imaginary

For constructive interference the distance PNQ travelled by 2-2' should be equal to nλ

Bragg law $n\lambda = 2d \sin\theta$ *Essential condition for diffraction*


Diffraction pattern recorded
Diffracted beam
Incident beam
$2\theta_B$
Y
Crystalline material
Transmitted beam

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

Constructive interference occurs only when

$n\lambda = AB + BC$

$AB = BC$

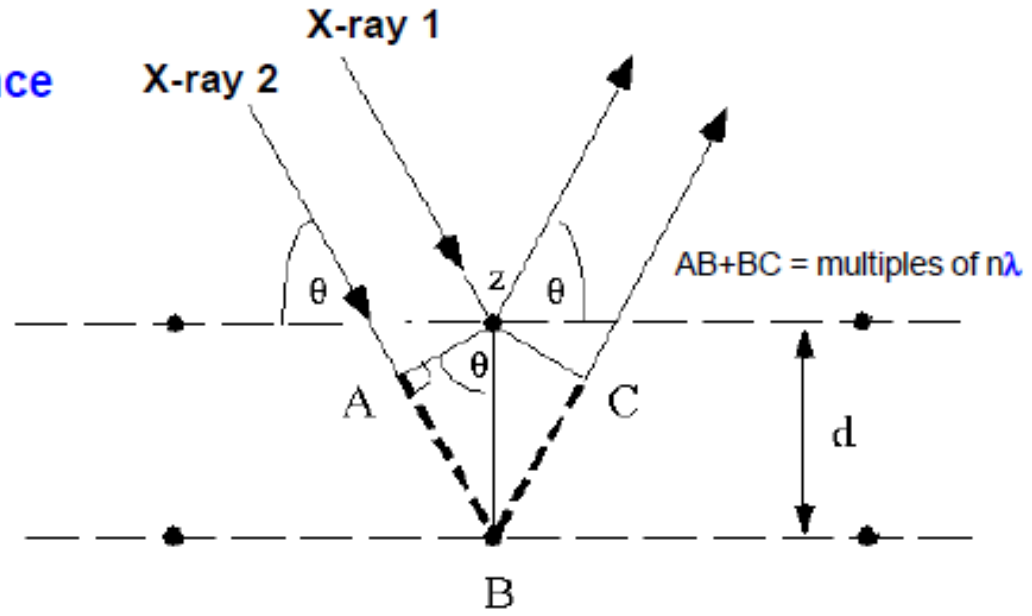
$n\lambda = 2AB$

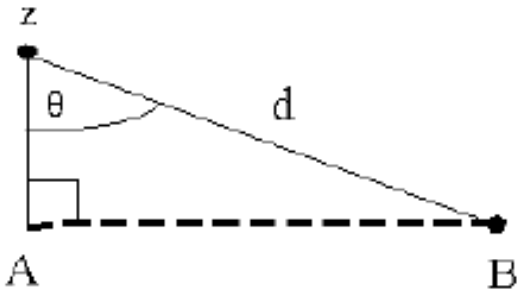
$\sin\theta = AB/d$

$AB = d\sin\theta$

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

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





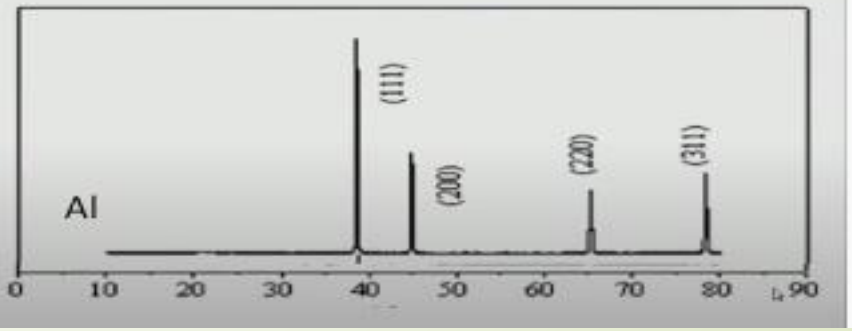
Crystal structure from X-ray diffraction peaks

Bravais lattice	Reflection present	Reflection absent
Simple	all	None
Base centered	h and k unmixed	h and k mixed
Body centered	(h+k+l) even	(h+k+l) odd
Face centered	h k and l unmixed	h k and l mixed

Crystal structure from X-ray diffraction peaks

Diffraction scan gives data in from of 2θ v/s Intensity

d spacing can be calculated from Bragg's law – If we know angle θand wavelength of X-ray used

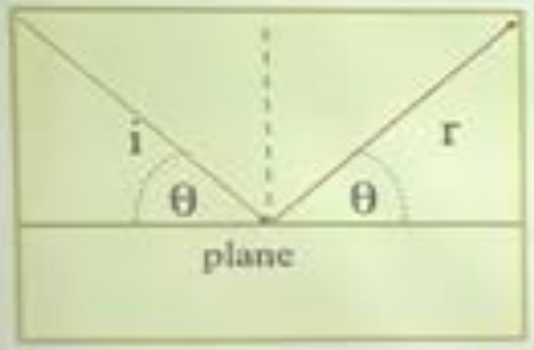


Why XRD?

- Measure the average spacings between layers or rows of atoms
- Determine the orientation of a single crystal or grain
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline regions

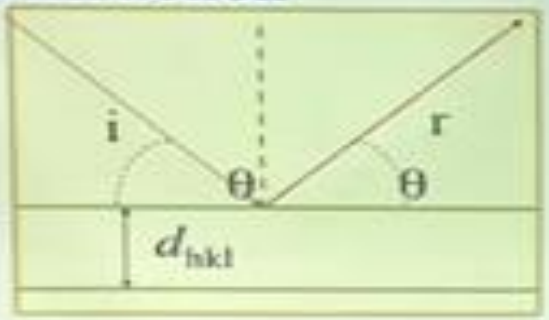
X-Ray Diffraction

Braggs Law (Part 1): the diffracted beam appears to be **specularly** reflected from a set of crystal lattice planes.



Specular reflection: Angle of incidence =Angle of reflection (both measured from the plane and not from the normal)

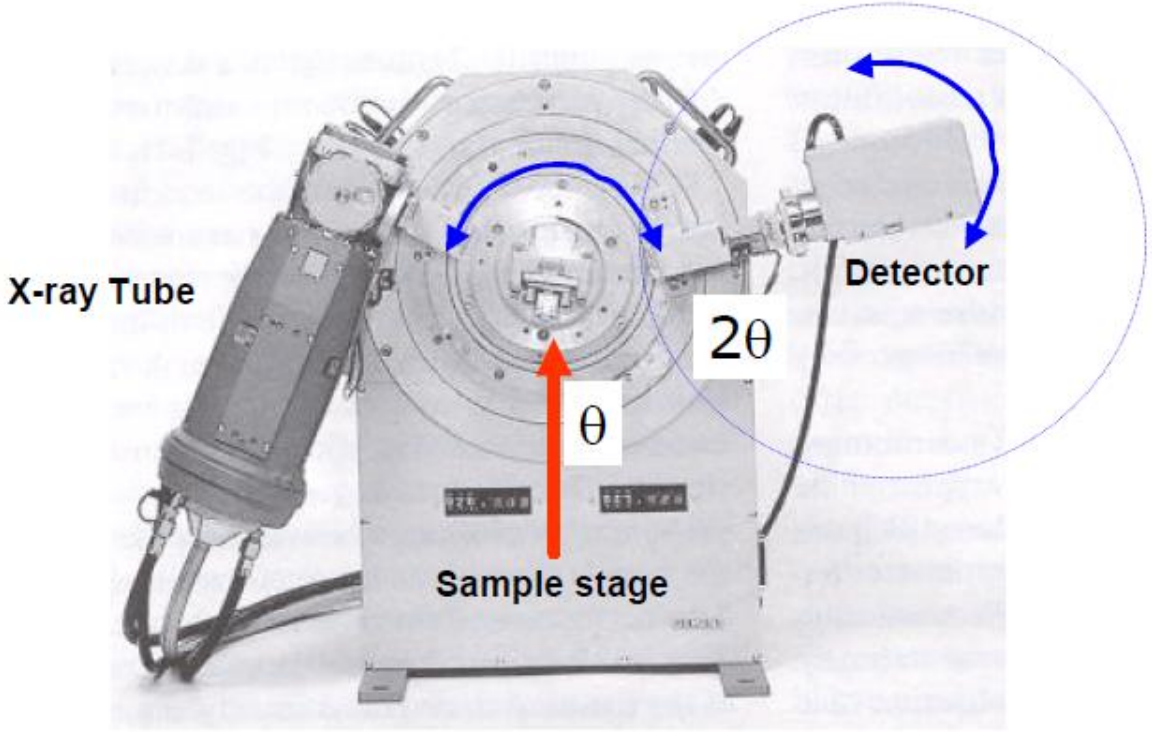
X-Ray Diffraction

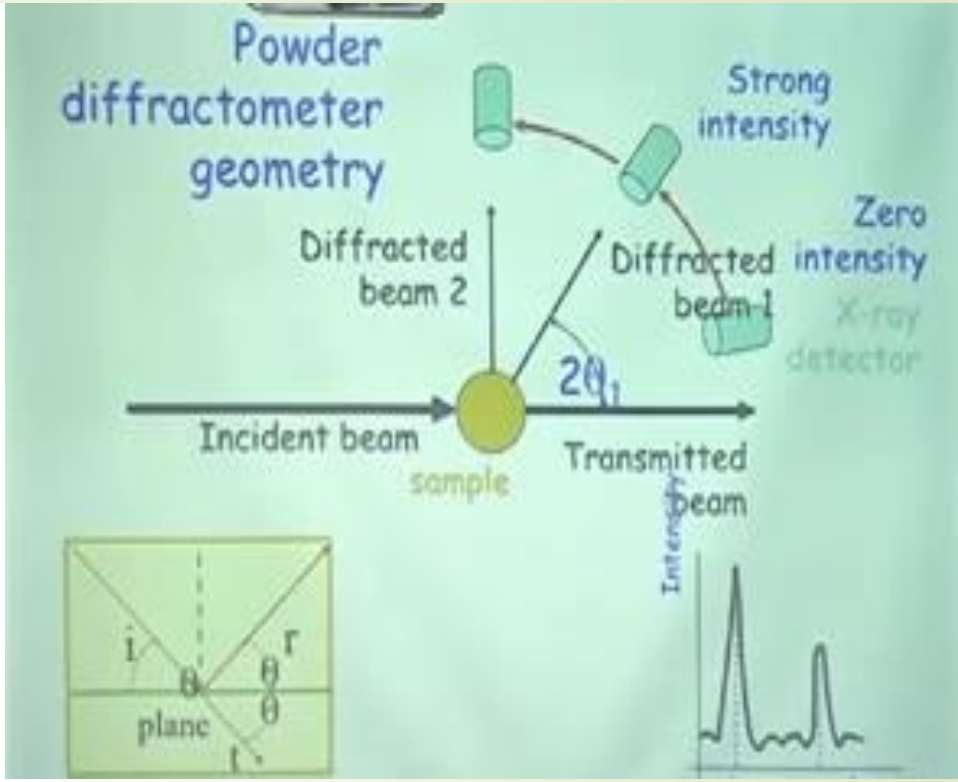


Bragg's law (Part 2):

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

A Modern Automated X-ray Diffractometer





X-rays
Characteristic Radiation, K_α

Target	*Wavelength, Å*
Mo	0.71
Cu	1.54
Co	1.79
Fe	1.94
Cr	2.29

What is XRD?

X-ray diffraction is a powerful non-destructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the atomic positions within the lattice planes. Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in a given material. An online search of a standard database for X-ray powder diffraction patterns enables quick phase identification for a large variety of crystalline samples

Working

X-ray diffraction is based on Bragg's law ($n\lambda = 2d\sin\theta$). A monochromatic beam of X-rays is allowed to incident on a sample, and reflected X-rays are detected by a detector. X-ray diffraction technique is useful in determining the percent crystallinity in the natural fibers before and after physical or chemical treatment. Generally, X-ray diffractogram of the sample is recorded on an X-ray diffractometer operating at known voltages and current using a Cu Kα X-rays (λ = 0.15406 nm) over the 2θ range from 10 to 100 degrees in the steps of 0.01 degree at room temperature in open quartz sample holders. Amorphous regions of the samples produce broad peak, whereas crystalline regions produce sharp peaks. The degree of crystallinity (X_c) can be determined by determining the intensities of the crystalline (I_c) and amorphous (I_a) contents in the sample:

$$X_c = \frac{I_c}{I_a + I_c} \times 100$$

What is X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

Fundamental Principles

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

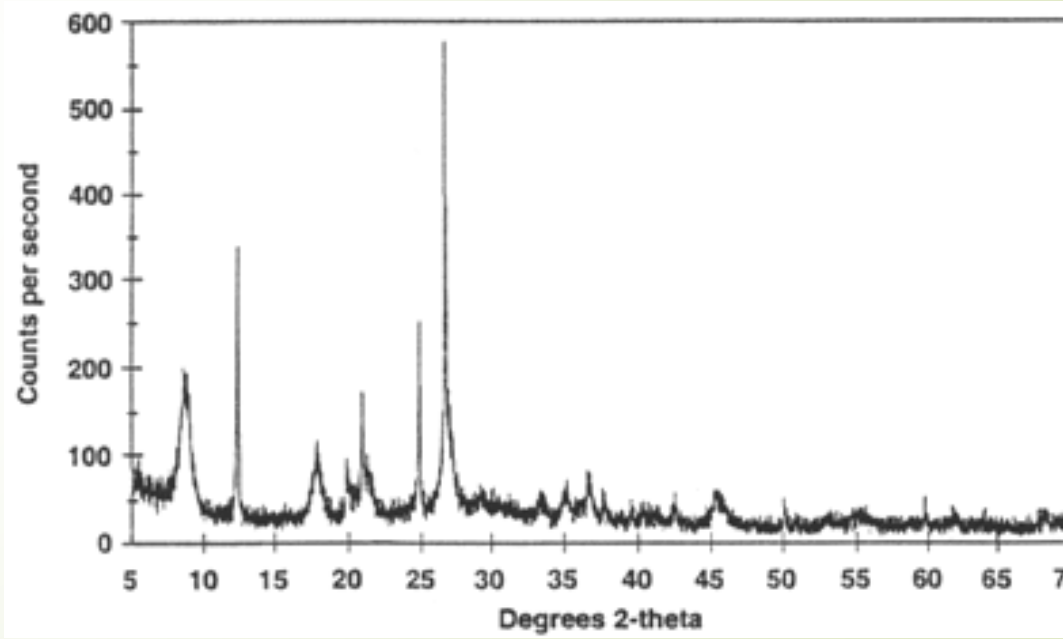
X-ray Powder Diffraction (XRD) Instrumentation - How Does It Work?

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector.

The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction.

Copper is the most common target material for single-crystal diffraction, with CuKα radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. 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.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.



Applications

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. Other applications include:

•characterization of crystalline materials

•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

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 an unambiguous mineral determination
•Minimal sample preparation is required
•XRD units are widely available
•Data interpretation is relatively straight forward

Limitations

- Homogeneous and single phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacings, hkls)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur and worsens for high angle 'reflections'

Sample Collection and Preparation

Determination of an unknown requires:
Requirement: The sample material, an instrument for grinding, and a sample holder.

•Obtain a few tenths of a gram (or more) of the material, as pure as possible

•Grind the sample to a fine powder, typically in a fluid to minimize inducing extra strain (surface energy) that can offset peak positions, and to randomize orientation. Powder less than ~10 μm(or 200-mesh) in size is preferred

•Place into a sample holder or onto the sample surface: Packing of fine powder into a sample holder.

Determination of an Unknown Substance

The d-spacing of each peak is then obtained by solution of the Bragg equation for the appropriate value of λ. Once all d-spacings have been determined, automated search/match routines compare the *d*s of the unknown to those of known materials. Because each mineral has a unique set of d-spacings, matching these d-spacings provides an identification of the unknown sample. A systematic procedure is used by ordering the d-spacings in terms of their intensity beginning with the most intense peak. Files of d-spacings for hundreds of thousands of inorganic compounds are available from the International Centre for Diffraction Data as the Powder Diffraction File (PDF). Many other sites contain d-spacings of minerals such as the American Mineralogist Crystal Structure Database. Commonly this information is an integral portion of the software that comes with the instrumentation.

Numerical based on Bragg's equation

A beam of X-rays of wavelength 0.071 nm is diffracted by (110) plane of rock salt with lattice constant of 0.28 nm. *Find the glancing angle for the second-order diffraction.*

Sol: Given data are:
Wavelength (λ) of X-rays = 0.071 nm
Lattice constant (*a*) = 0.28 nm
Plane (*hkl*) = (110)
Order of diffraction = 2
Glancing angle θ = ?
Bragg's law is $2d \sin\theta = n\lambda$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \text{because rock salt is FCC}$$

$$= \frac{0.28 \times 10^{-9}}{\sqrt{1^2 + 1^2 + 0^2}}\,\text{m} = \frac{0.28 \times 10^{-9}}{\sqrt{2}}\,\text{m}$$

Substitute in Bragg's equation

$$2 \times \frac{0.28 \times 10^{-9}}{\sqrt{2}} \sin\theta = 2 \times 0.071 \times 10^{-9}$$

$$\sin\theta = \sqrt{2} \times \frac{0.071}{0.28} = 0.3586$$

$$\theta = \sin^{-1}(0.3586) = 21.01^\circ \approx 21^\circ$$

Q2. Calculate the longest wavelength that can be analysed by a rock crystal of spacing d = 2.83Å in the (i) first order and (ii) second order.

(i) Here e = 2.28Å = 2.82×10^{-10} m, n = 1

For longest wavelength $(\sin\theta)_{max} = 1$

$$\therefore \lambda_{max} = \frac{2 \times 2.82 \times 10^{-10}}{1} = 5.64 \times 10^{-10} m = 5.64Å$$

(ii) Hence n = 2 and for longest wavelength $(\sin\theta)_{max} = 1$

$$\therefore \lambda_{max} = \frac{2d\sin\theta_{max}}{n} = \frac{2\times2.82\times10^{-10}\times1}{2} = 2.82 \times 10^{-10} m$$

$$= 2.82Å$$

Q3. Calculate the wavelength of an X-rays beam incident at 12^0 for the first order reflection from calcite crystal if the grating constant of the crystal is 3.035Å ($\sin 12^0 = 0.2079$).

$$\lambda = \frac{2d\sin\theta}{n}$$

Given $d = 3.035Å$, $\theta = 12^0$ and $n = 1$

$$\lambda = \frac{2 \times 3.035 \times \sin 12^0}{1} Å = 3.035 \times 0.2079Å = 1.25Å$$

Q4. The wavelengths of first-order X-rays are $2.20A^0$ at $27^08'$. Find the distance between the adjacent Miller planes.

Using Bragg's law,

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

Where,

$n = 1$

$\lambda = 2.29$ A°

$\theta = 27°8'$

Substituting the values, we get

$d = 2.51$ A°