162402 Instrumental Methods of Analysis

Unit – III

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X-Ray Diffraction Analysis

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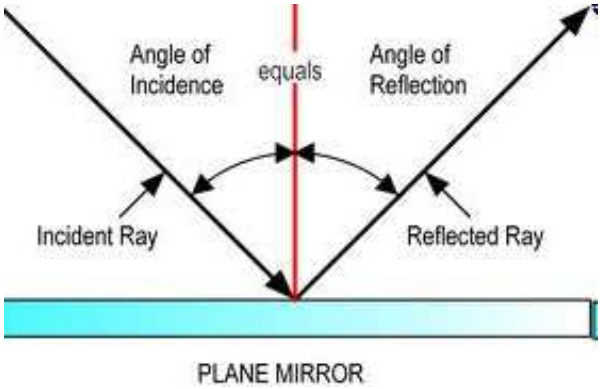
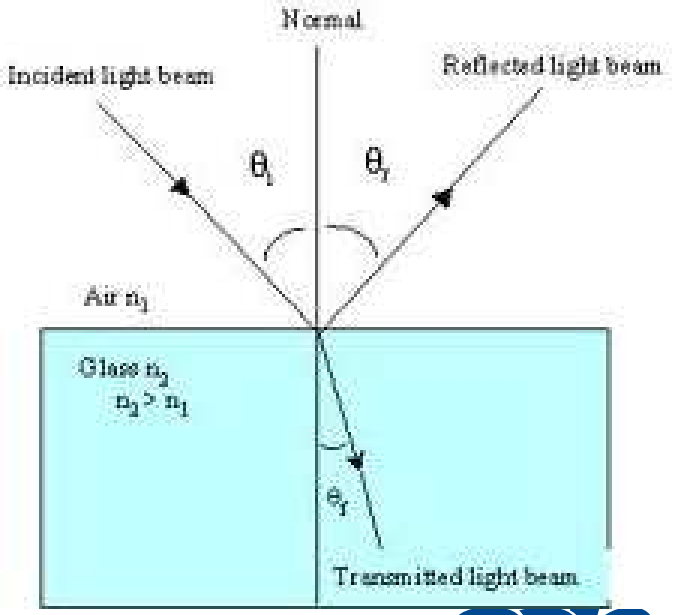
Light interaction with matter

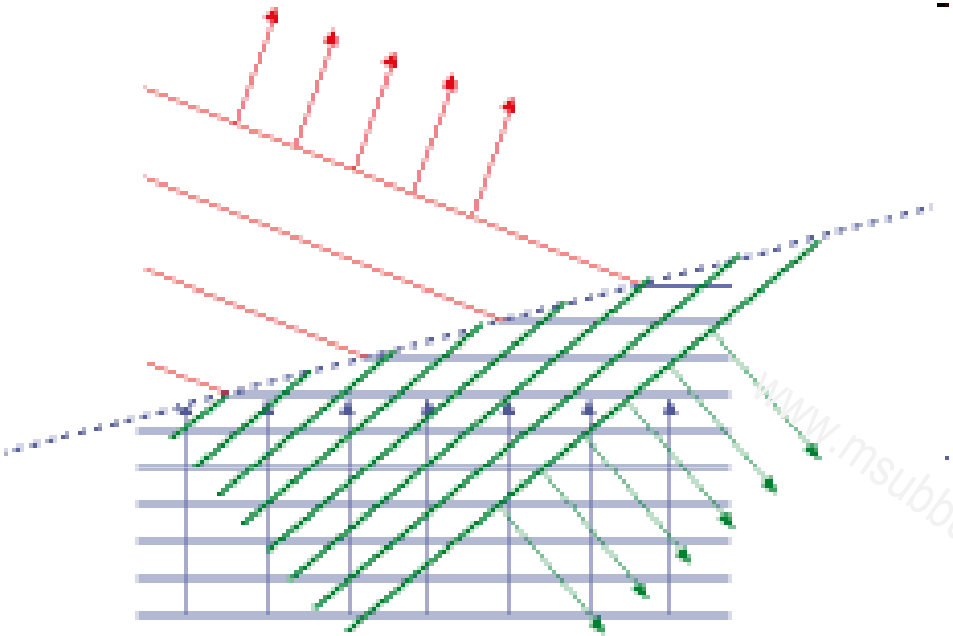
- Reflection- the bouncing of light when it hits a shiny surface



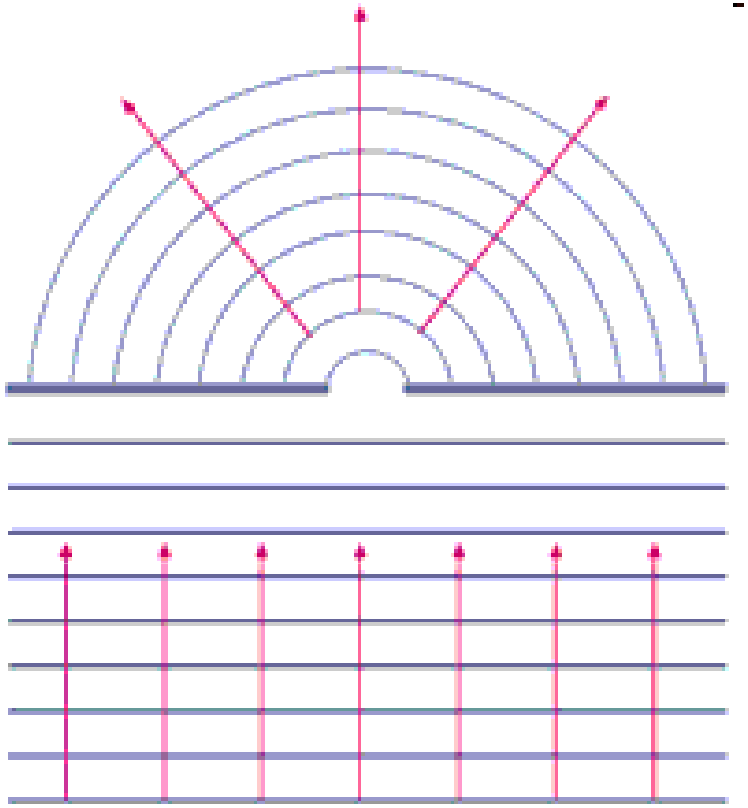
- Refraction- the bending of light when it passes from one median to another.

- Diffraction - refers to the "bending of waves around an edge" of an object. Diffraction depends on the size of the object relative to the wavelength of the wave.





When a wave meets the interface, it is either refracted or reflected.



A wave is diffracted by an aperture.

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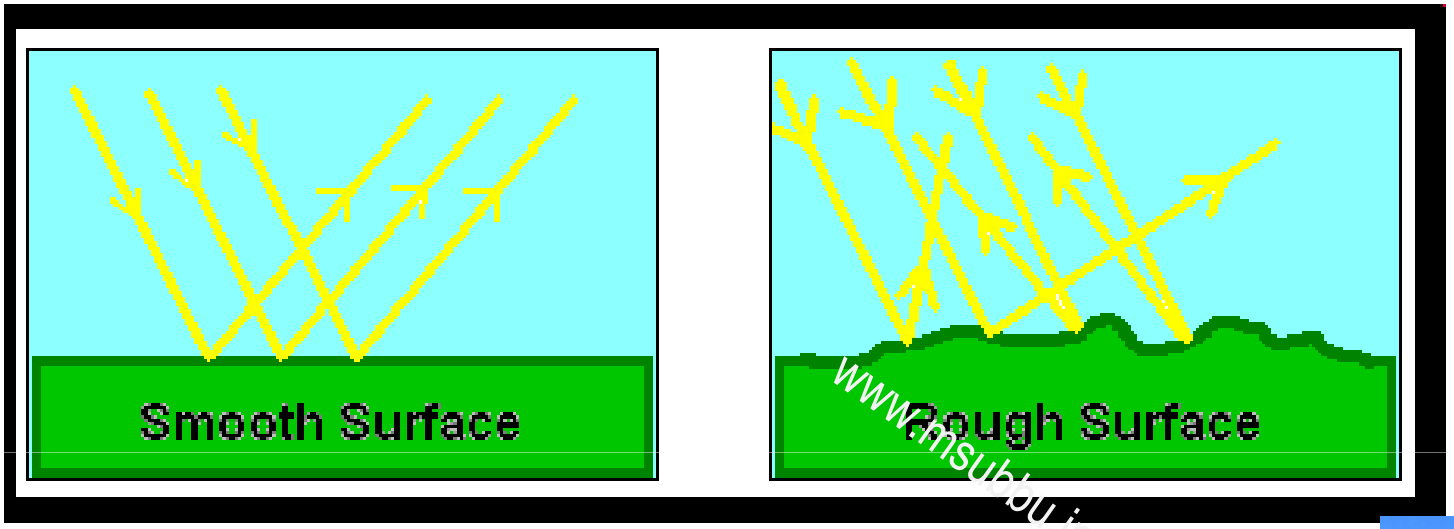
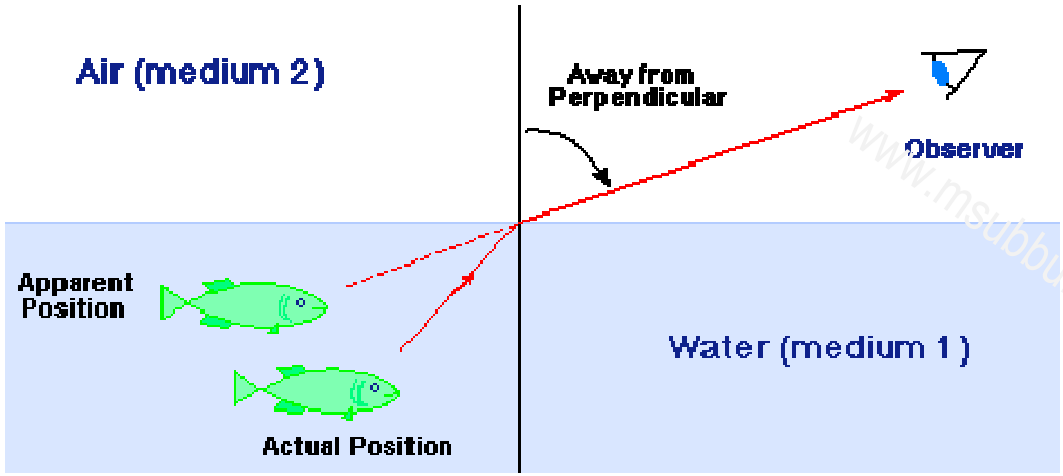
Reflection



Reflection occurs when light bounces off objects. How much reflection depends upon how even the surface is. If the surface is rough, the light scatters.

Refraction



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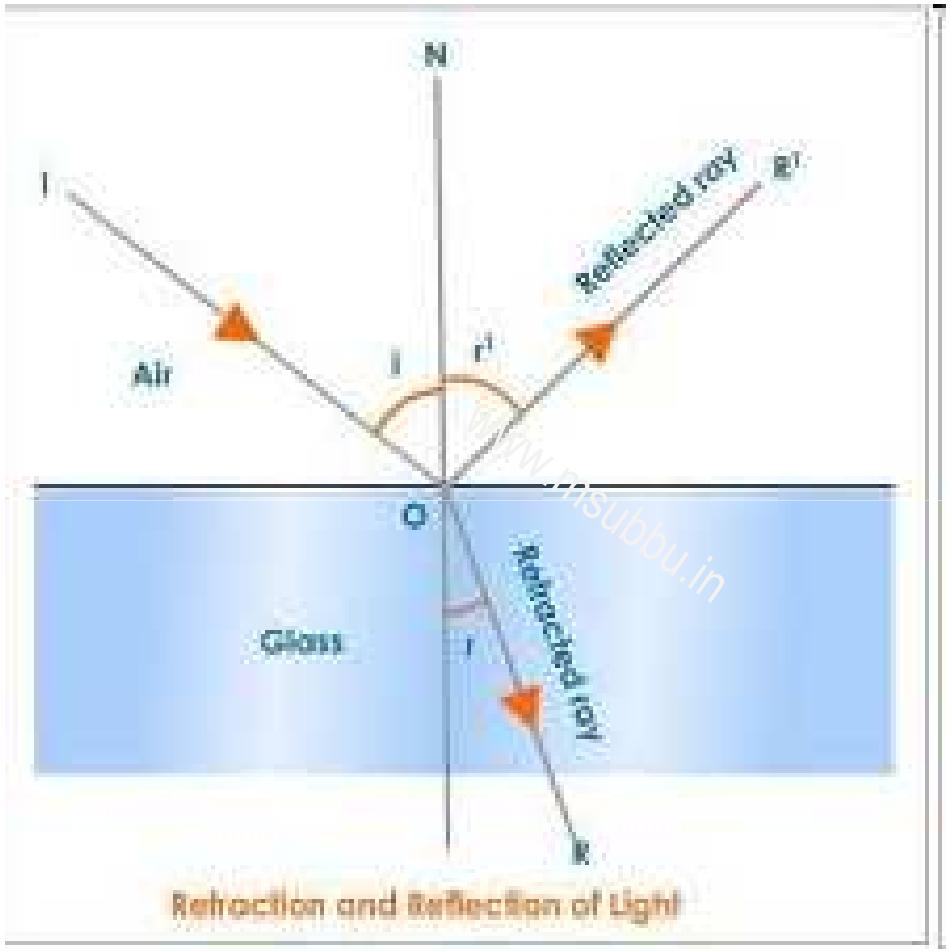

Refraction and Reflection of Light

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Diffraction

- Diffraction of light is the bending of light waves around an object.
- Appearance of a rainbow is the result of the diffraction of light. As sunlight encounters water droplets in the air, the light is broken into the colors of the rainbow. This typically occurs just before or after it rains and the air contains a large amount of water vapor or water droplets.
- Separation into the colors of the rainbow also occurs when a CD is placed at an appropriate angle in relation to a light source. The light waves bend around the edges of the groves cut into the CD and separates into the colors of the rainbow.
- Diffraction of light occurs when a light wave passes by a corner or through an opening or slit that is physically the approximate size of, or even smaller than that light's wavelength

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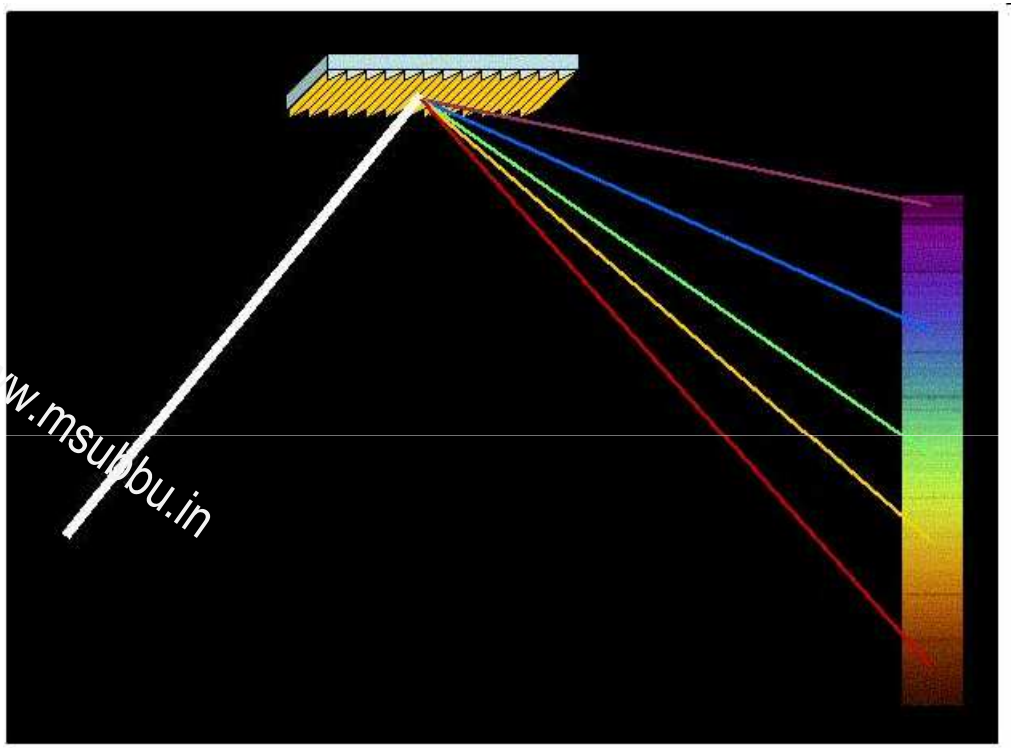
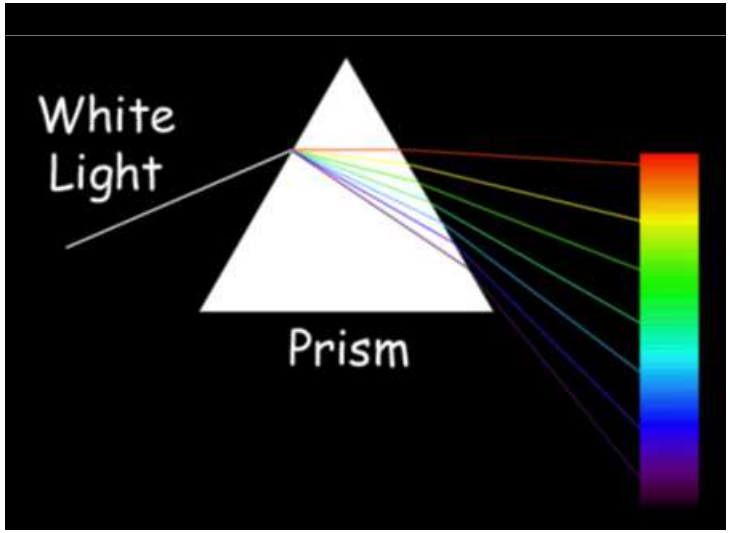
CD / DVD



Diffraction grating



Diffraction through a prism

Diffraction (contd.)

- The terms ***diffraction*** and ***scattering*** are often used interchangeably and are considered to be almost synonymous.

- Diffraction describes a specialized case of light scattering in which an object with regularly repeating features (such as a diffraction grating) produces an orderly diffraction of light in a diffraction pattern.

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X-Rays

- X-rays are electromagnetic radiation with wavelengths between about 0.02 ^{o}A and 100 ^{o}A. The wavelength of X-rays is on an atomic level and is much smaller than that of visible light.

- Since X-rays have a smaller wavelength than visible light, they have higher energy and are more penetrative. Its ability to penetrate matter, however, is dependent on density of the matter. Therefore, X-rays are useful in exploring structures of atoms.

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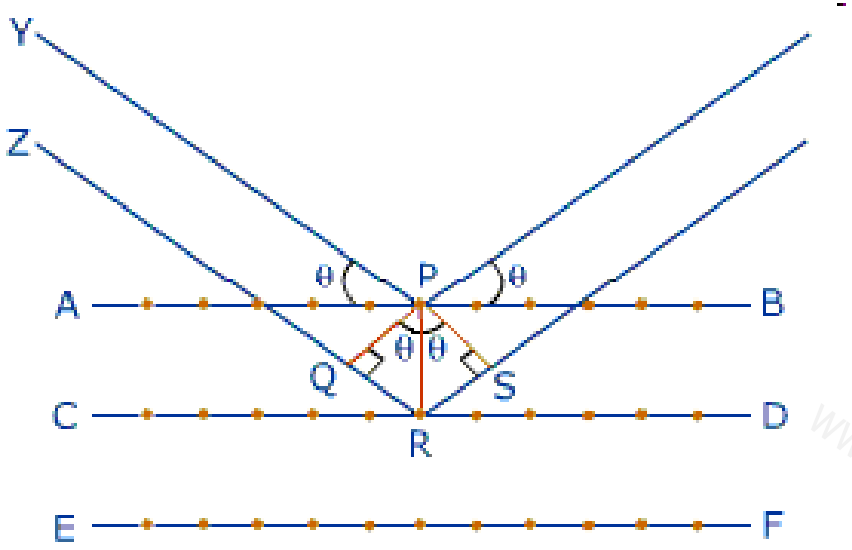
X-ray Diffraction

- When an X-ray beam strikes a crystal surface at some angle θ, a portion is scattered by the layer of atoms at the surface. The un-scattered portion of the beam penetrates to the second layer of atoms where again a fraction is scattered, and the remainder passes on to the third layer. The cumulative effect of this scattering from the regularly spaced centers of the crystal is a diffraction of the beam in much the same way as visible radiation is diffracted by a reflection grating

Bragg's Law Derivation



The XRD process is based upon the principle that a crystal may be considered to be made up of a number of parallel equidistant atomic planes, as represented by lines AB, CD and EF in the figure.

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Suppose two waves (Y and Z) of X-ray beams, which are in phase falls on the surface of the crystal. If the ray Y gets reflected from the first layer i.e., AB line and the ray Z is reflected from the second layer of atoms i.e., CD line, then it is evident that as compared to the ray Y, ray Z has to travel a longer distance, equal to QRS in order to emerge out of the crystal. If the waves Y and Z are in phase after reflection, the difference in distance traveled by the two rays must be equal an integral number of wavelength ($n\lambda$), for constructive interference.

Thus,
Distance QRS = nλ .....(i)
It is obvious from the figure that
QR = RS = PR sinθ
Therefore QRS = 2 PR sinθ .....(ii)
If the distance between the successive atomic planes is = d
Then, PR = d ...……(iii)
So, from equations (i), (ii) and (iii)

nλ = 2d sinθ

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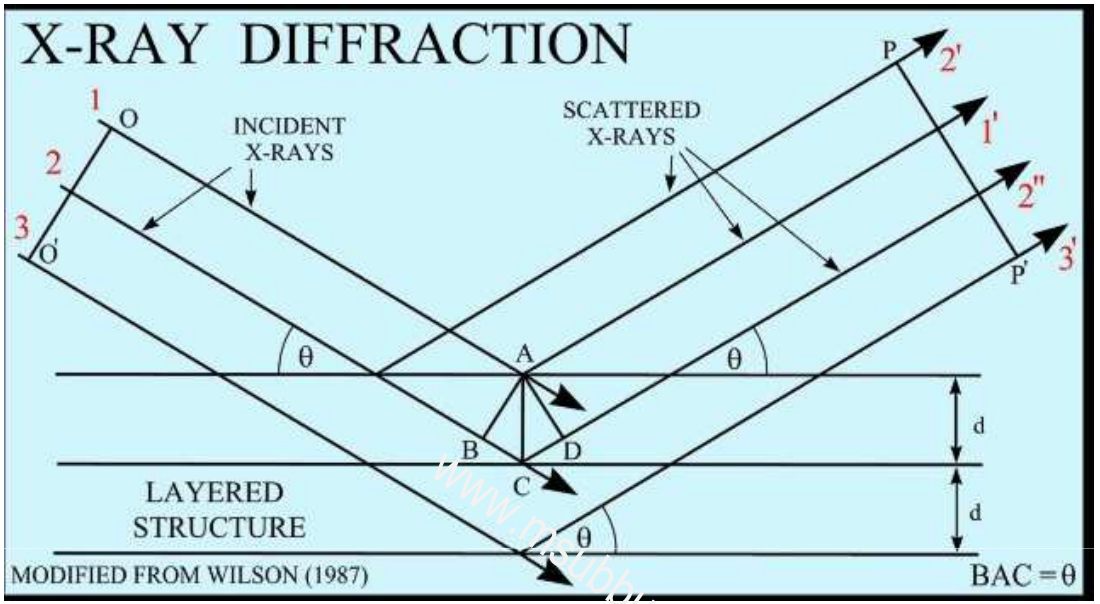
Thus, Bragg gave a mathematical equation to establish a relationship between wave length of the incident X-ray, the distance between the layers and the angle of diffraction.

Here, λ = wavelength of X-ray used
θ = Angle between incident X-rays and plane of the crystal. The diffracted beam makes an angle 2θ.
d = Distance between planes of the constituent particles in a crystal.
n = An integer (1, 2, 3, 4, …etc).

Bragg's law Usage



From Bragg's law, we know that $n\lambda = 2d \sin\theta$, therefore if we know the wavelength λ of the X-rays going in to the crystal, and we can measure the angle *theta* of the diffracted X-rays coming out of the crystal, then we can determine the spacing between the atomic planes. This spacing is the called the d-spacing. If we now reorient the crystal to a different atomic plane, we can measure the d-spacing in other planes. By doing multiple x-ray diffractions at different crystal orientations, we can determined crystal structure and the size of the unit cell of the crystal.

Energy Levels in Atoms

- An atom is composed of a nucleus and electrons.
- The electrons are arranged in shells around the nucleus with the valence electrons in the outer shell.
- The shells are named starting with the shell closest to the nucleus, which is called the K shell. The K shell is the lowest in energy.
- The shells moving out from the nucleus are named the L shell, M shell, and so on alphabetically.

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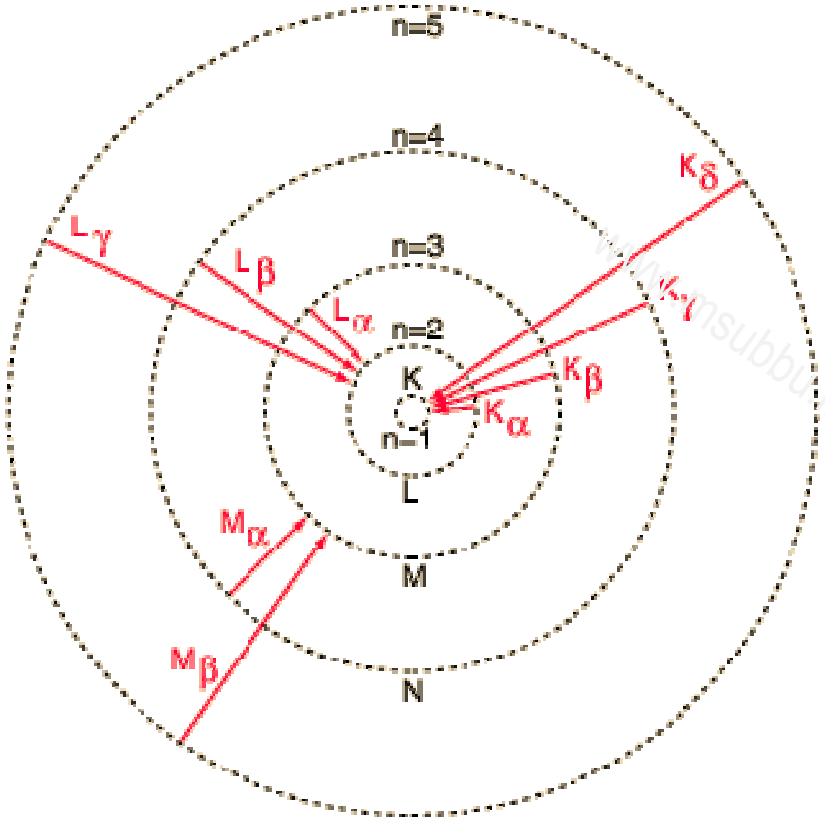
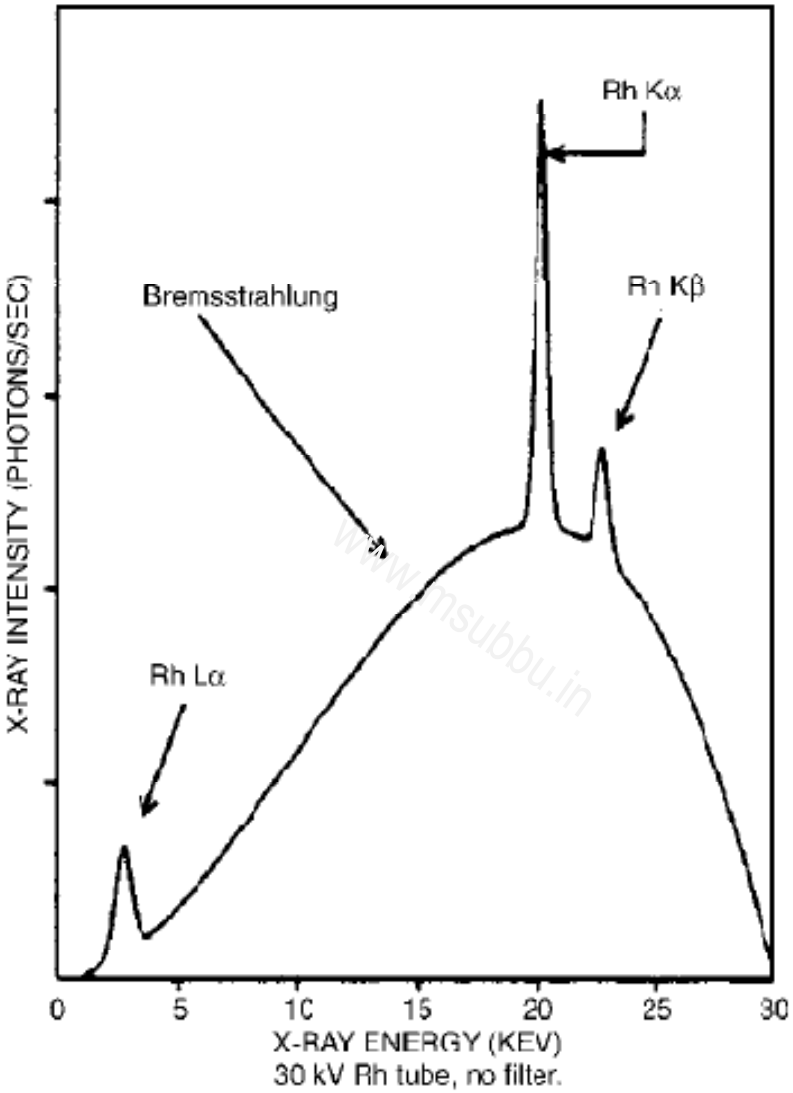
X-ray Transitions



X-ray emission lines from electron transitions terminating in the K shell are called K lines, lines from transitions terminating in the L shell are called L lines, and so on.



X-ray emission spectrum obtained by bombarding rhodium metal (Rh) with electrons.

Duane-Hunt Law

$$\text{Energy (keV)} = \frac{12.4}{\lambda\,(\text{Å})}$$

- The Duane–Hunt Law law gives the maximum frequency (or the minimum wavelength) of X-rays that can be emitted by Bremsstrahlung (radiation that arises from retardation by particles) in an X-ray tube by accelerating electrons through an excitation voltage *V* into a metal target.

- This law gives the conversion factor between energy and wavelength.

- Most X-ray systems express wavelength in angstroms and energy in keV.

Moseley’s Law

- **Moseley's law** is an empirical law concerning the characteristic x-rays that are emitted by atoms.

- According to this law, the frequencies of certain characteristic X-rays emitted from chemical elements are proportional to the square of a number which was close to the element's atomic number.

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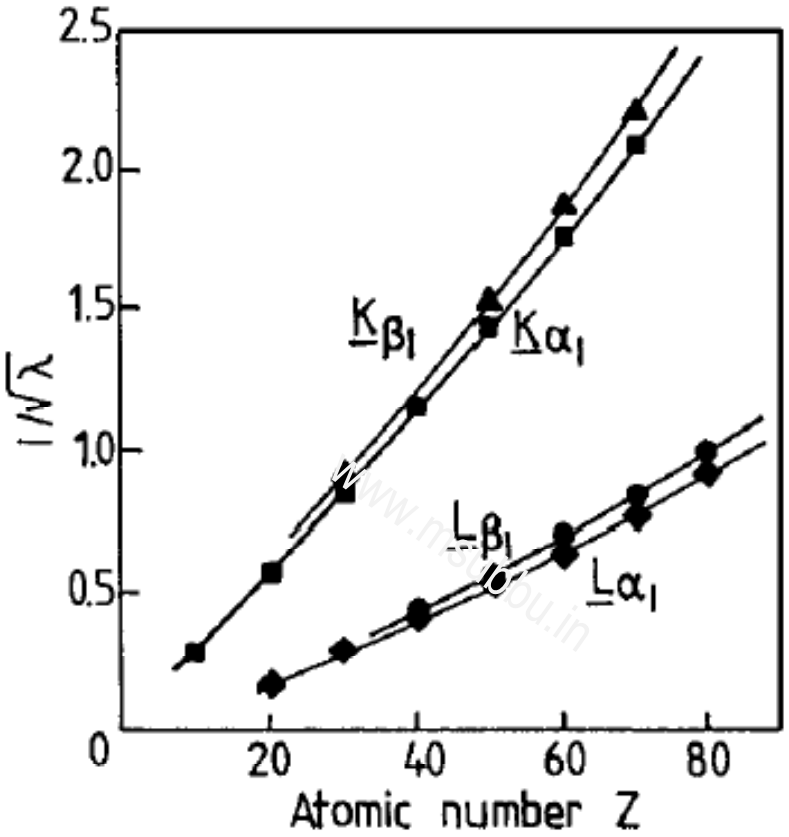

Partial Moseley's Law plots for selected K and L lines, showing the relationship between the X-ray emission wavelength and atomic number of the element. Using this relationship it was possible to predict undiscovered elements and to correctly assign atomic numbers to known elements.

Introduction to XRD

- About 95% of all solid materials can be described as crystalline. The rest 5% are amorphous. When X-rays interact with a **crystalline substance**, one gets a **diffraction pattern**.

- Every crystalline substance gives a pattern; and in a mixture of substances each produces its pattern independently of the others. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases

- As of now for about 50,000 inorganic and 25,000 organic single component crystalline phases, diffraction patterns have been collected and stored as standards. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample.

Introduction to XRD (contd.)

- In a crystalline solid, the constituent particles (atoms, ions or molecules) are arranged in a regular order. An interaction of a particular crystalline solid with X-rays helps in investigating its actual structure.

- Crystals are found to act as diffraction gratings for X-rays and this indicates that the constituent particles in the crystals are arranged in planes at close distances in repeating patterns.

- The phenomenon of diffraction of X-rays by crystals was studied by W.L.Bragg and his father W.H.Bragg in 1913.

Introduction to XRD (contd.)

- Samples may be in solid or powder form, and the technique is non-destructive .
- A crystal would diffract X-rays, just as a ruled grating will diffract light of a wavelength close to the distance between the ruled lines on the grating
- Diffraction of X-rays by crystals forms the basis of XRD for crystal structure determination

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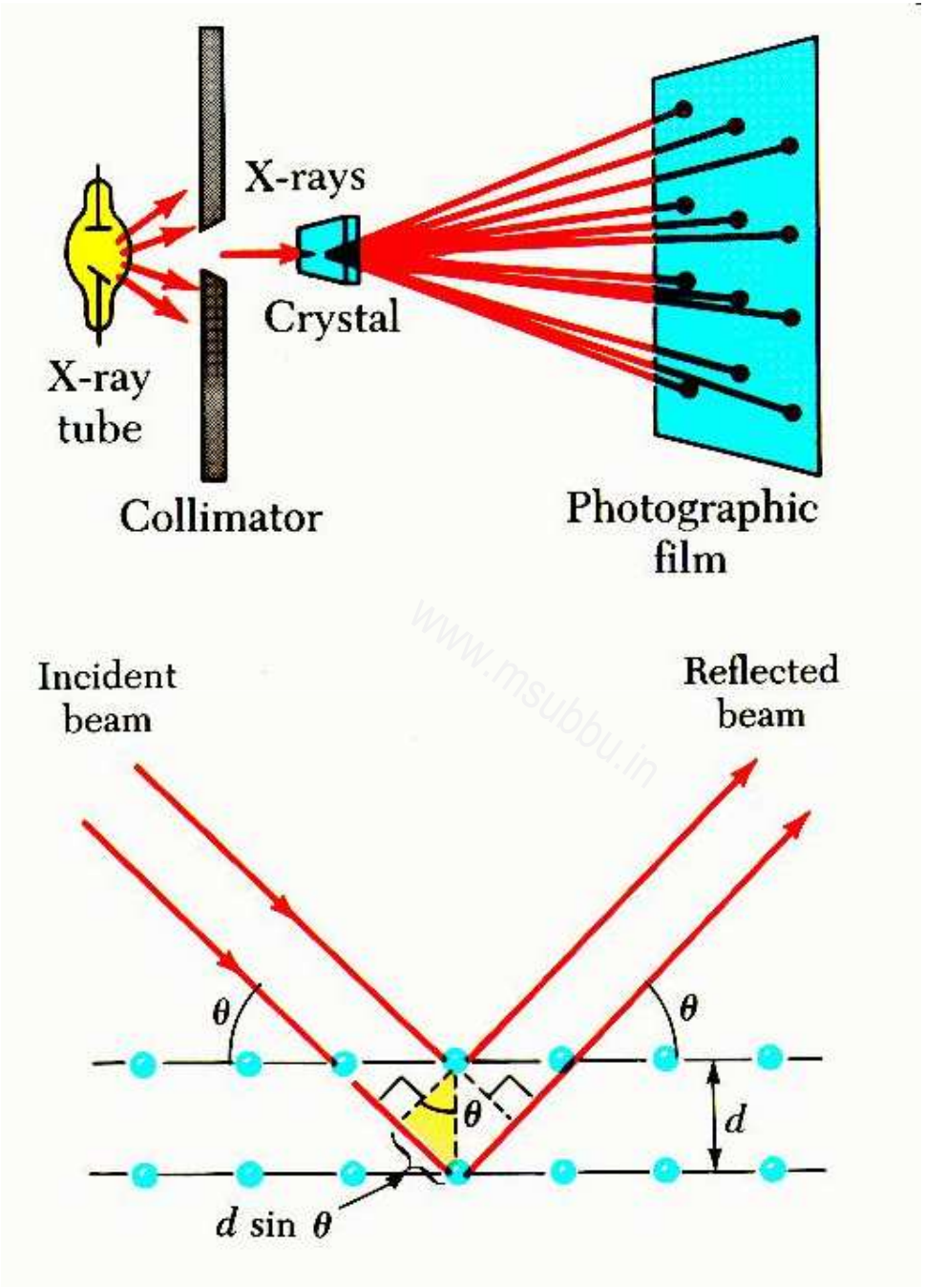

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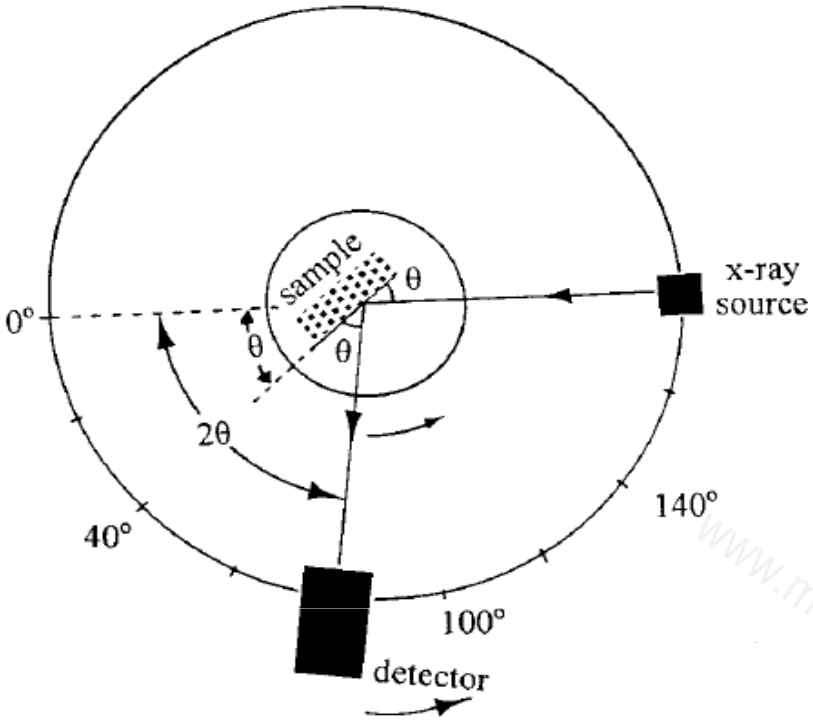
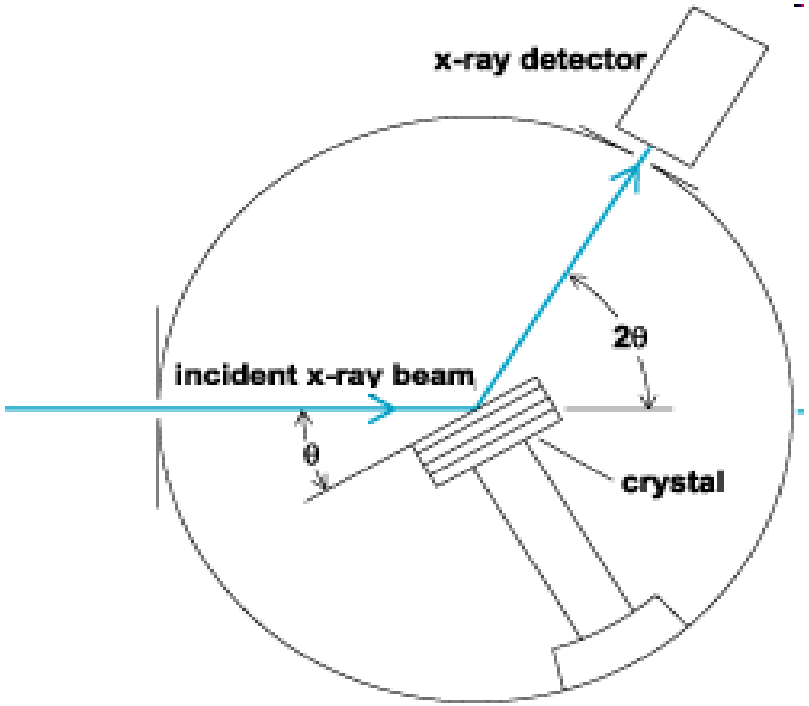


Figure 8.39 Schematic layout of a single-crystal XRD.



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Essential Parts of X-Ray Diffractometer

- X-ray Tube: the source of X Rays
- Incident-beam optics: condition the X-ray beam before it hits the sample
- The goniometer: the platform that holds and moves the sample, optics, detector, and/or tube
- The sample & sample holder
- Receiving-side optics: condition the X-ray beam after it has encountered the sample
- Detector: count the number of X Rays scattered by the sample

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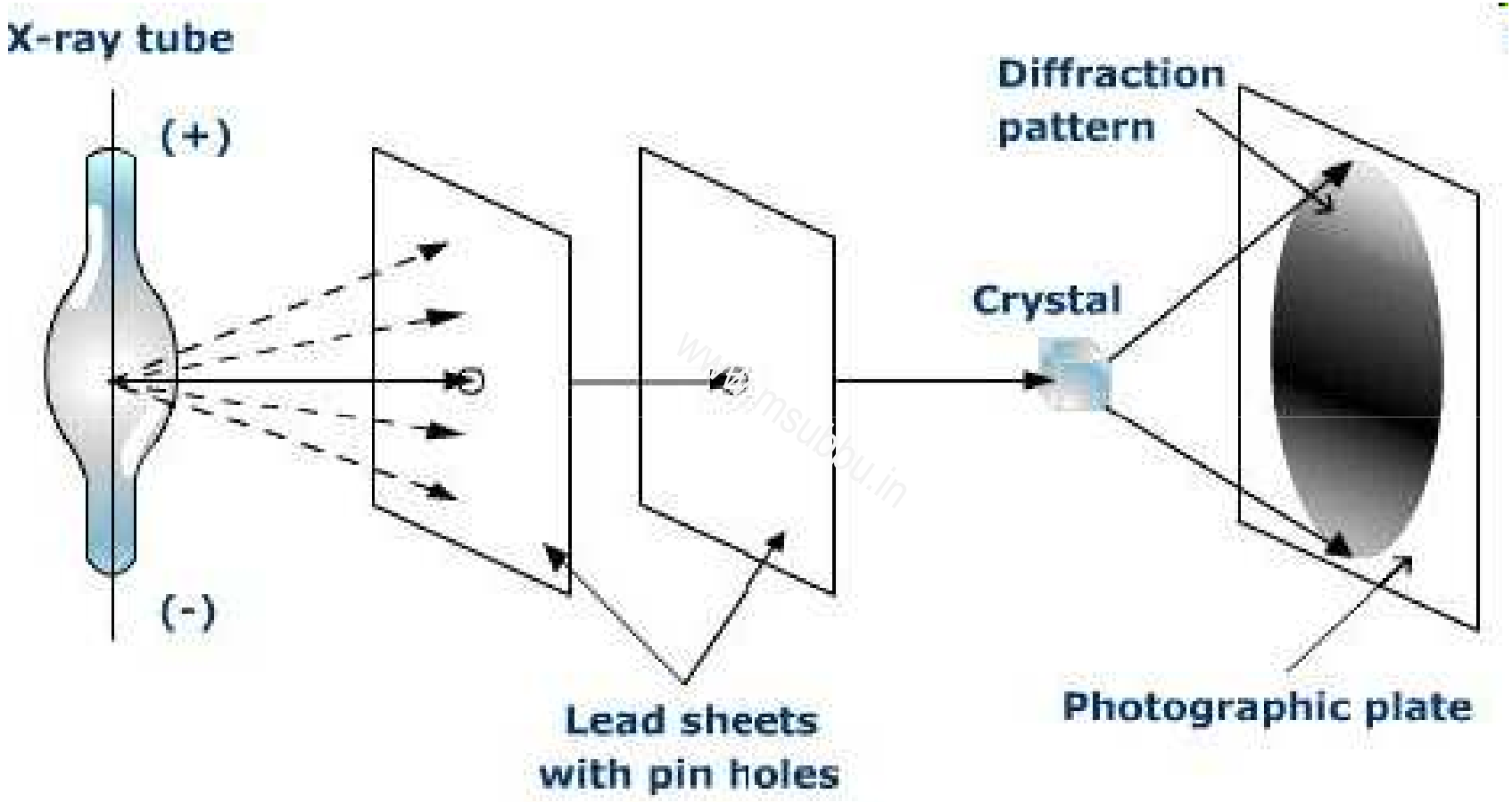
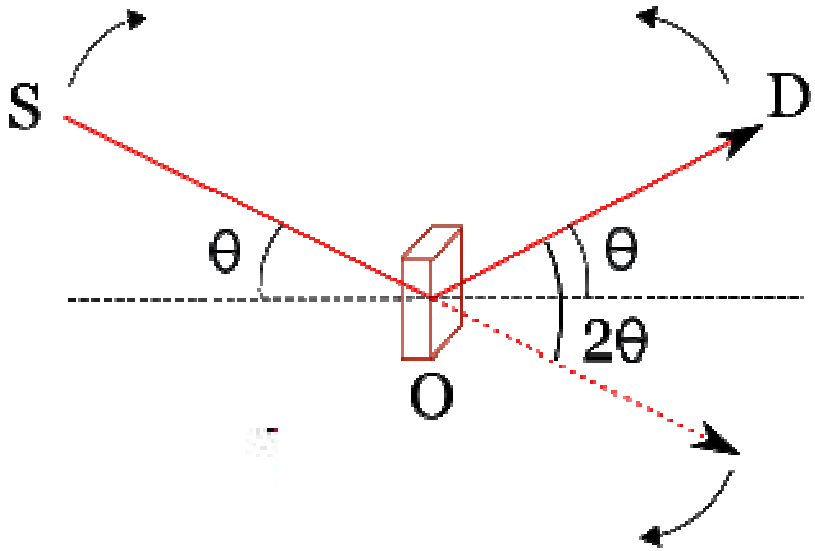
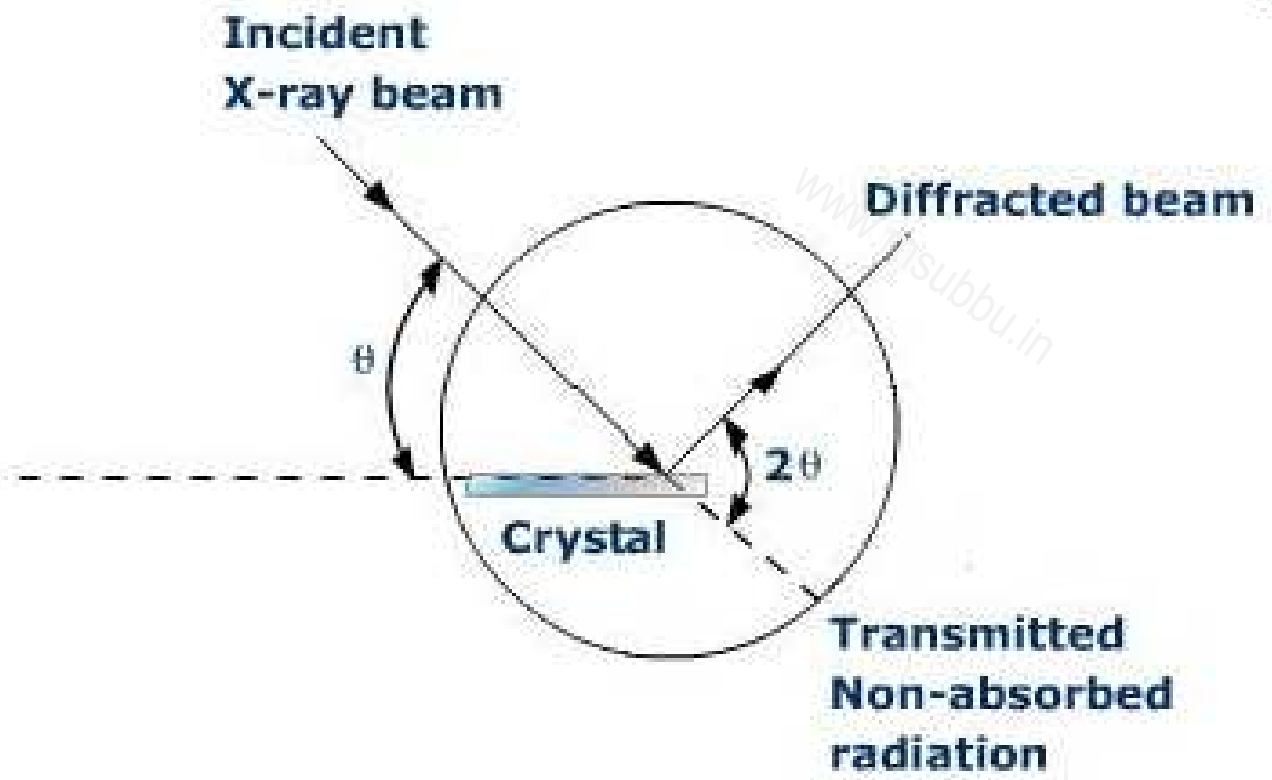
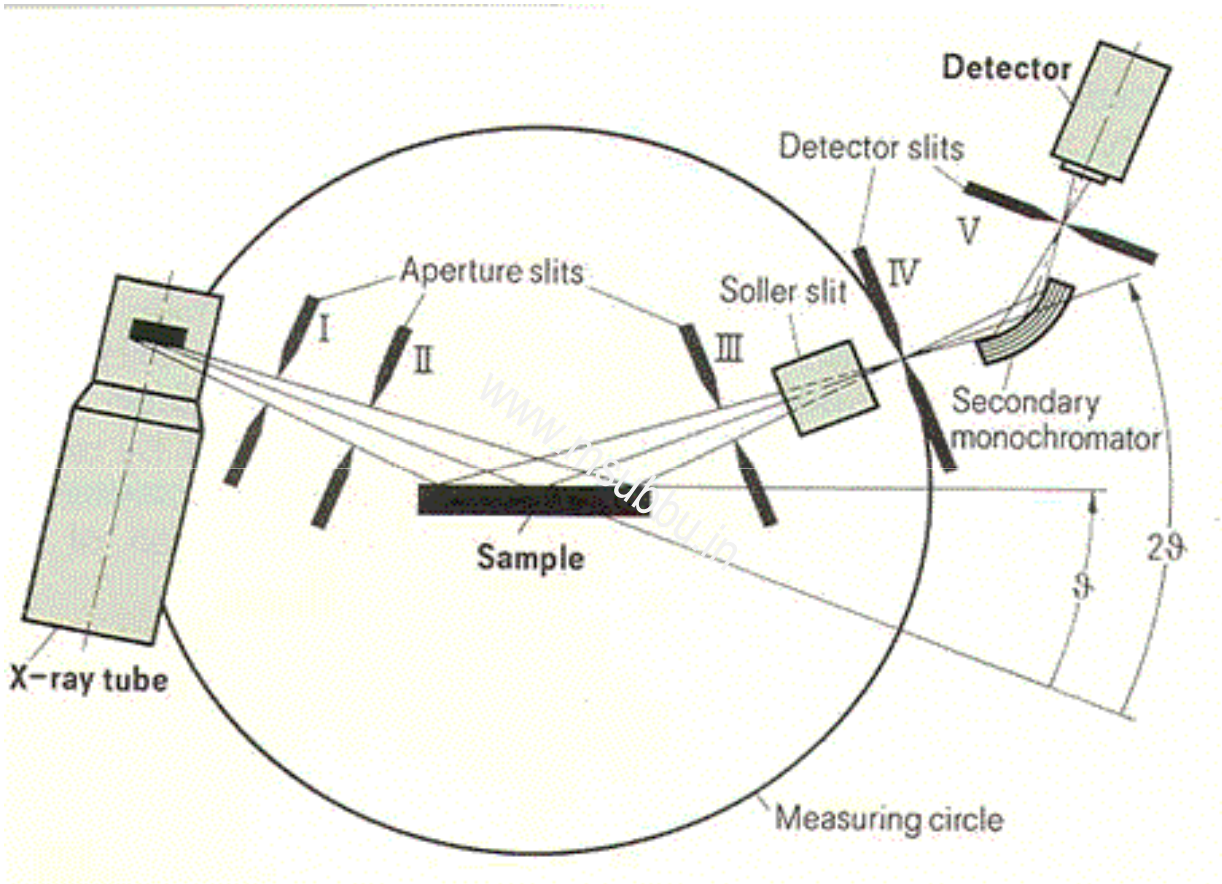

X-ray tube
(+)
(-)
Diffraction pattern
Crystal
Lead sheets with pin holes
Photographic plate


S
D
θ
θ
2θ
O


Incident
X-ray beam
Diffracted beam
θ
2θ
Crystal
Transmitted
Non-absorbed
radiation


Detector
Detector slits
V
Aperture slits
Soller slit
IV
I
II
III
Secondary
monochromator
Sample
θ
2θ
X-ray tube
Measuring circle

Samples

- In X-ray diffraction work we normally distinguish between single crystal and polycrystalline or powder applications.

- The single crystal sample is a perfect (all unit cells aligned in a perfect extended pattern) crystal with a cross section of about 0.3 mm. The single crystal diffractometer and associated computer package is used mainly to elucidate the molecular structure of novel compounds, either natural products or man made molecules.

- Powder diffraction is mainly used for "finger print identification" of various solid materials, e.g. asbestos, quartz. In powder or polycrystalline diffraction it is important to have a sample with a smooth plane surface. If possible, we normally grind the sample down to particles of about 0.002 mm to 0.005 mm cross section. The ideal sample is homogeneous and the crystallites are randomly distributed (we will later point out problems which will occur if the specimen deviates from this ideal state). The sample is pressed into a sample holder so that we have a smooth flat surface.

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Goniometer

- The mechanical assembly that makes up the sample holder, detector arm and associated gearing is referred to as goniometer.

- For the THETA : 2-THETA goniometer, the X-ray tube is stationary, the sample moves by the angle THETA and the detector simultaneously moves by the angle 2-THETA. At high values of THETA small or loosely packed samples may have a tendency to fall off the sample holder.

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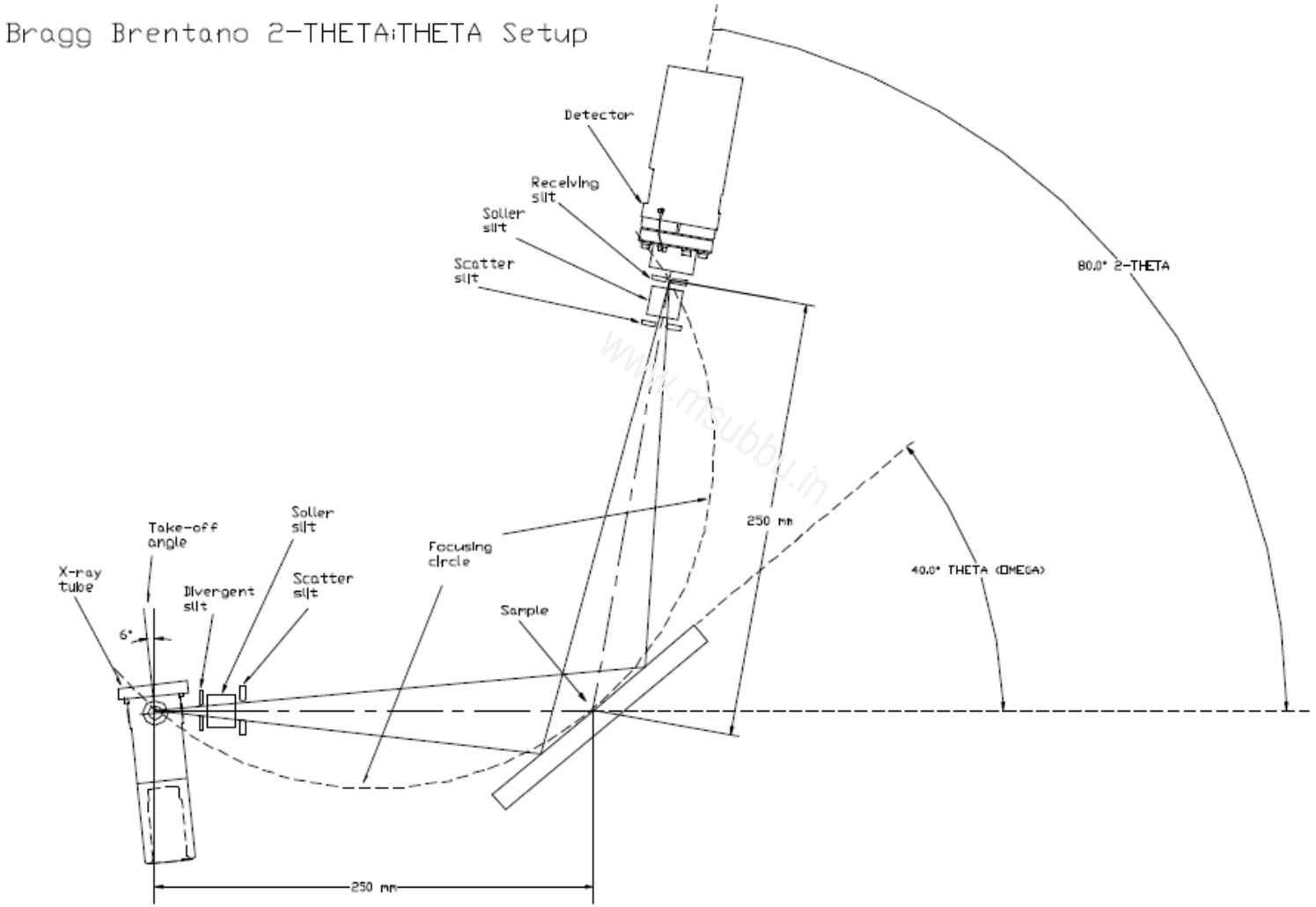
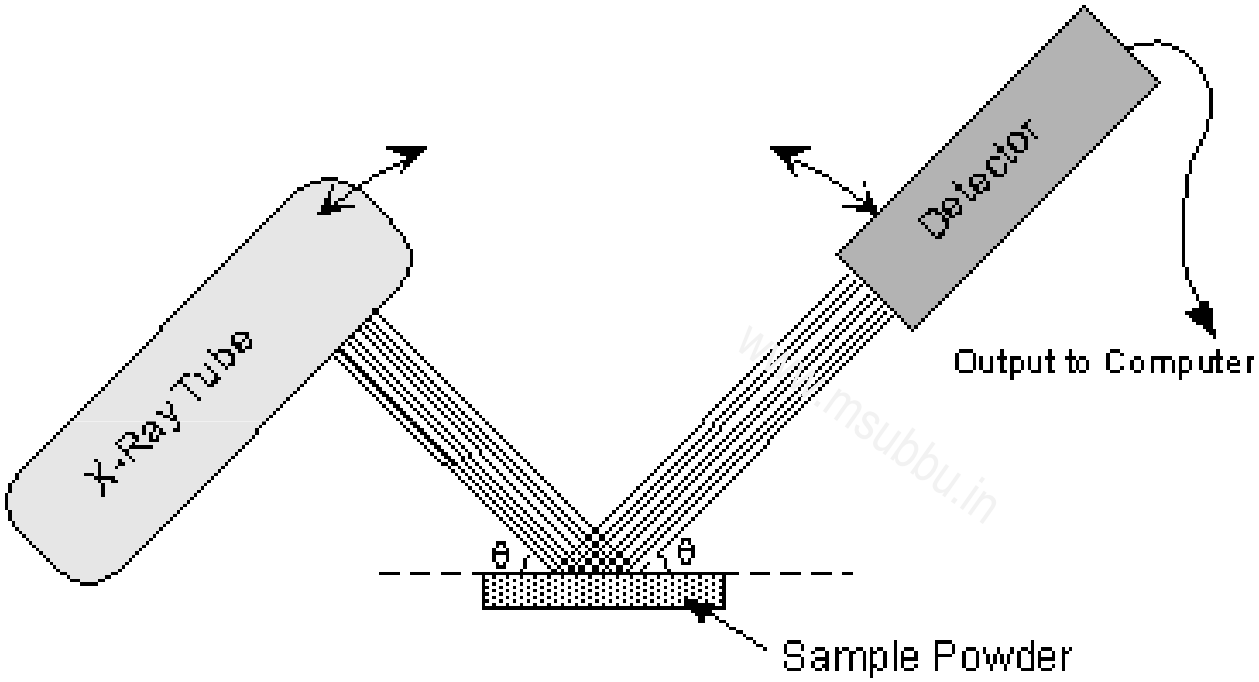
Theta – 2 Theta Goniometer



Theta-Theta Goniometer

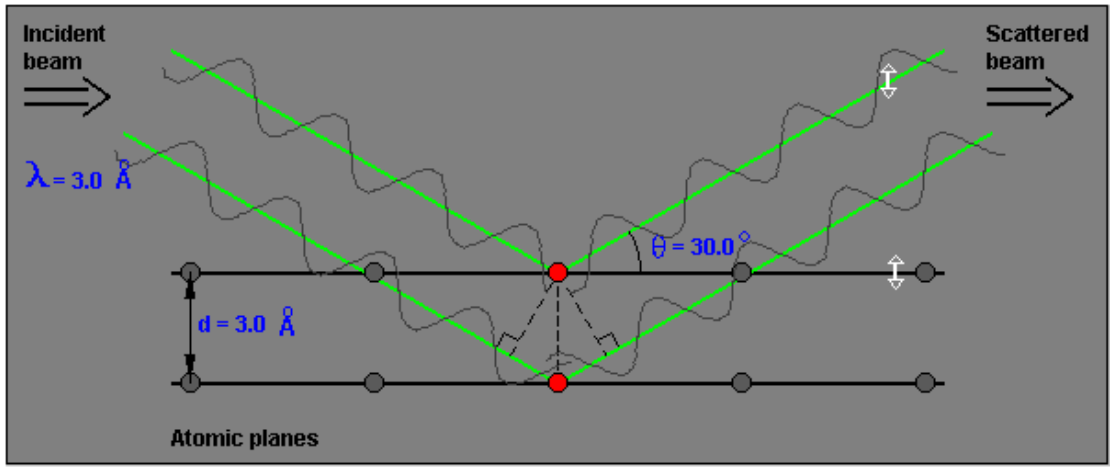


Bragg equation

- The resolution of an X-ray diffraction detector is determined by the **Bragg equation**:

$$d = \frac{1}{2}\left(\frac{\lambda}{\sin\theta}\right)$$

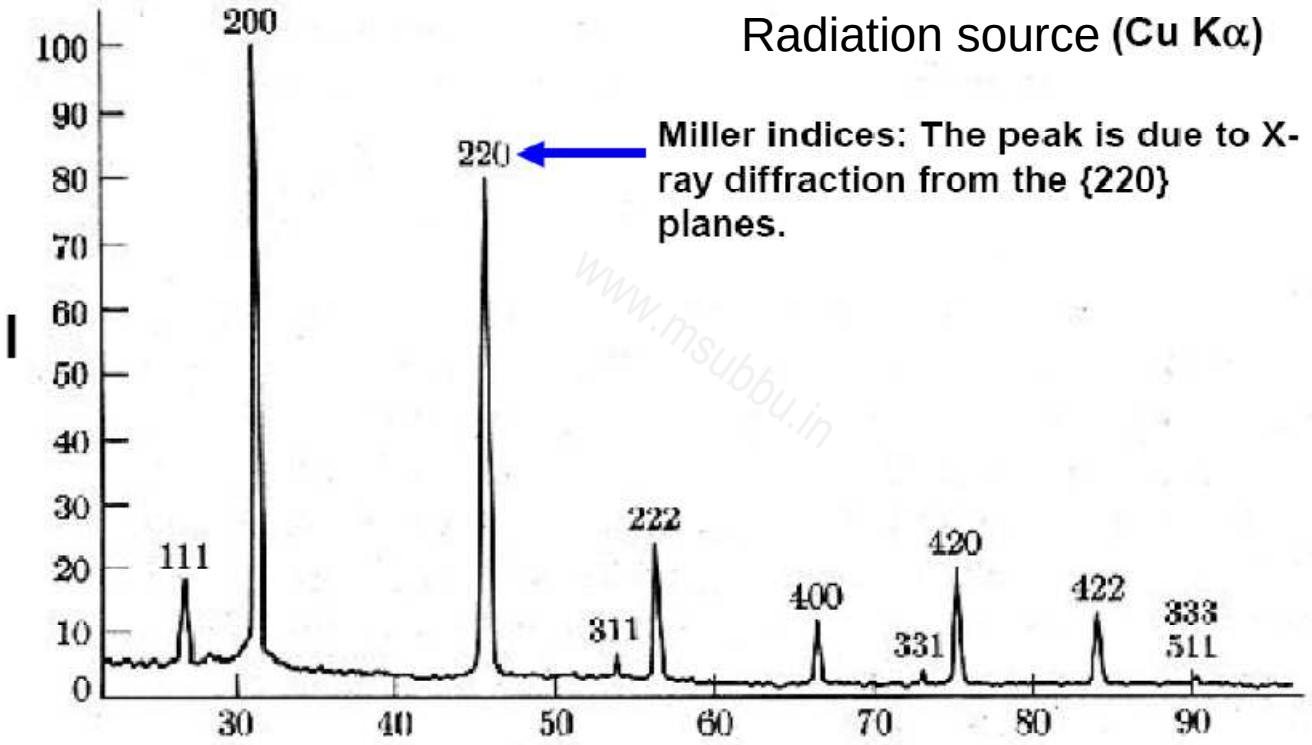
where *d* is the resolution of the detector, λ is the incident x-ray wavelength, and θ is the angle of diffraction.



XRD Pattern of NaCl Powder

1.54 ^{o}A for Cu Kα radiation

Radiation source (Cu Kα)



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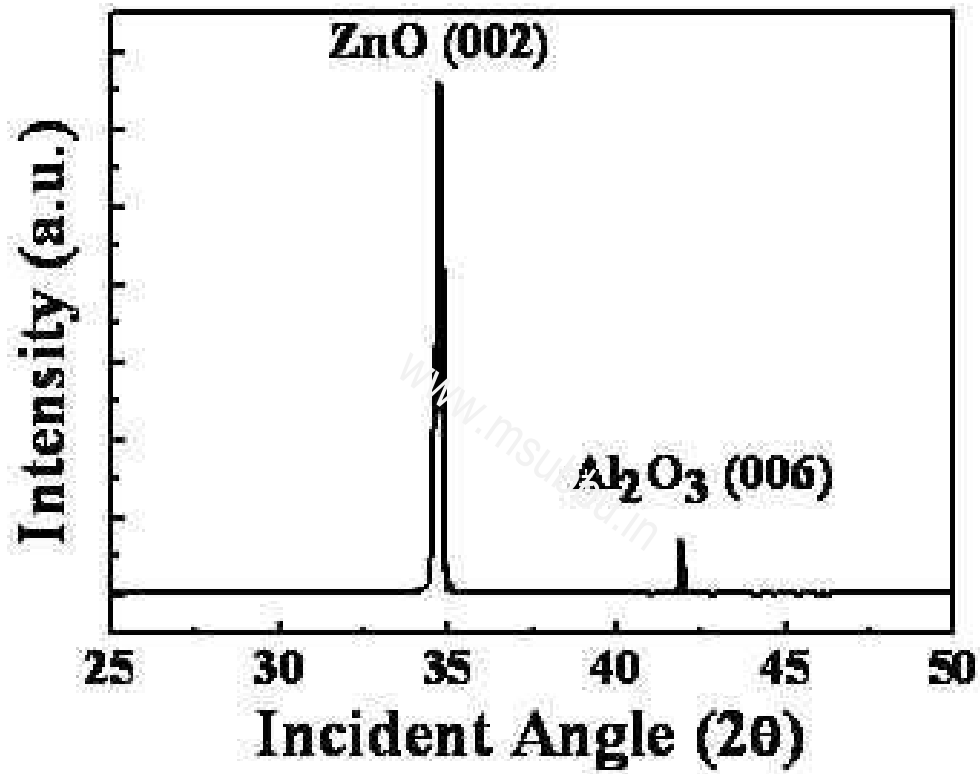
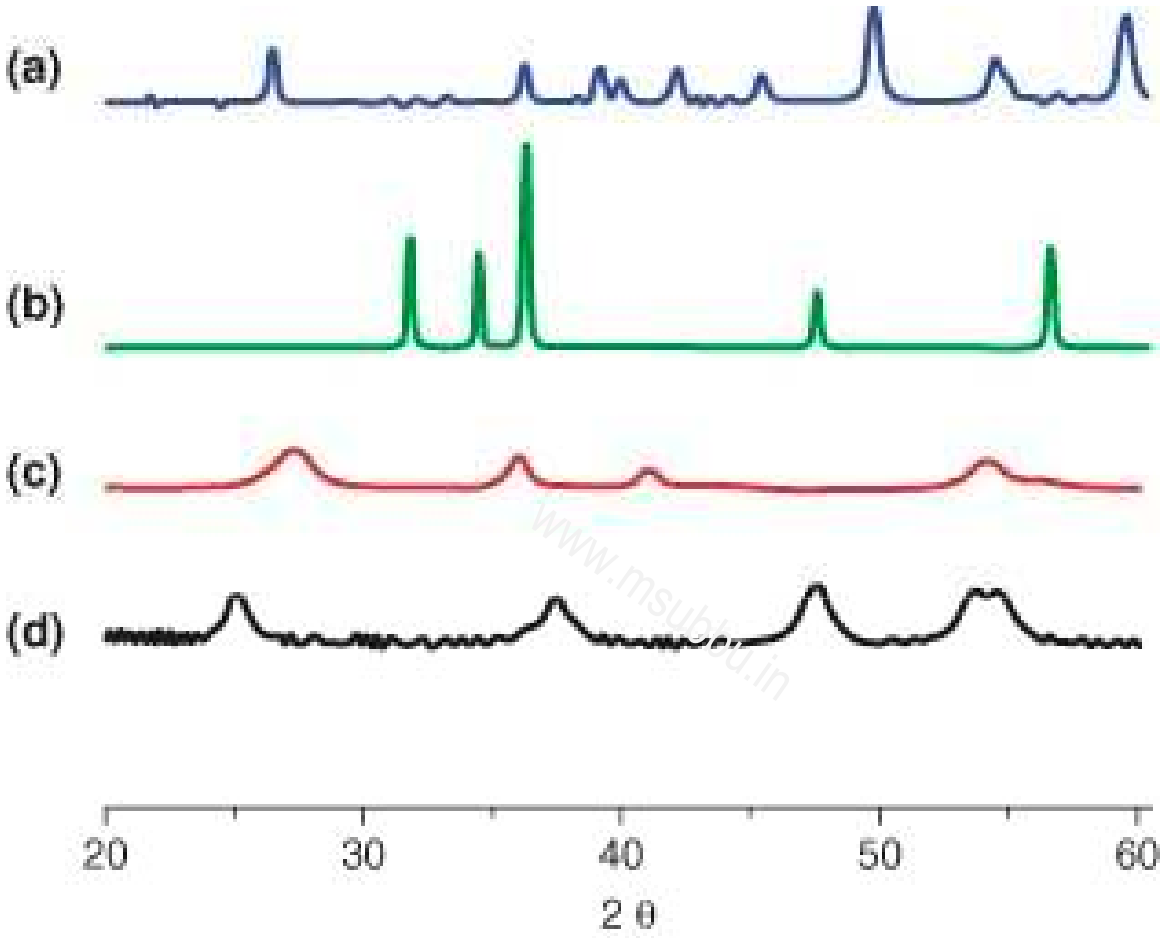
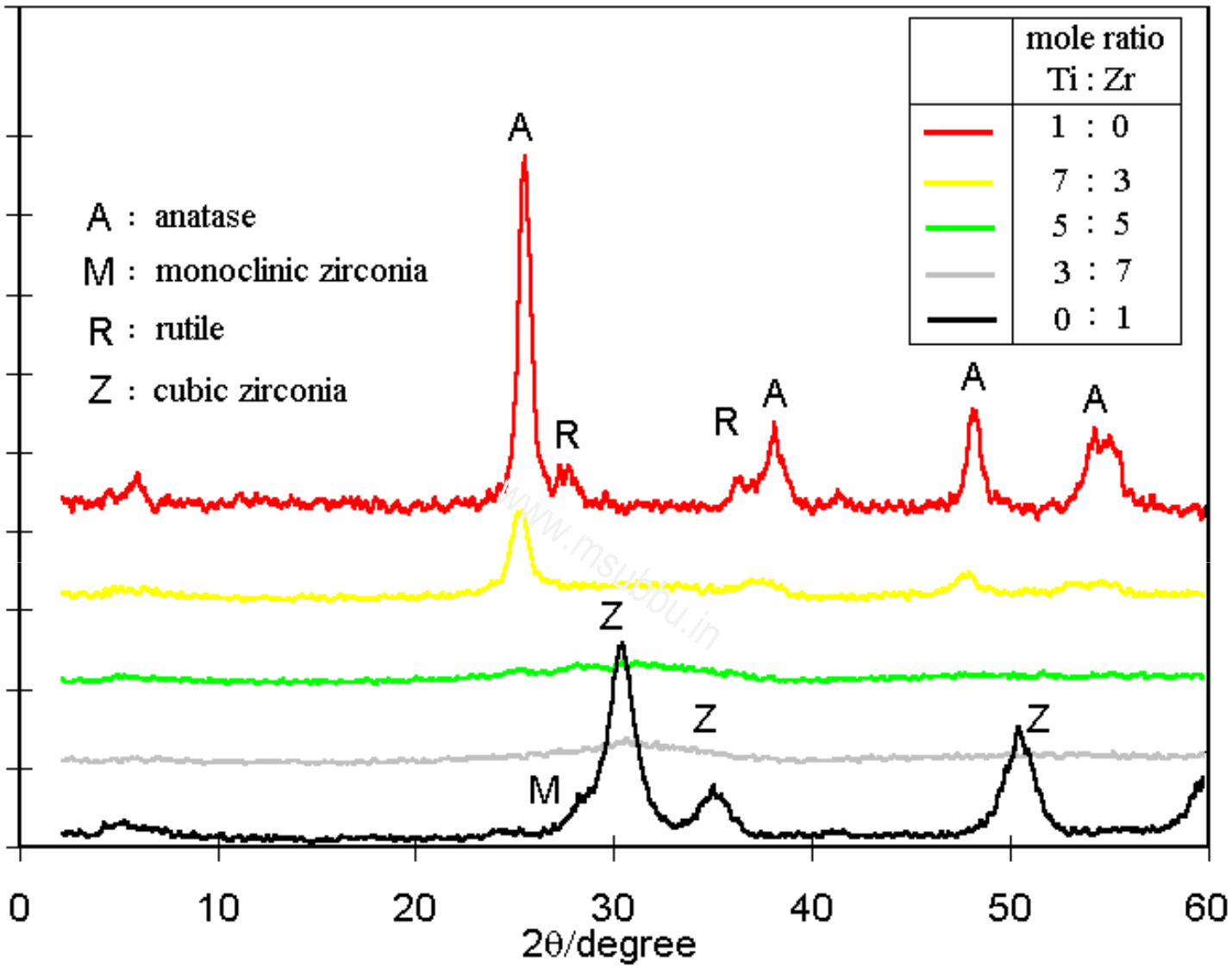


XRD spectrum of the epitaxial ZnO films prepared on sapphire substrate.

(XRD analysis of ZnO Ultraviolet photodiodes)



The spectra shows the XRD pattern of nanoscale (a) silicon dioxide (SiO2, alpha-quartz), (b) zinc oxide (ZnO, hexagonal), (c) titanium dioxide (TiO2, rutile), and (d) titanium dioxide (TiO2, anatase).



XRD diffraction pattern measured for a series of sulfated TiO2-ZrO2 mixed oxides of different composition

XRD Analysis

- Figure in the previous slide, illustrated X-ray diffraction pattern measured for a series of sulfated TiO2-ZrO2 mixed oxides of different composition. Pure TiO2 formed mainly the anatase phase, with a small amount of rutile.

- Pure ZrO2 was mainly cubic zirconia with a small amount of monoclinic phase. Mixed oxides of TiO2 and ZrO2 were mostly amorphous.

- A small amount of anatase was found in the mixed oxide with Ti : Zr mole ratio equal to 7 : 3. The difference in peak width in the X-ray diffraction patterns suggested that the ZrO2 formed much smaller crystals than TiO2.

Applications of XRD

- X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

- XRD is commonly used in the engineering, geological and materials sciences for applications such as corrosion studies, material fabrication, analysis of combustion products, mineral identification and determination of lattice parameters.

- Identification and quantification of the various phases is possible.

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Limitations of XRD

- Amorphous materials cannot be identified by XRD, so many polymeric and glassy materials cannot be studied.

- XRD is not a trace analysis technique. A component should be present at 3–5% by weight at a minimum in order for diffraction peaks to be detected.

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