

INTRODUCTION

X-ray diffraction (XRD) is a technique where compounds diffract (scatter) the X-rays of wavelength ranging from 10^{-6} to 10^{-10} cm, based on the inter atomic distance in a crystal. The resulting diffraction pattern of X-rays shows the arrangement of atoms within the crystalline structures. XRD is mainly used in qualitative analysis, including structure elucidation of organic and inorganic compounds.

Principle

When X-rays are passed on a crystal, the X-rays are scattered based on the arrangement of atoms in the crystals. Within a crystal, atoms are arranged in a plane with a particular distance in each axis viz., x, y and z. When X-rays of wavelength similar to inter planar distance falls on these atoms, they diffract, due to constructive interference (Fig 1). This pattern can be recorded on photograph film or measured using X-ray detectors. Interpretation of this pattern gives information on various aspects of the compound.

Bragg's equation:

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

where,

n = Integer

λ = Wavelength of x-ray used

d = distance between atomic layers in a crystal

θ = Theta (angle of incidence)

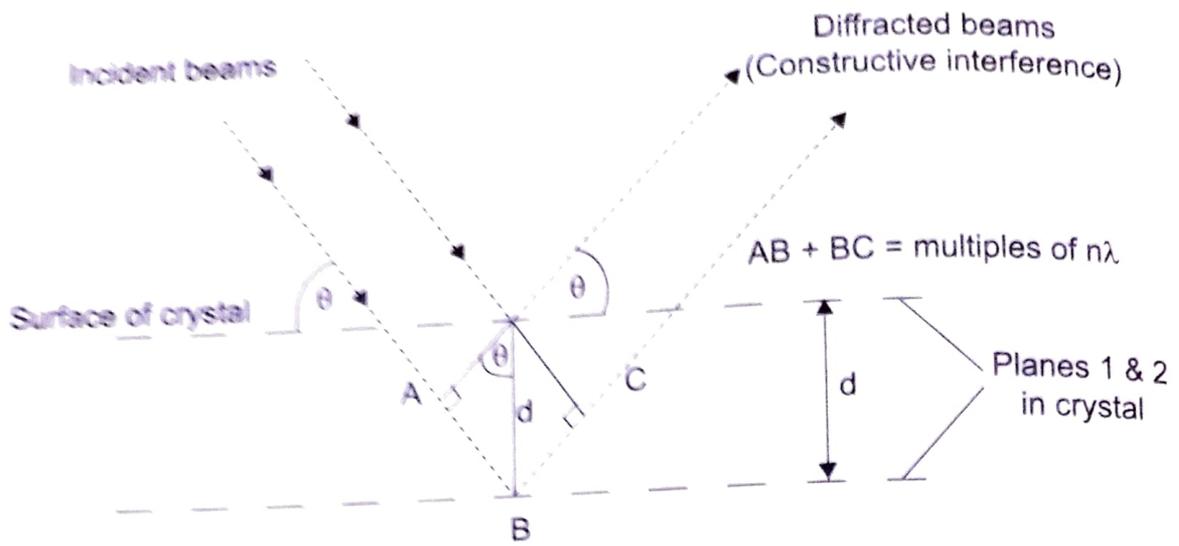


Fig 1. Diffraction of X-rays by a crystal

The derivation of the equation is as follows:

$$n\lambda = AB + BC$$

$$AB = BC$$

$$\text{Hence, } n\lambda = 2AB \quad \text{.....Equation 1}$$

$$\sin \theta = AB/d$$

$$d \sin \theta = AB$$

$$2d \sin \theta = 2AB \quad \text{.....Equation 2}$$

Based on Equation 1 & 2, $n\lambda = 2d \sin \theta$

When we know the wavelength λ and θ , the value of "d" i.e., spacing between the planes within the crystal can be determined.

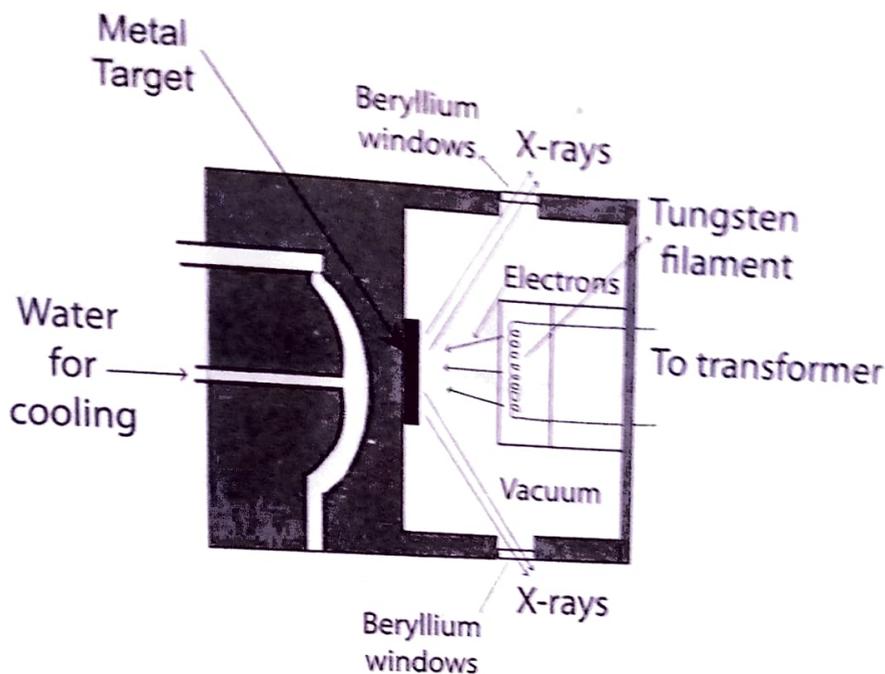
INSTRUMENTATION

Source of X-ray

X-rays are produced when high speed electrons collide with a metal target. High speed electrons are generated from hot tungsten filament (cathode) and after applying a high accelerating voltage (15-60 kilovolts) and are made

to fall on metal target (anode) like copper / aluminium, molybdenum or Magnesium. Water is circulated as coolant to copper block containing desired target metal (Fig 2).

Fig 2. Source of X-ray



Sample preparation & holder

As an ideal situation, sample to be analysed should be in the form of a single crystal, where the cross section is about 0.3mm. In case of powders or polycrystalline nature, they are ground to a particle size of 0.002 to 0.005mm and compressed to be present in a sample film holder.

In some of the XRD instruments, the sample holder is fixed, while the source as well as detector is rotated to a certain angle. Alternatively, sample holder can be rotated while the X-ray source is in fixed position.

Detector

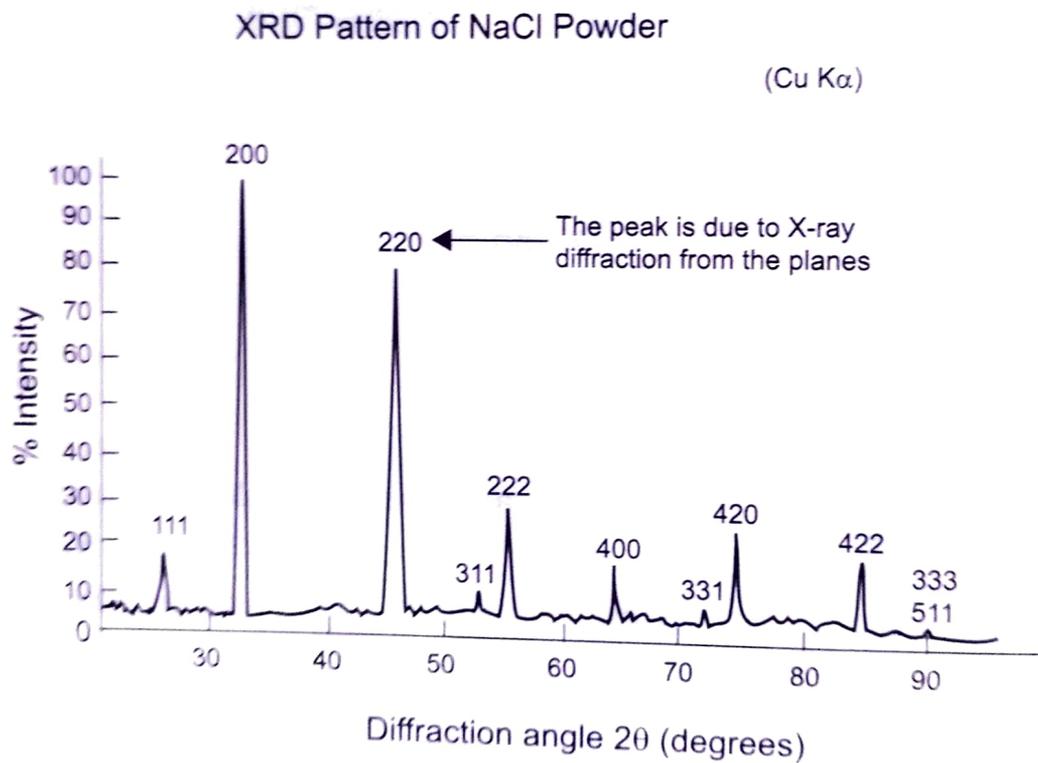
X-ray detector is used to capture the diffracted X-rays which produces signal and recorded. Alternatively, a photographic film is placed around the sample, where the diffracted X-rays produces image in the form of a pattern. This pattern is unique (like a finger print) to different crystals and serves

as identifying mechanism. In most of the models, the detector is capable of rotating and from the signal captured, the angle θ is measured.

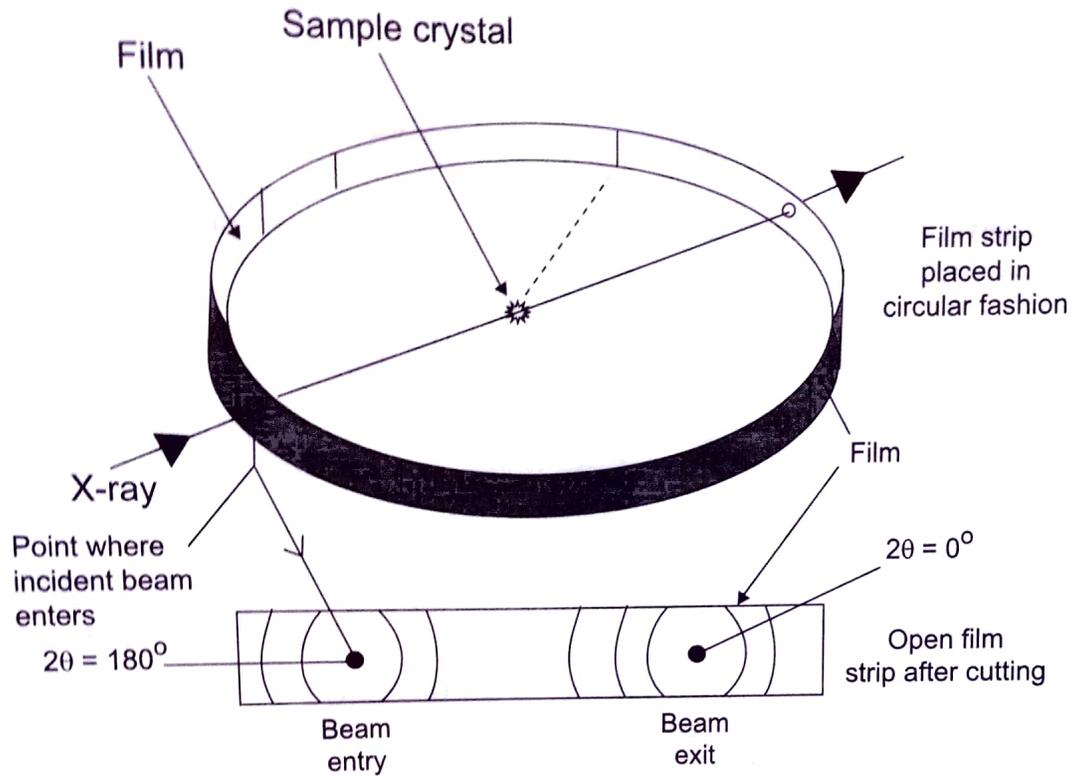
Recording and Interpretation

The signal from the detector is recorded or the pattern of diffraction is captured on a photographic film. This unique pattern is used for interpretation about the crystals.

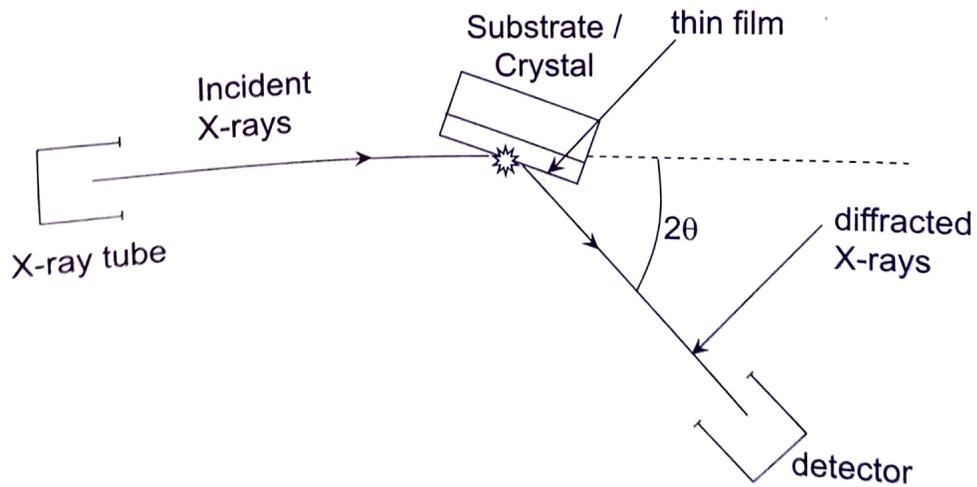
XRD signals



Recording XRD pattern on photographic film



Typical components of XRD instrument



Advantages of XRD

1. XRD is applied for crystalline (mono) as well as polycrystalline compounds and also for amorphous materials.
2. It is the easiest technique to find the "d" spacing in crystals.
3. Sample preparation is easy and fast (in some cases, no need to prepare a sample).
4. XRD patterns are available in the database and can be compared for easy interpretation.

Pharmaceutical and other related Applications

XRD is applied in wide variety of fields such as pharmaceutical industry, environmental science, geological applications, material science, chemistry (both organic and inorganic) and forensic science.

- Measurement of the average space "d" between layers of atoms
- Determination of the orientation of a single crystal and crystal structure of unknown material
- Measurement of size, shape and internal stress of small crystalline regions
- Measurement of thickness of thin films and multi layers
- Determination of each type in mixed crystals (up to 3% in a mixture)
- Comparison of XRD pattern with the database of thousands of compounds for interpretation

Pharmaceutical applications

Study of polymorphism in drugs eg. Carbamazepine (form I & III), enalapril maleate (form I & II), aspartame salts, etc. XRD is also used for qualitative and quantitative analysis of organic and inorganic compounds.