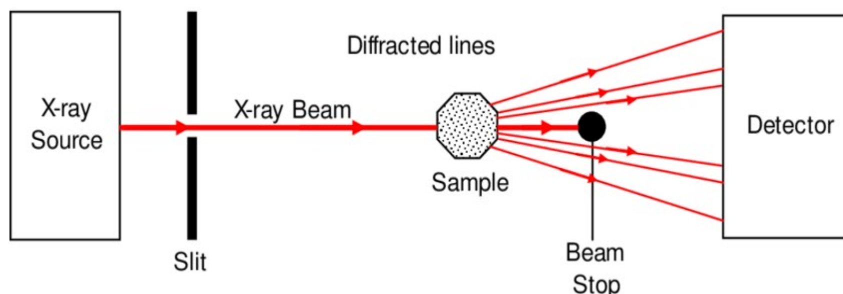
X-ray Diffraction (XRD)

Definition

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. It is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.



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. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. 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. 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. Conversion of the diffraction peaks to d−spacings allows identification of the mineral because each mineral has a set of unique d−spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

- **Bragg's Law:** Bragg showed that if the diffraction from a crystal was considered as reflections from imaginary planes of atoms within the crystal then an equation could be formulated to predict where diffraction maxima would occur in a diffraction pattern. Consider a pair of parallel X-rays striking a pair of horizontal parallel planes as shown in the Figure. The parallel rays hit the planes in phase but the lower ray has a longer distance to travel than the upper one by the time they are both reflected. By simple trigonometry it can be shown that $n\lambda = 2d\sin\theta$. The Bragg relationship shows that constructive interference of the waves will only occur when the path difference is some multiple of the wavelength, λ.

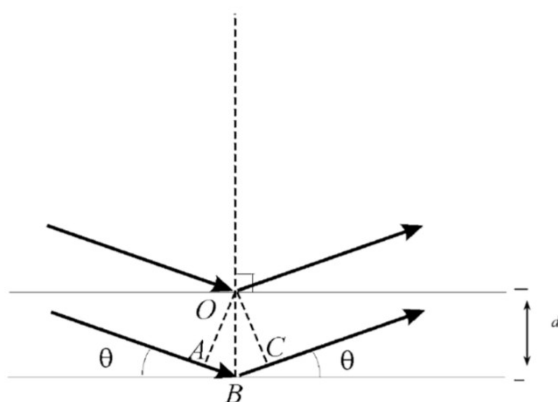
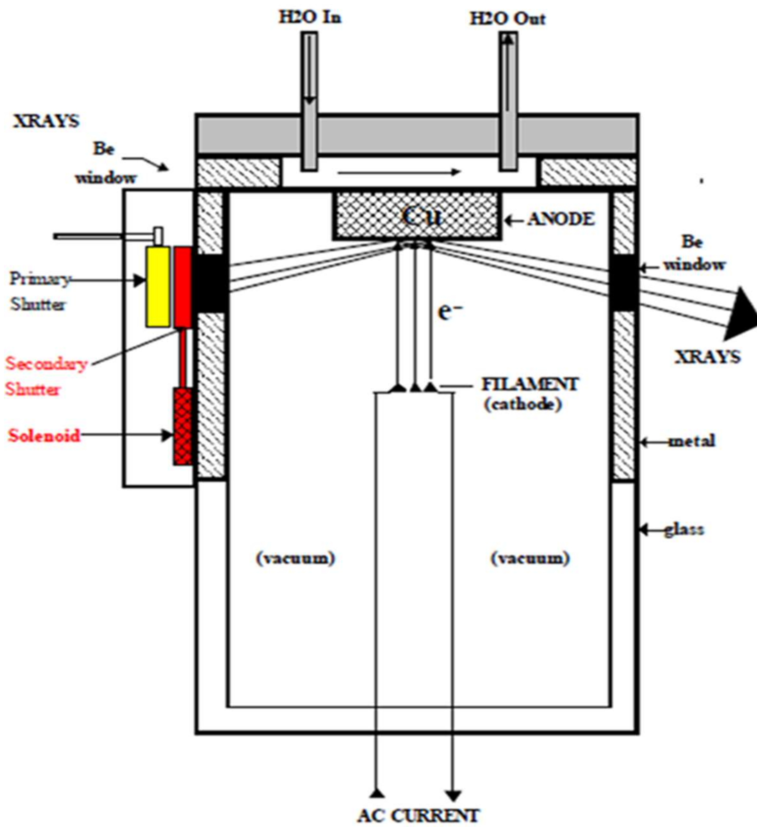


Figure: Bragg's Law of reflection.



The arrows indicate the electromagnetic waves that are reflected from a pair of parallel planes separated by distance d. The dashed line with one end at B is a normal to these planes. The bottom wave travels an extra distance, i.e. a path difference of AB + BC, and if it is to be in constructive interference with the top wave, AB + BC needs to be an integer multiple of the wavelength λ of the wave. Since the waves are parallel, OA and OC are perpendicular to AB and BC respectively, and by simple geometry, AB = BC = dsinθ. Hence, for the constructive addition of the waves, AB + BC =2 dsinθ = nλ. The amplitude of the reflected wave will depend on the electron density at the point of diffraction.

Figure: Cross section of safety filament X-ray tube

How Does It Work?

X-ray diffractometers consist of three basic elements: X-ray tube, sample holder, and X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons,

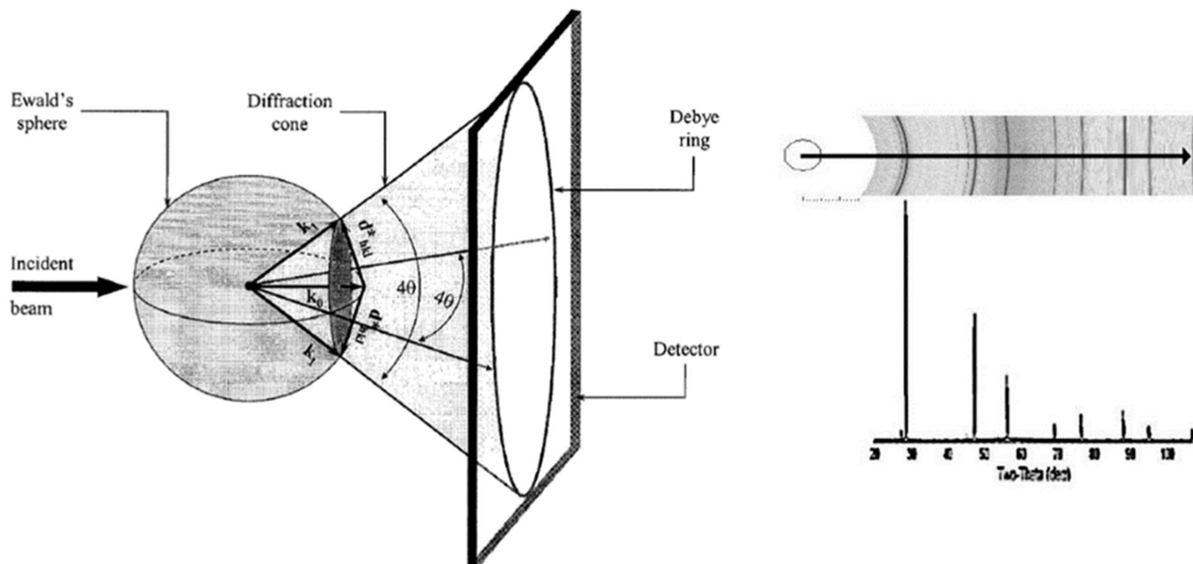
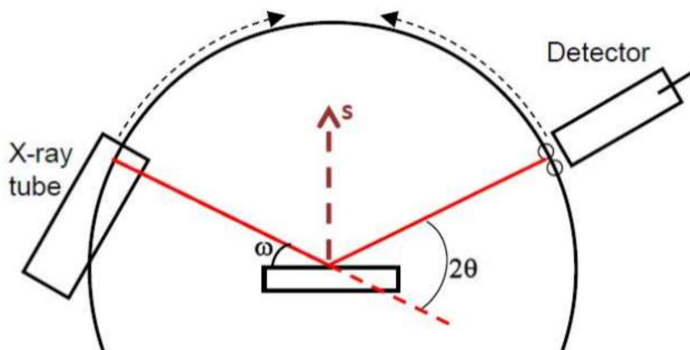
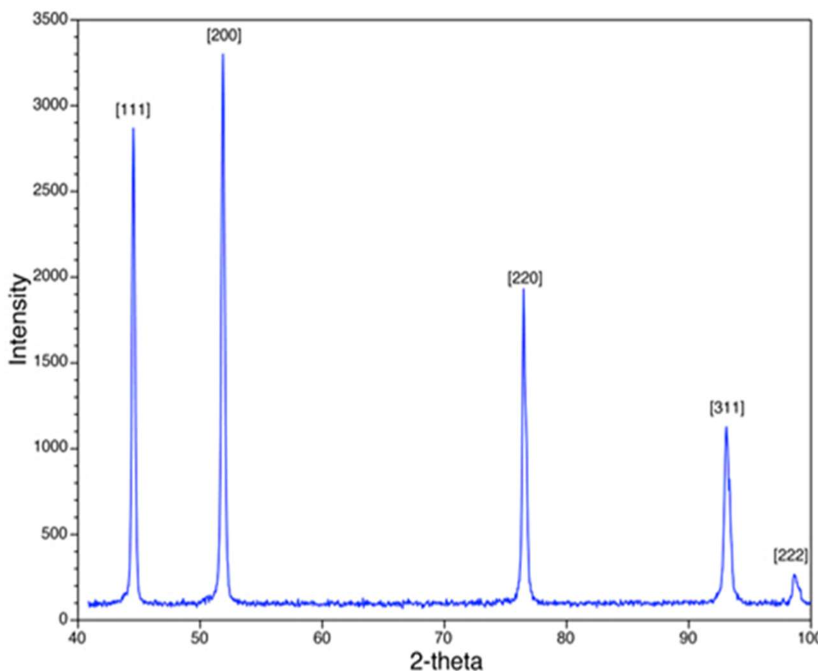


Figure: X-rays are scattered in a sphere around the sample.

accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. 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. Kα1and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. 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 present in the X-ray scan.

Applications

1. Determination of unit cell dimensions.
2. Whether the sample is a composite material consisting of multiple crystallographic phases and, if so, determine the fraction of each phase.

3. Differentiation between crystalline and amorphous materials.
4. Determining the grain/particle size of the material.
5. Determining the degree of texture (preferred orientation of grains) in material.
6. Determination of the texture of polygrained materials.
7. Measurement of sample purity.
8. Determination of orientation of single crystals.
9. Determination of electron distribution within the atoms and throughout the unit cell.
10. Determination of molecular structure and characterization of proteins and nucleic acid.

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'.