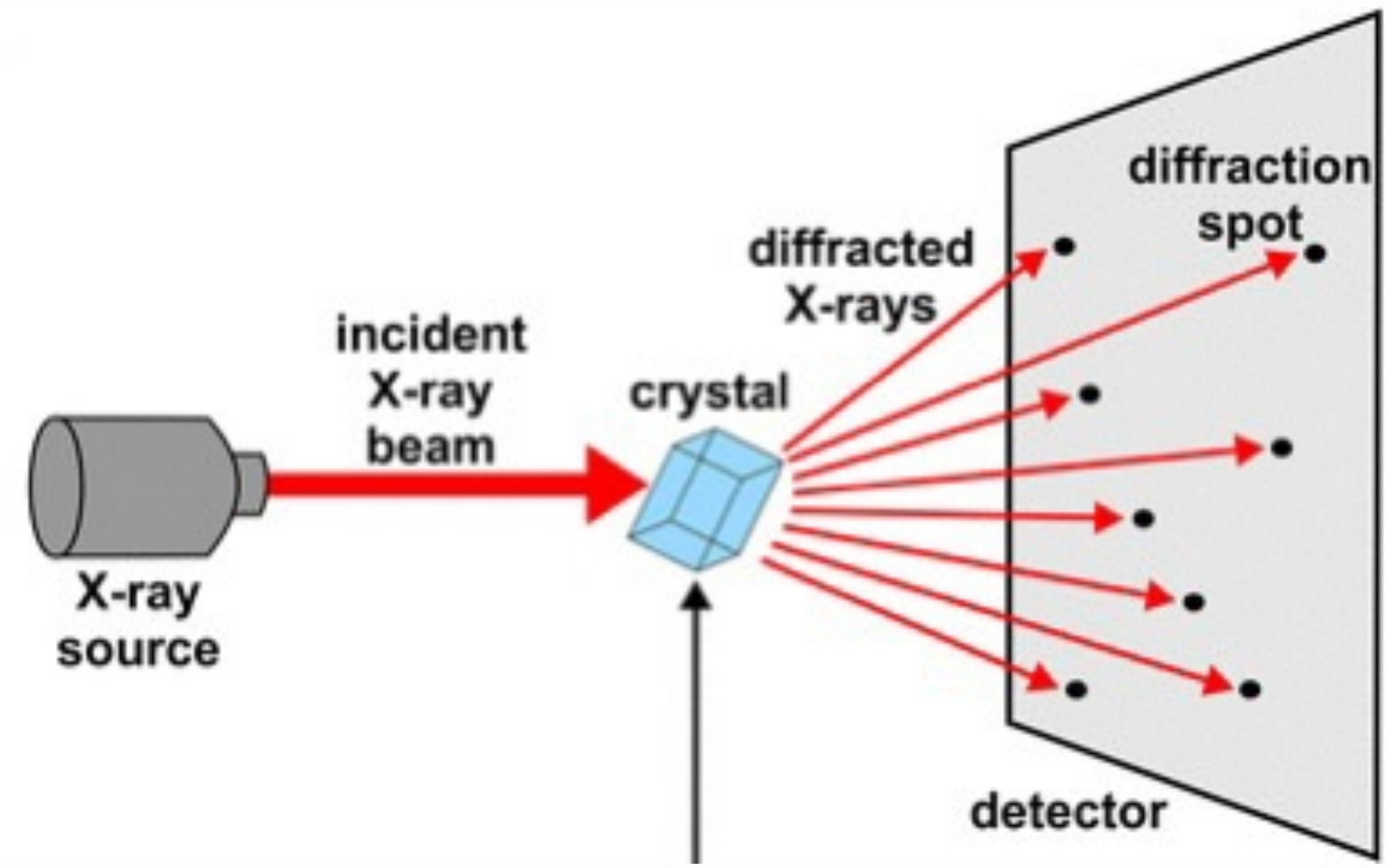
X ray Crystallography:



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X ray Crystallography:

X-ray crystallography is a technique used to determine the 3D structure of molecules.

Especially large biomolecules like proteins, nucleic acids (DNA, RNA), or small compounds — by analysing the pattern formed when X-rays are diffracted by their crystal lattice.

Principle-

When a beam of X-rays is directed at a crystal, the X-rays are scattered by the electrons in the crystal's atoms. This produces a diffraction pattern — a series of spots — which can be captured on a photographic plate or a detector.

Using mathematical methods (Bragg's Law and transform techniques), we can calculate the positions of the atoms in the crystal.

Production Of X - rays

Production of X-rays = making or generating X-rays. This typically happens when high-energy electrons collide with a metal target (such as tungsten) in a vacuum tube. The collision converts their energy into X-rays and heat.

1. Cathode emits electrons:

The tube contains a filament (cathode) made of tungsten.
When electric current is passed through it, the filament heats up (this is called thermal emission or thermionic emission).
This emits electrons into the vacuum tube.

2. Acceleration of electrons:

High voltage (typically 30–100 kV) is applied between the cathode (negative) and anode (positive).
This voltage accelerates the electrons toward the anode with high energy.

3. Collision with metal target:

The electron stream strikes a metal target (typically tungsten) placed at the anode.

The collision converts their kinetic energy into:

X-rays (about 1%) — due to sudden deceleration or energy transitions of electron clouds.

Heat (about 99%) — due to their energy being absorbed by the metal.

4. Emission of X-rays:

The X-rays exit through a window made of material that lets them pass (such as beryllium).

These rays can then be used for imaging, crystallography, or other applications.

Different x-ray methods

1. X-rays by X-ray Tube (General Method) -

Principle:
High-energy electrons collide with a metal target (typically tungsten) in a vacuum tube. This produces X-rays due to sudden deceleration (bremsstrahlung) and atomic transitions.

Application:
Medical imaging (radiography and CT scan)
Security scanning of luggage or packages
General scientific and industrial applications (defects in materials, structural analysis)

2. Synchrotron Radiation 🔷

✅ Principle:

Relativistic electrons (with very high energy) are forced to move in a circle by strong magnets (Bending magnets or undulators). This emits highly collimated and intense X-rays — called Synchrotron radiation.

✅ Application:

Protein crystallography (determining 3D structures of biomolecules)

Material science and nanotechnology (analyses of microstructures)

Spectroscopy (for elemental and electronic structure)

3. X-rays by Radioactive Isotopes 🔷

✅ Principle:

Some radioactive isotopes naturally release X-rays during their radioactive decay. This typically occurs when inner electron shells are filled by electron transitions following nuclear transformation.

✅ Application:

Fluorescence X-rays in analytical instruments (XRF) — used for elemental analysis of materials

Small, low-energy sources for educational or industrial applications

4. Fluorescent X-rays (Secondary Emission)

✅ Principle:

When high-energy radiation (such as an electron beam or higher-energy X-rays) knocks an electron out of a lower-energy (inner) electron shell, an electron from a higher-energy (outer) electron drops down to fill its place. This emits fluorescent X-rays with characteristic energy for each element.

✅ Application:

X-ray fluorescence (XRF) — used in elemental analysis, metal identification, or for art authentication

Determining the composition of archaeological samples or metal alloys

5. Bremsstrahlung (Braking Radiation)-

✅ Principle:

When high-energy electrons are deflected by nuclei of heavy atoms, they lose energy in the form of X-rays with a broad spectrum of energies (bremsstrahlung).

✅ Application:

General diagnostic radiography — most dental and medical imaging

Security scanning and industrial radiography — to inspect materials for defects

Material thickness and density measurements

Bragg's Law

Bragg's Law explains the condition under which X-rays are diffracted by a crystal's lattice planes.

When X-rays strike a crystal, they are scattered by the atoms. This scattering can produce constructive interference — which forms strong, visible diffraction spots — if the path difference between rays is an integer multiple of their wavelength.

Principle-

Picture crystal planes as parallel mirror-like sheets of atoms spaced at a distance d.

When X-rays are incident at an angle θ, they are reflected by these planes. The reflection from the lower plane lags behind the reflection from the upper plane by a path difference.

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

Where:

n = integer (order of reflection, typically 1)
λ = X-rays' wavelength
d = Distance Between Planes of Atoms in the crystal
θ = Bragg Angle, the incident angle at which reflection occurs

Applications -

Bragg's Law is used to:

-Determine atomic spacing in crystal structures.
-Identify phases of materials.
-Investigate structures of proteins and complex biomolecules.
-Develop new materials with desirable properties in materials science.
-Support pharmaceutical formulation by analyzing crystalline forms of drugs.

Rotating Crystal Technique

The rotating crystal technique is a method used to record X-rays diffracted by a single crystal as it is slowly rotatedin a beam of X-rays.

This rotation lets us collect reflection data from many different planes in the crystal — which is crucial for determining its 3D structure.

Principle-

-We have a single crystal placed in a holder.

-An X-rays beam is directed at the crystal.

-The crystal is gradually rotated (typically by a few degrees at a time) while retaining its orientation with its rotation axis perpendicular to the X-rays.
-This brings different sets of crystal planes into positions where Bragg's condition for constructive interference is satisfied.

Procedure-

Step 1 — Mount the crystal:
The crystal is placed on a goniometer — a holder that can be slowly turned.

Step 2 — X-rays exposure:
A collimated beam of X-rays is directed toward the crystal.

Step 3 — rotation:
While the crystal slowly rotates, different planes align with Bragg's condition.

Step 4 — recording:
The diffracted rays produce spots on a photographic plate or a detector placed behind the crystal.

Step 5 — data processing:
The positions and intensities of these spots are later used to compute the crystal's structure.

Applications-

Determining 3D structures of complex biomolecules, such as proteins and nucleic acids (DNA and RNA).

Analyzing atomic arrangement in crystalline materials (such as metals, alloys, and minerals).

Providing information about atomic distances, bond lengths, and bond angles within the crystal.

X-ray Powder Method

The X-ray powder method (also called powder diffraction) is a technique used to analyse crystalline materials in powder form instead of a single crystal.

This is especially useful when large or well-ordered single crystals are unavailable.

Principle-

When a fine crystal powder is placed in a beam of X-rays, each tiny crystallite is oriented in a random direction.

Therefore, for every set of crystallographic planes (with spacing d), there are many crystallites placed at the proper angle to satisfy Bragg's Law:

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

This results in diffraction rings instead of separate spots.

Procedure-

Step 1 — Prepare the sample:
Grind the crystalline substance into fine powder (typically < 10 μm).

Step 2 — Mount the sample:
Fill a glass tube or small holder with the powder. Sometimes, a small rod or flat plate is used.

Step 3 — Irradiate with X-rays:
Point a collimated X-rays beam toward the sample.

Step 4 — Detect the diffraction pattern:
Diffracted rays form concentric rings on a photographic plate or a detector placed behind the sample.

Step 5 — Measure the rings' radii or positions:
Using these, we can calculate the d-spacings of the crystal planes.

Applications-

✅ Identify unknown crystalline compounds (by comparing their diffraction patterns to standard databases).

✅ Analyze phases in a mixture of compounds (such as pharmaceuticals, ores, or ceramics).

✅ Determine lattice parameters, crystallite sizes, and degree of crystallinity in a material.

✅ Detect structural defects or stress in materials.

1. Ionic Crystals-

-Constituents: Positive and negative ions (cations and anions)

-Bond: Ionic bonds (electrostatic attraction)

-Properties:

Hard and brittle

High melting points

Mostly soluble in water

Do not conduct electricity in solid form (but conduct when molten or dissolved in water)

Examples: NaCl (table salt), KBr, CsCl, CaF_2

2. Covalent (Network) Crystals-

Constituents: Atoms connected by covalent bonds in a network structure

Bond: Covalent bonds

Properties:
Very hard (diamond) or brittle (silica)
Very high melting points
Mostly insoluble in water
Generally poor conductors of electricity

Examples: Diamond, Graphite, Quartz (Silicon dioxide, SiO_2)

3. Metallic Crystals -

Constituents: Metal atoms

Bond: Metal bonds (attraction between metal ions and a pool of free electrons)

Properties:
Good conductors of electricity and heat
Malleable (can be hammered into thin sheets)
Ductile (can be drawn into wires)
Lustrous (shiny)

Examples: Copper, Gold, Iron, Silver, Aluminium

4. Molecular Crystals-

Constituents: Molecules held together by weak forces

Bond: Van der Waals forces, hydrogen bonds, or dipole-dipole interactions

Properties:
Soft or brittle
Low melting points
Mostly poor conductors of electricity

Examples: Ice (H_2O), Sugar ($C_{12}H_{22}O_{11}$), Iodine (I_2), Naphthalene.

Applications of X-ray diffraction

1. Determining Crystal Structure-

Helps identify the arrangement of atoms in a crystal.

Allows us to compute atomic distances, bond lengths, and bond angles.

This forms the basis for understanding a material's properties.

2. Identification of Compounds-

Each crystalline substance produces a unique diffraction pattern — a kind of "fingerprint."

This is used to identify unknown compounds by comparing their patterns with standard databases.

3. Quantitative Phase Analysis

Determine relative amounts of phases in a mixture (by peak intensities).

4. Quality Control and Purity

Confirm purity of a substance (by matching its diffraction pattern to standard patterns).
Detect and identify impurities or secondary phases.

5. Crystallite Size and Strain Determination

Analyze peak broadening to estimate crystallite size (typically by Scherrer's formula).
Evaluate microstrain or lattice distortion.

6. Degree of Crystallinity

Calculate crystallinity percentage in polymers or composite materials.

7. Texturing and Preferred Orientations

Analyze texture (predominant crystallographic direction) in metal, ceramic, or thin film samples.

8. Thickness of Thin Films

Determining film thickness by interference fringe or reflection data.

9. Residue Stress Analysis

Measure residual stress and microstrain within materials.

10. Applications in Pharmacy

Identify polymorphs of drugs, which can affect their stability, bioavailability, and formulation properties.

Analyze crystalline form of raw materials and final products in pharmaceuticals.