Chapter #2:
X-Ray Diffraction and the Reciprocal Lattice

Lecture 1: Determination of Crystal Structure

1. Introduction

The interatomic spacing in crystalline solids is typically on the order of an angstrom (Å ≈ 10^{-10} m). To determine crystal structures and probe atomic arrangements, radiation with a comparable wavelength must be used. Diffraction techniques rely on the interaction between electromagnetic or particle waves and the periodic crystal lattice.

Common probes used in crystallography include:

• X-rays ($\lambda \approx 1$ Å) – interact primarily with electrons.
• Neutrons ($\lambda \approx 1$ Å) – interact with atomic nuclei.
• Electrons ($\lambda \approx 1$–2 Å) – interact strongly with electrons and are suitable for surface studies.

Typical X-ray wavelength range: $\lambda = 0.1$ Å – 10 Å

Typical atomic spacing order: $d \approx 1$ Å

Energy of Electromagnetic Wave (Photon)
$E = hc / \lambda = h\nu$

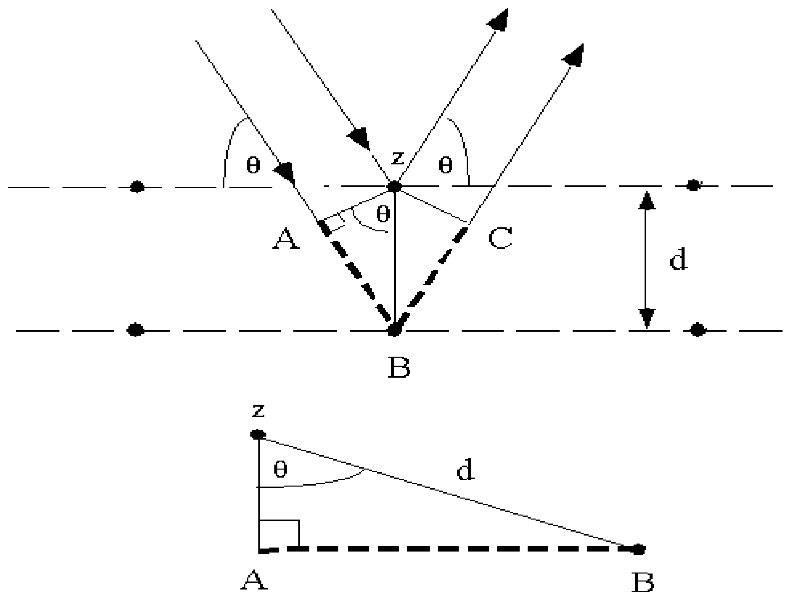
Where:
h : Planck's constant
c : Speed of light
λ : Wavelength
ν : Frequency

2. Bragg's Law

When a beam of monochromatic radiation is incident on a crystal, it is reflected by parallel atomic planes. Constructive interference occurs only when the path difference between reflected waves satisfies a specific condition.

2.1 Path Difference

For two rays reflected from adjacent parallel planes separated by distance **d**, the path difference is:



- From the figure above, we observe that there are two rays (Ray 1 and Ray 2), and the path difference (Δ) between them is given by the following relation:

$$\Delta = \overline{AB} + \overline{BC} = 2\overline{AB} = 2(d \sin\theta)$$

$$\Delta = 2\ d\ \sin_\theta$$

where **θ** is the angle between the incident beam and the reflecting plane (Bragg angle).

2.2 Condition for Constructive Interference

Constructive interference occurs when ***the path difference equals an integer multiple of the wavelength:***

$\Delta = n\lambda$

Combining the two expressions gives Bragg's Law:

$\mathbf{2\ d\ \sin_\theta = n\lambda}$

where:
n = order of reflection
λ = wavelength
d = interplanar spacing
θ = Bragg angle

A necessary condition for Bragg reflection is:

$\boldsymbol{\lambda \leq 2\, d_{(hkl)}}$

This also explains why visible light cannot be used to determine atomic-scale structures.

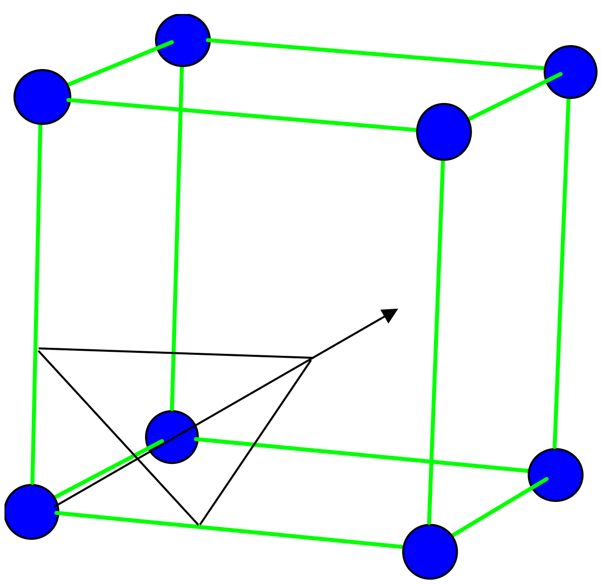
> X-rays are scattered by electrons of atoms arranged periodically in a crystal. The periodic arrangement makes the scattered waves interfere as if they were reflected from lattice planes.

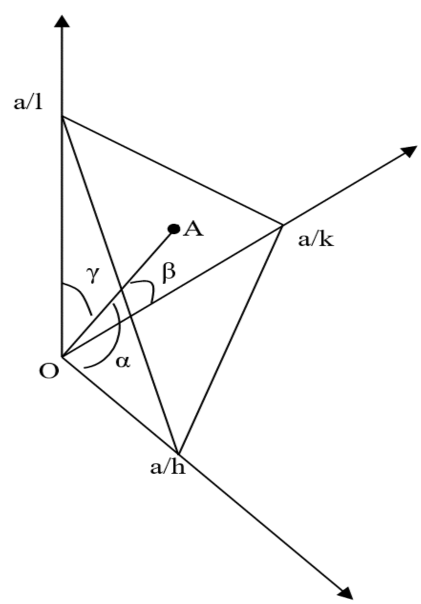
3. Interplanar Spacing in Cubic Crystals

For a **simple cubic lattice** with lattice parameter **a**, the interplanar spacing corresponding to Miller indices (*hkl*) is given by:

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2}}$$

This relation is derived geometrically by considering the intercepts of the plane with the crystal axes at a/*h*, a/*k*, and a/*l* as follows:





$\overline{OA}$ represents the interplanar spacing between the planes, and it is denoted by d.

$$\cos_{\alpha} = \frac{\overline{OA}}{a/h} = \frac{d}{a/h} = \frac{dh}{a}$$
$$\cos_{\beta} = \frac{\overline{OA}}{a/k} = \frac{d}{a/k} = \frac{dk}{a}$$
$$\cos_{\gamma} = \frac{\overline{OA}}{a/l} = \frac{d}{a/l} = \frac{dl}{a}$$
$$\cos^2{}_{\alpha} + \cos^2{}_{\beta} + \cos^2{}_{\gamma} = 1$$

Then,

$$(\frac{d\ h}{a})^2 + (\frac{d\ k}{a})^2 + (\frac{d\ l}{a})^2 = 1$$
$$d^2 = \frac{1}{\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}} = \frac{a^2}{h^2 + k^2 + l^2}$$
$$d = \sqrt{\frac{a^2}{h^2 + k^2 + l^2}}$$

Example-1:

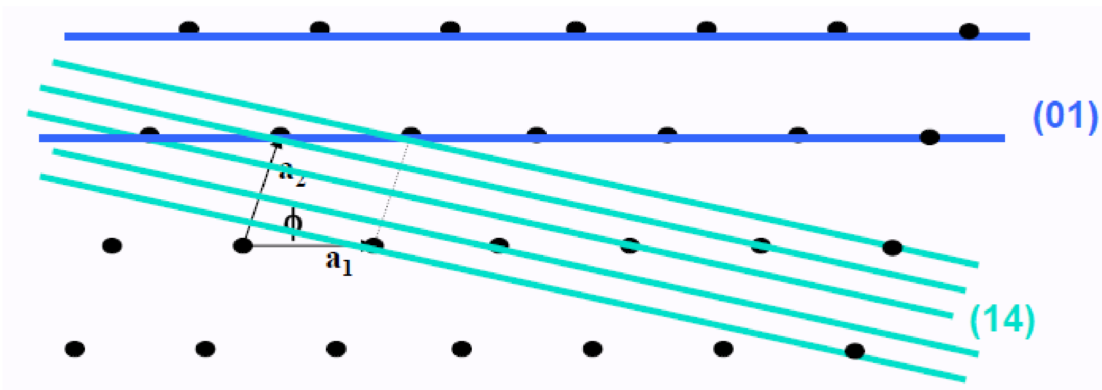
$$d_{(100)} = \frac{a}{\sqrt{(1+0+0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{(1+1+0}} = a/\sqrt{2}$$

$$d_{(111)} = \frac{a}{\sqrt{(1+1+1}} = a/\sqrt{3}$$

- **As the Miller indices increase, the interplanar spacing decreases.**

Think about it:



- There are different sets of parallel planes that can divide the crystal lattice.
- Small Miller indices indicate high plane density and large spacing between planes.
- Large Miller indices indicate low plane density and small spacing between planes.

For an orthorhombic lattice, the interplanar spacing is given by:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Using Bragg's law, the diffraction condition becomes:

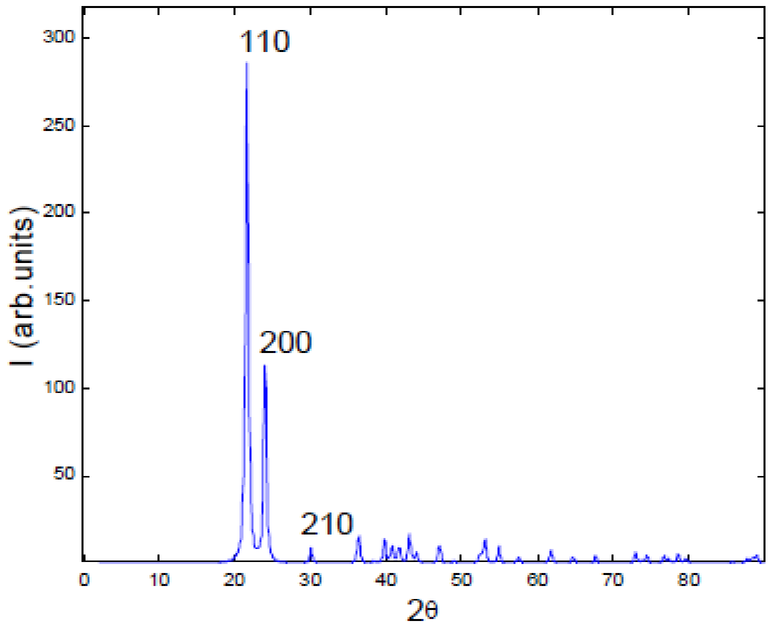
$$\sin^2\theta = (n^2\lambda^2/4)(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2})$$

5. Output of X-ray diffraction (XRD)

Output:

- Graph of **intensity vs angle (2θ)**
- Peaks correspond to diffraction from specific lattice planes

Only specific angles produce strong reflections due to interference conditions.



- Crystals can be viewed as sets of parallel atomic planes.
- Distance between planes = **interplanar spacing (d)**.
- Planes are labeled by Miller indices (*hkl*).
- Each set of planes can diffract X-rays.

4. Example Problem

Example-2:

If the spacing between two atomic planes is d = 5 Å, determine the maximum wavelength that can produce a Bragg reflection.

From the condition $\lambda \leq 2d$:
$\lambda_{max} = 2 \times 5$ Å $= 10$ Å

Example-3:

If the spacing between two different planes is 5 Å, calculate the maximum X-ray energy (in eV) required to produce a Bragg reflection.

Solution:

Given:

Interplanar spacing d = 5 A^0
Step 1: Bragg Law

$2\,d\,\sin(\theta) = n\,\lambda$

For maximum energy, the wavelength must be minimum.

Minimum wavelength occurs when $\sin(\theta) = 1$ and $n = 1$.

Therefore $\lambda = 2d$

$\lambda = 2 \times 5 = 10\ A^0$

$10\ A^0 = 1.0 \times 10^{-9}$ m

Step 2: Photon Energy Formula

$E = hc / \lambda$

$h = 6.626 \times 10^{-34}$ J.s

$c = 3.0 \times 10^{8}$ m/s

$E = (6.626 \times 10^{-34} \times 3.0 \times 10^{8}) / (1.0 \times 10^{-9})$

$E = 1.9878 \times 10^{-16}$ J

Step 3: Convert to eV

$1\ eV = 1.602 \times 10^{-19}$ J

$E = (1.9878 \times 10^{-16}) / (1.602 \times 10^{-19})$

$E = 1.24$ keV

5. Experimental Methods for Structure Determination (student presentations)

1. **Laue Method:**
A continuous spectrum of X-rays is directed onto a stationary single crystal. Different wavelengths satisfy Bragg's condition simultaneously.

2. **Rotating Crystal Method:**
A monochromatic X-ray beam is incident on a rotating single crystal, allowing various plane orientations to satisfy Bragg's condition.

3. **Powder Method:**
A monochromatic beam is directed onto a powdered sample containing randomly oriented microcrystals, producing diffraction rings.

See the following video to see how X-ray diffraction is used to determine atomic arrangements in materials:

https://app.jove.com/ar/v/10446/x-ray-diffraction-for-determining-atomic-and-molecular-structure?utm_source=chatgpt.com

Summary: