

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 ($\text{\AA} \approx 10^{-10} \text{ m}$). 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** ($\lambda \approx 1 \text{ \AA}$) – interact primarily with electrons and are widely used to determine crystal structures.
- **Neutrons** ($\lambda \approx 1 \text{ \AA}$) are electrically neutral and therefore interact primarily with atomic nuclei rather than the electron cloud. This makes neutron diffraction useful for studying crystal structures and magnetic ordering.
- **Electrons** ($\lambda \approx 1\text{--}2 \text{ \AA}$) have wavelengths comparable to atomic spacings and are strongly scattered by solids, making electron diffraction particularly useful for studying crystal surfaces.

Typical X-ray wavelength range: $\lambda = 0.1 \text{ \AA} - 10 \text{ \AA}$

Typical atomic spacing order: $d \approx 1 \text{ \AA}$

Energy of Electromagnetic Wave (Photon)

$$E = hc / \lambda = h\nu$$

Where:

h : Planck's constant

c : Speed of light

λ : Wavelength

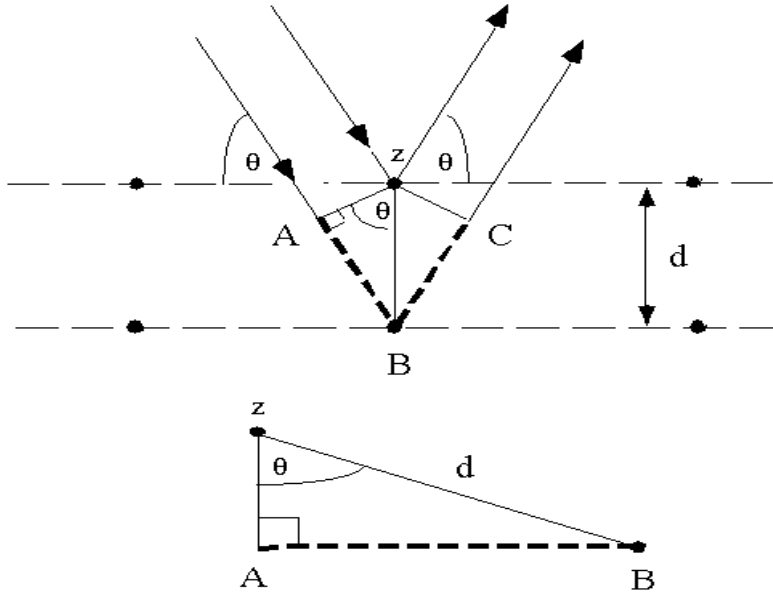
ν : Frequency

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:

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

where:

n = order of reflection

λ = wavelength

d = interplanar spacing

θ = Bragg angle

A necessary condition for Bragg reflection is:

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

- 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.
- **The corresponding Bragg angle is**

$$\theta = \sin^{-1}\left(\frac{\lambda}{2d_{hkl}}\right)$$

- Experimentally, the diffraction peak is often reported at the **scattering angle** 2θ , not at the Bragg angle θ . Thus,

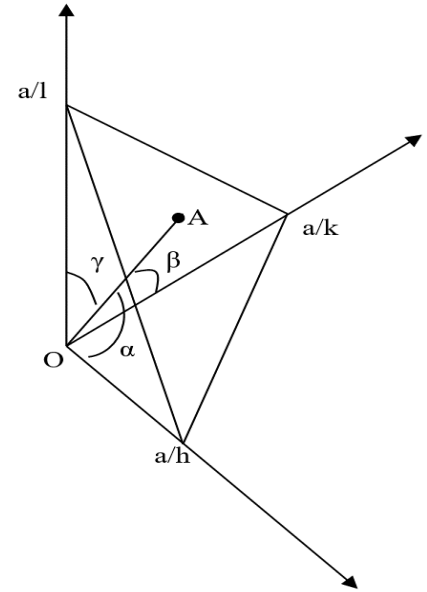
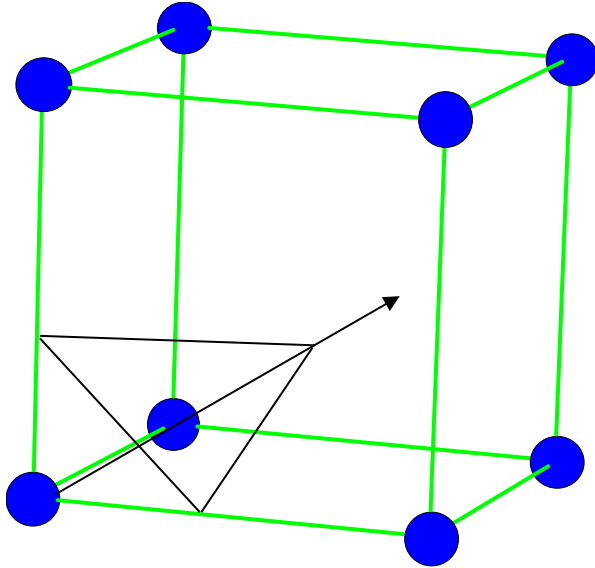
$$2\theta = 2 \sin^{-1}\left(\frac{\lambda}{2d_{hkl}}\right)$$

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,

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

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

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

Example-1:

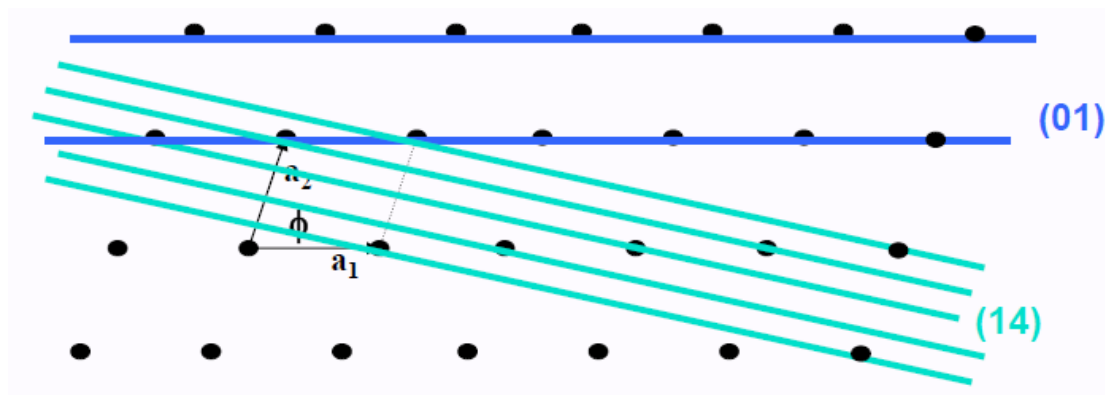
$$d_{(100)} = \frac{a}{\sqrt{(1+0+0)}} = a$$

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

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

- 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.
- Planar density tells us how many atoms are packed on that plane per unit area.

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:

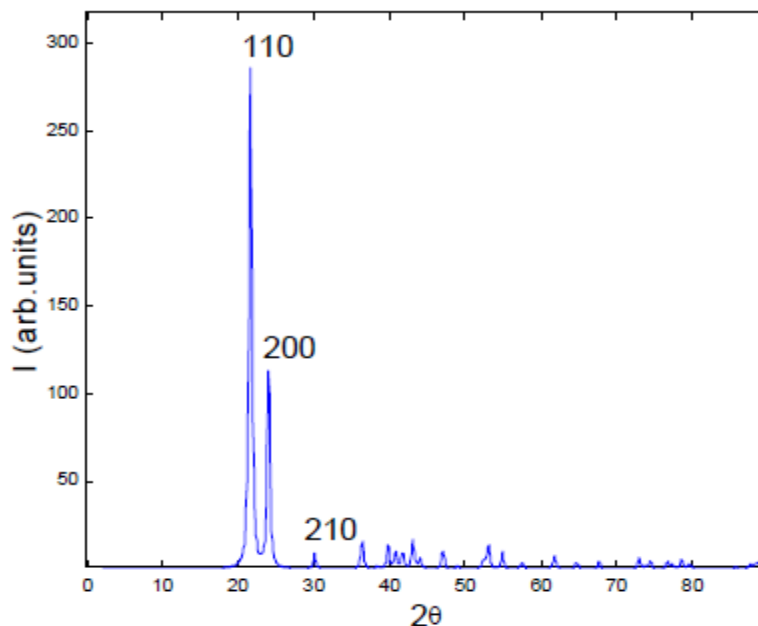
$$\sin^2 \theta = (n^2 \lambda^2 / 4) \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$$

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.

Key Insights

Diffraction arises from wave interference. Crystals behave as reflecting atomic planes. The path difference determines interference conditions. Only certain angles produce diffraction peaks. Bragg's Law connects diffraction geometry with crystal structure.

4. Example Problem

Example-2:

If the spacing between two atomic planes is $d = 5 \text{ \AA}$, determine the maximum wavelength that can produce a Bragg reflection.

From the condition $\lambda \leq 2d$:

$$\lambda_{\max} = 2 \times 5 \text{ \AA} = 10 \text{ \AA}$$

Example-3:

If the spacing between two different planes is $5 \text{ \AA}$, calculate the maximum X-ray energy (in eV) required to produce a Bragg reflection.

Solution:

Given:

Interplanar spacing $d = 5 \text{ \AA}$

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 $\lambda = 2 d$

$$\lambda = 2 \times 5 = 10 \text{ \AA}$$

$$10 \text{ \AA} = 1.0 \times 10^{-9} \text{ m}$$

Step 2: Photon Energy Formula

$$E = h c / \lambda$$

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

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

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

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

Step 3: Convert to eV

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

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

$$E = 1.24 \text{ keV}$$

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:

Path difference = $2d \sin\theta$

For Constructive Interference

Path difference = $n\lambda$

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

Braggs Law

d = Interplaner Spacing

θ = Braggs Angle

λ = Wavelength of X – ray

n = Order of Diffraction

Braggs Condition

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

$$\frac{n\lambda}{2d} = \sin\theta$$

$$\frac{n\lambda}{2d} \leq 1$$

$\sin\theta = 1 \text{ (Max)}$

For $n = 1$

$\lambda \leq 2d$

Wavelength of X-ray should be less than the double of interplanar spacing

$$\frac{2d}{\lambda} = n$$

As λ decreases, order of diffraction increases.

