UNIT-1(CRYSTALLOGRAPHY)

Thursday, August 7, 2025

1. INTRODUCTION TO CRYSTALLOGRAPHY

What is Crystallography?

Crystallography is the study of how atoms are arranged in solid materials, especially crystals.

- It uses special tools like **X-ray diffraction** to look inside crystals and see how the atoms are organized.
- This helps scientists learn about the **chemical bonds** and **physical properties** of different materials.
- Crystallography is very important in **science fields** like chemistry, physics, biology, and materials science.
- It has helped make big discoveries in areas like **medicine**, **nanotechnology**, and **electronics**.
- By knowing how atoms are arranged, scientists can understand **how materials behave**.
- It also helps in **creating new materials** with special features for specific uses.

Image of crystalline solid

1. MILLER INDICES (CUBIC SYSTEM)

What is a Crystalline Solid?

A crystalline solid is a type of solid where the tiny building blocks (like atoms, molecules, or ions) are arranged in a very neat and repeating pattern.

This pattern repeats in all directions (3D), which gives the solid a clear shape and strong structure.

The repeating pattern is called a crystal lattice.

Beautiful crystals like diamonds or salt look shiny and symmetric because of this special arrangement.

The fixed spots where the atoms sit in this pattern are called lattice sites.

What is a Single Crystal?

A single crystal is a solid where the atoms are arranged in a continuous and unbroken repeating pattern throughout the entire material.

The pattern extends without any breaks across the whole solid.

There are no grain boundaries (no interruptions in the pattern).

Single crystals are often transparent, shiny, and have uniform properties in specific directions.

Common examples include diamond, quartz, and silicon wafers used in electronics.

What is a Polycrystal?

A polycrystal (or polycrystalline solid) is a solid made up of many small crystals, called grains.

Each grain has a well-ordered atomic pattern, but the grains are not aligned with each other.

The areas where grains meet are called grain boundaries.

Polycrystals are usually stronger and tougher, but may not have uniform properties in all directions.

Common examples include metals like iron, copper, and ceramics.

1. Lattice

A lattice is a regular, repeating arrangement of points in space.

Each point represents the position of an atom, ion, or molecule.

It acts like a framework or grid that shows how particles are organized in a solid.

Think of it as the skeleton of a crystal.

2. Crystal Lattice

A crystal lattice is the 3D structure formed when atoms, ions, or molecules are placed on the lattice points.

It shows the actual arrangement of particles in a crystalline solid.

This pattern repeats in all directions, giving the crystal its shape and properties.

Examples: The crystal lattice of NaCl (salt) or diamond.

3. Unit Cell (PRIMITIVE)

A unit cell is the smallest repeating block of a crystal lattice that shows the full pattern.

It is like a building block of the entire crystal.

When unit cells are repeated in all directions, they form the whole crystal structure.

It defines the crystal's symmetry, shape, and dimensions.

Types: Cubic, Tetragonal, Hexagonal, etc.

4. **Multiple Cell (NON-PREMITIVE)**

A multiple cell is a larger block made by combining several unit cells together.

It helps in better visualizing the 3D structure of the crystal.

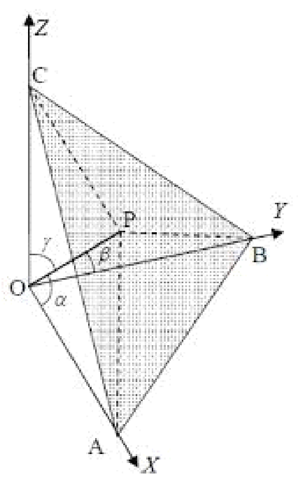
Often used in diagrams and models to show more of the crystal at once.

It’s not the smallest unit, but a bigger piece made by repeating the unit cell.

Got it! Here's the same text without using dollar signs for math expressions, keeping it clean and clear:

3. INTER PLANAR SPACING (CUBIC SYSTEM)

Interplanar Spacing (d_{hkl}) in a Cubic System



Interplanar spacing is the perpendicular distance between two adjacent, parallel crystal planes. It is denoted by d_{hkl}, where h, k, and l are the Miller indices of the crystal plane. This spacing is crucial for understanding crystal structures and plays a key role in techniques such as X-ray diffraction.

Derivation of the Formula

Consider a crystal plane with Miller indices (hkl). The plane intercepts the x, y, and z axes at distances OA, OB, and OC, respectively. By the definition of Miller indices, these intercepts relate to the lattice constants a, b, and c as follows:

- $OA = a / h$
- $OB = b / k$
- $OC = c / l$

Let d be the perpendicular distance from the origin to this plane. Define the direction cosines of this perpendicular line with respect to the x, y, and z axes as cos α, cos β, and cos γ, respectively.

From right triangle relationships,

- $\cos\alpha = d / OA = d / (a / h) = (d \times h) / a$
- $\cos\beta = d / OB = d / (b / k) = (d \times k) / b$
- $\cos\gamma = d / OC = d / (c / l) = (d \times l) / c$

A fundamental property of direction cosines states:

- $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

Substituting the above expressions gives:

- $(d \times h / a)^2 + (d \times k / b)^2 + (d \times l / c)^2 = 1$

Which simplifies to:

- $d^2 \times (h^2 / a^2 + k^2 / b^2 + l^2 / c^2) = 1$

Rearranging, the general formula for interplanar spacing is:

- $d_{hkl} = 1 / \sqrt{(h^2 / a^2) + (k^2 / b^2) + (l^2 / c^2)}$

Final Formula for Cubic Systems

In a cubic crystal system, all lattice parameters are equal, i.e., a = b = c. Substituting this into the general formula gives:

- $d_{hkl} = 1 / \sqrt{(h^2 / a^2) + (k^2 / a^2) + (l^2 / a^2)}$

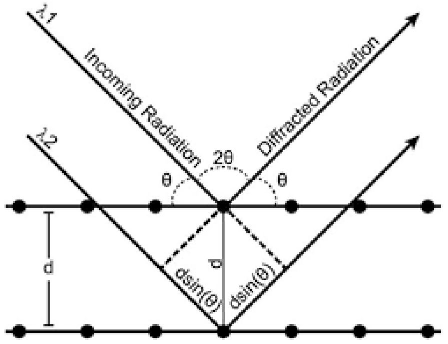
  $= 1 / \sqrt{(h^2 + k^2 + l^2) / a^2}$

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

This formula allows straightforward calculation of the interplanar spacing for any set of planes (hkl) in a cubic lattice, given the lattice constant a.

4. BRAGG'S LAW

What is Bragg's Law?



Bragg’s Law explains how X-rays reflect off layers of atoms in a crystal.

- When X-rays hit a crystal, they bounce off the layers of atoms inside it.
- If the X-rays reflect at a specific angle, they combine to make a strong signal.
- This only happens when the distance between atomic layers and the angle of the X-rays satisfy a special condition.
- This condition is called **Bragg’s Law**, and it helps scientists find out the distance between atomic layers in a crystal.

Bragg’s Law Formula

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

Where:

- **n** = Order of reflection (1, 2, 3,...)
- **λ** = Wavelength of the X-ray
- **d** = Distance between atomic layers (interplanar spacing)
- **θ** = Angle at which X-rays are reflected (glancing angle)

Derivation of Bragg's Law (Step-by-Step)

Let’s say X-rays hit a crystal and reflect off two atomic layers.

1. **Two X-rays enter the crystal:**

   One reflects from the top layer, the other goes deeper and reflects from the second layer.

2. **Extra Distance Traveled:**

   The second X-ray travels more distance before coming out.

   This extra path = **AB + BC** (see figure in textbook)

   Using geometry, AB = BC = **$d \sin\theta$**

3. **Total Extra Path**

   = AB + BC = **$2d \sin\theta$**

4. **Constructive Interference Condition**

   For the reflected X-rays to reinforce each other (constructive interference):

   Extra path = a whole number of wavelengths = **$n\lambda$**

5. **So, the condition becomes:**

   $n\lambda = 2d \sin\theta$ → This is Bragg’s Law

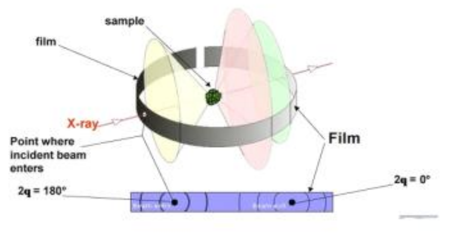
Why is Bragg’s Law Important?

- Helps find the atomic structure of crystals.
- Tells us the spacing between atomic planes.
- Used in **X-ray diffraction experiments**.

- Vital in material science, physics, chemistry, and biology (e.g. DNA structure).

5. POWDER DIFFRACTION METHOD

Powder Diffraction Method (Debye-Scherrer Method)



Construction:

Consider a polycrystalline material which is mixed with a little adhesive and placed in a sample holder. A thin film of X-rays is loaded in the cylindrical cassette of the camera, whose radius is 'R'. The thin film is perforated at the two ends that are the entry and exit point of the X-ray beam. The diffraction pattern is obtained at $\theta = 0^\circ - 90^\circ$.

Working:

A monochromatic X-ray beam is made to fall on the powder sample, which contains a large number of crystallites. When the X-ray beam is incident on the powder, it is scattered in all possible directions. At $\theta = 45^\circ$, the corresponding cone opens out as a circle by satisfying Bragg's conditions. If the angle θ is greater than 45°, back reflections are obtained. The diffraction pattern, as well as the lattice plane, are shown in the figure below. The mathematically derived diffraction angles with a known camera radius 'R' are evaluated.

Calculations:

$$4\theta = \frac{s}{R} \; RADIUS$$
$$\theta = \frac{s}{4R} \frac{180}{\pi}$$

The following calculations are derived from the experimental setup.

Here, S is the circumference of the diffracted ring, and R is the radius of the camera. The angle θ is the Bragg's angle.

6. CLASSIFICATION OF POINT DEFECTS

What are Point Defects?

Point defects are tiny mistakes in the way atoms are arranged in a solid.

- They happen when atoms are **missing**, **extra**, or **in the wrong place**.
- These defects can change how the material **looks, behaves, or conducts electricity**.
- Point defects are common in **metals, crystals, and ionic solids**.
- They are important in making **stronger, smarter, and better materials**.
- Scientists use these defects to improve **electronics, batteries**, and other high-tech things.

What is a Vacancy Defect?

A vacancy defect happens when an **atom is missing** from its spot.

- It's like a seat being empty in a row of chairs.
- This makes the solid **less dense**.
- It can change how heat or electricity moves through the solid.

- Vacancy defects are found in **metals and crystals**.

What is an Interstitial Defect?

An interstitial defect is when an **extra atom gets squeezed** into a small space between atoms.

- It's like stuffing an extra chair between others.
- This makes the material **more dense**.
- It changes how hard or strong the solid is.
- Found in things like **steel**.

What is a Substitutional Defect?

A substitutional defect is when **one atom is replaced** by a different kind of atom.

- It's like swapping one person's seat with someone else.
- This changes the **properties** of the material.
- Common in **alloys**, like brass (copper + zinc).
- It helps make **stronger and rust-resistant** materials.

7. SCHOTTKY DEFECTS AND FRANKEL DEFECTS

What is a Schottky Defect?

A Schottky defect happens when **a positive and a negative ion are both missing**.

- This keeps the charge balanced.
- It makes the material **lighter** (less dense).
- Found in salts like **NaCl (table salt)**.
- It affects how the solid **melts or conducts**.

What is a Frenkel Defect?

A Frenkel defect happens when a **small ion leaves its place** and goes into a gap in the solid.

- The number of atoms stays the same.
- It doesn't change the **density**.
- Seen in materials like **silver chloride (AgCl)**.
- It helps with **electric flow** in some solids.

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