PC-8 : PHYSICAL CHEMISTRY

UNIT-I Solid state

Symmetry in Crystals

Definition:

Symmetry in crystals refers to the orderly and repetitive arrangement of atoms or ions in a crystal lattice such that certain symmetry elements can be identified.

Symmetry Elements & Symmetry Operations

A **symmetry element** is a geometrical entity (point, line, or plane) about which a symmetry operation is performed.

A **symmetry operation** is the act of moving the crystal (rotation, reflection, inversion, etc.) in such a way that after the operation, the crystal appears indistinguishable from its original state.

The main symmetry elements in crystals are:

1. Plane of Symmetry (Mirror Plane, m)

Definition: An imaginary plane dividing the crystal into two equal halves that are mirror images of each other.

Types:

Horizontal plane (σh) – parallel to the base of the crystal.

Vertical plane (σv) – parallel to the vertical axis.

Diagonal plane (σd) – passes through edges or corners diagonally.

Example: Cubes have multiple planes of symmetry.

2. Axis of Symmetry (n-fold Axis)

Definition: An imaginary line through the crystal about which it can be rotated by **360°/n** and appear the same after each rotation.

Types:

Two-fold (C_2) → 180° rotation symmetry.

Three-fold (C_3) → 120° rotation symmetry.

Four-fold (C_4) → 90° rotation symmetry.

Six-fold (C_6) → 60° rotation symmetry.

Example: Quartz has a three-fold axis; NaCl crystal has four-fold axes.

3. Centre of Symmetry (Inversion Centre, i)

The three fundamental laws are:

Definition: A point inside the crystal such that every point on the surface has an identical point directly opposite to it, equidistant from the centre.

Example: NaCl and CsCl crystals have a centre of symmetry.

4. Rotation–Reflection Axis (Improper Axis of Symmetry, Sn)

Definition: A combination of rotation followed by reflection through a plane perpendicular to the axis.

Example: Certain tetrahedral molecules (like SF_4) exhibit this.

Importance of Symmetry in Crystals

Helps in **classification** of crystals into 32 crystal classes (point groups).

Determines **physical properties** such as optical behavior, cleavage planes, and growth habit.

Plays a role in **X-ray diffraction studies** for determining crystal structure

Laws of Crystallography

Crystallography deals with the study of the external form, internal structure, and physical properties of crystals.

The external shape of a crystal reflects its internal arrangement of atoms, ions, or molecules, and this arrangement follows certain natural laws known as **laws of crystallography**.

1. Law of Constancy of Interfacial Angles (Steno's Law – given by Nicolaus Steno, 1669)

Statement:

The angles between any two corresponding faces of a crystal of the same substance are always the same, **irrespective of size, shape, or method of formation** of the crystal.

Explanation:

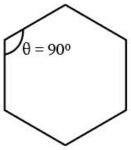
Even though crystals of the same substance may differ in size due to different growth conditions, the angle between corresponding faces remains constant.

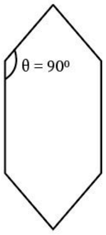
This is because the internal arrangement of atoms in a given crystal type is fixed, and external faces correspond to definite atomic planes.

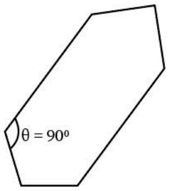
Example:

Sodium chloride crystals: Small cubic crystals and large cubic crystals both have interfacial angles of **90°** between adjacent faces.

Quartz crystals: The angle between certain prism faces is always about **120°**, no matter the crystal size.







2. Law of Rationality of Indices

(Weiss Law – given by Christian Samuel Weiss, 1784)

Statement:

The intercepts of any crystal face on the crystallographic axes are either equal to the unit intercepts or simple whole-number multiples of them.

Explanation:

A crystal lattice can be represented by crystallographic axes (imaginary reference lines).

A particular crystal face cuts these axes at distances proportional to small integers.

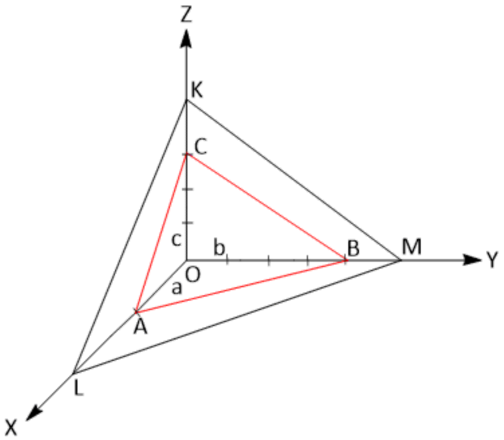
These intercepts, when expressed in terms of unit cell dimensions, are always in a rational ratio (not fractions like √2 or π, but whole numbers).

Example:

If a unit cell has axes a, b, c:

A face may intercept a at 1a, b at 2b, c at ∞ (parallel to c-axis).

These are expressed as Weiss indices (1, 2, ∞) → converted into Miller indices.



3. Law of Symmetry

(Haüy's Law given by René Just Haüy, 1784)

Statement:

All crystals of the same substance belong to the same **crystal class** and have the same elements of symmetry.

Explanation:

A crystal's external shape is determined by its internal atomic arrangement.

Therefore, all crystals of the same substance will show the same set of symmetry elements, no matter the size or growth conditions.

Weiss Indices

Definition

Weiss indices are a method of designating the orientation of crystal faces(planes) by expressing their intercepts on the crystallographic axes **in terms of unit lengths**. They are represented by symbols **a : b : c** (or simple multiples of these), where:

a = intercept along the x-axis
b = intercept along the y-axis
c = intercept along the z-axis

Origin

The system was proposed by **Christian Samuel Weiss** (1784–1856), hence the name. It was the first scientific attempt to describe the orientation of crystal faces mathematically.

Basic Idea

A crystal face can be described by the ratio of its intercepts on the crystallographic axes.

1. These intercepts are given as simple **whole-number multiples** (or fractions) of the unit cell dimensions.
2. If a plane is parallel to an axis, the intercept is written as ∞ for that axis.

Notation

Weiss indices are written as:

ha:kb:lc

where:

h,k,l = integers (possibly including ∞)

a,b,c = unit intercepts along the x, y, and z axes

Example

Suppose a crystal face intercepts:

a-axis at 2a

b-axis at 3b

c-axis is parallel (∞ intercept)

Weiss notation → 2a:3b:∞c

Special Cases

1. If a plane cuts an axis at one unit length → written as **a**.
2. If a plane is parallel to an axis → intercept = ∞.
3. If intercept is a fraction → expressed as multiple of the reciprocal.

2. Miller Indices

Definition:

Miller indices are a set of three small integers (h, k, l) used to denote the orientation of a crystal plane with respect to the crystallographic axes.

They are derived from the intercepts of the plane on the three axes of the crystal.

Steps to determine Miller indices:

1. **Determine intercepts** of the crystal plane along the crystallographic axes **a, b, c** (in terms of unit cell dimensions).
   Example: Intercepts = 2a, 3b, 1c.
2. **Take reciprocals** of these intercepts.
   Example: $\frac{1}{2} : \frac{1}{3} : 1$
3. **Clear fractions** to get the smallest set of whole numbers.
   Example: Multiply by 6 → (3, 2, 6)
4. **Write in parentheses** → **(3 2 6)** = Miller indices.

Rules:

If a plane is **parallel** to an axis → intercept = ∞ → reciprocal = 0.

Example: Plane parallel to z-axis → (h k 0).

Negative intercept → denoted by a bar over the number (e.g.,$\bar{1}$)

Example: A plane cutting a at a, b at 2b, parallel to c

→ intercepts = (1, 2, ∞)

→ reciprocals = (1, 0.5, 0)

→ multiplying by 2 → (2 1 0).

Relationship to Miller Indices

Miller indices are derived from Weiss indices by:

1. Taking **reciprocals** of the Weiss indices.
2. Clearing fractions to get the smallest set of whole numbers.
   Example:
   Weiss indices = 2a:3b:∞c
   → reciprocals = $\frac{1}{2}$: $\frac{1}{3}$: 0
   → multiply by 6 → (3 2 0) = **Miller indices**.

Lattice Point

Definition:

A lattice point is a fixed position in a crystal lattice that represents the location of atoms, ions, or molecules.

Features:

Every lattice point has an identical environment.

Lattice points repeat periodically in all three dimensions.

They are the **nodes** of the space lattice.

Example:

In NaCl crystal, each lattice point represents either a Na^+ ion or a Cl^- ion arranged in a regular pattern.

Space Lattice

Definition:

A space lattice is the three-dimensional arrangement of lattice points in space, showing the periodic arrangement of atoms in a crystal.

Unit Cell:

Definition:

The smallest repeating structural unit of a crystal lattice which, when repeated in all three dimensions, generates the entire lattice.

Parameters:

A unit cell is described by:

Edge lengths: a, b, c

Interaxial angles: α (between b and c), β (between a and c), γ (between a and b)

Types of Unit Cells:

Primitive (P) – points at corners only.

Body-centered (I) – points at corners + one at body center.

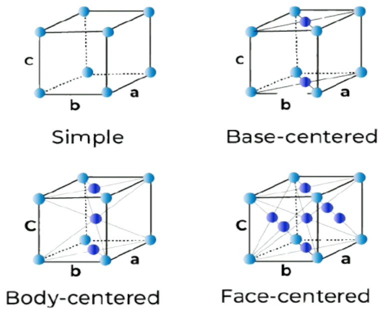
Face-centered (F) – points at corners + one at cent

Base-centered (C) – points at corners + one at center of each pair of opposite faces.

Example:

NaCl → Face-centered cubic (FCC)

CsCl → Body-centered cubic (BCC)



crystal systems:

The mathematical proof (done in crystallography using group theory) shows there are only 7**Types:** Based on edge lengths and angles, space lattices are grouped into **7 crystal systems**:

1.Cubic 2. Tetragonal 3.Orthorhombic 4.Hexagonal 5.Rhombohedral (Trigonal) 6.Monoclinic 7.Triclinic

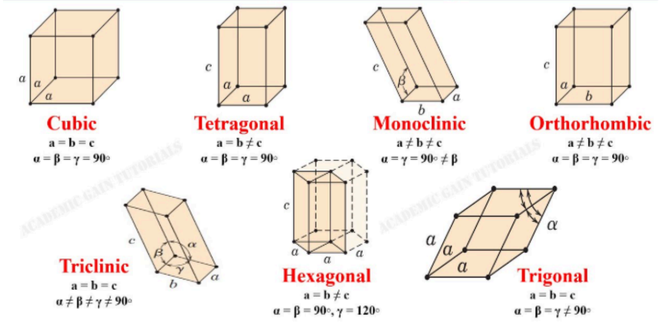


IMAGE TAKEN FROM ACADEMIC GAIN TUTORIALS

Bravais Lattices:

Definition:

A **Bravais lattice** is an infinite three-dimensional arrangement of points in space such that each point has an identical environment. It represents the periodic arrangement of lattice points in a crystal.

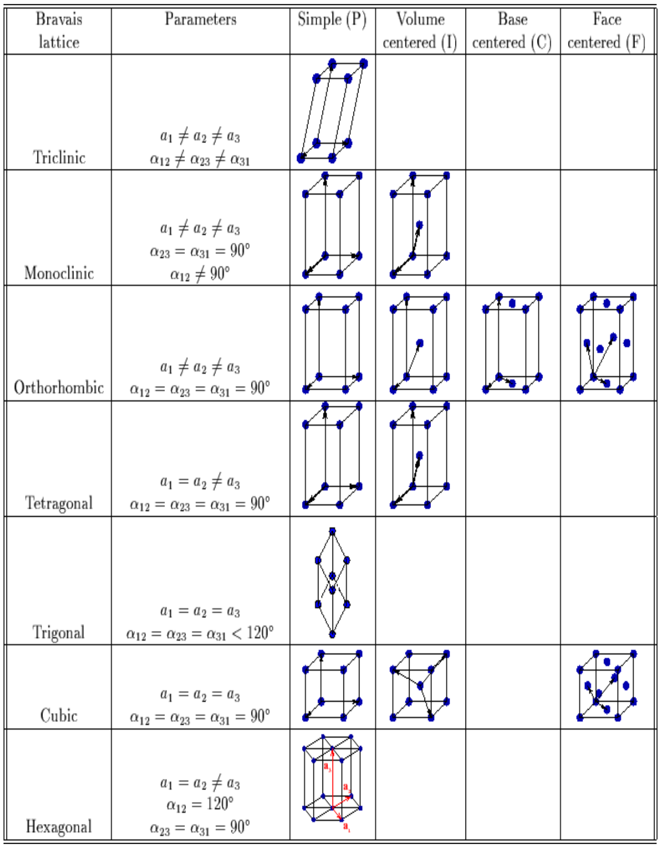
By considering centering of lattice points (primitive, body-centered, face-centered, base-centered), there are **14 Bravais lattices**.

Bravais Lattices and Crystal Systems

By combining 7 systems with different lattice centering types (P, I, F, C), we get 14 Bravais lattices.

Types of Lattice Centering:

1. **Primitive (P)** – points at corners only.
2. **Body-centered (I)** – points at corners + one at center of cell.
3. **Face-centered (F)** – points at corners + one at center of each face.
4. **Base-centered (C)** – points at corners + one at center of a pair of opposite faces.



Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

Bragg's Law

Statement: Bragg's law gives the condition for constructive interference of X-rays scattered by crystal planes:

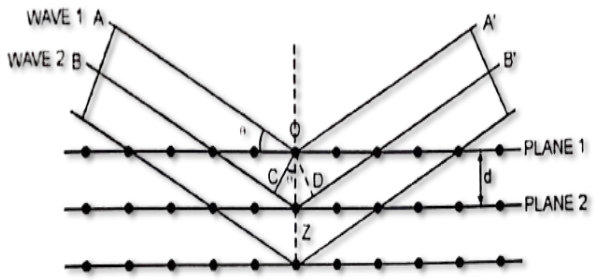
$n\lambda=2d\sin\theta$ Where: n = order of reflection (integer)

λ = wavelength of X-rays d = interplanar spacing

θ = glancing angle (angle between incident beam and crystal plane)

Derivation (Concept):

Consider two parallel atomic planes in a crystal separated by distance d. Two monochromatic X-rays (waves 1 and 2) strike the planes at the same glancing angle θ and are reflected. In the figure the rays hit the top plane at point O and hit the lower plane at point Z and the next lower plane at points directly below them.



Path difference:

Ray 2 travels extra distance compared to Ray 1 because it penetrates to the lower plane and then returns. This extra path consists of two segments (one on the incident side and one on the reflected side). Call these segments CZ and ZD. The total extra path length is

Δ=CZ+ZD.

For constructive interference (bright reflected beam) the path difference between the two rays must be an integer multiple of the wavelength λ

CZ+ZD = n λ where n = Integer and λ = wave length of X-ray used

Draw perpendiculars OC and OD from O to the ray 2 to form right angle triangles Δ OCZ and Δ ODZ. and **Δ OCZ & Δ OZD** are **similar triangles**

In Δ OCZ ∠C = 90° ∠O = θ° ∠Z = (90-θ)°

In Δ ODZ ∠D = 90° ∠O = θ° ∠Z = (90-θ)°

In Δ OCZ $\sin\theta = \frac{\text{opposite side to }\theta}{\text{hypotenuse}}$

$$\sin\theta = \frac{ZC}{OZ}$$

$$\sin\theta = \frac{ZC}{d}$$

$$ZC = d\sin\theta$$

Similarly In Δ ODZ

$$\sin\theta = \frac{\text{opposite side to }\theta}{\text{hypotenuse}}$$

$$\sin\theta = \frac{ZD}{OZ}$$

$$\sin\theta = \frac{ZD}{d}$$

$$ZD = d\sin\theta$$

The total extra path length Δ=CZ+ZD = n λ

n λ = CZ+ZD =d sin θ +d sin θ = 2d sin θ

n λ = 2d sin θ

X-ray Diffraction and Crystal Structure

X-ray Diffraction (XRD)

Definition:

XRD is an experimental method used to determine the arrangement of atoms in a crystal by studying the pattern in which a beam of X-rays is diffracted by the crystal.

Principle:

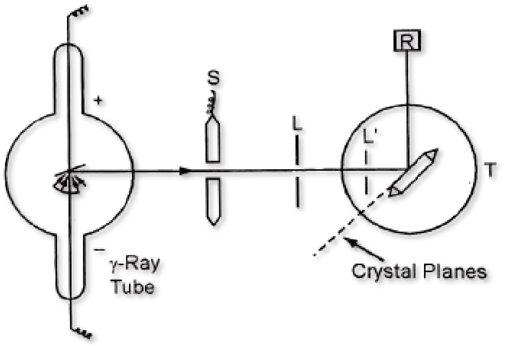
When X-rays of wavelength comparable to the spacing between atomic planes (~1 Å) strike a crystal, they are scattered by the atoms. Under certain conditions, constructive interference occurs, producing a diffraction pattern.

Common XRD Methods:

1. Laue Method – Uses a fixed crystal and polychromatic X-rays → studies orientation of crystals.
2. Rotating Crystal Method – Uses monochromatic X-rays → determines unit cell dimensions.
3. Powder Method (Debye–Scherrer) – Uses powdered sample → for unknown materials.

Rotating Crystal Method

In the **Rotating Crystal Method** of X-ray diffraction, a single crystal is carefully mounted on the rotation axis at the center of a cylindrical film camera. A narrow, monochromatic X-ray



beam is aligned so that it strikes the crystal exactly at the center. The crystal is then rotated about a fixed axis during exposure. As the crystal rotates, different sets of lattice planes come into position to satisfy **Bragg's condition**, producing a characteristic pattern of diffraction spots (called layer lines) on the surrounding photographic film. After the exposure, the film is developed and the positions of the spots are accurately measured. These positions are converted into diffraction angles 2θ, which are then used in **Bragg's law** to calculate the interplanar spacings ddd. The observed reflections are indexed by assigning appropriate **Miller indices** (h k l), and the corresponding lattice parameters of the crystal are calculated using the d_{hkl} formula appropriate for its crystal system.

Purpose in Crystallography:

To determine **interplanar spacing** (d)

To find **crystal structure** (FCC, BCC, HCP, etc.)

To measure **lattice constants** and identify materials