

Basics of Solid State Chemistry

Subject: Advanced Physical Chemistry-II
Subject Code: BCHE-602

Dr. Raj Kumar
Assistant Professor
Department of Chemistry
School of Basic & Applied Sciences
Maharaja Agrasen University
Email: rajkumar@mau.edu.in



Objectives

- ☐ To Understand the basics of crystallography and its role in solid-state chemistry.
- ☐ To Learn about crystal lattices and how they define crystal structures.
- ☐ To Explore Bragg's equation and its significance in X-ray diffraction.
- ☐ To Understand the importance of symmetry in crystal classification and material properties.

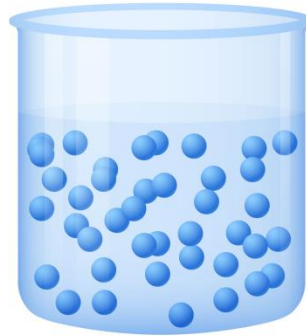
Matter

SOLID



- Rigid
- Fixed Shape
- Fixed Volume
- Cannot be squashed

LIQUID



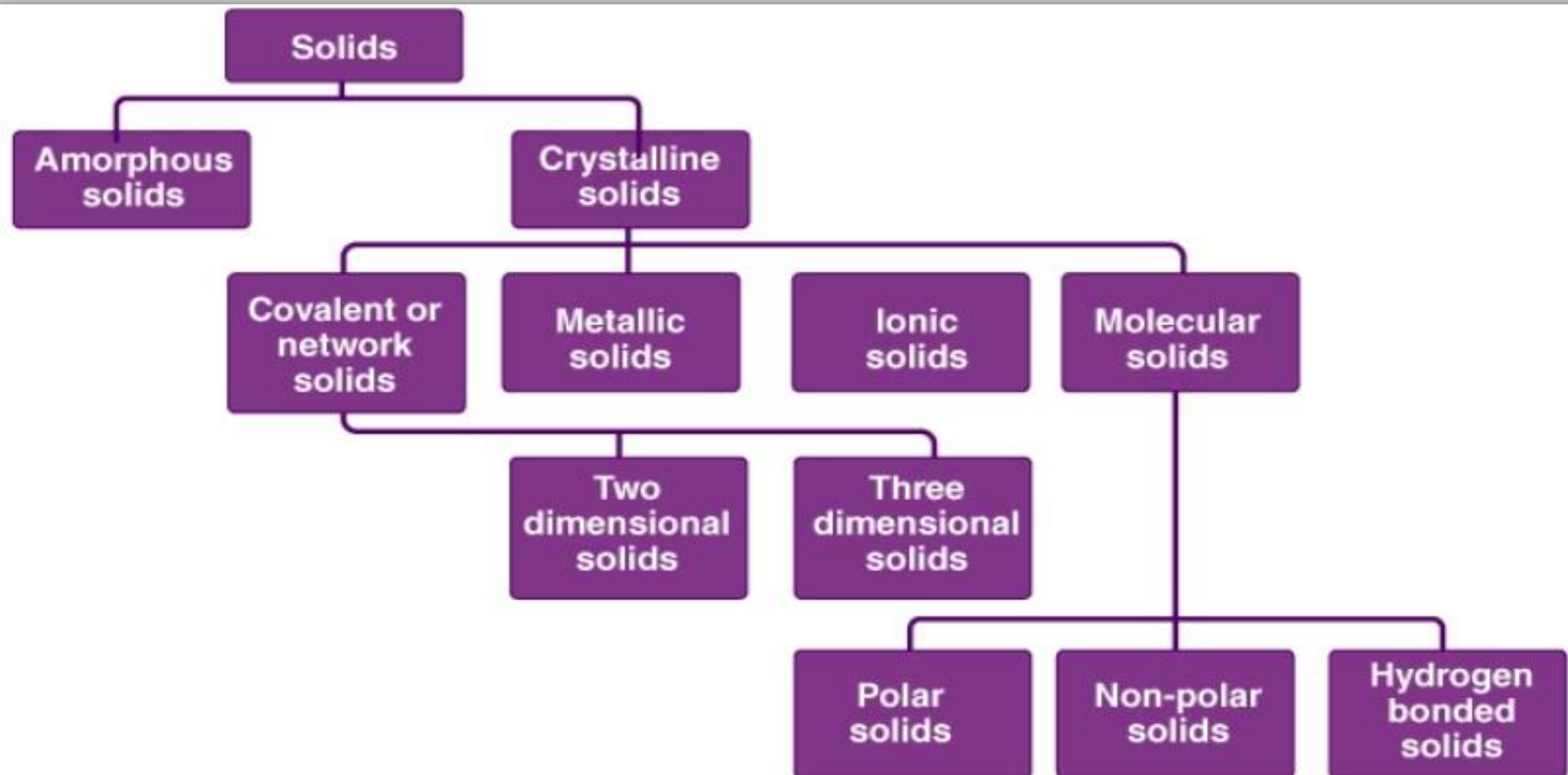
- Not Rigid
- No Fixed Shape
- Fixed Volume
- Cannot be squashed

GAS



- Not Rigid
- No Fixed Shape
- No Fixed Volume
- Can be squashed

Classification of Solids



How to Study geometric structure of solids?

Crystallography

- Crystallography is the study of the geometric description of crystals and their internal atomic arrangement.
- It helps in understanding how atoms are arranged in solids and how this affects their properties.

Crystallographic Axes: (ox, oy, oz)

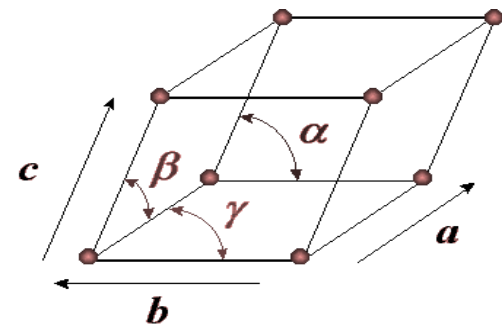
The lines drawn parallel to the lines of intersection of any three faces of a unit cell, which do not lie in the same plane.

Interfacial Angles: (α , β , γ)

The angles between three crystallographic axis

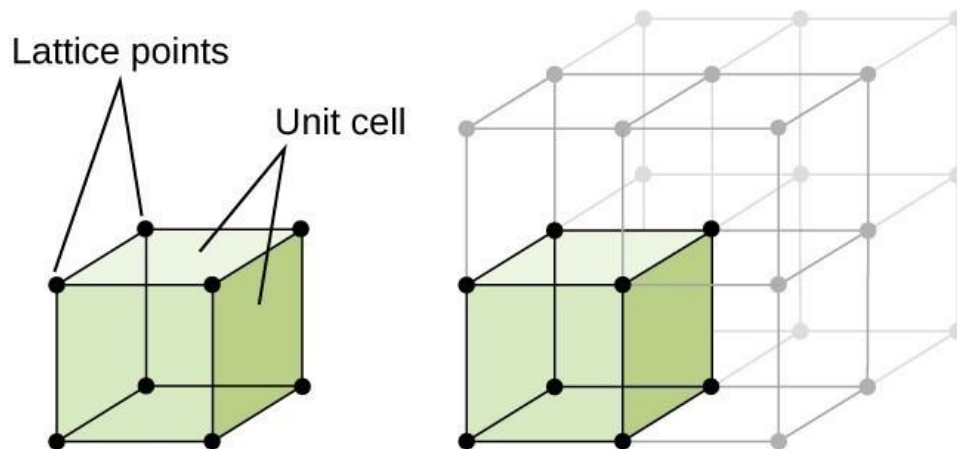
Primitives: (a, b, c)

The three sides of the unit cell



Crystal Lattice

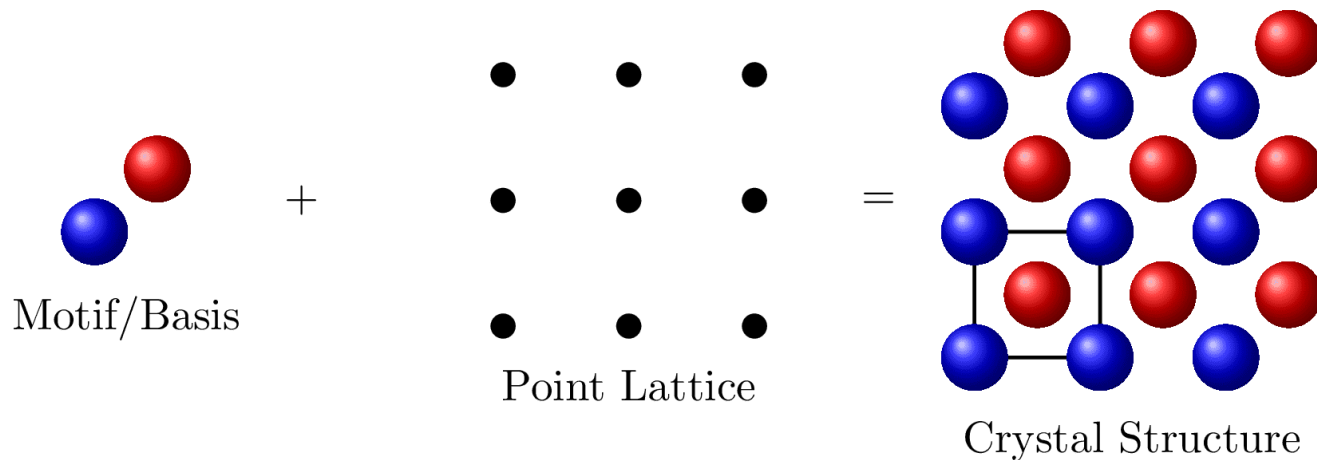
- A **crystal lattice** is a **three-dimensional arrangement** of atoms, ions, or molecules in a repeating and periodic pattern.
- It serves as the **framework** for the structure of a crystalline solid.
- In crystallography, only the geometrical properties of the crystal are of interest, therefore one replaces each atom by a geometrical point located at the equilibrium position of that atom.



- ✓ An infinite array of points in space,
- ✓ Each point has identical surroundings to all others.
- ✓ Arrays are arranged in a periodic manner.

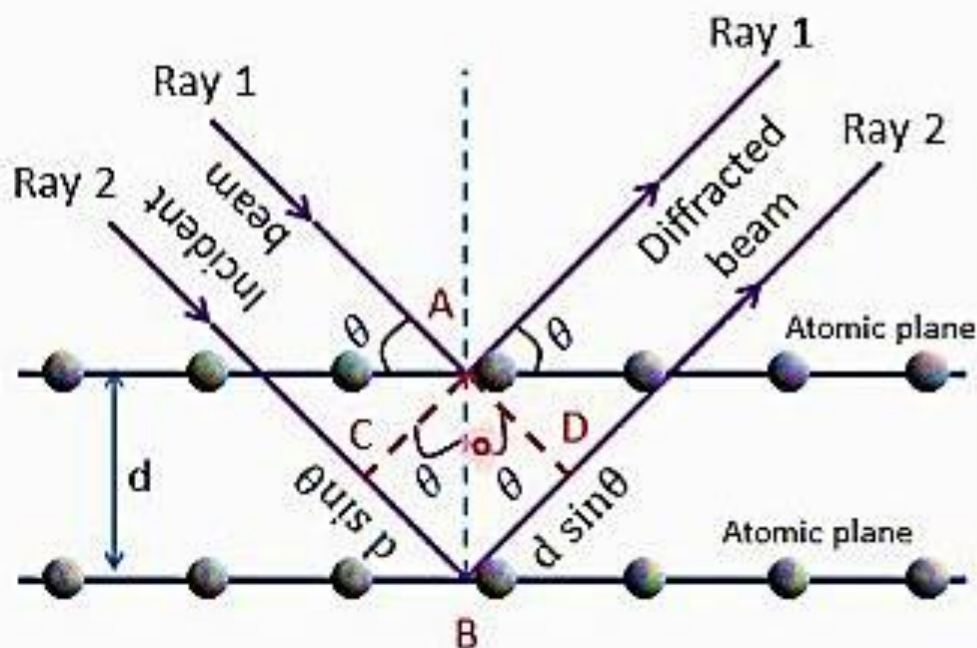
Crystal Structure

Crystals are structures that consist of a repeating pattern in space. A crystal structure is formed by placing atoms, groups of atoms, or molecules—known as the basis or motif—at the lattice points of a geometric framework called the crystal lattice.



Bragg's Equation

Bragg's Law of X-ray Diffraction



From figure, we can write -

$$CB = BD = d \sin \theta$$

Path difference between Ray 1 and Ray 2 is -

$$\Delta = CB + BD$$

$$= d \sin \theta + d \sin \theta = 2d \sin \theta$$

Condition for maximum is -

$$\text{path difference } \Delta = n \lambda$$

where $n = 1, 2, 3, 4, \dots$

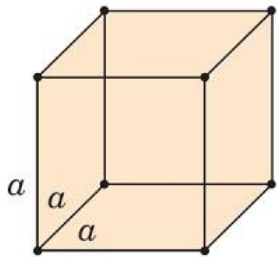
for 1st, 2nd, 3rd order maximum respectively

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

This is known as
Bragg's law of X-ray diffraction

Classification of Crystals

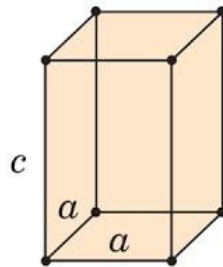
Seven Crystal Systems



Cubic

$$a = b = c$$

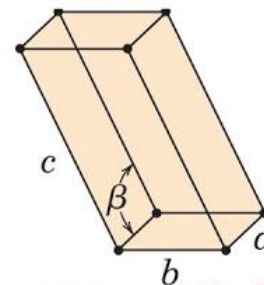
$$\alpha = \beta = \gamma = 90^\circ$$



Tetragonal

$$a = b \neq c$$

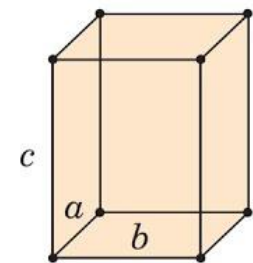
$$\alpha = \beta = \gamma = 90^\circ$$



Monoclinic

$$a \neq b \neq c$$

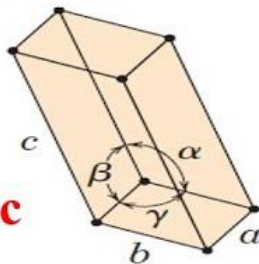
$$\alpha = \gamma = 90^\circ \neq \beta$$



Orthorhombic

$$a \neq b \neq c$$

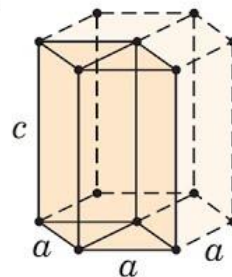
$$\alpha = \beta = \gamma = 90^\circ$$



Triclinic

$$a \neq b \neq c$$

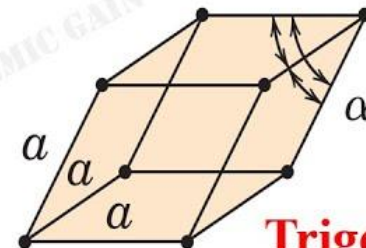
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



Hexagonal

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$



Trigonal

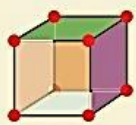
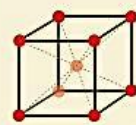
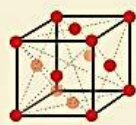
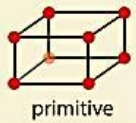
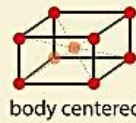
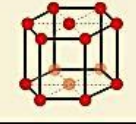
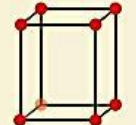
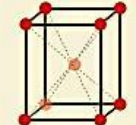
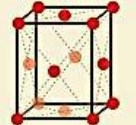
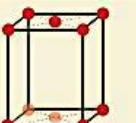
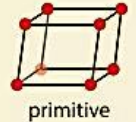

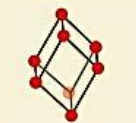
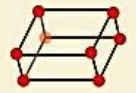
$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

Classification of Crystals

Crystals are categorized into 7 crystal systems based on their symmetry:

- Cubic
- Tetragonal
- Orthorhombic
- Hexagonal
- Trigonal (Rhombohedral)
- Monoclinic
- Triclinic

cubic	 primitive	 body centered	 face centered	
tetragonal	 primitive	 body centered		
hexagonal	 primitive			
orthorhombic	 primitive	 body centered	 face centered	 basis face centered
monoclinic	 primitive		 basis face centered	
trigonal	 primitive			
triclinic	 primitive			

Crystal Symmetry

- Symmetry plays a crucial role in defining crystal structures and their physical properties.
- Understanding symmetry operations helps in classifying materials
- Predicting their behavior in applications such as semiconductors, optics, and material science.

Symmetry Elements and Their Operations

Plane of Symmetry (Mirror Plane):

- Operation: Reflection in the plane.
- Example: A cube has multiple mirror planes dividing it into symmetrical halves.

Centre of Symmetry (Inversion Centre):

- Operation: Inversion of all atoms through the centre.
- Example: A diamond structure has an inversion centre.

Axis of Symmetry (Rotation Axis):

- Operation: One or more rotations about the axis.
- Example: A hexagonal crystal exhibits 6-fold rotational symmetry.

Improper Axis of Rotation:

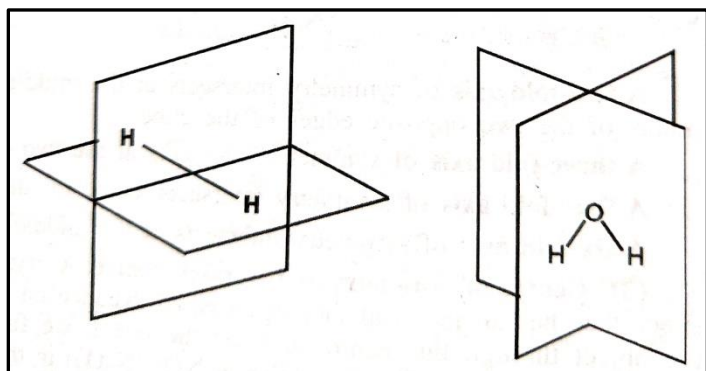
- Operation: Rotation followed by reflection in a plane perpendicular to the axis.
- Example: Some molecular structures exhibit improper rotational symmetry.

Axis of Rotation Inversion:

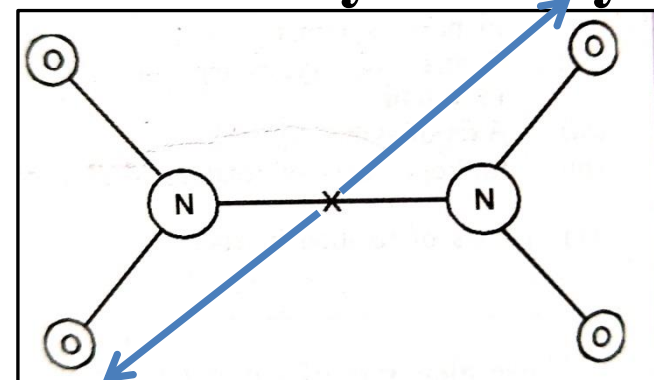
- Operation: Rotation followed by inversion through the centre.
- Example: Present in complex crystal systems.

Symmetry elements: Examples

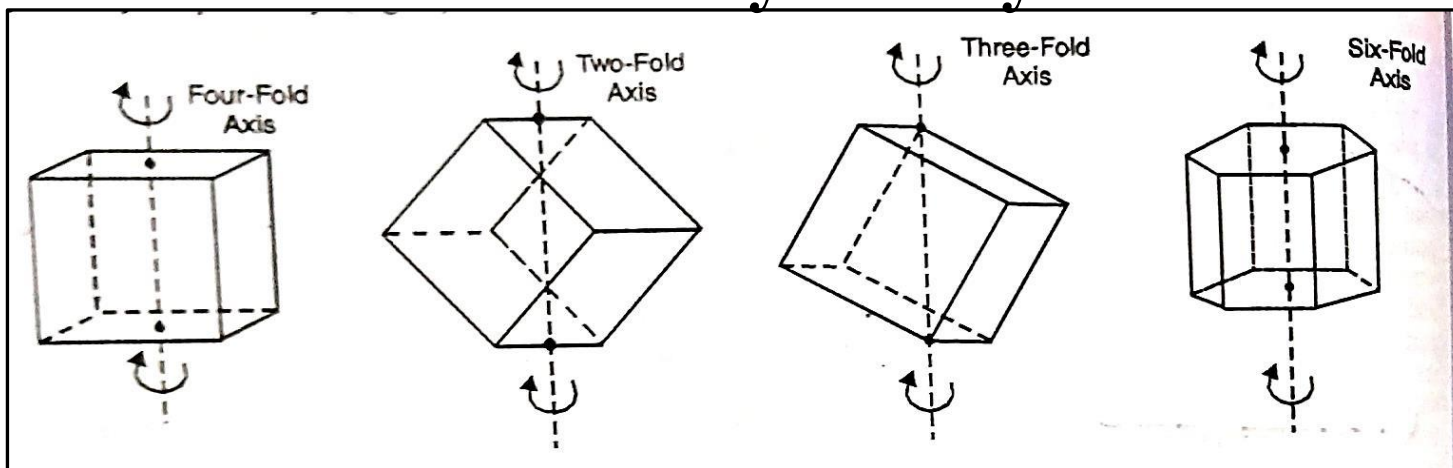
Plane of symmetry



Centre of symmetry



Axis of Symmetry



Summary

- Crystallography helps describe the geometric arrangement of atoms in solids.
- A crystal lattice is a periodic and three-dimensional arrangement of points that form the structural framework of crystals.
- A crystal structure is obtained by attaching atoms or molecules (motif) to lattice points.
- Crystals are categorized into 7 crystal systems based on symmetry.
- Bragg's equation is fundamental in X-ray diffraction analysis for studying crystal structures.
- Symmetry elements such as reflection planes, rotation axes, and inversion centers define the structural and physical properties of crystals.
- Understanding crystal symmetry is crucial for applications in material science, optics, and semiconductors.



Suggested Readings

"Solid State Chemistry and Its Applications" - Anthony R. West

- A comprehensive introduction covering crystal structures, defects, and electronic properties.

"Solid State Chemistry: An Introduction"- Lesley Smart & Elaine Moore

- A modern take on solid-state chemistry with practical applications.