

UNIT – I CRYSTALLOGRAPHY:

Crystallography: Crystal Symmetry Elements, Crystal Classes, Crystal Systems, Unit Cell, Bravais Lattices, Space Groups

1. Crystal Symmetry Elements:

- **Rotation Axes:** These are imaginary lines around which a crystal can be rotated to a position where it looks the same as before rotation. Examples include 2-fold, 3-fold, 4-fold, and 6-fold rotation axes.
- **Mirror Planes:** These divide the crystal into two halves, with one half being the mirror image of the other.
- **Center of Symmetry:** A point within the crystal where any line drawn through it intersects the crystal's surface at equal distances. It is also called an inversion center.
- **Screw Axes:** These combine translation and rotation, where the crystal is rotated around an axis and simultaneously translated along that axis.

2. Crystal Classes:

- There are 32 crystal classes, each characterized by specific combinations of symmetry elements.
- These classes are grouped based on their symmetry properties, such as presence or absence of rotation axes, mirror planes, and center of symmetry.

3. Crystal Systems:

- Crystal systems are based on the geometry of the unit cell and the relationships between its edges and angles.
- There are seven crystal systems: cubic, tetragonal, orthorhombic, monoclinic, triclinic, hexagonal, and rhombohedral.

4. Unit Cell:

- The unit cell is the smallest repeating unit in a crystal lattice that maintains the crystal's symmetry and structure.
- It is characterized by its dimensions (a , b , c) and interaxial angles (α , β , γ).

5. Bravais Lattices:

- Bravais lattices represent the different ways in which identical lattice points can be arranged in space.
- There are 14 Bravais lattices, categorized into seven crystal systems based on their lattice geometry.

6. Space Groups:

- Space groups describe the arrangement of atoms or ions within the unit cell, including their positions, orientations, and symmetries.
- There are 230 space groups, which combine the translational symmetry of the Bravais lattice with the rotational, mirror, and other symmetry elements present in the crystal.

Applications:

1. Materials Science:

- Understanding crystal symmetry and structure is crucial in materials science for designing materials with desired properties, such as strength, conductivity, and optical behavior.
- Knowledge of crystal classes and systems helps in predicting the physical and chemical properties of materials.

2. Drug Discovery:

- Crystallography is used in pharmaceuticals to determine the crystal structures of drug molecules and their interactions with target proteins.
- This information aids in drug design, optimization, and formulation.

3. Mineralogy and Geology:

- Crystallography plays a vital role in identifying and classifying minerals based on their crystal structures and symmetry properties.
- It helps in understanding geological processes, such as mineral formation and phase transformations.

4. Semiconductors and Electronics:

- Crystallography is essential in the design and fabrication of semiconductor materials and electronic devices.
- It helps in controlling the crystal structure and orientation of materials to optimize their electrical and optical properties.

Crystallography: Differences Between Point Group and Space Group, Screw Axis, Glide Planes, Relationship

Between Molecular Symmetry and Crystallographic

Symmetry

1. Differences Between Point Group and Space Group:

Point Group:

- Describes the symmetry operations that leave at least one point unchanged within a molecule or crystal.
- Specifies the rotational and reflectional symmetry elements present.
- Examples include C_{2v} (for ethylene molecule) and D_{6h} (for benzene molecule).
- Point groups are used to characterize molecular symmetry in chemistry.

Space Group:

- Describes the symmetry operations that leave at least one point unchanged within a crystal lattice.
- Specifies the translational symmetry in addition to rotational and reflectional elements.
- Examples include $P2_1/c$ (for monoclinic crystal system) and $Fm-3m$ (for cubic crystal system).
- Space groups are used to characterize the arrangement of atoms in crystals in crystallography.

2. Screw Axis:

- A screw axis is a type of rotational symmetry operation found in both point groups and space groups.
- In a screw axis, a rotation about an axis is combined with a translational component along that axis.
- Screw axes are denoted by notation like " n " for the rotation and " $1/n$ " for the translation.
- Example: 2_1 screw axis involves a rotation of $360^\circ/2$ followed by a translation of one-half of the unit cell length along the axis.

3. Glide Planes:

- Glide planes are symmetry operations that combine a reflection with a translation perpendicular to the plane.
- Glide planes are denoted by notation like " a " for the reflection and " b " for the translation.
- Example: b -glide plane involves a reflection followed by a translation of one-half of the unit cell length along the direction perpendicular to the plane.

4. Relationship Between Molecular Symmetry and Crystallographic Symmetry:

Molecular Symmetry:

- Describes the symmetry elements present within a molecule, such as rotation axes, reflection planes, and inversion centers.
- Molecular symmetry is important in determining the physical and chemical properties of molecules.
- Used in chemical bonding theories, spectroscopy, and stereochemistry.

Crystallographic Symmetry:

- Describes the arrangement of atoms or ions within a crystal lattice, including translational, rotational, and reflectional symmetry.
- Crystallographic symmetry determines the overall shape and symmetry of crystals, influencing their physical properties.
- Used in crystallography to determine crystal structures and study crystal properties like diffraction patterns and lattice parameters.

Application:

- Understanding the differences between point groups and space groups is crucial in crystallography for characterizing molecular and crystal symmetry, respectively.
- Knowledge of screw axes and glide planes helps in identifying additional symmetry elements beyond simple rotations and reflections.
- Recognizing the relationship between molecular symmetry and crystallographic symmetry aids in predicting crystal structures and understanding the physical properties of crystals.
- This understanding is essential in various fields such as materials science, solid-state chemistry, and drug design, where crystal structure plays a significant role in determining properties and behavior.

1. The Concept of Reciprocal Lattice and Its Application:

- **Reciprocal Lattice:** The reciprocal lattice of a crystal is a mathematical construct used to describe the periodic arrangement of the crystal's diffraction pattern in reciprocal space.
- **Miller Indices:** Reciprocal lattice vectors are denoted using Miller indices, which represent the plane spacing in the crystal lattice.
- **Brillouin Zone:** The reciprocal lattice plays a crucial role in understanding the electronic band structure of materials, particularly in solid-state physics.
- **Application:** Understanding the reciprocal lattice is essential in interpreting diffraction patterns obtained from techniques like X-ray crystallography and electron diffraction.

2. X-ray Diffraction by Single Crystal:

- **Bragg's Law:** Describes the relationship between the angle of incidence of X-rays, the spacing between crystal lattice planes, and the wavelength of the X-rays.
- **Diffraction Pattern:** When X-rays are incident on a single crystal, they are diffracted by the crystal lattice, producing a diffraction pattern characterized by bright spots.
- **Crystallographic Information:** Analysis of diffraction patterns provides information about the crystal structure, including the unit cell parameters and atomic positions.
- **Application:** X-ray diffraction is widely used to determine the atomic structure of crystalline materials, including small organic molecules, proteins, and inorganic compounds.

3. Structure Factor:

- **Definition:** The structure factor (F) describes the amplitude and phase of the scattered X-rays by a crystal lattice.
- **Calculation:** It is calculated using the Fourier transform of the electron density distribution within the unit cell.
- **Interpretation:** The magnitude of the structure factor provides information about the electron density at specific atomic positions, while the phase provides information about the relative positions of atoms.
- **Application:** Structure factors are essential in determining the crystal structure from X-ray diffraction data and refining atomic models.

4. Systematic Absence:

- **Definition:** Systematic absences in X-ray diffraction patterns occur when certain reflections are forbidden due to the crystal symmetry and lattice translation vectors.
- **Identification:** Systematic absences are identified by analyzing the diffraction pattern and comparing observed and expected reflections based on the crystal symmetry.
- **Information:** Systematic absences provide valuable information about the crystal symmetry and space group.
- **Application:** Systematic absences aid in the determination of crystal structures and the assignment of space groups.

5. Determination of Space Groups:

- **Space Group Definition:** Space groups describe the symmetry operations that leave the crystal lattice unchanged.

- **Analysis:** Determination of space groups involves analyzing diffraction patterns, systematic absences, and crystallographic symmetry elements.
- **International Tables for Crystallography:** Standard references are used to assign space groups based on experimental observations.
- **Application:** Determining the space group is crucial for accurately describing the crystal symmetry and refining the crystal structure.

6. Fourier Synthesis:

- **Principle:** Fourier synthesis is a mathematical technique used to reconstruct electron density maps from X-ray diffraction data.
- **Fourier Transform:** X-ray diffraction intensities are Fourier transformed to generate an electron density map, which represents the distribution of electron density within the crystal.
- **Interpretation:** The electron density map provides information about the spatial arrangement of atoms within the unit cell.
- **Application:** Fourier synthesis is essential in structure determination, refinement, and visualization in X-ray crystallography.

7. Heavy Atom Method:

- **Principle:** The heavy atom method is a technique used to determine the phases of X-ray diffraction data in cases where direct phase determination is challenging.
- **Introduction of Heavy Atoms:** Heavy atoms, typically containing high atomic numbers, are introduced into the crystal structure to provide additional phase information.
- **Isomorphous Replacement:** Involves substituting light atoms in the crystal with heavy atoms to induce changes in the diffraction pattern.
- **Application:** The heavy atom method is particularly useful in solving the phase problem and determining the crystal structure of macromolecules such as proteins and nucleic acids.

Applications:

- **Material Science:** Crystallography is used to determine the atomic structure of materials, providing insights into their properties and behavior.
- **Drug Design:** Understanding the crystal structure of biomolecules and their complexes aids in rational drug design and development.

- **Catalysis:** Knowledge of crystal structures is essential for designing and optimizing catalysts for various chemical reactions.
- **Geology:** Crystallography is used to study the structure and properties of minerals, aiding in geological exploration and resource extraction.

Crystallography: A Brief Account of

Cambridge Structural Database (CSD) and

Protein Data Bank (PDB)

1. Cambridge Structural Database (CSD):

Introduction:

- The Cambridge Structural Database (CSD) is a comprehensive repository of small molecule crystal structures determined by X-ray crystallography.
- It contains detailed three-dimensional structural data on organic, inorganic, metal-organic compounds, and organometallic complexes.
- CSD is maintained by the Cambridge Crystallographic Data Centre (CCDC) and is one of the most valuable resources in structural chemistry.

Key Features:

1. Extensive Collection:

- CSD contains over one million curated crystal structures, making it the largest database of its kind.
- Structures are accompanied by experimental details, such as unit cell parameters, space group, bond lengths, and angles.

2. Search and Analysis Tools:

- Users can search the database by chemical name, molecular formula, structural similarity, and various other criteria.
- Advanced analysis tools allow researchers to study trends in bond lengths, angles, and packing arrangements.

3. Applications in Chemistry:

- CSD is widely used in drug discovery, materials science, and organic synthesis.
- It aids in the interpretation of experimental results, validation of molecular models, and prediction of crystal packing.

4. **Structure Validation:**

- CSD provides tools for the validation of crystal structures, ensuring the accuracy and reliability of the reported data.
- Researchers can assess the quality of a crystal structure by comparing it with similar structures in the database.

Applications of CSD:

- **Drug Design and Discovery:** CSD facilitates the study of molecular interactions in drug-receptor complexes, aiding in the design of new pharmaceuticals.
- **Materials Science:** Researchers use CSD to understand the structure-property relationships in materials such as organic semiconductors, catalysts, and polymorphs.
- **Chemical Education:** CSD serves as a valuable teaching tool for students to learn about crystallography, molecular geometry, and chemical bonding.

2. **Protein Data Bank (PDB):**

Introduction:

- The Protein Data Bank (PDB) is an international repository of three-dimensional structural data of biological macromolecules, primarily proteins and nucleic acids.
- It provides structural information on the arrangement of atoms within proteins, DNA, RNA, and their complexes with ligands, drugs, and other biomolecules.

Key Features:

1. **Comprehensive Collection:**

- PDB contains thousands of experimentally determined structures of proteins, nucleic acids, and their complexes from various organisms and experimental methods.

2. **Standardized Format:**

- Structures deposited in PDB are represented using a standardized file format called the PDB format, which includes atomic coordinates, experimental metadata, and annotation information.

3. **Search and Analysis Tools:**

- PDB offers powerful search and visualization tools for exploring the structural data, including sequence alignment, structural superposition, and molecular visualization.

4. Integration with Other Databases:

- PDB collaborates with other bioinformatics resources to provide additional information on protein function, sequence, and evolution, enhancing the utility of the structural data.

Applications of PDB:

- **Biomedical Research:** PDB serves as a central resource for structural biology research, enabling scientists to study protein structure-function relationships, protein-ligand interactions, and drug design.
- **Drug Discovery:** Structural information from PDB is used in rational drug design to identify potential drug targets, design inhibitors, and optimize drug candidates.
- **Molecular Modeling:** PDB structures are used as templates for molecular modeling and simulation studies to understand protein dynamics, folding pathways, and conformational changes.

Neutron diffraction by crystals—magnetic scattering – measurement techniques – comparison with X-ray diffraction elucidation of structure of magnetically ordered unit cell.

Introduction to Neutron Diffraction: Neutron diffraction is a powerful technique used in crystallography to study the atomic and magnetic structure of materials. It involves the scattering of neutrons by the atomic nuclei within a crystal lattice. Neutron diffraction offers unique advantages over X-ray diffraction, particularly in elucidating the magnetic properties of materials.

Principles of Neutron Diffraction:

1. Neutron Source:

- Neutrons are typically obtained from nuclear reactors or particle accelerators.
- Neutron beams are collimated and directed towards the sample under investigation.

2. Scattering by Atomic Nuclei:

- Neutrons interact with the atomic nuclei in the crystal lattice through processes such as nuclear scattering and magnetic scattering.

3. Detection of Scattered Neutrons:

- Scattered neutrons are detected using detectors positioned around the sample.

- The intensity and direction of scattered neutrons provide information about the atomic and magnetic structure of the material.

Measurement Techniques:

1. Powder Neutron Diffraction:

- Used for analyzing powdered samples to obtain information about their crystalline structure and phase composition.
- Applications include the study of phase transitions, crystallographic phase identification, and determination of atomic positions.

2. Single-Crystal Neutron Diffraction:

- Utilized for determining the atomic structure of single crystals, including the positions of atoms within the unit cell.
- Provides detailed information about bond lengths, angles, and atomic arrangements.
- Particularly useful for investigating complex structures and materials with magnetic ordering.

Magnetic Scattering:

1. Nuclear Magnetic Scattering:

- Neutrons are scattered by the magnetic moments associated with atomic nuclei.
- Provides information about the distribution and orientation of nuclear magnetic moments in the crystal lattice.

2. Magnetic Structure Determination:

- By analyzing the magnetic scattering patterns, researchers can elucidate the magnetic structure of materials, including the direction and magnitude of magnetic moments within the unit cell.
- Allows for the study of magnetic ordering phenomena such as ferromagnetism, antiferromagnetism, and ferrimagnetism.

Comparison with X-ray Diffraction:

1. Sensitivity to Light Elements:

- Neutron diffraction is particularly sensitive to light elements such as hydrogen and lithium, which are often difficult to detect using X-ray diffraction.
- This sensitivity allows for the determination of hydrogen positions in crystal structures, crucial for understanding hydrogen bonding and chemical interactions.

2. Magnetic Structure Determination:

- Neutron diffraction is uniquely suited for studying magnetic materials and elucidating their magnetic structures.
- Unlike X-rays, neutrons are scattered by the magnetic moments associated with atomic nuclei, providing direct information about magnetic ordering.

Applications:

1. Material Science:

- Neutron diffraction is used to study the structural and magnetic properties of materials such as superconductors, multiferroics, and magnetic nanoparticles.
- Insights gained from neutron diffraction contribute to the development of new materials with tailored magnetic and electronic properties.

2. Geology and Mineralogy:

- Neutron diffraction is applied in the study of geological samples to determine their mineral composition, crystal structure, and phase transitions under extreme conditions.

3. Biology and Biochemistry:

- Neutron diffraction is used in structural biology to investigate the atomic structure of biological macromolecules such as proteins, nucleic acids, and membranes.
- It provides insights into biomolecular interactions, enzyme mechanisms, and drug binding sites.