INTRODUCTION to CRYSTALS and CRYSTAL SYMMETRY

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Crystallographers want to know how the atoms in a material are arranged in order to understand the relationship between atomic structure and properties of these materials.

1. Solve Structures
2. Understand Mechanisms of Crystal Growth
3. Use Properties of crystals

A. Geometric Crystallography
B. Cristallophysics
C. Cristallochemistry
Most of the Earth and other planets are made of solid rock. The basic units from which rocks are made are minerals.

Minerals are natural crystals, and so the geological world is largely a crystalline world.

The properties of rocks are determined by the properties of the constituent minerals, and many geological processes represent the culmination - on a very grand scale - of microscopic processes inside minerals.

Deformation of rocks or weathering are large scale processes controlled by small scale processes such as the diffusion, nucleation, crystallization or phase transformations.

The Crystalline State

- The states of matter may be distinguished in terms of their tendency to retain a characteristic volume and shape.

- **Solid**: shape and volume stable and are classified according to regularity and structure of their building blocks. In:
  - **CRYSTALLINE**: periodic and perfect arrangement of atoms.
  - **POLYCRYSTALLINE**: are solids that are composed of many **crystallites** of varying size and orientation.
  - **AMORPHOUS**: no periodic structure, atoms are disordered. Some of these amorphous compounds are called mineraloids. They usually form at low temperatures and pressures during the process of weathering and form botryoidal masses. Examples: Obsidian, Chrysocolla, Mn Oxides, Opal.

- **Obsidian** is amorphous solid formed as a result of quickly cooled lava.
- **Chrysocolla** (blue) is a hydrous amorphous copper silicate.
- **Pyrolusite** (MnO₂)
The Crystalline State

Crystallinity: refers to the degree of structural order in a solid. It can be measured with XRD.

Gemologic Mexican Fire Opal

Typical X-ray diffraction patterns of silica minerals arranged in order of increasing maturity and crystallinity.
The Crystalline State

- Non dense, **random** packing
- Dense, **ordered** packing

Dense, ordered packed structures tend to have lower energies & thus are more stable.
Polymorphism

Polymorphism is the ability of a compound to exist in more than one crystal form. The term *allotropy* is used for elements.

The allotropes of carbon include:

a. diamond (carbon atoms are bonded in a tetrahedral lattice arrangement)
b. graphite (carbon atoms are bonded in sheets of a hexagonal lattice)
c. graphene (single sheets of graphite)
d. fullerenes (carbon atoms are bonded together in spherical, tubular, or ellipsoidal formations)
Polimorphism in minerals

Andalusite, Kyanite and sillimanite are naturally occurring aluminosilicate minerals that have the composition $\text{Al}_2\text{SiO}_5$. The triple point of the three polymorphs is located at a temperature of 500 °C and a pressure of 0.4 GPa. These three minerals are commonly used as index minerals in metamorphism.

Polytipism is a type of polymorphism related with the way of individual layers are stacked in the mineral structure. Is common in clay minerals.
CRYSTAL Definitions

A CRYSTAL is a solid composed of atoms, ions or molecules that demonstrate **long range periodic order in three dimensions** that can be measured and quantified with crystallographic tools.

Is also a regular polyhedral form, bounded by smooth faces, which is assumed by a chemical compound, due to the action of its interatomic forces, when passing from the state of a liquid or gas to that of a solid.

**Crystallography originally evolved from the study of the morphology of mineral crystals:**

1611: J. Kepler speculated that snowflakes are hexagonal grids of water particles.

1669 Nicholas Steno enunciate: **Law of constancy of interfacial angles** observing that for quartz crystals with different sizes the angles between certain pairs of faces of is constant.

Legrandite: $\text{Zn}_2\text{AsO}_4(\text{OH})\cdot\text{H}_2\text{O}$
Properties of Crystals

1. **HOMOGENEITY**: chemical uniformity, different positions are equivalent

2. **ANISOTROPY**: different values of a physical property in different directions.

3. **PERIODICITY**

4. **SYMMETRY**
Properties of a Crystal: Periodicity

Periodicity: is the repetition in the space.

The smallest regularly-repeating blocks that contains the complete lattice pattern of a crystal is known as **unit cell**. The dimensions of a unit cell are described by the lengths of the three axes, $a$, $b$, and $c$, and the three interaxial angles, $\alpha$, $\beta$, and $\gamma$. 
The 7 Crystal Systems

Seven distinct unit cells can be recognized for 3-D lattices associated with seven systems of crystal axes called the seven crystal systems. The system to which a crystal belongs can be identified from its external symmetry.

<table>
<thead>
<tr>
<th>System</th>
<th>Axial lengths and angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>Three equal axes at right angles $a = b = c, \quad \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>Three axes at right angles, two equal $a = b \neq c, \quad \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Three unequal axes at right angles $a \neq b \neq c, \quad \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Rhombohedral*</td>
<td>Three equal axes, equally inclined $a = b = c, \quad \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c, \quad \alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>Three unequal axes, one pair at right angles $a \neq b \neq c, \quad \alpha = \gamma = 90^\circ \neq \beta$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \quad (\alpha \neq \beta \neq \gamma \neq 90^\circ)$</td>
</tr>
</tbody>
</table>

* Also called trigonal.

**Table:**

<table>
<thead>
<tr>
<th>Cubic</th>
<th>Tetragonal</th>
<th>Hexagonal</th>
<th>Trigonal</th>
<th>Orthorhombic</th>
<th>Monoclinic</th>
<th>Triclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galena</td>
<td>Zircon</td>
<td>Apatite</td>
<td>Quartz</td>
<td>Celestite</td>
<td>Gypsum</td>
<td>Albite</td>
</tr>
</tbody>
</table>
Quasicrystals

Quasicrystal: consists of arrays of atoms that are ordered but not strictly periodic. It lacks translational symmetry. They can show five-fold symmetry, which is impossible for an ordinary periodic crystal.

Tiling of a plane by regular pentagons is impossible but can be realized on a sphere in the form of pentagonal dodecahedron.
LATTICE: A collection of mathematical points (infinite in extensión) in a periodic arrangement and mathematically described by translation vectors.

BASIS: atoms attached to each lattice point.
• Ionic solids have ions at the lattice points.
• Molecular solids have (small) molecules at the lattice points.
• Atomic solids have atoms at the lattice points (includes Network Solids)
• Metallic solids have metal atoms at the lattice points
In 1849, Auguste Bravais found that all regular crystals could be described in terms of only 14 lattice types for the 7 crystal systems.

- **Primitive (P):** lattice points on the cell corners
- **Body-Centered (I):** lattice points on the cell corners with one additional point at the center of the cell
- **Face-Centered (F):** lattice points on the cell corners with one additional point at the center of each of the faces of the cell
- **Base-Centered (A, B, or C):** lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell (sometimes called end-centered.)
Perfect Crystals are not common

Crystalline Defects

Point Defects

A. vacancies/schottky defects
B. Interstitial Vacancies/Frenkel defects
C. Compositional defects

- Substitutional impurity
- Interstitial impurity

D. Electronic impurity

Line Defects

1. Edge Dislocation
2. Screw Dislocation

Surface Defects

- a. Grain boundaries
- b. Twin boundaries
- c. Tilt boundaries
- d. Stacking fault

Volume Defects

Non Crystalline regions of dimensions at least 10 to 30Å

Point defects of crystals

Vacancy
Interstitial Impurity
Self-interstitial
Substitutional impurity
Frenkel defect

Edge dislocation

www.subsitech.com
An object is described as *symmetric* with respect to a *transformation* if the object appears to be in a state that is identical to its initial state, after the transformation.

In crystallography, *most types of symmetry can be described in terms of an apparent movement (rotation, translation) of the object*. The apparent movement is called the *symmetry operation*. The locations where the symmetry operations occur (rotation axis, a mirror plane, an inversion center, or a translation vector) are described as *symmetry elements*.

In crystals, the axes of symmetry (rotation axes) can only be *two-fold* (2), *three-fold* (3), *four-fold* (4) or *six-fold* (6), depending on the number of repetitions of the motif which can occur (*order of rotation*). Thus, an axis of order 3 (3-fold) produces 3 repetitions of the motif, one every $360 / 3 = 120$ degrees of rotation.
Basic Symmetry Operations

The center of symmetry, or inversion center, is a point through which the operation moves an atom at \((x, y, z)\) to \((-x, -y, -z)\).
RotoInversion

ROTATION INVERSION
This set of operations define the **point group** of the crystal.

32 Combinations of symmetry: 32 Point group
2D Crystallographic Point Groups: 10

- 1
- 2
- 3
- 4
- 6
- M
- m
- 2mm
- 4mm
- 3m
- 6mm
3D Crystallographic Point Groups: 32

1. There is 1 unique 4 fold axis because each is perpendicular to a similar looking face.

2. There is one unique 3 fold rotoinversion axes (stick out of the coners of the cube)

3. There is 1 unique 2 fold axis.

4. So we can write: 4 -3 2

5. There are 3 mirror planes perpendicular to the 4 fold axis, and 6 mirror planes perpendicular to the 2-fold axis: 4/m -3 2/m
3D Crystallographic Point Groups: 32

<table>
<thead>
<tr>
<th>Crystal Class</th>
<th>Non-centrosymmetric Point Group</th>
<th>Centrosymmetric Point Group</th>
<th>Minimum Rotational Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>$\bar{1}$</td>
<td>One 1-fold</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$2, m$</td>
<td>$2/m$</td>
<td>One 2-fold</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>222, $mm2$</td>
<td>$mmm$</td>
<td>Three 2-folds</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4, 422, 4, 4$mm$, 4$2m$</td>
<td>$4/m$, $4/mmm$</td>
<td>One 4-fold</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>3, 32, 3$m$</td>
<td>$\bar{3}$, $\bar{3}m$</td>
<td>One 3-fold</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6, 622, 6, 6$mm$, 6$m2$</td>
<td>$6/m$, $6/mmm$</td>
<td>One 6-fold</td>
</tr>
<tr>
<td>Cubic</td>
<td>23, 432, 43$m$</td>
<td>$m\bar{3}$, $m\bar{3}m$</td>
<td>Four 3-folds</td>
</tr>
</tbody>
</table>
### 3D Crystallographic Point Groups: Stereograms

<table>
<thead>
<tr>
<th></th>
<th>Triclinic</th>
<th>Monoclinic (1st setting)</th>
<th>Tetragonal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>x</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
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<tr>
<td>2</td>
<td><img src="image4.png" alt="Diagram" /></td>
<td><img src="image5.png" alt="Diagram" /></td>
<td><img src="image6.png" alt="Diagram" /></td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Diagram" /></td>
<td><img src="image8.png" alt="Diagram" /></td>
<td><img src="image9.png" alt="Diagram" /></td>
</tr>
<tr>
<td><strong>y</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image10.png" alt="Diagram" /></td>
<td><img src="image11.png" alt="Diagram" /></td>
<td><img src="image12.png" alt="Diagram" /></td>
<td><img src="image13.png" alt="Diagram" /></td>
</tr>
<tr>
<td><strong>z</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image14.png" alt="Diagram" /></td>
<td><img src="image15.png" alt="Diagram" /></td>
<td><img src="image16.png" alt="Diagram" /></td>
<td><img src="image17.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Trigonal</th>
<th>Hexagonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>x</strong></td>
<td><img src="image18.png" alt="Diagram" /></td>
<td><img src="image19.png" alt="Diagram" /></td>
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<tr>
<td>3</td>
<td><img src="image21.png" alt="Diagram" /></td>
<td><img src="image22.png" alt="Diagram" /></td>
<td><img src="image23.png" alt="Diagram" /></td>
</tr>
<tr>
<td>6</td>
<td><img src="image24.png" alt="Diagram" /></td>
<td><img src="image25.png" alt="Diagram" /></td>
<td><img src="image26.png" alt="Diagram" /></td>
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<tr>
<td>23</td>
<td><img src="image27.png" alt="Diagram" /></td>
<td><img src="image28.png" alt="Diagram" /></td>
<td><img src="image29.png" alt="Diagram" /></td>
</tr>
<tr>
<td><strong>y</strong></td>
<td></td>
<td><img src="image30.png" alt="Diagram" /></td>
<td><img src="image31.png" alt="Diagram" /></td>
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<tr>
<td><img src="image32.png" alt="Diagram" /></td>
<td><img src="image33.png" alt="Diagram" /></td>
<td><img src="image34.png" alt="Diagram" /></td>
<td><img src="image35.png" alt="Diagram" /></td>
</tr>
<tr>
<td><strong>z</strong></td>
<td></td>
<td><img src="image36.png" alt="Diagram" /></td>
<td><img src="image37.png" alt="Diagram" /></td>
</tr>
<tr>
<td><img src="image38.png" alt="Diagram" /></td>
<td><img src="image39.png" alt="Diagram" /></td>
<td><img src="image40.png" alt="Diagram" /></td>
<td><img src="image41.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>
Compound Symmetry Operators

Screw Axis

Glide Planes
This set of operations define the point group of the crystal. There are 32 unique crystallographic point groups.

This set of operations define the Space group of the crystal.
2D Space Symmetry Groups
3D SPACE SYMMETRY GROUPS

They are all the ways in which motifs (atoms, molecules) can be distributed in a three-dimensional homogeneous space.

**Basis + Lattice = CRYSTALS**

32 POINT Symmetry Groups + 14 BRAVAIS Lattices = 230 SPACE Symmetry Groups

(The 230 space groups are collected in international tables of crystallography)
3D Space Symmetry Groups

A space group is designated by a capital letter identifying the lattice type (P, A, F, etc.) followed by the point group symbol in which the rotation and reflection elements are extended to include screw axes and glide planes.
Miller Index

**Miller indices** form a notation system in crystallography for planes in crystal lattices.

A plane is determined by three integers $h$, $k$, and $\ell$ that are the inverse intercepts along the lattice vectors (Law of Rational indices, Haüy 1784, 1801).

(hkl) represents a plane

\{hk\ell\} = set of all planes that are equivalent to (hk\ell) by the symmetry of the lattice.

[hk\ell], with square instead of round brackets, denotes a direction.

< hkl > represents a family of directions.

A crystal form is the set of faces related by symmetry.

There are 48 possible forms that can be developed.
CRYSTALS

- Homogeneity
- Anisotropy

Periodicity
- Translation

Symmetry
- Reflexion
- Rotation
- Inversion
- Rotoinversion

32 Point Groups

7 Crystal systems
- CUBIC
- TRIGONAL
- ROMBIC
- MONOCLINIC
- HEXAGONAL
- TETRAGONAL
- TRICLINIC

230 space Symmetry Groups
Under the microscope, I found that snowflakes were miracles of beauty; and it seemed a shame that this beauty should not be seen and appreciated by others. Every crystal was a masterpiece of design and no one design was ever repeated. When a snowflake melted, that design was forever lost. Just that much beauty was gone, without leaving any record behind.

Wilson A. Bentley (1865-1935)

He capture more than 5000 snowflakes potographs during his lifetime, not finding any two alike.

The Snowflake Man
Thank you for your attention!!!!!!