

## EPSc 352: Lecture Overview for Part 4, Symmetry

### **Order in Crystals: Internal and External Order; Symmetry**

Why do crystals have the shapes they do?

Conceptually move from 2-D ordered arrays to stacks in 3-D  
Reflect upon natural crystal forms/habits

**\*\*\* ESSENTIAL: Read K&D chapter 6 (to p. 131).**

Define symmetry:

“Regular arrangement of parts with reference to the corresponding parts.” (Blackburn and Dennen, p. 13)

“An object that consists of a systematic repetition of identical features is said to have ‘symmetry’.” (Bloss, p. 1)

“Symmetry refers to the regularity of the shape of a 2-D or 3-D object, such that the repetition of one segment of the object will (re-)create the entire object.” (Jill)

**Read hand-out about using CD to learn about symmetry.**

**\*\*Keep referring to hand-out entitled “Lattices, Point Groups, Space Groups”**

Why worry about symmetry?

Understanding symmetry is a means of making sense of geometric complexity, just as categorizing minerals by their anionic groups helps make sense of them chemically. Conclusion that there is a very limited number of types of patterns of repetition.

Physical and chemical properties of a mineral can be slightly different throughout the crystal – controlled by symmetry. Applications: electronics, optics, microbe-mineral interactions.

#### **Approach to Understanding Internal Order in Crystals**

Crystals consist of clusters of atoms; atoms have specific positions with respect to each other and with respect to whole structure

Look at patterns of atoms in crystals: only a limited number

Constraints on the number of patterns: atomic clusters are repeated, must fill space

Only certain kinds of patterns “work”

All the diverse crystal shapes we see are just variations on a few themes

In crystals, 3-D orderly arrays of atoms/ions define the crystal structure: “periodic duplication of”

any grouping of atoms along any line through the structure..." (Blackburn and Dennen, p. 11)

"A 3-D network of regularly arranged points to which the atoms in a crystal are related is called a lattice...the lattice itself is an imaginary geometrical framework." (B & D, p. 11)

Lattice is the framework, the basic "Lego block."

**\*\*\* ESSENTIAL: Read K&D chapter 7.**

### ⇒ Recognizing a lattice

Make successive translations of some initial point according to some fixed rules

Translation vectors: distance/length + direction

Create different parallelograms

Rule is that these parallelograms must "tile a plane" (i.e., fill space). Thus, there are only 5 distinct "mesh shapes" (K&D, p. 148, Fig. 7.5 and p. 150, Fig. 7.8)

Primitive vs. multiple cells: ownership of points

Points represent "motifs" (clusters of atoms, with their geometries)

Extend the cells into 3<sup>rd</sup> dimension: space lattices.

5 basic types of 2-D planar lattice types generate in 3-D only 6 geometrically distinct types of primitive cells. These are like 6 different shapes of Lego blocks (cf. Lab 6). Can also regard them as 6 geometrically distinct types of primitive cells.

*[If you allow for non-primitive 3-D cells, you get a total of 14 cell types (Bravais lattices). These 14 account for all possible point distributions (cf. Lab 6).]*

There is a symmetry of the lattice **and** within the lattice.

2-D and 3-D structure (i.e., ordering, symmetry) in a crystal arises from repetition of a motif such that the environment of and around each repeated motif is identical (Klein and Hurlbut, 20<sup>th</sup> ed., p. 18). This is the essence of a lattice.

Due to symmetry/shape of the motif and the arrangement of the motifs, certain symmetry relations arise in the pattern (lattice). [hand-out 27, bottom]

rotation, reflection, glide (= reflection + translation) [hand-out 28]

incompatible/inconsistent symmetries can be recognized as impossible

K&D, p. 148, Fig. 7.5 shows all the axes and mirrors consistent with the 5 plane lattices.

**Discuss Notation:** 2mm.

So, there is an orderliness to crystal structure, and there is a limited number of possible orderly structures.

[Only 10 symmetrically different kinds of 2-D motifs (i.e., symmetry content and direction); combining these 10 different motifs with all compatible members of 5 plane lattices produces 17 different plane groups.]

### ⇒ **Combining symmetry operations:**

Inversion: inversion center,  $i$ . Inversion “repeats motifs as though they were inverted by a simple lens (Blackburn and Dennen).”

So,  $i = 2\text{-fold rotation} + \text{reflection}$ . Concept of identical operations.

\*\*All possible combinations of symmetry lead to symmetrically unique products.

### ⇒ **Space Lattices**

“The periodic repetition of a plane lattice in some non-coplanar direction generates a space lattice that is a stack of identical plane lattices in parallel position separated by a translation  $t_3$ .” (Blackburn and Dennen, p. 18)

The way the planes are stacked must be consistent with the symmetry of the planes and their motifs. This restriction limits the stacking possibilities.

As stacking continues, eventually points/motifs on the top plane directly overlie/repeat the points on your 0-level (cf. CCP and HCP). Can connect these analogous points to form a 3-D cell.

See K&D, p. 162, Fig. 7.17: There are 14 types of space lattices (you worked with them in Lab 6)

- primitive cells: lattice points only at corners
- multiple cells: lattice points also on faces or in body center
- A-, B-, or C-face-centered cells
- all-face-centered cells (F)
- body-centered cells (I)
- note rhombohedral lattice

Note that you keep seeing the same kind of nomenclature:

- 14 Bravais lattices grouped into 6 categories (see Labs 6 and 7) according to their general symmetry
- named acc. to their symmetry elements and locations of their lattice points, e.g., 222F
- primitive cells and multiple (non-primitive) cells

We have the building blocks (space lattices). Now need 3-D coordinate axes to allow us to designate:

- specific faces or directions in a crystal
- kinds of symmetry and orientation of symmetry elements

## ⇒ Crystal Systems

6 different shapes of Bravais lattice building-blocks are reflected in:

# of defined axes  
relative lengths of the axes  
 proportions of axes of same and different lengths  
angular relations among axes

Cubic/isometric	tetragonal hexagonal	triclinic monoclinic orthorhombic	H.O. #29 and Dietrich & Skinner
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NOTE: We are discussing crystallographic/geometric axes. Once these are defined, we can investigate IF there is any symmetry along or perpendicular to these axial directions, or even with respect to the bisectors of the axes.

H.O. #29 shows properties of all 6 crystal systems as does the instruction packet for Lab #7.

\*\*\***Keep referring to hand-out entitled “Lattices, Point Groups, Space Groups”**, which summarizes the hierarchy of symmetry

## ⇒ Point Groups = Crystal Classes

All possible motif symmetries combined will all the possible (compatible) space lattice types gives us 32 possible point groups.

Point groups = all possible ways of distributing points or motifs about a central, fixed point.

One way to generate point groups is to begin with some original point and then operate on that point with combinations of rotation axes and mirrors (oriented along the crystallographic axes or their bisectors, or perpendicular to them).

\*\*Point groups represent the symmetry of all possible symmetric 3-D objects.

\*\*Point groups also are subdivided into the 6 crystal systems.

Useful way of pictorially representing the symmetry of each of the 32 point groups (crystal classes): H.O. #30, Klein and Dutrow, pp. 127-128.

Try some examples.

## ⇒ Space Groups (K&D, chapter 7, pp. 165-168)

Presently have considered rotation axes (including rotoinversion axes), mirror planes, and inversion centers to envision motions/operations around a fixed point.

Those 3 types of symmetry are all that are recognized macroscopically in crystals (or wooden blocks).

Add translation to the rotation and reflection operations → different symmetric relations, because translations are on order of fractions of lengths along crystallographic axes of unit cell.

Examine (in hand-out) diopside (pyroxene) structure (from Klein, 22<sup>nd</sup> edition, 2002, p. 285) as an example, on the atomic scale, of symmetry that includes more than just rotation and reflection.

Screw axes: orientation and motion (H.O. #33)

Handedness: if motif not symmetrical (like a hand), repeated motif may not be congruent with original. Compare  $4_1$  and  $4_3$  screw axes.

Glide planes: orientation and motion (H.O. #34)

“When we combine the 14 possible space lattice types (Bravais lattices) with the symmetry inherent in the 32 crystal classes (the translation-free point group symmetries), as well as the two symmetry elements that involve translation (screw axes and glide planes), we arrive at the concept of space groups...represent the various ways in which motifs (such as atoms in crystals) can be arranged in space in a homogeneous array (homogeneous meaning that each motif is equivalent to every other motif in the pattern).” (Klein and Hurlbut, 20<sup>th</sup> ed., p. 121)

**There are 230 space groups.**

If you ignore the translation components of the 230 space groups, you get the 32 point groups (see Klein and Dutrow, Table 7.4 on page 167).

Each space group:

is based on a Bravais lattice (compatible with a point group)

is isogonal with a specific point group

Each point group “is the translation-free residue” of one or more isogonal space groups (see Table 7.4 on p. 167, which is a list of all space groups and their corresponding point groups).

**Example:** space group  $P 6_2/m 2/m 2/c \Rightarrow 6/m 2/m 2/m$  point group

<b>P</b>	$6_2$	<b><i>x/c</i></b>
<b>Lattice</b>	<b>Screw</b>	<b>Glide</b>
<b>type</b>	<b>axis</b>	<b>along c-axis</b>

Various ways of determining unit cell dimensions and specific site occupancies of atoms

Direct measurement of distances between (images of) atoms and planes of atoms (high-resolution transmission electron microscopy: HRTEM)

Scanning tunneling microscopes that permit imaging of actual atoms and measurement of their spatial positions

X-ray diffraction off planes of atoms in a crystal

X-ray intensity measurements from single crystals to determine atomic distributions

Neutron and electron diffraction

Spectroscopic techniques such as visible-light, infrared (IR), Raman, Mössbauer, and nuclear magnetic resonance spectroscopy. Determine symmetry of structural sites.

## 👁️ Crystallography and its Reflection in External Form

Constancy of interfacial angles and axial ratios

1669: Nicolas Steno showed that no matter how badly formed a quartz crystal's faces were, the angles between adjacent faces were the same.

Dominant (broadest, best developed) faces on a crystal represent planes cutting through largest numbers of lattice points (greatest densities of atoms).

Orientations of dominant faces indicate orientations of lattice points and crystallographic axes. Examination of crystal faces indicates relative lengths of axes, i.e., axial ratios. Most accurate determination of axial lengths comes from X-ray crystallography (our next set of lectures).

In tetrag. & hexag., **a:c** = 1:c/a

In cubic/isometric, **a<sub>1</sub>:a<sub>2</sub>:a<sub>3</sub>** = 1:1:1

In mono., ortho., tric., **a:b:c** = a/b : 1 : c/b

\*\*\***Unit cell**: smallest “chunk” of the crystal that incorporates its composition (stoichiometry), symmetry, and its length scales of repetition (lengths of crystal axes). There is a specific relationship among the volume of the unit cell, the # of formula units per cell, and the density (specific gravity) of the mineral (you will do a calculational problem on this).

a, b, and c are used to designate the axial directions in a crystal and also the lengths of the edges of its unit cell. E.g., a = 2.79 Å, b = 12.65 Å, and c = 14.92 Å.

Those lengths along a, b, and c are also the lengths between the “tick marks” along the a, b, and c axes. These are the inherent repeat distances between identical clusters of atoms along each geometric direction in the crystal.

### ⇒ Crystal Shapes (Habits, Forms)

Crystal shape thus reflects underlying symmetry of atomic distribution

“The symmetry of crystals requires that parallel stacks of rational planes be chemically and physically as well as geometrically equivalent.” (Blackburn and Dennen, p. 44)

Not all possible faces grow on each crystal. The growth environment may favor certain atomic planes and their symmetrically identical counterparts.

Pick a plane of atoms in a crystal; envision how that plane (face on the crystal) is repeated by all the symmetry operations of its crystal class/point group (e.g., 4/m). The figure you derive is crystallographic “form” and a growth “habit.”

**\*\*\* ESSENTIAL: Read K&D chapter 6, pp. 131-137.**

### ☞ Indexing Faces and Directions (use your CD Module II !!)

You can index crystal faces, in the context of an axial system.

\*\*Remember (see Lab 7) the axial systematics (+ and - ends, orientation, etc.)

In order to index faces, you need to establish the spacing of tick marks along the axes.

I suggest: look at big faces parallel to two axes and/or that intersect third axis. Assume that the ratios of these intersected lengths represent the a:b:c of the real crystal. Thus, assume **shape of crystal reflects shape of unit cell**.

Klein and Dutrow (p. 132) suggest: Choose the biggest face that intersects all 3 axes and assume the intersected lengths represent the true a:b:c. The intercepts of this face are assigned values of 1a, 1b, 1c; this is the unit face.

For other unknown faces, designate intersection points of face (plane) on each axis in terms of how many axial lengths from 0,0,0 (center of figure). NOTE: Slope of that face is determined by relative lengths of axes, e.g., (111) face in cubic vs. tetragonal vs. orthorhombic systems.

\*\*\*Every crystal has an inherent l:w:h aspect ratio, as represented by the lengths of the edges of its unit cell. Its axial units have the same aspect ratio. From the example above, each unit along the a-axis is 2.79 Å, along the b-axis 12.65 Å, along the c-axis 14.92 Å.

For a crystal's faces/planes, what we really are interested in is their orientation, not their absolute position with respect to the central point (because parallel planes are identical). The orientation of the face/plane is what defines the pertinent lattice plane.

We can represent some plane of interest by its intercepts with each axis, by reference to the individual axial units (tick marks on the axes), e.g., (3a, -2b, 1/2c).

**Remember that axes have + and - ends!**

**Remember the conventions for labeling the axes (Lab 7 hand-outs, text p. 129).**

Indexing Planes ( ) through Miller indices: convention **(Read carefully text pp. 131-134)**

Miller indices capture the orientation of the plane, without regard for the absolute distance of the plane from the center (0,0,0).

Series of whole numbers derived by inverting the intercept parameters and then clearing all fractions.

Examples: intercepts are (-2a, 2b, 2/3c). [Note that this plane is parallel to (-1a, 1b, 1/3c).

Intercepts          Invert          Clear          Miller Index

$(-2a, 2b, 2/3c) \rightarrow -\frac{1}{2} \quad \frac{1}{2} \quad \frac{3}{2} \rightarrow \bar{1} \quad 1 \quad 3 \rightarrow (\bar{1} \ 1 \ 3)$

$(\infty a, \infty b, 2c) \rightarrow 0 \quad 0 \quad \frac{1}{2} \rightarrow 0 \ 0 \ 1 \rightarrow (001)$

In hexagonal/rhombohedral system, you have (hkil) index for 4 axes. Usually omit i, because  $h + k + i = 0$ .

Example:  $(1 \ 2 \ \bar{3} \ 1) = (1 \ 2 \ * \ 1)$  or  $(1 \ 2 \ 1)$

Law of rational indices: Miller indices of common faces of a mineral are small whole numbers or zero. This is because the larger, more dominant faces of the crystal intersect the largest number of nodes (lattice points) in the crystal lattice.

### ⇒ Notion of a form { }

Understanding of symmetry allows us to view crystals in a more organized fashion. Realize that the existence of a certain level of symmetry in the object (i.e., its crystal class) demands that certain orientations within the crystal are indistinguishable: sameness.

Can think of the symmetry elements in the crystal class as operating on a face (just as they operated on a single point in the dot-circle diagrams).

Create/recognize a crystal form by taking one designated face and performing all the symmetry operations of a crystal class on it.

Designate the **{form}** by the crystal face and crystal class, e.g.,

{111} form in the class  $4/m \bar{3} 2/m$  is an octahedron

General forms {hkl} have more faces than special forms:

General faces: (hkl), (211)

Special faces:

(001)	(00l)
(100)	(h00)
(110)	(hk0)

### ⇒ Indexing directions/lines [ ]

As for faces and planes, we are most interested in direction of a line, not in its distance from the origin.

So, picture all lines in a crystal as having been translated parallel to themselves so they now pass through the (0,0,0) origin.

Direction of line thus defined by designating a second point through which line passes.

Designate this point (a,b,c) [e.g., (2,3,1)] with coordinates derived from the units of length along all the crystallographic axes. These coordinates define the line **[hkl]**, e.g., **[231]**.

Note: When not all axes have same length, the [pqr] line may not coincide with the normal (perpendicular) to the (pqr) plane.

### Concept of zone

This concept is related to a line; do not confuse it with a form.

A group of crystal faces whose intersection edges are all parallel are said to lie in the same zone.

A zone axis is a line that passes through the center of the crystal and that is parallel to the face intersections, i.e., **[hkl] zone**.

**Next topic is X-ray diffraction: Read your text, Klein and Dutrow chapter 14 (pp. 307-321).**