

Symmetry

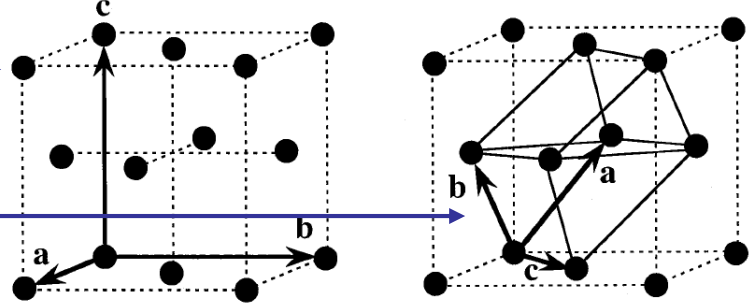
- Previously, we noted all crystal structures could be specified by a set of Bravais lattice vectors, when describing a lattice you must either use the primitive vectors or add a set of basis vectors (e.g., atom positions) to the conventional vectors,

For cubic F lattice, the conventional lattice vectors are: $\vec{a} = ax$ $\vec{b} = ay$ $\vec{c} = az$

The primitive lattice vectors are:

$$\vec{a} = \frac{a}{2}(y+z) \quad \vec{b} = \frac{a}{2}(x+z) \quad \vec{c} = \frac{a}{2}(x+y)$$

The cubic F lattice



- In practice, the number of basis atoms can be quite large and simply listing them is cumbersome., e.g. Al_2O_3 has 12 Al & 18 O=30 basis vectors with no translational centering**
- By acknowledging the symmetry of the atomic configuration, which must meet minimum symmetry criteria, it is possible to describe the basis down to a small number of parameters.
- Thus, crystal structure data are always presented with reference to
 - 32 point groups (macroscopic symmetry operations) or crystal classes and
 - 230 space groups (microscopic symmetry operations) or crystal structures.
 or the underlying symmetry of the structure.
- We need to define **symmetry operators** and **groups of operators** that are used to describe long-range configuration of atoms in a crystal, such as you will see in diffraction data.
 - Knowledge of symmetry is extremely important for understanding the thermal, optical, mechanical, electrical, ... properties (anisotropy) of solids, e.g. the presence of an inversion center eliminates piezoelectricity - electric polarization is induced by applying external forces/stresses.

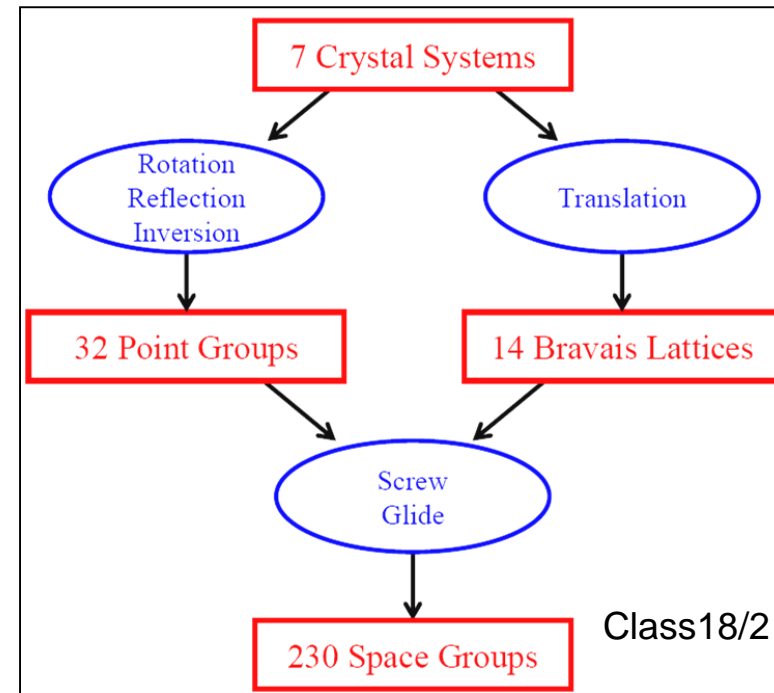


Symmetry Operators

- A symmetry operator describes an action that can be used to develop a pattern by changing the position and/or orientation of an object in space.
- The **7 symmetry operators** are : translation, rotation, reflection (mirror), inversion (center of symmetry), roto-inversion (inversion axis), glide (translation + reflection), and screw (translation + rotation).
- **Symmetry elements** are imaginary objects that perform the symmetry operation. It's used to specify the reference point about which an operation is performed. When performed on any object, the symmetry operation will bring equivalent points into coincidence (remain invariant).
- The above, first 5 macroscopic (for point groups) symmetry elements to consider are:

1. Translation vectors.
2. Rotation axes: symmetry about an axis of rotation (line).
3. Mirror planes: symmetry across a reflecting plane.
4. Centers of symmetry (inversion points): symmetry about a point.
5. Inversion axes (roto-inversion): combination of rotation and inversion.

Remember the operators in a point symmetry group leave at least one point in the pattern unchanged (i.e., perform symmetry operation(s) around a fixed/immobile point).



Symmetry Operators (continued)

1. Translation is the replication of an object at a new spatial coordinate. If the operator is the vector, \vec{R} , and if there is an object (e.g. atom) located at a position specified by the vector

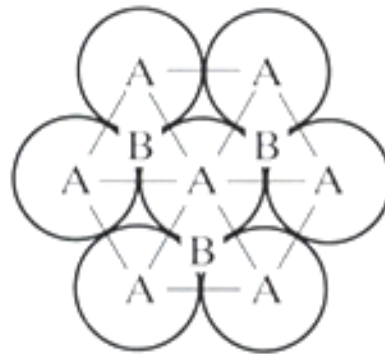
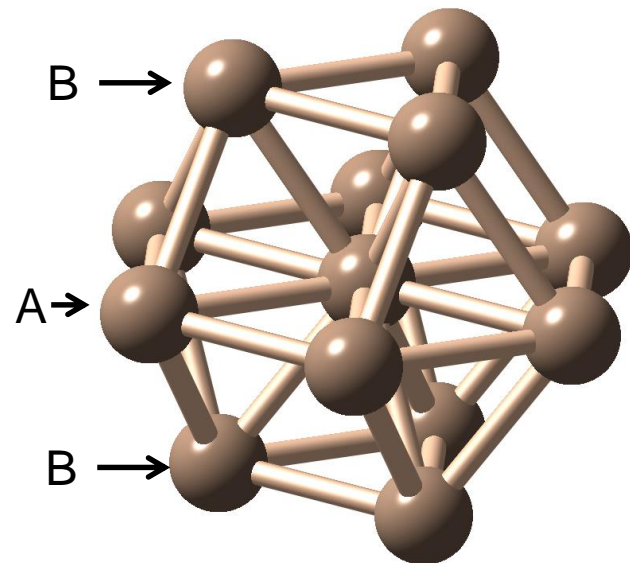
$$\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$$

then we know that an identical object will be located at $\vec{r} + \vec{R}$

- This operator is same as previously discussed Bravais lattice vector: $\vec{R} = u\vec{a} + v\vec{b} + w\vec{c}$
- Translation is used to build a crystal structure by replicating an object (basis) at each of the Bravais lattice points.

HCP Two atoms of the same kind are associated with the two lattice points

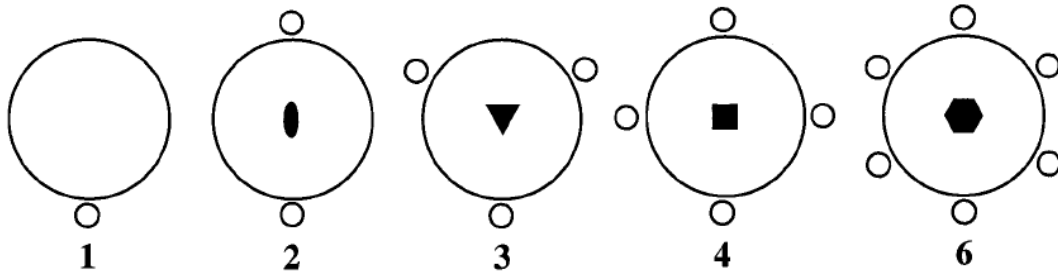
Lattice points at $(0,0,0)$ and $(1/3 \vec{x}, 2/3 \vec{y}, 1/2 \vec{z})$:



REMEMBER: For lattice points to be equivalent, you must be able to move from one position to the other with the same lattice translation vector.

Symmetry Operators (continued)

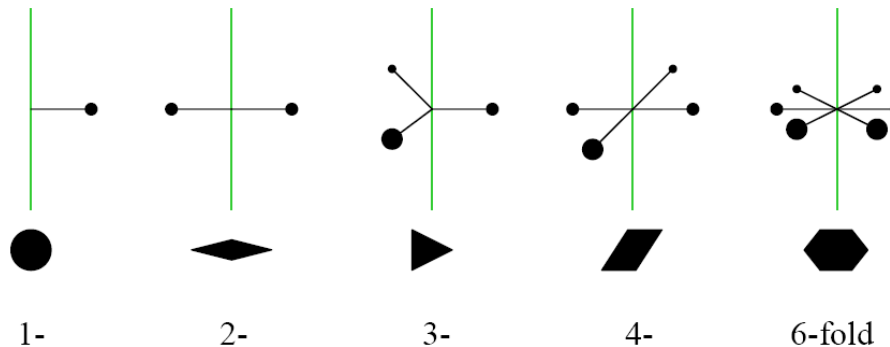
2. Rotation is motion through an angle about an axis, symmetry about a line. Rotation about a certain axis brings the lattice into a position indistinguishable from itself. Since repeated operations must eventually place the object in its original position, the possible angles are constrained by the condition that $n\alpha = 2\pi$, where n is integer number ($n=1, 2, 3, 4, \text{ and } 6$) of rotations, or times to bring it back to original position, and α is the angle of each rotation, in radians. ($\alpha=2\pi, \pi, 2\pi/3, \pi/2, \pi/3$)



The five rotation operators that are consistent with translational symmetry (Bravais lattice translations). The solid object in center shows the position of the rotation axes and small circle is the object which is repeated to form the pattern

These are 5 of the 32 point groups and easiest to visualize.

Symmetry about a line:



(Note: we saw these previously for the 10 2-D point groups)

Only certain rotations are possible. All lattice sites generated by a symmetry element must be equivalent.

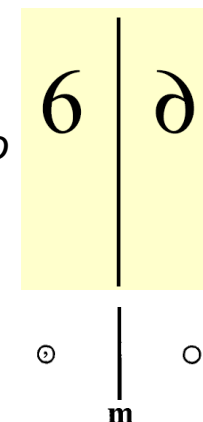
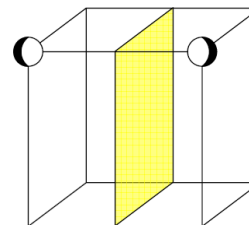
Symmetry Operators (continued)

3. Reflection describes operation of a mirror, or symmetry about a plane. The symmetry element is the mirror plane denoted by **m**:

L.H. \ominus | R.H. \circ *The reflection operator. The axis of a mirror refers to its normal. The right hand (R.H.) object is specified by an open circle and left hand (L.H.) replica is specified by a comma.*

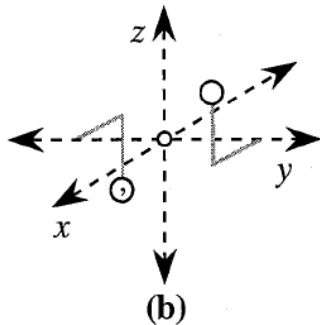
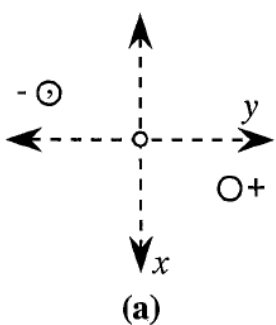
m

Reflection converts a right-handed object into a left-handed replica:



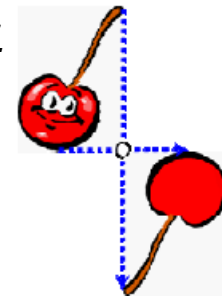
- Equivalent points are brought into coincidence by reflection across the plane (mirror).
- The positions of mirror planes on 32 point group stereograms are specified by **bold lines**.
- When a mirror plane is normal to an axis of rotation, "m" is placed in the denominator and a 1,2,3,4 or 6 is in the numerator, e.g. 4/m vs. when a mirror plane is parallel to rotation axis: 4mm

4. Inversion this operation occurs through an element called a center of symmetry, symmetry about a point. A center of symmetry at the origin transforms an object at (x,y,z) to the position (-x,-y,-z):



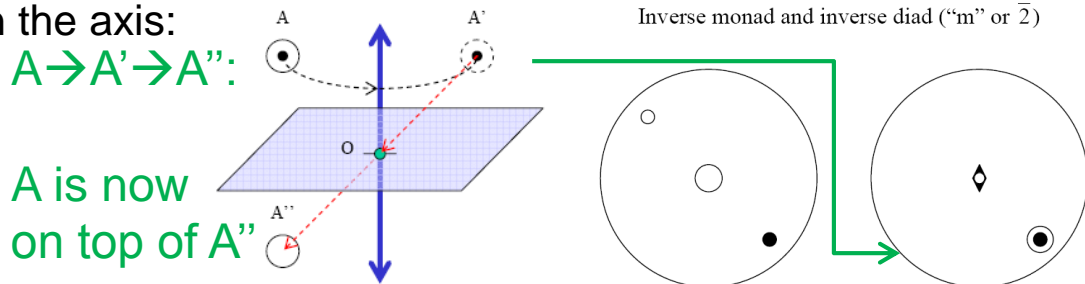
Projection (along z) of the pattern formed by an inversion center (a). The (+) and (-) sign indicate small vertical displacements above (+) and below (-) the plane of the paper/slide.

Written symbol is i or \bar{i} . Like the mirror, inversion also creates a left-hand replica.



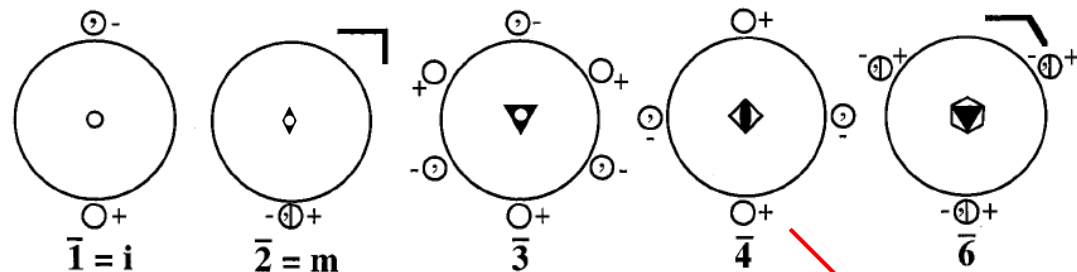
Symmetry Operators (continued)

5. Roto-inversion operator *rotates* an object in a pattern about its **axis** and then *inverts* the object through a center of symmetry on the axis:



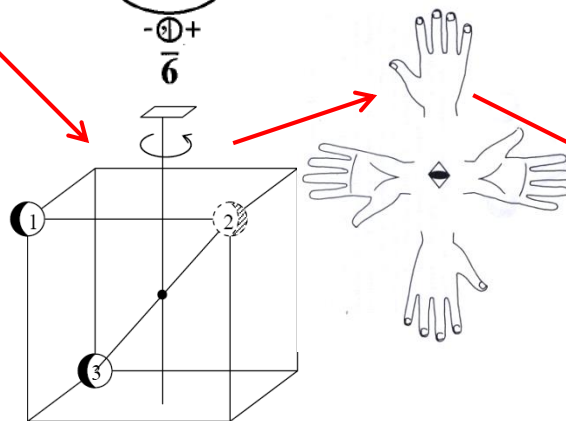
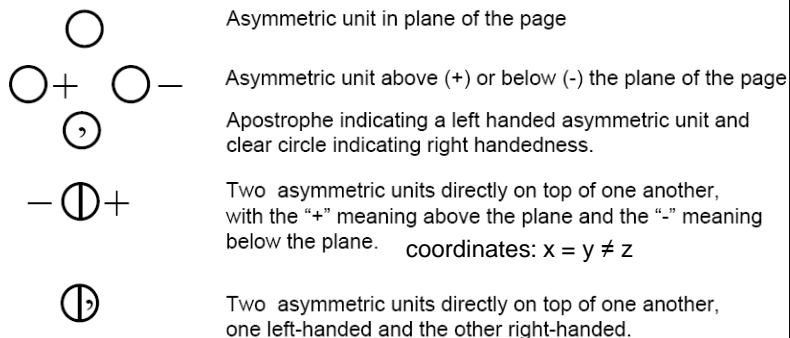
Equivalent points are brought into self-coincidence by a combined rotation and inversion.

- The roto-inversion axes produce only one pattern that could not be produced by other operators used alone or in combination.
- The roto-inversion operators written symbols is the same as n-fold rotation axes but with bar on top, e.g.



These are 5 more of the 32 point groups to total 10 so far:

Name	Rotation (°)	Symbols
Inverse monad	360 + inversion	$\bar{1}$
Inverse diad	180 + inversion	$\bar{2}$
Inverse triad	120 + inversion	$\bar{3}$
Inverse tetrad	90 + inversion	$\bar{4}$
Inverse hexad	60 + inversion	$\bar{6}$



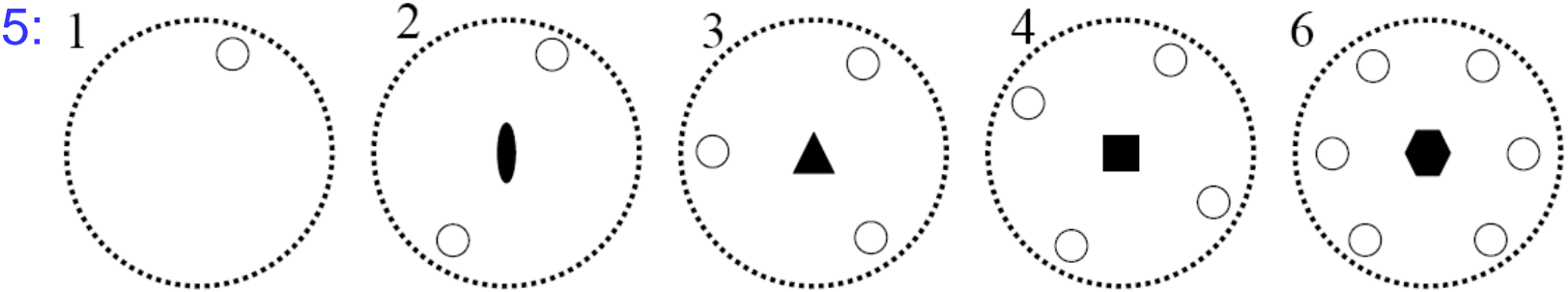


Summarize the first 10

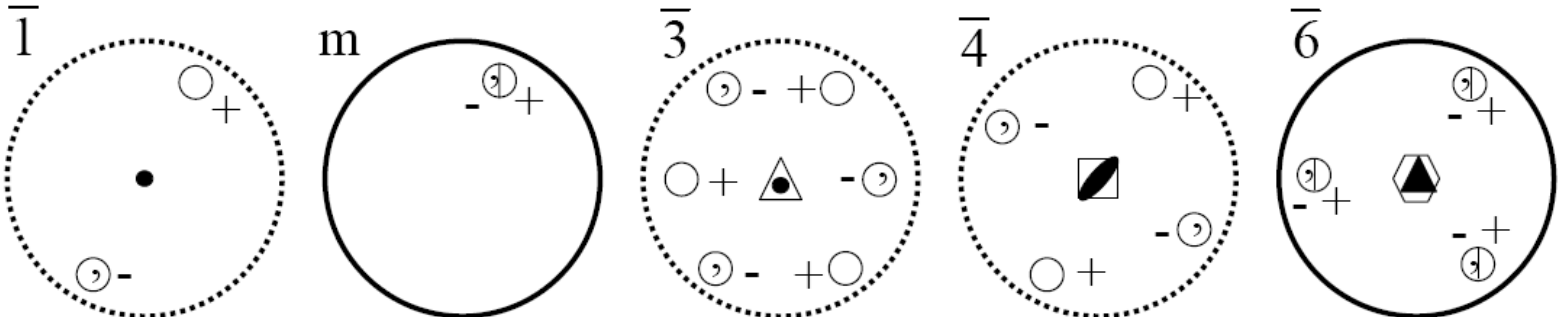
• Operators fall into 2 classes, those producing a right hand replica (**proper**) and those with left hand or mirror image replica (**improper**).

- RH Object
 - ⊙ LH Object
 - ⊕ 2 Objects Projected to the same location
- + above the plane
- below the plane

Proper Rotation (all objects are RH)



5: Improper Rotation (RH and LH objects)





Symmetry Operators (continued)

Transformation Matrix:

Inversion	Mirror normal to \hat{x}	Mirror normal to \hat{y}	Mirror normal to \hat{z}
$T = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$T = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

coordinates: $x = y \neq z$

How do we combine multiple symmetry operations about a point?

Recall: Symmetry operations cannot be combined so as to violate one of the other symmetry elements. Self-consistency must be maintained.

Mirror planes cannot be placed randomly.

Seven crystal systems in terms of symmetry elements

System*	Symmetry	Lattice Parameters	Angles
Triclinic	No axes of symmetry	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic	Single diad	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$
Orthorhombic	Three mutually perpendicular diads	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	A single tetrad	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	One hexad	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$
Rhombohedral (trigonal)	A single triad	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Cubic	Four triads	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

*Listed in order of increasing symmetry

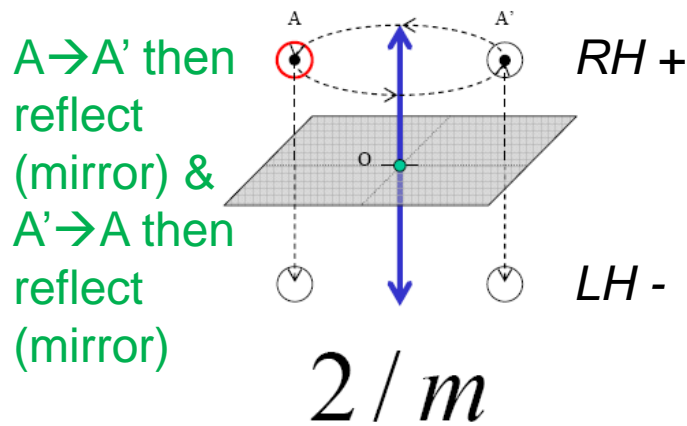


Rest of the Point Groups

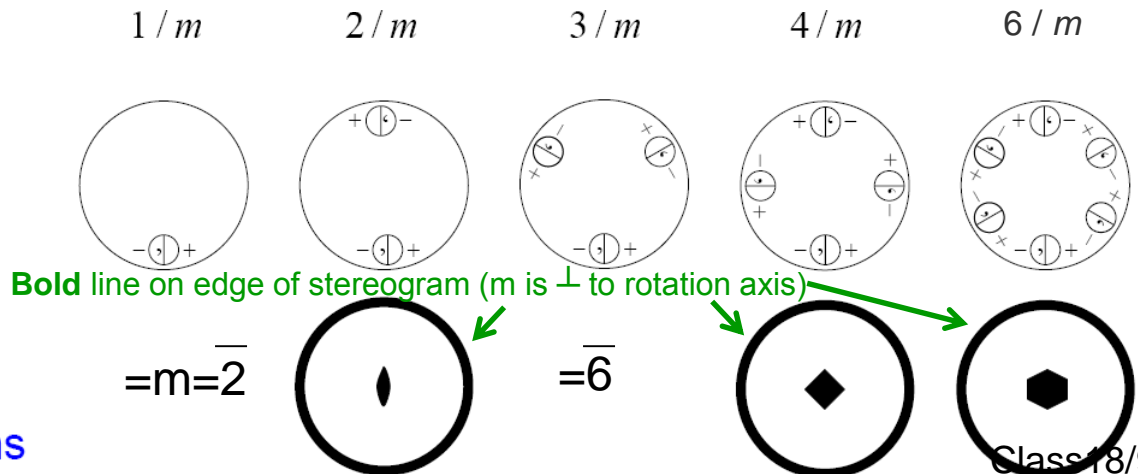
- In principle, there are a tremendous number of point symmetry groups that can be constructed from the 5 operators we just defined.
- However, we are only interested in the ones that can be combined with Bravais lattice vectors to build a crystal.
- Since the Bravais lattice translations themselves already have some symmetry, this limits the possibility.
- For example, tetragonal crystals have a rotation tetrad parallel to [001]. Thus, this operator must be part of any point symmetry group used in conjunction with tetragonal Bravais lattices vectors.
- There are 32 (distinct) point groups that are compatible with one of the 14 Bravais lattice translations. Let's look at the other 22:**

Mirror Planes \perp Rotation Axis

Mirror Planes \perp Rotation Axis



Rotate through symmetry operations then reflect (up or down)

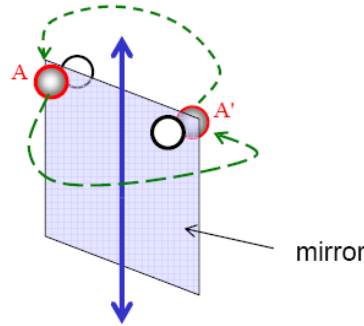


These are 3 more of the 32 point groups to total 13 so far.

Rest of the Point Groups (continued)

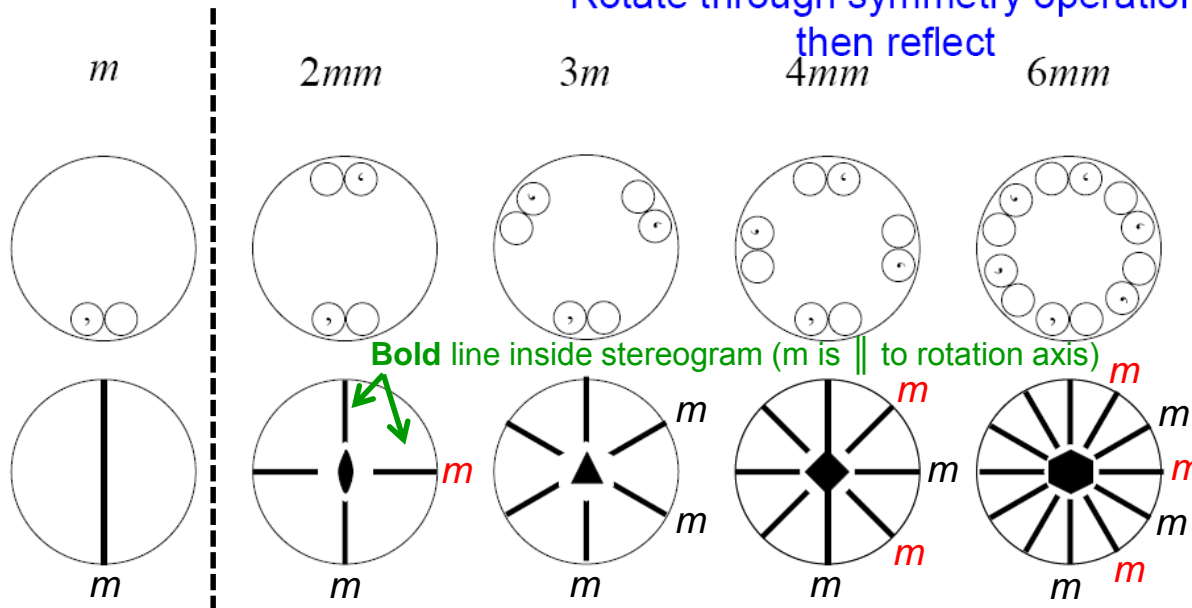
Mirror Planes // Rotation Axis

$A \rightarrow A'$ then
reflect
(mirror) &
 $A' \rightarrow A$ then
reflect
(mirror)



$2m$

Rotate through symmetry operations
then reflect



These are 4 more of the 32 point groups to total 17 so far. *(Note: we saw these previously for 10 2-D point groups)*