Crystallography

Morphology, symmetry operations
and crystal classification

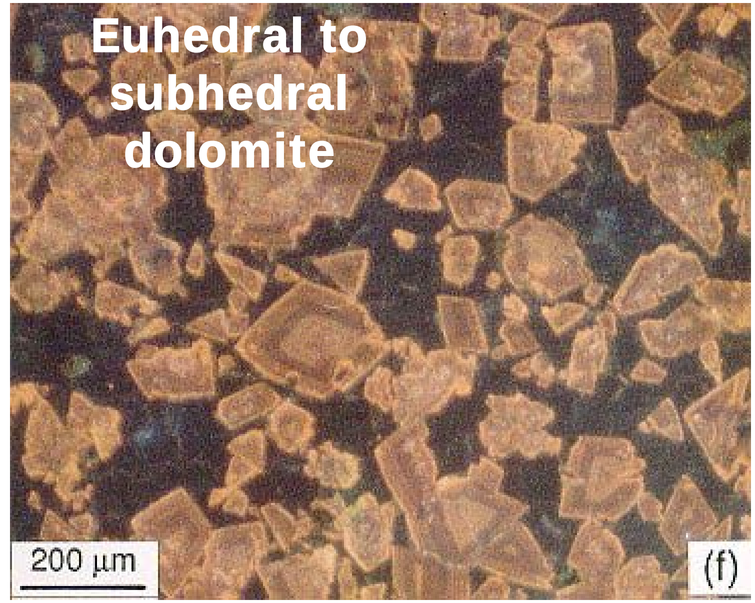
Morphology

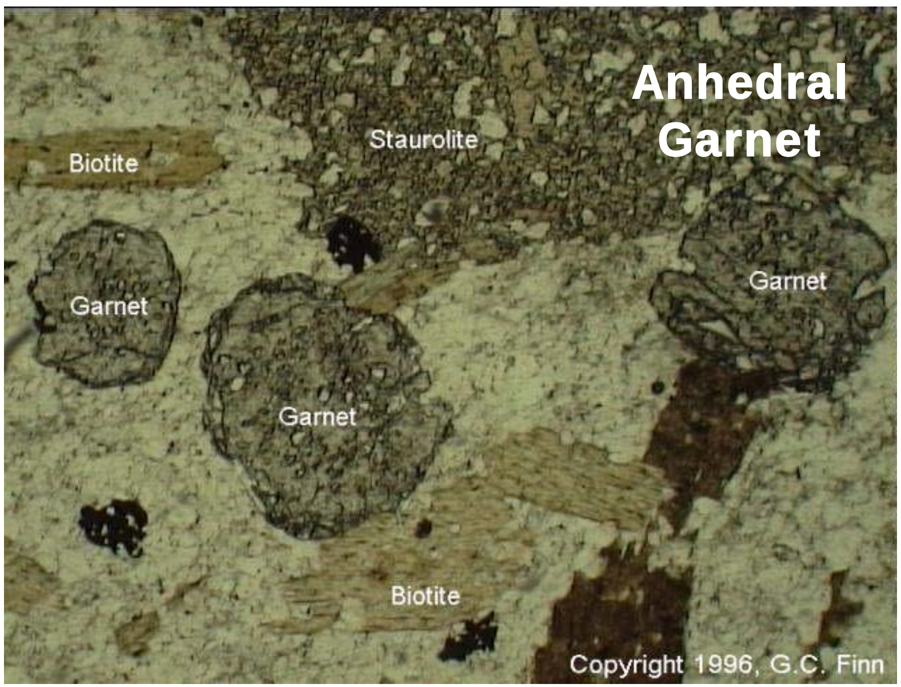
The study of external crystal form.

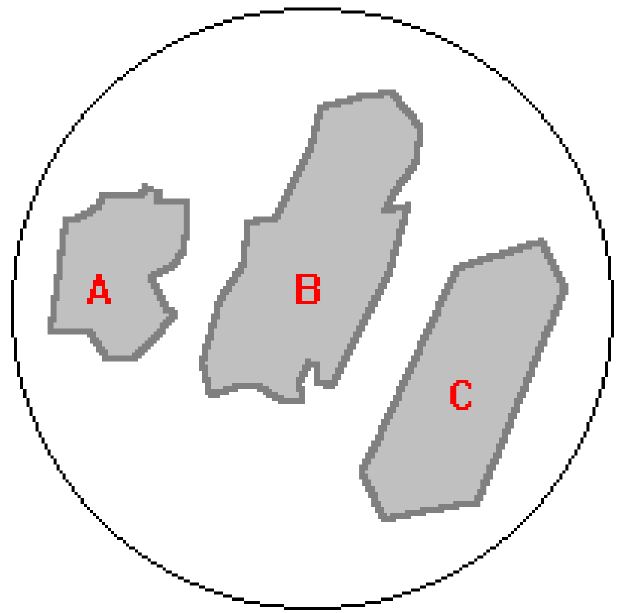
A crystal is a regular geometric solid, bounded by smooth plane surfaces.

Single crystals on the most basic level may be **euhedral**, **subhedral** or **anhedral**.

Hedron (Greek – face); *Eu* and *An* (Greek – good and without); *Sub* (Latin – somewhat).







Which is which in this sketch?

External crystal form is an expression of internal order

The Unit Cell

The smallest unit of a structure that can be indefinitely repeated to generate the whole structure.

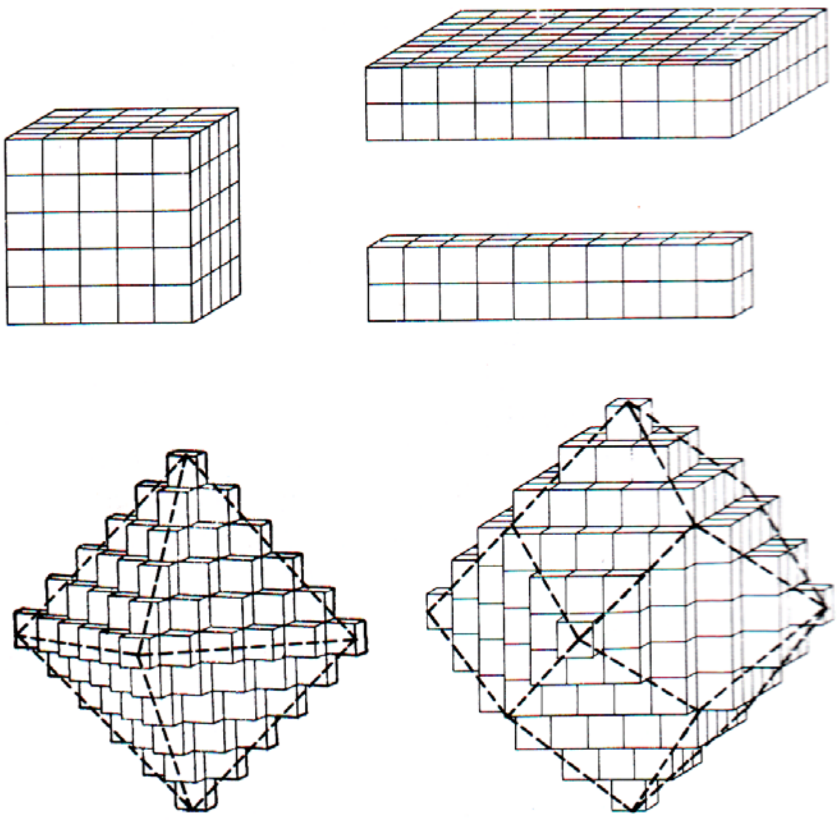
Irrespective of the external form (euhedral, subhedral, or anhedral) the properties and symmetry of every crystal can be condensed into the study of one single unit cell.

Repetition of unit cell creates a *motif*

In this example the unit cell is a cube.

It is a constant.

The arrangement and stacking differs between shapes.



Elements of symmetry identified in the unit cell will be present in the crystal

Elements without translation

Mirror (reflection)

Center of symmetry (inversion)

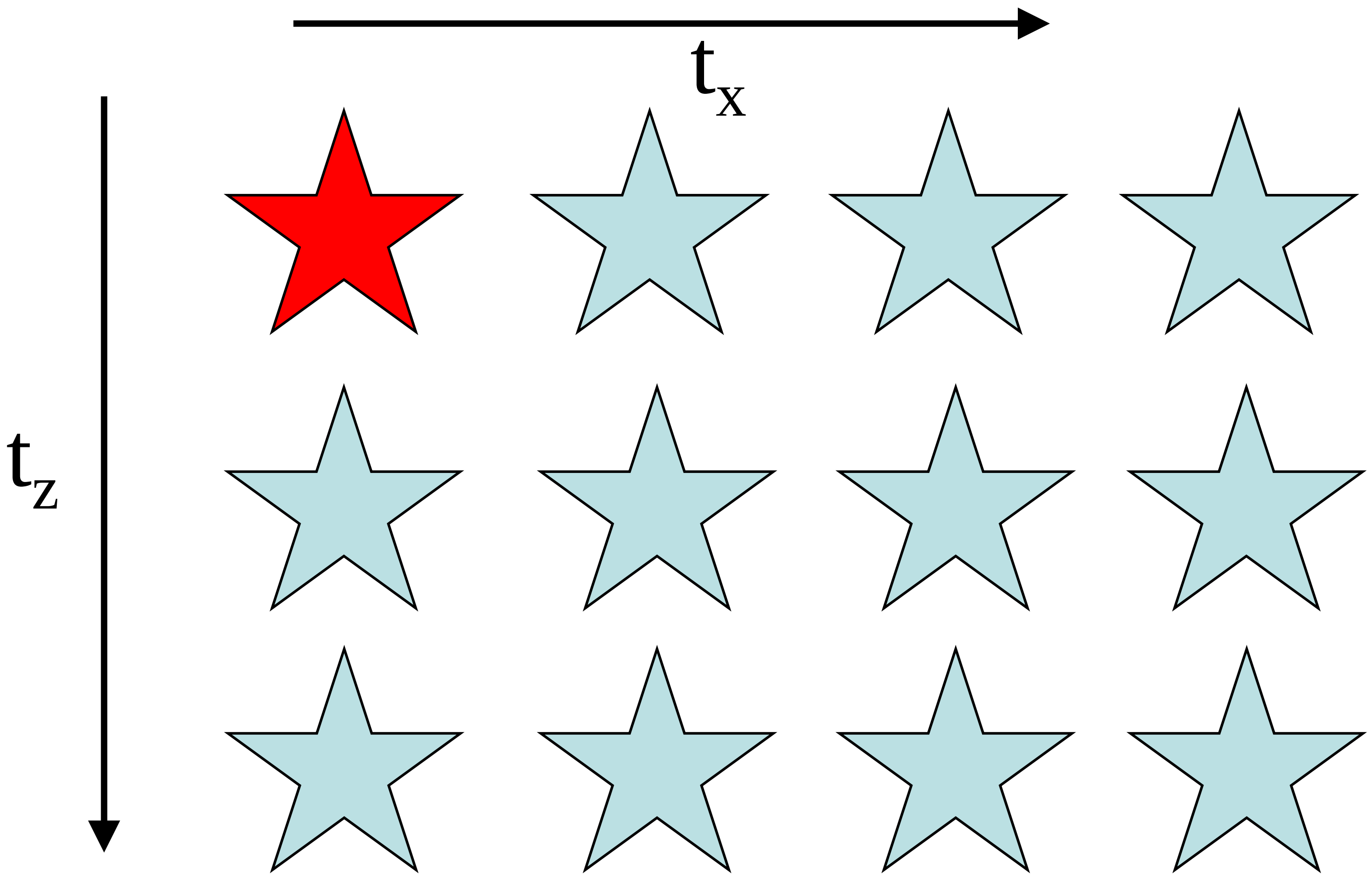
Rotation

Glide

These are all referred to as (a) *symmetry operation(s).*

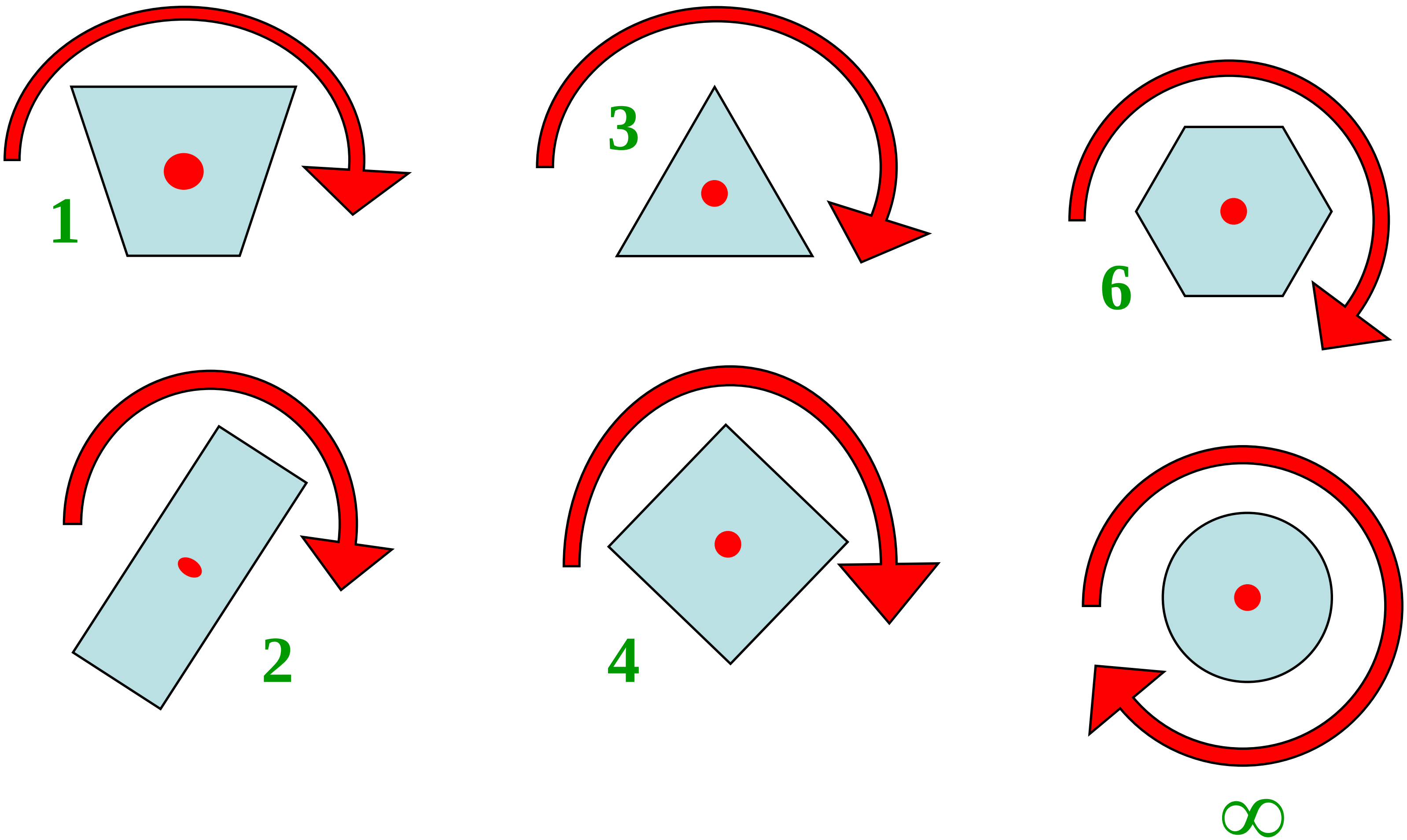
Translation

An operation (t) that generates a pattern a regular identical intervals.

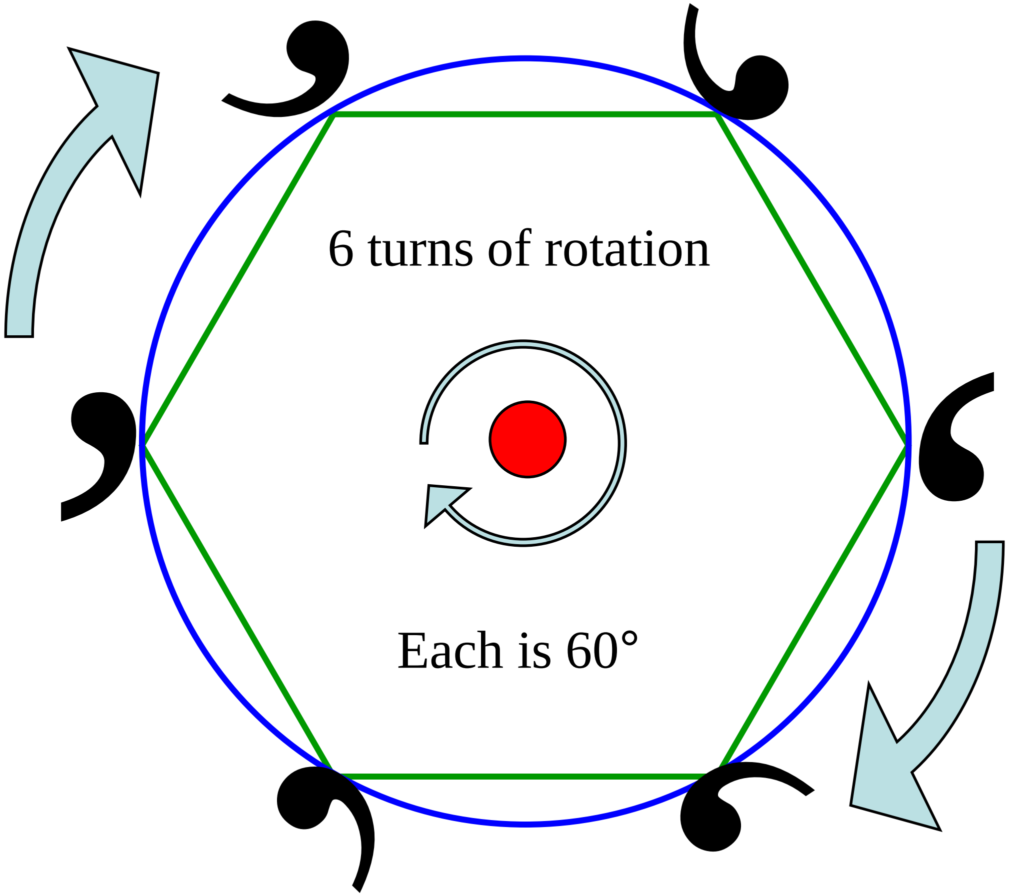


In 3 dimensional space the translations can be labelled x, y and z (or 1, 2 and 3).

Rotational symmetry is expressed as a whole number (n) between 1 and ∞. n refers to the number of times a motif is repeated during a complete 360° rotation.



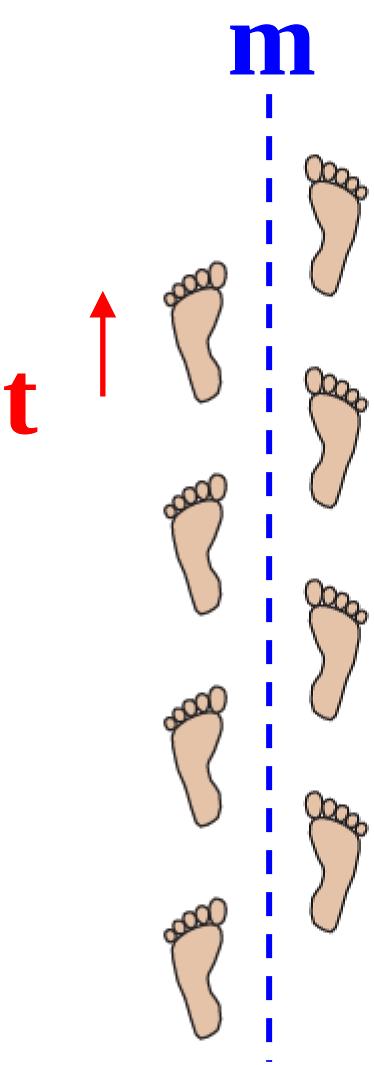
Rotation produces patterns where the original motif is **RETAINED**.



Both original and rotation have the same "handedness". They are **CONGRUENT**.

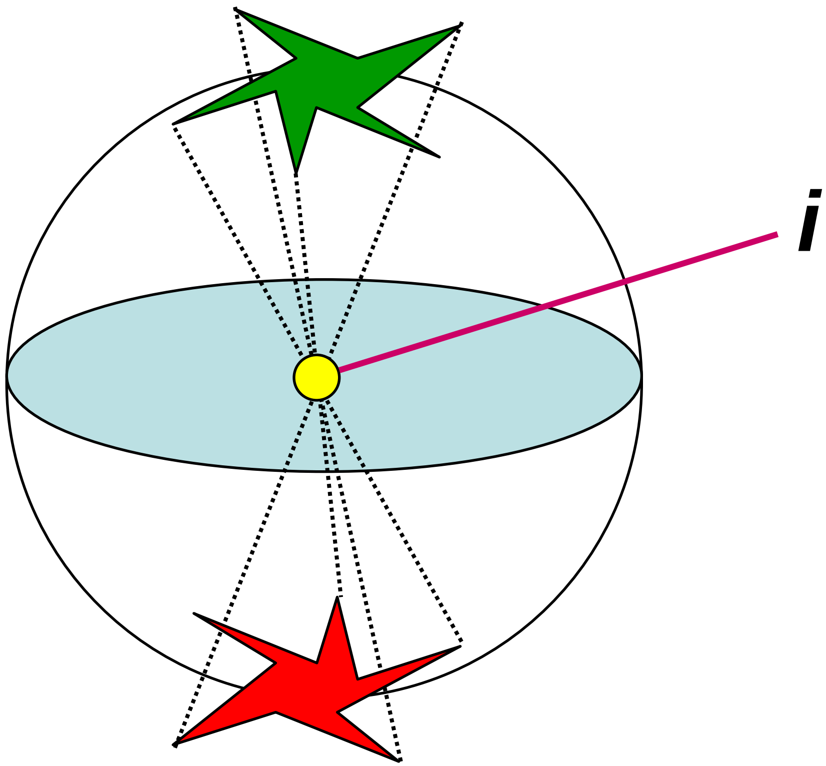
Glide

A two-step operation: reflection followed by translation (*g*)



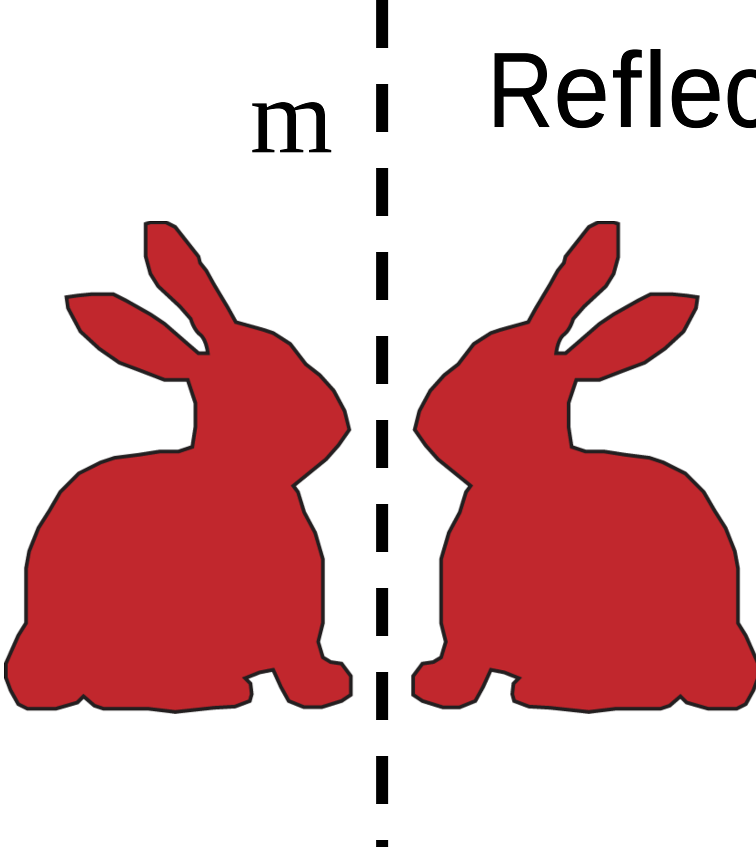
An *inversion (i)* produces an inverted object through an *inversion center*.

Draw lines from every point on the object through the inversion center and out an equal distance on the other side.



Is the operation ***congruent***, or does it create an ***enantiomorphic pair***?

Reflection versus Inversion

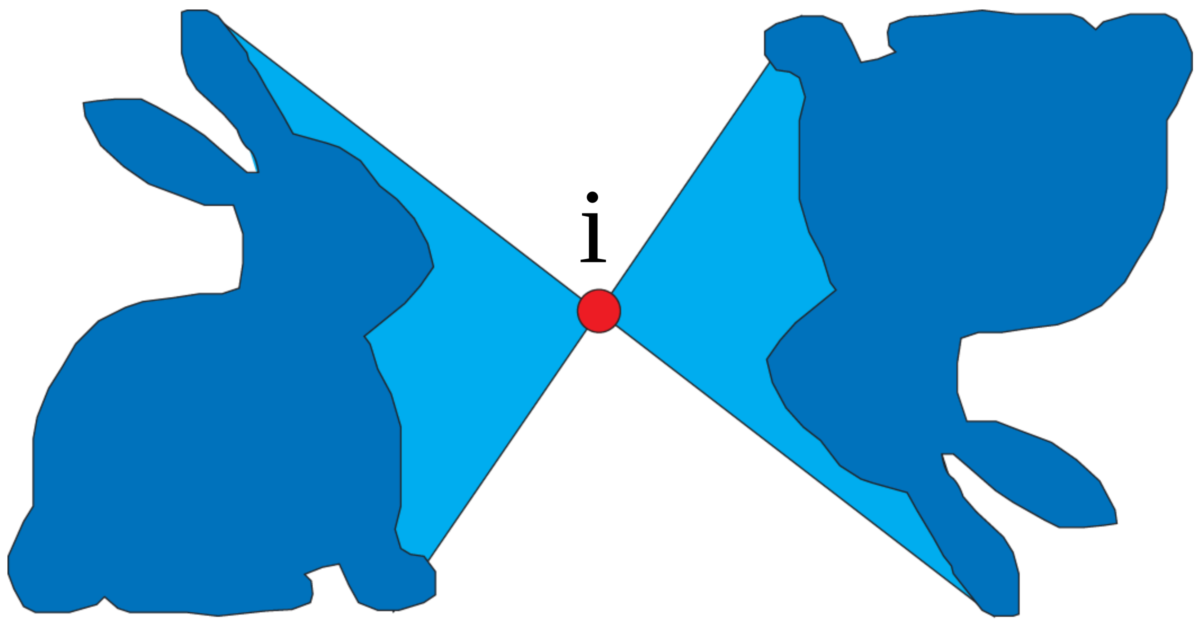


Let us look at this purely in 2 dimensions.

Reflection of a 2-dimensional object occurs across a plane (m)

After inversion everything is an equal and opposite distance through a single point *i*.

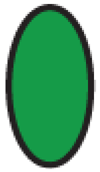
Results in congruent pairs.

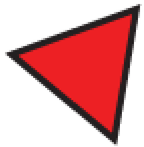


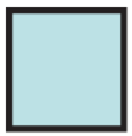
Combination of Rotations

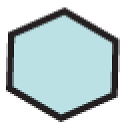
Moving from 2 dimensional to 3 dimensional systems (real crystals) multiple rotation axes may be identified.

RULE: All symmetry operators must intersect at a single point.

 2-fold rotation: 180° rotation

 3-fold rotation: 120° rotation

 4-fold rotation: 90° rotation

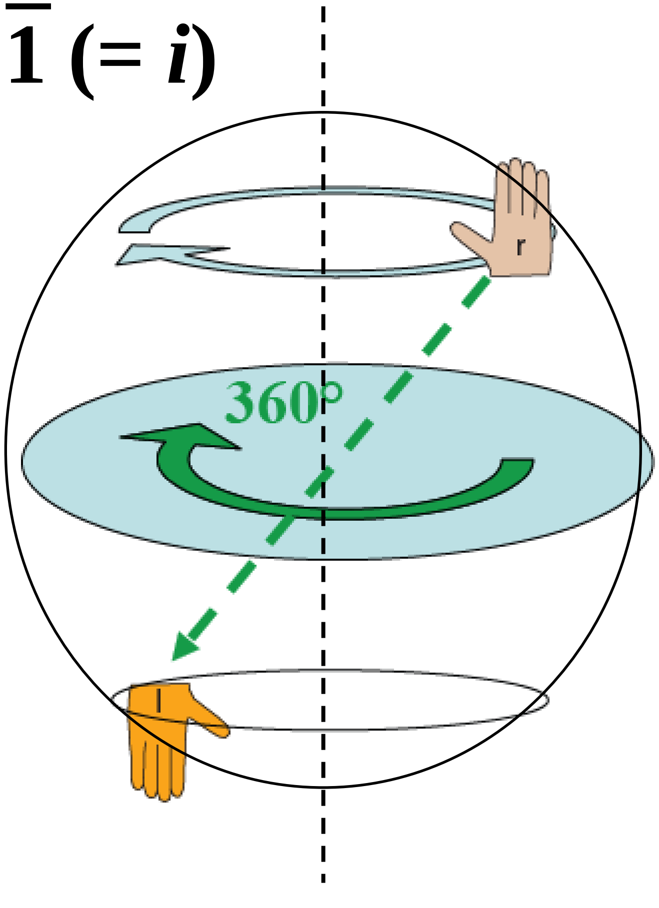
 6-fold rotation: 60° rotation

m mirror plane

The combining of the single operations, rotation and inversion, generates a ***rotoinversion operation***.

360°

$\bar{1}$ (= *i*)



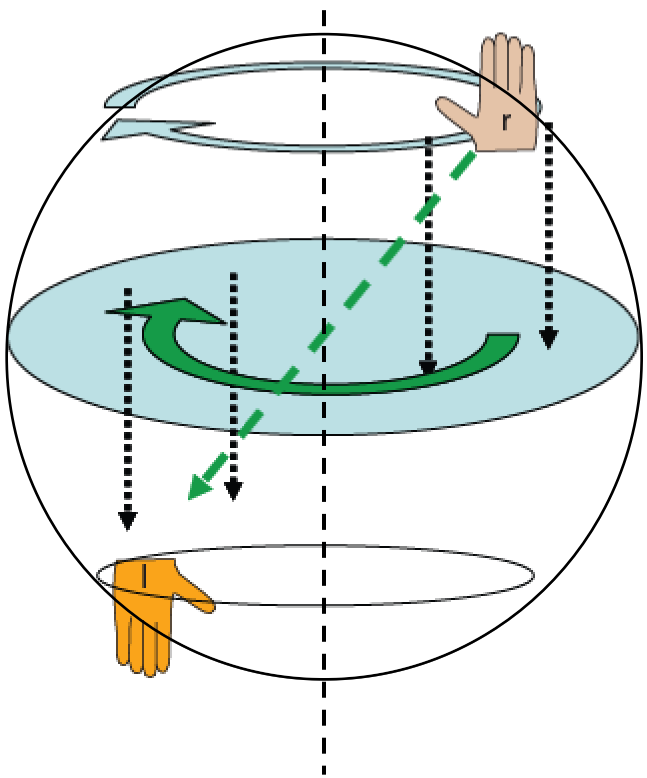
This may be viewed in one of two ways. Either, think of the diagram as two independent objects, a right hand in the upper hemisphere, and a left hand in the lower hemisphere.

The rotoinversion is the symmetry operation required to transpose one object onto the other.

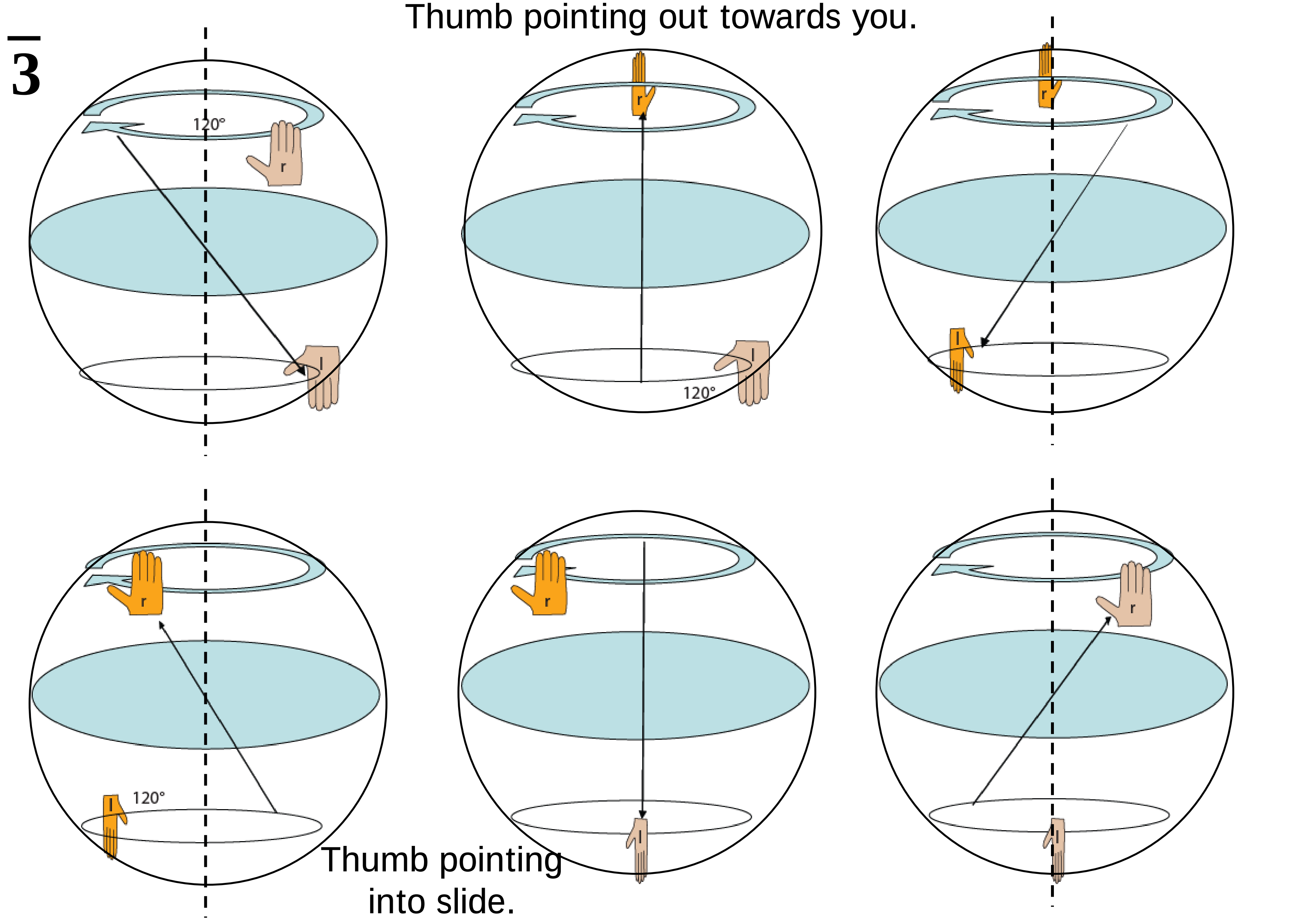
In this operation, rotate the hand through 360° and invert.

NOTE: 2D inversion results in ***congruent pairs***.
3D roto-inversion in ***enantiomorphic pairs.***

$\bar{2}$ (= *m*)



These figure shows a rotoinversion operation with n = 2.

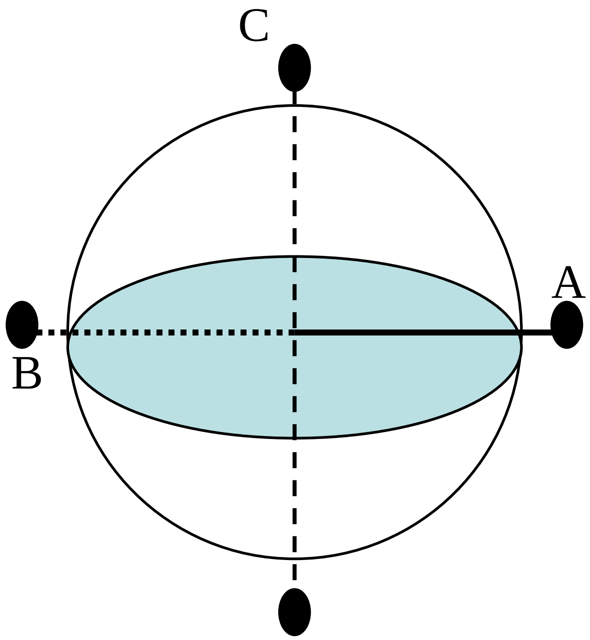


A second $\bar{3}$ rotoinversion returns the unit cell to its original position.

Simple Combination Systems

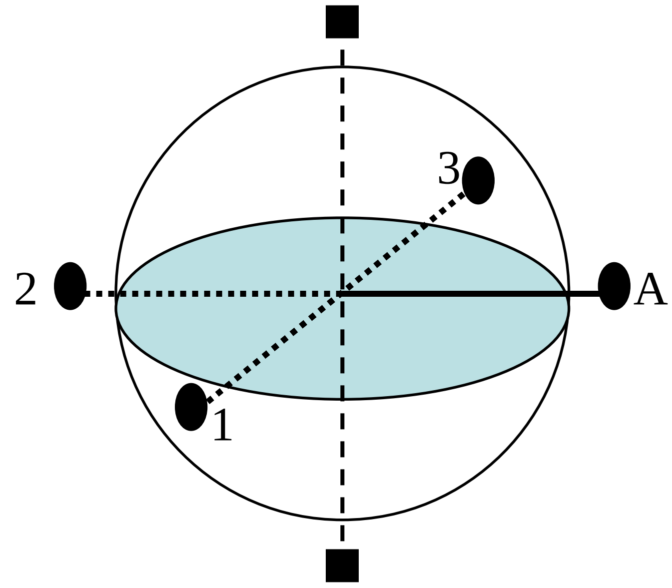
Combining various axes of rotation to generate regulate three dimensional patterns.

2-fold rotation + 2-fold rotation

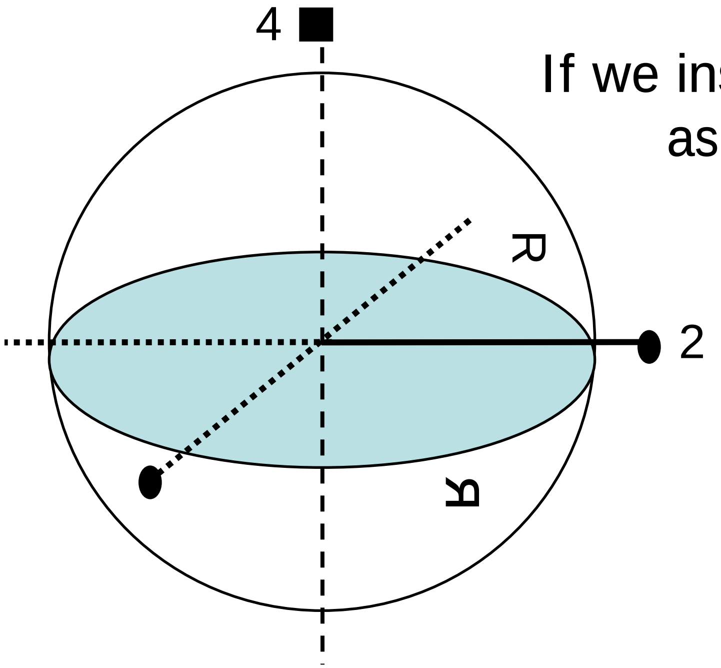


Vertical 2-fold axis (C) operates a 2-fold rotation on A.
This generates a second, identical axis B.

4-fold rotation + 2 x 2-fold rotation

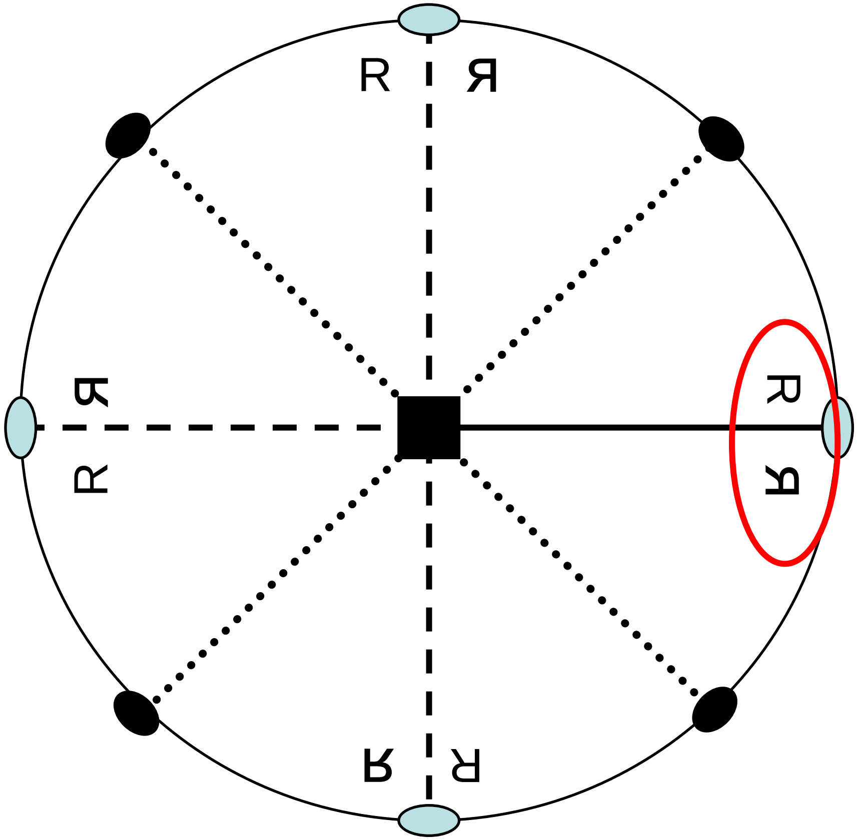


In this example, the 4-fold axis generates three identical 2-fold axis



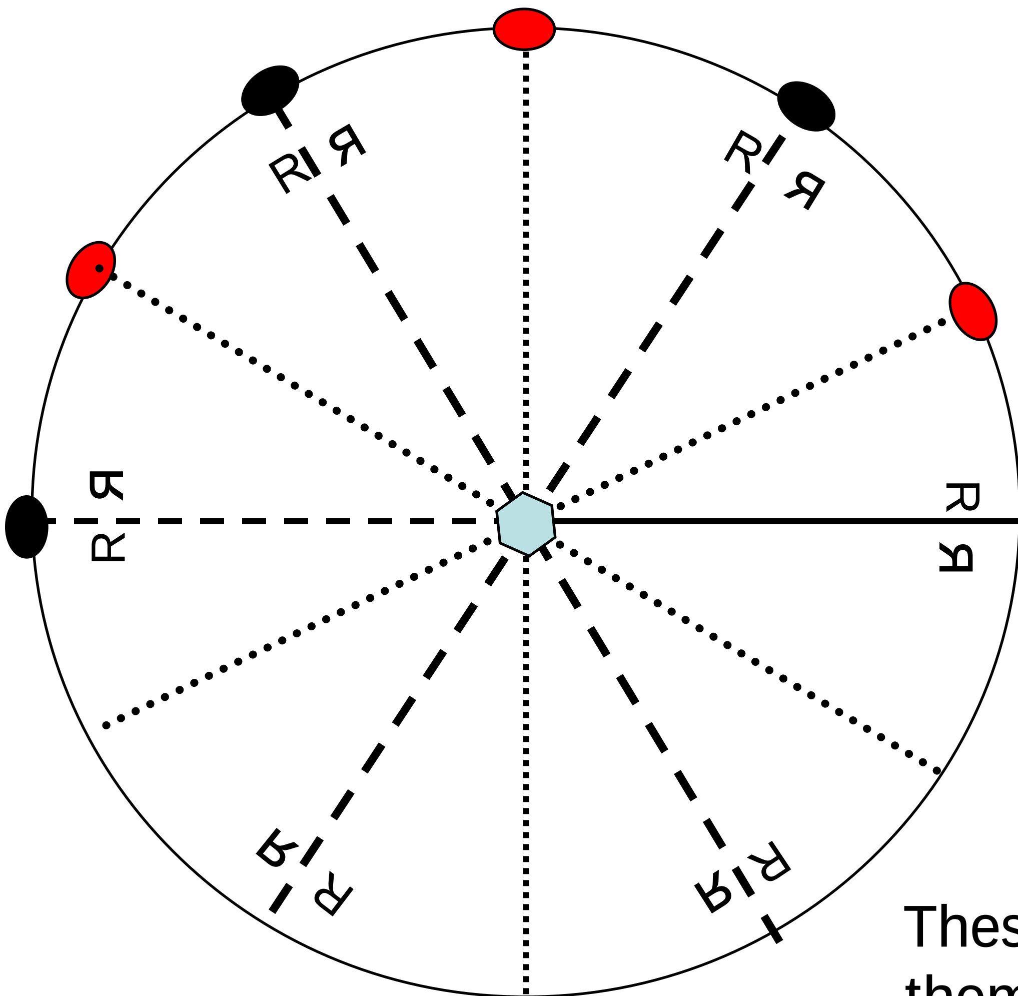
If we insert a “unit cell” we can track what happens as each symmetry operation is executed.

Viewing the image from above (down the 4-fold axis), 4-fold rotation of the original “R Я” results in the following distribution.



Remember – thinking with respect only to rotation – this new pattern has two new independent sets of 2-fold rotation. The first is highlighted by the markers. This set, themselves generate the second set of 2-fold rotations indicated by the markers.

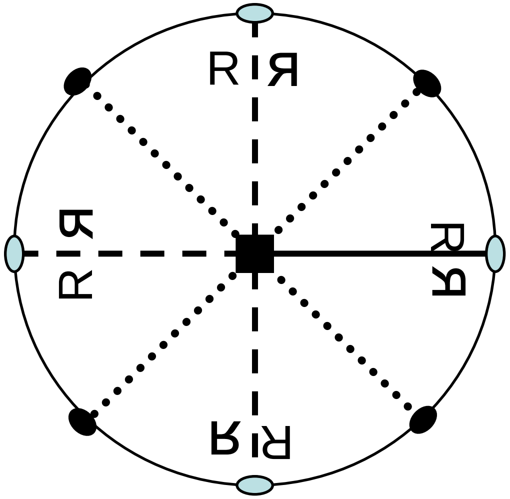
To test this, try it out on a circle of paper, marked with the “unit-cell”.



In the 6-fold system we generate 5 additional motif pairs (6 x “R Я”).

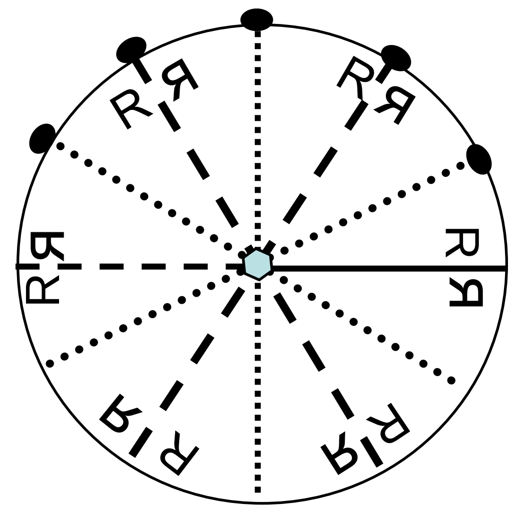
These 6 pairs them-selves, generate a further set of three 2-fold axes (⬬).

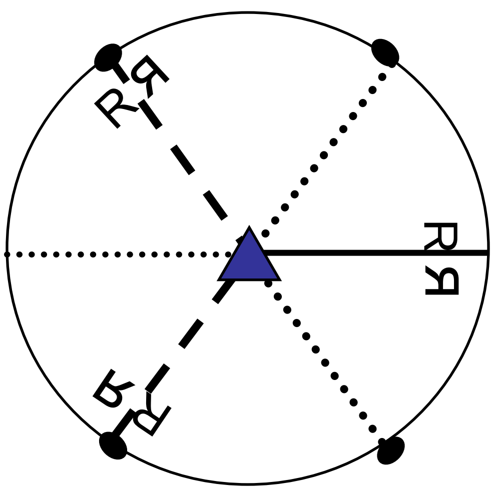
These three 2-fold axes in themselves generate a second set of three 2-fold rotational axes (⬬).



Motif is generated via a 4-fold axis, a set 2-fold axes, and subsequently, a second set of 2-fold axes.
The short-hand notation for this combination is 422.

Here, the motif is generated via a 6-fold axis, a set of 2-fold axes, and subsequently, a second set of 2-fold axes.
The short-hand notation for this combination is 622.





In a trigonal system there are only two rotational symmetries.
The short-hand notation is 32.

NOTE: The short-hand notation does not tell you how many axes of rotation are present, merely which operations are present.

A cube (or similar isometric shape) has very special symmetry. It has a very high degree of symmetry.

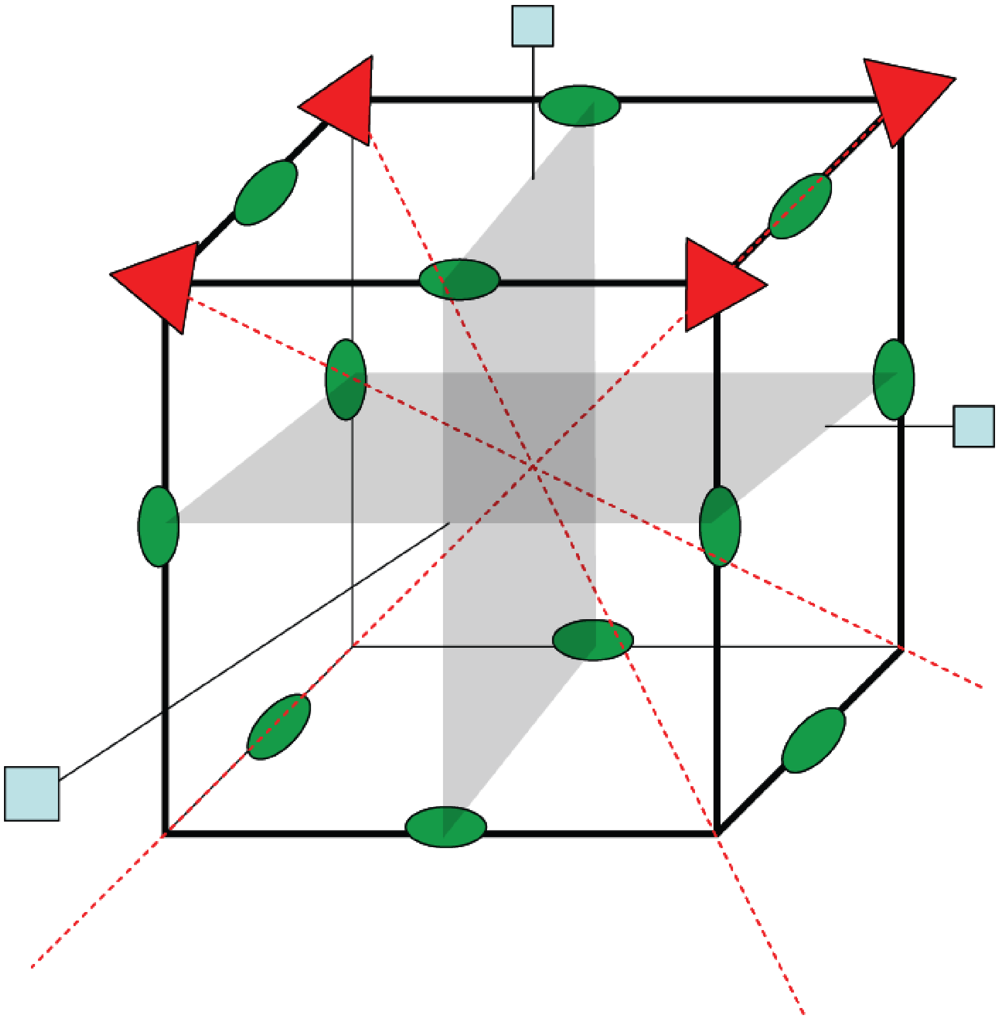
Can we identify the operations?

3 x 4-fold axes

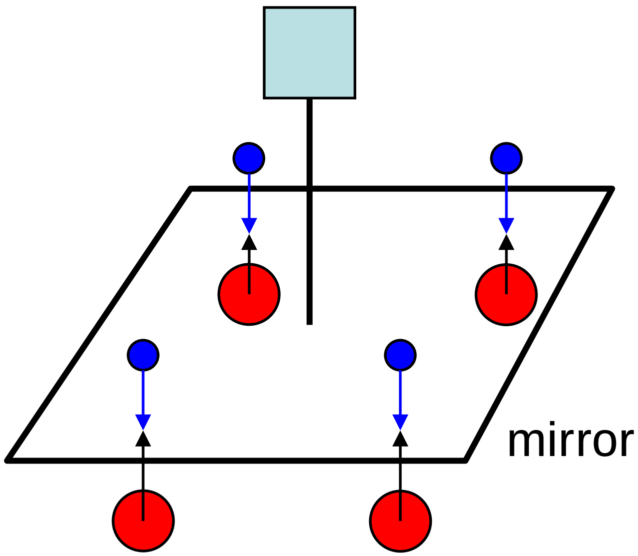
4 x 3-fold axes

6 x 2-fold axes

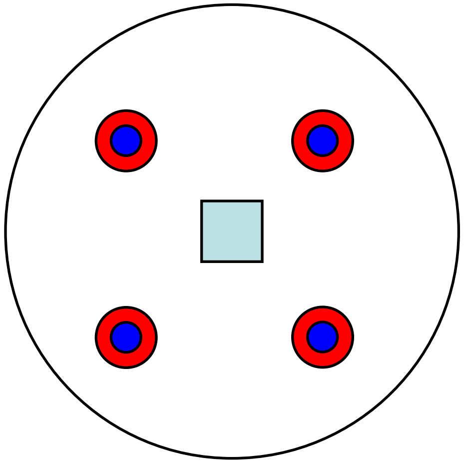
Label = 432



Combining Rotation and Mirrors

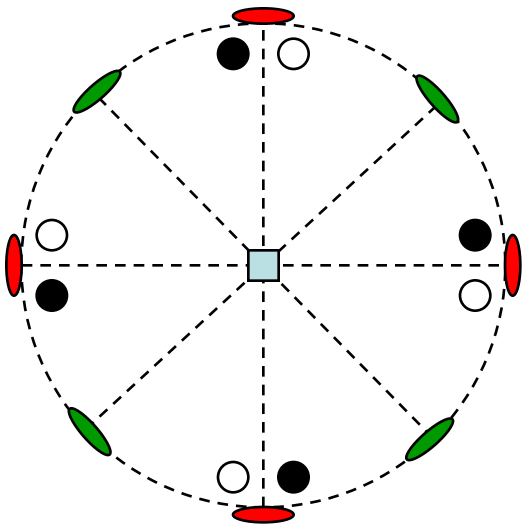


$\frac{4}{m}$

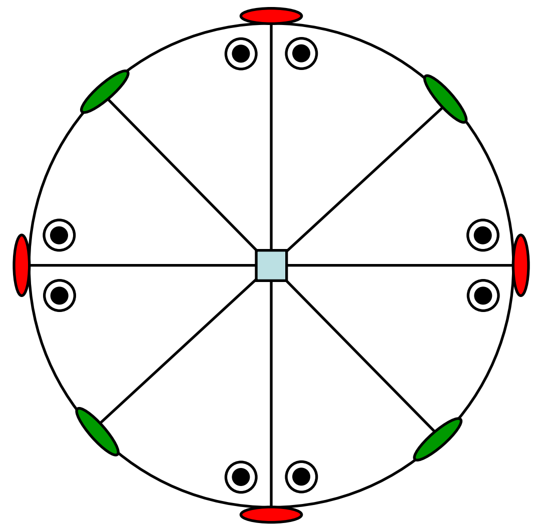


Mirror is in plane of “paper”

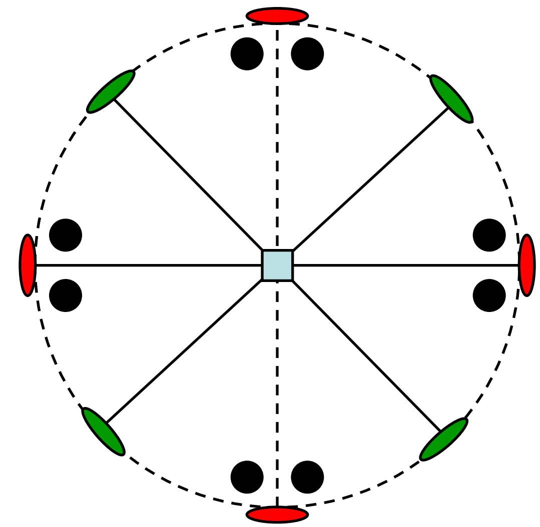
What would a projection of $\frac{6}{m}$ look like?



4 2 2
No mirrors



4 2 2
m m m
3 perpendicular mirrors
+
1 in plane of “paper” (horizontal)



4mm
3 perpendicular mirrors

Motifs above the horizontal plane (upper hemisphere) denoted by solid dots. Those below the page (lower hemisphere) are indicated by open circles. Dotted lines indicate “no mirrors”. Solid lines indicate the position of mirror planes.

3D operations

Screw axes: created by specifying a translation distance and a rotation angle

Rotoinversions:

- 2-fold: 180° + inversion = mirror plane (m)
- 3-fold: 120° + inversion
- 4-fold: 90° + inversion
- 6-fold: 60° + inversion = $3/m$

combinations of 3D operations

Must combine rotation & reflection with inversion and rotoinversion to generate the 32 point groups or *crystal classes*

X,Y,Z coordinate reversals:

- z-y plane reflection
- rotation around z
- inversion

Review

Rotation axes (n, where n=1, 2, 3, 4 and 6).

Rotoinversion axes ($\bar{1}$ $\bar{2}$ $\bar{3}$ $\bar{4}$ and $\bar{6}$).

Combination of rotation axes (622, 422, 222, 32).

And combined rotation with mirrors (i.e. 6/m 2/m 2/m)

As well as glide (g) and translation (t).

A reflection produces a mirror image across a mirror plane **(m)**

There is no rotational element.

They can not be superimposed on each other.

They are an **enantiomorphic** pair