



Symmetry in crystals
National Workshop on Crystal Structure Determination Using
Powder XRD

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I. WHAT IS SYMMETRY?

Symmetry is a common natural occurrence and appears in art forms, architecture, natural patterns (snowflakes, flower petals, honeycombs, skeletons, *etc.* Symmetry implies some (a) regularity, (b) proportion, and (c) the resulting beauty.

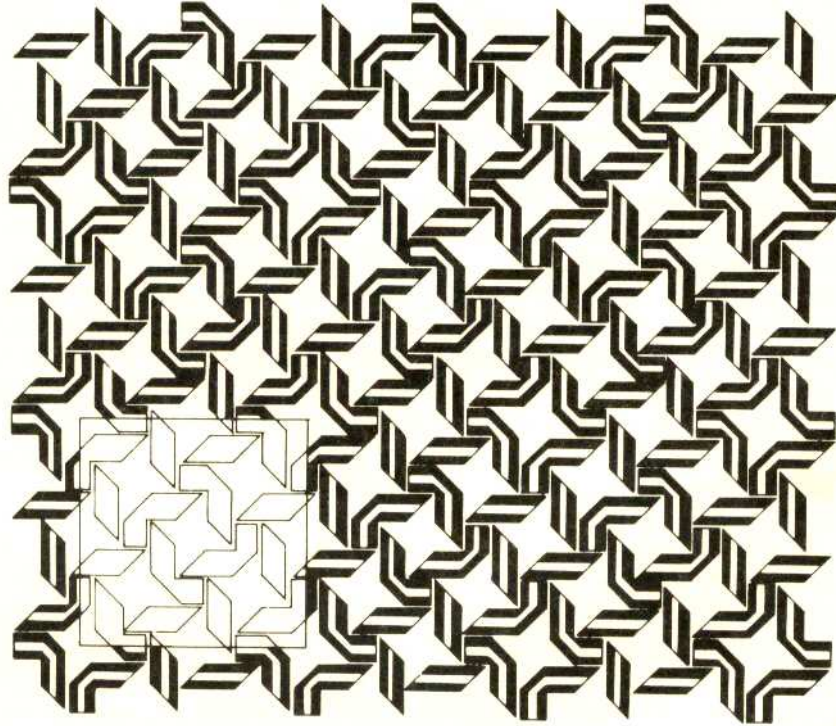


FIG. 1: A symmetric tile from a Persian painting.

A simple example of symmetry is considered in Figure 2, showing two symmetric units of a broken teacup.

II. ELEMENTS OF SYMMETRY

In the discussion, we will start from an understanding of symmetry in two-dimensions. We will observe symmetry in three kinds of objects, the three “p’s”:

polygons→**points**→**patterns**.

A **symmetry operation** is the process of transforming an object such that the initial and final states are indistinguishable. Refer to Fig. 2 again. We will see how the symmetry operations act on polygons, points and patterns.

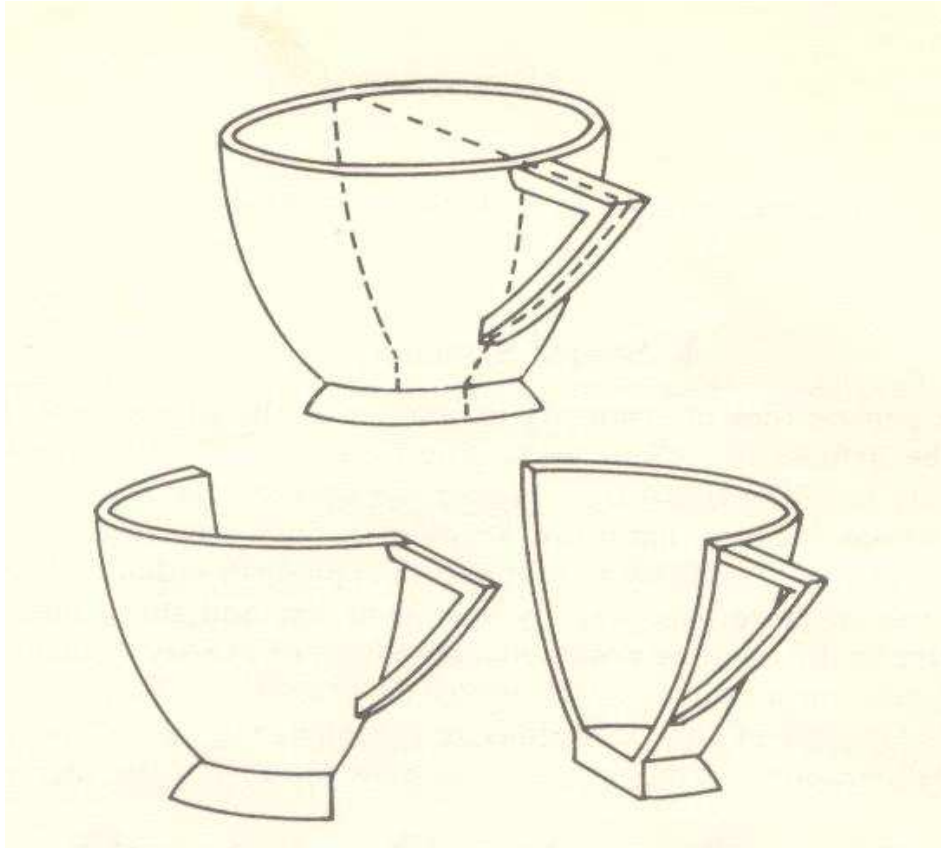


FIG. 2: A teacup.

A symmetry operation is defined by **symmetry elements**. There can be three kinds of elements:

1. points,
2. axes,
3. planes.

We will discuss these elements one by one, but not necessarily in the same order.

III. AXES OF ROTATION

There can be 1,2,3,4 and 6-fold axes of rotation. An n -fold rotation axes implies that a rotation around an axis through $2\pi/n$ or $360^\circ/n$ leaves the object in an indistinguishable state.

Hermann-Mauguin notation: **1**, **2**, **3**, **4**, **6**.

These elements can be represented by the symbols in Fig 3.

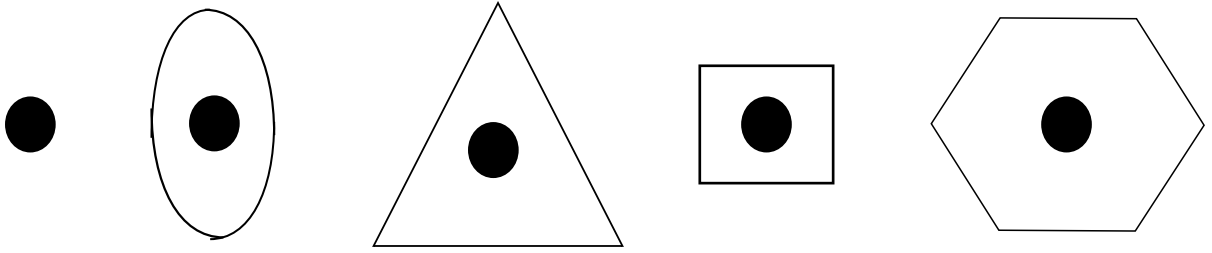


FIG. 3: Symbolic representations of axes of symmetry.

A. Examples on polygons

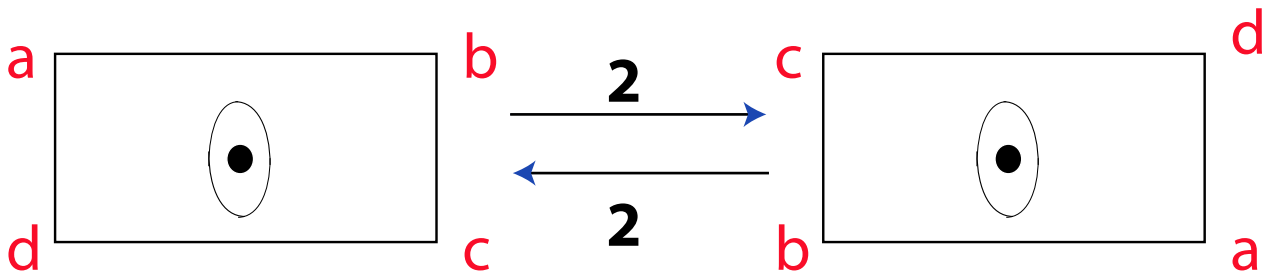


FIG. 4: **2** operation on a rectangle.

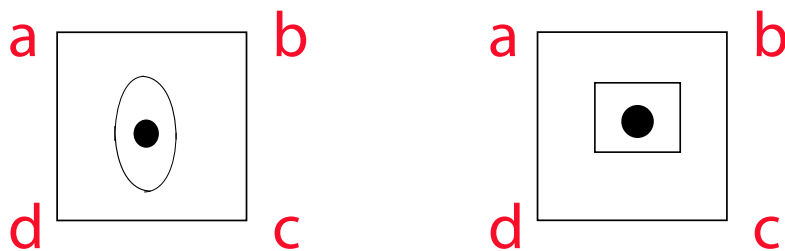


FIG. 5: A square has both **2**-fold and **4**-fold axes of rotation.

- Note that for convenience, the symmetry element (axis of rotation) and the symmetry operation (rotation) are represented by the same notation, **1**, **2**, **3**, **4**, **6**.
- The hexagon also possesses a **3** symmetry axis. Furthermore, one can show that $\mathbf{6} \cdot \mathbf{6} = \mathbf{3}$ or $\mathbf{6}^2 = \mathbf{3}$. The notation $\mathbf{a} \cdot \mathbf{b}$ represents the operation **b** followed by the operation **a**.

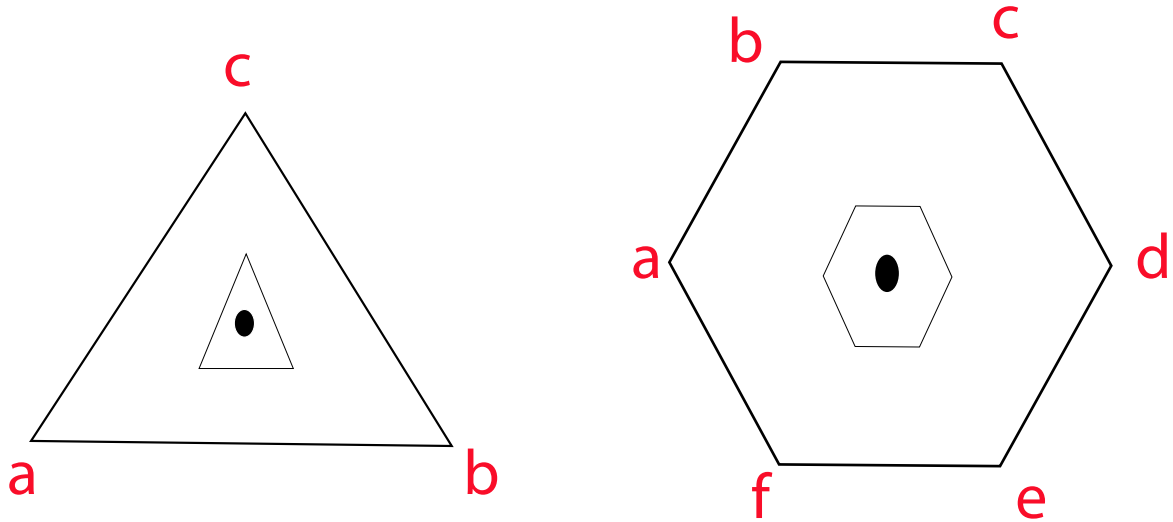


FIG. 6: **3**-fold and **6**-fold axes of rotation for a triangle and hexagon, respectively.

B. Examples on points

Suppose we have a distribution of points. Each “point” is just an object of zero size and has no dimensions. It is just a convenient place-holder as we will see in later talks (Dr. Siddiqi). It is very similar to what we would later on refer to as a **lattice**.

Note that *every* point of the infinite expanse of points is a **2** axis.

C. Examples on patterns

Suppose we affix an object at each point in the grid. What we now have is not an arrangement of points, but an arrangement of objects. Each object is called a **basis** or a **motif** and the resulting arrangement is called a **pattern**. You will note that this is similar to the concept of a crystal **structure** (Dr. Siddiqi).

- The maximum symmetry of a pattern is the symmetry of the points.
- A higher symmetry motif cannot increase the symmetry of the pattern.
- The symmetry of the pattern is determined by *both* the symmetry of the points and the motif.
- The symmetry operation **1**, in fact, means no symmetry at all.

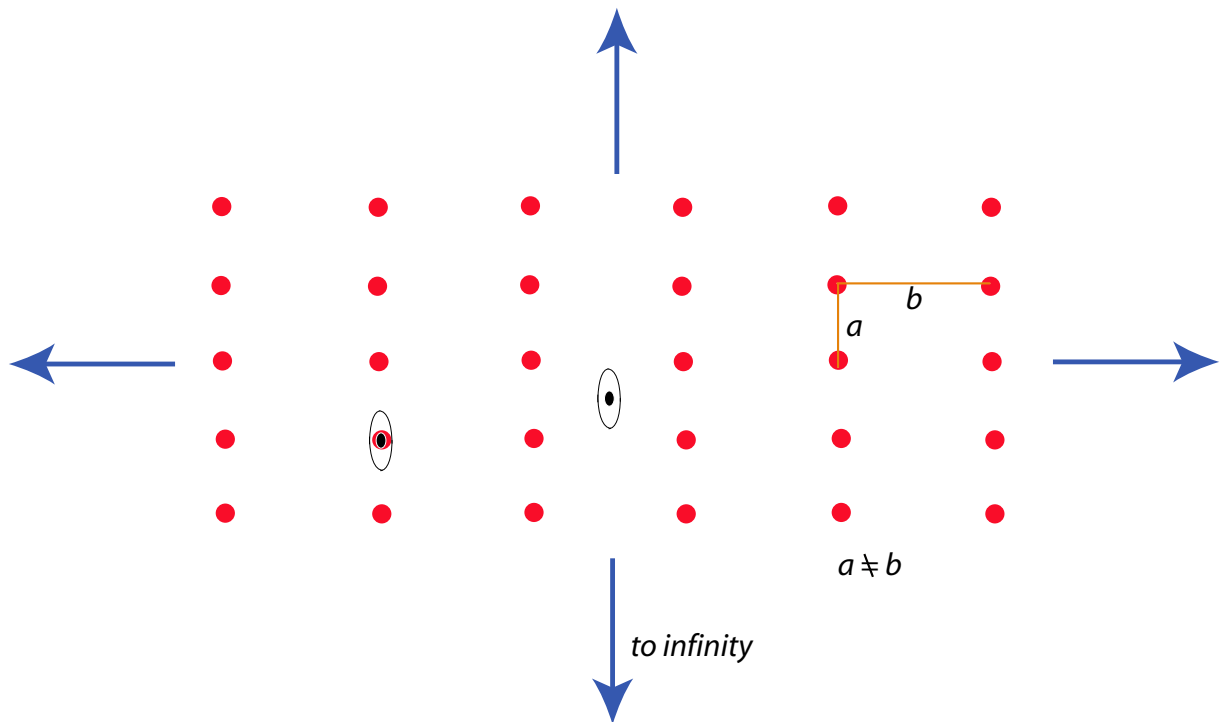


FIG. 7: The rectangular grid of points has **2**-fold symmetry axes.

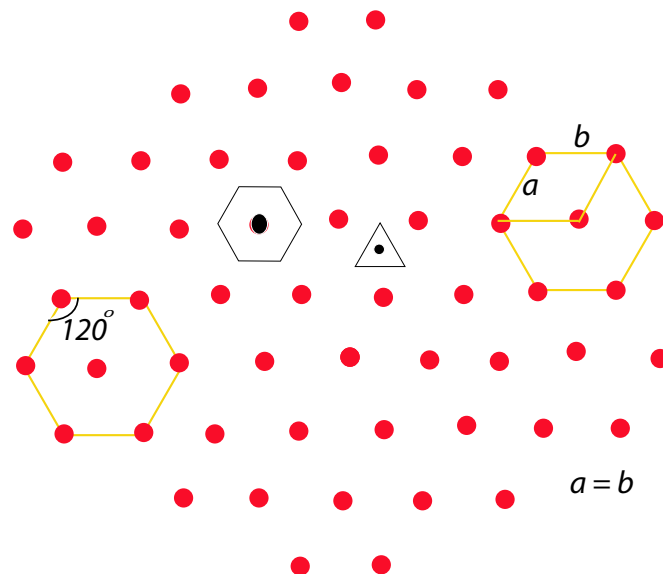


FIG. 8: The hexagonal grid of points has **3** and **6**-fold symmetry axes.

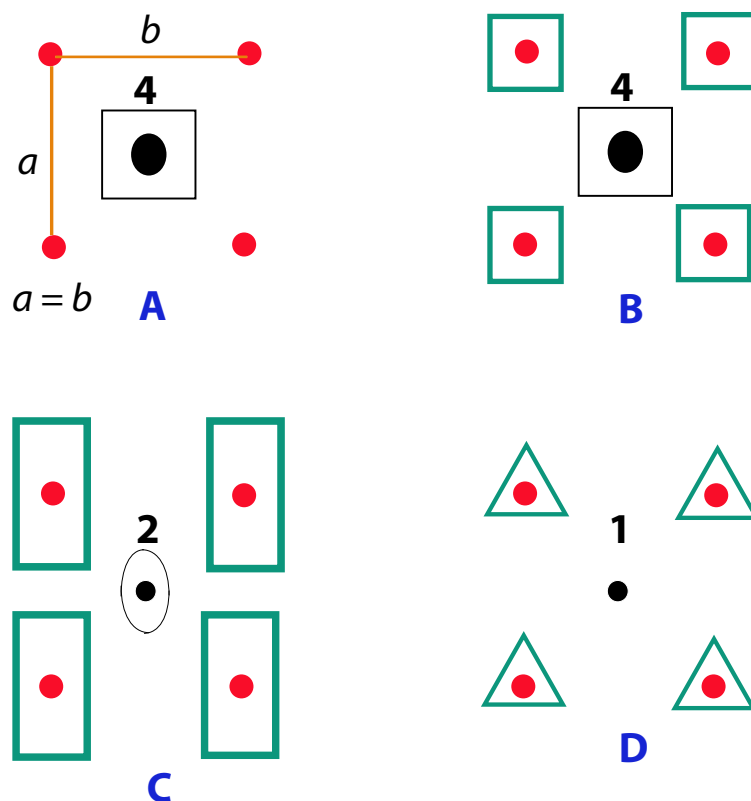


FIG. 9: A square set of points with different motifs.

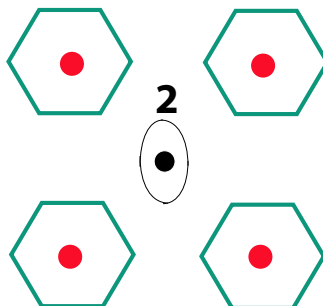


FIG. 10: A square set of points with a **4** axis but affixed with a hexagonal motif with a **6** axis.

IV. PLANES OF REFLECTION

We now discuss **planes of reflection** or **mirror planes**. The idea is very simple, if an object is reflected in a mirror, the image and the object are related by a symmetry transformation, denoted by **m**. An example was given in Figure 2. Mirror images of molecules are very common in inorganic and organic chemistries. The molecule and its mirror image

are called **enantiomers**. The molecule having an enantiomorph pair is said to exhibit **handedness** or **chirality**.

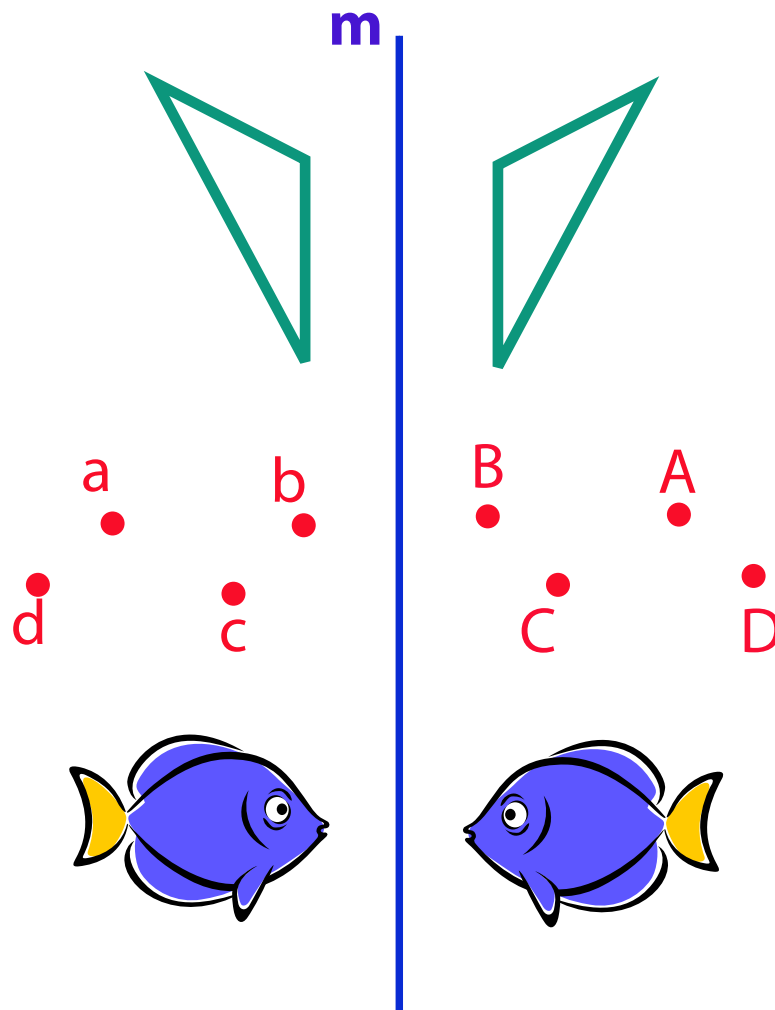


FIG. 11: Illustration of the reflection operation m for polygon, points and an arbitrary object.

V. POINT OF INVERSION

A point of **inversion** or an inversion operation is denoted by \bar{I} . It is also called a **centre of symmetry**. Objects with a centre of symmetry cannot exhibit electric polarizability, optical activity, *etc.*

- Unit cells (refer to Dr. Siddiqi's lecture) of all plane lattices have an \bar{I} centre of symmetry.

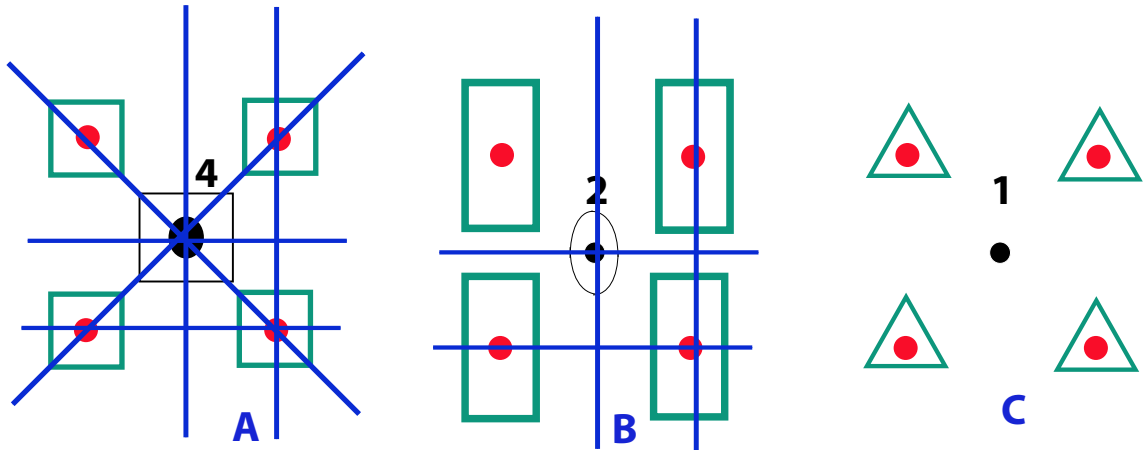


FIG. 12: Mirror planes for patterns based on a square set of points but different motifs.

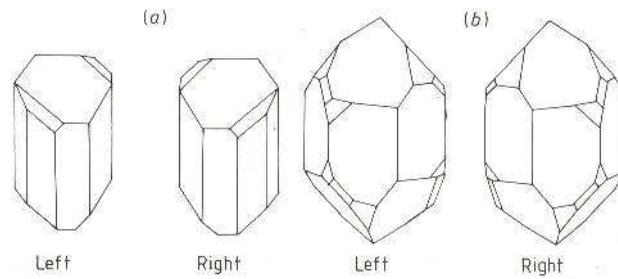


FIG. 13: Handedness in naturally occurring minerals (a) sodium ammonium tartarate and (b) calcite.

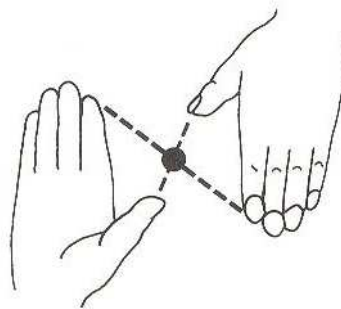


FIG. 14: Center of symmetry in a pair of hands.

- A pattern may or may not have a centre of symmetry depending on the symmetry of the motif.

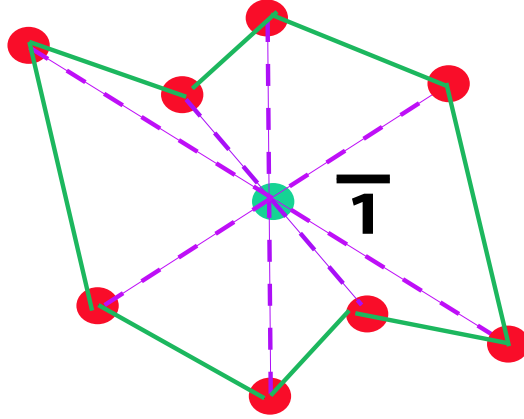


FIG. 15: Example of a centrosymmetric polygon or a set of points (lattice).

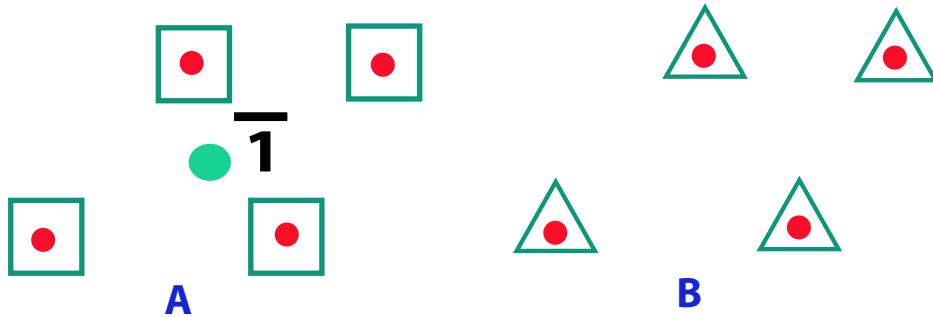


FIG. 16: The existence and non-existence of a point of inversion $\bar{1}$ for two oblique lattices with different kinds of motifs.

- In summary, for two dimensions, a polygon, set of points, or a pattern possesses one or more of these 7 symmetry elements:

Axes of rotation: **1, 2, 3, 4, 6**

Mirror plane: **m**

Point of inversion $\bar{1}$.

VI. EXTENSION TO THREE DIMENSIONS

All of the symmetry elements and operations discussed above, also exist in three dimensions, whether we are considering three-dimensional polygons, three-dimensional arrays of points (lattices) or three-dimensional patterns (crystal structures). However, there is an additional symmetry operation which only makes sense in three dimensions. This is the

operation of **rotoinversion**.

Most of the results that hold for two dimensions remain valid in three dimensions, *e.g.*,

- The maximum symmetry in a pattern is that of the array of points.
- The motif and the points, both control the symmetry of the pattern.

VII. OPERATION OF ROTATION INVERSION OR ROTARY INVERSION

The operation is a rotation followed by an inversion.

$\bar{1} = \bar{1} \cdot 1$ (pronounced as bar-one or one-bar!)

$\bar{2} = \bar{1} \cdot 2$

$\bar{3} = \bar{1} \cdot 3$

$\bar{4} = \bar{1} \cdot 4$

$\bar{6} = \bar{1} \cdot 6$.

The operation $\bar{1}$ is a simple inversion operation and hence, does not add to the list already formulated. Furthermore, one should check that $\bar{2} = \mathbf{m}$ and hence is not a new operation.

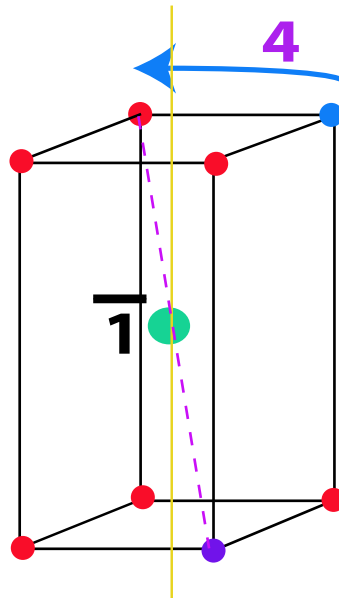


FIG. 17: Illustration of the $\bar{4}$ operation in a three dimensional lattice. Note that the points are coloured only for clarity.

Therefore, for three dimensional polygons, sets of points (lattices) and patterns (structures), we have ten distinct symmetry elements and operations:

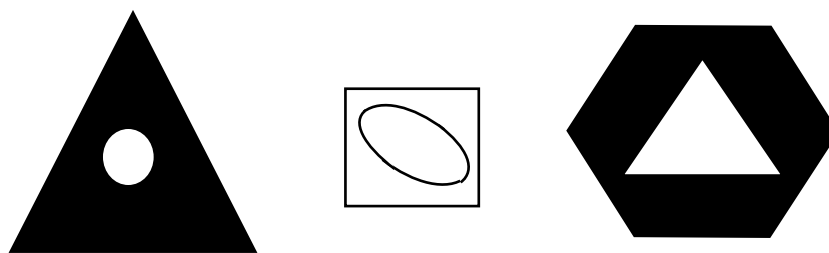


FIG. 18: Symbols for the roto-inversion axes.

Axes of rotation: **1**, **2**, **3**, **4**, **6**

Mirror plane: **m**

Point of inversion: $\bar{1}$

Rotary inversion axes: $\bar{3}$, $\bar{4}$, $\bar{6}$.

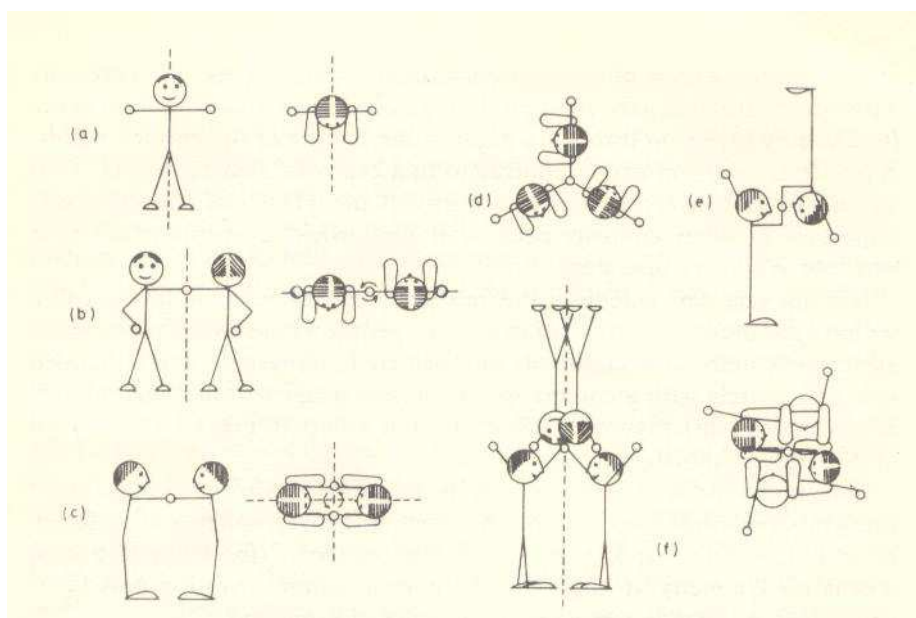


FIG. 19: Identical twins: (a) **m**; (b) **2** axis of rotation; (c) two mutually perpendicular mirror planes **m** and a **2** lying along the intersection between these planes; (d) **3**; (e) $\bar{1}$; (f) $\bar{1}$. (Taken from L.S. Dent Glaser, Chapter 19, The Chemistry of Cements: Academic Press, 1964.)

- The ten distinct symmetry elements control the external symmetry of an object. For this reason, they are also called the **macroscopic symmetry elements**.
- These symmetry elements can combine in different **classes**. In fact, only 32 classes can be made. Each class also satisfies the properties of a finite mathematical group.

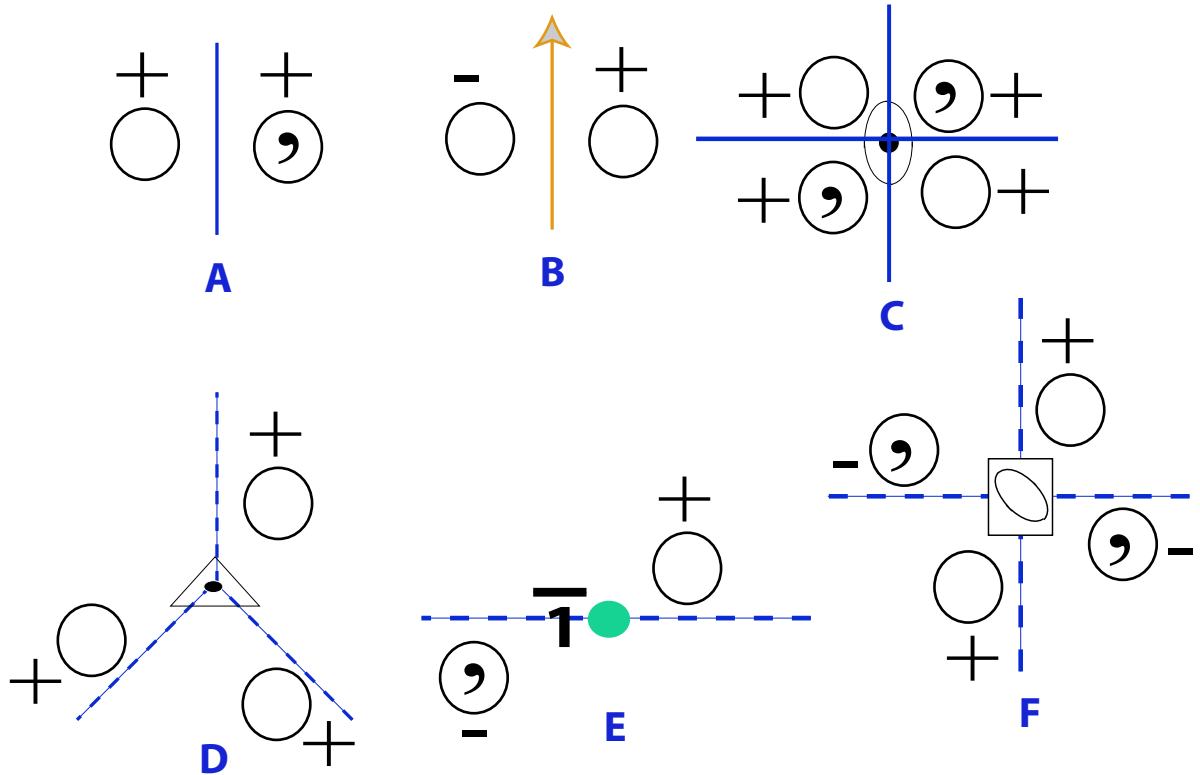


FIG. 20: Alternative notation for Figure 19: (a) \mathbf{m} ; (b) $\mathbf{2}$ axis of rotation; (c) two mutually perpendicular mirror planes \mathbf{m} and a $\mathbf{2}$ lying along the intersection between these planes; (d) $\mathbf{3}$; (e) $\bar{\mathbf{1}}$; (f) $\bar{\mathbf{1}}$.

These classes are called **point groups**. (Details in Dr. Falak Sher’s lecture!) These classes are called “point” groups because the symmetry elements necessarily intersect at a point — the geometrical centre of the object. Note that points as well as patterns can be classified into these point groups.

Two simple examples of point groups are presented in Figure 21. Consider (A). There are three symmetry elements, two mutually perpendicular mirror planes and a $\mathbf{2}$ axis located along the intersection of the planes. The group must contain *all* three elements, whenever two of them exist, they generate the third out of their combined action. (It is a property of a mathematical group that if g_1 and g_2 belong to the group \mathcal{G} then their composition $g_1 \cdot g_2$ must also be a member of \mathcal{G} .) So the symmetry elements in this group are $\mathbf{2mm}$, but as a short-hand, it suffices to mention just two, \mathbf{mm} , and this becomes a label for the point

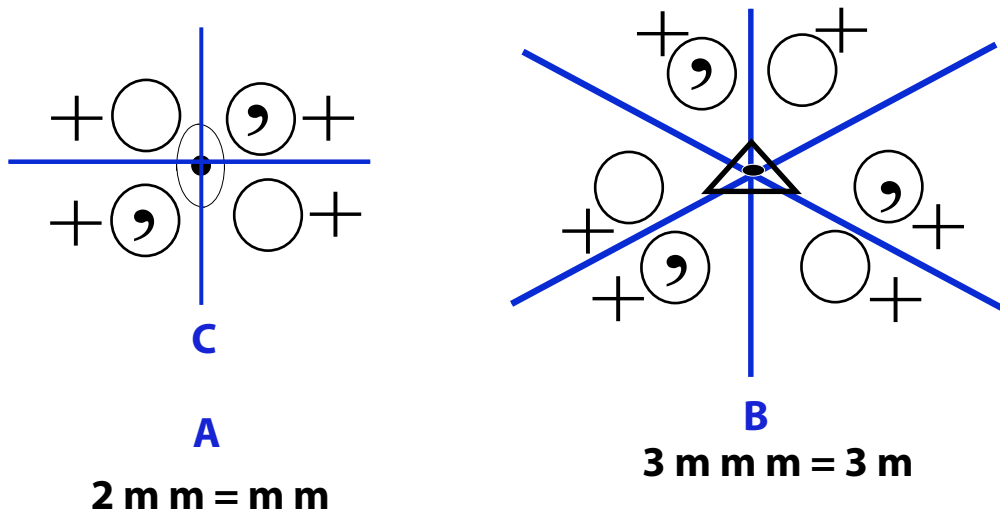


FIG. 21: Simple examples of two point groups.

group.

VIII. THREE DIMENSIONAL PATTERNS

For three dimensional patterns, two additional symmetry elements exist. These are non point symmetry elements and are based on the translation operation. These elements do not influence the macroscopic appearance of the crystal, rather they help define the **microscopic** symmetry. They are:

1. glide plane
2. screw axis.

IX. GLIDE PLANE

A **glide plane** represents a translation operation followed by a reflection in a mirror plane. Glide planes are symbolized as:

- a**: glide parallel to the x direction and a translation of $a/2$
- b**: glide parallel to the y direction and a translation of $b/2$
- c**: glide parallel to the z direction and a translation of $c/2$

- n**: glide along the face diagonal and a translation of 1/2 of the face diagonal
- d**: glide along the body diagonal and a translation of 1/4 of the body diagonal

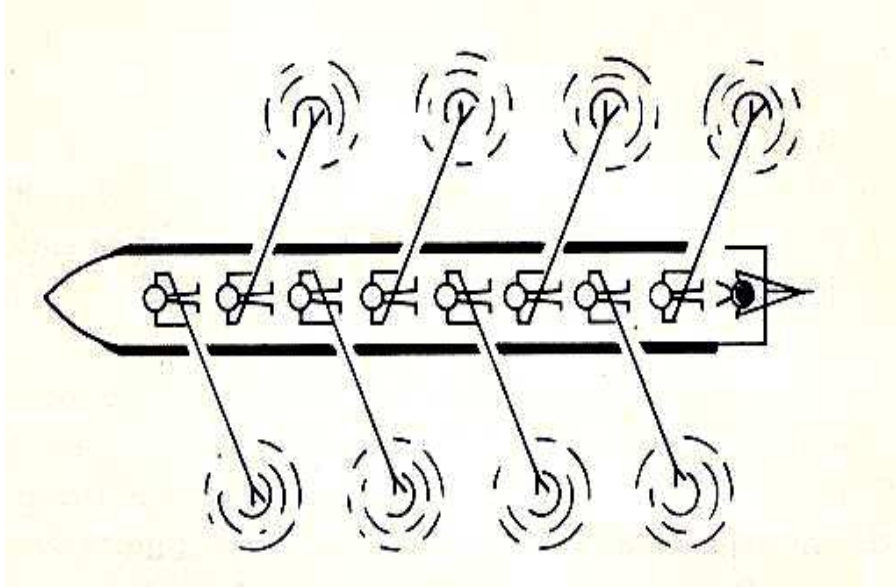


FIG. 22: A group of rowers exemplifying a glide operation.

- Note the possibility of defining a primitive versus a centred cell in Figure 23. We choose the centred cell because of (a) its simplicity, but more importantly, (b) because it preserves the symmetry of the unit cell that is characteristic of this structure (Refer to Dr. Siddiqi's talk!).

X. SCREW AXIS

The **screw axis** represents a translation followed by rotation. A screw axis is represented as N_n where N is the order of rotation and the translation distance is n/N . For example 4_1 represents a **4** rotation followed by a translation of 1/4 parallel to the axis of rotation.

Note that in totality, we have the following 26 symmetry elements in a three dimensional pattern (structure):

Axes of rotation: **1, 2, 3, 4, 6**

Mirror plane: **m**

Point of inversion: $\bar{1}$

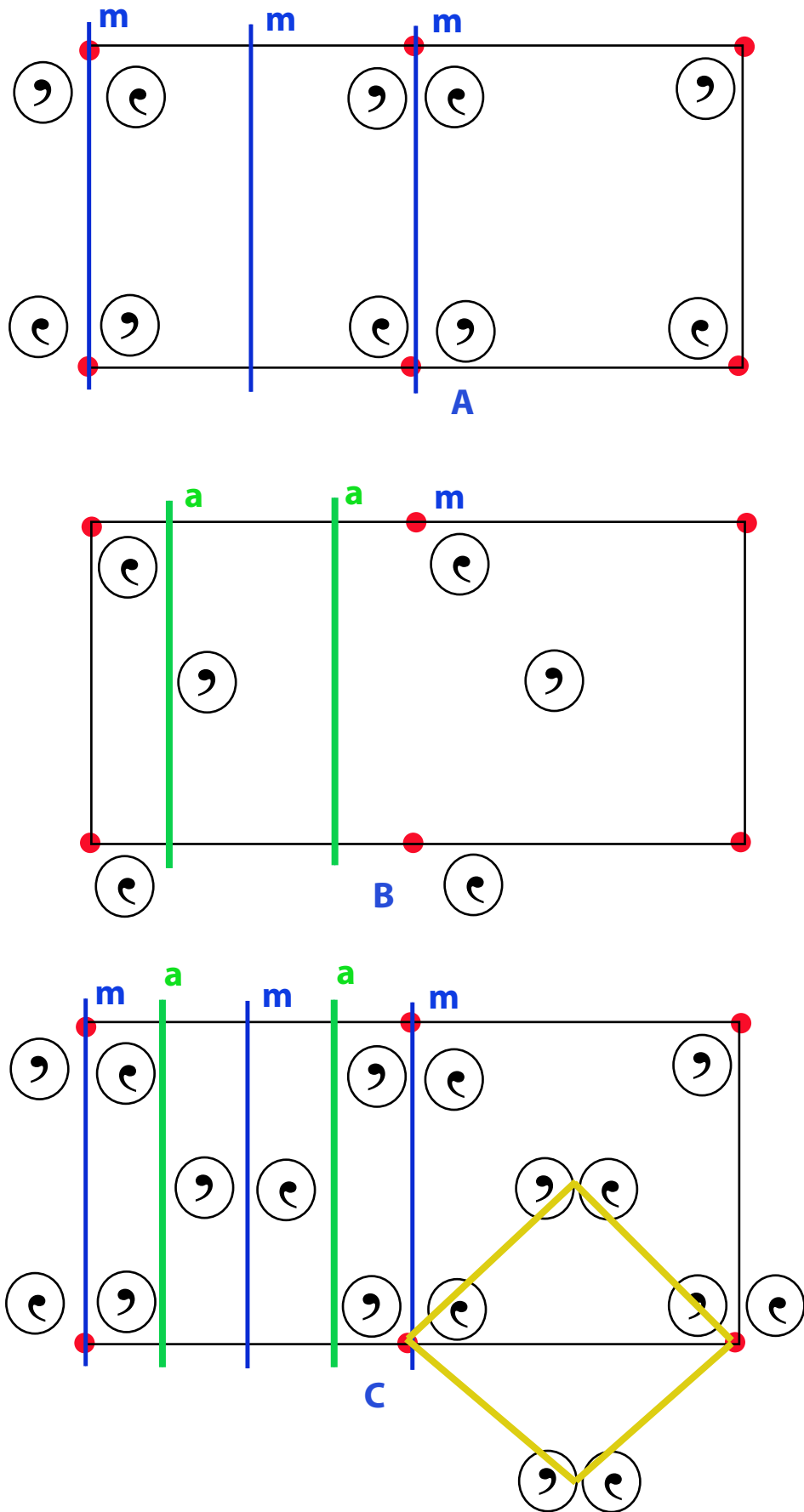


FIG. 23: The combined action of mirror and glide planes.

Rotary inversion axes: $\bar{3}$, $\bar{4}$, $\bar{6}$

Glide planes: **a**, **b**, **c**, **d**, **n**

Screw axes: 2_1 , 3_1 , 3_2 , 4_1 , 4_2 , 4_3 , 6_1 , 6_2 , 6_3 , 6_4 , 6_5 .

These symmetry elements occur in distinct combinations, but the presence of the screw and glide operations extend the number of these groups to 230. These groups are called **space groups** and define the internal symmetry of any structure or pattern. (Dr. Falak Sher's talk!)

XI. EXERCISES

1. Can a two-dimensional polygon have both a three and a four-fold symmetry axis? Can you draw such a structure?
2. Can you identify all two-fold rotation axes in Figure 7?
3. What is the relationship between **6** and 6^5 operations? What is the relationship between **6** and **3**?
4. Can we fill a flat space with arrays of pentagons? If not, what do we learn about the existence or non-existence of the **5** symmetry axis in space-filling sets of points?
5. Identify all axes of rotation in a square arrangement of points.
6. The hexagonal lattice of points in two dimensions has six mirror planes. Identify these planes and mark their geometrical coordinates. Note that you may have to draw many points of the lattice to show the planes.
7. Using a diagram similar to Figure 17, convince yourself that $\bar{2} = \mathbf{m}$. Also draw the mirror plane **m**. How is this plane geometrically arranged with respect to the **2** axis?
8. Convince yourself of the notation used in Figure 20.
9. Referring to Figure 21(B), show that it is possible to generate **3mmm** from just **3** and *m*.

10. What are the symmetry elements in your your hand, your face? Can a pair of your hands belong to a $\bar{1}$ point group?