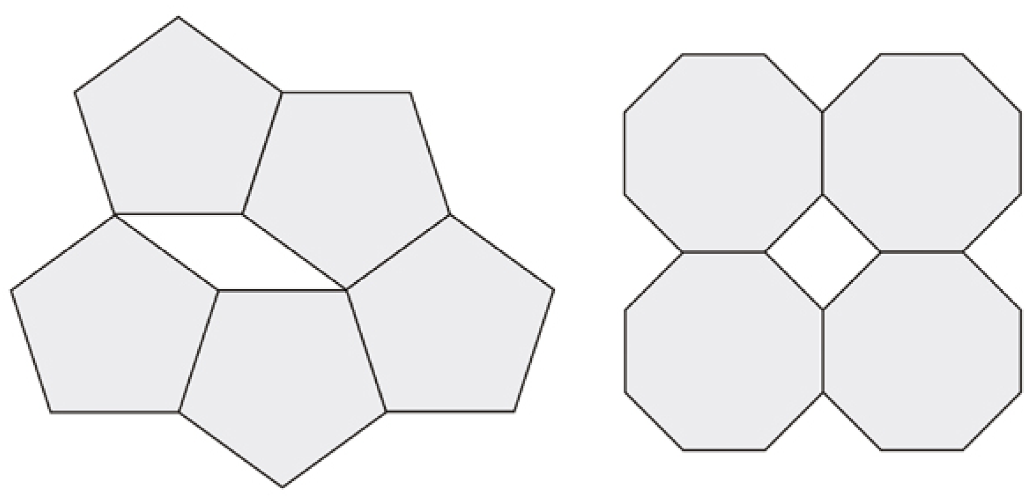
Crystallographic Restriction Theorem

Liam Rooney, Matt Keating and Aisling McSharry

Groups Poster Project

Introduction

The crystallographic restriction theorem in its basic form was based on the observation that the rotational symmetries of a crystal are usually limited to 2-fold, 3-fold, 4-fold, and 6-fold. Although objects themselves may appear to have 5-fold, 7-fold, 8-fold, or higher-fold rotation axes, these are not possible in crystals. Crystals can only show 2-fold, 3-fold, 4-fold or 6-fold rotation axes. The reason is that the external shape of a crystal is based on a geometric arrangement of atoms (vertices). In fact, if we try to combine objects with 5-fold and 8-fold apparent symmetry, we cannot combine them in such a way that they completely fill space, as illustrated below:



Explanation

A shape is said to have rotational symmetry if it can be mapped onto itself through rotation about a central point by some angle less than 2π. If the rotation angle is π/n, then the shape is said to have n-fold symmetry. All regular polygons have rotational symmetry (when working in the plane). In fact, an n-sided regular polygon has n-fold symmetry. For example, a regular pentagon has 5-fold rotational symmetry and can be mapped upon itself through rotation by an angle of 2π/n. However, when working in three-dimensional space as with crystals, there are a limited number of ways in which to rotate an object about a point mapping each of its vertices onto another. These rotations can come in the form of:

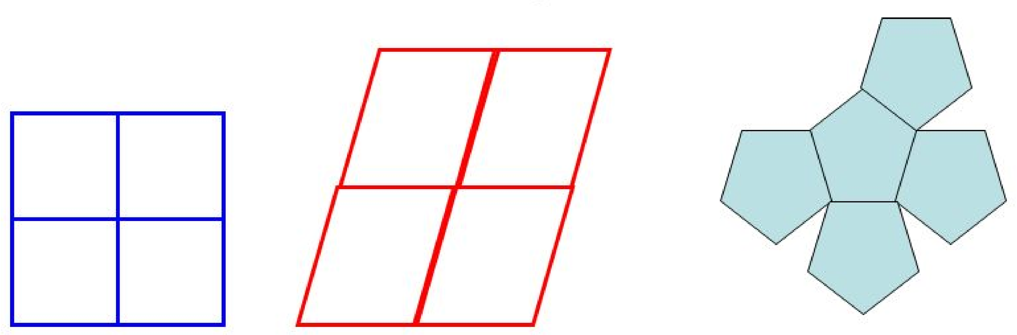
- 1 –fold rotation (rotation through 360 degrees)
- 2 - fold rotation (rotation through 180 degrees)
- 3 - fold rotation (rotation through 120 degrees)
- 4- fold rotation (rotation through 90 degrees)
- 6- fold rotation (rotation through 60 degrees)

In the case of crystals the only above rotation axes can occur!!

Lattice symmetries

Rotational symmetries of building blocks (polygons) must be consistent with translational symmetry

crystallographic restriction theorem: lattice can have only 2, 3, 4, and 6-fold rotational symmetries



Lattice Space

To fully understand this concept, we need to know what the term lattice means. In two dimensions, a lattice is a regular distribution of points across the plane. In three-dimensional space a lattice is a regular repeated arrangement of points. In simple terms, each point must be indistinguishable and have identical surroundings. The points must be distributed in such a fashion that they can successfully be mapped onto each other by rotating about a point. A unit cell is an object that will fill all space when translated by the lattice translation vectors. A basis is then an object assigned to each lattice point, for example an atom or molecule. In the figure below which is set in the Euclidean plane, we can see two example of unit cells and two invalid examples. In the top two diagrams, we see there is a square and hexagon shaded in. These are considered unit cells on these lattice spaces as for the top right example (4-fold (2-fold)), you can attach more squares to each side of the square infinitely along the lattice space. During this process all space will be filled (shaded). This will also work for the hexagonal (6-fold (3-fold)) shape in the top left diagram. However, when you try this with a pentagon or octagon, you will find you are unable to fill all space. Translating this into three dimensional space, in order to form a crystal, the arrangement of vertices must allow us to completely fill space, leaving behind no gaps, by repeating the arrangement.

Polygons.png Polygons.png

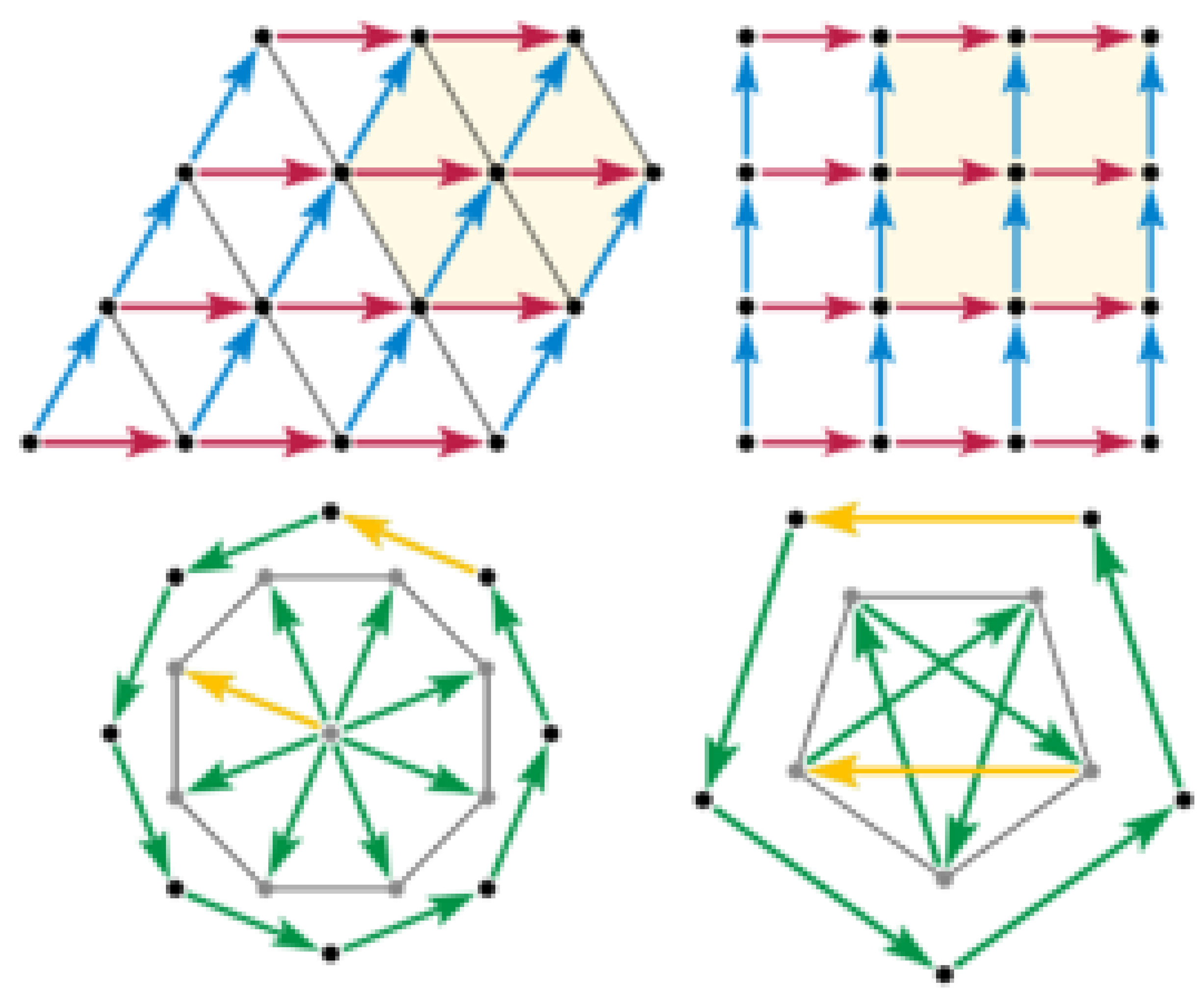


Fig. 3: Compatible: 6-fold (3-fold), 4-fold (2-fold)
Incompatible: 8-fold, 5-fold

Consider an 8-fold rotation (as in the bottom left of Fig. 3), and the displacement vectors between adjacent points of the polygon. If a displacement exists between any two lattice points, then that same displacement is repeated everywhere in the lattice. So collect all the edge displacements to begin at a single lattice point. The edge vectors become radial vectors, and their 8-fold symmetry implies a regular octagon of lattice points around the collection point. But this is impossible, because the new octagon is about 80$\%$ as large as the original. The significance of the shrinking is that it is unlimited. The same construction can be repeated with the new octagon, and again and again until the distance between lattice points is as small as we like; thus no discrete lattice can have 8-fold symmetry. The same argument applies to any k-fold rotation, for k greater than 6.

Comparison

In Fig. 4 we see a regular dodecahedron which is an object comprised of 12 pentagonal faces, 3 meeting at each vertex. Although this object has 5-fold rotational axes, we cannot infinitely arrange regular dodecahedrons together without leaving pockets of space in between.

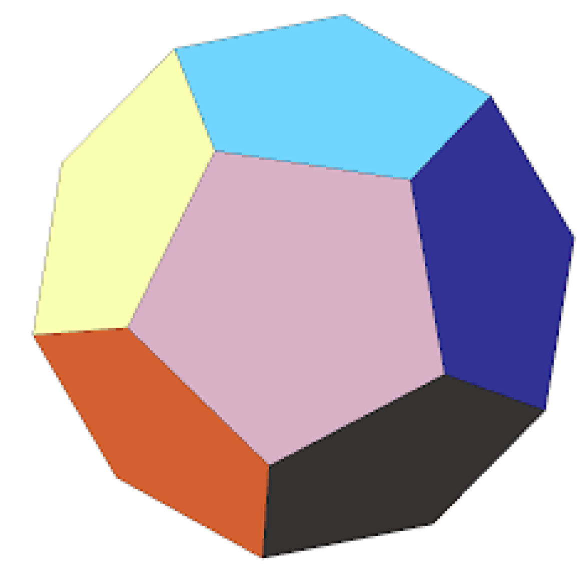


Fig. 4: Regular Dodecahedron

Importance of Crystallography

Computers and smart phones have become essential in our daily lives. Crystallography determines the functionality of many of their components. A few examples are screen backlights and batteries. Almost all pharmaceuticals are molecularly crystallographic substances. Understanding crystallography is important for the production of safe pharmaceuticals. Crytallography also helps in optimising fertilizers for maximising crop yield. Lastly, it can help in designing ideal membranes for desalination plants to treat drinking water.

Examples of Crystals

Here are some example of crystals. It is possible to arrange each one infinitely with itself so as to completely fill space, leaving no pockets of space in between.