

A historical outline of the interaction between two disciplines

Crystals and mathematics

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People have always been fascinated by crystals and surprised and delighted by their regular geometry, their special symmetry, and their mysterious color refraction. Many natural minerals are crystals. They are parts of stones, but due to the irregular grain boundaries their crystalline nature is often hidden. In cavities, however, minerals can freely grow into recognizable crystals. The crystal shape is also obvious in snowflakes, the growth of which is not limited. Crystals are often found on display in museums or private collections, or as polished gems. Less known is that the largest part (about 98%) of the solid ground is crystalline. This means that crystals are a stable state of the condensed matter.

The term “crystal“ is derived from the Greek “krystallos“ (meaning “ice“) and was used for the first time in connection with rock crystals. People probably thought that crystals formed in extreme cold, which is not true. Most crystalline minerals form at high temperatures and under extreme pressure during the cooling process of magma from the interior of the earth.

Crystals are solids whose components (atoms, ions, molecules) constitute a regular crystal structure – mathematically described as a lattice with a basis. In modern

crystallography, a crystal is defined and its geometrical structure described by means of diffraction patterns obtained through exposure to x-rays or other sources of radiation.

This article will briefly outline the history of crystallography and the mathematical-geometrical description of crystal structures.

1. The beginnings of research on crystals

The first known systematic treatise dedicated to minerals is that of natural scientist Theophrastus of Eresos (371-287 B.C.), a student of Plato and Aristotle. It is contained in his publication “On Stones“ (see [1]).

In the encyclopedia “Naturalis Historia“ by Pliny the Elder (23-79 AD), a comprehensive scientific work consisting of 37 volumes, there is also a treatise on rare stones and minerals (cf. [2]), which was the basis of mineralogical knowledge until the Middle Ages. During the Middle Ages, crystals and stones were also thought to have healing properties – a belief still shared by some New Ager today.

As neither the chemical composition, nor the optical characteristics of crystals could be determined before the beginning of the 19th century, these old studies are only of historical interest to scientists.

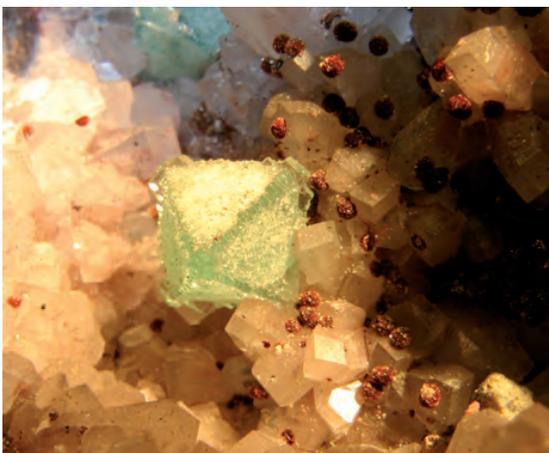


Fig. 1: Fluorite octahedron on calcite

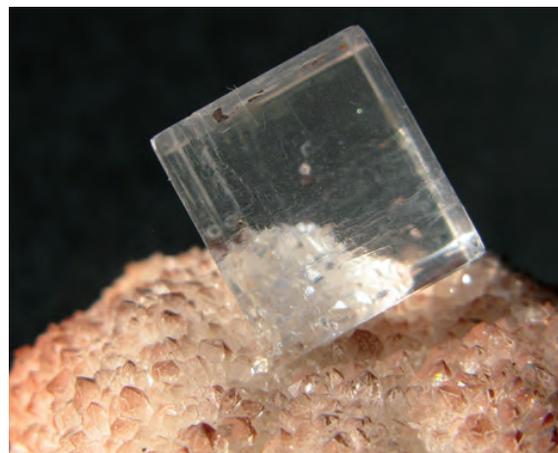


Fig. 2: Fluorite crystal – Grube Clara

2. Crystal shapes and polyhedra

The regular shapes of crystals immediately remind mathematicians of regular, convex polyhedra, especially the Platonic solids with congruent faces and the same number of faces meeting at each vertex. There are exactly five Platonic solids (tetrahedron, hexahedron or cube, octahedron, dodecahedron, and icosahedron, see Fig. 3); their faces are equilateral triangles, squares, or pentagons. The classification of regular polyhedra (claiming that there are only these five regular polyhedra) by the Greek mathematicians, in particular Plato and Euclid, may be considered the first strict approach to classification in mathematics.

In fact, there are minerals whose crystals are almost proper, regular tetrahedra, hexahedra (see Fig. 2), or octahedra (see Fig. 1). Dodecahedra and icosahedra, however, can never be crystal shapes (for reasons of translational symmetry, see chapters 8 and 10), but they can be found in living organisms, e.g., viruses.

Non-regular dodecahedra and icosahedra, on the other hand, exist as crystals. Pyrite, for example, can have the shape of a cubic pentagondodecahedron which by its appearance can be easily mistaken for a regular dodecahedron. Each of its faces is a pentagon, but with four shorter and one longer side. It has cubic symmetry.

An important role beside the Platonic solids play the *Archimedean solids*. They consist of various types of regular polygons and are symmetric in such a way that every vertex can be taken to any other vertex by rotation or reflection. Archimedean solids can be constructed as truncated Platonic solids, i.e. by cutting away a corner of the Platonic solid so that a regular face is formed (e.g., a regular triangle in place of the corner of a cube).

Even more important for crystallography are the *Catalan solids* or *Archimedean duals* that consist of only one type of face. They have, however, different types of vertices, because duality means that the face of a Catalan solid is formed at the vertex of an Archimedean solid. For example, the rhombic dodecahedron is a Catalan solid which is dual to the cuboctahedron. The rhombic dodecahedron is a typical crystal form and is present in garnets. Other frequent crystal structures are prisms, which consist of two parallel, congruent, regular polygons and the lateral surfaces that connect them.

3. Crystals and Greek mathematics

The Greek mathematicians certainly knew the crystal shapes and their symmetries. However, their studies on regular polyhedra were neither motivated by, nor related to crystals. At least, it seems that there is not any proof for this ([3], p. 342). On the contrary – platonic philosophers considered the total symmetry of the regular polyhedra an expression of perfect, everlasting beauty, independent of short-lived, earthly manifestations (cf. [3], p. 340).

In this, Greek philosophy shows some similarities to parts of modern, in particular to pure, mathematics, the research of which is directed towards mathematics-inherent structures and does not serve any particular purpose. It is only committed to its own axioms and logical deductions, without any need or regard for practicability or experience. Still we note that mathematics, also pure mathematics, is – today more than ever – indispensable for understanding scientific processes, and that it has become the driving force of industrial and economic innovation.



Fig. 3: Platonic solids

However, there is most certainly a connection between the crystal shape, which is considered beautiful by man, and the fact that Greek mathematicians were dealing with regular polyhedra. After all, they could have examined other things instead. But according to Plato, the search for everlasting perfection, for the Good, is related to beauty and regularity. „*The good is always beautiful, and the beautiful never lacks proportion*“. (Platon, *Timaios*, 87c, 4-5)

4. Kepler and the snowflake

It seems that the connection between examinations of the crystal shapes and the ancient studies on mathematical structures of polyhedra was only made in the Renaissance ([3], p. 342). Johannes Kepler (1571-1630) used the harmony of the Platonic solids as a means to describe the harmony of the celestial spheres. However, his attempt to prove that the distances of the planets can be defined by a model of nested, regular polyhedra encased by spheres failed. He therefore abandoned this model and developed for the first time the model of elliptical planetary orbits around the sun that is still in use today.

Kepler's interest for crystals is also reflected in his studies on the symmetry of snowflakes ([4], see Fig. 4). He discovered that the unique geometry and six-fold symmetry of the snowflake is caused by natural forces. The exact physical reason behind this, the fact that the components of matter – atoms and molecules – are always aligned in such a way that they are in a state of minimal energy, was still unknown at his times. This results in beautiful symmetrical structures in snowflakes and other crystals.

Kepler's attempt to describe the hexagonal structure of snowflakes as a structure of miniscule particles with minimal distance between them, caused him to study the maximum density of circle and sphere arrangements, published in the same work. He assumed that the most closely packed arrangement of spheres is the cubic close packing (as seen, for example, with oranges stacked in form of a pyramid at a market stall). Only some 400 years later, in 2003, this *Kepler conjecture* was proven by the American mathematician Thomas Hales, partly by complex computer calculations.

5. The beginnings of crystallography

As early as around 1669, Nicolaus Steno (1638-1686) discovered the law of constancy of the interfacial angle when examining quartz. This means that the angles between two identical faces of a crystal are always the same, independent of its size, shape, and the conditions under which it was formed. Steno assumed this law of



Fig. 4: Snowflake

constancy of the interfacial angle for all crystals, and his examinations marked the beginnings of crystallography, i.e. the science dealing with crystals.

The general validity of the law of constancy of the interfacial angle was empirically proven in later years, around 1783, by Jean Baptist Romé de L'Isle through systematic examination and detailed description of about 500 different crystals.

One step further goes the "Traité de minéralogie etc.", by René-Just Haüy, published in Paris in 1801. Based on the observation of fragments of a piece of calcite shattered on the ground, Haüy described the crystals as consisting of smaller units (which he called "integrating molecules") that always have the same structure as the crystal itself. That the external shape of crystals can be derived from a periodical alignment of elementary components is a fundamental finding for crystallography. For example, it makes it easy to explain the law of constancy of the interfacial angle. Therefore, Haüy is nowadays also referred to as the "Father of Crystallography".

6. Modern crystallography

The proof that crystals really consist of regularly aligned units, however, was only furnished by Max von Laue (1879-1960) and his colleagues in 1912. They discovered the *diffraction of x-rays by crystals* and the crystal-dependent, regular pattern of points resulting from it. This discovery and its theoretical substantiation won von Laue the Nobel Prize in Physics in 1914.

Already in 1913, William Henry and his son William Lawrence Bragg had shown that x-rays could even be used to exactly define the position of atoms within a crystal, thus identifying its three-dimensional structure. They both were awarded the Nobel Prize in Physics for this discovery in 1915.

While up to then geometrical optics had been the most popular analytical method in crystallography, *x-ray crystallography* or other sources of radiation are almost exclusively used in modern crystallography to determine diffraction patterns. So, today some hundreds of thousands of such structures, ranging from small inorganic and organic compounds to large biomolecules, have been stored in databases, with their number steadily growing.

The methods of x-ray crystallography were continuously refined, thus making it possible to determine also the structure of important biological molecules (e.g. cholesterol, penicillin, insulin) between 1920 and 1970. This had a great impact on healthcare. The most important discovery in this connection certainly was that of the structure of the DNA by James Watson and Francis Crick by analyzing diffraction experiments, for which they were awarded the Nobel Prize in 1962 in Physiology or Medicine together with Maurice Wilkens.

In recent times, two discoveries are particularly noteworthy: Graphene as the first example of a new class of two-dimensional crystalline materials with unique electronic and mechanical properties (Nobel Prize in Physics awarded to Andre Geim and Konstantin Novoselov in 2010) and the *quasicrystals* (Nobel Prize in Chemistry awarded to Dan Shechtman in 2011). Especially the discovery of the quasicrystals in 1982 was a total surprise for crystallography. These were materials whose diffraction patterns showed a clear pattern of points just like those of ordinary periodic crystals (unlike amorphous substances, which produce blurred diffraction patterns), but with five-fold symmetry – although this should not be possible, due to the periodicity of a crystal (see sections 9 and 10).

It is worth mentioning that nowadays, besides the mathematical crystallography (i.e., the classification of crystals by symmetry), which will be discussed in detail below, there are many more important aspects of crystallography. These include the mineralogical and biological crystallography, but also crystal physics, in particular diffraction physics and crystal growth, with manifold fields of applications, e.g. medicine and materials research.

7. Crystal lattices

The discovery made by Steno, Romé und Häüy, that crystals consist of periodically repeating basic units having the same shape as the crystal itself, leads us to the concept of the crystal lattice. However, for this purpose we are looking at *ideal crystals*. These are infinite and have translational symmetry, i.e., their basic units, or, from today's point of view, the atom positions, are merged into one another by a translational movement within space, so

that the whole crystal is formed by the translations of one basic unit.

Of course, ideal crystals do not exist. A real crystal is always finite and has defects, i.e. deviations from regularity. Still it suffices for many purposes, especially to classify crystals, to look at ideal crystals.

Each translation within the three-dimensional Euclidean space is defined by a translation vector that can be described as a combination of the multiples of three (once chosen) independent basic vectors. The total of all translations that transform the basic unit of a crystal into other basic units, and transform the (ideal) crystal into itself, have three linearly independent basic vectors so that each of these translations can be described as a combination of integer multiples of the basic vectors. All translation vectors (or their end points) that transform the crystal into itself form a three-dimensional lattice within the space, the *crystal lattice*.

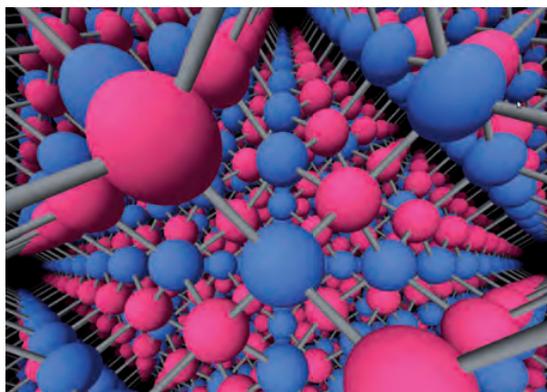


Fig. 5: Lattice of a diamond

The points of this lattice do not represent atoms but only depict the periodicity of the crystal structure. Of course, the crystal lattice depends on the outward shape of the crystal or the basic unit, but since it translates the basic units within the crystal (within the range of atom radii) it is not possible to deduce the crystal lattice from the shape of the crystal. The parallelepiped defined by the three basic vectors is called *unit cell* or *primitive cell*.

The choice of the basis of a lattice is not unambiguous. Therefore one tries to find a basis where the unit cell reflects the shape of the crystal as exactly as possible. Since this is not always possible, but, on the other hand, it is important to be able to easily view the crystal's symmetry, one waives the requirement that the vectors forming the unit cell be a lattice basis and uses three vectors forming larger (non-primitive) unit cells instead. In this case, the translations of the crystal lattice can be

described as a combination of rational multiples of these vectors. These vectors are also called a non-primitive basis of the lattice.

Around the year 1843, Auguste Bravais (1811-1863) classified the different possible crystal lattices by indicating both primitive and non-primitive unit cells. They are named *Bravais lattices* after him. In three dimensions there are exactly 14 Bravais lattices, i.e. exactly 14 translation groups of all possible ideal crystals.

8. Crystallographic groups

Crystals are classified according to their symmetric properties, i.e., we examine the isometries (distance- and angle-preserving mapping) of the three-dimensional Euclidian space that transform the crystal or crystal lattice (which is actually the same) into itself.

The inverse operation of such an isometry and subsequent random operations again result in isometries of the crystal lattice; mathematicians call this a group. The isometry group of a crystal lattice is called *crystallographic group* or (*crystallographic space group*).

Of course, the translations of the lattice belong to the crystallographic group. They describe the “long-range order” of the crystal. However, there are also isometries of the crystal lattice with (at least) one fixed point, e.g. rotations around an axis, point reflections or reflection in a plane, or combinations thereof. This group describes the symmetry of the basic unit and thus of the crystal itself. It is called the *crystal's point group*. There are exactly 32 of such crystallographic point groups, also called *crystal classes*. Being abstract groups, these groups are of mathematical interest, but for our purposes it is important to note that they are applied to the isometry of the crystals and serve to define the different crystal classes.

Each element of a crystal's point group operates on a crystal with a finite order, i.e. after a finite number of subsequent operations the crystal is back in its initial position (because there is only a finite number of positions of a vertex, an edge or a face of a crystal). For example, the reflection in a plane has order 2, the rotation of a cube around an axis through opposite plane centers (or edge centers or corners) has order four (or two or three).

So there are 32 crystallographic point groups (crystal classes) besides the 14 translation groups (crystal lattices). There are 230 different crystallographic groups in total, i.e., isometry groups of crystal lattices (in three dimensions). They were identified in 1891 by Arthur Moritz Schoenflies and Jewgraf Stepanowitsch Fjodorow independently.

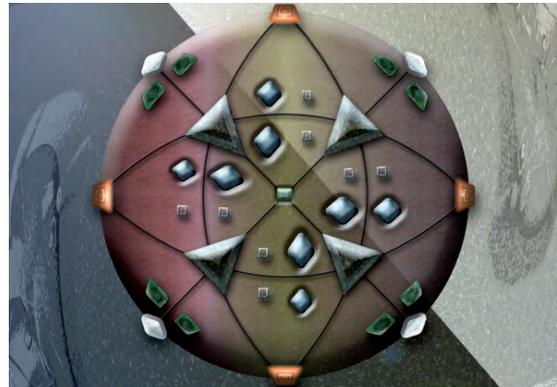


Fig. 6: Example of a point group

Different point groups are combined in one *crystal system*. Today, we differentiate between seven crystal systems: *triclinic*, *monoclinic*, *orthorhombic*, *tetragonal*, *trigonal*, *hexagonal*, and *cubic*. The crystal systems were introduced by Christian Samuel Weiss (1780-1856) when he translated the textbooks by Häüys. They were based on the analysis of the alignment of particularly striking directions of the crystals, the axes “around which everything was equally distributed”. Thus, the crystal systems constitute a symmetry-related classification of crystals by means of crystallographic axes of coordinates. Weiss used the axes to clearly denote for the first time the position of all crystal faces or planes within the lattice by the ratios between their intercepts on the axes, the *Weiss indices*. Nowadays we mainly use the lowest integral common multiples of the reciprocal intercepts, the *Miller indices*.

9. Mathematical groups

We can have a look at the isometries of space that transform any body into itself. These are called the isometry group or *symmetry group* of the body. Most bodies in nature are irregular or asymmetrical. In this case, there is no isometry besides the identity, which transforms the body into itself. A group that only consists of the identity is called *trivial*. Bodies with a trivial isometry group are thus asymmetrical, and bodies with a non-trivial isometry group are called symmetrical. The larger the isometry group of a body, the more symmetrical its appearance.

For example, the sphere as a symbol of a symmetrical body is transformed into itself through any isometry, and its symmetry group contains an uncountably infinite number of elements, i.e. as many as there are real numbers (e.g., every rotation around any angle and any axis and every reflection in any plane through the central point). The isometry group of a crystal is not trivial, but always countable, with the point group itself only containing a

finite number of elements. In any case, we have to note that the colloquial terms “symmetric” and “regular” are mathematically described by the concept of the group.

A (abstract) mathematical *group* consists of a set and an operation which assigns, to any two elements of the set, one element of the set. Several subsequently performed operations can be arbitrarily grouped into operations of two (put into brackets). In addition, each operation has an inverse operation, so that performing subsequent operations results in the identity, which is always one element of each group.

From a historical point of view, the abstract group concept defined in this manner (something taught today right at the beginning of mathematical studies) is still quite young and an abstraction of the concept of the symmetry group which has been in existence much longer. This is a good example of how mathematical concepts are derived from real experience (symmetrical, regular) by abstraction, and how these mathematical concepts are then exclusively defined by abstract axioms, independent of the original observation.

10. The impossibility of the icosahedron

Why can crystals not take the shape of regular icosahedra or dodecahedra? We will learn that this is due to the translational symmetry, which strongly limits the point group of the crystal.

Five regular triangles meet at each vertex of the icosahedron. If we look at a rotation around an axis through two opposite vertices, which transforms the icosahedron into itself and each triangle into the neighboring triangle, this rotation has order 5. The same applies to the dodecahedron if we are looking at the rotation axis through the centers of two opposite faces.

Now we are going to show that a crystal cannot have such a rotation of order 5. Let us look at a crystal rotating around any given axis. This axis has a finite order n , and transforms a unit cell of the crystal into a translated one. The case $n=2$, i.e. a rotation of 180° , is of course possible and we can therefore assume in the following that n is larger than or equal to 3. Now we imagine a plane located perpendicularly to the rotation axis and intersecting a vertex of the unit cell which is not located on the rotation axis. With a full rotation, the vertex describes a regular polygon with n edges within the plane. All vertices of this polygon are vertices of unit cells, i.e., they are transformed into each other by translation of the crystal grid. Each translation shifts the rotation axis so that the rotation around the shifted axis generates an adjacent

n -edged polygon within the same plane. This process can be repeated for an infinite number of times until the whole plane is completely (without any gaps or overlapping) tiled with regular, n -edged polygons.

By examining the angles we will now show that this is only possible if $n=3, 4$ or 6 . Let us assume that r regular polygons with n edges meet at a point within the plane, and that the vicinity of this point is completely tiled with these polygons.

The angle between two adjacent edges of a polygon with n edges is $180^\circ - 360^\circ/n$, and $r(180^\circ - 360^\circ/n) = 360^\circ$ applies accordingly. If we divide by 360° , then $r/2 - r/n = 1$. Multiplying by $2n$ and rearranging the equation gives $n(r-2) = 2r$. If we set $r-2 = s$, then $n = 2 + 4/s$. As n is a positive integer, s can only take the values of $1, 2$ or 4 , which means that n can only be $6, 4$ or 3 .

Therefore, the point group of a crystal can only contain rotations of orders $2, 3, 4$ or 6 . Thus, crystals cannot have the shape of an icosahedron or of a dodecahedron.

11. Quasicrystals

We have learned that a crystal's point group can only contain rotations of orders $2, 3, 4$ or 6 . The diffraction of x-rays in crystals shows a sharp pattern of points that allows to determine the crystal's point group. For a long time, scientist thought that purely point-shaped diffraction reflexes were only present in crystals and used this assumption to define a crystal. Accordingly, the translational symmetry or the crystal lattice were considered an equivalent for the existence of point-shaped diffraction patterns.

Therefore it came as a shock to crystallography when, in 1982, Dan Shechtman discovered clear, point-shaped diffraction patterns in materials having the same rotational symmetry as the icosahedron, i.e. of order 5. Since these new materials certainly could not be considered crystals in a traditional sense, they were named *quasicrystals*.

The discovery of quasicrystals led to a new crystallographic definition of (traditional) crystals: now, translational symmetry was required as an independent property. Quasicrystals have clear diffraction points, but no periodic translational-symmetric structure. A review article about quasicrystals published on the occasion of the awarding of the Nobel Prize to Shechtman is provided in [8].

If a quasicrystal is cut in an appropriate manner, the slice plane, e.g. in Shechtman's aluminum-manganese alloy, shows a local five-fold rotational symmetry and a tiling of the plane that is not periodic, but “quasi-periodic”. This

quasi-periodic tiling of the plane had already been discovered in the 1970s by the British mathematician Roger Penrose and is named *Penrose tiling* after him.

The Penrose tiling has many interesting properties. For example, any patch from the tiling (independent of its size) can occur for an infinite number of times, but cannot periodically repeat itself. An easily understandable description of many mathematically interesting characteristics of quasicrystals and Penrose tilings is provided by the mathematicians Baake, Grimm, and Moody in [9].

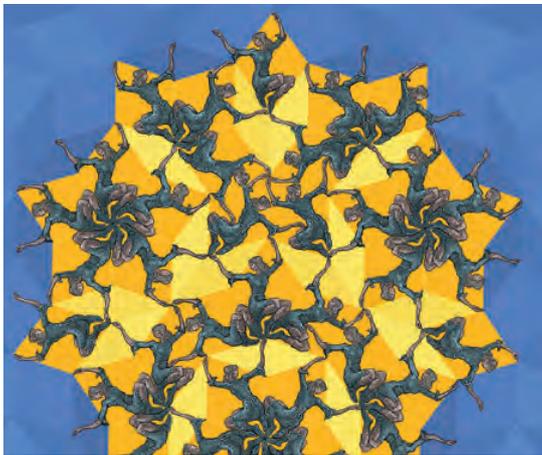


Fig. 7: Quasi-periodic rhombic penrose tiling

Quasicrystals are becoming increasingly important for technical applications because they can give special properties to materials when used as additives.

The discovery of quasicrystals has gained the Penrose tiling a lot of attention. One found out that similar quasi-periodic patterns had already been existing in Islamic ornaments of mosques and palaces from the Middle Ages. How these beautiful but complicated patterns were constructed, was only discovered a short time ago (cf. [10]).



Fig. 8: Jigsaw puzzle of a penrose tiling

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The following references are only a part of the sources I used. I think they contain particularly useful further information on the topic.

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Images:

Fig. 1: Fluoride octahectron on calcite, Photo: Werner Günter, Oberwolfach

Fig. 2: Fluorite crystal – Grube Clara, Photo: Werner Günter, Oberwolfach

Fig. 3: Platonic solids, Photo: Zumthie at de.wikipedia, source: http://commons.wikimedia.org/wiki/File:Platonische_Koerper_im_Bagno.jpg

Fig. 4: Snowflake, Photo: Jochen Burger, source: www.natur-portrait.de/foto-26022-frau-holles-erster-gruss.html

Fig. 5: Lattice of a diamond; screenshot from the Crystal Flight software, source: <http://imaginary.org/program/crystal-flight>

Fig. 6: Example of a point group; Author: Jean Constant; source: <http://imaginary.org/gallery/jean-constant-crystallographic-points-groups>

Fig. 7: Quasi-periodic rhombic penrose tiling; Author: Uli Gaenshirt source: <http://imaginary.org/gallery/quasicrystalline-wickerwork>

Fig. 8: Jigsaw puzzle of a penrose tiling; Mineralien- und Mathematikmuseum Oberwolfach (MiMa) source: <http://mima.museum/mathematik-penrose.php>