



The experience of the *Voyage dans le cristal* travelling museum exhibition

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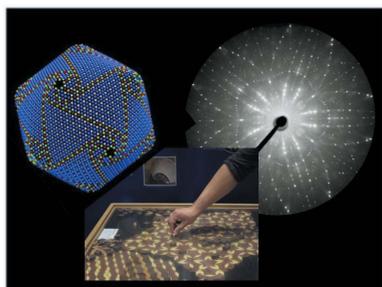
Crystallography is little known to the public, even though it underpins much of the research into matter in physics, chemistry, new materials and life sciences. On the one hand, crystallography is present in almost every field of scientific or technical activity and also in innovative applications. On the other hand, the origins of crystallography started with humanity's interrogation and interaction with crystals in prehistoric times, which has continued to the present day. These two 'views' can be used to focus public interest on crystallography and show children and students the importance of the scientific approach. As an example, this article describes the travelling exhibition *Journey into the crystal*, which presents to the general public the science and the beauty of matter in the crystalline state. This exhibition takes visitors on a journey of discovery about matter, but also on a journey through time to the beginnings of crystallography.

1. Introducing crystallography to a wider public

1.1. Issues that we have to face

Throughout the development of humanity, relations between human civilizations and science have had a rather nonlinear history. The Greek philosophers of the fourth and fifth centuries BC are known for their efforts to understand the world and matter, but these questions and the significance of science were much less preeminent in the Middle Ages.

In the middle of the 17th century, what is usually called the *siècle des lumières* began. This period, generally considered to extend roughly from 1650 to 1800, is characterized by an explosion of scientific knowledge. L'Accademia del Cimento was created in Florence in 1657, the Royal Society in London in 1660 and the Académie des Sciences in Paris in 1666. The first scientific journal, entitled *Philosophical Transactions of the Royal Society*, was first published in 1664. At that time, Immanuel Kant and many others proposed to address the understanding of all questions in all fields from the perspective of reason (Kant, 1784). This is the beginning of the modern age¹ of the triumph of science. Human progress is fundamentally linked to the rational understanding of the facts (Condorcet, 1794). Knowledge was disseminated in 'cabinets of curiosities' and literary salons (Fig. 1). The explosion of technological progress drove the social development that took place throughout the period that followed, starting from the end of the 18th century up to and including the greater part of the 20th century. According to Condorcet, people living at that time knew that this progress was strongly dependent on the global increase in scientific knowledge. However, by contrast, since the 1980s a clear indifference to science can be observed,



¹ The word 'modern' means here after the Middle Ages. Of course, the ancient Greek civilization and the Islamic societies of the beginning of the second millennium had previously developed very fundamental scientific knowledge.

particularly among young students. Science is associated with technological developments and sometimes appears to be the source of problems instead of the solution to them. In such a situation, it is both a difficult challenge and a duty to propose a scientific exhibition for the general public.

Initially, crystallography was the science of the drawing of crystals. Since the Stone Age, ‘angular stones’, one of the previous names for crystals, have prompted many questions and much astonishment. Since the description of the five platonic solids and right up to the current determination of the interatomic structure of sophisticated biological crystals, crystallography has been more generally defined as ‘the science of crystals’. It is a little strange to observe that some aspects of crystallography are very familiar to many people, while it is simultaneously considered to be a very specialized scientific domain. Indeed, everybody is attracted by the interplay between the light and a diamond or by the deep red colour of a ruby. Unfortunately, the establishment of accurate relationships between the symmetry of the atomic arrangement in diamond, as described in the appropriate space group and by the equations that correctly describe the propagation of the electromagnetic waves associated with light, appears to be less attractive. Unlike chemistry, for example, the science of crystals induces a positive *a priori* impression. Nevertheless, it suffers from its image of being quite a confined science that is influenced by a widely misunderstood part of applied mathematics.

When it comes to people with some scientific education, crystallography suffers from another drawback: it is usually considered to be an ‘old fashioned science’. An introduction to crystallography is usually provided during the first two years of undergraduate studies. Very often, it consists of a geometrical description of the hexagonal compact and cubic stacking. An extension to this may be the description of cubic, cubic centred and cubic face centred crystallographic cells. Instead

of presenting an internal explanation of the beauty of snowflakes² or the importance of biological macromolecules, the teacher illustrates the subject using the unexciting structure of iron. Too often, somewhere between physics and chemistry, the introduction to crystallography appears to be a very boring course of secondary importance.

Starting from this situation, our goal is to propose a rational approach which can promote the interests of science and, more specifically, of crystallography. Our challenge is not only related to students or people who are very involved in the development of science; we are also interested in the wider public. Our objective can be expressed by the following question: How can we promote an interest in crystallography in anyone, say, crossing the street, drinking a beer or going to the market?

1.2. Some answers that we can bring to the table

One of the major characteristics of crystallography is certainly that it is a largely interdisciplinary science. During the 19th century, science was divided into several parts that were classified relative to each other (Comte, 1830). Previously, one used to speak about *rex natura*, and in this sense crystallography is probably easier to describe as a science of nature. Crystallography is thus present, at least, in applied mathematics, physics, chemistry, earth science and biology. In the past crystallographers were often physicists or mathematicians; today the largest number of ‘diffractionists’, users of synchrotron radiation, are biologists. During the past ten years, the presentation of research activities, which were previously classified according to the classical scientific fields, has been reorganized in terms of general societal questions. Biologists are working with chemists and physicists on environmental questions and global climate change challenges, chemists and physicists join in their efforts to develop new energy sources, and so on. Regarding crystallography, an interesting aspect of this new approach to science is that it is involved in a large number of societal challenges. As an interdisciplinary science, crystallography appears to be one of the common elements of basic scientific knowledge that is mandatory in the design of many of the new emergent solutions. Thus, we can build our strategy on this new situation. Crystallography will be presented as a science that is able to surpass the conventional limits of the classical science fields, and thus it is well placed to provide answers on fundamental societal challenges. We hear about sustainable development every day; we will show that crystallography is also central to this field.

Our second approach is through the history of science. For more than two centuries a big philosophical debate has been taking place about the importance of the historical ‘view’ in the teaching of scientific concepts. The contradictors in this debate were often very famous scientists. Lavoisier thought that the history of science had nothing to do with scientific

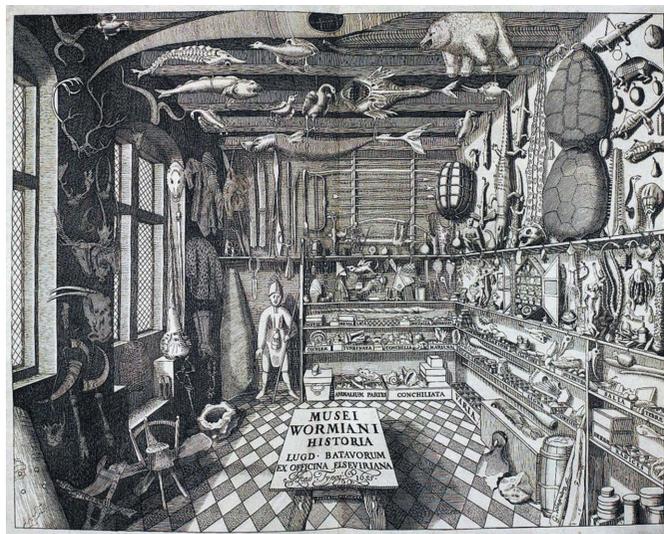


Figure 1
Musei Wormiani Historia, the frontispiece from the *Museum Wormianum* (1655), depicting Ole Worm's cabinet of curiosities. Source: Wikipedia. Original source: Smithsonian Institution Libraries.

² Anyone interested in the description of the interatomic structure of snowflakes may start by reading the beautiful short book *Strena seu de nive sexangula* (Kepler, 1611).

treatises (Lavoisier, 1789). On the other hand, more recently Langevin (1904, 1950) and Perrin, and, from a more theoretical point of view, Bachelard (1938), were great defenders of the introduction of historical facts into the teaching of science. As Bachelard remarked, one of the difficulties of the scientific approach is that it requires the shedding of all prejudices. One way to achieve this is to adopt a 'chronological approach'. We are fundamentally convinced that knowledge of the intellectual and experimental routes that have been developed to explain a specific fact or phenomenon is the best way to understand it. The scientific and historical foundations of crystallography are old, and they have already been described elsewhere (for example, Authier, 2013; Hodeau & Guinebretière, 2007). We want the visitors to our exhibition to rediscover the scientific facts by following the same paths of reasoning as those explored by the actual discoverers.

Pieces of rock that have surprisingly regular and flat surfaces can be found in nature. The very old and fundamental question is, why do these strange stones present such regular faces? Up until the discovery of X-ray diffraction by crystals, during the two millennia from Plato to Haüy, the scientific explanations for the structure of crystals alternated between external and internal factors. Throughout that time, the understanding of the nature of crystals intersected with some very general important questions about human civilization. Democrite suggested that the external shape is associated with the stacking of very small entities that he called 'atoms'. To Aristotle, inert matter could not have a specific shape. Only external causes may give their external shape to the crystals. One of the important questions here is, who has given these stones their external shape? Or in other words, who is the sculptor? Up to the end of the Middle Ages in Europe, this question accompanied the beginnings of crystallography. Nevertheless, at that time, Kepler had already proposed that only the regular stacking of identical entities is able to

reproduce a geometrical shape and thus explain the external hexagonal form of snowflakes (Kepler, 1611). Not only because of their shape but also owing to their optical properties (the beauty of precious stones) or their mechanical characteristics (the hardness of diamond), crystals have been the starting point of fundamental questioning throughout the development of human thought.

Scientific explanations are often felt to be *ex cathedra* assertions without a link to common knowledge. We propose to use both surprise and interrogation as the guidelines for our educational approach. By leading visitors beyond misunderstandings and supernatural invocations, we aim to promote rational explanations.

1.3. Means of use

Following the general approach described above, we built a travelling exhibition based on three types of components. First of all, there were a number of panels,³ most of which were richly illustrated, featuring text written in collaboration with more than 60 scientific specialists on various aspects of crystallography. All the written parts were polished by professionals involved in the field of communication. Posters are one of the common ways of communication used by the scientific community. However, as far as the wider public is concerned, they are largely insufficient. In our opinion, the crucial point is to associate these panels with a large number of objects (Fig. 2). Crystals have themselves a power to entice and attract. Some jewels may be exhibited, but the costs and security levels are important issues. We propose that visitors should be able to touch actual crystals, to rotate them, to see their interplay with light, to experiment with their hardness by striking a piece of glass, and so on. Of course, historical artefacts have to be introduced into the exhibition: instruments such as Haüy's wooden models, Crookes tubes or old diffractometers as well as a copy of a hand written laboratory book are all fascinating objects. The third component of the exhibition consisted of short computer-assisted interactive presentations of specific aspects of crystallography, which are a few minutes long and animated. Roughly 20 of these have been realized. Some basic explanations of chirality and of the continuous crossing made by crystallographers between real and reciprocal space are briefly illustrated. We think these three mainstays are mandatory. Nevertheless, a fourth aspect is probably the most important. People want to discuss, ask questions and meet scientists. So, the organization of conferences associated with the exhibition is a key point.

According to this approach, and starting from our experience in Grenoble in 2009, scientists and scientific organizations from the Steering Committee for the International Year of Crystallography in France (AICr2014) and from the Grenoble 100 Years of Crystallography group have joined forces to create a set of multilingual hands-on travelling exhibitions. *Voyage dans le cristal* (*Journey into the crystal*) is



Figure 2 Crystallography exhibitions can be diverse. In addition to panels, conferences, workshops, display objects and tools are an important key to their success. Furthermore, we have the chance to see that crystals are everyday objects. Source: *Voyage dans le cristal*.

³ In fact, two different arrangements were organized. The large version was made up of 39 panels, and a more concise exhibition contained 12 panels. Many other intermediate arrangements can be imagined.

organized in three main stages. In the first part, the crystal is presented as an object of desire. The central point of the second part is the presentation of the crystal as an object of science. Understanding the properties of condensed matter requires a basic knowledge of crystallography. The description of the internal organization of a crystal is a convenient starting point. Finally, the crystal is presented as being involved in many contemporary applications.

The *Journey into the crystal* exhibition recounts humanity's interaction with crystals, through art and science, from prehistoric times to the present day. It invites the public to go on a journey to discover crystals in their many aspects. To date, it has been translated into 13 languages.⁴ During 2014, it was presented in all the main towns in France (more than 70 exhibitions were scheduled). Thanks to the help of the International Union of Crystallography (IUCr), all the contents have been reorganized to make them well adapted to various forms of presentation. This exhibition is a modular tool devoted to spreading an interest in crystallography, nothing else; nevertheless, this is an essential task.

2. The travelling exhibition *Voyage dans le cristal*

Through this *Journey into the crystal*, the public discover why the crystal is intriguing, how it is so useful to science and how it plays such an important role in our daily lives. They learn about the birth of crystallography and the multiple facets of crystals as

- (a) objects of beauty,
- (b) objects of science and
- (c) contemporary objects with numerous applications.

2.1. Crystals provoke wonder, become symbols and inspire study

In their quest for the riches of the centre of the Earth, people have been discovering stones of varying shapes and substances since prehistoric times. Some stones have very unusual angular shapes, with flat, fairly smooth sides, as if they had been manufactured. These angular shapes are natural. They cover the walls of underground cavities called geodes, crypts or kilns. They inspire wonder (Fig. 3).

One of these stones, quartz, is a major component of the Earth's crust. It is a colourless transparent crystallized silica (SiO_2), commonly known as rock crystal, and its transparency is the origin of the word 'crystal'. The etymology of 'crystal' comes from the Greek *kryystallos*, meaning 'ice'. Could rock crystal actually be water that has been converted into a kind of permanent ice after being subjected to an intense level of freezing? This analogy between rock crystal and other transparent materials can be found in crystalware (or fine glassware), which is not actually crystal.

⁴ The complete version of the exhibition exists in English, French and Spanish. For smaller events, a short version of the exhibition already exists in Arabic, Brazilian, Catalan, English, Finish, Flemish, French, German, Russian, Slovakian, Spanish, Swedish and Turkish (see <http://www.iucr2014.org/resource-materials/voyage>).

Crystal shapes can be diverse. Of all the minerals, calcite (CaCO_3), which is the major component of limestone, has the greatest number of different geometrical shapes. Haüy described nearly 150, Palache recorded 630 and Goldschmidt distinguished 2544 distinct forms. These forms are sometimes subdivided into four main categories for classification: rhombohedron, prism, scalenohedron and bipyramid. Such diversity occurs in many other minerals and is due to the different growth rates of the different faces of a crystal. These rates depend on the structure of the crystal, and also the conditions of growth, such as the temperature, pressure and impurities in the composition of the mother liquid.

Crystals can present a multitude of colours, either in different crystals of the same type or in the same crystal, such as in ametrine (a variety of amethyst). In the past, colour and transparency were the main information that differentiated minerals; however, this is no longer the case, and such criteria rarely allow the type of mineral to be identified. We presently know colour as just a human perception of a marginal physical phenomenon: the absorption of light of a particular energy. There are many factors that affect our perception of colour: (i) the presence of a light-absorbing (or chromophorous) atom like azurite; (ii) the presence of a few chemical impurities, such as in amethyst and ametrine, or in sapphires and rubies; (iii) the inclusion of a minor mineral in a major one, such as rutile in quartz; (iv) deformation due to irradiation, as in smoked quartz; and (v) the size of the crystals, as in haematite. Thus, in most cases the colour of a crystal is related to an infinitesimal component of the crystal, and frequently it is the defects or impurities that play this role (Fig. 4).

The colour, transparency, rarity and stability of certain stones made them precious objects that were used in jewels and gems (*cf.* for example the exhibition *Gemmes, une brillante histoire*, which was held from July to October 2014 in the *Musée de St Antoine l'Abbaye*, France). Since ancient times, these precious stones have been polished to form rounded



Figure 3
Mexico's *Cueva de los Cristales* (Cave of Crystals) contains some of the world's largest known natural crystals of gypsum (as long as 11 m). 'They are the Sistine Chapel of crystallography', according to Juan Manuel García-Ruiz (García-Ruiz & Trueba, 2009). Source: *The Giant Crystal Caves of Naica*, copyright Madrid Scientific Films 2009, photograph Javier Trueba.

shapes. They were even carved as *intaglios* and *cameos*. The beauty of the crystals' facets naturally led to the cutting of precious stones, the first examples of which appeared in the 13th century in Europe. It was wonder at the flat faces that pushed people to cut crystals with numerous faces. Cutting is a difficult art which is carried out so as to favour the reflection of light both inside and outside the crystal, and it has evolved with the times. Its objective is to make the stone as attractive as possible. Certain facets are like mirrors, while others trap light within the stone so that it emerges more vividly or with the appearance of little rainbows known as 'fires'. Surprisingly, one stone, diamond, was for a long time resistant to polishing. A wide range of stones have been used for jewellery, from the most precious, such as diamond, sapphire, ruby and emerald, to the more modest, such as garnet, amethyst and carnelian. These stones are rare and expensive, so people started to produce imitations out of transparent glass.

In the past, people have had a curious and troubled relationship with nature. Among all the objects of nature, stones and crystals have played a special role. Their colours and forms and, above all, their apparent permanence and stability have appeared to give them the power to escape time. From the ancient megaliths to stones invested with mysterious powers like the philosopher's stone of the alchemists, which is capable of bringing wealth and immortality, a veritable 'popular belief' has grown up around these stones that still remains today. Fascinated by crystal colours and shapes, people have come to believe that stones, and particularly

crystals, have magical powers. For thousands of years, these powers have been supposed to offer healing and protection. During ancient times and the Middle Ages, stones were supposed to have the power to act in many ways; there are, therefore, healing stones, stones of madness, stones of lightning or of thunder, and so on. These beliefs are reported in many lapidaries and almanacs.

The best example of a stone with symbols and virtues attached to it is diamond. The name diamond derives from the Greek *adamas* (unconquerable), which referred initially to a very hard material. In ancient times, the Greeks gave it this name because they could neither cut nor saw it. People very soon bestowed it with extraordinary qualities and symbols like stability, then invincibility, and this stone came to represent power. By extension, the diamond became a symbol of protection and eternity, and also a symbol of eternal love and marriage.

2.2. Crystallography: the birth and triumph of a science

From the end of the 16th century, the discovery of mines rich in crystals led to more and more scientists becoming interested in the products produced deep below the ground. Scientists confirmed that certain minerals often have recognizable angular shapes, which do not appear to be random. How could the incredible shape of crystals be explained? In the 16th and 17th centuries, natural philosophers held two opposing points of view about crystals: did they grow faceted from inert matter, or were they sculpted solids? (Fig. 5). On the basis of his observations of quartz crystal forms, Stensen (1669) introduced the concept of crystal growth. In 1690, Huygens discovered an optical property of quartz (Huygens, 1690), which had already been observed in calcite by Bartholinus (1669), known as double refraction: a double image. These and other studies gave rise to the development of the scientific discipline of mineralogy. It was the birth of a science. The word 'crystallography' (or the description of crystals) was used for the first time by Capperell (1723).

In the 18th century, although it was still not possible to look inside crystals, crystallographers were able to imagine their internal structure by observing their outer geometry. Already in 1669, Stensen had suggested that the hexagonal form of the quartz crystal was preserved during growth created by the successive accumulation of parallel layers deposited by an outside liquid (Stensen, 1669). This theory was taken up by Guglielmini (1688), who proposed four different crystal forms (hexagonal prism, cube, rhombohedron and octahedron). Romé de l'Isle adopted the idea of Linnaeus (Carl von Linné), founder of the system for classifying living species, and used the forms of crystal as a classification criteria. In order to reproduce crystals from clay, he asked Carangeot to measure the angles between the faces: they are identical for the same type of crystal. This was the origin of the law proposed by Romé de l'Isle on the constancy of angles between the facets for a given type of crystal (Romé de l'Isle, 1772). While observing the form of pieces of broken calcite, Haüy built a model in which the crystals resulted from a stack of basic



Figure 4

In its purest form, quartz is colourless and transparent. Colouring is due to impurities and can be the result of proximity over millions of years to radioactive rocks. Smoky quartz contains aluminium impurities, but its colour disappears above 300–400°C (~570–670 K). The colours vary with the impurities, as in violet amethyst, which is merely an irradiated quartz with iron oxide impurities (Fe^{4+}); when heated, the iron impurities change their oxidation state (Fe^{3+}) and yellow citrine is obtained. Ametrine is a mix of citrine and amethyst. Source: *Voyage dans le cristal*. Photographs: quartz rock crystal (La Gardette, Isère, France) and amethyst (Montana, USA) (copyright Collection des Muséum de Grenoble); smoky quartz (Curie family, copyright Collection des Minéraux de Jussieu, UPMC, Paris); ametrine (copyright Eddy-Vleeschdrager).

cubes or bricks, which he called ‘integrant molecules’ (Fig. 6). Haüy also commented that the faces observed were the result of simple intercepts, that is, the ‘law of simple rational indices’ (Haüy, 1801). This observation led scientists to define a crystal as the regular stacking of an elementary building block. Thus, crystalline forms were not perceived as the result of a freak of nature, each one being a solid body composed of a solid chemical compound. All these studies gave rise to the new science of crystallography. Together with astronomy, mechanics and optics, this is one of the oldest of the physical sciences.

At the beginning of the 19th century, German and French crystallographers introduced the concept of symmetry. To classify minerals, these crystallographers developed a new meaning of the word symmetry, reserved until then for architecture (in Greek: ‘due proportion’). They spoke of centres and axes of symmetry of different orders, and rediscovered the concept of symmetry introduced independently in 1794 by the mathematician Legendre. Weiss rejected Haüy’s integrant molecules theory, and became a leader of a German school of thought which specialized in symmetry (Weiss, 1813). Hessel and Frankenheim showed that there are only 32 forms of crystallographic symmetry (Hessel, 1830). This classification of crystals using symmetry and the lattice system is still with us today. It is invaluable for studying the physical properties of

crystals, including their optical, mechanical and thermal properties.

During the 19th century, the notion of frequency (periodic repetition) and atomic order was established so as to help in understanding the form of crystals and their symmetry. In 1840, Delafosse replaced the ‘little blocks’ of Haüy with the notion of volumes, which could be molecules and space (Delafosse, 1867). In 1848, Bravais described all these volumes as a ‘lattice system’ that repeats itself, with an identical ‘motif’ at each lattice point (known as the ‘node’ of the mesh through its analogy with a fishing net). He showed that there are only 14 types of lattice system (Bravais, 1866). Bravais proposed that a crystalline face is especially developed when the bonding is stronger within its molecular plane. This suggests that these planes, which appear preferentially, have the greater molecular density. Georges Friedel observed a large number of natural crystals and proved that the frequency of the appearance of a face is linked to the density of the points of the lattice and, therefore, to the internal structure of the crystal (Friedel, 1921).

At the end of the 19th century, the hypothetical ‘molecules’ were usually replaced by more complex ‘motifs’, like those of wallpaper, containing atoms and potentially new symmetries. These motif groups of symmetry were identified by Sohncke (1879), opening the way for the studies of symmetry by Schoenflies (1891) and Fedorov (1885). This theory, in addition to the periodicity of the crystals, was to be confirmed in 1912 by the first X-ray diffraction experiments. By the beginning of the 20th century, without being able to ‘see into’ a crystal, crystallographers had developed an experimental and theoretical knowledge of crystals.

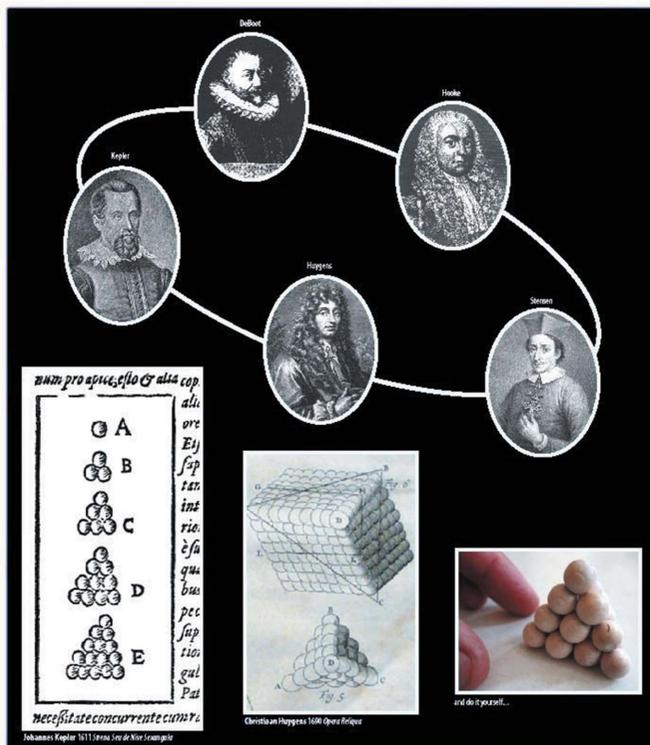


Figure 5
De Boodt, Kepler, Hooke, Huygens and Stensen considered the cause of the crystal shapes to lie within the crystal: stacks of particles, layering of planes, as can be shown by using educational pyramids. Source: *Voyage dans le cristal*; adapted from Johannes Kepler (1611), *Strena Seu de Nive Sexangula*; Christiaan Huygens (1690), *Opera Reliqua*.



Figure 6
Calcite crystal in scalahedron form and a wooden model produced by Haüy to illustrate his ‘stacked bricks’ theory on the shape of crystals. According to legend, René Just Haüy had this inspiration when he dropped and broke a calcite crystal (Iceland spar). He noticed that all the fragments were identical in form and were, without exception, parallelepipeds; these were totally different from the irregular shards obtained from broken glass. Source: *Voyage dans le cristal*; adapted from (i) calcite crystal (copyright Muséum de Grenoble), (ii) wooden model (copyright Collection des Minéraux de Jussieu, UPMC, Paris), (iii) painting of Haüy (copyright Musée de Minéralogie, Mines ParisTech, Paris).

2.3. X-rays, a breakthrough in crystallography

When X-rays were discovered in 1895, Röntgen was persuaded that they represented analogies with visible light, but despite his best efforts, he was unable to determine their precise nature. In the end, he gave up and called them ‘X-rays’ (Röntgen, 1895). To understand the nature of this unknown radiation, Röntgen placed different objects between a Crookes tube and a photographic plate and confirmed that these rays passed through solid matter. When he inadvertently placed his hand in the path of these strange rays, Röntgen observed an image of the bones of his hand on the plate. In 1901 he has awarded the first Nobel Prize for Physics.

This was the start of an intense period of research into the nature of X-rays. Scientists, particularly German scholars, were convinced that this was a wave. Röntgen’s work had already shown that this radiation possessed a high energy and a very short wavelength. Laue’s idea of using crystals to understand X-rays came about during a discussion with Ewald, one of Sommerfeld’s PhD students. Laue presumed that exposing a crystal to X-rays could give rise to an optical phenomenon with the separation of the beams of light, known as interference. To apply Laue’s idea, in April 1912 Friedrich and Knipping exposed a crystal to X-rays and observed a number of spots on the photographic plate placed behind it. Laue interpreted these spots as being due to interference, that is, the ‘diffraction’ of the X-rays by a periodically spaced lattice of atoms present within the crystal (Friedrich *et al.*, 1912). This was the beginning of a rush to publication; in a single year between June 1912 and June 1913 a large number of papers were published on X-ray diffraction, often in the journal *Nature*. It is difficult to cite all of them. The most important are the following: W. H. Bragg (1912*a,b*, 1913); W. L.

Bragg (1912*a,b*, 1913); Bragg & Bragg (1913*a,b*); Tutton (1912); Barkla & Martyn (1913); De Broglie (1913); De Broglie & Lindemann (1913); Hupka & Steinhaus (1913); Hupka (1913); Keene (1913); Terada (1913). In 1914, Laue received the Nobel Prize for Physics for his discovery that X-rays are waves, just like light, but with a wavelength a thousand times smaller (similar to the distances between atoms).

This experiment carried out to reveal the nature of the X-ray beam also established the frequency of the order in the crystals (periodicity) and opened up the extraordinary possibility of determining their atomic arrangement (Fig. 7). In 1912, William Henry Bragg and his son analysed Laue’s results in detail (W. H. Bragg, 1912*a*; W. L. Bragg, 1912*a*). The son, William Lawrence, then aged 22 years, worked out an equation which enabled him to calculate the position of the atoms within a crystal from the manner in which the atomic planes of the crystalline structure diffract the X-rays: Bragg’s Law,⁵ $\lambda = 2d\cos\theta$ (W. L. Bragg, 1912*a*), where λ is the wavelength of the incident radiation, d the spacing of the lattice planes and θ the scattering angle with respect to the normal of the reflection plane. As early as 1912, the Braggs invented a new type of X-ray diffractometer (W. L. Bragg, 1912*b*). Using this, they made numerous measurements and investigated the atomic structures of many types of crystal (W. L. Bragg, 1913; Bragg & Bragg, 1913*a,b*). Thus, they developed the science of X-ray crystallography. The diffraction of X-rays was not just a physical phenomenon, but became a tool for exploring the arrangement of atoms within the crystals. The Braggs received the Nobel Prize for Physics in 1915.

The first X-ray crystallography experiments had already given some surprising information, such as the relation between diamond and graphite. In the first century AD, Pliny the Elder wrote that not only is diamond resistant to fire, but, furthermore, the most intense flames do not even heat it up (because it transmits the heat). Also, against all expectations, in the middle of the 17th century the scholar Boyle discovered, without understanding why, that diamond ‘evaporates’ when subjected to great heat. Up to the 19th century, increasing numbers of experiments were carried out, most notably by Darcet, Hannay and Lavoisier (Lavoisier, 1772), in order to investigate the mechanism of this transformation. They discovered that diamond and graphite are made of the same material: carbon. But, they were unable to explain their difference: one is transparent and hard, while the other is black and crumbles. Diamond is denser than graphite, which, at that time, led them to believe that if you compressed graphite into a volume similar to that occupied by a diamond of the same weight then it would be possible to transform graphite into diamond. The final explanation came at the

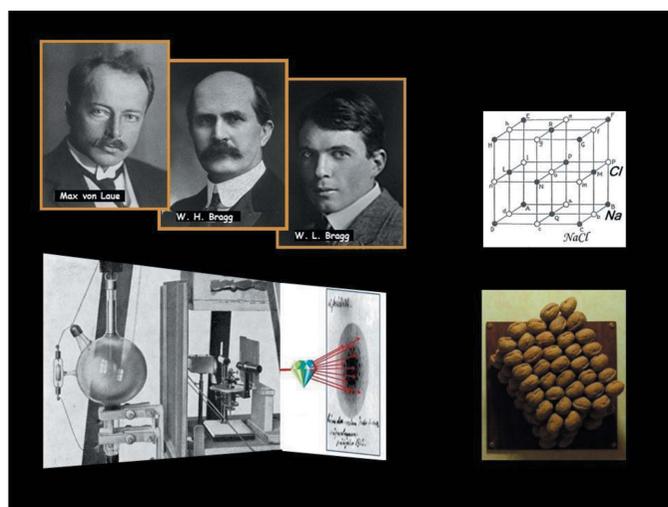


Figure 7
After the Laue experiment, which revealed that because of their periodicity crystals could cause X-rays to diffract, William Lawrence Bragg and his father, William Henry Bragg, developed the science of X-ray crystallography. This enabled them to determine the atomic structure of many crystals, like those of NaCl salt and diamond. Source: *Voyage dans le cristal*; adapted from photographs courtesy of <http://www.iucr.org> and <http://www.nobelprize.org>.

⁵ The so-called ‘Bragg law’ is usually written as $\lambda = 2d\sin\theta$, where θ is the scattering angle with respect to the reflection plane. We reproduce it here in its original form as written by W. L. Bragg (1912*a*). Indeed, following the conviction of his father who thought that X-rays were particles, W. L. Bragg imagined that these particles were reflected onto dense atomic planes. Thus, according to the Snell–Descartes law, he considered the reflection of these particles with respect to the normal of the reflection plane. According to this scheme, the convenient law must, of course, use cosines.

beginning of the 20th century, when X-rays allowed scientists to discover the internal structure of diamond and graphite: they both have the same carbon atoms, but their atomic arrangements are quite different.

Another surprise is the atomic characteristics of glasses and crystals. The word ‘crystal’ is often associated with transparency and brightness, and it is a synonym for beauty and wealth. Certain royal dinner services are made of rock crystal. These are imitated by the middle classes who use various fine-cut objects, also called ‘crystal’. Nevertheless, these items are made of glass, like volcanic silica glass, and are not true crystal, because they have been cooled too quickly. Diffraction experiments show glass is an amorphous material formed of atoms with a disordered arrangement, like an immobile liquid. These glasses have been synthesized since ancient times, but it took several centuries before people succeeded in making them as transparent as rock crystal. Quite different to this, the highly transparent rock crystal is made of crystallized silica, which thus has an ordered arrangement (Fig. 8).

Another material uses the word crystal in its denomination: ‘liquid crystal’. Liquid crystal is a phase that is between the liquid and solid states: it flows like a liquid but has the properties of a solid. The molecules of a liquid crystal are highly elongated and have the tendency to line up like matches or cigars in a box. They owe their name to their optical properties, which are similar to those of crystals.

In fact, the definition of the word ‘crystal’ has evolved with time: (i) in the 18th century the term crystal was used by scientists to describe any angular stone with specifically orientated plane surfaces; (ii) in the early 19th century, crystal referred to any homogeneous solid material characterized by planar faces; (iii) in the 20th and 21st centuries the term crystal refers to any material whose atoms are arranged in an ordered pattern; (iv) since 1992, and taking into account the discovery of quasi-crystals (Shechtman *et al.*, 1984), the IUCr has

defined a crystal as a material with an ordered arrangement of matter, periodic or aperiodic, manifested by relatively discrete diffraction spots.

2.4. Crystals for research and applications

In the 20th century, crystals were subject to many applications in different areas of science. Crystal chemistry was born at the beginning of the 20th century with the discovery of X-rays. Its objective was to explain the relationship between the properties, the chemical composition and the arrangement of the atoms in crystals. One example is the first X-ray study of stilbite, a stone that boils, as found by Cronstedt in 1756: hence its name, ‘zeolite’, from the Greek *zeo* (to boil) and *lithos* (stone). In 1930, Taylor (1930) and Pauling (1930) used X-ray diffraction to study zeolite crystals for the first time and revealed that, at an atomic level, these minerals are made up of a nanoporous matrix. Stilbite is a sodium calcium aluminium silicate which can hydrate or dehydrate in a reversible manner, according to its temperature. So, water is trapped within the cavities of the structure.

This crystallographic approach to atomic arrangement has represented a true revolution for chemists, who have therefore been able to visualize the structure and constitution of isolated solids, thus enabling them to focus on strategies for synthesizing new materials. The same methods have spread throughout the sciences of pharmacology and biology, where research has led to the synthesis of new pharmaceuticals.

In order to better understand the way a living organism functions and the role of the different proteins, scientists have looked for means to elucidate their structure. X-ray crystallography has proved to be an extremely efficient technique for this. Proteins, which are very large biological molecules (macromolecules) that are essential for life, are made up of amino acids. Each protein has a specific function, directly linked to its three-dimensional structure (*i.e.* the manner in which the amino acids are laid out, one against the other in space). Proteins do not naturally form crystals, so these crystals have to be made artificially in order to study them.

One of the first X-ray studies for understanding living organisms was that of DNA, which is present in all living cells. It carries the inherited information that holds the ‘secret of life’. DNA is made up of two complementary strands formed by two regular sequences of small molecules, wound into a double helix. DNA molecules can thus duplicate themselves to form identical molecules that characterize the entire genetic make-up. It was Rosalind Franklin’s image of a pseudo-crystal made of DNA fibres, obtained in 1952 by X-ray diffraction, which enabled the structure of the molecule to be determined (Franklin & Gosling, 1953). Between the 1920s and the 1960s, X-ray crystallography started to be used to elucidate biological molecules related the structure of life. Dorothy Hodgkin solved the structure of cholesterol (Crowfoot, 1941), penicillin, vitamin B12 (Hodgkin *et al.*, 1956) and insulin (Blundell *et al.*, 1971), and she was awarded the Nobel Prize for Chemistry in 1964. Sir John Kendrew and Max Perutz worked out the crystal structure of a protein, earning them the Nobel

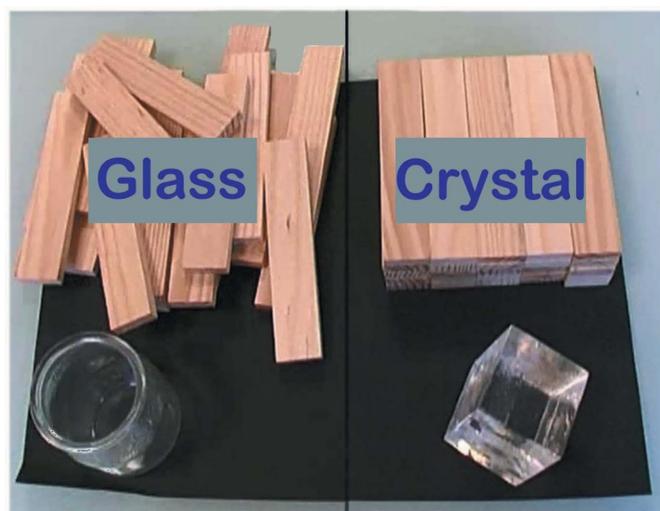


Figure 8
There’s crystal and ‘crystal’. In a true crystal the atoms are arranged like the wooden bricks in this wall. In glass the atoms are disordered, like the same bricks in this pile; if you try to build the wall too fast, you just get a pile of bricks. Source: *Voyage dans le cristal*.

Prize for Chemistry in 1962 (Perutz *et al.*, 1960). To date, crystallographers have solved the crystal structures of over 90 000 proteins and other biological molecules (Fig. 9). There is a very strong relationship between the atomic arrangement (the structure) of a biological macromolecule and its function: the precise knowledge acquired about its forms means that a hypothesis can be developed regarding its role and the manner in which it carries out its function. These studies relate to basic research, which concerns the acquisition of a precise understanding of the biological processes, and applied research, which leads to the synthesis of new medicines.

Crystallography is also important in earth science. Some natural crystals, because of their composition, structure and density, can be a marker of the composition of the Earth. Information about the Earth's core comes primarily *via* the crystals contained in materials recovered from volcanic eruptions, and also from zones created by the formation of mountain ranges. These materials can undergo a transformation during their journey to the surface, and their point of departure is unknown. In order to understand the deeper layers of our planet, researchers 'cultivate' these crystals under same high-pressure/temperature conditions as those found in the depths of the Earth. The higher the temperature and the pressure required to produce such crystals, the further down their natural analogues are supposed to originate from, with a consequent increase in their density and a modification in the materials. The crystals' stability zones can be linked to the different kinds of strata of the Earth, as shown by seismic waves. When carrying out a study of meteorites, crystals are

also a marker of the composition of the solar system. An analysis of the crystals contained in meteorites enables us to comprehend the history of the planets.

The messenger role of crystals is also useful in archaeology and in studies of heritage objects (Fig. 10). For example, objects found at burial sites are often made up of crystalline structures preserved under conditions favourable for their conservation. Such crystals are genuine archives for those who know how to read them. From a study of archaeological remnants, and in particular the crystals of which they are composed, it has been possible to obtain information about the way ancient people lived and their customs, everyday lifestyles and environment.

2.5. Crystals are an everyday object, found everywhere

In living organisms, mineralization is a very common process. Crystals are all around us. They are in shells, pearls, corals and bones – even sedimentary chalks were once life. This occurs by the process of 'biomineralization', by which living organisms produce and organize their mineral structure. This process is a controlled form of crystallization. Snails and oysters have different types of shells made of calcium carbonate (limestone) crystals (CaCO_3 calcite or aragonite). The differences in the arrangement (the microstructure) of the calcium carbonate crystals of these shells is biologically controlled by the living organisms.

In fact, crystals are present in animals' bodies, particularly in the bones. Studies of the chemical composition of bones and tooth enamel were quite perplexing for the first researchers, because these chemical compounds are very reactive nanocrystals, known as apatites. Using this information, researchers developed artificial biomineralization. Now, they are able to create crystalline prostheses that imitate nature.

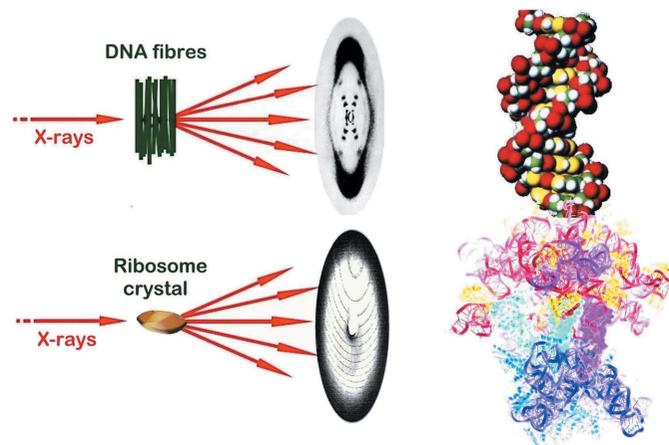


Figure 9

To understand the structure of DNA, Rosalind Franklin produced a kind of one-dimensional crystal aligning long fibres of DNA molecules. With this bundle-shaped crystal she obtained X-ray diffraction patterns of exceptional quality. When they saw these photographs, Watson & Crick (1953) deduced the structure of the double helix of DNA. Currently, the structures of very large biological macromolecules can be solved. For example, together with Venkatraman Ramakrishnan and Thomas Steitz, Ada Yonath has determined the structure of large ribosomes which are responsible for the production of all proteins in the living cells of humans, plants and bacteria; they were honoured by the Nobel Prize in 2009. Many others researchers have been awarded the Nobel price for their scientific achievements involving the use of crystallography (<http://www.iucr.org/people/nobel-prize>). Source: *Voyage dans le cristal*, adapted from IUCr Journals.



Figure 10

The crystals in archaeological paintings can be analysed by scientists using diffraction. These studies, together with the findings of archaeologists, enhance our understanding of how they were made, as it was in the case of the Maya blue colour. This research can be used in educational workshops to prepare Maya blue and build palygorskite/indigo models in schools. Source: Institut Neel-CNRS and Lycée Pontcharra. Photograph from Bonampak, Chiapas, Héctor Montaña/INAH.

Surprisingly, nanocrystals are present in spider webs, which helps to explain their properties. The spider's web, which includes up to seven types of thread, is one of the wonders of the natural world and can be related to high-level technological materials. Its robustness is linked to its composition: a succession of tiny rigid crystals and elastic polymer strands.

Crystals are everywhere: metals and alloys are also made up of many crystals. These crystals are at the heart of metallurgy, which is the science that studies the structure and properties of metals and alloys. Metallurgy began 3000–5000 years ago with the Bronze Age. Metallurgy is also concerned with describing the technologies used in the production of metals, their treatment and casting, particularly of steels. A metallic element is made up of a group of crystallites that are inter-linked, with sizes varying from one centimetre to a nanometre (one billionth of a metre). The defects existing in and between these crystals are at the heart of metallurgical behaviour. Even if the hardness can be associated with certain structures, it is often the defects that determine the mechanical properties of metals and alloys. These defects also play a key role in forging, laminating and milling. Metallurgy is always seeking to develop and shape materials for different sectors of the economy, such as the automobile, aeronautical and nuclear industries. Electron microscopy and diffraction by X-rays are used to determine the order in which the crystals are arranged, and to understand the processes involved during the elaboration (solidification, precipitation) and use (corrosion, ageing process, distortions) of metal alloys (Fig. 11). We can say that the Steel Age is the age of materials with controlled defects.

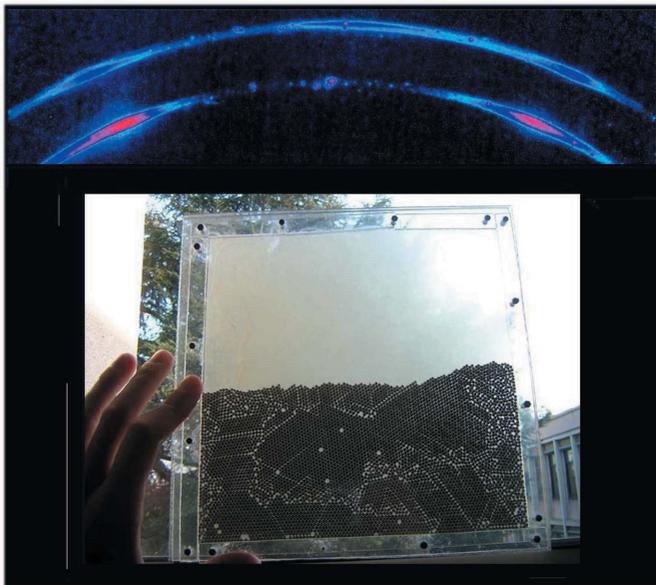


Figure 11

Defects in metals and alloys are at the heart of metallurgical behaviour. We can picture the order of atoms and some of these defects using a stack of metal balls in a box. Here, we see a partially ordered polycrystalline material, with defects, grain boundaries and crystal twinning. Scientists use microscopy and X-ray diffraction to distinguish deformed crystals from the recrystallized crystals (here the diffraction images of aluminium cans). Source: *Voyage dans le cristal*.

Most microelectronic components present in our everyday lives are made from near-perfect crystals. Silicon is the crystal most widely used in electronics. This crystal should be near perfect with just a few impurities added to allow its properties to be adjusted to suit demand (known as doping the crystal). Such crystals are currently used in the chips found in robots, smart cards and computers. In all areas, the general trend is to place more components onto smaller surfaces, and therefore the components themselves need to be smaller. In order to make these minute components, it is essential for perfect crystals to be 'made' with very few chemical and structural defects.

In microelectronics, other specific crystals can be used; these are 'magnetic crystals' where an order of 'magnetic moments' is superimposed onto the atomic order (Fig. 12). The magnetic moments of the atoms can be illustrated by the direction of tiny compass needles. Just as X-rays enabled us to 'see' the order of atoms, so neutrons enable us to observe the magnetic order (Shull & Smart, 1949) because neutrons are themselves like tiny compasses: they possess a magnetic moment. The different orders of these magnetic moments can be used for information storage, and this explains why such crystals are used as microelectronic components.

Crystals are also employed as solid state lasers or light sources for use in displays such as traffic signals or Christmas decorations. Some analogous microcomponents can produce light; these are called light-emitting diodes (LEDs), which are also produced with near-perfect crystals. By placing a fluorescent crystal between two mirrors, the light emitted by



Figure 12

A complex ferrimagnetic order exists in magnetite – the oldest known magnet – whose structure is represented here by the Nobel Prize winner Louis Néel's model, which he made out of wires and plugs to help himself understand the structure of the mineral. Source: *Voyage dans le cristal* (copyright Institut Néel-CNRS).

fluorescence can be amplified through a laser (light amplification by stimulated emission of radiation) effect.

Many applications are based on very common classic crystals such as quartz. Piezoelectricity, which transforms a force into electricity and *vice versa*, was first discovered in quartz by Jacques and Pierre Curie in 1880 (Curie & Curie, 1880). Piezoelectricity is used in sonars, and it is also used to measure the time in quartz watches and to define the precise frequencies of all electronic devices (telephones, computers, GPS *etc.*). On account of its remarkable properties, investigations very soon began into the structure of quartz, and several models were suggested for its molecular arrangement. Furthermore, the complexity of this element meant that its structure was only determined in 1925 by W. H. Bragg and R. E. Gibbs (Bragg & Gibbs, 1925). In quartz, all atoms are interlinked by short bond lengths between silicon and oxygen, making it appear like a spiral atomic arrangement. This spiral staircase lies at the heart of its chiral properties and its facility to polarize light.

'Chiral' comes from the Greek word *chiro*, which means 'hand: when the palms face in the same direction, the left hand cannot be superimposed on the right hand. Chirality is a fundamental concept used in chemistry and physics. It exists in certain crystals, and it is a fundamental property of the chemistry of living organisms and an indispensable condition of certain physical properties. The first observation of chirality in molecules was in 1848 by Pasteur (1848). He observed that crystals can have two identical and yet opposing forms, a mirror image of each other, which he interpreted as the existence of two chiral molecules. Crystallography is a key tool in determining asymmetry in the atomic arrangement. Asymmetric molecules have two chiral forms; generally, one of these two forms is dominant in nature. Our body is made up of basic chiral structures: amino acids and sugars. A chiral molecule in one form will not have the same effect on our

bodies as the same molecule in the other form (enantiomer). That is the case with certain medicines, and for the perception of certain tastes and smells.

Many applications are also based on the most famous crystal, diamond, a symbol of wealth but just one member of the carbon family (Fig. 13). To trace the history and origin of this enigmatic crystal, people had to understand its characteristics and contradictions. It was not until the middle of the 20th century that the first theoretical research enabled scientists to determine the conditions of stability of diamond and graphite: in order to produce a diamond, temperatures of 1100–1500°C (~1370–1770 K) are required, with pressures greater than 45 000 atmospheres (~4.56 GPa). Nowadays, it is possible to achieve such conditions, and we are, therefore, able to fabricate or 'cultivate' diamonds. We have succeeded in putting diamonds to many uses. Artificial diamonds are essential for industry (machining), energy (drilling for oil), surgery (scalpels) and the electronics of the future. Natural diamonds are mainly used for jewellery.

2.6. An exhibition for a wider public

In reaching conclusions about these different examples, we can say that crystals are an everyday object found everywhere. Thus, a crystallography exhibition can be attractive to a wider public. Nevertheless, for such a public we must present the information at different reading levels, and we must present objects, build some tools and organize workshops to explain the science in a way that is easy to understand.

By collaborating with a local museum, it can be easy to display wonderful natural crystals. By using a few laboratory tools like a microscope, the public can also observe some of

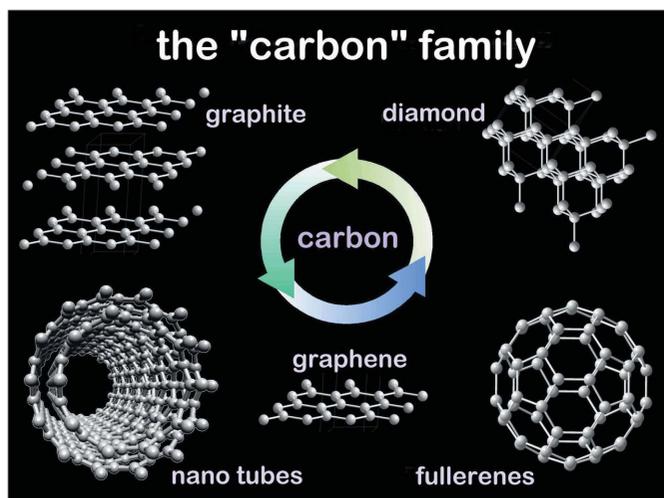


Figure 13
Studies of diamonds have enabled the discovery of new members of the carbon family for new applications. That family gives us graphite, the fullerenes (a 'nano football'), carbon nanotubes and graphene. The story continues with new nanomaterials, which include different arrangements of carbon atoms. Source: *Voyage dans le cristal*.

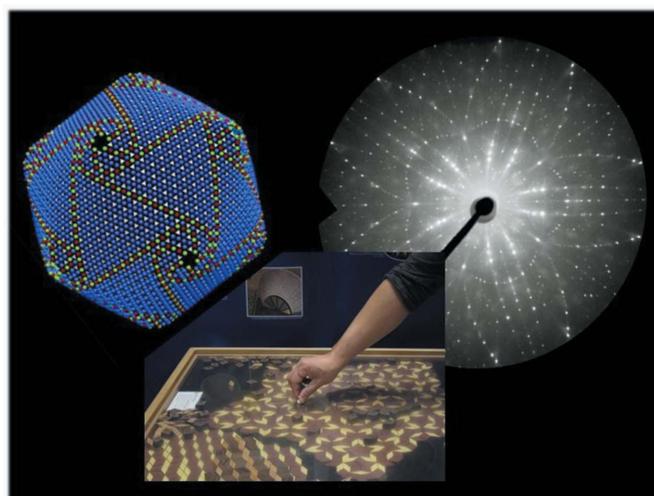


Figure 14
We can create mosaics and pave a surface with identical patterns or shapes (square, rectangular, hexagonal). These tiles with different symmetries can be used to allow the public to discover for themselves some symmetry rules. For example, paving with tiles having a symmetry of the order of five- or tenfold will not allow a surface to be covered completely, but quasi-crystals can be made by using the regular stacking of two different bricks. Source: *Voyage dans le cristal* (copyright IUCR Journals and Steurer; see also <http://www.krystallopolis.fr/>).

the crystals on a smaller scale. First, we observe their geometry, as was done in the 17th century. Using common feldspar–calcite and pyrite crystals, we can illustrate the measurement of the interfacial angles and study the symmetries of the geometric forms that enable us to differentiate crystals. Nevertheless, the more attractive way to observe crystals is to use microscopes with natural or polarized light. Observing crystals with a simple magnifying glass or an optical microscope will allow the public to discover many things about them. These observations can then be applied to help visitors gain a wider understanding. For example, an observation of the most common crystals, such as ice crystals, shows the diversity of the different forms of growth. This is fascinating to behold, but it also provides a source of information about the state and transformation of this material that enables us to understand natural phenomena such as snow avalanches. Another workshop can be organized to play around with symmetries, then to build yourself a crystal, and finally to understand what a crystal is (Fig. 14).

The crystallographer and French Research Minister Hubert Curien said in 1990 at the IUCr Bordeaux Congress:

It is not often the case in science that steps in the intellectual process are as clearly apparent as they are in crystallography. In crystallography, there is a constant alternation between considerations at the atomic scale and macroscopic observation. Observations of overall characteristics, such as crystal forms and cleavage, led Haüy to one of the earliest proofs of the discontinuous internal structure of matter... In crystallography, there is a constant alternation between the crystal space and its associated reciprocal space (Curien, 1990).

A study of the structure of crystals cannot be made directly with a microscope, but rather it has to rely on diffraction. The geometry of the locations of the different diffraction spots allows the structure to be represented in a virtual space, which is called ‘reciprocal space’. A mathematical relationship called a ‘Fourier transform’ exists between this reciprocal space, observed by diffraction, and the real structure of the crystal, which is called the ‘direct space’. We chose to explain this alternation between the crystal space and its associated reciprocal space, and the reality that diffraction is a ‘barcode’ of materials, by using the travels of Alice (in Wonderland) and Joseph (Fourier) in Crystal-land. We present on a screen a parallel to the vision of Alice, who had a direct view of the world of the crystal and its atoms, and that of Joseph, who can only see the patterns produced by the diffraction spots (Fig. 15). This can also be shown using a camera/computer to calculate in parallel the Fourier transform of images or objects.⁶ Such tools illustrate that the observation of reciprocal space using diffraction has enabled scientists to observe the symmetry of a crystal, to calculate the dimensions of its building block or ‘unit cell’ and, finally, to ‘see’ the atoms: the

diffraction pattern is the fingerprint that identifies each crystal.

In the same introductory speech to the IUCr Bordeaux Congress in 1990, Hubert Curien concluded:

Although the seductive power of solid matter has long depended on its perfect atomic ordering, nowadays one is inclined to value the lack of such perfect periodicity. Crystal defects are no longer viewed as mere imperfections... (Curien, 1990).

This was a key predictive point, since most properties are related to these imperfections and a present goal of crystallography is the quest for information about these imperfections. The key role played by these imperfections can be illustrated by the presentation of a stand on crystal growth, which shows the effect of impurities on their properties, as seen in silicon microelectronics, and sometimes on their values, as seen in sapphires and rubies, which are crystals of corundum (Al_2O_3) with some crucial Cr, Fe or Ti impurities. In a large number of technological fields the specific qualities of crystals are of paramount importance. For electronics, communications, energy, medicine and defence applications we need crystals with the appropriate properties, size and quality. Thus, crystal growth has become a major technological challenge.

The cultivation of crystals or crystallogenesis is based on a simple principle: the formation of a solid object with atoms that are organized in a periodic array. This organization is spontaneous, but time must be allowed for it to take place. When a molten compound is suddenly cooled (tempered) there is no long-range order of the positions of atoms (amorphous glass) as there was in the molten state. If cooling is sufficiently slow, then the atoms and molecules have time to move and thus optimize their interactions and compactness. These two factors lead to an atomic order which is regularly repeated. Each atomic layer reproduces the order of the inner layer and acts as a model or pattern for the following ones. The period of time taken may vary considerably according to each material. If you want to grow a few large crystals rather than a

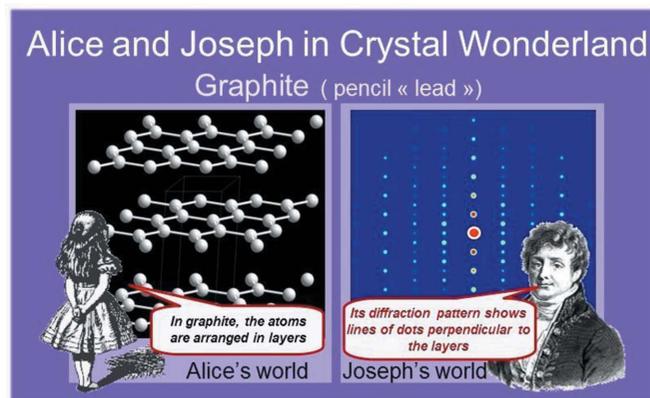


Figure 15

To visualize diffraction, we can present examples that show parallel views: (i) Alice (in Wonderland)’s view of the world, its crystals and atoms – the ‘direct space’; (ii) Joseph (Fourier)’s view – by diffraction in ‘reciprocal space’. Source: *Voyage dans le cristal*.

⁶ V. Jacques (LPS, Orsay, France) has built a transportable setup that is able to realize *in situ* the live Fourier transform of any image. Thanks to the support of the French Steering Committee for the AICr2014, this setup is available for everyone who is interested. Further information can be obtained from the French Crystallography Association.



Figure 16

Cultivating crystals: the key point is that it takes time to grow large crystals. Young people and schoolchildren can make crystals (large ones like for the IYCr2014 crystal-growing competition, or small ones like for Crystal Tree creation). Source: AICr2014, copyright LRF/CNRS-Alpes (<http://cristaux.udppclille.free.fr/>; <http://concourcroissancecristaux2014.blogspot.fr/>).

stack of small crystals, you will need more time (Fig. 16): however, not as long as was necessary for the formation of the crystals found in the Naica caves.

In conclusion, such an exhibition experience and all the International Year of Crystallography (IYCr2014) activities illustrate how we can present to the general public the beauty of matter in the crystalline state and the modernity of our science. The discoveries in crystallography of the 20th century have dispelled the mysteries about atomic structure and the physical properties of crystals, giving them 'a new place at the heart of modern civilization'. Crystals are now research tools used in investigations that cover an immense range, from the composition of our planet Earth to the microscopic structures of materials and the molecules of life.

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