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The Nobel Prizes of 2011

Crystallography and the Nobel Prizes: On the 2011 Nobel Prize in Chemistry, awarded to Dan Shechtman

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Summary. Crystallography has a considerable presence among Nobel Prize laureates. Indeed, 48 of them have close links to crystallography. The 2011 Nobel Prize in Chemistry was awarded to Dan Shechtman for his discovery of quasicrystals. In addition to the scientific merit of the work, the Prize is a personal recognition of Dan Shechtman, whose ideas were initially rejected by the international scientific community. Yet, reason prevailed in the end, supported by arguments that arrived from seemingly unrelated directions, such as the study of Arab building tiles and the mathematical concept of tessellation. Concepts of a more crystallographic nature, such as twinned crystals and modulated and incommensurate crystal structures, also played an important role. Finally, in 1992, the International Union of Crystallography modified the definition of "crystal" to include quasicrystals.

Keywords: crystal structure · electron diffraction · quasicrystals · tessellations

Resum. La cristal·lografia té una gran presència en els premis Nobel; així doncs, 48 guardonats estan estretament vinculats a la cristal·lografia. El Premi Nobel de Química 2011 va ser concedit a Dan Shechtman pel descobriment dels quasicristalls. A part del mèrit científic del descobriment, el Premi és un reconeixement al treball de Dan Shechtman, ja que les seves idees van ser rebutjades inicialment per la comunitat científica internacional. Finalment la raó es va imposar, amb el suport d'arguments que van venir per camins insospitats i aparentment sense cap relació, com ara l'estudi dels mosaics presents en edificacions àrabs i també del concepte de tessel·lació. També hi van contribuir conceptes més pròpiament cristal·logràfics com les macles i les estructures modulades. L'any 1992 la Unió Internacional de Cristal·lografia va modificar la definició de cristall per tal d'incloure-hi els quasicristalls.

Paraules clau: estructura cristal·lina · difracció d'electrons · quasicristalls · tessel·lacions

The number of scientists working in the field of crystallography whose studies have been recognized with a Nobel Prize is remarkable. Indeed, according to the website of The International Union of Crystallography (IUCR) [http://www.iucr.org /people/nobel-prize] there are 48 such laureates: 31 in Chemistry, 14 in Physics, and three in Physiology or Medicine. Given that, thus far, 166 scientists have been awarded the Nobel Prize in Chemistry and 198 the Nobel Prize in Physics, Nobel laureate crystallographers account for 18.7 % and 7.1 %, respectively. In the 21st century, nine crystallographers have been awarded the Nobel Prize in Chemistry and two the Nobel Prize in Physics.

As for female Nobel laureates in Chemistry, the proportion of those recognized for their work in crystallography is

Table 1. Noble Prizes in Chemistry awarded to women

Scientist	Year	Prize	Comments
Marie Curie	1911	"in recognition of her services to the advancement of chemistry by the discovery of the elements radium and polonium, by the isolation of radium and the study of the nature and compounds of this remarkable element"	Also awarded the 1903 Nobel Prize in Physics.
Irène Joliot-Curie	1935	"in recognition of their synthesis of new radioactive elements"	Awarded jointly with her husband, Frédéric Joliot. Daughter of Nobel Prize winners Pierre Curie and Marie Curie.
Dorothy Crowfoot Hodgkin	1964	"for her determinations by X-ray techniques of the structures of important biochemical substances"	Known as a founder of protein crystallography.
Ada E. Yonath	2009	"for studies of the structure and function of the ribosome"	Pioneer of ribosome crystallography. Awarded jointly with Venkatraman Ramakrishnan and Thomas A. Steitz.

particularly noteworthy: two of the four women laureates were recognized for their work in this field (Table 1). Table 2 provides a list of all the crystallography Nobel Prizes, beginning with the earliest awards of the prize, in 1901.

As can be seen in Table 2, initially all Nobel Prizes awarded to crystallography were in the field of Physics, a trend that later evolved towards Chemistry. In the most recent years, crystallography awards have honored an important number of works in the field of Biology—there is no Nobel Prize in Biology. Among the milestones noted in Table 2, we should mention the 1915 Nobel Prize, awarded to the Braggs, father and son; the two crystallography Nobel Prizes awarded in 1962; and the chemist Linus Pauling, who in 1954 received the Nobel Prize in Chemistry and in 1962 the Nobel Peace Prize.

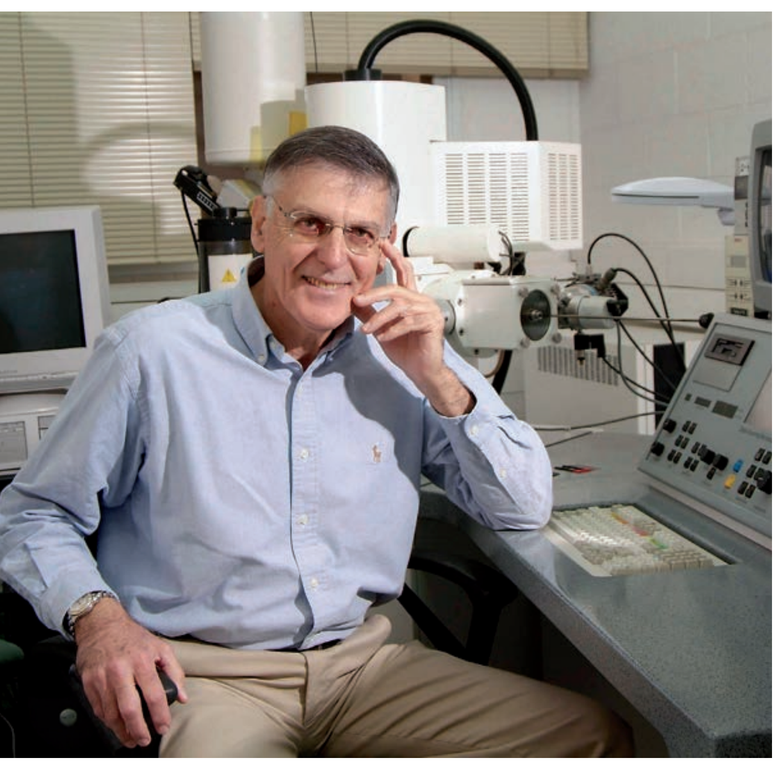

Fig. 1. Dan Shechtman and the electron microscope—the tool that enabled him to discover quasicrystals. (Image courtesy of Technion, Haifa, Israel © Technion Spokesperson).

Given this impressive history, it comes as no surprise that the 2011 Nobel Prize in Chemistry was once again awarded to a crystallographer, specifically to Professor Dan Shechtman, born in Tel Aviv (Israel) in 1941 (Fig. 1). In this particular case, not only was the Prize awarded to just one person, who carried out scientific work of great importance, but it also honored the perseverance of a man who confronted the international scientific community with ideas that took many years to be accepted.

Dan Shechtman and his experiment

This story starts in 1982, when Dan Shechtman was on sabbatical at the Johns Hopkins University in Baltimore (Maryland, USA). The focus of his research, carried out in collaboration with the U.S. National Bureau of Standards (Washington DC, USA), was alloys of aluminium and transition metals, obtained through fast cooling. Such alloys are of practical interest in the aeronautical industry.

One of the experiments consisted of measuring electron diffraction by means of an electron microscope, such as shown in Fig. 1. On the morning of April 8, 1982, Dan Shechtman obtained several electron diffraction images showing a 5-fold symmetry (Fig. 2). Not only was this observation unique, but scientifically this type of symmetry was considered to be impossible [20].

As can be readily imagined, Dan Shechtman's surprise was enormous, as he noted in his laboratory logbook (Fig. 3) with the comment: "(10 fold ???)." As any good scientist would do, Shechtman repeated the experiments many times and under different conditions, but those impossible

Table 2. Nobel Prizes related to crystallography

Year, category	Awarded to	Awarded for
1901, Physics	Wilhelm Conrad Röntgen	"the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him"
1914, Physics	Max von Laue	"his discovery of the diffraction of X-rays by crystals"
1915, Physics	Sir William Henry Bragg, Sir William Lawrence Bragg	"their services in the analysis of crystal structure by means of X-rays"
1917, Physics	Charles Glover Barkla	"his discovery of the characteristic Röntgen radiation of the elements"
1929, Physics	Prince Louis-Victor Pierre Raymond de Broglie	"his discovery of the wave nature of electrons"
1936, Chemistry	Petrus (Peter) Josephus Wilhelmus Debye	"his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases"
1937, Physics	Clinton Joseph Davisson, George Paget Thompson	"their experimental discovery of the diffraction of electrons by crystals"
1946, Chemistry[a]	James Batcheller Sumner	"his discovery that enzymes can be crystallized"
1954, Chemistry	Linus Carl Pauling	"his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances"
1962, Physiology or Medicine	Francis Harry Compton Crick, James Dewey Watson, Maurice Hugh Frederick Wilkins	"their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material"
1962, Chemistry[a]	John Cowdery Kendrew, Max Ferdinand Perutz	"their studies of the structures of globular proteins"
1964, Chemistry[a]	Dorothy Crowfoot Hodgkin	"her determinations by X-ray techniques of the structures of important biochemical substances"
1972, Chemistry[a]	Christian B. Anfinsen	"his work on ribonuclease, especially concerning the connection between the amino acid sequence and the biologically active conformation"
1976, Chemistry	William N. Lipscomb	"his studies on the structure of boranes illuminating problems of chemical bonding"
1982, Chemistry[a]	Aaron Klug	"his development of crystallographic electron microscopy and his structural elucidation of biologically important nucleic acid-protein complexes"
1985, Chemistry	Herbert A. Hauptman and Jerome Karle	"their outstanding achievements in the development of direct methods for the determination of crystal structures"
1988, Chemistry[a]	Johann Deisenhofer, Robert Huber, Hartmut Michel	"the determination of the three-dimensional structure of a photosynthetic reaction centre"
1991, Physics	Pierre-Gilles de Gennes	"discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers"
1992, Physics	George Charpak	"his invention and development of particle detectors, in particular the multiwire proportional chamber"
1994, Physics	Clifford G. Shull, Betram N. Brockhouse	"pioneering contributions to the development of neutron scattering techniques for studies of condensed matter"
1996, Chemistry	Robert F. Curl Jr., Sir Harold W. Kroto, Richard E. Smalley	"their discovery of fullerenes"
1997, Chemistry[a]	Paul D. Boyer, John E. Walker, Jens C. Skou	"their elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP)"
2003, Chemistry[a]	Peter Agre, Roderick MacKinnon	"structural and mechanistic studies of ion channels"
2006, Chemistry[a]	Roger D. Kornberg	"his studies of the molecular basis of eukaryotic transcription"
2009, Chemistry[a]	Venkatraman Ramakrishnan, Thomas A. Steitz, Ada E. Yonath	"studies of the structure and function of the ribosome"
2010, Physics	Andre Geim, Konstantin Novoselov	"groundbreaking experiments regarding the two-dimensional material graphene"
2011, Chemistry	Dan Shechtman	"the discovery of quasicrystals"
2012, Chemistry[a]	Robert J. Lefkowitz, Brian K. Kobilka	"studies of G-protein-coupled receptors"
2013, Chemistry[a]	Martin Karplus, Michael Levitt, Arieh Warshel	"the development of multiscale models for complex chemical systems"

[a]The research awarded was related to biology

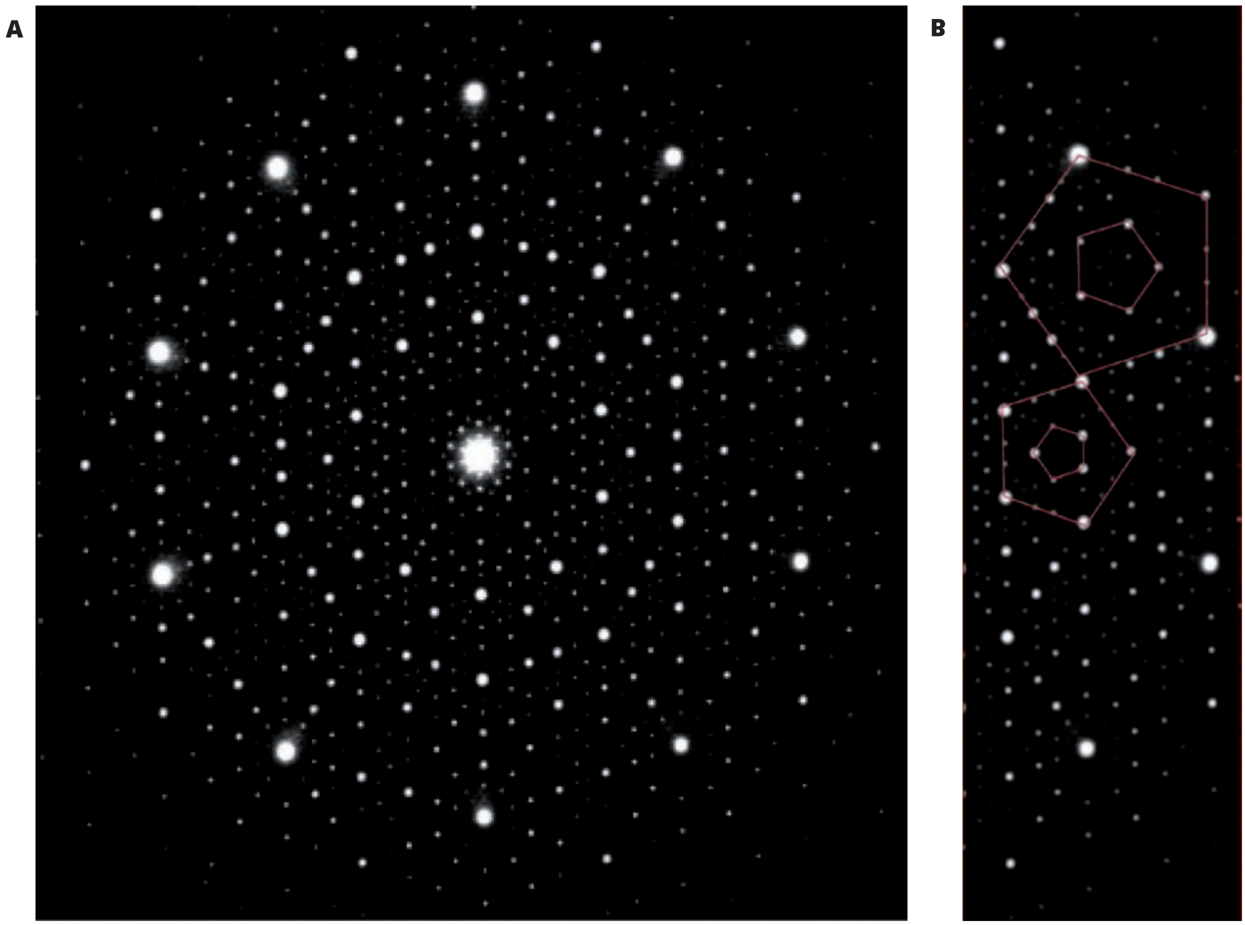

Fig. 2. (**A**) The electron diffraction of a quasicrystal. (**B**) Detail. The 5-fold symmetries are highlighted in color. (Image courtesy of Prof. Sven Lidin).

5-fold symmetries stubbornly kept appearing. The seeming impossibility was due to the fact that, given their periodicity, crystals can only present rotational symmetries of 2-fold, 3-fold, 4-fold, and 6-fold, as can be shown mathematically (crystallographic restriction theorem). The symmetry of periodic media, such as crystals, had been firmly established by the end of the 19th century and had culminated in the enumeration of 230 symmetry space groups.

Figure 4 provides a graphic demonstration of the crystallographic restriction theorem in the case of a 4-fold rotation axis. Thus, when two parallel quaternary axes are rotated 90º, new quaternary axes are generated that place themselves periodically. Figure 5 illustrates the analogous situation for a 6-fold rotation axis (60º). With 2-fold and 3-fold axes, the same result is obtained; in other words, a periodic medium is also generated.

When trying the same procedure for the 5-fold axis (Fig. 6) or any other rotation axis other than those listed above, the result is not a periodic medium, but rather many points that continue to densely fill the space.

The reaction of the scientific community

When Dan Shechtman tried to publicize his results, he was met with strong opposition, as has so often happened in the history of science (think of Miguel Servet, Galileo Galilei, and others). Luckily, in the 20th century being burned at the stake or sentenced to prison was no longer considered an appropriate response to controversial ideas such as Shechtman's. Nevertheless, he ended up leaving the laboratory where he had worked and his findings continued to receive intense criticism from the scientific community. Even such an important personality as the double Nobel Prize laureate L. Pauling was of the opinion that "there is no such thing as quasicrystals, only quasi-scientists."

His results were repeatedly denied publication in the scientific journals until two long years later, when they were published in the journal *Physical Review Letters,* in 1984 [20]. Meanwhile, the work of other scientists furthered the doubt of the scientific community regarding the existence of quasicrystals.

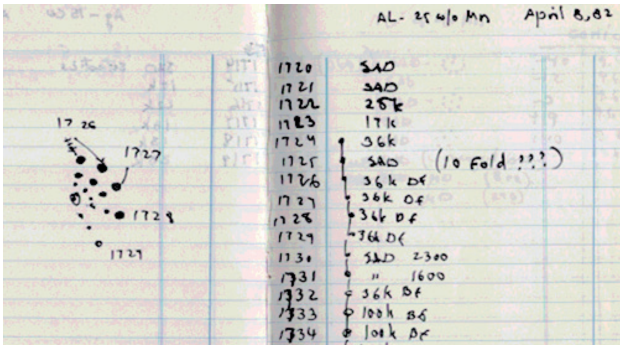

Fig. 3. Dan Shechtman's laboratory logbook for April 8, 1982.

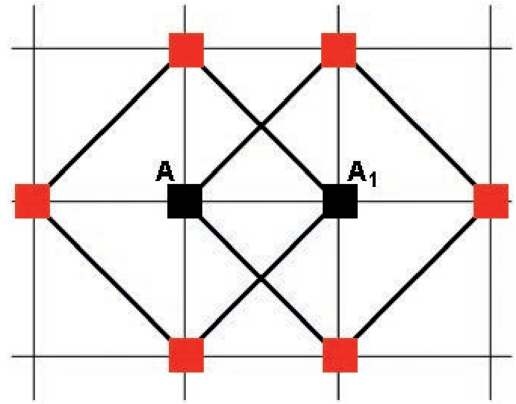

Fig. 4. The action of a 4-fold rotation axis generates four new axes. If the process is repeated, a periodical medium is obtained. To illustrate this, axis A has been applied first, and axis A_1 after.

Acceptance of quasicrystals and new discoveries

Nonetheless, Dan Shechtman and other scientists were ultimately able to build support for the existence of quasicrystals [16,18,21,23] such that by the early 1990s this phenomenon had gained general acceptance.

Most quasicrystals described to date correspond to alloys, but others of different composition were discovered as well. Thus, quasicrystals turned out to be a more general phenomenon than had originally been thought and they have been observed in, for example, chalcogenides [9], polymers [13], liquid crystals [25], and nanoparticles [22]. There is even a natural quasicrystal, a mineral called icosahedrite [5,6].

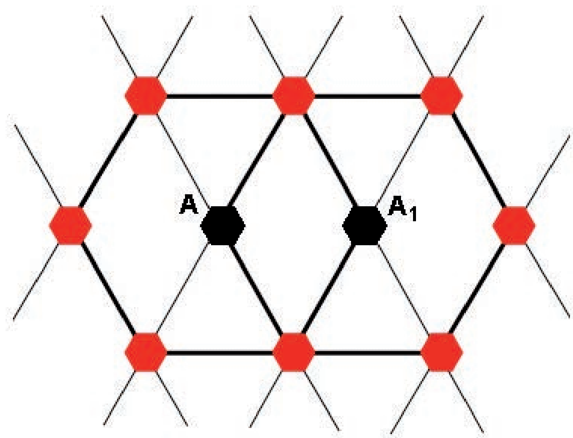

Fig. 5. Action of a 6-fold rotation axis. As with the axis in Fig. 4, a periodic medium is obtained.

Properties and applications

The first quasicrystals obtained were metastable, which made them difficult to study and seemed to limit their possible applications, as their structure would disappear rapidly. In 1987, the first stable quasicrystal, with the formula $Al_{65}Cu_{20}Fe_{15}$, was discovered [23], followed by reports of other stable quasicrystals. These were essentially aluminum alloys and they opened the door both to detailed studies of their properties and to their possible applications [10].

Along these lines, important differences were observed regarding the thermal and electrical properties of alloys with a quasicrystalline vs. crystalline structure. For example, the thermal conductivity of AlFeCu and AlPdMn, two alloys with a quasicrystalline structure, is 100 times lower than that of either pure aluminum or zirconium dioxide (ZrO_2), which is known to be a good thermal insulator [11].

The electrical conductivity of quasicrystals is also highly inferior to that of metals, but they cannot be considered as standard insulators, since their conductivity increases substantially as the temperature rises. However, their behavior differs from that of semiconductors, too [4]. Quasicrystals also have an atypical magnetic behavior, with alloys con-

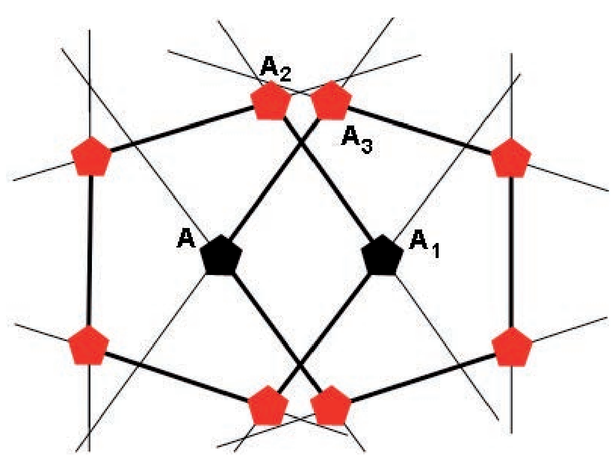

Fig. 6. The action of a 5-fold rotation axis produces close points (for instance, A_2 and A_3), which as the process continues densely fill the plane with 5-fold axes. There is no periodicity.

A B C

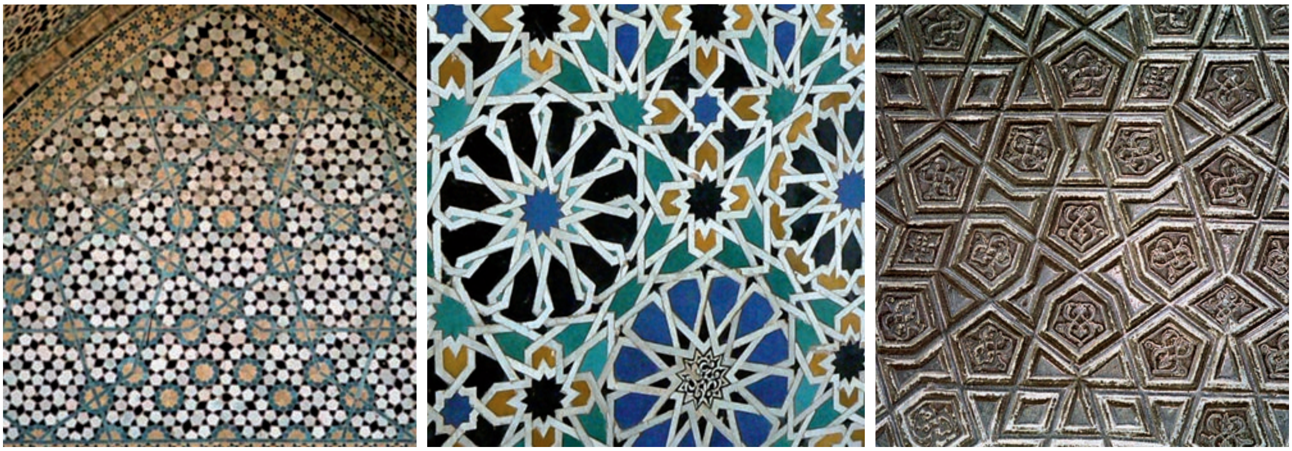

Fig. 7. (**A**) Darb-e Imam, Isfahan (Iran). (Image courtesy of Prof. Dudley / Elliff, www.kendalldudley.com, Arlington, MA). (**B**) The Alhambra, Granada (Spain). (Image courtesy of Roberto Veturini,"Alhambra Tiles 15" November 7, 2008 via Flickr, Creative Commons Attribution). (**C**) Sultan Ahmed Mosque, Istanbul (Turkey). (Image courtesy of Prof. Mehmet Erbudak, Bogaziçi University, Istanbul).

taining transition metals, such as Fe or Mn, tending to be diamagnetic rather than paramagnetic [3].

In terms of their mechanical properties, quasicrystals are exceptionally hard [24]. This is a function of their non-periodic nature, which hinders the presence and propagation of dislocations. For this same reason, quasicrystals are also fragile, which limits their practical use when they appear in massive form. At the same time, however, when used as coatings or surface treatments their inherent fragility is reduced.

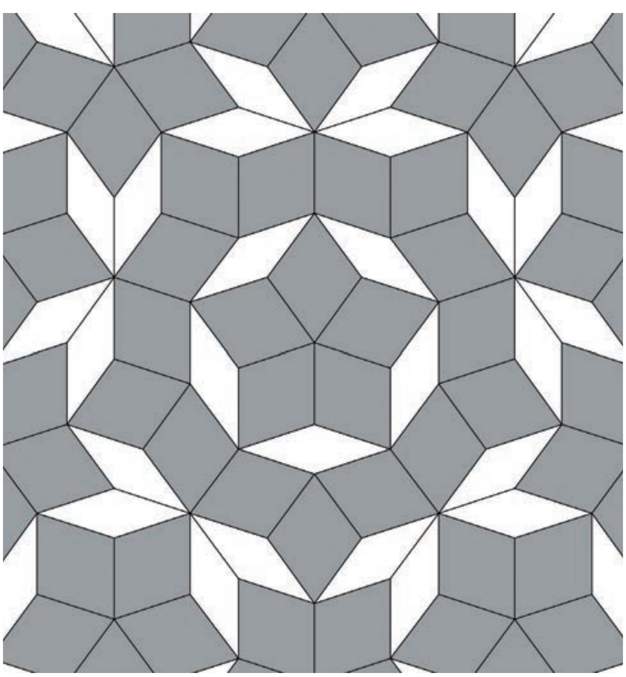

Fig. 8. Penrose tiling. The mosaic is made up of two types of rhombuses that, once coupled, produce a 5-fold symmetry. There is no periodicity. (Image courtesy of Domesticat, June 8, 2012 via Flickr, Creative Commons Attribution-Noncommercial-ShareAlike).

Chemically, quasicrystals are highly resistant to oxidation and corrosion, comparable to stainless steel [8], which has encouraged their patented application in surgical material, acupuncture needles, and razor blades [17]. In addition, quasicrystal surfaces have very small coefficients of friction and are therefore of interest as antiadhesive materials [12], e.g., in cookware and in parts of combustion engines. In the case of cooking utensils, superficial treatment with Teflon has been replaced by quasicrystal coatings, as these are much more heat resistant [1]. A disadvantage is that the antiadherence of Teflon is slightly better and that with quasicrystals spallation of the material must be avoided, as it can result in toxicity.

Numerous potential applications of quasicrystals have been described, including the storage of hydrogen [15], catalysis [14], and the strengthening of composites [7]. These and other applications of quasicrystals are currently fields of active investigation that will no doubt eventually yield interesting results.

The structure of quasicrystals

Soon after the discovery of quasicrystals, efforts were made to elucidate the distribution of their atoms, i.e., to determine their crystalline structure and thus why their diffractions violate the sacred rules of crystallography. In 1986, P. Bak published an article with the title, "Icosahedral Quasicrystals: Where Are the Atoms?" [2].

A rigorous explanation of the structure of quasicrystals is beyond the scope of this report, but a basic explanation can be attempted. Quasicrystals can be described as groupings of ordered atoms that have long-distance symmetry (just like conventional crystals) but no periodicity. It is this organization of matter that was previously considered to be scientifically impossible.

An excellent bidimensional model of the structure of quasicrystals can be found in some of the tiling of mosques and other Islamic buildings. Indeed, it is quite remarkable that a structure that puzzled 20th century science was in full view for centuries and been seen and admired by thousands of people for centuries [19]. Figure 7 provide representative examples of the typical symmetries of quasicrystals.

In addition, in 1970, the mathematician and physicist Roger Penrose described what came to be called “Penrose tiling,” which are basically mosaics made up of two pieces of rhombic shape that can fill (*tile*) the whole plane while never repeating (i.e., there is no periodicity) and which present pentagonal symmetry, as do quasicrystals. Figure 8 shows one of these mosaics.

* * *

Given the great number of cases of quasicrystals described experimentally, and the convincing theories that explain their structure and properties, in 1992 the International Union of Crystallography changed the definition of “crystal” to incorporate quasicrystals. This was, all things considered, a great triumph for Dan Shechtman… and for science in general.

Main publications underpinning the award

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To learn more

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