Article

The 2011 Nobel Prize in Chemistry

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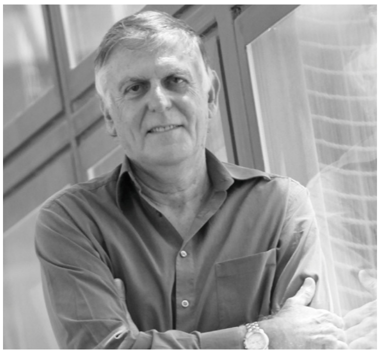

2011 Nobel Laureate Daniel Shechtman; courtesy of the Technion – Israel Institute of Technology

The Royal Swedish Academy of Sciences has awarded the 2011 Nobel Prize in Chemistry to Dan Shechtman of Technion - Israel Institute of Technology, Haifa, Israel, for the discovery of quasicrystals. In 1982, Shechtman, a materials scientist, discovered crystals with structures that many believed to be impossible but he held his ground against fierce opposition, scorned even by luminaries including double-Nobel-prizewinner Linus Pauling. The crystals have the fascinating mosaics of the Arabic world reproduced at the level of atoms with regular patterns that never repeat themselves. This Nobel Prize in Chemistry is for work that has fundamentally altered the way in which chemists conceive of solid matter.

Dan Shechtman recorded an image counter to the laws of nature in electron microscope on the morning of 8 April 1982. He was working at the National Institute of Standards and Technology (NIST) in the US while on leave from the Technion. On entering the result into his notebook apparently he followed it with three question marks, saying to himself "There can be no such creature". The material he was studying was an unusual looking aluminium/manganese mix, which he hoped would yield useful information from electron microscopy at the atomic level. The microscope produced an image of concentric circles, each made of ten bright dots at the same distance from each other (Fig. 1) and contrary to all logic.

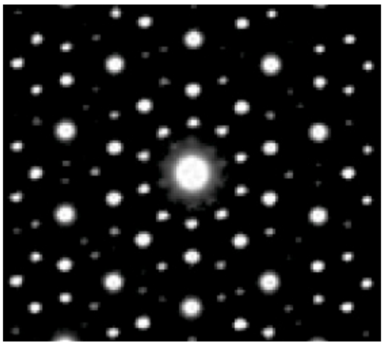

Fig. 1. Shechtman's ten-fold diffraction pattern; rotating the image through 36^o results in the same pattern (adapted from *Scientific Background on the Nobel Prize in Chemistry 2011*, with permission from The Royal Swedish Academy of Sciences; www.nobelprize.org/nobel_prizes/chemistry/laureates/2011/info.htm).

Shechtman had rapidly chilled the glowing molten metal hoping for complete disorder among the atoms, but what he recorded was a pattern contrary to the laws of nature. There were ten dots in each circle - not the four or six accepted theory would generate. The crystal symmetry was not represented in the International Tables for Crystallography, and science plainly stipulated that a pattern with ten dots in a circle was impossible, and the proof for that was as simple as it was obvious. All solid matter consists of atoms symmetrically packed inside a crystal in a pattern that repeated periodically over and over again. Three-, four- and six-fold symmetries are common, but five-, seven- and higher-fold symmetries were regarded as impossible. Shechtman's image, with its ten concentric dots, showed that the atoms in his crystal were packed in a pattern that could not be repeated. In addition, having shown that he was not dealing with a twinned crystal, he rotated the crystal in the electron microscope in order to see how far he could turn it before the ten-fold diffraction pattern reappeared. That experiment showed that the crystal itself did not have ten-fold symmetry like the diffraction pattern, but instead was based on an equally impossible five-fold symmetry. If correct, the scientific community had to be mistaken in its assumptions.

When Shechtman advised colleagues of the discovery, he was faced with total opposition, even ridicule. Many claimed that he had a twin crystal, but he was sure this was not the case. Eventually, he was asked to leave his research group. However, he persisted with his study and, in 1983, he persuaded Ilan Blech, a colleague at the Technion, to look at his peculiar research findings. Together they attempted to interpret the diffraction pattern and translate it to the atomic pattern of a crystal. They submitted an article to the *Journal of Applied Physics* in the summer of 1984, but the article came back rapidly; seemingly the editor had decided it was inappropriate for publication. Shechtman then asked John Cahn, the renowned NIST physicist, to take a look at his data. Eventually Cahn did this, and then in turn, consulted with French crystallographer, Denis Gratias, in order to see if Shechtman could have missed something. According to Gratias, Shechtman's experiments were reliable and the data obtained in a manner he himself would have adopted had he conducted the experiments. Thus, it was that in November 1984 Shechtman finally published his data jointly with Cahn, Blech and Gratias in *Physical Review Letters*.[1]

The article had a dramatic impact on the crystallography community as it questioned the most fundamental truth of their science, namely, that all crystals consist of repeating, periodic patterns. Following the appearance of the paper, the wider audience subjected Daniel Shechtman to even more criticism, but, at the same time, other crystallogra-

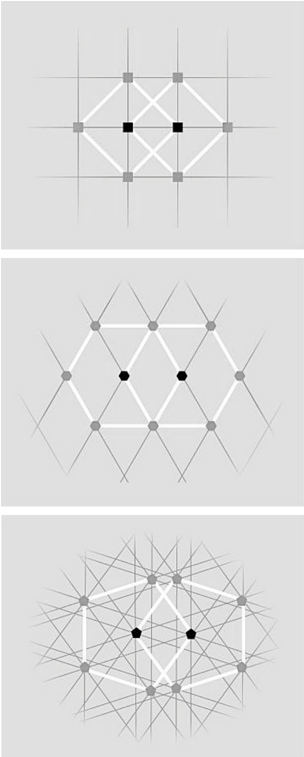

Fig. 2. Two 4-fold (upper) or 6-fold (centre) axes of rotation generate new rotational axes at the same distance of separation as in the original pair. Repeating the procedure yields periodicity. For the pair of 5-fold axes (lower), the procedure instead generates a new, shorter distance. An iterative procedure will thus fill the plane densely with 5-fold axes, and no periodicity will result (adapted from *Scientific Background on the Nobel Prize in Chemistry 2011*, with permission from The Royal Swedish Academy of Sciences; www.nobelprize.org/nobel_prizes/chemistry/laureates/2011/sci.html).

phers began to reassess results they had obtained, but presumed to be generated by a twinned crystal. Examples of quasicrystals flooded in from around the globe. Over the next while, other crystals began to appear with equally seemingly impossible patterns, such as eight- and twelve-fold symmetry.

At the time that Shechtman published his discovery, he still had no clear grasp of what the interior of the strange crystal looked like. Evidently its symmetry was five-fold, but how were the atoms packed? The answer to that question came from an unexpected quarter – that of mathematical games with mosaics.

During the 1960s, mathematicians began to explore whether a mosaic could be laid with a limited number of tiles so that the pattern never repeated itself, to create a so-called *aperiodic mosaic*. First successful in 1966, British professor Roger Penrose subsequently provided a more elegant solution by creating mosaics with just two different tiles, *e.g.* a fat and a thin rhombus.[2] His findings have since been used to analyze medieval Islamic Girih patterns, and it is now known that Arabic artists produced aperiodic mosaics out of five unique tiles as early as the 13th century. Such mosaics decorate the extraordinary Alhambra Palace in Spain and portals and vaults of the Darb-i Imam Shrine in Iran. Crystallographer Alan Mackay took to applying the Penrose mosaic to the atomic world to see whether atoms could form aperiodic patterns like the mosaics. An experiment in which circles (representing atoms) were substituted at intersections in the Penrose mosaic and then used as a diffraction grating actually provided ten-fold symmetry – ten bright dots in a circle.[3] The connection between Mackay's model and Shechtman's diffraction pattern was made by physicists Paul Steinhardt and Dov Levine.[4] During the review process of Shechtman's1984 article,[1] Steinhardt got the opportunity to read the manuscript and he realized that Mackay's theoretical tenfold symmetry really existed in Shechtman's laboratory. On Christmas Eve, 1984, only five weeks after Shechtman's article appeared in print, Steinhardt and Levine published an article where they described quasicrystals and their aperiodic mosaics.[4] The name "quasicrystals" was coined in this article and is a material that exhibits long-range order in a diffraction experiment and yet does not have translational periodicity.

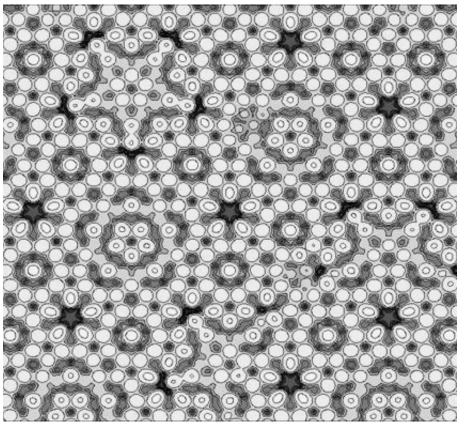

Fig. 3. Atomic model of an Al-Pd-Mn quasicrystal surface (*en.wikipedia.org/wiki/File:Quasicrystal1.jpg*).

In order to describe Shechtman's quasicrystals, a concept that comes from mathematics and art - *the golden ratio (τ)* – has to be invoked. In quasicrystals, the ratio of various distances between atoms is related to the golden mean. This mathematical constant occurs over and over again. Thus, the ratio between the numbers of fat and thin rhombi in Penrose's mosaic and the ratio of various distances between atoms in quasicrystals is always related to τ. In the mathematical number sequence 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, 233, *etc*., each number is the sum of the two preceding numbers. Moreover, if a higher number in the sequence is divided by the preceding number, *e.g.* 233 by 144, the resulting number is close to the golden ratio. Both this *Fibonacci sequence* and the golden ratio are important in crystallography when a diffraction pattern is used to describe quasicrystals at the atomic level. Prior to the acceptance of Shechtman's results, chemists interpreted regularity in crystals as a periodic and repeating pattern, three-, four- and six-fold symmetries. The Fibonacci sequence too, is regular, despite never repeating itself, simply because it follows a mathematical rule. Thus, the golden ratio τ appears naturally in all manifestations of five-fold symmetry as the relation between the diagonal and the edge in a regular pentagon; it is inextricably linked to the Fibonacci sequence.

The interatomic distances in a quasicrystal are patterned in an orderly manner, and the diffraction data allow one to see what a quasicrystal looks like on the inside. Importantly, however, this regularity is not the same as that for a periodic crystal. This realization led the International Union of Crystallography, in 1992, to alter its definition of a crystal. Previously, a crystal had been defined as *a substance in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating three-dimensional pattern*, but now the definition is broader and is *any solid having an essentially discrete diffraction diagram.* This allows for possible future discoveries of other kinds of crystals.

The quasicrystals discovered by Shechtman in 1982 were synthetic intermetallics, and since then such systems have afforded very many quasicrystalline materials. The first quasicrystalline material in a different system came from dendrimer liquid crystals, but it was only in 2009 that the first report of naturally occurring quasicrystals appeared.[5] An alloy of aluminium, copper and iron, acquired by an Italian museum in 1990, but reported to have come from 200-million-year-old rocks in the Khatyrka River in Chukhotka, Eastern Russia, provided a diffraction pattern with ten-fold symmetry. The mineral was named icosahedrite, after the geometrical solid with sides consisting of twenty regular three-cornered polygons and with the golden ratio integrated into its geometry. Quasicrystals have also been found in very durable steel made by a Swedish company. They formulated a steel the analysis of which showed it to consist of two different phases - hard steel quasicrystals embedded in a softer kind of steel. Enhanced strength is seen because the quasicrystals function as armour; this product is now used in razor blades and thin needles for eye surgery. Despite being very hard, like glass, quasicrystals can easily fracture. Their unique atomic structure makes them poor conductors of heat and electricity. They have non-stick surfaces and are useful thermoelectric materials. Today, quasicrystals are being examined for use as in, amongst other things, surface coatings for frying pans, components for energy-saving light-emitting diodes (LEDs), and for heat insulation in engines.

References

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