Daniel Shechtman, Quasicrystals, and Golden Ratio: A Review of the Great Discovery

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1. INTRODUCTION :

Solids have definite mass, volume, and shape due to the fixed positions of their constituent particles. Up to the early 1980s, based on the structure of the material, there were only two different types of solids: amorphous (e.g., coal, glass, plastic, rubber, etc.) and crystals [e.g., copper(Cu), copper sulphate ($CuSO_4$), $NiSO_4$, diamond, graphite, NaCl, sugar, etc.]. However, after the early 1980s, three types of solids were known, namely, amorphous, crystals, and quasicrystals. Quasicrystals are found most commonly in aluminium alloys (Al-Li-Cu, Al-Mn-Si, Al-Ni-Co, Al-Pd-Mn, Al-Cu-Fe, Al-Cu-V, etc.), but are also found in several other compositions (Cd-Yb, Ti-Zr-Ni, Zn-Mg-Ho, Zn-Mg-Sc, In-Ag-Yb, Pd-U-Si, etc.). (Maclá, 2006)

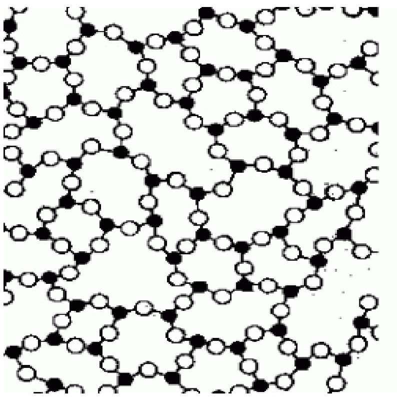

Fig. 1: Amorphous structure of a glassy solid

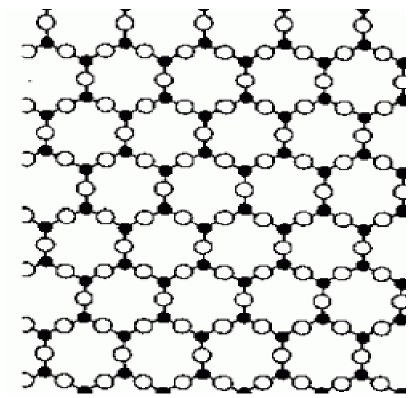

Fig. 2: Lattice structure of a crystalline solid

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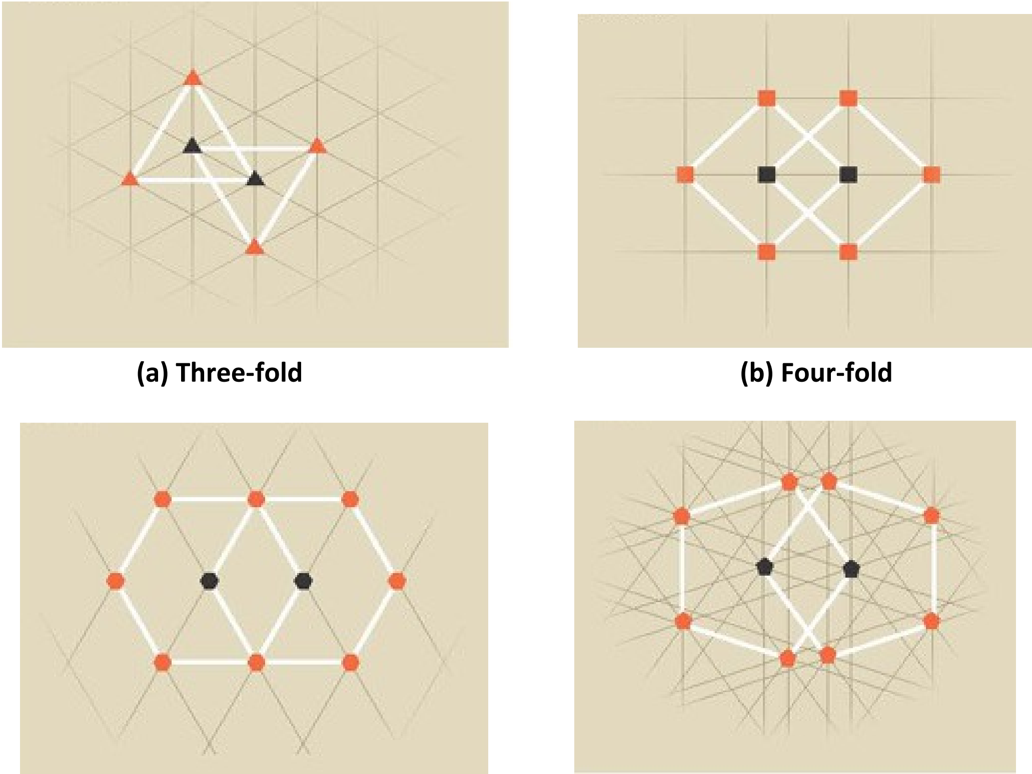
Remark: *The word amorphous is derived from the Greek word 'morphe'. In Greek the word 'morphe' means shape or form; and hence, amorphous (a + morph + ous) means 'without shape' or 'shapeless'. In condensed matter physics and materials science, an amorphous solid is any non-crystalline solid in which the atoms and molecules are not organized in a definite lattice pattern. (A lattice is a regular arrangement of particles like atoms, ions, or molecules.) Thus an amorphous solid is a solid that lacks the long-range order characteristic of a crystal. Such solids include glass, plastic, and gel. Solids and liquids are both forms of condensed matter, and both are composed of atoms in close proximity to each other. In some older books, the term has been used synonymously with glass. Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays.*

Most crystals in nature, such as those in sugar, salt, or diamonds, are symmetrical and all have the same orientation throughout the entire crystal. In all solid matters, atoms were believed to be packed inside crystals in symmetrical patterns that were repeated periodically over and over again. For scientists, this repetition was required in order to obtain a crystal.

Fig. 3: Crystalline faces: the faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS_2), or at other angles, as in quartz. (Courtesy U C Davis, ChemWiki)

Fig. 4: Cleavage surfaces of an amorphous solid: Obsidian, a volcanic glass with the same chemical composition as granite (typically $KAlSi_3O_8$), tends to have curved, irregular surfaces when cleaved (Courtesy: U C Davis, ChemWiki)

Traditional crystallography has defined a crystalline structure as an arrangement of atoms (in a lattice) that is periodic in three dimensions with two-, three-, four-, and six-fold (or hexagonal) rotational symmetry. Crystals have a *lattice structure.* It has a regular geometrical arrangement of points in crystal space, i.e., a three-dimensional array of points or lattice points with identical arrangements of atoms with space filling cubes or hexagonal prisms. It was always believed that all metals had crystallized materials which were usually made up of unit cells of atoms that are repeated to form a single uniform structure.



(a) Three-fold **(b) Four-fold**

(c) Six-fold **(d) Five-fold**

Fig. 5: Different kinds of symmetries in crystals - the pattern within the crystal with five-fold symmetry will never repeat itself

Remark: *The structure of a crystal can be seen to be composed of a repeated element in three dimensions. This repeated element is known as the 'unit cell'. The unit cell is defined in terms of the lattice (set of identical points). It is the building block of the crystal structure. In crystallography, the crystal structure is a description of the ordered arrangement of atoms, ions, or molecules in a crystalline material. The unit cell is repeated many billions of times in every direction to obtain acrystal. In three-dimension, the unit cell is any parallelepiped whose vertices are lattice points, and in two-dimension, it is any parallelogram whose vertices are lattice points.*

As stated above, inside a crystal, atoms are ordered in repeating patterns and depending on the chemical composition, they have different symmetries. In Fig. 5(a), it is seen that each atom is surrounded by three identical atoms in a repeating pattern, yielding a three-fold symmetry. If the image is rotated 120^o, the same pattern can be obtained. The same principle applies to four-fold symmetries [Fig. 5(b)] and six-fold symmetries [Fig. 5(c)]. The pattern repeats itself, and if the image is rotated 90 degrees and 60 degrees, respectively, the same pattern appears. However, with five-fold symmetry [Fig. 5(d)], this is not possible, as distances between certain atoms will be shorter than those between others. The pattern does not repeat itself, which was proof enough to scientists that it was not possible to obtain five-fold symmetries in crystals. The same applies to seven-fold or higher symmetries.

2. DISCOVERY OF QUASICRYSTALS:

On the morning of April 8, 1982, an image counter to the laws of nature appeared in Daniel Shechtman's electron microscope, while on sabbatical (as a visiting scholar) at the National Bureau of Standards in Gaithersburg, Maryland, USA. Professor Shechtman was busy examining a rapidly cooled metal alloy (a mix of aluminium and manganese). He observed a strange looking crystal that did not obey the physical laws that crystals are supposed to obey. "Eyn chaya kazo", Shechtman said to himself, — "There can be no such creature" in Hebrew, and he had turned to the electron microscope in order to observe it at the atomic level. However, the picture that the microscope produced was counter to all logic: he saw concentric circles, each made of ten bright dots at the same distance from each other (Fig. 6).

Fig. 6: Daniel Shechtman's diffraction pattern was ten-fold: rotating the picture to a tenth of a full circle (36°) results in the same pattern (Credit: Shechtman; Royal Swedish Academy of Sciences)

It was always believed that metals had crystallized materials which were usually made up of unit cells of atoms that are repeated to form a single uniform structure. However, while examining a rapidly cooled mix of aluminium (Al) and manganese (Mn), an alloy with potential uses in aerospace technologies, Daniel Shechtman found that the atoms packed in this alloy were in a pattern that could not be repeated — something that was forbidden according to known chemistry. The atoms in the sample seemed to be arranged in a pattern that had a five-fold rotational symmetry.

For the first time Daniel observed a three-dimensional example of a Penrose pattern (to be discussed in Section 4) in the material world — *quasiperiodic crystals*, also known as *quasicrystals*. (Shechtman, Blech, Gratias, and Cahn, 1984) An alloy of aluminium and magnesium (Al_6Mn) was discovered in the laboratory which exhibited the symmetry of an icosahedron with five-fold axis — it showed the kind of symmetries and non-periodic patterns previously known only theoretically from Penrose's thick and thin rhombs (or kites and darts).

Shechtman's image showed that the atoms in his crystal were packed in a pattern that could not be repeated. Such a pattern was considered just as impossible as creating a football — a sphere — using only six-cornered polygons, when a sphere needs both five- and six-cornered polygons. With 5-fold symmetry, once thought to be impossible, they were first observed by Daniel Shechtman in an aluminium-manganese alloy. Daniel named these structures as *quasicrystals*.

It was always believed that metals had crystallized materials which were usually made up of unit cells of atoms that are repeated to form a single uniform structure. However, Daniel Shechtman, while examining a rapidly cooled mix of aluminium and manganese, a metal alloy with potential uses in aerospace technologies, found that the atoms packed in this alloy were in a pattern that could not be repeated — something that was forbidden according to known chemistry. The atoms in the sample seemed to be arranged in a pattern that had a five-fold rotational symmetry.

Daniel moved out from his office into the corridor at the U.S. National Institute of Standards and Technology (NIST) (in the City of Gaithersburg, in Montgomery County, Maryland) wanting to find someone with whom he could share his discovery. But the corridor was empty, so he went back to the microscope to carry out further experiments on the peculiar crystal. Among other things, he double-checked if he had obtained a twin crystal: two inter-grown crystals whose shared boundary gives rise to strange diffraction patterns. Many claimed that what he had observed was in fact a twin crystal; but he could not detect any signs that he was in fact looking at a twin crystal.

Furthermore, he rotated the crystal in the electron microscope in order to see how far he could turn it before the tenfold diffraction pattern reappeared. That experiment showed that the crystal itself did not have ten-fold symmetry like the diffraction pattern, but was instead based on an equally impossible five-fold symmetry. Daniel Shechtman concluded that the scientific community must be mistaken in its assumptions.

Shechtman had rapidly chilled the glowing molten metal, and the sudden change in temperature should have created complete disorder among the atoms. But the pattern he observed told a completely different story: the atoms were arranged in a manner that was contrary to the laws of nature. Shechtman counted and recounted the dots. Four or six dots in the circles would have been possible, but absolutely not ten. He made a notation in his notebook: 10-fold???

The diffraction pattern showed that the atoms inside the metal were packed into an ordered crystal. That in itself was nothing extraordinary; almost all solid materials, from ice to gold, consist of ordered crystals. However, unexpected appearance of ten bright dots in each concentric circle in the material's diffraction pattern (Fig. 6) initially baffled Shechtman (and others) — it was something he had never seen before, despite his vast experience using electron microscopes. Furthermore, such a crystal was not represented in the International Tables for Crystallography — the main crystallographic reference guide. At the time, 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.

Shechtman's image showed that the atoms in his crystal were packed in a pattern that could not be repeated. He followed up the initial data with other experiments that also indicated the material had a five-fold symmetry, a characteristic that was thought to be impossible.

It was shown that rapid solidification of an aluminum-manganese alloy (Al_6Mn) can produce a solid that diffracts electrons like a crystal but has no lattice-based translational symmetry (as crystals do). A quasiperiodic structure is generated using a pair of polyhedral, the three-dimensional analogues of the two-dimensional Penrose tiles, which tile the plane aperiodically (discussed in detail Section 4). These polyhedra will produce a diffraction pattern when bombarded with gamma rays (a method of analyzing crystal structures) which suggests that the two polyhedra occur in the ratio of 1.618:1 (or ϕ:1, where ϕ is the golden ratio). These crystals are now called *quasicrystals*, or *quasiperiodic crystals* ('quasi' means 'apparently but not really'), and they have changed the way chemists view solid state chemistry. (Shechtman, 1986) The NGR (Nuclear Gamma-ray Resonance) spectrum of this crystal structure appears as shown in Fig. 7.

Rather than finding a random collection of atoms as expected, Shechtman observed a diffraction pattern with ten-fold rotational symmetry, something which was thought to be impossible (subsequent experiments would demonstrate that what Shechtman had discovered was actually five-fold symmetry). Shechtman's five-fold symmetry defied the basic definition of a crystal which had stood unchallenged since crystallography's inauguration as a science some 70 years prior (as stated above). Shechtman later described them as "fascinating mosaics of the Arabic world reproduced at the level of atoms." (Lannin and Veronica, 2011) "An intriguing feature of such patterns, also found in Arab mosaics, is that the mathematical constant known as the the 'golden ratio', denoted by the Greek letter ϕ (Phi), occurs over and over again. Underlying it is a sequence worked out by the great Italian mathematician Leonardo Fibonacci in the 13th century CE, where each number is the sum of the preceding two." (Lannin and Veronica, 2011)

The foregoing spectrum (Fig. 7) displays two quadripole doublet peaks. The least-squares regression fit for these curves saw minimized standard deviations (which is statistically a good thing — the lower the standard deviation, the closer the data is to the mean) when the intensity ratio was constrained to be 1.618, the golden ratio (Phi). This suggests that Phi is involved in determining the spacing between the atoms in the quasicrystalline lattice structure. (Swartzendruber et al, 1985, p. 1384-85)

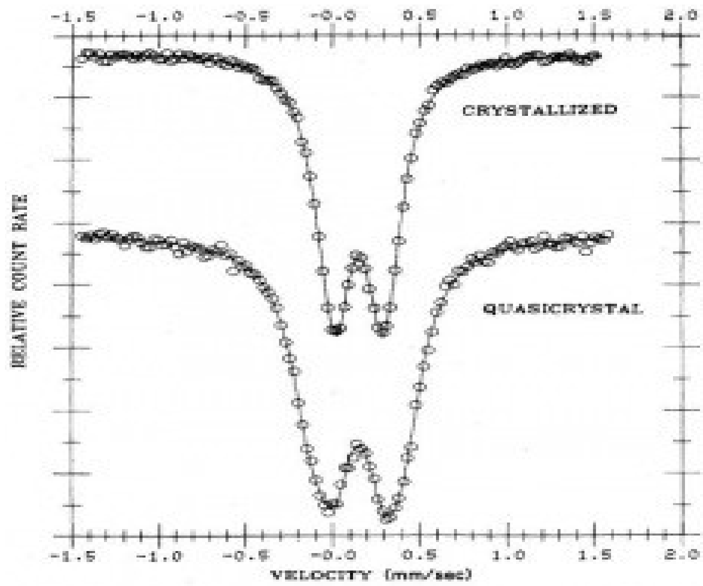


Fig. 7: The Nuclear Gamma-ray Resonance (NGR) Spectrum for crystallized Al-Mn alloy (the image from Swartzendruber et al, 1985, p. 1384). The circles are data points and the solid line is the least squares fit obtained as described in text. The zero of velocity represents the centre of a pureiron spectrum at room temperature and positive velocity represents source and absorber approaching.

Quasiperiodic crystals are regular; yet, they form non-repeating patterns (that never repeat themselves) which usually appear in aluminum alloys. Quasicrystalline patterns comprise a set of interlocking units whose pattern never repeats, even when extended infinitely in all directions, and possess a special form of symmetry.

Fig. 8: Daniel Shechtman, who discovered quasicrystals, displays a model at his lab in Haifa, Israel (Photograph: David Blumenfeld)

However, Shechtman's discovery was viewed with skepticism; this form of matter, i.e., the configuration found in quasicrystals, was believed to be impossible to create, and Daniel Shechtman had to fight a fierce battle against established science. "I told everyone who was ready to listen that I had material with pentagonal symmetry. People just laughed at me," Shechtman recalls when he was interviewed in his office at the Israel Institute of Technology at Haifa, surrounded by numerous prizes he has won before the crowning glory of the Nobel award. In fact, Shectman lost his job soon after his discovery.

In early 1982, the head of the laboratory where Daniel Shechtman worked came to his desk "smiling sheepishly". Shechtman recalls what happened next: "He put a (crystallography) book on my desk and said, 'Danny, why don't you read this and see that it is impossible what you are saying.' And I said, 'You know, I teach this book. I don't need to read it. I know it's impossible, but here it is. This is something new!' That person expelled me …. He said, 'You are a disgrace to our group. I cannot bear this disgrace.' And, he asked me to leave the group; so I left the group. He was a good friend of mine." (Dibben, 2011; Jha, 2013) Shectman was kicked out of his university research group, of course this situation had become too embarrassing. However, Daniel found a new group that adopted a scientific orphan. Shechtman recapitulates, "The scandal of polywater was still in the air, and I feared for my scientific and academic career."

That should have been the end of the story were it not for Linus Pauling — a two-time Nobel prize winner, once for chemistry (in 1954) and a second time for peace (in 1962) — accused him of "talking nonsense", and delivered the ultimate insult: "There is no such thing as quasicrystals, only quasiscientists." (Ho, 2011; Jha, 2013) This Pauling said at a science conference in front of an audience of hundreds. Pauling was apparently unaware of a 1981 paper by Hagen Kleinert (Polish-born German theoretica Physicist) and Kazumi Maki (world-renowned Japanese physicist in the field of superconductivity) which had pointed out the possibility of a non-periodic Icosahedral Phase in quasicrystals. (Kleinert and Maki, 1981)

Shechtman had obtained his PhD degree from Technion, Israel Institute of Technology, Haifa, Israel, and in 1983, he managed to get Ilan Blech, a colleague at his alma mater, interested in his peculiar research findings. So, he moved to Technion where Dr. Ilan Blech was perhaps the only colleague who not only believed in him but who agreed to cooperate with him. Blech was able to decipher Shechtman's experimental findings and offered an explanation, known as the *Icosahedral Glass Model*. Together they attempted to interpret the diffraction pattern and translate it to the atomic pattern of a crystal. They wrote an article that contained the model and the experimental results, and submitted it to the Journal of Applied Physics in the summer of 1984. But, the paper was immediately rejected by the editor, and came back seemingly by return of post. They resubmitted it to the journal Metallurgical Transactions, and was published (on the second try) in 1985, but his results were still mocked and derided.

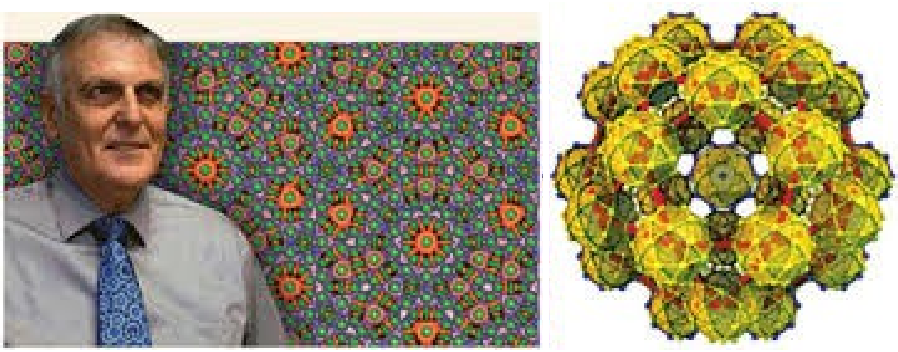


Fig. 9: Daniel Shechtmanand 3-D model of his quasicrystal

Meanwhile, Shechtman asked John Werner Cahn, a renowned German-born American physicist who had lured him over to NIST in the first place, to take a look at his data. The otherwise busy researcher Cahn eventually did, and in turn, he consulted with a French crystallographer, Denis Gratias, in order to see if Shechtman could have missed something. But according to Gratias, Shechtman's experiments were reliable. Gratias would have proceeded in the same manner had he conducted the experiments himself. In November 1984, Physical Review Letters published Shechtman's discovery in a scientific paper co-authored with three other scientists: Ilan Blech (Israel), Denis Gratias (France), and John Cahn (USA). (Shechtman, Blech, Gratias, and Cahn, 1984) Wider acclaim followed, mainly from physicists and mathematicians and later from crystallographers. Cahn et al's contribution to Shechtman's work was primarily to confirm his findings and conclusions about the existence of what came to be known as quasicrystals.

In its 5th October 2011 issue, The American Ceramic Society writes, "Shechtman's assertions made him an outcast for a few years, but his dogged pursuit of an explanation of his findings eventually put him ahead of other researchers who, as it turns out, had observed similar patterns and data but had too-hastily dismissed the diffractions as being the result of twinned or intermingled crystals."

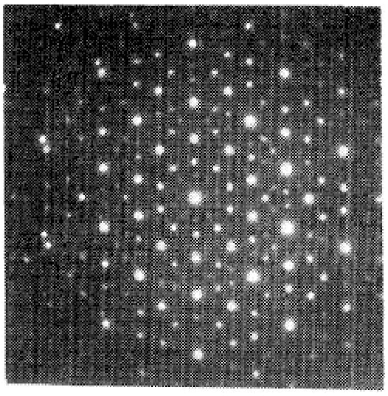


Fig. 10: Ten-fold way: Quasiperiodic patterns have small repeating elements but on a larger scale do not exactly repeat (top). Daniel Schechtman's electron diffraction pattern from a metal alloy shows spots with a ten-fold rotational symmetry, which researchers in 1984 thought was impossible for a crystal (bottom). Today researchers call the material a quasicrystal because its structure is quasiperiodic. *(Levine and Steinhardt, 1984)*

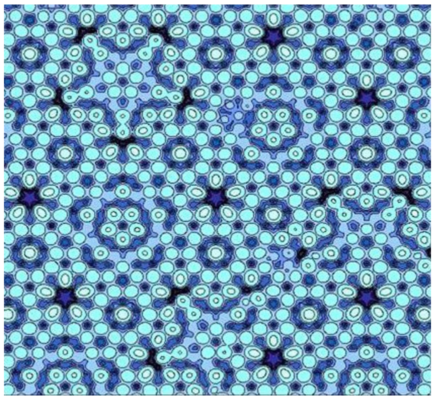


Fig. 11: A quasicrystal of silver aluminum similar to the first quasicrystal of magnesium aluminum discovered by Daniel Shechtman. Although the pentagons in this quasicrystal can't fit together as squares and triangles do, other atomic shapes fill the gaps — patching holes. *(Photograph: Wikimedia Commons)*

"When I came out with my results, people found it difficult to accept. It was easier to say 'Don't they know anything about crystallography at Technion? Don't they read the books?' I had to defend it a while," said Shechtman. It took two years from the initial discovery for Shechtman to publish his results. After their publication, according to Shechtman, "all hell broke loose."

"Shortly after the first publication, there was a growing community of avant-garde young scientists from around the world who all supported me and joined the fight, so I was not alone anymore," he said. "But in the first two years I was alone."

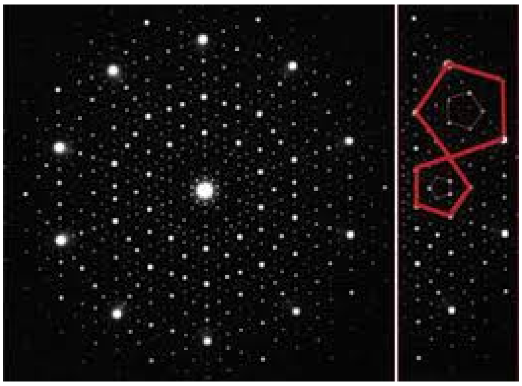


Fig. 12: Electron diffraction pattern from an icosahedral quasicrystal containing perfect pentagons (the presence of perfect pentagons highlighted in the diagram to the right)

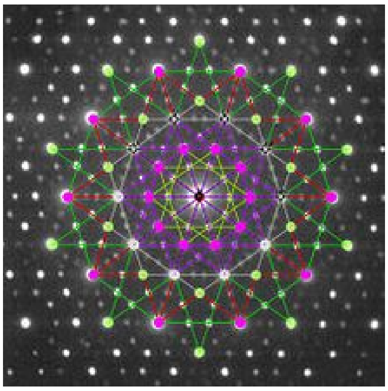


Fig. 13: A penteract (5-cube) pattern using 5-D orthographic projection to 2-D using Petrie polygon basis vectors overlaid on the diffractogram from an icosahedral Ho-Mg-Zn quasicrystal *(Courtesy: Wikipedia)*

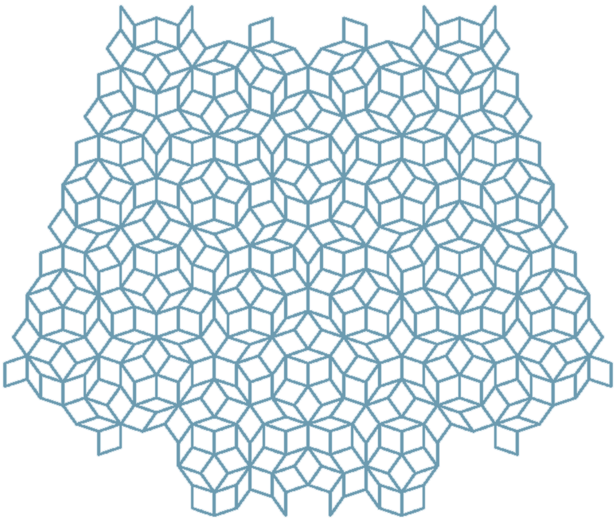


Fig. 14: Penrose tiling that produced the X-ray diffraction pattern above found new form of matter imagined in Islamic art. *(Source: http://imageshack.com/f/n7penrosepattern1p)*

During the same time (within six weeks) when Daniel's results were published, (Shechtman, Blech, Gratias, and Cahn, 1984) an American physicist Paul Joseph Steinhardt of the University of Pennsylvania and his student Dob Levine (an Israeli physicist) had quite independently identified similar geometrical structure, and coined the term 'quasicrystal' because it shared some defining properties of crystals but lacked their regular repeating structure. (Levine and Steinhardt, 1984; Steinhardt, 2013, 2007)

Quasicrystals are the crystals found in the atoms of metals / materials that are structured in certain pattern, but unlike a normal crystal, they do not repeat their patterns — they are non-repeating regular patterns of atoms. They represent a new state of matter that was not expected to be found, with some properties of crystals and others of non-crystalline (amorphous) matter, such as glass. Quasicrystals once thought impossible have changed understanding of solid matter and since Daniel's discovery, they have been found in other substances.

Twenty nine years after Shechtman's discovery, the Royal Swedish Academy of Sciences awarded him the 2011 Nobel Prize in Chemistry, in recognition of his finding of quasicrystals, metallic alloys with atoms arranged in orderly, infinite, aperiodic, crystal-like patterns with theoretically forbidden (typically 5-fold) symmetry.

3. WHAT ARE QUASICRYSTALS?

A 'quasiperiodic crystal', also called 'quasicrystal', is a structure that is ordered but not periodic. Quasicrystal is a form of solid matter whose atoms are arranged like those of a crystal but assume patterns that do not exactly repeat themselves. It is a body of solid material that resembles a crystal in being composed of repeating structural units but that incorporates two or more unit cells into a quasiperiodic structure. Basically, a quasicrystal is a crystalline structure that breaks the periodicity (i.e., the ability to shift the crystal one unit cell without changing the pattern — translational symmetry) of a normal crystal for an ordered, yet aperiodic arrangement. This means that quasicrystalline patterns will fill all available space, but in such a way that the pattern of its atomic arrangement never repeats.

"Quasiperiodic crystals are still crystals — they have nothing to do with amorphous materials," said Daniel Shechtman. He further added, "Amorphous materials are non-ordered (like glass); quasicrystals are crystals; but the atomic relation within them is different than periodic crystals. It is perfectly ordered, but not periodic."

Earlier, chemists interpreted regularity in crystals as a periodic and repeating pattern. But, the Fibonacci sequence is also regular, even though it never repeats itself, because it follows a mathematical rule. The inter-atomic distances in a quasicrystal correlate with the Fibonacci sequence; atoms are patterned in an orderly manner, and chemists can predict what a quasicrystal looks like on the inside. But, this regularity is not the same as when a crystal is periodic. In 1992, this realization led the International Union of Crystallography to alter its definition of what acrystal is. 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". The new definition became "any solid having an essentially discrete diffraction diagram". This definition is broader and allows for possible future discoveries of other kinds of crystals.

Thus, a quasicrystal is a structure that is ordered but not periodic — a form of solid matter whose atoms are arranged like those of a crystal but assume patterns that do not exactly repeat themselves. Quasicrystals are a type of solid minerals or metals with structures in between those of crystals and glasses (amorphous solids). A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry. In other words, it is a locally regular aggregation of molecules resembling a crystal in certain properties (such as that of diffraction) but not having a consistent spatial periodicity.

Before the discovery of quasicrystals, the prevailing paradigm in crystallography held that crystals are defined by a repeated unit cell and are mathematically constrained to only 2-, 3-, 4-, or 6-fold symmetry. Symmetry simply means that one can rotate the crystal's unit cell a certain number of degrees (e.g., 45 degrees, 60 degrees, etc.) and the unit cell will look the same as it did before he / she rotated it. This does not apply just to unit cells, but to 2-dimensional geometric figures as well. For example, if one rotates a square 90-degrees it will appear indistinguishable from how it looked before he / she rotated it; but if the square is rotated 45 degrees it does not look the same — it has 4-fold symmetry. If an equilateral triangle is rotated 120 degrees, it will look indistinguishable from before it was rotated, so it has 3-fold symmetry. If one rotates a hexagon 60 degrees it is indistinguishable from its initial position, so it has 6-fold symmetry because it can be rotated six times before it is back to where it started. Forms that were not regular and periodic (e.g., the pentagonal form Daniel Shechtman identified, as explained below) were deemed impossible. Five-fold symmetry was prohibited in classical crystallography.

Remark: A 'unit cell' is the smallest group of atoms which has the overall symmetry of a crystal, and from which the entire lattice can be built up by repetition in three dimensions. It is the smallest building block of a crystal, consisting of atoms, ions, or molecules, whose geometric arrangement defines a crystal's characteristic symmetry and whose repetition in space produces a crystal lattice — a geometric arrangement of the points in space at which the atoms, molecules, or ions of a crystal occur.

X-rays first revealed the internal structure of crystals in 1912, and from that time onward, scientists concluded that all crystals possessed rotational symmetry and a periodic structure. According to the received wisdom at the time, a crystal was something which by definition was both ordered and periodic, meaning that it exhibited a certain pattern at regular intervals. This consensus held for more than 70 years. (Shtull-Trauring, 2011)

But symmetry is not the only important feature of a crystal. These unit cells have to pack themselves together tightly. Mathematically, only 2-, 3-, 4- and 6-fold symmetry can form crystals; otherwise, there are gaps or holes in the structure. If we think of a tiled floor, we will never see a tiled floor with all (regular) pentagons (5-fold symmetry) because they cannot pack tightly.

This nice, neat theory was overturned by Daniel Shechtman's discovery of the crystal with 5-fold symmetry, which was later named *quasicrystal*. Generally, quasicrystals are crystals that display *'forbidden' symmetry*. An additional characteristic of a crystal with forbidden symmetry is that it is aperiodic. That is, it lacks a repeating pattern.

The atoms in the crystal in front of him yielded a forbidden symmetry. Such a pattern was considered just as impossible as creating a football — a sphere — using only six-cornered polygons, when a sphere needs both five- and six-cornered polygons. But, since Daniel Shechtman's discovery, Islamic mosaics with intriguing patterns and the golden ratio in mathematics and art have helped scientists to explain Shechtman's bewildering observation.

Mathematician Roger Penrose had theorized a 2-dimensional pattern consisting of 5-fold symmetry that was aperiodic. Shechtman's quasicrystals seemed to follow Penrose's pattern. Using X-ray diffraction studies, Shechtman found that his material (an aluminum-manganese alloy, Al_6Mn) had all of the features of a crystal but it had *forbidden symmetry*.

The quasicrystals are found in almost every metal and these quasicrystals have an uneven structure which means they do not have obvious cleavage (sundering) planes thereby making them particularly hard in nature.

4. QUASICRYSTALS AND ISLAMIC MOSAICS:

Mathematicians like to challenge themselves with puzzles and logic problems. During the 1960s, they began to ponder 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. The first successful attempt was reported in 1966 by an American mathematician Robert Berger, but it required 20,426 different tiles and was thus far from pleasing mathematicians' penchant for parsimony. (Berger, 1966) As more and more people took on the challenge, the number of tiles required steadily shrank. After Berger's discovery, various mathematicians considered the question of finding a smaller set of aperiodic prototiles and discovered sets of aperiodic prototiles with fewer and fewer prototiles. One well-known set of six aperiodic prototiles was discovered in 1971 by Raphael Mitchel Robinson (1911-1995), another American mathematician from the University of California, Berkley. (Robinson, 1971)

Finally, in the mid-1970s, a British professor of mathematics, Roger Penrose, provided a most elegant solution to the problem. He created aperiodic mosaics with just two different tiles, for example, a fat and a thin rhombus (Fig. 15). Penrose tiling is the first aperiodic tiling constructed by Roger Penrose with two types of rhombic tiles, where the entire pattern is generated by a local joining rule referred to as the 'matching rule', which requires each of the tiles to complete types and directions of the arrowheads on the tile edges, as shown in Fig. 15(b).

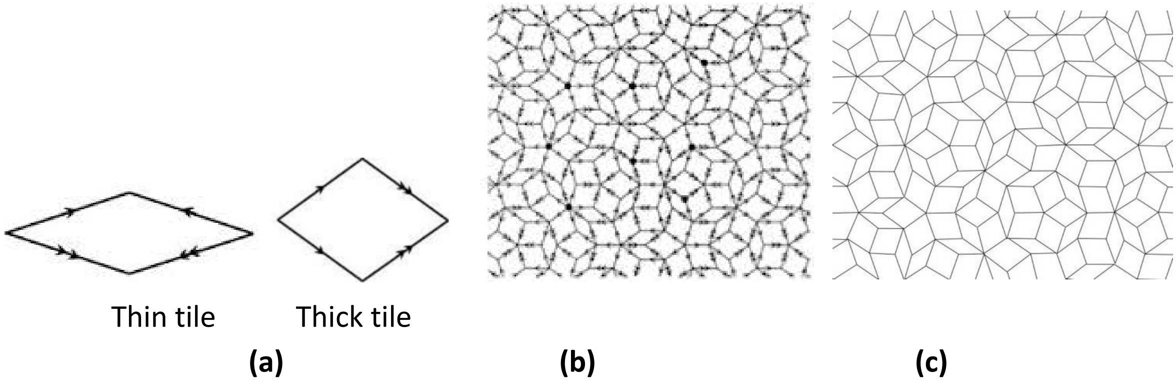


Fig. 15: (a) The two prototiles (the thick and thin rhombs) in the aperiodic set discovered by Penrose; (b) Penrose tiling by thick and thin rhombs with arrows indiacting the matching rules; (c) Penrose tiling by thick and thin rhombs (the arrows indicating the matching rules are omitted)

Penrose's mosaics inspired the scientific community in several different ways. Among other things, his findings have since been used to analyze medieval Islamic Girih patterns, and now it has been learned that Islamic artists produced aperiodic mosaics out of five unique tiles (the Girih tiles) as early as the 13th century CE. Such mosaics decorate the extra-ordinary Alhambra Palace in Spain, for example, and portals and vaults of the Darb-i Imam Shrine in Isfahan, Iran. *Girih tiles* are a set of 5 different tile shapes (Fig. 16) that were used (in intricate girih patterns) in the creation of tiling patterns for decoration of buildings in Islamic architecture since the 13th century CE. They are known to have been used since about the year 1200 CE and their arrangements found significant improvement starting with the Darb-i Imam shrine built in 1453 CE. The details of the aforesaid five shapes of the tiles are:

- a regular decagon with ten interior angles of 144°;
- an elongated (irregular convex) hexagon with interior angles of 72°, 144°, 144°, 72°, 144°, 144°;
- a regular pentagon with five interior angles of 108°;
- a rhombus with interior angles of 72°, 108°, 72°, 108°; and
- a bow-tie (non-convex hexagon) with interior angles of 72°, 72°, 216°, 72°, 72°, 216°.

All sides of the five different tile shapes are of the same length; and all their angles are multiples of 36° (π/5). These five figures, except the pentagon, have bilateral (reflection) symmetry through two perpendicular lines. Some have additional symmetries. Specifically, the decagon has tenfold rotational symmetry (rotation by 36°); and the pentagon has fivefold rotational symmetry (rotation by 72°).

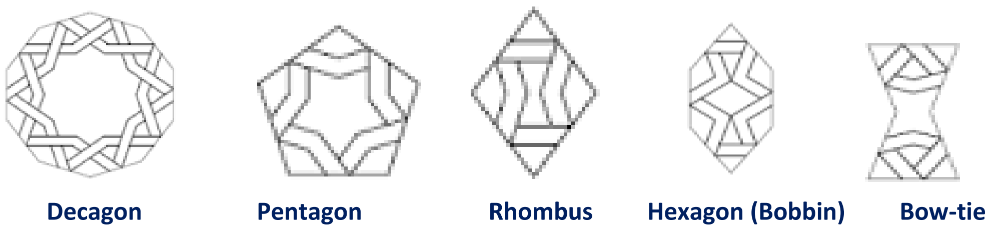


Fig. 16: Girih tiles: Lu's description of five shapes as 'girih tiles' (Source: Prange, 2009)

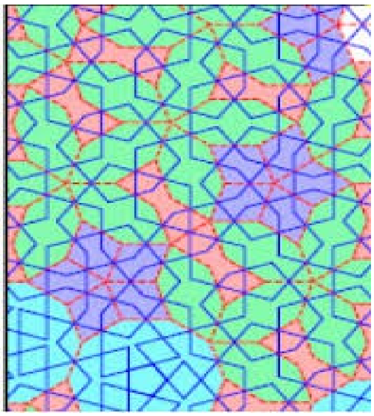


Fig. 17: Girih tiling *(Prange, 2009)*

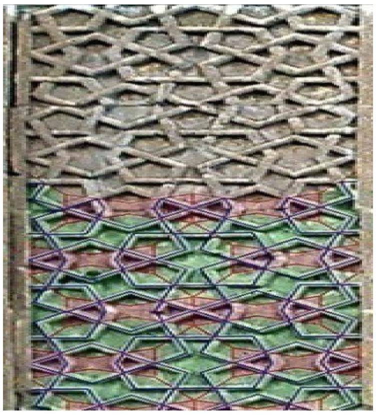


Fig. 18: Periodic girih pattern from the Seljuk Mama Hatun Mausoleum in Tercan, Turkey (~1200 CE), with girih-tile reconstruction overlaid at bottom *(Source: Al-Hassani, 2010)*

The British crystallographer Alan Mackay applied the Penrose mosaic in yet another manner. He was curious as to whether atoms, the building blocks of matter, could form aperiodic patterns like the mosaics. In 1982, he conducted an experiment with a model where he substituted circles, representing atoms, at intersections in the Penrose mosaic (Fig. 19). He then illuminated the model and obtained a ten-fold diffraction — a tenfold symmetry — with ten bright dots in a circle (Fig. 19).

Fig. 19: Mackay's simulated diffraction pattern from a Penrose tiling

Mackay made significant scientific contributions related to the structure of materials. In a 1962 paper, he showed how to pack atoms in an icosahedral fashion — a first step towards five-fold symmetry in materials science — these arrangements are now known as *Mackay icosahedra*. (Mackay, 1962) A pioneer in the introduction of five-fold symmetry in materials, in another paper in 1981, Mackay predicted quasicrystals in which he used a Penrose tiling in two and three dimensions to predict a new kind of ordered structures not allowed by traditional crystallography. (Mackay, 1981) In a later paper, in 1982, he took the optical Fourier transform of a 2-D Penrose tiling decorated with atoms, obtaining a pattern with sharp spots and five-fold symmetry. (Mackay, 1982) This brought the possibility of identifying quasiperiodic order in a material through diffraction, and almost during the same time, Quasicrystals with icosahedral symmetry were found by Daniel Shechtman and co-workers. (Shechtman, Blech, Gratias, and Cahn, 1984)

The connection between Mackay's model and Shechtman's diffraction pattern was subsequently made by the physicists Paul Steinhardt and Dov Levine. (Levine and Steinhardt, 1984) Before Shechtman's article appeared in Physical Review Letters, the editor sent it off to other scientists for review. During this process, Steinhardt got the opportunity to read it. He was already acquainted with Mackay's model, and realized that Mackay's theoretical ten-fold symmetry existed in real life in Shechtman's laboratory at NIST.

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. (Levine and Steinhardt, 1984) Quasicrystals got their name in this article.

In every metal, atoms are arranged in a typical symmetrical form. Daniel Shechtman discovered that the atoms had crystal structures in frozen gobbets of metal that had beautiful patterns, similar to those found on Islamic mosaics. In quasicrystals, he found the fascinating mosaics of the Islamic world reproduced at the level of atoms: regular patterns that never repeat themselves. Aperiodic mosaics, such as those found in the medieval Islamic mosaics of the *Alhambra Palace* in Spain and the *Darb-i Imam Shrine* in Iran, have helped scientists understand what quasicrystals look like at the atomic level. In those mosaics, as in quasicrystals, the patterns are regular — they follow mathematical rules — but they never repeat themselves. Shechtman found that the atoms were arranged in such a way that they broke the rules of how crystals are formed, and altered the views of other scientists.

Penrose tiles allow a two-dimensional area to be filled in five-fold symmetry, using two shapes based on *Phi* (ϕ), the golden ratio. It was thought that filling a three-dimensional space in five-fold symmetry was impossible, but the answer was again found in *Phi*. Where the solution in 2-D required two shapes, this can be accomplished in 3-D with just one shape. The shape has six sides, each one a diamond whose diagonals are in the ratio of *Phi* (ϕ).

For the first time Daniel observed a three-dimensional example of a Penrose pattern in the material world — quasiperiodic crystals, also known as quasicrystals. (Shechtman, Blech, Gratias, and Cahn, 1984) An alloy of aluminum and magnesium (Al_6Mn) was discovered in the laboratory which exhibited the symmetry of an icosahedron with five-fold axis — it showed the kind of symmetries and non-periodic patterns previously known only theoretically from Penrose's tiling by thick and thin rhombs (or kites and darts). Shechtman's image showed that the atoms in his crystal were packed in a pattern that could not be repeated. Atoms of quasicrystals pack space with pentagonal symmetry based on *Phi* (the golden ratio) (Fig. 22).

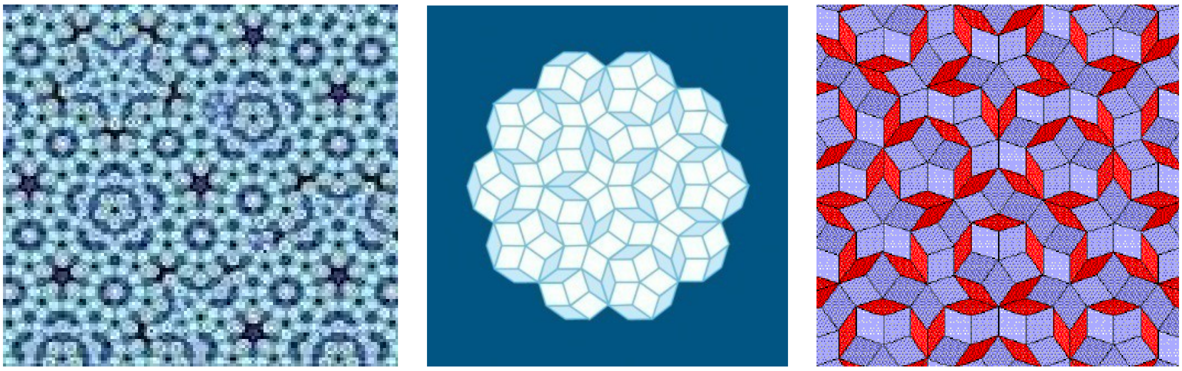


Fig. 20: Quasicrystals

Muslim artists had discovered and used quasicrystal geometry 500 years before it was discovered in the West. David R. Nelson, Professor of Physics at Harvard University writes:

"Shechtmanite quasicrystals are no mere curiosity. The study of quasicrystals has tied together two existing branches of theory: the theory of metallic glasses and the mathematical theory of aperiodic tilings. In doing so it has brought new and powerful tools to bear on the study of metallic alloys. Questions about long- and short-range icosahedral order should occupy solid-state physicists and materials scientists for some time to come." (Nelson, 1986)

(a) (b) (c)

Fig. 21: Islamic mosaics [Fig. 21 (b) shows the decagonal pattern on the 17th-century lodging complex of Nadir Divan Beg in Uzbekistan — an example of how the mathematical pattern of crystals discovered by Shechtman had been used in architecture for centuries — art imitates Science.]

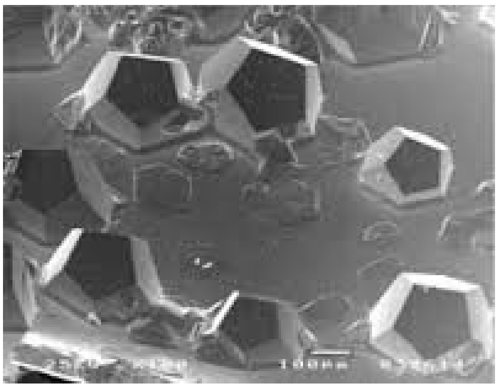


Fig. 22: Metallic quasicrystals: photo, courtesy of Division of Applied Physics, Graduate School of Engineering, Hokkaido University, Japan

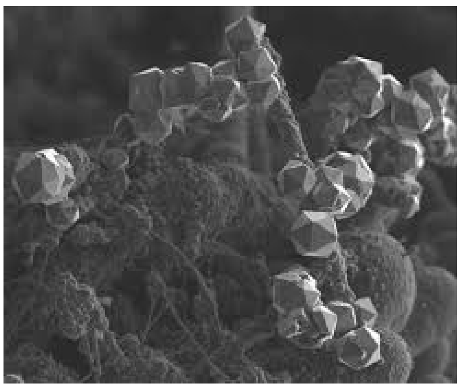


Fig. 23: Scanning electron microscopy of quasicrystal isocahedra: photo, Science Stuff, Epic Science, Random

When one translates Penrose tiling to a three-dimensional atomic lattice, he / she has the essence of a quasicrystal. The important takeaway here, according to Shechtman, is that "there is not a motif of any size that repeats itself. So there is order, and yet there is no periodicity." The order is derived from the fact that anyone could reconstruct the Fibonacci sequence or Penrose tiles, yet despite this order, if the sequence or tiling is shifted in any way it is impossible to derive an exact repetition.

Among several ways to mathematically define quasicrystalline patterns, one definition, the 'cut and project' construction, is based on the work of Harald Bohr (mathematician brother of Niels Bohr, the 1922 Nobel Laureate Danish physicist who made foundational contributions to understanding atomic structure and quantum theory). The concept of an almost periodic function (also called a *quasiperiodic function*) was studied by Bohr, including works of Piers Bohl (Latvian mathematician) and Ernest Esclangon (French astronomer and mathematician). (Bohr, 1925) He introduced the notion of a superspace. Bohr showed that quasiperiodic functions arise as restrictions of high-dimensional periodic functions to an irrational slice (an intersection with one or more hyperplanes), and discussed their Fourier point spectrum. These functions are not exactly periodic, but they are arbitrarily close in some sense, as well as being a projection of an exactly periodic function. In order that the quasicrystal itself be aperiodic, this slice must avoid any lattice plane of the higher-dimensional lattice. De Bruijn (1981) showed that Penrose tilings can be viewed as two-dimensional slices of five-dimensional hypercubic structures.

Non-periodic tilings can also be obtained by projection of higher-dimensional structures into spaces with lower dimensionality and under some circumstances there can be tiles that enforce this non-periodic structure and so are aperiodic. The Penrose tiles are the first and most famous example of this, as first noted in the pioneering work of de Bruijn. (De Bruijn, 1981) There is yet no complete (algebraic) characterization of cut and project tilings that can be enforced by matching rules, although numerous necessary or sufficient conditions are known. (Le, 1997)

5. QUASICRYSTALS AND GOLDEN RATIO:

When scientists describe Shechtman's quasicrystals, they use a concept that comes from mathematics and art: the *golden ratio*(Phi). This number had already caught the interest of mathematicians in ancient Greece, as it often appeared in geometry. In quasicrystals, for instance, the ratio of various distances between atoms is related to the golden ratio (*Phi*).

Remark: *Phi (Φ), the golden ratio, or the divine proportion, or the proportion of beauty, is an irrational and transcendental number named after the Greek architect Phidias who designed the magnificent Parthenon temple in Greece, dedicated to the Goddess Athena, whom the people of Athens considered their patron. Phi is the first three characters of Phidias. It is the division of a line with any given length into a larger part and a smaller part so that the ratio of the whole line to the larger part is the same as the ratio of the larger part to the smaller part. This occurs only when the whole is 1.618033... times the larger part and the larger part is 1.618033... times the smaller part.*

A fascinating aspect of both quasicrystals and aperiodic mosaics is that the golden ratio of mathematics and art, the mathematical constant *Phi* (ϕ), occurs over and over again. For instance, the ratio between the numbers of fat and thin rhombi in Penrose's mosaic is ϕ. Similarly, the ratio of various distances between atoms in quasicrystals is always related to ϕ.

The mathematical constant ϕ is described by a sequence of numbers that the great 13th-century Italian mathematician Leonardo Fibonacci worked out from a hypothetical experiment dealing with rabbit reproduction. In this well-known sequence, each number is the sum of the two preceding numbers: 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, etc. If one of the higher numbers in the Fibonacci sequence is divided by the preceding number — for instance, 144/89 — a number close to the golden ratio is obtained. Both the Fibonacci sequence and the golden ratio are important to scientists when they want to use a diffraction pattern to describe quasicrystals at the atomic level. The Fibonacci sequence can also explain how the discovery awarded the Nobel Prize in Chemistry 2011 has altered chemists' conception of regularity in crystals. [See Livio (2008) and Dunlap (2003) for details about golden ratio and Fibonacci numbers.]

The Fibonacci sequence can be seen as a 1-D analog to Daniel Shechtman's quasicrystal, in which there is order without repetition. The 2-D analog was discovered in 1974 by the famous English mathematician and physicist Roger Penrose. (Oberhaus, 2015)

The Golden Ratio continues to open new doors in our understanding of life and the universe. As we progress through the 21st century, *Phi* seems to be having a rebirth in integrating knowledge across a wide variety of fields of study, including time and quantum physics.

6. ATOMIC THEORY:

In the world of atoms, there are four fundamental asymmetries (structure of atomic nuclei, distribution of fission fragments, distribution of numbers of isotopes, and the distribution of emitted particles), and it is significant that "the numerical values of all of these asymmetries are equal approximately to the `golden ratio', and that the number forming these values are sometimes Fibonacci or `near' Fibonacci numbers." (Wlodarski, 1963) In changing states of a quantity of hydrogen atoms, as the atoms gain and lose radiant energy at succeeding energy levels, the changing proportion of the histories of the atomic electrons form Fibonacci numbers. (Huntley, 1969)

The golden ratio (ϕ) provides a quantitative link between various known quantities in atomic physics. While searching for the exact values of ionic radii and for the significance of the ionization potential of hydrogen, Heyrovska (2005, 2009) has found that the Bohr radius can be divided into two golden sections pertaining to the electron and proton. More generally, it was found that ϕ is also the ratio of anionic to cationic radii of any atom, their sum being the covalent bond length. After that she showed, among other facts, that many bond lengths in organic and inorganic molecules behave additively, and are the sum of the covalent and / or the ionic radii, whether partially or fully ionic or covalent. In addition, a new interpretation and a very accurate value of the *fine structure constant* α has been discovered in terms of the golden angle. (The fine-structure constant is a fundamental physical constant characterizing the strength of the electromagnetic interaction between elementary charged particles. The fine-structure constant is a unitless numerical constant — whose value is approximately equal to 1/137.508.) Thus, it is to be noted that α is quite a small number, very nearly 1/137, i.e., $\alpha^{-1} = (360 - 2/\varphi)/\varphi^2 = 137.036$ or $\alpha = \varphi^2/(360 - 2/\varphi) = 0.0072974$.

"In the last few years, the Golden proportion has played an increasing role in modern physical research and it has a unique significant role in atomic physics. (Heyrovska, 2005) The Golden proportion is found to govern the transition from Newtons physics to relativistic mechanics and the Golden rectangle has been used to derive the dilation of time intervals and the Lorentz contraction of lengths in special relativity." (Sigalotti and Mejias, 2006)

7. QUASICRYSTALS IN NATURE:

Since their discovery in 1982, hundreds of quasicrystals have been synthesized in laboratories around the world. In the summer of 2009, however, scientists first reported quasicrystals occurring in nature. Scientists led by Paul Joseph Steinhardt, an American physicist and cosmologist from Princeton University, have discovered a new kind of mineral (a rare form of solid) — an icosahedral quasicrystal that includes six distinct five-fold symmetry axes — in a rock sample taken from the Khatyrka River in Koryak Mountains in North Eastern Russia. The mineral (quasicrystal) in question is an alloy of aluminum, copper, and iron (with composition $Al_{71}Ni_{24}Fe_5$), and yields a diffraction pattern with ten-fold symmetry. It is called icosahedrite, after the icosahedron, a geometrical solid with sides consisting of 20 regular three-cornered polygons and with the golden ratio integrated into its geometry. It was discovered in the Khatyrka meteorite (Bindi, Steinhardt, Yao, and Lu, 2009) — nature's quasicrystal seems to come from a meteorite some 4.5 billion years old: far from an artificial innovation, the quasicrystal may be one of the oldest minerals in existence, formed at the birth of the Solar System. The finding was published in the Proceedings of the National Academy of Sciences. (Bindi, 2012)

Fig. 24: World's Only Known Natural Quasicrystal Traced to Ancient Meteorite — Scientific American (Credit: Paul J. Steinhardt who discovered it in Russian Koryak Mountains)

Fig. 25: Image of Paul J. Steinhardt and his team at the Russian excavation site (Credit: Paul J. Steinhardt)

Quasicrystals have unusual properties and have previously been made only in the laboratory. Its discovery in nature could redefine the field of mineralogy and expand our understanding of how quasicrystals form, leading to new applications. The results suggest that quasicrystals can form and remain stable under geologic conditions, although there remain open questions as to how this mineral formed naturally.

8. HOW QUASICRYSTALS ARE GOING TO CHANGE OUR LIFE?

This new form of matter possesses some unique and remarkable crystallographic and physical properties, embodying a novel kind of crystalline order. Daniel's findings demonstrated a clear diffraction pattern with a five-fold symmetry. Since then, quasi-crystals have been found in other substances. The materials have interesting properties, often being harder or tougher than their crystalline counterparts, and having low surface friction or unusual optical behaviour.

With the discovery of quasicrystals, a lot of changes are bound to occur in our everyday life. Background material provided by the Royal Swedish Academy of Sciences reports that hundreds of different types of quasicrystals have now been synthesized and that at least one natural mineral has been found to have that structure. Many more such crystals are expected to be discovered in near future for different metals. Our day-to-day applications may change. For example, a Swedish company found them in one of the most durable kinds of steel, which is now used in products such as razor blades and thin needles made specifically for eye surgery, the academy said. With quasicrystals, there is a likelihood of possible merge of applications in near future to make our life simpler and easier. Quasicrystals are also being studied for use in new materials that convert heat to electricity.

Here is what the Royal Swedish Academy says about the uses of quasicrystals (as quoted by The American Ceramic Society, October 5, 2011):

"When trying out different blends of metal, a Swedish company managed to create steel with many surprisingly good characteristics. Analyses of its atomic structure showed that it consists of two different phases: hard steel quasicrystals embedded in a softer kind of steel. The quasicrystals function as a kind of armor. This steel is now used in products such as razor blades and thin needles made specifically for eye surgery.

"Despite being very hard, quasicrystals can fracture easily, like glass. Due to their unique atomic structure, they are also bad conductors of heat and electricity, and have non-stick surfaces. Their poor thermal transport properties may make them useful as so-called thermoelectric materials … Today, scientists also experiment with quasicrystals in surface coatings for frying pans, in components for energy-saving light-emitting diodes, and for heat insulation in engines, among other things."

Professor Daniel Shechtman describes the quasicrystals as the most beautiful and potential protective layer in future alloys and protective coatings in various applications. This discovery is truly a celebration of fundamental research.

“Quasicrystals are very hard and are poor conductors of heat and electricity, offering uses as thermoelectric materials, which convert heat into electricity. They also have non-stick surfaces, handy for frying pans, and appear in energy-saving light-emitting diodes (LEDs) and heat insulation in engines.” (Lannin and Veronica, 2011) The Nobel Prize recognizes a breakthrough that has fundamentally altered how chemists conceive of solid matter.

The lesson: *"A good scientist is a humble and listening scientist and not one that is sure 100 percent in what he read in the textbooks." — Daniel Shechtman*

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References:

1. Al-Hassani, Salim T.S. (2010), New Discoveries in the Islamic Complex of Mathematics, Architecture and Art, Islamic Heritage, Foundation for Science, Technology and Civilization (FSTC), Vol. 2, Issue 5, Manchester, UK. (This essay is a revised and expanded version of a lecture presented at the 28th Annual Conference on the History of Arabic Sciences organized by the Institute for the History of Arabic Sciences, Aleppo University, Aleppo, Syria, in 25-27 April 2007. It was published in the proceedings of the conference.)
2. Berger, Robert (1966), *The undecidability of the domino problem*, Memoirs of the American Mathematical Society (66): 1-72.
3. Bindi, Luca (2012), Evidence for the extraterrestrial origin of a natural quasicrystal, Proceedings of the National Academy of Sciences, vol. 109 no. 5, p. 1396-1401.
4. Bindi, Luca; Steinhardt, P.J.; Yao, N.; and Lu, P. (2009), *Natural Quasicrystals*, Science 324 (5932): 1306-1309.
5. Bohr, H. (1925), *Zur Theorie fastperiodischer Funktionen I,* Acta Mathematicae, 45: 580.
6. De Bruijn, N.G. (1981), *Algebraic Theory of Penrose’s Non Periodic Tilings of the Plane*, Part I, II, Indagationes mathematicae 43 (1), 39-66.; Nederl. Akad. Wetensch, Amsterdam, Proc. A84: 39.
7. Dibben, Andrea (2011), *Shechtman Scaled Walls of Skepticism En Route to Nobel Prize*, Socionomist, October 2011 issue.
8. Dunlap, R.A. (2003), *The Golden Ratio and Fibonacci Numbers*, World Scientific Publishing Co. Pte. Ltd., Singapore; first Published in 1997.
9. Heyrovska, R. (2005), *The Golden ratio, ionic and atomic radii and bond lengths*, Molecular Physics, 103, p.877-882.
10. Heyrovska, Raji (2009), *The Golden ratio in the creations of Nature arises in the architecture of atoms and ions*, in Innovations in Chemical Biology (Chapter 12), edited by B. Sener, Springer, New York.
11. Ho, Mae-Wan (2011), *Golden Mean Wins Chemistry Nobel Prize*, Institute of Science in Society (ISIS) Report, 11 July 2011.
12. Huntley, H.E. (1970), *The Divine Proportion: A Study in Mathematical Beauty*, Dover Publications, New York, ISBN 0-486-22254-3.
13. Jha, Alok (2013 Jan 5), *Dan Shechtman: 'Linus Pauling said I was talking nonsense',* Guardian, London.
14. Kleinert H. and Maki K. (1981), *Lattice Textures in Cholesteric Liquid Crystals* (PDF), Fortschritte der Physik 29 (5): 219-259.
15. Lannin, Patrick and Veronica, E.k. (2011), *Ridiculed crystal work wins Nobel for Israeli*, Reuters, Stockholm, Thursday, October 6, 2011, 10:12am EDT.

16. Le, T.T.Q. (1997), *Local rules for quasiperiodic tilings, The mathematics of long range aperiodic order*, NATO Adv. Sci. Inst. Ser. C. Math. Phys. Sci. 489: 331–366.
17. Levine, D. and Steinhardt, P.J. (1984), *Quasicrystals: A New Class of Ordered Structures* (PDF), Phys. Rev. Lett 53 (26): 2477-2480.
18. Livio, Mario (2008), *The Golden Ratio: The Story of Phi, The World's Most Astonishing Number*, Crown Publishing Group, New York, ISBN 0307485528; first published in 2002 by Broadway Books (Random House), New York City, ISBN 0-7679-0815-5.
19. Mackay, Alan Lindsay (1962), *A dense non-crystallographic packing of equal spheres*, Acta Crystallogr. Vol. 15, 916.
20. Mackay, Alan Lindsay (1981), *De Nive Quinquangula* (in Russian), Krystallografiya, Vol. 26, 910-9.
21. Mackay, Alan Lindsay (1982), *Crystallography and the Penrose Pattern*, Physica 114 A, 609.
22. Maclá, Enrique (2006), *The role of aperiodic order in science and technology*, Reports on Progress in Physics 69 (2): 397-441.
23. Oberhaus, Daniel (2015 May 3), Quasicrystals *Are Nature's Impossible Matter*, http:// motherboard.vice.com/read/quasicrystals-are-natures-impossible-matter, retrieved 29 May 2016.
24. Prange, Sebastian R. (2009 September–October), *The Tiles of Infinity*, Saudi Aramco World, Vol. 60, No. 5, p. 24-31.
25. *Robinson,* Raphael M. *(1971), Undecidability and non-periodicity for tilings of the plane, Inventiones Mathematicae 12 (3): 177-190.*
26. Shechtman, Daniel (1986 July), *Quasiperiodic Crystals – Experimental Evidence*, Journal de Physique, 47(C3), p.C3-1-C3-7.
27. *Shechtman, D.; Blech, I.; Gratias, D.; and Cahn, J. (1984 Nvember 12), Metallic Phase with Long-Range Orientational Order and No Translational Symmetry, Physical Review Letters 53 (20):1951-54.*
28. Shtull-Trauring, A. (2011, January 4). *Clear as crystal*, Haaretz.com, Retrieved from http:// www.haaretz.com/weekend/magazine/clear-as-crystal-1.353504.
29. Sigalotti, L.D.G. and Mejias, A. (2006), *The Golden ratio in special relativity*, Chaos, Solitons & Fractals, 30:521-4.
30. Steinhardt, Paul J. (2007), *A New Paradigm for the Structure of Quasicrystals*, Archived from the original on 23 February 2007, Retrieved 2007-03-26.
31. Steinhardt, Paul J. (2013), *Quasicrystals: a brief history of the impossible*, Rendiconti Lincei 24: 85-91.
32. Swartzendruber, L.J.; Schectman, D.; Bendersky, L.; and Cahn, J.W. (1985), *Nuclear gamma-ray resonance observations in an aluminum-based icosahedral quasicrystal*, Physical Review B 32.2: 1383-1385, Web, 23 April 2010.
33. Wlodarski, J. (1963 December), *The Golden Ratio and the Fibonacci Numbers in the World of Atoms*, Fibonacci Quarterly, 1(4), p. 61-63.