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Scientific Background on the Nobel Prize in Chemistry 2011

THE DISCOVERY OF QUASICRYSTALS

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The Discovery of Quasicrystals

The Nobel Prize in Chemistry 2011 is awarded to Dan Shechtman for the discovery of quasicrystals.

Background

Solid state matter always displays substantial short-range and long-range order to various degrees. Short-range order is imposed by the typical local bonding requirements of chemistry. Even in materials such as silica glass, which are normally considered to be completely amorphous, substantial local order is present: Each silicon atom is tetrahedrally surrounded by four oxygen atoms at 1.62 Å, and the typical oxygen–oxygen separation is 2.65 Å. While it is possible to detect one or two more distinct structural traits in silica glass, the material lacks the hallmark of crystallinity: long-range order.

Ever since the work of Abbé Haüy in 1784[1], where he showed that the periodic repetition of identical parallelepipeds (*molécules intégrantes,* now known as unit cells) can be used to explain the external shape of crystals, long-range order has been assumed to be inextricably linked to translational periodicity. Hence, the classical definition of a crystal is as follows: *A crystal is a substance in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating three-dimensional pattern.*[2]

Implicitly, this means that a crystal is infinite, and given the size of the unit cell (tens to hundreds of ångströms) in comparison to the size of the physical crystal (hundreds of microns), practically, this is not too far off the mark. The vast majority of the unit cells form the bulk of the crystal, and only a very small part form the surface.

Real crystals are, of course, not only finite in size but also contain imperfections, and the borders between crystalline and amorphous are to some extent defined by the measurement method. A sample that appears crystalline to a local probe such as selected area electron diffraction may appear amorphous to powder X-ray diffraction.

One of the most striking characteristics of crystals is their space-group symmetry. The 230 space groups were enumerated in the late 19th century independently by Fedorov[3], Barlow[4] and Schoenflies[5]. Many local symmetry operations that are incompatible with translational symmetry may still be realized by isolated molecular assemblies. Among the rotational symmetries, 2-, 3-, 4- and 6-fold axes are allowed, while 5-, 7- and all higher rotations are disallowed. The proof is very simple, and it is instructive to consider how two parallel 4-fold or

[1] R.J. Haüy (1784) *"Essai d'une théorie sur la structure des cristaux"*.
[2] International Union of Crystallography [prior to 1992]
[3] E.S. Fedorov (1891) "Симмтрія правильныхъ системъ фигуръ" ("The symmetry of regular systems of figures"), Zapiski Imperatorskogo S. Petersburgskogo Mineralogichesgo Obshchestva (Proceedings of the Imperial St. Petersburg Mineralogical Society), **2**(28), pp 1-146. English translation: David and Katherine Harker, (1971) "Symmetry of Crystals", American Crystallographic Association Monograph No. 7, Buffalo, N.Y. Am. Cryst. Ass. pp 50-131.
[4] W. Barlow (1894) "Über die Geometrischen Eigenschaften homogener starrer Strukturen und ihre Anwendung auf Krystalle" ("On the geometrical properties of homogeneous rigid structures and their application to crystals"), *Zeitschrift für Krystallographie und Minerologie*, **23**, pp 1-63.
[5] A. Schoenflies (1892) *Krystallsysteme und Krystallstruktur*.

6-fold axes of rotation generate translational symmetry, while two parallel 5-fold axes of rotation clearly cannot coexist (figure 1).

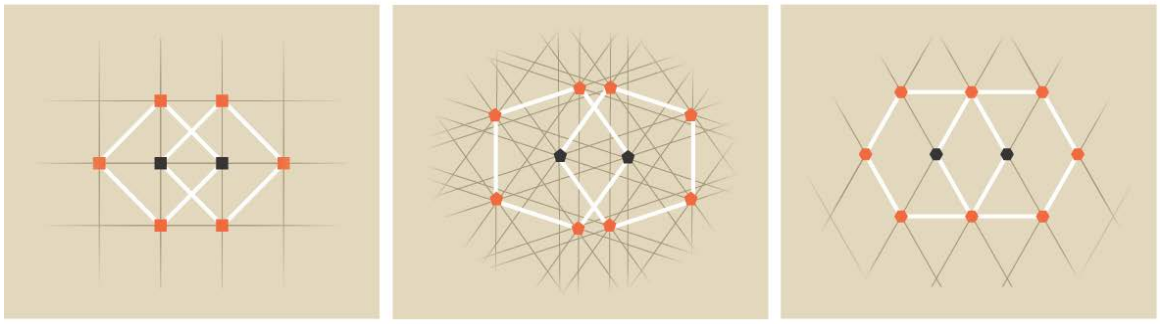

Figure 1. Two 4-fold (left) or 6-fold (right) axes of rotation generate new rotational axes at the same distance of separation as in the original pair. Repeating the procedure yields periodicity. For the pair of 5-fold axes (centre), the procedure instead generates a new, shorter distance. An iterative procedure will thus fill the plane densely with 5-fold axes, and no periodicity will result.

This proof makes it obvious that 5-fold symmetry is incompatible with translational symmetry, and hence with crystallinity.

The discovery

In a seminal paper published in November 1984[6], rapidly solidified alloys of Al with 10–14% Mn were shown by means of electron diffraction to possess icosahedral symmetry in combination with long-range order, in clear violation of the results above (figure 2). In a second paper that was submitted earlier, but that appeared later in print, the researchers detailed their synthetic procedure and proposed a model based on packing of icosahedra[7].

The phenomenon was rapidly christened “quasicrystallinity” by Levine and Steinhardt in a paper[8] that appeared a mere five weeks later (24 December 1984). Clearly, the old definition of crystallinity was insufficient to cover this new class of ordered solids, and as a consequence, the definition of “crystal” given by the International Union of Crystallography was changed.

While formal definitions may be more or less important to science, this one is interesting because it makes no attempt to define the concept of “crystal” directly, but rather provides an operative definition based on the diffraction pattern of the material: *By "Crystal" is meant any solid having an essentially discrete diffraction diagram*. The discovery of quasicrystals has taught us humility. As pointed out in a recent review[9]: “We do not know when the next class of non-periodic exciting crystal structures will be discovered, or if there will be such a discovery at all.” Rather than making the mistake of again being overly restrictive, science now treats exclusive statements about long-range order with caution.

[6] D. Shechtman, I. Blech, D. Gratias, J.W. Cahn (1984) “Metallic phase with long range orientational order and no translation symmetry”, *Physical Review Letters* **53**(20), pp 1951-1954.
[7] D. Shechtman, I. Blech (1985) “The microstructure of rapidly solidified Al_6Mn”, *Metallurgical Transactions* **16A**, pp 1005-1012.
[8] D. Levine, R. Steinhardt (1984) “Quasicrystals: a new class of ordered structures”, *Physical Review Letters* **53**(26), pp 2477-2480.
[9] W. Steurer, S. Deloudi (2008) “Fascinating quasicrystals”, *Acta Crystallographica A* **64**, pp 1-11.

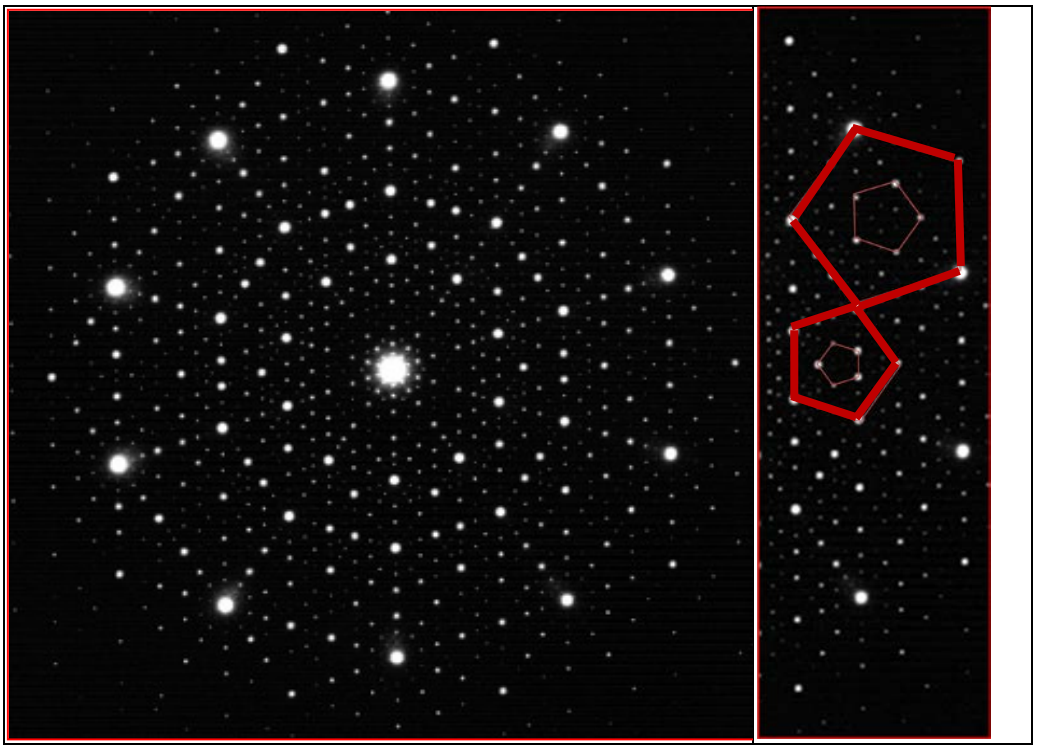

Figure 2. Electron diffraction pattern from an icosahedral quasicrystal. Note the presence of perfect pentagons highlighted in the diagram to the right. The linear scale between pentagons is τ, and the scale between a pentagon inscribed in another pentagon is τ^2. One of the great challenges of quasicrystal structure work is also apparent in this image. The intensity distribution of the diffraction pattern varies over many orders of magnitude, even in electron diffraction, and measuring the crucial weak reflections in an X-ray diffraction pattern within a reasonable time frame has only become possible with modern area detectors that were not around at the time of discovery.

While the discovery process can often be difficult to retrace, the singular nature of the discovery of quasicrystals makes it possible to date exactly when it was made. In the notebook from Dan Shechtman recording his electron microscopy session on 8 April 1982, the entry for exposure 1725 has the comment: 10 Fold ??? (figure 3).

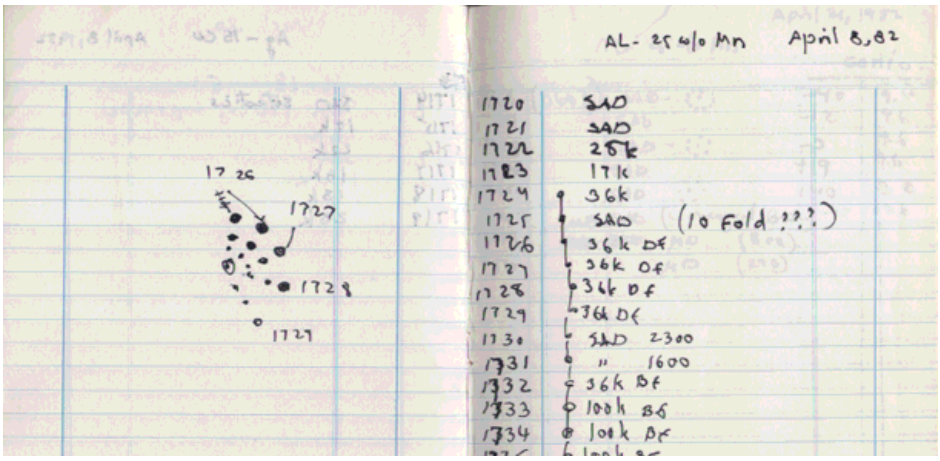

Figure 3. The notebook of Dan Shechtman dating the discovery of quasicrystals to 8 April 1982 (www.quasi.iastate.edu/discovery.html).

To make the discovery even more astounding, Shechtman found that by rotating the sample he could identify additional 5-fold axes as well as 3-fold and 2-fold. It became clear that the symmetry of his sample was not merely 5-fold but icosahedral (figure 4).

Naturally, Dan Shechtman was not unaware of the fundamental crystallographic laws that forbid 5-fold symmetry, but a crucial component of the discovery is the superb quality of his electron diffraction work, providing a solid experimental underpinning of the discovery. While 5-fold symmetry may be explained by twinning, twinning was a phenomenon with which Shechtman was familiar and this looked nothing like it.

After the discovery, Shechtman spent a long time convincing colleagues about the veracity of his interpretation (local icosahedral symmetry rather than twinning), and the two original papers on the discovery were published more than two years later. The achievement of Dan Shechtman is clearly not only the discovery of quasicrystals, but the realization of the importance of this result and the determination to communicate it to a skeptical scientific community.

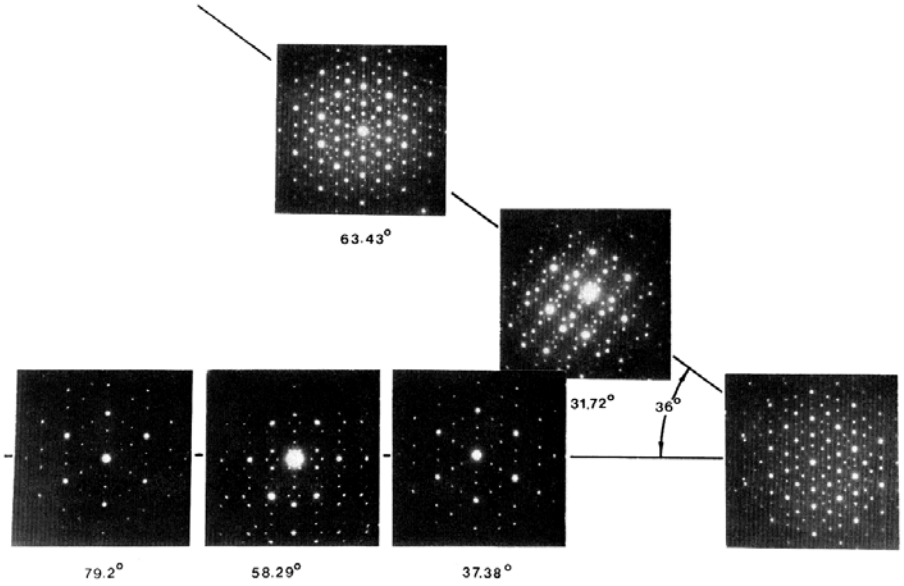

Figure 4. Original electron diffraction images taken by Dan Shechtman. The angular relationship between the various zones examined by Shechtman shows that the sample exhibits icosahedral symmetry[6].

The discovery spurred a lot of debate, but also frantic activity aimed at synthesizing examples. Within a few years, the icosahedral quasicrystals were joined by axial quasicrystals with decagonal and pentagonal symmetry[10,11], octagonal symmetry[12], dodecagonal symmetry[13] and enneagonal symmetry[14]. Furthermore, within each symmetry class of quasicrystals, different superspace-group symmetries are allowed and realized. Thus among the icosahedral quasicrystals there are two distinct classes: P-type and F-type quasicrystals, with names that

[10] L. Bendersky (1985) "Quasicrystal with one-dimensional translational symmetry and a tenfold rotation axis", *Phys. Rev. Lett.* **55**, pp 1461–1463.
[11] P.A. Bancel, P.A. Heiney (1986) "Icosahedral aluminum-transition-metal Alloys", *Phys. Rev.* **B33**, pp 7917–7922.
[12] N. Wang, H. Chen, K.H. Kuo (1987) "Two-dimensional quasicrystal with eightfold rotational symmetry", *Phys. Rev. Lett.* **59**, pp 1010–1013.
[13] T. Ishimasa, H.U. Nissen, Y. Fukano (1985) "New ordered state between crystalline and amorphous in Ni–Cr particles", *Phys. Rev. Lett.* **55**, pp 511–513.
[14] S. Fischer, A. Exner, K. Zielske, J. Perlich, S. Deloudi, W. Steurer, P. Lindner, S. Förster (2011) "Collodial quasicrystals with 12-fold and 18-fold rotational symmetry", *PNAS* **108**, pp 1810-1814.

refer to their respective centering symbols in 6-dimensional superspace. However, while quasicrystals allow non-crystallographic symmetry, they are not defined by it, and quasicrystals with rotational symmetries allowed in normal 3-dimensional space have been found.

A very important factor for the successful determination of quasicrystal structure has been the discovery of stable quasicrystals. Stable quasicrystals may be grown to considerable size and exhibit the typical features of well-ordered crystalline phases. These high-quality samples were necessary for the detailed structural studies that have led to an understanding of quasicrystal structure. The first stable icosahedral quasicrystals were synthesized as early as 1987 in the ternary system Fe-Cu-Al[15], and stable axial quasicrystals followed the year after[16]. A breakthrough came with the discovery of a binary stable icosahedral quasicrystal in 2000, using Ca-Cd and Yb-Cd[17]. The binary system, which has less disorder, was crucial for providing the high-quality samples subsequently used for the detailed structural elucidation of icosahedral quasicrystals.

What are quasicrystals?

A quasicrystal is a material that exhibits long-range order in a diffraction experiment and yet does not have translational periodicity. In fact, the assumption that a crystal must be 3-dimensionally periodic had already been challenged by the discovery of incommensurately modulated structures. These are crystal structures that are subject to periodic distortions with a period that is incompatible with that of the underlying parent lattice. The existence of incommensurability was inferred in the structure of cold-worked metals as early as 1927[18], but a comprehensive treatment in terms of the now-prevalent superspace approach was not introduced until the work of de Wolff[19] and Janner and Jansen[20,21,22,23]. In contrast to quasicrystals, these structures may however be regarded as distortions of periodic structures, and their point-group symmetries allow 3-dimensional periodicity. In lieu of translational periodicity, quasicrystals exhibit another intriguing symmetry property, namely self-similarity by scaling. In icosahedral and decagonal quasicrystals, the self-similarity is related to the scaling properties of the golden ratio τ, $(\sqrt{5}+1)/2$. This feature is clearly apparent in direct space models and diffraction patterns alike (figure 2).

The superspace formalism developed to treat incommensurately modulated structures was well-adapted to deal also with quasicrystals. Hermann[24] showed that symmetries that are non-crystallographic for 3-dimensional lattices may become crystallographic if treated in higher-dimensional space. Icosahedral symmetry is allowed together with translational symmetry in 6-

[15] A.P. Tsai, A. Inoue, T. Masumoto (1987) "A stable quasicrystal in Al-Cu-Fe system", *Jpn. J. Appl. Physics* **26**, L1505-L1507.
[16] L.X. He, Z. Zhang, Y.K. Wu, K.H. Kuo (1988) "Stable decagonal quasicrystals with different periodicities along the tenfold axis in $Al_{65}Cu_{20}Co_{15}$", *Inst. Phys. Conf. Ser.* 93 (2), Chapter 13, Conf. EUREM, pp 501–502.
[17] A.P. Tsai, J.Q. Guo, E. Abe, H. Takakura, T.J. Sato (2000) "A stable binary quasicrystal" *Nature* **408**, pp 537-538.
[18] U. Dehlinger (1927) "Uber die Verbreiterung der Debyelinien bei kaltbearbeiteten Metallen", *Zeitschrift für Kristallographie* **65**, pp 615–631.
[19] P.M. de Wolff (1974) "The pseudo-symmetry of Modulated crystals", *Acta Crystallographica* **A 30**, pp 777-785.
[20] A. Janner, T. Janssen (1977) "Symmetry of periodically distorted crystals", *Physical Review* **B15**(2), pp 643–658.
[21] A. Janner, T. Janssen (1979) "Superspace groups", *Physica* **99A**, pp 47–76.
[22] A. Janner, T. Janssen (1980) "Symmetry of incommensurate crystal phases. I. Commensurate basic structures", *Acta Crystallographica* **A36**, pp 399–408.
[23] A.Janner, T.Janssen (1980) "Symmetry of incommensurate crystal phases. II. Incommensurate basic structures", *Acta Crystallographica* **A36**, pp 408–415.
[24] C.Hermann (1949) "Kristallographie in Raumen Beiliebiger Dimenzionszahl .1. Die Symmetrieoperationen", *Acta Crystallographia* **2**(3) 139-145.

dimensional space, where each coordinate axis is perpendicular to a hyperplane spanned by the other five. Projection to a 3-dimensional external space is straightforward according to the projection matrix,

$$M = (\tau^2+1)^{-1/2} \begin{pmatrix} 1 & \tau & 0 & -1 & \tau & 0 \\ \tau & 0 & 1 & \tau & 0 & -1 \\ 0 & 1 & \tau & 0 & -1 & \tau \end{pmatrix}.$$

The golden ratio τ appears naturally in all manifestations of 5-fold symmetry as the relation between the diagonal and the edge in a regular pentagon, and it is inextricably linked to the Fibonacci sequence.

Application of the projection matrix to the vertices of a 6-dimensional hypercube yields a regular icosahedron as the projection. In the 3+1–dimensional incommensurate example shown in figure 5, the atomic surfaces are 1-dimensional objects, while in the case of the 6-dimensional hyperspace needed for icosahedral quasicrystals, they are 3-dimensional objects of the appropriate symmetry.

The natural question that quickly arose out of the discovery of quasicrystals is “Where are the atoms?”[25] There are several ways to obtain information about the arrangements based on microscopy and diffraction techniques. An important limiting factor is the relative paucity of information in a quasicrystal diffraction pattern because many reflections are weak. It is particularly important to get information on the shape of the atomic surfaces in perpendicular space, and the reflections carrying that information are often weak. In general, the intensity distribution in quasicrystals covers many orders of magnitude, and only in highly perfect samples is it possible to measure weak reflections with any accuracy.

Two different methods are generally used for modelling quasicrystals. The higher dimensional reciprocal-space approach has the advantage that it utilizes the full power of diffraction methods developed for periodic crystals over the course of a century.

An important aspect of the higher dimensional analysis is that it also yields the structures of classically crystalline phases that often occur at compositions close to those of quasicrystals. These approximant phases provide important information on the structure of the corresponding quasicrystals because they are expected to have similar local atomic arrangements. While aperiodic structures such as quasicrystals are generated for irrational cuts of hyperspace, periodic structures come out of rational cuts.

[25] P. Bak (1986) “Icosahedral Quasicrystals: Where are the atoms?”, *Phys. Rev. Lett.* **56**, pp 861–864.

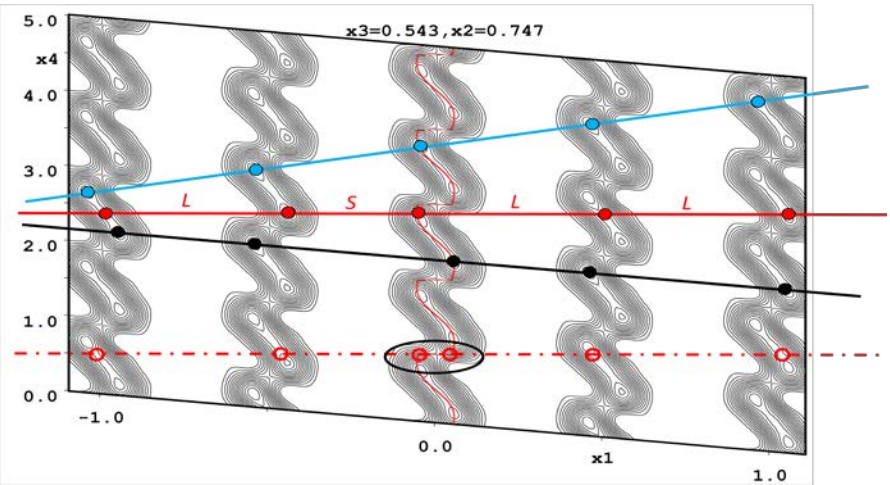

Figure 5. The 3+1–dimensional space representation of the electron density in an incommensurately modulated structure can be used as a simplified model for the 5- (for axial cases) or 6-dimensional (for icosahedral cases) representation of a quasicrystal. The concept of atomic position is replaced by an atomic surface along the extra dimension (internal space or perpendicular space, vertical) and the intersection of that surface with real space (external space or parallel space, horizontal) generates the local atomic arrangement. In this example, a saw-tooth–shaped modulation function generates a sequence of short and long distances in the incommensurate structure (red). The two simplest periodic commensurate approximants represent a sequence of equal distances (blue) and a simple alternating sequence (black). They are generated by cuts at angles rational to the coordinate axes. The dashed line, finally, represents a cut that intersects the atomic surface at a point where the modulation function is indeterminate and where two possible local structures are available. The encircled position on the dashed line indicates the uncertain position where a minute fluctuation of the position of the cut will produce different local structures. In real quasicrystals, such fluctuations, called phasons, contribute to entropic stabilization above absolute zero.

Approximants are labeled by the axial relation of the generating cut. For an icosahedral quasicrystal, that relation is τ:1 (or in fact τ:1, τ:1, τ:1, given the six dimensions of the hypercubic lattice) while the simplest cubic approximants are 1:1 and 2:1 (figure 6).

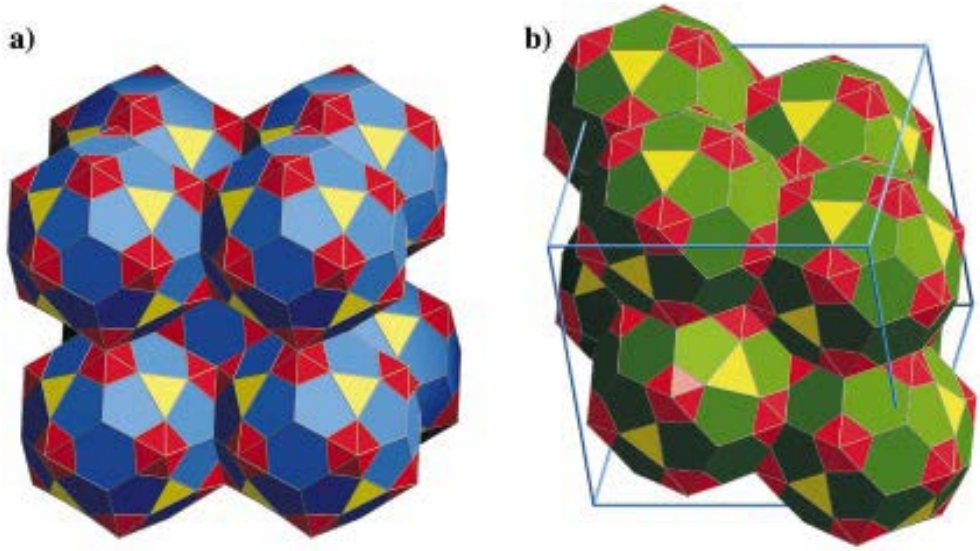

Figure 6. Polyhedral arrangement in the a) 1:1 and b) 2:1 icosahedral quasicrystal approximants in the system Ca-Cd[26].

[26] C. Pay-Gomez, S. Lidin (2001) "Structure of $Ca_{13}Cd_{76}$: a novel approximant to the $MCd_{5.7}$ quasicrystals", *Angewandte Chemie* **40**, pp 4037-4039.

An important discovery that helped pave the way for the understanding of the discovery of quasicrystals was the construction and analysis by Penrose of his famous pentagonal tiling[27]. The pentagonal Penrose tiling (figure 7) is a self-similar pattern with 5-fold symmetry, long-range order and no translational periodicity. de Bruijn applied the higher dimensional approach to Penrose tiles[28], and Mackay subjected an image of the vertices of a Penrose tiling to optical diffraction and was able to show that it has a discrete diffraction diagram[29]. These early results were certainly instrumental in allowing Levine and Steinhardt to accomplish their remarkable early analysis (and resulting paper) on quasicrystals, and helped establish the credibility of the discovery.

In the 3-dimensional direct-space method, clusters from approximant phases are packed using tiling models or covering models that may be random or ordered according to the rules for Penrose tilings. The result of this approach can be evaluated qualitatively by comparison with microscopy or diffraction experiments. In practice, the 3-dimensional direct-space approach and the 6-dimensional reciprocal-space approach are complementary and they are often used together. The higher dimensional approach yields numerical reliability factors that are entirely analogous to those for periodic structures, while the strength of the tiling models is that they are intuitively understandable and may be directly compared to results from microscopy. They may also provide some help in generating starting models for higher dimensional refinement.

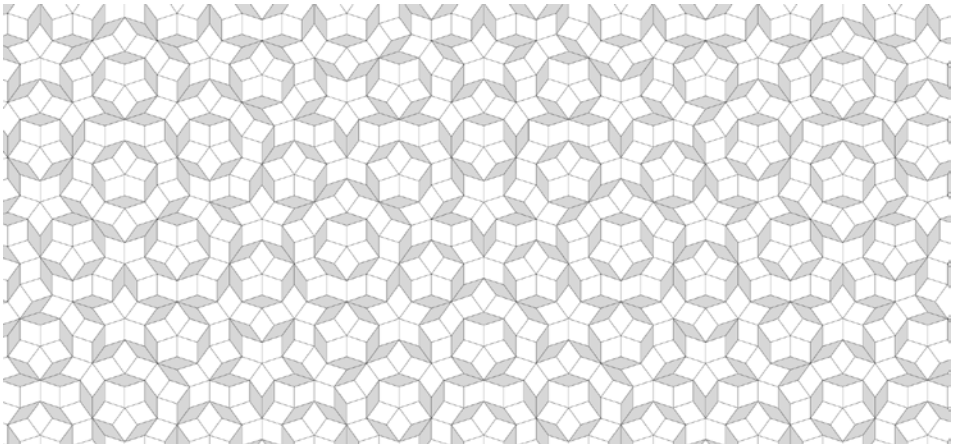

Figure 7. Pentagonal Penrose tiling. Note the local 5-fold symmetry that even in the absence of any translational symmetry pervades the image. Decorating the two tiles with structural motifs or, as in the experiment of Mackay[29], simply identifying the vertices as atomic positions generates a quasiperiodic structure.

The highly successful direct methods for phasing diffraction data for periodic structures are not directly transferrable to higher dimensional problems, but recent years have seen the development of novel methods that address this[30,31,32].

[27] R. Penrose (1974) "Role of aesthetics in pure and applied research" *Bulletin of the Institute of Mathematics and Its Applications* **10**:266.
[28] N.G. de Bruijn (1981) "Algebraic theory of Penrose's non-periodic tilings of the plane, I, II", *Indagationes mathematicae* **43**(1), pp 39–66.
[29] A. Mackay (1982) "Crystallography and the Penrose Pattern", *Physica* **A114**, pp 609-613.
[30] A. Yamamoto, H. Takakura (2004) "Structure Refinement of Quasicrystals", *Ferroelectrics* **305**, pp 223–227.
[31] A. Yamamoto, H. Takakura, T. Ozeki, A.P. Tsai, Y. Ohashi (2004) "Structure refinement of i-Al-Pd-Re quasicrystals by synchrotron radiation data", *J. Non-Cryst. Solids* **334**, pp 151–155.
[32] S. Katrych, T. Weber, M. Kobas, L. Massüger, L. Palatinus, G. Chapuis, W. Steurer (2007) "New decagonal quasicrystal in the system Al-Ir-Os", *J. Alloys Compd.* **428**, pp 164–172.

Refinement of quasicrystal models involves the refinement of the position and shape of the atomic surfaces in 5-dimensional space for axial quasicrystals and 6-dimensional space for icosahedral quasicrystals. A detailed model involves a high degree of complexity, which requires a large number of independent observations, and achieving this is challenging in quasicrystals because the intensity distribution typically covers many orders of magnitude. Furthermore, as is typical for intermetallics, most quasicrystals exhibit occupational disorder, introducing ambiguities in the model.

These have been issues in many quasicrystal refinements. Refined structures started appearing in the late 1980s[33] and have been continuously improving. The structural resolution in the analysis of decagonal quasicrystals has undergone gradual improvement to reach a level approaching that of periodic crystals[34], and recent[35] state-of-the-art structural analysis of stable binary icosahedral quasicrystals bridges the last gap (figures 8 and 9).

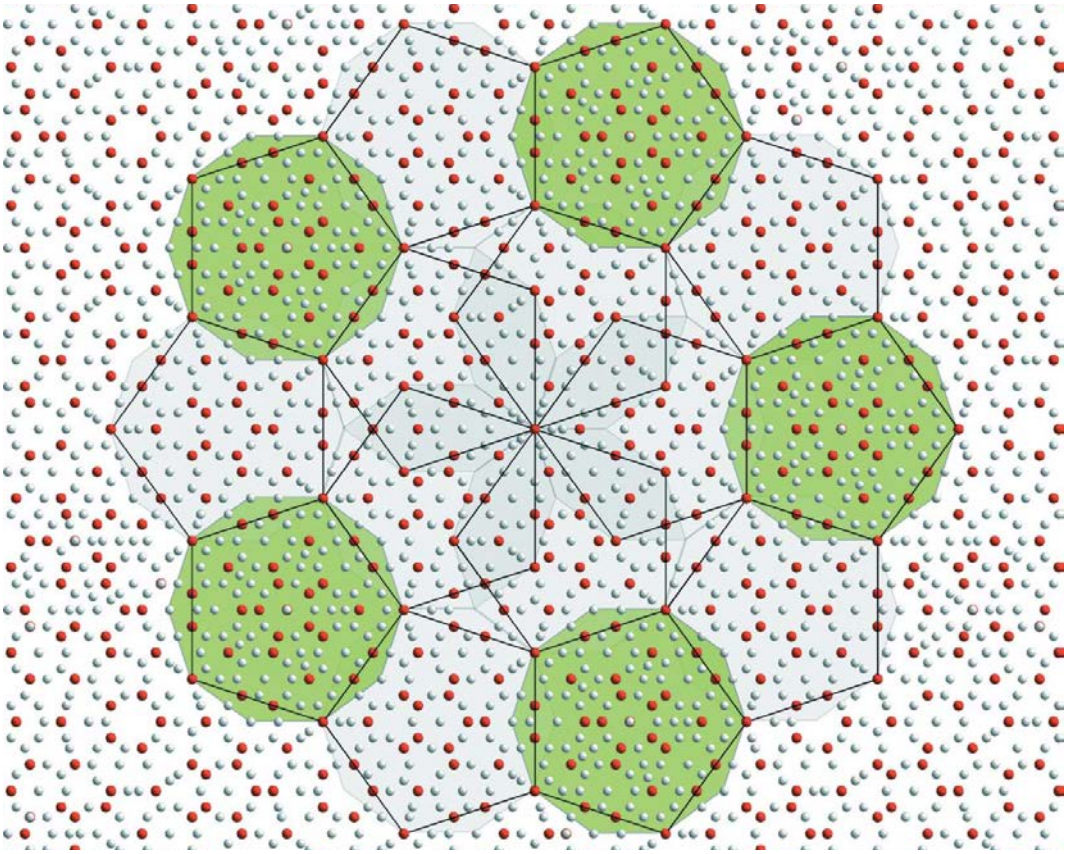

Figure 8. Section perpendicular to the decagonal axis of Al-Co-Ni[36].

The question asked by Bak in the infancy of quasicrystal research — "Where are the atoms ?" — has now received a satisfactory answer. The reliability of today's models is on par with that of

[33] J.W. Cahn, D. Gratias, B. Mozer (1988) "A 6-D structural model for the icosahedral (Al,Si)-Mn quasicrystal", *J. Phys. Fr.* **49**, pp 1225–1233.
[34] A. Cervellino, T. Haibach, W. Steurer (2002) "Quasicrystal structure analysis, a never-ending story?", *Acta Cryst.* **B58**, pp 8–33.
[35] H. Takakura, C.P. Gomez, A. Yamamoto, M. de Boissieu, A.P. Tsai (2007) "Atomic structure of the binary icosahedral Yb-Cd quasicrystal", *Nature Mater.* **6**, pp 58–63.
[36] S. Deloudi, W. Steurer (2007) "Systematic cluster-based modeling of the phases in the stability region of decagonal Al-Co-Ni", *Philos. Mag.* **87**, pp 2727–2732.

models for conventional crystals, and this leaves science in a position where the physical properties of quasicrystals may be understood directly in terms of their structures. Modelling of quasicrystals is still challenging, given that the theoretical methods for dealing with extended systems rely on periodicity. Theoretical models for quaiscrystals normally treat large approximants that are known to have similar properties because at the moment, this is the only viable option.

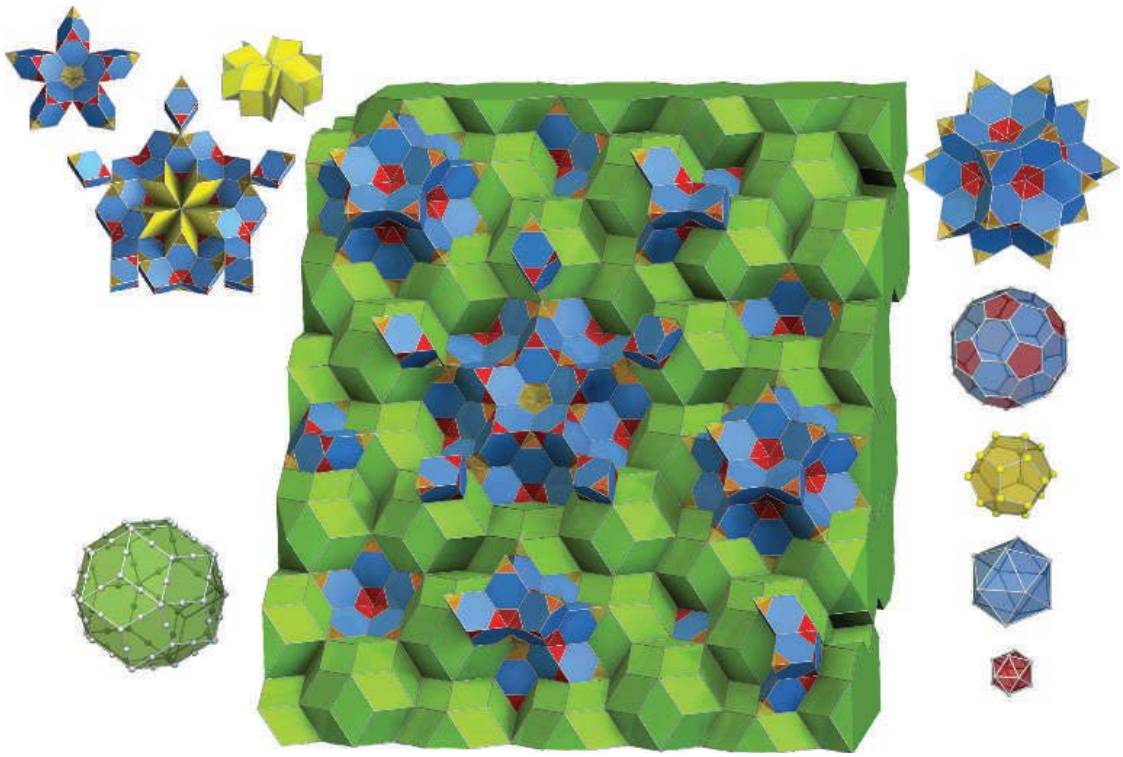

Figure 9. Slab from the structural model for i-$YbCd_{5.7}$ showing the two distinct clusters that build the structure[35].

Properties of quasicrystals

Intermetallic quasicrystals are typically hard and brittle materials with unusual transport properties and very low surface energies. Thermal and electronic transport in solid materials is normally enhanced by phonons and Bloch waves that develop as a consequence of the periodic nature of crystals. In quasicrystals, the absence of such collective transport modes generates behaviors more like those found in glasses than in normal crystals. The low surface energy of quasicrystals make them corrosion- and adhesion-resistant and imparts them with low friction coefficients.

Occurrence of quasicrystals

The first quasicrystals discovered by Dan Shechtman were synthetic intermetallics, and while hundreds of intermetallic systems have been shown to yield quasicrystals, so far few other types of systems have been reported to be quasicrystalline. The first report of quasicrystals in other systems was from dendrimer liquid crystals[37], followed by star copolymers[38] and most recently

[37] X. Zeng et al (2004) "Supramolecular dendritic liquid quasicrystals", *Nature* **428**, pp 157-160.
[38] K. Hayashida et al (2007) "Polymeric quasicrystal: mesoscopic quasicrystalline tiling in ABS star polymers", *Physical Review Letters* **98**, 195502.

as self-assemblies of nanoparticles[39]. Very recently, the naturally occurring quasicrystalline mineral icosahedrite has been identified in a sample from the Khatyrka River in Chukhotka, Russia[40,41].

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Member of the Nobel Committee for Chemistry

[39] D.V. Talapin (2009) "Quasicrystalline order in self-assembled binary nanoparticle superlattices", *Nature* **461**, pp 964-967.
[40] L. Bindi, P.J. Steinhardt, N. Yao, P.J. Lu (2009) "Natural Quasicrystals", *Science* **324,** pp 1306-1309.
[41] L. Bindi, P.J. Steinhardt, N. Yao, P.J. Lu (2011) "Icosahedrite, $Al_{63}Cu_{24}Fe_{13}$, the first natural quasicrystal", *American Mineralogist* **96**, pp 928-931.