

Quasicrystals: a brief history of the impossible

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Abstract The 30-year history of quasicrystals is one in which, time after time, the conventional scientific view about what is possible has been proven wrong. First, quasicrystals were thought to be mathematically impossible; then, physically impossible; then, impossible unless synthesised in the laboratory under carefully controlled conditions. One by one, these strongly held views have been disproven, the last only recently as the result of the discovery of a natural quasicrystal found in a meteorite dating back to the formation of the solar system. This paper is a brief personal perspective on this history of misunderstanding and discovery.

Keywords Quasicrystals · Icosahedral symmetry · Diffraction · Icosahedrite

This précis is based on a presentation delivered at the Accademia dei Lincei for a meeting commemorating the 100th anniversary of X-ray diffraction. The topic was *quasicrystals*, a subject that has captivated me for over 30 years with its never-ending ability to surprise. The recent awarding of the Nobel Prize in Chemistry to Dan Shechtman for his discovery of the first icosahedral solid and the centenary of X-ray diffraction made this a timely occasion for a historical reflection. This essay is intended

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as a brief personal perspective rather than a formal history. Over 11,000 papers have been written on this subject by other authors whose important contributions to the field could not be included in these few pages. I strongly commend the reader to reviews and other reminiscences to obtain a complete account.

1 Mathematically impossible

When the concept of quasicrystals was first introduced in 1984 (Levine and Steinhardt 1984), it met resistance because it appeared to contradict mathematical theorems that had been proven over the last two centuries and that had been adopted as essential truths in crystallography and solid state physics. Solids were thought to come in one of two forms, ordered and disordered, where ordered meant periodic and disordered meant amorphous or glassy. (Incommensurate crystals were known, but they are subject to the same symmetry restrictions as periodic crystals.) The classic theorems of Schoenflies and Fyodorov proven in the 19th century established that periodic solids are only allowed two-, three-, four-, or sixfold symmetry axes, limiting the number of possibilities in three dimensions to 32 point groups. Five-, seven- and all higher-order symmetry axes—an infinite number of possibilities—are incompatible with periodicity. Most forbidden of all is icosahedral symmetry, because it contains six independent disallowed fivefold symmetry axes, the maximum number possible in three dimensions. The historic work of von Laue and the Braggs showed that periodic solids exhibit point-like (Bragg) diffraction patterns with the same symmetry restrictions. By contrast, amorphous solids and glasses have isotropic diffuse diffraction patterns. All this is rigorously true.

Somehow, after several decades, point-like diffraction, order, and crystal became incorrectly conflated as mathematically equivalent. This was the conventional belief in 1981 when quasicrystals began to emerge as a hypothetical idea. Now, after quasicrystals, it is recognized that the terms are inequivalent, though the field has not yet broadened its view as much as it needs to, as discussed in the concluding remarks.

A small crack in the establishment view came with the theory of dislocation-mediated two-dimensional melting by Nelson and Halperin (1979), in which they argued for a two-stage melting process from crystal to liquid punctuated by an intermediate “hexatic phase”. Hexatic diffraction is neither Bragg nor simply diffuse; rather the pattern consists of a hexagonal arrangement of algebraically decaying finite-width peaks. The rotational symmetry is not remarkable, since it is crystallographically allowed, but the introduction of a “bond orientational order parameter” is, since it opens the possibility of a new type of ordered phase that had not been considered previously for monatomic systems.

In a study with David Nelson and Marco Ronchetti (Steinhardt et al. 1981), we examined whether a similar effect occurs in three-dimensional supercooled liquids and glasses composed of a single type atom with Lennard–Jones interactions. Earlier, Nelson and Toner (1981) had proposed the possibility of a cubic bond orientationally ordered phase, and the original intent of the investigation was to search for it. The effort failed, but something curious turned up instead: *icosahedral* bond orientational order extending many interatomic spacings. This was not a new phase, since the icosahedral correlations only spanned a finite distance, but it introduced a new element: crystallographically forbidden symmetry.

In a colloquium given in fall 1981, shortly after joining the faculty at the University of Pennsylvania, the hypothesis was floated that, by including two or more atomic species, it may be possible to have a truly new phase of matter with infinite-range icosahedral bond orientational order that evades the crystallographic theorems. In the audience was a young graduate student, Dov Levine, who approached afterward to ask if he could join in pursuing this idea. Warnings that the project was highly risky and may have not physical relevance did not deter him, and so the quest started.

Within a matter of months, the concept of quasicrystals developed. An inspiration was the two-dimensional Penrose tiling invented by Sir Roger Penrose (Penrose 1974) 7 years earlier. Penrose had identified a pair of tile shapes that can only fit together non-periodically, forming a self-similar pattern full of fivefold symmetric clusters of tiles. Penrose’s tiling attracted the attention of diverse theorists; several independently speculated that there might

be some analogy for solids [Conway (unpublished); Mackay 1981, 1982; Kramer and Neri 1984; Elser 1986], though in most cases it was not made clear what this meant. The approach in Levine and Steinhardt 1984 was systematic in first identifying the precise symmetries and order parameters that underlie the Penrose tiling and can be used to define a new phase of matter, namely *quasiperiodicity* and *bond orientational order*, and then showing that they generalize to arbitrary non-crystallographic symmetries in two and three dimensions.

Icosahedral symmetry became the first target. A three-dimensional quasicrystal was constructed using polyhedral units and certain “face-to-face matching” rules that force a quasiperiodic arrangement with perfect long-range icosahedral orientational order. The existence of matching rules was an important advance because it meant that, conceivably, local interactions (e.g., between atoms or molecules) could be sufficient to make the new phase a ground state. The hypothetical phase was ultimately dubbed *quasicrystal*, short for quasiperiodic crystal (Levine and Steinhardt 1984).

The mathematical properties are subtle. In real space, the lack of periodicity means that there is no translation of a quasicrystal pattern that *exactly* overlays the original; consequently, each atom or cluster of atoms in a quasicrystal has a distinct global arrangement of atoms surrounding it. On the other hand, there is a sequence of translations of the pattern that *almost* overlay the original except for a small density of misalignments; and that density can be made arbitrarily small by going to ever larger translations. This is the closest to translational symmetry without being periodic. Similarly, there is sequence of points such that a rotation by $2\pi/5$ about the point *almost* overlaps the original (see Steinhardt and Bindi 2012 for illustrations of these properties).

In reciprocal space, the *almost* translational symmetry guarantees a diffraction pattern consisting only of true point-like peaks just like the Bragg peaks in a periodic crystal. The peaks are arranged in a reciprocal space lattice of points described by an integer sum of basis vectors set by the rotational symmetry, just as for periodic crystals, but with a symmetry that is forbidden to crystals. However, unlike the case for crystals, the number of integer linearly independent basis vectors D in d -dimensions exceeds d , resulting in a reciprocal lattice with a dense arrangement of peaks labeled by D quasi-Miller indices. For example, the reciprocal lattice for three-dimensional icosahedral quasicrystals has $D = 6$ quasi-Miller indices. The result is a diffraction pattern that is distinctive and instantaneously recognizable.

An important corollary is that the real space structure can be viewed as a projection or cut through a subset of points in a six-dimensional hypercubic lattice; and the diffraction pattern can be computed as the convolution of the

six-dimensional crystal diffraction pattern with the window function that defines the projection (Kramer and Neri 1984; Kalugin et al. 1985; Duneau and Katz 1985; Elser 1986).

2 Physically impossible, part I

Although the quasicrystal concept is mathematical sound, it was not clear at first whether it had physical relevance. A patent disclosure filed in 1983 was rejected on the grounds that it was unlikely to find real materials with this symmetry (Levine and Steinhardt 1983). Similar comments were made by reviewers of grant proposals. As a result, the decision was made to take a sabbatical leave in fall 1984 at the Thomas J. Watson Research Laboratory in Yorktown Heights, NY, with the goal of stimulating the search for a physical example.

The search was interrupted in October 1984 by a visit by David Nelson. The meeting provided the first opportunity to present him the concept of quasicrystals and the signature diffraction patterns that had been computed. As it turned out, Nelson had come with news of his own: a preprint, by Dan Shechtman, Ilan Blech, Denis Gratias and John Cahn, describing their study of a puzzling new alloy of aluminum and manganese (Shechtman et al. 1984; the paper ultimately earned Shechtman the Nobel Prize). The highlight of the paper, which the four authors could not explain, was a series of diffraction patterns showing sharp diffraction spots, like a crystal, but arranged with a three-dimensional pattern with forbidden icosahedral symmetry. The reaction to seeing the experimental pattern was joyous amazement, for it matched the computed pattern of a quasicrystal sitting on the desk.

After contacting Cahn and Shechtman, we learned that, working a few hundred miles to the south and with no knowledge of our theoretical work on quasicrystals, Dan Shechtman had discovered an icosahedral solid 2 years earlier, on April 8, 1982, in the midst of a survey of aluminum-transition metal alloys at the National Bureau of Standards (now NIST). Within NBS, his observation met with skepticism, but Shechtman persisted. Two years later, after a series of cross-checks, the paper was submitted and some preprints distributed. One was the preprint that Nelson carried. The paper had no theoretical explanation (though see below the discussion of Shechtman and Blech 1985). Immediately following the meeting with Nelson, a draft was begun explaining the theory of quasicrystals, emphasizing how they opened the possibility of infinitely many new symmetries, including icosahedral, and proposing that Shechtman's alloy might be a physical realization of a quasicrystal. (The Shechtman et al. data at the time was not convincing, as described below, so this part of the paper was somewhat tentatively stated.) The theory

paper appeared in *Physical Review Letters* a month after the Shechtman et al. experimental paper, and, almost immediately, the name of the theory became attached to icosahedral alloys. That association was premature, though.

3 Physically impossible, part II

Despite the qualitative agreement between the predicted and observed diffraction patterns, the quasicrystal explanation for Shechtman's icosahedral aluminum–manganese phase was not readily accepted. First, as shown by X-ray studies (Bancel et al. 1985), the diffraction peaks are not truly point-like, as predicted by the quasicrystal theory: the diffraction peaks of the aluminum–manganese alloy have experimentally resolved finite widths. Annealing could not be used to sharpen the peaks because the phase is unstable to crystallization.

Adding to the skepticism was a seemingly compelling heuristic argument suggesting that the quasicrystal phase is physically impossible to achieve in realistic atomic systems. In a quasiperiodic structure, it was argued, no two atoms or clusters occupy identical positions in the overall structure, so they cannot self-organize into a perfect quasicrystalline arrangement (unless the atoms have long-range interactions, which is physically implausible). Tessellating with Penrose tiles appears to reinforce this conclusion: randomly adding tiles sequentially to a cluster of Penrose tiles leads to frequent mismatches and defects. The combination of the finite-peak widths and the seemingly unshakable theoretical argument opened the door to alternative theories.

Pauling (1985) dismissed the quasicrystal theory and proposed instead that the phase is a multiply twinned crystal. Because of the prominence of the author, his strongly worded criticisms and his proposal have received more attention in histories than they actually merit. In actuality, the twinning hypothesis never took hold because test after test failed to find any evidence of individual crystallites.

The serious contender was the *icosahedral glass model*, first described by Shechtman and Blech (1985) and, then, fully developed by Stephens and Goldman (1986). An icosahedral glass consists of random densely packed arrangement of icosahedral clusters arranged with common orientation. Despite the translational disorder, the icosahedral glass model produces surprisingly sharp finite-width peaks whose positions fit the measured results well. Even today, the data from aluminum–manganese is not good enough to distinguish clearly whether Shechtman et al.'s phase is icosahedral glass or a defective quasicrystal.

Three years later, though, two developments totally reversed opinion. On the theoretical front, Onoda et al. (1988) announced alternative local rules for adjoining

Penrose tiles that allow perfect growth of a quasicrystal tiling around a single point defect (analogous to crystal growth around a screw dislocation). The heuristic argument was proven wrong—there is no theoretical barrier to growing perfect quasicrystals after all. On the experimental front, Tsai et al. (1987) discovered a quasicrystal phase [with composition later determined by Bancel (1991), $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$] that can be very slowly quenched and exhibits resolution-limited point-like peaks, decisively ruling out the icosahedral glass picture. Less known is that Linus Pauling visited our group at the University of Pennsylvania in 1989 to compare his twinning theory to the exquisite data obtained by Bancel and Heiney on $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$; after conceding that his twinning model would now require unrealistically large unit cells, Pauling offered to sponsor and edit back-to-back papers by him and by the Penn group that together made clear that the quasicrystal picture is superior (Pauling 1989; Bancel et al. 1989; Pauling, private communication).

The $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ alloy, which plays an important role later in this story, should perhaps be viewed as the first *bonafide* quasicrystal to be synthesised in the laboratory. Since then, well over one hundred high-quality quasicrystalline materials have been identified, many with icosahedral symmetry, but also with other forbidden symmetries predicted by the quasicrystal theory.

4 Naturally impossible

Despite the successes of the quasicrystal picture, there was still not a consensus concerning the status of quasicrystals as a fundamental state of matter even two decades after the icosahedral glass and multiple-twinning pictures were disproven. A common view remained that quasicrystals are too complicated to be stable states of matter and that all ground states are crystalline. This view led to an alternative “entropic” quasicrystal picture based on considering random tilings (think of random arrangements of Penrose tiles without matching rules) and showing that icosahedral symmetry can emerge for entropic reasons even though it is not energetically preferred (Henley 1991). According to the entropic picture, quasicrystals are always inherently delicate, metastable oddities that may only be synthesised for ideal compositions and under highly controlled artificial conditions. Yet, the original theory (Levine and Steinhardt 1984), supported by the construction of tilings with matching rules and kinetic growth rules that can force quasicrystallinity, argued that quasicrystals can be as energetically stable and robust as crystals and can form even when conditions are not ideal.

A search for natural quasicrystals serves as a litmus test. If quasicrystals are energetically stable and on the same

footing as crystals, as the latter view suggests, then it is plausible that quasicrystals formed under natural conditions within complex rocks, just like crystalline minerals. According to this view, the oldest quasicrystal on Earth is not likely a synthetic sample made in the last century, but a mineral formed eons ago. Of course, there are other reasons for conducting a search. A successful find would also open a new chapter in the study of mineralogy, forever altering the conventional classification of mineral forms. Below is a brief description of the search; a more complete discussion with figures can be found in Steinhardt and Bindi (2012).

After informally searching for quasicrystals in museums failed, a decade-long systematic quest for natural quasicrystals began in 1999 in collaboration with Ken Deffeyes in the Department of Geoscience; Nan Yao, Director of the Imaging and Analysis at Princeton, and a bright senior thesis student, Peter Lu. My concept was to begin with a computer-database search based on powder diffraction data. The advantage of using powder diffraction data is that there exists a collection of over eighty thousand patterns in the International Center for Diffraction Data Powder Diffraction File (ICDD-PDF) that includes nearly nine thousand mineral patterns. With Lu, quantitative figures-of-merit were derived that can be used to rank powder patterns to identify the most promising quasicrystal candidates in the ICDD-PDF. One figure-of-merit measures how closely the powder peak wavevectors match those for an ideal icosahedral pattern, and the other measures how closely the relative intensities match. Scanning the database using these figures-of-merit identified the most promising mineral candidates. As many of the minerals as possible were acquired and studied by TEM and X-ray diffraction, but, in the end, no new quasicrystals were discovered in the original 2-year study (Lu et al. 2001). However, the paper included an offer to collaborate with others interested in joining the quest.

Six years later, the call was answered by Luca Bindi, Head of the Division of Mineralogy of the Museo di Storia Naturale of the Università di Firenze (Italy). The fact the Bindi was the one to answer was a remarkable stroke of luck, not only because of what he had in his collection, but also because of the talent and dedication he brought to the project, often saving the project over the next few years when it became mired. Bindi began by testing samples on the list that were also in his museum collections. A year later, when no successes were found among candidates on the list, the decision was made to test minerals not listed in the ICDD-PDF catalog altogether but whose compositions were similar to known quasicrystals synthesised in the laboratory. The search soon focused on a sample labeled “khatyrkite” (catalog number 46407/G), acquired by the Florence museum in 1990 and cataloged as coming from the Khatyrka region of the Koryak mountains in the

Chukotka autonomous okrug on the north eastern part of the Kamchatka peninsula (Bindi et al. 2009, 2011). As first reported by Razin et al. (1985), khatyrkite, nominally (Cu, Zn) Al₂, is a tetragonal crystal found in association with cupalite, nominally (Cu, Zn) Al, which is orthorhombic. The Florence sample was thin-sliced and examined by electron microprobe, which revealed a variety of metallic phases aside from khatyrkite. Among them were two whose chemical composition did not match those of known minerals. The sample was pulverized and powder diffraction patterns of each of the two unknown phases were obtained. One scored high according to the figures-of-merit. That sample was sent to Princeton for analysis by transmission electron microscopy.

Working with Yao, the diffraction pattern of the new phase was obtained in the early morning hours of January 1, 2009 and found to reveal the unmistakable signature of an icosahedral quasicrystal. Patterns of sharp peaks form straight lines in an incommensurate lattice with five-, three- and twofold symmetry (Levine and Steinhardt 1984). In addition, the angles between the symmetry axes are consistent with icosahedral symmetry. Twenty-five years after the concept of quasicrystals was first introduced and a decade into the systematic search, the first natural quasicrystal had been discovered. The composition was measured to be Al₆₃Cu₂₄Fe₁₄, the same composition (Bancel 1991) as the first *bonafide* quasicrystal synthesised by Tsai et al. (1987) in the laboratory.

The road to acceptance was not simple. Consultations with renowned petrologist Lincoln Hollister (Princeton) and meteorite expert Glenn Macpherson (Natural History Museum, Smithsonian Institution) led to a familiar response: impossible! This time, though, the quasicrystal was not the issue; rather, the problem was that the quasicrystal, khatyrkite and other metallic alloy phases found in the sample contain metallic aluminum, which requires extraordinary reducing conditions that were thought to be unattainable naturally. Establishing that the sample is indeed natural took nearly 2 years of laboratory (Bindi et al. 2012) and detective work, and, ultimately, a geological expedition to the Koryak Mountains of Chukotka in far eastern Russia to find additional samples. The extraordinary story, recounted elsewhere (Steinhardt and Bindi 2012) established that the quasicrystal and the rock containing it are part of a carbonaceous chondrite with calcium aluminum inclusions that dates back 4.5 Gya to the formation of the solar system.

The first natural quasicrystal has been officially accepted by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association and named *icosahedrite* for the icosahedral symmetry of its atomic structure (Bindi et al. 2011). The mineral is classified as icosahedral (with a face-centered icosahedral

symmetry abbreviated as $Fm\bar{3}5$) with peaks labeled by six-indices (corresponding to the six basis vectors that define the reciprocal lattice).

From the perspective of condensed matter physics, the discovery of icosahedrite constitutes significant new support for the original proposal that icosahedral quasicrystals can be energetically stable states of matter, on the same footing as crystals (Levine and Steinhardt 1984). The alternative entropic picture is hard to reconcile with the extreme conditions under which icosahedrite formed and annealed. The finding of natural quasicrystal enclosed within stishovite and other evidence not presented here indicates that formation likely occurred under shock conditions and rapid cooling where entropic effects were unimportant compared to energetics and kinetics in forming the phase. Furthermore, all the icosahedrite grains that have been studied thus far have the same composition, to within better than one per cent, even though the phases surrounding them are different. This observation is expected if the composition corresponds to an energetically preferred structure, whereas the entropic model generally allows a continuous range of composition (corresponding to crystal approximant structures). Further laboratory studies could shed light on this issue.

5 Concluding remarks

For more than half a century, “X-ray diffraction” and “crystallography” were synonymous. Quasicrystals shattered the connection, demonstrating that other kinds of order are possible, leading to a new phase of matter. Why did it take so long for quasicrystals to be discovered, and why was there the large degree of resistance and misunderstanding recounted above? Perhaps the answer is curiously human: anything but periodicity is hard to envision. Consider, for example, that studies of patterns created by the ancient Egyptians show that they discovered all seventeen of the two-dimensional plane crystallographic groups, but, with one possible exception (Lu and Steinhardt 2007), no one prior to the 20th century constructed a quasicrystalline pattern. This is not because quasicrystalline patterns are rare: there are only a finite number of rotational symmetries compatible with periodic patterns but an infinite number compatible with quasiperiodicity. Even today, only a few examples (5-, 8-, 10-, 12-fold symmetry in the plane and icosahedral symmetry in three dimensions) have been found in solids, even though there is no known physical restriction ruling out the other symmetry possibilities. Clearly, there is plenty of opportunity for new quasicrystal discoveries using X-ray diffraction in the century ahead.

In considering the future of diffraction science, though, a broader vision is called for. Is the human imagination

preventing us from envisaging other kinds of ordered phases? Almost certainly, yes. Solids whose diffraction patterns consist of sharp reflections are well mined by now, but recently there have been interesting investigations of matter with long-range correlations but no sharp reflections at all. An example is a new class of solids called “hyperuniform disordered” (Torquato and Stillinger 2003; Florescu et al. 2009), homogeneous materials with the short-to-intermediate characteristics of a glass (isotropic, random) and the long-range characteristics of a crystal (density fluctuations that grow as the surface area rather than the volume). The diffraction pattern is distinctive: the scattering intensity is diffuse, like a glass, except that the intensity approaches zero as the wavenumber approaches zero, like a crystal. There are many subspecies, such as solids where the scattering intensity is zero for a finite range of wavenumbers surrounding zero in addition. It is hard to imagine a structure that has these properties, yet it is possible (see Florescu et al. 2009 to see examples). Furthermore, hyperuniform disordered solids are potentially important because they have large band gaps despite the lack of translational order, resulting in novel types of semiconductors. Using designer material techniques, examples have been fabricated in the laboratory on the microwave scale and their photonic properties have been studied (Man et al. 2012).

Hyperuniform disordered solids are probably the tip of a huge iceberg of novel possibilities without point-like diffraction. Our ability to discover them is limited only by the human imagination. My hope is that the bicentenary celebration of X-ray diffraction will feature many new classes of novel materials that have yet to be envisioned.

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