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Quasicrystals: Sections of Hyperspace

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It was, and still is, a fundamental law of crystallography that fivefold rotational symmetry and three-dimensional (3D) lattice periodicity are mutually incompatible. With this in mind, the Israeli materials scientist Dan Shechtman did not trust his eyes when he inspected electron diffractograms of rapidly solidified Al-Mn. What he expected to see was either diffraction patterns with sharp Bragg reflections exhibiting one of the crystallographic symmetries 1, 2, 3, 4, or 6, or a few diffuse rings indicating a metallic glass. But he saw the apparently crystallographically impossible: tenfold rotational symmetry *and* sharp Bragg reflections, the latter indicating lattice periodicity. Shechtman, puzzled by this observation, had a closer look on the diffraction symmetry and found it to be overall icosahedral (Figure 1 and 2).

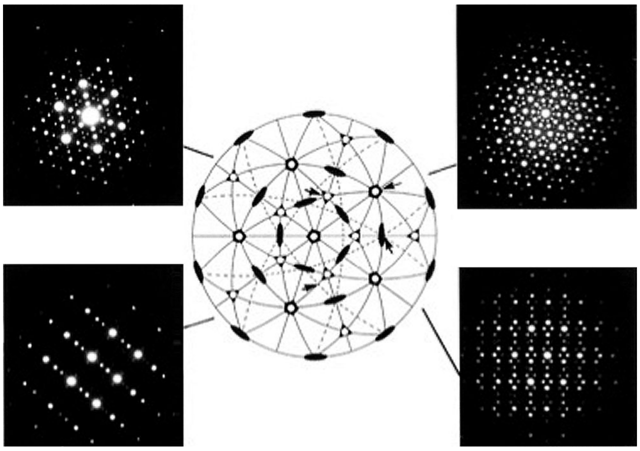
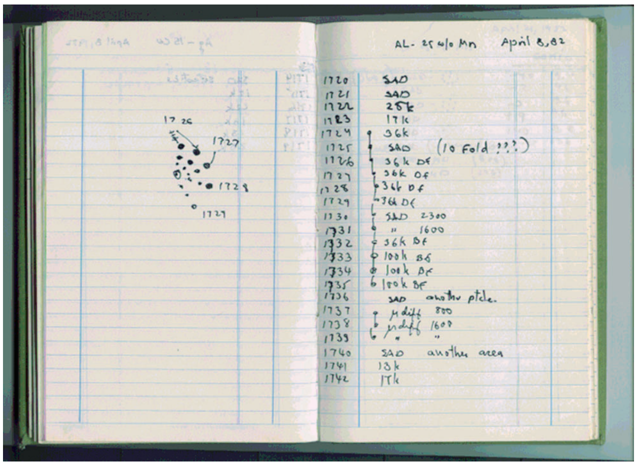


Figure 1. Electron diffraction patterns of the Al-Mn quasicrystal taken along different symmetry directions indicating icosahedral diffraction symmetry. Reprinted from Ref. [1].

His colleagues at the National Institute of Standards (NIST), Gaithersburg, Maryland, where he worked on leave from his home institution, the Technion in Haifa, Israel, were skeptical. The reactions were similar to that of the eminent metallurgist John W. Cahn: "*Go away, Dany. These are twins and that's not terribly interesting*".[2] Indeed, twinning is a frequently observed phenomenon. Even simple metals, such as silver for instance, can form icosahedral twins mimicking icosahedral diffraction symmetry (for a review on fivefold twinning, see Ref. [3]).



AL- 25 w/o Mn April 8, 82

1720	SAD	
1721	SAD	
1722	25k	
1723	17k	
1724	36k	
1725	SAD	(10 Fold ???)
1726	36k DF	
1727	36k DF	
1728	36k DF	
1729	36k DF	
1730	SAD	2300
1731	"	1600
1732	36k DF	
1733	100k DF	
1734	100k DF	
1735	100k DF	
1736	SAD	another ptcle.
1737	μdiff	800
1738	μdiff	1600
1739	"	"
1740	SAD	another area
1741	13k	
1742	17k	

Figure 2. Shechtman's notes of April 8, 1982, with the observation of tenfold symmetry highlighted by three question marks.

Heated Debate

Shechtman was not able to publish his unexpected findings before November 1984. He was supported by three co-authors: John W. Cahn, who changed his mind after the French crystallographer Denis Gratias, a co-author as well, confirmed Shechtman's experimental work; Ilan Blech, from the Technion contributed an interpretation of the diffraction patterns in terms of a "*random packing of nonoverlapping parallel icosahedra attached by edges*". In this paper,[1] the authors had to explicitly state that crystals "*cannot and do not exhibit the icosahedral point-group symmetry*".

There were many sceptics in the first years, with the double Nobel laureate Linus Pauling, the most prominent, refusing to accept the existence of this novel kind of structural ordering. "*Apparent icosahedral symmetry is due to directed multiple twinning of cubic crystals*"[4] was their mantra. Trying to keep pace with the increasing quality of quasicrystals and their diffraction patterns, however, Pauling was forced to increase the number of atoms per cubic unit cell for his twinning model from a mere 1120[4] to a remarkable 19400.[5]

Predecessors

Looking back, it is hard to understand why it took such a long time until full acceptance of this novel ordering state of

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matter was reached. Already in 1974, the British mathematician Roger Penrose discussed quasiperiodic tilings with fivefold orientational symmetry of the tiling edges.[6] Martin Gardner popularized these tilings in his column “Mathematical Games” in the journal Scientific American three years later.[7] The British crystallographer Alan L. Mackay was the first envisioning crystal structures based on these Penrose tilings. He even performed optical diffraction experiments resulting in the first diffraction patterns with tenfold symmetry *and* sharp Brag reflections.[8] Paul J. Steinhard and his collaborator Dov Levine were aware of these papers and published the outline of a first theory of quasicrystals[9] only six weeks after Shechtman.[1]

Higher-Dimensional Approach

How can we explain the apparent violation of crystallographic laws as indicated by sharp Bragg reflections arranged with icosahedral diffraction symmetry? Already in the year 1949, the German crystallographer Carl Hermann discussed the possible point-group symmetries of lattices in arbitrary dimensions.[10] He found fivefold and icosahedral symmetries to be compatible with 4D and 6D hyperlattices, respectively. If we consider the 3D diffraction pattern of a quasicrystal as projection from 6D reciprocal space, then the quasicrystal structure results as 3D section of the corrresponding 6D hypercrystal structure. This powerful approach, which is commonly used today, has been first applied to quasicrystals by the Dutch mathematician Nicolas G. de Bruijn by defining matching rules for the Penrose tiling.[11] The principle is shown on the example of the 1D quasiperiodic Fibonacci sequence (Figure 3).

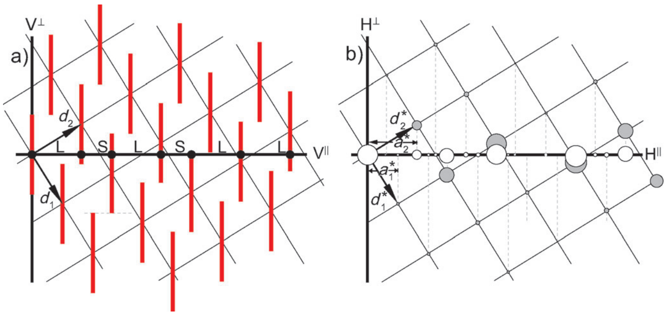

Figure 3. The 1D Fibonacci sequence ..LSLSLL.. in the 2D description: a) The Fibonacci sequence results as a cut of a 2D hypercrystal by the physical space $V^{\parallel}$, and b) its Fourier transform (diffraction pattern) as a projection onto the physical reciprocal space $H^{\parallel}$.

Occurrence

Quasicrystals are binary or ternary phases that have so far been found in more than fifty intermetallic systems (Figure 4), frequently accompanied by periodic approximants. Approx-

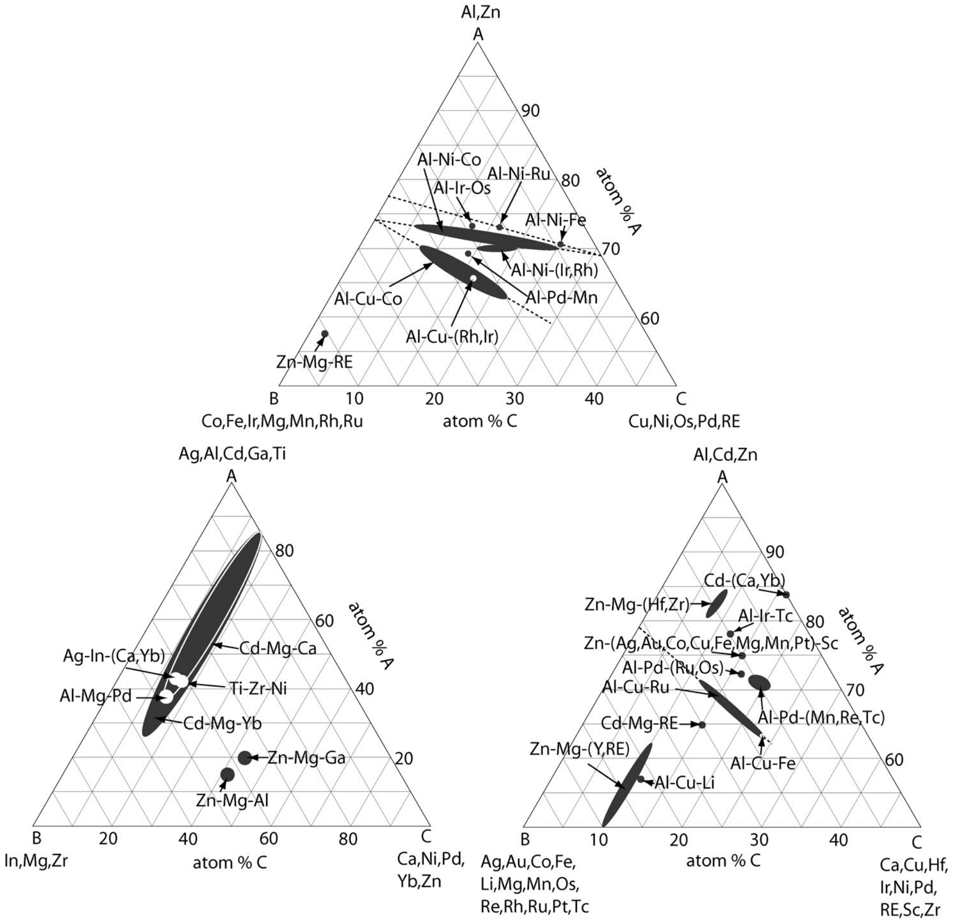

Figure 4. Stability regions of (top) decagonal and (bottom) icosahedral quasicrystals. RE denotes rare-earth metals. Note that only the A-rich parts of the concentration diagrams are shown (reprinted from Ref. [12]).

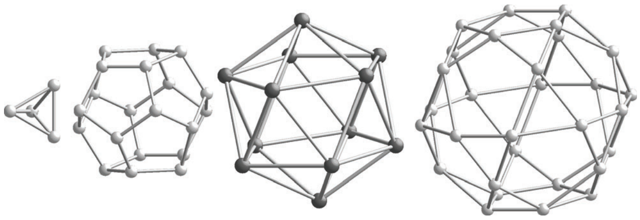

Figure 5. Shell structure of the $Cd_{54}Yb_{12}$ Tsai cluster (Cd light spheres, Yb dark spheres).

imants possess periodic structures built from the same large structural subunits ("clusters"[13]) as quasicrystals (Figure 5).

Most stable quasicrystals show either icosahedral or decagonal diffraction symmetry. They can be grown by standard methods as perfectly as any other metal crystal. Recently, quasiperiodic structures have also been identified in self-organized colloidal systems with 12- and 18-fold symmetries (see for example Ref. [14] and references therein).

Structure, Properties, and Applications

A simple model of a 2D quasiperiodic structure can be obtained by properly decorating a quasiperiodic tiling. Such a model is not far from reality as illustrated on the example of a decagonal quasicrystal in the ternary system Al-Co-Ni (Figure 6).

Generally, quasiperiodic structures can be described as packings of partially overlapping clusters with non-crystallographic symmetry. It can be shown that quasiperiodicity allows the most efficient packing while maintaining the cluster symmetry.[15,16] Furthermore, structural subunits present in each cluster match together resulting in an interpenetrating network of flat atomic layers, extended over the whole crystal (Figure 7).[17]

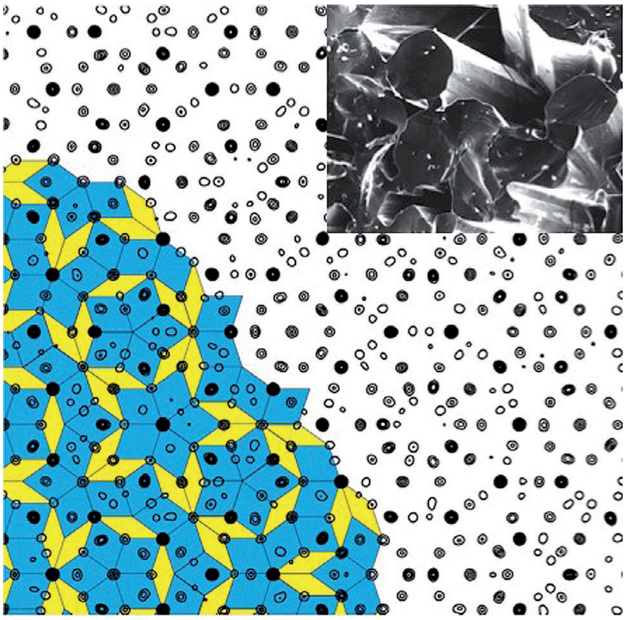

Figure 6. Projected electron density map of decagonal Al-Co-Ni with underlying Penrose tiling. In the insert (upper right), some intergrown decaprismatic quasicrystals are depicted.

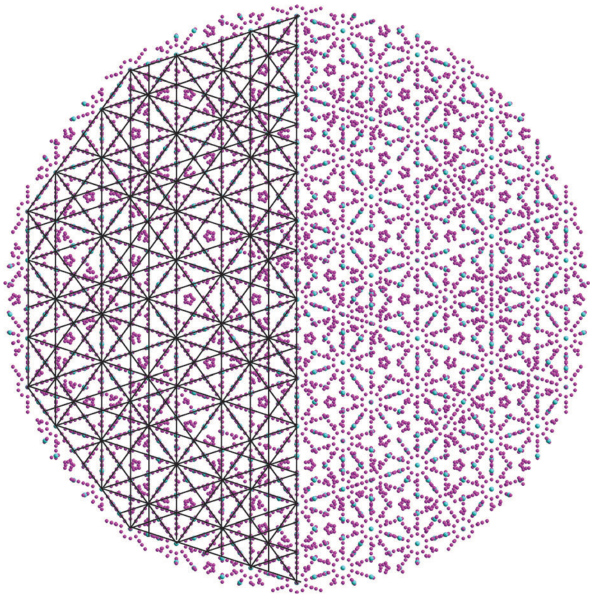

Figure 7. Projection of a spherical section (diameter 100 Å) of the structure of icosahedral Cd-Yb[20] along a fivefold axis. Almost all atoms are arranged in flat atomic layers, forming a framework compatible with fivefold symmetry. The atomic layers interpenetrate each other in a way that is only possible in quasiperiodic structures.

Strange structures may give rise to strange properties. Indeed, quasicrystals have a special electronic structure leading to low electronic and thermal conductivity as well as a small surface energy. Remarkably, the temperature dependence of these conductivities is opposite to that of simple metals.

To date there are only niche applications known for quasicrystals that are based on their non-stick properties in frying pans and because of their aging resistance and hardness in surgical steels. For more information, see the book *Useful Quasicrystals*.[18]

Perhaps more promising applications are emerging in the field of photonic and phononic quasicrystals.[19] Their arbitrarily high symmetry allows the creation of omnidirectional bandgaps, even for low-contrast heterostructures; their quasiperiodicity offers increased flexibility in bandgap engineering by specific defect incorporation. Photonic crystals can be of interest for optical devices to be used in the communication industry or optical computers. Phononic crystals can for example be used as thermal barriers (nanometer scale) and acoustic barriers (meter scale).

Paradigm Shift

Quite a few textbooks still tell us that the thermodynamic equilibrium state of any single-phase solid is crystalline, that is, shows 3D lattice periodicity on time and space average. The discovery of incommensurately modulated structures and composite crystals in the first half of the last century did not really have any influence on this classical view. These cases could be just seen as regular distortions or intergrowths, respectively, of periodic structures. After the discovery of quasicrystals, however, these constructs to conserve periodicity were not applicable anymore. With the discovery of quasicrystals, a fundamentally new category of long-range order had to be constituted.

The origin of quasiperiodicity is still not fully understood. Since quasiperiodic ordering can take place in materials with completely different interaction potentials, from intermetallics to terpolymers and self-assembled colloids, several different ordering and stabilization mechanisms must be in place. For more detailed and comprehensive information on quasicrystals and their fundamentals, see the book *Crystallography of Quasicrystals*.[21]

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