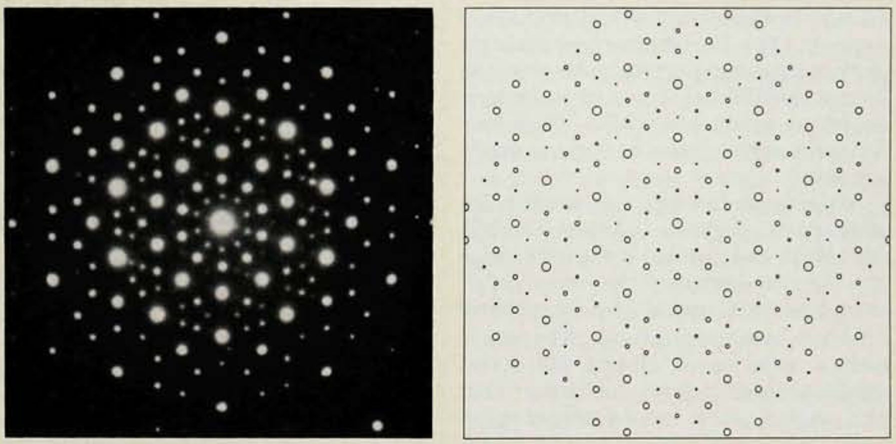
Forbidden fivefold symmetry may indicate quasicrystal phase

You can't tile a bathroom floor with regular pentagons. The crystallographic equivalent of this mundane truth is the inviolate classical rule that no crystal structure—in two or three dimensions—can possess fivefold rotational symmetry. It was with complete surprise, therefore, that Dan Shechtman and his colleagues recently discovered[1] a fivefold symmetric *point* diffraction pattern for micron-size grains of metallic alloy prepared by rapid cooling in their National Bureau of Standards laboratory.



Electron diffraction pattern (left) of a rapidly cooled grain of Al_6Mn alloy, measured by Dan Shechtman *et al.*, indicates crystallographically *forbidden* icosahedral rotation symmetry. With the beam directed along one of the 6 fivefold rotation axes, ones sees something quite new and surprising—a pentagonal (in fact tenfold) pattern of sharp Bragg peaks. Quite independently, theorists Dov Levine and Paul Steinhardt, imagining materials organized like three-dimensional generalizations of the nonperiodic Penrose tiling, calculated a Bragg delta-function diffraction pattern (right) for such a "quasicrystal." The calculated intensities, indicated by circle size, are in good agreement with the data, of which the theorists knew nothing. The peaks lie along quasiperiodically spaced lines, as do the points of the quasilattice.

A diffraction pattern exhibiting fivefold symmetry would have been astounding enough, even if it had not been a *point* pattern—a pentagonal array of sharp Bragg peaks. A diffraction pattern of diffuse circles, for example, with intensity maxima at five equidistant points on each circle would indicate something quite novel, but nonetheless comprehensible—a noncrystalline material with fivefold bond-orientational order, but without the rigorous translational periodicity that is the defining criterion of a crystal. But a pattern of sharp Bragg peaks, so the conventional wisdom went, can only be produced by a crystal—and a crystal quite definitely cannot exhibit pentagonal symmetry.

The NBS group's puzzling data may well have revolutionary implications for condensed-matter physics. They lead us to the notion of a quasicrystal, a highly organized phase of solid material quite distinct from crystals, glasses or anything else one has seen before.

What Shechtman and his colleagues found, in fact, was a diffraction pattern indicating a structure possessing the rotational symmetry of a regular icosahedron—the last of the five Platonic solids, with 20 equilateral triangular faces, 10 threefold axes and 6 fivefold axes of rotational symmetry. Although the icosahedral group is a forbidden symmetry of classical crystallography, it has in recent years held a certain fascination for crystallographers and recreational mathematicians. Alan Mackay (Birkbeck College, London) and other crystallographers have noted that in the formation of crystallites around gas atoms there is often a tendency of the first few shells of atoms to arrange themselves icosahedrally around the seed atom. As the crystal grows beyond the first few shells, the lattice must of course abandon the forbidden icosahedral symmetry if it is to acquire translational periodicity.

Recreational mathematicians have been attracted by the crystallographically forbidden icosahedral group because it is the largest finite subgroup of the rotation group in three dimensions. Starting from some avocational work in the theory of tiling by particle theorist Roger Penrose (Oxford)—which made its first public appearance in Martin Gardner's "Mathematical Games" column in the January 1977 issue of *Scientific American*—a number of people have undertaken to generalize Penrose's aperiodic fivefold-symmetric tiling scheme to three dimensions, some just for fun, others like Mackay in the hope that it might have some relevance to the arrangement materials occurring in nature.

Jut as the NBS group was making its experimental discovery, and knowing nothing of this work, theorists Paul Steinhardt and Dov Levine at the University of Pennsylvania were undertaking a rigorous mathematical treatment[2] of the Penrose tiling generalized to three dimensions. They showed that these aperiodic "quasilattices" would possess infinitely long-range icosahedral rotation symmetry. More important, in defiance of the conventional wisdom among crystallographers, they showed that the Fourier transform (diffraction pattern) of these lattices, despite their lack of translational periodicity, turns out to be a point pattern of Bragg delta functions. When they first saw the NBS diffraction data last fall, Steinhardt (on leave at IBM) and Levine were astonished and pleased to find that they appeared almost identical to their calculated Fourier transforms.

Electron diffraction. Shechtman was a visitor at NBS from the Technion in Haifa. The other members of the group were John Cahn (NBS), Denis Gratias, a visitor from the Centre d'Études de Chimie Metallurgique in Vitry, France, and Ilan Blech (Technion). The discovery of the peculiar diffraction pattern was as fortuitous as it was unexpected. The group had been studying the properties of alloy structures produced by

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the rapid cooling of molten aluminum with small admixtures of transition metals such as iron or manganese. Splattering the melt onto a cold disk rotating at 6000 rpm, one hopes that very fast solidification will yield interesting crystalline alloy structures.

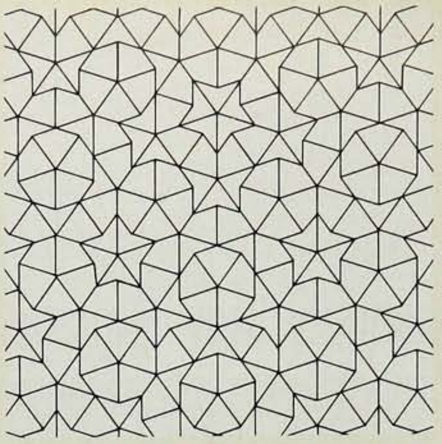
Examining—under a transmission electron microscope—micron-size grains produced in this way from a 6-to-1 (atomic ratio) melt of Al and Mn, Shechtman happened to notice that the image contrast varied strongly with the orientation of the grains in the electron beam. Because this would ordinarily suggest that the grains are strongly diffracting single crystals, he went on to use the 100-keV beam of the microscope to produce electron diffraction patterns of the grains at various orientations.

What he found was a series of point diffraction patterns having twofold, threefold and fivefold symmetry, with the angles between the axes corresponding to those of the icosahedral rotation symmetry group. The sharp point patterns of Bragg diffraction peaks seemed a clear indication that the grains were indeed single crystals—but every crystallography text tells us the icosahedral group is an inadmissible crystal symmetry. It could not be a crystal, but it was clearly a highly organized structure, maintaining bond-orientational order over micron distances—10^4 atomic diameters.

"My first reaction was that this must be twinning," Cahn told us. Fivefold point diffraction patterns are known to occur when several different crystals grow as a single entity in such a way that they mimic a fivefold rotational symmetry. But further imaging studies with the electron microscope soon convinced the group that this was not twinning. The electron micrographs also indicated that this particular ordered state—whatever it was—grew outward from a nucleation center like an ordinary crystal. Such nucleation and growth indicate that the transition from the liquid state is a first-order phase transition.

This new phase turns out to be metastable. At room temperature it persists indefinitely, but at 350 °C it reverts to an ordinary crystalline Al_6Mn structure in a few hours; at 400 °C it's a matter of minutes. The transition from the icosahedral phase to the crystalline phase is also observed to be first order.

Back in Haifa shortly after the discovery of the new phase, Shechtman and Blech tentatively proposed a model to explain it. Every Mn atom, they suggested, sits at the center of an icosahedron at each of whose 12 vertices sits an Al atom. Because there are only six Al for each Mn, however, adjacent icosahedra must share Al



Penrose tiling, a two-shape scheme devised by Roger Penrose that can only tile the plane aperiodically. In this example the shapes are "darts" and "kites." His rules forbid combining them to form rhombi, which *can* tile periodically. Side ratios are the golden mean, and angles are multiples of $\pi/5$.

atoms; and it is this sharing that orients all the icosahedra in the same direction throughout a grain. The attachment of these unit icosahedra to one another would be random; there could, of course, be no long-range translational order. But an approximate periodicity would appear, they argue, sufficient to explain the general features of the observed diffraction pattern.

Cahn told us that this fairly simple picture is now known to be wrong. Very recent Mössbauer studies by Lydon Swartzendruber at NBS have shown that there are two distinguishable kinds of Mn sites in the array, both quite asymmetric with respect to the Al sites. An intriguing discovery from the Mössbauer data is that the relative frequency of occurrence of these sites is 1.6 ± 0.2, tantalizing close to the "golden mean" of Hellenic architecture, given by $(\sqrt{5}+1)/2$. This golden mean recurs like a *leitmotif* in Penrose tiling and in its three-dimensional quasicrystal generalization.

Penrose tiling. Most geometric shapes cannot tile a plane or pack space. Cubes can; icosahedra can't. But sometimes when a single shape won't do, a pair of shapes used together can. Until recently, it was conventional wisdom among tiling theorists, albeit without proof, that any finite set of different tiles that can tile the plane can do it periodically. In 1974, Penrose devised the simplest possible counterexample—a pairs of shapes that could tile the plane, but *only* without translational periodicity. Many different pairs of quadrilateral shapes will do the trick; they all have two characteristic lengths whose ratio is the golden mean. Because of its potential commercial value for games and decorations, Penrose was reluctant to disclose this tiling scheme until he had applied for patents two years later.

In 1981 Mackay pointed out that one could generalize the Penrose tiling with a pair of rhombohedra, one acute, the other obtuse. He noted that such nonperiodic structures would have local fivefold symmetry axes, and he studied their Fourier transforms empirically by shining light through masks to form diffraction patterns. In France, Remy Mosseri (CNRS, Meudon) and Jean François Sadoc (Orsay) used Penrose patterns to model real physical systems.

Shortly before the NBS data became known last fall, Peter Kramer and R. Neri (Tübingen) published[3] a three-dimensional Penrose pattern which they derived by projecting down from higher-dimensional hyperlattices. Veit Elser did much the same thing "just for fun" in 1982, while he was a graduate student in particle physics at Berkeley. But his work, like that of Robert Amman (Cambridge, Mass.), another important "recreational" contributor, remains unpublished.

Theoretical work. Steinhardt and Levine were motivated by the suggestive results of computer stimulations Steinhardt had undertaken in 1982 with David Nelson (Harvard) and Marco Ronchetti (Free University of Trento). Supercooling a simulated liquid of about a thousand idealized argon atoms below its equilibrium melting temperature, they observed the beginnings of extended icosahedral bond-orientation order. Nelson and Steinhardt then set out on different paths in search of an explanation. While Steinhardt was led by the Penrose tiling patterns to the idea of a quasicrystal, Nelson sought a solution through the periodic packing of icosahedra in curved spaces, where symmetry prohibitions are relaxed.

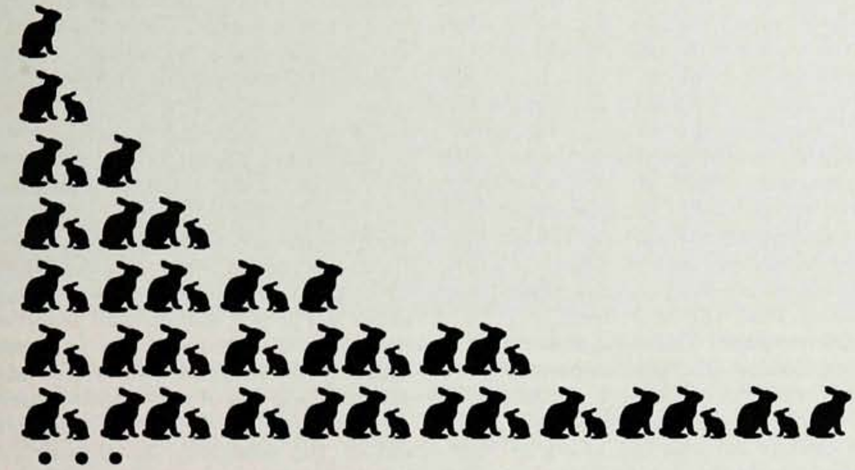
Returning to the real Euclidean world, however, requires the introduction of disclination fault lines. Nelson and his student Subir Sachdev have recently shown[4] that certain arrays of disclination lines will exhibit extended icosahedral order similar to that observed by the NBS group. Nelson describes this as a more microscopic approach that the quasicrystal model of Steinhardt and Levine.

Last year, Steinhardt and his student, Levine, undertook a detailed mathematical analysis on the Penrose problem. They devised "inflation rules" for building these "quasicrystals" out to infinity, and they showed that their icosahedral symmetry is not just local; it extends with perfect orientational alignment to infinite range.

Quasiperiodicity. Steinhardt stresses that these quasicrystal lattices are neither random nor truly aperiodic. An infinite number of different patterns is allowed, but each, once begun,

Quasiperiodic rabbit breeding

The Fibonacci sequence that determines the alternation of long and short spacings along a quasicrystal axis first arose when the medieval mathematician Leonardo Fibonacci of Pisa considered the idealized propagation of rabbits. If at the end of every year every adult rabbit produces one baby and every one-year-old baby becomes an adult, one sees the following evolution from year to year (assuming rabbits are immortal):



The sequence never becomes periodic. If "adult" and "baby" are regarded as spatial intervals whose ratio is 1.618 . . ., the golden mean, one has what Steinhardt calls a quasiperiodic sequence. With other generation rules one gets other quasiperiodic sequences having different length ratios, but the ratio must be an algebraic, irrational number.

is rigorously deterministic. He characterizes the Penrose patterns and their three-dimensional generalizations as "quasiperiodic" rather than aperiodic. The quasilattice points are generated by the intersections of families of parallel planes (or lines) whose consecutive spacings alternate between two characteristic lengths in a Fibonacci sequence (see box). It should come as no surprise that the ratio of the longer to the shorter spacing is the golden mean.

Thus, in the direction of each of the fivefold symmetry axes, one has a nonperiodic but quite deterministic alternation between two incommensurable lengths (the golden mean being an irrational number). Working out the Fourier transform of such quasilattices, Steinhardt was amazed to find that they reduce to series of delta functions in reciprocal lattice space—a result the crystallographers would only have expected for a truly periodic lattice. Unlike the Fourier transform of a true crystal, however, whose peaks are separated by finite intervals, the reciprocal space of a quasilattice turns out to be infinitely dense in diffraction peaks. But with finite intensity resolution one would not be able to tell the difference between diffraction patterns of a crystal and a quasicrystal—except that a quasicrystal diffraction pattern can exhibit forbidden rotational symmetry. The diffraction peak intensities observed by the NBS group are in good qualitative agreement with those calculated by Steinhardt and Levine. Penrose patterns, quasicrystals and their Fourier transforms all have the property of "self similarity"; the patterns repeat themselves on ever larger scales as the quasilattice grows.

Prospects. If the quasicrystal theory turns out to be a correct description of the new metastable state of bulk Al_6Mn, it will have explained the general symmetry properties of the quasilattice, but it does not uniquely specify the unit cells, nor how the actual atomic sites "decorate" the cells. That will require detailed treatment of the interatomic forces and a thermodynamic explanation of why they should seek out this metastable state. Steinhardt, Nelson and Ronchetti, making use of theoretical results obtained in 1978 by Shlomo Alexander and John McTague at UCLA, have already shown that the phase transition to the icosahedral quasicrystalline state would have to be of first order.

Just how pointlike the Al_6Mn diffraction pattern really is remains an open experimental question. With higher-resolution diffraction measurements now being carried out in several laboratories, it may turn out that the diffraction peaks are more diffuse than they first appeared to be, indicating that the bond-orientational order extends only over a finite correlation length.

But the data thus far and the theory point to a novel class of ordered structures in the solid state, neither glassy nor crystalline. Steinhardt suggests that we will have to do the quantum and classical mechanics of solids all over again. The nice, simple properties of crystals result from their periodic potentials. With quasiperiodic potentials, analogous properties arise, Steinhardt argues, but always a bit "bizarre." In place of a finite number of finite electronic band gaps, for example, one gets an infinite density of gaps. "Between every two band gaps there's another gap. That's a reflection of the self-similarity of these quasicrystals."

One will have to calculate in detail the electronic and elastic properties implied by the quasicrystal theory. Comparison with actual materials will then determine its relevance to the physical world. —BMS

References

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High-resolution photo of protoplanetary disk orbiting star

Before the summer of 1983 we had no serious evidence of nonstellar, solid material orbiting any star other than our own. As far as we knew, our solar system might be a rare—perhaps even unique—curiosity in the Galaxy. But in the last 18 months we've learned a lot. Infrared investigations by the Infrared Astronomy Satellite (IRAS) and several ground-based telescopes have provided strong evidence for aggregates of small particles orbiting as many as 40 stars in our extended neighborhood (PHYSICS TODAY, May 1984, page 17).

Convincing as these infrared data may be, they have not offered us an explicit "picture" of such a "protoplanetary" system. But now we finally have such a picture. Employing a highly sensitive charge-coupled-device camera with a sophisticated coronograph at the 2.5-meter Las Campanas Telescope in Chile, Bradford Smith (University of Arizona) and Richard Terrile (JPL) have produced a high-resolution image of a thin, Saturn-like