Where Are the Atoms in the Icosahedral Phase?

Researchers disagree on whether it is even possible to specify atomic positions; they do not know whether the icosahedral phase is more like a glass or a quasi-periodic crystal

Two years ago this November, an astonishing report appeared in *Physical Review Letters* that described an aluminum-manganese compound whose structure appeared to violate one of the most sacred rules of crystallography. Dubbed the icosahedral phase, the material exhibited an electron diffraction pattern with sharp spots, which is indicative of crystallinity, but the pattern had a forbidden fivefold symmetry. It is not possible to build a crystal lattice from the periodic repetition of a single unit cell having this symmetry.

This apparent contradiction, which was reported by Dan Shechtman of the Israel Institute of Technology (Technion) in Haifa, Ilan Blech (now at the Zoran Corporation, Sunnyvale, California), Denis Gratias of the Centre d'Etudes de Chimie Métallurgique in Vitry, France, and John Cahn of the National Bureau of Standards (NBS) in Gaithersburg, Maryland, stimulated an enormous interest. By now, icosahedral phases of various compositions have been made in numerous laboratories around the world by several methods, and the number of published papers continues to grow exponentially.

Despite all the effort, researchers still do not understand the structure of the icosahedral phase. At the moment, opinions are divided between two alternative models. "The situation is rather turbulent on the theoretical side at the moment," says Paul Steinhardt of the University of Pennsylvania. The quasi-crystal model derives from the early realization that it was possible to construct so-called quasi-periodic lattices based on two "unit cells" that accounted for the diffraction pattern. Description of the quasi-crystal then becomes a matter of discovering the specific quasi-periodic lattice and the locations of the atoms in the unit cells. The more recent icosahedral glass model postulates the existence of icosahedral structural units that are packed together in a special way that is simultaneously ordered and random.

Before the original publication by Shechtman and his co-workers announcing the icosahedral phase in aluminum-manganese, Shechtman and Blech had also prepared a paper describing a possible model for its structure. The model was based on an icosahedral structural unit having a manganese atom at the center and an aluminum atom at each of the 12 vertices. A regular icosahedron has 20 faces, each of which is an equilateral triangle. The rotational symmetry at a vertex is fivefold; at the center of a face it is threefold; and on an edge it is twofold.

To preserve these symmetries, all of which occur in the icosahedral phase, the icosahedra were packed together in such a way that they all had the same orientation but were randomly joined along edges in the first version of the model or at vertices in a later one. This model was a forerunner of the type now called icosahedral glasses, but it did not catch on at the time.

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The first publication with a quasi-crystal interpretation of the aluminum-manganese icosahedral phase, by Dov Levine and Steinhardt at Pennsylvania, who coined the term quasi-crystal, appeared only 1 month after the announcement that the material had been found. Their idea was to generalize in three dimensions two-dimensional objects called Penrose tiles, after Roger Penrose of the University of Oxford.

Although it is well known that it is not possible to cover a flat surface with a single pentagonal unit cell or tile, Penrose discovered that it is possible to generate a pattern having fivefold symmetry from two tiles shaped like parallelograms whose edges are the same length but whose angles are different. In three dimensions, the unit cells are rhombohedra. While there are certain rules for arranging the rhombohedra, the unit cells do not appear in any fixed or periodic arrangement. In particular, the ratio of the number of cells of each type is a famous irrational number in mathematics called the golden mean and has the value $(1 + \sqrt{5})/2$.

Quasi-crystals caught on quickly because physicists were already familiar with quasi-periodicity in so-called incommensurate structures, because mathematically inclined crystallographers were already contemplating uses for Penrose tiles, and because quasi-crystals adequately accounted for the observed diffraction patterns. In short order, several methods for generating quasi-periodic lattices appeared. But the question of where to put the atoms remained.

The approach to locating the atoms that has generated the most attention is to consider the structure of a crystalline phase of a material that also has an icosahedral phase. The crystalline phase of interest is that for which the diffraction patterns in orientations other than those showing the fivefold symmetry (or high-resolution transmission electron microscope images) of the two phases are similar. Two groups, Marc Audier and Pierre Guyot of the Ecole Nationale Supérieure d'Electrochimie et d'Electrométallurgie in Saint Martin d'Heres, France, and Veit Elser of AT&T Bell Laboratories and Christopher Henley of Cornell University, independently took this tack last year with the same materials and constructed similar models.

Using crystallographic data taken from the literature for the α phases of aluminum-silicon-manganese and aluminum-silicon-iron, Audier and Guyot obtained an icosahedral structural unit that consists of two concentric icosahedra. The outer icosahedron has 12 manganese (or iron) atoms at the vertices, while the inner has 12 aluminum and silicon atoms at its vertices. This structural unit is associated with each vertex and the center of a cubic unit cell (body-centered cubic lattice), so that each unit has eight equally distant nearest neighbors, all with the same orientation. Extra aluminum atoms arranged in strings of octahedra connect the aluminum icosahedra at each lattice point and also make the composition come out correctly.

To convert this structure into the icosahedral phase, Audier and Guyot used the same structural units to decorate two rhombohedral unit cells. In one cell the units are associated with the vertices and with an interior point, whereas in the other they are associated only with the vertices. As it works out, each unit has either five, six, or seven nearest neighbors. The investigators were not able to specify all the positions of the connecting aluminum atoms, however.

Elser and Henley initially took a different

tack. They showed that the α phase structure could be generated from the same rhombohedral unit cells that make up the quasiperiodic lattice. However, the ratio of the number of units was the rational fraction 5/3, which is similar in value to the golden mean. This demonstrates the similarity of the two structures.

In the end, however, Elser and Henley arrived at a structural unit similar to that found by the French researchers. The unit they found was known previously and is called a Mackay icosahedron, after Alan Mackay of Birkbeck College (London), who devised it many years earlier in another context. The Mackay icosahedron contains 54 atoms arranged in two shells. The inner shell is an icosahedron with 12 aluminum and silicon atoms at its vertices. The outer shell is also an icosahedron with 12 manganese (or iron) atoms at its vertices, which are immediately above those of the inner shell, as before, and 30 additional aluminum and silicon atoms on the edges of the icosahedron between the manganese atoms.

There is recent experimental evidence to support the existence of an icosahedral structural unit, although not enough to specify exactly what it is. At the Workshop on Aperiodic Crystals, held in Les Houches, France, last March, Bernard Mozer of NBS, Cahn, Gratias, and Shechtman reported on powder neutron diffraction studies of aluminum-manganese. From the relative intensities of the peaks in the neutron diffraction pattern as compared to those in x-ray patterns, the researchers deduced that a quasiperiodic lattice was decorated by a complex structural unit. Further analysis suggested a unit the size of the Mackay icosahedron.

Extended x-ray absorption fine structure (EXAFS) spectra provide local structural information in both periodic and nonperiodic materials. At the Les Houches workshop, Edward Stern, Yanjun Ma, and Karen Bauer of the University of Washington and Charles Bouldin of NBS discussed spectra taken on the α and icosahedral phases of aluminum-silicon-manganese and the icosahedral phase of aluminum-manganese. The spectra suggested the existence of a manganese icosahedron in both phases with a distance of 5 angstroms between manganese atoms. Moreover, the icosahedra in the icosahedral phase were slightly farther apart than in the α phase, suggesting fewer nearest neighbors in the icosahedral phase. The spectra did not give the positions of aluminum atoms, although some information may be extractable with further analysis.

In their discussion of possible ways to arrange these structural units, Stern and his co-workers eschewed the quasi-crystal model and adopted the icosahedral glass concept,

Al-Li-Cu Icosahedral Phase

To nail down the structure of the icosahedral phase (see story), as well as to explore its still mostly unknown physical properties, researchers need samples with dimensions considerably larger than the 20 micrometers or less that have been available up to now. This requirement is now on the verge of being met. Several groups are making ingots of an aluminum-lithium-copper alloy that contain icosahedral phase regions having dimensions up to 3 millimeters. Moreover, the first "single crystal" x-ray diffraction data are coming in. These confirm the icosahedral symmetry of the new material, but have not yet yielded a structure.

The icosahedral phase of aluminum-lithium-copper appeared unrecognized in the literature as long ago as 1955. But last year, M. D. Ball and D. J. Lloyd of Alcan International Limited in Kingston, Ontario, reported the existence of small particles of an apparent icosahedral phase at the boundaries between crystal grains in an aluminum-lithium-copper-magnesium alloy. Aluminum-lithium is an increasingly important high-strength and lightweight material, while copper, magnesium, and other elements are added to improve its fracture toughness. Although the particles showed a fivefold symmetry in electron diffraction patterns, the Canadian researchers concluded that the symmetry was an artifact due to a crystal imperfection known as microtwinning.

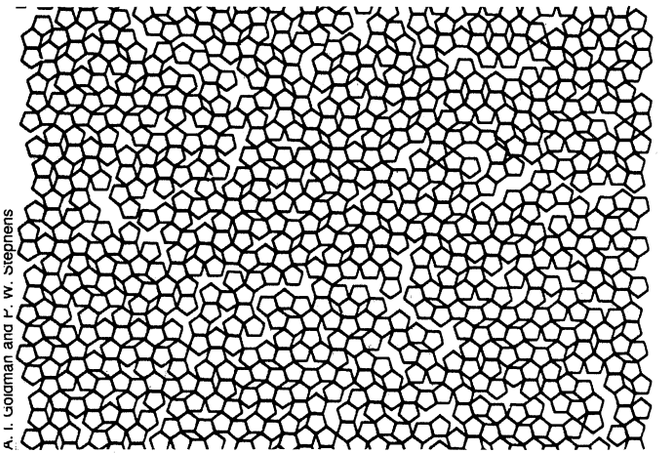
The first researchers to report large samples of the stable icosahedral phase were Pierre Sainfort and Bruno Dubost of the French aluminum company Cegedur-Pechiney in Voreppe. Last spring at the Workshop on Aperiodic Crystals in Les Houches, France, they described the formation of the icosahedral phase of aluminum-lithium-copper produced simply by melting high-purity elemental aluminum, lithium, and copper in a preheated mold and cooling. The icosahedral phase took the form of dendritic "crystals" that occupied about 83% of the volume of the cast ingot. The longest dendrites exceeded 2 millimeters in length.

More recently, Charles Bartges and Earle Ryba of the Pennsylvania State University have made samples containing roughly cylindrical single-phase regions of the icosahedral phase up to 0.2 millimeter in diameter and 3 millimeters in length. They were unable to obtain such large chunks until they cooled the molten alloy from 850°C by quenching it in ice water rather than cooling slowly. The investigators then heated it back to 450°C for 1 week in an attempt to bring the material to a thermal equilibrium structure. Single-crystal x-ray diffraction studies aimed at determining the structure of the icosahedral phase are under way. Already completed are diffraction studies on samples up to 0.2 millimeter long that were made earlier and reported at the American Crystallographic Association meeting in Hamilton, Ontario, last June. These data, obtained by the precession method, confirm the icosahedral symmetry. But the Penn State researchers are not yet certain whether they can rule out the microtwinning explanation for the symmetry.

Two groups at AT&T Bell Laboratories, working independently, have succeeded in making millimeter-sized samples of the aluminum-lithium-copper icosahedral phase. A. Refik Kortan, Ho Sou Chen, and Joseph Waszczak make their material by slowing cooling molten alloy initially at 700°C in a furnace. The resulting material is very sensitive to preparation conditions, and sometimes the researchers obtain spherical single-phase regions and sometimes dendritic shapes. The group has completed preliminary single crystal x-ray diffraction studies. The findings not only confirm the icosahedral symmetry but, according to Chen, rule out a twinning explanation. A qualitative analysis suggests that the intensities of the diffraction peaks are consistent with a quasi-crystal structural model, although the atoms seem to be in different positions from those proposed for aluminum-manganese.

Joseph Remeika, Gerald Espinosa, and Ann Cooper, also of Bell Labs, make their icosahedral phase in a similar way. They are able to grow columnar single-phase regions with characteristic dimensions of about 2 millimeters. Electron diffraction studies by Cheng-Hsuan Chen of Bell Labs definitely establishes the icosahedral symmetry of this material, according to Remeika.

All in all, other researchers in the field cannot wait to obtain samples of the new material for themselves. "The stable icosahedral phase gives a big shot to the field; we've done almost everything we could with the old material," says Matthew Marcus of Bell Labs, who is investigating the properties of aluminum-lithium-copper made there. ■ **A.L.R.**



A. I. Goldman and P. W. Stephens

Two-dimensional pentagonal glass

This computer simulation of the packing of pentagonal structural units shows how orientational order is maintained across a two-dimensional sample. In three-dimensional materials, the structural units are icosahedrons.

which was just becoming popular at the time because of a difficulty with the quasi-crystal model. Whatever the details of its structure, the quasi-crystal model predicts that the width of the peaks in x-ray powder diffraction patterns should be arbitrarily narrow (delta functions), whereas the experimental line widths for icosahedral phase materials are relatively broad. The icosahedral glass model became a serious alternative late last winter, when Peter Stephens of the State University of New York at Stony Brook and Alan Goldman of Brookhaven National Laboratory showed that the diffraction pattern for such a material would in fact have nonzero peak widths.

In their computer simulations, Stephens and Goldman considered icosahedral structural units, all with the same orientation but packed randomly so that they shared either vertices, faces, or edges. "Randomly packed" refers to which vertices, edges, or faces are joined. There are 20 faces, for example, but a maximum of eight of these can be joined without overlapping of the icosahedra. The quasi-crystal models in effect specify which are to be joined, whereas the icosahedral glass model leaves it to chance. The EXAFS spectra discussed above suggested that neighboring icosahedra meet at faces.

For the face-packed icosahedra, the calculated positions of the strongest diffraction peaks agreed with those in high-resolution patterns obtained from synchrotron radiation experiments on aluminum-manganese that were done several months earlier by Peter Bancel and Paul Heiney of the University of Pennsylvania in collaboration with Stephens and Goldman and Paul Horn at the IBM Yorktown Heights Laboratory. Moreover, the size of the icosahedral units precisely matched that of the Mackay icosahedra in α aluminum-silicon-manganese. In more recent work that is not yet published, they have added what Stephens calls second-nearest-neighbor correlations; that is, there is some reduction in the randomness. Incorporation of these correlations improves the fit with the positions of the weaker peaks in the diffraction pattern and produces agreement with the measured peak widths.

Quasi-crystal proponents have also been looking more deeply into their model to see if there is a way to explain the peak widths observed experimentally. One concept that shows some promise in this regard is that of phason strain. Like quasi-periodicity, phasons first appeared some time ago in the theory of incommensurate structures. In the context of quasi-crystals, they refer to a kind of local reshuffling of the rhombohedral unit cells in the quasi-periodic lattice. It is possible, for example, to remove a few rhombohedra from a small volume of the lattice and replace them in a different order without leaving any gaps.

Disordered regions of this sort are expected to form naturally during the formation of an icosahedral phase, which is usually formed by rapid cooling of a blob of molten material brought about by, for example, dropping it on a spinning metal wheel. The temperature drops so rapidly that the diffusion of atoms necessary to repair phason strain cannot occur before the strain is "frozen in." At Pennsylvania, Tom Lubensky, Joshua Socolar, Steinhardt, Bancel, and Heiney have completed an analysis of phason strain and other possible sources of peak broadening in powder diffraction patterns and find evidence for its presence.

The earlier high-resolution x-ray data obtained by Bancel and his colleagues had shown that the peak widths did not increase uniformly with the diffraction angle, as should have been the case if the inhomogeneous compressive strain that is often present in rapidly solidified materials and that is a possible source of peak broadening were dominant. Moreover, newer electron diffraction data recorded by Bancel and Heiney show that there are small and systematic distortions in the positions and shapes of the spots in the pattern as compared to the ideal quasi-crystal positions. The new analysis of Lubensky and his colleagues shows that the frozen-in phason strain can, qualitatively at least, account for these phenomena.

In another new study, Horn, Wolfram Malzfelt, David DiVincenzo, John Toner, and Richard Gambino of IBM have taken a crack at comparing the quasi-crystal model with frozen-in phason strain and the icosahedral glass model by means of x-ray diffraction data they obtained for aluminum-manganese and aluminum-silicon-manganese material. The researchers carried out measurements on both as-prepared and annealed samples. Annealing would presumably remove some of the inhomogeneous compressive strain or some other disorder that might be present in as-prepared material but not the phason strain. The idea was to observe the variation of the peak width with a parameter related to the diffraction angle called the phason momentum. Both models predict a smoothly increasing peak width as the phason momentum grows, although the shapes of the curves are slightly different. Only the annealed samples showed this behavior. Because of variations from sample to sample, however, the scatter in the data precluded making a distinction between the two models.

An unanswered question is whether the quasi-crystal and icosahedral glass models simply represent the extremes of a continuum of possibilities or whether there is an unbridgeable philosophical difference between them that will eventually be reflected in experimental data that only one model will be able to explain. In the first view, the models are already evolving toward one another, as exemplified by the invocation of frozen-in phason strain in quasi-crystal and second-nearest-neighbor correlations in the icosahedral glass. If they continue to converge, says Horn, who strongly prefers the glass explanation, "it will be a matter of taste how you describe the structure."

Some help in resolving the issue may not be far off. A number of groups have begun making an icosahedral phase of another material, an aluminum-lithium-copper compound, in sizable chunks of up to 3 millimeters in at least one dimension (see box). Such large samples would be of enormous help in unraveling the structure of this icosahedral phase because classical "single crystal" x-ray diffraction studies of its structure could be undertaken. ■ **ARTHUR L. ROBINSON**

ADDITIONAL READING

J. Phys. (Paris) **47**, Colloque C3 (Supplement to No. 7, July 1986) contains the proceedings of the Workshop on Aperiodic Crystals, Les Houches, France, 11–20 March 1986.

D. R. Nelson and B. I. Halperin, "Pentagonal and icosahedral order in rapidly cooled metals," *Science* **229**, 233 (1985).