Quasicrystalline Materials

Although the science of crystals took centuries to mature, the science of quasicrystals is developing in a matter of years. This time around, scientists have all the tools

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Quasicrystals, a class of materials discovered in 1984, are rather like oobleck, a form of precipitation invented by Dr. Seuss. Both the quasicrystals and the oobleck are new and unexpected. Since the discovery of a new class of materials is about as likely as the occurrence of a new form of precipitation, quasicrystals, like oobleck, suffered at first from a credibility problem. Many scientists thought it possible that instead of being new materials, they were actually anomalous forms of familiar materials, either crystals or glasses.

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Among the doubters was the celebrated chemist Linus Pauling, who maintained that quasicrystals were really crystals that weren't yet understood. Pauling's skepticism was aroused by the claim that the diffraction pattern obtained by scattering electrons or x rays from the new alloy could not be mapped to any known crystal structure. As Pauling knew, if the structural building block is carefully chosen, it is possible to come arbitrarily close to matching any diffraction pattern. Indeed, Pauling eventually suggested several complex crystalline models that very nearly described the diffraction patterns obtained from quasicrystalline alloys.

Even those who acknowledged the existence of quasicrystals had trouble absorbing their novelty. Although the diffraction patterns from quasicrystals were reasonably sharp, which is a sign of an ordered structure, many scientists found it hard to believe that, in their own way, quasicrystals are as well ordered as crystals. After a century of modern crystallography the notion of order was so tightly bound up with the notion of periodicity—the simple stacking of a building block called a unit cell—that the prejudice was that the aperiodic quasicrystals must somehow be less ordered than the periodic crystals.

These debates were settled and the structure and properties of quasicrystals clarified over the past 10 years by the techniques of materials science, a discipline that is a silent partner in many scientific endeavors. The general picture of quasicrystalline structures that has emerged from this research is not very different from that given a decade ago by Paul Steinhardt of the University of Pennsylvania (*American Scientist*, November–December 1986), and this article focuses instead on the properties of quasicrystals as materials. Particular emphasis is given to our research at the Ames Laboratory, a Department of Energy laboratory located in Ames, Iowa, but it is important to point out that many groups in the United States and throughout the world (most notably in France, Germany, Japan, China, India, Canada and Mexico) have very active programs in quasicrystal research. Many of the most recent results in this field can be found in the proceedings of the fifth international conference on quasicrystals, which was held last summer in France (Janot and Mosseri 1995).

Over the past decade these groups have collectively demonstrated that quasicrystals are indeed a new class of materials, both well ordered and different from other classes. The insights into the properties of the quasicrystals provided by this work are now guiding efforts to put them to practical use.

A Fortuitous Discovery

Quasicrystals were discovered by Dan Shechtman of the Technion in Israel during a project at the National Institute of Standards and Technology (NIST) to find lighter and stronger aluminum alloys. One of the alloys of aluminum and manganese produced diffraction patterns characteristic of neither a crystal nor a glass, and Shechtman, after first convincing himself, went about the arduous task of convincing others that what he had seen was indeed real. Together with Ilan Blech, also of the Technion, Denis Gratias of CECM-CNRS in Vitry, France, and John Cahn of NIST, Shechtman published the now-famous announcement of this discovery in November 1984.

At first glance, the diffraction patterns from the novel alloy resembled crystal diffraction patterns. Crystals are ordered solids that can be constructed by repetition of a unit cell, much as a wall is constructed by laying bricks. The atomic "decoration" of each unit cell is identical to that of the other unit cells. Crystals possess both positional and orientational order, which means that if the size and shape of one unit cell and its atomic decoration are known, the positions of all the other atoms in the solid can be determined.

Because electrons, photons (x rays) and neutrons are coherently scattered by this orderly arrangement of atoms, a crystal produces a diffraction pattern made of well-defined spots (if the sample is a single crystal) or rings (if the sample is made up of many small crystallites with random orientations). In addition, the diffraction patterns from single crystals exhibit rotational symmetries; when a pattern is rotated through a specific angle about a particular axis, the rotated pattern matches the unrotated one. These symmetries provide insight into the shape of the unit cell.

Like a crystal, the novel aluminum-manganese alloy produced electron-diffraction patterns that were composed of well-defined spots. The diffraction patterns also had two features that distinguished them from crystal diffraction patterns. Because only certain geometrical shapes can be stacked together periodically to completely fill space, a crystal's diffraction pattern can have only certain rotational symmetries. The lowest-order rotation is a full 360-degree rotation about an axis perpendicular to the pattern that always

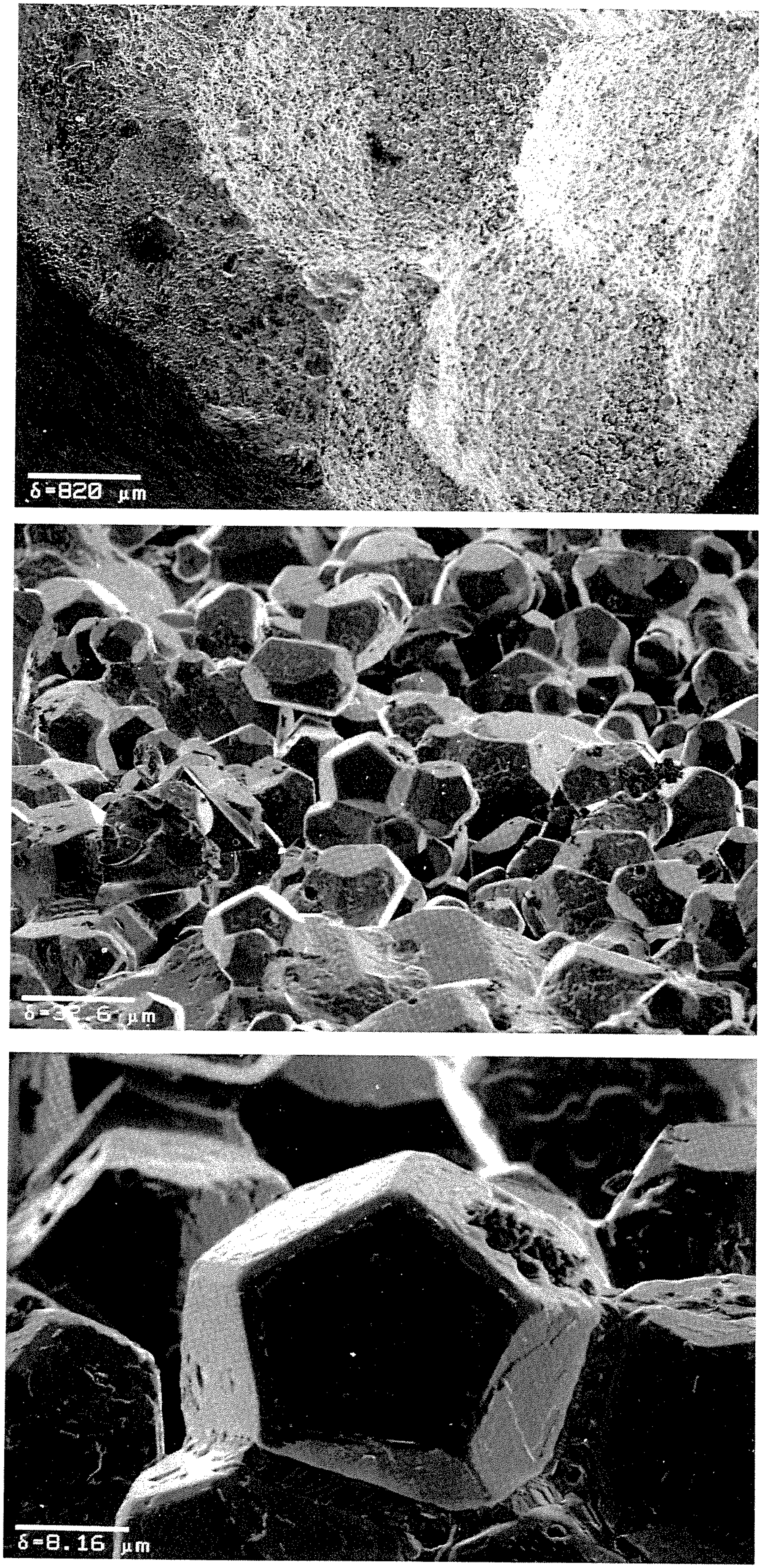


Figure 1. Grains of aluminum-copper-iron (shown here at increasing magnification from top to bottom) have striking pentagonal facets. This geometry arises because the solidifying alloy tends to grow along planes of atoms that have fivefold rotational symmetry. Fivefold symmetry is one of the distinguishing marks of quasicrystals, a new class of materials discovered in 1984. (The secondary electron microscope images were taken by Tamara Bloomer.)

brings it back into coincidence with itself. Twofold, threefold, fourfold and sixfold rotational axes are also allowed, but all other rotational symmetries are forbidden. The aluminum-manganese alloy, however, clearly exhibited a fivefold rotational axis. By rotating the novel alloy through various angles, Shechtman and his coworkers showed that the alloy had icosahedral symmetry; like the 20-sided solid called an icosahedron, it had six fivefold axes.

Second, the spots in a crystal's diffraction pattern occur at regular intervals, a spacing that reflects the underlying periodicity of the crystal lattice and that can be used to determine the dimensions of the crystal's unit cell. The spots in the novel alloy's diffraction pattern, however, were aperiodically spaced. The ratio of the distances between adjacent spots in any quasicrystalline diffraction pattern is an irrational number. In the case of the

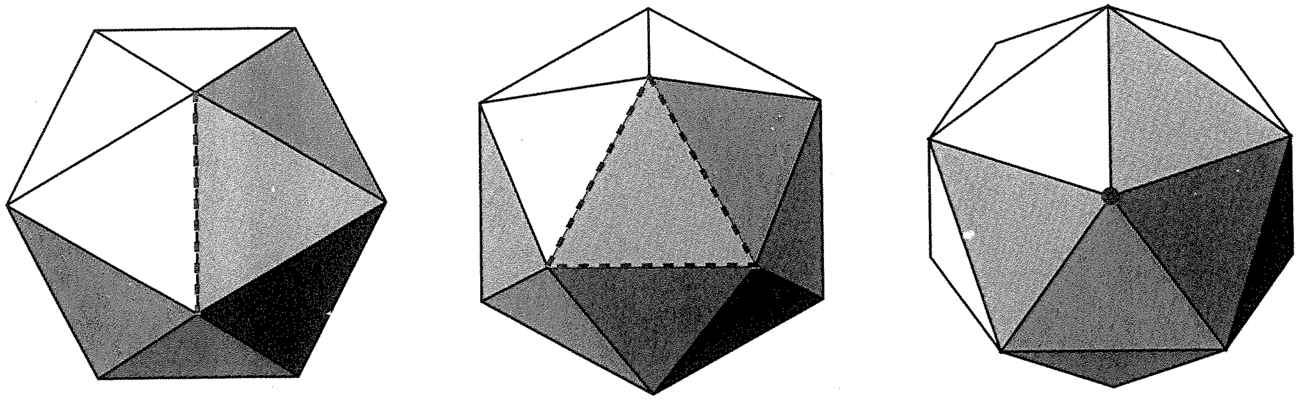


Figure 2. Icosahedral symmetry is a property of the most-studied quasicrystalline alloys: They share the rotational symmetries of the 20-sided polyhedron called an icosahedron. They have 15 twofold, 10 threefold and 6 fivefold rotational symmetry axes. Lines connecting edges of the icosahedron on opposite sides of the solid are twofold symmetry axes *(left)*. Lines connecting triangular faces on opposite sides of the solid are threefold symmetry axes *(middle)*. Lines connecting vertices on opposite sides of the solid are fivefold symmetry axes *(right)*.

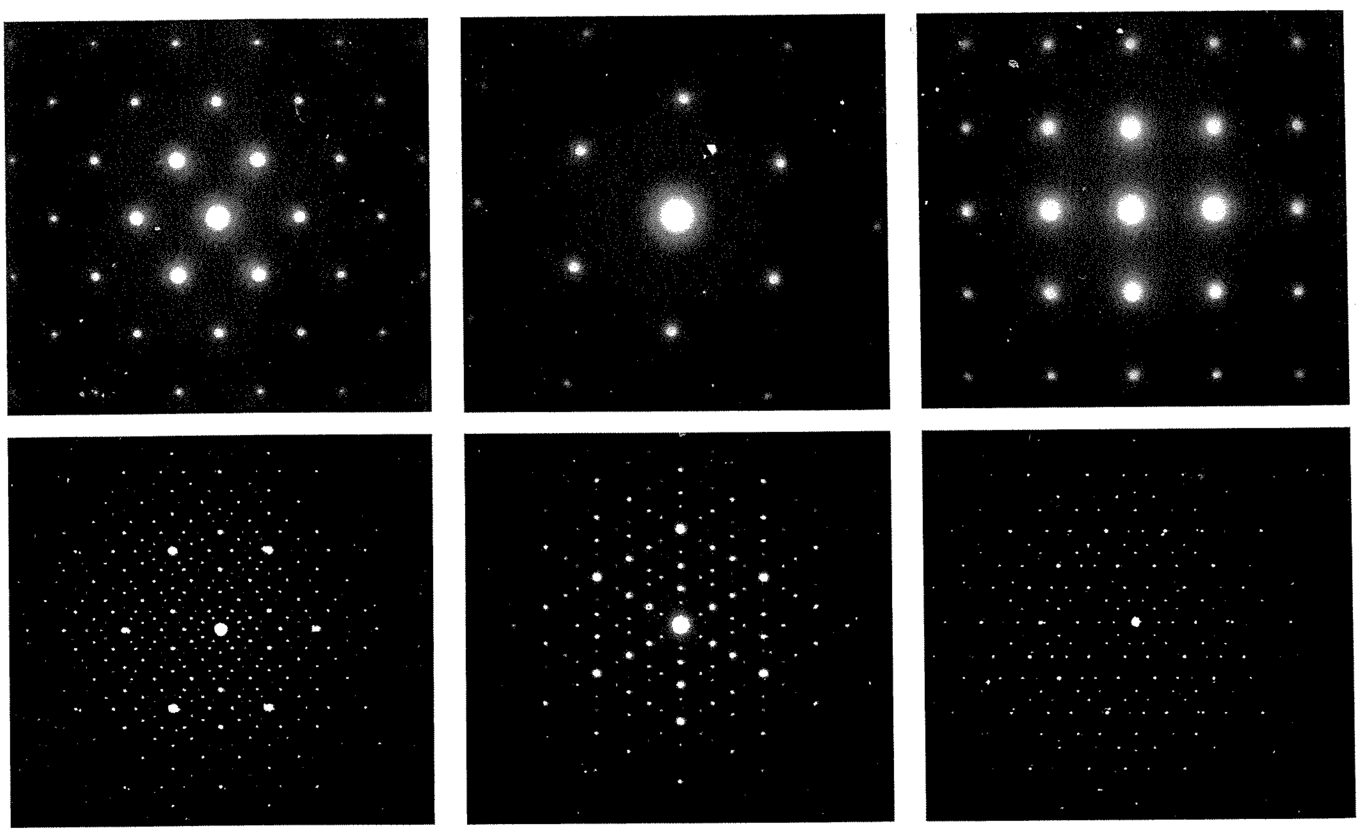


Figure 3. Structural differences between a crystal and a quasicrystal can be seen by comparing the electron diffraction patterns of crystalline *(top)* and quasicrystalline *(bottom)* phases of an aluminum alloy. The spots are made by electrons coherently scattered from planes of atoms parallel to the beam direction. Each spot corresponds to a set of parallel planes. A crystal's symmetry can be seen by picking a motif of spots and determining how often it recurs in the pattern. Patterns along different directions in the cubic crystalline alloy have twofold *(left)*, threefold *(middle)* and fourfold *(right)* rotational symmetry. The quasicrystal, on the other hand, exhibits twofold *(left)*, threefold *(middle)* and fivefold *(right)* rotational symmetry. The fivefold rotational symmetry is forbidden to crystalline materials. Another difference is that the quasicrystal has aperiodic rather than periodic translational order, as the spacing of spots of the diffraction patterns shows.

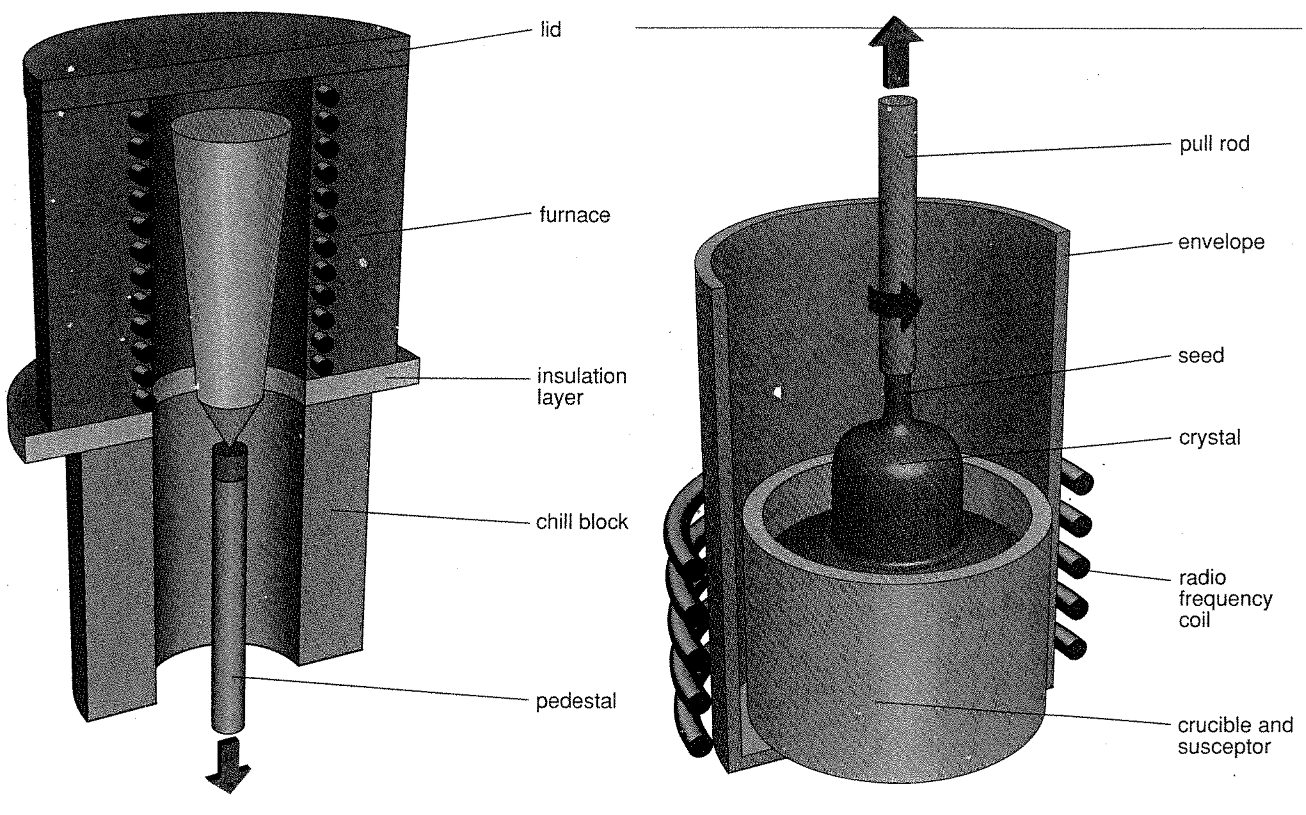
icosahedral alloys, this irrational number is related to tau (τ), the golden mean, $(\sqrt{5} + 1)/2$, a number that arises in the geometry of pentagons and icosahedra.

Over the next five years many similar materials came to light. For instance, new icosahedral alloys were discovered among aluminum-based alloys, as well as among alloys of titanium and transition metals (such as titanium-chromium and titanium-manganese), among alloys of gallium, magnesium and zinc, and even among alloys of uranium, palladium and silicon. Other aperiodic systems were also discovered. The decagonal phase of aluminum-manganese, for example, was discovered soon after its icosahedral phase. As its name implies, the decagonal phase produces a diffraction pattern with a tenfold rotational axis. Perpendicular to this axis, however, the spacing of diffraction spots is periodic, indicating that the material can be described as a periodic stacking of aperiodically ordered planes. All of these novel materials are now called quasicrystals.

Building Quasicrystals

Quasicrystals are the products of human ingenuity rather than of nature. In most instances, the quasicrystalline phase of an alloy is not the alloy's preferred (equilibrium) phase at any temperature. Shechtman produced his samples by melt-spinning, a solidification technique that cools the molten metal at a million degrees per second, fast enough to lock the alloy into a metastable structure it would not have assumed had it been allowed to cool more slowly. The drawback was that melt-spinning produced short ribbons of metal containing small grains. (In this context, a grain is a region of the solid that contains atomic clusters with a single coherent orientation.) Furthermore, upon heating, the quasicrystalline structure relaxed back to a stable crystalline phase. Shechtman's ribbons had grains only a few micrometers across, too small for single-grain x-ray diffraction studies and the many other probes that require relatively large "single quasicrystals."

Then in 1988 An-Pang Tsai, Akihisa Inoue and Tsuyoshi Masumoto of Tohoku University in Sendai, Japan, discovered the aluminum-copper-iron and aluminum-copper-ruthenium families of icosahedral quasicrystals. Unlike the earlier alloys, these compounds have a stable quasicrystalline phase at elevated temperatures. If the alloy is cooled slowly, however, the quasicrystalline phase can decompose into crystalline phases. Large quasicrystalline grains can be made by heating solid ingots into the appropriate temperature regime, allowing the quasicrystalline grains to grow, and then cooling the ingots quickly enough that the crystalline phases that form at lower temperatures have little time to



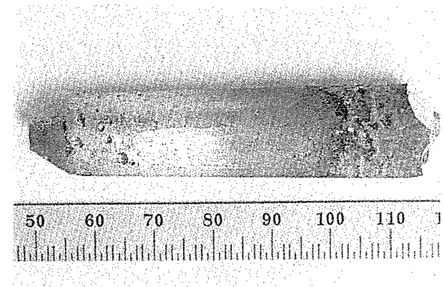


Figure 4. Much of recent work on quasicrystals was made possible by the discovery that certain quasicrystals can be produced by conventional crystal-growing techniques. In the Bridgman method *(above left)*, a crucible containing the alloy is placed in a furnace at a temperature above the melting point of the alloy. After an hour, the crucible is slowly withdrawn (at a rate of about a millimeter per hour) from the furnace. Because the crucible has a conical bottom, only a small volume of liquid is initially cooled below its melting point; this encourages a single nucleation event and the formation of only one grain. An ingot from a Bridgman furnace is shown at right. In the Czochralski method *(above right)*, a seed crystal is lowered into the molten metal and then withdrawn at a controlled rate. The orientation of the atomic lattice with respect to the faces of the grain is controlled by the orientation of the seed crystal's lattice. The ability to control the lattice orientation is useful for some analytical studies.

nucleate and grow. The largest single grain of aluminum-copper-iron produced at the Ames Laboratory so far is about 0.25 cubic centimeters.

Another breakthrough came in 1989 when the Japanese group discovered the icosahedral phase of aluminum-palladium-manganese. The quasicrystalline phase of this alloy system is thermodynamically stable down to room temperature. As a result, quasicrystalline grains can be produced by traditional crystal-growing techniques, which are characterized by cooling rates of about 10 degrees an hour. Several groups, including those at the Ames Laboratory, the LTPCM/ENSEEG in St. Martin d'Heres, France, the CECM-CNRS, Tohoku University and the Institüt für Festkörperforschung in Jülich, Germany, have used these methods to produce quasicrystalline grains much larger than a cubic centimeter in size. With grains this large, virtually any

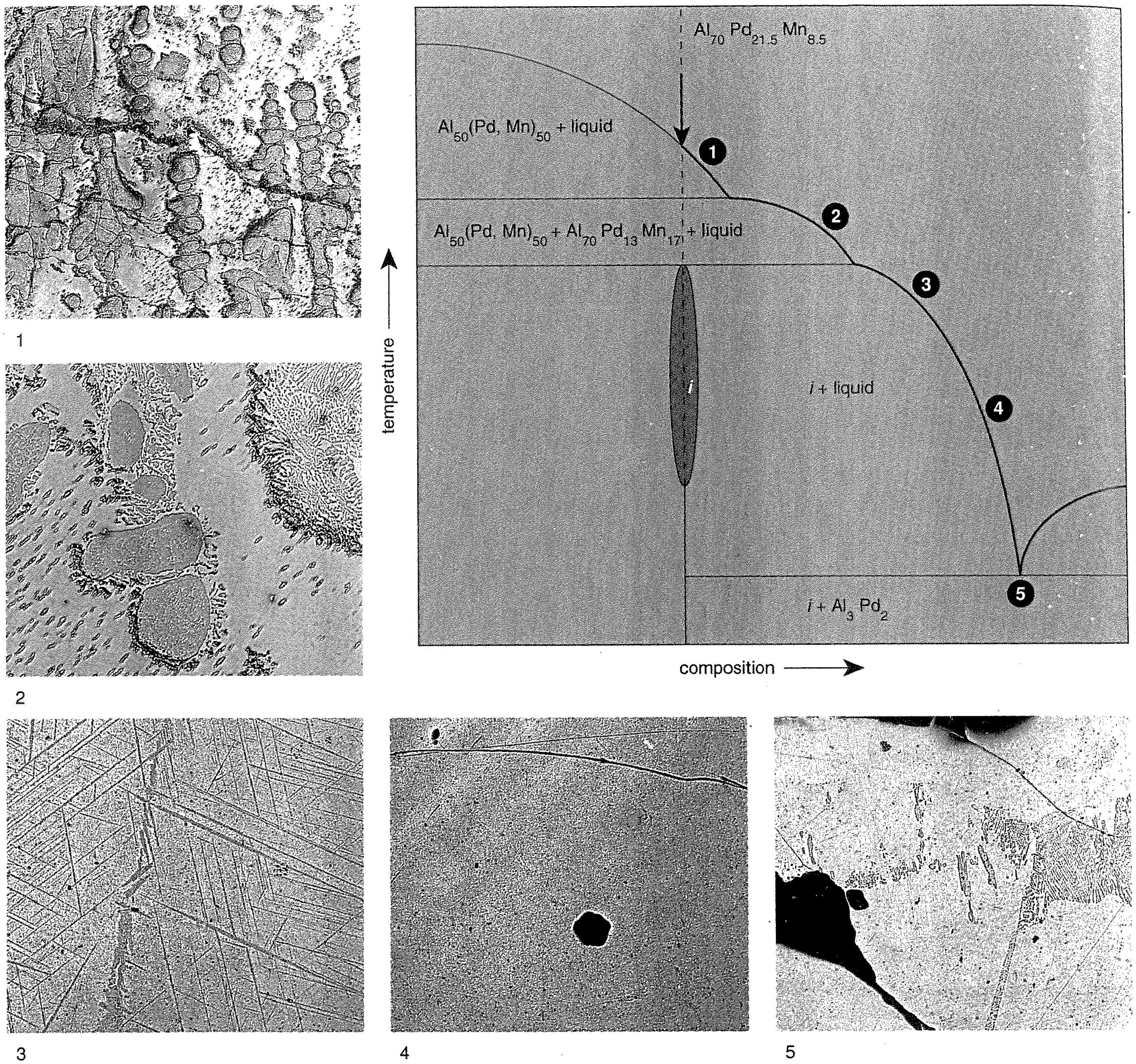


Figure 5. Grains of quasicrystalline material must typically be harvested from a solidified ingot that contains regions with other phases or mixtures of phases. Solidification of $Al_{70}Pd_{21.5}Mn_{8.5}$ quasicrystals (the *i*, or icosahedral, phase) begins with the precipitation of dendrites, or finger-like projections, of $Al_{50}(Pd,Mn)_{50}$, a crystalline phase *(1)*. As solidification continues, aluminum accumulates in the liquid until the composition favors a reaction in which two phases—$Al_{50}(Pd,Mn)_{50}$, a crystalline phase, and $Al_{70}Pd_{13}Mn_{17}$, a decagonal phase—solidify simultaneously, forming a lamellar structure in which the phases alternate *(2)*. Aluminum continues to accumulate in the liquid until the composition of the liquid favors the direct precipitation of the quasicrystalline phase. Because the first quasicrystalline material to form is supersaturated, when it cools to room temperature, plates of the decagonal phase form in it by the process of solid-state precipitation *(3)*. Only then are conditions right for the precipitation of good quasicrystalline material that does not undergo further transformations. This region of the ingot is represented here by a micrograph of a pore with pentagonal faces, formed by the evolution of gases dissolved in the liquid metal *(4)*. At the top end of the ingot, the composition of the liquid again drifts away from that favoring precipitation of the quasicrystalline phase toward one favoring the simultaneous solidification of a crystalline phase (Al_3Pd_2) and the quasicrystalline phase *(5)*. (Micrographs were taken by Hal Salisbury.)

analytical study can be done, including angle-resolved photoemission (a technique for determining electronic structure) and single-grain inelastic neutron scattering (a technique for studying vibrational excitations called phonons).

Although crystal growers routinely produce ingots of metals or alloys that are a single grain, until recently the best ingots of quasicrystalline material contained a handful of small single grains together with other material. The underlying difficulty is that the quasicrystalline alloys are typically three-element (ternary) compounds that can form a wide variety of phases. Solidification is therefore not a simple process, nor does it necessarily yield a single solid phase. This complexity is apparently inherent to the quasicrystalline alloys, because they all have similar phase equilibria.

The central problem in growing single-grain quasicrystals by conventional techniques is that the first solid phase to come out of the melt is generally a crystalline phase. The quasicrystalline phase is formed at a lower temperature, when the remaining liquid reacts with the high-temperature crystalline phase. Shechtman was able to produce quasicrystalline samples by melt-spinning because rapid cooling suppressed the formation of the primary crystalline phase. At crystal-growth cooling rates, however, the crystalline phase is not suppressed. The bottom third of an ingot of aluminum-palladium-manganese alloy (the first portion to solidify) typically contains a mix of crystalline and quasicrystalline phases, and only the upper two-thirds is single-phase quasicrystalline material.

By manipulating the overall composition of the melt, however, it is possible to exercise control over the sequence in which the phases solidify. The reason is that the composition of the liquid from which the quasicrystalline phase precipitates directly is not the same as the composition of the solid quasicrystalline phase. Thus, as the primary crystalline phase precipitates out, the remaining liquid is continually enriched in some elements and depleted in others until it reaches a composition that favors precipitation of the quasicrystalline phase. By starting with a composition off the stoichiometry for the quasicrystalline phase itself, it is possible to increase the yield of high-quality single-grain quasicrystalline material.

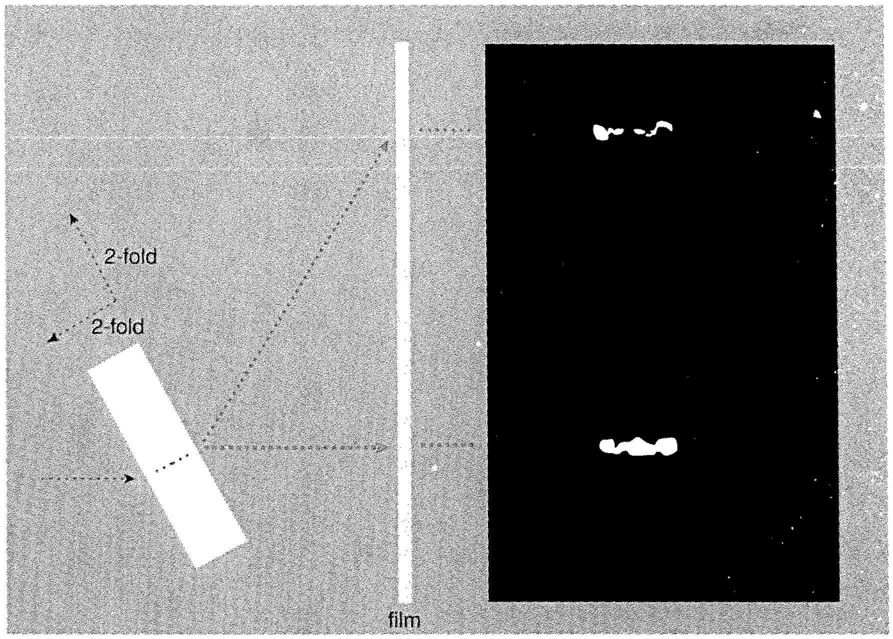


Figure 6. Single-grain quasicrystals have recently been shown to match or exceed the structural perfection of many intermetallic crystals. That quasicrystals are well ordered was clearly demonstrated by the observation of the Borrmann effect in a single quasicrystal of aluminum-palladium-manganese. The grain was set at the correct angle to the x-ray beam to achieve an intense diffracted beam *(purple)*. A second forward-diffracted beam was then observed behind the sample *(pink)*. This beam is observed only if a sample has nearly perfect positional order, even if that order is aperiodic rather than periodic.

Traditional crystal-growing methods work for aluminum-palladium-manganese because the temperature difference between the onset of solidification (the precipitation of the primary crystalline phase) and the solidification of the quasicrystalline phase is less than 10 degrees Celsius. The temperature difference is small because the composition of the liquid from which the quasicrystalline phase precipitates is relatively close to the composition of the solid phase. As a result, a planar growth front can be established between the newly formed solid and the remaining liquid as the quasicrystalline phase begins to solidify, and planar growth promotes the growth of large grains. The temperature and compositional differences in aluminum-copper-iron are much larger, and this prevents the establishment of planar growth, discouraging the growth of large grains.

Exploring Order

The availability of large aluminum-palladium-manganese grains permitted experiments to be done that conclusively showed quasicrystals are well-ordered materials. Although the diffraction patterns from early quasicrystalline alloys were composed of well-defined spots, the spots were not quite as sharp as those produced by periodic crystals, which suggested these materials were somehow less than perfectly ordered. One structural model, for example, proposed that they might have long-range orientational order but only short- or medium-range positional order. Although samples of aluminum-copper-iron produced much sharper diffraction patterns, doubts about the structural perfection of quasicrystals lingered until 1993.

One clear indicator of a material's structural perfection is whether the diffraction of x rays by the material is best described by the kinematical or the dynamical scattering theory. In the kinematical theory of diffraction, which is applicable to most materials, a light quantum, or photon, enters the sample, is scattered once by the atomic electrons and leaves without additional interactions. Although this theory is appropriate for imperfect materials containing many defects, it falls short in the case of nearly perfect crystals, such as the large silicon or germanium crystals that are routinely made for the electronics industry. In a perfect crystal, multiple interactions between photons and atomic electrons set up a wavefield within the material, with the consequence that a more sophisticated theory, the dynamical theory of scattering, must be invoked.

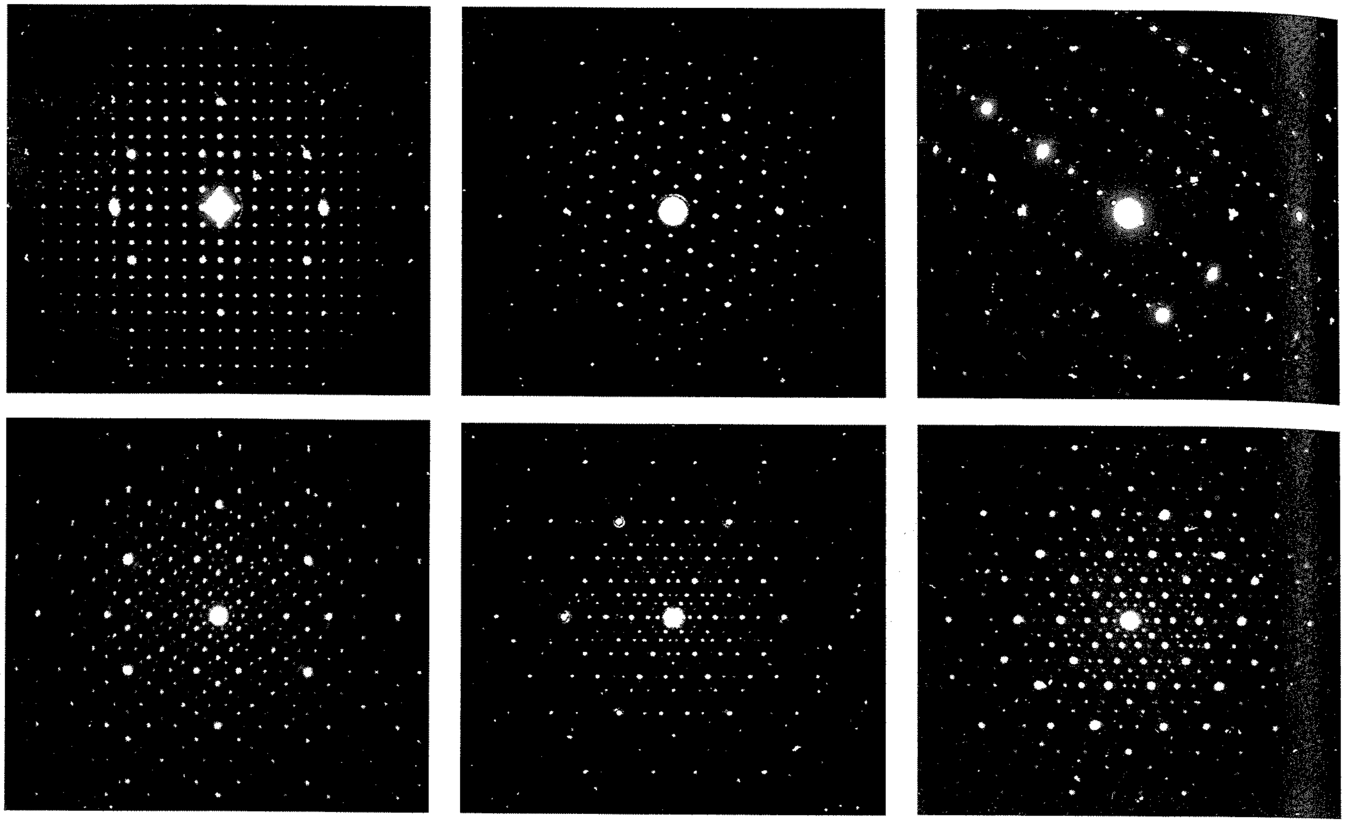


Figure 7. One of the more intriguing products of quasicrystal research is the discovery of crystalline approximants, crystals whose unit cells have quasicrystalline atomic "decorations." Comparison of the twofold, threefold and "pseudo-fivefold" electron diffraction patterns from an approximant phase *(top)* and twofold, threefold and fivefold diffraction patterns from a quasicrystalline phase *(bottom)* in the aluminum-copper-ruthenium system illustrates the difference between them. The more intense patterns of spots indicate the presence of icosahedral clusters in both structures; the arrangement of these spots is nearly the same in both sets of diffraction patterns. Closer inspection of the two sets of patterns, however, reveals the periodicity inherent to the approximant phase and the aperiodicity of the quasicrystalline phase.

How does one know whether the dynamical or kinematical theory applies to a specific sample of material? A striking effect within the competence of the dynamical but not the kinematical theory is the "anomalous" transmission of x rays through a sample (the Borrmann effect). To check for this effect, a single-grain sample is oriented in an x-ray beam in such a way that the diffraction condition is satisfied. (To form a diffracted beam, the x rays scattered from the regular array of atoms in the crystal must interfere constructively, and this happens only at certain angles.) The sample itself is so thick that if it were rotated away from the correct angle for diffraction, it would absorb all of the x-ray beam. If the sample has a high degree of structural perfection and the condition for diffraction is satisfied, the dynamical theory shows that the normal absorption by the sample is greatly reduced. As a result, both the diffracted and a forward-scattered beam (a beam with the same direction as the incident beam) appear behind the sample.

The Borrmann effect was observed in a sample of aluminum-palladium-manganese in 1993 by Stefan Kycia and colleagues at Ames Laboratory, NIST and McGill University in Montreal. The observation is striking confirmation that quasicrystals can achieve a degree of structural perfection comparable to that of the best periodic metallic crystals. Furthermore, it demonstrates that the dynamical theory, which was originally proposed for periodic crystalline systems, can also be used to describe diffraction in aperiodic materials.

Quasi Quasicrystals

Insight into the relation between periodic and aperiodic materials has been gained by studying transformations among them. For example, several of the icosahedral alloys, including aluminum-copper-ruthenium, undergo reversible transformations from crystalline to quasicrystalline phases at high temperatures. (The highest-temperature phase of aluminum-copper-ruthenium has a cubic structure, but as the temperature is lowered below about 900 degrees Celsius, an icosahedral quasicrystalline phase is formed.) These transformations demonstrate that the quasicrystalline phase is thermodynamically stable; at some temperatures it is the structure with the minimum free energy and the one nature therefore prefers.

A 1991 study of the phase transitions of aluminum-copper-ruthenium at elevated temperatures showed that a crystalline phase transforms into a quasicrystalline phase by passing through a series of crystalline "approximants" (a term coined by Veit Elser and Christopher Henley at Cornell University) with progressively larger unit cells. A crystalline approximant is a phase whose composition is close or identical to that of the quasicrystalline phase and whose unit cell has atomic "decorations," that look quasicrystalline, such as icosahedral clusters of atoms, but which is nonetheless a crystal. In a sense, these crystalline approximants are the missing link between periodic crystals and their quasicrystalline cousins.

As this lengthy definition suggests, it can be difficult to determine whether a particular alloy is a quasicrystal or a crystal with a very large unit cell. Indeed, confidence in the claim that an alloy is a quasicrystal depends on how precisely the diffraction pattern from that alloy can be measured. Careful measurements of the positions of spots in diffraction patterns made at synchrotron-radiation sources establish the minimum dimensions the material's unit cell must have if it is indeed a crystalline material masquerading as a quasicrystalline one. For instance, if the aluminum-copper-iron icosahedral alloy were crystalline, it would require a cubic-unit-cell edge length of about 200 Angstroms—that is, a unit cell big enough to contain about a million atoms. To put this in perspective, the unit cells of even the most complex intermetallic alloys typically contain only a few hundred atoms. Furthermore, in most cases, replicating the observed icosahedral rotational symmetry would require twinning (the close juxtaposition of several crystallites at specific angles to one another).

This is not to suggest that large-unit-cell periodic approximants have not been discovered in the course of research on quasicrystals. At Washington University in St. Louis, for example, Ken Kelton's group found an alloy of aluminum, cobalt and copper with a unit cell whose edge length is about 100 Angstroms. More typically, crystalline approximants have unit cell sizes in the range of 10 to 40 Angstroms. The existence of these large-unit-cell crystalline alloys, with length scales and numbers of atoms more characteristic of organic than inorganic structures, is one of the more fascinating discoveries to come out of quasicrystal research.

Insights into Bulk Properties

Perhaps the most fundamental principle of materials science is that a material's atomic structure determines many of its properties. How do the properties of quasicrystals differ from those of crystals, and how are these differences related to their structure?

Even though quasicrystalline alloys are made up of metallic elements, they are poor electrical and thermal conductors. A metal conducts electricity and heat easily because many of its electrons occupy states with energies above a certain critical value called the Fermi energy. Electrons above the Fermi level can move freely, carrying charge or conducting heat. Insulators, on the other hand, have an electron distribution with a large gap at the Fermi energy. Electrons in these materials must obtain a substantial boost to reach states where they can move freely. Almost from the start, the poor conductivity of quasicrystals was attributed to a scarcity of electrons at the Fermi energy.

At first, however, arguments about the electron distributions of quasicrystals had to be made from indirect evidence, such as measurements of resistivity as a function of temperature. Experimental groups at the Laboratoire d'Études des Propriétés Electroniques des Solides in Grenoble, the University of Tokyo and the University of Virginia, for example, exhaustively measured the electronic properties of quasicrystalline alloys and crystalline approximants.

A more direct way of probing a material's electron distribution is a technique called photoemission. In a photoemission study, a sample is irradiated with photons of known energy. The absorption of photons provides enough energy to eject electrons from the sample, and the kinetic energy of these electrons is measured experimentally. The energy of the electrons in the material is then calculated by subtracting the incident photon energy from the kinetic energy of the ejected electrons. High-resolution photoemission studies done on an aluminum-palladium-manganese sample showed that its electron distribution is intermediate between those of a conductor and an insulator; as had been suspected, there is a deep dip, or pseudo-gap, in the density of states near the Fermi energy.

How is the pseudo-gap related to the

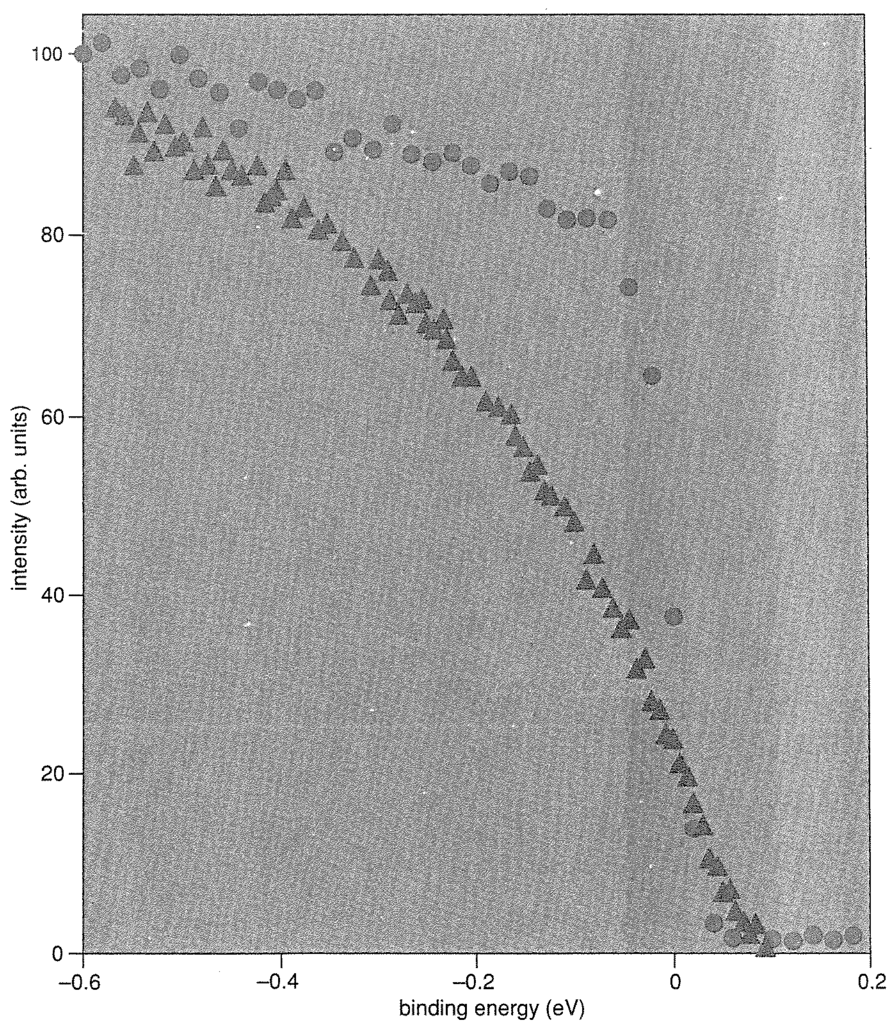


Figure 8. Although they are composed of good metals, quasicrystals exhibit electrical conductivity thousands of times smaller that those of their constituents. Measurements made by a technique called photoemission showed that compared to a typical metal such as platinum *(pink)*, an aluminum-palladium-manganese quasicrystal *(purple)* has fewer states with energies near the Fermi energy (a binding energy of 0 electron volts). This valley, or pseudo-gap, explains the material's poor conductivity.

quasicrystals' aperiodic structure? Quasicrystals fall into a class of materials, called Hume-Rothery alloys, in which a progressive change in composition is accompanied by a progressive increase in valence-electron density. As the electron density increases, the material adopts a succession of different structures. In the copper-zinc system, for example, as the zinc content increases, the structure changes from the face-centered cubic structure of copper, to a structure like that of cesium chloride, to a structure called gamma brass, to two hexagonal close-packed geometries like those found in magnesium.

Although most of these structures are geometrically simple, the gamma-brass structure is not. It consists of cubes, but each cube encloses an octahedron that encloses a tetrahedron that encloses a second tetrahedron. Why would nature prefer a structure so elaborate? The answer, it turns out, is that a complicated structure sometimes allows a material to lower its overall energy by a kind of symmetry breaking that results in a decrease in the number of states with energies near the Fermi energy. In this way, the poor electrical conductivity of the quasicrystals and of their periodic approximant brethren is linked to the motifs assumed by the atoms of which they are composed.

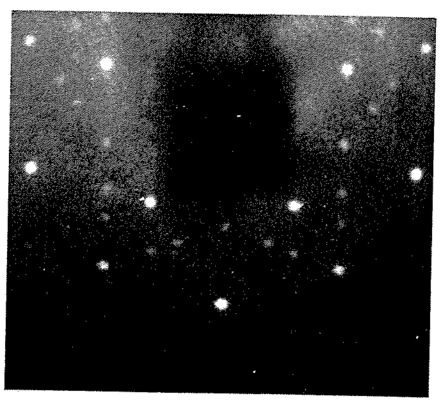


Figure 9. The surface properties of a quasicrystalline alloy are not necessarily the same as those of the bulk. To determine the atomic arrangement at the surface, the sample is probed with electrons that have lower energies than those used to make diffraction patterns of the bulk. A low-energy electron-diffraction pattern made by exposing a clean sample whose surface plane is perpendicular to the fivefold axis to electrons with an energy of 75 electron-volts still clearly shows the fivefold symmetry of the bulk. The pattern is not identical to the diffraction pattern for the fivefold axis in Figure 3 because the lower-energy electrons probe a thinner slice of the sample. (Figure printed with permission from S.-L. Chang *et al.*, 1995, *Surface Science* 337:135-146.)

In related research, the Ames Lab group has been collaborating with groups at the Centre d'Études Nucleaires in Saclay, France, and the Institute Laue Langevin in Grenoble on the study of phonon excitations in the icosahedral alloys. A phonon is a normal-mode vibration of the crystalline lattice, the three-dimensional equivalent of the vibrational pattern of a plucked guitar string. The possible modes of vibration in a solid include low-energy acoustic modes in which neighboring atoms vibrate longitudinally or transversely in synchrony with one another and high-energy optical modes in which neighboring atoms vibrate in opposition to one another.

The study of the electronic and vibrational properties of quasicrystals is an area where experiment leads theory in some ways. The reason is that the usual techniques for calculating these properties in crystalline solids rely on the fact that crystals have unit cells that repeat at regular intervals. Because their structure is periodic, comparatively simple mathematical expressions called Bloch functions can be used to extend the description of electronic and vibration characteristics of a single unit cell to a lattice of many unit cells. But if a material is aperiodic, these calculational shortcuts no longer apply.

Does the failure of the standard calculational tools mean that the electronic and vibrational excitations are actually different in aperiodic materials? The electronic properties of quasicrystalline materials generally resemble those of crystalline materials of similar composition. Some measurements indicate, however, that the quasicrystals' electronic properties are more perturbed than those of the crystalline approximants, perhaps because an aperiodic structure scatters electrons more effectively than a periodic structure. Similarly, the low-energy vibrational excitations of quasicrystals generally resemble those of crystalline solids, but at high energies there appear to be subtle differences between them. In other words, despite the striking differences in atomic-scale structure, there are generally only small differences between the electronic and vibrational properties of crystalline and quasicrystalline materials.

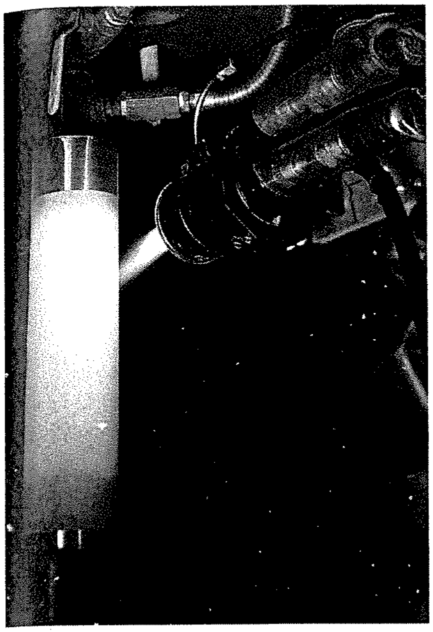
How Quasicrystals Deform

How do the mechanical properties of quasicrystals differ from those of crystals, and how are the differences related to their structure? Differences in the strengths of materials with different structures can be understood by examining the mechanisms by which they deform under stress.

Crystalline materials, most notably metals, can be deformed a great deal before they crack. They are plastic because their grains contain defects that can move about with relative ease. These defects, called dislocations, are line imperfections in the otherwise perfect crystal lattice. Their presence allows two sections of the lattice to move past one another a step at a time, and this incremental motion requires much less energy than breaking all of the bonds between the sections at once. This explains why metals are much less strong than one would predict from the strength of metallic bonds.

Moving a dislocation still requires external energy, however. In other words, there is a "hurdle," or barrier, the material must overcome to break a bond and move the dislocation forward a step. In a crystalline material composed of one elemental species, the hurdles are all the same height and are evenly spaced, much like the hurdles Edwin Moses ran in the Olympics. He would have had a much more difficult time of it if the hurdles weren't evenly spaced and all the same height. Similarly, a dislocation has a more difficult time moving in quasicrystals, where the aperiodicity creates hurdles that are irregularly spaced. Furthermore, because quasicrystalline alloys are made up of several different elements, the hurdles' heights also vary. The motion of a dislocation is limited by its ability to jump the highest barrier.

Because of the difficulty of moving a dislocation through a quasicrystal, at first few scientists believed quasicrystals could deform by the motion of defects within grains. Even after experiments revealed that quasicrystalline alloys could exhibit remarkable plasticity at elevated temperatures, they were still thought to deform by other mechanisms. Researchers at Ames Laboratory and the Institüt für Festkörperforschung have shown, however, that at sufficiently high temperatures quasicrystals do indeed deform by dislocation motion. (The high temperatures contribute thermal



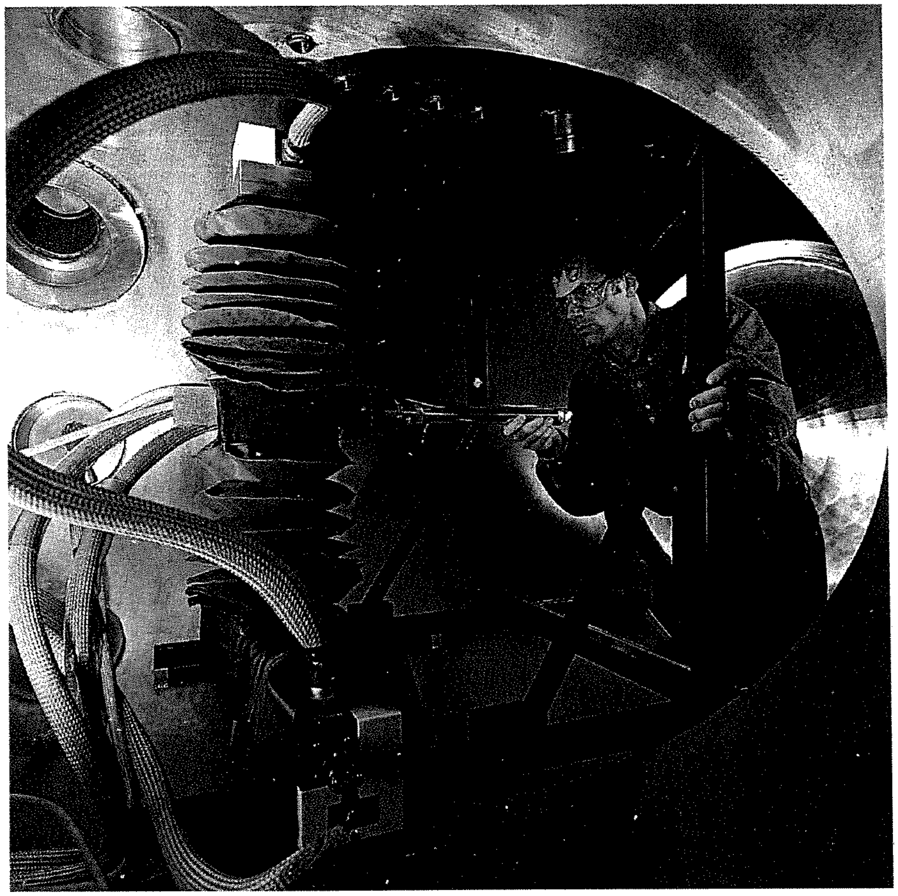


Figure 10. Quasicrystal coatings can be applied to metal parts by a technique called plasma arc spraying. A plasma, or highly energetic gas of electrons and ions, melts a quasicrystalline feedstock powder and accelerates it out through the nozzle of a "gun" (*above*). To improve the quality of the coatings, the process is sometimes carried out in a controlled atmosphere (*right*).

energy toward overcoming the energy barrier; at room temperature quasicrystals fracture instead of deforming.) But as might be expected, the quasicrystals were determined to have a comparatively large energy barrier for dislocation motion. The energy barrier in aluminum-copper-iron, for example, is roughly twice that in most crystalline aluminum alloys.

Surface Characteristics

The properties of a material's surface are not necessarily the same as those of the bulk material. Like bulk properties, surface properties are determined by the atomic arrangements and the chemical composition. But crystalline surfaces often reconstruct, which means that the atoms at the surface adopt an arrangement different from that of the bulk material. It also sometimes happens in crystalline alloys that one element segregates and forms a skin on the surface, so that the surface composition as well as the surface arrangement is different from that of the bulk material.

To investigate the atomic arrangements of the quasicrystal surfaces, groups at Bell Laboratories, the University of Basel in Switzerland, and a collaboration between the Ames group and Michel van Hove of Lawrence Berkeley Laboratory are using surface-specific structural probes such as low-energy electron diffraction and scanning tunneling microscopy. To investigate the composition of the quasicrystalline surface these groups are using a variety of techniques, including x-ray photoelectron and Auger electron spectroscopies. What insights are likely to come from these studies? At the Ames Laboratory, preliminary results suggest that aluminum-palladium-manganese is oxidation-resistant because aluminum tends to segregate at the surface, where it forms a thin skin of aluminum oxide that prevents oxidation of the bulk of the material.

Another goal of surface studies is to explain the low surface friction of quasicrystal coatings. Low coefficients of friction were first reported by Jean Marie Dubois and coworkers at the Ecole des Mines in Nancy, France, for coatings containing the icosahedral phase of aluminum-copper-iron. The Ames group is collaborating with Andrew Gellman of Carnegie Mellon University to determine whether, and under what conditions, low coefficients of friction might be related to the unique structure of clean alloy surfaces. Since the surfaces oxidize when they are exposed to air, it is also possible that the coefficients of friction are controlled by the surface oxide layer, not by the alloy itself. In order to distinguish between these possibilities, experiments must be conducted in an ultra-high-vacuum environment.

A final goal of the surface studies is to determine whether the surface chemistry of the aluminum-based quasicrystalline alloys differs from that of aluminum. The possibility of a difference arises from the fact that the density of states at the Fermi edge is much lower in the quasicrystalline alloys than in aluminum. Differences in the electron distribution of solids can lead to differences in the availability of electrons for bonding to other substances and therefore in their chemistry.

Quasicrystal Applications

The results of these mechanical studies began to suggest potential applications for quasicrystals. From the practical point of view, quasicrystals are exceptionally hard materials that combine low density with high strength. Their

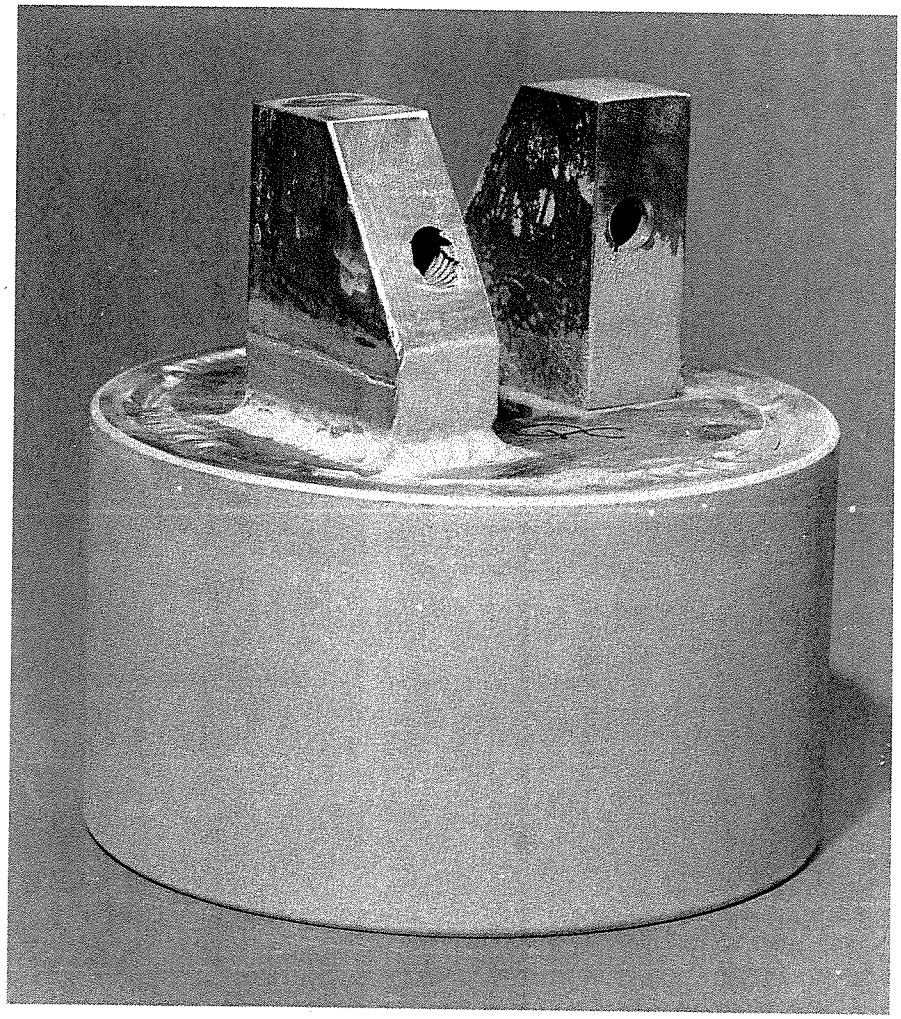


Figure 11. One of the most promising applications for the quasicrystalline alloys is as a hard facing material for equipment that suffers abrasive wear. One example is this mold component, which is forced through wet concrete to form the central cavity of concrete drainage pipe. So abrasive is the slurry that the mold must typically be replaced every few weeks. A coating of quasicrystalline aluminum-copper-iron may extend its lifetime.

brittleness further defines the range of suitable applications. Unfortunately, a body of knowledge usually available in the application of metals was missing for quasicrystals.

Most metals had been used for millennia and their complex behavior codified in recipes for smelting, refining and working before scientists got around to explaining their physical basis. In the case of quasicrystals, however, the situation is reversed. There is no art encoding a subtle understanding of properties gained through practical experience. Instead the metallurgist is in the somewhat uncomfortable position of having to trust the physicist's science.

Turning the quasicrystalline alloys into engineering materials requires simultaneous consideration of all of the material properties discussed in this article, as an example illustrates. Groups at Ames Lab, the Ecole des Mines and Tohoku University are working to develop a process for applying quasicrystalline coatings to surfaces. The French group has already used this process to coat cookware, in what may be the first commercial application for quasicrystals. The same process might eventually be used to apply coatings to engine components, injection molds, and agricultural or mining equipment.

The project aims to exploit the unusual hardness of aluminum-copper-iron, a quality that can be traced back to its aperiodic atomic structure. Aluminum-copper-iron is harder, for example, than sand or even martensitic steel. In addition, aluminum-copper-iron shares aluminum's low weight and is potentially less expensive than many of the coating materials now in use. These typically contain expensive metals or ones that require expensive processing techniques because they are considered to be carcinogenic, such as nickel, chromium or cobalt.

The coatings will be applied by plasma arc spraying, a process commonly used in industry to make coatings of other materials. In plasma arc spraying a fine powder of the feedstock material is fed into a plasma spray gun. The plasma (a highly energetic gas of ions and electrons) within the gun melts the powder and accelerates it out through the nozzle. The molten droplets smack into a substrate, flow outward and build up to form a coating.

Adapting this process to aluminum-copper-iron meant wrestling with the complex solidification behavior of quasicrystalline alloys. For a variety of reasons, including the low thermal conductivity of the quasicrystalline phase, the smaller powder particles can overheat in the plasma. Because the vapor pressure of aluminum is far higher than that of copper or iron, if the particles overheat, the aluminum may vaporize. Enough aluminum can be lost to carry the coating outside the compositional range of the quasicrystalline phase. If this happens, the coating may contain very little quasicrystalline material, even though the feedstock powder itself is largely quasicrystalline.

This problem can be avoided by balancing the transfer of thermal and kinetic energy from the plasma to the powder particles. In particular the best results are obtained using smaller particles and a very-high-velocity plasma. The velocity of the plasma limits the dwell time, or the time any one particle remains in the plasma "flame," and so reduces the likelihood of overheating. Keeping the particles small ensures that, despite the short dwell time, they melt completely.

Then there is a second solidification problem to overcome. When aluminum-copper-iron cools slowly, the first phase to precipitate out is a crystalline phase. It is possible to bypass the crystalline phase and to form the quasicrystalline coating by undercooling the liquid metal. But if the liquid does not cool uniformly, a crystalline phase may still form between solidified quasicrystalline regions. The Ames group is also investigating the relation between process parameters and the solidification rate, with the goal of maximizing the quasicrystalline content of the as-deposited coatings.

The Path Ahead

In just ten years, the materials science of quasicrystals has caught up with the materials science of other intermetallic compounds. Indeed, given the flurry of activity in this field over the past decade, quasicrystals may now rank as the most studied of the complex intermetallic phases.

The field matured rapidly in part because scientists had at their disposal all of the analytical techniques and tools that were developed for the materials science of crystals and glasses over the past hundred years. Those working on quasicrystals were therefore in the enviable position of being able to do new science with well-established tools.

Many of the basic issues regarding the structure and stability of quasicrystalline alloys have now been resolved, at least in general terms. But along the way, new periodic intermetallic phases were discovered, and their fascinating stories are only beginning to unfold.

In the meantime, quasicrystal research is moving toward finding applications for these materials. Unlike oobleck, which proved so noxious it had to be conjured away to preserve life in the kingdom of Didd, quasicrystals offer many attractive properties: high strength, relatively low density, low surface friction and good oxidation resistance. Novel applications promise to make the next decade of quasicrystal research as much of an adventure as novel physics made the past decade.

Acknowledgments

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