

SEARCH AND DISCOVERY

Binary Quasicrystals Discovered That Are Stable and Icosahedral

Like *The Cosby Show* and the Macintosh computer, quasicrystals made their debut in 1984. By rapidly cooling an alloy of aluminum and manganese, a group led by Technion's Dan Shechtman created a solid whose sharp x-ray diffraction patterns indicated a high degree of order.¹ But the patterns also exhibited symmetries that are impossible to realize in a regular repeating array in three dimensions. Neither amorphous nor crystalline in the traditional sense, quasicrystals have long-range orientational order but lack periodic translational order.

The first quasicrystalline materials were thermodynamically unstable. When heated, they formed regular crystals. But in 1987, the first of many stable quasicrystals were discovered, making it possible to produce large samples for study and opening the door to potential applications. Unlike Shechtman's prototype, these stable quasicrystals contained three chemical elements, leading some to believe that quasicrystal stability required three elements.

That state of affairs changed two years ago when Matthias Conrad and Bernd Harbrecht of the University of Marburg and Frank Krumeich of the Swiss Federal Research Institute in Zurich succeeded in creating stable quasicrystals from two elements, tantalum and tellurium.² Those quasicrystals are two-dimensional in that the stacking is periodic along one axis, but along the other two it's quasiperiodic with dodecagonal (12-fold) symmetry.

Now, a team led by An Pang Tsai from Japan's National Research Institute for Metals in Tsukuba has discovered quasicrystals of cadmium-ytterbium that are stable and exhibit three-dimensional icosahedral symmetry.³ The icosahedron, which has 20 identical triangular faces, has the largest finite group of symmetries in the three-dimensional world but its symmetry is off-limits to regular crystals. "Tsai's discovery is one of the most exciting things to happen in quasicrystals in a long time," says Iowa State University's Pat Thiel.

You don't need three chemical elements to make thermodynamically stable quasicrystals. Two will do.

Tsai didn't stumble on Cd-Yb crystals by chance. In 1994, his team discovered stable icosahedral phases in ternary compounds of zinc and magnesium coupled with various rare earth (RE) elements. Four years ago, Tsai tried replacing Zn with Cd, which appears in the same column of the periodic table. But, not knowing the right stoichiometry in advance, he couldn't find any trace of the quasicrystal.

Then, in March last year, Tsai revisited the Cd-Mg-RE system with a fresh approach and discovered eight to nine stable icosahedral quasicrystals. Among those alloys, Cd-Mg-Yb turned out to be particularly stable in that its formation didn't require annealing. Curious about this property, Tsai looked up the Cd-Yb phase diagram (see figure 1). Next to the cubic Cd₆Yb is a stable phase, Cd_{5.7}Yb, which metallurgists had dubbed "unknown" and whose odd structure they had attributed to a very large lattice constant.

Tsai realized that Cd₆Yb could be

what quasicrystallographers call an approximant, a crystalline phase whose composition is very close to that of its quasicrystal relative but whose components (atomic clusters) are arranged periodically rather than quasiperiodically. If Cd₆Yb really is an approximant, then the unknown phase was an excellent candidate for a quasicrystal. Inspired by this hunch, Tsai's colleague Junqing Guo made grains of Cd_{5.7}Yb in an induction oven. Electron microscope images confirmed the material's quasicrystalline nature, as did x-ray diffraction patterns, one of which is reproduced on the cover.

Why should Yb, alone among the rare earths, form a stable quasicrystal with Cd? Tsai sees a clue in the size of the Yb atom, which comes in divalent and trivalent forms. Divalent Yb—the sort that forms the quasicrystal—has a radius of 1.94 Å, whereas trivalent Yb measures 1.74 Å. Europium is the only other rare earth that has both divalent and trivalent forms, but it doesn't form binary quasicrystals with Cd. Most other rare earths have atomic radii between 1.75 and 1.85 Å; divalent Eu's is 2.04 Å; so, reasons Tsai, Cd's atomic partner must be bigger than 1.85 Å and smaller than 2.04 Å. Calcium, though not a rare earth, fits in that range, and, as Tsai's team has recently discovered, also forms stable binary icosahedral quasicrystals with Cd.

Energy versus entropy

Despite 18 years of quasicrystal research written up in more than 5000 papers, not one quasicrystal structure is known with the completeness and accuracy that crystallographers take for granted. Nor has a definite explanation emerged for how and why quasicrystals form. Although the discovery of stable binary quasicrystals won't lead directly to a solution, it does at least simplify the calculations.

The atoms in nearly all regular crystals arrange themselves in a symmetric repeating pattern because that arrangement has the lowest energy. But some regular crystals adopt the

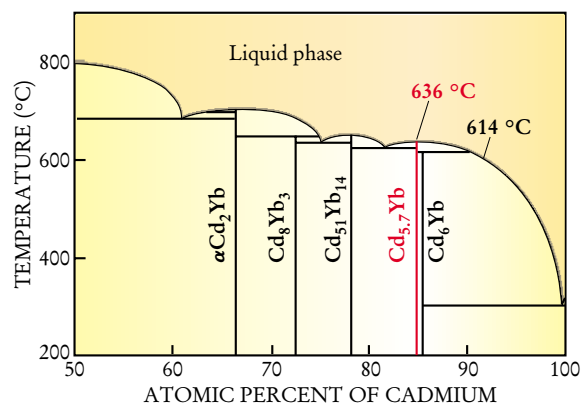


FIGURE 1. BINARY PHASE DIAGRAM of cadmium-ytterbium alloys. The looping curved line marks the boundary between the liquid phase above and the solid phases below. Shown in red is the quasicrystalline Cd_{5.7}Yb, whose stoichiometry is almost identical to its closest neighbor on the phase diagram, the cubic Cd₆Yb.

arrangement—or, rather, an ensemble of arrangements—that gives them the highest entropy. This energy-versus-entropy dichotomy exists in the field of quasicrystals, too, but with the difference that some theorists believe that most, if not all, quasicrystals could be stabilized by entropy.

Advocates of both energy and entropy stabilization find evidence in Tsai's discovery to support their cases. Cornell University's Veit Elser of the entropy camp notes that $\text{Cd}_{5.7}\text{Yb}$ is a congruent melter—that is, the solid can be in equilibrium with the liquid, suggesting entropic kinship between the two phases. Says Elser: "When you take the high-temperature liquid cadmium-ytterbium and cool it down, the first thing that forms is the quasicrystal. And to get the approximant, you need a solid-state reaction involving the quasicrystal and the other crystal phase at lower temperature. That, for me, is a key point."

Elser also finds support for the entropy picture in the structure that Tsai proposed for $\text{Cd}_{5.7}\text{Yb}$'s atomic building blocks (see figure 2). At the center of the cluster is a tetrahedron of Cd atoms that breaks the cluster's overall icosahedral symmetry. The energetic view relies on the deterministic packing of identical units, but in the entropic picture the units don't have to be arranged so carefully. "You just don't care how the tetrahedron is oriented. All orientations are just as

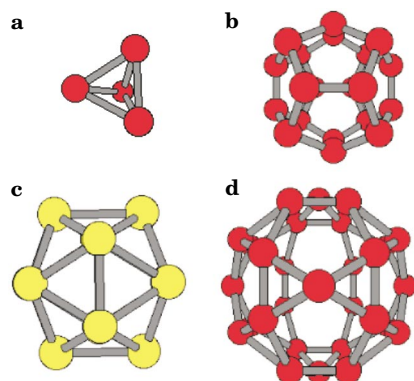


FIGURE 2. A PRELIMINARY STRUCTURE for the atomic cluster that forms the basis of $\text{Cd}_{5.7}\text{Yb}$ quasicrystal. Cadmium atoms are shown in red, ytterbium in yellow. Like a Russian doll, the successively smaller units (c, b, a) fit within the largest unit (d).

likely," says Elser.

In the energy camp, Princeton University's Paul Steinhardt sees the cluster's tetrahedron as providing the asymmetry that energy stabilization needs. In the energy picture, a repeating unit, the quasi-unit cell, finds the lowest energy state by maximizing its density. "The discovery of stable binary quasicrystals," says Steinhardt, "is consistent with a simple relationship with crystals. Energy stabilization, local growth rules, simple repeating units—all these features, which are

found in crystals, are also found in quasicrystals."

The key difference between quasicrystals and regular crystals is that the units in quasicrystals can overlap, making it possible to realize symmetries that are forbidden to regular crystals. Though once rather complicated, the rules for overlapping atomic clusters are now simpler in the latest version of the energy-stabilization theory and don't require the long-range collusion that was a feature of earlier versions.

Despite their differences, both camps agree that more and better structural data are needed on the Cd-Yb and Cd-Ca systems. For one thing, Tsai's atomic cluster model is a first guess based on the Cd_6Yb approximant. Also needed are measurements of the materials' mechanical, thermal, and electrical properties. But don't expect too many applications for $\text{Cd}_{5.7}\text{Yb}$. Cadmium is poisonous. "The allure of these new materials will remain intellectual for the foreseeable future," says Thiel.

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References

1. D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, *Phys. Rev. Lett.* **53**, 1951 (1984).
2. M. Conrad, F. Krumeich, B. Harbrecht, *Angew. Chem. Int. Ed.* **37**, 1384 (1998).
3. A. P. Tsai, J. Q. Guo, E. Abe, H. Takakura, T. J. Sato, *Nature* **408**, 537 (2000).

Hydrodynamics May Explain Like-Charge Colloidal Attraction

We are taught from the first lectures in electrostatics that like charges repel each other. That expected behavior breaks down, however, in some colloidal suspensions. There, large colloidal particles (called macroions), typically all with the same charge, are surrounded by smaller, oppositely charged counterions, not to mention a polar fluid, charged surfaces on the walls of the container, and possible additional ions. In such complex fluids, many varied experiments over the past 15 years have produced evidence of attractive interactions between the macro-ions.

In many regards, latex colloidal suspensions, with their spherical particles of nearly identical diameter, are useful models for studying behavior in more complex systems (see, for instance, the article by Alice Gast and William Russel in *PHYSICS TODAY*,

As two like-charged particles are repelled by a nearby charged wall, the resulting fluid flow can make them move toward each other.

December 1998, page 24). Attractions in such systems at short length scales—on the order of a few nanometers—are well established and attributable to correlations among multivalent counterions; such attraction in biological systems is discussed in the article by William Gelbart and coauthors in *PHYSICS TODAY*, September 2000, page 38. But in some systems, attraction has been observed at length scales of several microns, and an understanding of that behavior has been elusive. Recently, Todd Squires of Harvard University and Michael Brenner of MIT have proposed an explanation for some of the

experimental results, incorporating hitherto overlooked effects of hydrodynamics.¹ Their model produces quantitative agreement with measurements, by Amy Larsen and David Grier at the University of Chicago, of the behavior of two colloidal particles near a single wall.²

Hints of attraction

A typical charge-stabilized latex colloidal suspension consists of spheres with diameters on the order of $1\text{ }\mu\text{m}$ or smaller, dispersed in water. Sulfate or other groups on the spheres dissociate in solution, producing a large surface charge density on the spheres. The spheres are surrounded by counterions that are many times more numerous and much smaller than the spheres. As a result, the dynamics of the counterions have a significantly faster time scale than that of the