Quasicrystals soldier on?

Attempts continue to account for the occurrence of quasicrystals with fivefold symmetry, and are to be applauded. The case for believing them important is less sure.

THERE seems still to be life in the problem of quasicrystals, and of whether they are explicable. The essence of the problem, it will be recalled, is that fivefold symmetry is flatly forbidden for a crystal lattice in which the crystallizing units have both an intrinsic symmetry and the translational symmetry of a crystal lattice as well. Yet, as the world knows, we have been living with exceptions to that rule for the best part of three years. Apart from the original intermetallic compound of Al and Mn, there are now ternary compounds such as Al-Cu-Li and Ga-Mg-Zn which have phases showing distinct icosahedral symmetry.

Not that explanations are impossible. The earliest were essentially generalizations of the way in which it is possible completely to fill a plane surface by a suitable arrangement of tiles of two distinct but related rhombi — the arrangement called the Penrose tiling. The ratio of the major and minor diagonals of each rhombus is the golden mean, also the natural number that crops up in the definition of a Fibonacci series.

This tiling is not a two-dimensional crystal, for there is nothing corresponding to a unit cell, nor to directions in two-dimensional space that would correspond to crystal axes, but that is an academic question provided that the arrangement can be essentially infinite. Then, there is no reason why such a tiling of the plane should not represent a two-dimensional solid of some kind, whence the term "quasicrystal". By now, there are three and even many-dimensional generalizations of the Penrose tiling, and thus models for the existence of three-dimensional quasicrystals. There is no doubt that some of the elements of these structures do, indeed, have fivefold symmetry. The interesting question is whether these structures are those of the solids that actually exist.

Observationally, the issue is clouded by the difficulty of making structural measurements with materials that are usually made at high temperatures, and by the likelihood that the conditions in which most specimens are made are far from equilibrium.

On balance, three distinct positions are recognizable in the range of opinion on offer — quasicrystals which are infinite in extent do indeed exist; quasicrystals of infinite extent are possible, but in reality are so shot through with dislocations and

other internal defects that quasicrystallinity is limited to a few hundred interatomic distances; and, on the radical (or is it "conservative"?) extreme, Pauling's view that the structures called quasicrystals are really solid materials formed by the interspersing of microscopic crystallographic twins.

One way of telling which of these possibilities, or which combination of them, may arise in practice is to concentrate on gross features of the actual specimens made in the laboratory, asking simple questions such as "If they have fivefold symmetry on an atomic scale, should they not also have faces, or facets, with fivefold symmetry?" This problem is first that of calculating the equilibrium shape of the facets of a quasicrystal (which will be a function of the temperature). A diagnostic test that bears on this is whether the facets of a small quasicrystal should be rough or smooth, on a scale measured by a few interatomic spacings, for this will determine how readily atoms will migrate to their equilibrium positions within a structure.

Richard Lipowsky (from the nuclear research centre at Jülich in West Germany) and Christopher L. Henley (Boston University) have made an interesting attack on the second problem (*Phys. Rev. Lett.* **60**, 2394; 1988). The issue is that of what the most likely (Boltzmann-weighted) configuration of a surface will be in a quasicrystal. The calculation is simply that of the enumeration of the numbers of bonds between neighbouring Penrose-like tiles broken as surfaces of different configuration are formed. The equilibrium is determined by the increase of energy on breaking the bonds and the loss of entropy that results.

What emerges is that the stability of a surface formed by breaking apart a quasicrystal is sharply different in the two- and the three-dimensional cases. The energy term is an interfacial term, but the entropy is a function of the dimensions of the bulk. Lipowsky and Henley accordingly conclude that two-dimensional quasicrystals will have decagonal shape at absolute zero, but will become rounded at the corners as the temperature is increased.

Three-dimensional crystals are a different kettle of fish, because the relatively greater importance of the entropy will keep decagonal faces decagonal for longer. By the same test, of course, badly

formed quasicrystals with no recognizable fivefold symmetry on the outside will convert to forms in which the internal symmetry is externalized as they are annealed. Indeed, the message here is that the way to tell the internal symmetry of a quasicrystal is to anneal it, when its internal symmetry will be revealed.

The same issue of the same journal has a more recondite quarrel on a related topic. Kevin Ingersent and Paul J. Steinhardt (co-discoverer of the Al-Mn quasicrystalline material) have obviously been belatedly cut to the quick by an earlier paper (Ho *et al. Phys. Rev. Lett.* **59**, 1116; 1987) asserting that a model of a quasicrystal in which the forces between atoms are strictly attractive leads to the conclusions that decagonal faces cannot exist.

"So what?", Ingersent and Steinhardt stoutly protest (*Phys. Rev. Lett.* **60**, 2444; 1988). They construct a model allowing for the surface energy of a quasicrystal, and wrapping the entropy term within a variable called the "surface free energy". The interest of this brief note is a sequence of diagrams showing the shapes of the quasicrystals that will arise with different proportions of repulsion and attraction. The repulsive component of the interatomic force, they say, is crucial: the greater its relative amount, the more faceted and less spherical the quasicrystallites become.

Lipowsky and Henley have made essentially the same point; perhaps the best way to tell the structure of a quasicrystallite is to make a few specimens (usually a few micrometres across) and to anneal them. Then the internal structures will be externalized. Maybe the experimentalists in the field will be sufficiently challenged to try.

Meanwhile, we have all learned a great deal about what may be called, not unreasonably unfairly, the great quasicrystal ramp (which will continue). First, there is such a thing as dodecahedral (fivefold) symmetry, at least on the scale of atoms in a three-dimensional atomic array. Second, there are ways of making (or at least modelling) three-dimensional arrays of atoms which hold together and may be infinite, or at least large, in extent. Third, so little has been discovered, in the past three years, from the properties of quasicrystals about the nature of the solid state that the whole episode may have served merely to sharpen people's teeth for more interesting battles.

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