Origins of five-fold symmetry

That solids with five-fold symmetry may exist seems plausible enough, but a brief bout of calculation serves chiefly as a proof of how much more remains to be done.

LAST year's gust of excitement at the recognition of five-fold symmetry in a binary alloy (of Al and Mn) by Shechtman, Blech, Gratias and Cahn (*Phys. Rev. Lett.* **53**, 1951; 1984) has already spawned its own mini-industry. The surprise, then, was that there should be evidence of any kind for five-fold symmetry when this is strictly forbidden, on geometrical grounds, in a crystal with regular translational periodicity (see *Nature* **313**, 263; 1985).

By the end of the year, D. Levine and P.J. Steinhardt had produced an outline explanation of how such a structure could exist (*Phys. Rev. Lett.* **53**, 2477; 1984). They showed how to construct "quasi-crystalline" structures in two or three dimensions which, although devoid of translational symmetry, could have local five-fold symmetry. Now attention has turned to the question whether such structures will be energetically preferred to regular crystals. But the clutch of three papers published (in *Phys. Rev. Lett*, 8 April 1985), all of which follow the same track, show such discordancies as to suggest that the issue is far from settled.

The starting point is the Landau theory of the evolution of symmetry by means of phase transitions from, say, a liquid in the process of solidification, or one solid phase in the process of transition to another. The trick, following Landau, is to suppose that the free energy is a function of parameters which describe the degree of geometrical order in the system. The first task is to determine what order parameters are allowed by geometry.

Everybody agrees that the order parameters to use are quantities D_k which are the coefficients of mass-density waves within the aggregated system, and which turn up in mathematical expressions of the form $D_k\exp(i\mathbf{Q}_k.\mathbf{R})$, where $\mathbf{Q}_k$ is some fixed vector and $\mathbf{R}$ is the vector representing position. (The symbol i is the square root of -1.) This, of course, is a periodic function of a kind that might describe plane waves travelling in direction $\mathbf{Q}_k$.

A single order parameter, associated with a single vector $\mathbf{Q}$, suffices to describe the smectic phase of a liquid crystal (in which molecules assume a periodic arrangement in only one dimension within the medium in which they are dissolved). The ordering of regular crystals, on the other hand, requires at least three order parameters, each of them associated with a different vector $\mathbf{Q}_k$. These must jointly describe how it is possible to choose an infinite number of directions within the crystal in which identically constituted layers of atoms are periodically repeated (and which are defined, in crystallography, by the Miller indices *hkl*). The basic vectors describing these recurring planes of atoms are not those defining the translational symmetry of the crystal, represented by the repeated translation of the unit cell, but rather the vectors of what is called the reciprocal lattice. All this is standard textbook stuff.

The neatness of the Landau treatment stems from its representation of the free energy as a power series expansion in terms of the mass-density distribution, itself the sum of terms such as $D_k\exp(i\mathbf{Q}_k.\mathbf{R})$ taken over all possible vectors $\mathbf{Q}_k$ in the reciprocal lattice. The separate terms are themselves harmonics of similar expressions involving only the basis vectors of the reciprocal lattice.

Structures with the symmetry of a body-centred cubic lattice are thus signalled by terms which are products of six *D*-coefficients, each corresponding to one of the six independent vectors of the tetrahedron which is the unit structure of the reciprocal lattice. Face-centred cubic symmetry is similarly signalled by terms of the eighth power, where the corresponding vectors are those of the unit octahedra of the reciprocal lattice. Telling whether a melt will crystallize in one form rather than the other may then simply be a matter of guessing whether one form of symmetry will give a smaller free energy than the other, which in practice entails much arm-waving.

The novelty now reported is that the same argument can be used to judge the likelihood that symmetries not allowed in ordinary crystallography will occur. Per Bak from the Brookhaven National Laboratory puts the case most simply by enumerating the terms in a Landau expansion corresponding to five-fold symmetry (*Phys. Rev. Lett.* **54**, 1517; 1985). The simplest case is that of fifth-power terms (products of five *D*-coefficients) corresponding to the five vectors represented by the sides of an equilateral planar pentagon, but this corresponds in three dimensions merely to a structure built of parallel rods whose cross-sections are the elements of the Penrose tiling of the plane.

Bak gets true five-fold symmetry by picking out the Landau terms corresponding to the null combinations of the fifteen pairs of vectors along the edges of a regular icosahedron. These show up as ten third-degree terms and six fifth-degree terms, corresponding to the ten triangles and five pentagons that can be drawn on the surface of an icosahedron. Bak readily concludes that a structure with five-fold symmetry can be stable relative to body-centred cubic structures if only the parameters are suitably adjusted.

Levine and Steinhardt (see above), together with a number of colleagues at the University of Pennsylvania and John Toner from the IBM research centre, follow a similar tack but calculate the elastic constants of a solid with five-fold symmetry to demonstrate its stability (*Phys. Rev. Lett.* **54**, 1520; 1985). As in the simple Landau treatment, symmetry restricts the range of terms occurring in the equations, but this line of argument has the virtues of showing how dislocations may be introduced into structures with five-fold symmetry (by means of pretty pictures made by driving a dot-matrix printer by the expressions calculated for the mass-density distribution) and of making explicit the hidden symmetry of these perplexing five-fold structures, which emerge as the representation in three dimensions of much simpler structures in six dimensions.

So far, there is very little physics in these discussions, but M.D. Mermin and Sandra M. Troian from Cornell University have a novel twist (*Phys. Rev. Lett.* **54**, 1524; 1985). They say that they find only metastable states for a solid with one component and with five-fold symmetry (but they appear not to have included fifth-degree terms, corresponding to the six pentagons on the surface of an icosahedron, in their Landau calculation). But how relevant is it that the only real solid in which five-fold symmetry has been found so far is an alloy, with two components?

In an alloy, there is scope for a dimension of disorder beyond those specified by the wave vectors of the simple Landau calculation. On this view, the argument goes, there is scope for generating five-fold symmetry from a blend of geometrical shape and occupancy by one or other of two components. So far as it goes, the argument is suggestive only, although the most telling evidence is a pair of dot-matrix diagrams, said to represent a cross-section from a structure with five-fold symmetry, in which one component almost exactly fills the gaps in the distribution of the other. Time, and some tangible experimental investigation, will no doubt tell whether this is what five-fold symmetry is like.

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