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Perfect quasicrystals?

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Quasicrystals are crystalline solids exhibiting icosahedral symmetry. Their discovery in Al–Mn alloys in 1984 caused great surprise, because the classical laws of crystallography forbid icosahedral symmetry in periodic crystals. This discovery required there to be a new kind of crystalline order, quasiperiodicity, which had rarely been considered before except by mathematicians. There was speculation that quasicrystals would qualify as a new phase of matter, with unique properties unknown to other crystalline solids, such as fractal electronic behaviour. Unfortunately, the properties of the dozens of real icosahedral alloys discovered subsequently were dominated by disorder and no novel phenomena were uncovered. Thus, excitement has been generated by the recent report by C. A. Guryan *et al.* (*Phys. Rev. Lett.* **62**, 2409–2412; 1989) who show that the icosahedral alloy, $Al_{65}Cu_{20}Ru_{15}$, is much less disordered, by the usual crystallographic criterion of the sharpness of X-ray diffraction lines, than any previous quasicrystal. Indeed, a recent study by P. A. Bancel at IBM, Yorktown Heights, shows that after annealing, the diffraction lines of the sister compound $Al_{65}Cu_{20}Fe_{15}$ are sharper than instrumental resolution — as good as the best conventional crystals. In short, these materials seem to be perfect quasicrystals, rekindling the search for unusual physical properties.

These developments give greater significance to important work on the mathematics of tilings done by Roger Penrose and others beginning in the 1970s. Penrose discovered a nonperiodic tiling of the plane, using two types of tiles, which, to use our present language, is a quasiperiodic crystal with pentagonal symmetry. He also found matching rules — local rules for how the two types of tiles may join — which force the quasiperiodicity; that is, the rules forbid both disordered tilings and ordered, periodic tilings. Later work by G. Y. Onoda and co-workers at IBM showed how the matching rules could be extended to a specific algorithm for growing the tiling from a seed. The resulting structure, the Penrose tiling, is unique and perfectly ordered in a mathematical sense.

Soon after the discovery of the quasicrystal alloys, three-dimensional generalizations of the Penrose tiling and the matching rules were found for icosahedral tilings. It became natural to assume that the alloys had atomic arrangements that correspond to the tile shapes in the three-dimensional Penrose tiling, and this was confirmed in studies of various alloy systems. Thus, there is general agreement that the new Al–Cu–Fe and Al–Cu–Ru alloys are actual physical realizations of these mathematical constructions — they are icosahedral tilings with long-range quasiperiodic order. Other models, like Pauling's 'multiple twin' ideas, have been virtually ruled out.

Recent theoretical work, however, shows that there are other variants of the Penrose tiling model that are consistent with the data of Guryan *et al.*. In the original ideal Penrose tiling model, the dominant contribution to the free energy $F = U - TS$ would come from the energy U (T is temperature). It is hypothesized that the local atomic interactions enforce Penrose's matching rules, favouring the quasiperiodic ground state. Calculations by M. Widom *et al.* (*Phys. Rev. Lett.* **63**, 310–313; 1989) and K. Strandburg *et al.* (*Phys. Rev. Lett.* **63**, 314–317; 1989) show that the Penrose tiling can also be stabilized by the entropy S. If Penrose's matching rules are relaxed, the entropy is large because more varied packings of tiles are permitted. This has become known as the random-tiling model, although the randomness is very constrained by the requirements of icosahedral packing; the resulting state still has long-range icosahedral quasiperiodic order, despite the short-range disorder.

There is really no sharp distinction between the ideal Penrose tiling and this random tiling. They represent two extremes of a continuous range of possibilities in which the quasicrystal is stabilized by a mixture of energy and entropy. Both models are based on the Penrose tiling, and both predict perfect long-range order as seen in the new alloys. However, it is important to determine which model most accurately describes $Al_{65}Cu_{20}Ru_{15}$ and $Al_{65}Cu_{20}Fe_{15}$, because it is only in the ideal-tiling limit that we would expect to find some of the truly unique features of the quasiperiodic state, like fractal properties in the electronic behaviour as described in the model of M. Kohmoto *et al.* (*Phys. Rev.* **B35**, 1020–1033; 1987).

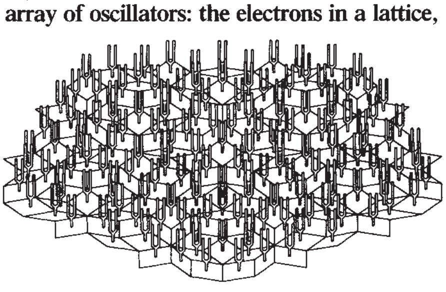
Further experiments are now being done that will help determine the version of the Penrose tiling that actually applies to the real materials. None of the results so far is conclusive, although some recent reports tend to support the random-tiling ideas. The electical resistivity, as measured recently by A. P. Tsai *et al.* (*J. mat. Sci. Lett.* **8**, 253–256; 1989) and J. L. Wagner *et al.* (*Phys. Rev.* **B39**, 8091–8095; 1989) is fairly high, indicating a large degree of local disorder in these compounds. Also, recent X-ray diffraction studies by Bancel of Al–Cu–Fe at high temperatures indicate that the icosahedral phase is actually better ordered at elevated temperatures, which is consistent with entropy playing the dominant role in stability.

So it seems that researchers will have to seek further to find the truly perfect Penrose tiling, because even the new

In tune with quasiperiodicity

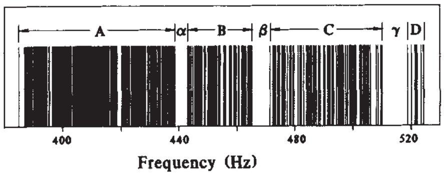
As noted by DiVincenzo, quasiperiodicity can be expected to generate features entirely alien to normal periodic lattices. In an off-beat contribution to quasicrystal research, Shanjin He and J. D. Maynard have used 150 tuning forks arranged in a two-dimensional Penrose tiling to simulate the spectrum of electronic states in a quasicrystal (*Phys. Rev. Lett.* 62, 1888–1891; 1989).

The tines of the tuning forks are joined to their nearest neighbours by arcs of steel wire. The connection with a real quasicrystal is that the forks make a coupled array of oscillators: the electrons in a lattice,



equally, comprise a coupled set of oscillators. By 'humming' at this pentagonal aeolian harp and listening — with an electric-guitar pickup — the authors effectively find the spectrum of frequencies at which the entire ensemble vibrates — which is equivalent to revealing the eigenvalue spectrum of the electronic structure.

The striking outcome is that the resonant frequencies form a set of bands — marked



A, B, C and D in the spectrum — much as one finds for the states in a crystalline solid. But the gaps between the bands (α, β, γ) are in the ratio of the golden mean ($(\sqrt{5} + 1)/2$ — the ratio of the areas of the two rhombi in the tiling pattern — and the bandwidths themselves are in the ratio of powers of this number. The observation of such ratios in a real quasicrystal might be indicative of perfect quasiperiodicity.

The patterns traced by the tines of the tuning forks, revealed by tiny mirrors fixed to their points, typically bear the 5-fold symmetry of the Penrose tiling. The wave-functions of the electrons in the quasiperiodic potential of a quasicrystal could be expected to have this characteristic too. □