Quasicrystals

Amorphous, crystalline or both?

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THE structure of icosahedral quasicrystals[1], discussed in a News and Views article[2] last month, remains a mystery and a source of controversy. Two leading models, the quasiperiodic-crystal model of Levine and Steinhardt[3] and the icosahedral-glass model of Stephens and Goldman[4], both disagree with details of the experimental findings. At a recent meeting*, proposals were made for modifying each model to obtain agreement with details of the X-ray diffraction pattern. Various experimental and theoretical results suggest that the truth combines elements of both models. Quasicrystals may be a unifying link between crystalline and amorphous metals.

Quasicrystals, discovered by D. Shechtman (Israel Institute of Technology), are metallic alloys whose electron-diffraction patterns combine sharp, crystallographic peaks with non-crystallographic, icosahedral symmetry. Efforts to explain the structures by twinning[5] fail to account for the observed golden-mean ratios between peak positions (A. R. Kortan, AT&T Bell Labs) and need double diffraction to explain the peaks observed in X-ray diffraction patterns (P.A. Bancel, University of Pennsylvania). The quasiperiodic-crystal and icosahedral-glass models overcome these flaws.

The quasiperiodic-crystal model[3] uses a three-dimensional generalization of the Penrose pattern to produce a structure that combines long-range, icosahedral bond-orientational order with translational quasiperiodicity. The icosahedral-glass model[4], in contrast, packs oriented icosahedra joined at random on their faces. The peak positions for both models are in excellent agreement with X-ray diffraction experiments. The peak intensities agree qualitatively with experiments in that the intensities fall off at large values of the perpendicular momentum. (Perpendicular momentum measures mismatch between the quasiperiodicity of the quasicrystal and the periodicity of the X-rays.) Both models fail to explain properly the observed widths of the X-ray diffraction peaks, which are slightly broadened, their width proportional to the perpendicular momentum (P.M. Horn, IBM, Yorktown Heights). The icosahedral-glass model produces broadened peaks, but the widths are proportional to a higher power of the perpendicular momentum (A.I. Goldman, Brookhaven National Lab). Thus, the two models straddle the true behaviour of the peak widths.

The quasiperiodic-crystal can be modified by the inclusion of 'phasons', which are like phonons but carry perpendicular momentum instead of ordinary momentum. These excitations correspond to rearrangements of atoms that destroy the quasiperiodicity but do not otherwise distort the structure. The inclusion of random, phason excitations leads to the correct behaviour of the peak widths[6,7] and also predicts unusual peak shapes (J.E.S. Socolar and D.C. Wright, University of Pennsylvania; D.R. Nelson and M.V. Jaric, Harvard University) which can be observed experimentally (J.D. Budal, Oak Ridge Labs; D.M. Follstaedt and J.A. Knapp, Sandia Labs). Modifying the icosahedral-glass model is harder. The original model puts new icosahedra indiscriminately on any face of the growing cluster where they can fit. Invariably, these clusters contain many cracks that cannot be filled with atoms in their optimal environments. More careful growth modelling that reduces the number of cracks, and the introduction of higher-order positional correlations, are unable to reproduce the observed linear dependence of peak width on perpendicular momentum.

Intrinsic disorder provides circumstantial evidence favouring models such as the icosahedral glass. The peak widths were first oberved in splat-cooled AlMn in which the grain size is typically a micrometre[8]. Recently, quasicrystals of AlLiCu have been produced with slower cooling rates achieving grain sizes of centimetres and showing beautiful faceting. Curiously, the peak widths in the supposedly high-quality AlLiCu quasicrystals were comparable to those in the splat-cooled AlMn quasicrystals. Horn suggested this shows a source of intrinsic disorder in quasicrystals on a scale of hundreds of angstroms.

S.C. Moss (University of Houston) warned against drawing strong conclusions based on the assumption that the AlLiCu samples are the most ordered possible quasicrystal. The actual rate of quasicrystal growth in slowly cooled AlLiCu is comparable to that in the splat-cooled AlMn because the grains of AlLiCu are so large. Thus it is not surprising that both have similar degrees of disorder. The beautiful facets on the AlLiCu quasicrystals may also be misleading. J. Toner (IBM, Yorktown Heights) said that even highly defected crystals may have facets which appear macroscopically flat. The issue will not be decided experimentally until defects are removed from the AlLiCu samples. In fact, ion-channelling experiments in carefully grown quasicrystals (M.A. Marcus, AT&T Bell Labs) indicate translational order on a scale of micrometres.

There are already theoretical models that bridge the gap between the perfect, quasiperiodic crystal and the icosahedral glass. K.J. Strandburg and I presented Monte Carlo simulations of a binary mixture of Lennard–Jones atoms in two dimensions. The mixture spontaneously forms a quasicrystalline equilibrium state at low temperatures[9]. Thermodynamic stability depends on the configurational entropy produced by randomly rearranging the tiles of the Penrose pattern. The structure is thus equivalent to the perfect, quasiperiodic crystal, modified by the inclusion of phasons. C.L. Henley (Cornell University) described models of three-dimensional quasicrystals that also allow local deviations from perfect quasiperiodicity. In these models the diffraction spots are delta functions (Henley) with power-law, diffuse background (Nelson, Jaric).

An exciting view of quasicrystals emerged from many of the experimental talks. This places quasicrystals between crystals and amorphous metals, sharing features of both. Quasicrystals possess sharp diffraction peaks, and there is also strong evidence for crystalline short range order. X-ray absorption fine structure studies of AlLiCu quasicrystals (Y. Ma and E.A. Stern, University of Washington) find that the chemical environment of the copper atoms are virtually identical to those of a crystalline phase of similar composition. Comparison of the Patterson functions of crystalline and quasicrystalline phases of AlMnSi inspired J.W. Cahn (NBS) to remark that the local environments are extraordinarily similar. Glassy behaviour in quasicrystals was found by observing tunnelling systems (N.O. Birge, AT&T Bell Labs). Finally, Moss demonstrated structural similarities between icosahedral quasicrystals and amorphous metals. He compared the size-broadened, quasicrystalline AlMn structure function with the glassy phase of the same composition and remarked "It is as if glasses are microquasicrystalline". ☐

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