

Evidence from electron micrographs that icosahedral quasicrystals are icosahedral twins of cubic crystals

(Al₅Mn/cubic morphology)

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ABSTRACT An analysis of electron micrographs of Al₅Mn quasicrystals obtained by rapidly cooling a molten alloy with composition Al₁₇Mn and removing the Al matrix by electro-solution, revealing aggregates of 20 microcrystals at the corners of a pentagonal dodecahedron, supports the proposal that these microcrystals are cubic crystals twinned about an icosahedral seed, with each cubic microcrystal sharing a threefold axis and three symmetry planes with the seed.

The question of the nature of the so-called icosahedral quasicrystals has attracted great attention since their discovery 6 years ago (1). Several somewhat different structures involving violation of the usually accepted principles of crystallography have been proposed (a survey is given in ref. 2). A few investigators, however, have contended that these substances are icosahedral twins of cubic crystals (3). I now point out that some recently obtained electron micrographs provide additional strong support of the twinning proposal.

In a recent analysis of a twofold-axis electron-diffraction photograph of the quasicrystal with composition approximately Al₅Mn, it was pointed out that four sets of parallel layer lines can be recognized on the pattern of diffraction maxima (3). Two of these sets of layer lines are at angles with the planes of symmetry corresponding to diffraction by large atomic clusters with approximate icosahedral symmetry. The other two sets correspond to a face-centered cubic unit of structure with cube edge 66.306 Å. Diffraction maxima occur at intersections of the icosahedral and cubic sets, indicating that the cubic crystals that by icosahedral twinning constitute the quasicrystal are composed of very large approximately icosahedral atomic complexes in a face-centered arrangement. There are ≈19,400 atoms in the cube, ≈4850 per lattice point (cubic close packing). It was suggested that each large icosahedral complex consists of 45 104-atom clusters; each 104-atom cluster involves a triple-shell icosahedral arrangement of atoms, and the 45 clusters are in a double-shell icosahedral arrangement. The structure factors of the very large doubly icosahedral complexes account for the icosahedral sets of layer lines, and those for the cubic lattice account for the other set.

A similar discussion was also presented for the quasicrystal Al₁₃Cu₄Fe₃, for which the twofold-axis electron-diffraction photographs also show four sets of parallel layer lines—two diagonal sets corresponding to large icosahedral complexes containing ≈4680 atoms and vertical and horizontal sets corresponding to a body-centered unit with edge 52.00 Å containing ≈9960 atoms. A third structure was suggested for Al₁₃CuLi₃ (3). A discussion of the formation of the large icosahedral structures in the molten alloys and the ways in which they can be packed together when the molten alloy is

chilled has also been published, together with a proposed structure for the decagonal quasicrystal Al₆Pd and a summary of the evidence supporting the twinning hypothesis (4). One kind of evidence is that the values of angles between lines of atoms on high-resolution transmission electron micrographs of icosahedral Al₅Mn taken with the incident beam parallel to the fivefold axis of the specimen are much closer to the values expected for cubic crystals than to those for icosahedral packing (5).

The new evidence was reported in a series of papers by Csanády and her collaborators (6–9). They prepared samples by very rapid chilling on a rotating copper drum of molten alloys with composition either Al₆Mn or Al₁₇Mn. In each case Al₅Mn icosahedral quasicrystals were obtained, embedded for the first composition in a small amount and for the second composition in a large amount of the matrix Al (6). They carried out partial electro-solution of the quasicrystals with a solvent (2% KI in methanol) that dissolved the Al matrix or another solvent (10% HCl in aqueous solution) that dissolved the quasicrystals, leaving cavities with the shape of the quasicrystals in the matrix.

The molten alloys with different compositions produce quasicrystals with different morphologies. The Al₆Mn alloy produces dendrites composed of quasicrystals ≈500 nm in diameter with the shape of pentagonal dodecahedra with planar pentagonal faces (8). On the other hand, the Al₁₇Mn alloy produces aggregates of crystallites, usually 1000–2000 nm in overall diameter, usually consisting of 20 individual crystallites arranged at the corners of a pentagonal dodecahedron, and in parallel orientation (6–9). There seems to be a central crystallite or icosahedral complex that acts as a seed for the 20 that surround it and that orients them in definite orientations.

The Rate of Formation of Seeds and Its Relation to the Morphology of the Quasicrystals

The difference in morphology of the two alloys can be understood by consideration of the rate of formation of the seeds that initiate the crystallization. Let us assume that the seed has the same composition as the crystallites, Al₅Mn. To form a seed in the Al₁₇Mn alloy requires the considerable time during which the Mn atoms in a volume >3 times that of the seed diffuse into the volume of the seed. We see that the rate of formation of the seed and the rate of growth of the crystallites are of a rather high order of the Mn concentration in the alloy and are without doubt far larger for Al₆Mn than for Al₁₇Mn.

In the electron micrograph of figure 1a of ref. 8 it is shown that the dendrites have branches consisting of 10–20 crystallites in directions consistent with icosahedral symmetry and that dendritic clusters with different orientations are roughly 20 μm apart. Each cluster originates from a single seed, the formation of which is the rate-determining step in

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the formation of the cluster, with the rate some hundreds of times slower than the growth rate of the dendrites. The individual crystallites in a dendrite are in parallel orientation (figure 1b of ref. 8), as is found in general for dendritic crystals.

The Structure of the Twins of 20 Cubic Microcrystals About a Central Seed Obtained by Rapid Cooling of the $Al_{17}Mn$ Molten Alloy

An example of the aggregate of 20 microcrystals shown in the electron micrograph of the quasicrystal preparation from the $Al_{17}Mn$ melt after removal of the Al matrix by electrosolution is shown in Fig. 1 (figure 2e of ref. 9). These aggregates are from 1 to 4 μm apart and are sometimes separated by a thin layer of undissolved matrix, presumably by Al containing enough Mn to resist solution by the solvent (figure 7 of ref. 6).

(It is found by application of the laws of diffusion to the problem that for a system of sinks in a three-dimensional array in a medium with a solute at 0 time uniformly distributed there are formed at a later time points, lines, and layers between the sinks at which the solute concentration is a maximum or has a saddle point.)

The observed morphology of the crystallites supports the interpretation of the quasicrystals as icosahedral twins of cubic crystals, each with a threefold axis and three planes of

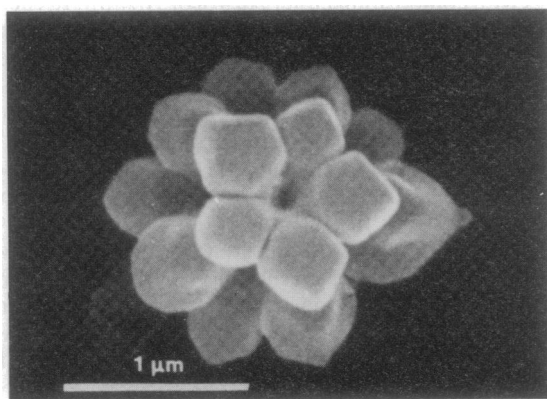


FIG. 1. Scanning electron micrograph of a cluster of 20 $Al_{17}Mn$ cubic microcrystals showing twinning about an icosahedral seed. The cubic morphology of the microcrystals can be seen (figure 2e of ref. 9). (Reproduced with permission of Á. Csanády.) [Reprinted by permission of VCH Publishers, Inc., 220 East 23rd St., New York, NY 10010, from: The Journal *Symmetry*, Volume 1, page 75 (1990); one figure.]

symmetry in common with the icosahedral seed. The crystallites in Fig. 1 can be seen to have approximately cubic face development, somewhat distorted in the inner regions and with rounded edges. The outer angles of the top faces are measured to be $\approx 90^\circ$, as expected for cubes. Moreover, the faces of sets of five crystallites are seen not to be coplanar, but to be tipped. The angle of tip between the direction [100] and the fivefold axis of the five microcrystals is measured to be $22^\circ \pm 2^\circ$, in close agreement with the value 22.34° calculated for this sort of twinning.

Another test of the twinning structure of the quasicrystals might be carried out. If a single crystallite of an aggregate of 20 were to be isolated and subjected to study by electron diffraction, it is predicted that the horizontal and vertical layer lines characteristic of the cubic structure would be found on the twofold-axis photographs with the electron beam parallel to any one of the six twofold axes of the cubic unit but not on those with the beam along any one of the 9 other twofold axes of the similarly oriented icosahedron.

Discussion

The foregoing discussion of the morphology of the 20 crystallites in a quasicrystal aggregate isolated by solution of the matrix of excess Al provides some additional evidence that the $Al_{17}Mn$ quasicrystal consists of icosahedral twins of cubic crystals, each of which has a threefold axis and three symmetry planes in common with an icosahedral seed.

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