Quasicrystal with One-Dimensional Translational Symmetry and a Tenfold Rotation Axis

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Studies of phase formation in rapidly solidified Al-Mn alloys (composition range 18–22 at.% Mn) show that an icosahedral phase is replaced by another noncrystallographic phase, a decagonal phase. The decagonal phase is another example of quasicrystal: It has a noncrystallographic point group ($10/m$ or $10/mmm$) together with long-range orientational order and one-dimensional translational symmetry. The decagonal phase is an intermediate phase between an icosahedral phase and a crystal both from the symmetry and from the solidification condition points of view.

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An icosahedral phase with long-range orientational order and noncrystallographic point-group symmetry $m\overline{3}\overline{5}$ (icosahedral) was recently discovered by Shechtman *et al.*[1] The phase forms in rapidly solidified Al-Mn alloys in the composition range 10–20 at.% Mn, but also has been observed in some other aluminium-transition-metal systems (Fe, Cr, and Rh). The incompatibility of icosahedral symmetry and long-range order was explained by the construction of an ordered aperiodic structure (three-dimensional Penrose tilting).[2] A complementary approach has been used as a method involving direct projection of a six-dimensional periodic grid into a three-dimensional hyperplane.[3] It was suggested that those new types of quasiperiodic structures be termed "quasicrystals."[2]

Studies of phase formation at higher compositions of Mn, or at slower solidification rates than melt spinning have shown that the icosahedral phase is replaced by the so-called T phase. The phase was first observed by Schaefer *et al.*[4] and Bendersky *et al.*[5]; however, no crystallographic study was published. In this work I report that the T phase is another example of quasicrystal: It has a noncrystallographic point group ($10/m$ or $10/mmm$) together with long-range orientational order and one-dimensional translational symmetry, therefore belonging to the cylindrical family of groups G_1^3.[6] I will refer to this phase as the decagonal phase. The growth morphology of the phase from the alloy melt is cylindrical with the tenfold rotation axis along the cylinder axis. The cylinder axis is also the direction of one-dimensional translational symmetry. Cross sections of the cylinders show ten faceted planes con-

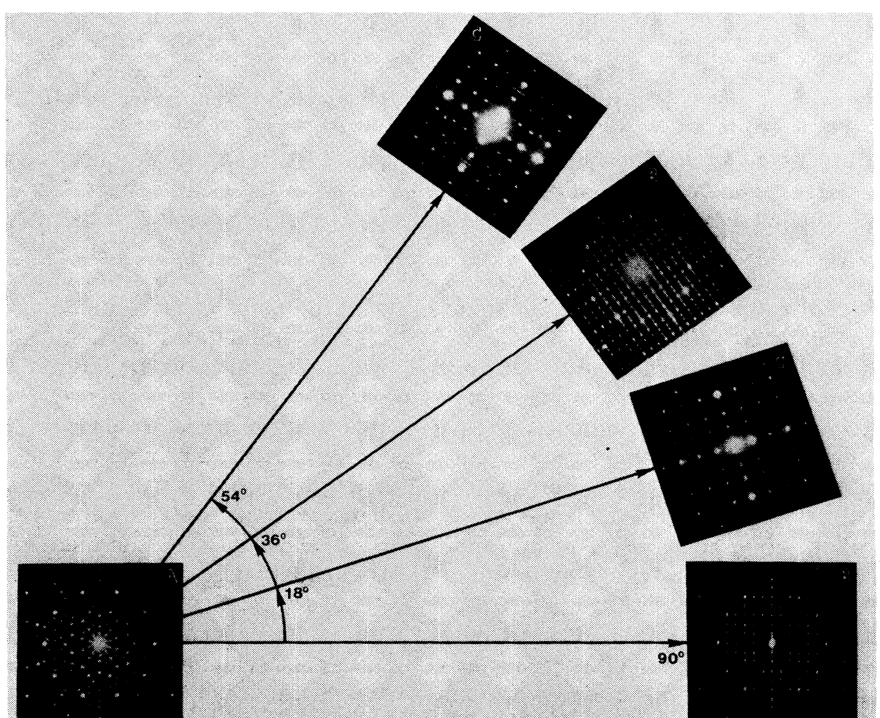

FIG. 1. Selected-area electron diffraction patterns taken from a single grain of the decagonal phase.

sistent with the $10/m$ point-group form. Because the diameter of these cylindrical quasicrystals is approximately 1 μm, the study of this phase is best performed by means of transmission electron microscopy.

Figure 1 shows a series of selected-area electron diffraction patterns (SADP's) from the decagonal phase, obtained by tilting. There are one tenfold (A) and ten equivalent twofold (B) diffraction patterns, where the angle between A and B zone axes is 90° and the angle between adjacent B zone axes is 36°. Another type of twofold diffraction pattern (C) has a zone axis 18° away from the B zone axis *b*, with a 36° angle between adjacent C axes. Figures 2(a) and 2(b) show convergent-beam diffraction patterns (CBDP's) from the decagonal phase and the icosahedral phase at the tenfold zone-axis orientations. The advantage of CBDP's compared to conventional (parallel electron beam) SADP's is the presence of higher-order Laue-zone (HOLZ) lines which result from significant electron scattering into diffraction maxima in the HOLZ's due to the beam convergency.[7,8] Therefore, three-dimensional crystallographic information from the crystal axis parallel to the incident beam is available. The whole-pattern symmetries are 10 (or $10mm$) and $\bar{5}m$, respectively, and are consistent with the results of Fig. 1 for the decagonal phase and with the point group $m\bar{3}\bar{5}$ for the icosahedral phase. Another difference between the CBDP's is the presence of HOLZ rings for the decagonal phase. The diameter of the HOLZ rings in Fig. 2(a) suggests the existence of a 1.24-nm^{-1} periodicity of the reciprocal lattice along the tenfold zone axis. The same periodicity can be measured in the SADP's B and C (Fig. 1). An analysis of CBDP's obtained at orientations C and B indicates that the whole-pattern symmetry is *m* for both, where the mirror plane is perpendicular to the tenfold axis. Furthermore, consideration of the different cylindrical point groups with rotational symmetry five or ten shows that the only point group which satisfies the observed experimental results is $10/m$. However, the presence of a high density of planar defects, collinear with the tenfold symmetry axis (see later discussion), could possibly destroy a mirror plane parallel to this axis on CBDP's at B and C. Because of this possibility the point group $10/mmm$ may not be ruled out.

The point group obtained plus the translational symmetry suggest that the decagonal phase is crystalline with a one-dimensional periodicity and planar quasiperiodicity in the other two dimensions. Apparent decagonal planar quasiperiodicity could occur by multiple twinning of a conventional crystal. To test this, experiments of the same kind used by Ref. 1 were performed with an electron microscope: (1) Microdiffractions (with beam size ~ 20 nm) taken across a grain from point to point show the same tenfold diffraction that appears in the selected-area diffraction pattern.

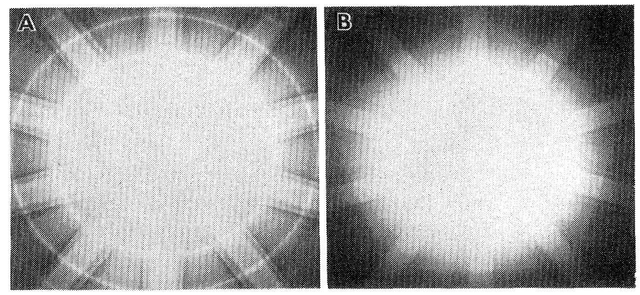

FIG. 2. Convergent-beam electron diffraction patterns from the (a) decagonal and the (b) icosahedral phases. Whole-pattern symmetries are 10 (or $10mm$) and $\bar{5}m$, respectively.

This suggests that the entire grain has long-range orientational order. (2) A set of dark-field images reveals no twins or microscrystallinity. (3) High-resolution (structural) images show no evidence of twinning on the scale of nanometers, and full restoration of the tenfold diffraction pattern after optical Fourier transformation was obtained.[9] On the basis of these experiments we conclude that the decagonal phase does not consist of multiple-twinned crystal structure.

Diffraction patterns from the decagonal phase (except the tenfold SADP) show the presence of streaking (see Fig. 1, SADP's B and C). However, tilting experiments demonstrate the existence of sheets of intensity in reciprocal space, normal to the unique tenfold axis with a spacing between sheets corresponding to $1/1.24\ (\mathrm{nm})^1$. The tenfold SADP shows very intense background, indicating that the zero-order Laue-zone reflections and the sheet of intensity are in the same plane for this orientation. The presence of planar intensity in reciprocal space can be due to the presence of one-dimensional objects in real space, aligned normal to the planes. Two possibilities can be considered:

(1) The first is the presence of cylindrical domains with domain walls containing the tenfold axis. For crystal orientations with a large angle between the beam direction and the tenfold axis, the domain boundaries should image as long planar defects, and indeed, this was observed frequently. The domain structure could be caused by chemical ordering, as suggested by the presence of extra reflections or diffuse intensity between basic spots in some of the diffraction patterns.

(2) Alternatively, the one-dimensional crystal of the decagonal phase can be considered as linear chains, ordered perpendicular to the chains according to Penrose tilting,[10] or also as another type of planar quasiperiodicity preserving tenfold symmetry.[2,3] Modulation of the chains in an uncorrelated way can give rise to the planar diffuse scattering.[11]

The decagonal phase forms by liquid freezing. The formation is a first-order transition involving nucleation and growth. At low Mn concentration (17 at.% Mn) the phase nucleates frequently on surfaces of growing dendrites of the icosahedral phase,[2,3] where at higher Mn concentrations ($-$ 22 at.% Mn) it nucleates directly from the melt. The microstructure of melt-spun Al–22.4-at.%-Mn alloy is a single-phase multigrain structure, where the phase is decagonal. At compositions between 18 to 22 at.% Mn dendritic growth of the phase is observed where the primary growth direction is the tenfold symmetry axis, along which the structural periodicity is developed. This one-dimensional periodicity is believed to develop at slower solidification velocities than those required for the icosahedral phase. Thus, this decagonal phase appears to be intermediate between the icosahedral and the crystal phases both from the symmetry and from the solidification condition points of view.

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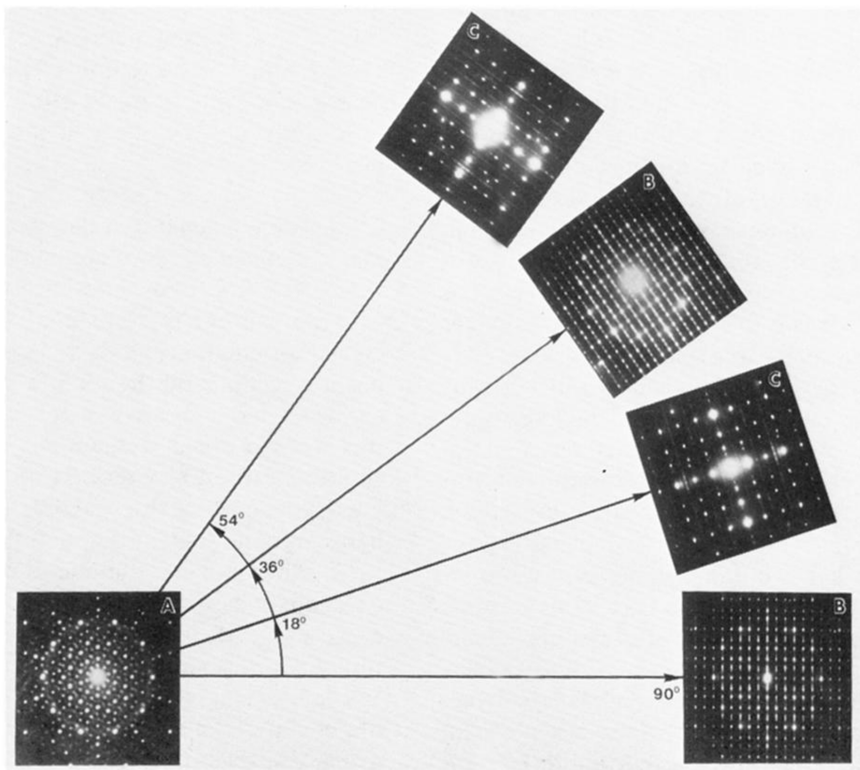

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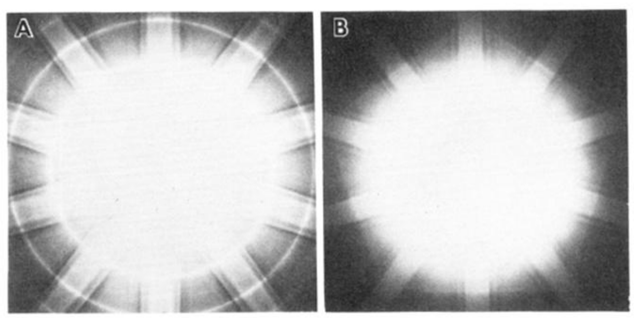

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