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Formation of icosahedral Al-Mn by ion implantation into oriented crystalline films

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The icosahedral quasicrystal phase has been produced by precipitation from the solid phase during ion implantation of Mn into oriented films of fcc Al on NaCl. Implantations at substrate temperatures of 20 °C, 150 °C, and 275 °C resulted in amorphous, icosahedral, and crystalline phases, respectively. Microdiffraction patterns were obtained from individual icosahedral grains which had precipitated within the bulk of the Al grains. They are oriented with three mutually perpendicular twofold axes of the icosahedral structure parallel to the [001], [110], and [1$\bar{1}$0] directions of the fcc Al matrix.

In experiments on rapidly quenched Al-Mn alloys, Shechtman, Blech, Gratias, and Cahn[1] have reported electron diffraction patterns exhibiting both icosahedral point symmetry and sharp Bragg peaks. Since these two properties were commonly considered inconsistent, the observations have generated a large number of theoretical and experimental investigations into the nature of the atomic ordering in this new structure. In one promising theoretical approach, several authors[2–4] have shown that icosahedral ordering can be described as the three-dimensional (3D) quasicrystal generalization of the 2D Penrose tiling. By packing 3D space with two different polyhedra in a nonperiodic way, they find that the locations of the vertices preserve true long-range bond-orientational order with tenfold symmetry. Moreover, the Fourier transform of their structure appears quite similar to the electron diffraction patterns observed in Al-Mn alloys. This 3D description of a structure which lacks translational order but preserves bond-orientational order differs from the hexatic phase[5] analog in 2D in that it can be generated from a crystal by introducing defects only as a spatially ordered array. Alternative theoretical models which use the Landau theory to describe icosahedral ordering in terms of mass-density waves have also been presented.[6–8]

Experimental studies of Al-Mn quasicrystals thus far have produced electron diffraction patterns[1] and high-resolution electron microscopy images[9] indicating the icosahedral point symmetry, and have presented high-resolution powder x-ray diffraction profiles yielding more quantitative diffraction information.[10] In addition, the materials exhibiting metastable quasicrystalline order have thus far been produced by means of rapidly quenching a molten alloy on a cool rotating wheel, and very recently, by noble-gas ion-beam mixing.[11,12] In spite of the numerous studies undertaken, however, investigations have not yet established the atomic locations in a quasicrystal structure.

In this paper, we report the observation of solid-phase precipitation of quasicrystals during implantation of Mn into a crystalline Al matrix. The resulting precipitates are highly oriented with respect to the fcc matrix. We establish a unique orientation relationship between the symmetry axes of the icosahedral phase and the crystallographic directions of the Al matrix. This relationship provides important clues for the atomic structure of the icosahedral phase and leads to speculation concerning the coherence of the quasicrystal and crystal structures.

Thin-film samples were prepared by vacuum deposition of approximately 1000-Å Al films onto cleaved (100) NaCl substrates at room temperature. The Al films were then implanted with $^{55}Mn^{+}$ ions at two energies (35 and 75 keV) in order to produce roughly uniform Mn concentrations typically in the range of 13–24% near the center of the films. Implantation at these energies placed minimal amounts of Mn near the film surfaces, thus making subsequent kinetic processes characteristic of those in the bulk. The doses, dose rates, and substrate temperatures during implantation are listed in Table I. After implantation the films were removed from the substrates by placing the samples in distilled water.

A transmission-electron-microscopy (Philips 400) examination of the Al films before implantation showed that they consist of small (typically less than ~2000 Å) grains oriented with a ⟨111⟩ axis normal to the film. The grains were randomly oriented about the film normal. Figure 1 shows typical selected area diffraction patterns for samples labeled *B* (implantation temperature 20 °C), *C* (150 °C), and

TABLE I. Parameters for implantation of Mn into Al film samples.

Sample	Temperature (°C)	Energy (keV)	Dose (10^{16} cm^{-2})	Current density (μA/cm^2)
A	20	35, 75	2.9, 2.9	2.1, 3.4
B	20	35, 75	2.7, 4.0	2.1, 3.4
C	150	35, 75	1.9, 2.9	2.3, 3.4
D	150	35, 75	2.7, 4.0	2.7, 2.7
E	275	35, 75	1.9, 2.9	2.7, 2.7
F	275	35, 75	2.7, 4.0	2.7, 2.7

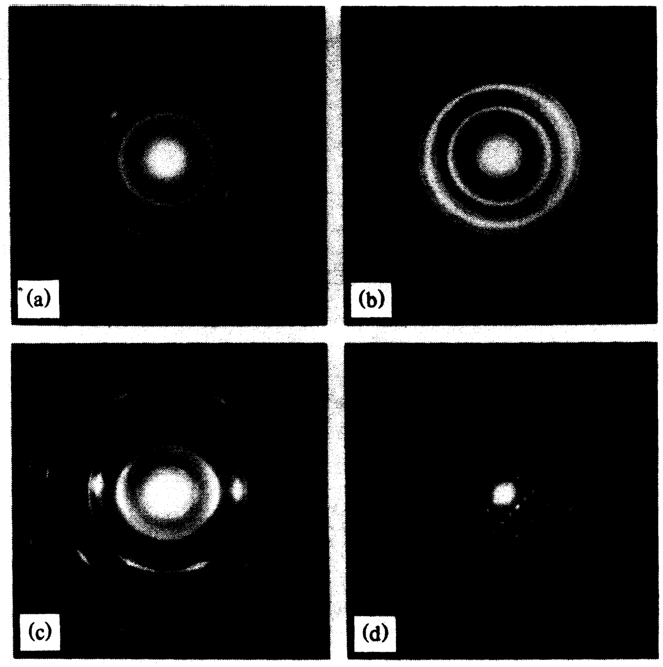

FIG. 1. Selected area diffraction patterns from Al films implanted with Mn ions at three different substrate temperatures. (a) 20 °C; (b) 150 °C, beam normal to film; (c) 150 °C, sample tilted 10°; (d) 275 °C.

E (275 °C). For each of the three temperatures, the higher- and lower-dose samples showed the same diffraction results. In Fig. 1(a), the diffraction patterns associated with the lowest-temperature implantation shows a diffuse ring centered at a scattering vector of approximately $q = 2.96$ Å^{-1} as well as sharp partial rings corresponding to the textured aluminum film. A comparison of the position of this amorphous ring with the x-ray powder pattern peaks listed for the icosahedral phase by Bancel *et al.*[10] shows that it lies midway between the expected positions for the two strongest quasicrystal lines, and hence suggests that the short-range interatomic distances in the implanted phase are similar to those in the icosahedral phase.

Figures 1(b) and 1(c) shows the patterns for an Al-Mn sample implanted at 150 °C which has been oriented with the electron beam parallel and tilted ~10° respectively to the film normal. In these patterns, additional rings are observed which we have indexed. All ring spacings are found to agree within experimental error with either the published peak positions for the icosahedral Al-Mn phase or with expected positions due to multiple scattering of the electrons between the Al matrix and the icosahedral phase. High-resolution x-ray diffraction measurements are in progress using the Oak Ridge National Laboratory beam line at the National Synchrotron Light Source. Preliminary measurements confirm the predicted icosahedral peak positions for the strongest lines to within 0.005 Å and more detailed measurements will be reported elsewhere.

Bright-field and dark-field images of the icosahedral phase showed it to consist of small (less than ~500 Å) irregularly shaped grains with no preference for locating at the boundaries between Al grains. A comparison of Figs. 1(b) and 1(c) shows different relative intensities for the icosahedral rings as well as nonuniform intensity around individual rings. These observations indicate that the icosahedral grains display an orientational texturing. For example, the strongest icosahedral powder line {100000} (Ref. 13) is not observed in fcc ⟨111⟩ pole patterns such as in Fig. 1(b).

Figure 1(d) shows a typical selected area diffraction pattern from a sample implanted at a substrate temperature of 275 °C. Various patterns were indexed and found to exhibit reciprocal-lattice planes indicating the crystalline Al_6Mn structure.

Considering the implantation results at different temperatures, we note that if the icosahedral phase were created as a direct result of the collision cascades during ion implantation, we would also expect the phase to form at room temperature. If it were created by precipitation from an amorphous intermediate phase, we should observe no texturing. Our observations thus indicate that the icosahedral phase forms in our 150 °C samples by solid phase precipitation during the period when there are many mobile point defects after the cascade is completed.

We gain insight into the nature of the observed orientational texturing from microdiffraction patterns of individual grains. Figure 2(a) shows a typical convergent-beam diffraction pattern from sample *C* with the ~475-Å-diameter electron beam normal to the Al-Mn film. The sixfold pattern characteristic of the fcc Al [$\bar{1}$11] pole is clearly seen. From an analysis of many such patterns, it can be concluded that the icosahedral reflections result from several different grains, each of which is oriented with an icosahedral ⟨110000⟩ direction parallel to one of the three Al ⟨110⟩ directions. Further, each icosahedral grain is only a few degrees from a fivefold icosahedral axis which gives rise to additional reflections of the {110000} type separated by $2\pi/10 = 36°$. At first glance, the alignment of the

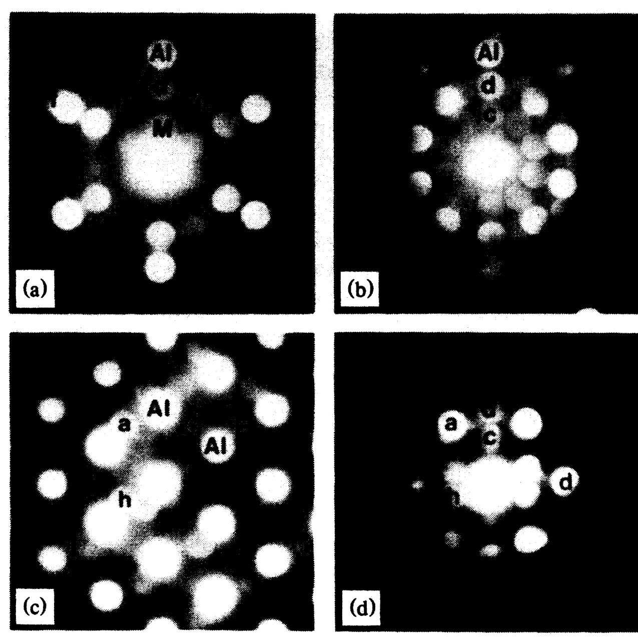

FIG. 2. Microdiffraction patterns at various orientations. fcc spots are labeled Al, multiple scattering is labeled *M*, and other letters correspond to the icosahedral indexing scheme presented in Ref. 10 as follows: {100000} = *a*, {110000} = *d*, {11101̄0} = *c*, {110001} = *h*, {101000} = *f*. (a) fcc [$\bar{1}$11] pole; (b) icosahedral fivefold axis; (c) fcc [110] pole; and (d) icosahedral twofold axis.

icosahedral {110000} reflections, labeled *d*, with the fcc peaks in Fig. 2(a) would seem to indicate a threefold icosahedral axis. However, a closer comparison of the observed and expected (see Fig. 2 of Ref. 10) reflections reveals reflections located between neighboring {110000} spots are not observed at the positions expected for a threefold pattern, but instead lie further from the origin and at approximately 36° from a nearby {110000} reflection.

Our conclusion was verified by microdiffraction patterns obtained while tilting the sample such that the film normal was approximately 3° from the direction of the electron beam. A typical fivefold icosahedral pattern is shown in Fig. 2(b). Although the small size and close proximity of the icosahedral grains often resulted in extraneous reflections from neighboring grains, many fivefold patterns could easily be found at a tilt angle of 3° ± 1° from the Al [$\bar{1}$11] pole and were not observed at other tilt angles up to 30°.

Further experimental observations were obtained by orienting the Al-Mn film for other fcc poles. For example, Fig. 2(c) shows an fcc ⟨110⟩ reciprocal lattice section upon which is superimposed an icosahedral twofold pattern as well as reflections due to multiple scattering. This superposition was observed for many, but not for all Al ⟨110⟩ poles investigated. A twofold icosahedral pattern that was not oriented along a major fcc axis is shown in Fig. 2(d) for comparison.

From stereographic analysis of the convergent beam diffraction patterns, we conclude that the icosahedral grains are oriented such that three mutually perpendicular twofold axes lie along the fcc [001], [110], and [1$\bar{1}$0] crystallographic directions as shown in Fig. 3. The icosahedral grains appear to be equally divided among the three equivalent sets of crystallographic directions of this type.

It is worthwhile to consider possible explanations for the observed texturing. Since the atomic locations within the icosahedral precipitates are not known, it is not possible to construct models of specific interfaces between the two phases which may be energetically favored. Further, the icosahedral phase is not consistent with truly crystalline translational periodicity. However, on average, the atomic density is localized to planes[14] which give rise to Bragg peaks in the diffraction patterns. Considering atomic planes in this manner, it is found that in the implanted Al-Mn films, the icosahedral {110000} planes lie parallel to Al {001} or {110} planes but not to the close-packed {111} planes. A comparison of plane spacings shows the icosahedral (110000) plane and the Al (002) plane can be

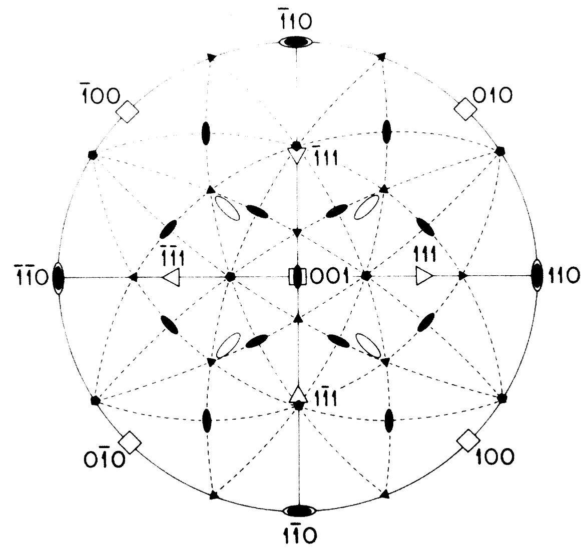

FIG. 3. Stereographic projection showing the orientation relationship between the icosahedral (solid symbols) and fcc Al (open symbols) phases.

made quasicoherent throughout the two phases if a 2% strain is allowed over distances of a few hundred angstroms. This speculation is particularly interesting since it has direct consequences for quantitative x-ray diffraction patterns. Speculation involving coherency of atomic planes implies that the peak position of different reflections of the {110000} type would probably be shifted and broadened by different amounts for planes which lie parallel or tilted away from the Al (002) plane. Clearly high-resolution x-ray diffraction studies of oriented samples, together with the demonstrated orientation relationship between precipitate and parent phase, should provide insight into questions concerning quasicrystal atomic structure.

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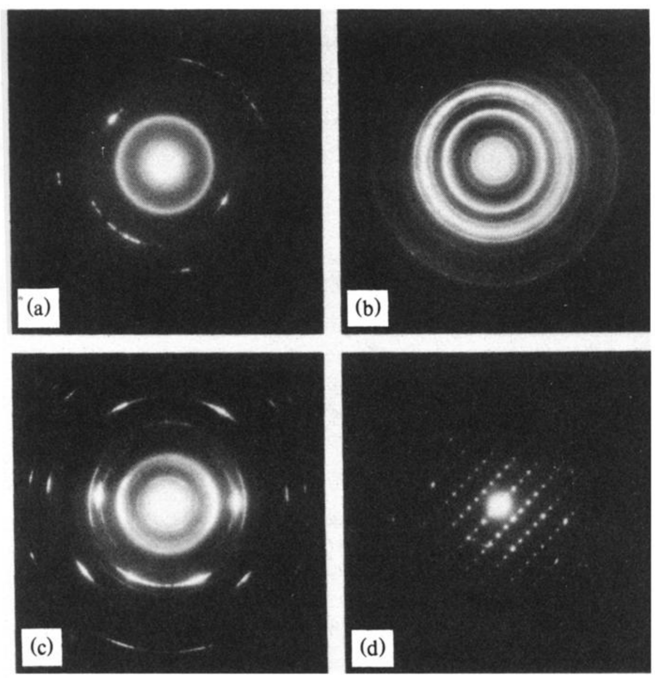

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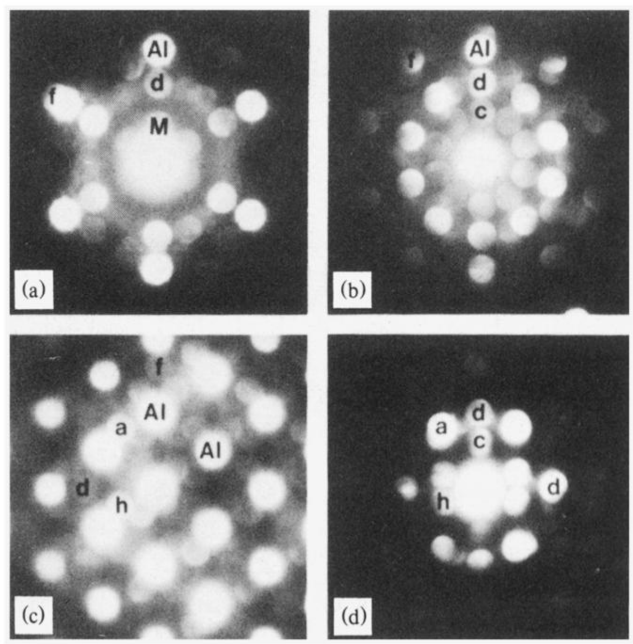

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