X-Ray Diffraction Study of Phason Strain Field in Oriented Icosahedral Al-Mn

J. D. Budai, J. Z. Tischler, A. Habenschuss, and G. E. Ice
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

and

V. Elser
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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We have produced large-area (some square centimeters), crystallographically oriented icosahedral-phase material by implanting Mn ions directly into single-crystal Al substrates. High-resolution x-ray measurements of the positions and line shapes of the quasicrystal diffraction peaks reveal systematic deviations from perfect icosahedral symmetry. A quantitative analysis of the data shows that the samples contain a simple form of phason strain field which depends on the kinetics of grain formation. The results rule out the icosatwin model proposed by Pauling.

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Theoretical descriptions involving projections from higher dimensions[1] or arrangements of more than a single packing unit[2] have shown that quasicrystals with noncrystallographic point symmetries can exist. However, scattering studies of quasicrystals have consistently found broad diffraction peaks,[3] indicating a high degree of disorder. Consequently, theoretical descriptions have been expanded to include defects in quasicrystalline structures.[4,5] In particular, the presence of incommensurate length scales in quasicrystals gives rise to the possibility of a phason strain field which is predicted to shift and broaden diffraction peaks in a manner which is qualitatively very different from usual crystal strain fields.[6,7] Large amounts of quenched random phason strain can disorder a quasicrystal enough to produce "icosahedral glass"[8] structures.[9]

Experimentally, the most extensively studied quasicrystals are the Al–transition-metal icosahedral phases. However, detailed atomic studies have been limited in that all Al–transition-metal samples produced thus far have consisted of randomly oriented powders.[3,7,10] In this Letter, we report an ion implantation technique for producing large-area (some square centimeters) samples containing oriented grains of Al–transition-metal icosahedral phase. High-resolution x-ray scattering measurements using these samples reveal broad linewidths and systematic shifts of peak positions away from perfect icosahedral symmetry. Analysis of the shifts yields the first quantitative description of the 3D phason strain field. Although recent x-ray measurements of oriented Al-Li-Cu quasicrystals clearly demonstrate the phason character of peak widths,[11] the precise form of the strain field has not been identified. Even uniformly oriented Al-Li-Cu samples will usually consist of a high multiplicity of differently strained regions which complicate the analysis of diffraction data. A major advantage of the ion implantation technique, used here, is the presence of a bias for a particular strain field.

In previous studies of ion-implanted thin Al films,[12] we found that quasicrystal grains precipitate within matrix Al grains with a crystallographic orientational relationship. Specifically, they align with three mutually perpendicular icosahedral twofold axes parallel to the [$1\bar{1}0$], [110], and [001] directions of the fcc Al matrix. We have verified that this relationship holds for Al-Cr quasicrystals as well, and expect that it is generally valid for other Al–transition-metal icosahedral phases which can be formed using ion beams. In the present study, large Al single crystals were polished, etched, heated to 140 °C in vacuum, and then implanted at six different energies ranging from 39 to 183 keV to obtain a uniform concentration of ~17 at.% Mn to a depth of approximately 1500 Å. Precipitation of quasicrystals during ion implantation occurs in the solid phase slowly over a period of several hours and thus involves qualitatively different formation kinetics than the more common technique of rapid quenching.

The Al crystal was oriented with the Mn implantation beam nearly parallel with one of the ⟨001⟩ axes, the surface normal. Consequently, the three ⟨001⟩ axes were no longer equivalent in the precipitation process. We identify precipitates in Fig. 1 as type I (multiplicity = 2) or type II (multiplicity = 4) depending on whether an icosahedral twofold axis is, or is not, aligned with the [001] surface normal. The icosahedral twofold axes aligned with the fcc poles provide a convenient orthogonal coordinate system and have been labeled H,K,L. To investigate these expected orientations and obtain high-resolution x-ray diffraction measurements, ion-implanted samples were examined by use of a Huber four-circle diffractometer on the Oak Ridge National Laboratory beam line X-14 at the National Synchrotron Light Source. By use of a sagittally focusing Si(111) monochromator crystal and a Ge(111) analyzer crystal, the

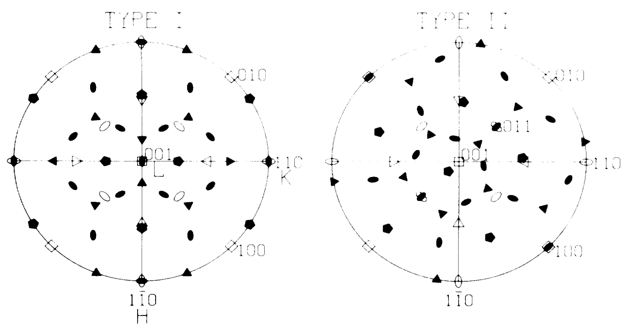

FIG. 1. Stereographic projections of the two distinct alignments of icosahedral axes (solid symbols) with respect to fcc Al poles (open symbols).

resolution in the diffraction plane was typically less than 0.001 $Å^{-1}$ in both the longitudinal (θ-2θ) and transverse (θ) directions.

Longitudinal scans such as those plotted in Fig. 2 show the intensity along particular symmetry axes as a function of momentum transfer. As expected, scans along twofold axes contain a sequence of peaks at positions which scale approximately as $\tau=(1+\sqrt{5})/2$. The peaks in Fig. 2 have been indexed by using the orthogonal H,K,L axes from Fig. 1 as well as the letter designation used by Bancel *et al.*[3] Other types of x-ray scans provide additional confirmation of the quasicrystal alignment shown in Fig. 1. For example, intensity scans obtained while rotating the sample and holding the scattering angle fixed verify the presence of the icosahedral twofold, threefold, and fivefold symmetry axes. No evidence for any unaligned quasicrystalline or other alloy phase is seen. Having established the icosahedral nature of the aligned Al-Mn grains and chosen an indexing scheme, reflections could be precisely located by use of orthogonal scans in reciprocal space. The peak positions and line shapes were determined by fitting the intensity scans to the Pearson VII function.[13]

A striking observation seen in our x-ray measurements on ion-implanted samples is that the diffraction peaks are shifted away from positions of perfect icosahedral symmetry. Although the shifts are different in nature for type-I and type-II quasicrystal grains, systematic trends can be identified. The peaks associated with type-I grains have symmetric line shapes and are shifted by small amounts which are typically less than 0.01 $Å^{-1}$ in magnitude. The shifts for the series of peaks labeled b,c,d,f (see Fig. 2) along any particular twofold axis are oscillatory, reversing direction for successive reflections in this sequence. Reflections which are located such that $H=0$, $K=0$, or $H=\pm K$ (see Fig. 1) do not move out of these high-symmetry planes. The peaks associated with type-II grains are similar in that they show oscillatory shifts along twofold axes and do not move out of planes of high symmetry with respect to the fcc substrate. However, the type-II peaks differ in that they often show

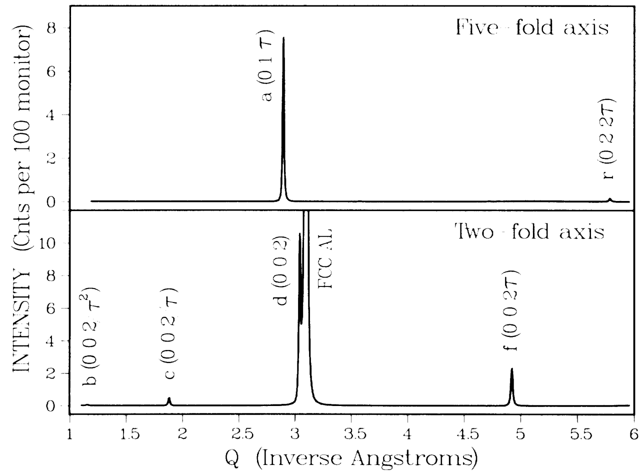

FIG. 2. Intensity vs momentum Q along (lower) surface normal and (upper) fivefold axis 31.7° from normal.

asymmetric or split line shapes. In addition, the peak shifts are typically much larger in magnitude than those observed for type-I peaks.

In order to understand the origin of the observed peak shifts, it is convenient to describe the icosahedral structure as a 3D projection from a 6D cubic lattice. Following the notation proposed by Elser,[1] we express the icosahedral reciprocal-lattice vectors as the direct sum of the "physical" reciprocal vector $\mathbf{G}_\parallel$ with a complementary vector $\mathbf{G}_\perp$, i.e., $\mathbf{G}=\mathbf{G}_\parallel\oplus\mathbf{G}_\perp$. The effect of defects in a quasicrystal can then be understood by considering the phase change for a Bragg reflection $\phi_G=\mathbf{u}(\mathbf{x})\cdot\mathbf{G}_\parallel+\mathbf{w}(\mathbf{x})\cdot\mathbf{G}_\perp$ when positionally varying translational, $\mathbf{u}(\mathbf{x})$, and phason, $\mathbf{w}(\mathbf{x})$, strain fields are introduced. Unlike the ordinary strain field, the phason field does not represent a continuous deformation of a perfect quasicrystal.[14] Rather, $\mathbf{w}(\mathbf{x})$ represents a coarse-grained property of the structure that is truly continuous only on large length scales. A useful definition that encompasses both the "defected ideal quasicrystal" and "icosahedral glass" points of view is the following: A framework for the structure consists of a discrete set of quasilattice points $\mathbf{x}_\parallel$ relative to which the local atomic positions may be expressed as a "decoration" with the possibility of an additional strain displacement $\mathbf{u}(\mathbf{x})$. Each quasilattice point can be supplemented with a 3D vector $\mathbf{x}_\perp$ such that the combination $\mathbf{x}_\parallel\oplus\mathbf{x}_\perp$ forms a 6D lattice point. The actual subset of lattice points $\{\mathbf{x}_\parallel^i\oplus\mathbf{x}_\perp^i\}$ utilized in the structure forms a connected three-surface in 6D space, the average properties of which are given by $\mathbf{w}(\mathbf{x})$. Specifically, $-\mathbf{w}(\mathbf{x})$ is the average of the $\mathbf{x}_\perp^i$ vectors of the reference quasilattice points $\mathbf{x}_\parallel^i$ near $\mathbf{x}$. A linear change in $\mathbf{w}(\mathbf{x})$ is described by the 3×3 matrix $A_{\alpha\beta}$, i.e.,

$$-\mathbf{w}(\mathbf{x})=\left[\sum_{\alpha,\beta=1}^{3}\mathbf{b}_\perp^\alpha A_{\alpha\beta}\mathbf{b}_\parallel^\beta\right]\cdot\mathbf{x},$$

where $\mathbf{b}_\parallel^\alpha$ and $\mathbf{b}_\perp^\alpha$ are suitable bases for the two 3D spaces. In the present situation, we choose the set $\{\mathbf{b}_\parallel^\alpha\}$ as well as the set $\{\mathbf{b}_\perp^\alpha\}$ to consist of three mutually orthogonal unit vectors directed along corresponding twofold icosahedral axes in their respective 3D spaces.

In considering the type-I precipitates, we further choose $\mathbf{b}_\parallel^1$ to be along the fcc [001] surface normal so that $\mathbf{b}_\parallel^2$ and $\mathbf{b}_\parallel^3$ are parallel to the $[1\bar{1}0]$ and [110] axes. From the equivalence of the $\mathbf{b}_\parallel^2$ and $\mathbf{b}_\parallel^3$ directions, both with respect to the fcc matrix and the growth kinetics, we deduce $A_{22}=A_{33}$ and further relations among the off-diagonal elements. However, in analyzing the observed shifts in three orthogonal directions of 37 different reflections, a satisfactory fit was achieved by retaining only the diagonal terms. The shift in reciprocal space is given by the transpose of $A_{\alpha\beta}$ which in our case reduces to

$$\delta\mathbf{G}_\parallel=\lambda_1\mathbf{b}_\parallel^1(\mathbf{b}_\perp^1\cdot\mathbf{G}_\perp)+\lambda_2[\mathbf{b}_\parallel^2(\mathbf{b}_\perp^2\cdot\mathbf{G}_\perp)+\mathbf{b}_\parallel^3(\mathbf{b}_\perp^3\cdot\mathbf{G}_\perp)].$$

Fitting this expression to the experimental *HKL* coordinates, we find $\lambda_1=-0.0065\pm0.0015$ and $\lambda_2=+0.004\pm0.002$, with the largest deviation between the calculated and observed magnitude for any reflection being 0.0015 Å^{-1}. In agreement with previous work on Al-Mn icosahedral phase, we obtain a quasilattice parameter[1] $a_R=4.6008\pm0.0005$ Å. It is also interesting to note that the near vanishing of the trace of $A_{\alpha\beta}$ implies, at least in the formulation of the detected ideal quasicrystal, a constancy in the density of quasilattice points.

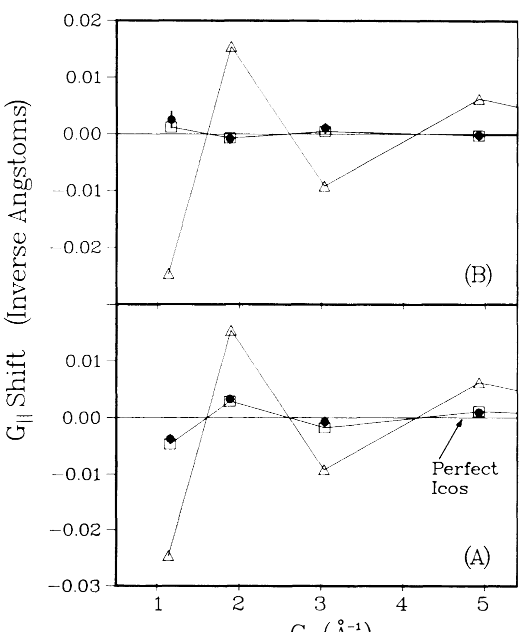

FIG. 3. Shift in $|\mathbf{G}_\parallel|$ for type-I peaks along (a) surface normal and (b) twofold axis 36° from normal. Experimental data (solid circles), phason strain model (open squares), and Pauling twinning model (open triangles).

Figure 3 shows examples of simple peak-shift patterns which result from the phason strain. Both the magnitude and sign of the observed characteristic damped oscillatory behavior for $\delta\mathbf{G}_\parallel$ along various twofold axes is accurately described using the fitted values for λ_1 and λ_2. A similar pattern is predicted by the icosatwin model proposed by Pauling.[15] His model simply represents a particular choice of linear phason strain for which the peak positions are approximated by rational cubic indices ($a_0=23.4$ Å). As shown in the figure, the observed peak shifts are clearly inconsistent with the twinning model. It is interesting to note that it is possible to describe the observed positions along the surface normal as arising from a larger periodicity of 43.4 Å for which the strong reflections are indexed as 8, 13, 21, and 34 times the fundamental. However, this approach fails for other twofold axes and a more complete description is given simply by specifying λ_1 and λ_2 for type-I grains.

Since the details of the atomic arrangements depend on the growth environment particular to each icosahedral grain, we expect the observed difference between the type-I and type-II peak shifts. Although certain general characteristics, such as the damped oscillations along twofold axes, are also present for type-II precipitates, we are unable to determine the explicit form for the strain field in this case. The appearance of asymmetric and split peaks for type-II grains suggests a superposition of different strain fields. This is not unexpected, since for these precipitates the icosahedral axes have no simple relationship to the surface normal during the growth process.

While the positions of x-ray diffraction peaks describe average properties of the sample, additional information concerning deviations from the average structure can be obtained by considering the shapes of individual reflections. As seen in Fig. 4, the transverse widths for reflections that lie along the surface normal increase monotonically with $|\mathbf{G}_\parallel|$, as expected for an ordinary crystal containing defects. The major contributions to

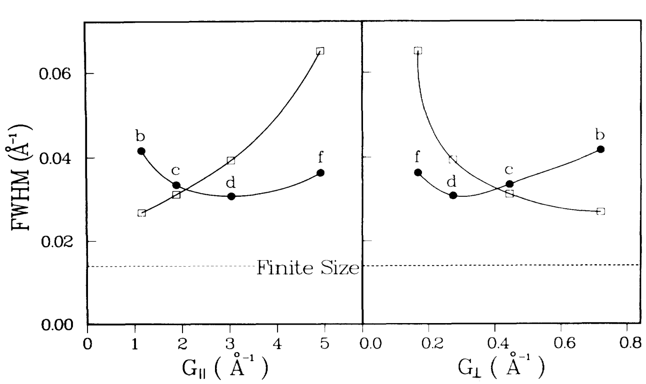

FIG. 4. Radial (solid circles) and transverse (open squares) FWHM plotted vs $|\mathbf{G}_\parallel|$ and $|\mathbf{G}_\perp|$ for peaks along the surface normal.

the transverse widths appear to be a mosaic spread of ~0.7° convolved with a finite grain size of typically 450 Å (consistent with transmission-electron-microscopy images). The radial widths, however, show a very different behavior, which can be expressed as a monotonic increase with large $|\mathbf{G}_\perp|$. A simple explanation of this effect, already observed in Al-Li-Cu icosahedral phase, was advanced by Bancel *et al.*[11] in terms of phason disorder. If phason strain is correlated with growth conditions, then it is unrealistic to assume a specific linear strain or matrix $A_{\alpha\beta}$ for the entire sample (even when assuming a fixed growth direction). Rather, one expects a distribution for, in our case, λ_1 and λ_2 that reflects a distribution in growth conditions (perhaps as a function of grain size or depth below the surface). To explain the region of linear rise in radial width with increasing $|\mathbf{G}_\perp|$ shown in Fig. 4, the corresponding width of the distribution must be roughly 0.03, considerably larger than the mean.

In summary, we have used ion implantation to form large areas of oriented Al-Mn icosahedral phase which scatter x rays as single-quasicrystal samples. The observed x-ray peak positions and line shapes are well described by a quasicrystal model biased towards a particular linear phason strain field. The range of strain about the average, as well as the difference in scattering between type-I and type-II orientations leads us to conclude that the phason strain for individual grains depends on the local growth conditions.

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