Structure of Rapidly Quenched Al-Mn

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We report electron-microscopy and high-resolution x-ray-scattering measurements of rapidly quenched Al_6Mn. The electron-diffraction pattern shows icosahedral symmetry. Peaks in the x-ray-diffraction pattern can be indexed to a mixture of fcc Al and a phase whose reciprocal lattice is described by a sum of icosahedral vectors. The half-width of the sharpest x-ray peak is 0.01 Å^{-1}. A comparison is made with current theories of quasicrystalline order.

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Recent electron-microscopy measurements by Shechtman *et al.*[1] and by Field and Fraser[2] have indicated that rapidly quenched samples of Al alloyed with Mn, Fe, or Cr can produce electron-diffraction patterns with sharp spots and icosahedral point symmetry. The diffraction from a single ~ 2-μm grain shows twofold, threefold, and fivefold patterns when the grain is rotated through the appropriate icosahedral angles. This result is apparently at variance with a well-known crystallographic theorem, which states that long-range periodic translational order is incompatible with icosahedral point symmetry.

The results of Shechtman *et al.* can be understood in several theoretical contexts. By extending the concept of hexatic bond-orientational order (BOO) to three dimensions, Steinhardt, Nelson, and Ronchetti[3] showed that under some circumstances glasses might show icosahedral BOO. This predicted orientational order was accompanied by at most short-range translational order, and it was not compatible with sharp diffraction peaks. Levine and Steinhardt[4] have recently described a new class of ordered structures based on quasiperiodic rather than periodic translational order. By generalizing the properties of two-dimensional nonperiodic tilings of a plane[5,6] to three-dimensional space-filling structures, they can construct nonperiodic lattices which still maintain long-range BOO. One particular quasicrystal structure studied by Levine and Steinhardt has perfect icosahedral symmetry, and consists microscopically of two unit cells which are arranged nonperiodically but according to definite mathematical rules. Remarkably, a calculation of the diffraction intensity from this structure predicts sharp peaks and shows strikingly good agreement with the icosahedral diffraction patterns from quenched Al-Mn samples.[7,8] Bak,[9] Levine *et al.*,[10] Mermin and Troian,[11] and Nelson and Sachdev[12] have presented phenomenological models based on Landau theory with icosahedral point symmetry and quasiperiodic or incommensurate translational order. An alternative model[2,13] for the observed diffraction peaks suggests that by combining clusters of twenty or more twinned orthorhombic Al_6Mn microcrystals and including the effect of multiple electron diffraction, it may be possible to reproduce the entire icosahedral electron-diffraction pattern.[14] While dark-field imaging has the potential for determining the twinning structure of a grain, interpretations of the experimental results have varied.[1,2]

In this Letter we present the first detailed high-resolution x-ray powder-diffraction study of the Al-Mn system. Our x-ray data, combined with electron microscopy, allow a quantitative comparison with icosahedral models for the structure of this system. Additionally, the shape of the x-ray diffraction peaks can yield information about the range of translational order.

Thin metallic ribbons were prepared by quenching a

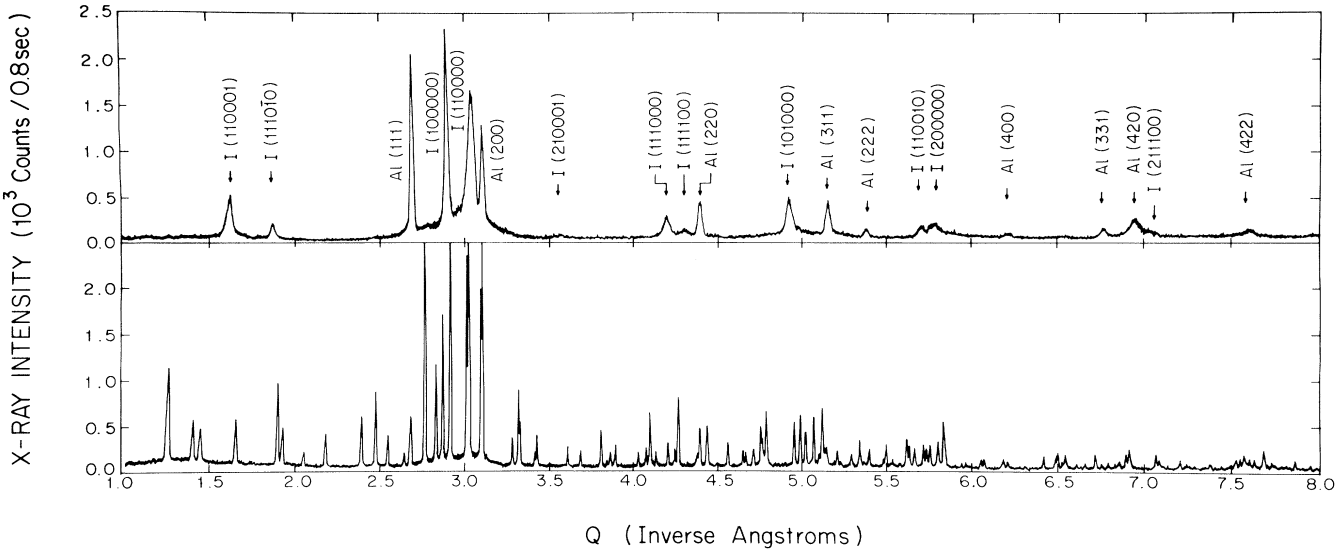

FIG. 1. Top: High-resolution x-ray diffraction pattern of quenched Al-Mn powder. Labels are Al and icosahedral Miller indices as discussed in text. Bottom: Diffraction pattern of annealed Al-Mn powder. The four strongest peaks have been truncated.

molten alloy of Al–14-at.%-Mn on a 9-in. Cu wheel rotating at 3250 rpm. Specimens for electron microscopy were thinned by standard ion-milling techniques. The samples were composed of two phases with grain sizes extending up to several microns. Some samples were annealed by heating to 410 °C for 75 min in an argon atmosphere. High-resolution x-ray experiments on powdered samples were done with 14.6-keV bending-magnet synchrotron radiation at the Cornell High Energy Synchrotron Source (CHESS). The instrumental resolution was approximately 0.001 Å^{-1} half width at half maximum (HWHM). Additional low-resolution x-ray-diffraction measurements on ribbon samples were done with use of rotating-anode Mo $K\alpha$ or Cu $K\alpha$ radiation. The resolution was approximately 0.01 Å^{-1} and the peak scattered intensity 10000 counts/100 sec.

The bottom panel of Fig. 1 shows a high-resolution powder-diffraction profile for the annealed Al-Mn sample. Comparison of the annealed profile to the x-ray powder file index[15] for orthorhombic Al_6Mn gives a match for all listed peak positions and intensities. Gaussian fits to the line shapes of the peaks yield widths of $\Delta q = 0.004$ Å^{-1} HWHM, implying a mean crystallite size of 600–800 Å. The top panel of Fig. 1 shows a high-resolution x-ray powder-diffraction profile for the quenched Al-Mn sample. A weak peak at 2.79 Å^{-1} is best indexed as the orthorhombic Al_6Mn (131); none of the other measured peaks are at the orthorhombic positions. This allows us to establish an

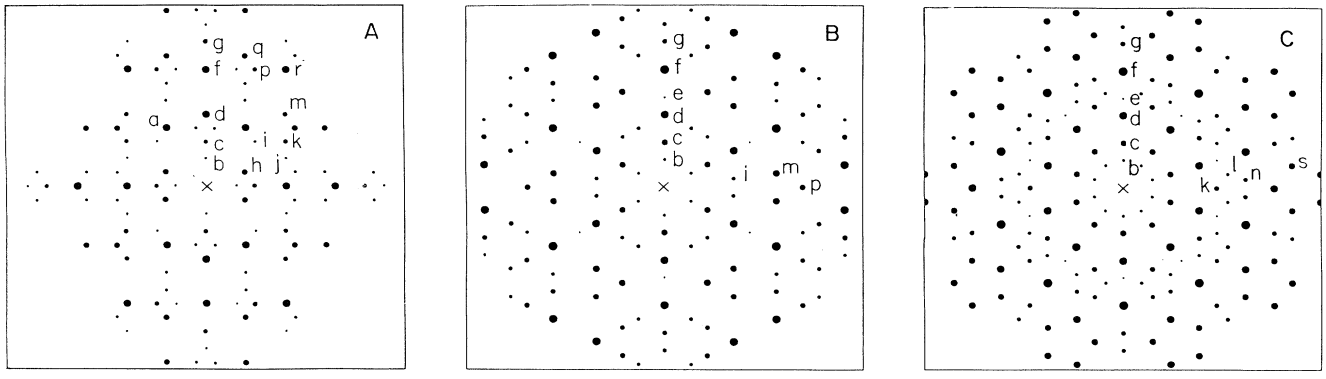

FIG. 2. Schematic of electron-diffraction patterns, showing the strongest spots. (A) twofold axis. (B) threefold axis. (C) fivefold axis. Letters labeling spots correspond to entries in Table I.

upper limit of (2–3)% orthorhombic phase in this sample. Except for a subset of the peaks that index to fcc Al, none of the other peaks in this high-resolution profile can be indexed to any known Al-Mn crystal structure. Table I shows measured parameters for various peaks. The patterns that we obtain in the twofold, threefold, and fivefold axes, shown schematically in Fig. 2, are identical to those reported elsewhere.[1,2] By rotating 32° from the twofold pattern shown in Fig. 2, passing through a threefold pattern, we observe another twofold pattern which is a subset of the original. Our ten fitted high-resolution peaks are all matched by strong electron-diffraction peaks, with scattering vectors matching to within experimental error. Our low-resolution data contain fifteen additional peaks which also match with observed electron-diffraction peaks. Additional weak peaks in the low-resolution data also belong to the orthorhombic phase. The electron-diffraction peaks that are not found in the x-ray data are either among the weakest in the patterns or overlap with fcc-Al peaks in the x-ray patterns. Since samples from the same batch yield icosahedral + Al peaks in the quenched phase, and only orthorhombic Al_6Mn peaks in the annealed phase, the Mn:Al ratio in the icosahedral phase is apparently greater than 1:6. (Preliminary studies suggest an optimal Mn content of 22 at.%.)

We can index all of the x-ray and electron-diffraction peaks using the twelve vectors pointing to the vertices of an icosahedron, which are generated by cyclic permutations of $(q_x,q_y,q_z)=(\pm 1,\pm\tau,0)$. We take our six independent vectors to be

$$\mathbf{q}_1=(1,\tau,0),\quad \mathbf{q}_2=(1,-\tau,0),\quad \mathbf{q}_3=(0,1,\tau),$$
$$\mathbf{q}_4=(0,1,-\tau),\quad \mathbf{q}_5=(\tau,0,1),\quad \mathbf{q}_6=(-\tau,0,1),$$

where τ is the golden mean, $(1+\sqrt{5})/2$. As an example, the (110001) peak is found at $\mathbf{q}=Q_0^*(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_6)$ or $\mathbf{q}=Q_0^*(2-\tau,0,1)$. By comparing the electron- and x-ray-diffraction peaks, we find that the peak at 2.896 Å^{-1} is a natural choice for the fundamental (100000) reciprocal lattice vector.[16] All other peaks are then found at their calculated positions with experimental error. Note that the peak at 3.043 Å^{-1} is obtained from that at 2.896 Å^{-1} by adding two distinct fundamental vectors. A family of icosahedrally oriented twins can produce [100000] peaks such as that at 2.896 Å^{-1}, yielding twofold, threefold, and fivefold electron-diffraction symmetry planes. However, such a twinning model requires multiple scattering to generate the entire diffraction pattern. The presence of high-order peaks in our x-ray data strongly supports the existence of *true single-domain icosahedral point symmetry,* and we can exclude any model for the structure of rapidly quenched Al-Mn that requires multiple scattering to explain the diffraction pattern. (Of

TABLE I. Measured parameters for various peaks: icosahedral indices, peak labels and symmetry planes, and results of Gaussian fits of peak position, peak intensity, and peak width to the high-resolution powder profile. Entries for which an intensity but no HWHM is shown are from the low-resolution measurements. Low-resolution fitted widths were approximately 0.015 Å^{-1}. When an x-ray peak was not observed, the scattering vector was extracted from the electron-diffraction pattern. Icosahedral x-ray peaks at 2.64, 5.23, and 6.15 Å^{-1} could not be fitted as a result of large nearby fcc-Al peaks. Peaks with harmonic order greater than seven have been indexed by use of the lowest-order vector with the observed magnitude and symmetry.

Index		Planes	Q (Å^{-1})	I (arb. units)	HWHM (Å^{-1})
(21$\bar{1}\bar{1}\bar{1}$1)		2	0.66		
(220011)	b	2,3,5	1.16		
(110001), (32$\bar{1}$112)	h	2 2,3	1.632	22	0.018
(1110$\bar{1}$0)	c	2,3,5	1.876	8	0.014
(2210$\bar{2}$0)		2	2.00		
(31$\bar{1}\bar{1}$11)		2	2.20	1.5	
(21$\bar{1}$001), ($\bar{3}$31021)		2 5	2.49	3	
(21$\bar{1}\bar{1}$01)	i	2,3	2.64		
(100000), (32$\bar{1}$002)	a	2 5	2.896	100	0.009
(110000)	d	2,3,5	3.043	78	0.022
(220002), (2211$\bar{1}$1)	j	2 2,3	3.24	1	
(111101)		2	3.44		
(210001)	k	2,5	3.576	1.5	0.04
(3200$\bar{1}$1)		2	3.63		
(220001)		2	3.92	0.5	
(2210$\bar{1}$0)	l	5	4.04		
(111000), ($\bar{3}$300$\bar{1}$1)	e	2 2,3,5	4.200	11	0.021
(111100)	m	2,3	4.307	3	0.020
(2110$\bar{1}$0)		2	4.60	0.5	
(2110$\bar{1}$1)	n	5	4.70	0.5	
(101000)	f	2,3,5	4.928	20	0.021
(42$\bar{2}$002)		2	4.99	0.5	
(210000), (21$\bar{1}$000)	p	2 2,3	5.23		
(2111$\bar{1}$1)		2	5.51	1	
(110010)	q	2	5.708	5	0.020
(200000), (111$\bar{1}$00)	r	2 2,5	5.79	7	0.04
(221002), (43$\bar{1}$002)		2 5	5.83	3	
(220000)	g	2,3,5	6.06	1	
(3211$\bar{1}$1)		2	6.15		
(211000), (440004)	s	5 2	6.53	1	

course, multiple diffraction may still act to alter the relative intensities of the observed electron-diffraction peaks.)

The correlation lengths in the quenched phase are shorter than those found in the annealed samples. The $I(100000)$ and most Al peaks have a width of $\Delta q = 0.01$ Å^{-1}; most of the other icosahedral peaks are somewhat broader. Our observation of 100–300-Å correlation lengths in the icosahedral phase must be reconciled with the electron-microscopy observation of BOO across grains 1 μm or greater in diameter. High-resolution convergent-beam microscopy suggests that many grains are locally distorted on length scales much less than the 1-μm crystallite size.[17] It is possible that the x-ray linewidths are due to local strains or defects such as dislocations which destroy positional but not orientational order over length scales greater than several hundred angstroms. Note that nearby diffraction peaks of different symmetries appear to have quite different widths. For example, the (110000) peak at 3.043 Å^{-1} is nearly twice as broad as the nearby (100000) peak. This symmetry-dependent broadening is not predicted by a distribution of lattice constants or by a naive description of finite-size broadening, but may be due to strains or other defects. This phase may best be described as the icosahedral analog of a hexatic phase[18] with long-range BOO and finite positional order. Our measurements are also consistent with theoretical models incorporating intrinsic icosahedral symmetry and long-range positional order[4,8–12] plus metastable defects. We note that in the present data the x-ray intensity drops rapidly with increasing harmonic order.

We have also studied a variety of other bimetallic alloys. Rapidly quenched samples of 6:1 Al-Pd and Al-Pt contain a phase apparently related to the icosahedral phase; we are presently conducting a more detailed study of these materials.[19] Rapidly quenched samples of 6:1 Al-Ru show the full icosahedral symmetry in the electron-diffraction patterns and also produce x-ray diffraction profiles that are almost identical to those produced by rapidly quenched Al-Mn.

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