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Nuclear γ-ray resonance observations in an aluminum-based icosahedral quasicrystal

L. J. Swartzendruber
Center for Materials Science, National Bureau of Standards, Gaithersburg, Maryland 20760

D. Shechtman
Department of Materials Engineering, Israel Institute of Technology,
Technion, 3200 Haifa, Israel

L. Bendersky
Center for Materials Research, The Johns Hopkins University, Baltimore, Maryland 21218

J. W. Cahn
Center for Materials Science, National Bureau of Standards, Gaithersburg, Maryland 20760

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Nuclear γ-ray resonance (Mössbauer effect) results are presented from rapidly solidified Al-(Mn,Fe) alloys which contain the orientationally ordered phase with icosahedral point-group symmetry. Detailed analysis of the spectra obtained is consistent with an icosahedral quasicrystalline model for the structure of this phase.

It has recently been shown[1] that rapid solidification of Al-rich Al-Mn alloys by melt spinning can produce a metallic solid which diffracts electons like a single crystal but has point-group symmetry $m\bar{3}\bar{5}$ (icosahedral) which is inconsistent with lattice translations. Following Ref. 1 we refer to this phase as the icosahedral phase. It has long-range orientational order giving rise to sharp diffraction patterns, but lacks periodic translational order. It is a metastable phase which forms by a first-order transition. Once formed, heating above 350 °C is required for it to crystallize to the stable Al_6Mn phase.

Thus far two models have been proposed which claim to explain the observed diffraction patterns from this icosahedral phase. One model consists of a packing of parallel icosahedra attached by the edges, each containing one transition metal atom at its center.[2] The second proposes a quasiperiodic filling of space by rhombohedra with two distinct shapes filling space in a quasiperiodic manner.[3,4] We present here nuclear γ-ray resonance (NGR) data that are incompatible with the first model and which, at the same time, are consistent with the present form of the second model.

The icosahedral phase has been found to form readily in melt-spun Al-rich Al-Mn alloys,[1] but only in small amounts in melt-spun Al-rich Al-Fe alloys.[5] In order to observe the NGR of ^{57}Fe, ternary alloys were used. Two melt-spun ribbons were prepared with the compositions Al–22 wt.% Mn–4 wt.% Fe and Al–16 wt.% Mn–10 wt.% Fe. These correspond to the formulas $Al_6(Mn_{0.85}Fe_{0.15})_{1.03}$ and $Al_6(Mn_{0.62}Fe_{0.38})_{1.03}$, respectively. These two alloys produced essentially equivalent spectra. Optical microscopy on cross sections and transmission electron microscope (TEM) examination on thin foils of this alloy showed only two phases: the icosahedral phase and a small amount of fcc Al. Electron and x-ray diffraction patterns from this icosahedral phase were indistinguishable from those published[1] for the binary Al-Mn alloy. Since Fe is known to be insoluble in fcc Al (less than 3 at.% dissolves at the highest achievable quenching rates[6]), and considering the small amount of fcc Al present, we believe it is valid to assume that nearly all of the Fe atoms in the as-spun ternary alloys reside as random substitutions for Mn atoms in the icosahedral phase. Contributions to the observed NGR spectra from other phases will be insignificant.

The as-spun alloys were also heat treated in vacuum at 500 °C for 1 h. TEM examination after this heat treatment revealed that all the icosahedral phase had transformed to the crystalline Al_6Mn structure.

The model based on iron atoms centered in aluminum icosahedra is inconsistent with the rather strong quadrupole splitting in the observed spectra (see Fig. 1). Icosahedral first-neighbor coordination of the transition metal atoms would imply high local symmetry[7] resulting in little or no electric field gradient, and therefore at most a weak quadrupole splitting. Any contributions to the electric field gradient from asymmetries in the second- and further-neighbor coordination shells would be insufficient to produce the observed splitting.

In the quasicrystalline model proposed by Levine and Steinhardt,[3] a quasiperiodic structure is generated using a pair of polyhedra which are the three-dimensional analogs of the two-dimensional Penrose tiles.[4,8,9] These two polyhedra form a space-filling quasilattice of infinite extent which is nonperiodic and from which a diffraction pattern can be calculated.[3,10] The calculated pattern[3] is consistent with the three- and fivefold symmetry, spacing, intensity, and sharpness in the observed diffraction pattern[1,2] (although the positions of the atoms in this structure have not been determined). In filling all space, the two polyhedra must occur in the ratio 1.618. . . to 1 (the golden mean) with the more frequent polyhedron being less distorted than the less frequent one. (In Mackay's rhombic triacontahedron the two polyhedra would occur in equal numbers.[9]) Packing the two kinds of polyhedra leads to a quasicrystalline lattice which is self-similar in the sense that one can eliminate a subset of lattice points and increase all distance scales by a constant factor to obtain another quasicrystalline lattice. This inflation procedure can be reversed but it must cease to have

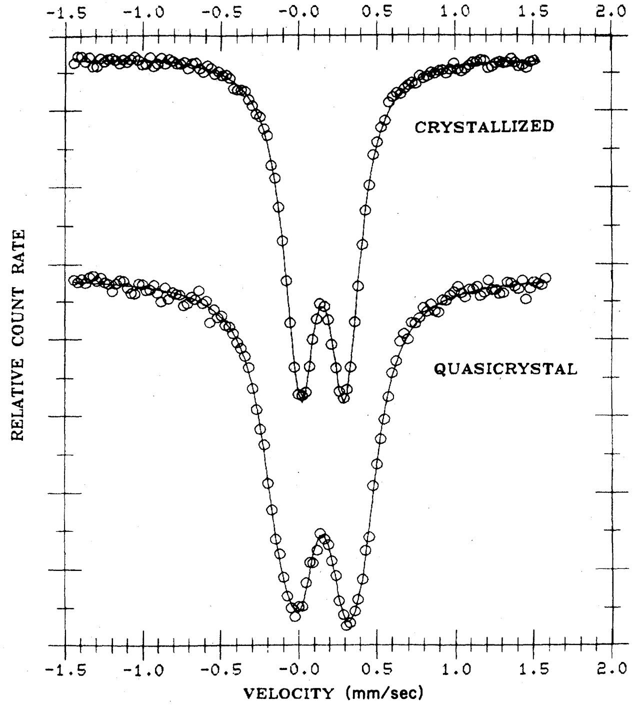

FIG. 1. Room-temperature NGR absorption spectra from the heat-treated (crystallized) and from the as-spun (quasicrystal) alloy $Al_6(Mn_{0.85}Fe_{0.15})10.3$. The circles are data points and the solid line is the least-squares fit obtained as described in the text. The zero of velocity represents the center of a pure iron spectrum at room temperature and positive velocity represents source and absorber approaching.

validity beyond the point where the number of transition metal atoms per quasilattice point or polyhedron becomes 1. We therefore assume that there are two kinds of asymmetric sites for the transition metal atoms and that the ratio for the numbers of atoms of each kind should be the golden mean. This would produce an NGR spectrum consisting of two quadrupole doublets with a golden mean amplitude ratio.

The spectra obtained for the $Al_6(Mn_{0.85}Fe_{0.15})_{1.03}$ alloy both as spun and after heat treatment are shown in Fig. 1. The spectrum from the heat-treated sample has been least-squares fitted to a symmetric doublet. The parameters obtained for these samples and for the $Al_6(Mn_{0.62}Fe_{0.38})_{1.03}$ samples are given in Table I. The values obtained for the quadrupole splitting of the crystallized samples, 0.287 and 0.296 mm/sec, are very close to the 0.288-mm/sec splitting observed previously by Stickels and Bush[11] in metastable Al_6Fe. The linewidths of the crystallized samples 0.244 and 0.239 mm/sec are only slightly greater than the natural linewidth for ^{57}Fe (0.21 mm/sec) and the slight broadening is largely attributable to instrumental effects (≈ 0.02 mm/sec). By fitting to separate lines it was determined that these doublets are, within experimental error, completely symmetric.

The spectra obtained from the as-spun icosahedral samples are least-squares fitted to a pair of symmetric doublets (cf. Fig. 1). In the least-squares fit the height ratio of the two doublets was constrained to be 1.618. All other parameters, i.e., the isomer shifts, linewidths, and quadrupole splittings, were unconstrained. The parameters obtained from this fit are shown in Table I. Note that the more intense doublet, which we associate with the less distorted polyhedron, has an isomer shift and quadrupole splitting very close to that observed for the crystallized material with the Al_6Mn structure, whereas the less intense doublet, which we associate with the more distorted polyhedron, has a considerably larger quadrupole splitting. This larger splitting indicates a larger electric field gradient. It can be noted that this type of two-doublet fit gave a significantly lower residual standard deviation (0.14% compared to 0.22% at a count level of 6.3×10^5) than did an unconstrained fit to two individual lines. It is thus clear that, although the quasicrystal spectra might be fitted in more complicated ways than used here, there must be more than one type of iron site in the quasicrystalline material, with each site having a relatively large quadrupole splitting. Attempts at fitting were also made using other doublet intensity ratios. For ratios of 1.8 and 1.4 the residual standard deviations were slightly larger, although the difference could not be considered significant. At ratios of 2.0 and 1.2 the deviations were significantly larger. An equally valid fit was obtained when the

TABLE I. Parameters obtained by least-squares fitting the spectra of Fig. 1 for $Al_6(Mn_{0.85}Fe_{0.95})_{1.03}$ and for a sample of $Al_6(Mn_{0.62}Fe_{0.38})_{1.03}$. Isomer shifts are given with respect to pure iron at room temperature.

	Doublet 1				Doublet 2			
Sample	Relative intensity	Splitting (mm/sec)	Isomer shift (mm/sec)	Width (mm/sec)	Relative intensity	Splitting (mm/sec)	Isomer shift (mm/sec)	Width (mm/sec)
Crystallized ($Fe_{0.15}$)	1.0	0.287	0.152	0.244	0	. . .	. . .	. . .
As spun ($Fe_{0.38}$)	1.618	0.298	0.150	0.289	1	0.550	0.141	0.272
Crystallized ($Fe_{0.38}$)	1.0	0.296	0.185	0.239	0	. . .	. . .	. . .
As spun ($Fe_{0.38}$)	1.618	0.294	0.191	0.297	1	0.523	0.174	0.288

linewidths of the two doublets were constrained to be equal. In that case the linewidth obtained was between the linewidths given in Table I. The larger linewidth in the quasicrystals over those in the crystallized material has two likely causes: (1) variations in the second and third near-neighbor environments expected in a nonperiodic quasicrystal, and (2) the presence of vacancies and other defects expected in a rapidly quenched solid.

The NGR spectrum of an iron atom is essentially a probe of the local environment of that atom, being most sensitive to the first one or two near-neighbor shells. Although the spectra obtained here do not establish the location of the Fe atoms in the crystal, they are consistent with the quasicrystalline model of Levine and Steinhardt[3] and cannot be consistent with models which place the transition-metal atoms at centers of icosahedra.

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