Mössbauer-effect study of the Fe hyperfine-field distributions in the ferromagnetic quasicrystal $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$

R. A. Dunlap and V. Srinivas
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5
(Received 20 March 1989)

The alloy $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$ has been prepared by rapid quenching from the melt. This alloy is shown to be a single-phase icosahedral quasicrystal and is ferromagnetic at room temperature. ^{57}Fe Mössbauer-effect spectra have been obtained at 110 and 293 K. A spectrum was also obtained at 293 K in an external magnetic field of 4.8 kOe in order to obtain the sign of the hyperfine magnetic field. These results show a mean Fe hyperfine field of +17 kOe and suggest an average Fe magnetic moment of $0.11\mu_B$. These results are discussed in terms of recent magnetization measurements on other ferromagnetic quasicrystals and possible models for the magnetic structure.

I. INTRODUCTION

Since the first report of quasicrystals by Shechtman *et al.*[1] in 1984, the magnetic properties of these materials have attracted considerable interest.[2–4] A variety of magnetic behaviors have been reported ranging from diamagnetism[5] to paramagnetism[6] and spin-glass behavior.[7] Recently, ferromagnetism has been reported in icosahedral Al-Ce-Fe by Zhao *et al.*,[8] in icosahedral Al-Mn-Si by Dunlap *et al.*,[9] and in icosahedral Al-Mn-Ge based alloys by Tsai *et al.*[10] The availability of such ferromagnetic quasicrystals allows for the comparison of experimental results with theoretical predictions on the effects of icosahedral symmetry on magnetic ordering.[11–15] In the present work we report on ^{57}Fe Mössbauer-effect measurements in an icosahedral quasicrystal which exhibits ferromagnetism at room temperature: $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$. This alloy is an extension of the ferromagnetic Al-Mn-Cu-Ge alloys reported by Tsai *et al.*[10] We have chosen to substitute Fe into this system rather than the simpler Al-Mn-Ge system because of the larger saturation magnetization.

II. EXPERIMENTAL TECHNIQUES

An alloy of $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$ was prepared by rapid quenching from the melt onto the surface of a single Cu roller with a surface velocity of 60 m/s. A Cu $K\alpha$ x-ray-diffraction pattern was obtained using a Siemens scanning powder diffractometer. As illustrated in Fig. 1, this alloy was found to be a well-ordered single-phase icosahedral quasicrystal. The figure shows the indexing of the diffraction peaks according to the scheme of Bancel *et al.*[16] This pattern yields a quasilattice constant[17] of 4.488 Å, in good agreement with the value of 4.504 Å reported for $Al_{40}Mn_{25}Cu_{10}Ge_{25}$ by Tsai *et al.*[10] The present alloy is found to be clearly ferromagnetic at room temperature as expected on the basis of a value of T_C of 467 K reported for icosahedral $Al_{40}Mn_{25}Cu_{10}Ge_{25}$.[10]

Fe Mössbauer-effect spectra were obtained at 110 ± 5 K (liquid-nitrogen cold finger) and 293 ± 2 K (room temperature) using a Pd^{57}Co source and a Wissel System II Mössbauer spectrometer. Spectra were collected using a conventional constant acceleration mode and the spectrometer was found to have an intrinsic line width for a thin α-Fe absorber of 0.24 mm/s full width at half maximum (FWHM). Room-temperature spectra were also obtained in an external magnetic field of 4.8 kOe for the purpose of determining the sign of the internal hyperfine field.

III. RESULTS AND DISCUSSION

^{57}Fe Mössbauer-effect spectra obtained at 110 and 293 K are illustrated in Fig. 2. These spectra are clearly distinct from the quadrupole-split doublets with ~0.4 mm/s previously reported in all cases for paramagnetic Al-based quasicrystals.[18–20] Acceptable computer fits to these spectra could not be obtained on the basis of a Lorentzian doublet or a distribution of Lorentzian doublets [e.g., the shell model or a similar distribution (Refs. 5, 21, and 22)]. The spectra could, however, be satisfactorily fit to a Zeeman-split Lorentzian sextet with broadened lines or to a distribution of Lorentzian sextets. To illustrate this

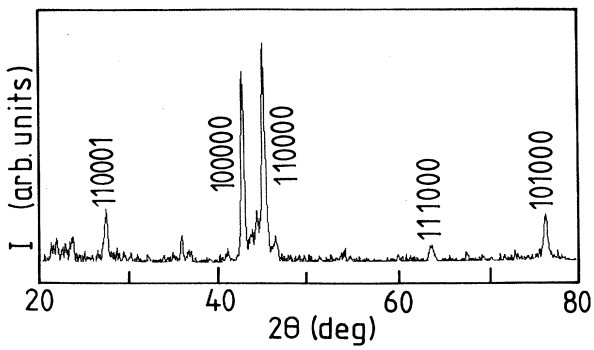

FIG. 1. Cu $K\alpha$ x-ray-diffraction pattern of icosahedral $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$. Indices of the major peaks are given according to the scheme of Ref. 16.

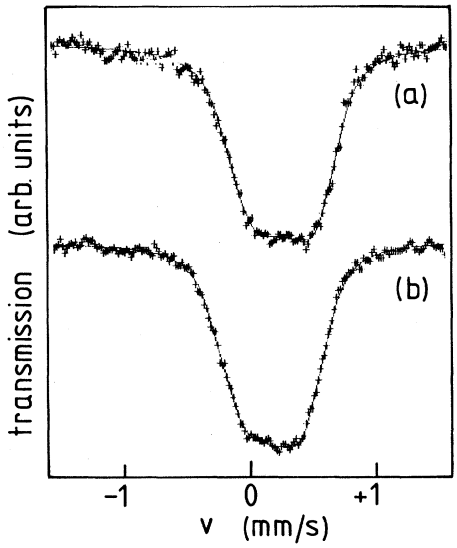

FIG. 2. ^{57}Fe Mössbauer-effect spectra of icosahedral $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$ obtained for zero external magnetic field at (a) 110 K and (b) 293 K. Solid lines represent fits according to method 2 described in the text.

point, a fit to the room-temperature spectrum to an asymmetric Lorentzian doublet (seven fitting parameters) gave a misfit[23] of 1.34 while a fit to a Lorentzian sextet (six fitting parameters) gave a misfit of 0.52. For the fit to the sexet, all linewidths were constrained to be equal and the relative line amplitudes were constrained to be symmetric and of the form $3{:}b{:}1{:}1{:}b{:}3$, where b was a free-fitting parameter. As well, the fit to a doublet yielded anomalously broad lines (~0.47 mm/s FWHM at room temperature) and this width was found to be temperature dependent.

Results of the computer fits to Lorentzian sextets for the three spectra are given in Table I (method 1). The following observations can be made on the basis of these results: The isomer shift becomes less positive with increasing temperature as is expected on the basis of the second-order doppler effect. The room-temperature isomer shift, however, does not seem to be a function of applied field. The value of b changes slightly between 110 and 293 K indicating a partial realignment of domains. This effect is commonly observed in amorphous materials[24] and results from thermally induced strains in the sample. This effect is highly dependent on the method of mounting the sample (in this case on cellophane tape). The introduction of a magnetic field in the plane on the ribbons significantly increases b, indicating a partial alignment of the domains by the external magnetic field. On the basis of coercive forces in excess of 2 kOe reported by Tsai *et al.*[10] for a similar alloy, it is not surprising that the domain alignment is not complete ($b=4$). The linewidth, as expected, is independent of both temperature and applied field. The linewidth values obtained here, ~0.37 mm/s, are essentially identical to those typically observed for fits to the asymmetric Lorentzian doublets seen in Fe Mössbauer spectra of paramagnetic Al-based quasicrystals. This excess linewidth is undoubtedly due to a distribution of Fe sites within the icosahedral structure. The details of such distributions in paramagnetic quasicrystals has been somewhat controversial (Refs. 3, 5, 18, and 19–22). However, the linewidths obtained from the Lorentzian sextet fits to the present spectra indicate that this ferromagnetic quasicrystal has a degree of Fe site disorder which is consistent with that seen in paramagnetic icosahedral alloys. The change in the hyperfine field observed here between 110 and 293 K is consistent with a value of the Curie temperature T_C in the neighborhood of 500 K, as has been reported for similar quasicrystals by Tsai *et al.*[10] The observed increase in the room temperature H with the application of an external magnetic field shows that the sign of the field is positive. This is in contrast to the sign of the Fe field in α-Fe but is the same as that found in many Heusler alloys[25] where the ferromagnetic order is also the result of Mn-Mn coupling. Finally, the quadrupole splitting observed in all of these fits is essentially zero.

We have, as well, fitted these spectra to a distribution of hyperfine fields, $P(H)$, using the method of LeCaer and Dubois[26] (method 2). This method makes no *a priori* assumptions concerning the functional form of $P(H)$. In or-

TABLE I. ^{57}Fe Mössbauer-effect parameters for icosahedral $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$. Method 1 is a fit to a Lorentzian sextet and method 2 is a fit using the method of LeCaer and Dubois (Ref. 26). H_a is the externally applied magnetic field. The isomer shift δ is measured relative to room temperature α-Fe and for method 2 is δ_0 from Eq. (1). b is the relative spectral line amplitudes given by $3{:}b{:}1{:}1{:}b{:}3$, Γ is the FWHM of the Lorentzian lines. For method 2 the FWHM was fixed to the intrinsic Fe linewidth for our spectrometer, 0.24 mm/s. H for method 2 is the mean hyperfine field given by $P(H)$. The quadrupole splitting Δ is given as $\Delta=[(L_6-L_5)-(L_2-L_1)]/4$. Misfit is defined in Ref. 23. All velocities are in mm/s and are ± 0.01 mm/s, and α is given in mm/(s kOe).

Method	T (K)	H_a (kOe)	δ	b	Γ	α	H (kOe)	Δ	Misfit
1	110	0	+0.335	1.98	0.367	· · ·	17.4	−0.005	1.84
	293	0	+0.252	1.60	0.374	· · ·	15.9	−0.007	0.52
	293	4.8	+0.254	2.42	0.363	· · ·	17.2	−0.002	1.52
2	110	0	+0.328	1.97	0.24	+0.007	18.8	−0.005	1.33
	293	0	+0.243	1.59	0.24	−0.003	17.4	−0.006	0.49
	293	4.8	+0.255	2.41	0.24	+0.01	18.9	+0.003	1.24

der to account for any possible spectral asymmetry we have, in the application of this method, included a correlation between hyperfine splitting H and the isomer shift δ of the form

$$\delta(H) = \delta_0 + \alpha H . \quad (1)$$

The parameters resulting from these fits are given in Table I. The hyperfine-field distributions observed for the room-temperature spectra are illustrated in Fig. 3. The $P(H)$ obtained at 110 K is of the same general form as the zero field $P(H)$ obtained at 293 K. Values of δ_0 obtained here are in agreement with the average values found using method 1. This is expected on the basis of the reasonably symmetric spectra and the corresponding small values (essentially zero) for the parameter α. Asymmetry indicating both positive and negative, as well as zero, values of α has been seen in the Fe Mössbauer spectra of Al-based quasicrystals,[20,27] showing that particular values of α are not an intrinsic property of the quasicrystalline structure. In the present case, the fitted values of α are zero to within the anticipated accuracy of these measurements. Values of the parameter b obtained from method 2 for each spectrum are consistent with those values found using method 1. Although the mean values of H found using method 2 are higher than the average values obtained with fitting method 1, they are systematically so, and the resulting H values follow the same trends as a function of both temperature and applied field. Again, this fitting method gives a quadrupole splitting of, essentially, zero. As we might anticipate, the misfit for the fits to a distribution of hyperfine fields is, for each spectrum, somewhat lower than that for the fit to a simple Lorentzian sextet. The $P(H)$ observed at room temperature as a function of applied field, as illustrated in Fig. 3, shows a well-defined shift to higher H. This is consistent with the conclusion based on fits using method 1 that the internal Fe hyperfine field is positive.

On the basis of the measured magnitude of the Fe hyperfine field, ~ 17 kOe, and the usual relationship for Fe magnetic moment of 150 kOe/μ_B, the present measurements suggest an average Fe magnetic moment of $0.11\mu_B$. The bulk magnetization measurements on the closely related icosahedral alloy $Al_{40}Mn_{25}Cu_{10}Ge_{25}$ by Tsai *et al.*[10] give an average Mn moment in the neighborhood of $0.06\mu_B$. While the small average Fe moment, as indicated by the present Mössbauer measurements, does not necessitate a correspondingly small average Mn moment, it is certainly consistent with it. It is, on the other hand, not uncommon for transferred Fe hyperfine fields to be fairly small in systems which order ferromagnetically as a result of large ferromagnetically coupled Mn moments (e.g., Ref. 25). In the present case, however, the average Mn moment appears, on the basis of magnetization measurements, to be very small. This is true not only in the related Al-Mn-Ge and Al-Mn-Cu-Ge alloys reported by Tsai *et al.*,[10] but in ferromagnetic Al-Mn-Si alloys reported by Dunlap *et al.*[9] as well. The reason for the relatively high values of T_C in alloys which show such small average magnetic moments remains, at present, unknown.

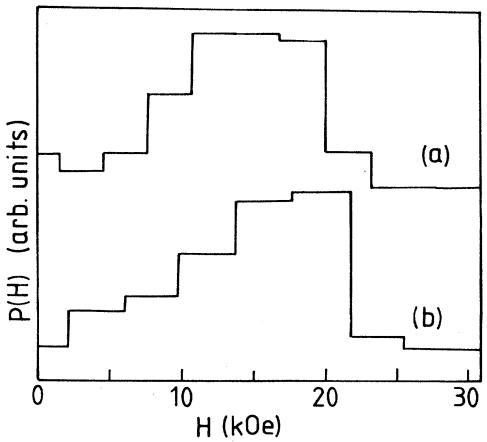

FIG. 3. ^{57}Fe hyperfine-field distributions for $Al_{40}Mn_{25}Fe_3Cu_7Ge_{25}$ as obtained by the method of Ref. 26 (method 2) at room temperature for (a) zero external magnetic field and (b) an external magnetic field of 4.8 kOe.

The present Mössbauer measurements are consistent with the interpretation that these unusual magnetic properties are intrinsic properties of ferromagnetic quasicrystals rather than, for example, the result of a small quantity of crystalline precipitate. The fact that the present Mössbauer measurements are probing inherent properties of the same phase which exhibits, in magnetization measurements, an ordering of the Mn moments, is further evidenced by a consistent picture of the magnetic hardness in the magnetization measurements by the large coercivity and in the Mössbauer measurements by the difficulty in forcing $b = 4$ in applied field. A possible interpretation of the above facts along with the data of Table I, which shows that less than half of the applied field is actually seen at the Fe nuclei, is that the apparent small average Mn moment results from a magnetic alignment which is not true collinear ferromagnetism. In this context, it is interesting to note that these systems show relatively large effective moments [$\sim 1.3\mu_B$ in Al-Mn-Si (Ref. 7) and up to $2.2\mu_B$ in Al-Mn-Ge (Ref. 28)] for stoichiometries which are paramagnetic. This suggests as well the possibility that the ferromagnetism is highly itinerant.

In conclusion, the present Fe Mössbauer measurements are consistent with the previously reported novel magnetic properties of quasicrystalline ferromagnets, and emphasize the fact that considerable work is still necessary for a full understanding of the magnetic properties of these materials.

ACKNOWLEDGMENTS

The authors are grateful to Dr. R. C. O'Handley and Dr. M. E. McHenry for numerous helpful comments and suggestions during the course of this work. This research was funded by grants from the Natural Sciences and Engineering Research Council of Canada.

[1]D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **54**, 1951 (1984).
[2]J. J. Hauser, H. S. Chen, and J. V. Waszczak, Phys. Rev. B **33**, 3577 (1986).
[3]M. Eibschutz, M. E. Lines, H. S. Chen, J. V. Waszczak, G. Papaefthymiou, and R. B. Frankel, Phys. Rev. Lett. **59**, 2443 (1987).
[4]K. Fukamichi, T. Goto, T. Masumoto, T. Sakakibara, M. Oguchi, and S. Todo, J. Phys. F **17**, 743 (1987).
[5]Z. M. Stadnik, G. Stroink, H. Ha, and G. Williams, Phys. Rev. B **39**, 9797 (1989).
[6]M. E. McHenry, V. Srinivas, D. Bahadur, R. C. O'Handley, D. J. Lloyd, and R. A. Dunlap, Phys. Rev. B **39**, 3611 (1989).
[7]M. E. McHenry, R. A. Dunlap, R. Chatterjee, A. Chow, and R. C. O'Handley, J. Appl. Phys. **63**, 4255 (1988).
[8]J. G. Zhao, L. Y. Yang, Q. Fu, and H. Q. Guo (unpublished).
[9]R. A. Dunlap, M. E. McHenry, V. Srinivas, D. Bahadur, and R. C. O'Handley, Phys. Rev. B **39**, 4808 (1989).
[10]A. P. Tsai, A. Inoue, T. Masumoto, and N. Kataoka, Jpn. J. Appl. Phys. **27**, L2252 (1988).
[11]M. A. Marcus, Phys. Rev. B **34**, 5981 (1986).
[12]A. P. Smith and N. W. Ashcroft, Phys. Rev. Lett. **59**, 1365 (1987).
[13]M. E. McHenry and R. C. O'Handley, Mater. Sci. Eng. **99**, 377 (1988).
[14]M. E. McHenry, R. C. O'Handley, W. Dmowski, and T. Egami, J. Appl. Phys. **61**, 4232 (1987).
[15]M. E. McHenry, M. E. Eberhart, R. C. O'Handley, and K. H. Johnson, Phys. Rev. Lett. **56**, 81 (1986).
[16]P. A. Bancel, P. A. Heiney, P. W. Stephens, A. I. Goldman, and P. M. Horn, Phys. Rev. Lett. **54**, 2522 (1985).
[17]V. Elser, Phys. Rev. B **32**, 4892 (1985).
[18]R. A. Dunlap, D. W. Lawther, and D. J. Lloyd, Phys. Rev. B **38**, 3649 (1988).
[19]L. J. Swartzendruber, D. Shechtman, L. Bendersky, and J. W. Cahn, Phys. Rev. B **32**, 1383 (1986).
[20]Z. M. Stadnik and G. Stroink, Phys. Rev. B **38**, 10447 (1988).
[21]V. Srinivas, R. A. Dunlap, D. Bahadur, and E. Dunlap (unpublished).
[22]M. Eibschutz, H. S. Chen, and J. J. Hauser, Phys. Rev. Lett. **53**, 169 (1986).
[23]S. Ruby, Mössbauer Effect Methodology **8**, 263 (1973).
[24]R. A. Dunlap and G. Stroink, J. Phys. F **14**, 3083 (1984).
[25]G. R. MacKay, Ph.D. thesis, Dalhousie University, 1984 (unpublished).
[26]G. LeCaer and M. Dubois, J. Phys. E **12**, 1083 (1979).
[27]R. A. Dunlap, V. Srinivas, and M. E. McHenry (unpublished).
[28]M. E. McHenry, V. Srinivas, and R. A. Dunlap (unpublished).