Magnetic properties of icosahedral Al-Mo-Fe and Al-Ta-Fe alloys

V. Srinivas
Deparment of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5

M. E. McHenry
MST-6, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

R. A. Dunlap
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5
(Received 27 April 1989)

Single-phase icosahedral quasicrystals of the composition $Al_{80}Mo_9Fe_{11}$ and $Al_{70}Ta_{10}Fe_{20}$ have been prepared by rapid quenching from the melt. X-ray-diffraction measurements have yielded quasilattice constants of 4.600 ± 0.003 Å for both alloys. Room-temperature ^{57}Fe Mössbauer-effect measurements show a nearly symmetric doublet in Al-Mo-Fe and an asymmetric doublet in Al-Ta-Fe. These results are analyzed in terms of various distributions of Fe quadrupole splittings. Magnetization measurements for both alloys show a magnetization that exhibits Curie paramagnetism at low temperatures ($T \lesssim 100$ K) and Pauli paramagnetism at higher temperatures. These results show a localized Fe moment of $0.19\mu_B$ in Al-Mo-Fe and $0.48\mu_B$ in Al-Ta-Fe.

I. INTRODUCTION

The existence of icosahedral quasicrystals was first demonstrated experimentally in the Al-Mn system by Shechtman *et al.*[1] Since then, quasicrystallinity has been found in a wide variety of alloy systems. The existence of an icosahedral phase in binary Al–transition-metal alloys (Al-TM) has been studied extensively. For example, Dunlap *et al.*[2] have investigated the Al-Fe system and have found that although an icosahedral phase forms, the alloys are not single phased and are not well ordered. Similar results have been found for other Al-TM systems.[3] Among Al-TM systems, Al-Cr and Al-Mn form the purest, best-ordered quasicrystals. It is now clearly established that transition-metal sites of different sizes exist in these structures[4–6] and that $3d$ elements too far either side of Mn are either too large or too small to be readily accommodated in all sites. The details of this site distribution, both from a magnetic and from a size standpoint,[7] are not yet clear. Thus, pseudobinary alloys containing two transition metals, one from the left of Mn and one from the right of Mn, have been found to yield particularly stable, well-ordered, single-phase icosahedral alloys.[7] Two alloys of interest which fall into this general category are $Al_{80}Mo_9Fe_{11}$ (Ref. 8) and $Al_{70}Ta_{10}Fe_{20}$.[9] In the present work, we have investigated structural and magnetic properties of these alloys using x-ray diffraction, Mössbauer spectroscopy, and SQUID (superconducting quantum-interference device) magnetization measurements. The study provided the first report of Pauli paramagnetization in a quasicrystalline alloy. This is of particular importance in the context of the recent suggestion[10] that ferromagnetic quasicrystals may be very weak itinerant ferromagnets.

II. EXPERIMENTAL METHODS

Single-phase quasicrystals of the compositions $Al_{80}Mo_9Fe_{11}$ and $Al_{70}Ta_{10}Fe_{20}$ were prepared by quenching from the melt onto the surface of a single copper roller with a surface velocity of ~ 60 m/s. Cu $K\alpha$ x-ray diffraction patterns obtained on a Siemens scanning powder diffractometer showed both alloys to be well-ordered single-phase icosahedral quasicrystals, as reported in the literature,[8,9] with quasilattice constants[11] of 4.603 Å (Al-Mo-Fe) and 4.597 Å (Al-Ta-Fe).

Room-temperature ^{57}Fe Mössbauer-effect measurements were made on a Wissel System II Mössbauer spectrometer using a Pd^{57}Co source. The intrinsic spectrometer linewidth was found to be 0.23 mm/s (FWHM) for α-Fe. Magnetization measurements were made using a SHE-VTS-905 SQUID magnetometer in external fields of up to 10 kOe.

III. RESULTS

Room-temperature ^{57}Fe Mössbauer spectra of icosahedral $Al_{80}Mo_9Fe_{11}$ and $Al_{70}Ta_{10}Fe_{20}$ are illustrated in Fig. 1. To obtain average values of the isomer shift and quadrupole splitting, these spectra were fitted to asymmetric Lorentzian doublets. Parameters obtained from these fits are given in Table I. The solid lines in Fig. 1

TABLE I. Room-temperature ^{57}Fe Mössbauer-effect parameters obtained from fits to an asymmetric Lorentzian doublet.

Alloy	δ (mm/s)	Δ (mm/s)	Γ_1 (mm/s)	Γ_2 (mm/s)	A_1/A_2
$Al_{80}Mo_9Fe_{11}$	+0.274	0.483	0.397	0.399	1.006
$Al_{70}Ta_{10}Fe_{20}$	+0.216	0.447	0.433	0.371	0.948

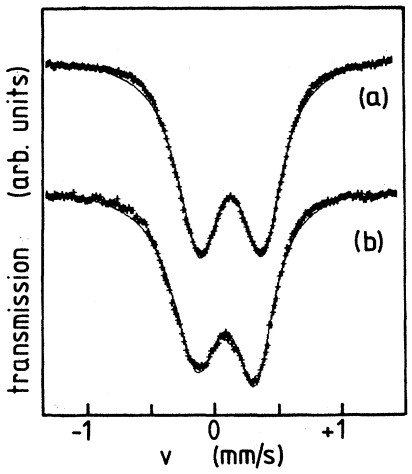

FIG. 1. Room-temperature ^{57}Fe Mössbauer-effect spectra of (a) $Al_{80}Mo_9Fe_{11}$ and (b) $Al_{70}Ta_{10}Fe_{20}$. Solid lines are fits to asymmetric doublets.

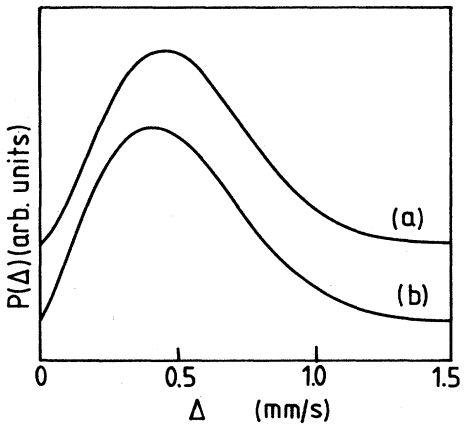

FIG. 2. $P(\Delta)$ obtained for the Gaussian distribution [Eq. (1)] for (a) $Al_{80}Mo_9Fe_{11}$ and (b) $Al_{70}Ta_{10}Fe_{20}$.

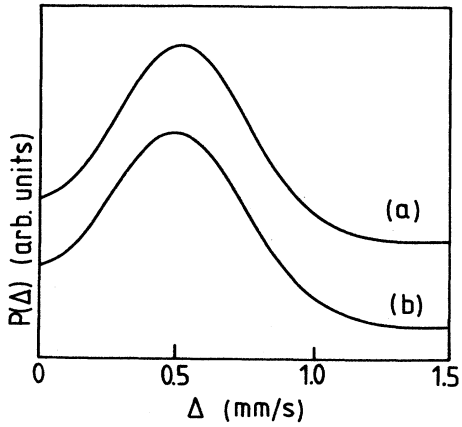

FIG. 3. $P(\Delta)$ obtained for the shell-model distribution [Eq. (3)] for (a) $Al_{80}Mo_9Fe_{11}$ and (b) $Al_{70}Ta_{10}Fe_{20}$.

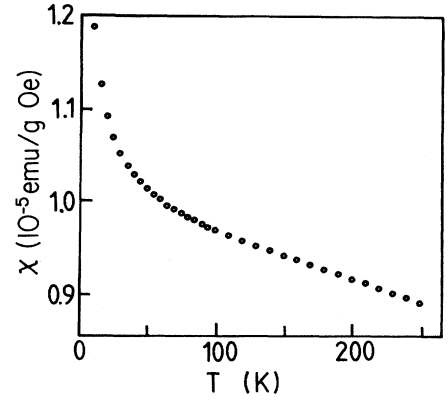

FIG. 4. Susceptibility as a function of temperature obtained in an applied field of 10 kOe for $Al_{80}Mo_9Fe_{11}$.

show these fitted curves. As is generally the case in icosahedral alloys, we observe the following: (1) The fitted line widths Γ_i are much greater than the intrinsic ^{57}Fe linewidth, and (2) a significant misfit occurs in the wings of the spectra. Both of these features are clear evidence that there is a distribution of quadrupole splitting present in these alloys. A number of different approaches have been taken concerning the quarupole distributions in icosahedral alloys.[12–16] In order to compare the present Mössbauer spectra, we have chosen two methods[17] which have been used with some success previously. These are as follows.

(1) The first method is a Gaussian distribution of quadrupole splittings Δ of the form

$$P(\Delta)=\frac{1}{\sqrt{2\pi}}\{\exp[-\ln 2(\Delta-\Delta_0)^2/\sigma_g^2] + \exp[-\ln 2(\Delta+\Delta_0)^2/\sigma_g^2]\}\ , \quad (1)$$

where Δ_0 is the most probable splitting and σ_g is the full width (FWHM) of the distribution. The linewidth of the

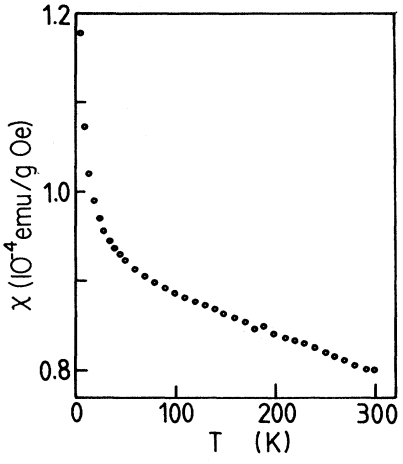

FIG. 5. Susceptibility as a function of temperature obtained in an applied field of 10 kOe for $Al_{70}Ta_{10}Fe_{20}$.

TABLE II. Room-temperature ^{57}Fe Mössbauer-effect parameters obtained from a fit to a Gaussian distribution of quadrupole splittings as described in the text.

Alloy	δ_0 (mm/s)	Δ_0 (mm/s)	σ (mm/s)	α
$Al_{80}Mo_9Fe_{11}$	+0.274	0.485	0.546	+0.003
$Al_{70}Ta_{10}Fe_{20}$	+0.237	0.465	0.568	−0.051

component spectra was fixed to be intrinsic α-Fe linewidth. In order to account for the spectral asymmetry, we have expressed the correlation between the isomer shift and the quadrupole splitting as

$$\delta(\Delta)=\delta_0+\alpha\Delta \ . \tag{2}$$

(2) The second method is a shell distribution[18] of the form

$$P(\Delta)\propto(\Delta/\sigma_s)^n\exp(-\Delta^2/2\sigma_s^2) \ , \tag{3}$$

where n and σ_s are fitted parameters. A correlation between isomer shift and quadrupole splitting, as given in Eq. (2), was used in this case also.

Table II gives the parameters obtained from the Gaussian distribution. The resulting $P(\Delta)$ for the two alloys studied here are shown in Fig. 2. The fitting parameters obtained from the shell-model distribution are given in Table III, and the resulting $P(\Delta)$ are illustrated in Fig. 3. Both of these fits show an improvement in the quality of fit over the asymmetric doublet, although there is no significant difference between the two different distributions.

Susceptibility versus temperature curves for the Al-Mo-Fe and Al-Ta-Fe alloys are shown in Figs. 4 and 5. These results show Curie-like behavior at temperatures below about 100 K and a linear decrease at higher temperatures. This behavior, as discussed below, is characteristic of the formation of a local magnetic moment as well as Pauli paramagnetism at higher temperatures. These data were fit to a susceptibility of the form

$$\chi(T)=a+bT+c/(T-\Theta) \ , \tag{4}$$

where the constant c is related to the localized moment in Bohr magnetons μ_B as

$$\mu=\left[\frac{3k_BCA}{N_Af\mu_B^2}\right]^{1/2} \ . \tag{5}$$

In Eq. (5) k_B is Boltzmann's constant, A is the atomic weight, N_A is Avagadro's constant, and f the fraction of magnetic atoms. The results of these fits are given in Table IV.

IV. DISCUSSION AND CONCLUSIONS

The anomalous line widths observed for the fits of the Mössbauer spectra to asymmetric doublets indicate that there is a reasonable degree of disorder. In fact, the present line widths indicate that these alloys contain somewhat more intrinsic disorder than, for example, icosahedral Al-Cu-Fe.[14] Although the details of this disorder have been the subject of considerable controversy,[4–7,12–17] we do not believe that Mössbauer spectroscopy, in the case of quasicrystals, provides a definitive method of characterizing this disorder.[17] Computer fits to Fe Mössbauer spectra of quasicrystals using two doublets have typically yielded superior goodness-of-fit measures compared with those fits to a single broadened doublet.[12] While these fits still yield anomalous line widths, there is no reason why these results cannot be interpreted on the basis of two distinct but disordered classes of sites.[17] On the other hand, fits to single-peaked distributions have been used successfully as well,[15,17,19] and fits to distribution which involved no assumed functional form[10,16] have sometimes yielded singly peaked distributions and have sometimes yielded bimodal distributions. The following considerations are of importance in viewing these results. (1) Alloys of different compositions may possess differences in microstructure ranging from minor differences in the degree of disorder to major differences such as different decorations of the Penrose tiles.[20] (2) Differences in sample preparation procedures for alloys of the same nominal composition can yield differences in the degree of disorder.[16] (3) As it is known that Fe substitutes preferentially into certain sites in the icosahedral structure,[5,6] the distribution of Fe site environments should not be interpreted as indicative of the distribution of transition-metal sites in the alloy. Therefore, in the present analysis, we have not attempted to differentiate between the validity of different site distribution models on the basis of the Mössbauer spectra, but rather have used parameters obtained on the basis of different models in a more general way, to characterize these alloys.

While the isomer shifts δ of Fe in Al–transition-metal alloys show a general trend to less positive values with increasing d-electron density,[21] the present results for the

TABLE III. Room-temperature ^{57}Fe Mössbauer-effect parameters obtained from a fit to the shell model, as described in text. n and σ_s are fitted parameters from Eq. (3), and $\bar{\Delta}$ and $\langle\Delta\rangle$ are the resulting most probable splitting and width (FWHM) of the distribution of quadrupole splittings, respectively.

Alloy	δ_0 (mm/s)	n	σ_s (mm/s)	α	$\bar{\Delta}$ (mm/s)	$\langle\Delta\rangle$ (mm/s)
$Al_{80}Mo_9Fe_{11}$	+0.274	1.48	0.351	+0.002	0.444	0.579
$Al_{70}Ta_{10}Fe_{20}$	+0.237	1.14	0.363	−0.051	0.410	0.585

TABLE IV. Results of magnetization measurements of Al-Mo-Fe and Al-Ta-Fe as fit to Eqs. (4) and (5). μ is the average moment per Fe atom.

Alloy	a (emu/g Oe)	b (emu/g Oe K)	c (emu K/g Oe)	$\mu(\mu_B)$	Θ (K)
$Al_{80}Mo_9Fe_{11}$	1.02×10^{-5}	-5.15×10^{-9}	1.4×10^{-5}	0.19	3.9
$Al_{70}Ta_{10}Fe_{20}$	9.28×10^{-5}	-4.32×10^{-8}	1.13×10^{-4}	0.48	2.6

average δ, given in Table I, show the opposite trend. Although similar anomalies have been seen between other alloys containing VIB and VIIB group elements, e.g., Al-Cr and Al-Mn,[13,21] the present isomer-shift variations are no doubt related to differences in Al content and differences in occupied d-orbitals between the Al-Mo-Fe and Al-Ta-Fe alloys. Values of the relative line intensities A_1/A_2 shown in Table I are indicative of the degree of asymmetry of the Mössbauer spectrum. Clearly, the present results indicate a much larger spectral asymmetry for Al-Ta-Fe than for Al-Mo-Fe, and, as well, that these asymmetries are of opposite sign. This is illustrated by the relative sign and magnitude of the parameter α from Eq. (2) given in Tables II and III for both fits to distributions of splittings. The results for Al-Ta-Fe form an interesting contrast with those reported for Mössbauer spectra of Al-Cu-Fe, where α is large but positive.[14] These results clearly indicate that a particular sign or magnitude for the parameter α are not characteristics of quasicrystals. The isomer-shift values, δ_0 from Tables II and III are consistent for the two different distributions. For Al-Mo-Fe, the values of δ_0 are essentually identical to the average isomer-shift values from Table I, as is expected from the corresponding small value of α. For Al-Ta-Fe, the values of δ_0 are significantly larger than the average values as expected for a spectrum which exhibits a large negative α. The width of the distributions, as evidenced by σ for the Gaussian fit and $\langle\Delta\rangle$ for the shell-model fit, are measurably larger for the Al-Ta-Fe alloy than for the Al-Mo-Fe alloy. The value of the exponent n from the shell-model fit, as given in Table III, shows a decrease between Al-Mo-Fe and Al-Ta-Fe. This correlation between n and $\langle\Delta\rangle$ for the shell-model fit has been reported previously in other quasicrystalline alloys,[17] and it has been suggested[17] that this correlation is indicative of the degree of atomic disorder in these alloys.

The magnetization measurements shown in Figs. 4 and 5 are the first instance of combined Curie and Pauli paramagnetization in icosahedral alloys. The related alloy Al-Cu-Fe, in contrast to present results, has recently been shown to be diamagnetic.[19] On the other hand, icosahedral Al-Ce-Fe has been found to order ferromagnetically.[22] In icosahedral Al-Ce-Fe,[22] as well as in the ferromagnetic icosahedral quasicrystals Al-Mn-Si (Ref. 23) and Al-Mn-Cu-Ge,[10,24] it has been suggested that the ferromagnetism is highly iterant. In this context, the observation of Pauli behavior in Al-Mo-Fe and Al-Ta-Fe is particularly significant. As Pauli paramagnetism is indicative of a high density of states (DOS) at the Fermi energy, the significance of differences between the band structure of Al-Mo-Fe and Al-Ta-Fe and that of Al-Cu-Fe is important and is presumably based on the difference between the nearly empty d bands of Mo and Ta in contrast to the filled d bands of Cu. This distinction is presumably responsible, not only for the Pauli behavior at high temperatures, but the formation of a localized Fe moment in Al-Mo-Fe and Al-Ta-Fe, while Al-Cu-Fe remains diamagnetic. In cases where the d-band DOS shows a maximum relative to alloys with fewer or more d electrons than the temperature dependence of the Pauli suspectibility is typically characterized by a negative value of b in Eq. (4).[25] The formation of a local Fe moment has not previously been observed in Al-TM-Fe (TM denotes transition metal) or Al-TM-Fe-M (M denotes metalloid) quasicrystals when TM is a $3d$ metal. The present results are the first reported for Al–TM-Fe alloys with $4d$ or $5d$ transition metals and certainly suggest that Fe moment formation in these alloys is not uncommon. The results in Al-Ce-Fe reported by Zhao *et al.*[22] suggest that this is the case for Al rare-earth Fe quasicrystals as well.

In conclusion, we have presented Fe Mössbauer-effect measurements in two single-phase icosahedral quasicrystals. These have been interpreted in the context of a disordered Fe-site environment. Also, we have reported the first case of observed Pauli paramagnetization in a quasicrystal and have illustrated that this behavior may be related to the weak ferromagnetic behavior recently reported in related icosahedral systems.

ACKNOWLEDGMENTS

The authors are grateful to Dr. E. Dunlap for developing software for the analysis of Mössbauer spectra. This work was supported 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]R. A. Dunlap, D. J. Lloyd, I. A. Christie, G. Stroink, and Z. M. Stadnik, J. Phys. F **18**, 1329 (1988).
[3]P. A. Bancel and P. A. Heiney, Phys. Rev. B **33**, 7917 (1986).
[4]M. E. McHenry, V. Srinivas, D. Bahadur, R. C. O'Handley, D. J. Lloyd, and R. A. Dunlap, Phys. Rev. B **39**, 3611 (1989).
[5]M. Eibschutz, M. E. Lines, H. S. Chen, and J. V. Waszczak (unpublished).
[6]M. Eibschutz, M. E. Lines, H. S. Chen, J. V. Waszczak, G. Papaefthymiou, and R. B. Frankel, Phys. Rev. Lett. **59**, 2443 (1987).
[7]D. W. Lawther, R. A. Dunlap, and V. Srinivas, Can. J. Phys. **67**, 463 (1989).

[8]M. Hui and X. Chen, Solid State Commun. **68**, 813 (1988).
[9]A. P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys. **27**, L5 (1989).
[10]R. A. Dunlap and V. Srinivas, Phys. Rev. B **40**, 704 (1989).
[11]V. Elser, Phys. Rev. B **32**, 4892 (1985).
[12]L. J. Swartzendruber, D. Shechtman, L. Bendersky, and J. W. Cahn, Phys. Rev. B **32**, 1382 (1985).
[13]R. A. Dunlap, D. W. Lawther, and D. J. Lloyd, Phys. Rev. B **38**, 3649 (1988).
[14]Z. M. Stadnik and G. Stroink, Phys. Rev. B **38**, 10 447 (1988).
[15]M. Eibschutz, H. S. Chen, and J. J. Hauser, Phys. Rev. Lett. **56**, 169 (1986).
[16]D. Bahadur, V. Srinivas, and R. A. Dunlap, J. Phys. Condens. Matter **1**, 2561 (1989).
[17]V. Srinivas, R. A. Dunlap, D. Bahadur, and E. Dunlap, Philos. Mag. B (to be published).
[18]G. Czjzek, Phys. Rev. B **25**, 4908 (1982).
[19]Z. M. Stadnik, G. Stroink, H. Ma, and G. Williams, Phys. Rev. B **39**, 9797 (1989).
[20]R. A. Dunlap, R. C. O'Handley, M. E. McHenry, and R. Chatterjee, Phys. Rev. B **37**, 8484 (1988).
[21]R. A. Dunlap, G. Stroink, K. Dini, and D. F. Jones, J. Phys. F **16**, 1247 (1986).
[22]J. G. Zhao, L. Y. Yang, and H. Q. Guo (unpublished).
[23]R. A. Dunlap, M. E. McHenry, V. Srinivas, D. Bahadur, and R. C. O'Handley, Phys. Rev. B **39**, 4808 (1989).
[24]A. P. Tsai, A. Inoue, T. Masumoto, and N. Kataoka, Jpn. J. Appl. Phys. **27**, L2252 (1988).
[25]R. M. White, *The Quantum Theory of Magnetism* (McGraw-Hill, New York, 1970).