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Ferromagnetism in icosahedral Al-Mn-Si alloys

R. A. Dunlap*
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 and Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5

M. E. McHenry†
MST-5, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

V. Srinivas and D. Bahadur‡
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5

R. C. O'Handley
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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Alloys of $Al_{50}Mn_{20}Si_{30}$ and $Al_{55}Mn_{20}Si_{25}$ have been prepared by rapid quenching from the melt onto a single Cu roller. As-quenched alloys have been found to be fully amorphous. This amorphous phase crystallizes at approximately 600 K. Alloys annealed below the crystallization temperature transform into single-phase icosahedral quasicrystals. Both the amorphous and quasicrystalline phases are weakly ferromagnetic with Curie temperatures around 120 K and saturation magnetization in the order of 0.1 emu/g.

I. INTRODUCTION

Since the first report of long-range icosahedral symmetry in rapidly solidified $Al_{86}Mn_{14}$ by Shechtman, Blech, Gratias, and Cahn,[1] similar symmetry has been reported in numerous other alloy systems [e.g., Al-Cu-Li,[2] Pd-U-Si,[3] Ti-Ni-V,[4] Al-Mg-Zn,[5] and Ti-Ni-Fe-Si.[6] Subsequently, single-phase icosahedral quasicrystals have been prepared (e.g., Ref. 7) and recently thermodynamically stable alloys with long-range icosahedral symmetry have been reported.[8,9]

Unlike conventional crystals, quasicrystalline materials show no long-range translational periodicity. Unlike glasses, they show sharp diffraction peaks indicating long-range orientational ordering. Structural models of quasicrystals are typically based on either a three-dimensional Penrose tiling,[10] a distortion of analogous crystalline structures (e.g., α-Al-Mn-Si),[11] or an icosahedral glass.[12]

In general the microscopic details of the atomic arrangement within a quasicrystal are unknown. Drawing analogies to crystalline counterparts has suggested, in the case of Al-Mn-Si, that transition-metal atoms (Mn) do not occupy sites of icosahedral symmetry.[13] While an increase in the Mn moment observed between the crystalline and quasicrystalline phases of Al-Mn-Si has cast some doubt on this interpretation,[14] Mössbauer measurements of Fe-doped samples have suggested that Fe, at least, occupies sites of lower symmetry (e.g., Ref. 15). Ti-Ni-V and Ti-Ni-Fe-Si alloys have, on the other hand, shown evidence of transition-metal sites with local icosahedral symmetry.[4,6,16,17]

While careful theoretical work has been reported[18,19] on the effects of icosahedral symmetry on magnetic-moment formation, the absence of experimental data has resulted from the inability to produce a ferromagnetically ordered quasicrystal. Previous comparisons[20] have considered the properties of crystalline materials with local icosahedral symmetry, e.g., Frank-Kasper phases.[21] In the present work, we report the formation of the first single-phase icosahedral quasicrystals, $Al_{50}Mn_{20}Si_{30}$ and $Al_{55}Mn_{20}Si_{25}$, which show ferromagnetic ordering.

II. EXPERIMENTAL METHODS

Samples of $Al_{50}Mn_{20}Si_{30}$ and $Al_{55}Mn_{20}Si_{25}$ were prepared by arc melting high-purity elemental components followed by melt spinning onto the surface of a single Cu roller. The surface velocity of the roller was ~60 m/s. Further details of the sample preparation have been given previously.[22] Resulting ribbons were shown to be fully amorphous, as indicated by the typical x-ray diffraction scan shown in Fig. 1(a).

Differential scanning calorimetry (DSC) measurements performed at a heating rate of 20 K/min are illustrated in Fig. 2. On the basis of calorimetry measurements, we chose to anneal the samples in argon at a temperature about 25 K below the main crystallization exotherm. The $Al_{50}Mn_{20}Si_{30}$ sample was annealed at 648 K for 90 min

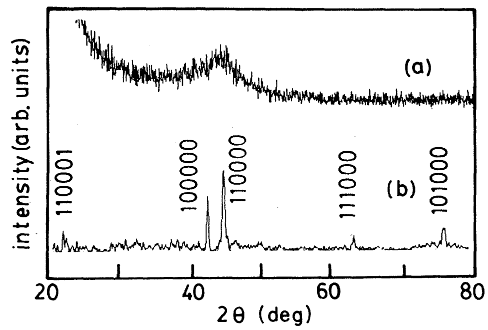

FIG. 1. Cu $K\alpha$ x-ray diffraction scans of $Al_{50}Mn_{20}Si_{30}$ (a) as-quenched (amorphous) and (b) annealed (icosahedral) as described in the text. Icosahedral diffraction peaks are indexed as described in the text.

and the $Al_{55}Mn_{20}Si_{25}$ sample was annealed at 623 K for 45 min. Resulting annealed samples were found to be single-phase icosahedral structures, as illustrated by the x-ray diffraction scan in Fig. 1(b). Peaks are indexed in the figure according to the scheme of Bancel *et al.*[23]

Magnetization measurements were performed on as-quenched amorphous alloys and annealed icosahedral alloys using a SHE superconducting quantum interference device magnetometer.

III. RESULTS

Results of x-ray diffraction measurements of the icosahedral phase are summarized in Table I. Values of the quasilattice constant[24,25] have been found from the data in Table I to be 0.4580 ± 0.0003 nm for both alloys studied here. This is only 0.65% smaller than the value of 0.461 nm reported for $Al_{74}Mn_{20}Si_6$.[24,25]

The differential-thermal-analysis (DTA) scan of amorphous $Al_{50}Mn_{20}Si_{30}$ is consistent with that obtained by

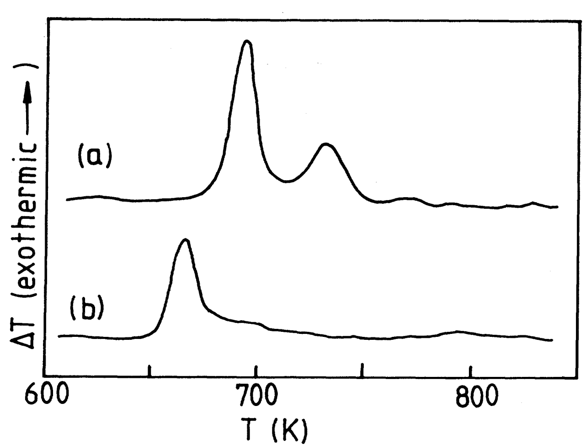

FIG. 2. DSC results obtained at a heating rate of 20 K/min for (a) amorphous $Al_{50}Mn_{20}Si_{30}$ and (b) amorphous $Al_{55}Mn_{20}Si_{25}$.

TABLE I. Major x-ray diffraction peak positions and intensities for the icosahedral phase of $Al_{50}Mn_{20}Si_{30}$ and $Al_{55}Mn_{20}Si_{25}$. Indices are given according to the scheme of Bancel *et al.* (Ref. 23).

Reflection	$Al_{50}Mn_{20}Si_{30}$ q (nm^{-1})	$Al_{50}Mn_{20}Si_{30}$ I(relative)	$Al_{55}Mn_{20}Si_{25}$ q (nm^{-1})	$Al_{55}Mn_{20}Si_{25}$ I(relative)
110001	15.46	26	15.41	23
100000	29.22	67	29.20	67
110000	30.69	100	30.68	100
111000	42.37	17	42.43	8
101000	49.72	27	49.61	23

Inoue, Bizen, and Masumoto[26] for the same alloy, and shows two exothermic peaks. Onset temperatures for the peaks are slightly shifted with respect to those of Inoue *et al.*,[26] being 676 and 720 K in the present work and 640 and 738 K in the previous work. Inoue *et al.*[26] have identified the larger (lower temperature) exotherm with an amorphous to quasicrystalline transition, and the smaller (higher temperature) exotherms with a quasicrystalline to crystalline transition. DSC measurements indicate an enthalpy associated with the larger peak of 20.0 J/g and with the smaller peak 3.6 J/g. The ratio of these two values, 5.6, is somewhat larger than the value of 3.6 obtained by Inoue *et al.*,[26] but is consistent with their interpretation that the internal energy of the quasicrystalline phase is closer to that of the crystalline phase than to that of the amorphous phase. While Inoue *et al.*[26] have annealed their sample of amorphous $Al_{50}Mn_{20}Si_{30}$ for a short period of time, 5*s*, at a temperature between the two exothermic peaks, we have produced a quasicrystalline phase with sharper diffraction peaks by annealing just below the crystallization temperature for an extended period.

The DTA of $Al_{55}Mn_{20}Si_{25}$ shows only a single exothermic peak with an onset at 650 K and does not permit us to distinguish between the amorphous to quasicrystalline and the quasicrystalline to crystalline transitions. Annealing just below the temperature of the exotherm has yielded a single-phase quasicrystal. It is interesting to note, as well, that quenching at a rate slightly lower than that used to prepare the amorphous phase has also yielded the quasicrystalline phase but, in this case, the x-ray diffraction peaks are somewhat broader and a minor crystalline impurity phase is present.

Magnetization measurements of both amorphous and both icosahedral samples indicated that they are ferromagnetic at low temperatures. A typical magnetization curve for the icosahedral phase at 10 K is illustrated in Fig. 3. The curve shows a partial saturation at about 500 Oe but exhibits a significant paramagnetic component at higher applied fields. The low-field behavior is illustrated in Fig. 4. There is measurable hysteresis with a remanence, M_r, of about 0.03 emu/g, or about 10% of the saturation value.

Values of the spontaneous magnetization and the Curie temperature are given for both alloys in Table II. Also listed are the ferromagnetic moment, μ_f, per Mn atom, based on the values of M_s and the paramagnetic moment,

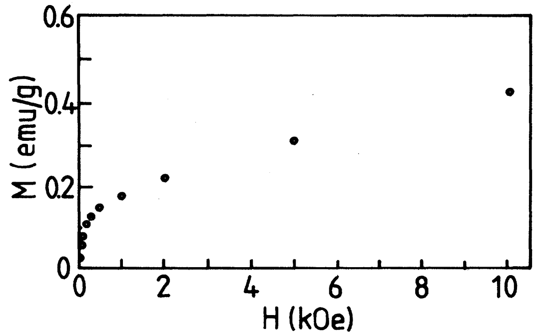

FIG. 3. First quadrant M-H curve for icosahedral $Al_{55}Mn_{20}Si_{25}$ at 10 K.

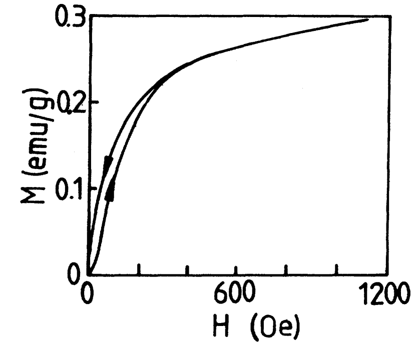

FIG. 4. Low-field magnetization curve at 10 K for icosahedral $Al_{50}Mn_{20}Si_{25}$. As indicated by the arrows, the figure shows the initial magnetization curve and the remanent curve.

μ_p, per Mn based on a Curie law for the paramagnetic susceptibility, $\chi(T)$, of the form

$$\chi(T) = \frac{\mu_B \mu_p^2}{3k_B T}, \quad (1)$$

where the effective paramagnetic moment is measured in units of μ_B. Values of $\chi(T)$ for the paramagnetic component were calculated by subtracting a spin $\frac{5}{2}$ Brillouin function for the measured M_s values from the $M(T)$ data obtained in an applied field of 10 kG (Fig. 5). We note the presence of ferromagnetic and paramagnetic contributions in this typical high-field curve. Resulting values of the effective paramagnetic moment are substantially less than the value of $\sim 1.3\mu_B$ typically found in icosahedral $Al_{74}Mn_{20}Si_6$ (e.g., Ref. 14), and suggest either that only a small fraction of the Mn atoms carry paramagnetic moments or that these moments are drastically reduced as a result of the increased Si content of the alloys.

Magnetization curves of the amorphous alloys showed ferromagnetic behavior with Curie temperatures which were slightly lower than those of the corresponding icosahedral phase. Typical magnetization versus temperature curves for the amorphous alloys are shown in Fig. 6. For a similar amorphous alloy, $Al_{50}Mn_{20}Si_{30}$, Hauser, Chen, and Waszczak[27] have reported a value of $T_c = 120$ K. The present results are in good agreement with this previous value for amorphous Al-Mn-Si. The amorphous alloys show purely weak ferromagnetic behavior without the additional paramagnetic phase observed in the icosahedral alloys at low temperatures in large applied fields. We note that the upturn in M at low temperatures is easily observed for the icosahedral alloy in applied fields of ~ 100 Oe but, as illustrated in Fig. 6, is not found in the magnetization curve of the amorphous alloy.

IV. DISCUSSION

The present results are, to our knowledge, the first report of an icosahedral quasicrystal exhibiting ferromagnetic ordering. The alloys investigated here are distinguished from Al-Mn-Si alloys showing paramagnetic and spin-glass behavior by the presence of a higher Si content (at the expense of the Al content). This alloy, and the commonly studied $Al_{74}Mn_{20}Si_6$ quasicrystal, which shows a spin-glass transition at about 5 K (e.g., Ref. 13), both contain 20% Mn. The exceptionally small ferromagnetic moment given in Table II, both for the icosahedral and amorphous phases, certainly indicates that only a small fraction of the Mn atoms are contributing to the ferromagnetism. This is consistent with the observation of Hauser *et al.*[27] It is interesting to note that Hauser *et al.*[27] observed ferromagnetism only in melt-spun amorphous alloys of Al-Mn-Si and not in alloys of the same composition which were prepared by sputtering. It is possible that the ferromagnetic properties result from the precipitation of a small quantity of magnetic Mn-rich alloy at the grain boundaries. If such a crystalline phase is responsible, then the proportion of this phase must be very small in order to avoid detection in the x-ray diffraction patterns. This is particularly the case for the amorphous samples. However, the relatively small change in M_s that we observe between the amorphous and icosahedral phases would be surprising if the ferromagnetism were the result of precip-

TABLE II. Magnetic properties of icosahedral and amorphous Al-Mn-Si alloy studies in the present work. Values of μ are per Mn atom.

Alloy	Phase	M_s (emu/g)	T_c (K)	$\mu_F(\mu_B)$	$\mu_p(\mu_B)$
$Al_{50}Mn_{20}Si_{30}$	Icosahedral	0.23	112	0.0069	0.24
	Amorphous	0.12	110	0.0036	···
$Al_{55}Mn_{20}Si_{25}$	Icosahedral	0.18	115	0.0054	0.32
	Amorphous	0.062	107	0.0016	···

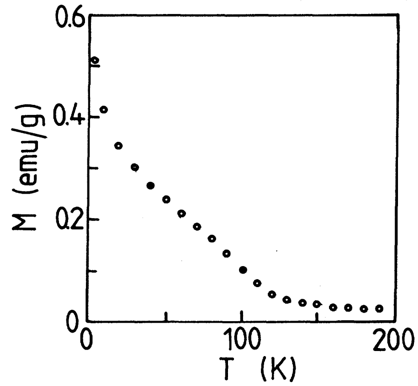

FIG. 5. Magnetization vs temperature obtained in an applied field of 10 kOe for icosahedral $Al_{55}Mn_{20}Si_{25}$.

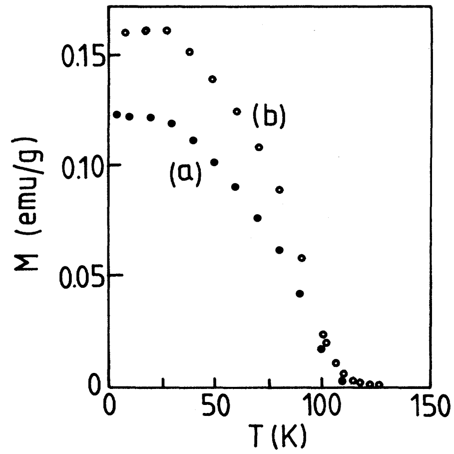

FIG. 6. Magnetization vs temperature curves for amorphous $Al_{55}Mn_{20}Si_{25}$ using applied fields of (a) 50 Oe and (b) 100 Oe.

itates at grain boundaries rather than being an intrinsic property of the microstructure of these alloys. At present, the relationship between the ferromagnetic properties and the icosahedral and amorphous phases remain unclear. Hauser *et al.*[27] suggested the possibility that Heusler-like ordering in amorphous Al-Mn-Si is responsible for the ferromagnetism. It seems, however, unlikely that Al would be suitable to fill the role of the late transition-metal alloy present in a conventional Heusler alloy.

In conclusion, we have found that amorphous and icosahedral alloys of $Al_{55}Mn_{20}Si_{25}$ and $Al_{50}Mn_{20}Si_{30}$ show ferromagnetic ordering below 115 K, although the details of the relationship of this ordering to the amorphous and icosahedral structures is yet to be determined.

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*Permanent address: Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5.

†Present address: MST-5, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

‡Permanent address: Advanced Center for Materials Science, Indian Institute of Technology, Kanpur, India 208016.

[1]D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2]W. A. Knapp and D. M. Follstadt, Phys. Rev. Lett. **55**, 1591 (1985).

[3]S. J. Poon, A. J. Drehman, and K. R. Lawless, Phys. Rev. Lett. **55**, 2325 (1985).

[4]Z. Zhang, H. R. Ye, and K. H. Kuo, Philos. Mag. A **52**, 149 (1985).

[5]R. Ramachandra Rao and G. Sastry, Pramana **25**, L225 (1985).

[6]R. A. Dunlap. R. C. O'Handley, M. E. McHenry, and R. Chatterjee, Phys. Rev. B **37**, 8484 (1988).

[7]C. H. Chen and H. S. Chen, Phys. Rev. B **33**, 2814 (1986).

[8]W. Ohashi and F. Spaepen, Nature (London) **330**, 555 (1987).

[9]A. P. Tsau, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys. **26**, L1505 (1987).

[10]D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).

[11]P. Guyot and M. Audier, Philos. Mag. B **52**, L15 (1985).

[12]D. Shechtman and I. A. Blech, Metall. Trans. A **16**, 1005 (1985).

[13]V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985).

[14]M. E. McHenry, R. A. Dunlap, R. Chatterjee, A. Chow, and R. C. O'Handley, J. Appl. Phys. **63**, 4255 (1988).

[15]M. Eibschutz, H. S. Chen, and J. J. Hauser, Phys. Rev. Lett. **56**, 169 (1986).

[16]R. A. Dunlap, M. E. McHenry, R. C. O'Handley, D. Bahadur, and V. Srinivas, J. Appl. Phys. **64**, 5956 (1988).

[17]D. Bahadur, V. Srinivas, R. A. Dunlap, R. C. O'Handley, and M. E. McHenry (unpublished).

[18]M. E. McHenry and R. C. O'Handley, Mater. Sci. Eng. **99**, 377 (1988).

[19]M. E. McHenry, M. E. Eberhart, R. C. O'Handley, and K. H. Johnson, Phys. Rev. Lett. **56**, 114 (1986).

[20]M. E. McHenry, R. C. O'Handley, K. Dmowski, and T. Egami, J. Appl. Phys. **61**, 4232 (1987).

[21]F. C. Frank, Proc. R. Soc. London, Ser. A **15**, 43 (1952).

[22]R. A. Dunlap and K. Dini, J. Phys. F **16**, 11 (1986).

[23]P. A. Bancel, P. A. Heiney, P. W. Stephens, A. I. Goldman, and P. M. Horn, Phys. Rev. Lett. **54**, 2522 (1985).

[24]V. Elser, Phys. Rev. B **32**, 4892 (1985).

[25]C. L. Henley and V. Elser, Philos. Mag. B **53**, 159 (1986).

[26]A. Inoue, Y. Bizen, and T. Masumoto, Metall. Trans. A **19**, 383 (1988).

[27]J. J. Hauser, H. S. Chen, and J. V. Waszczak, Phys. Rev. B **33**, 3577 (1986).