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Nonuniform local magnetism in Al-Mn quasicrystals

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The distribution of local magnetism in Al-Mn quasicrystal alloys has been studied by NMR spin-echo techniques. The ^{55}Mn resonance is found to be close to the position observed in nonmagnetic orthorhombic Al_6Mn and α-$Al_{73}Si_{10}Mn_{17}$ despite large paramagnetic susceptibilities in the quasicrystals. Analysis of spectral intensities shows that the paramagnetism is due to a class of Mn sites having local environments which do not occur in the crystals.

Since the initial discovery of icosahedral symmetry in the diffraction patterns of rapidly quenched Al-Mn alloys,[1] attention has been focused primarily on the structure of these unusual materials. There was little indication of interesting electronic properties in the so-called quasicrystals until the recent discovery by Hauser, Waszczak, and Chen[2] that quasicrystalline alloys of the type $Al_{1-x}Mn_x$ and $(AlSi)_{1-x}Mn_x$ show strong Curie-Weiss paramagnetism and, in low fields, spin-glass behavior. In contrast the equilibrum crystalline phases orthorhombic(*o*)-Al_6Mn and α-$Al_{73}Si_{10}Mn_{17}$ exhibit only weak, temperature-independent paramagnetism.[2,3] In quasicrystalline and amorphous alloys the average moment per Mn atom, characterized by an effective number of Bohr magnetons, $\langle p_{\mathrm{eff}}\rangle$, increases systematically with Mn concentration in the range 14–22 at.% Mn. In this paper we describe nuclear magnetic resonance (NMR) results for quasicrystalline alloys which show that the paramagnetism of the quasicrystalline phases is distributed nonuniformly among the Mn sites. In particular, we find a large fraction of Mn sites which are magnetically similar to those in the crystals and carry no moment. The magnetism is provided by a subset of sites having moments substantially larger than the average value $\langle p_{\mathrm{eff}}\rangle$. An increasing proportion of magnetic sites at higher Mn concentrations explains much of the apparent increase in $\langle p_{\mathrm{eff}}\rangle$.

Alloy ribbons with compositions $Al_{86}Mn_{14}$, $Al_{80}Mn_{20}$, $Al_{78}Mn_{22}$, and $Al_{72}Si_6Mn_{22}$ were prepared by spin quenching and gently crushed to form powdered samples of 50–100 mg for NMR studies. Electron diffraction examination of these ribbons revealed the characteristic icosahedral (*i*) symmetry[2] except for $Al_{80}Mn_{20}$ which also contained an appreciable amount of the decagonal "*T*" phase (referred to as *i/T*), and $Al_{78}Mn_{22}$ which was pure *T* phase. A 20-h anneal of an $Al_{86}Mn_{14}$ ribbon at 825 K yielded the orthorhombic phase sample. After crushing the ribbons, we checked the powders by x-ray diffraction to confirm that no phase changes (i.e., recrystallization) occurred during the powdering process. The so-called α phase (α-$Al_{73}Si_{10}Mn_{17}$) (Ref. 4) was prepared as a bulk, polycrystalline ingot and subsequently powdered. NMR spin-echo spectra were obtained by integrating the echo with a boxcar integrator and recording the boxcar output while sweeping the magnetic field. We averaged repeated sweeps to obtain adequate signal-to-noise ratios. For a measurement at 300 K, for example, the data-acquisition time was about 30 h while at 4.2 K, less than an hour was required for typical measurements. All data reported in this paper were obtained using a fixed frequency of 18.3 MHz.

Spin-echo spectra of crystalline and quasicrystalline Al-Mn alloys at 4.2 K are compared in Fig. 1. The spectra show the dominant $m=\pm\frac{1}{2}$ transition of ^{27}Al and, in some cases, the ^{55}Mn resonance at higher field. An underlying quadrupolar satellite structure extends over 4–5 kG. The low-field quadrupolar structure evident in the spectrum of *i*-$Al_{86}Mn_{14}$ and discussed in a previous paper[5] is absent in the quasicrystals having higher Mn content.

The ^{55}Mn resonance is relatively narrow in the crystalline phases, broadens in *i*-$Al_{86}Mn_{14}$, and can be discerned in *i/T*-$Al_{80}Mn_{20}$ and *i*-$Al_{72}Si_6Mn_{22}$ only by the asymmetry of the spectra. While this broadening might be attributed to increased disorder in the local electric field gradient distribution in the higher-Mn-content alloys, it is significant that it correlates with the increasing Curie-Weiss paramagnetism in these alloys. In fact, it is clear from the temperature dependence of the spectra shown in Fig. 2, that the ^{55}Mn line is subject to magnetic broadening at low temperatures. Spectra for *i/T*-$Al_{80}Mn_{20}$ at 4.2, 77, and 300 K show a striking narrowing of the ^{27}Al central line and improved resolution of the ^{55}Mn line which correlates with the strong decrease in susceptibility at higher temperatures. Yasuoka, Soyama, Kimura, and Takeuchi[6] recently reported that the ^{27}Al linewidth scales with the susceptibility in the range 2–160 K although they were unable to resolve the ^{55}Mn resonance at the lower magnetic field they employed. By folding the ^{27}Al spectrum symmetrically about the central transition, we were able to separate the ^{55}Mn spectra at 77 and 300 K [insets, Figs. 2(a) and 2(b)]. These show that the ^{55}Mn linewidth is essentially unchanged above 77 K with a residual linewidth appreciably broader than in the crystalline phases. Thus, after removal of the low-temperature magnetic broadening, there remains evidence of a relatively broad distribution of local electric field gradients in the $Al_{80}Mn_{20}$ quasicrystal. The spectrum of *T*-$Al_{78}Mn_{22}$ at 77 K was found to be similar to that of *i/T*-$Al_{80}Mn_{20}$ but with a somewhat broader ^{55}Mn peak.

The central point of this paper is that the position of the ^{55}Mn resonance is inconsistent with a uniform distribution of local magnetism in the quasicrystals. The ^{55}Mn resonance occurs at essentially the same position in both the

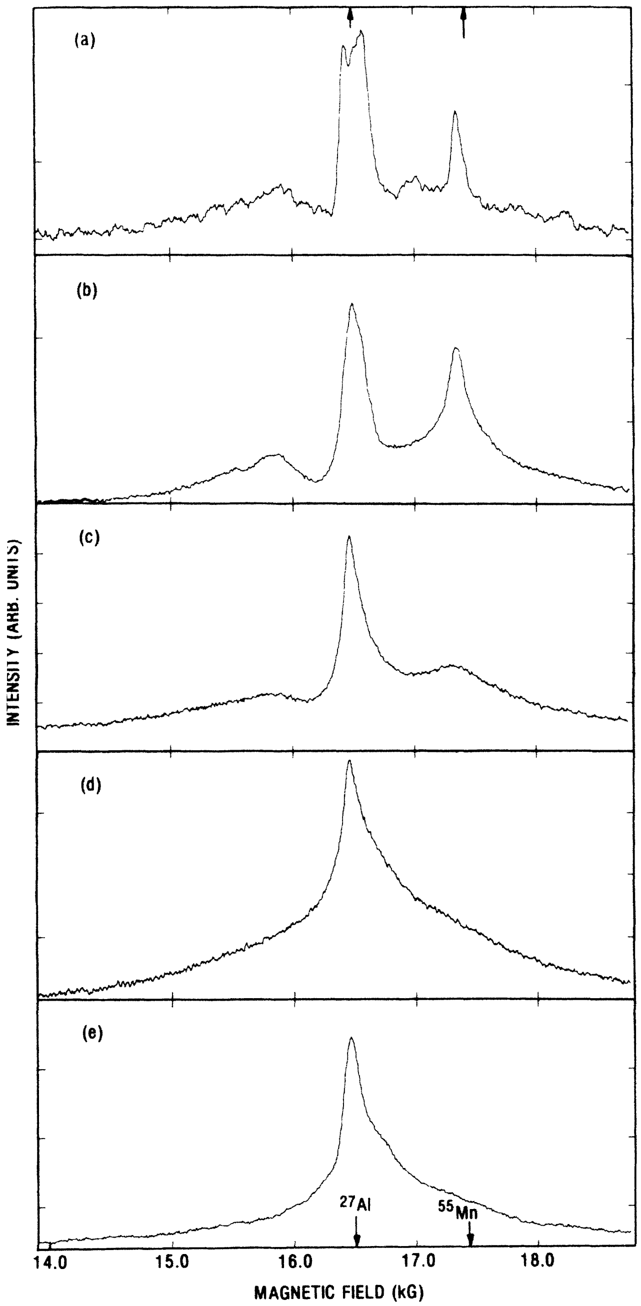

FIG. 1. Field-swept spin-echo spectra obtained at 4.2 K and 18.3 MHz (a) *o*-$Al_{86}Mn_{14}$, (b) α-$Al_{73}Si_{10}Mn_{17}$, (c) *i*-$Al_{86}Mn_{14}$, (d) *i*/*T*-$Al_{80}Mn_{20}$, (e) *i*-$Al_{72}Si_6Mn_{22}$. Arrows indicate reference positions for ^{27}Al and ^{55}Mn resonances.

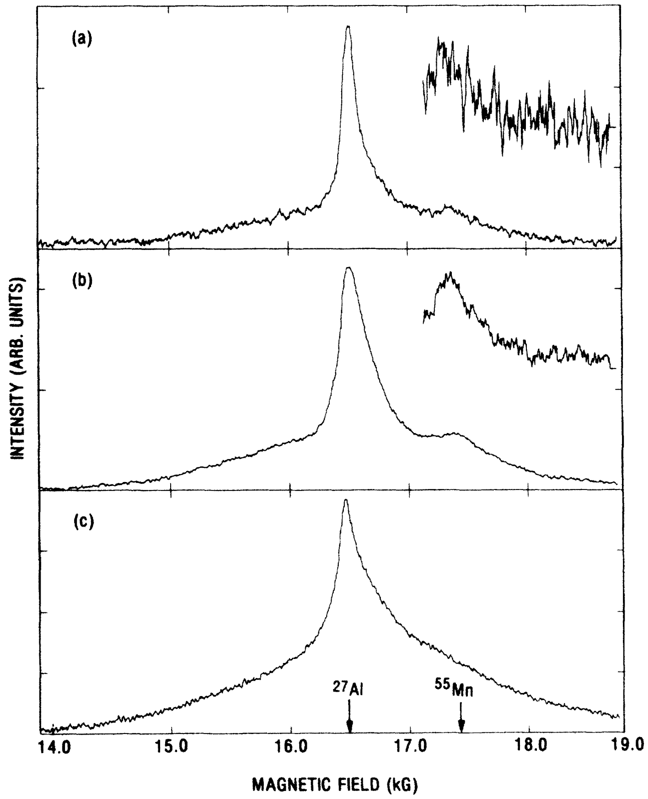

FIG. 2. Spin-echo spectra of *i*/*T*-$Al_{80}Mn_{20}$ at (a) 300 K, (b) 77 K, and (c) 4.2 K. Insets (a) and (b) display deconvolved ^{55}Mn resonance. Arrows have the same meaning as in Fig. 1.

quasicrystals and the nonmagnetic crystalline phases. This corresponds to a positive Knight shift $K \simeq 0.5\%$. In contrast, the measured susceptibilities and typical ^{55}Mn *d*-spin hyperfine field values[7] imply large negative Knight shifts. For example, the resonance in *i*-$Al_{86}Mn_{14}$ would be shifted more than 1 kG for a hyperfine field of ~ -100 kG/μ_B, where μ_B is the Bohr magneton. Now the core-polarization hyperfine field is a local, quasiatomic property determined mainly by the inner-core electronic structure.[8] It maintains a value of roughly -100 kG/μ_B (within about a factor of 2) for ^{55}Mn in a variety of ionic insulators and metallic environments having widely different valence-electron structures.[8,9] There is no reason to expect vanishingly small hyperfine fields in amorphous and quasicrystalline Al-Mn alloys so we are led to conclude that the observed ^{55}Mn NMR signal is due to Mn sites which do not contribute in an essential way to the bulk paramagnetism. The remaining sites must carry local moments which are larger than the average values $\langle p_{\text{eff}} \rangle$ obtained by assuming that all Mn atoms contribute equally to the magnetization. Resonances from these magnetic sites can be expected to be unobservably broad due to rapid nuclear relaxation by the localized electron spin fluctuations. The absence of any observable temperature-dependent shift argues against a linewidth contribution from a distribution of small shifts (weak moments) on the nonmagnetic sites. Rather, the resonance of the observed (nonmagnetic) sites are broadened by indirect interactions with the local moments in a manner analogous to that proposed for the ^{27}Al nuclei in Ref. 6.

The fraction of nonmagnetic Mn sites can be estimated from the relative intensity of the ^{55}Mn and ^{27}Al contributions to the spectra. The accuracy with which this may be done is limited by differences in the spin-echo decay times T_2 and the optimum pulse-width settings at different points in the 5-kG-wide combined spectrum. In addition, some spectra were obtained under conditions in which the narrowest part of the ^{27}Al spectrum was partially saturated. With these limitations, we estimated the intensity ratio $I(^{55}\mathrm{Mn})/I(\mathrm{total})$ to roughly $\pm 10\%$ by integrating separately the ^{55}Mn peak and the combined spectrum. This was done for i-$\mathrm{Al_{86}Mn_{14}}$ at 4.2 K [Fig. 1(a)] and i/T-$\mathrm{Al_{80}Mn_{20}}$ at 77 K [Fig. 2(b)] and 300 K [Fig. 2(a)]. As a check we carried out the same analysis on o-$\mathrm{Al_{86}Mn_{14}}$ for which we expect that all Mn sites contribute to the resonance. We obtained the expected mole fraction within experimental error: $x_{\mathrm{nm}} = 0.15 \pm 0.02$. The result for the quasicrystal phases yielded a roughly constant nonmagnetic mole fraction $x_{\mathrm{nm}} \simeq 0.12 \pm 0.01$ at all temperatures and compositions measured except for T-$\mathrm{Al_{78}Mn_{22}}$ for which a somewhat lower value was obtained. Thus in i-$\mathrm{Al_{86}Mn_{14}}$ a small minority of sites is responsible for the observed paramagnetism while in i/T-$\mathrm{Al_{80}Mn_{20}}$, the magnetic fraction $x - x_{\mathrm{nm}}/x$ rises to about 40%. In T-$\mathrm{Al_{78}Mn_{22}}$ roughly 60% of the Mn sites are magnetic. Using this result, and interpolating the value of x_{nm} for alloys with $x = 0.16$ and 0.18, we can calculate the average moment p_{eff} of the magnetic sites between $x = 0.14$ and 0.20 using

$$\langle p_{\mathrm{eff}}^2 \rangle = [(x - x_{\mathrm{nm}})/x] p_{\mathrm{eff}}^2 , \qquad (1)$$

where values of $\langle p_{\mathrm{eff}}^2 \rangle$ are taken from the work of Hauser *et al.*[2] The results plotted in Fig. 3 show that the p_{eff} values of the magnetic sites are substantially larger than $\langle p_{\mathrm{eff}}^2 \rangle^{1/2}$, as expected, and increase by only about 30% from $x = 0.14$ to 0.20.[10] It is interesting that for $\mathrm{Al_{80}Mn_{20}}$, argued to be close to the ideal for formation of the quasicrystal,[11] the p_{eff} value approaches the values ($1.7\mu_B$ and $1.9\mu_B$) found for the magnetic sites in elemental α-Mn. Our observed shifts for the nonmagnetic sites in the quasicrystals are comparable with those of the least magnetic sites in α-Mn.

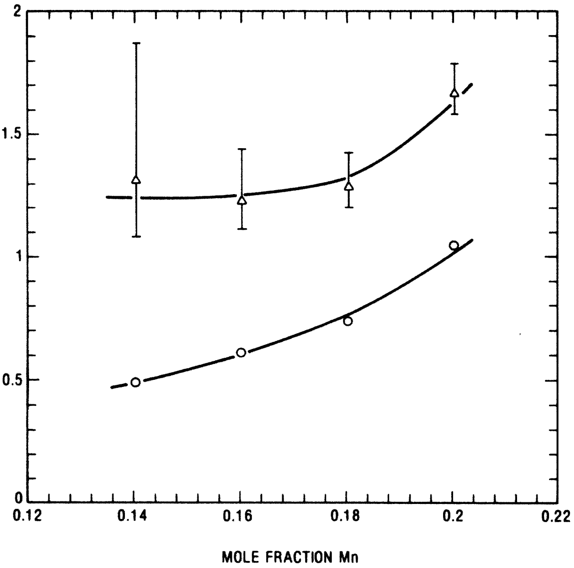

FIG. 3. Effective Bohr magneton numbers for Al-Mn quasicrystalline alloys. Open circles: average values determined from susceptibility (Ref. 2); triangles: inferred values for magnetic sites.

To summarize, the crystalline phases o-$\mathrm{Al_{86}Mn_{14}}$ and α-$\mathrm{Al_{73}Si_{10}Mn_{14}}$ show no local moment paramagnetism and NMR spectra of these materials exhibit typical quadrupolar structure with a relatively narrow central transition. The icosahedral phases, in contrast, contain a certain fraction of magnetic Mn sites which increases at higher Mn concentration. In the context of models based on clusters found in the α phase,[12–15] this means that the increased disorder present in the quasicrystals permits Mn environments which are favorable for moment formation. We emphasize that the distinction between magnetic and nonmagnetic sites does not necessarily imply the existence of two unique structural environments. The residual linewidth of i/T-$\mathrm{Al_{80}Mn_{20}}$ shows, for example, that there remains a distribution of local environments among the nonmagnetic sites. Rather, we suggest that there are two *classes* of site, one group much more magnetic than the other. The analogy of α-Mn with its two strongly magnetic crystallographic sites and two weakly magnetic sites may be helpful, but of course the details of the interactions are quite different at the Mn-Mn separations found in the elemental metal. Finally, we would like to note again the similarity of the magnetic behavior of the icosahedral and amorphous alloys.[2] This suggests strongly that the appearance of magnetic sites in the quasicrystals is related to the inherent disorder in these structures and is not a consequence of icosahedral or decagonal symmetry.

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