NMR and Mössbauer study of spin-glass behavior in $FeAl_2$

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We have used NMR and Mössbauer spectroscopy to investigate the magnetism and spin-glass behavior in $FeAl_2$. The results show that the observed behavior can be interpreted as local-moment magnetism residing on the Fe sites. An increase in ^{57}Fe Mössbauer magnetic hyperfine field was observed at the 35-K spin-glass freezing temperature, with a reduced low-temperature value consistent with unquenched fluctuations in the spin-glass state. However, the ^{27}Al NMR shifts and spin-lattice relaxation behavior are consistent with transfer hyperfine interactions to Fe local moments, with a magnitude of approximately 2.5 μ_B. This value is consistent with the bulk magnetization, but surprising compared to other Fe aluminides, given the small Fe-Fe coordination number and associated weakening expected for the magnetic moment.

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I. INTRODUCTION

$Fe_{1-x}Al_x$ alloys exhibit a variety of magnetic properties, including ferromagnetism for low-Fe compositions, going over to reentrant spin-glass behavior for compositions near $x=0.3$.[1,2] In low-Fe intermetallics, the moments become smaller, with ordered FeAl and dilute-Fe alloys having zero moment.[3–5] Al-rich quasicrystalline phases such as $Al_{62}Cu_{25}Fe_{13}$ are also essentially nonmagnetic.[6,7] However, $FeAl_2$ is an anomaly, exhibiting a large effective moment 2.55 μ_B per Fe,[8] and a spin-glass freezing temperature of 35 K. There is considerable fundamental interest in moment formation in the Fe aluminides[4,5,9–13] and in questions of local versus itinerant magnetism in these systems.[9,12,13] Therefore, we have undertaken local-probe studies utilizing ^{27}Al NMR and ^{57}Fe Mössbauer spectroscopy to investigate the $FeAl_2$ moments and the dynamics of the ordering process.

The structure of $FeAl_2$ is shown in Fig. 1, as solved by Corby and Black.[14] This structure is a distorted close-packed configuration, with three mixed Al-Fe sites among the 18 per cell. Despite the high coordination, the preference for Fe-Al bonding is apparent, with Fe-Al neighbors exhibiting the smallest bond lengths. A recent set of measurements indicated $FeAl_2$ to be semimetallic.[15] Strong covalent bonding is characteristic of this and related materials,[16,17] and the resulting pseudogap presumably helps to stabilize the structure. Generally, a reduction in transition metal-aluminum hybridization leads to a larger local moment,[11,18] and this has led to interesting magnetic behavior in a number of related transition-metal aluminides.[16,19–22]

II. EXPERIMENTAL METHODS

The sample for this study was synthesized by arc melting the elemental constituents under argon, followed by further annealing in vacuum. The resulting polycrystalline ingot was used for all measurements. This was a different sample than that used in the previous study in this laboratory,[8] however the spin-glass freezing temperature was found to be identical. The sample was characterized by powder x-ray diffraction (Bruker D8 Advance) using Cu K_α radiation. Structural refinement was carried out using the GSAS software suite.[23,24]

Mössbauer spectra were measured using a homebuilt spectrometer. The sample for Mössbauer studies was powdered and sieved and the center shift was calibrated relative to α-Fe at room temperature. Dilution studies showed saturation effects on the Mössbauer line shapes to be minimal. NMR experiments were performed at a fixed field using a 9-T homebuilt pulse spectrometer.[19] We used 1-M aqueous $AlCl_3$ as a NMR reference.

III. RESULTS AND DISCUSSION

X-ray diffraction results are shown in Fig. 2. The analysis showed no evidence for a second phase. Atomic occupation

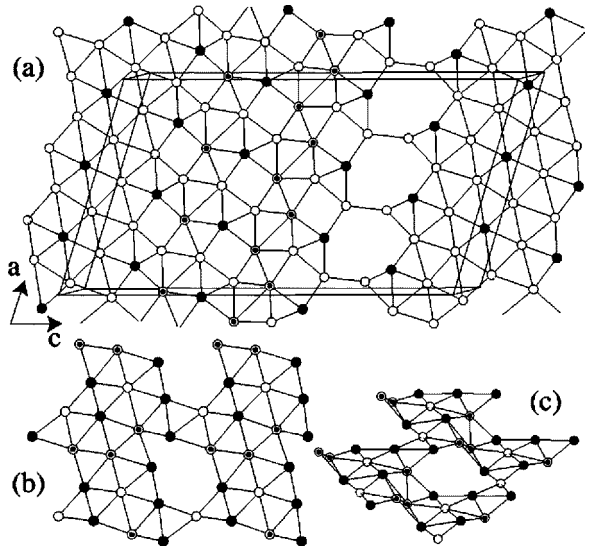

FIG. 1. $FeAl_2$ structure. Filled circles: Fe (5/cell); open circles: Al (10/cell); dot-filled circles: mixed-occupancy sites (3/cell). (a) (021) plane, with frame showing a 3×3 set of triclinic unit cells. (b) View along (101) showing Fe pairs/triads. This Fe-containing layer alternates with an Al-only layer. (c) Rotated view of layer pictured in (b).

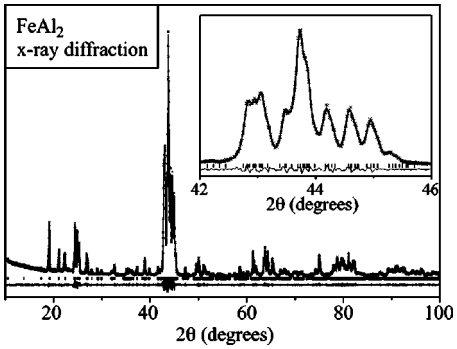

FIG. 2. Powder x-ray results for $FeAl_2$, with results of refinement and difference plot. The vertical marks are fitted reflections.

parameters are in reasonable agreement with the atomic weights reported earlier,[14] though the refinement indicated Al occupation on Fe sites as well as mixed sites (up to 0.29 relative Al occupation of Fe site 1′ [site labeling convention of Ref. 14]). No Fe occupation of Al sites was found, and the mixed sites had Al occupation parameters in the range 0.36–0.53. The fit yielded $a=0.4868$ nm, $b=0.6454$ nm, $c=0.8796$ nm, $\alpha=91.76°$, $\beta=73.35°$, and $\gamma=96.90°$, for the triclinic unit cell, with R values $R_{wp}=0.0599$ and $R_p=0.0455$. The Al/Fe ratio resulting from the refinement was 2.03.

Using the occupation parameters thus obtained, we calculated mean atomic coordination numbers, including partially occupied sites. This gave 2.5 Fe neighbors per Fe atom, and 3.5 Fe neighbors per Al atom. For this calculation, neighbors were assumed to be those at a distance less than 0.3 nm.

Figure 3 shows Mössbauer spectra versus temperature. At room temperature, a broadened doublet is observed, consisting of unresolved spectra for the different Fe sites. To fit these we used a superposition of three multiplets, and found that additional multiplets did not further improve the goodness of fit. Theoretical curves followed a standard (Lorentz) model for Mössbauer spectra. Quadrupole splittings were allowed to vary with temperature, however their contributions to line-shape changes are small. Line shapes obtained from this procedure are shown in Fig. 3.

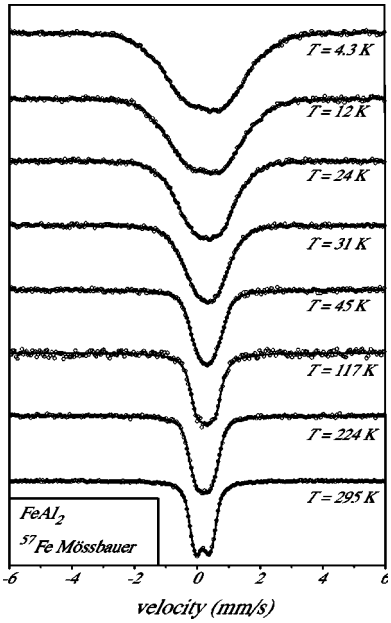

FIG. 3. ^{57}Fe Mössbauer spectra for $FeAl_2$, with theoretical fits described in the text plotted as solid curves.

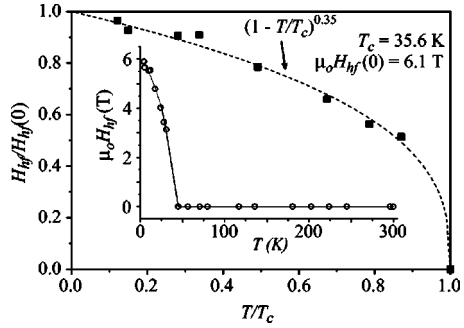

FIG. 4. Reduced hyperfine field vs reduced temperature, from the Mössbauer fitting for $FeAl_2$. The dashed curve is a fit according to $(1-T/T_c)^{\beta}$, with $\beta=0.35$, $T_c=35.6$ K, and $\mu_o H_{hf}(0)=6.1$ T. The inset shows the full temperature dependence.

The mean isomer shift obtained was 0.20 mm/s at room temperature, increasing smoothly to 0.33 mm/s in the zero-temperature limit, with no change observed at T_f. Fitting to a Debye vibrational model yielded a Debye temperature of 410 K. The large increase in linewidth between 45 and 31 K could be accounted for by the development of a nonzero hyperfine magnetic field (H_{hf}) at T_f. The temperature dependence of H_{hf} is shown in Fig. 4.

The main plot of Fig. 4 shows the reduced hyperfine field, and a power-law fit to the relation,

$$H_{hf}/H_{hf}(0) = (1 - T/T_c)^{\beta}, \tag{1}$$

yielding $\beta=0.35$, $T_c=35.6$ K, and $\mu_o H_{hf}(0)=6.1$ T. The T_c matches the observed 35-K spin glass T_f. The value of $\mu_o H_{hf}(0)$ is relatively small; for example, in dilute body-centered cubic Fe alloys,[25] $\mu_o H_{hf}$ may be approximated by a local value of 8.6 T per μ_B (21.9 T for a local moment of 2.55 μ_B), and a transfer hyperfine field of 1.2 T per μ_B per Fe neighbor. Using the mean Fe-Fe coordination number 2.5 obtained above, and even for complete antialignment of neighbors, the field is $\mu_o H_{hf}=14.2$ T. The observed value is significantly smaller, but this is typical of spin glasses, due to unquenched low-temperature spin dynamics during the metastable ^{57}Fe lifetime.[26,27] The exponent $\beta=0.35$ is a value found in three-dimensional (3D) ferromagnets,[28,29] but smaller than that obtained for short-range spin glasses, $\beta \approx 0.5$,[30] and dipolar superspin glasses, $\beta \approx 1.0$.[31,32] The susceptibility is also atypical below T_f, continuing to increase as if some spins remain loosely coupled.[8]

Figure 5 shows ^{27}Al NMR spectra recorded between 4 and 468 K, using a standard $\pi/2-\tau-\pi$ spin-echo sequence. From the NMR pulse-length dependence, we find that the

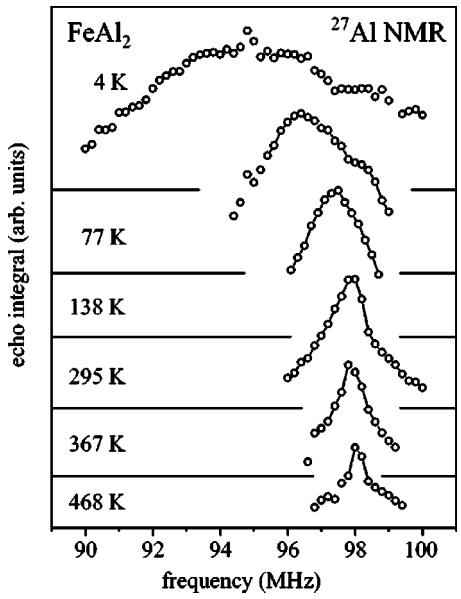

FIG. 5. ^{27}Al NMR spectra for $FeAl_2$. The data are offset vertically for clarity.

observed spectra correspond to $1/2$ to $-1/2$ transitions for the $I=5/2$ ^{27}Al nucleus, implying that the other transitions are suppressed due to quadrupole broadening. Figure 6 shows the relative shift obtained from the center of mass of these peaks. The shifts can be expressed by

$$K = K_1 + K_2(T). \tag{2}$$

A Curie-Weiss-type fit for K_2 (T) is shown by the dashed curve in Fig. 6, yielding $K_1=-0.155\%$, with the Weiss temperature fixed at $\theta=-38$ K according to the susceptibility.[8] The 4-K point was excluded from this fit since it is below T_f. (Allowing θ to vary yielded an optimized value $\theta=-33$ K, with a large error bar of 15 K indicating insensitivity to that parameter.) The results correspond to ^{27}Al directly coupled to neighboring Fe moments, with a negative transfer hyperfine coupling. Note that the ^{27}Al shift does not increase relative to the Curie-Weiss curve below T_f as would be expected in the case of cluster-glass behavior, for which local ferromagnetic

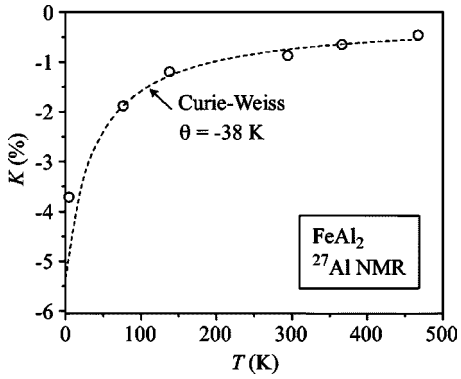

FIG. 6. ^{27}Al center-of-mass NMR shifts vs temperature. Dashed curve: Curie-Weiss fit with $\theta=-38$ K.

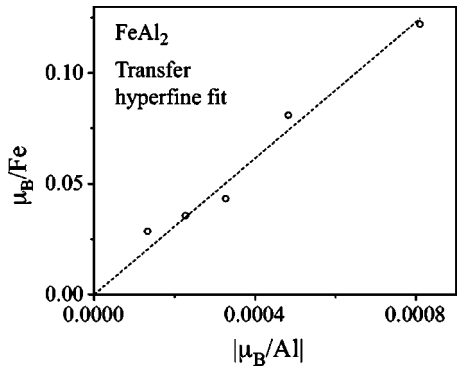

FIG. 7. $FeAl_2$ paramagnetic moment per Fe obtained from the magnetization curve, plotted vs magnitude of effective on-site Al moment obtained from the mean NMR shift. The dashed curve is a least-squares linear fit.

couplings should guarantee spin saturation in the large applied NMR field.

The transfer hyperfine coupling can be obtained from $K_2(T)$ [Eq. (2)] and the Fe moment calculated using $p_{eff}=2.55$ and $\theta=-38$ K. This is shown in Fig. 7, where the moment per Al was obtained from $K_2(T)$ using $\mu_o H_{hf}=190$ T as the Al *s*-spin hyperfine field.[33] From the least-squares slope we obtain a net Al hyperfine field of 1.2 T per μ_B on Fe. Dividing by 3.5, the mean Al-Fe coordination number, yields $\mu_o H_{hf}^{tr}=0.35$ T per μ_B per Fe neighbor. A similar value of 0.24 T was found in Al_3V,[22] while for dilute Al in Fe, the ^{27}Al shift[34] corresponds to $\mu_o H_{hf}^{tr}=0.31$ T. (The latter is obtained from the quoted shift[34] by dividing by 2.2 μ_B and the coordination number, 8 for BCC Fe.) Thus the $FeAl_2$ couplings are not particularly large despite the anomalous Fe moment.

The negative $K_1=-0.155\%$ implies an Al spin polarization opposing that of the Fe *d* orbitals, and in aluminides such behavior is observed in systems with open *d* shells: in nonmagnetic FeAl (Ref. 35) and for a magnetic decagonal Al-Pd-Mn quasicrystal,[36] values between -0.3% and -0.6% have been reported. Since this term is temperature independent, it implies a Pauli susceptibility, and a predominant Fe *d* contribution to the Fermi surface. This contrasts the

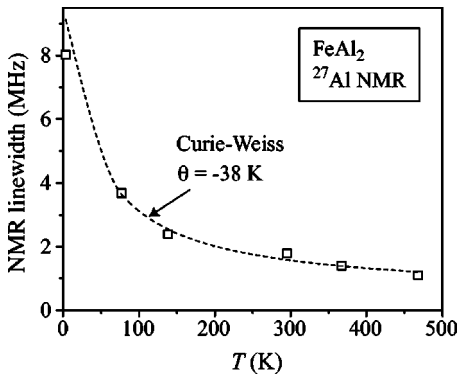

FIG. 8. ^{27}Al NMR FWHM linewidths for $FeAl_2$. The dashed curve is a Curie-Weiss fit with $\theta=-38$ K.

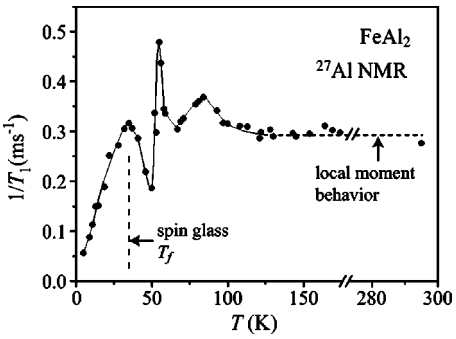

FIG. 9. ^{27}Al NMR spin-lattice relaxation rate vs T in $FeAl_2$. The dashed horizontal line shows T-independent local-moment behavior at high temperatures. The solid curve is a guide to the eye.

semiconducting behavior calculated for $FeAl_2$ in simpler geometries.[5,17]

The full width at half maximum (FWHM) of the NMR line is plotted in Fig. 8, along with a fitted curve proportional to $1/(T-\theta)$, plus a T-independent background term. To see whether statistical occupation of Fe and mixed sites alone could account for this, we performed a Monte Carlo-type calculation assuming Fe having identical paramagnetic moments, $H_{hf}^{tr}=0.35$ T for all neighbors, and statistical site occupation according to the x-ray occupation parameters. The resulting Curie-Weiss contribution to the linewidth was smaller than observed by a factor of $1/3$. Local variations in transfer couplings and/or moments may account for this difference, thus the observed widths appear reasonable.

The spin-lattice relaxation rate (T_1^{-1}) was measured by inversion recovery, irradiating the central portion of the ^{27}Al line, and using the integral of the spin echo. T_1 was extracted by fitting to multiexponential curves for magnetic relaxation of an $I=5/2$ ^{27}Al central transition. Figure 9 shows the results. At low temperatures, several peaks are observed, while at high temperatures the spin-relaxation rate is nearly constant with a value of 0.3 ms^{-1} (dashed line). These data resulted from two separate runs, showing consistent behavior.

The lowest-temperature peak in T_1^{-1} appears at 35 K, due to the slowing down of magnetic spins at T_f, as observed in other spin-glass systems.[37] The maxima in T_1^{-1} above T_f do not correspond to observed features in magnetization[8] or specific heat.[15] These features are reminiscent of the behavior of AlPdMn quasicrystals[36,38] for which multiple T_1^{-1} peaks are also seen. For that case, there is a reduction of Mn moment at low T associated with the anomalous T_1 behavior. For $FeAl_2$, there is no large change in moment above T_f, as evidenced by the susceptibility.[8] However, it is possible that the alignment of adjacent spins, such as the Fe pairs or triads (Fig. 1), to form combined moments, may be responsible for these features. A gradual reduction in electron density, as shown by the changes in thermopower below 100 K,[15] could contribute to such spin-alignment behavior by changing the indirect spin coupling.

The temperature-independent T_1^{-1} above 100 K is characteristic of concentrated local-moment systems in which J couplings rather than thermal fluctuations control the spin dynamics. Weak itinerant ferromagnets can exhibit similar behavior,[39] however for the nearly antiferromagnetic itinerant case, more appropriate in the present situation, $T^{1/2}$ relaxation behavior is expected. Much different behavior is also observed in Al-Fe-Cu quasicrystals, where the moments are widely separated and found on a small fraction of the sites.[7] Concentrated local moments produce a rate given by[40]

$$1/T_1 = (2\pi)^{1/2}(A/\hbar)^2(3\omega_E)^{-1}S(S+1)z', \tag{3}$$

where A is the transfer hyperfine energy and $\omega_E=[8J^2zS(S+1)/3\hbar^2]^{1/2}$ is the electron exchange frequency, with J the interaction strength, S the local-moment spin, and z the Fe-Fe coordination number, assuming that each Fe carries a local moment. Equation (3) differs from Ref. 40 in that A is a transfer hyperfine coupling, so we include z', the number of local moments interacting with each nucleus. In our case $z'=3.5$ and $z=2.5$, as described above. A is the nuclear Zeeman energy corresponding to the hyperfine field $\mu_o H_{hf}^{tr}=0.35$ T obtained above, which is $A=-2.6\times10^{-27}$ J. Given the magnitude of p_{eff}, we assumed that $S=1$. In the mean-field approximation,[41] J is related to the Weiss temperature through $Jz=3k_B\theta/2S(S+1)$, giving $J=1.6\times10^{-22}$ J. This yields $T_1^{-1}=0.6$ ms^{-1}. The observed $T_1^{-1}=0.3$ ms^{-1} (dashed line in Fig. 9), is in good agreement with this calculated value. Thus, the T_1^{-1} behavior provides compelling evidence that the magnetic fluctuations in this system can be attributed to stable local moments localized on Fe atoms.

The local moment in $FeAl_2$ is surprising in light of the expected Al-Fe covalency and corresponding weakening of the moment.[17,18] A standard picture for BCC Fe-Al alloys has been that a Fe-Fe coordination number 4 or greater is required for Fe to assume its full moment,[1] thus the coordination in $FeAl_2$ would appear to oppose such behavior. The Knight shifts do indicate an apparent d contribution at the Fermi level, nevertheless from the relaxation behavior we conclude that a stable local moment, rather than an itinerant mechanism, best characterizes the observed magnetism.

IV. CONCLUSIONS

NMR and Mössbauer measurements show that $FeAl_2$ can be characterized as a concentrated local-moment system. An increase in Mössbauer hyperfine field was observed to coincide with the spin-glass freezing temperature, while the ^{27}Al NMR is dominated by transfer hyperfine interactions to Fe. An analysis assuming independent local moments with mean values equivalent to the value obtained from bulk susceptibility gave good quantitative agreement with the observed shifts and relaxation times.

ACKNOWLEDGMENTS

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