Coupled atomic motion and spin-glass transition in FeAl$_2$

Yang Li, F. G. Vagizov, V. Goruganti, and Joseph H. Ross, Jr.
Department of Physics, Texas A&M University, College Station, TX 77843-4242

Zuxiong Xu and Guohui Cao
Department of Physics, University of Science and Technology Beijing, Beijing 100083, China

Cheng Dong
National Laboratory for Superconductivity, Institute of Physics, Beijing 100080, China

Zhaosheng Feng
Department of Mathematics, University of Texas-Pan American, Edinburg, TX 78541
(Dated: November 2, 2018)

We have used $^{57}$Fe Mössbauer spectroscopy and x-ray diffraction to study the magnetic and vibrational properties of FeAl$_2$. FeAl$_2$ is an ordered intermetallic with a large Fe local moment, and a complex crystal structure with site-occupation disorder on some sites. This material exhibits spin-glass freezing below 35 K. From the $^{57}$Fe recoilless fraction, we find that there is a vibrational mode which freezes out concurrently with the spin freezing. X-ray powder diffraction measurements confirm this result, indicating an anomalous change in the Debye-Waller factor at temperatures below the spin-freezing temperature.

Coupling of structural distortions to a magnetic transition can lead to a number of interesting physical phenomena. For instance, in the manganite La$_{1-x}$Ca$_x$MnO$_3$, a Jahn-Teller distortion coupled to the ferromagnetic transition significantly enhances the magnetoresistance, leading to the colossal magnetoresistive effect. Furthermore, in a range of manganite and cuprate materials, the competition between magnetism and structural distortions contributes to the development of stripes and related textures, which has led to a wealth of new physics, and plays an important role in high-$T_c$ superconductivity. The interplay of structural distortion and a spin glass transition has also been identified in the highly frustrated pyrochlore lattice: the pyrochlore Y$_2$Mo$_2$O$_7$ exhibits a lattice distortion driven by a spin-glass transition, which allows the magnetic frustration to be reduced. In this letter, we describe Mössbauer and x-ray measurements indicating that FeAl$_2$ has a soft mode which is coupled to its spin-freezing transition. This soft mode becomes activated above the spin freezing temperature ($T_f$), thus is coupled to the magnetic excitations.

FeAl$_2$ is an ordered intermetallic with a complex structure that can be described as containing layers which are roughly close-packed. Inset within Fig. I is a view of this structure perpendicular to these layers. There are ten Al and five Fe sites per unit cell, with three additional sites having mixed Fe-Al occupation, plus one vacancy site per cell, forming channels along $a$. The vacancies presumably help to adjust the electron count in order to provide energy stabilization via a pseudogap at the Fermi surface; hence the observed semimetallic behavior. The Fe-Fe coordination number is small, however the effective magnetic moment per Fe atom (2.5 $\mu_B$) is large, and has been shown to be a stable local moment on Fe.

The magnetic behavior of FeAl$_2$ is dominated by a spin freezing transition at $T_f = 35$ K, below which the magnetization exhibits the typical frequency dependence and hysteretic behavior of a spin glass. The coupling between Fe spins is dominated by superexchange through Al orbitals, which is antiferromagnetic in sign. The complex structure and mixed occupancy of some sites contribute to the magnetic frustration, and hence the spin glass configuration. NMR measurements have shown that the spin fluctuations at temperatures well above $T_f$ are dominated by non-thermal flip-flop processes between super-exchange-coupled Fe moments. Here we show, using Mössbauer spectroscopy and x-ray diffraction, that these fluctuations are tied to a soft vibrational mode that persists to low temperatures, and which is strongly coupled to the magnetic behavior.

Samples for this study were prepared by arc melting...
Fe and Al, and subsequent solid-state reaction, to yield polycrystalline ingots. Rietveld analysis of the powder x-ray diffraction pattern for this sample has been discussed previously [11]; no additional phases could be detected. Mössbauer spectra were obtained using a $^{57}$Co source in a Rh matrix. The sample was ground and sieved to less than 20 µm. Shift and velocity calibrations are referred to α-Fe at room temperature.

Mössbauer spectra taken at 4.3 K and 295 K are shown in Fig. 1. A large increase in linewidth commences at $T_f$, which can be attributed to the development of quasi-static magnetic hyperfine fields ($H_{hf}$) at low temperatures [11]. Absorption lines include a superposition of five inequivalent Fe sites, plus the three mixed sites, within the triclinic FeAl$_2$ structure (space group P1; see inset of Fig. 1). To fit the hyperfine field distributions, here we have used a Voigt-based fit according to a method described previously [12, 13]. The fit used three broadened multiplets to approximate the distribution of quadrupole and magnetic hyperfine fields, with a low-temperature distribution of $H_{hf}$ shown as an inset to Fig. 1. The resulting weighted average $H_{hf}$, shown as the inset to Fig. 2, develops sharply below $T_f$, quite similar to the previous result [11], but with slightly larger average values of $H_{hf}$ obtained with this model.

The temperature dependence of the relative Mössbauer spectral areas is shown in Fig. 3. The data were obtained for a sample containing 4 mg/cm$^2$ FeAl$_2$. The area was obtained directly from the measured spectra by means of Simpson integration using a fitted-background subtraction, so as to be independent of the spectral fitting (Fig. 1). The area is related to the recoilless fraction ($f$) [14]; above $T_f$ the gradual reduction follows the normal trend, due to increased atomic motion because of the population of phonon modes. Further changes in $f$ at low temperatures imply the freezeout of an additional lattice vibrational mode, or perhaps a localized mode involving loosely-bound atoms [12, 14].

Mössbauer areas are related to nonlinear absorption in thick samples, as well as to $f$. To investigate the thickness dependence, we prepared a lower density sample. The inset of Fig. 3 shows area ratios between $T = 0$ K and 50 K, encompassing the magnetic changes. $T = 0$ values were obtained by fitting to a function of the form, \( \exp(-T^2/T_0^2) \) (dashed curve in the main plot of Fig. 3). The inset plot shows a fit to the change vs. thickness, based on the known behavior of Mössbauer spectral areas [14]. This calculation assumed a change from a doublet to a sextet; although in our case the individual lines are not resolved, this assumption agrees well with the observed linewidth change. The only adjustable parameter for the inset curve was an additive constant, found equal to 0.1 (seen by the intercept), which represents the change in $f$ once the thickness effect is removed. Thus the observed changes in area are due in large part to a change in vibrational properties at low-temperatures.

For the case of nuclear motion, $f$ is reduced due to dynamical phase shifts of the radiation, averaged over the radiative lifetime. Harmonic motion yields to good approximation [13] $f = \exp(-k^2\langle x^2 \rangle) \equiv \exp(-2W)$ where $2W$ is Lamb-Mössbauer factor, $k$ is the x-ray wavevector and \( \langle x^2 \rangle \) the mean square linear displacement. Using a Debye phonon model one finds [13]

$$2W = \frac{6E_R}{k_B\Theta_D} \left[ \frac{1}{4} + \frac{T^2}{\Theta_D^2} \int_0^{\Theta_D/T} \frac{\xi d\xi}{e^\xi - 1} \right],$$  \hspace{1cm} (1)

where $E_R$ and $\Theta_D$ are the recoil energy and Debye tem-
perature respectively. A fit of the high-temperature data gives $\Theta_D = 413$ K, shown as a solid curve in Fig. 3. This is comparable to that of other intermetallic compounds (for example Zr(Fe,Al)$_2$ has $\Theta_D = 420$ K [19]). The increased area below $T_f$ is a departure from the Debye model. Lattice softening at a structural phase transition typically gives an enhancement of $f$ only in the critical region near $T_c$ [18]. In manganites and related colossal magnetoresistive materials, $f$ increases at temperatures somewhat below $T_c$ [20], attributed to fluctuations confined to nanoscale clusters associated with polarons. For FeAl$_2$, the reduction in $f$ from $T = 0$ to $T_f$ corresponds to the activation of a vibrational mode with $\sqrt{\langle x^2 \rangle} = 0.0044$ nm for Fe, calculated according to $f = \exp(-k^2/\langle x^2 \rangle)$.

Low temperature x-ray diffraction measurements also support the presence of a low-temperature vibration anomaly. We examined the diffraction profile at temperatures between 10 and 300 K, over a restricted angular range of 19° to 27°, which contains some of the characteristic peaks. (A full powder spectrum was shown in Ref. [11].) The relative peak intensities were obtained by means of Simpson integration using a fitted-background subtraction [21]. From the diffraction profiles we see no evidence of any structural transition down to 10 K (the instrument limitation), though the limited angular range precludes a detailed structural analysis. The inset to Fig. 4 compares data from 10 K and 35 K, for the region containing the most intense peaks, showing the amplitude increase with little or no peak shift. A striking feature is that the relative intensities exhibit a rapid increase below 35 K, similar to the Mössbauer results. This implies an anomalous stiffening as the temperature decreases below $T_f$.

The main plot of Fig. 4 shows the evolution of the peak areas. The solid curve is a fit of the high-temperature data to $\exp(-2M)$, where the Debye-Waller factor is

$$2M = \frac{12h^2 \sin^2 \theta}{mk_B \Theta_D \lambda^2} \left[ \frac{1}{4} + \frac{T^2}{\Theta_D} \int_0^{\Theta_D/T} \frac{\xi d\xi}{\xi^2 - 1} \right],$$

where $m$ is the atom mass, $\theta$ the scattering angle, and $\lambda$ the x-ray wavelength. To evaluate the results, we approximated $m$ as the average mass, weighted according to form factors and atom concentrations, yielding $\Theta_D = 430$ K. This is in good agreement with the (more precise) Mössbauer value of 413 K. However, below $T_f$ there is an additional increase, corresponding to an enhancement of 6.5% between 35 and 10 K.

The mean square displacement can be obtained from the x-ray diffraction intensities in a similar way to the Mössbauer recoilless fraction, although the x-ray average includes static as well as dynamic lattice displacements, and scattering from Al as well as Fe. The x-ray results give $\sqrt{\langle x^2 \rangle} = 0.014$ nm at 35 K, approximately 3 times larger than the value found via Mössbauer. Note that these averages assume that all atoms are vibrating in an equivalent way; if instead only one Fe atom per cell were involved in the anomalous vibrational mode, for example, the result would instead be $\sqrt{\langle x^2 \rangle} \approx 0.13$ nm for this atom (depending upon the phase factors involved in the particular reflections observed). A localized vibration involving only a single Al yields instead 0.52 nm. These large values seem unlikely to be accommodated by the lattice, despite the presence of the vacancy site (Fig. 4). Rietveld refinement [11] yielded room-temperature thermal ellipsoids (assumed isotropic) with sizes in the range 0.01–0.03 nm. While the sensitivity to such parameters for a single atom is not high for such a complex structure, these results make it seem unlikely that the anomalous vibrational mode is a localized mode. More likely, the difference between the x-ray and Mössbauer results can be ascribed to larger-amplitude motion for the lighter Al atom, combined with displacements that are in part quasi-static. The results are consistent with vibrations due to magnetic interactions among Fe atoms which are modulated by random magnetic fluctuations. In the spin glass regime, these fluctuations freeze out, reducing the associated atomic motions. This is the only instance of this type of behavior of which we are aware.

Returning to the Mössbauer center shifts of Fig. 2, the decrease with $T$ is a second-order Doppler (SOD) shift [18], due to the activation of phonon vibrations. This shift is proportional to $\Delta E/E_o = -(v^2)/(2c^2)$. A fit according to the Debye approximation [18] is shown by the dashed curve, giving $\Theta_D = 414$ K, very close to the value obtained from $f$. Since the SOD shift contains $\langle v^2 \rangle$ rather than $\langle x^2 \rangle$, the center shift is typically sensitive only to higher-frequency vibrational modes. No change can be seen in the center shift for the tempera-
ture range of spin-glass freezing, which implies that the low-temperature change in $f$ is due to activation of a low frequency mode. For example, the spin exchange frequency was estimated from NMR \[11\] to be about $10^{12}$ Hz, which corresponds to the frequency of a relatively low-energy acoustic phonon. Therefore, the observed results are consistent with the activation of a vibrational mode which is coupled to the $T$-independent spin fluctuations in the paramagnetic regime.

Anomalous low-temperature atomic motion is seen in another Fe-Al system: Fe localized at an interstitial site in irradiated fcc Al exhibits such behavior \[13\], \[14\], \[15\], and a similar low-temperature Mössbauer response. However, in the present case the freeze-out is coupled to a magnetic freezing transition. The behavior is also somewhat different from that observed for the $Y_2Mn_2O_7$ pyrochlore \[6\], in which a structural distortion accompanies the freezing transition. In FeAl$_2$ the magnetic fluctuations activate a soft mode, which however does not completely soften so as to cause a structural transition (as evidenced by the absence of change in x-ray diffraction).

The closely related quasicrystalline and approximant phase aluminides provide a useful comparison. For example, Al$_{65}$Cu$_{35}$Fe$_{15}$ is a stable icosahedral phase, while Fe$_3$Al$_{13}$ is a decagonal approximant, however the range of Fe-Al metastable binary quasicrystals does not extend to Fe concentrations as large as in FeAl$_2$. Quasicrystals exhibit significantly enhanced diffusion and plasticity, which has been attributed to the motion of phasons, characterized by coordinated atomic jumps which individually cover a fraction of a lattice constant. There have been direct observations of phason motion \[24\], \[25\], and of anomalous motion at surprisingly low temperatures, extending however to crystalline as well as quasicrystalline phases \[26\]. It would be useful to further characterize the soft mode evidenced in FeAl$_2$ in order to gain further understanding of the lattice vibrational properties of this class of materials.

To summarize, from Mössbauer and x-ray measurements we have demonstrated that FeAl$_2$ undergoes a change in vibrational behavior which accompanies its spin-glass transition. This change takes the form of a soft mode which is activated by the magnetic fluctuations in the material. This result is somewhat different from the behavior previously observed in frustrated magnetic systems, however it seems likely that similar behavior might also be present in other concentrated spin glasses.

This work was supported by the Robert A. Welch Foundation, Grant No. A-1526, by the National Science Foundation (DMR-0103455), and by Young Teachers Program of MOE China (EYTP) and National Natural Science Foundation of China (Grant No.50372005).

[1] A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, Nature (London) 373, 407 (1995).
[2] A. P. Ramirez, J. Phys.: Condens. Matter 9, 8171 (1997).
[3] C. Renner, G. Aepli, B. G. Kim, Y. A. Soh, and S. W. Cheong, Nature (London) 416, 518 (2002).
[4] T. Becker, C. Streng, Y. Luo, V. Moshtynaga, B. Damascake, N. Shannon, and K. Samwer, Phys. Rev. Lett. 89, 237203 (2002).
[5] N. Mathur and P. Littlewood, Physics Today 68, 25 (2003).
[6] A. Keren and J. S. Gardner, Phys. Rev. Lett. 87, 177201 (2001).
[7] R. N. Corby and P. J. Black, Acta Cryst. 29, 2669 (1973).
[8] M. Krajčí and J. Hafner, J. Phys.: Condens. Matter 14, 5755 (2002).
[9] C. S. Lue and Y.-K. Kuo, J. Phys.: Condens. Matter 15, 877 (2003).
[10] C. S. Lue, Y. Öner, D. G. Naugle, and J. H. Ross, Jr., Phys. Rev. B 63, 184405 (2001).
[11] J. Chi, Y. Li, F. G. Vagizov, V. Goruganti, and J. H. Ross, Jr., Phys. Rev. B 71, 024431 (2005).
[12] Z. X. Xu, Z. D. Xu, H. S. Yang, and R. Z. Ma, Chinese Science Bulletin 38, 1767 (1993).
[13] D. G. Rancourt and J. Y. Ping, Nucl. Instrum. Meth. B 58, 85 (1991).
[14] A. Vértes, L. Korecz, and K. Burger, Mössbauer Spectroscopy (Elsevier Scientific, 1979), p. 32.
[15] G. Vogl, W. Mansel, and P. H. Dederichs, Phys. Rev. Lett. 36, 1497 (1976).
[16] W. Petry, G. Vogl, and W. Mansel, Phys. Rev. Lett. 45, 1862 (1980).
[17] L. Pauling, J. Solid State Chem. 40, 266 (1981).
[18] S. Dattagupta, in Mössbauer Spectroscopy, edited by D. P. E. Dickson and F. J. Berry (Cambridge University Press, 1986), p. 198; E. R. Bauminger and I. Nowik, ibid., p. 219.
[19] A. Israel, I. Jacob, J. L. Soubeyroux, D. Fruchart, H. Pinto, and M. Melamud, J. Alloys Comp. 253, 265 (1997).
[20] A. Nath, Z. Klenčsár, E. Kuzman, Z. Homonnay, A. Vértes, A. Simopoulos, E. Devlin, G. Kallias, A. P. Ramirez, and R. J. Cava, Phys. Rev. B 66, 212401 (2002).
[21] C. Dong, F. Wu, and H. Chen, J. Appl. Cryst. 32, 850 (1999).
[22] A. I. Goldman and R. F. Kelton, Rev. Mod. Phys. 65, 213 (1993).
[23] E. Huttunen-Saarivirta, J. Alloys Comp. 363, 150 (2004).
[24] K. Edagawa, K. Suzuki, and S. Takeuchi, Phys. Rev. Lett. 85, 1674 (2000).
[25] E. Abe, S. J. Pennycook, and A. P. Tsai, Nature (London) 421, 347 (2003).
[26] J. Dolinšek, T. Apih, P. Jeglič, M. Feuerbacher, M. Calvo-Dahlborg, U. Dahlborg, and J. M. Dubois, Phys. Rev. B 65, 212203 (2002).