Hyperfine field distributions and transverse spin freezing in iron-rich amorphous Fe-Zr alloys

D. H. Ryan and Hong Ren
Centre for the Physics of Materials, Department of Physics, McGill University, Rutherford Building, 3600 University Street, Montréal, Québec H3A 2T8, Canada

In order to settle the question of homogeneous versus inhomogeneous ordering in amorphous Fe-Zr alloys, we have obtained Mössbauer spectra with well-defined magnetic texture and without line overlap by subtracting spectra measured with and without a small polarizing field. These spectra allow us to show that $P(B_{hf})$ has no bimodal structure at any temperature, and there is no paramagnetic component in the spectra above T_{xy}. We therefore rule out the possibility that magnetically isolated clusters or precipitates play a role in the ordering. We also present high-field spectra which show homogeneous transverse-spin freezing at $\sim$28 K in a-$Fe_{90}Zr_{10}$.

INTRODUCTION

Iron-rich alloys of the form Fe_xM_{100-x} ($x \geqslant 90$; M = Sc,Y,Zr,Hf) exhibit complex magnetic structures and ordering behavior as a result of competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange.[1] On cooling, these alloys exhibit two magnetic transitions: first at T_c to a collinear FM state with substantial, unfrozen, transverse-spin components; then at T_{xy} the transverse degrees of freedom freeze and the spin system enters an asperomagnetic state.[2] At higher levels of frustration, a single transition directly from paramagnet to asperomagnet is found.[3] These observations are consistent with the original mean-field models of spin glasses,[4] and both local mean-field simulations[5] and recent full Monte Carlo simulations[6] of the exchange-frustrated three-dimensional (3D) Heisenberg model with nearest-neighbor interactions.

However, an alternative model of these alloys is that exchange frustration, and possibly some chemical segregation, leads to magnetic phase separation into small spin glass or AFM clusters weakly coupled to the FM matrix,[7,8] and it is the freezing of these clusters that leads to the change in magnetic properties at T_{xy}. Indeed, it has been suggested that the transverse-spin freezing recently observed in $Fe_{92}Zr_8$ is due to the ordering of AFM γ-Fe clusters,[9] although the main evidence in favor of this interpretation is the coincidence between the Néel temperature T_N for some γ-Fe precipitates in copper ($\sim$70 K) (Refs. 10 and 11) and T_{xy} in $Fe_{92}Zr_8$ (76 K).[2]

Hyperfine field distributions, $P(B_{hf})$, measured by Mössbauer spectroscopy, should allow spins in the isolated clusters (if they exist) to be distinguished from those in the FM matrix, especially above T_{xy} where the clusters are predicted to be paramagnetic. Some support for an inhomogeneous picture of spin freezing in a-Fe-Zr comes from a bimodal $P(B_{hf})$: The high-field peak is interpreted as being due to the FM matrix, and the much smaller peak at lower fields represents the cluster spins.[7,9] However, competition between quenched-in stresses and demagnetizing fields in the ribbon samples leads to magnetic texture (a tendency for the moments to lie in a particular direction), and both the position and area of the low-field feature are highly dependent on the the magnetic texture assumed in the fit,[7] complicating the interpretation of the results.

Deconvolution of $P(B_{hf})$ from a measured spectrum is not trivial in amorphous materials. First, most deconvolution routines fit a truncated series expansion to obtain $P(B_{hf})$, a procedure which necessarily yields oscillatory results, particularly in the presence of significant counting noise. Second, overlap among the six lines of a magnetically split spectrum makes all such deconvolution routines unstable.[12] Finally, the presence of magnetic texture affects the intensities of the $\Delta m_I = 0$ transitions (lines 2 and 5) and can substantially modify the derived $P(B_{hf})$. The first problem can be reduced by improving the fitting procedure and data quality; however, the second represents a fundamental limitation: Significant line overlap reduces the reliability of $P(B_{hf})$ determinations. Standard solutions to the magnetic texture problem are either to ignore it, i.e., to argue that spin directions will be essentially random and set the intensity ratio $R = I_{2,5}/I_{3,4}$ equal to 2, or else to allow R be a variable parameter in the fit. Neither procedure is satisfactory. The first is simply wrong as $R = 2$ is rarely observed for ribbon samples, while the second, allowing R to vary, exacerbates the problems of line overlap, since the distribution shape and R are highly correlated fitting parameters.

The subtraction procedure described here yields spectra with a well-defined magnetic texture which may be fitted unambiguously to obtain $P(B_{hf})$. We present data on a-$Fe_{90}Zr_{10}$ which has previously been shown[13] to be less frustrated than the a-$Fe_{92}Zr_8$ used in the earlier study of transverse spin freezing.[2] It has a lower T_{xy} and a smaller transverse spin component. We find no evidence for any bimodality in $P(B_{hf})$; nor do we observe a zero-field or nonmagnetic component above T_{xy} where any clusters should be paramagnetic.

EXPERIMENTAL METHODS

Amorphous ribbons of nominal composition $Fe_{90}Zr_{10}$ were melt spun under helium from ingots prepared from the pure metals by argon arc melting. The absence of crystallinity was confirmed by x-ray diffraction and room-temperature Mössbauer spectroscopy. Spectra were obtained on a conventional constant-acceleration spectrometer with

 0021-8979/91/085057-03$03.00

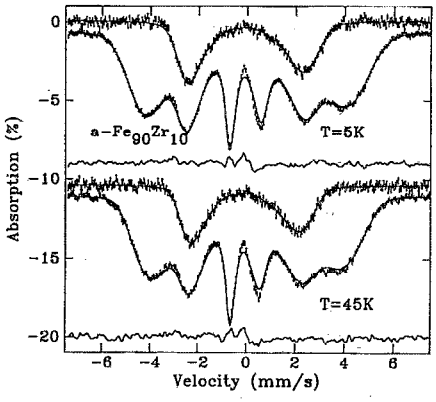

FIG. 1. Two-line spectra obtained by subtraction of polarized ($B_\perp$ = 50 mT) and unpolarized six-line spectra for temperatures above and below T_{xy} (28 K). The six-line unpolarized spectra are shown with fits using the hyperfine field distribution obtained from the two-line spectra, along with a plot of the residual error in each case.

a 1 GBq ^{57}CoRh source at room temperature. Polarized spectra were obtained by cooling the sample from above T_c [226 K (Ref. 13)] in a field of 50 mT applied parallel to the sample plane (and hence perpendicular to the γ beam) using a small permanent magnet. High-field spectra were recorded with 3 T applied parallel to the γ beam using a superconducting solenoid. For these measurements, the source was located inside the cryostat at the null point of the magnet, and the spectrometer was operated in sinusoidal mode. As before,[2] the field was applied above T_c and spectra were obtained on field cooling. A field of 3 T was selected to place the material well onto the flat region of the magnetization curve (after demagnetizing fields are taken into account) where the system is technically saturated.[13]

Subtracting the small- and zero-field spectra yields two-line spectra with a minimum possible line overlap and well-determined magnetic texture.[14,15] A modified version of Window's method[16] was used to obtain $P(B_{hf})$, which was then checked by using the distribution to fit the original six-line spectra. Typical two- and six-line spectra are shown with fits and residuals in Fig. 1.

HYPERFINE FIELD DISTRIBUTIONS

At no temperature below T_c is the hyperfine field distribution bimodal (Fig. 2). There is some weak low-field structure, but it appears and disappears at random and exhibits no consistent temperature dependence. We have traced it to statistical fluctuations in the central region of the subtracted spectra. Subtraction leads to a reduction in the signal-to-noise ratio in the resultant spectrum, and even in the absence of overlap, the fitting procedure is still sensitive to noise. The refitting procedure also yields unambiguous values for R, which we found to lie in the range $1.3 < R < 1.9$ for the zero-field spectra. We never observed $R = 2$, which is expected for random spin orientations and generally assumed for metallic glass samples.

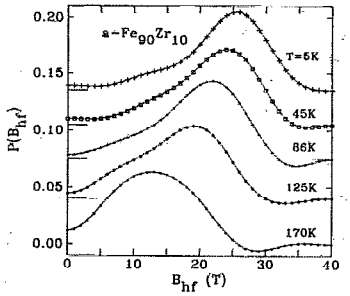

FIG. 2. Hyperfine field distributions obtained from the difference spectra for a series of temperatures above and below T_{xy} (28 K).

Strictly speaking, the distributions obtained by this subtraction procedure only sample the *polarizable* fraction of the spin population since it is only sensitive to those spins whose direction changes in response to the 50-mT applied field. If magnetic inhomogeneities, such as AFM clusters, were indeed present, the distribution could not be expected to be representative of the sample as a whole. However, we were able to use $P(B_{hf})$ derived in this manner to fit both the polarized and unpolarized six-line spectra at all temperatures. Furthermore, the residuals shown with the data in Fig. 1 show no change in form on passing through T_{xy}, particularly near zero velocity: Thus, there is no evidence of a paramagnetic component in the spectra above T_{xy}. We therefore conclude that the spin system responds homogeneously to small polarizing fields and that no clusters are present.

TRANSVERSE SPIN FREEZING

Spectra measured in a field of 3 T show the characteristic signature of transverse-spin freezing[2]: the development of noncollinearity on field cooling though T_{xy} as the transverse-spin components order (Fig. 3). These spectra were fitted using the same hyperfine field distributions shown in Fig. 2 with only R and a field shift as adjustable parameters. The latter parameter takes account of the applied field which reduces the hyperfine field at the iron nucleus, and the former allows the detection of the onset of noncollinearity. For a sample fully magnetized parallel to the γ beam, R is zero; however, as the transverse spin components order, they do so perpendicular to the beam

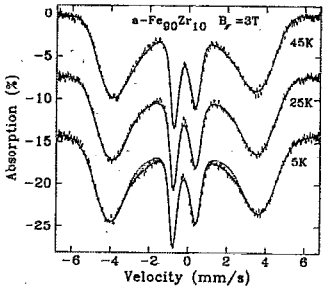

FIG. 3. Spectra measured with $B_\parallel = 3$ T showing the growth of lines 2 and 5 as the transverse-spin components freeze below $T_{xy} = 28$ K. The spectrum at 5 K is shown with two fitted lines: one where R is forced to be zero, the other where R is allowed to take its optimum value. Note that the hyperfine field distribution used for these fits was derived from the subtraction procedure described in the text.

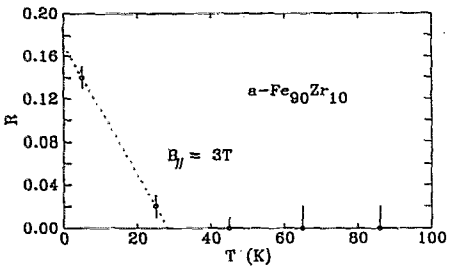

FIG. 4. Intensity ratios for lines 2 and 5 (R) with $B_{\parallel} = 3$ T showing the increase in R below T_{xy}.

and R increases. Derived values of R are plotted on Fig. 4 and show that $T_{xy} = 28 \pm 3$ K. Although the effect is quite small, the highly constrained fitting procedure allows reliable identification of lines 2 and 5, and both the magnitude of R and the onset temperature are consistent with earlier measurements.[13] The fact that we are able to fit spectra obtained in a field of 3 T with the *same* distribution used for the zero-field spectra is further evidence for homogeneous magnetic ordering in this system. It is extremely unlikely that decreasing the iron concentration by 2 at. % would cause the composition of a precipitated minority phase to change enough to account for a 50% reduction in ordering temperature. Moreover, the observed T_{xy} in $Fe_{90}Zr_{10}$ is unrelated to T_N in γ-Fe. We can therefore rule out any role for either precipitated phases or magnetically isolated components in the ordering behavior of a-Fe-Zr alloys.

CONCLUSIONS

Subtraction of polarized and unpolarized spectra can be used to eliminate both line overlap and the effects of unknown magnetic texture so as to allow unambiguous determination of $P(B_{hf})$. There is no evidence of a bimodal structure in $P(B_{hf})$; nor is there any substantial change in its shape through T_{xy}. At any given temperature, one field distribution may be used to fit spectra obtained with $B = 0$, $B_{\perp} = 50$ mT, and $B_{\parallel} = 3$ T, demonstrating the homogeneous nature of the magnetic order and allowing us to rule out the presence of magnetic clusters or precipitated phases. The magnetic phase diagram for iron-rich a-Fe-Zr (Ref. 13) shows $Fe_{90}Zr_{10}$ to be far less frustrated than $Fe_{92}Zr_8$, and as expected, transverse spin freezing occurs at a lower temperature ($T_{xy} = 28$ K) to a more closely collinear state.

ACKNOWLEDGMENTS

This work was supported by grants from the Graduate Faculty of McGill University, the Natural Sciences and Engineering Research Council of Canada, and Fonds pour la formation de chercheurs et l'aide à la recherche, Québec.

[1] K. Moorjani and J. M. D. Coey, *Magnetic Glasses* (Elsevier, Amsterdam, 1984).
[2] D. H. Ryan, J. O. Ström-Olsen, R. Provencher, and M. Townsend, J. Appl. Phys. **64**, 5787 (1988).
[3] D. H. Ryan, J. O. Ström-Olsen, W. B. Muir, J. M. Cadogan, and J. M. D. Coey, Phys. Rev. B **40**, 11208 (1989).
[4] M. Gabay and G. Toulouse, Phys. Rev. Lett. **47**, 201 (1981).
[5] C. M. Soukoulis, G. S. Grest, and K. Levin, Phys. Rev. B **28**, 1510 (1983).
[6] J. R. Thomson, H. Guo, D. H. Ryan, M. J. Zuckermann, and M. Grant, these proceedings.
[7] S. N. Kaul, C. Bansal, T. Kumeran, and M. Havalgi, Phys. Rev. B **38**, 9248 (1988).
[8] D. A. Read, G. C. Hallam, and M. Chirwa, J. Magn. Magn. Mater. **82**, 83 (1989).
[9] D. A. Read, T. Moyo, S. Jassim, R. A. Dunlap, and G. C. Hallam, J. Magn. Magn. Mater. **82**, 87 (1989).
[10] G. J. Johanson, M. B. McGirr, and D. A. Wheeler, Phys. Rev. B **7**, 3208 (1970).
[11] Y. Tsunoda, S. Imada, and N. Kunitomi, J. Phys. F **18**, 1421 (1988).
[12] G. Le Caer, J. M. Dubois, H. Fischer, U. Gonser, and H.-G. Wagner, Nucl. Instrum. Methods B **5**, 25 (1984).
[13] D. H. Ryan, J. M. D. Coey, E. Batalla, Z. Altounian, and J. O. Ström-Olsen, Phys. Rev. B **35**, 8630 (1987).
[14] I. Vincze and E. Babic, Solid State Commun. **27**, 1425 (1978).
[15] D. Kaptas and I. Vincze, Hyperfine Interact. **55**, 987 (1990).
[16] B. Window, J. Phys. E **4**, 401 (1971).