Cluster relaxation in iron-rich amorphous FeZr alloys near T_c

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A cluster relaxation model has been used to fit the Mössbauer spectra of iron-rich amorphous Fe–Zr alloys near their ordering temperatures. While the results are consistent with the presence of relaxation, deduced cluster sizes are an order of magnitude smaller than expected. Incorporating static magnetic and structural disorder into the model extends the temperature range over which the data may be fitted.

I. INTRODUCTION

Competing ferromagnetic and antiferromagnetic exchange in iron-rich amorphous Fe_xZr_{100-x} ($x \geqslant 88$) leads to complex magnetic ordering behavior and a noncollinear ground state at $T = 0$ K. Two magnetic transitions have been observed for these alloys: on cooling through T_c, collinear components of the spins order with substantial transverse spin components, which precess rapidly and time average to zero. Below the second transition at T_{xy}, the transverse components freeze and the spin system becomes noncollinear.[1,2] The manner in which the order develops at T_c is unclear. Recent Monte Carlo simulations indicate that, in a moderately frustrated Heisenberg system like a-FeZr, a normal ferromagnetic transition should occur,[3,4] and this is consistent with both critical exponent measurements[5] and the appearance of well-defined magnetic domains.[6] However, small angle neutron scattering measurements show only short range (~ 100 Å) spin correlations below T_c,[7] while above T_c both Mössbauer spectra in applied fields[8] and magnetization measurements[9] show evidence of correlated spin clusters. Comparison of average hyperfine fields derived from Mössbauer spectra with and without applied fields suggests that such clusters persist even below T_c.[2,10] Finally, the temperature dependence of the average effective hyperfine field for $Fe_{91}Zr_9$ is consistent with theoretical results for intrinsically ferromagnetic clusters.[11] ^{57}Fe Mössbauer spectroscopy probes the nuclear environment on a time scale of $\sim 10^{-7}$ s. If the environment varies significantly in this period, due for example to slow relaxation of the local moments, then the observed spectrum is modified in a characteristic manner. In order to calculate the spectral shape some form for the relaxation must be assumed. A simple model for paramagnetic systems is to consider the local field as flipping between two values $+h$ and $-h$ (i.e., up and down) with some frequency f.[12] To obtain a net magnetization for the system, unequal flipping frequencies are assumed: $f_1(+h \rightarrow -h)$ and $f_2(-h \rightarrow +h)$. This latter model has been used to fit frustrated crystalline magnetic systems[13] but the presence of substantial static disorder reduces its applicability to glasses. At $T = 0$, even ferromagnetic glassy alloys exhibit extremely broad spectra as a result of wide variations in local atomic environments and this static disorder remains significant right up to T_c. On approaching T_c from below in frustrated materials, standard static distribution fitting methods fail as the effects of relaxation become significant. We report here attempts to combine a relaxation model with information on the broad moment distribution present at $T = 0$ in order to describe the observed spectra of a-FeZr over the widest possible range of temperatures.

II. EXPERIMENTAL METHODS

Amorphous ribbons of $Fe_{90}Zr_{10}$, $Fe_{92}Zr_8$, and $Fe_{93}Zr_7$ were melt spun under helium from ingots prepared from the pure metals by arc melting under argon. The absence of crystallinity was confirmed by x-ray diffraction and room temperature Mössbauer spectroscopy. Compositions were determined by electron microprobe analysis and were all found to be within 0.4 at. % of the nominal values.

Mössbauer spectra were obtained over a temperature range from 5 K to room temperature on a conventional constant acceleration spectrometer with a ^{57}CoRh source at room temperature. Fitting was carried out using a standard least-squares minimization routine with fit quality being determined both by the appearance of the residual plot and from the reduced χ^2 value returned by the program. The low temperature spectra could be fitted with standard static distribution methods such as that due to Window;[14] however these fail at around 0.8 T_c. The fitting range may be extended by adding more terms (six were used here) to the model, but unphysical negative probabilities appear in the hyperfine field distributions as the procedure becomes unstable. The simple one-site asymmetric relaxation model[13] only works over a very narrow temperature range ($0.97\ T_c \geqslant T \geqslant 0.91\ T_c$ or about 10 K in $Fe_{92}Zr_8$). Above $\sim 0.97\ T_c$ the quadrupole splitting in the paramagnetic state becomes significant and while it is possible to extend the range of the fit by including the effects of the quadrupole distribution determined at room temperature ($\sim 1.7\ T_c$), the model still fails below $\sim 0.91\ T_c$ as the effects of static magnetic disorder start to dominate.

Two models combining static disorder with relaxation broadening were developed in order to extend the fit fur-

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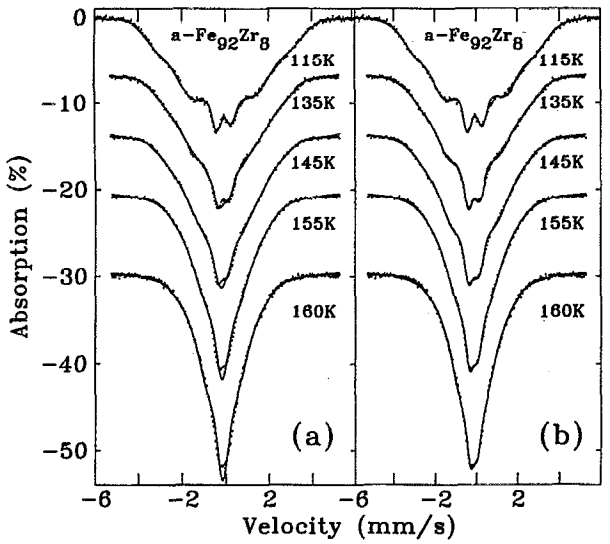

FIG. 1. Mössbauer spectra of $Fe_{92}Zr_8$ at several temperatures below T_c (170 K) fitted with (a) the static and (b) relax-2 models described in the text.

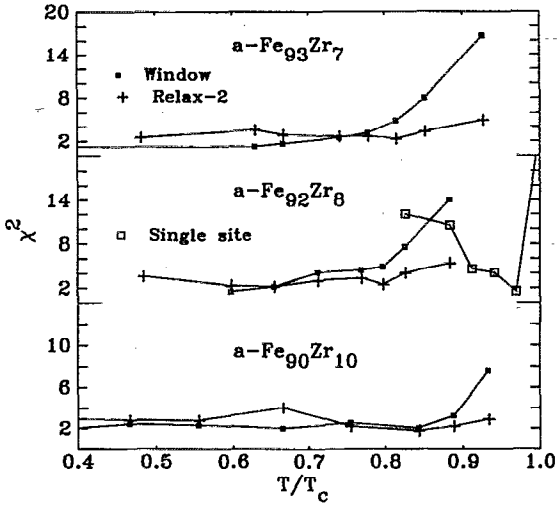

FIG. 2. χ^2 vs reduced temperature for the three alloys studied here. Results for static distributions (Window) and dynamic fits (relax-2) are compared showing the improvement in fit quality close to T_c for the relaxation model. Results for the single site model are also shown for $Fe_{92}Zr_8$ above 0.8 T_c.

ther below T_c. The static hyperfine field distribution for a given alloy was determined at 5 K using a simplified form: an asymmetric Gaussian distribution with a variable maximum probability and independent widths to higher and lower fields. This fits the low temperature spectra quite well and simplifies subsequent analysis by ensuring a smooth hyperfine field distribution and minimizing the number of fitting parameters used. Relaxation effects were added in two ways. In "relax-1" all of the components in the hyperfine field distribution were assumed to relax at the same rate and f_1 and f_2 are varied in order to obtain the best fit. This procedure does not significantly extend the useful range of the model as it ignores the possibility that there is a spectrum of cluster sizes relaxing at different rates. A more satisfactory fit was found when the two flipping frequencies were assumed to be correlated with the magnitude of the hyperfine field (relax-2): high field components were allowed to relax more slowly than those at lower fields. This is equivalent to assuming that the larger moments are associated with the larger clusters. An exponential dependence of the frequency on field was used to model an (assumed) activated flipping process.

III. RESULTS AND DISCUSSION

Mössbauer spectra of $Fe_{92}Zr_8$ measured at different temperatures are shown with the fits obtained by Window's method and relax-2 in Figs. 1(a) and 1(b), respectively. At 115 K both methods fit well, however above 135 K, only relax-2 still gives reasonable agreement with the data. As noted above, adding more terms to the Window fit does reduce the fitting error but at the expense of stability. In Fig. 2, we show plots of reduced χ^2 obtained from the static and relaxation fits as function of reduced temperature for the three samples studied here. In all cases, Window's method and the relaxation fit are of comparable quality at low temperatures, but the static distribution fails on approaching T_c. In the case of $Fe_{92}Zr_8$ the values of χ^2 for the one-site relaxation fit are also shown.

The temperature range over which the relaxation model yields a significant improvement in fit quality and the degree of improvement should be related to the importance of cluster relaxation in the material, which is in turn expected to be related to the degree of exchange frustration present. $Fe_{90}Zr_{10}$ is the least frustrated system studied here and the relax-2 model does not show any advantage until 0.85 T_c, whereas for the more frustrated $Fe_{92}Zr_8$ relax-2 is better than Window above $\sim$0.7 T_c although only above 0.8 T_c is the difference marked. Finally, for $Fe_{93}Zr_7$, the relax-2 model is clearly superior above $\sim$0.75 T_c.

Although the improvement in fit is significant near T_c, and the temperature range over which the improvement is observed corresponds to the level of frustration in the material, little new insight into the magnetic properties of the material is obtained. In order to obtain stable fits, a number of rather artificial assumptions have to be made about the shape of the moment distribution, its temperature dependence and, more significantly, the form of the cluster relaxation. Fixing the distribution to be that observed at $T = 0$ assumes that the shape is temperature independent and further assumes that relaxation is the only mechanism by which order is lost—i.e., all demagnetizing processes found in normal ferromagnets are neglected. The form of the correlation between relaxation rate and field, while reasonable (there must be a distribution of cluster sizes and hence relaxation rates) is somewhat artificial since it assumes the larger moments are associated with the larger clusters and therefore precludes the extraction of meaningful cluster sizes from the fits.

In principle, some information about the clusters may be obtained from the simple one-site fits above T_c. For Invar ($Fe_{65}Ni_{35}$), plots of the temperature dependences of

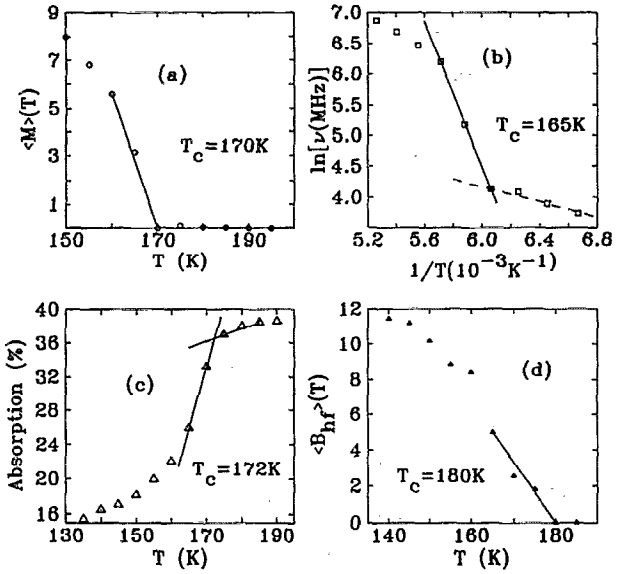

FIG. 3. Comparison of T_c determinations from single site relaxation fits (a) & (b) and static distribution fits (c) & (d). Essentially identical results are obtained from all four parameters. See text for definitions of $\langle M \rangle$ and ν.

magnetization $[\langle M \rangle = (f_1 - f_2)/(f_1 + f_2)]$ and average relaxation frequency $[\nu = (f_1 + f_2)/(f_1 f_2)]$ allowed a clearer definition of the characteristic temperature than was possible on the basis of zero velocity thermal scans or average hyperfine fields.[13] These parameters are plotted in Figs. 3(a)–3(d) for $Fe_{92}Zr_8$ and show that all methods give about the same T_c with the same clarity. Finally, $d \ln(\nu)/d(1/T)$ above T_c may be used to derive the size of the relaxing clusters. The slope of the solid line in Fig. 3(b) is about 6000 K, following the analysis of Rancourt[13] and using a T_c of 170 K, we obtain an average cluster size of ~ 10 Å, far smaller than the neutron scattering value of 100 Å.[7]

IV. CONCLUSIONS

Relaxation models have been used to fit the Mössbauer spectra of iron-rich a-Fe–Zr and significant improvement has been achieved in fit quality for spectra recorded near T_c compared to Window's method, a standard static model. The behavior of the Mössbauer spectra around T_c is consistent with the presence of slowly relaxing spin clusters; however the effects of static disorder (quadrupole splitting above T_c and moment distributions below T_c) severely limit the temperature range over which the analysis may be performed. Cluster sizes derived from a simple model are an order of magnitude smaller than values obtained from small angle neutron scattering. Attempts to extend the useful fitting range by including the effects of static disorder, while successful in reproducing the form of the data, are of little value as the restrictions which have to be imposed in order to obtain a stable fit make interpretation of the derived parameters impossible.

[1] D. H. Ryan, J. M. D. Coey, E. Batalla, Z. Altounian, and J. O. Ström-Olsen, Phys. Rev. B **35**, 8630 (1987).
[2] D. H. Ryan, J. O. Ström-Olsen, R. Provencher, and M. Townsend, J. Appl. Phys. **64**, 5787 (1988).
[3] J. R. Thomson, Hong Guo, D. H. Ryan, M. J. Zuckermann, and Martin Grant, J. Appl. Phys. **69**, 5231 (1991).
[4] J. R. Thomson, Hong Guo, D. H. Ryan, M. J. Zuckermann, and Martin Grant (to be published).
[5] S. N. Kaul, J. Phys. F **18**, 2089 (1988).
[6] S. Hadjoudj, S. Senoussi, and D. H. Ryan, J. Appl. Phys. **67**, 5958 (1990).
[7] J. J. Rhyne, R. W. Erwin, J. A. Fernandez-Baca, and G. E. Fish, J. Appl. Phys. **63**, 4080 (1988).
[8] S. M. Fries, C. L. Chien, J. Crummenauer, H. G. Wagner, and U. Gonser, Hyp. Int. **27**, 405 (1986).
[9] H. Yamamoto, H. Onodera, K. Hosoyama, and H. Yamauchi, J. Magn. Magn. Mater. **31–34**, 1579 (1983).
[10] M. Ghafari, N. Chmielek, W. Keune, and C. P. Foley, Hyp. Int. **54**, 527 (1990).
[11] S. J. Morup, J. Magn. Magn. Mater. **37**, 39 (1983).
[12] M. Blume and J. A. Tjon, Phys. Rev. **165**, 446 (1968).
[13] D. G. Rancourt, Hyp. Int. **40**, 183 (1988).
[14] B. Window, J. Phys. E **4**, 401 (1971).