Transverse spin freezing in a-$Fe_{92}Zr_8$ (invited)

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High field magnetization measurements combined with Mössbauer spectroscopy with and without an external magnetic field have been used to study the evolution of magnetic order from wandering axis ferromagnet to asperomagnet at the transverse spin freezing transition ($T_{xy} = 76 \pm 3$ K) in amorphous $Fe_{92}Zr_8$. Below T_{xy}, the total iron moment derived from the Mössbauer spectra is larger than its z component, determined by magnetization measurements. Mössbauer spectra measured with an external field of 3 T parallel to the γ beam show absorption due to the $\Delta m_I = 0$ transitions only below T_{xy} and confirm ordering of transverse spin components. Unlike the irreversibility in the dc susceptibility, the transition is not suppressed by the large measuring field, and therefore the fundamental nature of the transition is being probed rather than a sympton or side effect. The transition may be broadly interpreted in terms of a mean-field mixed exchange model, although the detailed behavior is somewhat different. A phase diagram describing the effect of exchange frustration on magnetic ordering is presented, and the observed properties of the phases are outlined.

INTRODUCTION

The magnetic behavior of amorphous Fe_xZr_{100-x} alloys exhibits a number of unusual features as $x \to 100$. Although the iron moment is essentially constant for $x > 85$, the magnetic ordering temperature falls rapidly from 270 K at $x = 88$ to 160 K at $x = 93$, and high field magnetization curves demonstrate the presence of a substantial noncollinear component to the magnetic order at 4.2 K.[1] Order is not established homogeneously throughout the sample at T_c, but appears to develop gradually through the growth of magnetic clusters and slow relaxation of these clusters is observed well above T_c.[2,3] Small angle neutron scattering (SANS) shows that the magnetic correlation length fails to diverge at T_c but remains finite down to 10 K, and does not exceed 20 nm.[4]

As a further complication, several authors have reported a second magnetic transition at a temperature well below T_c. The existence of the transition was first suggested by Hiroyoshi and Fukamichi[5] on the basis of irreversible dc susceptibility χ_{dc}, and further evidence for the transition has since been seen in a peak in χ_{ac} in the presence of a small dc field,[6] in the appearance of a field-induced uniaxial anisotropy,[7] in an increase in the SANS strength[4,8] and in a step in the average hyperfine field measured by Mössbauer spectroscopy.[9] Despite the range of techniques used, the nature and even the existence of the second transition remain controversial. Antiferromagnetic exchange between some nearest-neighbor iron atoms arising through the distance dependence of the iron-iron direct exchange[10] is generally used to explain the existence of the transition, but opinions on its nature vary and include the freezing of antiferromagnetic clusters in a ferromagentic matrix (often called mictomagnetism)[6] and a reentrant spin-glass transition.[1,9] Read, Moyo, and Hallam[11] rejected these hypotheses and showed that the irreversible χ_{dc} data could be due to failing to correct for the effects of the demagnetizing field in the presence of exponentially increasing magnetic hardness at low temperatures, and that the second transition was merely an artefact of the measurement technique.

While this last description does have the attraction of simplicity, it fails to address the collapse of T_c and the development of noncollinear order with increasing iron content. We therefore proposed a model and phase diagram for a-Fe_xZr_{100-x} (Ref. 1) based on the mean-field mixed exchange theory of Gabay and Toulouse[12] which characterizes the exchange distribution by the ratio of its average value (J) to its width (Δ). In this picture, the addition of small amounts of antiferromagnetic exchange ($J/\Delta \gg 1$) leads to both a rapid reduction in T_c and the appearance of noncollinear order. In the limit of $J/\Delta \to 0$ spin-glass ordering is predicted, but for $J/\Delta \sim 1$ the order is almost collinear. The gross behavior of the a-Fe_xZr_{100-x} system (rapid reduction in magnetic ordering temperature and the development of noncollinearity at $T = 0$) may therefore be understood in terms of a buildup of negative exchange with increasing x. The model also allows extrapolation to $x = 100$, and suggests that pure amorphous iron would be a highly concentrated spin glass. Furthermore, for $J/\Delta > 1$ the model predicts that the magnetic order develops in two stages: first, at T_c, the collinear components of the spin order, then at a lower temperature, T_{xy}, the transverse spin components freeze and the magnetic structure becomes noncollinear. If we associate T_{xy} with the low-temperature transition observed by other workers then the transition represents a fundamental change in the nature of the magnetic order, from an essentially collinear structure above T_{xy}, to a noncollinear or asperomagnetic structure below T_{xy}. The other effects seen in susceptibility meausurements, which are easily suppressed by modest applied fields (~ 50 mT), reflect the development of some exchange induced anisotropy as the transverse degrees of freedom are lost.

 0021-8979/88/225787-05$02.40

Mössbauer spectra obtained with a magnetic field applied parallel to the γ-beam direction offer the clearest method of observing the freezing of transverse spin components. The six lines observed in a magnetically split spectrum have intensities $3{:}R{:}1{:}1{:}R{:}3$ where $R = 4\sin^2\theta/(1+\cos^2\theta)$, and θ is the angle between the magnetic moment and the direction of the γ beam. Thus, the $\Delta m_I = 0$ transitions (lines 2 and 5) are forbidden when the moments are parallel to γ beam ($\theta = 0°$) and the appearance of intensity in these lines signals the freezing out of transverse components. Such experiments have been carried out on $Au_{100-x}Fe_x$ ($x = 16.8$)[13] and transverse spin freezing was observed. Also Mössbauer spectra obtained in zero external field showed a sudden rise in the average hyperfine field $\langle B_{hf}\rangle$ at T_{xy} as the extra spin components froze out. While such results are encouraging, the compositions of *Au*Fe for which transverse spin freezing is expected correspond to a region of the binary phase diagram where compositional uniformity cannot be guaranteed. Much evidence for the presence of iron-rich platelets parallel to the [420] planes has been presented[14] and the possible role of compositional modulations clouds the issue of the nature of the magnetic order.[15–17]

Iron-rich amorphous Fe_xZr_{100-x} provides a very attractive alternative system for studying the effects of varying exchange frustration on magnetic ordering. The rapid quenching and low concentration of alloying element make any significant compositional modulation unlikely, and indeed SANS shows no evidence of such effects[4]; therefore a metallurgical explanation of any magnetic transitions may be ruled out. Also, the magnetic phase diagram is well established[1] and contains a wide range of values for both T_c and T_{xy}. We selected $Fe_{92}Zr_8$ for this study as, with $T_c \sim 180$ K and $T_{xy} \sim 80$ K, it combines a wide intermediate region with a large degree of noncollinearity at 4.2 K, so that the transition from collinear to asperomagnetic order should be well defined.

EXPERIMENTAL METHODS

Amorphous ribbons of nominal composition $Fe_{92}Zr_8$ 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. Magnetization measurements were performed on a vibrating sample magnetometer with a superconducting solenoid which provided a field of up to 5.5 T. $\langle M_z\rangle$, the average parallel component of the iron moment was determined by extrapolating the high field region of the magnetization curves, which is roughly linear, back to zero applied field.[1] Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer both with a field of 3 T applied parallel to the γ beam, and in zero field. In all cases where spectra were measured in an external field, the full field was applied well above T_c; then the sample was cooled in this field to the measuring temperature. This was done in order to ensure that the appearance of the $\Delta m_I = 0$ transitions was due to a spontaneous rearrangement of the spin structure, and not to a failure to polarise the sample. A field of 3 T was selected so as to place the material well on to the flat region of the magnetization curve (after demagnetizing fields are taken into account) where all domains, if such exist, have been swept out.

Three different forms of the hyperfine field distribution were used in fitting the Mössbauer spectra to obtain average hyperfine fields $\langle B_{hf}\rangle$ and the intensities of lines 2 and 5 ($\Delta m_I = 0$). These were: (i) Lorentzian lines, broadened according to their distance from the spectrum center (equivalent to assuming a Lorentzian distribution), (ii) an asymmetric Gaussian distribution with a variable maximum probability, and independent widths to higher and lower fields, (iii) Window's method[18] which involves no *a priori* assumptions about the shape of the hyperfine field distribution. The quality of the fits obtained increased from (i) to (iii) but with little variation in the information obtained. In all cases a linear correlation between the isomer shift and the hyperfine field was used to account for the observed asymmetry in the spectra, and variable intensity ratios of the form $3{:}R{:}1{:}1{:}R{:}3$ for the six lines, with R constrained to be between 0 and 4, were used to detect the transverse components of the spins. The fitting sequence used was as follows: with R constrained to be zero, the rest of the parameters were optimized; R was released and the optimization repeated; finally the stability of the solution was tested by displacing R from its fitted value, either to 1 if it was zero, or zero if the fit had returned a nonzero value, the fit was then optimized again. The fit always returned to its previous values, within statistical uncertainties. A conversion factor of 15 T/μ_B was used to relate the hyperfine field to the iron moment.[1,2]

RESULTS

Mössbauer spectra obtained with and without an external field at various temperature above and below T_{xy} are shown in Fig. 1. It is immediately apparent from a visual inspection of Fig. 1(b) that the $\Delta m_I = 0$ transitions are absent at high temperatures, and develop on cooling. The fitting procedures described above were used to determine the temperature at which the transverse spin freezing occurs (signaled by $R \neq 0$). Figure 2 shows the fitted values of R as a function of T for the various methods. There is some variation in the value of R determined by the different methods (this reflects the relative ease with which the distribution can compensate for absorption in lines 2 and 5 by broadening to low fields), but all three methods lead to the *same* value for T_{xy} of 76 ± 3 K.

Another expected characteristic of transverse spin freezing is the development of a discrepancy between moments determined by Mössbauer spectroscopy, and M_z deduced from magnetization curves. This arises because between T_c and T_{xy} only the z components of the spins are ordered and both techniques observe the same moment. Below T_{xy} the *total* moment increases and Mössbauer spectra measure this, but the z component remains the same so magnetization curves show no change except for the gradual increase expected from the reduction of thermal disorder. Figure 3 shows magnetization curves for a-$Fe_{92}Zr_8$ at a number of temperatures. M_z values together with average hyperfine fields, measured both with and without an external field, are given in Fig. 4. The expected difference between M_z and

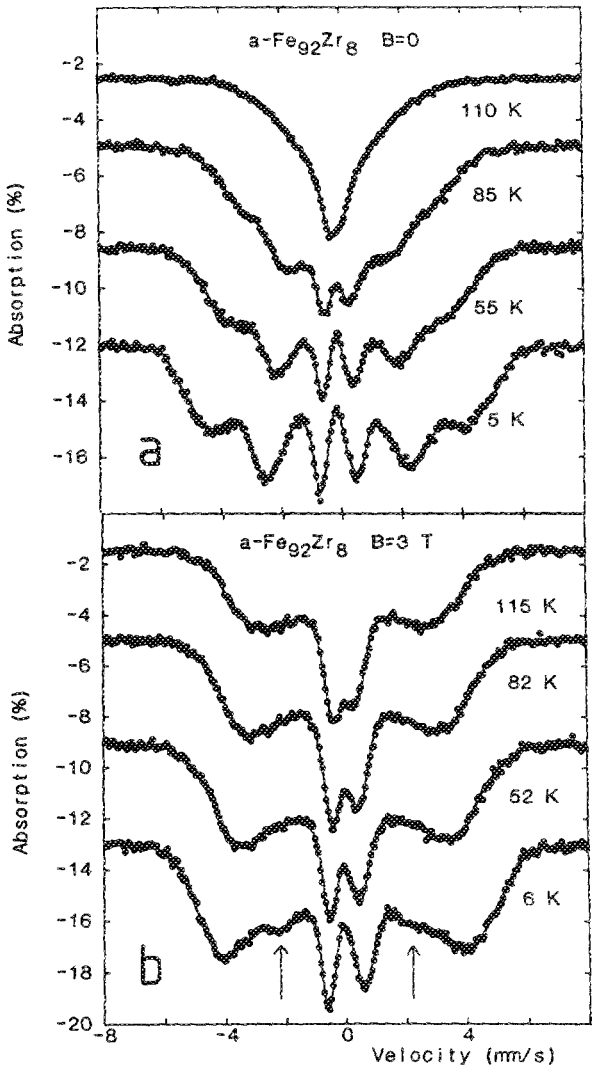

FIG. 1. Mössbauer spectra of a-$Fe_{92}Zr_8$ obtained above and below the transverse spin freezing temperature ($T_{xy} = 76$ K). (a) In zero field, (b) with a field of 3 T applied parallel to the γ direction. Note the development of the $\Delta m_I = 0$ transitions (arrows) below T_{xy}.

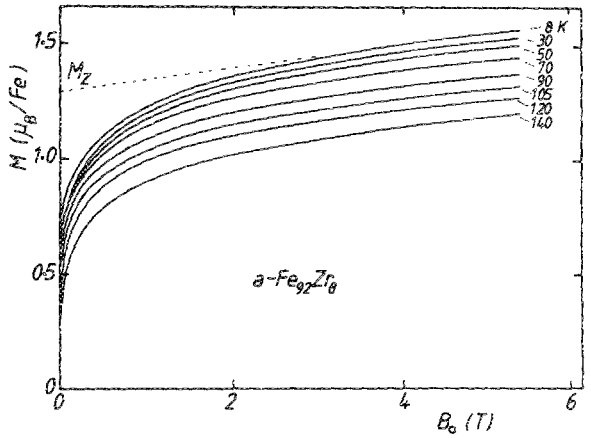

FIG. 3. Magnetization curves for a-$Fe_{92}Zr_8$ for a number of different temperatures. The dotted line indicates the extrapolation of the high field region back to zero field to obtain M_z.

$\langle B_{hf}\rangle_{3\,T}$ below T_{xy} is observed. The difference between $\langle B_{hf}\rangle_0$ and $\langle B_{hf}\rangle_{3\,T}$ also disappears at T_{xy}, but this is almost certainly fortuitous. The persistence of a significant magnetic splitting even close to T_c in spectra measured in an external field shows that the ordering for this sample is dominated by the relaxation of large magnetically coupled clusters in this temperature regime. An alloy with a higher T_c and lower T_{xy} such as Fe_9Zr_9 would show agreement between $\langle B_{hf}\rangle_{3\,T}$ and $\langle B_{hf}\rangle_0$ well above T_{xy} and in $Au_{83.2}Fe_{16.8}$ this agreement does not occur until well below T_{xy}.[19]

DISCUSSION

The two characteristic features of transverse spin freezing have been observed at the expected temperature. Both the appearance of the $\Delta m_I = 0$ transitions and difference between M_z and $\langle B_{hf}\rangle_{3\,T}$ are clear signals of the transition. We do not however observe the previously reported abrupt rise in $\langle B_{hf}\rangle_0$ at T_{xy} (Refs. 9 and 13); this may be due to T_{xy} being too close to T_c for a break in slope to be distinguished.

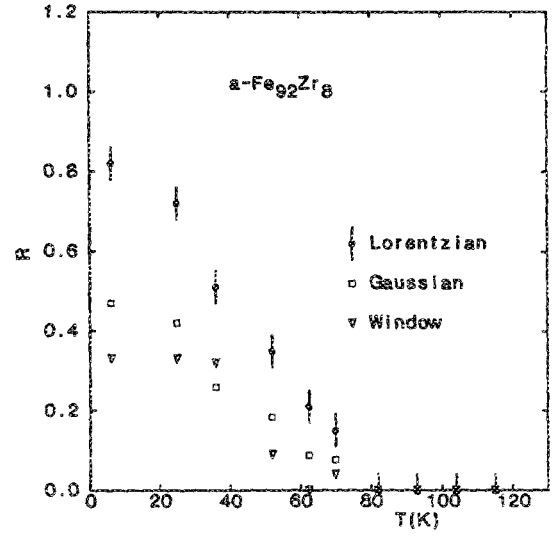

FIG. 2. Variation of the normalized intensity in the $\Delta m_I = 0$ Mössbauer transitions as a function of temperature for various fitting techniques.

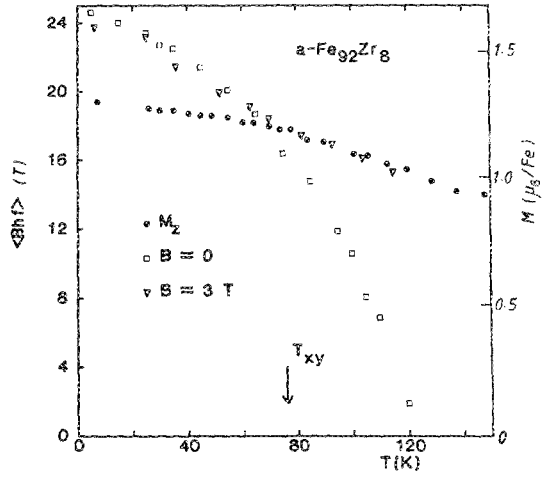

FIG. 4. Variation of the ordered iron moment in a-$Fe_{92}Zr_8$ with temperature, measured by both magnetization and Mössbauer spectroscopy. Note the deviation of M_z from $\langle B_{hf}\rangle_{3\,T}$ below T_{xy}.

As a magnetically concentrated system dominated by direct exchange, $Fe_{92}Zr_8$ provides a useful comparison with other alloys in which transverse spin freezing is more usually observed close to the percolation threshold[19] where a crossover from long-ranged to short-ranged coupling occurs. Furthermore, as it is also amorphous, compositional modulations are unlikely, and spatially ordered segregation (like [420] platelets) is impossible. Transverse spin freezing must therefore be due solely to the distribution of magnetic exchange, as originally predicted,[12] and a metallurgical origin as suggested for *Au*Fe,[17] may be ruled out.

Our results suggest that the phase diagram of Gabay and Toulouse should be modified in a manner which is illustrated in Fig. 5. In this phase diagram the conventional spin glass and the true ferromagnet are separated by regions in which the system exhibits properties common to both. At high J/Δ ($\gg 3$ in the Gabay and Toulouse diagram) lowering the temperature induces a well-defined phase transition to a true ferromagnet with moments fully aligned and an infinite correlation length. If we remain at low temperature and progressively reduce J/Δ we reach a point (somewhere on line 5) where the correlation length becomes finite and enter a region which has been described as a wandering axis ferromagnet,[1,20] but which is perhaps more properly viewed as a strongly correlated spin glass (SGII). In this phase there is a locally preferred axis whose direction is maintained over the coherence length [20 nm in $Fe_{92}Zr_8$ (Ref. 8)] but which is random over longer distances. In zero field there is no spontaneous moment, but a very small field is sufficient to align the local axes and produce a substantial magnetization, though one which remains below saturation because the perpendicular components of spin remain unfrozen. As we continue to reduce J/Δ we pass through the T_{xy} line (3) below which the perpendicular components of spin are frozen, although in random directions, since there is no observed change in correlation length. This phase is often called an asperomagnet. At still lower values of J/Δ the ferromagnetically correlated regions gradually disappear (line 4) and we finally reach the conventional spin glass (SGI). Experiments with hydrogen doping, which allows a continuous increase in J/Δ, suggest that line 5 does not mark a sharp transition, but rather that the system evolves continuously from asperomagnetic to ferromagnetic.[21] Similarly T_c (line 2) evolves from a spin freezing transition into a ferromagnetic phase transition.

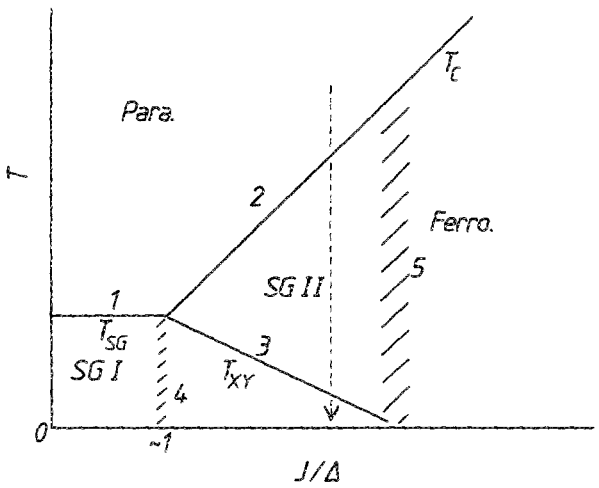

FIG. 5. Proposed magnetic phase diagram for systems with mixed exchange, showing the separation of the ferromagnetic region (Ferro) from the conventional spin glass (SGI) by a strongly correlated spin-glass region (SGII). See text for a description of the phases and the transitions.

The phase SGII may be distinguished from SGI, lying below it in temperature, by the ordering of transverse spin components. At $T = T_c$, the system spontaneously selects a direction "z" and only spin components parallel to this direction order. Transverse components remain free and the spins precess rapidly. The selection of the z axis is essentially arbitrary and is probably controlled by local anisotropy fields,[22] with the result that the axis will vary slowly throughout the sample (particularly in an amorphous system where no global axis exists). On cooling through T_{xy} the transverse components freeze but the z components and the correlation length remain unchanged. Table I shows the variation of the order parameters on cooling through the two transitions along the arrow marked on Fig. 5.

While the transition at T_{xy} may appear equivalent to the spin-canting transition predicted by both mean-field spin-glass theory[12,23] and two-dimensional computer modeling,[24] in that both involve the transformation of an initially collinear spin structure into one with significant transverse components, it is quite different. In the latter case the xy spin components appear via the tilting of the ordered spins away from the z axis, and lead to a *reduction* of Q_z, whereas in the former transition the transverse components are always present, but above T_{xy} they are not frozen and so time average to zero. Transverse spin freezing leads to an increase in the total ordered moment (Q), but does not involve the collinear component (Q_z) which remains unchanged. The $T = 0$ ground states are probably the same, but the routes taken from the high-temperature paramagnetic phase are clearly different.

CONCLUSIONS

Transverse spin freezing has been observed. It is characacterized by the appearance of transverse spin components at a well-defined temperature (T_{xy}) below that at which the

TABLE I. Variation of magnetic order parameters in the double transition region of the phase diagram in Fig. 4 (between lines 4 and 5). M is the average magnetization and remains zero at all temperatures in zero external field since the correlation length is finite. Q is the time average of the spin at each site, averaged over the whole sample, and may be divided into a component parallel to the local axis, Q_z, and one perpendicular to it, Q_{xy}.

Order parameter	$T > T_c$	$T_c > T > T_{xy}$	$T < T_{xy}$
$M = \langle S_i \rangle$	0	0	0
$Q = \langle S_i(0) \cdot S_i(t) \rangle$	0	>0	>0
		$= Q_z$	$= Q_z + Q_{xy}$
$Q_z = \langle S_i^z(0) \cdot S_i^z(t) \rangle$	0	>0	>0
		$= Q$	$< Q$
$Q_{xy} = \langle S_i^{xy}(0) \cdot S_i^{xy}(t) \rangle$	0	0	>0

collinear components order (T_c). The magnetic order both above and below T_{xy} has a short correlation length and is therefore spin-glass-like. The two states are distinguished by the value $\langle S_i^{xy}(0) \cdot S_i^{xy}(t) \rangle$ which is only nonzero below T_{xy}.

ACKNOWLEDGMENTS

We are grateful to Dr. Geoffrey Grinstein for many useful discussions during his recent visit to McGill. This work was supported in part by a grant from the Natural Science and Engineering Research Council, Canada.

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