The ferromagnet to spin-glass cross-over: A neutron depolarisation study

D.H. Ryan\textsuperscript{a,}, Zin Tun\textsuperscript{b}, J.M. Cadogan\textsuperscript{c}

\textsuperscript{a} Department of Physics, Center for the Physics of Materials, McGill University, 3600 University St., Montreal, Quebec H3A 2T8, Canada
\textsuperscript{b} AECL, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada
\textsuperscript{c} School of Physics, The University of New South Wales, Sydney, NSW 2052, Australia

Abstract

Mössbauer spectroscopy, magnetisation, susceptibility and neutron depolarisation have been used to investigate the evolution of magnetic order in a-Fe\textsubscript{90-x}Ru\textsubscript{x}Zr\textsubscript{10}. Ru additions cause exchange frustration leading to a rapid reduction in $T_c$ and the appearance of transverse spin freezing at $T_x$. At $x_c = 2.5$, $T_c$ drops abruptly to meet $T_x$, and the system becomes a spin glass with no long-range order. The magnetic phase diagram is fully consistent with results of mean field and Monte Carlo simulations. The anomalous peak in the neutron depolarisation signal observed close to $x_c$ in this and other systems is shown to be due to the formation of a uniformly magnetised state induced by the 1 mT guide field. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Frustration; Spin glasses; Mössbauer spectroscopy; Neutron depolarisation; Metallic glasses

1. Introduction

Magnetic materials with randomly competing positive and negative exchange interactions exhibit a rich variety of magnetic behaviour. Mean-field calculations [1] and numerical simulations [2] of partially frustrated magnetic systems of Heisenberg spins yield results consistent both with each other and with the experimental measurements. With no frustration, the material is a ferromagnet, with \( R \)-ranged correlations and collinear order. As frustration is introduced, the order at \( T = 0 \) becomes increasingly non-collinear and the magnetisation is reduced. The ground state appears to be an $xy$-spin glass co-existing with perpendicular ferromagnetic order (i.e. along the $z$-axis). On heating from zero temperature, the $xy$-spin glass melts at $T_{xy}$ to form a collinear ferromagnet with substantial transverse degrees of freedom that fluctuate rapidly and time-average to zero. Further heating takes the system to $T_c$ where the ferromagnet undergoes a conventional 3-D Heisenberg phase transition to a paramagnetic state. As the degree of frustration increases, the features characteristic of ferromagnetic order decline (both $T_c$ and magnetisation fall) while the spin-glass character becomes more pronounced ($T_{xy}$ rises and irreversibilities at low temperatures become stronger). Eventually, $T_c$ and $T_{xy}$ meet, and further increases in frustration lead to a pure 3-D spin glass with a transition temperature ($T_{sg}$) that is largely independent of the frustration level. Both calculations and simulations predict that the composition $x_c$ at which $T_c$ and $T_{xy}$ meet marks a significant change in properties and there is some evidence from scaling analysis of fluctuations through $x_c$ that a phase transition separates the spin glass from the ferromagnet [2].

One of the clearest examples of a partially frustrated magnetic system is provided by amorphous iron-rich Fe–Zr alloys [3]. The frustration in these alloys arises through the distance dependence of the direct exchange interaction ($J(r)$) coupled with short Fe–Fe contacts in the glass which lead to significant numbers of antiferromagnetic (AF) bonds that compete with the dominant ferromagnetic (FM) interactions. The effects of exchange frustration start to appear at \( \sim 90 \) at\% Fe and become
more pronounced with increasing iron content. All of the features described above have been observed in the a-Fe$_{x}$Zr$_{100-x}$ system, and quantitative agreement with the predictions has been obtained [3]. Unfortunately, some impurities (in this case Zr) must be present to stabilise a metallic glass, and the FM–SG boundary is expected to lie near $x = 94.5$ at% Fe, or about 1.5 at% beyond the limits of glass stability. The truncated phase diagram has led to a number of other explanations for the magnetic behaviour. These invariably appeal to the presence of magnetically distinct clusters that freeze at some reduced temperature, and destroy the ferromagnetic order established at $T_e$ [4–8]. A more complete discussion of the limitations of these models has been presented elsewhere [3]; we note here that there is no evidence for the existence of the distinct spin populations demanded by the extrapolation models introduced above [1–3]. We also investigated especially on the FM–SG cross-over region. The work presented here is intended to characterise the Ru-induced changes in the magnetic order, concentrating especially on the FM–SG cross-over region. Magnetisation, neutron depolarisation and Mössbauer measurements were used to probe the magnetic correlations on macro-, meso- and microscopic length scales. Our results confirm the destruction of magnetic order and show that by $x \geq 2.5$, no long-range ferromagnetic order is present above 2 K. The magnetic phase diagram is fully consistent with the homogeneous exchange-frustration models introduced above [1–3]. We also investigate the region around $x_e$ and show that the apparent formation and collapse of ferromagnetic order on cooling is an artefact of the measurement technique.

2. Experimental methods

The alloys were prepared by arc-melting the appropriate ratio of pure elements (Fe: 99.95%, Zr: 99.5% and Ru: 99.9%) under Ti-gettered argon to yield ~3 g ingots. Melt-spinning was carried out under a partial pressure of helium onto a copper wheel at 55 m/s. Absence of crystallinity was confirmed using Cu K$_\alpha$ X-ray diffraction and room temperature Mössbauer spectroscopy.

A susceptibility system with a closed-cycle fridge was used to record $X_{AC}$ versus $T$ down to 12 K. Magnetisation data were obtained in fields of up to 9 T over the temperature range 2–300 K. Mössbauer measurements were made on a constant acceleration spectrometer with a 1 GBq $^{57}$CoRh source calibrated using an α-Fe foil. Samples were mounted in a vibration-isolated closed-cycle fridge for spectra at temperatures down to 12 K.

Neutron depolarisation data were obtained using the DUALSPEC triple-axis spectrometer at AECL, Chalk River. Initial polarisations of $\sim 96\%$ at $\lambda = 0.237 \text{ nm}$ were achieved with Cu$_2$MnAl single crystals as polariser and analyser. Measurements were made between 2 and 300 K in a 1 mT guide field, on stacks of one or more 5 mm lengths of 20 µm thick ribbons. Three orthogonal pairs of 1 m diameter Helmholtz coils was used to provide guide fields oriented along X (parallel to the neutron flight path), Y (horizontal and parallel to the long axis of the sample) and Z (vertical). These allowed all three components of the sample magnetisation to be probed so that variations in magnetic texture could be detected.

3. Basic characterisation

$Z_{AC}$ measurements show a steady reduction in $T_e$ (taken as the point of maximum slope on a plot of $Z_{AC}$ versus $T$) and an evolution from ferromagnetic behaviour to a spin-glass-like cusp with increasing Ru content. The cusp develops at $x = 2.35$ and there is an abrupt drop between $x = 2.35$ and $x = 2.5$, where $T_e$ falls by 60 K, followed by a more gradual decline. Modified Arrott plots (using standard 3-D Heisenberg exponents) yield ordering temperatures in accord with those derived from $Z_{AC}$ and Mössbauer measurements for $x \leq 2.35$. Beyond this point no spontaneous magnetisation is observed at any temperature. We therefore conclude that the FM–SG boundary lies in the range: 2.35 $\leq x_e \leq 2.5$. Magnetisation curves at 5 K show a steady decline with increasing Ru content (Fig. 1), with a gradual increase in high field slope and coercivity. There is no discontinuity in its behaviour at $x_e$.

Mössbauer spectra for these materials exhibit the usual broadened six-line pattern below the ordering temperature. The decline in average hyperfine field ($\langle B_{mh} \rangle$) (and hence iron moment) with increasing Ru content is far less than that observed in the magnetisation, reflecting the expected increase in non-collinearity as exchange frustration drives the system towards the spin glass. $\langle B_{mh} \rangle$ versus $x$ shows no break in slope at $x_e$, confirming that the breakdown in the long-range order is not related to a collapse in the iron moment. The temperature dependence of $\langle B_{mh} \rangle$ in Fig. 2 shows two remarkable features.
First, an abrupt change in behaviour occurs between $x = 2.0$ and $2.2$, significantly below $x_c$. Second, for $0.5 \leq x \leq 2.0$ there is a clear break in the temperature dependence at $\sim 80$ K. We found that $\langle B_{hf} \rangle(T)$ can be fitted within $0.1$ T by a combination of a modified Brillouin function [12] and a linear term that starts at $T_{br}$, the break point [11]. Fitting the data with two Brillouin functions adds more parameters and tends to degrade the fit quality.

The phase diagram in Fig. 3 summarises the characteristic temperatures determined by the various techniques used here. The boundary between ferromagnetic and spin-glass behaviour is clearly visible as an abrupt drop in ordering temperature and a loss of long-range order. $T_{br}$ rises to meet $T_c$ with increasing Ru content and they meet at $x_c$, behaviour consistent with $T_{br}$ being associated with transverse spin freezing. However, Mössbauer measurements in an applied field are needed before $T_{br}$ can be conclusively identified with $T_{sy}$. The parallels between the phase diagram in Fig. 3 and that of the binary a-Fe–Zr system [3] are quite striking. Up to $x = 2.0$ the rate of decline in $T_c$ and the composition dependence of $T_{sy}$ are very similar. Indeed, if a Mathon plot of $T_c^2$ versus $x$ is made, it predicts a loss of magnetic order at $x = 4$ in much the same way as is claimed for a-Fe–Zr [7, 8]. However, in the Ru-doped system we can achieve much higher levels of frustration and so observe that magnetic order is not lost. The decline in $T_c$ is cut off by $T_{sy}$ as the spin glass is formed and $T_{sy}$ is largely independent of $x$. These results are in full agreement with theoretical predictions for exchange frustration.

Window fits [13] to the Mössbauer spectra yield strongly bimodal hyperfine field distributions $P(B_{hf})$, and while this structure may simply be mathematical in origin [3], it is clearer here than in any other alloy system that we have studied. The bimodal structure is not associated with the break in temperature dependence at $T_{br}$ as it is present in samples that do not exhibit a break point. Were we to argue that the magnetic behaviour in this system arose from a cluster–matrix competition, then it would be natural to associate the low-field feature in $P(B_{hf})$ with the clusters and the stronger, high-field feature with the matrix. This assignment fails for two reasons. (1) We observe no significant shift in the position of the low-field component on passing through $x_c$ so this component cannot be associated with the freezing of clusters. (2) The area of the low-field feature never dominates the distribution, even as we cross into the spin glass. The low-field feature is always a minority component and likely to be a mathematical artefact.

The most direct evidence for the disappearance of long-range order comes from neutron depolarisation data [11]. Ordering temperatures for $x < x_c$ agree with values determined by other methods and are included in Fig. 3. The depolarisation caused at $T = 0$ decreases with increasing Ru far more rapidly than either the magnetisation or $\langle B_{hf} \rangle$ (Fig. 4). We attribute this to a rapid reduction in domain size from $1.64 \pm 0.01$ $\mu$m at $x = 0$ to $0.4 \pm 0.1$ $\mu$m by $x = 2$. For $x > 3$ no depolarisation is
observed at any temperature ($\Delta P < 5 \times 10^{-4}$) and we can rule out the presence of ferromagnetic correlations on a length scale greater than 10 nm. This confirms our conclusion that for $x \geq 2.5$ the system is a spin glass.

4. The FM–SG cross-over region

The change in behaviour at $x_c$ is remarkably sharp. Over a range of $\sim 0.2$ at% in Ru content, $T_c$ changes by nearly a factor of 2 and all long-range order is lost. We emphasise that this is solely an exchange effect, as Mössbauer spectra show that there is no significant change in either the average iron moment or its distribution through this region.

The critical region is the only place where there is a significant difference in ordering temperature determined by the various techniques, and then only for the Mössbauer data at $x = 2.2$ and 2.35. The Mössbauer values lie $\sim 30$ K below the other methods. While it is easy to attribute an upward shift in the Arrrott values to the large applied field used in their measurement, it is far less obvious that the 1 and 0.5 mT used in the depolarisation and $I_{AC}$ measurements could have a significant effect. However, in view of the effect described below, it is possible that some shift is present. Furthermore, as the cusp in $I_{AC}$ develops there is an associated ambiguity in the definition of $T_c$. It is not clear at which composition it becomes appropriate to switch from using the point of maximum slope to define $T_c$ (used below $x_c$), to the peak of the cusp (used above $x_c$). No such ambiguity is present in the Mössbauer data and the onset of magnetic splitting marks ordering in both spin glass and ferromagnetic systems. It is likely that $I_{AC}$ overestimates $T_c$ for these two alloys.

For $x = 1$ and 2, we previously observed a striking recovery in the neutron depolarisation below about 80 K [11] and suggested that a stress-driven re-orientation of the domain magnetisation might be an explanation. This was consistent with changes in the line intensities in the Mössbauer spectra of these alloys. However, measurements of all three components of the depolarisation signal do not support such a rotation. Furthermore, as we move into the cross-over region the recovery structure becomes even more pronounced, even as the maximum effect weakens. For the $x = 2.35$ sample shown in Fig. 4 there is a striking peak at 120 K with only weak depolarisation observed below 80 K. We observed such peaks as far as $x = 3$. Similar behaviour has been reported for $a-(Fe_{0.3}Mn_{0.7})_{5}P_{16}B_{6}Al_{3}$ [14], $Au_{84}Fe_{16}$ [15] and $a-(Fe_{0.13}Ni_{0.87})_{5}P_{16}B_{6}Al_{3}$ [16]. In this last study, the polarisation recovery evident in our less heavily Ru-doped samples was also reported.

For a multi-domain sample the series of brief precessions of the neutron moment in each domain leads to a polarisation that decays as: $P = \exp(-x^2)$ with $x = \frac{\gamma}{\pi} (B^2) d$. $d$ is the sample thickness, $\gamma$ is the mean domain size along the neutron flight path, $\langle B^2 \rangle$ is the mean-square domain magnetisation perpendicular to the beam polarisation, and $c$ has the value $4.633 \times 10^{14} \text{m}^{-2} \text{T}^{-1}$ [17]. Given this expression, the simplest explanation for a depolarisation signal that fades on cooling is that either or both of the domain size $d$ or the domain magnetisation, $B$, are decreasing. Lorentz microscopy studies (albeit of less frustrated alloys), showed no evidence of domain shrinkage on cooling, and attributed the irreversibilities observed at low temperatures in these systems to pinning of domain walls [18]. We therefore eliminate changes in domain size from consideration. A reduction in magnetisation on cooling could be considered attractive for many reasons. As we move through the composition range around $x_c$ where the peak occurs, the saturation magnetisation of the samples clearly falls. The formation and subsequent collapse of a ferromagnetic state would be consistent with the various cluster models identified in the introduction [4–8]; however, such agreement is only found in the extremely narrow composition range around the FM–SG boundary, and appears coincidental. Alternatively, results of a homogeneous 2-D ‘local mean field’ simulation [19] have been used to support a canting driven loss of magnetisation at low temperatures. Apart from the inconsistency in the use of this 2-D model (the canting transition is only observed on heating, but it is interpreted as a cooling curve) we repeated the simulations in the course of our own 3-D Monte Carlo work [2] and found that the ‘local mean field’ model exhibits extremely poor dynamics and is easily trapped in local minima. The canting transition is an artefact of such trapping: a system quenched into a low magnetisation state remains there until the temperature is raised enough for it to jump to the equilibrium high magnetisation state. A drop in magnetisation was never observed on cooling. Our own 3-D simulations showed no evidence for a loss of magnetisation; on the contrary, we observed a consistent
increase in magnetisation on cooling for all those systems that initially entered a ferromagnetic state. Finally, it is not clear that the spontaneous loss of a ferromagnetic state on cooling is thermodynamically reasonable.

If the domain size is fixed, and ferromagnetic order does not decay, where does the peak in the depolarisation signal come from? To answer this question we turn to the full polarisation data shown in Fig. 5. For an isotropic domain distribution, the depolarisation signal should be independent of the direction of polarisation of the incident neutron beam, and this was generally observed for the ferromagnetic samples. However, Fig. 5 shows that the Z signal is always the weakest, indicating that the magnetisation tends to lie in the horizontal plane defined by the ribbon long axis and surface normal. This is consistent with low-temperature Mössbauer spectra recorded in zero applied field which also showed a clear tendency for the moments to lie perpendicular to the ribbon plane, i.e. along X. The data shown in Fig. 5 were obtained on heating, following cooling in the 0.5 mT stray field along Z from the guide boxes. We attribute the differences between the X and Y channels to imperfect guide fields that were not truly orthogonal for these axes.

A conventional interpretation would call for the development of a ferromagnetic domain state on heating, followed by its collapse at $T_c$. Similar curves were obtained on cooling and presumably would be explained in the same way. However, a comparison of the depolarisation in Fig. 5 with the Mössbauer data in Fig. 2 shows that the signal persists about 40 K above the temperature at which the hyperfine field, and hence all spontaneous magnetic order, disappears. It is, therefore, extremely unlikely that conventional ferromagnetic order is causing the depolarisation signal, especially in view of the excellent agreement in ordering temperatures observed at less frustrated compositions (Fig. 3).

Some small guide field is essential to maintain the neutron polarisation, and it can also be used, as here, to control the polarisation direction. The field of 1 mT used here is typical, and generally does not significantly influence the sample magnetisation, especially when samples have saturation magnetisations of 1–1.5 T. For such samples the guide field may bias the domain magnetisations slightly but the dominant effect is still the randomising of the polarisation due to transits through multiple, uncorrelated domains. Even quite severe bias will not suppress the signal. For samples near $x_c$ the situation is totally different. The spontaneous magnetisation is close to or actually zero, so the unperturbed sample cannot affect the beam. However, both DC and AC susceptibility yield significant signals for these materials, and modest magnetisations are readily achieved by quite small fields. The origin of this magnetisation is easily understood. Both numerical [2] and analytical [1] work show that at the FM–SG boundary, 75–85% of the exchange bonds are still ferromagnetic, so that a field applied near $T_{sg}$ can elicit a significant ferromagnetic response. At higher temperatures, thermal fluctuations dominate and no polarisation of the spins is possible, while at low temperatures frustration effects dominate, again preventing polarisation. In small fields the frustration prevents the field cooling of a polarisation, and $\chi_{AC}$ follows the decline of $\chi_{DC}$. Our explanation of the depolarisation peak observed in samples close to $x_c$ is therefore as follows: it is an artefact of the guide field that induces a weak uniform polarisation of the sample.

To test this model we cooled a 100 µm thick sample of a-Fe$_{80}$Ru$_{20}$Zr$_7$ in a field of 76 mT parallel to Y and recorded the signal shown in Fig. 6 on heating in the orthogonal guide fields. This material is on the FM–SG side, and shows only a weak (~3%) depolarisation signal [20]. Two features are immediately apparent: (i) there is no signal in the Y channel at any temperature confirming that the sample is indeed polarised along Y and that the decay of this polarised state does not involve the formation of domains; (ii) the polarised state is uniform as the neutrons are able to complete a full 2π rotation within the sample. As the temperature is increased, the magnetisation relaxes and the neutrons complete progressively smaller fractions of a rotation. Similar results were obtained for a-Fe$_{90}$Sc$_{10}$ which is a spin glass.
which decays on heating without forming domains. The sample is cooled into a uniformly magnetised state and does not depolarise the beam at any temperature [21], however the internal magnetisation is weaker and we did not obtain a complete inversion of the neutron polarisation. The a-Fe$_{93}$Zr$_{7}$ data are shown here because the neutron polarisation is clearly rotated by a uniform field, and not scrambled by domains. The a-Fe$_{93}$Zr$_{7}$ data were rescaled by up to 30% (see caption) which is a minor correction in view of the fact that the neutron depolarisation data were obtained in fields of 1 mT for the same samples. The magnetisation curves were rescaled by up to 30% (see caption) which is a minor correction in view of the fact that the neutron depolarisation data were obtained in fields of ±X, ±Y and ±Z at each temperature, rather than the static value used in the magnetometer. Despite these limitations, the agreement in shape, position and amplitude is remarkably good. An examination of the a-Fe–Mn [14] and a-Fe–Ni [16] data suggests that uniform polarisations of 16 and 10 mT, respectively, would also account for those observations.

5. Conclusions

a-Fe$_{90-x}$Ru$_x$Zr$_{10}$ provides a clear example of the evolution from ferromagnet to spin glass under the influence of exchange frustration. Two magnetic transitions are observed, the first at $T_c$ as ferromagnetic order appears, while at the second ($T_{sg}$) transverse degrees of freedom freeze to form a co-existing x-y-spin glass. There is a clear break in behaviour at the FM–SG boundary with $x_c \approx 2.5$ at% Ru. At $x_c$, $T_c$ and $T_{sg}$ merge and the system becomes a spin glass with no ferromagnetic order. The loss of ferromagnetic correlations is confirmed by neutron depolarisation. We have also shown that the maximum in the depolarisation signal seen near $x_c$ in this and other systems does not reflect the formation and decay of ferromagnetic order, but rather is an artefact of the guide field used in the measurement.

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, Fonds pour la formation de chercheurs et l’aide à la recherche, Québec, the Australian Research Council and The University of New South Wales.

References