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Neutron depolarisation study of magnetic order in a-$Fe_{90}Sc_{10}D_x$ ($0 \le x \le 28$)

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Abstract

Ac susceptibility and neutron depolarisation have been used to study magnetic order in a-$Fe_{90}Sc_{10}$ loaded with between 0 and 28 at% deuterium. The addition of 3 at% D more than doubles T_C and converts the as-cast alloy from a spin glass to a ferromagnet with 0.4 μm domains. Saturating the material with deuterium leads to a further doubling of both the domain size and T_C.

Keywords: Spin glass; Magnetic order; Metallic glass; Metal hydrides; Neutron depolarisation; Exchange frustration

1. Introduction

Ac susceptibility measurements on a-$Fe_{90}Sc_{10}$ show a cusp at about 100 K [1], indicating the onset of magnetic order. Unlike iron-rich a-Fe–Zr alloys, the ordering temperature is not sensitive to the Sc content, remaining constant across the range accessible to melt-spinning ($89 \le x \le 91$) [1,2]. In further contrast with the a-Fe–Zr system, where two magnetic transitions are observed [3], a-$Fe_{90}Sc_{10}$ goes directly from the paramagnetic state to a random, non-collinear ordered state, without first passing through a ferromagnetic regime [4]. More detailed investigation of χ_{ac} [5] and low-field magnetisation [3] showed that the critical behaviour at the ordering temperature is more characteristic of a spin glass, and that the ordered state exhibits no spontaneous magnetisation. We therefore regard a-$Fe_{90}Sc_{10}$ to be a spin glass below $T_{sg} \sim 100$ K.

The addition of hydrogen to any of the iron-rich a-Fe–ETM glasses (where ETM = Sc [2], Y [6], Zr [7] or Hf [8]) has been shown to raise the ordering temperature, often by factors of 3 or more, and also to lead to ferromagnetic ordering below the increased T_C. These transformations have been attributed to the lifting of exchange frustration which arises from short Fe–Fe contacts present in the glasses. Hydrogen expands the glass, increasing the interatomic distances and eliminating the antiferromagnetic exchange that causes the frustration [3]. Within this view, a-$Fe_{90}Sc_{10}$ represents the extreme case of complete frustration leading to a spin glass. An alternative view of the ordering at T_{sg} is that it results from the blocking of non-interacting, or possibly weakly interacting, 1 nm superparamagnetic

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clusters [9]. However, the absence of a frequency dependence on the ordering temperature is not consistent with this model [4].

Since Mössbauer spectroscopy, which probes the ordering on an atomic scale, and magnetisation measurements, which are sensitive to sample-sized ordering, have each been interpreted as supporting both the cluster and exchange frustration models, we decided to use neutron depolarisation measurements to provide a check on the 10 nm to 10 μm length scale. We have also investigated the effects of varying the level of deuterium loading on the observed ordering.

2. Experimental methods

The alloys were prepared by arc-melting the appropriate ratio of pure elements (Fe 99.95% and Sc 99.9% pure) under Ti-gettered argon to yield ~ 2 g ingots. Melt-spinning was carried out under a partial pressure of helium onto a copper wheel at 50 m/s. Absence of crystallinity was confirmed using Cu K_α powder X-ray diffraction and room temperature Mössbauer spectroscopy. A LakeShore susceptibility system with a closed-cycle fridge was used to record χ_{ac} vs. T down to 12 K using an ac field of 500 A/m. Deuterium was added electrolytically [10] to saturation, and the final deuterium contents were determined from the mass loss on heating to 300°C in a Perkin-Elmer TGA-7 thermogravimetric analyser. This instrument was also used to determine the magnetic ordering temperature of those deuterides ordering above room temperature, by operating with a small field gradient applied. Samples with deuterium contents below saturation were prepared by annealing saturated material in the TGA and monitoring the mass loss. Deuterium ($^2_1$H) was used rather than $^1_1$H to avoid possible complications from the large incoherent cross-section of the lighter isotope. We do not expect the difference in mass to play any role in modifying the magnetic properties, and both the saturation loadings and the T_C shifts observed here in a-Fe–Sc–D, and previously in a-Fe–Zr–D [11], are the same as those reported for ^{1}H-loaded alloys.

The neutron depolarisation measurements were carried out on the long wavelength polarised neutron spectrometer (LONGPOL) at the High Flux Australian Reactor (HIFAR) operated by the Australian Nuclear Science and Technology Organisation (ANSTO). The incident beam, with a wavelength of 0.36 nm, is polarised vertically by scattering from saturated polycrystalline iron sheets. A similar arrangement is used as an analyser. Typical beam polarisations were in the range 32–36%. The instrument has been described in more detail elsewhere [12]. A cadmium plate with a 5 mm × 5 mm square hole served as the sample holder. Several ribbons were laid side-by-side to cover the opening, with Cd wire covering any gaps between ribbons. One or two layers of ribbon were used. The holder was mounted on the cold stage of a closed-cycle fridge which operates down to 12 K.

3. Results and discussion

The high mobility of hydrogen isotopes in intermetallic compounds and glasses makes uniform loading relatively easy, but complicates the measurement of many of the hydrogen-induced effects. Fig. 1 shows the loss of deuterium from a-$Fe_{90}Sc_{10}D_{28}$ at a heating rate of 40 K/min. Since the estimated T_C for this sample (Fig. 2) is 400 K, it is clear that there is a substantial loss of deuterium before T_C is reached. Indeed, all of the samples heated through T_C showed no evidence of ordering above room temperature when cooled. As a result, the value of T_C given in Table 1 can only be regarded as a lower limit. At lower heating rates, the hydrogen loss problem becomes more severe and greatly limits the measure-

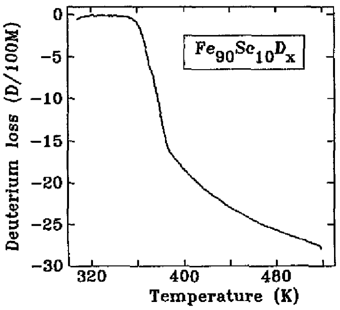

Fig. 1. Deuterium loss vs. temperature for a-$Fe_{90}Sc_{10}$ at a heating rate of 40 K/min. The rapid loss starting at 360 K makes accurate measurements of T_C for the saturated alloy impossible, and only a lower limit may be estimated.

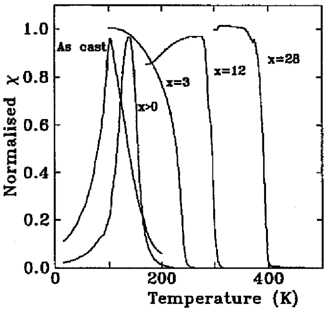

Fig. 2. Susceptibility vs. temperature for a range of deuterium loadings. Note the evolution from a cusp, characteristic of a spin glass at $x = 0$, to a steep rise and plateau typical of ferromagnetic materials for $x > 3$. The sample marked $x > 0$ contains residual deuterium that could not be removed by annealing (see text).

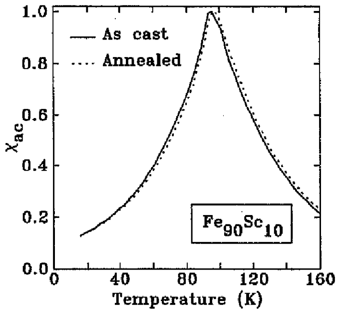

Fig. 3. Comparison of χ_{ac} vs. temperature for an as-cast (solid line) and annealed (dotted line) samples of a-$Fe_{90}Sc_{10}$ showing that the shift in T_{sg} apparent in the $x > 0$ sample in Fig. 2 is not due to annealing.

ments that can be made. For example, Mössbauer spectroscopy data gave a value of ~ 300 K for a-$Fe_{90}Sc_{10}H_{30}$ [2] compared with the value of 400 K obtained here on a similar composition, and a-$Fe_{91}Hf_9H_y$ has been shown to lose its hydrogen in a matter of hours at room temperature permitting only the limited observation that T_C is initially greater than 300 K [8].

We have exploited the reversibility of the deuterium loading process to prepare a number of samples with different deuterium contents. Approximately 1 m of ribbon was initially saturated with deuterium, then different annealing temperatures were used to partially unload pieces. χ_{ac} measurements (Fig. 2) show that T_C falls as the deuterium is removed, and eventually the original cusp is restored. The 35 K shift in peak position for the $x > 0$ sample shown in Fig. 2 is not due to the annealing used to extract the deuterium. Annealing a deuterium-free sample under the same conditions yields a shift of less than 2 K as can be seen in Fig. 3. Metallic glasses always contain a number of deep traps in which hydrogen is not mobile, and from which it is essentially impossible to extract the hydrogen without crystallising the glass [13]. We expect the trap concentration in this alloy to be of order 1/100 metal atoms, and it is the effects of this residual deuterium that lead to the shift in the $x > 0$ sample shown in Fig. 2.

Table 1
Summary of fitted parameters from data shown in Fig. 1 and Fig. 3. $T_C(\chi)$ and T_C(ndep) are ordering temperatures derived from susceptibility and depolarisation measurements, respectively. δ is the mean domain size

Deuterium content	$T_C(\chi)$ (K)	T_C(ndep) (K)	δ (μm)
0	95 [a]		< 0.01
3±0.5	244±4	216±3	0.37±0.01
9±0.5	257±4	227±3	1.02±0.06
12±0.5	302±4		
28±0.3	395±5	390±40	1.0±0.1

[a] Note: the as-cast a-$Fe_{90}Sc_{10}$ is a spin glass, so the value given in the T_C column is for T_{sg}.

Having established that deuterium loading leads to a reversible increase in the ordering temperature, and expecting both from earlier work [2] and from the χ_{ac} data in Fig. 2 that there is a switch from spin glass to ferromagnetic order associated with the T_C increase, we turn to neutron depolarisation to confirm that the as-cast material is indeed a spin glass and that deuterium loading does indeed yield a ferromagnet. On passing through a uniformly magnetised region such as a domain, the neutron moment experiences a torque which causes it to precess about the magnetisation direction. The total rotation increases with the internal magnetisation, the thickness of the domain and the wavelength of the neutron. If the neutron now passes through many such domains it will undergo multiple rotations. If the magnetisation direction within each domain can be assumed to be a random vector, and the angle through which the

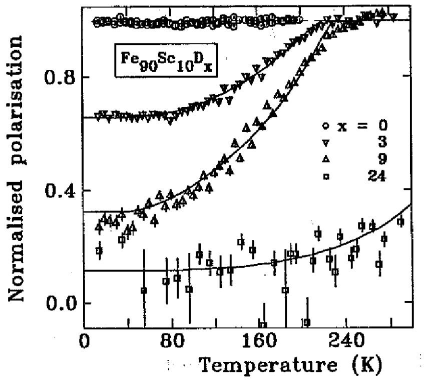

Fig. 4. Neutron depolarisation signals for an as-cast sample of a-$Fe_{90}Sc_{10}$ and three different deuterium loadings. The solid lines are fits assuming a constant domain size (see text).

neutron moment turns in each domain is $\ll 2\pi$, then the initial polarisation is scrambled and decays according to [14]:

$$P = \exp(-\alpha\lambda^2), \tag{1}$$

with

$$\alpha = \tfrac{1}{2}c^2\langle B_\perp^2 \rangle d\delta, \tag{2}$$

where λ is the neutron wavelength, $\langle B_\perp^2 \rangle$ is the mean square domain induction perpendicular to the neutron polarisation, d is the sample thickness and δ is the mean domain size. c is a constant which takes the value 4.63×10^{14} $m^{-2}\,T^{-1}$ in SI units. In a paramagnet, the temporal variations in local magnetisation are too rapid for the neutron moment to follow, and no depolarisation is observed. Similarly, in a spin glass where the spins are frozen in random orientations, the spatial variations in internal field occur on too short a length scale to affect the neutron moment, and again no depolarisation occurs. This means that once we know a sample is ordered, from χ_{ac} for example, we can readily distinguish a ferromagnet from a spin glass as the former will depolarise the neutron beam, while the latter does not.

Fig. 4 shows the results of neutron depolarisation measurements for four different deuterium loadings. The as-cast sample ($x = 0$) does not depolarise the beam at any temperature, consistent with the ordered state being a spin glass. In order to consider the superparamagnetic cluster model, we need a value for the cluster magnetisation. Taking the average hyperfine field from Mössbauer measurements [1–3] as an estimate of the iron moment, and assuming collinear order within a cluster, then the internal magnetisation should be about 1.3 T. A fit to Eq. (1) then puts an upper limit of ~ 10 nm on the cluster size. This is probably too small for the analysis to be valid, and is too large to allow us to rule out the presence of 1 nm clusters.

As the deuterided samples are expected to be soft ferromagnets [2], demagnetisation effects will cause the domain magnetisations to lie preferentially within the plane of the ribbons. We included this anisotropy by approximating $\langle B_\perp^2 \rangle$, in Eq. (2), as $\frac{1}{2}B^2$. All of the deuterium loaded samples depolarise the beam in the ordered state, and fits to Eq. (1) (summarised in Table 1) show that the ordering temperature, T_C, and the domain size, δ, both increase with the loading x. It is interesting to note that the ordering temperatures for the $x = 28$ sample derived from TGA and depolarisation measurements are in good agreement, despite the fact that the TGA value is expected to be affected by deuterium loss and a severe extrapolation is needed to get T_C from the depolarisation curve. Even small amounts of deuterium have a profound effect on the magnetic order, since the sample with $x = 3$ is clearly ferromagnetic, with an ordering temperature more than double that of the as-cast alloy. Further additions of deuterium do not have as dramatic an effect, the domain size and ordering temperature both double between $x = 3$ and $x = 28$, but this translates into only $dT_C/dx \sim 7$ K/at% D compared with six times that rate from $x = 0$ to $x = 3$. It is not clear how a cluster view of the ordering can account for the observed behaviour. At 1 μm the units are far too big to be considered superparamagnetic clusters and the deuterium loaded alloys must be ferromagnetic. Somehow, 3 at% of deuterium would have to eliminate the segregation that caused the system to exhibit clusters, and this process must also be reversible. Within the bond frustration model of this system [3], the low ordering temperature and spin glass state result from exchange frustration due to the presence of short Fe–Fe contacts. Adding deuterium expands the glass and eliminates the short contacts. Clearly a-$Fe_{90}Sc_{10}$ is very close to the spin glass boundary and only a few at% of deuterium is enough to lift most of the frustration. T_C rises abruptly, and ferromagnetic order develops. More deuterium causes further expansion and eliminates the remaining frustration but the T_C increases are more modest.

4. Conclusions

χ_{ac} shows that the addition of deuterium to a-$Fe_{90}Sc_{10}$ causes a rapid and progressive increase in the ordering temperature. This change is reversible, as driving out the deuterium (apart from about 1 at% D located in deep traps) restores the original properties. Neutron depolarisation shows that the as-cast alloy is a spin glass, and that the increase in ordering temperature caused by the addition of deuterium is accompanied by the development of ferromagnetic order and a rapid growth in domain size.

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