A single magnetic transition in *a*-$Fe_{91}Sc_9$

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The magnetic ordering behavior of $Fe_{91}Sc_9$ has been studied by Mössbauer spectroscopy and magnetization measurements. Mössbauer spectra in an external field parallel to the γ beam clearly shows that the noncollinearity develops as soon as magnetic order appears, indicating a single transition to an asperomagnetic state, in contrast to the mean-field theory and Monte Carlo simulations which predict a transition from paramagnet to spin glass for strongly frustrated alloys. A possible origin for this discrepancy is discussed.

I. INTRODUCTION

Iron-rich amorphous alloys are magnetically frustrated materials and have been studied extensively. For Fe–Zr and Fe–Hf alloys, two distinct magnetic transitions are observed on cooling.[1–4] The first, at T_c, marks the onset of long range collinear ferromagnetic order, however, substantial spin components persist transverse to the collinear order and precess rapidly so that their time average is zero. At the second transition (T_{xy}), these transverse spin components freeze randomly without affecting the collinear order of the longitudinal components and the system enters an asperomagnetic state. It is also found that as the frustration level is raised by increasing the iron content, the two transitions approach each other and the degree of noncollinearity increases.[5] All of these observations have been reproduced by Monte Carlo simulations[6,7] where the only mechanism used is exchange frustration modeled by randomly replacing a fraction of ferromagnetic interactions with antiferromagnetic interactions. For systems with an intermediate level of frustration, the simulations predict two magnetic transitions exactly as described above. When the frustration level is high enough, the two transitions merge to form a single transition from paramagnet to spin glass. These features have also been predicted by mean-field theory.[8]

The magnetic behavior of Fe–Sc alloys seems very similar to that described by Monte Carlo simulations and mean-field theory for highly frustrated materials. Melt-spun amorphous $Fe_{90}Sc_{10}$ was first prepared and studied by Day *et al.*[9] A sharp cusp at 99 K in ac susceptibility (χ_{ac}) was observed, suggesting spin-glass-like behavior at low temperatures. Ryan *et al.*[10] have shown that all of the samples they studied (Fe_xSc_{100-x}, $x=89$, 90, and 91) exhibited nonzero hyperfine fields in their Mössbauer spectra at almost the same temperature that the irreversibility in thermomagnetic measurements appeared, suggesting a single sharp transition to an asperomagnetic state characterized by noncollinearity and nonzero magnetization. In recent studies of $Fe_{90}Sc_{10}$ using Mössbauer spectroscopy in external fields, Ghafari *et al.*[11,12] found evidence for superparamagnetic clusters above T_c, and attributed the onset of noncollinear order at T_c to a blocking of these clusters in random orientations.

We have performed Mössbauer spectroscopy and magnetization measurements in order to obtain a clearer understanding of the magnetic ordering in $Fe_{91}Sc_9$. Our experimental observations are compared to the mean-field theory and Monte Carlo simulations.

II. EXPERIMENTAL METHODS

Amorphous ribbons of nominal composition $Fe_{91}Sc_9$ 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. The sample composition was checked by electron microprobe analysis and found to be within 0.2 at. % of the nominal value.

Mössbauer spectra were obtained over a temperature range from 5 to 140 K on a conventional constant acceleration spectrometer with a 25 mCi ^{57}Co*Rh* source at room temperature. High field spectra were recorded with a 6-T field applied parallel to the γ beam using a superconducting solenoid with the source located at the null point of the magnet, inside the cryostat at the same temperature as the sample. The field was applied above T_c and the spectra were obtained on field cooling. All spectra were fitted using Window's method.[13] Magnetization was measured with a vibrating-sample magnetometer in fields of up to 19 T.

III. RESULTS AND DISCUSSION

Mössbauer spectra were measured in zero field and the temperature dependence of average hyperfine field is plotted in Fig. 1. The transition temperature T_c is determined to be 102 ± 5 K, in good agreement with previous results.[9,10] From the average hyperfine fields, the corresponding average iron moments can be obtained by using a con-

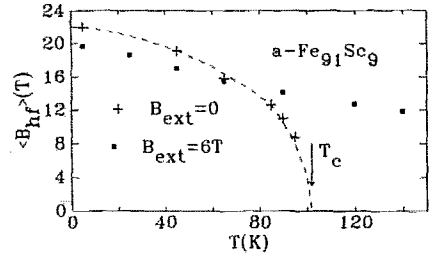

FIG. 1. Average hyperfine fields ($\langle B_{hf}\rangle$) for $Fe_{91}Sc_9$ derived from Mössbauer spectra with and without an external field.

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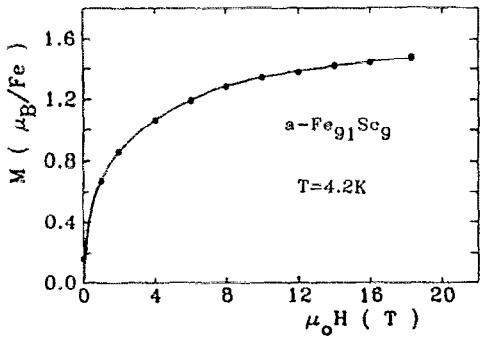

FIG. 2. Magnetization curve for $Fe_{91}Sc_9$ measured at 4.2 K.

version factor of 15 T/μ_B as found in α-Fe and crystalline Fe–Y alloys.[14] This gives an average iron moment μ_{av} of 1.47 μ_B/Fe at 5 K.

Magnetization measured at 4.2 K does not saturate in fields up to 19 T (Fig. 2), remaining below the average moment deduced from the average hyperfine field. A measure of the longitudinal component M_z may be obtained by extrapolating the segment of the magnetization curve between 2 and 6 T to $\mu_0 H=0$ T. M_z is 0.71 μ_B/Fe, much smaller than the moment derived from the average hyperfine field. This indicates that the system has a noncollinear ground state. However, since the alloy also shows a nonzero magnetization below the transition temperature, the ground state is not a pure spin glass, rather it is an asperomagnet. A measure of the degree of noncollinearity may be obtained by considering the iron moments to be oriented randomly within a cone of half-angle ψ, the ratio of μ_{av} and M_z given above, yield a half angle of $92\pm5°$.

Direct evidence for the noncollinear state comes from Mössbauer spectra measured in a 6-T field applied parallel to the γ beam (Fig. 3). 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 γ beam. For a collinear system, θ is zero and lines 2 and 5 are absent. The measured spectra clearly show the presence of the two lines

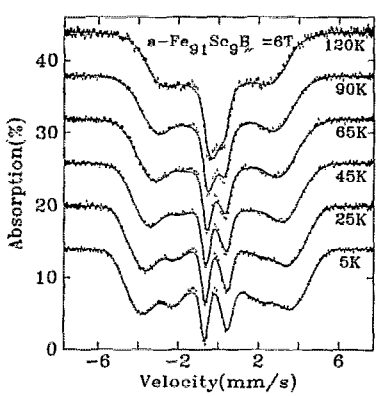

FIG. 3. Mössbauer spectra measured with a 6-T field applied parallel to the γ beam. The growth of lines 2 and 5 is clearly observed as the temperature is decreased.

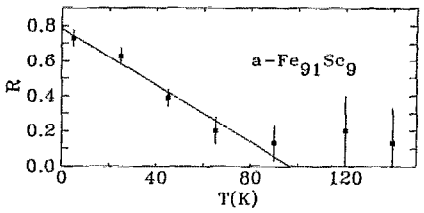

FIG. 4. Relative intensity of lines 2 and 5 (R) with $B_\parallel=6$ T. The onset of R at 97 ± 7 K (determined from the linear fit to the data shown by the solid line) coincides with T_c (102 ± 5 K), the onset of $\langle B_{hf}\rangle$ in zero field.

at low temperatures. A plot of R as a function of temperature (Fig. 4) shows that while lines 2 and 5 are present at all temperatures, R increases strongly below T_c. The nonzero values above T_c are not related to the long range ordering of the system and may be attributed to the presence of clusters which relax slowly in the applied ficld[11,12] and lead to the large enhancement of $\langle B_{hf}\rangle$ seen in Fig. 1. Fitting the low temperature behavior to a straight line indicates that the onset of noncollinearity occurs at 97 ± 7 K,[15] i.e., at T_c. This is consistent with χ_{ac} work[9,16] which also indicates a single magnetic ordering event in this system.

Thus, unlike the Fe–Zr and Fe–Hf alloys, which first enter a collinear state at T_c and develop noncollinearity only below the second transition, $Fe_{91}Sc_9$ undergoes a single transition and enters the noncollinear state directly.

Compared to Fe–Zr and Fe–Hf alloys with the same Fe content, $Fe_{91}Sc_9$ has a lower T_c, a larger ψ, and its magnetization curve exhibits a greater slope, indicating that the system is more frustrated. While the reason for the higher level of frustration is not clear, we can rule out the possibility of size effect. First, the radii of Sc (1.62 Å) and Zr (1.60 Å) are almost same, so the average Fe–Fe separation in $Fe_{91}Sc_9$ and $Fe_{91}Zr_9$, which determines the frustration level due to direct exchange, should also be quite close. Second, hydrogenation (which expands the lattice, increasing the Fe–Fe distance and reducing the incidence of direct antiferromagnetic couplings) does not convert Fe–Sc alloys into ferromagnets.[16] Hydriding Fe–Zr and Fe–Hf alloys lifts the exchange frustration and converts them into collinear ferromagnets with greatly increased T_c. By contrast, hydriding Fe–Sc alloys does reduce the degree of noncollinearity and raise the ordering temperature, but it does not restore the ferromagnetic character of the transition at T_c.[16] There must therefore be a further source of exchange frustration in the Fe–Sc system. One possible origin of this extra frustration could be indirect exchange via conduction band polarization. Since the direct exchange is already partially frustrated, this indirect exchange would further enhance the exchange frustration and would not be affected by hydrogenation.

It is instructive to compare our observations with mean-field theory[8] and Monte Carlo simulations.[6,7] Although the expected high degree of frustration and observed single transition in $Fe_{91}Sc_9$ are broadly consistent with the theory and simulations, the asperomagnetic state

in Fe–Sc is reached via a single transition with no intervening ferromagnetic phase. It has been suggested that the presence of magnetic clusters near T_c may be related to the discrepancy. However, the observed transition at T_c cannot simply reflect the blocking of superparamagnetic clusters, as measurements on very different time scales give almost identical values of T_c. For Fe_xSc_{100-x} ($89 \leqslant x \leqslant 91$), the transition temperatures (102 ± 5 K) measured by Mössbauer spectroscopy, which is sensitive on a time scale of $10^{-7} \sim 10^{-9}$ s, are almost the same as those obtained from χ_{ac} measurements where a driving field of several kHz was used [99 K (Ref. 9) and 95 K (Ref. 16) for $Fe_{91}Sc_{10}$]. The relaxation rate for magnetization reversal in zero field (the field is really zero in Mössbauer spectroscopy and only 5 μT in the χ_{ac} measurements) may be written

$$\tau^{-1} = \tau_0^{-1} \exp(-\Delta E / k_B T), \tag{1}$$

where τ_0 is the attempt frequency (assumed constant) and ΔE is an energy barrier. χ_{ac} measurements give $T_c \sim 100$ K at $\tau^{-1} \sim 1$ kHz from these we estimate ΔE to be ~ 1800 K (assuming a "reasonable" value of 10^{11} Hz for τ_0^{-1}).[17] For Mössbauer measurements where $\tau^{-1} \sim 10$ MHz, the blocking temperature is then predicted to be ~ 200 K, far above the experimentally observed value of ~ 100 K. This result is relatively insensitive to the actual choice of ΔE or τ_0^{-1} and thus we can rule out a simple blocking transition as the origin of the ordering at T_c.

It is not yet clear what really happens at the transition. One possibility is that clusters form well above T_c and expand to include more weakly coupled moments as the temperature is lowered toward T_c. The transition temperature then corresponds to a percolation threshold where the clusters form a continuous path throughout the sample. Below T_c, the ordered fraction continues to grow as the more weakly interacting moments couple to the percolating cluster. An external field applied above T_c slows the relaxation of the clusters and leads to a large hyperfine field. We note that the presence of slowly relaxing clusters does not necessarily lead to anomalous behavior at T_c, as similar relaxation behavior has been observed near T_c in the a-Fe–Zr system which has a ferromagnetic phase transition at T_c.[1]

IV. CONCLUSIONS

A single transition to an asperomagnetic state is observed for $Fe_{91}Sc_9$ with a transition temperature of 102 ± 5 K. This transition is distinct from that predicted by mean-field theory and Monte Carlo simulations for highly frustrated systems. The difference may be attributed to the presence of magnetic clusters near T_c but the observed transition cannot simply reflect the blocking of these clusters.

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