Relaxation and spin correlations in ^{119}Sn-doped a-Fe$_{90}$Sc$_{10}$

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Combined ^{119}Sn and ^{57}Fe Mössbauer measurements have been made on a Sn-doped sample of a-Fe-Sc both around T_{sg} (117±2 K) to examine the onset of order, and at 12 K to investigate spin correlations. The different time scales probed by the Sn and Fe Mössbauer transitions allow us to confirm that cluster relaxation effects do not contribute to the ordering at T_{sg}, while the large transferred hyperfine field (B_{hf}) at the Sn sites, in an alloy known to exhibit isotropic spin freezing, is inconsistent with the simple view of the transferred field arising as a vector sum over the nearest-neighbor moments.

I. INTRODUCTION

Amorphous iron-rich Fe-Sc alloys are unique among the iron-rich early transition metal-iron glasses, in that they do not exhibit a strong dependence of the magnetic ordering temperature on composition.[1] In contrast to a-Fe$_x$Zr$_{100-x}$ where the ordering temperature drops from 260 K at $x=88$ to 160 K at $x=93$,[2] the ordering temperature in a-Fe$_x$Sc$_{100-x}$ is essentially constant at 105 K in the range $89 \leqslant x \leqslant 91$ accessible by melt spinning.[3] Examination of the scaling behavior of the susceptibility around T_{sg} indicates that the material is a borderline spin glass, just sufficiently frustrated to destroy the ferromagnetic order,[4] a result that is confirmed by in-field Mössbauer measurements[5] which show that the system directly enters a noncollinear state at T_{sg}, and does not pass through the intermediate ferromagnetic phase seen in less frustrated materials.[1] More recent magnetization measurements have demonstrated that the system does not exhibit a spontaneous moment at any temperature.[6] An alternative view of the ordering proposes the existence of superparamagnetic clusters, which block in random orientations at T_{sg}.[7] This seems extremely unlikely in view of the close agreement between χ_{ac}[4,8] and Mössbauer[3] determinations of the ordering temperature, measurements with vastly different characteristic time scales.[5]

We present here a combined ^{57}Fe and ^{119}Sn Mössbauer study of a ^{119}Sn-doped a-Fe-Sc alloy. The two Mössbauer measurements are made in the same way, and on the same equipment, thus eliminating instrumental and calibration differences; however, the lifetime of the ^{119}Sn excited state is a factor of 5.5 times shorter than that of ^{57}Fe, so that the two measurements probe very different time scales, allowing us to examine the possible role that cluster freezing may play in the ordering at T_{sg}. Furthermore, as Sn has no local moment, the transferred hyperfine field at the ^{119}Sn nuclei contains information about the magnetic correlations among the neighboring Fe moments.

II. EXPERIMENTAL METHODS

Ingots for melt spinning were prepared in an arc furnace under titanium-gettered argon. The Sc (99.9%) was first premelted and then alloyed with the ^{119}Sn. Enriched ^{119}Sn (isotopic purity 82.9%) was used in order to get ~8 mg ^{119}Sn per 1 g sample weight and ensure a convenient absorption in the ^{119}Sn spectra. The Sc-Sn alloy was then added to an appropriate quantity of Fe (99.98%), and melted several times to ensure homogeneity. Melt spinning was done under a helium atmosphere onto a copper wheel, and yielded ribbons ~1 mm wide and ~10 μm thick. The amorphous structure of the sample was verified by x-ray diffraction and room-temperature Mössbauer spectroscopy. Differential scanning calorimetry showed that the crystallization temperature for this material was 810 K, close to the value of 822 K reported for a-Fe$_{90}$Sc$_{10}$,[3] confirming that the addition of 1% Sn does not significantly affect the glass. The amorphous ribbons were mounted on tape in order to make a Mössbauer absorber. A single thickness was used for the ^{57}Fe spectra while six layers were used for the ^{119}Sn measurements. The Mössbauer spectra were taken using a conventional constant acceleration spectrometer with a ^{57}CoRh source for the ^{57}Fe spectra and a Ca^{119}SnO$_3$ source for the ^{119}Sn spectra. The temperature was varied by means of a vibration-isolated closed-cycle He cryostat.

The ^{57}Fe spectra were fitted using two Gaussian distributions to describe the hyperfine field distribution. For the ^{119}Sn spectra a single Gaussian distribution with different widths on the low- and high-field side of the peak field was used. As the sample is an amorphous ribbon, the relative intensity of lines 2 and 5 cannot be fixed *a priori* to its powder average value. Therefore it was fitted in the ^{57}Fe spectra and then set to 2 (the value found in the fits to the ^{57}Fe spectra) for the ^{119}Sn spectra. A linear correlation between the isomer shift and the hyperfine field was assumed in order to fit the slight asymmetry in the spectra.

III. RESULTS AND DISCUSSION

A conventional method for determining magnetic ordering temperatures is to record the transmitted intensity of Mössbauer radiation at zero velocity as a function of temperature. As the spectrum broadens at T_{sg}, the peak absorption falls, and the zero-velocity count rate increases. The data for the ^{57}Fe thermal scan are shown in Fig. 1. T_{sg} is identified with the marked change in slope at 119±1 K. The procedure has to be modified for ^{119}Sn as the isomer shift displaces the peak absorption above T_{sg} to +1.8 mm/s relative to the source at rest. The spectrometer is therefore run at a constant velocity chosen to maximize the absorption at room temperature, and the observed drift in count rate on cooling above
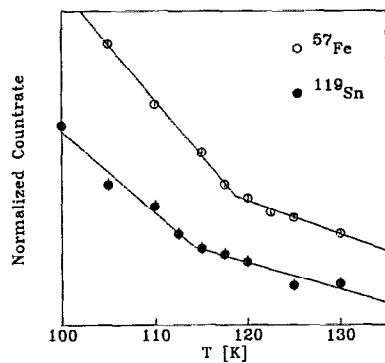
FIG. 1. Mössbauer thermal scans for a-Fe$_{90}$Sc$_9$Sn$_1$ at zero velocity for ^{57}Fe (O) and at $\sim$1.8 mm/s for ^{119}Sn ($\bullet$), showing the discontinuity at T_{sg}.

FIG. 2. Mössbauer spectra measured at 12 K a-Fe$_{90}$Sc$_9$Sn$_1$ for ^{57}Fe (top) and ^{119}Sn (bottom).

T_{sg} seen in Fig. 1, is due to the spectrum center moving as a result of the second-order Doppler shift. A clear break in slope is observed at 114$\pm$2 K.

Given that ^{119}Sn samples on a shorter time scale than ^{57}Fe, we would expect the Sn data to give a significantly higher ordering temperature if blocking of superparamagnetic clusters were the origin of the magnetic order. Such clusters would appear frozen at higher temperatures when observed at higher frequencies. However, the two Mössbauer measurements yield the same ordering temperature within error (it is interesting to note that the Sn value is actually slightly lower, rather than significantly higher). Assuming that T_{sg} does reflect a blocking of superparamagnetic clusters, we can calculate the energy barrier for magnetization reversal[9] and thus the change in blocking temperature on going from ^{57}Fe to ^{119}Sn. This calculation indicates that the ^{119}Sn transition would be at $\sim$150 K if such a model were appropriate, rather than 114 K as observed. We can therefore rule out relaxation effects or cluster blocking as contributing to the ordering of a-Fe-Sc.

Unlike earlier work on Sn-doped a-Fe-Zr which showed no effect of the Sn additions on the magnetic ordering temperature,[10] the Sn-doped sample does exhibit a slightly higher ordering temperature than that of earlier materials; however, we do not believe that the $\sim$14 K increase reflects a significant modification of the magnetic structure. The most convenient way to modify the magnetic properties of a-Fe-Sc is to add hydrogen. This leads to profound changes in both T_c (rises to $\sim$310 K) and the iron moment (increases to $\sim$2.2μ_B, the average hyperfine field rises to 31.3 T),[3] but the material still lacks the critical behavior characteristic of a ferromagnet.[4] Therefore it seems reasonable to conclude that if a 200 K increase in T_c leaves the system still in a strongly spin-glass like state, a 14 K increase will have negligible effects on the magnetic structure.

The Mössbauer spectra obtained at 12 K for the two transitions are shown in Fig. 2. Both are clearly magnetically split, reflecting the ordering of the iron moments. The fit to the ^{57}Fe spectrum yields an average hyperfine field of 22.8 T, indistinguishable from previous values obtained on Sn-free materials,[3,5] and further reinforcing the view that the addition of Sn has not significantly affected the magnetic ordering. Curiously, the ^{119}Sn spectrum also yields a large average
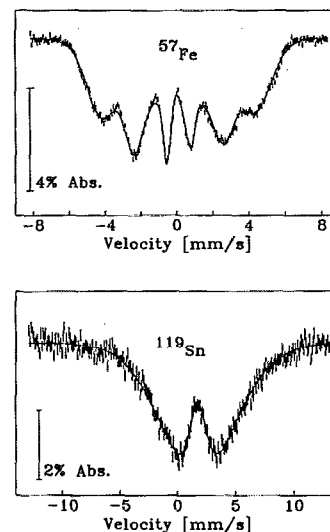
field: 5.1$\pm$0.2 T. If the local magnetic order were essentially isotropic, as would be expected in a spin glass, the contributions from the neighboring Fe moments would be random and therefore largely cancel at a Sn site. Such a situation would then yield a small ratio between the observed transferred Sn field and the Fe field (assumed proportional to the Fe moments). The value obtained here is 0.22$\pm$0.01, essentially the same as that found in the less frustrated a-Fe$_{92}$Zr$_7$Sr$_1$ (Ref. 10) and the almost ferromagnetic a-Fe$_{90-x}$Ni$_x$Zr$_9$Sn$_1$.[11] Assuming that the transferred field at the ^{119}Sn results from a vector sum over the moments on the Fe nearest neighbors, and that the coordination number in the glass is $\sim$12, then going from fully collinear to isotropic order should lead to a factor of 4 drop in the Sn/Fe hyperfine field ratio, a prediction that is completely inconsistent with our observations. Similar measurements on Mn-containing spin glasses[12,13] have also reported large transferred fields, leading to the rather unlikely speculation that the spin glass is dominated by significant ferromagnetic short-ranged correlations.[13] Since it is highly unlikely that the addition of 1 at % Sn makes the a-Fe-Sc alloy essentially ferromagnetic, without increasing either T_c or the iron moment, we are forced to conclude that even in an isotropically ordered material (i.e., a spin glass), the ^{119}Sn nuclei measure the magnitude of the average iron moment, rather than the vector sum of the randomly oriented neighboring moments.

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