Mössbauer measurements of spin correlations in a-$(Fe,Ni)_{90}Zr_9Sn$

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The local spin structure of the partially frustrated amorphous $Fe_{90-x}Ni_xZr_9Sn$ system was investigated by Mössbauer spectroscopy for $x=1,3$. The magnetic probe atom ^{57}Fe and the nonmagnetic ^{119}Sn were used to monitor the local correlation of the spins. The additional Ni renders the system less frustrated. We measured the temperature dependence of the hyperfine fields of the two probe atoms. The ratio $\langle B_{hf}(^{119}Sn)\rangle/\langle B_{hf}(^{57}Fe)\rangle$ rises with increasing temperature. This is in contrast to the temperature independence found for this ratio in $Fe_{92}Zr_7Sn$. A similar rise was found in the crystalline spin-glass AuFe where the slope was much larger and was related to a loss of longitudinal correlations.

INTRODUCTION

In amorphous and crystalline materials with competing antiferromagnetic (AF) and ferromagnetic (FM) exchange couplings two magnetic transitions have been observed in the low to medium frustration range.[1] The first transition marks the onset of ferromagnetic ordering at T_c. At the second transition temperature, T_{xy}, the transverse degrees of freedom freeze.[1,2] Overlaying the gross ordering behavior, are a series of phenomena associated with magnetic correlations and excitations. Neutron depolarization[3] and Lorentz microscopy[4] clearly show the existence of long-range ($\sim$10 μm) magnetic correlations which appear at T_c and persist through T_{xy}, consistent with the formation of a ferromagnetic state. By contrast, small angle neutron scattering reveals significant contributions from short-range ($\sim$10 nm) correlations,[5] which are sensitive to both magnetic transitions, and exist well above T_c.

One way to probe short-range magnetic correlations is to use Mössbauer spectroscopy. For a magnetic probe atom like ^{57}Fe the main contribution to the measured hyperfine field stems from the local moment of the atom itself. For a nonmagnetic probe atom like ^{119}Sn only the transferred fields from the neighboring magnetic moments contribute to the measured hyperfine field. If the spin structure is collinear, then the fields from the neighboring moments should add coherently, and a large transferred field should be observed at the nonmagnetic site, while a noncollinear or random spin structure should lead to a partial cancellation of the contributions and thus a smaller transferred field. The ratio of the (transferred) ^{119}Sn field to the (generating) ^{57}Fe field contains information about the degree of collinearity, and the temperature dependence of the ratio can be used to scale out the large changes due to thermal fluctuations, and reveal smaller effects due to changes in spin structure. This technique has been used to study spin correlations in several frustrated magnetic systems. In amorphous $Fe_{92}Zr_7Sn_1$, where the frustration arises through the distance dependence of the Fe-Fe direct exchange interaction, the transverse spin components were found to be correlated[6] as no change in the field ratio was observed on cooling through T_{xy}. Similarly, in AuFe, where the frustration is due to competition between long-ranged Ruderman–Kittel–Kasuya–Yosida (RKKY) and nearest-neighbor direct exchange interactions, both ^{196}Au and ^{119}Sn Mössbauer resonances have been employed, and clear evidence for strongly correlated transverse spin components was obtained.[7,8] However, more detailed examination of the temperature dependence of the $^{119}Sn/^{57}Fe$ field ratio, revealed evidence for a decay in the longitudinal spin correlations on cooling,[6] a result that is consistent with observations on similar compositions by neutron depolarization.[3]

In order to further understand the behavior of the field ratio it is necessary to study a range of frustrated magnetic systems. We have previously reported work on the a-$(Fe_{1-x}Mn_x)_{78}G_{22}$ system (G is a mixture of glass forming elements like Si, B, Al, P), which is frustrated through the addition of manganese,[9] however interpretation is complicated by the large magnetic moment of the Mn atoms. Here we report work on a simpler system, a-$(Fe_{90-x}Ni_x)_{90}Zr_{10}$, in which the addition of Ni reduces the frustration in the alloy, raising T_c and suppressing the transverse spin freezing transition.[10] In addition to the reduction of noncollinearity with increasing nickel content, the excitations become better behaved.[11] No spin waves were observed by inelastic neutron scattering for $x=0$, and while spin waves are seen below T_c for $x=1$, they soften on cooling, and were not resolved below $0.1T_c$. Well-defined spin waves are present for $x\geqslant 5$. Nickel carries a relatively small moment in this system ($\sim 0.6\mu_B$[12]) and as it is only present in low concentrations, its direct effects on the ^{119}Sn hyperfine field should be small. Therefore, the dominant contributions to the ^{119}Sn field should come from changes in the magnetic structure. The two samples considered here contain 1 and 3 at. % nickel; insufficient nickel to render the materials ferromagnetic.

EXPERIMENTAL METHODS

Ingots for melt spinning were prepared by first melting appropriate quantities of Zr (99.8%) and Ni (99.99%) in an arc furnace under titanium-gettered argon, then the Fe (99.98%) was added and the constituents were alloyed by rf melting under an Ar atmosphere. Enriched ^{119}Sn was used in order to get approximately 8 mg ^{119}Sn per 1 g sample weight to ensure a usable absorption in the ^{119}Sn spectra. Melt spinning was done under a helium atmosphere on to a copper wheel. The amorphous structure of the sample was verified by x-ray diffraction, DSC measurements, and room-temperature Mössbauer spectroscopy. The resultant amor-

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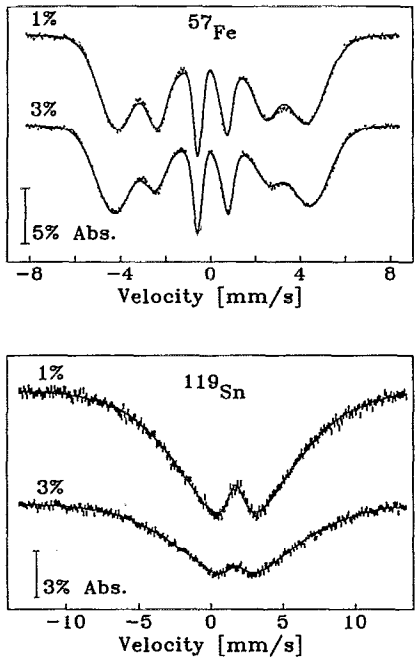

FIG. 1. ^{57}Fe and ^{119}Sn Mössbauer spectra for $Fe_{90-x}Ni_xZr_9Sn$ taken at 12 K.

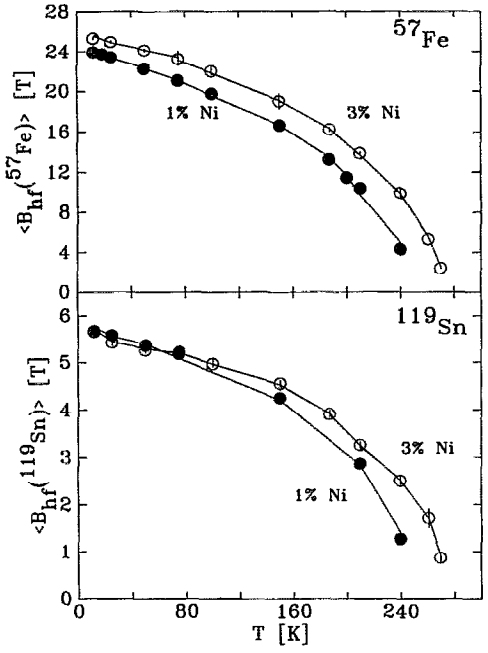

FIG. 2. Temperature dependence of the average ^{57}Fe and ^{119}Sn hyperfine fields for the two compositions of $Fe_{90-x}Ni_xZr_9Sn$.

phous ribbons were mounted on tape in order to make a Mössbauer absorber. The MS spectra were taken with a conventional constant acceleration spectrometer with a ^{57}Co/Rh 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 or a continuous flow 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 was used. As the sample is an amorphous ribbon the intensity of the 2nd and 5th lines could not be fixed to its powder average value. Therefore the intensity was fitted in the ^{57}Fe spectra, and then set to the value found in those fits (~1) in order to fit 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. Spectra taken at 12 K for the different compositions and the two probe atoms along with the fits are shown in Fig. 1.

RESULTS

As expected, T_c increases on adding Ni, being 247±5 K for $x=1$ and 270±5 K for $x=3$, compared with 230±5 K for $x=0$. The temperature dependence of the average ^{57}Fe and ^{119}Sn hyperfine fields is given in Fig. 2. The curves show Brillouin-like behavior in all cases, and the derived T_c for each alloy is the same for both the Fe and Sn measurements, confirming that the Sn probes the same magnetic behavior as Fe.

The ^{57}Fe hyperfine field at 12 K rises on adding nickel, increasing 4% on going from $x=0$ to $x=1$, and a further 6% on going to $x=3$. The width of the hyperfine field distribution also narrows slightly. These results are in accordance with more collinear ordering, and the increased magnetization observed in this system on adding Ni.[10]

The behavior of the ^{119}Sn transferred hyperfine field however, is less straightforward. The shapes of the ^{119}Sn spectra shown in Fig. 1 are different, reflecting a 4% increase in the width of the hyperfine field distribution on going from $x=1$ to $x=3$, however, this broadening does not translate into an increased average. It is immediately apparent from Fig. 2, that the average Sn field at 12 K does not match the increase in the iron moment derived both from magnetization measurements and the ^{57}Fe Mössbauer spectra. In clear contrast to the ^{57}Fe data, the average ^{119}Sn hyperfine field does not change with composition, and the slight difference in temperature dependence, apparent in Fig. 2, simply reflects the higher T_c of the $x=3$ sample.

Plotting the ratio: $\langle B_{hf}(^{119}\mathrm{Sn})\rangle/\langle B_{hf}(^{57}\mathrm{Fe})\rangle$ (Fig. 3) reveals another puzzle. Since the Sn field does not increase with the Ni content, the Sn/Fe field ratio decreases on moving to the less frustrated, and thus more collinear, sample. Furthermore, a clear temperature dependence is apparent, with a slope of $\sim 1.5\times10^{-4}$ K^{-1}, at least an order of magnitude greater than the largest slope consistent with the data from $Fe_{92}Zr_7Sn_1$.[6] This slope should also be compared with the much stronger temperature dependence of $\sim 9\times10^{-4}$ K^{-1} observed in AuFe by ^{119}Sn Mössbauer spectroscopy. In the case of AuFe, the decline in the field ratio on cooling was interpreted as evidence for a loss of longitudinal order, a conclusion consistent with neutron depolarization measurements. However in the case of a-$Fe_{90-x}Ni_xZr_{10}$ no temperature dependence was seen for $x=0$, and adding nickel reduces frustration, making the system more ferromagnetic.

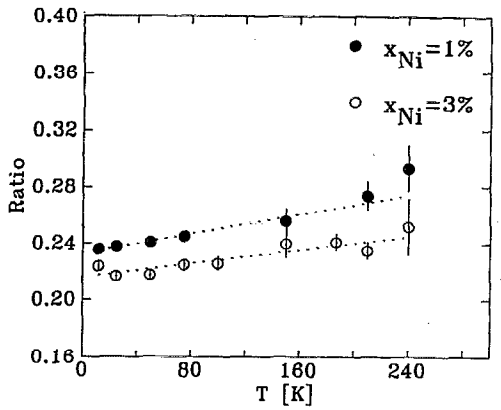

FIG. 3. Temperature dependence of the ratio $\langle B_{hf}(^{119}\mathrm{Sn})\rangle/\langle B_{hf}(^{57}\mathrm{Fe})\rangle$ for the two compositions of $Fe_{90-x}Ni_xZr_9Sn$.

Two possible conclusions can be reached. (i) There is, in fact, a loss of collinear order on cooling in a-$Fe_{90-x}Ni_xZr_{10}$. Independent confirmation of this behavior will be difficult to obtain, as the effect is quite small. The reduction of thermal fluctuations on cooling from 100 to 0 K, leads to a factor of two increase in the magnetization, while the change in the field ratio, and hence in the degree of collinearity, over the same temperature range is only about 1%. Unambiguously separating these two contributions would be extremely difficult. The existence of a collinearity loss in this system is unexpected since magnetization and neutron scattering measurements both show that the material becomes more ferromagnetic with increasing Ni content. Moreover, a more frustrated, binary a-Fe-Zr alloy showed no evidence of a collinearity decay. (ii) The Sn hyperfine field does not probe correlations between the neighboring Fe moments in the simple manner proposed, perhaps as a result of a greater tendency to form covalent bonds. The failure of the Sn field to rise with the increase in the Fe moment certainly provides support for this view. However, both ^{196}Au and ^{119}Sn Mössbauer measurements in AuFe yielded the same result, and confirmed neutron depolarization measurements. This agreement suggests that Sn does not sample its environment any more selectively than Au, and also shows that a loss of collinear order does yield the correct signature in the hyperfine field ratio. It is possible that the additional Ni leads to changes in the Fe moments which are not probed by the Sn. For example, even small changes in the orbital contribution to the iron moment can have significant effects on the ^{57}Fe hyperfine field,[13] but would not be seen by neighboring Sn atoms. It is not clear why the temperature dependence of such effects should differ from that of the average moment so as to yield a temperature dependent field ratio.

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