Amorphous magnetism in Mn_xSn_{1-x} alloys

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We present systematic low-temperature *in situ* ^{119}Sn Mössbauer-effect studies in vapor-quenched amorphous Mn_xSn_{1-x} ($0.09 \leq x \leq 0.95$) alloys between 150 and 4.2 K. It is shown that the magnetic behavior of the system is correctly displayed by the transferred magnetic hyperfine (hf) interactions detected at the ^{119}Sn site. Combining the results of the concentration dependence of the transferred magnetic hf field and the ordering temperature with recent ac magnetic susceptibility data reported on this system, a complete magnetic phase diagram is proposed. The effect of an external magnetic field (up to about 3 T) on the spin correlations in the spin-glass state is also discussed.

I. INTRODUCTION

The variety of magnetic properties displayed by most amorphous magnetic alloys are known to be connected with their topological and chemical disorder. Particularly interesting are amorphous magnetic alloys which are suitable for the basic study of magnetic phase diagrams (e.g., Fe_xSn_{1-x}).[1] Among this class of systems, manganese alloys are of considerable interest in the study of 3*d* amorphous magnetism because Mn is intermediate between paramagnetic and ferromagnetic metals.

Recently, amorphous Mn_xSn_{1-x} alloys ($0.05 \leq x \leq 0.60$) have been successfully prepared using the vapor-quenching technique at low temperatures.[2,3] *In situ* ac magnetic susceptibility (χ_{ac}) measurements have shown that (i) the manganese atoms exhibit localized magnetic moments and (ii) the system displays a spin-glass (SG) type of behavior in the concentration range $0.05 \leq x \leq 0.60$.[3]

In this work we present *in situ* ^{119}Sn Mössbauer-effect (ME) measurements performed on vapor-quenched Mn_xSn_{1-x} in an extended concentration range of $0.09 \leq x \leq 0.95$ condensed near 4.2 K. ^{119}Sn ME experiments on Mn_xSn_{1-x} are very useful due to the fact that the Sn atoms do not carry any magnetic moments. However, if the system orders magnetically, it is expected to observe a transferred hyperfine (hf) field, B_{thf}, due to the ordering of Mn moments. The magnitude of the observed B_{thf} and the shape of its distribution, $P(B_{thf})$, are known to be very sensitive to the type of the local spin correlations and to the distribution of their directions, respectively.[4,5] Thus, it is hoped that such studies shed light on the nature of the local magnetic states in the amorphous Mn_xSn_{i-x} ($0.09 \leq x \leq 0.95$) alloys. ^{119}Sn ME results obtained on the same samples in the paramagnetic state have been published elsewhere.[6]

II. EXPERIMENTAL DETAILS

The elements (85% enriched ^{119}Sn and pure Mn) were evaporated by means of two thermally heated tantalum ovens. The double-vapor beam was condensed onto a quartz plate substrate cooled at liquid-helium temperature. The vacuum during evaporation was better than 4×10^{-8} mbar. The concentration ratio of Mn and Sn could be measured during the deposition by a system of three quartz 5-MHz oscillators acting as microbalances. The deposition rate of the condensed films on the substrate was less than 0.2 nm/s. Typical thicknesses of the films were between 100 and 2000 nm. The amorphous nature of the condensed alloys was checked by *in situ* electrical resistivity measurements. A conventional Mössbauer spectrometer for transmission geometry operating in the constant acceleration mode was used. The source was 6-mCi ^{119m}Sn in $CaSnO_3$. The source and absorber were kept at the same temperature during measurements. ^{119}Sn ME spectra of some of the SG samples ($x=0.16$ and $x=0.47$) were measured in an external magnetic field (B_{ext}) up to 2.7 T. The magnetic ordering temperature (T_0) for all samples was measured by the ME using the thermal scanning technique.[7]

III. RESULTS AND DISCUSSION

A. Magnetic properties versus alloying composition

Figure 1(a) shows some typical ^{119}Sn ME spectra for different concentrations ($x=0.16$, 0.30, 0.47, 0.68, and 0.95) collected at 4.2 K. As it is usual in disordered systems, the ME spectra exhibit broad lines. They were fitted using the Window method.[8] All ME spectra display transferred hf fields (B_{thf}) at the ^{119}Sn site, which reflect the ordering of the Mn moments at low temperatures. Hyperfine field distributions [$P(B_{thf})$] corresponding to the measured ME spectra are shown in Fig. 1(b). We observe for the sample with $x=0.16$ an unresolved magnetic-split pattern (very broad single line) which becomes resolved with increasing Mn concentration [see Fig. 1(a)]. The variation of the average transferred hf field, $\bar{B}_{thf}$, with Mn concentration is best seen in Fig. 2. Here the saturation values of $\bar{B}_{thf}$ ($\bar{B}_0$) are plotted against x.

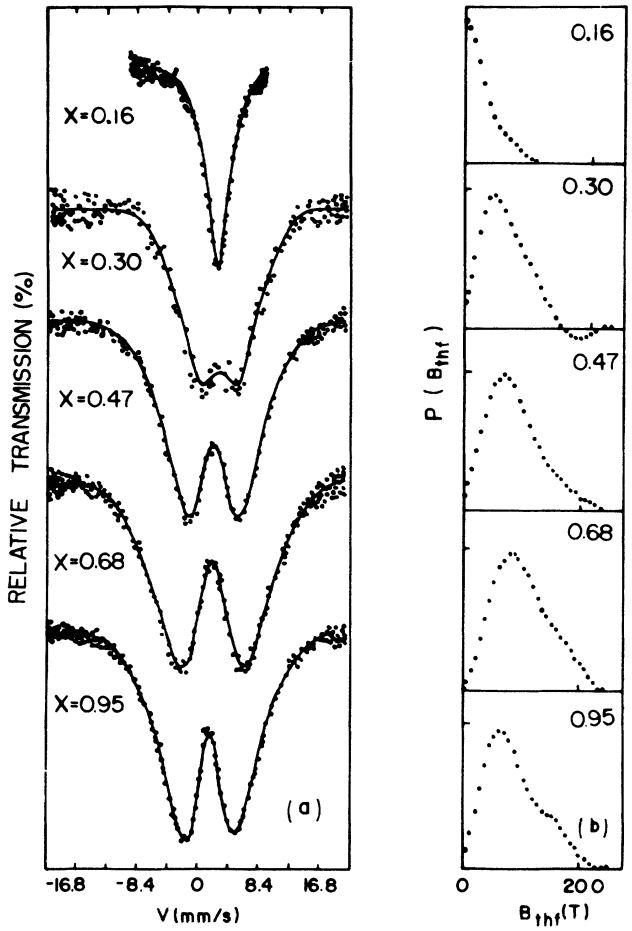

FIG. 1. (a) ^{119}Sn ME absorption spectra of amorphous Mn_xSn_{1-x} at $T=4.2$ K for different Mn concentration x. (b) Hyperfine field distribution $P(B_{hf})$ from the analysis of the corresponding ME spectra.

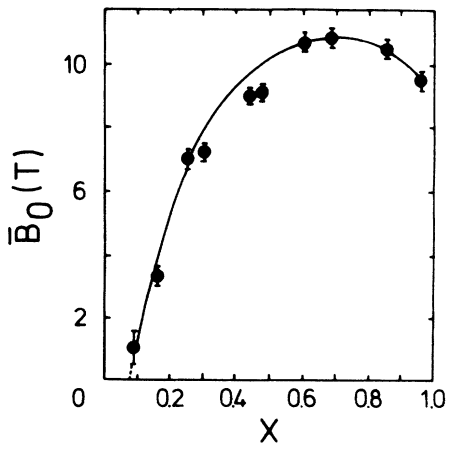

FIG. 2. Saturation value of the transferred hyperfine field, $\bar{B}_0$, as a function of Mn concentration x, for the amorphous Mn_xSn_{1-x} alloys.

As shown in Fig. 2, $\bar{B}_0$ increases rapidly with increasing Mn concentration above $x=0.09$ up to $x<0.60$, goes through a broad maximum (plateau) around $x=0.68$ and then decreases for $x>0.85$.

The concentration dependence of T_0 deduced from our ME measurements is in fair agreement[9] with that obtained from the χ_{ac} data in the concentration range $0.05\leq x\leq 0.60$ (Ref. 3) (see Fig. 3). Most interesting is the finding that the variation of T_0 with x (Fig. 3) is very similar to that of $\bar{B}_0$ (Fig. 2). This means that we have a simple correlation between the change of $\bar{B}_0$ and T_0 with increasing Mn concentration.

On the other hand, the concentration dependence of both the isomer shift and the quadrupole splitting of the system measured in the paramagnetic state[6] is quite different than that of $\bar{B}_0$ and T_0. From this it can be concluded that the variation of $\bar{B}_0$ and T_0 with Mn concentration is related to changes of the magnetic properties of the system and not to changes of the short-range chemical order.

Thus, the simple correlation between $\bar{B}_0$ and T_0 with changing Mn concentration, as well as the agreement of our T_0 values with those obtained from χ_{ac} measurements,[3] demonstrate that the magnetic behavior of the Mn_xSn_{1-x} system is correctly displayed by the transferred hf interactions detected at the Sn atoms. On this basis, we discuss, in the following the change of the type of the local magnetic order with concentration, despite the fact that this information cannot be simply deduced from Mössbauer spectroscopy alone.

1. The spin-glass phase: $0.05\leq x\leq 0.60$

The spin-glass behavior in this concentration range has been already proved by previous χ_{ac} measurements on Mn_xSn_{1-x}.[3] In the same concentration range we obtain a linear increase of $\bar{B}_0$ and T_0 with increasing x up to $x=0.30$. Above this value ($0.30<x<0.60$), the rate of increase of $\bar{B}_0$ and T_0 levels off (see Figs. 2 and 3). As will be discussed in detail in section B, the linear increase of $\bar{B}_0$ and T_0 with increasing x in the range $0.09\leq x\leq 0.30$ is caused by the enhancement of local ferromagnetic spin-correlations in the SG phase. Such a linear behavior is expected only if the system remains in a

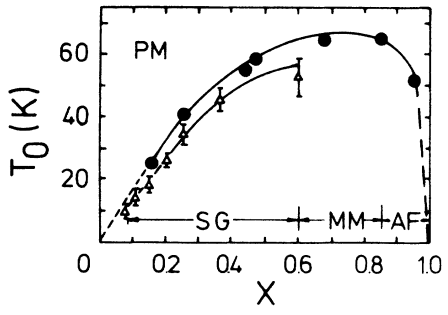

FIG. 3. Proposed magnetic phase diagram of Mn_xSn_{1-x} amorphous system. Data points are results of this work (●) and Ref. 3 (△): PM (paramagnetic); SG (spin-glass); MM (mixed magnetic) and AF (antiferromagnetic).

unique magnetic regime. Obviously, any change in the type of the local spin correlations with increasing Mn concentration will modify the rate and sign of the change of $\bar{B}_0$ and T_0 with x; transferred magnetic hf contributions from antiferromagnetic spin correlations are expected to cause a rapid decrease of $\bar{B}_0$ due to the antiferromagnetic coupling of Mn spins around the Sn atoms. Thus, we attribute the decrease of the slopes of $\bar{B}_0$ and T_0 with increasing x ($0.30 < x \leq 0.60$) to a gradual increase of considerable antiferromagnetic spin correlations in this region. In fact, as will be shown later, the magnetic behavior of the system for $0.30 < x \leq 0.95$ is governed by the relative strength of these two types of local spin correlations.

2. *Mixed magnetic phase:* $0.60 < x < 0.85$

In this intermediate concentration range we observe almost no change of $\bar{B}_0$ and T_0 with increasing Mn concentration (see Figs. 2 and 3). This clearly indicates that in this region both ferromagnetic and antiferromagnetic spin correlations are of comparable strength. In fact, the local nature of this mixed magnetic (MM) phase is found to be complex: careful measurements of the temperature dependence of $\bar{B}_{\rm thf}$ for a sample with $x = 0.68$ showed a second magnetic transition at $T = 13.5$ K, well below the ordering temperature T_0 at $T = 65$ K. This behavior is similar to that observed in several reentrant SG systems (e.g., Fe-Au).[10] However, the shape of hf distribution curves [see Fig. 1(b) for $x = 0.68$] are found to be asymmetric below 13.5 K, indicating a possible magnetic inhomogeneity. Thus, it is difficult to derive a clear conclusion about the local nature of the magnetic state in the MM phase.

3. *The antiferromagnetic phase:* $0.85 \leq x \leq 0.95$

At high concentrations, $0.85 \leq x \leq 0.95$, we observe a decrease of both $\bar{B}_0$ and T_0 (see Figs. 2 and 3). The only possible type of *local* magnetic order which causes a decrease of $\bar{B}_0$ is the dominance of antiferromagnetic (AF) spin-correlations of Mn spins around Sn atoms in this concentration region. This assumption is supported by previous ^{119}Sn ME measurements on crystalline β-Mn doped with 5% Sn.[11] This system displayed magnetic order below 36 K, indicating that it is most probably antiferromagnetic, similar to pure α-Mn. It is interesting to mention that in pure amorphous Mn no magnetic order has been observed down to 1.5 K.[12,13] The dashed line in Fig. 3 between $x = 0.95$ and $x = 1$ denotes a linear extrapolation to this experimental point.

On the other hand, we observe a narrowing of the width of the hf field distribution of the samples in this concentration range [see Fig. 1(b)]. This may indicate an increase of the structural short-range order in the Mn-rich side ($x > 0.85$) of the phase diagram.[6]

B. Local nature of the spin-glass state

After discussing the magnetic phase diagram of the system Mn_xSn_{1-x}, we want to focus on two interesting aspects of the nature of the SG state: (i) the evolution of the magnetic order at low Mn concentration, and (ii) the effect of applying an external magnetic field on the spin correlations. Regarding the change of the magnetic behavior of the SG state as a function of Mn concentration, Figs. 2 and 3 show that $\bar{B}_0$ and T_0 vary linearly with increasing Mn concentration in the range $0.09 \leq x \leq 0.60$, indicating their strong correlation. However, as can be seen from Figs. 2 and 3, at low concentrations ($0 < x < 0.09$) $\bar{B}_0$ and T_0 do not correlate. This finding is most obvious if one linearly extrapolates $\bar{B}_0$ and T_0 to lowest Mn concentration. We obtain for zero values of $\bar{B}_0$ and T_0 two different values of x ($x \cong 0.08$ for $B = 0$ T and $x \cong 0$ for $T_0 = 0$ K). This can be understood if we assume the following picture for the diluted SG state ($0 < x < 0.08$): (i) the magnetic behavior of the system is dominantly determined by the ordering of Mn moments in the nearest neighbor (NN) shells, and (ii) these Mn moments are randomly frozen below T_0. In such a situation the transferred hf fields detected by Sn atoms will be averaged to zero. At higher Mn concentrations, $0.09 \leq x \leq 0.60$, the increase of the value of $\bar{B}_0$ is caused by transferred magnetic hf contributions from a considerable number of NN Mn spins which are ferromagnetically correlated.

The last point to be discussed is how the spin correlations will be affected by an external magnetic field. Figures 4(a), 4(b) and 5(a), 5(b) show some typical ^{119}Sn ME spectra for two SG samples ($x = 0.16$ and $x = 0.47$) in different $B_{\rm ext}$ (up to 2.7 T) and corresponding $P(B_{\rm thf})$ curves, respectively. As evident from Figs. 4(a) and 4(b), we obtain for the sample (with $x = 0.16$) a positive shift (increase) of $\bar{B}_{\rm thf}$ and narrowing of the width of $P(B_{\rm thf})$ curves with increasing $B_{\rm ext}$. For the concentrated SG

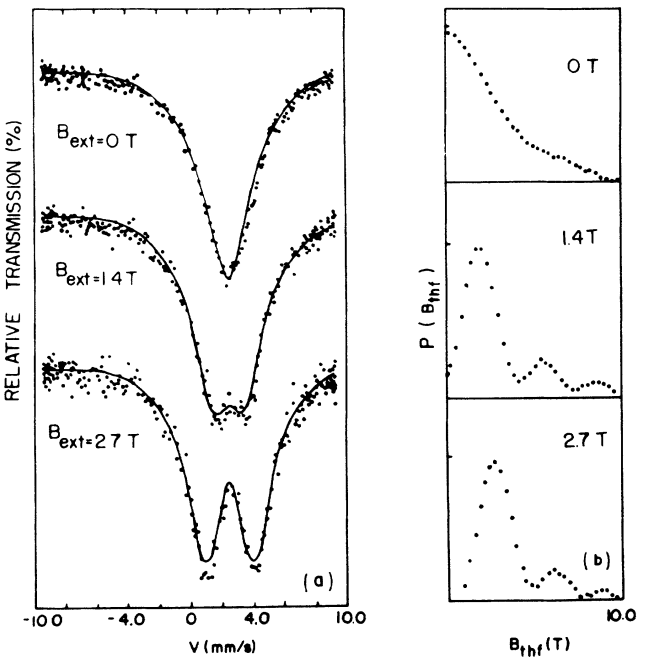

FIG. 4. (a) ^{119}Sn ME absorption spectra at 4.2 K in different external applied magnetic fields; and (b) the corresponding hf field distributions $P(B_{\rm thf})$.

sample [$x=0.47$, Figs. 5(a) and 5(b)] we find again a narrowing of the width of the $P(B_{thf})$ distribution; however, no clear shift of $\bar{B}_{thf}$ is observed.

The narrowing of $P(B_{thf})$ in both SG samples with increasing B_{ext} can be explained by the enhancement of the spin correlations between Mn moments in the NN shells. This conclusion is supported by the observed increase (shift) of $\bar{B}_{thf}$ with increasing B_{ext} in the $x=0.16$ sample [Fig. 4(b)].

Such an increase of $\bar{B}_{thf}$ with B_{ex} is not observed in the concentrated SG sample with $x=0.47$. This different response of the two SG samples ($x=0.16$ and 0.47) to B_{ex} is consistent with our finding (see Sec. III A) that considerable local AF spin correlations do exist in the concentrated SG sample ($x=0.47$). This, however, does not modify the macroscopic SG magnetic behavior of the sample.

IV. CONCLUSIONS

On the basis of the results of our *in situ* ^{119}Sn Mössbauer-effect measurements on vapor-quenched amorphous Mn_xSn_{1-x} alloys ($0.09 \leq x \leq 0.95$) we were able to suggest a magnetic-phase diagram for the system as well as to shed light on the local nature of the spin-glass state in the region $0.05 \leq x \leq 0.60$.

The magnetic behavior of the system is shown to be correctly reflected by the measured transferred hf field and the ordering temperature in the whole concentration range. Combining the concentration dependence of $\bar{B}_0$ and T_0 with recent experiment results reported from ac susceptibility measurements[3] in the concentration range $0.05 \leq x \leq 0.60$, we propose the following magnetic phase diagram: (i) a spin-glass phase, $0.05 \leq x \leq 0.60$, which is already proved by ac-magnetic susceptibility (here the local spin correlations are found to be dominantly ferromagnetic); (ii) a mixed magnetic region, $0.60 < x < 0.85$, where both ferromagnetic and antiferromagnetic spin correlations are assumed to be of equal strength; (iii) a dominantly antiferromagnetic-type order above $x > 0.85$, which causes a decrease of $\bar{B}_0$ due to the antiparallel coupling of Mn spins around the Sn atoms.

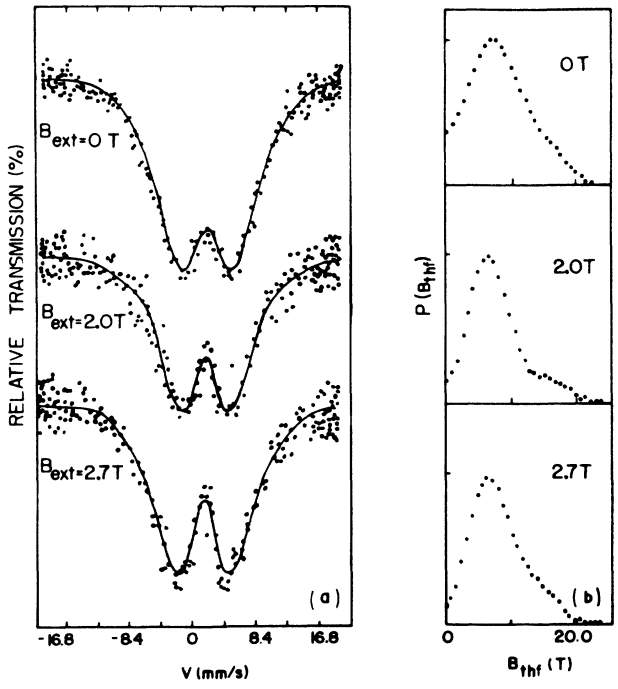

FIG. 5. (a) ^{119}Sn ME absorption spectra at 4.2 K for the SG sample with $x=0.47$ in different external magnetic fields; (b) corresponding hf field distributions, $P(B_{thf})$.

The application of an external magnetic field on diluted ($x=0.16$) and concentrated ($x=0.47$) SG samples showed an increase of the local spin correlations with increasing B_{ext}. This finding demonstrates that the SG state exhibits a considerable distribution of the local spin directions of Mn around the Sn atoms.

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