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AMORPHOUS MAGNETISM IN Mn_xSn_{1-x} ALLOYS

by

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ABSTRACT

We present systematic low temperature *in situ* 119Sn Mössbauer effect (ME) 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 119Sn 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.

Key-words: Amorphous alloys; Mössbauer spectroscopy; Hyperfine field distribution; Magnetic phase diagram; Metal vapor quenching.

INTRODUCTION

The variety of magnetic properties displayed by most of 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 3d amorphous magnetism because Mn lies 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 behavior in the concentration range $0.05 \leq x \leq 0.60$/3/.

In this work, we present *in situ* 119Sn 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 4.2K. 119Sn ME experiments on Mn_xSn_{1-x} are very useful due to the fact that the Sn atoms dont carry any magnetic moment. 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 as well as the distribution of their directions respectively /4,5/.

It is, thus, hoped that such studies shed light on the nature of the local magnetic states in the amorphous Mn_xSn_{1-x}, $0.09 \leq x \leq 0.95$, alloys. 119Sn ME results obtained on the same samples in the paramagnetic state have been published elsewhere /6/.

II EXPERIMENTAL DETAILS

The elements (85% enriched 119Sn 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 like microbalances. The deposition rate of the condensed films on the substrate was less than 0.2 nm/s. Typical thickness of the films was between 100 and 2000 nm. The amorphous nature of the condensated 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 119mSn in CaSn03. Source and absorber were kept at the same temperature during measurements. 119Sn 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_o) for all the samples was measured using the thermal scanning technique /7/.

III RESULTS AND DISCUSSION

A. *MAGNETIC PROPERTIES VERSUS ALLOYING COMPOSITION*

Fig. 1(a) shows some typical 119Sn 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 known Window method /8/. All ME spectra display transferred hf fields (B_{thf}) at the 119Sn site, which reflect the ordering of the Mn moments at low temperatures. Hf 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 splitted pattern (very broad single line), which becames resolved with increasing Mn concentration (s. Fig. 1a). 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 B ($\bar{B}_o$) are plotted against x. As shown in Fig. 2, $\bar{B}_o$ 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 rapidly decreases for $x > 0.85$.

The concentration dependence of T_o deduced from our ME measuremants is in fair agreement /9/ with that obtained from the χ_{ac} data in the concentration range $0.05 \leq x \leq 0.60$ /3/ (s. Fig. 3). Most interesting is the finding that the variation of T_o with x (Fig. 3) is very similar to that of $\bar{B}_o$ (Fig. 2). This means that we have a simple correlation between the change of $\bar{B}_o$ and T_o 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 $\bar{B}_o$ and T_o. From this it can be concluded that the variation of $\bar{B}_o$ and T_o with Mn concentration is related to changes of the magnetic properties of the system and not to changes of the chemical short range order.

Thus, the simple correlation between $\bar{B}_o$ and T_o with changing Mn concentration as well as the agreement of our T_o 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 can not be simply deduced from Mössbauer Spectroscopy alone.

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 $\bar{B}_o$ and T_o with increasing x up to x = 0.30. Above this values ($0.30 < x < 0.60$), the rate of increase of $\bar{B}_o$ and T_o levels off, (s. Fig. 2 and 3). As will be discussed in details in section B, the linear increase of $\bar{B}_o$ and T_o with increasing x in the range $0.09 \leq x \leq 0.30$ is caused by the enhancement of local ferromagnetic in the correlations in the SG phase. Such a linear behavior

is only expected, if the system remains in an unique magnetic region. 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 $\bar{B}_o$ and T_o with x: transferred magnetic hf contributions are expected from antiferromagnetic spin correlations to cause a rapid decrease of $\bar{B}_o$ due to the antiferromagnetic coupling of Mn spins around the Sn atoms. Thus we attribute the decrease of the slopes of $\bar{B}_o$ and T_o with increasing x, $0.30 < x \leq 0.60$, to a gradual increase of considerable antiferromagnetic spin correlations in the region. In fact, as it 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.

MIXED MAGNETIC PHASE: $0.60 < x < 0.85$

In this intermediate concentration range we observe almost no change of $\bar{B}_o$ and T_o with increasing Mn concentration (s. Fig. 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 $\bar{B}_{thf}$ for a sample with x = 0.68 showed a second magnetic transition at T = 13.5 K, well bellow the ordering temperature T_o at T = 65 K. This behavior is similar to that observed in several re-entrant SG systems (e.g. Fe-Au /10). However, the shape of hf distribution curves (s. Fig. 1b for x = 0.68) are found to be asymmetric below 13.5 K, indicating a pos

sible magnetic inhomogeneity. Thus, it is difficult to drive a clear conclusion about the local nature of the magnetic state in the MM phase.

THE ANTIFERROMAGNETIC PHASE: $0.85 \leq x \leq 0.95$

At high concentrations $0.85 \leq x \leq 0.95$, we observe a rapid decrease of both $\bar{B}_o$ and T_o (s. Figs. 2 and 3). The extrapolation of the experimental points to $x = 1.0$, in Fig. 2 and 3, is based on the fact that no magnetism has been observed in pure amorphous Mn down to 1.5 K /11,12/. The only possible type of local magnetic order which causes a sharp decrease of $\bar{B}_o$ is the dominance of antiferromagnetic (AF) spin correlations of Mn spins around Sn atoms in this concentration region. The existence of dominatly AF is supported by previous 119Sn ME measurements on crystalline β-Mn alloy dopped with 5% Sn /13/: this system displayed below 36 K magnetic order which is most probably antiferromagnetic similar to pure α-Mn.

On the other hand, we observe a narrowing of the width of the hf field distribution of the samples in this concentration range (s. Fig. 1). This may indicate an increase of the structural short range order in 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, Fig. 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 $\bar{T}_0$ 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 bellow 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 can be affected by an external magnetic field. Figs. 4(a,b) and 5(a,b) show some typical 119Sn ME spectra for two SG samples ($x = 0.16$ and $x = 0.47$) in different B_{ext} (up to 2.7 T) and corresponding $P(B_{thf})$ curves, respectively. As evident from Fig. 4 (a,b), we obtain for the sample with $x = 0.16$ a positive shift

(increase) of $\bar{B}_{thf}$ and narrowing of the width of $P(B_{thf})$ curves with increasing B_{ext}. For the concentrated SG sample (x = 0.47, Fig. 5(a,b)) we find again a narrowing of the width of $P(B_{thf})$ 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 B_{thf} with increasing B_{ext} in the x = 0.16 sample (s. Fig. 4b). However, such an increase is *not* observed in the concentrated SG sample with x = 0.47. This behavior may be related to the existence of considerable antiferromagnetic spin correlations in the concentrated SG sample (s. section II A).

IV CONCLUSIONS

On the basis of the results of our "*in situ*" 119Sn 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 $\bar{B}_o$ and T_o with recent experimental 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 rapid decrease of $\bar{B}_o$ due to the antiparallel coupling of Mn spins around the Sn atoms.

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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FIGURE CAPTIONS

Fig. 1: (a) 119Sn ME absorption spectra of amorphous Mn_xSn_{1-x} at T = 4.2 K for different Mn concentration x. (b) Hyperfine fields distributions $P(B_{thf})$ from the analysis of the corresponding ME spectra.

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

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

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

Fig. 5: 119Sn 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, $P(B_{thf})$.

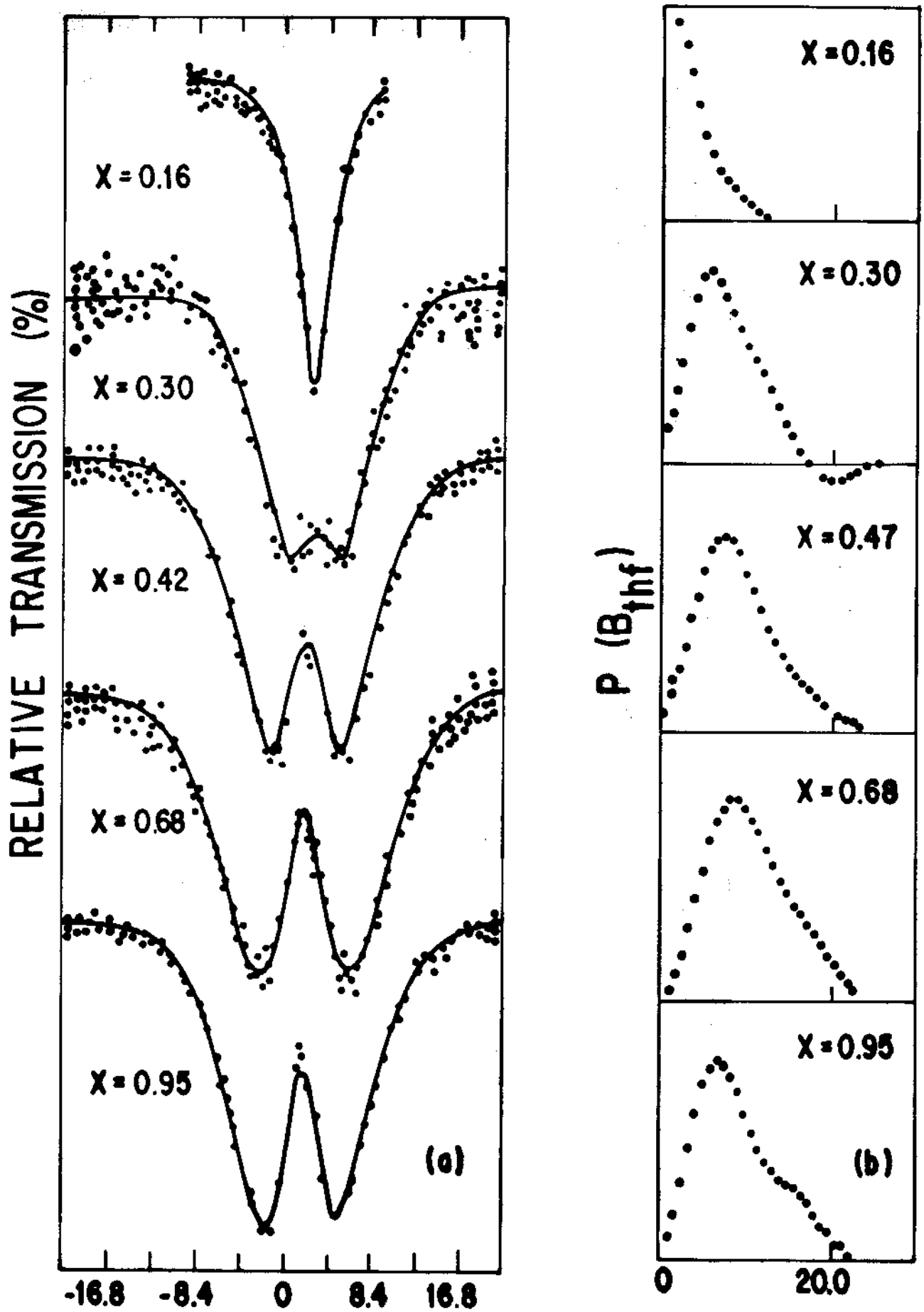
RELATIVE TRANSMISSION (%)
X = 0.16
X = 0.30
X = 0.42
X = 0.68
X = 0.95
(a)
-16.8
-8.4
0
8.4
16.8
P (B_hf)
X = 0.16
X = 0.30
X = 0.47
X = 0.68
X = 0.95
(b)
0
20.0

Fig. 1

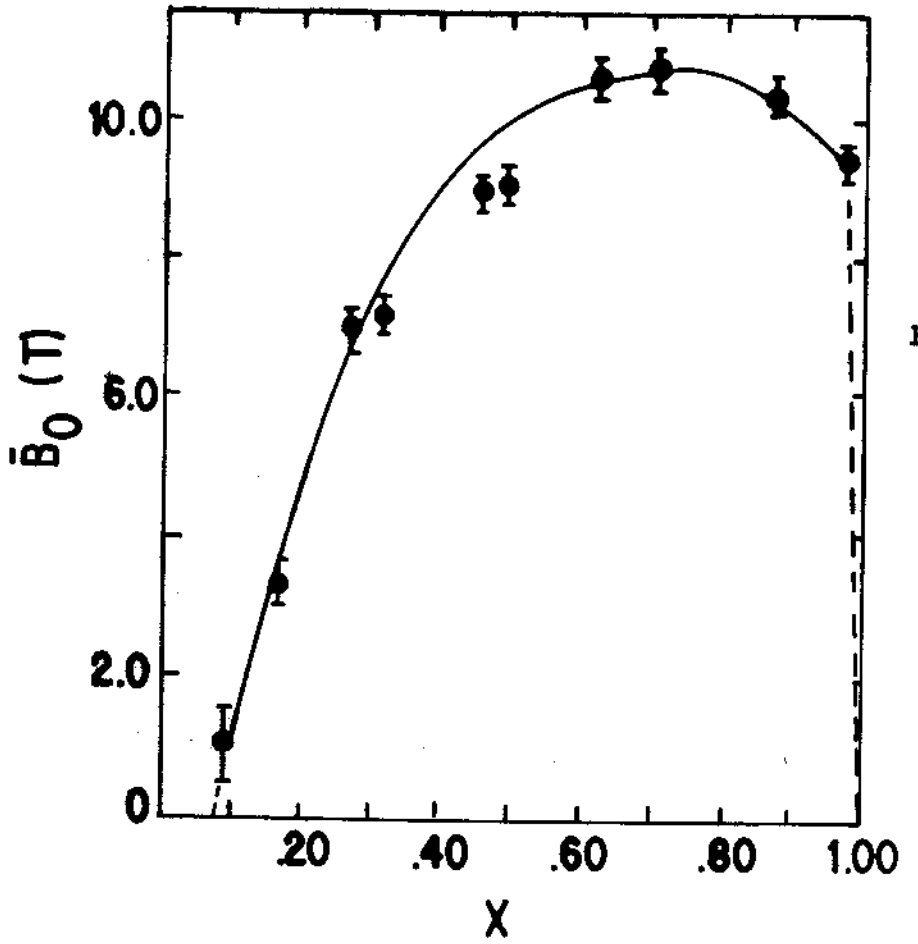
10.0
6.0
2.0
0
$\bar{B}_0$ (T)
.20
.40
.60
.80
1.00
X

Fig. 2

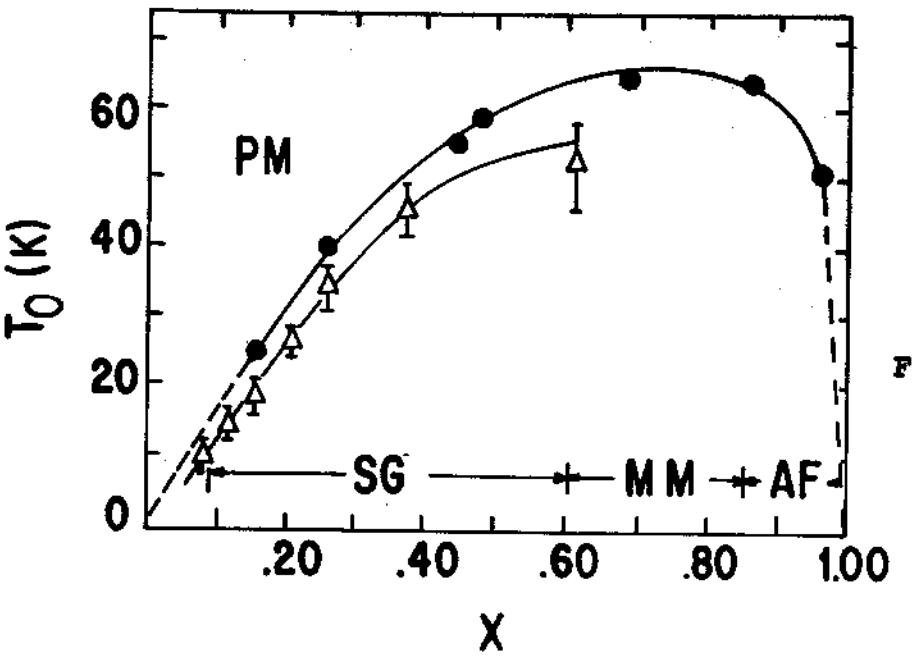
60
40
20
0
T_0 (K)
PM
SG
MM
AF
.20
.40
.60
.80
1.00
X

Fig. 3

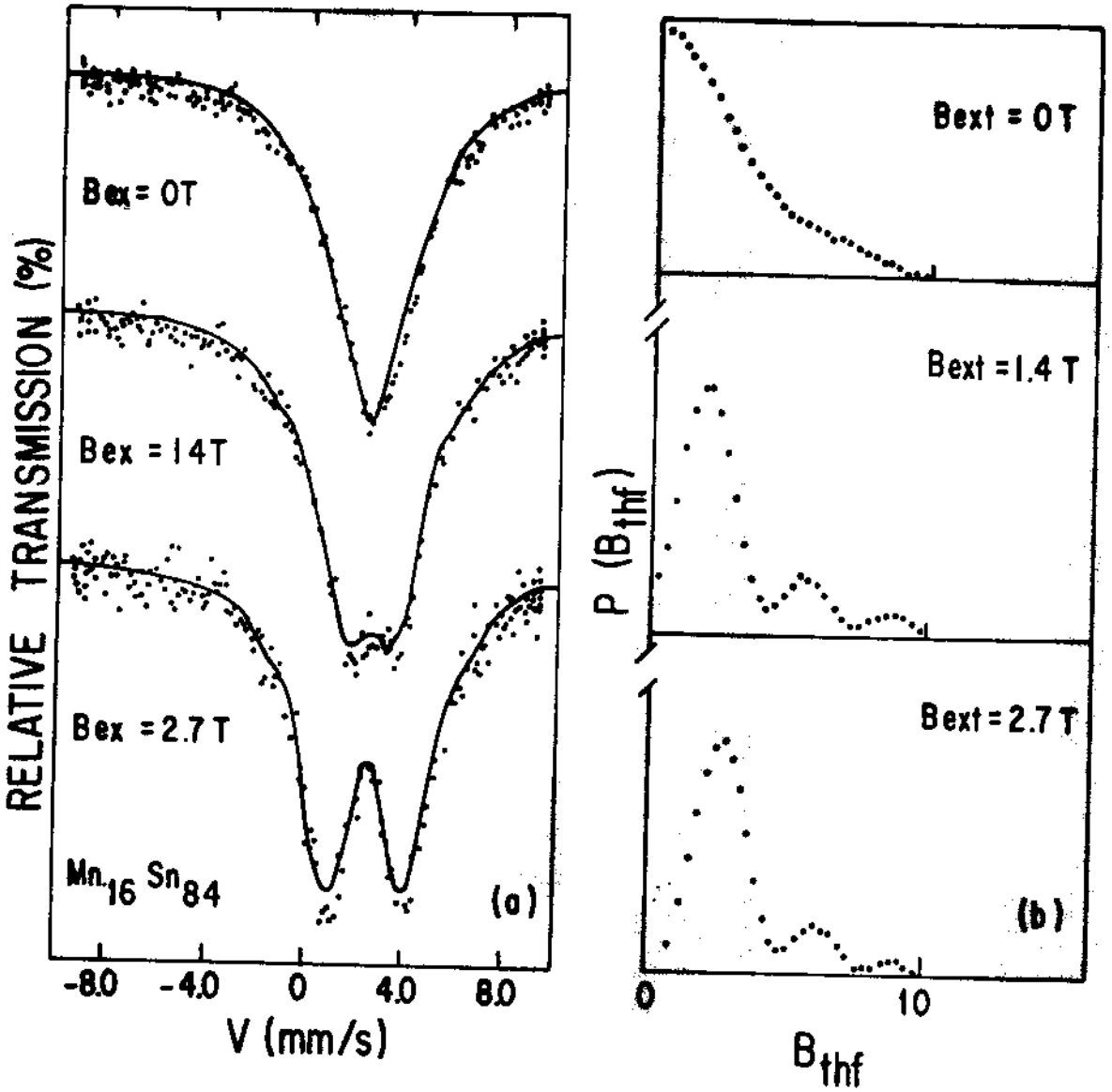
RELATIVE TRANSMISSION (%)
Bex = 0T
Bex = 1.4T
Bex = 2.7T
Mn16 Sn84
(a)
-8.0
-4.0
0
4.0
8.0
V (mm/s)
P (Bthf)
Bext = 0T
Bext = 1.4 T
Bext = 2.7 T
(b)
0
10
Bthf

Fig. 4

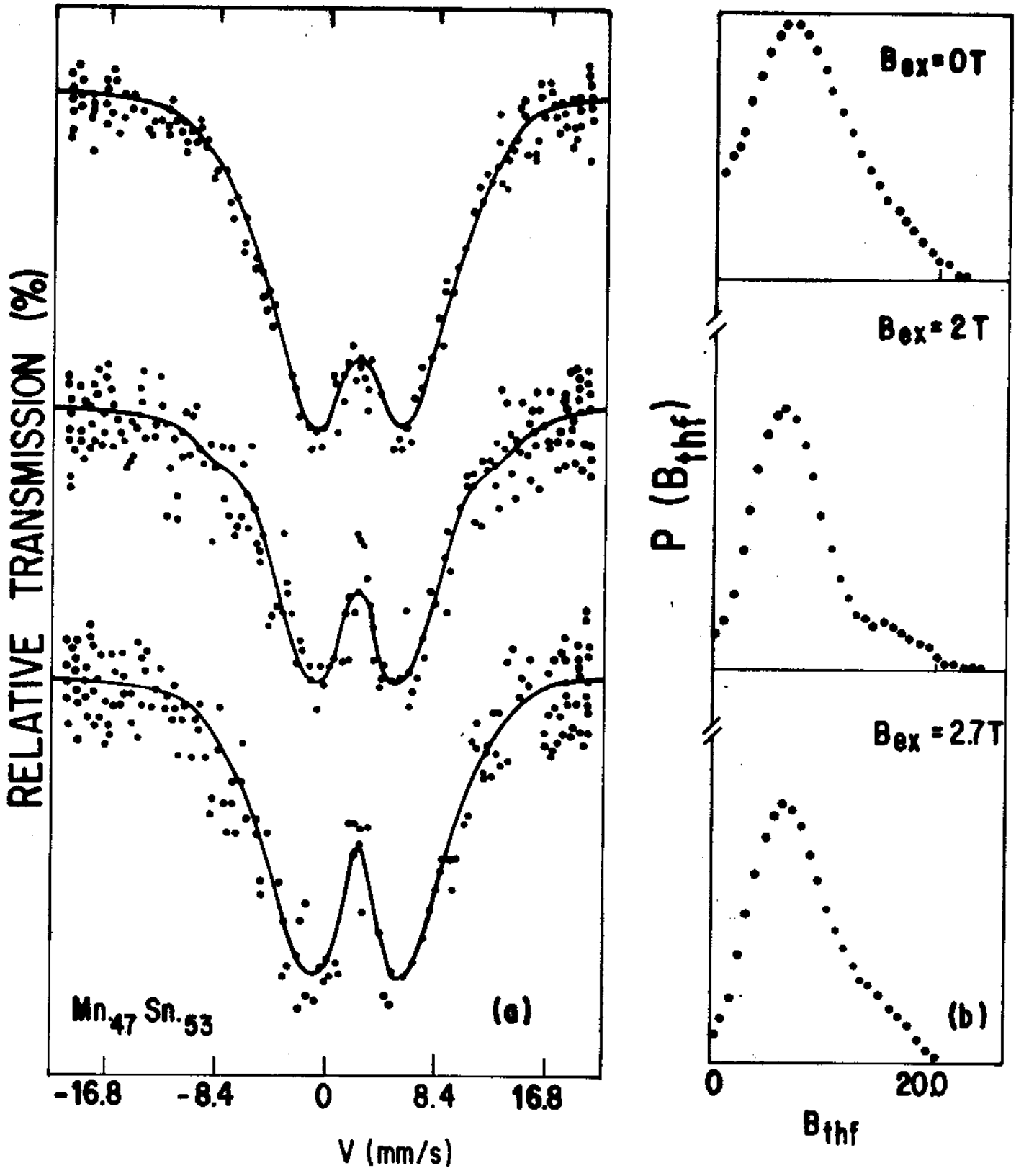
RELATIVE TRANSMISSION (%)
Mn47 Sn53
(a)
-16.8
-8.4
0
8.4
16.8
V (mm/s)
P (Bthf)
Bex=0T
Bex=2T
Bex=2.7T
(b)
0
20.0
Bthf

Fig. 5

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/9/ Values of the magnetic ordering temperature, T_o, deduced from 119Sn ME measurements are slightly higher than those obtained from χ_{ac} method /3/. This is known to be related to the dynamical nature (relaxation effects) of the SG freezing.

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