SHORT RANGE ORDER IN VAPOR QUENCHED AMORPHOUS Mn_xSn_{1-x} ALLOYS USING IN SITU ^{119}Sn MÖSSBAUER SPECTROSCOPY

by

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We present the first systematic in situ ^{119}Sn Mössbauer studies on vapor quenched amorphous Mn_xSn_{1-x} $(0.09 \leq x \leq 0.95)$. A comparison of the values of the isomer shift and quadrupole splitting at different concentrations x with those of related MnSn intermetallic compounds suggests the existence of a crystalline like short range order in this amorphous system.

INTRODUCTION

The problem of short range order in amorphous alloys is a highly debated subject in the literature for the last years [1-4]. The proposed structural models for amorphous systems are based on either dense random packing of hard spheres [5] (DRPHS) or short range order [6] (SRO) where the symmetry of the chemical bondings are essentially preserved.

Among the microscopic experimental techniques used to account for the SRO in amorphous systems, e.g. NMR [7], neutron scattering [8], the Mössbauer effect (ME) is known as a powerful tool to inspect the nearest neighbor configuration of the Mössbauer nucleus (via the isomer shift, IS) as well as its local site symmetry (via the quadrupole splitting, QS). Therefore a large number of ME studies on amorphous systems have been reported (e.g. Fe-B [9] and Fe-Zr [10]).

A promissing candidate for such ME investigations is the system Mn-Sn where Sn is a proper ME isotope (^{119}Sn). The phase diagram of Mn-Sn shows a very limited solubility in the solid phase around the three intermetalic compounds: $MnSn_2$, Mn_2Sn and Mn_3Sn [11]. Also no pronounced eutetic points have been found in all the concentration range [11]. For this reason Mn-Sn can only be prepared in the amorphous phase by the vapor quenching technique [12]. Moreover, due to the high sensitivity of the amorphous films produced [13], all the measurements must be performed in situ at low temperatures. Indeed, Korn [13] has performed low temperature in situ electrical resistivity measurements on vapor quenched amorphous thin films of Mn_xSn_{1-x} (0.05 $\leq$ x $\leq$ 0.60). Magnetic susceptibility (χ_{ac}) in situ measurements on this system also have been recently reported by the same group [14]. However, both macroscopic experimental methods (electrical resistivity

and χ_{ac}) could not offer any clear conclusion about the SRO in this system.

In order to obtain informations about the SRO in the amorphous Mn-Sn (a-SnMn) system we have performed the first in situ [119]Sn ME (5 K and 150 K) measurements on vapor quenched $Mn_x Sn_{1-x}$ in a broad concentration range of $0.09 \leq x \leq 0.95$. Following the concentration dependence of the IS and QS, it should be possible to obtain information about the SRO of the system, especially at concentrations where the ME parameters in the amorphous system can be compared with the crystalline counterparts.

Here we will present only the results in the paramagnetic phase taken at 150 K. The low temperature magnetic results will be published elsewhere [15].

EXPERIMENTAL DETAILS

The elements (85% enriched [119]Sn and pure Mn) where 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 condensated 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 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 6mCi ^{119}Sn in $CaSnO_3$. Source and absorber were kept at the same temperature during the measurements.

RESULTS AND DISCUSSION

Fig. 1(a) shows some typical ^{119}Sn ME spectra for different con-centrations of a-MnSn samples, collected in the paramagnetic phase at T=150 K. This temperature is well above the highest magnetic or-dering temperature (T_o) in the Mn_xSn_{1-x} system $(T_o=66$ K for $x=0.85$ [15]). No crystallization could be detected from the in situ elec-trical resistivity measurements up to 150 K. The fitting of the ME spectra was based on the known Window method [16], and assuming (for x=0.16 to 0.73) a linear correlation between IS and QS, i.e. $IS=IS_o+$ αQS. The constant α obtained from such a fitting procedure changes considerably with composition x, being negative for $x \lesssim 0.6$ and posi-tive for $x \gtrsim 0.6$. This finding is supported by the different behavior of IS and QS with the composition x as shown in figs. 2 and 3 (see below). For x=0.09 the ME spectrum shows a single narrow line with an unresolved QS. ME spectra between x=0.16 and 0.73 display a well de-fined asymmetric doublet (see Fig. 1(a)), where the asymmetry changes sign above x=0.60. The corresponding QS distributions P(QS) for the presented ME spectra are shown in Fig. 1(b).

In the following we discuss first the concentration dependence of the isomer shift and then that of the quadrupole splitting in the a-MnSn alloys.

Fig. 2 shows the variation of the average isomer shift (IS) in-dicating a decrease of the s electron density, $\rho(o)$, at the Sn nu-cleus with increasing x. The change of IS with x follows qualitative

ly that of the known intermetallic MnSn compounds (see Fig. 2). Similar behavior of IS has been also observed in amorphous and crystalline Fe_xSn_{1-x} as a function of x [17]. The observed decrease of $\rho(o)$ at the Sn nucleus with increasing x, in principle can be attributed to two different charge transfer processes: (i) a gradual increasing Mn (3d) $\rightarrow$ Sn (5p) or (ii) a gradual increasing Sn (5s) $\rightarrow$ Mn (4s or 3d) transfer. Process (i) is excluded on the basis of the band struc ture calculations, which have shown for example for Fe_3Si [18] that the Fe (3d) states are below the ' metalloid sp states. Process (ii), on the other hand, is supported by the results of ^{57}Fe ME experiments on amorphous Fe_xSn_{1-x}: the experimental data showed an increase in $\rho(0)$ at the Fe nucleus with increasing x between 0.5 and 1. This would favor a Sn(5s) $\rightarrow$ Mn(4s) transfer in this *high* concentration range. The observed decrease in the IS of ^{119}Sn in amorphous Mn_xSn_{1-x} between x=0 and x=1 corresponds to a decrease in the Sn(5s) occupation number of about 0.4 electrons.

The above results reveal the strength and the nature of the chemical bonds in the system. To make this point more clear the isomer shift of Sn in amorphous and crystalline Cu_xSn_{1-x} is compared in Fig. 2 [19,20]. Here the isomer shift increases with x for amorphous Cu_xSn_{1-x} (x $\leq$ 0.2) while it decreases for the crystalline alloys [19]. Such an opposite behavior of IS for amorphous and crystalline Cu-Sn alloys denies any correlation between the SRO in these systems. In contrast to this, we observe in Mn-Sn quite similar behavior of IS with x for both amorphous and crystalline phases (see Fig. 2). From this we conclude that the SRO in amorphous MnSn should be related to that in the different intermetallic compounds. This last finding will be further supported from the results of the QS.

Fig. 3 shows the variation of the average QS (QS) as obtained in

the paramagnetic phase as a function of x. We observe a rapid in-
crease in the value of QS at low concentration (x $\lesssim$ 0.16). Also the
magnitude of QS $\approx$ 0.9mm/s is much larger than that expected for
amorphous Sn metallic system. For example no QS could be resolved
in amorphous CuSn (18 at.%Cu) [19]. The large value of the QS observed
in the all concentration range (x = 0.16 to 0.95) is an indication for
a local site symmetry around the Sn atoms that deviates considerably
from that typical for amorphous DRPHS systems. It is interesting to
mention that the experimental data for the QS of a-MnSn are located
in the average close to those for the known MnSn intermetallic com-
pounds (see Fig. 3). From this it can be concluded that local site symme-
try in a-MnSn alloys is related in the average to that of the corres
ponding intermetallic MnSn compounds. This is again a clear support
for a crystalline like SRO in this amorphous system.

ACKNOWLEDGEMENTS

FIGURE CAPTIONS

Fig. 1: (a) [119]Sn ME absortion spectra of amorphous $Mn_x Sn_{1-x}$ at T = 150 K and for different Mn concentration x. (b) Quadrupole splitting distribution P(QS) as obtained from the analysis of the corresponding ME spectra.

Fig. 2: Variation of the average isomer shift (IS) at 5 K with Mn(Cu) concentration x for: (•) a-$Mn_x Sn_{1-x}$ (present work). (o) MnSn intermetallic compounds: 1-$MnSn_2$ (Ref. 21), 2-$MnSn_2$ (present work), 3-$Mn_3 Sn$ (Ref. 22). $Cu_x Sn_{1-x}$ alloys: (▼) amorphous (Ref. 19, and (▽) crystalline (Ref. 20). All IS values are corrected to the same temperature (5 K). Lines through data points are only guide ot the eye.

Fig. 3: Variations of the average quadrupole splitting (QS) with Mn concentration x: (o) a-$Mn_x Sn_{1-x}$ (present work). (o) MnSn intermetallic compounds: 1-$MnSn_2$ (Ref. 21), 2-$Mn_2 Sn$ (Ref. 22), 3-5 at.% Sn in crystalline beta-manganes (Ref. 23). The solid line through data points is only guide to the eye.
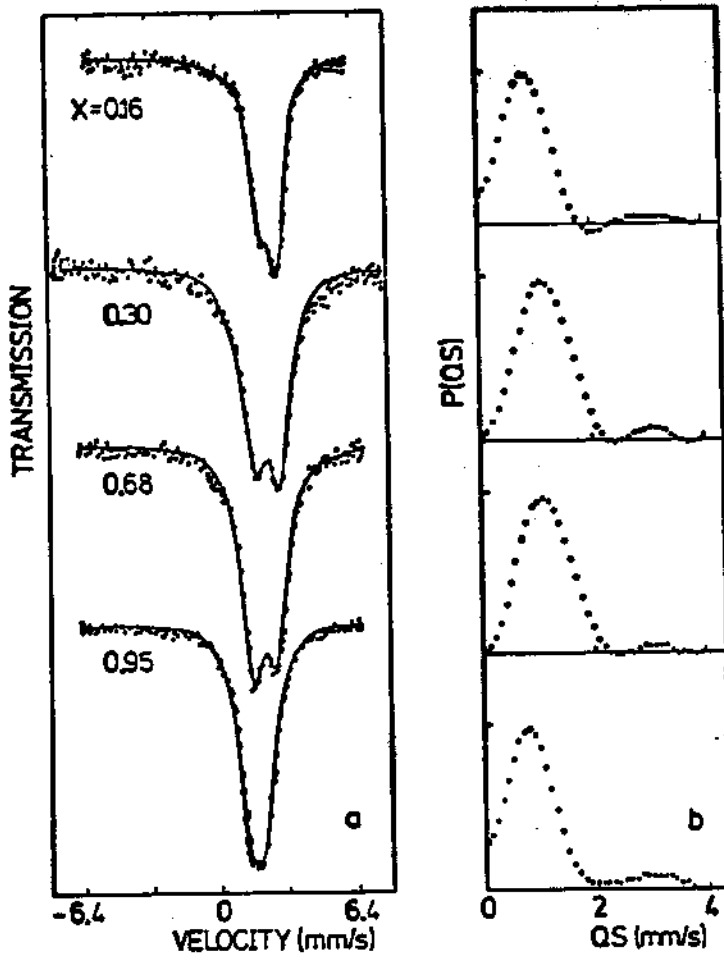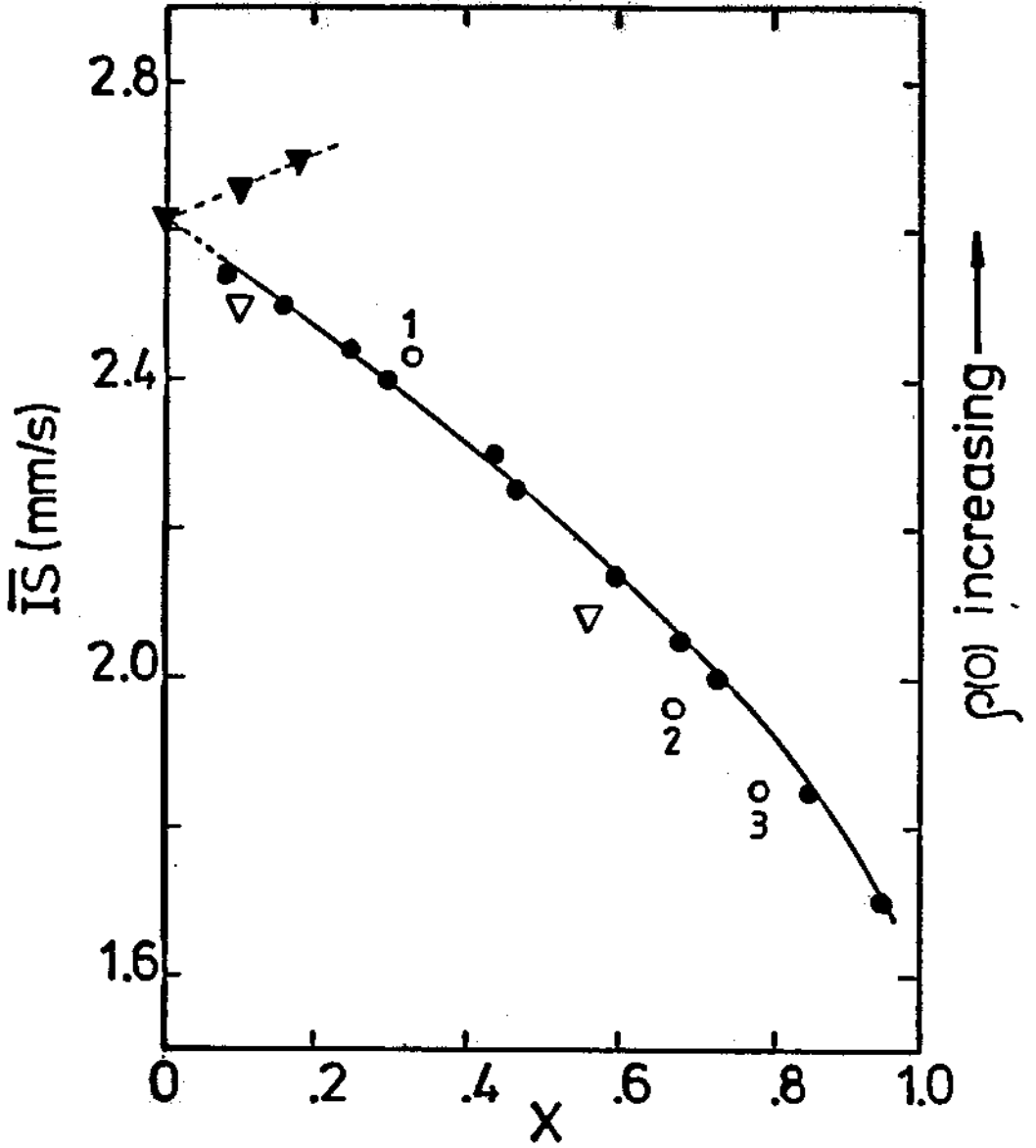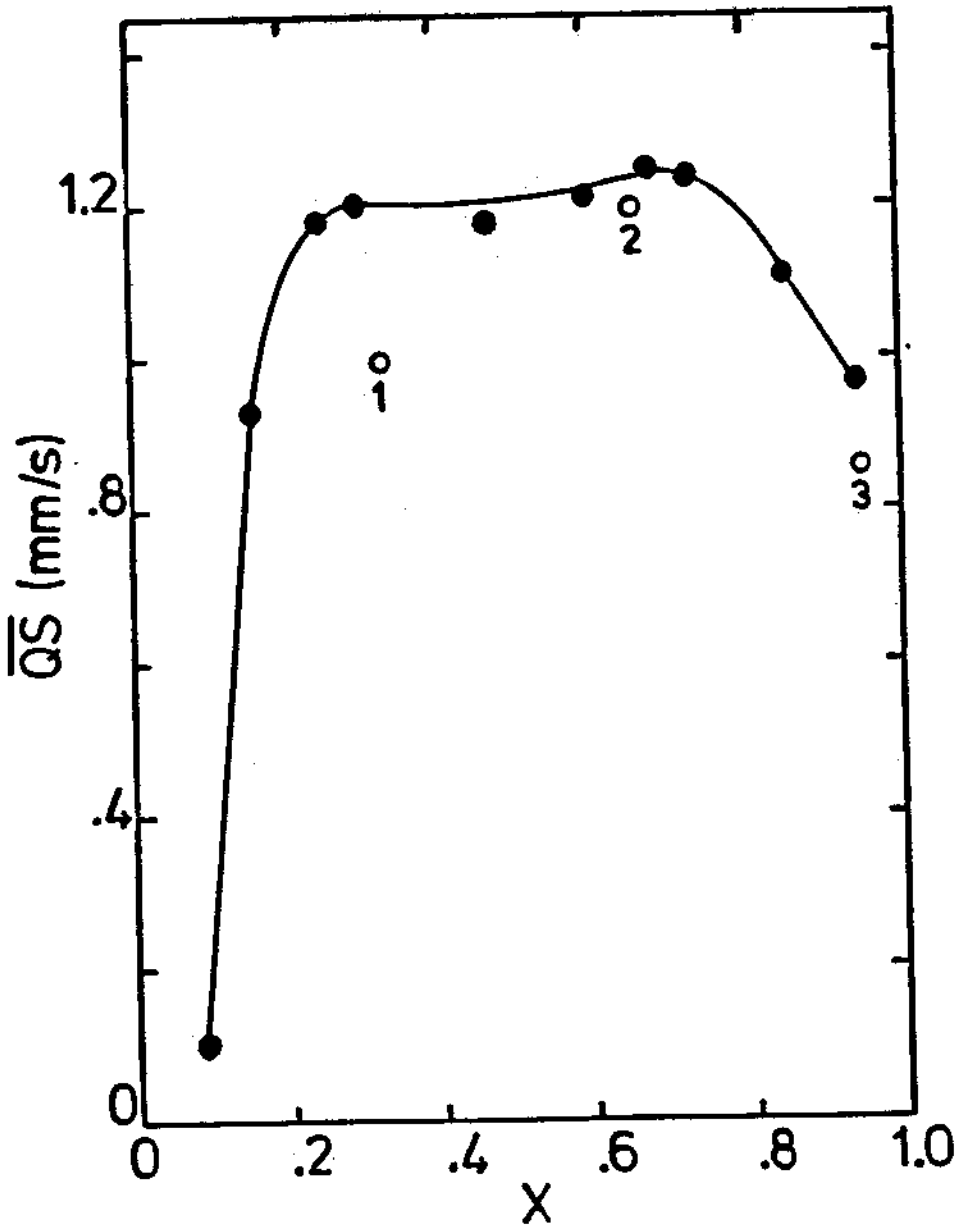
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