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^{119}Sn Mössbauer study of Mn_3SnH_x

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Abstract

Hydrides of the intermetallic compound Mn_3Sn have been prepared at 350°C and pressures of molecular hydrogen between 2.8 and 4.0 GPa. The hydrides with an approximate composition Mn_3SnH were found to have a cubic perovskite structure. A ^{119}Sn Mössbauer study revealed that they are magnetically ordered between 4.2 and 300 K and undergo a magnetic transition at $T_M \lesssim 200$ K.

Keywords: Mössbauer spectroscopy; Hydride; Magnetic transition; Perovskite structure

1. Introduction

A cubic phase with the approximate composition Mn_3SnH was found in a recent study of hydrides of $Mn_{1-y}Sn_y$ alloys [1]. It formed together with hcp ε-Mn(Sn)–H solid solutions upon high pressure hydrogenation of alloys with Sn contents $y \gtrsim 0.05$, and its metal lattice was found to be of the Cu_3Au type. The crystal structure of the Mn_3SnH_x hydrides was recently studied by neutron diffraction [2]. Hydrogen atoms were found to occupy the position at the cube center of the Cu_3Au unit cell, which leads to a structure of the perovskite type, as detailed in Table 1.

Mn_3SnH can be considered as the hydride of the intermetallic compound Mn_3Sn. Like the isostructural compounds Mn_3Ge and Mn_3Ga, Mn_3Sn has the hexagonal DO_{19} structure. It exhibits a complex magnetic behaviour and has been subject to a number of studies (see e.g. [3–9] and references therein). Below its Néel temperature, $T_N = 420$ K, Mn_3Sn was shown to have a triangular antiferromagnetic spin structure [4–6]. A weak ferromagnetic remanence below T_N, first observed by Yasukochi et al. [3], disappears below a temperature T_1, which has been reported to lie in the range 150–270 K, depending on stoichiometry and details of thermal treatment [6]. Below T_1 an incommensurate modulation of the spin structure is observed [6,8,10], which becomes commensurate below about 120 K [10].

Despite their different symmetry, the structures of Mn_3Sn and its hydride are closely related. This relationship, which is analogous to that of the fcc and the hcp structure, is illustrated in Fig. 1, which shows the two

Table 1
Proposed structure of the hydrides $Mn_{3+y}Sn_{1-y}H_x$. The occupied sites of space group *Pm*3*m* with Wykoff notation, site symmetry, coordinates *x*, *y*, *z*, and occupancy *N*. For the studied samples: $x = 0.92(3)$ and $0 \lesssim y \lesssim 0.2$.

Atom	Site	*x*	*y*	*z*	*N*
Sn	1a *m*3*m*	0	0	0	1-*y*
Mn1	3c 4/*mmm*	0	1/2	1/2	1
Mn2	1a *m*3*m*	0	0	0	*y*
H	1b *m*3*m*	1/2	1/2	1/2	*x*

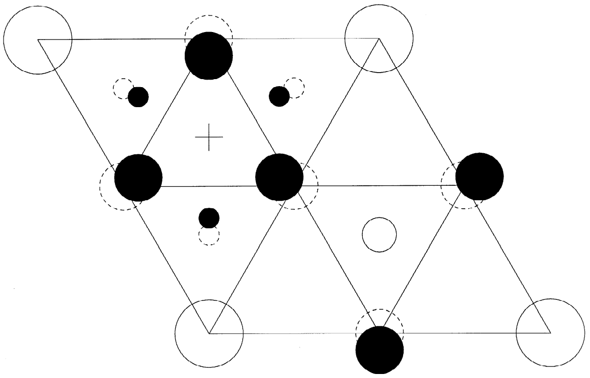

Fig. 1. [001] projection of the hexagonal DO_{19} structure of Mn_3Sn. Filled circles represent Mn atoms, the smaller ones at $z = \frac{1}{4}$ (layer A), the larger ones at $z = \frac{3}{4}$ (layer B). Of the Sn atoms shown as empty circles, the smaller ones are again in layer A and the larger ones in layer B. This projection corresponds to a [111] projection of the cubic perovskite structure of Mn_3SnH_x. The cross indicates the octahedral interstitial site between layers A and B which is occupied by hydrogen in the cubic structure, and which is surrounded by six Mn atoms. The position of the Sn atoms in the C layer (not shown) is above this hydrogen site.

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hexagonal layers (A and B) of a [001] projection of the hexagonal DO_{19} structure. This projection corresponds to a [111] projection of the cubic perovskite structure. The cubic symmetry requires that the Mn atoms occupy the positions indicated by dashed circles in Fig. 1, and that a third layer, C, is added. The DO_{19} structure of Mn_3Sn is generally stable only in the presence of excess Mn, which replaces Sn atoms on 2c sites of the space group $P6_3/mmc$ [5]. Likewise, the excess Mn atoms in the hydride randomly occupy 1a sites of the space group $Pm3m$ of Mn_3SnH_x [2], which are regularly occupied by Sn (Table 1).

By its cubic perovskite structure, Mn_3SnH is also related to a large group of nitrides and carbides of Mn with the general formula Mn_3MX, where M is a metal and X=N or C. An extensive review on these compounds, many of which have interesting magnetic properties, can be found in Ref. [11].

2. Experimental details

Compounds of nominal composition $Mn_{3.0}Sn_{1.0}$, $Mn_{3.08}Sn_{0.92}$ and $Mn_{3.2}Sn_{0.8}$ were prepared by arc-melting from the elements in an argon atmosphere and subsequent annealing in an evacuated quartz tube at 850°C for 10 h in the case of $Mn_{3.0}Sn_{1.0}$ and at 900°C for 140 h in the case of $Mn_{3.08}Sn_{0.92}$ and $Mn_{3.2}Sn_{0.8}$. The starting materials, Mn flakes and Sn pellets, were of 99.98% and 99.96% purity, respectively. Prior to the melting, a MnO_2 layer covering the Mn flakes was removed by reduction to MnO in a H_2 flow at 800°C and subsequent etching in 1 *N* HCl.

The samples were ground to a powder and characterized by X-ray diffraction. $Mn_{3.08}Sn_{0.92}$ and $Mn_{3.2}Sn_{0.8}$ were single phase samples with the DO_{19} structure, whereas the sample of nominal composition $Mn_{3.0}Sn_{1.0}$ contained a few percent of Mn_2Sn with a B8 structure. ^{119}Sn Mössbauer spectra of the initial samples confirmed these findings.

Hydrides of these compounds were prepared by exposing the samples to molecular hydrogen at 350°C and a pressure of 2.8 GPa in the case of $Mn_{3.08}Sn_{0.92}$ and of 4 GPa in the case of $Mn_{3.0}Sn_{1.0}$ and $Mn_{3.08}Sn_{0.92}$ in a high pressure cell described previously [12]. Before releasing the pressure, the samples were cooled to below room temperature. To avoid hydrogen losses, the samples were stored in liquid nitrogen. It turned out, however, that hydrides stored at ambient temperature did not lose hydrogen within several months.

X-ray powder patterns of the hydrides showed that these had a cubic structure with a lattice parameter $a=3.985(5)$ Å at 100 K, in agreement with the structure proposed in Table 1 and Fig. 1. The diffraction lines of the hydrides were slightly broadened compared to those of the initial samples. The hydrogen content of the samples was determined with an accuracy of 2–3% by hot extraction into a calibrated volume at temperatures around 500°C. All investigated $Mn_{3+y}Sn_{1-y}H_x$ samples had a hydrogen content of $x=0.92(3)$.

The Mössbauer spectra were obtained with a source of ^{119m}Sn in $CaSnO_3$. The temperature of the Mn_3SnH_x absorbers was varied between 4.2 and 300 K. Measurements at higher temperatures have not been performed since hydrogen losses during the measurement time of about one day per spectrum could not be ruled out. The spectra were analysed by fitting transmission integral curves comprising Gaussian distributions of magnetic sextet patterns to the measured data. The effective absorber thicknesses were determined by simultaneous measurement of a β-Sn reference absorber of known thickness.

3. Results

Over the whole investigated temperature range from 4.2 to 300 K, the ^{119}Sn Mössbauer spectra of $Mn_{3.0}Sn_{1.0}H_x$, $Mn_{3.08}Sn_{0.92}H_x$ and $Mn_{3.2}Sn_{0.8}H_x$ (Fig. 2) show a distribution of magnetic hyperfine splittings. At ambient temperature the corresponding hyperfine field distributions (Fig. 3) are essentially single-peaked with hyperfine fields around 5.9 T depending only slightly on the Sn content. As the temperature is lowered, the distributions broaden and new peaks with smaller hyperfine fields emerge. In the case of $Mn_{3.2}Sn_{0.8}H_x$ the distribution also exhibits higher fields. At 4.2 K the spectra of $Mn_{3.0}Sn_{1.0}H_x$ and $Mn_{3.08}Sn_{0.92}H_x$ show a main peak at 1.3–1.7 T and two smaller peaks at 3.2–3.5 T and 5.4–6.0 T, the larger hyperfine fields being observed in the sample with the lower Sn content. The 4.2 K spectrum of $Mn_{3.2}Sn_{0.8}H_x$ is considerably more complex and shows significant peaks at hyperfine fields as high as 20 T and 24 T, a main peak at 7 T, and smaller peak at 1.7 T.

All components have the same isomer shift of +1.67 mm/s relative to $CaSnO_3$ with both source and absorber at 4.2 K. This shift is slightly smaller than that of the initial Mn_3Sn compounds (1.69–1.70 mm/s).

The spectra are symmetric around their center of gravity. This implies that electric field gradients caused by local deviations from the cubic $m3m$ symmetry of the Sn sites are small and randomly oriented and therefore do not lead to an asymmetry of the unresolved sextet patterns.

The complex variation of the Mössbauer spectra with temperature is reflected in the temperature dependence of the average hyperfine fields (Fig. 4). For $Mn_{3.0}Sn_{1.0}H_x$ and $Mn_{3.08}Sn_{0.92}H_x$, after a slight increase which is typical of magnetically ordered substances, the average hyperfine field drops with decreasing temperature between 200 and 100 K from about 6 T to about 2 T. In the case of $Mn_{3.2}Sn_{0.8}$, a somewhat less pronounced increase of the average hyperfine field below $T\approx110$ K is connected with the appearance of the high-field peaks in the hyperfine field distribution.

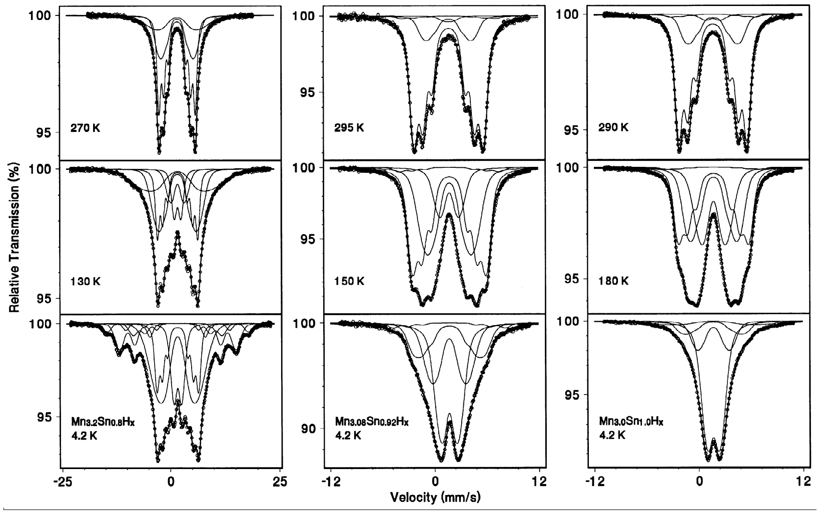

Fig. 2. Typical ^{119}Sn Mössbauer spectra of Mn_3SnH_x hydrides at different temperatures. The shown temperatures were choosen to illustrate the limiting cases of the high and the low temperature magnetic state as well as the spectra observed at intermediate temperatures.

4. Discussion

The temperature dependence of the average ^{119}Sn hyperfine fields clearly indicates that a transition between different magnetic states occurs in the Mn_3SnH_x hydrides. The temperature dependence of the hyperfine fields suggests a somewhat smeared out second order phase transition with a critical temperature of $T_C \approx 200$, 160 and 110 K for the hydrides $Mn_{3.0}Sn_{1.0}H_x$, $Mn_{3.08}Sn_{0.92}H_x$ and $Mn_{3.2}Sn_{0.8}H_x$, respectively.

Several reasons may account for the complexity of the hyperfine field distributions at low temperatures. One possibility is, of course, a complex magnetic state giving rise to several magnetically inequivalent Sn sites. There are, however, two factors that are more likely to lead to a complex distribution of sites with different hyperfine fields: the partial occupation of 1b sites by hydrogen and the excess Mn atoms replacing Sn on 1a sites. Since the hydrogen content of the studied samples is largely the same, we believe that additional magnetic moments carried by excess Mn atoms on 1a sites are the essential cause, as this can account also for the different distributions observed in the samples with different amounts of excess Mn. (Note that the $Mn_{3.0}Sn_{1.0}H_x$ sample is only nominally stoichiometric due to the presence of the Mn_2Sn impurity.) Direct influences of the 1a Mn atoms on the isomer shift or the quadrupole splitting of the Sn probes are expected to be small because of the strong shielding by the twelve nearest Mn neighbours of the Sn atoms. The same holds for the hydrogen atoms on 1b sites. The additional magnetic moments may, however, influence the local magnetic order and thus the hyperfine field of the nearby Sn probes.

A quantitative estimation can be endeavoured for the samples $Mn_{3.08}Sn_{0.92}H_x$ and $Mn_{3.2}Sn_{0.8}H_x$, for which the concentration of excess Mn is approximately known:

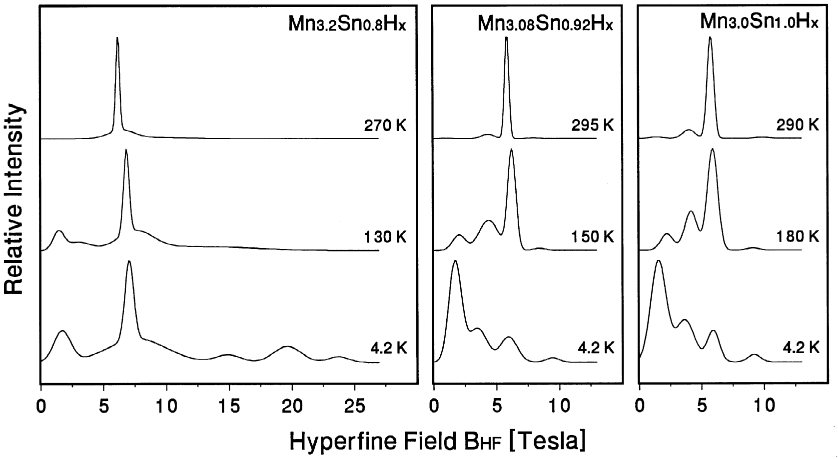

Fig. 3. Hyperfine field distributions corresponding to the Mössbauer spectra shown in Fig. 2. The distribution curves are normalized to equal maximum intensity.

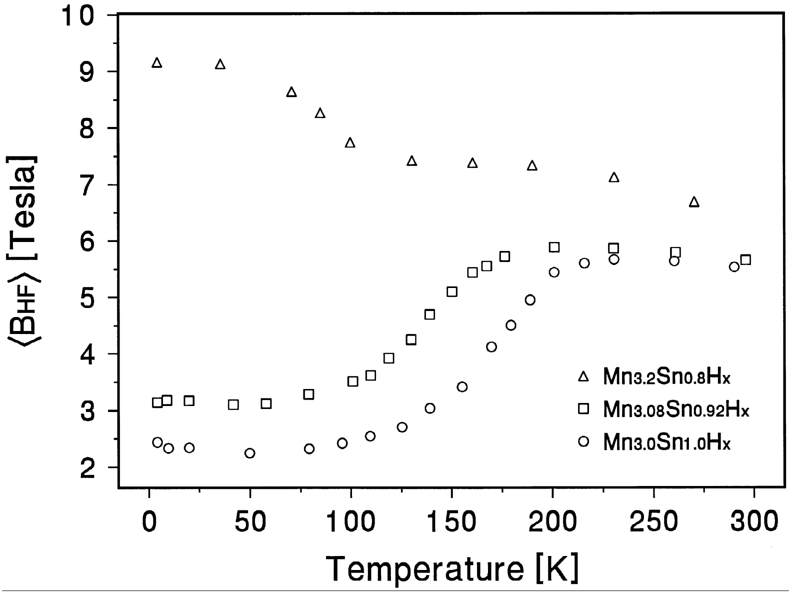

Fig. 4. Average ^{119}Sn hyperfine field $\langle B_{HF} \rangle$ of the Mn_3SnH_x hydrides as a function of temperature.

assuming a binomial distribution for the number of Mn atoms on the 6 1a sites at a distance of one lattice constant from a Sn probe, one finds that only 60% and 26% of the Sn atoms in $Mn_{3.08}Sn_{0.92}H_x$ and $Mn_{3.2}Sn_{0.8}H_x$, respectively, have an undisturbed local surrounding up to this distance. These fractions largely agree with the relative intensity of the 1.3–1.7 T peak in the hyperfine field distributions of these samples at 4.2 K, which is the main peak in the B_{hf} distribution of $Mn_{3.0}Sn_{1.0}H_x$ and $Mn_{3.08}Sn_{0.92}H_x$, and might thus be associated with an undisturbed local environment of the Sn probes.

It must be noted, however, that at ambient temperature the relative intensity of the main peak is much higher. Furthermore, excess Mn is also present in the parent compound Mn_3Sn. The Mössbauer spectra of Mn_3Sn, however, show essentially one hyperfine field, $B_{hf} \approx 4$ T, at room temperature and a relatively narrow field distribution at 4.2 K, which is only somewhat broader for samples with a higher concentration of excess Mn. The reason for this different behaviour is unknown and therefore further studies of this system by complementary methods such as NMR or neutron diffraction are highly desirable.

Acknowledgments

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