

## INFLUENCE OF DISSOLVED HYDROGEN ON THE NÉEL TEMPERATURE OF $\alpha$ -Mn(Sn) SOLID SOLUTIONS

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### Abstract:

An interstitial solution of hydrogen in an  $\alpha$ -Mn(Sn) solid solution with a hydrogen-to-metal ratio  $x = 0.05$  was prepared by exposing  $\alpha$ -Mn(Sn) containing 0.2 at.% Sn to molecular hydrogen at a pressure of 0.85 GPa and a temperature of 350°C. The Néel temperature of this hydride and those of hydrogen-free  $\alpha$ -Mn(Sn) solid solutions containing 0.2 and 0.5 at.% Sn were determined by <sup>119</sup>Sn Mössbauer spectroscopy. The values found are 128.3 K for the hydride and 97.3 and 107 K for the hydrogen-free solid solutions with 0.2 and 0.5 at.% Sn respectively.

### 1. Introduction

$\alpha$ -Mn is the allotropic modification of manganese that is stable at ambient temperature. It has a complex structure with 58 atoms in the cubic unit cell and four crystallographically inequivalent sites [1]. Below its Néel temperature of 95 K,  $\alpha$ -Mn is ordered antiferromagnetically [2,3] with a complex, non-collinear magnetic structure with six magnetically inequivalent sites [4, 5, 6].

Up to about 5 at.% hydrogen can be dissolved interstitially in  $\alpha$ -Mn at pressures of molecular hydrogen up to about 1 GPa and elevated temperatures [7]. In a recent neutron diffraction study hydrogen atoms were found to occupy the 12-fold e sites of the space group  $I\bar{4}3m$  of  $\alpha$ -Mn in these interstitial solutions [8]. While the magnetic properties of 3d transition metal hydrides with close packed metal lattices have been thoroughly studied and can be understood in terms of a rigid d-band model [9], nothing is known to date about the influence of interstitial hydrogen on the magnetic properties of  $\alpha$ -Mn.

In the present work we used <sup>119</sup>Sn Mössbauer spectroscopy to study the effect of hydrogen on the magnetic ordering in  $\alpha$ -Mn. As a non-magnetic atom, <sup>119</sup>Sn has turned out to be a very sensitive probe for hyperfine fields in hydrides of manganese [10]. Its use, however, requires the addition of small amounts of Sn to the manganese. In order to separate the effects of substitutional Sn and interstitial hydrogen, hydrogen-free  $\alpha$ -Mn(Sn) solid solutions were also studied in the present work. Such an investigation appeared also worthwhile since recently an unusually strong effect of Sn impurities on the Néel temperature of  $\alpha$ -Mn has been reported [11].

### 2. Experimental

Dilute alloys of enriched <sup>119</sup>Sn in Mn were prepared by arc-melting from the elements in an argon atmosphere of 99.998 % purity. Two samples with 0.2 at.% and one with 0.5 at.% Sn were made. Prior to the melting, a MnO<sub>2</sub> layer covering the surface of the Mn pieces (purity 99.99 %) was removed by reduction in an H<sub>2</sub> flow at 800°C and subsequent etching in 1 n HCl. The melted ingots were crushed and annealed in evacuated quartz tubes at 600°C for about one day. After grinding, X-ray diffraction patterns were measured from the annealed samples. These showed that the

samples containing 0.2 at.% Sn were pure  $\alpha$ -Mn(Sn), whereas the sample with 0.5 at.% Sn contained a small amount of a  $\beta$ -Mn(Sn) impurity.

One  $\alpha$ -Mn(Sn) sample with 0.2 at.% Sn was loaded with hydrogen in a high pressure cell described elsewhere [9] at a pressure of 0.85 GPa and a temperature of 350°C. Before releasing the pressure the sample was quenched to room temperature. To avoid hydrogen losses the sample was kept in liquid nitrogen thereafter and handled only briefly at ambient temperature when necessary. The X-ray diffraction pattern of the hydrogenated sample showed that it had the  $\alpha$ -Mn structure with a lattice parameter that had increased from 8.892 to 8.916 Å at 100 K. The hydrogen-to-metal ratio  $x = 0.049$  of the sample was determined with an accuracy of about 2 % by hot extraction into a calibrated volume.

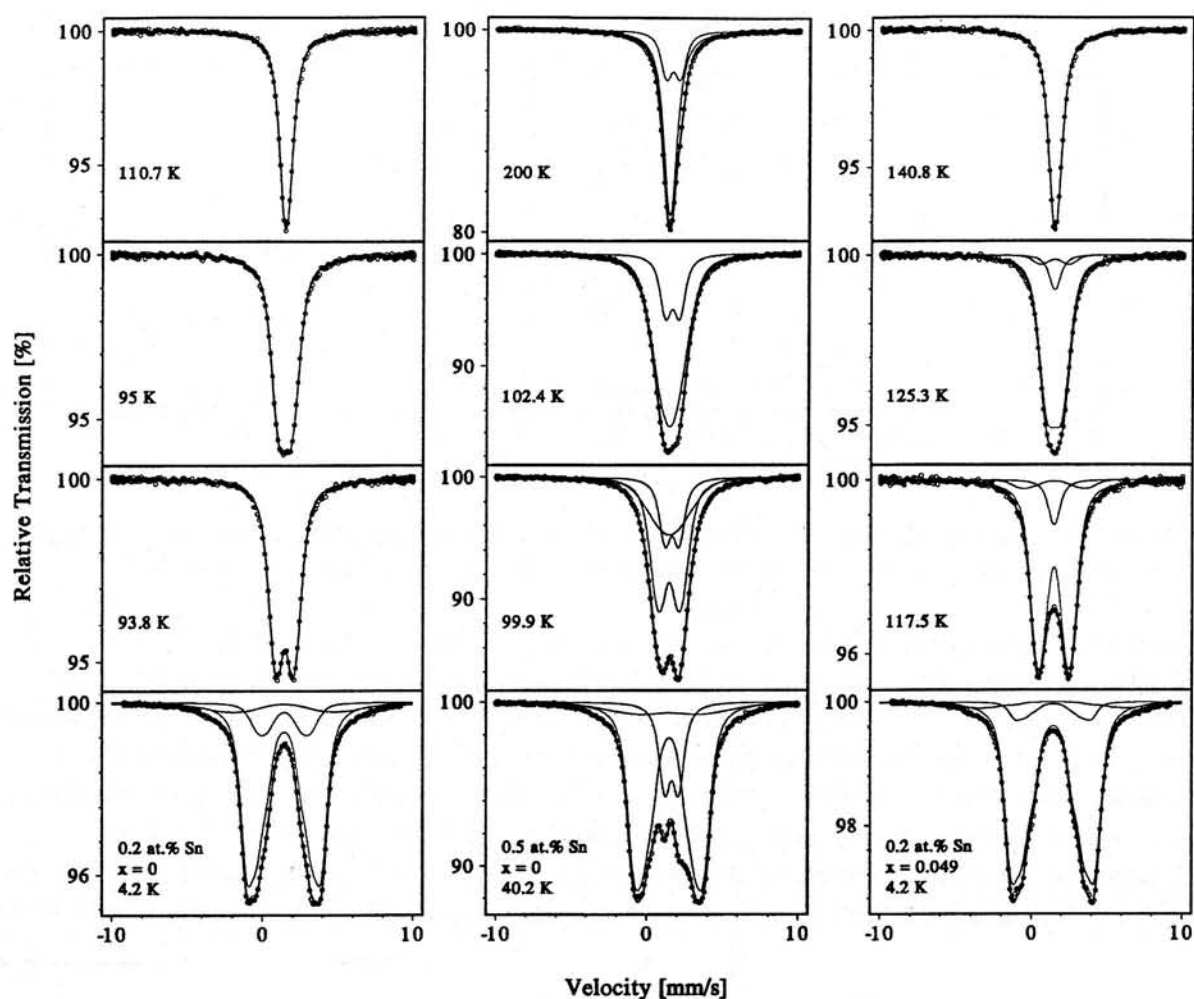
The Mössbauer measurements were done in a He-cooled gas flow cryostat, which allowed the variation of the absorber temperature between 10 and 300 K, and in a He bath cryostat at 4.2 K. The spectra were evaluated by fitting with transmission integral curves comprising magnetic sextets with a Gaussian distribution of hyperfine fields.

### 3. Results

Typical Mössbauer spectra of an  $\alpha$ -Mn(Sn) solid solution containing 0.2 at.% Sn are shown in the left column of Fig. 1. Above  $T \approx 98$  K the spectra consist of a slightly broadened single line with an isomer shift of 1.45 mm/s with respect to  $\text{CaSnO}_3$  at the same temperature. Below this temperature, a magnetic broadening sets in and below  $T \approx 94$  K the spectra show a distinct magnetic splitting. The magnetically split or broadened spectra could be fitted well by a single Gaussian distribution of hyperfine fields, which shows considerable intensity at zero hyperfine field near the Néel temperature. The more accurately measured 4.2 K spectrum, however, is better fitted by three magnetically split components (Fig. 1, bottom left). The main component in this spectrum with about 80 % relative intensity shows a hyperfine field of 3.6 T. In Fig. 2, the average hyperfine fields calculated from the Gaussian distribution functions are plotted against temperature as solid circles. A Néel temperature of 97.3 K was determined by linearly extrapolating the data points below and above the bending point (Fig. 2, on the right).

The spectra of the  $\alpha$ -Mn(Sn) sample with 0.5 at.% Sn (Fig. 1, middle column) exhibit clearly a non-magnetic  $\beta$ -Mn(Sn) impurity with about 20 % relative intensity.  $\beta$ -Mn(Sn) shows as a quadrupole doublet with an isomer shift of 1.63 mm/s relative to  $\text{CaSnO}_3$  and a quadrupole splitting of 0.8 mm/s [12]. The average hyperfine fields of the  $\alpha$ -Mn(Sn) component of this sample are shown as solid squares in Fig. 2. The  $\alpha$ -Mn(Sn) in these spectra shows a magnetically split shoulder at temperatures as high as 140 K, which contributes to the average hyperfine field. The steepest increase of the hyperfine field, however, occurs at considerably lower temperatures. By linear extrapolation a critical temperature of 106.6 K was determined for this sample (Fig. 2, on the right).

Spectra of the hydrogen loaded  $\alpha$ -Mn(Sn) sample with 0.2 at.% Sn are shown in the right column of Fig. 1. They closely resemble those of the hydrogen-free  $\alpha$ -Mn(Sn) solid solutions with 0.2 at.% Sn, but the magnetic splitting sets in already at higher temperatures and the hyperfine field of 4.05 T of the main component in the 4.2 K spectrum is considerably larger. No significant change in the isomer shift could be observed on hydrogenation. Linear extrapolation of the average hyperfine fields (solid triangles in Fig. 2), yielded a Néel temperature of 128.3 K. Additionally, with about 8 % relative intensity a component which splits only at about 110 K is observed in the spectra. Mössbauer spectra taken of this sample after hot extraction of the hydrogen did not differ significantly from those of the hydrogen-free sample discussed above. The average hyperfine fields calculated from these spectra are shown in Fig. 2 as empty circles.



**Fig. 1:** Typical Mössbauer spectra of  $\alpha$ -Mn(Sn) solid solutions with 0.2 at.% (on the left) and 0.5 at. Sn (in the middle) and of an interstitial solution of hydrogen in  $\alpha$ -Mn(Sn) with a hydrogen-to-metal ratio  $x = 0.049$  and 0.2 at.% Sn (on the right). Spectra measured at temperatures well above, near and well below the respective Néel temperatures are shown.

#### 4. Discussion

While the Néel temperature of 97.3 K determined for a  $\alpha$ -Mn(Sn) solid solution with 0.2 at.% Sn is slightly higher than the value of 95 K usually quoted for pure  $\alpha$ -Mn, it differs drastically from the value of about 180 K given by Nakai [11] for the Néel temperature of a  $\alpha$ -Mn(Sn) solid solution with this Sn content. The reason for these contradictory results is not clear, in particular because Nakai also used  $^{119}\text{Sn}$  Mössbauer spectroscopy to determine the Néel temperature. It is worthwhile to note that a Néel temperature near 97 K for an  $\alpha$ -Mn(Sn) solid solution with 0.2 at.% Sn could be reproduced in the present work even with a sample that was melted separately, hydrogenated under high pressure and then outgassed again (empty circles in Fig. 2).

The results of the present work for  $\alpha$ -Mn(Sn) with 0.5 at.% Sn are less conclusive, because due to the  $\beta$ -Mn(Sn) impurity the Sn content in the  $\alpha$ -Mn(Sn) phase is not exactly known. Assuming a Sn concentration of 2 at.% in the  $\beta$ -Mn(Sn) phase, which is the lower limit for the Sn content in the  $\beta$ -Mn phase at the annealing temperature of 600°C [13], one can estimate the average Sn content of the  $\alpha$ -Mn phase from the relative intensities of the respective components in the Mössbauer spectra to be about 0.42 at.%. The critical temperature of 107 K obtained for this sample shows clearly that the Néel temperature of  $\alpha$ -Mn(Sn) solid solutions increases steeply with increasing Sn concentration. The magnetically broadened shoulder appearing already well above this temperature might therefore be due to an inhomogeneous distribution of Sn in the  $\alpha$ -Mn(Sn) phase.

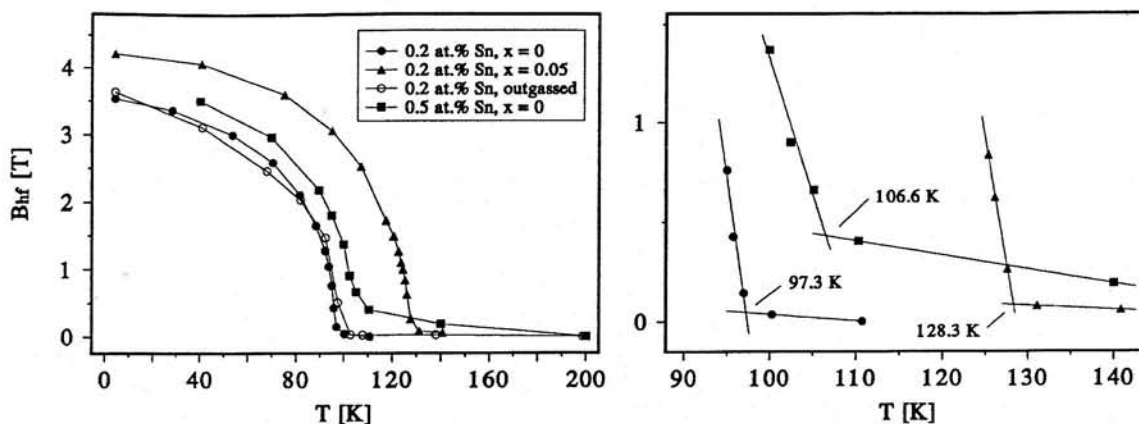


Fig. 2: Temperature dependence of the average hyperfine fields of the investigated  $\alpha$ -Mn(Sn) samples. On the right the linear extrapolations used to determine the Néel temperatures are shown.  $x$  is the hydrogen-to-metal ratio.

For the hydrogenated  $\alpha$ -Mn(Sn) sample, a Néel temperature of 128.3 K could be deduced from the Mössbauer spectra. Thus interstitial hydrogen with a hydrogen-to-metal ratio  $x = 0.05$  increases the ordering temperature by more than 30 K. The observed increase in the 4.2 K hyperfine field suggests that the magnetic moments also increase by about 10 % upon hydrogenation. The hydrogen-induced changes are reversible since after outgassing the Mössbauer spectra of this sample showed the same behaviour as a hydrogen-free  $\alpha$ -Mn(Sn) solid solution with 0.2 at.% Sn. A component with a lower Néel temperature observed in the spectra of the hydrogenated sample is presumably due to a not quite homogeneous hydrogen distribution resulting in regions with lower hydrogen concentration and thus lower ordering temperature.

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