

⁵⁷Fe MÖSSBAUER STUDY OF HYDRIDES AND DEUTERIDES OF MANGANESE

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Hydrides and deuterides of manganese with hydrogen-to-metal ratios x between 0.65 and 0.93 were studied by Mössbauer spectroscopy on dilute substitutional ⁵⁷Fe probes. No traces of magnetic ordering were found. Experiments on ⁵⁷Fe in MnD_{0.77} in external magnetic fields show that the iron has no measurable magnetic moment. The shapes of the Mössbauer patterns are compatible with superstructure ordering of the interstitials of the anti-CdI₂ type near $x = 0.5$, while the dependence of the isomer shifts on x shows that there are no substantial iron-hydrogen interactions.

1. Introduction

Under high pressures of molecular hydrogen or deuterium, manganese forms hcp hydrides and deuterides with hydrogen-to-metal ratios in the range of $0.65 \lesssim x \lesssim 0.95$ [1-3]. According to neutron diffraction experiments [4], these are antiferromagnetic. Their Néel temperatures presumably lie near 350 K, where a direct observation has been impossible because the hydrides decompose rapidly above 300 K at ambient pressure. A weakly ferromagnetic behaviour observed in both MnH _{x} and MnD _{x} [5,6] has been attributed to either spin canting or structural defects causing parasitic ferromagnetism [4]. The present Mössbauer experiments on dilute substitutional ⁵⁷Fe probes in MnH _{x} and MnD _{x} were prompted by the open questions concerning the magnetic properties of these systems. To avoid decomposition of the hydrides above room temperature, part of the experiments were performed in a high pressure cell permitting measurements at temperatures up to about 600 K. Additional experiments were performed at ambient pressure and 4.2 K in external magnetic fields up to 6 T.

2. Experimental details

The hydrides were prepared as described by Ponyatovsky et al. [3] at temperatures between 325 and 350 °C and pressures between 2.5 and 3.8 GPa from arc-melted alloys of α -Mn with 0.2 or 0.5 at.% of enriched ⁵⁷Fe. The deuterides contained a few percent of hydrogen. In order to avoid hydrogen losses during storage, the samples were kept in liquid nitrogen except during

the Mössbauer measurements. The Mössbauer experiments at high pressure were performed in a pressure cell using B_4C anvils [7], in which the powdered samples were enclosed in teflon capsules of 7 mm diameter with methanol as the pressure transmitting medium and silica as a filler. The hydrogen contents were determined by outgassing into a calibrated volume at elevated temperatures.

3. Results and Discussion

The Mössbauer spectra of hydrides and deuterides of manganese taken at 4.2 K (fig. 1) show no evidence of a magnetic hyperfine splitting. The isomer shifts increase with the hydrogen content, while the linewidths are largest near $x = 0.75$ (fig. 2). As for ^{57}Fe in hydrides of Ni and Pd [8-10], the broadening of the patterns can be attributed to a superposition of absorption lines with different isomer shifts resulting from the different numbers of nearest hydrogen neighbours around the ^{57}Fe probes in the disordered hydride phases, with at best very small electric quadrupole splittings. The fits shown in fig. 1 were made with a maximum of 7 single lines corresponding to between zero and 6 hydrogen neighbours with a shift of +0.12 mm/s per hydrogen neighbour like in the case of the PdH_x and NiH_x systems [8-10]. A magnetic contribution to the linewidths should be most clearly revealed in the vicinity of the Néel temperature, where any such broadening should disappear. Therefore the temperature dependence of the spectra was measured for $\text{MnD}_{0.77}$ at a pressure of about 2 GPa, by which decomposition could be avoided up to about 600 K, the highest temperature that could be reached in the pressure cell, although some loss of deuterium occurred above 450 K. The latter can be seen from the temperature dependence of the isomer shift (fig. 2), which increases slightly with temperature up to about 450 K and then decreases steeply. This decrease is irreversible, as is shown by the shift obtained at 100 K after the sample had been kept at 584 K for about 4 days (fig. 2). The hydrogen content of the sample after this treatment could not be determined because of the contamination with debris from the pressure cell, but is estimated to be near the lower limit of existence of the hcp hydride phase of $x \approx 0.65$, since the Mössbauer pattern taken at 4.2 K (fig. 1) shows the presence of about 10 % of $\alpha\text{-Mn}$. The temperature dependence of the linewidths (fig. 2) decreases smoothly with increasing temperature but shows no anomaly near the supposed [4-6] magnetic ordering temperature of about 350 K. If MnD_x is indeed antiferromagnetic, the absence of an observable magnetic hyperfine interaction of the iron nuclei is surprising since iron in antiferromagnetic hcp Mn-Fe alloys exhibits magnetic hyperfine fields between 1 and 2 T [11-14], which cause at least an easily detectable line broadening.

In a further search for magnetic hyperfine effects, Mössbauer spectra of ^{57}Fe in $\text{MnD}_{0.77}$ were measured at 4.2 K in external magnetic fields of 2, 4 and 6 T. The resulting hyperfine patterns can be explained by a magnetic field at the iron nuclei that is equal to the external field within the limits of error of about 1 %. The iron thus bears no measurable localized magnetic moment, in agreement with the rigid band model, which predicts non-zero magnetic moments at iron in hcp phases only at substantially higher electron numbers than those reached in manganese hydrides.

The isomer shift in MnH_x and MnD_x increases with the hydrogen content (fig. 2). Since the shift of iron in hydrogen-free hcp Mn is not known because of the instability of this phase, we take the mean isomer shift of the complex Mössbauer pattern of ^{57}Fe in $\alpha\text{-Mn}$ [15] as representative for unloaded manganese. For this we found a shift of -0.26 mm/s with respect to the source of ^{57}Co in Rh. Relative to this value, the hydrogen-induced shift is $+0.27$ mm/s at

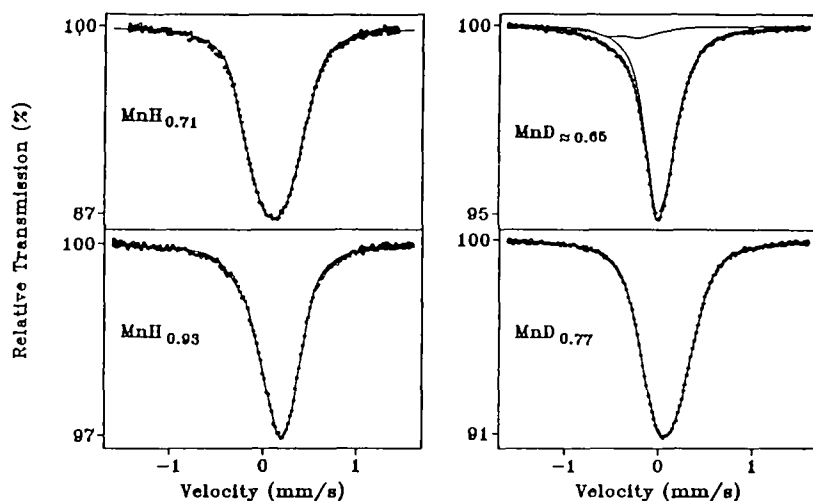


Fig. 1: Mössbauer spectra of ^{57}Fe in hydrides and deuterides of manganese measured at 4.2 K with a source of ^{57}Co in Rh at the same temperature.

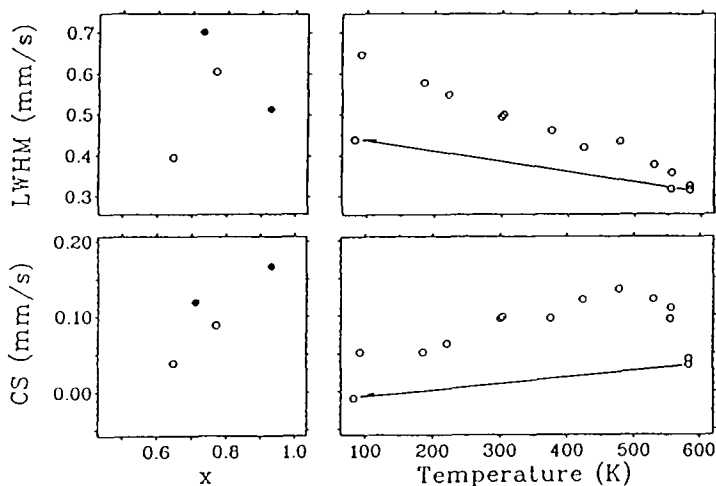


Fig. 2: Centre shifts (CS) and full linewidths at half maximum (LWHM) of the ^{57}Fe Mössbauer patterns of hydrides (full symbols) and deuterides (open symbols) of manganese as a function of the hydrogen-to-metal ratio x at 4.2 K (left) and as a function of temperature (right) for a sample with an initial hydrogen content of $x = 0.77$. The centre shifts are given with respect to the source of ^{57}Co in Rh at the same temperature as the absorber, which largely eliminates the second order Doppler shift.

$x \approx 0.65$ and $+0.43$ mm/s at $x = 0.93$. The nearly linear dependence of these shifts on the hydrogen content indicates that, other than for ^{57}Fe in Ni and Pd [7-9], there is no sizeable influence of a repulsive interaction between the iron solutes and the interstitials, which would lead to a reduced hydrogen site occupancy near the iron probes and to a nonlinear dependence of the centre shift on x [7-9]. For a distribution of hydrogens near the iron that is unperturbed by iron-hydrogen interactions and superstructure ordering, the width of the Mössbauer pattern

should be largest near $x = 0.5$ and decrease towards higher hydrogen contents. However, fig. 2 shows that the width is small at $x \approx 0.65$, has a maximum near $x = 0.75$ and then decreases again when all interstitial sites become filled as x approaches unity. This behaviour suggests a superstructure ordering of the hydrogen near $x = 0.5$, confirming the neutron diffraction results [4] that have been interpreted in terms of an anti- CdI_2 type superstructure, in which alternate hexagonal layers of octahedral interstitial sites are filled and each metal atom has 3 nearest hydrogen neighbours at $x = 0.5$.

4. Conclusions

The ^{57}Fe Mössbauer data for the hydrides and deuterides of manganese do not reveal magnetic ordering and show that iron solutes in these systems have no measurable localized magnetic moment. Considering these results, it will be of interest to extend the ^{57}Fe Mössbauer studies to the fcc manganese hydrides described recently [16,17], which have also been found to be antiferromagnetic [16].

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