Pergamon

NEUTRON DIFFRACTION INVESTIGATION OF γ MANGANESE HYDRIDE

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A profile analysis of the neutron diffraction spectrum of the *fcc* high pressure hydride γ-MnH$_{0.41}$ measured under ambient conditions showed that hydrogen is randomly distributed over the octahedral interstices of the *fcc* metal lattice and that the hydride is an antiferromagnet with the same collinear spin structure as pure γ-Mn, but with a smaller magnetic moment of about 1.9 Bohr magnetons per Mn atom. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

Under high hydrogen pressures manganese is known to form non-stoichiometric ε hydrides with a *hcp* metal lattice [1, 2] and non-stoichiometric γ hydrides with either *fcc* or *fct* metal lattices [3, 4]. The crystal and magnetic structures of the antiferromagnetic ε hydrides were studied by neutron diffraction [5] and by Mössbauer spectroscopy [6, 7], and their lattice dynamics by inelastic neutron scattering [8]. The γ manganese hydrides with H/Mn atomic ratios of $x = 0.04$–0.36 were also found to be antiferromagnets and the dependence of their Néel temperature, T_N, on the hydrogen concentration was studied by magnetization measurements and by neutron diffraction [3].

A room temperature X-ray examination of γ-MnH$_x$ [3] revealed a surprisingly low hydrogen induced lattice expansion of $\partial V_a / \partial x = 0.7(3)$ Å^3/H atom. This might be an indication for an essential difference between the crystal structure of the γ-MnH$_x$ hydrides and those of other known hydrides which show lattice expansions of the order of $\partial V_a / \partial x = 1.5$–$3$ Å^3/H atom [9, 10]. Neither the hydrogen positions in the manganese lat-

tice, nor the magnetic structure of the γ hydrides were, however, determined from the neutron diffraction data in [3].

The present article reports on the results of a neutron diffraction (ND) investigation of the crystal and magnetic structure of γ-MnH$_x$ with $x \approx 0.41$.

2. EXPERIMENTAL

To prepare the hydride, powdered manganese metal of 99.99 wt.% purity and a grain size of 0.05 to 0.1 mm was loaded with hydrogen by a 20 min. exposure to a hydrogen pressure of 2 GPa at 800 °C, which is well within the region of thermodynamic stability of γ manganese hydrides in the T–P phase diagram of the Mn–H system [11]. The hydrogen content of the γ-MnH$_x$ sample was determined to be $x = 0.411(5)$ by hot extraction at temperatures up to 500 °C. Under ambient conditions, no release of hydrogen from the sample was observed in the course of two weeks.

The ND spectrum of a 300 mg sample of this hydride was measured at 300 K for 20 h with the high luminosity time-of-flight diffractometer DN-2 installed at the pulsed reactor IBR-2 of the JINR, Dubna. The data were analysed with a computer program [12]

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based on the Rietveld profile refinement technique.

3. RESULTS

The ND spectrum of γ-MnH$_{0.41}$ and the results of its profile analysis are presented in Fig. 1. The smooth background has been subtracted from the shown spectrum to allow a better visual comparison with the calculated profiles.

An X-ray examination of the γ-MnH$_{0.41}$ sample at 300 K (DRON-2.0 diffractometer, FeK$_\alpha$ radiation) showed that it has a *fcc* manganese lattice. As is seen from Fig. 1, the ND spectrum of this sample contains intensive superstructure lines corresponding to the primitive cubic cell, space group *Pm3m*.

The superstructure lines can be due to both hydrogen ordering and magnetic ordering. With the unpolarized neutron beam used in the experiment, magnetic and nuclear scattering are incoherent with respect to each other and the corresponding intensities are additive. Since the lines (001) and (003) are not observed in the ND spectrum, this means that only atomic and magnetic superstructures which give zero intensity for these reflections need to be considered in the analysis.

Assuming a collinear spin structure, only four types of antiferromagnetic superstructures are compatible with the *fcc* lattice of the magnetic atoms [13]. Of these, only one (type I) can be described with a cubic unit cell of the same size $a = a_0$ as the crystallographic *fcc* cell, while all others have unit cells twice as large in at least one dimension. Since all observed superstructure lines have integral indices of the cubic structure with $a = a_0$, the magnetic structure must be of the type I.

The type I structure consists of ferromagnetic (001) planes coupled antiferromagnetically. From the observation that the (001) reflection is missing in the ND spectrum one can conclude that the magnetic moments of the Mn atoms are oriented perpendicular to these planes, since the neutron scattering intensity from magnetic planes is proportional to the square of the projection of the magnetic moments onto the planes. The resulting magnetic structure is shown in Fig. 2. Its symmetry is tetragonal, Shubnikov space group P_I4/mmm. The magnetic Bravais cell with $a = a_0/\sqrt{2}$ and $c = a_0$ is shown by dashed lines.

The diffraction lines of the collinear antiferromagnetic superstructures in the *fcc* lattice do not overlap with any of the *fcc* nuclear lines. Their profiles can therefore be analysed independently. As shown in Fig. 1, curve *b*, the modelling of the proposed type I superstructure provides a good description of all superstructure lines in the ND spectrum of γ-MnH$_{0.41}$. The magnetic form-factor of Mn was taken from [14].

Table 1. Positional parameters (x, y, z), thermal factors (B) and site occupancies (ω) for γ-MnH$_{0.41}$ according to the Rietveld analysis of the neutron diffraction data collected at 300 K. The obtained and expected profile factors are R_p = 1.43% and R_{ex} = 1.40%. Collinear antiferromagnetic structure, Shubnikov space group P_I4/mmm, a = 2.670(3) Å, c = 3.776(3) Å, magnetic moment of σ = 1.88(15) μ_B/Mn atom directed along the c-axis

Atom	x	y	z	B, Å^2	ω
Mn, $\sigma_\uparrow$	0	0	0	0.55	1.00
Mn, $\sigma_\downarrow$	1/2	1/2	1/2	0.55	1.00
H	0	0	1/2	1.80	0.41(3)
H	1/2	1/2	0	1.80	0.41(3)

In transition metal hydrides with close packed metal lattices hydrogen occupies either octahedral or tetrahedral interstices, the occupation of the tetrahedral ones occurring only in the dihydrides of titanium and vanadium group metals [15]. A model assuming hydrogen randomly occupying octahedral positions in the *fcc* metal lattice gives a good profile fit of the *fcc* lines in the ND spectrum (curve c in Fig. 1). It also yields a value of x = 0.41(3) hydrogen atoms per Mn atom which agrees well with x = 0.411(5) measured by hot extraction.

Together with the magnetic contribution (curve b), the calculated nuclear component (curve c) provides a rather good description of the whole ND pattern, as one can see from the difference curve d. The intensity ratio of the magnetic and nuclear contributions yields σ = 1.88(15) μ_B/Mn atom for the magnetic moment of the Mn atoms at 300 K. The final refined values of the structure parameters of γ-MnH$_{0.41}$ are given in Table 1.

Neither tetrahedral hydrogen coordination nor the formation of an octahedral hydrogen superstructure in γ-MnH$_{0.41}$ are consistent with experiment. The former is illustrated by the difference curve e in Fig. 1. As to hydrogen ordering on octahedral interstices, eight types of octahedral superstructures stable with respect to formation of antiphase domains are possible in *fcc* interstitial solid solutions [16]. Only two of them give rise to reflections with only integral indices and in both cases these reflections include the (001) one. The absence of the (001) reflection and of any reflections with fractional indices in the ND spectrum of γ-MnH$_{0.41}$ therefore shows that hydrogen is distributed randomly over octahedral sites.

4. DISCUSSION

The γ modification of pure manganese is stable between 1263 and 1410 K. Its properties at lower temperatures were estimated by extrapolation from substitutional γ Mn alloys [17–19]. The γ-Mn phase
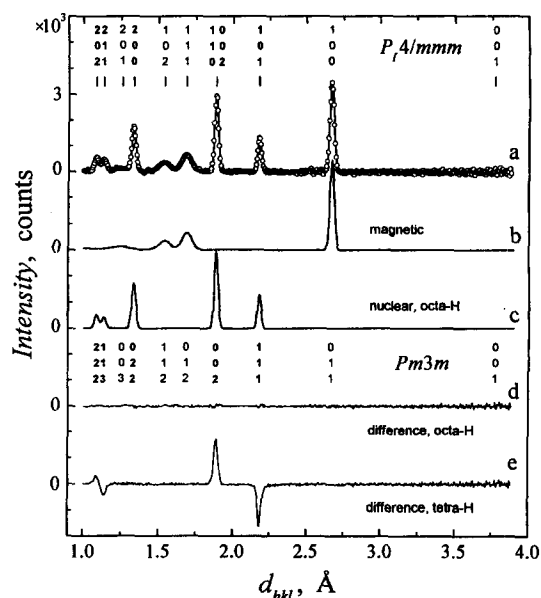
Fig. 1. Powder neutron diffraction spectrum of the γ-MnH$_{0.41}$ sample measured at 300 K (circles) and results of its Rietveld analysis (solid lines). (a) is the profile calculated with the structure parameters listed in Table 1 and represents the sum of the magnetic (b) and nuclear (c) contributions. (d) is the difference between the experimental (dots) and calculated (a) spectra, (e) the difference between the experimental spectrum and that calculated for $x = 0.41$ hydrogen atoms randomly occupying tetrahedral interstices in the *fcc* metal lattice of γ-MnH$_x$, the other fitting parameters being the same as in Table 1. Bold indices are for the lines of the *fcc* lattice.
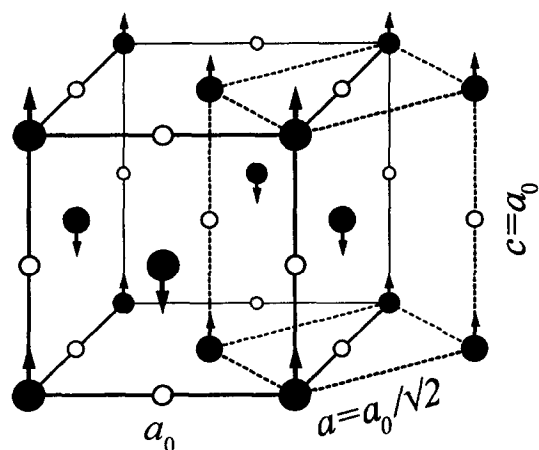

Fig. 2. Crystal (solid lines) and magnetic (dashed lines) Bravais cells of γ-MnH$_{0.41}$. Solid circles represent manganese atoms, open circles show the positions partly occupied by hydrogen, arrows indicate the positions and directions of the magnetic moments.

was shown to be an antiferromagnet with the type I collinear structure (as in Fig. 2) and with $T_N \approx 660$ K and $\sigma_0 \approx 2.4$ μ_B/Mn atom at $T = 0$ K. The magnetic ordering causes a tetragonal distortion of the *fcc* crystal lattice of γ-Mn below T_N. At room temperature, the *fct* lattice of this phase has $c/a \approx 0.95$ and $V_a(0) \approx 12.7$ Å^3/Mn atom [19].

The γ-MnH$_{0.41}$ sample studied in the present work has $V_a(0.41) = 13.46(3)$ Å^3/Mn atom. Relative to pure γ-Mn this yields $\partial V_a / \partial x \approx [V_a(0.41) - V_a(0)]/0.41 \approx 1.85$ Å^3/H atom which lies well in the range of 1.5–3 Å^3/H atom characteristic of transition metal hydrides [9, 10] and is close to $\partial V_a / \partial x \approx 1.8$ Å^3/H atom found for *hcp* hydrides of Mn and Co [10]. In this respect, γ-MnH$_{0.41}$ behaves as a typical interstitial hydrogen solution in a transition metal.

The decrease of the magnetic moment from $\sigma_0 \approx 2.4$ μ_B/Mn atom at 0 K for γ-Mn to $\sigma \approx 1.9$ μ_B/Mn atom at 300 K for γ-MnH$_{0.41}$ observed in this work, as well as a value of $T_N > 300$ K of γ-MnH$_{0.41}$ are in line with the rigid d-band model [10] which semiquantitatively describes the magnetic properties of all transition metal hydrides studied so far [20]. According to this model, these properties vary with hydrogen concentration as if the hydrogen was merely donating about 0.5 electrons per atom into the otherwise unchanged metal d-band. The dissolution of $x = 0.41$ of hydrogen in γ-Mn then increases its effective d-band occupation by the same amount as alloying with ≈ 20 at.% Fe, and it should lead to the same changes in the magnetic properties because Mn and Fe are neighbours in the periodic table and the concentration dependence of their magnetic properties is expected to obey the rigid band model. An extrapolation from the γ Mn–Fe–C alloys shows [21] that a γ-Mn$_{80}$Fe$_{20}$ alloy should be an *fcc* antiferromagnet with the type I magnetic structure and with $\sigma_0 \approx 2.0$ μ_B/Mn atom and $T_N \approx 600$ K. After a temperature correction using this T_N value, the model predicts $\sigma \approx 1.9$ μ_B/Mn atom at 300 K for γ-MnH$_{0.41}$, in agreement with experiment.

The structure and magnetic properties of γ-MnH$_x$ hydrides studied in [3] are inconsistent with both our data and the generally established properties of transition metal hydrides. In particular, the reported decrease in T_N from ≈ 660 K for γ-Mn to below 200 K for a *fcc* hydride with $x = 0.22$ exceeds the estimate from the rigid d-band model by an order of magnitude.

As to the X-ray data reported in [3], the linear dependence of $V_a(x)$ for γ-MnH$_x$ hydrides yields $V_a(0.41) \approx 13.7$ Å^3/Mn atom which is higher than our value of 13.46(3) Å^3/Mn atom. Due to the anoma-

lously small slope of $\partial V_a/\partial x = 0.7(3)$ Å^3/H atom [3], the extrapolation of this dependence to zero hydrogen concentration gives $V_a(0) \approx 13.4$ Å^3/Mn atom for γ-Mn, which is much higher than $V_a(0) \approx 12.7$ Å^3/Mn atom obtained by extrapolation from γ Mn–Pd alloys [19] and γ Mn–Cu alloys [17]. (This fact was not mentioned in [3] because the authors mistakenly adopted $V_a(0) \approx 13.43$ Å^3/Mn atom for the atomic volume of γ-Mn as a value estimated from the data on γ Mn–Cu alloys.) Additionally, even for a γ-MnH$_x$ sample with $x = 0.04$, the c/a ratio reported in [3] did not decrease below 0.99, while γ-Mn has $c/a \approx 0.95$ [19]. Possible reasons for these inconsistencies, however, cannot be analysed conclusively, because the experimental ND and X-ray spectra of the samples studied in [3] were neither shown nor discussed.

5. CONCLUSIONS

The *fcc* manganese hydride with $x \approx 0.41$ formed at a high hydrogen pressure can be considered as an interstitial solid solution of hydrogen in the γ modification of manganese. The hydride has the same antiferromagnetic spin structure as γ-Mn, but a smaller magnetic moment of ≈ 1.9 μ_B/Mn atom at 300 K in agreement with the predictions of the rigid d-band model for γ hydrogen solutions. The dissolved hydrogen expands the crystal lattice of γ-Mn at a rate of $\partial V_a/\partial x \approx 1.85$ Å^3/H atom, which is typical of transition metal hydrides.

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