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Giant tunnelling effect of hydrogen and deuterium in α manganese

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Abstract

The crystal structure of a solid solution of 3.5 at.% deuterium in α-Mn was determined by neutron diffraction and the spectrum of optical deuterium vibrations at 5 K was studied by inelastic neutron scattering (INS). The results give conclusive evidence of the tunnelling origin of the strong peaks at 6.4 and 1.6 meV observed earlier at temperatures up to 100 K in the INS spectra of hydrogen and deuterium solutions in α-Mn, respectively. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen/deuterium tunnelling; Neutron spectroscopy; Neutron diffraction

1. Introduction

The solubility of hydrogen in α-Mn was recently found to reach a few atomic percent under high hydrogen pressures [1]. A neutron diffraction investigation showed that hydrogen forms an unusual sublattice in the α-$MnH_{0.073}$ high-pressure phase and occupies the 12*e* type interstitial positions arranged in small dumb-bells 0.68 Å long [2]. An inelastic neutron scattering (INS) study [2] of α-$MnH_{0.073}$ at 90 K revealed a high-energy band of optical hydrogen vibrations split into three peaks, in accordance with the low site symmetry of the hydrogen positions, and also a strong low-energy peak at 6.4 meV which was tentatively attributed to the splitting of the vibrational ground state of hydrogen due to tunnelling between the adjacent 12*e* sites.

Hydrogen tunnelling in metals has been studied for many years already, but the tunnelling splitting of the hydrogen ground state never exceeded 0.2 meV; the integral intensity of the tunnelling peak was by orders of magnitude less than in α-$MnH_{0.073}$ and the effect was observed only at temperatures below 10 K [3]. Taking also into account that the observation of a quantum effect at temperatures as high as 90 K is a rare event, the nature of the giant tunnelling effect in α-$MnH_{0.073}$ deserved thorough justification.

Further results of INS studies nevertheless strongly corroborated the assumption of the tunnelling origin of the 6.4 meV peak in the spectrum of α-$MnH_{0.073}$ [4]. The results include the temperature and the neutron momentum-transfer dependences of the intensity of this peak and also the temperature dependence of the intensity of a similar peak at 1.6 meV in the INS spectrum of α-$MnD_{0.05}$. The most stringent argument, however, was the very fact that the peak moves from 6.4 meV for hydrogen to 1.6 meV for deuterium, because this decrease in energy is too large to result from mechanisms other than tunnelling. Moreover, the positions of these H and D peaks agree with roughly estimated values, $\Delta_0^H = 5$ meV and $\Delta_0^D = 1.5$ meV, for the splitting of the hydrogen and deuterium vibrational ground states due to tunnelling. These values follow from the relation:

$$\Delta_0 \approx (1/2)\hbar\omega_0 \exp(-m\omega_0 \ell^2/\hbar)$$

[5] if one substitutes the measured energy $\hbar\omega_0^H = 73$ meV [2,4] and the energy $\hbar\omega_0^D = \hbar\omega_0^H/\sqrt{2} \approx 51$ meV of H and D local vibrations along the line $2\ell = 0.68$ Å which connects the 12*e* sites in a dumb-bell. *m* is the mass of the H or D atom.

This estimation, which is a key argument in favour of the tunnelling nature of the observed effects, was nevertheless based on the rather questionable assumptions that the crystal structure and the distance 2ℓ between the adjacent 12*e* positions are the same for α-$MnH_{0.073}$ and α-$MnD_{0.05}$

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and that the ratio of frequencies of the H and D optical vibrations is harmonic. In the present work, the crystal structure of a deuterium solid solution in α-Mn was determined by neutron diffraction and the spectrum of deuterium optical vibrations was studied by INS.

2. Sample preparation and experimental details

A 6.5 g sample of a solid solution of deuterium in α-MnH was prepared from freshly powdered manganese metal of 99.99 wt.% purity and a grain size of 0.05–0.1 mm. To load the sample with deuterium, the powder was exposed to a deuterium pressure of 0.6 GPa at 350°C for 5 h with subsequent rapid cooling to room temperature. The method was the same as previously applied to load α-Mn with hydrogen [1], the only difference being that thermal decomposition of AlD_3 instead of AlH_3 was used to produce the high-pressure gaseous deuterium. Regretfully, the AlD_3 was contaminated with hydrogen. The synthesised sample therefore also contained hydrogen and, as the INS investigation showed (Section 3.2), had an atomic ratio of $H/D \approx 0.08$. The total content $(H+D)/Mn = 0.0377(2)$ of both hydrogen isotopes was determined by hot extraction into a calibrated volume at temperatures up to 550°C using a 25 mg portion of the sample. The composition of the sample was thus α-$MnD_{0.035}H_{0.003}$.

The neutron diffraction spectrum of this sample was measured at room temperature with a high-resolution Fourier diffractometry system (HRFD) installed at the pulsed reactor IBR-2 of the JINR, Dubna. The data were analysed with a computer program [6] based on the Rietveld profile refinement technique.

The INS spectrum of the α-$MnD_{0.035}H_{0.003}$ sample and, for comparison, also of the 8 g powder α-$MnH_{0.073}$ sample from Refs. [2,4] were measured at 5 K with the neutron spectrometer IN1 BeF at the hot source of the high-flux reactor at the ILL, Grenoble. The scattering angle was fixed at 90° and a Cu(220) monochromator was used to scan the energy of incoming neutrons. The final energy of neutrons that passed through the cold Be filter analyser and were recorded by the counters was assumed to be 3 meV. The energy resolution of the spectrometer was $\Delta\omega/\omega \approx 7\%$. A background spectrum from an empty aluminium sample holder was measured under the same conditions and then subtracted from the raw INS spectra of the samples.

3. Results and discussion

3.1. Neutron diffraction

_The cubic unit-cell of the α-Mn structure, space group *I43m*, contains 58 atoms located on the four crystallographically inequivalent sites 2*a*, 8*c*, $24g_1$, and $24g_2$. A profile analysis of the neutron diffraction patterns of α-$MnH_{0.073}$ showed [2] that hydrogen randomly occupies interstitial positions 12*e* inside distorted octahedra of manganese atoms on $24g_1$ and $24g_2$ sites, as schematically shown by the right inset in Fig. 1. The 12*e* sites form dumb-bells positioned rather far apart, at the centres of the edges and faces of the unit cell of α-Mn with $a = 8.9403$ Å, see the left inset in Fig. 1. Because of the small distance of $2\ell = 0.68$ Å between the 12*e* sites in a dumb-bell, these positions cannot be occupied by hydrogen at the same time due to the 'blocking effect' [7] requiring that the distance between hydrogen atoms in a metal should not be less than 2 Å. An occupancy of half of the 12e sites corresponds to an H/Mn atomic ratio of $x = 6/58 \approx 0.103$. In the $MnH_{0.073}$ sample hydrogen therefore filled about 70% of the accessible interstices.

The structure parameters of α-Mn and α-$MnH_{0.073}$ studied by neutron diffraction in Ref. [2] with the HRFD diffractometer at 300 K are given in Table 1. In the present work, the parameters of α-$MnH_{0.073}$, corrected for the lattice parameter, the type of the hydrogen isotope and its concentration, were used as starting parameters for the profile analysis of the neutron diffraction pattern of α-$MnD_{0.035}H_{0.003}$ shown in Fig. 2. The quality of the refinement is illustrated by the difference spectrum at the bottom of Fig. 2. The final refined values of the structure parameters of α-$MnD_{0.035}H_{0.003}$ are given at the bottom of Table 1.

In the course of refinement of the α-Mn, α-$MnH_{0.073}$ and α-$MnD_{0.035}H_{0.003}$ structures, the site occupancies for Mn atoms were fixed to one, and the other structure parameters listed in Table 1 were subject to fitting. The

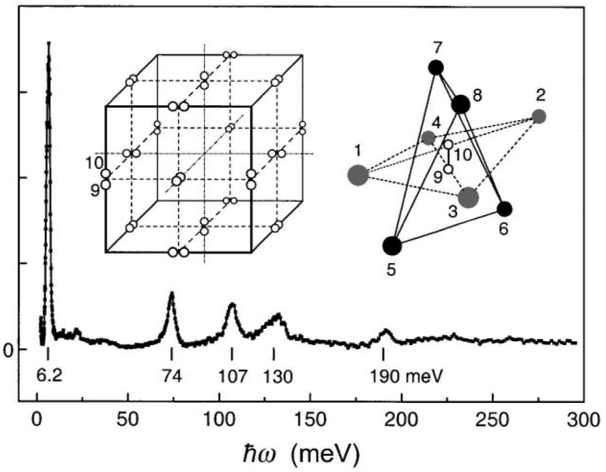

Fig. 1. The α-$MnH_{0.073}$ solid solution. On the right: two adjacent positions 12*e* partly occupied by hydrogen (open circles 9 and 10) and their nearest environment of two tetrahedra formed by manganese atoms on positions $24g_1$ (shaded circles 1–4) and on positions $24g_2$ (solid circles 5–8); the Mn atoms 1–4, 5, and 6 form a distorted octahedron around the H atom on position 9. On the left: the arrangement of dumb-bells of 12*e* positions in the unit cell of α-Mn. Bottom: the INS spectrum measured at 23 K with the TFXA spectrometer at ISIS, UK [10].

Table 1
Positional parameters (X, Y, Z), thermal factors (B) and site occupancies (ω) for α-Mn [2] and for the solid solutions α-$MnH_{0.073}$ [2] and α-$MnD_{0.035}H_{0.003}$ (present work) according to a Rietveld profile refinement of the neutron diffraction data collected at 300 K with the HRFD diffractometer at JINR, Dubna

Phase	Atom	Site	X	Y	Z	B (Å^2)	ω
α-Mn	Mn	2a	0	0	0	0.72	1.00
$a=8.9138(3)$ Å	Mn	8c	0.315(2)	0.315(2)	0.315(2)	0.45	1.00
$R_p/R_{ex}=5.0/3.1$	Mn	24g_1	0.354(2)	0.354(2)	0.033(2)	0.48	1.00
	Mn	24g_2	0.090(2)	0.090(2)	0.280(2)	0.44	1.00
α-$MnH_{0.073(1)}$	Mn	2a	0	0	0	0.74	1.00
$a=8.9403(3)$ Å	Mn	8c	0.319(2)	0.319(2)	0.319(2)	0.45	1.00
$R_p/R_{ex}=5.2/4.0$	Mn	24g_1	0.355(1)	0.355(1)	0.034(1)	0.61	1.00
	Mn	24g_2	0.091(1)	0.091(1)	0.281(1)	0.45	1.00
	H	12e	0	0	0.538(2)	1.57	0.34(2)
α-$MnD_{0.035}H_{0.003}$	Mn	2a	0	0	0	0.5	1.00
$a=8.9279(2)$ Å	Mn	8c	0.318(2)	0.318(2)	0.318(2)	0.3	1.00
$R_p/R_{ex}=3.6/2.2$	Mn	24g_1	0.356(1)	0.356(1)	0.035(1)	0.36	1.00
	Mn	24g_2	0.090(1)	0.090(1)	0.281(1)	0.36	1.00
	D	12e	0	0	0.539(2)	1.2	0.18(2)

R_p and R_{ex} are the obtained and expected profile factors. Cubic structure, space group $I\bar{4}3m$ (No. 217).

resulting site occupancy of the H atoms in α-$MnH_{0.073}$ and of the D atoms in α-$MnD_{0.035}H_{0.003}$ corresponds to the ratios H/Mn=(12/58)ω=0.070(4) and D/Mn=0.037(4), which agree with the compositions of the solutions. Within the experimental error the coordinates obtained for the Mn atoms in the unit cell of α-Mn do not change on hydrogen/deuterium uptake. The coordinates of the H and D atoms coincide within the experimental error and give $2\ell_H=$ 0.68(3) Å and $2\ell_D=0.70(3)$ Å.

As seen from Fig. 3, the values of the lattice parameter of α-$MnD_{0.035}H_{0.003}$ and α-$MnH_{0.073}$ form a single linear dependence if plotted as a function of the atomic ratio $x=(H+D)/Mn$. This implies that the dissolution of H and D results in virtually the same lattice expansion of the α-Mn metal. The increase in the atomic volume, V_a, of α-Mn corresponds to a value of $\partial V_a/\partial x=1.50(3)$ Å^3/H atom which lies near the lower limit of the interval 1.5–3 Å^3/H atom characteristic of hydrides of transition metals [8,9].

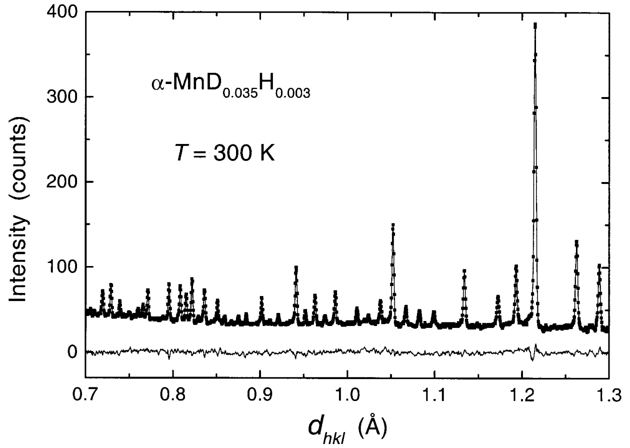

Fig. 2. The neutron powder diffraction pattern of α-$MnD_{0.035}H_{0.003}$ measured at 300 K with the HRFD diffractometer at JINR, Dubna (dots), its profile fit calculated with the structure parameters listed in Table 1 (solid line) and the difference between the experimental and calculated spectra (the curve at the bottom). For clarity, the smooth incoherent component is subtracted from the experimental spectrum.

3.2. Inelastic neutron scattering

A representative INS spectrum of α-$MnH_{0.073}$ that was measured recently [10] with better resolution than in Ref. [2] is shown in Fig. 1. The strong peak attributed to hydrogen tunnelling is centred at 6.2 meV, three peaks of the fundamental optical H modes are observed at 74, 107

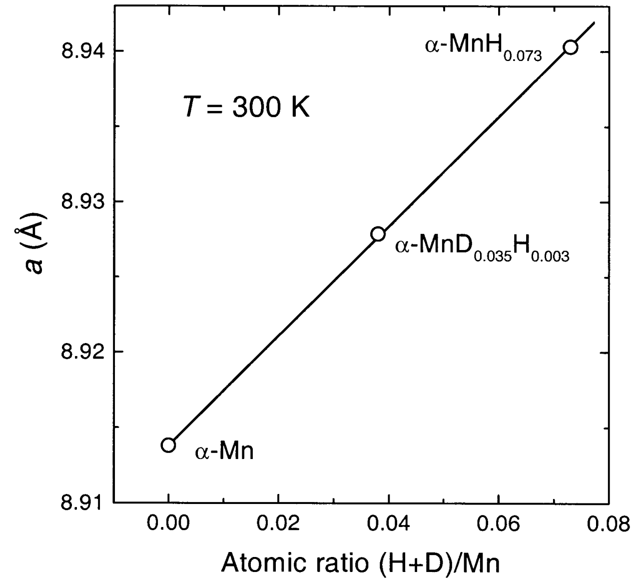

Fig. 3. The lattice parameter of solid H and D solutions in α-Mn at 300 K as a function of the total content $x=(H+D)/Mn$ of both hydrogen isotopes, the data from Table 1. The solid line shows the linear fit $a=(8.9139+0.363x)$ Å.

and 130 meV, and one peak of the second optical H band is seen at around 190 meV, all in reasonable agreement with the results in Ref. [2]. The peak at 74 meV presumably corresponds to a low-energy mode of H vibrations along the line connecting the sites in a dumb-bell because relative to this line the nearest-neighbour Mn atoms are most distant and positioned symmetrically (see the right inset in Fig. 1). The peaks at 107 and 130 meV can be assigned to vibrations perpendicular to this line.

Fig. 4a shows the INS spectra of α-$MnH_{0.073}$ and α-$MnD_{0.035}H_{0.003}$ in the range of optical vibrations measured in the present work at a temperature of 5 K. The peak positions in the spectrum of α-$MnH_{0.073}$ are virtually the same as in Fig. 1. Hydrogen and deuterium peaks in the spectrum of α-$MnD_{0.035}H_{0.003}$ have comparable intensities due to the large incoherent neutron scattering cross-section of hydrogen.

Under the assumption that the energy of similar optical modes is by a factor of $\sqrt{m_D/m_H} \approx \sqrt{2}$ lower for D atoms than for H atoms (a harmonic case) and that only excitations from the lower ground state take place at a temperature as low as 5 K (the upper ground state is nearly empty), the INS spectrum of deuterium in α-$MnD_{0.035}H_{0.003}$ in the range of optical vibrations can be approximated by the spectrum of hydrogen in α-$MnH_{0.073}$ plotted as a function of $\hbar\omega_D = \Delta_0^D/2 + (\hbar\omega_H - \Delta_0^H/2)/\sqrt{2}$. This modelled deuterium spectrum is plotted in Fig. 4b by the dashed line. Its comparison with the experimental spectra in Fig. 4a shows that the peak at about 107 meV in the spectrum of α-$MnD_{0.035}H_{0.003}$ is due to neutron scattering on H atoms only.

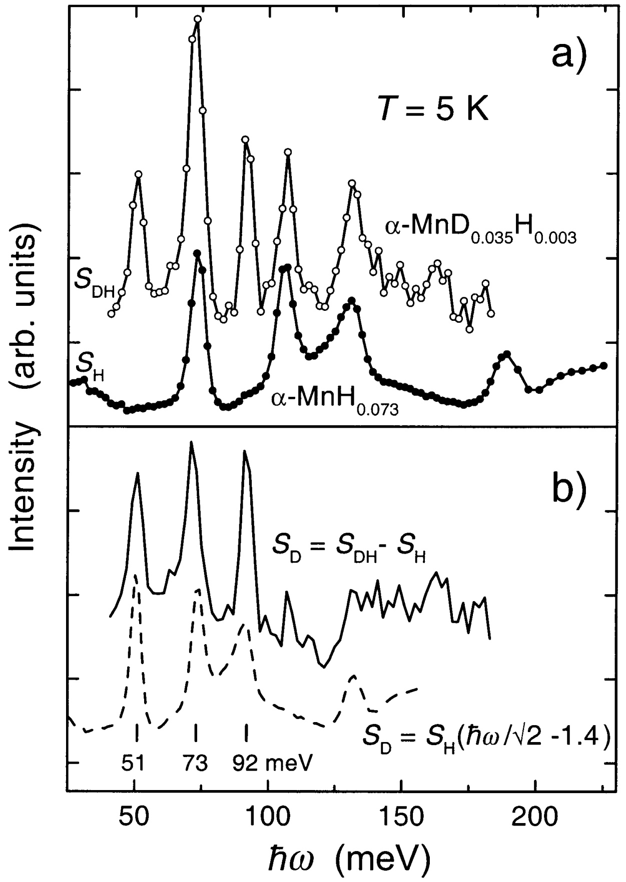

Fig. 4. (a) The experimental INS spectra of α-$MnD_{0.035}H_{0.003}$ (open circles) and α-$MnH_{0.073}$ (solid circles) measured at 5 K with the IN1 BeF spectrometer at ILL, Grenoble. (b) The difference between the above spectra considered as the INS spectrum of α-$MnD_{0.035}$ (solid curve) and the INS spectrum of α-$MnH_{0.073}$ plotted as a function of $\hbar\omega_D = \Delta_0^D/2 + (\hbar\omega_H - \Delta_0^H/2)/\sqrt{2}$ to simulate the spectrum of α-MnD_x in a harmonic approximation (dashed line).

The difference between the spectra of α-$MnD_{0.035}H_{0.003}$ and α-$MnH_{0.073}$ normalised to the integral intensity of the 107 meV peak yields the 'experimental' spectrum of deuterium in α-$MnD_{0.035}H_{0.003}$ plotted in Fig. 4b by the solid line. The elimination of the H contribution in the difference spectrum is not perfect, however, because the peaks in the spectrum of α-$MnH_{0.073}$ are broader than those in the spectrum of α-$MnD_{0.035}H_{0.003}$. In particular, a small peak at 107 meV still remains in the difference spectrum and the deuterium peak at 73 meV is noticeably deformed. The difference spectrum is nevertheless very similar to the deuterium spectrum calculated in a harmonic approximation (dashed line in Fig. 4b) and the positions of the two peaks at 51 meV and 92 meV, which do not overlap with the hydrogen peaks in the spectrum of α-$MnD_{0.035}H_{0.003}$, coincide with the calculated ones within the experimental error.

The fundamental modes of hydrogen and deuterium vibrations in α-Mn thus demonstrate harmonic behaviour, and the value $\hbar\omega_0^D = 51$ meV used in Ref. [4] to estimate the energy of tunnelling splitting in α-$MnD_{0.05}$ was correct.

The ratio of integral intensities of the 73 meV and the 51 meV peak in the INS spectra, respectively, of α-$MnH_{0.073}$ and α-$MnD_{0.035}H_{0.003}$ normalised to the intensity of the 107 meV peak gives an atomic ratio of $H/D \approx 0.08$ for the deuterated sample. This is the isotopic composition of that sample referred to throughout the paper.

4. Conclusions

The experiment shows that hydrogen and deuterium dissolved in α-Mn occupy interstitial positions of the same type 12*e* and with the same distance 2ℓ between the adjacent positions. The energies $\hbar\omega_0^H$ and $\hbar\omega_0^D$ of the H and D optical vibrations follow a harmonic ratio, $\sqrt{m_D/m_H} \approx \sqrt{2}$. These findings strongly corroborate the assumption of the tunnelling origin of the 6.4 meV and 1.6 meV peaks in the spectrum of α-$MnH_{0.073}$ and of α-$MnD_{0.05}$, respectively [4], because the difference between the energies of these peaks is too large to result from mechanisms other than tunnelling. In fact, the energy 6.4 meV of the H peak should almost not depend on the mass of the hydrogen isotope if the peak were due to crystal field or magnetic effects or due to 'lattice' vibrations. The peak energy should only decrease to $6.4/\sqrt{2} \approx 4.5$ meV when H is substituted for D if the peak were due to optical hydrogen vibrations. At the same time, the observed positions of the H and D peaks both agree with the energies $\Delta_0^{\mathrm{H}} \approx 5$ meV and $\Delta_0^{\mathrm{D}} \approx 1.5$ meV of the tunnelling splitting of the hydrogen and deuterium vibrational ground states as roughly estimated using the experimental values of 2ℓ, $\hbar\omega_0^{\mathrm{H}}$ and $\hbar\omega_0^{\mathrm{D}}$ [4].

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