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The vibrational spectrum and giant tunnelling effect of hydrogen dissolved in α-Mn

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Abstract

Vibrational spectra of α-$MnH_{0.07}$ and α-$MnD_{0.05}$ were studied by inelastic neutron scattering at temperatures from 1.7 to 200 K over a wide range of energy and momentum transfers. Together with the high-energy bands of the optical vibrations, pronounced peaks at 6.3 and 1.6 meV were observed in the spectra of the samples loaded with H and D, respectively. The study of the temperature, momentum-transfer and isotope dependence of the spectra demonstrated the tunnelling origin of these peaks.

Keywords: Hydrogen/deuterium tunnelling; Neutron spectroscopy

A recent high-pressure study showed that the solubility of hydrogen in α-Mn can be increased up to a few atomic percent [1]. The neutron diffraction investigation of α-$MnH_{0.07}$ revealed [2] that hydrogen randomly occupies interstitial sites of the 12e type (space group $I\bar{4}3m$) which form dumb-bells positioned rather far apart, at the centres of the edges and faces of the cubic unit cell of α-Mn. Because of the small distance of 0.68 Å between the 12e sites in a dumb-bell, each dumb-bell can accommodate only one hydrogen atom.

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An inelastic neutron scattering (INS) study [2] of α-$MnH_{0.07}$ at 90 K with the KDSOG-M spectrometer at JINR (Dubna, Russia) revealed a band of optical hydrogen vibrations split into three peaks at 73, 105 and 123 meV in accordance with the low site symmetry of the hydrogen positions and also a strong 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 12e sites forming a dumb-bell.

This paper reports on the results of further INS studies which strongly support the assignment [2] of the tunnelling origin of the 6.4 meV peak. These include the INS spectra of α-$MnH_{0.07}$ at 5–200 K (Fig. 1) measured with the TFXA spectrometer at ISIS, RAL (UK), the INS spectra of α-$MnD_{0.05}$ at

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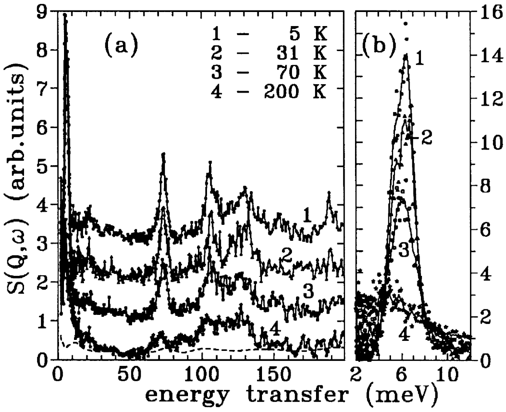

Fig. 1. The INS spectra of α-$MnH_{0.07}$ in the energy range (a) 2–200 meV and (b) 2–12 meV. The spectra in Fig. 1a are shifted along the *y*-axis. TFXA spectrometer, RAL.

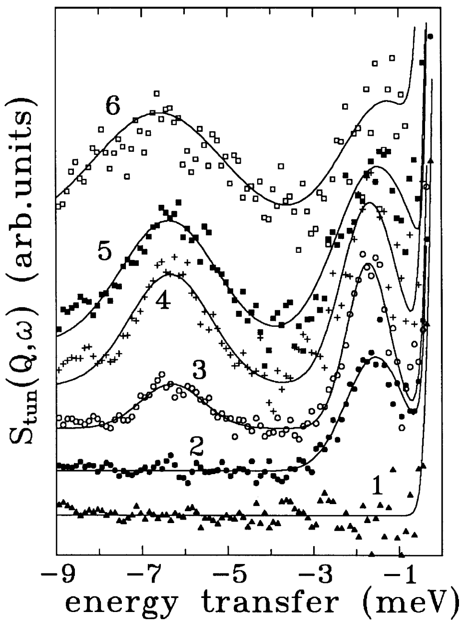

Fig. 2. The difference between the INS spectra of α-$MnD_{0.05}H_{0.005}$ and α-Mn at 2, 15, 29, 44, 60 and 100 K (curves 1–6). The curves are shifted along the *y*-axis. IN6 spectrometer, ILL.

1.7–180 K (Fig. 2) measured with the IN6 spectrometer at ILL (Grenoble, France) and the neutron momentum transfer dependence of the INS spectra of α-$MnH_{0.07}$ at 5–200 K (Fig. 3) measured with the MARI spectrometer at ISIS.

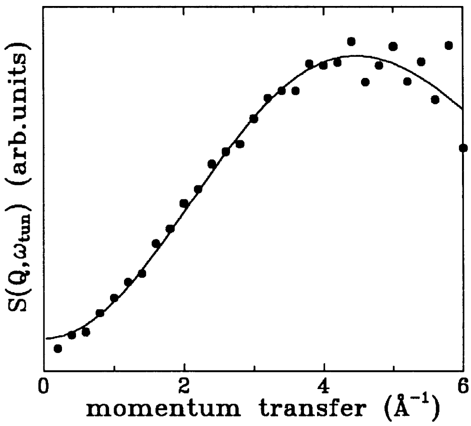

Fig. 3. The H tunnelling peak intensity in the INS spectrum of α-$MnH_{0.07}$ measured at 20 K as a function of momentum transfer. MARI spectrometer, RAL. The solid line shows the result of fitting based on equation of Ref. [4] (see text).

As seen from Fig. 1a, the peaks of the fundamental H optical modes in α-$MnH_{0.07}$ are observed at 74, 107 and 130 meV in fair agreement with Ref. [2]. The intensity of the peak at 6.2 meV decreases with increasing temperature and at 200 K the peak exhibits relaxation behaviour (Fig. 1b).

Fig. 2 shows the difference between the INS spectra of the α-$MnD_{0.05}$ sample and a sample of pure α-Mn measured under the same conditions. The α-$MnD_{0.05}$ sample was contaminated with about 0.5 at% H which manifested itself by the peak at 6.3 meV. The peak at 1.6 meV was due to 5 at% D. The positions of these H and D peaks agree with the roughly estimated values, $\Delta_0^H = 5$ meV and $\Delta_0^D = 1.5$ meV, of the splitting of the hydrogen and deuterium vibrational ground states due to tunnelling. These values follow from the equation $\Delta_0 \approx (1/2)\omega_0 \exp(-m\omega_0\ell^2/\hbar^2)$ of Ref. [3] if one substitutes $\omega_0^H = 73$ meV [2] and $\omega_0^D = 73/\sqrt{2}$ meV for the energy of H and D local vibrations along the line $2\ell = 0.68$ Å which connects the 12e sites in a dumb-bell [2]; *m* is the mass of the H or D atom.

The temperature dependencies of the integral intensities of the H and D tunnelling peaks are shown in Fig. 4 and can be well explained by a Boltzmann thermal population of the corresponding ground states (solid curves in the figure),

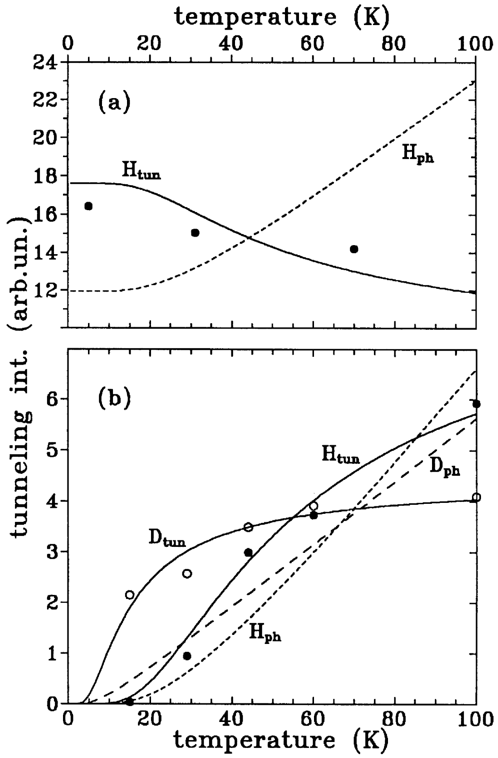

Fig. 4. The temperature dependencies of the tunnelling peak intensities for H and D in α-Mn obtained from the INS data measured in the regime of neutron energy loss (a, TFXA spectrometer) and neutron energy gain (b, IN6 spectrometer).

which is proportional to $1/[1+\exp(-\Delta_0/k_BT)]$ and $\exp(-\Delta_0/k_BT)/[1+\exp(-\Delta_0/k_BT)]$ for the lower and upper states, respectively. The use of a phonon or harmonic oscillator population factor is qualitatively inadequate (dashed curves in the figure).

As seen from Fig. 3, the intensity of the 6.3 meV peak of hydrogen in α-Mn as a function of momentum transfer, Q, can also be described fairly well by the dependence characteristic of tunnelling peaks: $S(Q,\omega_{tun}) \sim [1/2 - \sin(2\ell Q)/(4\ell Q)]\exp(-Q^2u^2)$ [4]. The value of the fitting parameter, u^2, the effective mean-square displacement of H atoms, is 0.0256 Å^2.

The remarkable features of the hydrogen tunnelling peak in the INS spectrum of α-$MnH_{0.073}$ are its anomalously large integral intensity compared to that of the optical hydrogen band and its anomalously high energy of 6.3 meV which is about 15 times higher than the energy of tunnelling splittings observed earlier for hydrogen in other metals [5]. Deuterium tunnelling in metals was not detected earlier by neutron spectroscopy.

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