

Solid State Communications 113 (2000) 569-572

solid state communications

www.elsevier.com/locate/ssc

Neutron spectroscopy of γ manganese hydride

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Received 5 November 1999; accepted 22 November 1999 by A.L. Efros

Abstract

The vibrational spectrum of fcc γ -MnH_{0.41} synthesized under high pressure of gaseous hydrogen was studied by inelastic neutron scattering at 2 K in the range of energy transfers from 25 to 400 meV. The fundamental band of optical hydrogen vibrations consists of a peak at 111 meV with a broad shoulder towards higher energies, which extends up to about 140 meV. At higher energy transfers, the spectrum originates from multiphonon neutron scattering and exhibits approximately harmonic behaviour. The results are compared with the available data for other metal hydrides. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Metals; E. Neutron scattering

1. Introduction

Hydrides of the group VI–VIII transition metals have close-packed metal sublattices with fcc (γ), hcp (ε) or dhcp (ε') structure [1,2], in which hydrogen occupies octahedral interstitial positions [3–5]. The lattice dynamics of the γ hydrides of Ni [6–8] and Pd (see [9] and references therein), of the ε hydrides of Cr [7], Mn [10] and Mo [7] and of the ε' hydride of Fe [11] have been studied by inelastic neutron scattering (INS).

Manganese forms both ε hydrides [12,13] and γ hydrides [14,15] under high hydrogen pressure. An INS investigation of these hydrides therefore provides the opportunity to compare the vibrational spectra of the two most widespread modifications of transition metal hydrides for one and the same host metal.

Manganese hydrides are non-stoichiometric compounds with wide composition ranges. In terms of the H-to-metal atomic ratio *x* these are 0.65 < x < 1 for the ε hydride [1] and 0.3 < x < 0.5 for the γ hydride [16]. An ε hydride of manganese studied earlier by INS [10] had x = 0.86. The present paper reports on the results of an INS investigation of a γ hydride with x = 0.41. According to neutron diffraction data, γ -MnH_{0.41} [5] as well as ε -MnH_{0.86} [17] are collinear antiferromagnets with a Néel point much above room temperature. Both hydrides display no atomic ordering of hydrogen, which randomly occupies octahedral interstices in the close-packed metal lattice. At room temperature, the lattice parameter of fcc γ -MnH_{0.41} is a = 3.776 Å [5] and the hydrogen-metal distance is R = a/2 = 1.888 Å. The hcp hydride ε -MnH_{0.86} has a = 2.964 Å, c = 4.357 Å [10] and a hydrogen-metal distance $R = \sqrt{a^2/3 + c^2/16} = 1.899$ Å.

2. Experimental

The INS measurement was carried out with the same sample of γ manganese hydride that was recently studied by neutron diffraction [5]. 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°. These conditions lie well within the region of thermodynamic stability of γ manganese hydrides in the *T*-*P* phase diagram

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of the Mn–H system [16]. Hot extraction and neutron diffraction gave the same value of x = 0.41 for the hydrogen content of the sample.

The INS spectrum of a 390 mg sample of γ -MnH_{0.41} was measured at 2 K with the neutron spectrometer IN1 at the hot source of the high flux reactor at the Institute Laue-Langevin in Grenoble. The spectrometer was operated in the beryllium filter mode, with a fixed scattering angle of 44°. Cu(200) and Cu(220) monochromators were used to obtain incoming neutrons with energies below and above ~120 meV, respectively. The corresponding energy resolutions were $\Delta \omega / \omega \approx 7$ % and 10 %.

The γ -MnH_{0.41} powder sample was enclosed in a flat aluminium container. A background spectrum from an empty container was measured separately under the same conditions and then subtracted from the raw INS spectrum of the γ -MnH_{0.41} sample in order to obtain the scattering intensity from γ -MnH_{0.41} alone.

3. Results and discussion

The INS spectrum $S(Q, \omega)$ of γ -MnH_{0.41} is shown in Fig. 1. It originates nearly exclusively from neutron scattering on hydrogen atoms. The contribution from manganese atoms is negligibly small, as the incoherent neutron scattering cross-section of H is about 40 times larger than that of Mn [18]. Furthermore, in the case of optical vibrations the scattering intensity is inversely proportional to the mass of the atom, which is about 50 times smaller for H than for Mn. With the hydrogen content x = 0.41 of the sample, this yields an intensity ratio of about 800 for scattering from H and Mn in the γ -MnH_{0.41} sample.

Significant inelastic scattering intensity from hydrogen is observed in three energy regions around 111, 230 and 340 meV (Fig. 1). The feature around 111 meV consists of a peak with a full width at half maximum of 12 meV, which exceeds the energy resolution $\Delta \omega \approx 8$ meV, and of a large shoulder towards higher energies, extending up to about 140 meV. The peak position and the shape of this intensity distribution are typical of the fundamental band of optical hydrogen vibrations in the ε and γ hydrides of 3*d*-metals studied so far. The scattering intensities in the regions around 230 \approx 2.111 meV and 340 \approx 3.111 meV can then be attributed to multiphonon processes involving the creation of two and three optical phonons, respectively.

3.1. Multiphonon scattering

The estimated contribution from multiphonon neutron scattering (MPNS) including processes involving up to four phonons is shown as a dashed line in Fig. 1. The calculation was done by an iterative technique based on an isotropic and harmonic approximation [8,10]. As one can see from Fig. 1, the calculated dashed line rather well describes the main features of the multiphonon part of the INS spectrum



Fig. 1. The dynamical structure factor $S(Q, \omega)$ of γ -MnH_{0.41} as a function of the energy loss ω of the inelastically scattered neutrons. The points connected by a solid line represent the data measured at 2 K with the IN1 BeF spectrometer at ILL, Grenoble. The dashed line is the calculated multiphonon contribution.

of γ -MnH_{0.41} at energies above 150 meV. The spectrum of multiphonon scattering from this hydride thus exhibits approximately harmonic behaviour. It seems rather probable, however, that similar to the case of fcc γ -PdH [9], this harmonic appearance is a result of averaging a highly anisotropic and anharmonic spectrum of the single crystallites in the γ -MnH_{0.41} powder over all orientations.

In [9], polycrystalline plates of γ -PdH with strong texture were studied by INS in two different orientations of the sample, with the [100] axis of the texture parallel and at an angle of 45° to the incoming neutron beam. The analysis of the observed anisotropy of the high-energy part of the INS spectrum showed that in the directions along the [110] axis and close to the [111] axis, the potential well for hydrogen at the octahedral positions in the fcc metal lattice of PdH is rather shallow and harmonic. Along the [100] axis, in the direction towards the nearest Pd atom neighbour, it is initially shallow too, but then very steep and strongly anharmonic. At the same time, the high-energy part of the INS spectrum of a powder PdH sample studied in the same work [9] exhibited only small deviations from the MPNS spectrum calculated in an isotropic harmonic approximation. The character of the bonding of hydrogen in γ -MnH_{0.41} and γ -PdH being similar, one can expect that the main features of the atomic potentials and, accordingly, of the INS spectrum of γ -MnH_{0.41} are the same as those of γ -PdH.

3.2. The fundamental band of optical hydrogen vibrations

As can be seen in Fig. 1, multiphonon neutron scattering significantly contributes to the intensity of the high-energy shoulder of the main optical peak at 111 meV in the INS spectrum of γ -MnH_{0.41}. Nevertheless, the total intensity in this range is much larger and the shoulder is also clearly seen in the "one-phonon" spectrum shown in Fig. 2, which was obtained by subtracting the calculated MPNS spectrum



Fig. 2. The "one-phonon" INS spectra $S(Q, \omega)$ of γ -MnH_{0.41} at 2 K (open circles, data of the present work) and of ε -MnH_{0.86} at 100 K (solid circles, data of Ref. [10]). The inset shows the same data, but the spectrum of γ -MnH_{0.41} has been broadened to simulate the lower resolution of the measurement on the ε -MnH_{0.86} sample.

from the experimental data. Such a shoulder is characteristic of the INS spectra of all hydrides of the VI–VIII group transition metals studied so far. Based on results for palladium hydride [19,20], its occurrence is usually ascribed to the dispersion of longitudinal optical phonon modes caused by long-range repulsive H–H interactions.

Fig. 2 also shows the "one-phonon" spectrum of ε -MnH_{0.86} obtained in [10] in the same way. As can be seen, the positions of the main optical H peaks in the spectra of γ -MnH_{0.41} and ε -MnH_{0.86} coincide within the experimental error. In fact, even the whole intensity distributions of the spectra coincide, if one takes into account that the spectrum of ε -MnH_{0.86} was measured with a lower resolution. This is shown in the inset of Fig. 2, where the spectrum of γ -MnH_{0.41} has been broadened to simulate this lower resolution.

The similarity of the optical vibrational spectra of the fcc and hcp hydrides of manganese allows the conclusion that in general the position of the main hydrogen peak in the INS spectra of *d*-metal hydrides with close-packed metal lattices in which hydrogen occupies octahedral interstices does not depend much on the particular structure of the hydride, fcc, hcp or dhcp. It is therefore reasonable to consider the dynamical properties of all these hydrides jointly, as a function of parameters applicable to every close-packed structure.

One such parameter is the hydrogen-metal distance *R*. In the case of the dihydrides with a close-packed fluorite-type structure (an fcc metal lattice with hydrogen on tetrahedral interstices) formed by various *d* transition metals, rare earths and even alkali earths, the energy of the main optical hydrogen peak as a function of *R* well obeys the dependence $\omega_0(R) = A \cdot R^{-3/2}$ [21]. Fig. 3 shows these data together with the available data on $\omega_0(R)$ for the transition metal monohydrides with close-packed structures.

As one can see from Fig. 3, the $\omega_0(R)$ values of the monohydrides show a quite different behaviour than those of the dihydrides. They steeply increase with decreasing atomic



Fig. 3. Energy of the main optical hydrogen peak ω_0 vs. the distance *R* between the nearest hydrogen and metal atoms for various dihydrides (crosses) [21] and for monohydrides of 3*d*-metals (open circles) and 4*d*-metals (solid circles): ε -CrH [7], ε -MnH_{0.86} [10], γ -MnH_{0.41} — the present work, ε' -FeH [11], γ -NiH [8], ε -MoH [7], γ -PdH [9], γ -PdH_{0.63} [22] and γ -PdH_{0.002} [22]. The upper dashed curve is a least-squares fit to the data for the dihydrides, the lower dashed curve has been included for comparison.

number of the host metal and, correspondingly, with increasing *R*, and are significantly different for 3*d*- and 4*d*-metals. At the same time, the $\omega_0(R)$ values for fcc γ hydrides of Pd with different hydrogen concentrations¹ decrease with increasing *R*, but much more steeply than the $\omega_0 \propto R^{-3/2}$ dependence valid for the dihydrides.

The factors resulting in the $\omega_0 = A \cdot R^{-3/2}$ dependence common for all the fluorite-type dihydrides are not well understood yet. What can be said is that the increase in Rby itself should decrease the strength of the interatomic interaction in a hydride and should therefore decrease ω_0 . The opposite behaviour of the $\omega_0(R)$ values of the monohydrides with decreasing atomic number of the host metal (Fig. 3) therefore indicates a significant increase in the hydrogen-metal interaction in the series of the 3d-metals $Ni \rightarrow Fe \rightarrow Mn \rightarrow Cr$ and also of the 4*d*-metals $Pd \rightarrow Mo$. This effect agrees with predictions of first-principles calculations [23,24] that the reduction of the number of valence electrons from right to left along the transition metal rows in the periodic table should lead to a steepening of the potential well for interstitial hydrogen due to a less efficient screening of the ionic core charges.

4. Conclusions

The INS investigation showed that the fundamental band of optical hydrogen vibrations in the fcc manganese hydride

¹ The fcc hydrides of palladium depleted and rich in hydrogen are often called the α and β phase, respectively.

with x = 0.41 extends over an energy interval from 90 to 140 meV and consists of a peak at 111 meV with a broad shoulder towards higher energies. The peak position and the shape of the intensity distribution are typical of fcc and hcp hydrides of 3*d* transition metals and coincide with those of the hcp manganese hydride with x = 0.86. The similarity of the optical vibrational spectra of the fcc and hcp manganese hydrides suggests that the main factors which determine the hydrogen dynamics are common to all close-packed crystal modifications of monohydrides of transition metals. The available data on the energy of the main optical H peak as a function of the hydrogen–metal distance indicate a significant increase in the metal–hydrogen interaction in such hydrides with decreasing atomic number of the host metal.

Acknowledgements

This work was supported by the Grants No. 99-02-17299 and 96-15-96806 from the Russian Foundation for Basic Research.

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