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Journal of Alloys and Compounds 446–447 (2007) 508–511

Journal of ALLOYS AND COMPOUNDS

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Anharmonicity of optical hydrogen vibrations in RhH

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Received 13 September 2006; received in revised form 19 November 2006; accepted 22 November 2006

Abstract

A polycrystalline sample of nearly stoichiometric *fcc* rhodium hydride was synthesised under high hydrogen pressure and then studied at ambient pressure and 5 K by inelastic neutron scattering in the range of energy transfers 35–380 meV. The fundamental band of optical hydrogen vibrations was shown to consist of a strong peak centred at 74 meV and broadened towards higher energies. The second and third band demonstrated essentially anharmonic behaviour, which is not typical of monohydrides of 3*d*- and 4*d*-metals with close-packed metal lattices.

Keywords: Interstitial alloys; Inelastic neutron scattering

1. Introduction

Hydrides of the group VI–VIII transition metals have close-packed metal lattices with *fcc* (γ), *hcp* (ε) or *double hcp* (ε') structure, in which hydrogen occupies octahedral interstitial positions [1]. An occupancy of all octahedral positions corresponds to an H-to-metal atomic ratio of $x = 1$. The lattice dynamics of most monohydrides synthesised so far has already been studied by inelastic neutron scattering (see [2–4] and references therein). The present paper reports on the INS study of rhodium monohydride.

Rhodium metal has an *fcc* structure and forms hydride with an *fcc* metal lattice, too, at hydrogen pressures higher than 4.5–5 GPa and $T > 250\,^\circ$C [5]. The composition of the hydride is close to RhH and it can be retained in a metastable state at ambient pressure and $T < 170$ K, if the sample is previously cooled under high hydrogen pressure. A neutron diffraction investigation at 120 K demonstrated [6] that γ-RhH has a NaCl-type crystal structure with H atoms occupying every octahedral site in the *fcc* Rh lattice with the parameter $a = 4.010$ Å, which is expanded by 5.6% compared to $a = 3.799$ Å of *fcc* Rh metal without hydrogen.

Earlier INS investigations showed that, despite the cubic symmetry of the octahedral interstitial sites, the second and third bands of optical hydrogen vibrations in γ-PdH [7,8] and γ-NiH [9] are anisotropic. This was disclosed by varying the orientation of textured polycrystalline samples [7,9] or single crystals [8] relative to the direction of neutron momentum transfer. To examine if the spectrum of H vibrations in γ-RhH is also anisotropic, the sample was prepared from textured polycrystalline Rh foil and measured by INS in two different orientations.

2. Sample preparation and experimental details

The starting material was a 0.1 mm foil of 99.99% Rh metal. To characterise its texture, pole figures {2 0 0} and {2 2 0} were constructed at room temperature by the Schultz method [10] at tilt angles up to $\vartheta_{\max} = 70^\circ$ using Mo Kα radiation (Fig. 1). The sample of RhH weighting 0.9 g was composed of 30 plates $5 \times 5 \times 0.1\ \mathrm{mm}^3$ cut out of that foil and loaded with hydrogen by a 24 h exposure to a H_2 pressure of 7 GPa at a temperature of 325 °C for 24 h and subsequent cooling to 100 K in the high-pressure cell. The hydrogenation method is described in [11].

To ensure the homogeneity of the sample, a few small portions (about 2 mg each) of different plates were analysed for hydrogen content by hot extraction into a calibrated volume at temperatures up to 200 °C and shown to contain $x = 0.98(3)$ hydrogen.

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doi:10.1016/j.jallcom.2006.11.150

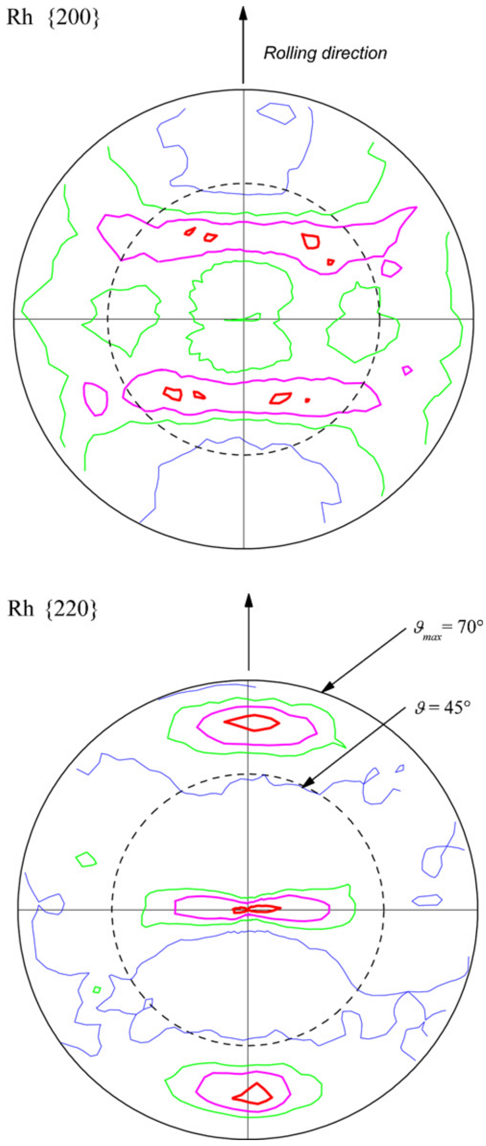

Fig. 1. Pole figures {2 0 0} and {2 2 0} of the initial *fcc* Rh foil used to prepare the RhH sample. The isolines are drawn at levels of 0.1, 0.3, 0.5 and 0.8 of the maximum intensity for each figure.

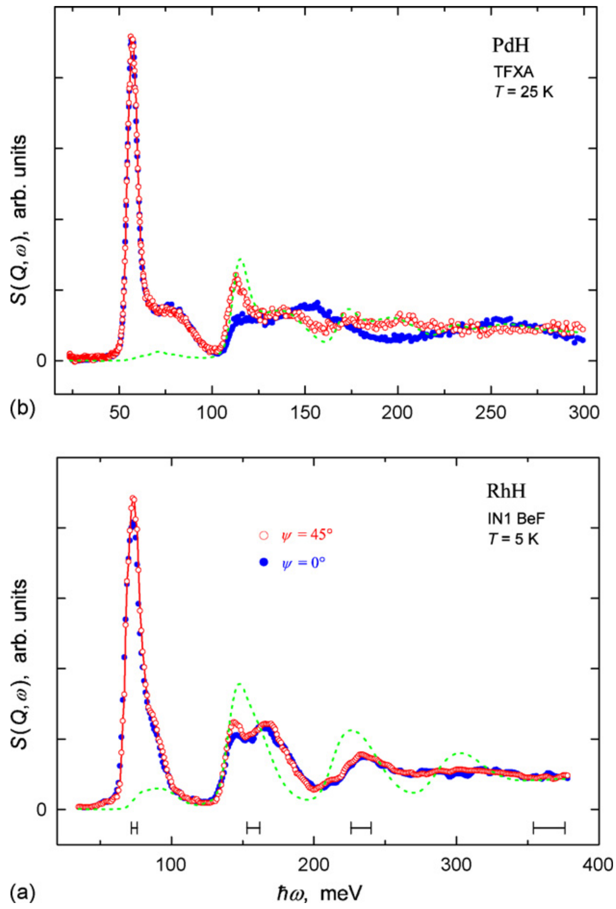

Fig. 2. The INS spectra of RhH measured at 5 K with the IN1-BeF spectrometer at ILL, Grenoble ((a), data of the present work) and those of PdH measured at 25 K with the TFXA spectrometer at ISIS, UK ((b), data of Ref. [7]). The dashed lines represent the multiphonon contributions calculated in an isotropic harmonic approximation using an iterative technique [15]. The horizontal bars indicate the energy resolution of the IN1-BeF spectrometer.

A few hydrogenated plates were examined by X-ray diffraction ($T = 100$ K, Cu Kα radiation) and shown to be single-phase *fcc* hydride with approximately the same texture as the starting Rh foil.

The INS spectra from the RhH sample were measured at 5 K in the range of neutron energy transfers, $\hbar\omega$, from 35 to 380 meV using the IN1-BeF neutron spectrometer installed at the hot source of the high-flux reactor at the Institute Laue-Langevin in Grenoble. The $\hbar\omega$ value was calculated by subtracting 3.5 meV, the mean energy of neutrons that passed through the Be filter, from the energy of the incoming neutrons. Due to this small final energy of the recorded neutrons, the deviation of the momentum transfer vector, $\boldsymbol{Q}$, from the direction of the incident neutron beam was only a few degrees in the range $\hbar\omega > 70$ meV of optical hydrogen vibrations in RhH.

The hydrogenated plates of Rh were brittle and easily cracked to about a hundred small pieces, which were placed in a flat aluminium container and arranged in one layer, side by side, randomly with respect to their rolling direction. The sample was measured in two different orientations, with an angle $\psi = 0°$ and 45° between the vector of the neutron momentum transfer, $\boldsymbol{Q}$, and the normal to the sample plane. Background spectra from an empty container were measured separately under the same conditions and then subtracted from the corresponding raw INS spectra in order to obtain the scattering intensity from the sample alone.

3. Results

The obtained INS spectra $S(Q,\omega)$ of the RhH sample in two different orientations are shown in Fig. 2 together with the spectra of PdH measured earlier [7] in the same manner and presented for comparison. The first (fundamental) band of optical H vibrations in RhH consists of a peak centred at $\hbar\omega_0 = 74$ meV with a shoulder extending towards higher energies. The shape of the band is typical of monohydrides of all other 3*d*- and 4*d*-metals of groups VI–VIII [2–4]. The main peak is usually ascribed to nearly nondispersive transverse optical modes, while the shoulder is assumed to arise from longitudinal optical modes, which

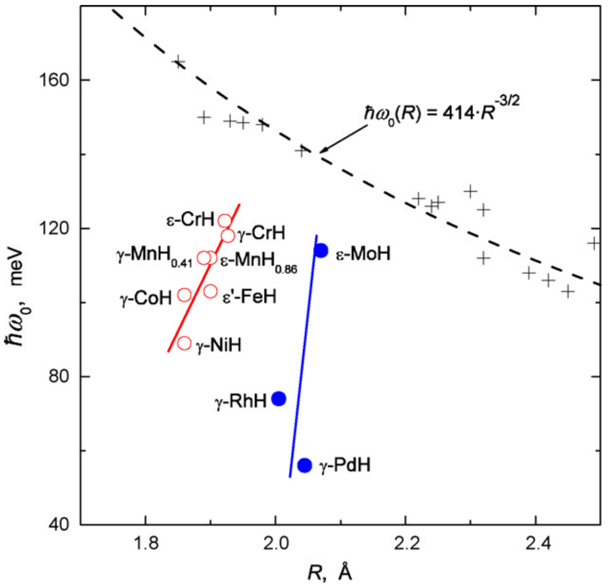

Fig. 3. Energy of the main optical hydrogen peak, $\hbar\omega_0$, vs. the shortest hydrogen-metal distance R for various dihydrides with a fluorite-type structure (crosses) [16] and for monohydrides of 3*d*-metals (open circles) and 4*d*-metals (solid circles) with octahedral coordination of hydrogen (see [2] for references and discussion; the points for γ-CoH [3] and γ-CrH [4] are from later works). The dashed curve is a least-squares fit to the data for the dihydrides.

show significant dispersion due to long-range repulsive H–H interactions.

The position $\hbar\omega_0$ of the main peak in the spectrum of RhH is plotted in Fig. 3 as a function of the hydrogen-metal distance R, which equals $a/2 = 2.005$ Å for the NaCl-type structure of this hydride. As one can see, the point for RhH is consistent with the approximately linear dependence $\hbar\omega_0(R)$ for hydrides of 4*d*-metals (solid line) that one could expect by analogy with the dependence for hydrides of 3*d*-metals.

The second and the third optical H bands in RhH have a smoother intensity distribution and appear at energies approximately two and three times the energy of the fundamental band, respectively. These bands result from multiphonon neutron scattering, and the shape of such bands in the INS spectra of powder samples of every other monohydride studied so far is fairly well described in the harmonic approximation. As seen from Fig. 2(b), the bands in RhH are strongly deformed and shifted towards higher energies compared to the calculated harmonic spectrum. This indicates that the H potential well in γ-RhH is significantly steeper than parabolic, at least in some directions.

4. Discussion

Earlier INS studies demonstrated that the H potential well in γ-PdH [7,8] and γ-NiH [9] is anisotropic at energies above the range of the first optical band. It is steep and anharmonic along the <1 0 0> axes (which are the directions towards the nearest metal atom neighbours), but nearly parabolic along any other direction, in particular, along the <1 1 0> directions. These INS results also agree with *ab initio* calculations for γ-PdH [12] and γ-NiH [13].

The INS intensity is roughly proportional to $(\boldsymbol{Q}\times\boldsymbol{e})^{2n}$, where e is the polarisation of the n hydrogen vibrations created by the scattered neutron. For the fundamental band ($n = 1$), virtually no anisotropy can be observed on symmetry grounds [9]. The anisotropy of the second ($n = 2$) and third ($n = 3$) band is clearly seen in Fig. 2(b) for the PdH sample with a strong texture of the (0 0 1)[1 0 0] type, from the difference between the INS spectra measured with $\boldsymbol{Q}$ directed predominantly along the [1 0 0] axis of the grains ($\psi = 0°$) and along the <1 1 0> axes ($\psi = 45°$). Averaged over all orientations of $\boldsymbol{Q}$, the contribution from the anharmonic hydrogen vibrations along the <1 0 0> directions is small, and the high-energy part of INS spectra of powder PdH samples looks like that for $\psi = 45°$ in Fig. 2(b) and exhibits only small deviations from isotropic, harmonic behaviour [7].

An analysis of the {2 2 0} and {2 0 0} pole figures of the Rh foil (Fig. 1) showed that it had a texture with preferred orientations from {1 1 2}<1 1 0> to {1 1 1}<1 1 2>, which is typical of rolled *fcc* metals after recrystallisation [14]. To take the random orientation of the rolling directions of the RhH pieces in the container plane into account, the orientation probability density $P_{hk\ell}$ was averaged over all directions in the sample plane for each measuring angle ψ. The relative probability densities for the orientations <1 0 0> and <1 1 0> at the experimental angles $\psi = 0°$ and 45° can be estimated by averaging the corresponding pole figure intensities at $\vartheta = 0°$ and at $\vartheta = 45°$ (at the centres and along the inner dashed circles in Fig. 1). This gives the ratios: $P_{110}(0°)/P_{110}(45°) \approx 5$; $P_{100}(0°)/P_{100}(45°) \approx 0.9$; $P_{110}(0°)/P_{100}(0°) \approx 5$; $P_{110}(45°)/P_{100}(45°) \approx 0.9$.

The largest deviation from isotropy should be expected for $\boldsymbol{Q}$ directed along the <1 0 0> axes, when hydrogen vibrations towards the nearest metal atoms are excited. As the orientation probability ratios show, the contribution from H vibrations polarised in these directions is significantly different for the INS spectra of the RhH sample measured at $\psi = 0°$ and 45°. In particular, the contribution from the <1 0 0> vibrations to the $\psi = 0°$ spectrum should be small, because the probability density $P_{110}(0°)$ of the <1 1 0> orientations alone already exceeds $P_{100}(0°)$ of the <1 0 0> orientations by a factor of 5. At the same time, the second and third bands in both $\psi = 0°$ and $\psi = 45°$ spectra are strongly anharmonic and nearly identical. This suggests that the potential well for H atoms in γ-RhH is anharmonic in most directions.

5. Conclusions

The potential well for H atoms in the cubic hydride γ-RhH proved to be strongly anharmonic as a whole at energies of the second and third optical H bands. This distinguishes γ-RhH from monohydrides of other group VI–VIII transition metals and, in particular, from γ-PdH and γ-NiH, in which significant anharmonicity is only observed for hydrogen vibrations polarised along the <1 0 0> axes.

Acknowledgements

This work was supported by grant No. 05-02-17733 from the Russian Foundation for Basic Research and by the Program

"Physics and Mechanics of Strongly Compressed Matter" of the Russian Academy of Sciences. Work at ANL was performed under the auspices of the US DOE-BES, contract No. W-31-109-ENG-38.

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