ANHARMONICITY OF OPTICAL HYDROGEN VIBRATIONS IN RhH

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Introduction

Hydrides of the group VI–VIII transition metals have close-packed metal sublattices 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 (INS) (see [2–4] and references therein). The present paper reports on the INS study of the γ-RhH hydride.

Results and discussion

A 0.9 g sample of RhH was made by exposing 0.1 mm foils of 99.99% Rh to a hydrogen 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 [5]. The cooling prevented loss of hydrogen from the sample in the course of its further studies at ambient pressure.

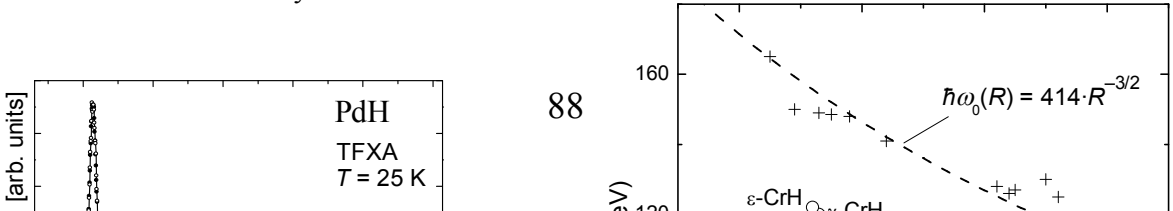
The INS study of the RhH sample was carried out at 5 K with the IN1 BeF spectrometer installed at ILL in Grenoble. The hydrogenated foils of Rh were brittle and cracked to about a hundred small pieces, which were placed in a flat aluminium container and arranged in one layer, side by side, randomly with 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. The results are presented at the bottom of Fig. 1.

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. The position $\hbar\omega_0$ of the main peak plotted in Fig. 2 as a function of the hydrogen-metal distance R agrees with the approximately linear dependence $\hbar\omega_0(R)$ for hydrides of 4*d*-metals that one could expect by analogy with the dependence for hydrides of 3*d*-metals.

The second and the third optical H band resulting from multiphonon neutron scattering in RhH have a smoother intensity distribution and

Fig. 1. The dynamical structure factor, $S(Q,\omega)$, of RhH (present paper, IN1 BeF spectrometer, ILL, France) and PdH [6] (TFXA spectrometer, RAL, UK) as a function of the energy loss $\hbar\omega$ of the inelastically scattered neutrons. The dashed line is the contribution from multiphonon neutron scattering calculated in an isotropic and harmonic approximation using the iterative technique of Ref. [8].

appear at energies approximately two and three times the energy of the fundamental band, respectively. 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. 1, 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.



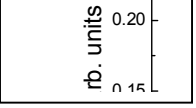


Fig. 2. Energy of the main optical hydrogen peak, $\hbar\omega_0$, versus the shortest hydrogen–metal distance R for various dihydrides with a fluorite-type structure (crosses) [9] and for monohydrides of 3*d*-metals (open circles) and 4*d*-metals (solid circles) with octahedral co-ordination of hydrogen (see [2–4] and references therein).

Earlier INS studies demonstrated that the H potential well in γ-PdH [6] and in γ-NiH [7] is anisotropic. It is steep along the <100> axes (which are the directions towards the nearest metal atom neighbours), but nearly parabolic along any other direction, in particular, along the <110> and <111> directions. The INS intensity is roughly proportional to $(\boldsymbol{Q}\cdot\boldsymbol{e})^{2n}$, where $\boldsymbol{e}$ is the polarisation of the n hydrogen vibrations created by the scattered neutron. As shown in the upper part of Fig. 1, the anisotropy of the spectrum is clearly seen, for example, in the PdH sample with a strong texture of the (001)[100] type, when the sample is measured [6] with $\boldsymbol{Q}$ directed predominantly along the [100] axis of the grains (ψ = 0°) and along the [110] axis (ψ = 45°).

The Rh foil had a texture with the preferred orientations from (112)[110] to (111)[112], which is typical of *fcc* metals. The probability densities $P_{hkl}(\varphi)$ for the crystal directions [110] and [100] to be tilted at φ = 0°and 45° to the sample plane were estimated from {220} and {200} pole figures. This gave the ratios:

$P_{110}(0°)/P_{110}(45°) \approx 5.5$;

$P_{100}(0°)/ P_{100}(45°) \approx 0.8$ и $P_{110}(0°)/P_{100}(0°) \approx 5$.

By analogy with PdH and NiH, one could expect that RhH would mostly show anharmonicity of H vibrations along the <100> axes. Experiment demonstrated that the H vibrational spectrum of RhH was anharmonic throughout.

In fact, the volume fraction of the RhH grains with the [100] axis directed perpendicular to the sample plane was small compared to that of grains with the [110] axis. Therefore, hydrogen vibrations along the <100> axes could not significantly contribute to the INS spectrum measured at ψ = 0°. These were apparently vibrations along the <110> axes and, as may be supposed, in many other directions different from <100> that mostly determine the strongly anharmonic behaviour of the 0°-spectrum.

The volume fraction of grains with the [110] axis directed at 45° to the sample plane was much less than perpendicular to it. Meanwhile, the INS spectrum measured at ψ = 45° nearly coincided with the 0°-spectrum. This suggests that the potential well for H atoms in RhH is rather equally anharmonic in most directions.

Summing up, the potential well for H atoms in the cubic hydride γ-RhH proved to be strongly anharmonic as a whole. This distinguishes γ-RhH from γ-PdH and γ-NiH (and, presumably, from any other monohydride of the group VI–VIII transition metals), which all have a mostly harmonic potential well so that anharmonicity is only observed for hydrogen vibrations along the <100> axes.

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