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Phonon spectra of ordered PdCuH and PdAgH prepared under a high hydrogen pressure

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Abstract

PdCuH and PdAgH ordered phases, synthesized under a high pressure of gaseous hydrogen, were studied by inelastic neutron scattering. The results showed a large difference between the Pd–H, Cu–H and Ag–H interactions. Values of 93 and 116 meV were predicted for the local H vibrations in dilute Ag–H and Cu–H solid solutions, respectively.

1. Introduction

Some years ago, an effect of atomic ordering was observed in the hydrides of Pd–Cu [1] and Pd–Ag [2] disordered alloys produced under high hydrogen pressures and elevated temperatures. Neutron diffraction investigations [3,4] have shown that the nearly stoichiometric PdAgH_{≈0.9} and PdCuH_{≈0.9} hydrides have a primitive tetragonal cell formed from the initial FCC cell of the disordered Pd–Cu(Ag) alloys due to ordering of the Pd and Cu(Ag) atoms into alternate layers perpendicular to the tetragonal *c*-axis, with the hydrogens occupying octahedral sites within the Pd layers.

It therefore seemed hopeful that an inelastic neutron scattering (INS) investigation of such ordered hydrides, due to their specific layered structure, would permit an isolation of the contributions from the H–Pd and H–Cu(Ag) interactions and allow an estimate of the latter (Cu–H and Ag–H hydrides are not known, and the dynamics of the dilute Cu–H and Ag–H solid solutions have never been investigated).

In this work we present the results of INS studies of the ordered PdCuH_{0.9} and PdAgH_{0.86} hydrides as well as that of the PdAgH_{0.50} depleted in hydrogen in order to investigate the dependence of the phonon spectrum upon hydrogen concentration [4, 5].

2. Experimental

The procedures and technique used to prepare and test the PdCuH and PdAgH samples were the same as in Ref. [6]. The initial samples of about 2.0 and 3.2 g were made out of 0.3 mm thick PdCu and PdAg plates. After hydrogenation for 24 h in an atmosphere of molecular hydrogen at 30 ± 2 kbar and 600 and 470 K for PdCuH and PdAgH, respectively, they were rapidly cooled to 100 K in order to avoid hydrogen loss. The ordered hydrides had composition PdCuH_{0.90±0.05} and PdAgH_{0.86±0.03}, and the cell parameters at 100 K and normal pressure were, respectively, $a = 2.792 \text{ \AA}$ and $c = 3.671 \text{ \AA}$; and $a = 2.826 \text{ \AA}$ and $c = 4.270 \text{ \AA}$. The depleted PdAgH_{0.50±0.03} sample ($a = 2.828 \text{ \AA}$, $c = 4.160 \text{ \AA}$) was prepared by exposing PdAgH_{0.86} to room temperature and atmospheric pressure for 35 h.

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The INS measurements on the PdCuH and PdAgH hydrides were carried out at 35 and 24 K, respectively on the time-focused crystal analyzer (TFXA) spectrometer [7] at the spallation neutron source, ISIS (DRAL, UK). The data were transformed to $S(Q, \omega)$ versus energy transfer using standard programs. The contributions from the multiphonon neutron scattering (up to four-phonon processes) were calculated in a harmonic isotropic approximation by the multiconvolution of the one-phonon spectrum using an iterative technique [8].

3. Results and discussion

The obtained INS spectra, Figs. 1 and 2, may be divided into three regions: (i) below 30 or 40 meV, where the lattice vibrations are mainly determined by motions of the metal atoms; (ii) between 50 and 115 meV, or 60

and 130 meV, the range of hydrogen optic modes; and (iii) above 115 or 130 meV, the range of multiphonon neutron scattering (the values are for the palladium–silver and palladium–copper hydrides, respectively).

As is seen from Figs. 1 and 2, the agreement between the calculated and experimental multiphonon spectra is rather good. Note, that even the fine structure of the two-phonon bands is well reproduced with the calculations in a harmonic approximation. This allows us to conclude that the behaviour of the hydrogen vibrations in the studied hydrides is mainly harmonic, and certain discrepancies between the calculations and experiments are probably due to the application of the isotropic approximation for description of obviously anisotropic objects.

The range of hydrogen optic phonon spectra of the PdAgH_x samples and, for comparison, that of PdH measured recently at TFXA [9] are presented in Fig. 3. It is well known that the INS spectra of PdH_x [8–12] exhibit one optic vibrational peak (transverse modes) with a strong shoulder at higher energies originating from dispersion caused by the H–H interaction (longitudinal modes). The optic peak is centred at 56 meV in β-PdH ($r_{\text{Pd-H}} = 2.048 \text{ \AA}$) [8, 9], at 69 meV the dilute Pd–H α -solution ($r_{\text{Pd-H}} = 1.945 \text{ \AA}$) [12], at 74 meV in the disordered Pd₃MnH_{0.03} and at 76 and 83 meV in the ordered Pd₃MnH_{0.4} ($r_{\text{Pd-H}} = 1.950 \text{ \AA}$) [13].

Analyzing the split hydrogen optic-phonon bands of the PdAgH_x samples we can conclude that the left-hand peak, positioned at about the same energy ($\omega_1 = 63$ and 64 meV for $x = 0.86$ and 0.50, respectively) as the peak from the transverse optic modes in PdH, is due to the Pd–H interaction, whereas the right-hand one at much higher energy ($\omega_2 = 86$ and 90 meV) should mainly originate from the Ag–H interaction. This also agrees with the fact that the difference between the ω_1 -values for the PdAgH_{0.86} and PdAgH_{0.50} samples with nearly

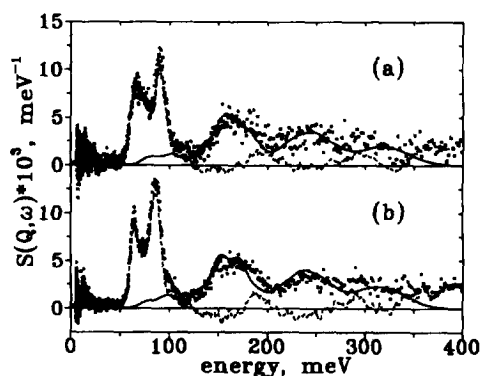


Fig. 1. The INS spectra $S(Q, \omega)$ for PdAgH_{0.50} (a) and PdAgH_{0.86} (b) as measured on TFXA at 24 K; solid lines – calculated multiphonon contributions, dashed lines – the difference between the experimental data and the calculated multiphonon spectra (the one-phonon spectra).

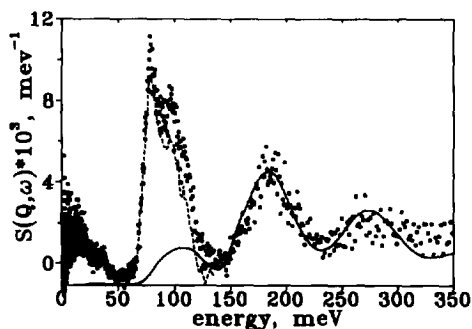


Fig. 2. The INS spectra for PdCuH_{0.9} at 35 K; solid lines – calculated multiphonon contributions, dashed lines – one-phonon spectra.

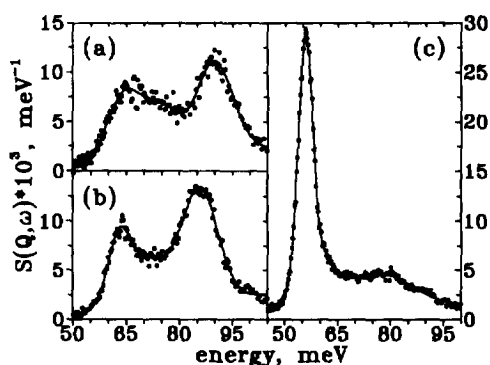


Fig. 3. The INS spectra for PdAgH_{0.50} (a), PdAgH_{0.86} (b) and PdH [9] (c); solid lines – fits with three Gaussians.

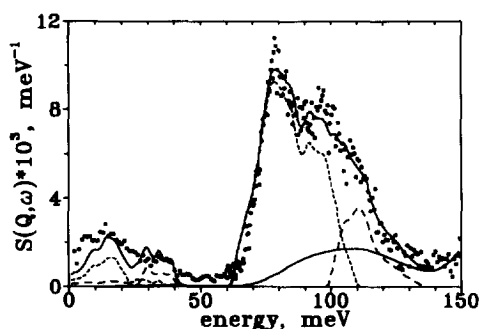


Fig. 4. Experimental (points) and calculated (upper solid line) $S(Q, \omega)$ spectra for $\text{PdCuH}_{0.9}$. To get the calculated spectrum, the spectrum resulting from the Born-von Kármán model was convoluted with the resolution function for the TFXA spectrometer and then summed with the calculated multiphonon contributions (lower solid line). The contributions to the calculated spectrum from vibrations of H atoms in the ab -plane and along the c -axis are shown by the short and long dashed lines respectively.

coinciding Pd–H distances was much smaller than between the ω_2 -values. As for the ω_2 -values, an increase in ω_2 by 4 meV with x decreasing from 0.86 to 0.50 was ascribed to the shortening of the Ag–H distances (the c -parameter decreased from 4.270 to 4.160 Å).

The INS spectrum of the $\text{PdCuH}_{0.9}$, in Fig. 4, revealed a broad hydrogen optic peak with peculiarities at energy transfers of 79 and 95 meV and of 113 meV which were ascribed to the H vibrations in the Pd–H planes and along the Cu–H chains, respectively. Note, however, that the energy of the optic peak in the $\text{PdCuH}_{0.9}$ ordered phase is the highest among those in the hydrides of palladium and its alloys, and that its value does not agree with the correlation between the energies of such peaks and palladium-to-hydrogen distances observed in these hydrides. Thus, the potential for hydrogen atoms in the $\text{PdCuH}_{0.9}$ ordered phase was noticeably different, even in the Pd–H plane, from that in the Pd–H hydrides.

From the obtained data one could extrapolate a value of 93 and 116 meV for the energy of local H vibrations in dilute pure Ag–H ($a \approx 4.074$ Å) and Cu–H ($a \approx 3.615$ Å) solid solutions, respectively.

The one-phonon spectra derived from the experimental data on $\text{PdCuH}_{0.9}$ and $\text{PdAgH}_{0.86}$ hydrides were then fitted [4, 5] using a conventional Born-von Kármán model, and we used the UNISOFT program [14] for the calculations. The principal adjustable parameters

were the force constants for the Pd–H and Cu–H or Ag–H interactions, which determine on the average the positions of the peaks forming the hydrogen optic band, and those for the H–H interaction, which are responsible for the shape of the band due to dispersion of the optic modes. The calculated phonon spectra permitted a reasonably good description of the measured INS spectra, and the results of our best fit for the PdCuH are presented in Fig. 4.

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