

NEUTRON SCATTERING STUDIES OF ORDERED PdCuH AND PdAgH PREPARED UNDER A HIGH HYDROGEN PRESSURE

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Abstract. Atomically ordered PdAgH_x and PdCuH_x hydrides with $x \approx 0.9$ were synthesized in an atmosphere of gaseous hydrogen at $P = 3$ GPa. Their metal lattices with primitive tetragonal cells were formed on the basis of *fcc* lattices of the initial PdAg or PdCu disordered alloys due to the ordering of the Pd and Ag or Cu atoms into alternate layers perpendicular to the tetragonal *c*-axis. Rietveld refinement of the neutron diffraction pattern of the PdCuH_{≈0.9} measured at 80 K, showed the H atoms to occupy octahedral interstitials within the Pd layers. The inelastic neutron scattering study of PdCuH_{≈0.9} and PdAgH_{≈0.9} 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.

1 INTRODUCTION

Some years ago, an effect of atomic ordering was observed in the hydrides of Pd-Cu¹ and Pd-Ag² disordered alloys produced under high hydrogen pressures and elevated temperatures. The neutron diffraction investigation³ has shown that the nearly stoichiometric PdAgH_{≈0.9} hydride has a primitive tetragonal cell formed from the initial *fcc* cell of the disordered PdAg alloy due to ordering of the Pd and Ag atoms into alternate layers perpendicular to the tetragonal *c*-axis, with the hydrogens occupying octahedral sites within the Pd layers.

The layered ordering of the metal atoms in the $\text{Pd}_{0.6}\text{Cu}_{0.4}\text{-H}$ hydrides determined by X-ray diffraction^{1,4} was similar to that observed in the PdAg-H hydrides. As copper is a chemical analogue of silver, one could expect the crystal structures of the PdCu-H and PdAg-H hydrides also to be similar.

It seemed thus hopeful that because of a specific layered structure of these ordered hydrides, their inelastic neutron scattering (INS) investigation would permit an isolation of the contributions originating from the H-Pd and H-Cu and H-Ag interactions and allow an estimation of the two latter (Cu-H and Ag-H hydrides are not known, dynamics of the dilute Cu-H and Ag-H solid solutions has never been investigated).

In the present work, we determined the positions of hydrogen atoms in the metal lattice of the ordered $\text{PdCuH}_{\approx 0.9}$ hydride by neutron diffraction and measured INS spectra of the ordered $\text{PdCuH}_{0.9}$, $\text{PdAgH}_{0.86}$ and $\text{PdAgH}_{0.50}$ hydrides and then fitted them using a conventional Born-von Kármán model^{5,6}.

2 EXPERIMENTAL

The procedures and technique used to prepare and test the PdCu-H and PdAg-H samples were the same as in⁷. The initial samples weighing about 2.0 and 3.2 g, were made of 0.3 mm thick PdCu and PdAg plates. After a 24 h hydrogenation in an atmosphere of molecular hydrogen at 3 ± 0.2 GPa and 600 K and 470 K for the $\text{PdCuH}_{0.9 \pm 0.05}$ and $\text{PdAgH}_{0.86 \pm 0.03}$, respectively, they were rapidly cooled to 100 K in order to avoid hydrogen losses. The $\text{PdAgH}_{0.50 \pm 0.03}$ sample depleted in hydrogen was prepared by a 35 h exposure of the $\text{PdAgH}_{0.86}$ one to room temperature and ambient pressure.

The neutron diffraction examination of the powdered $\text{PdCuH}_{0.9}$ sample was performed at 80 K using the time-of-flight diffractometer DN-2⁸ at the IBR-2 reactor (JINR, Dubna, Russia). The top loading cryostat with quartz windows was used in the experiment, and the neutron scattering angle was $2\theta = 90^\circ$.

The INS measurements on the PdCu-H and PdAg-H hydrides were carried out at 35 K and 24 K, respectively, on the time-focused crystal analyzer (TFXA) spectrometer⁹ at the spallation neutron source, ISIS (DRAL, UK). The data were transformed to $S(Q, \omega)$ vs. 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 technique¹⁰.

3 RESULTS AND DISCUSSION

3.1 Neutron Diffraction

According to the X-ray data, the PdCuH_x hydride had an atomically ordered

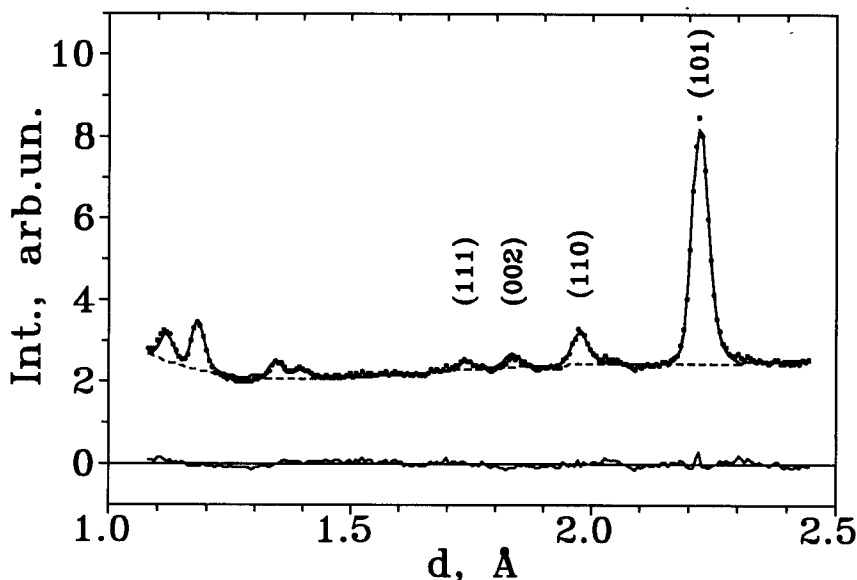


FIGURE 1 Powder neutron diffraction pattern for the $\text{PdCuH}_{\approx 0.9}$ at 80 K. Experimental points, fitting and differential curves (solid lines) and estimated incoherent background (dashed line).

tetragonal metal lattice with the cell parameters $a = 2.794 \pm 0.005$ Å and $c = 3.678 \pm 0.007$ Å at 100 K.

The neutron diffraction data (Figure 1) were analyzed using the Rietveld profile refinement program adapted to a time-of-flight diffractometer¹¹. The refinement converged to weighting and profile factors $R_w = 0.03$ and $R_p = 0.02$ for a primitive tetragonal structure of PdCuH_x , space group $P4/mmm$, with the lattice parameters $a = 2.792 \pm 0.010$ Å and $c = 3.671 \pm 0.013$ Å, Cu atoms at $(0, 0, 0)$, Pd atoms at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, H atoms at $(0, 0, \frac{1}{2})$ and hydrogen content $x = 0.95 \pm 0.05$.

Note, that despite of a large incoherent background from the hydrogen atoms and poor statistics of the experiment, a good convergence of the fit with respect to the hydrogen positioning clearly indicated that the hydrogen atoms occupy only octahedral interstitials within the Pd layers. The crystal structure of the $\text{PdCuH}_{\approx 0.9}$ sample was thus similar to that of the $\text{PdAgH}_{\approx 0.9}$ hydride³ with only one exception: the interatomic distance $r_{\text{Pd-H}} = 1.974$ Å in $\text{PdCuH}_{\approx 0.9}$ was longer than $r_{\text{Cu-H}} = 1.836$ Å whereas the distance $r_{\text{Pd-H}} = 1.999$ Å in $\text{PdAgH}_{\approx 0.9}$ was shorter than $r_{\text{Ag-H}} = 2.135$ Å.

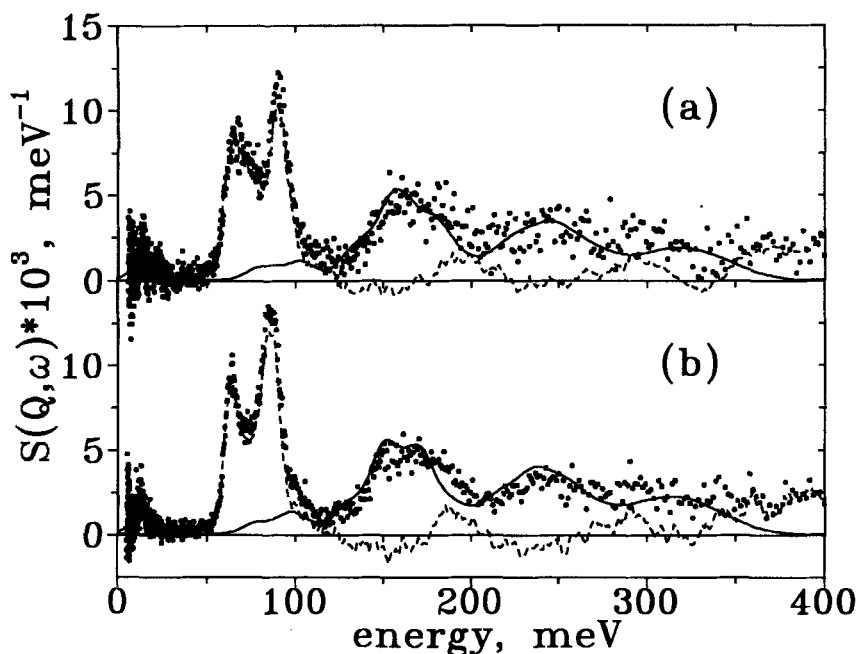


FIGURE 2 The INS spectra $S(Q, \omega)$ for $\text{PdAgH}_{0.50}$ (a) and $\text{PdAgH}_{0.86}$ (b) as measured on TFXA at 24 K; solid lines – calculated multiphonon contributions, dashed lines – the difference between the experimental data and the calculated multiphonon spectra (the one-phonon spectra).

3.2 Inelastic Neutron Scattering

The obtained INS spectra, Figures 2 and 3, may be divided into three regions, *i*) below 30 or 40 meV, where 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 Figures 2 and 3, the agreement between the calculated and experimental multiphonon spectra is rather good. Note, that even a fine structure of the two-phonon bands is well reproduced with the calculations in a harmonic approximation. This allowed us to conclude that the behaviour of 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 the obviously anisotropic objects.

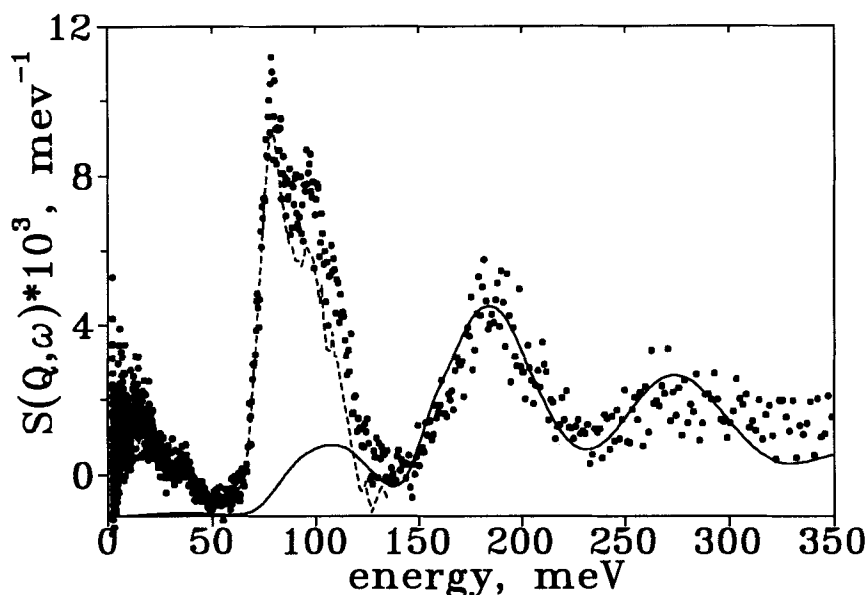


FIGURE 3 The INS spectra for PdCuH_{0.9} at 35 K; solid lines – calculated multiphonon contributions, dashed lines – one-phonon spectra.

The range of hydrogen optic phonon spectra of the PdAgH_x samples and, for comparison, that of PdH measured recently at TFXA¹² are presented in Figure 4. The INS spectra of PdH_x have been thoroughly studied^{10,12–15} and shown to exhibit one optic vibrational peak (transverse modes) with a strong shoulder at higher energies originating from a dispersion caused by the H-H interaction (longitudinal modes). The optic peak is centred at 56 meV in the β-PdH ($r_{\text{Pd-H}} = 2.048 \text{ \AA}$)^{10,12}, at 69 meV in the dilute Pd-H α-solution ($r_{\text{Pd-H}} = 1.945 \text{ \AA}$)¹⁵, at 74 meV in the disordered Pd₃MnH_{0.03} and at 76 and 83 meV in the ordered Pd₃MnH_{0.4} ($r_{\text{Pd-H}} = 1.950 \text{ \AA}$)¹⁶.

Analyzing the split hydrogen optic phonon bands of the PdAgH_x samples one can conclude that the left 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 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

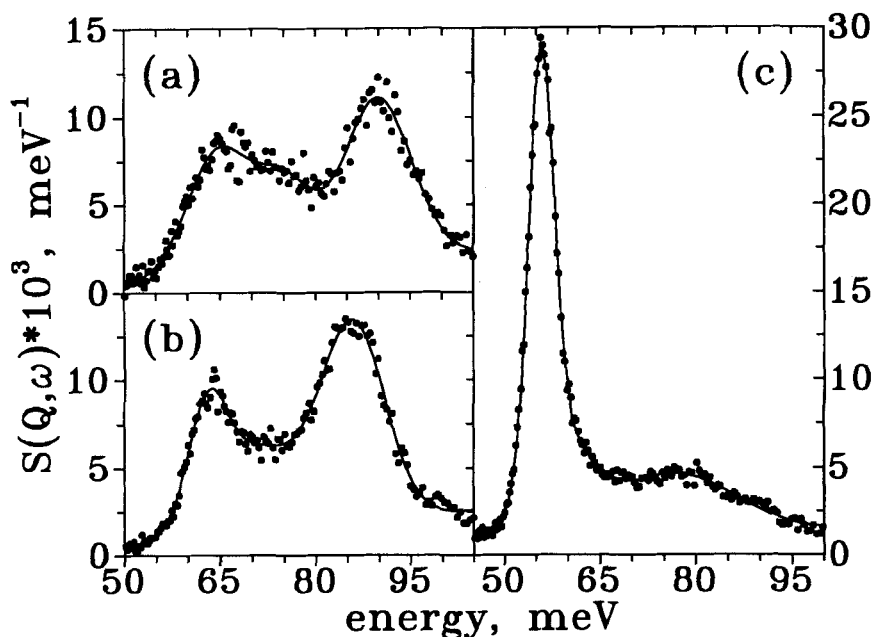


FIGURE 4 The INS spectra for $\text{PdAgH}_{0.50}$ (a), $\text{PdAgH}_{0.86}$ (b) and PdH^{12} (c); solid lines – fits with three gaussians.

coinciding Pd-H distances ($a=2.826$ and 2.828 Å) 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 reasonable to ascribe to the shortening of the Ag-H distances (the c -parameter decreased from 4.270 to 4.160 Å).

The INS spectrum of the $\text{PdCuH}_{0.9}$, Figure 5, 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 obey the correlation between the energies of such peaks and the Pd-H distances observed in these hydrides. The potential for hydrogen atoms in the $\text{PdCuH}_{0.9}$ ordered phase was thus noticeably different, even in the Pd-H plane, from that in the Pd-H hydrides.

An extrapolation of the obtained data to the Me-H distances for the hydrogens on octahedral sites in *fcc* Ag and Cu indicates values of 93 meV and 116 meV for the energy of local H vibrations in dilute pure Ag-H ($a \simeq 4.074$ Å) and Cu-H ($a \simeq 3.615$ Å) solid solutions, respectively.

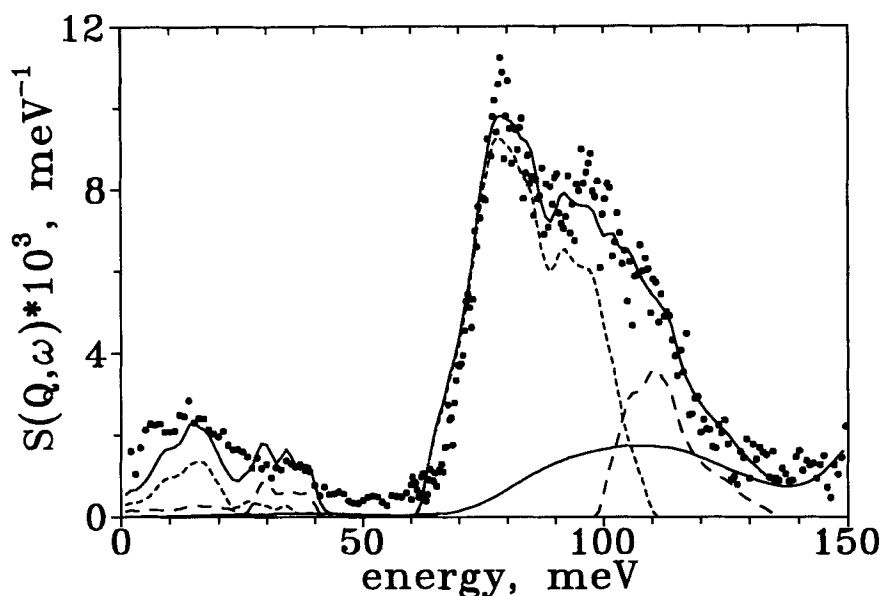


FIGURE 5 Experimental (points) and calculated (upper solid line) $S(Q, \omega)$ spectra for PdCuH_{0.9}. To get the calculated spectrum, the spectrum resulting from the Born-von Kármán model was convoluted with the resolution function for TFXA spectrometer and then summed with the calculated multiphonon contributions (lower solid line). The contributions to the calculated spectrum from vibrations of the H atoms in the *ab*-plane and along the *c*-axis are shown by short and long dashed lines.

The one-phonon spectra derived from the experimental data on PdCuH_{0.9} and PdAgH_{0.86} hydrides were then fitted^{5,6} with the help of the UNISOFT program¹⁷ using a conventional Born-von Kármán model. The principal adjustable parameters were the force constants for the Pd-H and Cu-H or Ag-H interactions, which determined on the average the positions of the peaks forming the hydrogen optic band, and those for the H-H interaction, which were 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 PdCu-H are presented in Figure 5.

4 CONCLUSIONS

Owing to the specific layered crystal structures of the ordered PdAgH and PdCuH hydrides, it appeared possible to study Ag-H and Cu-H interactions for the first time. The values of 93 meV and 116 meV were predicted for the local H vibrations in dilute Ag-H and Cu-H solid solutions, respectively.

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