

# Strong anisotropy in the inelastic neutron scattering from PdH at high energy transfer

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The dynamics of stoichiometric palladium hydride have been investigated using high-resolution inelastic-neutron-scattering experiments at 25 K in the energy-transfer region 2–800 meV. Strong anisotropy of the high-energy part of the spectra was observed. These features, which are similar to those seen previously in  $\beta$ -V<sub>2</sub>H, have energies remarkably close to the predictions of recent first-principles calculations. [S0163-1829(98)04129-0]

## I. INTRODUCTION

Measurements of the vibrational spectrum of the palladium-hydrogen system have attracted interest for many years. Dispersion curves and densities of phonon states in both the  $\alpha$  and  $\beta$  phases have been thoroughly studied for Pd-H( $D, T$ ) by the inelastic neutron-scattering (INS) technique.<sup>1–10</sup> The incoherent INS (IINS) spectrum of the  $\beta$ -phase hydride in the optic mode range consists of a sharp peak at around 60 meV with a broad high-energy shoulder. These features originate mainly from the transverse- and longitudinal-optic modes, respectively. Attempts to describe the phonon spectrum for nonstoichiometric PdH <sub>$x$</sub>  using the force constants derived from Born–von Kármán fits to the dispersion curves measured for PdD<sub>0.63</sub> (increased by about 10–20% after mass ratio correction),<sup>1</sup> gave substantially smaller heights for the high-energy shoulder, as compared to those observed in the INS measurements. Ross *et al.*<sup>8</sup> have shown that an increase in the H concentration does indeed tend to reduce the height of this shoulder. We report here IINS measurements on stoichiometric PdH which confirm this trend. The most interesting result of the present work, however, is the strong angular dependence of the spectra and the anharmonicity of the higher excited levels. These features, which are very similar to features of the  $\beta$ -V<sub>2</sub>H spectrum,<sup>11</sup> yield energy levels that are remarkably close to the predictions of recent first-principles calculations by El-sässer *et al.*<sup>12</sup>

## II. EXPERIMENTAL DETAILS

Two PdH samples of about 5 g each were made from palladium powder and from 0.3 mm thick palladium plates, respectively. The plates were cold-rolled and then annealed at 800 °C. This process resulted in strong texture, the [100] axis of this preferred orientation being approximately normal to the surface of the plates. The samples were hydrogenated in an atmosphere of molecular hydrogen at 40 kbar and 300 °C, the method employed being described in detail elsewhere.<sup>13</sup> The resulting hydrides had the same composi-

tion, PdH<sub>0.99±0.03</sub>. The superconducting transition temperature (9.33 K, midpoint) and lattice parameter of the fcc metal lattice ( $a=4.095$  Å at 100 K) were also the same for both samples. When not in use, the samples were stored in liquid nitrogen to prevent loss of hydrogen.

The IINS measurements were carried out at 25 K on the time-focused crystal analyzer (TFXA) spectrometer<sup>14</sup> on the ISIS spallation neutron source, at the Rutherford Appleton Laboratory, UK. The spectrometer provides good energy resolution,  $\Delta\omega/\omega\cong 2-3\%$  in the measured range of energy transfer, from 2 to 800 meV. The neutron-scattering angle was about 135°. Because of the small fixed final energy (4 meV) used, for the larger energy transfers, the wave vector transfer  $\mathbf{Q}$  was approximately parallel to the direction of the incident neutron beam. The deviation of  $\mathbf{Q}$  from this direction was approximately 9° for an energy transfer of 56 meV [which corresponds to the energy of the fundamental (100) peak] and 6° for 112 meV [the energy transfer for the (200) harmonics]. To study the possibility of anisotropy of the hydrogen vibrations, the measurements on the PdH plates were carried out for two different orientations of the sample where the angles  $\psi$  between incoming neutron beam ( $\mathbf{Q}$  direction) and the normal to the sample surface ([100] direction in the preferred orientation) were equal to 0° and 45°, respectively. After the subtraction of backgrounds determined in separate empty-can measurements, the data were transformed to  $S(Q, \omega)$  vs energy transfer (meV) using standard programs.

The contributions to the measured spectra from the multiphonon neutron scattering were calculated in an isotropic harmonic approximation using an iterative technique.<sup>10,15</sup> In the first iterative step, the experimental data in the range 2–100 meV were considered to be entirely due to one-phonon scattering. These data were then used to calculate the multiphonon (up to four-phonon processes) spectrum. After proper normalization, this calculated spectrum was subtracted from the experimental data over the same energy range (2–100 meV), and the resulting spectrum was taken to be an improved estimate of the one-phonon spectrum. The new one-phonon spectrum was again “self-folded” to produce the second approximation to the “real” multiphonon

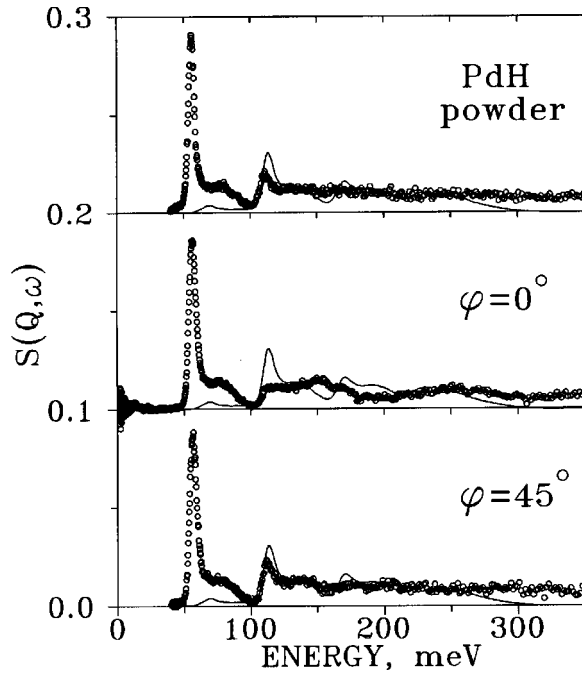


FIG. 1. The IINS spectra  $S(Q, \omega)$  of PdH at  $T=25$  K. Points indicate experimental data, lines indicate calculated multiphonon contributions. Upper part is for the powder sample, middle and bottom parts are for the plates at two different orientations  $\psi$ , see text.

contribution in the experimental IINS data, and so on. This iterative procedure gave a rather rapid convergence—after only 3–4 iterations, the one-phonon spectrum extracted from the experimental spectrum did not change any more.

### III. RESULTS AND DISCUSSIONS

Figure 1 shows the dynamic structure factors  $S(Q, \omega)$  for the PdH samples, both for the powder and for the plates in two different orientations. In the range of the fundamental H vibrations up to 100 meV, the three spectra nearly coincide indicating that the one-phonon terms are isotropic, as they ought to be. A comparison of the one-phonon spectrum for our powder sample in the range of the H optic modes with the calculated frequency distribution (solid line) for PdH<sub>0.63</sub> from the paper by Rowe *et al.*<sup>1</sup> is given in Fig. 2. The dashed curve represents a fit to the experimental one-phonon spectrum using three Gaussians. The positions and the full widths at half maximum of these Gaussians are presented in Table I (peak numbers 1<sub>1</sub>–1<sub>3</sub>) and they are the same for all three

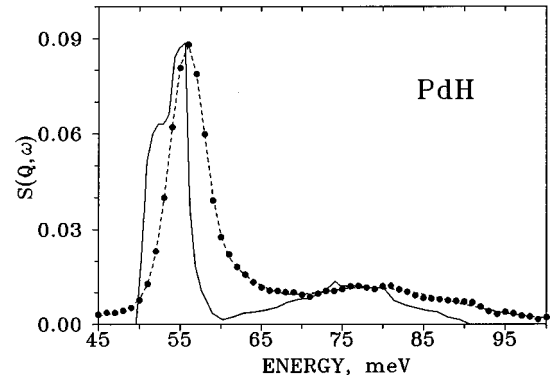


FIG. 2. The  $S(Q, \omega)$  spectrum for PdH powder after a multiphonon correction (points) and calculated frequency distribution for PdH<sub>0.63</sub> (solid curve) based on the force constants obtained from the Born–von Kármán model for PdD<sub>0.63</sub> (Ref. 1). The dashed curve is a fit to the experimental data using three Gaussians (see Table I).

spectra—PdH powder and PdH plates in two orientations.

In Ref. 1 the phonon density of states for PdH was obtained using the force constants from the Born–von Kármán fits to the dispersion curves measured for PdD<sub>0.63</sub>. As is seen from Fig. 2, the calculated position of the main optic peak is shifted to lower energies, and estimates show that the force constants for PdH<sub>x</sub> should be increased by about 8% compared to those for PdD<sub>x</sub>. The agreement between the calculated and measured widths of the main optic peak as well as the intensity ratios of the main optic peak (transverse modes) to high-energy shoulder (longitudinal modes) is good. The observed peak energy is 55.8 meV. This is about what one would estimate by extrapolation of the peak positions measured at lower concentrations. (It is well established that the peak energy decreases as the concentration and therefore the lattice parameter increases.<sup>8</sup>)

The lattice (acoustic) part of the generalized vibrational density of states  $G(\omega)$  for the PdH plates at  $\psi=0^\circ$  is shown in Fig. 3 (this measurement was selected because of having the best statistics). The spectrum consists of two peaks, one at about 13.7 meV (the transverse zone-boundary modes) and the second at around 22.5 meV (the longitudinal modes) with an upper frequency cutoff at 26 meV. These results are in agreement with the literature data.<sup>1</sup>

The high-energy ( $>100$  meV) part of the spectrum of the PdH plates at  $\psi=45^\circ$  exhibits approximately harmonic behavior. The first peak above the one-phonon hydrogen optical band is seen at about 112 meV in the experimental data

TABLE I. Peak positions  $\omega_i$  and full width at half maximum  $\Delta_i$  (in brackets) for different optic bands of the IINS spectrum of palladium hydride samples; all values are in meV. The parameters for the band 1 were obtained after the multiphonon corrections, and they are the same for all three measured spectra—PdH powder and two orientations ( $\psi$ ) for PdH plates.

No. of band	1 <sub>1</sub>	1 <sub>2</sub>	1 <sub>3</sub>	2 <sub>1</sub>	2 <sub>2</sub>	2 <sub>3</sub>	3	4	5
$\psi=0^\circ$	55.8 (4.8)	58.0 (11.6)	78.5 (22.8)		116.2 (14.2)	148.7 (41.8)	252.8 (50.5)	363.8 (55.8)	474.5 (44.6)
$\psi=45^\circ$	55.8 (4.8)	58.0 (11.6)	78.5 (22.8)	110.4 (9.0)	116.8 (14.2)	135.3 (35.3)	173.3 (24.0)	200.2 (20.9)	290 (52)

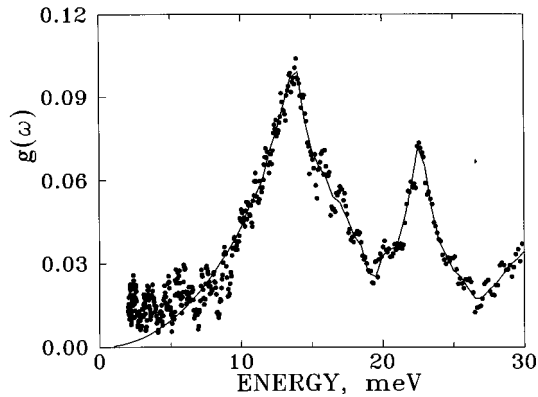


FIG. 3. The lattice part of generalized vibrational density of states  $G(\omega)$  for PdH plates at  $\psi=0^\circ$ .

and at 113.5 meV in the calculated multiphonon spectrum, the second maximum (at  $\sim 173$  meV) and the first and second minima (at about 125 and 160 meV, respectively) coincide in the experimental and calculated spectra. There is less observed intensity in the first harmonic peak at 113.5 and the second harmonic at 171 meV, though. The peaks in the bands 2–4 could be fitted with 3, 2, and 1 Gaussian functions with the parameters listed in the Table I.

In the case of the PdH plates at  $\psi=0^\circ$ , corresponding to  $\mathbf{Q}$  parallel to the  $[001]$  direction, the high-energy part of the spectrum looks completely different. The peak at 112 meV is

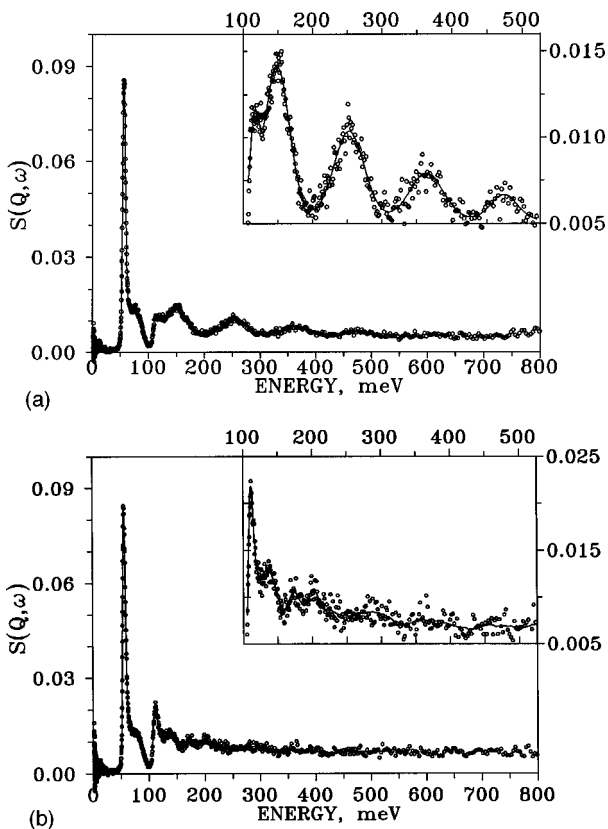


FIG. 4. (a) The  $S(\mathbf{Q}, \omega)$  spectrum for PdH plates at  $\psi=0^\circ$ . The inset is the high-energy part of the spectrum on a large scale. The solid lines are fits by Gaussians with the parameters listed in Table I. (b) The same as for (a) but for PdH plates at  $\psi=45^\circ$ . The solid lines are fits by Gaussians (for energies up to 225 meV) and polynomial spline (for higher energies).

suppressed, being replaced by other well-defined structure. The spectrum (see Fig. 4 and Table I) has split (200) band with peaks at 116 and 149 meV (their center of gravity is around 144 meV). Above 200 meV the spectrum consists of equally spaced peaks at 253, 364, and 475 meV with an energy difference of 111 meV, twice as large as the value for the fundamental mode frequency indicated by the main optic peak. The center of gravity of the second band, (002) transition, also follows this sequence because the difference  $253 - 111 = 142$  meV is very close to the experimental value of 144 meV.

Thus, we can conclude that the potential well for hydrogen at the octahedral interstitial position in an fcc  $\beta$ -PdH crystal is rather shallow and close to harmonic (or slightly anharmonic) and strongly damped in the directions which are approximately  $45^\circ$  to the  $[100]$  axis (along the  $[110]$  and close to the  $[111]$  axis) and initially shallow but then very steep and strongly anharmonic along the  $[100]$  axis (in the direction of the nearest Pd atom neighbor).

In the case of the powder sample, these two spectra are averaged. If we sum the spectra for PdH plates at  $\psi=45^\circ$  and  $\psi=0^\circ$  with the coefficients  $2/3$  and  $1/3$ , respectively, the resulting spectrum looks very close to spectrum for powder PdH.

It is interesting to note that in our previous experiment<sup>10</sup> on the same sample of PdH plates with  $\psi=45^\circ$  made in Dubna on a KDSOG-M spectrometer, the calculated multiphonon contributions agreed quite well with the observed spectra. The data in Ref. 10 were obtained by summing up the neutron spectra recorded at eight scattered angles from  $30^\circ$  to  $140^\circ$ , and the energy resolution at high energy transfer was about 10%. We think that the observed discrepancy is due to the differences in the experimental conditions.

#### IV. COMPARISON WITH THEORETICAL PREDICTIONS

The first attempt to explain the anharmonicity of the energy levels of H and its isotopes in palladium used the perturbation approach. Rush, Rowe, and Richter<sup>9</sup> were able to explain the energy levels up to the second harmonic in the  $\alpha$  phase using a single anharmonic potential up to the quartic term, assumed to have the same shape in each Cartesian direction. This approach does explain the isotope dependence of the observed energy transfers, but it does not work for higher energy levels. Moreover, it would not explain the anisotropic nature of the present data.

Our data for PdH samples are much more reminiscent of the results for  $V_2H$ .<sup>11</sup> The H atom in this hydride is located in the octahedral site in the bcc phase. In this site, the nearest-neighbor vanadium atoms are much closer in the  $[001]$  direction than in the basal plane. In the  $[100]$  direction, they observed peaks at 50.2, 131.8, 249.5, 340, 435, 539, 639, 720, 820, 930, 1140, 1270, and 1380 meV. The spectrum thus has one low-energy peak at 50.2 meV; an intermediate peak at 131.8 meV which is more than twice the fundamental energy; and approximately equidistant peaks at high energy transfer where the energy difference is about 100 meV (approximately twice the energy of the fundamental peak). This potential well was modeled with a parabolic potential with tetragonal symmetry augmented by an inverted Gaussian at the center of the well. It gives a good description of the narrow separation of the low-lying levels and the uniform separation of the higher levels.

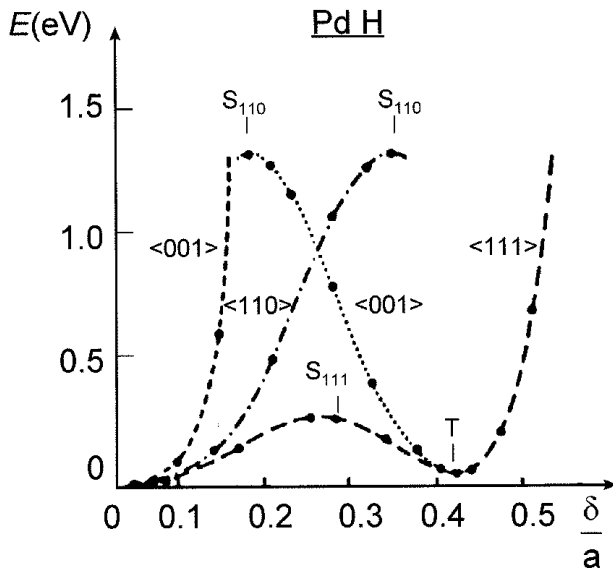


FIG. 5. The calculated profile of the potential energy for H in PdH ( $a=4.07$  Å) in the [100], [110], and [111] directions: origin, octahedral minimum; T, tetrahedral minimum;  $S_{111}$ ,  $S_{110}$ , saddle points. The diagram is taken from Elsässer *et al.* (Ref. 12).

It should be noted that the differentiation of the IINS spectra in the two crystal orientations is valid providing that energy can only be transferred to the excitations with Cartesian wave functions extending in a direction in which there is a finite component of the wave-vector transfer  $\mathbf{Q}$ . The success of the model in this case depends on the fact that the main deviations from a parabolic potential are the tetragonal distortion and the flatness of the bottom of the well which is such that a Cartesian representation of the potential works rather well. In contrast, the present spectra show anisotropy in spite of the site having cubic symmetry. Moreover, the variation is based on a  $45^\circ$  rotation, which means that it cannot be represented using Cartesian coordinates.

However, since these earlier experiments, first-principles total-energy calculations have made very significant progress. Elsässer *et al.*<sup>12</sup> have used the mixed-basis pseudo-potential method within the framework of the local-density-functional approximation to obtain the total energy and internal forces in the metal hydride lattice. The calculations were performed in superlattice cells with a series of H stoichiometries up to 1. The resulting energy surfaces for the PdH<sub>1.0</sub> case are reproduced in Fig. 5 and immediately offer a qualitative explanation of our results.

Thus, the potentials in the [111] and [110] directions initially lie close together with a parabolic shape, while the potential in the [001] direction is initially close to those in the other directions but then rises with a much steeper parabolic shape, this being the direction from the octahedral site to the nearest Pd atom. If it were simply a matter of the direction of  $\mathbf{Q}$  selecting energy levels from a one-dimensional potential, the explanation would be clear. In the [110] and [111] directions the separation would be small and constant, while in the [100] direction, the low-energy levels would be close with the same separation as in the other directions but then the separation would become large and uniform because of the steeper parabola in this direction.

Not surprisingly, the perturbation theory method, using an anharmonic Cartesian description of the potential well, does

not work well as it provides no way of representing the difference between the [100] and [110] directions. However, the Fourier series technique<sup>16</sup> produced good agreement. The calculated wave functions for the PdH<sub>1.0</sub>, which has a calculated lattice parameter of 4.07 Å (compared with the present experimental value of 4.095 Å) yield a first excited-state energy ( $E_{100}-E_{000}$ ) of 62 meV compared with an experimental value of 55.8 meV. Three of the six wave functions at the second levels are degenerate, being denoted (110) by analogy with the perturbation case, have an energy difference ( $E_{110}-E_{000}$ ) of 117 meV as compared with the experimental value seen in the [110] direction at 112 meV (see Fig. 1, at the bottom). The other three second level wave functions yield transition energies of 132 meV (singly degenerate) and 147 meV (doubly degenerate) compared with the broad experimental feature at 148.7 meV for the spectrum in [100] direction. These authors do not quote the higher energy levels but a simple approach involving fitting a parabola to the outer parts of the potential in the [100] direction confirms a spacing of 111 meV which agrees well with the spacing seen.

The model in Ref. 12 also predicts a threshold energy between adjacent sites in the [111] direction of about 250 meV. This would suggest that the higher energy levels would have somewhat delocalized wave functions in this direction, explaining the absence of the higher energy levels in the spectrum measured in this direction. It should be noted that these authors did not calculate the matrix elements that would define the intensity of the peaks for different magnitudes and directions of  $\mathbf{Q}$ . However, it is reasonable to assume, as here, that the direction of  $\mathbf{Q}$  will accentuate the energy levels determined predominantly from the profile of the potential well in that direction but that some of the other levels will also have a finite cross section.

An important point that still needs to be settled is whether the same potential well can be used for all isotopes. The calculations of Elsässer *et al.* were certainly performed on this assumption and predict that, after allowing for the mass difference, the fundamental energy for H should be 10% higher than for D (62 and 40 meV, respectively) because of the anharmonicity of the potential. This ratio is close to the estimated 8% difference in effective force constants quoted above.<sup>1</sup> There is of course, the possibility that because the electronic structure relaxes adiabatically, there will be some effect due to the different zero-point motions of the different isotopes.

## V. CONCLUSIONS

The present paper extends the inelastic neutron-scattering measurements on H in Pd to the stoichiometric hydride and the energy transfer range to 800 meV. Moreover, because of the preferred orientation in the plate samples, the strong anisotropy and anharmonicity of the IINS spectra were observed. The energy levels and directional dependence of the corresponding intensities were in remarkably good agreement with the results of first-principles calculations, confirming the shape of the calculated potential well.

## ACKNOWLEDGMENTS

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