VIBRATIONAL PROPERTIES OF HYDROGEN IMPURITY IN HIGH-PRESSURE PALLADIUM DEUTERIDE

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Local vibrations of a light-atom defect chemically identical to heavy atoms of the host lattice were experimentally studied only once in the work of ref. [1], in which a solid solution of 3.7 at.% H in $PdD_{0.6}$ was investigated by inelastic neutron scattering (INS). The experiment demonstrated the occurrence of a local-mode peak shifted beyond the band of optical vibrations of the D atoms. No other details of H or D vibrations could be seen in the INS spectrum because it was broadened due to the non-stoichiometric composition of the deuteride.

Homogeneous samples of stoichiometric PdD and PdH can only be prepared at high pressures. The present work reports on an INS study of three $PdD_{1-x}H_x$ powder samples with $x = 0.050$, 0.072 and 0.091 synthesised in a deuterium-hydrogen atmosphere at $P = 50$ kbar and $T = 600$ K. To analyse and interpret the obtained spectra, the lattice dynamics of $PdD_{1-x}H_x$ solid solutions was simulated using the Born-von Kàrmàn model.

The $PdD_{1-x}H_x$ samples weighing about 2 g each were prepared at ISSP RAS and studied with the IN1-BeF neutron spectrometer at the Institute Laue-Langevin in Grenoble. The background from the sample holder and cryostat was separately measured under similar conditions and subtracted from the INS spectra. The resulting INS spectra normalized to the sample weight and the number of incoming neutrons are shown in Fig. 1.

The optical spectra in Fig. 1 can formally be split into the contribution S_{PdD} from the undisturbed PdD matrix and the contribution S_H resulting from neutron scattering on the H atoms and also the neighbouring D atoms, whose motions are influenced by the H impurity. If the hydrogen content x is low and the interaction among the H atoms is negligibly small, the total scattering intensity S can be written as:

$$S = xS_H + (1-x)S_{PdD}. \tag{1}$$

From the experimental S spectra written in the form of equation (1) for any two different $PdD_{1-x}H_x$ samples one can get S_{PdD} and S_H. Figs. 2 and 3 show these dependences calculated for the pairs of samples with $x = 0.05$ and 0.091 and with $x = 0.05$ and 0.072. The calculated two S_{PdD} spectra (Fig. 2) coincide within the line thickness and the two S_H spectra (Fig. 3) are close to each other, too. This suggests the applicability of equation (1) to the solid $PdD_{1-x}H_x$ solutions with hydrogen concentrations up to $x = 0.091$ at least.

The S_{PdD} spectrum in Fig. 2 is very similar to the experimental spectrum $S(Q, \omega)$ of stoichiometric PdH [2] if the latter is plotted as a function of $\omega/1.51$. The deviation of the scaling factor from the
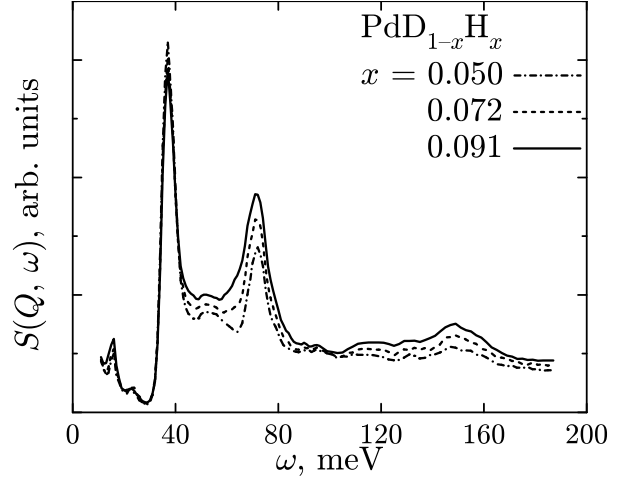

Fig. 1. The dynamic structure factor, $S(Q, \omega)$, of powder $PdD_{1-x}H_x$ samples measured at 5 K using the IN1-BeF neutron spectrometer at ILL, Grenoble. The peaks at 40 and 70 meV are mostly due to the optical vibrations of D and H atoms, respectively. The spurious intensity at energies below 30 meV results from two- and three-phonon scattering of admixed neutrons of half the wavelength in the incoming monochromared beam.
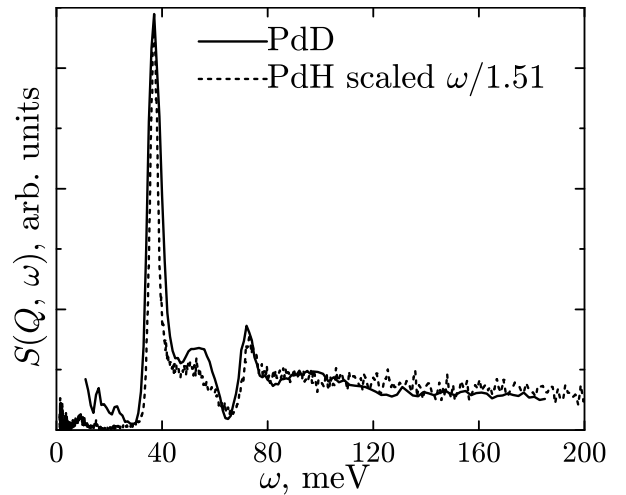

Fig. 2. Solid line: INS spectrum for PdD, extracted from the experimental $PdD_{1-x}H_x$ spectra. Dashed line: INS spectrum for PdH [2], scaled $\omega/1.51$.

harmonic value $\sqrt{m_D/m_H} \approx \sqrt{2}$ well agrees with earlier estimates [3].

The contribution S_H from the H impurity (Fig. 3) proved to have a rather unexpected profile. First, it showed a negative scattering intensity at energies near 35 meV, in the energy range of the main peak
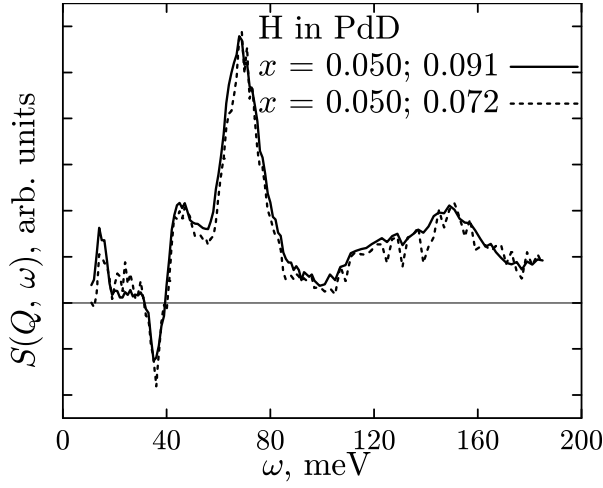
Fig. 3. INS spectrum corresponding to H impurity in PdD, extracted from two different pairs of experimental $PdD_{1-x}H_x$ spectra.

of D optical vibrations (see Fig. 2). Second, the broad H peak at 70 meV with an intense shoulder towards lower energies demonstrated no tendency to transforming into a narrow local-mode peak with decreasing H concentration in the deuteride.

To ascertain the origin of such an unusual profile, we have calculated the lattice dynamics for Pd_4D_3H ($x = 0.25$), Pd_8D_7H ($x = 0.125$), $Pd_{16}D_{15}H$ ($x = 0.0675$) and PdD crystals using the Born-von Kàrmàn model. The Pd-Pd, Pd-D and D-D force constants were taken from ref. [4]. The constants for H atoms were set equal to those for D atoms. The dispersion curves calculated for PdD without H impurities (NaCl-type cubic crystal structure, space group $Fm\bar{3}m$) are shown in Fig. 4.
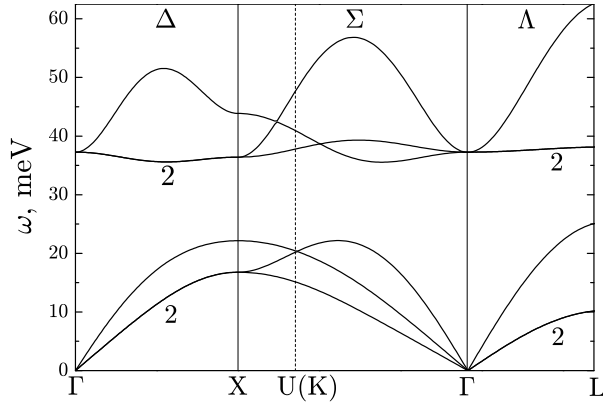

Fig. 4. Phonon dispersion curves for PdD calculated in the Born-von Kàrmàn model using force constants from ref. [4]. The numbers indicate the degeneracy; $\hbar = 1$.

Eigenvalues $\omega^2(j, \vec{q})$ and eigenvectors $\vec{e}_i(j, \vec{q})$ for each atom i in the unit cell were calculated for sampling points uniformly distributed over the irreducible part of the Brillouin zone (BZ) and further used to obtain densities of phonon states according

to

$$g(j,\omega) = \int\limits_{\vec{q}\in BZ} \delta(\omega - \omega(j,\vec{q}))d\vec{q} =$$

$$= \iint\limits_{\omega(j,\vec{q})=\omega} \frac{d^2q}{|\nabla_{\vec{q}}\omega(j,\vec{q})|}, \quad (2)$$

where $\vec{q}$ is varied over the BZ. Hereafter, the eigenvectors are normalized as $\forall j, \vec{q} \colon \sum_i m_i |\vec{e}_i(j,\vec{q})|^2 = 1$, m_i being the mass of atom i. To integrate in equation (2), we interpolated $\omega(j,\vec{q})$ linearly within tetrahedrons with vertices at the nearest sampling points chosen so as to completely fill the BZ. The total number of the sampling points varied from 32000 for PdD to 1000–2000 for the $PdD_{1-x}H_x$ structures.

Fig. 5 shows the total density of phonon states (phonon DOS) for PdD calculated as $g(\omega) = \sum_j g(j,\omega)$. One can see that the optic part of $g(\omega)$ qualitatively reproduce the intensity distribution in the experimental $S(Q,\omega)$ spectrum of PdD.
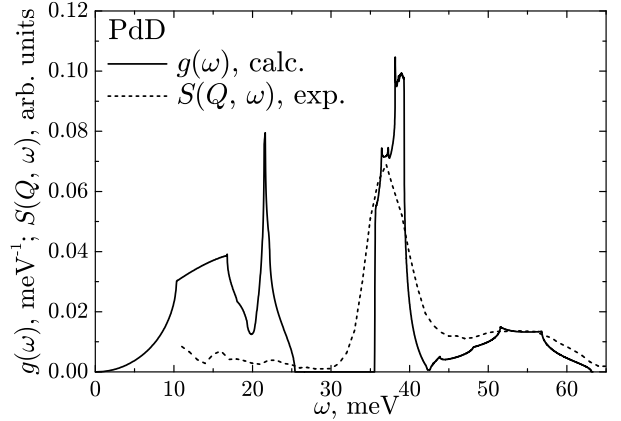

Fig. 5. Solid line: the phonon DOS of PdD calculated using 32000 sampling points in the irreducible BZ. Dashed line: the experimental INS spectrum of PdD from Fig. 2.

The calculated $g(\omega)$ spectra of the $PdD_{1-x}H_x$ solutions cannot be directly compared with their experimental $S(Q,\omega)$ spectra because of the significantly different cross-sections for neutron scattering by H and D atoms. To calculate the $S(Q,\omega)$ spectra from the $g(\omega)$ spectra, we did the following.

First, a partial generalized phonon density of states, $G_i(\omega) = \sum_j G_i(j,\omega)$, was computed for each atom in the unit cell using $G_i(j,\omega)$'s calculated as:

$$G_i(j,\omega) = \int\limits_{\vec{q}\in BZ} |\vec{e}_i(j,\omega)|^2 \delta(\omega - \omega(j,\vec{q}))d\vec{q} =$$

$$= \iint\limits_{\omega(j,\vec{q})=\omega} \frac{|\vec{e}_i(j,\omega)|^2 d^2q}{|\nabla\omega(j,\vec{q})|}, \quad (3)$$
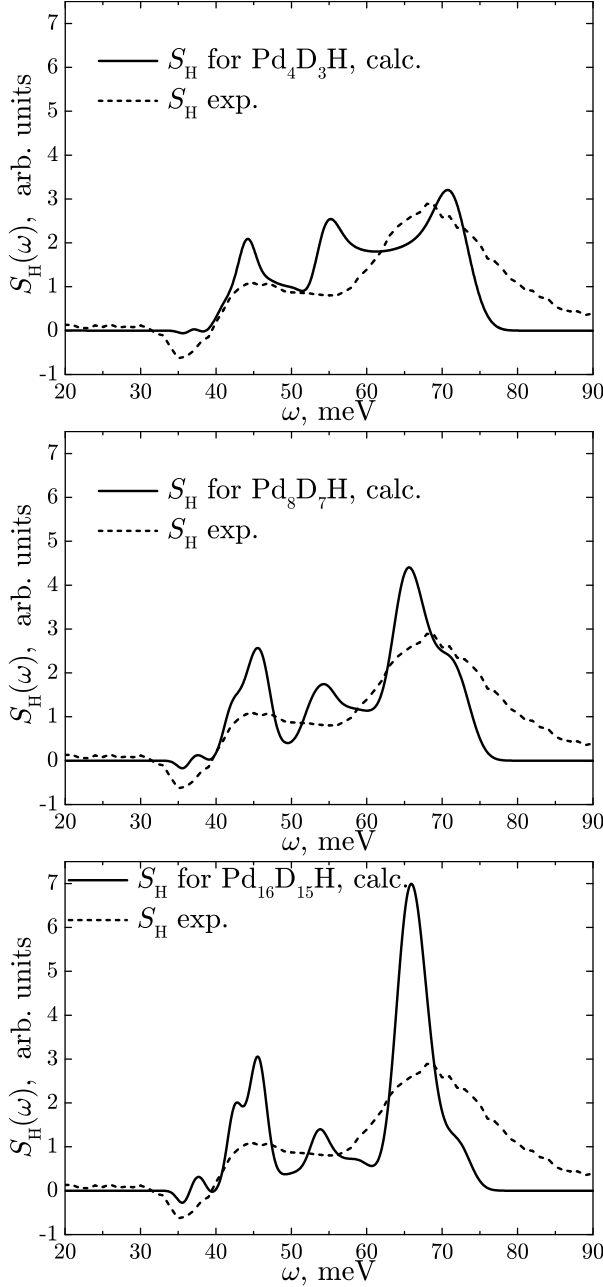
Second, the computed $G_i(\omega)$ were used to calcu-

Fig. 6. Contributions $S_H(Q, \omega)$ to the total dynamical structure factor of the solid $PdD_{1-x}H_x$ solutions due to the presence of H impurity. The dashed curves represent the experimental S_H from Fig. 3. The solid curves are results of the model calculations.

late the dynamical structure factor $S(Q, \omega)$ at 0 K according to:

$$S(Q, \omega) = \frac{\hbar^2 Q^2}{2\omega} \sum_i \frac{\sigma_i}{m_i} \exp(-2W_i(Q)) G_i(\omega),$$

where σ_i is the total (incoherent and coherent) neutron scattering cross section for atom i and

$$W_i(Q) = \frac{\hbar^2 Q^2}{12m_i} \int \frac{G_i(\omega)}{\omega} d\omega$$

is the Debye-Waller factor for atom i.

Finally, using the $S(Q, \omega)$ spectra calculated for PdD and for each of the three model solutions, Pd_4D_3H, Pd_8D_7H and $Pd_{16}D_{15}H$, the contribution S_H due to the H impurity in these solutions was calculated via equation (1). The resulting S_H contributions convoluted with the resolution function (a Gaussian with FWHM = 0.05ω) of the IN1-BeF spectrometer are shown in Fig. 6.

As seen from Fig. 6, the decrease in the H concentration and, correspondingly, in the H-H interaction leads to a sharpening of peaks in the calculated S_H spectra. At the same time, even in the $Pd_{16}D_{15}H$ structure with the minimum $x = 0.0675$, this interaction is strong enough to broaden the peak of local H vibrations over a wide interval of 60–75 meV.

Regretfully, none of the calculated spectra in Fig. 6 can quantitatively reproduce the profile of the experimental S_H spectrum because of the simple model used [4]. Nevertheless, the calculation confirms and explains some principle features of the S_H contribution. One of these features is the broad peak at 40–50 meV. According to the calculation, it originates from the low-frequency modes of co-vibrations of H atoms together with the D atoms. In its turn, the involvement of the D atoms in co-vibrations with the H atoms leads to the increase in their vibrational frequencies. The resulting shift of the main peak of optical D vibrations to higher energies produces a negative scattering intensity near 36 meV in the calculated difference spectra S_H. The negative intensity in the experimental S_H spectrum is observed at the same energies therefore it is likely to have this very origin.

To briefly summarize, three samples of solid $PdD_{1-x}H_x$ solutions with $x = 0.050$, 0.072 and 0.091 synthesised at high pressures are studied by inelastic neutron scattering. The vibrational spectrum of stoichiometric palladium deuteide has been constructed for the first time. The contribution from H impurity to the vibrational spectrum of PdD is shown to significantly differ from earlier estimates [1]. The main features of the obtained experimental profile of this contribution are explained by simulating the lattice dynamics of the solid $PdD_{1-x}H_x$ solutions using the Born-von Kàrmàn model.

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