# ANISOTROPY OF OPTICAL VIBRATIONS IN PdD

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## Introduction

Lattice dynamics of $PdH_x$ hydride and $PdD_x$ deuteride ($x > 0.6$) has been extensively studied for more than two decades. The H(D) atoms in $PdH_x$ ($PdD_x$) occupy octahedral interstitial positions in the *fcc* lattice of Pd metal. The phonon dispersion curves for $PdD_x$ and the density of vibrational states for $PdH_x$ with various concentrations of x were measured by many groups (see [1,2]).

Recent inelastic neutron scattering (INS) studies of textured foils of stoichiometric PdH demonstrated [3] that, despite of the cubic symmetry of octahedral hydrogen positions, the second and higher bands of optical H vibrations are strongly anisotropic.

The first optical H band in the INS spectra of PdH was found to be isotropic [3]. Nevertheless, this did not necessarily imply that the H potential well was also isotropic in the corresponding energy range, because the high symmetry of the first excitation state of the H atoms made it insensitive to possible anisotropy of the potential well [4].

To learn more about the anisotropy of the hydrogen potential well in palladium hydride at energies below the second excitation state of H atoms, now we exploited the fact that the vibrational energies of deuterium in the same potential well should be smaller by a factor of approximately $\sqrt{2}$ than the energies of protium, and therefore studied the second optical D band in a textured sample of palladium deuteride.

## Experimantal details

A textured sample of $PdD_{1-x}H_x$ with $x = 0.052$ was prepared using the same Pd foil with cubic texture as in [3,4]. We could not avoid contamination of the deuteride with hydrogen, and to isolate the contribution from H to the INS spectrum, we also studied $PdD_{1-x}H_x$ powder samples with $x = 0.050$, 0.072 and 0.091. All samples were synthesized at ISSP RAS in an atmosphere of gaseous deuterium/hydrogen mixtures at P = 50 kbar and T = 600 K. The samples were quenched under high pressure to 140 K and further stored in liquid nitrogen to prevent deuterium losses. The isotopic composition x of the synthesized samples was measured by mass spectrometry at the Institute for Inorganic Materials.

The INS measurements were carried out with the IN1-BeF spectrometer at ILL, Grenoble. The INS spectra were normalized to the mass of the sample and to the neutron flow.

## Results and discussions

From each pair of the measured powder INS spectra of $S(Q,\omega)$ (Fig.1), one can obtain the $S_{PdD}$ spectrum of pure PdD and the $S_H$ spectrum due to the H impurity in the deuteride, if he uses the equation

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

This equation should be correct for small x. The $S_{PdD}$ spectrum (Fig.2) and the $S_H$ spectrum (Fig.3a) proved to be the same for different S pairs that verified the validity of (1) at concentrations up to $x = 0.091$.

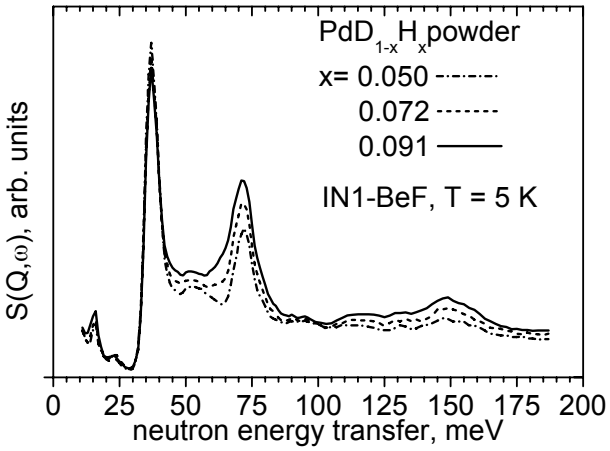


Fig.1. The INS spectra $S(Q,\omega)$ for the powder $PdD_{1-x}H_x$ samples.

As seen from Fig.2, the $S_{PdD}$ spectrum can be well approximated by the INS spectrum of a powder PdH sample [3] compressed along the energy axis by a factor of 1.51. The deflection of this factor from $\sqrt{m_D/m_H} \approx \sqrt{2} \approx 1.41$ indicates that the force constants for H in PdH are slightly larger than those for D in PdD.

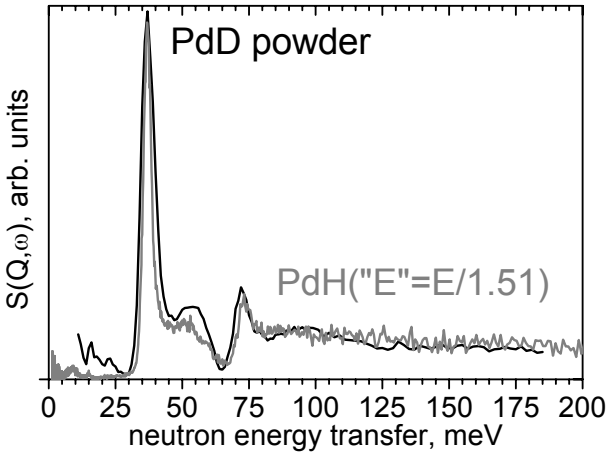


Fig.2. The $S_{PdD}(Q,\omega)$ spectrum of PdD powder (dark line) and the experimental PdH spectrum from ref. [3] plotted as a function of E/1.51 (light line).

The peak in the second vibrational band of PdD is positioned at 72meV, which is lower by 2meV than the doubled energy of 37meV of the peak in the first optical band. This suggests anharmonicity of the potential well for D atoms at energies as low as 2.5*37meV ≈ 90meV, counting from the bottom of the well.

A noteworthy feature of the $S_H$ contribution to the INS spectra of the powder $PdD_{1-x}H_x$ samples (curve at the bottom of Fig.3(a)) is the occurrence of negative intensities in the energy range 35–40meV. Our estimates using the Born-von Kàrmàn model showed that this feature originated from the increase in the vibrational frequencies of D atoms located near the H impurity atoms.

The palladium foil used to prepare the $PdD_{1-x}H_x$ sample with x = 0.052 was characterized by a very strong (001)[100] texture making the sample similar to a single crystal. The spectra shown in Fig.3(a) were measured with two different sample orientations – with the neutron momentum transfer **Q** directed, respectively, along the [100] and [110] axes of the texture. The same spectra with a subtracted isotropic H contribution $S_H$ are shown in Fig.3(b).

As seen from Fig.3(b), the intensity distribution in the first optical band of the PdD sample at energies of 35–60meV depends on the direction of **Q**. This is a result of coherent neutron scattering, because in this energy range, the volume in the reciprocal space covered by admissible neutron momentum transfers was smaller than the volume of the Brillouin zone. In the INS spectra of the textured PdH sample measured earlier [3], the coherent contribution was negligibly small due to the anomalously large incoherent neutron cross-section of the H atoms.

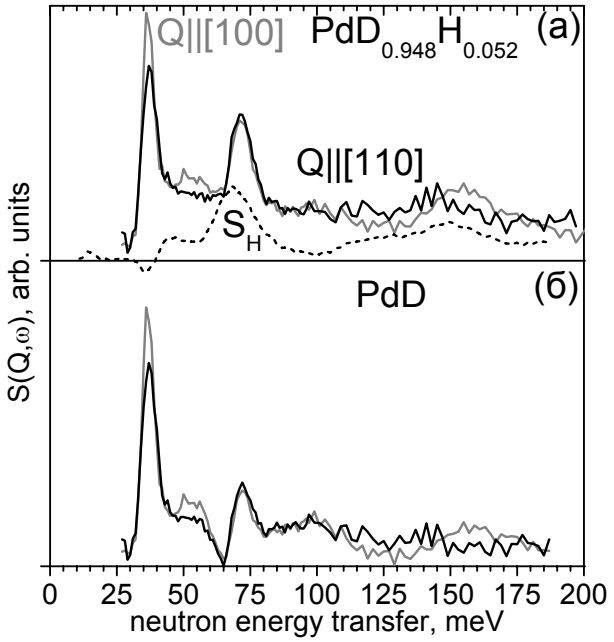


Fig.3. INS spectra of the $PdD_{1-x}H_x$ foil with x = 0.052 measured with the direction of neutron momentum transfer **Q** parallel to the [100] texture axis (light curve) and to the [110] axis (dark curve). The dashed line at the bottom of (a) is the contribution $S_H$ from the protium impurity.

The conditions for incoherent approximation were well satisfied for the second and higher optical bands of PdD. As follows from Fig.3(b), the second band of optical vibrations in PdD was isotropic in the energy range 65–110meV, whereas the INS spectrum was strongly dependent on the **Q** direction at higher energies.

**Conclusions**

Our investigation has shown that the potential well for D atoms in PdD is isotropic at energies up to 125meV (counting from the bottom of the well) and becomes strongly anisotropic at higher energies. Earlier, it was only known that the nearly identical potential well for H atoms in PdH is strongly anisotropic at energies higher than 130meV [3].

**References**

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4. Antonov VE et al. Europhys Lett 2000; 51(2):140–146.