PHYSICAL REVIEW B **80**, 134302 (2009)

Neutron spectroscopy of H impurities in PdD: Covibrations of the H and D atoms

V. E. Antonov,[1] A. I. Davydov,[2] V. K. Fedotov,[1] A. S. Ivanov,[3] A. I. Kolesnikov,[4] and M. A. Kuzovnikov[1,5,*]
[1]*Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia*
[2]*Bochvar All-Russian Scientific Research Institute for Inorganic Materials, Rogova Street 5a, 123060 Moscow, Russia*
[3]*Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France*
[4]*Neutron Scattering Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[5]*Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Moscow District, Russia*

(Received 23 July 2009; published 15 October 2009)

Three powder samples of solid isotopic solutions $PdD_{1-x}H_x$ with $x=0.050$, 0.072, and 0.091 are prepared under high pressure, and the spectra of their optical vibrations are studied by inelastic neutron scattering at ambient pressure and 5 K using the high-luminosity IN1-BeF spectrometer at ILL, Grenoble. These spectra are shown to be well represented by a linear combination of a contribution from the undisturbed matrix of stoichiometric PdD and a contribution due to the H impurity. The optical spectrum of PdD consists of a strong peak at 37 meV with a shoulder extending to 65 meV. The spectrum due to the H impurity is composed of a broad peak of defect H modes centered at 68 meV and superimposed on a broad N-shaped feature with a range of negative intensity near 36 meV and a shallow maximum at 45 meV. Simulations using the Born-von Kármán model show that this unusual feature is a result of the formation of a band of optical vibrations of the D and H atoms with equal frequencies (covibrations) caused by H-D interactions.

DOI: 10.1103/PhysRevB.80.134302 PACS number(s): 78.70.Nx, 63.20.D−, 63.20.Pw

I. INTRODUCTION

Due to the very large incoherent neutron-scattering cross section, hydrogen atoms substituting for deuterium atoms in deuterides provide a good model system for studying the dynamics of light-atom defects using inelastic neutron scattering (INS). Hydrogen defect modes were earlier observed and studied by INS in a few metal deuterides, e.g., $YD_{0.18}$,[1] YD_2,[2] CeD_2,[3] $LaD_{2.5}$,[4] and AlD_3.[5] In each case, the defect underwent a localized vibration producing one or more (depending on the H-site symmetry) sharp peaks detached from the host phonon band. An INS investigation of a solid solution of 3.7 at. % H in $PdD_{0.6}$ also demonstrated the occurrence of a local-mode peak shifted beyond the band of optical vibrations of the D atoms.[6] The peak was significantly broadened, but rather symmetric and positioned exactly at the energy $E_H=71$ meV predicted by the simple theory for the local vibrations of an isotropic light-atom mass defect.[7]

No other features of lattice vibrations in H-doped deuterides could be derived from experiment so far. In the case of the H solution in $PdD_{0.6}$,[6] the main obstacle was the broadening of the INS spectra due to the nonstoichiometric composition of the deuteride, which contained 40% vacancies in the D sublattice.

Homogeneous samples of nearly 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 synthesized in a deuterium-hydrogen atmosphere at $P=5$ GPa and $T=600$ K. The samples were prepared at ISSP RAS and studied by INS with the statistical accuracy a few times better than in earlier experiments[6] using the high-luminosity IN1-BeF neutron spectrometer at ILL. Together with the elimination of vacancies in the H/D sublattice and the higher H/D ratio of the samples, the better statistical accuracy of the INS experiment made it easier to investigate the changes induced by a light impurity inside the host phonon band.

II. SAMPLES PREPARATION AND EXPERIMENTAL DETAILS

The three $PdD_{1-x}H_x$ samples weighing about 2 g each were collected in batches about 0.5 g each prepared from powder of 99.98 wt. % pure Pd metal exposed to an atmosphere of gaseous deuterium/hydrogen mixtures at $P=5$ GPa and $T=600$ K for 24 h. The gas mixtures were produced by thermal decomposition of mixtures of aluminum deuteride and hydride in the necessary proportions and used as internal D_2 and H_2 sources in the high-pressure cell (the hydrogenation method is described in more detail elsewhere[8]). After the hydrogenation was completed, the batch was cooled to −140 °C to prevent its decomposition while releasing the pressure. When not in use, the samples thus prepared were stored in liquid nitrogen.

To ensure the homogeneity of the samples, a portion of a few milligrams of every batch was analyzed for D+H content by hot extraction into a pre-evacuated volume. With a heating rate of 20 K/min, the gas evolution began at approximately 160 K and ceased at about 500 K. The total $(D+H)/Pd$ atomic ratio of all batches was within the range of 1.00 ± 0.03. Every batch was also examined by x-ray diffraction ($T=100$ K, Cu $K\alpha$ radiation) and shown to be a single-phase $PdD_{1-x}H_x$ isotopic solution with the fcc metal lattice and the lattice parameter $a=4.087(4)$ Å close to $a=4.084$ Å for stoichiometric PdD.[9]

The atomic ratios of $x=H/(D+H)$ of the three $PdD_{1-x}H_x$ samples were determined by mass spectrometry of the gas produced by the complete thermal decomposition of a portion of each sample. The measurements were carried out with a high-resolution spectrometer designed for the isotopic analysis of hydrogen-helium mixtures. The obtained x

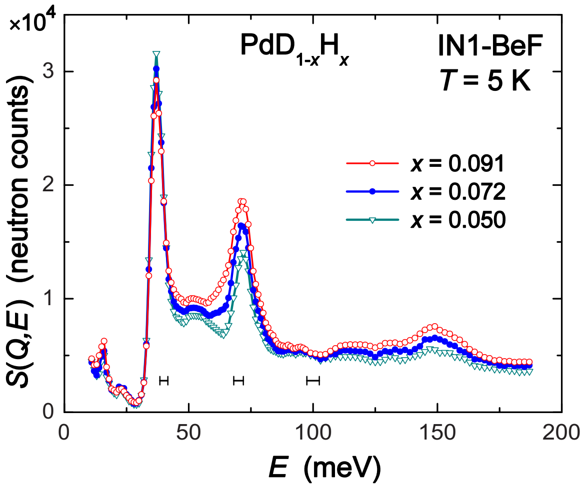

FIG. 1. (Color online) The dynamical structure factor $S(Q,E)$ of three powder $PdD_{1-x}H_x$ samples as a function of the energy loss E of the inelastically scattered neutrons. Q is the neutron momentum transfer and its dependence on E is a characteristic of the spectrometer used. The horizontal bars at the bottom of the figure show the energy resolution. The spurious intensity at energies below 30 meV results from one- and two-phonon scattering of admixed neutrons of half the wavelength in the incoming monochromated beam.

$=0.050(2)$, 0.072(2), and 0.091(2) proved to be significantly higher than the values of $x_{gas}=0.03$, 0.05, and 0.07, respectively, for the gaseous deuterium/hydrogen mixtures used in the high-pressure synthesis of the samples. This agrees with the equilibrium separation factor $(H/D)_{Pd}/(H/D)_{gas}>1$ for palladium in a deuterium/hydrogen atmosphere (see e.g., Ref. 10 for discussion and references).

The INS spectra from the $PdD_{1-x}H_x$ samples were measured at 5 K using the IN1-BeF spectrometer at ILL in Grenoble. The energy of the incoming neutrons was selected with a focusing Cu(220) single crystal. The inelastically scattered neutrons were registered at a scattering angle of 90°. The energy of the registered neutrons was fixed at an average value of 3.5 meV using a cold beryllium filter. The neutron energy transfer, E, was calculated by subtracting 3.5 meV from the energy of the incoming neutrons. In the studied range of 30–180 meV of energy transfers, the spectrometer provided the resolution $\Delta E/E \approx 5-8\%$. The background spectrum from the cryostat and an empty flat sample holder made of thin aluminum foil was measured separately and then subtracted from the raw INS spectra of the $PdD_{1-x}H_x$ samples.

III. RESULTS AND DISCUSSION

Figure 1 shows the experimental INS spectra of the three $PdD_{1-x}H_x$ samples normalized to the mass of the sample and to the neutron flux. In the range of optical vibrations at $E>30$ meV, the contribution from neutron scattering from palladium atoms is vanishingly small due to the mass dependence of polarization eigenvectors of the corresponding vibrational modes, and the spectra nearly entirely originate from scattering from the deuterium and hydrogen atoms.

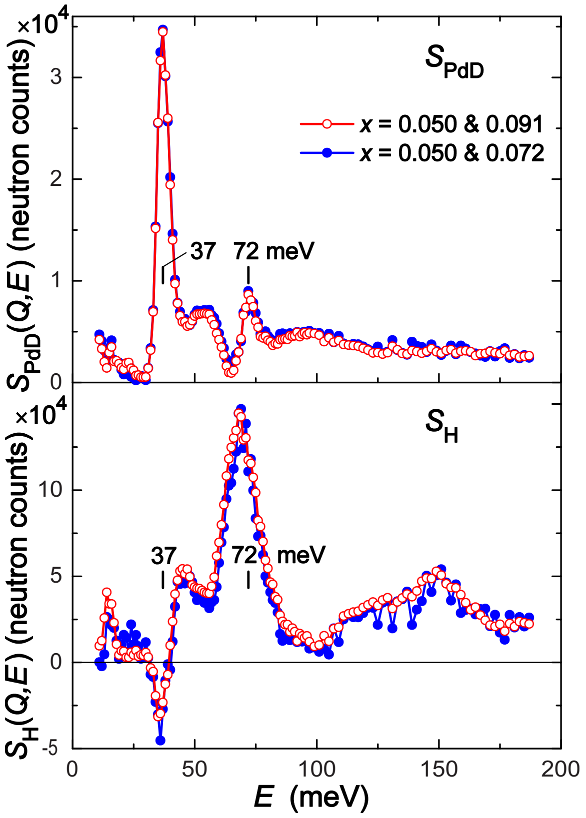

FIG. 2. (Color online) Two INS spectra S_{PdD} for the defect-free PdD (top) and two spectra S_H due to the H impurity in PdD (bottom) extracted from two different pairs of experimental $PdD_{1-x}H_x$ spectra.

We could not produce a sample of isotopically pure PdD because the aluminum deuteride used in the high-pressure synthesis was contaminated with protium and had $x=0.029(2)$. Nevertheless, from any pair of the INS spectra $S(Q,E)$ presented in Fig. 1, one can obtain the S_{PdD} spectrum of the undisturbed PdD matrix and the S_H spectrum due to the H impurity in the deuteride, if the total scattering intensity for each sample is written in the form

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

The S_{PdD} and S_H spectra being the same for all samples, Eq. (1) suggests that the S_H spectrum should result from neutron scattering on the H atoms and also from changes in the scattering from the D atoms caused by their interactions with differently vibrating H atoms.

Equation (1) should be valid for small x. As seen from Fig. 2, the S_{PdD} and S_H spectra calculated using different S pairs coincide within the experimental error. This verifies the validity of Eq. (1) at concentrations up to $x=0.091$. We will further analyze the S_{PdD} and S_H spectra derived from $S(Q,E)$ of the $PdD_{1-x}H_x$ samples with the most different $x=0.050$ and 0.091 because of their better statistical accuracy.

A. Spectrum S_{PdD} of stoichiometric PdD

As seen from Fig. 3, the S_{PdD} spectrum is very similar to the experimental spectrum $S(Q,E)$ of stoichiometric PdH,[11]

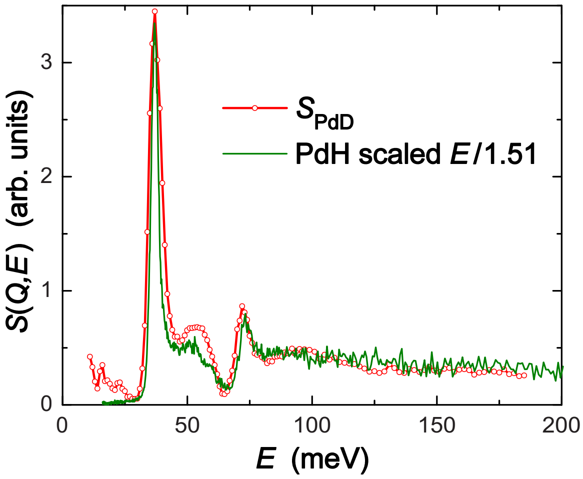

FIG. 3. (Color online) The S_{PdD} spectrum for PdD extracted from a pair of experimental $S(Q,E)$ spectra of the $PdD_{1-x}H_x$ samples with $x=0.050$ and 0.091 (open circles connected with a thick line) and the experimental $S(Q,E)$ spectrum of PdH (Ref. 11) compressed by a factor of 1.51 along the energy scale (thin solid line without circles). The scaling factor 1.51 was chosen to reproduce the energy position of 37 meV of the maximum of the main optical peak in the spectrum of PdD. The INS spectrum of PdH was measured in Ref. 11 at 25 K using the TFXA spectrometer at ISIS, U.K., and had a better energy resolution of $\Delta E/E \approx 1.5\%$ and a lower statistical accuracy than the S_{PdD} spectrum.

if the latter is compressed by a factor of 1.51 along the energy scale. The harmonic isotopic behavior would suggest an inverse proportionality of the vibrational energy E to the square root of the mass m of the vibrating atoms. The deviation of the scaling factor $E_H/E_D=1.51$ from the harmonic value $\sqrt{m_D/m_H} \approx \sqrt{2} \approx 1.41$ indicates that the force constants for H in PdH are slightly larger than those for D in PdD and well agrees with the earlier estimate[12] of $E_H/E_D=1.49(2)$ for optical vibrations in $PdH_{0.63}$ and $PdD_{0.63}$.

The first fundamental band of optical D vibrations in PdD consists of a strong peak centered at 37 meV with a shoulder toward higher energies extending up to about 65 meV. The second optical H band resulting from multiphonon neutron scattering has a smoother intensity distribution and appears at energies approximately twice the energy of the fundamental band. The third and higher optical bands merge into a rather featureless intensity distribution.

The intensity at energies below 30 meV in the INS spectrum of PdD in Fig. 3 is spurious. It mostly results from one- and two-phonon scattering of neutrons of half the wavelength admixed with the monochromated incoming beam at the IN1-BeF spectrometer. An INS spectrum of PdD with an improved low-energy part is shown in Fig. 4(a). The intensity distribution at $E<30$ meV in this spectrum was constructed using the INS spectrum of PdH measured in Ref. 11 and shown in Fig. 4(b) for comparison. We exploited the fact that the phonon density of states (PDOS) of acoustic vibrations that are only observed in this energy range should be nearly the same for PdH and PdD. This is because the scaling factor E_H/E_D for acoustic vibrations is equal to $\sqrt{(m_{\text{Pd}}+m_D)/(m_{\text{Pd}}+m_H)}$ in the harmonic approximation and its value is very close to unity due to the large mass m_{Pd} $=106.4$ a.u. of the Pd atom. Therefore, we took the acoustic part of the experimental $S(Q,E)$ spectrum of PdH from Ref. 11 and only rescaled it to have the correct intensity relative to the optical part of the spectrum of PdD. The relative intensity of the acoustic and optical parts of the $S(Q,E)$ spectrum of PdD was estimated using the Born-von Kármán model discussed in more detail later in this paper.

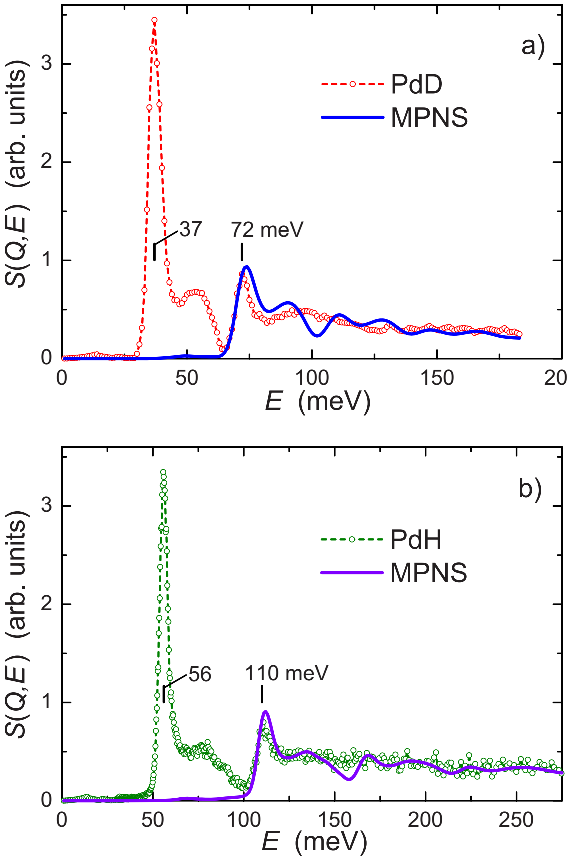

FIG. 4. (Color online) The open circles connected with a dashed line represent the dynamical structure factor $S(Q,E)$ of (a) PdD and (b) PdH (Ref. 11). The spectrum of PdD is a combination of the optical part ($E>30$ meV) determined from the INS measurements of this work and the acoustic part ($E<30$ meV) produced by rescaling the experimental spectrum of PdH (see text). The vertical bars indicate the peak positions in the first and second optical bands. The solid curves in (a) and (b) show multiphonon contributions calculated in a harmonic isotropic approximation.

With the low-energy part of the vibrational spectrum of PdD estimated in this manner, the contribution from multiphonon neutron scattering was calculated in a harmonic isotropic approximation using the iterative technique of Ref. 13. As seen from Fig. 4(a), the calculated multiphonon contribution (thick solid curve) is negligibly small in the range of 30–65 meV of the first optical band and semiquantitatively describes the intensity distribution in the second and higher bands. The remaining discrepancy between the calculated and experimental spectra of the second and higher optical bands in PdD suggests a certain anharmonicity of D vibrations in these bands. To characterize this anharmonicity numerically, note that the peak in the second band is positioned at 72 meV, which is lower by 2 meV than the doubled energy of 37 meV of the peak in the first band.

All said about the $S(Q,E)$ spectrum of PdD shown in Fig. 4(a) is applicable to the spectrum of PdH in Fig. 4(b). The calculated multiphonon contribution to the H vibrations in the first optical band of PdH is very small; the H vibrations in the second and farther optical bands are noticeably anharmonic; the peak in the second band is observed at 110 meV, which is 2 meV lower than twice the energy of 56 meV of the peak in the first band.

B. Spectrum S_H due to the H impurity in PdD

Based on theoretical and experimental results in the literature (see Ref. 6) one could expect that the H impurity in PdD should manifest itself by a peak of defect mode detached from the optical phonon band of the host PdD matrix and located at energies around 70 meV. As seen from Fig. 2, a strong and broad peak centered at about 68 meV is actually observed in the S_H spectrum of the studied $PdD_{1-x}H_x$ samples. In other aspects, the spectrum proved to be much more complex than expected. First, the 68 meV peak had an intensive shoulder toward lower energies with a clear maximum at about 45 meV. Second, the spectrum showed negative scattering intensity at energies in the vicinity of 36 meV. Both features were stable in the appearance and did not noticeably change their shapes, positions, and intensities if calculated with the H concentration in each $PdD_{1-x}H_x$ sample varying within the experimental error of $\delta x = \pm 0.002$.

To ascertain the origin of such an unusual profile of S_H, we have calculated the lattice dynamics for Pd_4D_3H, Pd_8D_7H, $Pd_{16}D_{15}H$, $Pd_{32}D_{31}H$, and PdD crystals ($x=0.25$, 0.125,0.0625, 0.03125, and 0, respectively) using the Born-von Kármán model. The Pd-Pd, Pd-D, and D-D force constants were taken from Ref. 14 that presented this data as results of a coherent neutron-scattering study[15] of the phonon-dispersion relations in a single crystal of $PdD_{0.63}$. The constants for H atoms were set equal to those for D atoms.

In our calculations, we used a primitive unit cell for the NaCl-type structure of the PdD crystal. In the case of the $Pd_ND_{N-1}H$ crystals, the unit cell was cubic or tetragonal and contained one H atom, N atoms of Pd, and $N-1$ atoms of D. Eigenvalues $E^2(j,\vec{q})$ and eigenvectors $\vec{e}_i(j,\vec{q})$ for every atom i in the unit cell and every phonon mode j were calculated for sampling points $\vec{q}$ uniformly distributed over the irreducible part of the Brillouin zone (BZ) and further used to obtain phonon densities of states according to

$$g(j,E) = \int_{\vec{q}\in \mathrm{BZ}} \delta[E - E(j,\vec{q})]d\vec{q} = \int\int_{E(j,\vec{q})=E} \frac{d^2\vec{q}}{|\nabla_{\vec{q}}E(j,\vec{q})|}, \tag{2}$$

where $\vec{q}$ was varied over the BZ. (Hereafter, the eigenvectors are normalized so that $\forall j,\vec{q}: \Sigma_i m_i |\vec{e}_i(j,\vec{q})|^2 = 1$, where m_i is the mass of atom i). To integrate in Eq. (2), we interpolated $E^2(j,\vec{q})$ 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 32,000 for PdD to 1,000–2,000 for the $PdD_{1-x}H_x$ structures.

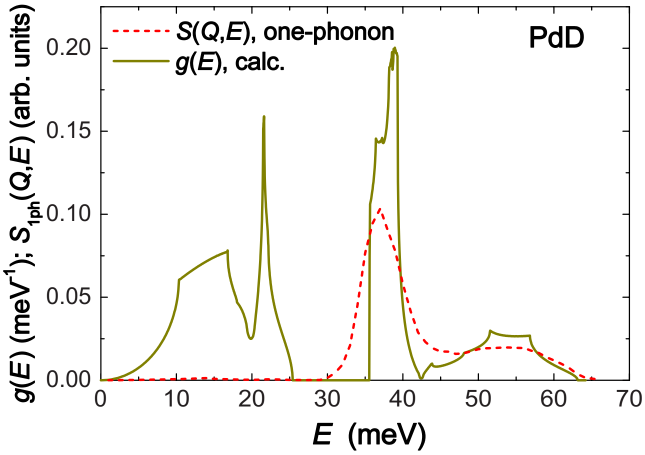

FIG. 5. (Color online) The PDOS $g(E)$ of PdD calculated using 32,000 sampling points in the irreducible part of the BZ (solid curve) and the one-phonon spectrum $S_{1ph}(Q,E)$ produced by subtracting the multiphonon spectrum from the $S(Q,E)$ spectrum of PdD in Fig. 4(a) (dashed curve).

To illustrate the applicability of the Born-von Kármán model with the set of force constants proposed in Refs. 14 and 15, the total phonon density of states of PdD calculated as $g(E)=\Sigma_j g(j,E)$ is shown in Fig. 5. The $g(E)$ spectrum thus obtained coincides with that calculated in Ref. 15 and its optical part semiquantitatively reproduces the intensity distribution in the experimental $S(Q,E)$ spectrum of PdD. The latter suggests that the model should be capable of describing the principal features of the effect of H impurity on this spectrum, too.

The calculated $g(E)$ spectra of the $PdD_{1-x}H_x$ solutions, however, could not be directly compared with the experimental $S(Q,E)$ spectra because of the significantly different cross sections for neutron scattering by H and D atoms.

To calculate the $S(Q,E)$ spectra from the $g(E)$ spectra we did the following. First, a partial generalized phonon density of states, $G_i(E)=\Sigma_j G_i(j,E)$, was computed for each atom in the unit cell using $G_i(j,E)$'s calculated as

$$G_i(j,E) = \int_{\vec{q}\in \mathrm{BZ}} |\vec{e}_i(j,E)|^2 \delta[E - E(j,\vec{q})]d\vec{q} = \int\int_{E(j,\vec{q})=E} \frac{|\vec{e}_i(j,E)|^2 d^2\vec{q}}{|\nabla_{\vec{q}}E(j,\vec{q})|},$$

and normalized so that $\int G_i(E)dE=1$. Second, the computed $G_i(E)$'s were used to calculate the dynamical structure factor $S(Q,E)$ at 0 K according to

$$S(Q,E) = \sum_i S_i(Q,E) = \frac{Q^2}{E}\sum_i \frac{\sigma_i}{m_i}\exp[-2W_i(Q)]G_i(E), \tag{3}$$

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

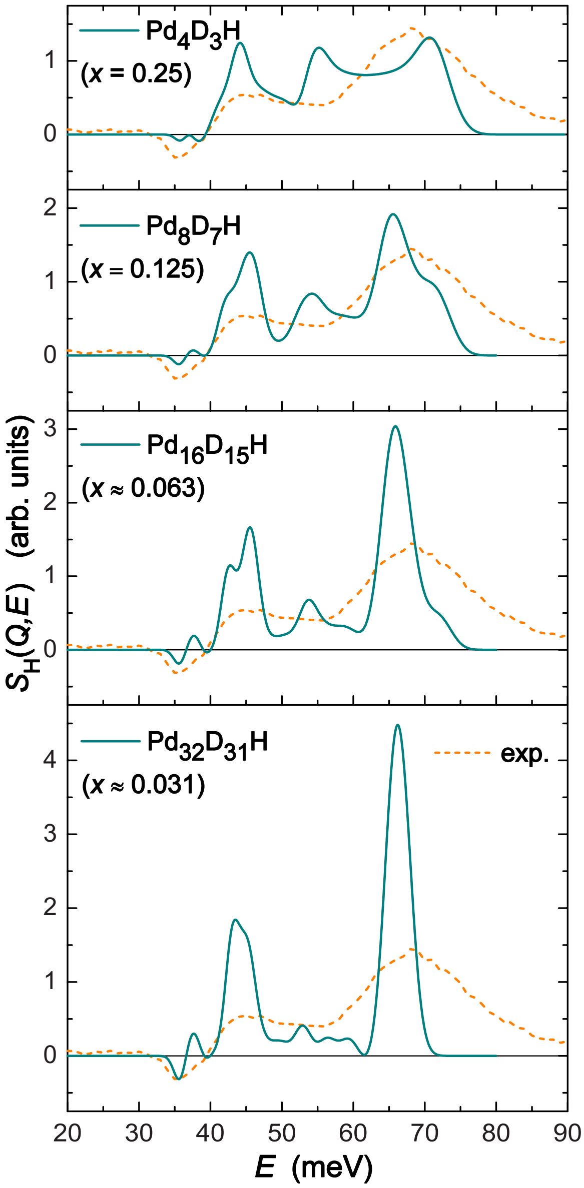

FIG. 6. (Color online) Contributions $S_H(Q,E)$ to the total dynamical structure factor of the solid $PdD_{1-x}H_x$ solutions due to the presence of H impurity. The dashed curves represent the experimental S_H from Fig. 2. The solid curves are results of the model calculations.

$$W_i(Q) = \frac{\hbar^2 Q^2}{4m_i} \int_0^{E\,\max} \frac{G_i(E)dE}{E}$$

is the Debye-Waller factor for atom i.

Finally, using the $S(Q,E)$ spectra calculated for PdD and for each of the four model $PdD_{1-x}H_x$ solutions, the contributions S_H due to the H impurity in PdD were calculated via Eq. (1). The resulting S_H spectra convoluted with the resolution function of the IN1-BeF spectrometer approximated by a Gaussian with FWHM=0.05E are shown in Fig. 6.

As seen from Fig. 6, the calculated S_H spectra are in qualitative agreement with experiment. The calculations reproduce the occurrence of a broad asymmetric peak at energies around 70 meV. The peak has a shoulder toward lower energies and the intensity distribution definitely shows a maximum at energies near 45 meV. The calculations also reproduce the presence of negative scattering intensity in the experimental S_H spectrum at energies in the vicinity of 36 meV.

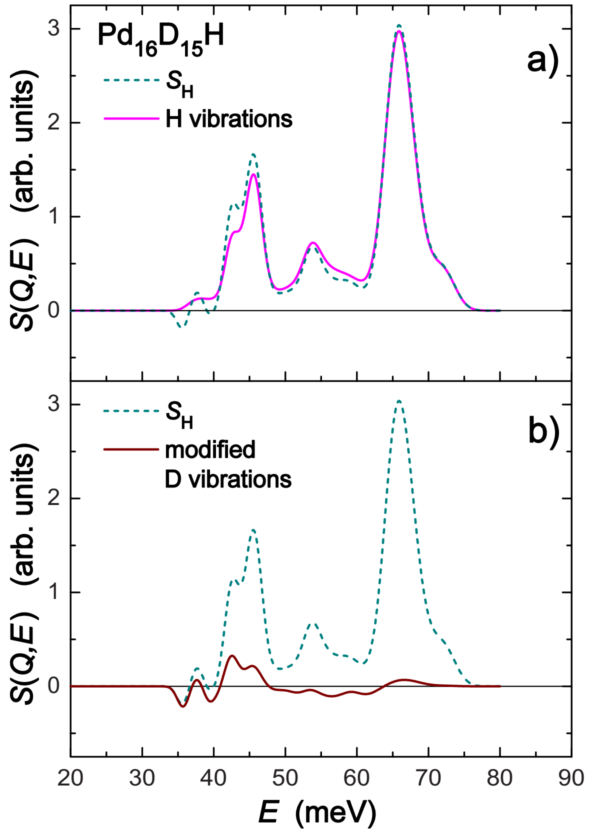

FIG. 7. (Color online) The dashed curve shows the $S_H(Q,E)$ spectrum calculated for the $Pd_{16}D_{15}H$ crystal (x=0.0625). The solid curves represent the contributions to this spectrum from neutron scattering on the H atoms (a) and due to changes in the vibrational spectrum of the D atoms (b).

It was clear enough that neutron scattering from the H atoms alone could not produce negative intensity in the S_H spectrum because the scattering intensities from all atoms were additive. In fact, together with the contribution from the H atoms, S_H should also contain a contribution due to the changes in the neutron scattering from the D atoms resulting from the changes in their vibrational spectrum caused by interactions with the H atoms. Figure 7 shows these two contributions calculated for the $Pd_{16}D_{15}H$ crystal.

Figure 7 illustrates the principal features that are characteristic of the calculated spectra of all four model $PdD_{1-x}H_x$ solutions. The peak at about 70 meV is nearly entirely produced by the H vibrations. As seen from Fig. 6, this peak gets narrower with decreasing H concentration. It splits from the optical D band at $x=1/32$ and should transform to the threefold degenerate local mode when the H concentration tends to zero.

The intensity distribution in Fig. 7(a) in the interval 50–60 meV with a shallow maximum at 55 meV is due to the H-H interactions and represents the incipient optical band

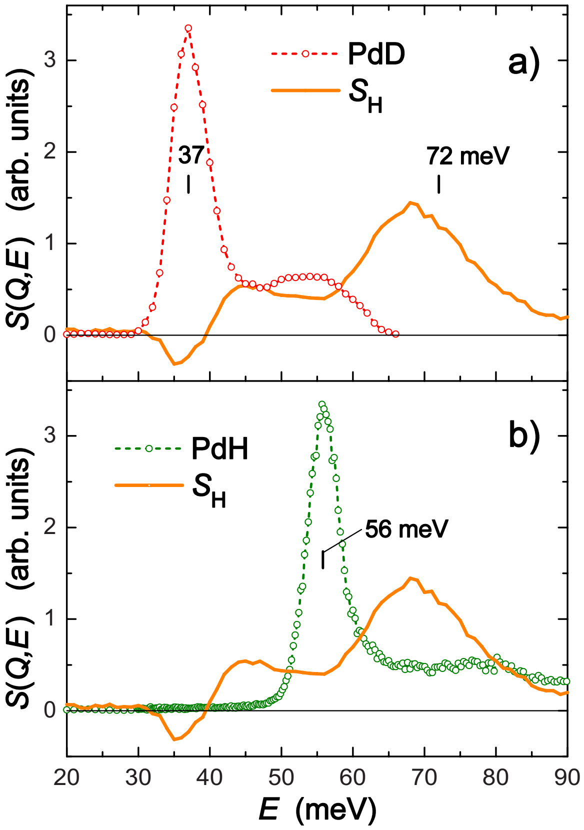

FIG. 8. (Color online) The solid line shows the S_H spectrum calculated by applying Eq. (1) to a pair of experimental $S(Q,E)$ spectra of the $PdD_{1-x}H_x$ samples with $x=0.050$ and 0.091. The circles connected with a dashed line show the one-phonon spectra $S_{1ph}(Q,E)$ of (a) PdD and (b) PdH produced by subtracting the multiphonon contributions from the corresponding $S(Q,E)$ spectra in Fig. 4.

of palladium hydride. As one can see from Fig. 6, the intensity of this band decreases with decreasing hydrogen concentration.

The broad peak at 45 meV originates from covibrations of the H and D atoms caused by H-D interactions. The peak is formed by neutron scattering from both the hydrogen [Fig. 7(a)] and deuterium [Fig. 7(b)] atoms, the contribution from the H atoms being larger due to the larger neutron-scattering cross section σ_H and smaller mass m_H [see Eq. (3)].

The negative scattering intensity at energies near 36 meV—in the range of the main D optical peak—is also caused by the H-D interactions. This is a result of the reduction in the density of states of D vibrations [Fig. 7(b)] due to the increase in the energy of vibrations of those D atoms that were located near the atoms of H impurity and were partly involved in their high-frequency motions.

Discussing the experimental S_H spectrum of the $PdD_{1-x}H_x$ samples, it is more illustrative to superimpose it on the experimental one-phonon spectra $S_{1ph}(Q,E)$ of PdD and PdH as shown in Fig. 8.

In view of the results of the computer modeling, the broad peak in the experimental S_H with the maximum at an energy of about 68 meV is mostly formed by modes of H vibrations located above the upper cutoff of the optical band in PdD [Fig. 8(a)]. The low-energy shoulder of this peak in the range of 50–60 meV is partly formed by H vibrations resulting from H-H interactions and resembling optical vibrations in PdH that have the maximum density of states at 56 meV [Fig. 8(b)].

The N-shaped dependence of S_H in the interval 30–50 meV with the minimum at 36 meV and maximum at 45 meV is caused by interactions between the neighboring D and H atoms. The H-D interactions lead to the formation of a new band of optical covibrations of D and H atoms with energies near 45 meV, right above the main peak at 37 meV in the density of vibrational states of PdD. The vibrational states of D atoms in the new band are mostly borrowed from this very peak and the resulting deficit in its intensity manifests itself by the negative values of S_H with the minimum at 36 meV. As the strength of the H-D interactions does not virtually depend on the H concentration if the concentration is small, the N-shaped feature cannot vanish with decreasing hydrogen content and, as the computer simulations show, this feature even gets sharper (Fig. 7).

The position E_H of the H peak located above the D optical band can accurately be obtained in the framework of a simple theory[7] for the local vibrations of isotropic light-atom mass defect in a NaCl-type crystal structure

$$\int_0^\infty \frac{G(E)dE}{E_H^2 - E^2} = \frac{1}{\varepsilon E_H^2}, \tag{4}$$

where $G(E)$ is the generalized density of vibrational states of D atoms in the host PdD crystal normalized so that $\int G(E)dE=1$ and $\varepsilon=(m_D-m_H)/m_D \approx 1/2$. The $G(E)$ spectrum can be calculated as

$$G(E) = \frac{E}{Q^2} S_{1ph}(Q,E)\exp[2W_D(Q)],$$

using the experimental $S_{1ph}(Q,E)$ of PdD shown in Fig. 5 and the Debye-Waller factor $W_D(Q)$ determined while calculating the multiphonon contribution to the S_{PdD} spectrum. Substituting this $G(E)$ in Eq. (4) gives $E_H=68.5$ meV in good agreement with the experimental $E_H \approx 68$ meV.

With the $G(E)$ spectrum of PdD calculated in the Born-von Kármán model, the solution of Eq. (4) is $E_H=66.5$ meV, which actually coincides with the position $E_H=66.3$ meV of the detached H peak in the $S(Q,E)$ spectrum of $Pd_{32}D_{31}H$ calculated in the same model (solid curve at the bottom of Fig. 6).

The simple theory, therefore, well predicts the frequency of the local H mode detached from the optical band of the host phase of PdD. Our INS investigation of the $PdD_{1-x}H_x$ system showed that a light H impurity can also produce changes in the intensity distribution inside the host phonon band of deuterides that are not small, having the same order of magnitude as the integral intensity of the peak of local H vibrations. The computer simulations demonstrated that these changes stem from the H-D interactions.

IV. CONCLUSIONS

Due to experimental limitations, previous studies on the effect of a light impurity on the vibrational spectrum of the host phase were mainly aimed at determining the frequency of the defect modes arising outside the vibrational band of the host atoms. Along with a peak of such modes, our INS investigation of solid hydrogen solutions in stoichiometric palladium deuteride revealed profound changes inside the optical D band due to covibrations of heavy D atoms and light H atoms. These covibrations form a band located above the main peak in the optical band of PdD. The vibrational states of D atoms in this new band are mostly borrowed from the main peak that considerably decreases its intensity. The integral intensity of the new band is comparable with that of the peak of defect H modes.

The observed changes inside the optical D band are caused by interactions of H atoms with the neighboring D atoms, so the strength of this interaction is nearly independent of the H concentration, when the concentration is low. Therefore, even in infinitely diluted H solutions in PdD, the magnitude of changes induced by the H impurity inside the optical D band should remain comparable with the intensity of the defect, local modes of H vibrations. We think that strong changes inside the vibrational band of the host phase due to a light impurity should be intrinsic to many systems.

ACKNOWLEDGMENTS

This work was supported by Grants No. 05-02-17733 and No. 08-02-00846 from RFBR, and by the Program “Physics of Strongly Compressed Matter” of RAS. A.I.K. wishes to acknowledge ORNL/NSSD that is managed by UT-Battelle, LLC, for DOE under Contract No. DE-AC05-00OR22725.

---

*kuz@issp.ac.ru

[1] I. S. Anderson, N. F. Berk, J. J. Rush, and T. J. Udovic, Phys. Rev. B **37**, 4358 (1988).

[2] T. J. Udovic, J. J. Rush, and I. S. Anderson, Phys. Rev. B **50**, 15739 (1994).

[3] P. Vorderwisch, S. Hautecler, and J. Eckert, J. Alloys Compd. **253-254**, 252 (1997).

[4] T. J. Udovic, J. J. Rush, Q. Huang, and I. S. Anderson, J. Alloys Compd. **253-254**, 241 (1997).

[5] A. I. Kolesnikov, V. E. Antonov, Yu. E. Markushkin, I. Natkaniec, and M. K. Sakharov, Phys. Rev. B **76**, 064302 (2007).

[6] J. J. Rush, J. M. Rowe, and D. Richter, Phys. Rev. B **31**, 6102 (1985).

[7] A. A. Maradudin, Rep. Prog. Phys. **28**, 331 (1965).

[8] V. E. Antonov, J. Alloys Compd. **330-332**, 110 (2002).

[9] J. E. Schirber and B. Morosin, Phys. Rev. B **12**, 117 (1975).

[10] E. Wicke and H. Brodowsky, in *Hydrogen in Metals*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), Vol. 2, p. 73.

[11] D. K. Ross, V. E. Antonov, E. L. Bokhenkov, A. I. Kolesnikov, E. G. Ponyatovsky, and J. Tomkinson, Phys. Rev. B **58**, 2591 (1998).

[12] J. J. Rush, J. M. Rowe, and D. Richter, Z. Phys. B: Condens. Matter **55**, 283 (1984).

[13] V. E. Antonov, I. T. Belash, A. I. Kolesnikov, J. Mayer, I. Natkaniec, E. G. Ponyatovskii, and V. K. Fedotov, Sov. Phys. Solid State **33**, 87 (1991).

[14] A. Rahman, K. Sköld, C. Pelizari, S. K. Sinha, and H. Flotow, Phys. Rev. B **14**, 3630 (1976).

[15] J. M. Rowe, J. J. Rush, H. G. Smith, M. Mostoller, and H. E. Flotow, Phys. Rev. Lett. **33**, 1297 (1974).