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Isotopic dependence of the frequency of optical vibrations in molybdenum monohydride

Mikhail A. Kuzovnikov[a,b,*], Vladimir E. Antonov[a,c], Thomas Hansen[d], Alexandre S. Ivanov[d], Alexander I. Kolesnikov[e], Valery I. Kulakov[a], Vitaly D. Muzalevsky[a], Stanislav Savvin[d], Marek Tkacz[f]

[a] Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia
[b] Centre for Science at Extreme Conditions and School of Physics and Astronomy, University of Edinburgh, Edinburgh EH9 3FD, United Kingdom
[c] National Research University Higher School of Economics, 20 Myasnitskaya ulitsa, 101000 Moscow, Russia
[d] Institut Laue-Langevin, 71 avenue des Martyrs CS 20156, 38042 Grenoble Cedex 9, France
[e] Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[f] Institute of Physical Chemistry PAS, 44/52 Kasprzaka, 01-224 Warsaw, Poland

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ABSTRACT

It is currently known that three hydrides – PdH_x, MoH_x, and TiH_x – exhibit an inverse isotope effect in superconductivity. Namely, the phase with a heavier hydrogen isotope, deuterium, has a higher critical temperature. Hydrides and deuterides of palladium have intensively been studied both experimentally and theoretically, but the origin of the isotope effect has not been established with certainty. The commonly accepted explanation is that the effect is likely to be due to the strong anharmonicity of the optical hydrogen vibrations, which was considered to be responsible for the large deviation of the ratio of the fundamental optical frequencies $\omega_H/\omega_D = 1.51$ from the harmonic value $\sqrt{2} \approx 1.41$. In the present paper, powder samples of $MoH_{1.1(1)}$ and $MoD_{1.07(3)}$ were synthesized under a hydrogen / deuterium pressure of several gigapascals and studied by inelastic neutron scattering (INS) at ambient pressure and $T = 10$ K. The INS study demonstrated that optical vibrations of H atoms in $MoH_{1.1}$ and D atoms in $MoD_{1.07}$ are harmonic and the ratio of fundamental optical frequencies $\omega_H/\omega_D = 1.44$ is close to the harmonic value $\sqrt{2} \approx 1.41$. This shows that anharmonicity is not a necessary condition for the presence of the inverse isotope effect. The $MoD_{1.07}$ sample was additionally studied by neutron diffraction (ND) at ambient pressure and $T = 100$ K. In agreement with previous ND results for $MoH_{1.2}$, the ND study of $MoD_{1.07}$ showed that deuterium atoms occupied almost all octahedral interstitial sites in its hexagonal close-packed metal lattice and formed a NiAs-type crystal structure with the composition close to MoD. The overstoichiometric composition $MoD_{1.07}$ of the deuteride is likely to result from a small fraction D/Mo ~ 0.07 of deuterium atoms partially occupying the tetrahedral interstices.

1. Introduction

The discovery of superconductivity with the critical temperature $T_c = 203$ K in body centered cubic (*bcc*) H_3S [1] formed under a pressure of about 150 GPa, resulted in a renewed interest in the fundamental properties of metallic hydrides. Recently, a series of new metallic superhydrides was synthesized in diamond anvil cells, and superconductivity was observed at ~215 K and 172 GPa in *bcc*-CaH_6 [2], at ~220 K and ~170 GPa in *bcc*-YH_6 [3,4], at 243 K and 201 GPa in hexagonal close packed (*hcp*) YH_9 [4], and at 250 K and 170 GPa in face centered cubic (*fcc*) LaH_{10} [5,6]. The nearly room critical temperatures of superconductivity resulted from favorable properties of these materials, such as the strong electron-phonon interaction and the presence of high-frequency phonons of optical hydrogen vibrations. The Bardeen-Cooper-Schrieffer (BCS) theory of phonon-mediated superconductivity in a harmonic approximation suggests that the critical temperature should be proportional to these phonon frequencies [7]. Since the frequency of the oscillator decreases with increasing mass, the isotopic substitution of H by heavier D should normally decrease T_c of the hydride.

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[*] Correspondence to: Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia.
E-mail address: kuz@issp.ac.ru (M.A. Kuzovnikov).

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Presently known superconducting hydrides can be classified into three categories depending on the sign of the isotope effect in superconductivity determined experimentally. There is a large group of the hydrides with the normal isotope effect in accord with the theoretical predictions: *bcc*-$H(D)_3S$ [1], *fcc*-$LaH(D)_{10}$ [5], *bcc*-$YH(D)_6$ [3,4], *hcp*-$YH(D)_9$ [4], and *hcp*-$CeH(D)_9$ [8]. One hydride, *cI*16-$Th_4H(D)_{15}$ [9], shows a zero isotope effect. Three hydrides, *fcc*-PdH(D) [10], *fcc*-$TiH(D)_{0.71}$ [11], and *hcp*-MoH(D) [12], exhibit the inverse isotope effect. Among the hydrides of the last group, *fcc*-PdH(D) has been studied most extensively both theoretically and experimentally.

Theoretical considerations suggest that the inverse isotope effect in *fcc*-PdH(D) is likely to originate from the strong anharmonicity of the potential well for H(D) atoms (see [13] and references therein), which manifests itself in a large deviation of the ratio $\omega_H/\omega_D \approx 1.5$ of the fundamental frequencies of optical vibrations in PdH and PdD from the harmonic value $\sqrt{m_D/m_H} \approx \sqrt{2} \approx 1.41$, where m_D and m_H are the atomic masses of D and H. However, we previously studied strongly textured samples of stoichiometric *fcc*-PdH(D) by inelastic neutron scattering (INS) [14,15] and did not observe any detectable anharmonicity and anisotropy in the first (fundamental) band of its optical vibrations, which are supposed to couple to the electron system and enhance superconductivity of palladium hydrides [13,16]. In agreement with theoretical predictions [17,18], the INS spectrum of PdH became strongly anisotropic only at neutron energy transfers of the second and higher optical bands and showed a strong anharmonicity for neutron momentum transfers, ***Q***, directed close to the < 100 > axes, these being the directions from the H atom to the nearest Pd atoms. For other directions of ***Q***, the INS spectrum remained almost harmonic. Averaged over all orientations of ***Q***, the contribution from the anharmonic hydrogen vibrations along the < 100 > directions was small, and the high-energy part of the INS spectrum of a powdered PdH sample (which was also studied in Ref. [14]) exhibited only small deviations from isotropic, harmonic behavior. No anharmonicity and anisotropy was observed in the INS spectra of optical vibrations in powder PdD samples either [15]. Since calculations of the effect of hydrogen on superconductivity of metal hydrides include the summation over all polarizations of hydrogen optical vibrations, this practically excludes a significant contribution from the anharmonicity of these vibrations.

As for the “anharmonic” ratio $\omega_H/\omega_D \approx 1.5$ of the frequencies of optical vibrations in PdH and PdD, it may result from strengthening the H-Pd interaction compared to the D-Pd interaction due to the larger amplitude of zero-point vibrations of the H atoms [19]. Note that this mechanism of the increase in the ω_H/ω_D ratio should not necessarily lead to anharmonicity of the H optical vibrations. In particular, the energy and shape of the first optical peak in the strongly textured PdH sample coincided with those of the powdered PdH sample and did not depend on the direction of the neutron momentum transfer [14]; the energies of the second optical peak in the powdered PdH sample [14,20] and in the powdered PdD sample [15] were well described in an isotropic harmonic approximation; the energies of the first and second optical peaks in the powdered PdH sample almost did not change in heating the sample from 15 to 200 K [20].

The scaling factor ω_H/ω_D was earlier experimentally determined for rather many binary metal hydrides with different crystal structures and different types of chemical bonds, and most hydrides were shown to have $\omega_H/\omega_D < \sqrt{2}$. For example, this factor equals to 1.34 for TaH(D), with H(D) atoms at the tetrahedral (T) interstices of the *bcc* metal lattice [21]; 1.35–1.37 for $AlH(D)_3$ with H(D) atoms between two Al atoms in a distorted primitive simple cubic metal lattice [22]; 1.37 for $YH(D)_2$ (T-sites in the *fcc* lattice) [23]; 1.37 for γ-ZrH(D) (T-sites in the face centered orthorhombic lattice) [24,25]; 1.37–1.41 for $NbH(D)_{0.85}$ (T-sites in the *bcc* lattice) [26]; 1.40 for $LaH(D)_3$ (octahedral (O) and T-sites in the *fcc* lattice) [27]; 1.40 for $UH(D)_3$ (T-sites in the A15-type metal lattice) [28]; 1.41 for LiH(D) (O-sites in the *fcc* lattice) [29]; 1.43 for NiH(D) (O-sites in the *fcc* lattice) [30]. The values of $\omega_H/\omega_D < \sqrt{2}$ are characteristic of the hydrides with “soft” (trumpet-like) anharmonicity of the potential wells for H(D) atoms. Large $\omega_H/\omega_D = 1.49 > \sqrt{2}$ was observed for the second optical peak in the strongly anisotropic and anharmonic INS spectra of *bcc*-$V_2H(D)$ [31], in which H(D) atoms vibrate inside the O-sites with a double-well potential [32].

Among the hydrides studied to date, only palladium hydride combines the harmonicity of the fundamental optical vibrations with the ratio $\omega_H/\omega_D \approx 1.5$ [15,33] considerably exceeding $\sqrt{2}$. It is reasonable to associate the unusual inverse isotope effect in the superconductivity of this hydride with its unusually large value of ω_H/ω_D. Molybdenum hydride is also a superconductor with an inverse isotope effect ($T_c = 0.92$ and 1.11 K for the hydride and deuteride, respectively [12]) and optical INS spectra of a powdered $MoH_{1.2}$ sample showed no anharmonicity [34,35]. In the present paper, we determined the ω_H/ω_D ratio for molybdenum hydride by inelastic neutron scattering in order to find out whether or not a large ω_H/ω_D value is characteristic of superconducting hydrides with the inverse isotope effect. For easier comparison of the INS spectrum of molybdenum deuteride with that of the hydride, we synthesized new samples of both deuteride $MoD_{1.07(3)}$ and hydride $MoH_{1.1(1)}$ and measured them with the present experimental setup.

Similar to many other hydrides of transition metals [36,37] molybdenum hydride and deuteride are not stoichiometric compounds. In particular, a room-temperature X-ray diffraction investigation in a diamond anvil cell at pressures up to 30 GPa showed [38] that an increase in the hydrogen pressure to 4.3 GPa leads to the transformation of *bcc*-Mo metal to *hcp*-MoH_x hydride with $x \approx 1.1$; at higher pressures, the hydrogen content of the hydride gradually increases, reaches $x = 1.35(10)$ at 15 GPa, and stops changing. There are two tetrahedral (T) and one octahedral (O) interstitial sites per each Mo atom available for hydrogen in the *hcp* metal lattice of the hydride, so that the hydrogen content x is related to the site occupancies $w(O)$ and $w(T)$ in the following way: $x = H/Mo = x_{octa} + x_{tetra} = w(O) + 2w(T)$. Presumably [38], hydrogen atoms completely occupied the O-sites, which gave $x_{octa} = 1$, and partially filled the T-sites, so that x_{tetra} grew from $x_{tetra} \approx 0.1$ at 4.3 GPa to $x_{tetra} \approx 0.35$ at 15 GPa. However, the neutron diffraction pattern of a powder sample $MoH_{1.19}$, measured in a metastable state at atmospheric pressure and $T = 120$ K, could only be interpreted as if the hydride composition was $MoH_{0.95(5)}$ and hydrogen atoms occupied the O-sites only [39]. Using a structural model with H atoms partially occupying the T-sites and a model with vacancies in the metal lattice, which could explain the “over-stoichiometric” hydrogen content $x > 1$ of the hydride, significantly worsened the agreement between calculation and experiment. To check the reproducibility of this puzzling result, we performed a neutron diffraction investigation of the $MoD_{1.07}$ sample in the present work.

2. Material and methods

Single-phase samples $MoD_{1.07(3)}$ weighing 99 mg and $MoH_{1.1(1)}$ weighing 1114 mg were collected from several separately synthesized samples made of high-purity single-crystal molybdenum foil 0.2 mm thick with the electrical resistance ratio $R_{300\,K}/R_{4.2\,K} \approx 1000$ loaded with deuterium (hydrogen) in high-pressure chambers of the “Toroid” type [40] using AlD_3 (AlH_3) as an internal source of the deuterium (hydrogen) gas [36]. The synthesis conditions were 7.4 GPa, 300 °C, 24 h for the deuterides and 5 GPa, 350 °C, 24 h for the hydrides (in the latter case, a high-pressure chamber with a larger working volume was used). After the synthesis was completed, the

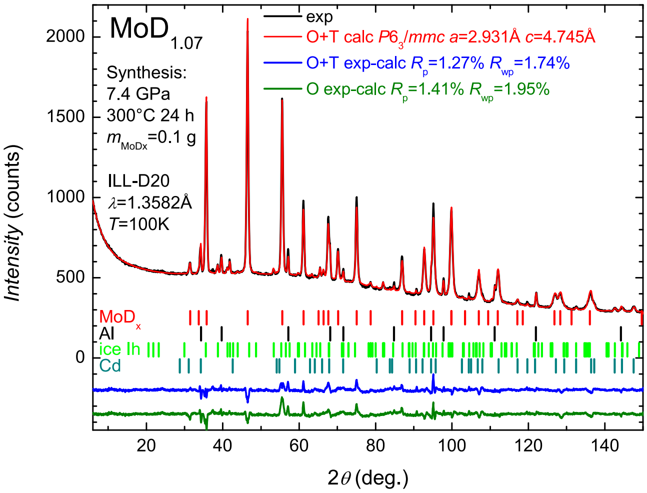

Fig. 1. Neutron powder diffraction pattern of the $MoD_{1.07}$ sample (black curve) measured at $T = 100$ K with the D20 instrument at ILL, and the results of its Rietveld analysis using the structural model with deuterium atoms occupying O+T sites (red curve). The two bottom curves show the refinement residuals for this structural model (blue curve) and for an alternative model with D atoms only at the O sites (olive curve). The minor contributions from the aluminum sample capsule, ice, and cadmium mask were accounted for in both Rietveld refinements using the same set of refinable parameters. The refined structural parameters for the main $MoD_{1.07}$ phase are listed in Table 1.

sample was rapidly cooled (quenched) together with the chamber to the liquid N_2 temperature; the pressure was released; the chamber was disassembled under liquid nitrogen; the sample was recovered from the chamber and further stored in liquid nitrogen in order to prevent deuterium (hydrogen) losses. These precautions were necessary, because at ambient pressure molybdenum deuteride and hydride decompose when heated above −50 °C [12].

Each quenched sample was then examined by X-ray diffraction at 85 K to ensure that it was a single-phase *hcp* molybdenum deuteride (hydride), and a small piece of the sample (a few milligrams) was also analyzed by hot extraction to verify that its deuterium (hydrogen) content is close to $x = 1.1$; the hot extraction method is described elsewhere [41]. The deuterated and hydrogenated samples were brittle. Prior to the neutron scattering experiments, the $MoD_{1.07(3)}$ and $MoH_{1.1(1)}$ samples collected from these deuterides and hydrides were ground in an agate mortar under liquid nitrogen to reduce texture effects.

Regretfully, the AlD_3 compound used to synthesize molybdenum deuteride was noticeably contaminated with protium and the sample of molybdenum deuteride proved to be contaminated with protium, too. The protium concentration in this sample could roughly be estimated as $H/(D+H) = 0.07$, based on the intensity of the local (defect) mode of hydrogen vibrations in the INS spectrum (see Section 3.2). For brevity, we will continue to refer to the deuterated sample as $MoD_{1.07}$.

The $MoD_{1.07}$ and $MoH_{1.1}$ samples were studied by inelastic neutron scattering at $T = 10$ K with the IN1-Lagrange inverted geometry spectrometer [42] installed at the hot source of the high-flux reactor at the Institute Laue-Langevin in Grenoble [43]. A background from the cryostat without the samples, but with the sample holder made of aluminum foil and the water ice condensed on it while loading, was measured separately under the same conditions and subtracted from the experimental INS spectra. The resulting spectra were normalized to the neutron flux at the sample. More details on the neutron scattering experiments can be found elsewhere [44].

The $MoD_{1.07}$ sample was studied by neutron diffraction at $T = 100$ K with the high-luminosity D20 diffractometer at ILL [45,46]. While still in liquid nitrogen, the powdered $MoD_{1.07}$ sample was wrapped in thin aluminum foil and placed into a standard vanadium holder with an inner diameter of 5 mm. Unwanted parts of the sample holder were masked with cadmium foil, which produced some weak sharp peaks at large angles of 2θ > 140°. The data acquisition time was 10 h. Rietveld refinements were done with the FULLPROF 7.00 program [47]. The neutron wavelength and detector zero-shifts were determined from a Rietveld analysis of the diffraction pattern of a $Na_2Ca_3Al_2F_{14}$ standard measured separately.

3. Results and discussion

3.1. Neutron diffraction

Fig. 1 shows the neutron powder diffraction pattern of our $MoD_{1.07}$ sample. The results of the Rietveld analysis of this ND pattern using structural models with deuterium at O-sites only and at both O+T sites are shown in Table I. The residuals for these two models are plotted in Fig. 1 by the olive and blue curves, respectively.

Due to the heavy contamination of the sample with protium, the ND results can only be considered semi-quantitative. In particular, the protium contamination leads to an effective reduction in the calculated occupation factor for D atoms by $w_{eff} = 1 + \frac{\mathrm{H}}{\mathrm{D+H}}\left(\frac{b_{\mathrm{H}}}{b_{\mathrm{D}}} - 1\right)$, where $b_H = -3.74$ fm and $b_D = 6.67$ fm are the amplitudes of neutron scattering by H and D atoms, respectively. Based on the total content (D+H)/Mo = 1.07 of hydrogen isotopes of the deuterated sample determined with the thermal desorption method, its protium contamination can roughly be estimated as $\frac{\mathrm{H}}{\mathrm{D+H}} = \left(\frac{w(\mathrm{O}) + 2w(\mathrm{T})}{(\mathrm{D+H})/\mathrm{Mo}} - 1\right)/\left(\frac{b_{\mathrm{H}}}{b_{\mathrm{D}}} - 1\right)$, where w(O) and w(T) are the refined occupancies presented in Table 1. For the O model with $w(\mathrm{O}) = 0.88$ and $w(\mathrm{T}) = 0$ and for the O+T model with $w(\mathrm{O}) = 0.83$ and $w(\mathrm{T}) = 0.04$, this equation gives virtually the same values of $H/(D+H) = 0.11(3)$ and $0.10(3)$, respectively. These values are in reasonable agreement with a more accurate INS-based estimate of $H/(D+H)_{octa} = 0.07(2)$ for the occupancy of the O-sites (see Section 3.2).

If the O model is true, this suggests that the “overstoichiometric” compositions $x > 1$ are due to the vacancies in the molybdenum lattice. If the O+T model is correct, the "overstoichiometric" deuterium and hydrogen atoms partially occupy the T-sites as

Table I

Refined parameters of the O and O+T structural models for molybdenum deuteride. Both refinements were carried out with the same set of refinable parameters, which included the profile functions, instrumental parameters, background, and absorption correction. The refinement residuals for each model are shown at the bottom of Fig. 1. Both model structures belong to the space group $P6_3/mmc$ (No. 194), and their refined lattice parameters $a = 2.931(4)$ Å; $c = 4.745(6)$ Å agree with previous results [12]. A CIF file for the O+T model can be found in the Supplementary Materials.

Model	Atom	Wyckoff position	*x*	*y*	*z*	*w*	U_{iso}, Å^2	R_p, %	R_{wp},%	R_{exp}, %	χ^2
O-sites only	Mo	2c	1/3	2/3	1/4	1	0.006(2)	1.41	1.95	0.59	11.0
	D(octa)	2a	0	0	0	0.88(2)	0.020(1)				
O+T sites	Mo	2c	1/3	2/3	1/4	1	0.007(1)	1.27	1.74		8.7
	D(octa)	2a	0	0	0	0.83(2)	0.021(1)				
	D(tetra)	4f	1/3	2/3	0.66(1)	0.04(1)	0.021(1)				

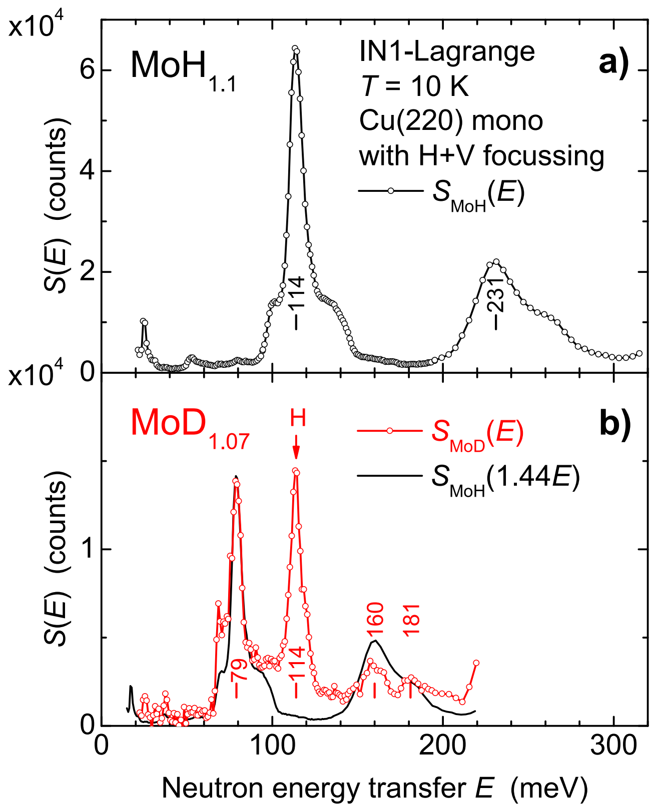

Fig. 2. Top: the dynamical structure factor $S(E)$ of the $MoH_{1.1}$ sample as a function of the neutron energy loss E (black curve). The vertical ticks show the positions of the experimental peaks. Bottom: $S(E)$ for the $MoD_{1.07}$ sample (red curve), experimental peak positions (red ticks with numbers) and the INS spectrum of $MoH_{1.1}$ from the top panel, scaled down by a factor of 1.44 along the energy axis (black curve). The peak at 114 meV marked with “H” is the local (defect) mode of protium impurity in the O-sites of the hcp metal lattice of $MoD_{1.07}$.

conjectured in Ref. [38]. The latter is more likely, because the inclusion of the T-site occupancy in the refinement led to a small but plausible decrease in the R-factors (see Table 1). The puzzling conclusion of the neutron diffraction investigation [39] that the powder $MoH_{1.19}$ sample contained $x = 0.95(5)$ of hydrogen and all this hydrogen occupied only O-sites was probably the result of an unfortunate combination of some negative factors such as the anomalously large amplitude of incoherent neutron scattering by H atoms.

Note in this regard that partial T-site occupancy in the hydrides of group VI-X transition metals was previously directly observed only in *fcc*-FeD_x [48] and *fcc*-PdD_x [49,50] using *in situ* neutron diffraction at high pressures and temperatures. However, the T-sites filling in those materials was temperature-induced via the Boltzmann mechanism, whereas in molybdenum hydrides and deuterides, the filling is purely pressure-induced.

The O+T model considered above assumes the same H/D ratio and a random distribution of D and H atoms over the O- and T-sites. To assess the possibility of preferential T-site occupancy by D or H atoms, we performed two additional refinements using O_{D+H}+T_D and O_{D+H}+T_H models, in which the T-sites were filled only with D and only with H atoms, respectively. In both models, the O-sites were completely filled by a mixture of D and H atoms with the occupancies $w_H(O) = 0.07$ and $w_D(O) = 0.93$ corresponding to the INS-based estimate $H/(D+H)_{octa} = 0.07$. The occupancy of the T-sites was fixed at $w(T) = 0.035$ in accordance with the sample composition $(H+D)_{octa+tetra}/Mo = 1.07$ determined by thermal desorption analysis.

Using the O_{D+H}+T_H model led to a significant deterioration of the fit quality compared to the original O+T model. Thus, the T-sites in hcp-$MoD_{1.07}$ could not be filled exclusively by H atoms. Filling these sites exclusively with D atoms in the O_{D+H}+T_D model resulted in approximately the same fit quality as in the O+T model. That is, the simple O+T model with the same ratio H/(D+H) for the O- and T-sites is quite adequate for the studied sample of hcp-$MoD_{1.07}$.

3.2. Inelastic neutron scattering

The INS spectra of the $MoH_{1.1}$ and $MoD_{1.07}$ samples measured at $T = 10$ K with the IN1-Lagrange neutron spectrometer are shown at the top and bottom of Fig. 2 with the black and red curves, respectively. The background from the cryostat and aluminum sample holder is subtracted, and the spectra are normalized to the neutron flux.

In agreement with the previous results [34], the fundamental band of optical hydrogen vibrations in the O-sites of the *hcp* metal lattice of $MoH_{1.1}$ consists of an intense peak at $E = 114$ meV asymmetrically broadened due to the H-H interaction. The vibrations of the H atom in the O-site along the z-axis and in the x,y-plane have the same frequency. This is typical of monohydrides of d-metals with close-packed crystal lattices, in which hydrogen atoms are located exactly at the centers of the O-sites [51]. The high-energy shoulder of the 114 meV peak originates from the H-H interaction between the nearest-neighbor atoms in the z-direction.

In the $S(E)$ spectrum of $MoH_{1.1}$, the scattering intensity at energies below 60 meV is mostly spurious and results from the neutrons scattered elastically by the sample and then inelastically by the beryllium filter, as well as from minor contamination of the incoming neutron beam with λ/2-neutrons [52]. Nevertheless, this part of the experimental spectrum is also useful, as it clearly shows the absence of the peak at $E = 29$ meV characteristic of the $J = 1 \rightarrow J = 2$ transition in molecular H_2 (the sample was rapidly cooled from the liquid N_2 temperature down to 10 K at the beginning of the INS experiment and therefore the molecular hydrogen, if existed, should have contained a considerable fraction of H_2 molecules in the non-equilibrium ortho-state with $J = 1$). The absence of molecular hydrogen in our $MoH_{1.1}$ sample indicates that it is unlikely that previous neutron diffraction failed to reveal the “overstoichiometric” hydrogen in the quenched $MoH_{1.19}$ sample [39], because this hydrogen was less tightly bound to the metal lattice and released from the hydride and formed bubbles inside the sample before the ND measurement at ambient pressure (similar effect was, for example, observed in the Al-H solid solutions [53,54]). Thus, of the three possible explanations for the overstoichiometric composition of molybdenum monohydride considered in Sections 3.1 and 3.2 (partial filling of the T-sites along with the complete filling of the O-sites; H atoms in the O-sites of the metal lattice with vacancies; molecular H_2 trapped in macropores of the sample) the first one is most likely.

However, the INS study provided no reliable evidence of the occupancy of T-sites in the $MoH_{1.1}$ sample. In particular, an extrapolation of the fundamental frequency of hydrogen optical vibrations at the T-sites in hypothetical *hcp*-MoH_2, predicted by *ab initio* calculations [55], to the lattice parameters of $MoH_{1.1}$ gave a broad peak at ~200 meV. As seen from Fig. 2(a), near this energy there is neither a peak, nor a hump, nor any other feature, which could be attributed to the H vibrations at the T-sites. In further analysis of the INS spectrum of molybdenum hydride we assumed that the intensity $S_{MoH}(E)$ in the range 0–180 meV is entirely due to neutron scattering by H atoms occupying the O-sites.

In order to describe the scattering intensity $S_{MoH}(E)$ of the second optical band of $MoH_{1.1}$ with a peak at 231 meV and to estimate the contribution of the multiple phonon scattering to the first (fundamental) band, we calculated the spectrum of multiphonon scattering by MoH in the harmonic isotropic approximation applying an iterative model-independent technique [56]. This technique uses the

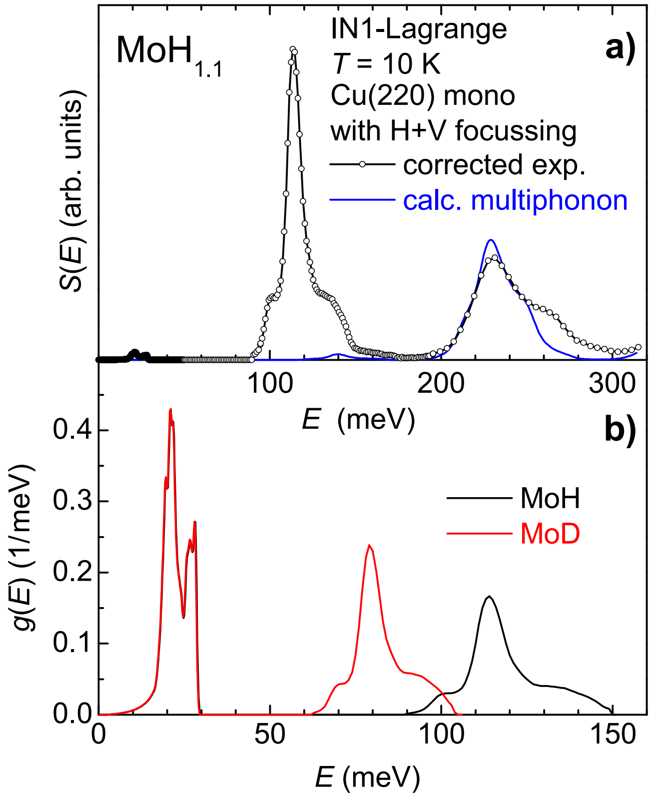

Fig. 3. Top: the corrected dynamical structure factor $S(E)$ of $MoH_{1.1}$ (black curve) and simulated multiphonon contribution to $S(E)$ (blue curve). Bottom: phonon densities of states $g(E)$ for $MoH_{1.1}$ (black) and $MoD_{1.07}$ (red).

distribution of the experimental INS intensity over the entire energy range of the one-phonon acoustic and optical vibrational bands from $E = 0$ to the maximum one-phonon energy equal to ~150 meV for $MoH_{1.1}$ (see Fig. 2(a)). The calculations were carried out with a "corrected" experimental spectrum $S_{MoH}(E)$, in which the spurious scattering intensity at $E < 90$ meV was replaced by a properly normalized acoustic part calculated with Density Functional Theory (DFT) using a procedure described elsewhere [44].

The corrected $S_{MoH}(E)$ and calculated multiphonon contribution are shown in Fig. 3(a) with the open black circles and with the solid blue curve, respectively. As seen from the figure, the multiphonon calculation in the harmonic isotropic approximation reproduces the position of the experimental two-phonon peak at 231 meV very well. This indicates the absence of a noticeable anharmonicity in the INS spectrum of the powdered $MoH_{1.1}$ sample in the energy range of the first and second bands of optical vibrations of H atoms at the O-sites. The excess intensity in the 250–300 meV range, which is not reproduced by our calculation, may result from the neglected vibrations of the H atoms at the T-sites.

The experimental INS spectrum $S_{MoD}(E)$ of the $MoD_{1.07}$ sample is presented in Fig. 2(b) by the open red circles connected with a red curve. Except for the peak of the local (defect) H-impurity mode at 114 meV, the fundamental region of $S_{MoD}(E)$ can be reasonably well approximated by the $S_{MoH}(E)$ spectrum of $MoH_{1.1}$, if the latter is scaled down by a factor of 1.44 along the energy axis, as shown by the black curve. This scaling factor is close to the harmonic value $\omega_H/\omega_D = \sqrt{2} \approx 1.41$, which suggests that the potential wells for H and D atoms at the O-sites in *hcp*-MoH(D) are harmonic and nearly identical. Another sign of the harmonic shape of potential wells for D atoms is that the two-phonon peak in $S_{MoD}(E)$ is observed at 160 meV, which is approximately twice the energy of the fundamental peak positioned at 79 meV (see Fig. 2(b)). The close similarity of the potential wells for H and D atoms in $MoH_{1.1}$ and $MoD_{1.07}$ indicates the absence of noticeable differences in the force constants that determine the spectra of optical vibrations of these atoms.

A weak peak in the $S_{MoD}(E)$ spectrum at 181 meV probably has the same origin as the excess intensity at 250–300 meV in the $S_{MoH}(E)$ spectrum of $MoH_{1.1}$ (Fig. 3(a)). In particular, the 181 meV peak could result from vibrations of D atoms in the T-sites.

To summarize, both molybdenum and palladium hydride are superconductors with an inverse isotope effect and both demonstrate predominantly harmonic behavior of optical hydrogen vibrations. At the same time, as shown in the present paper, the force constants for H and D atoms in, correspondingly, molybdenum hydride and deuteride do not practically differ from each other, whereas the differences between the analog force constants in palladium hydride and deuteride are anomalously large [14,15]. Neutron studies of molybdenum hydride and deuteride, therefore, lead to the conclusion that neither the anharmonicity of the optical vibrations of hydrogen, nor the strong difference in the force constants for the vibrations of H and D atoms is necessary for the appearance of the inverse isotope effect in superconductivity of metal hydrides.

The protium contamination of our sample of molybdenum deuteride can roughly be estimated as H/(D+H) = 0.07(2) based on the intensity of the local (defect) mode of hydrogen vibrations at 114 meV. This result does not contradict the diffraction-based estimate of H/(D+H) = 0.10(3) (see Section 3.1) and is slightly more accurate.

To obtain the phonon density of states $g(E)$ of molybdenum hydride shown in Fig. 3(b) by the black curve, the corrected $S(E)$ spectrum and the calculated multiphonon contribution to it shown in Fig. 3(a) were transformed to the almost spectrometer-independent, generalized vibrational density of states $G(E)$ according to:

$$G(E) = \frac{S(E)E}{Q^2[n(E,T)+1]}\exp(<u^2>Q^2),$$

where Q is the neutron momentum transfer, $n(E,T)$ is the Bose factor, $\exp(<u^2>Q^2)$ is the Debye-Waller factor, and $T = 10$ K is the temperature of the sample in the INS experiment. Subtracting the multiphonon $G(E)$ spectrum from the experimental one gave the one-phonon $G_{1st}(E)$ spectrum, which was further converted to the phonon density of states $g(E)$ by normalizing the well-separated acoustic and optical parts of $G(E)$ to 3 states each. The Debye-Waller factor was estimated in a self-consistent way using the relation $<u^2>Q^2 = \frac{\hbar^2 Q^2}{2m_n}\int\frac{G_{1st}(E)}{E}dE/\int G_{1st}(E)dE$.

Using the scaling factor $\omega_H/\omega_D = 1.44$ for the optical part of the phonon spectrum of $MoH_{1.1}$ and the factor $\omega_H/\omega_D = \sqrt{(m_{Mo}+m_D)/(m_{Mo}+m_H)} \approx 1.005$ for its acoustic part, we also constructed the phonon density of states of $MoD_{1.07}$ shown by the red curve in Fig. 3(b). The dependences $g(E)$ thus calculated are presented in numerical format in files g_MoH.DAT and g_MoD.DAT in the Supplementary Material and correspond to the stoichiometric compositions MoH and MoD of the molybdenum hydride and deuteride.

The heat capacities $C_V(T)$ of MoH and MoD at constant volume were also calculated at temperatures $0 \le T \le 1000$ K using the equation

$$C_V(T) = R\int\left(\frac{E}{k_B T}\right)^2 g(E)n(E,T)[n(E,T)+1]\,dE,$$

where R is the universal gas constant and k_B is the Boltzmann constant. Results of the calculation are presented in Fig.1S and files CV_MoH.DAT and CV_MoD.DAT in the Supplementary Material.

4. Conclusions

Massive powder samples of molybdenum hydride MoH$_{1.1(1)}$ and deuteride MoD$_{1.07(3)}$ were synthesized under high pressures and elevated temperatures and studied by neutron diffraction and inelastic neutron scattering in a metastable state at ambient pressure and low temperature. In agreement with the previous results for molybdenum hydride [39], neutron diffraction showed that deuterium atoms occupy most of the octahedral (O) interstitial sites in the *hcp* metal lattice of the MoD$_{1.07}$ deuteride. Inelastic neutron scattering demonstrated that optical vibrations of H and D atoms in the O-sites are harmonic and that the ratio of fundamental optical frequencies $\omega_H/\omega_D = 1.44$ is also close to the harmonic value $\sqrt{2} \approx 1.41$. That is, the H and D atoms vibrate in virtually the same harmonic potential well. This result is rather unexpected because it precludes from any simple explanation of the inverse isotope effect in superconductivity of molybdenum hydride. The currently available *ab-initio* calculations [57] also failed to determine the correct sign of the isotope effect for *hcp*-MoH(D).

It is worth noting in this connection that out of a wide variety of metal hydrides synthesized and studied to date, only three (those of palladium [10], molybdenum [12], and titanium [11]) turned out to be superconductors with the inverse isotope effect. Palladium hydride has been studied in detail for many years, and its inverse isotope effect was finally attributed to the anomalously strong anharmonicity of the optical hydrogen vibrations [13]. However, this explanation contradicts the results of earlier INS studies [14,15], which showed no detectable anharmonicity in the fundamental band of optical vibrations in stoichiometric fcc-PdH(D).

Thus, the reasons for the inverse isotope effect in both molybdenum and palladium hydride still remain a mystery to be solved.

CRediT authorship contribution statement

Mikhail A. Kuzovnikov: Investigation, Writing – original draft. **Vladimir E. Antonov:** Investigation, Writing – review & editing. **Thomas Hansen:** Investigation. **Alexandre S. Ivanov:** Investigation. **Alexander I. Kolesnikov:** Formal analysis. **Valery I. Kulakov:** Investigation. **Vitaly D. Muzalevsky:** Investigation. **Stanislav Savvin:** Investigation. **Marek Tkacz:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.162299.

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