An x-ray study of palladium hydrides up to 100 GPa: Synthesis and isotopic effects

Bastien Guigue, Grégory Geneste, Brigitte C. Leridon, Paul Loubeyre

► To cite this version:

Bastien Guigue, Grégory Geneste, Brigitte C. Leridon, Paul Loubeyre. An x-ray study of palladium hydrides up to 100 GPa: Synthesis and isotopic effects. *Journal of Applied Physics*, 2020, 127 (7), pp.075901. 10.1063/1.5138697 . hal-03024503

HAL Id: hal-03024503

<https://hal.science/hal-03024503>

Submitted on 11 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

An x-ray study of palladium hydrides up to 100 GPa: Synthesis and isotopic effects.

Bastien Guigue,^{1,2} Grégory Geneste,² Brigitte Leridon,¹ and Paul Loubeyre^{2, a)}

¹⁾LPEM, ESPCI Paris, PSL Research University, CNRS, Sorbonne Université, 75005 Paris, France

²⁾CEA, DAM, DIF, F-91297 Arpajon, France

(Dated: 10 December 2020)

The stable forms of palladium hydrides up to 100 GPa were investigated using the direct reaction of palladium with hydrogen (deuterium) in a laser-heated diamond anvil cell. The structure and volume of PdH(D)_x were measured using synchrotron x-ray diffraction. The Pd atoms remain on a *fcc* lattice. The stoichiometry of the hydride is inferred from the volume expansion due to the hydrogen solubility in the Pd lattice. No evidence for hydrogen to palladium ratio greater than 1 is observed for both isotopes. An inverse isotope effect on the formation enthalpy of the stoichiometric Pd hydride is disclosed by measuring the equilibrium formation pressure of PdH and of PdD, 1.9 GPa and 2.7 GPa respectively. An isotopic shift between the compression curves of PdH and of PdD is also measured, in good agreement with *ab initio* calculations quantifying the contribution of the hydrogen zero-point vibrational energy.

I. INTRODUCTION

PdH is a prototypical metallic hydride. Since its discovery in 1866¹, it has been extensively studied for its unusual properties and its applications. PdH is probably the best known superconducting hydride. Incorporation of hydrogen in the Pd lattice induces superconductivity, with a critical temperature (T_C) as high as 9 K for PdH². A peculiar aspect of the PdH superconductivity is the existence of an inverse isotope effect, with a T_C of 11 K in PdD³. Only recently, the explanation of this effect was quantitatively given by including anharmonic phonons contributions⁴. Palladium is one of the few elements that readily absorb hydrogen, forming PdH_x with $x \sim 0.7$ under 1 atm pressure⁵, and so it is used as a safe storage of large tritium amounts in the form of Pd-tritides⁶.

The absorption of hydrogen by palladium forms two distinct phases: a solid solution α -phase at lower hydrogen concentrations and a lattice expanded β -phase at higher hydrogen concentrations⁷. In the P-T-x space the boundary line between the α and β phases ends with a critical point, reported to be (2.4 MPa, 273°C) in the Pd-H₂ system, and (30.9 MPa, 283°C) in the Pd-D₂ system⁷. For both the α and β phases, hydrogen is assumed to occupy octahedral (O) interstitial sites of the Pd *fcc* lattice. While for $x > 0.7$ both neutron experiments on metastable samples and first principle calculations indicate that only the (O) sites are occupied^{4,8,9}, on the other hand neutron measurements showed a significant tetrahedral (T) interstitial sites occupancy for $x \sim 0.6$ ^{10,11}. Thereof, the T-occupancy, under certain P-T-x conditions, cannot be ruled out. Indeed, metastable phases at ambient pressure, related to both (O) and (T) sites occupancies and to a hydrogen-to-palladium (H:Pd) ratio larger than 1, have been invoked to explain claimed extraordinary properties of palladium hydride, such as a high temperature superconductivity with a T_C at least about 50 K¹² or even higher¹³ and an anomalous release of energy interpreted as a cold fusion process¹⁴. The suspected

large amount of hydrogen in Pd could be achieved either by electrochemical loading or by rapidly quenching a high temperature metastable phase. However, both claims remain unconfirmed. The possibility to create highly H loaded Pd hydrides is thus worth exploring.

The first aim of the present study is to investigate the existence of overstoichiometric Pd hydride by applying high hydrogen pressure. Near ambient pressure, the β -phase is limited to a stoichiometry of 0.7⁷. Further hydrogen absorption into the β -phase requires an increase of the hydrogen pressure¹⁵. The equilibrium hydrogen pressures for the formation of the stoichiometric PdH and PdD, estimated in the GPa range, have still not been precisely determined. Some experimental results suggest that by compressing the Pd-H system, hydrides with H:Pd ratio greater than 1 might be obtained and at sufficiently high pressure the Pd dihydride could be stabilized. By putting Pd under a 5 GPa hydrogen pressure at 700°C, a stoichiometry of 1.33 was reported in the form of a vacancy-ordered structure¹⁶. That is the highest documented H:Pd ratio. Also, over the past decade, a novel view on the chemistry of hydrogen with metals has emerged, with the discovery of the dramatic increase of hydrogen solubility in metals under pressure. An evolution from interstitial hydrides to compounds, having unusual hydrogen-to-metal ratios, is observed under pressure. Transition metal hydrides usually have an hydrogen-to-metal ratio close to 1, with hydrogen in the interstitial sites of the close-packed lattice. Until recently, at ambient pressure, dihydride configurations were only known for five transition metals from groups IV and V (Ti, Zr, Hf, V and Nb)⁵. By compressing metals embedded in hydrogen using a diamond anvil cell, other dihydrides were discovered: TaH₂ at 5 GPa¹⁷, RhH₂ at 8 GPa¹⁸, FeH₂ at 67 GPa¹⁹ and CrH₂ at 30 GPa²⁰. In particular, with the discovery of RhH₂¹⁸ and IrH₃²¹, respectively the first dihydride and trihydride of the platinum group, it seems promising to look for the formation of PdH₂ under pressure. In a recent study limited to 20 GPa, the formation of a Pd-Rh dihydride was observed, for Rh rich alloys²². For Pd-rich alloys, it was suspected that a fraction of H atoms could also occupy (T) sites, that could lead to extra solubility of H in Pd and a H:P ratio over 1 above 20

^{a)}paul.loubeyre@cea.fr

GPa²². PdH was observed to remain the stable phase in a recent compression experiment of Pd in hydrogen to 100 GPa²³. However, in this experiment, no laser-heating of the sample was coupled to high pressure so as to overcome a possible kinetic barrier for the diffusion of H atoms in (T) sites. The present study explores the formation of palladium hydrides under pressures of hydrogen up to 100 GPa. Laser-heating of the Pd samples embedded in hydrogen eliminates any possible kinetic hindrance for the H diffusion in Pd.

The second aim of this study is to quantify the isotopic difference between the compression curves and formation pressures of palladium hydride and deuteride. Are the isotopic effects normal or inverse as for the superconductivity temperature?

II. METHODS

The sample preparation and the synchrotron x-ray diffraction measurements were similar to those used in our previous studies on the synthesis of Fe, S and Cr hydrides at high pressure^{19,20,24}. In total, six pressure runs were performed on palladium samples embedded in different pressure transmitting media in the diamond anvil cell: 1 run using neon to measure a reference compression curve, 3 runs using hydrogen and 2 runs using deuterium. Two diamond tip diameters, 300 μm and 150 μm , were used to go up to and above 60 GPa respectively. Samples were confined in rhenium gaskets, with a gold coating of about 700 Å to prevent the loss of hydrogen by diffusion. The gases were loaded in the diamond anvil cell (DAC) under 140 MPa. As shown in Fig. 1, the palladium flake was always surrounded by a much larger volume of hydrogen or deuterium, to be able to synthesize the hydride with the highest stoichiometry stable on the convex hull at a given pressure. Pressure was measured either using the equation of state of a small marble of gold²⁵ or using the luminescence of a ruby²⁶, loaded close to the Pd sample. The ruby gauge was favored below 40 GPa to determine pressure with good accuracy. The random uncertainty in pressure is of 0.05 GPa with the ruby gauge, and about 2% with the gold gauge. The systematic uncertainty, due to the calibration of the pressure scales, should increase these error bars by about a factor 2. For the isotopic shift determinations shown below, which are based on a relative pressure shift at a given volume, only the random uncertainty is limiting the data accuracy. X-ray diffraction (XRD) data were collected at the ID27 beamline of the ESRF with a wavelength of 0.3738 Å. The XRD data were then analyzed using DIOPTAS²⁷, the FULLPROF software suite²⁸ and the XRDsuite²⁹. The uncertainty in volume is $\pm 0.04 \text{ Å}^3/\text{formula unit (f.u.)}$. For each run, the sample was heated at different pressures, as indicated in Fig. 1, to overcome possible kinetic hindrance for the formation of the stable Pd hydride. The temperatures reached during heating were at least about 1300 K (lower thermoemission visible through the camera setup used), and were sometimes above since the Pd sample could be partially melted.

Calculations were also performed to discuss the mechanism of the isotopic shift on the compression curve of PdH. Ground

FIG. 1. (a) Schematic representation of the different experimental runs. The pressure domains explored are represented in red for Pd+Ne sample, in back for Pd+H₂ (three runs, one with ruby and two with gold as pressure gauges) and in blue for Pd+D₂ (two runs, one with ruby and one with gold as pressure gauges). Laser-heating sequences are represented with yellow vertical ticks, together with the corresponding heating pressure. (b) Photograph of the 10 μm Pd sample with a gold marble, surrounded by solid H₂ in excess. The rhenium gasket was coated with a protective 700 Å gold layer. (c) Unrolled recorded XRD image of PdH at 3.8 GPa. The spotty character of the XRD pattern explains why its Rietveld refinement could not be satisfactorily performed.

FIG. 2. A selection of XRD patterns: PdH before and after laser-heating (LH) at 3.8 GPa; PdD after LH at 24.5 GPa; PdH after LH at 79 GPa. Le Bail refinement (as black line) of the diffraction data (as red dots) is made using a $Fm\bar{3}m$ unit cell symmetry (corresponding Bragg peaks are shown as red ticks). The difference between the experiment and the fit is plotted in blue. When present, the rhenium Bragg peaks are shown as black ticks.

FIG. 3. Volume of Pd hydride (deuteride) in equilibrium with a hydrogen (deuterium) pressure. The squares of different colors indicate the 3 runs performed in hydrogen; the red stars indicate the volume measured after laser-heating in run 3. The circles indicate the run performed in deuterium. Error bars in pressure and in volume are smaller than the symbols. The triangles indicate the measured volumes at ambient pressure for the metastable stoichiometric hydrides, PdH and PdD given by Schirber³⁴ and Burch³⁵. The equilibrium volumes for Pd hydride measured by Fukai at 5 GPa²² are also indicated, both for PdH and Pd₃VacH₄.

state Density Functional Theory (DFT) calculations have been performed using the ABINIT code³⁰ in the framework of the Local Density Approximation (LDA). The Projector Augmented Wave (PAW) method³¹ was used with atomic datasets taken from the GBRV table³². PdH is simulated in its 2-atom primitive unit cell (space group $Fm\bar{3}m$), using a $24 \times 24 \times 24$ k-point mesh. The plane-wave cutoff is 35 Hartrees (and 70 Hartrees for the double grid). The phonon modes of PdH and PdD are computed on a $6 \times 6 \times 6$ q-point mesh, using Density-Functional Perturbation Theory as implemented in ABINIT³³.

III. FORMATION OF PdH AND PdD ONLY

As shown in Fig. 2, the compounds formed through the spontaneous reaction of Pd with hydrogen or deuterium, and those after laser-heating, all preserved the cubic structure of Pd. The Rietveld refinement of the structural positions of the Pd atoms could not be performed because of insufficient quality of the powders. The quality of the powder deteriorated further upon laser-heating, with a tendency to form a multi-grains sample. However, for each spectra, a Le Bail refinement confirms that the Pd atoms remained arranged in the cubic unit cell with the $Fm\bar{3}m$ symmetry and allowed an accurate volume determination. The hydrogen stoichiometry was estimated using the volumetric expansion caused by the hydrogen (deuterium) insertion inside the palladium lattice.

FIG. 4. Compression curves for PdH and PdD (a) Volume vs. pressure for PdH compressed in hydrogen and for Pd in neon. Symbols: black dots and red dots indicate PdH data after pressure increase at 300 K and after laser-heating at a given pressure respectively; circles indicate Pd data in Ne. (b) Volume vs. pressure for PdD compressed in deuterium. Symbols: black dots and red dots indicate PdD data after pressure increase at 300 K and after laser-heating at a given pressure. Error bars are shown, with the uncertainty in pressure being $\pm 2\%$ and in volume $\pm 0.04 \text{ \AA}^3/\text{f.u.}$

A. Compression curve

Below 5 GPa, as shown in Fig. 3, the volume of Pd in hydrogen first expands under pressure and then follows a linear compression. The increase in volume of Pd embedded in hydrogen reflects the loading of hydrogen in the Pd lattice. That evolution was reproducibly followed on the three samples measured and also reversibly obtained upon pressure release. Furthermore, in one run, laser-heating of the sample was performed at several pressures, and the volume of the Pd hydride then falls exactly on the same curve. That curve hence

gives the equilibrium volume of Pd embedded in hydrogen at a given pressure. Knowing the volume expansion caused by the insertion of a hydrogen atom inside an (O) site of the *fcc* lattice of Pd, around $2.5 \text{ \AA}^3$ below 5 GPa, the equilibrium volume of the hydride *vs.* pressure can be analyzed in terms of the evolution of the H:Pd ratio *vs.* pressure. As a first approximation, we can assume that the H:Pd = 1 ratio is obtained above 3 GPa for Pd compressed in hydrogen and deuterium. However, two differences are clearly seen in Fig. 3 between Pd in hydrogen and Pd in deuterium, namely: the volume of Pd in hydrogen is greater than the volume of Pd in deuterium above 3 GPa when stoichiometric PdH and PdD are stable; the pressure to reach the stoichiometric PdH seems lower than the one for PdD. These two isotope effects are discussed in specific sections below.

The compression curves of PdH and PdD, embedded in their respective hydrogen isotope pressure medium from 3 GPa to 100 GPa, are plotted in Fig. 4. The data points fall on the same curve, regardless of whether there was previously a laser-heating of the sample. None of the usual signatures of a change of the stoichiometry for hydrides under pressure, *i.e.* an upward discontinuity of volume or a continuous positive deviation from the compression trend, are observed here. We can assume that, above 3 GPa, stoichiometric PdH (PdD) is the hydride with the largest H (D) concentration on the convex hull up to 100 GPa at least. The Vinet equation of state function is used to fit the data points for PdH and PdD. The corresponding parameters are: for PdH, $V_0 = 17.33(4) \text{ \AA}^3$, $K_0 = 159(3) \text{ GPa}$ and $K'_0 = 5.6(11)$; for PdD, $V_0 = 17.29(4) \text{ \AA}^3$, $K_0 = 159(2) \text{ GPa}$ and $K'_0 = 5.6(13)$. PdH and PdD have exactly the same isothermal bulk modulus, K_0 , and the same pressure derivative of K_0 , K'_0 . Consequently, PdH and PdD follow exactly the same curve when V/V_0 is plotted *vs.* P . A similar behavior was previously measured for the compression curve of LiH and LiD³⁶. The volumes at ambient pressure for metastable PdH and PdD are $V_0 = 17.33(4) \text{ \AA}^3$ and $V_0 = 17.29(4) \text{ \AA}^3$ respectively. It should be noted that for the estimation of the isotopic shift, systematic uncertainties in the volume determination cancel out, so an isotopic effect can be clearly measured even though its magnitude is of the order of the volumic uncertainty. These two volumes are compared to previous estimations at ambient pressure measured on metastable hydrides, see Fig. 3. The present estimation of V_0 for PdH is in good agreement with the value given by Burch³⁵. However, it is larger than the value of Shirber³⁴. Part of the disagreement with Shirber's volume, which was measured at 77 K, is thus due to thermal expansion. Shirber also measured the isotopic volume difference between metastable PdH and PdD at ambient pressure, which is in good agreement with the present determination. The Vinet fits for PdH, PdD and Pd compression curves at 300 K are given in Table I.

	$V_0 (\text{\AA}^3)$	$K_0 (\text{GPa})$	K'_0
Pd	14.75(4)	162(2)	6.2(9)
PdH	17.33(4)	159(3)	5.6(11)
PdD	17.29(4)	159(2)	5.6(13)

TABLE I. EOS parameters measured from the Vinet fits of the compression curves for Pd in Ne, PdH and PdD.

B. Volume expansion per hydrogen atom

The compression curve of Pd was measured by embedding Pd in Ne. The volume-pressure data points are plotted in Fig. 4. The Vinet fit of the Pd compression curve gives the following parameters: $V_0 = 14.75(4) \text{ \AA}^3$, $K_0 = 162(2) \text{ GPa}$ and $K'_0 = 6.2(9)$. The volume expansion associated to the transition from *fcc* Pd to *Fm $\bar{3}m$* PdH is given by the subtraction of the volume of pure Pd from the volume data of PdH at a given pressure. The results are plotted in Fig. 5. The volume expansion due to 1 H atom per Pd atom in the *Fm $\bar{3}m$* lattice is then $2.5 \text{ \AA}^3$ at pressures around 3 GPa, which is consistent with the filling of (O) sites. From the synthesis of RhH₂, the increase in volume due to an H occupation of a (T) site was measured around $3.2 \text{ \AA}^3$ under a pressure of a few GPa and it is reasonable to assume that it would be the same value for the occupancy of (T) sites in Pd²². From 3 GPa to 100 GPa, the volume expansion per H atom decreases under pressure, as it was observed for CrH and FeH monohydrides^{19,20}, both having a *hcp* lattice. The volume per H atom is slightly bigger in the case of PdH. Two previous measurements of the volume of PdH under pressure give experimental values of the volume expansion per H atom bounding the present data, the determination of Brownsberger²³ above and the one of Kuzovnikov below²². The calculated volume expansion per hydrogen atom under pressure is in good agreement with the present determination from 3 GPa to 100 GPa. The H or D atoms are thus likely to fill the (O) sites of Pd up to 100 GPa. The filling of the (T) sites, even partially, was expected above 20 GPa from the observation of dihydrides in palladium-rhodium alloys²². As theoretically shown by Errea³⁷, anharmonic effects play a stabilizing role for H atoms in (O) sites, so populating (T) sites could be favored in PdD. Yet, that is not observed.

Finally, it is interesting to note that the possibility to reach H:Pd ratio greater than 1 by rapidly cooling the Pd hydride after loading it with hydrogen at elevated temperature has already been reported twice. Under 10 MPa hydrogen pressure and temperature around 500°C and at 5 GPa under 700°C for a few hours¹⁶. In the latter case, the superabundant vacancies Pd hydride, Pd₃VacH₄, was well characterized. As plotted in Fig. 2, the Pd₃VacH₄ compound has a much smaller volume/Pd atom than PdH. By laser-heating the Pd sample in hydrogen above 1300 K and rapidly quenching it at ambient temperature by turning off the laser, no formation of an overstoichiometric hydride could be observed over the pressure range investigated from 0.5 GPa to 100 GPa. Therefore, long resistive heating might be needed to reach metastable forms of Pd hydrides with H:Pd ratio larger than 1, such as implemented for the synthesis of superabundant vacancies Pd₃VacH₄.

FIG. 5. Volume expansion per H atom for PdH as a function of pressure. Experimental data points are plotted as red dots. The black dashed line is the *ab initio* calculation. Previous determinations from ref.²³ and ref.²² are plotted as blue dashed line and green triangles respectively.

IV. ISOTOPIC SHIFT

A. Formation pressure

The non-monotonic evolution under pressure of the volume of Pd embedded in excess hydrogen up to 5 GPa, as plotted in Fig. 3, can be analyzed as the variation under pressure of the H concentration in Pd. For a quantitative analysis of the change of the H:Pd ratio with pressure, the volume difference between the present measurements and the expected volume of the stoichiometric hydride and deuteride (as given by the fits of the compression curves of PdH and PdD extrapolated below 3 GPa) is divided by the volume expansion per hydrogen atom below 3 GPa ($2.5 \pm 0.1 \text{ Å}^3$, as measured here and in very good agreement with accepted literature value⁵). The isotopic difference between the volume expansion due to the filling of (O) sites of bulk Pd by H or D atoms is here neglected (much smaller than error bars). The evolution of the hydrogen concentration vs. pressure is thus plotted in Fig. 6 for PdH and PdD. That reflects an equilibrium evolution since no scatter was observed between the 3 runs in hydrogen corresponding to different sample sizes and different time scales (from a few minutes to a few hours). Furthermore, laser-heating the sample at 1 GPa and at 4 GPa did not induce any deviation. It is known that at ambient pressure, the H(D):Pd ratio is around 0.7. The lowest pressure investigated here is about 0.3 GPa for which the H to Pd ratio is already around 0.9. A clear isotopic difference is observed, the D:Pd ratio being lower than the H:Pd one at a given pressure. Hence, the stoichiometric PdH hydride is stable above 1.9 GPa whereas the PdD hydride is stable above 2.7 GPa. Such an isotope effect in the formation of hydrides has already been largely investigated with applications for hydrogen separation or storage.

FIG. 6. Isotopic shift on the formation pressure. Evolution of the H:Pd ratio and D:Pd ratio in palladium hydrides vs. pressure, as black squares and blue dots respectively. The equilibrium pressures of stable stoichiometric PdH and PdD are indicated by the vertical dotted lines.

It is commonly quantified by comparing the measured formation pressures of the hydride, deuteride and if possible tritide. The lowest equilibrium pressure corresponds to the most stable compound. This normal isotope effect is observed when the tritide is more stable than the deuteride, itself more stable than the hydride; the equilibrium pressure of the deuteride is then lower than the one of the hydride. Here, we thus observed an inverse isotope effect. The isotopic effect should be canceled when the hydrogen atom contribution to the hydride's Zero-Point Energy (ZPE) is equal to half of the H_2 molecule's ZPE^{38,39}.

B. Compression curve

Although PdH and PdD have identical values for K_0 and K'_0 , the difference in the values of the ambient pressure V_0 induces an isotopic shift for the volume at a given pressure. The volume of PdH is greater than the one of PdD from ambient pressure up to 100 GPa, or equivalently, for a given volume the pressure of PdH is greater than the one of PdD, and increasing with pressure from 0.4 GPa near 3 GPa to 1.2 GPa near 80 GPa. This result is quantitatively in agreement with a similar measurements performed on lithium hydride and deuteride³⁶. This is at odds with the findings of Brownsberger²³, reporting a crossing between the PdH and PdD compression curves around 100 GPa. The need for small error bars on the data points to disclose the isotopic shift is illustrated in Fig. 7. Furthermore, the random uncertainty is here statistically reduced by having a large number of data points.

The isotopic shift on the EOS of palladium hydride is due to the ZPE of the hydrogen atom. Being larger for H than for

FIG. 7. Isotopic shift on the compression curves of PdH and PdD between 30 and 60 GPa. The Vinet fits of the EOS of PdH and PdD are plotted as full red line and black dash line respectively. The data points for PdD are shown with their error bars.

D, PdH has a larger lattice parameter than PdD at a given pressure. A normal isotope effect is observed here. The ZPE contribution was estimated from the calculation of phonon spectrum in PdH and PdD under pressure. By performing calculations within the LDA approximation, we somehow circumvent the instability problem of PdH at low pressure if using the GGA-PBE functional and for which the renormalization of the phonon spectra by anharmonicity is necessary³⁷. Anharmonicity contributions are not taken into account in our calculation, thus certainly less rigorous and semi-quantitative. However, as shown below, the isotopic shift is based on the volume derivative of the phonon frequencies and so the derivative of the anharmonicity contribution should be of a second order effect. The evolution of the phonon structure of PdH between 3 GPa and 30 GPa is shown in Fig. 8. The modes associated to H(D) motion are well separated from those associated with Pd motion, except at low pressure where the two partial vibrational densities of states (for Pd and for H(D)) begin to overlap. This overlap occurs around 10 – 15 GPa in PdD and around 0 – 3 GPa in PdH. As the pressure is increased, the branches associated to H(D) are rather rigidly shifted to higher wave numbers, while those associated to Pd are almost unchanged with pressure. The volume-dependence of the hydrogen of the hydrogen projected phonon energies suggests that hydrogen zero-point motions should contribute to the pressure, offering an explanation for the isotope effect which is observed on the experimental EOS. In order to estimate this contribution, we set up a simple model, in which H motion is replaced by that of a single 3D-Einstein oscillator, with pulsation ω_E . ω_E is determined by averaging the phonon density of states projected on H/D. The evolution of the effective Einstein frequency vs. the unit cell volume is plotted in Fig. 8. A linear evolution is observed, with a slope being larger for H than for D by almost the expected $\sqrt{2}$ factor. The isotopic pressure difference at 300 K and at a given volume is

FIG. 8. Phonon bandstructures of PdH at 29.6 GPa (a) and 3.0 GPa (b). The Pd projections are plotted in black, the H projections in red. (c) Evolution vs. volume of the effective Einstein frequencies corresponding to the H and D projections of the phonon bandstructures in PdH and in PdD, plotted as triangles in the bottom graph. A linear evolution is observed with: $\hbar\omega_E$ (meV) = $360.5 - 18.98V$ ($\text{\AA}^3/\text{PdH}$) for PdH and $\hbar\omega_E$ (meV) = $255.6 - 13.45V$ ($\text{\AA}^3/\text{PdD}$) for PdD.

then estimated using this linear fit as follows:

$$\hbar\omega_E = K - AV \quad (1)$$

$$P_{vib} = -dF/dV = \frac{3}{2}A \left(1 + \frac{2}{\exp(\hbar\omega_E/K_B T) - 1} \right) \quad (2)$$

with $3/2A \sim 4.56$ (resp. 3.23) GPa for H (resp. D). The calculated isotopic shift in pressure at a given volume is plotted in Fig. 9 and compared to experiment. The agreement is very satisfactory, showing an increase in pressure shift vs. pressure.

FIG. 9. Isotopic shift on the compression curve of Pd hydride. Experimental determination, as the difference between the Vinet fit of PdH and PdD EOS, is plotted as a blue dashed line. Calculation, estimated from the Einstein frequency effective modes for H and D in PdH and PdD, is plotted as a black dashed line.

V. CONCLUSION

The equilibrium H:Pd (D:Pd) ratio for Pd embedded in excess hydrogen (deuterium) was studied up to 100 GPa. No evidence for a H:Pd nor D:Pd ratio larger than 1 was observed. No metastable phases with H:Pd ratio larger than 1 could be synthesized by laser-heating Pd in excess hydrogen, even after rapid quenching. The compression curves of PdH and of PdD were measured up to 100 GPa. A normal isotopic shift on the compression curve is reported in good agreement with calculations. On the other hand, an inverse isotopic shift is observed for the stability pressure of PdH and of PdD.

ACKNOWLEDGMENTS

The authors acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation on beam line ID27. More particularly, we would like to thank M. Mezouar, G. Garbarino and V. Svitlyk for their precious help with the XRD experiments.

¹T. Graham, “XVIII. On the absorption and dialytic separation of gases by colloid septa,” *Philosophical Transactions of the Royal Society of London* **156**, 399–439 (1866), <https://royalsocietypublishing.org/doi/pdf/10.1098/rstl.1866.0018>.

²T. Skoskiewicz, “Superconductivity in the palladium-hydrogen and palladium-nickel-hydrogen systems,” *Physica Status Solidi A* **11**, K123–K126 (1972), <https://onlinelibrary.wiley.com/doi/pdf/10.1002/pssa.2210110253>.

³H. Hemmes, A. Driessen, R. Griessen, and M. Gupta, “Isotope effects and pressure dependence of the T_C of superconducting stoichiometric PdH and PdD synthesized and measured in a diamond anvil cell,” *Phys. Rev. B* **39**, 4110–4118 (1989).

⁴I. Errea, M. Calandra, and F. Mauri, “First-Principles Theory of Anharmonicity and the Inverse Isotope Effect in Superconducting Palladium-Hydride Compounds,” *Phys. Rev. Lett.* **111**, 177002 (2013).

⁵Y. Fukai, *The Metal-Hydrogen System: Basic Bulk Properties* (Springer, 2005).

⁶R. C. J. Bowman, R. S. Carlson, and R. J. De Sando, “Characterization of metal tritides for the transport, storage, and disposal of tritium,” in *Trans. Am. Nucl. Soc. (United States)* (1976).

⁷F. D. Manchester, A. San-Martin, and J. M. Pitre, “The H-Pd (hydrogen-palladium) System,” *Journal of Phase Equilibria* **15**, 62 (1994).

⁸J. E. Worsham, M. Wilkinson, and C. Shull, “Neutron-diffraction observations on the palladium-hydrogen and palladium-deuterium systems,” *Journal of Physics and Chemistry of Solids* **3**, 303 (1957).

⁹A. I. Kolesnikov, I. Natkaniec, V. E. Antonov, I. T. Belash, V. K. Fedotov, J. Krawczyk, J. Mayer, and E. G. Ponyatovski, “Neutron spectroscopy of $MnH_{0.86}$, $NiH_{1.05}$, $PdH_{0.99}$ and harmonic behaviour of their optical phonons,” *Physica B: Condensed Matter* **174**, 257–261 (1991).

¹⁰G. A. Ferguson, A. I. Schindler, T. Tanaka, and T. Morita, “Neutron Diffraction Study of Temperature-Dependent Properties of Palladium Containing Absorbed Hydrogen,” *Phys. Rev.* **137**, A483–A487 (1965).

¹¹M. P. Pitt and E. M. Gray, “Tetrahedral occupancy in the Pd-D system observed by in situ neutron powder diffraction,” *Europhysics Letters (EPL)* **64**, 344–350 (2003).

¹²H. M. Syed, T. J. Gould, C. J. Webb, and E. MacA. Gray, “Superconductivity in palladium hydride and deuteride at 52–61 kelvin,” *arXiv e-prints*, arXiv:1608.01774 (2016), 1608.01774.

¹³P. Tripodi, D. Di Gioacchino, and J. D. Vinko, “A review of high temperature superconducting properties of PdH system,” *International Journal of Modern Physics B* **21**, 3343–3347 (2007).

¹⁴C. P. Berlinguette, Y.-M. Chiang, J. N. Munday, T. Schenkel, D. K. Fork, R. Koningstein, and M. D. Trevithick, “Revisiting the cold case of cold fusion,” *Nature* **570**, 45–51 (2019).

¹⁵B. Baranowski, “High Pressure Research on Palladium-Hydrogen Systems,” *Platinum Metals Rev.* **16**, 10 (1972).

¹⁶Y. Fukai and N. Okuma, “Formation of Superabundant Vacancies in Pd Hydride under High Hydrogen Pressures,” *Phys. Rev. Lett.* **73**, 1640–1643 (1994).

¹⁷M. A. Kuzovnikov, M. Tkacz, H. Meng, D. I. Kapustin, and V. I. Kulakov, “High-pressure synthesis of tantalum dihydride,” *Phys. Rev. B* **96**, 134120 (2017).

¹⁸B. Li, Y. Ding, D. Y. Kim, R. Ahuja, G. Zou, and H.-K. Mao, “Rhodium dihydride (RhH_2) with high volumetric hydrogen density,” *Proceedings of the National Academy of Sciences* **108**, 18618 (2011).

¹⁹C. M. Pépin, A. Dewaele, G. Geneste, P. Loubeyre, and M. Mezouar, “New Iron Hydrides under High Pressure,” *Phys. Rev. Lett.* **113**, 265504 (2014).

²⁰A. Marizy, G. Geneste, P. Loubeyre, B. Guigue, and G. Garbarino, “Synthesis of bulk chromium hydrides under pressure of up to 120 GPa,” *Phys. Rev. B* **97**, 184103 (2018).

²¹T. Scheler, M. Marqués, Z. Konôpková, C. L. Guillaume, R. T. Howie, and E. Gregoryanz, “High-Pressure Synthesis and Characterization of Iridium Trihydride,” *Phys. Rev. Lett.* **111**, 215503 (2013).

²²M. A. Kuzovnikov and M. Tkacz, “Dihydride formation in the palladium–rhodium alloys under high hydrogen pressure,” *International Journal of Hydrogen Energy* **42**, 340–346 (2017).

²³K. Brownsberger, M. Ahart, M. Somayazulu, C. Park, S. A. Gramsch, and R. J. Hemley, “X-ray Diffraction, Lattice Structure, and Equation of State of PdH_x and PdD_x to Megabar Pressures,” *The Journal of Physical Chemistry C* **121**, 27327–27331 (2017).

²⁴B. Guigue, A. Marizy, and P. Loubeyre, “Direct synthesis of pure H_3S from S and H elements: No evidence of the cubic superconducting phase up to 160 GPa,” *Phys. Rev. B* **95**, 020104 (2017).

²⁵K. Takemura and A. Dewaele, “Isothermal equation of state for gold with a He-pressure medium,” *Phys. Rev. B* **78**, 104119 (2008).

²⁶H. K. Mao, J. Xu, and P. M. Bell, “Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions,” *J. Geophys. Res. Sol. Ea.* **91**, 4673 (1986).

²⁷C. Prescher and V. B. Prakapenka, “DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration,” *High Pressure Research* **35**, 223–230 (2015).

- ²⁸T. Roisnel and J. Rodriguez-Carvajal, “WinPLOTR: a Windows tool for powder diffraction patterns analysis,” *Proc. EPDIC 7*, 118–123 (2000).
- ²⁹S. Desgreniers and K. Lagarec, “XRDA: a program for energy-dispersive X-ray diffraction analysis on a PC,” *Journal of Applied Crystallography* **27**, 432–434 (1994).
- ³⁰X. Gonze, F. Jollet, F. Abreu Araujo, D. Adams, B. Amadon, T. Applencourt, C. Audouze, J.-M. Beuken, J. Bieder, A. Bokhanchuk, E. Bousquet, F. Bruneval, D. Caliste, M. Côté, F. Dahm, F. Da Pieve, M. Delaveau, M. Di Gennaro, B. Dorado, C. Espejo, G. Geneste, L. Genovese, A. Gerossier, M. Giantomassi, Y. Gillet, D. R. Hamann, L. He, G. Jomard, J. Laflamme Janssen, S. Le Roux, A. Levitt, A. Lherbier, F. Liu, I. Lukačević, A. Martin, C. Martins, M. J. T. Oliveira, S. Poncé, Y. Pouillon, T. Rangel, G.-M. Rignanese, A. H. Romero, B. Rousseau, O. Rubel, A. A. Shukri, M. Stankovski, M. Torrent, M. J. Van Setten, B. Van Troeye, M. J. Verstraete, D. Waroquiers, J. Wiktorski, B. Xu, A. Zhou, and J. W. Zwanziger, “Recent developments in the ABINIT software package,” *Computer Physics Communications* **205**, 106–131 (2016).
- ³¹P. E. Blöchl, “Projector augmented-wave method,” *Phys. Rev. B* **50**, 17953–17979 (1994).
- ³²K. F. Garrity, J. W. Bennett, K. M. Rabe, and D. Vanderbilt, “Pseudopotentials for high-throughput DFT calculations,” *Computational Materials Science* **81**, 446–452 (2014).
- ³³C. Audouze, F. Jollet, M. Torrent, and X. Gonze, “Projector augmented-wave approach to density-functional perturbation theory,” *Phys. Rev. B* **73**, 235101 (2006).
- ³⁴J. E. Schirber and B. Morosin, “Lattice constants of β -PdH_x and β -PdD_x with x near 1.0,” *Phys. Rev. B* **12**, 117–118 (1975).
- ³⁵R. Burch, “Theoretical aspects of the absorption of hydrogen by palladium and its alloys. Part 2.—Possible effects of lattice expansion on the solubility of hydrogen in palladium,” *Trans. Faraday Soc.* **66**, 749–755 (1970).
- ³⁶P. Loubeyre, R. Le Toullec, M. Hanfland, L. Ulivi, F. Datchi, and D. Hausermann, “Equation of state of LiH and LiD from x-ray diffraction to 94 GPa,” *Phys. Rev. B* **57**, 10403–10406 (1998).
- ³⁷I. Errea, M. Calandra, and F. Mauri, “Anharmonic free energies and phonon dispersions from the stochastic self-consistent harmonic approximation: Application to platinum and palladium hydrides,” *Phys. Rev. B* **89**, 064302 (2014).
- ³⁸N. Bourgeois, J.-C. Crivello, P. Cenedese, V. Paul-Boncour, and J.-M. Joubert, “Vibration analysis of hydrogen, deuterium and tritium in metals: consequences on the isotope effect,” *Journal of Physics: Condensed Matter* **30**, 335402 (2018).
- ³⁹N. Bourgeois, J.-C. Crivello, P. Cenedese, and J.-M. Joubert, “Systematic First-Principles Study of Binary Metal Hydrides,” *ACS Combinatorial Science* **19**, 513–523 (2017).