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Zachary M. Geballe, Maddury Somayazulu, Nicolas Armanet, Ajay K. Mishra, Muhtar Ahart, and Russell J. Hemley

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High pressure synthesis and thermodynamic stability of $PdH_{1\pm\epsilon}$ to 8 GPa

Zachary M. Geballe
Earth and Planets Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

Maddury Somayazulu
HPCAT, X-ray Science Division, Argonne National Laboratory, Lemont IL 60439, USA

Nicolas Armanet
International Institute for Hydrogen Materials Research (i2-HMR), Bourgoin Jallieu, France

Ajay K. Mishra
HP&SRPD, Bhabha Atomic Research Center Mumbai-85, India

Muhtar Ahart
Department of Physics, University of Illinois at Chicago, Chicago, IL, 60607, USA

Russell J. Hemley
Department of Physics, University of Illinois at Chicago, Chicago, IL, 60607, USA and Department of Chemistry, University of Illinois at Chicago, Chicago, IL, 60607, USA

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Abstract

Palladium hydride alloys are superconductors and hydrogen storage materials. One synthesis route is compression of Pd to high pressure in a hydrogen-rich environment. Here we report the evolution of the unit cell volume of PdH_x synthesized by compressing Pd in a pure H_2 medium to pressures from 0.2 to 8 GPa in a diamond anvil cell at room temperature. The volume of the face-centered cubic unit cell changes non-monotonically with pressure, increasing upon compression from 0.2 to 1 GPa and decreasing upon compression from 1 to 8 GPa. Volume is reversible upon decompression and is independent of whether the sample was heated to 600 K at low pressure ($P < 2$ GPa). The X-ray diffraction data show no evidence for a phase transition between 0.2 and 8 GPa. The volume maximum at 1 GPa must be caused by progressive hydrogenation from 0 to 1 GPa. Assuming a pressure-volume-composition equation of state derived from previously published data, the [H]:[Pd] ratio in this study increases to a maximum value of $x = 1 \pm 0.02$ at 2 ± 0.5 GPa and remains stable upon further compression to and from 8 GPa. These results add to a mounting body of evidence that $PdH_{1\pm\epsilon}$ is in thermodynamic equilibrium with pure H_2 at room temperature from 2 GPa to at least 8 GPa. The simplest interpretation is that H atoms occupy all octahedral sites and no tetrahedral sites in face centered cubic $PdH_{1.0}$.

I. INTRODUCTION

Palladium metal is a useful hydrogen filter in industrial applications, and it can store a large amount of hydrogen, even at low pressures [1]. At sufficiently high ratios of hydrogen to palladium, PdH_x alloys are superconductors [2]. The superconducting transition temperature, T_C, increases with x, from about 0 K at $x = 0.75$ to about 9.6 K at $x = 1.0$ [2–8], and slightly higher for palladium deuteride [2–5], the so-called inverse isotope effect [9, 10]. In fact, much higher values of T_C have been claimed in experiments designed to generate $x \geq 1.0$; T_C up to 60 K [11, 12], 70 K [13–16], and even 298 K [17–22], but none of these results have been confirmed by independent groups and some claims have sparked controversy [23, 24]. The search for high T_C superconductivity continues to motivate synthesis experiments aimed at maximizing the hydrogen content of PdH_x. Synthesis routes for $x = 0$ to 1 include the commonly used gas phase and electrochemical loading techniques [5, 25, 26], and three methods that generate the highest hydrogen contents detected so far:

high pressure synthesis [27–32], electrolysis [33–37], and hydrogen ion implantation [38–44]. High pressure has also been combined with high temperature to generate an exotic crystal with "superabundant vacancies" (SAVs) in place of palladium atoms [27–31].

Most recently, the behavior of PdH_x in an H_2 medium [45–47] and in paraffin oil [48, 49] at very high pressures has been reported. Brownsberger et al. [45] and Guigue et al. [47] report X-ray diffraction measurements and equations of state of PdH_x and PdD_x to 100 GPa. Together, the studies show that the hydrogen content increases to $x \approx 1$ at pressures up to ~ 2 GPa, and that up to 100 GPa the fcc lattice steadily compresses without an apparent loss or gain of hydrogen (i.e., $x \approx 1$). PdH_x with the same lattice volume was also synthesized by laser heating elemental Pd in paraffin oil at 39 GPa [48]. Moreover, Guigue et al. [47] shows that crystal structure and volume do not change upon laser-heating to > 1300 K at pressures from 0.8 to 85.5 GPa. Both Brownsberger et al. [45] and Guigue et al. [47] estimate that $x \approx 1$, but they obtained different X-ray volumes at ambient pressure (0.1 MPa). Moreover, no synchrotron-based study reports data collected during decompression from pressures above 2 GPa to pressures between 2 GPa and 0.1 GPa, causing uncertainty in the composition of PdH_x that is in thermodynamic equilibrium with H_2 over the pressure range 0.1 to 2 GPa at room temperature.

Here we present the results of synchrotron X-ray diffraction of PdH_x in a pure H_2 medium at room temperature in the lower pressure range of 0.2 to 8 GPa, with and without resistive heating to 600 K, and upon compression and decompression. These results include the four data points labeled "Geballe et al." in Fig. 3 of Brownsberger et al. [45].

II. METHODS

Palladium foil of < 2 μm thickness purchased from Goodfellow (99.9% purity, "as-rolled" temper) were placed in the $\sim$ 400 μm diameter holes of Cu-Be gaskets that were pre-compressed to $\sim$ 200 μm-thickness, leaving $> 98\%$ of the volume for an H_2 medium. In two runs, a small pile of gold powder was also placed in the gasket hole, $\sim$ 100 μm away from the palladium sample, and used as a pressure marker. H_2 was loaded as a supercritical fluid at 25,000 psi (0.2 GPa), 300 K, trapped inside the gasket at 0.1 to 0.2 GPa, and compressed to at most 0.3 GPa inside the gas loading device. In two runs, the sample chamber was heated to and from 600 K at 1 ($\pm$ 1) GPa using external resistive heating for $\sim$ 10 minutes before further compressing to > 4 GPa at room temperature. The cooling rate was ~ 10 K/minute. In the third run, the sample was compressed to 6 GPa at room temperature with no heating whatsoever. Two samples were also decompressed to $P < 0.2$ GPa. Angle-dispersive X-ray diffraction data were collected at many pressures during compression and decompression at Sector 16 of the Advanced Photon Source, Argonne National Lab. We used 0.4959 and 0.4066 Å X-rays focused to a ~ 50 μm spot and ~ 10 μm spots at endstations 16-BM-D and 16-ID-B, respectively. Pressure was determined at room temperature using the gold equation of state and the Raman shift of the H_2 vibron [50, 51]. Prior to gas loading to 0.2 GPa, the Pd starting material was not heated, exposed to hydrogen, or characterized by X-ray diffraction.

III. RESULTS AND DISCUSSION

The X-ray diffraction measurements indicate that Pd atoms form an fcc lattice at all conditions studied here (Fig. 1). The spacing of Pd atoms varies with pressure, but is independent of the pressure-temperature history of the sample (Fig. 2). The increase in lattice parameter from 4.08 Å to 4.090 (±0.004) Å over the range 0.2 to 1 GPa is monotonic and reversible. Upon further increase in pressure, the lattice parameter decreases monotonically to 8 GPa. We argue below that this is caused by a constant [H]:[Pd] ratio from 2 to 8 GPa, but note that our X-ray diffraction data alone cannot rule out a change in the [H]:[Pd] ratio. The palladium lattice expansion from 0.1 GPa to 1 GPa must be caused by hydrogenation upon compression; the lattice contraction on lowering the pressure must be caused by dehydrogenation upon decompression. Otherwise, our volume data would imply a negative isothermal compressibility, which is not thermodynamically allowed.

Further assumptions must be made to assess the likelihood of hydrogenation or dehydrogenation of the PdH_x lattice at pressures beyond 1 GPa. We compare our measurements of lattice volume to an equation of state that we create by combining three previously published data sets. The three data sets constrain volume, V, along three different axes in pressure-temperature-composition space, i.e., $V(P, T, x)$. Schirber and Morosin [52] constrains V(1 bar, 77 K, 0.8 to 0.98). Hemmes et al. [53] constrains V(1 bar, 10 to 250 K, 0.76). Tkacz and Baranowski [54] constrains V(1 bar to 12 GPa, 300 K, 0.6). We ignore the higher pressure data from Tkacz and Baranowski [54], because anomalous volumes are measured at $P > 12$ GPa due to a possible phase separation. Note that we do not assume the $\mathrm{PdH}_{1.0}$ stoichiometry is reached in any of our experiments, unlike the studies of Brownsberger et al. [45] and Guigue et al.[47], which make this assumption. Those studies are focused on a much higher pressure range (up to 100 GPa) that is not reached in the study of $V(P$, 300 K, 0.6) [54], eliminating the possibility to use our approach to analyze their entire data sets.

To interpret the above results, we assume an equation of state separable into the product of pressure-dependent, temperature-dependent, and composition-dependent terms:

$$V(P, T, x) = V_{0,\mathrm{PdH}} \times b(P) \times c(T) \times d(x) \tag{1}$$

The pressure term, $b(P)$, is derived from a second-order Birch-Murnaghan equation of state of the form,

$$P = \frac{3K_0}{2}\left(b^{-7/3} - b^{-5/3}\right) \tag{2}$$

where K_0 comes from our fit of the data from Tkacz and Baranowski [54] from 0 to 12 GPa. We find $V_0 = 16.30$ (± 0.06) Å^3/formula unit and $K_0 = 182$ (± 18) GPa, with K' fixed to 4. The temperature term is given by a third order polynomial fit to the dilatation data for $\mathrm{PdH}_{0.76}$ in Table 1 of Hemmes et al. [53]:

$$c(T) = \left(\frac{\alpha T^3 + \beta T^2 - \gamma T + 1}{\alpha(300\text{ K})^3 + \beta(300\text{ K})^2 + \gamma(300\text{ K}) + 1}\right)^3$$

for $\alpha = -5.98 \times 10^{-11}$ K^{-3}, $\beta = 5.82 \times 10^{-8}$ K^{-2}, and $\gamma = 1.57 \times 10^{-6}$ K^{-1}. The composition term is given by Schirber and Morosin [52]: $d(x) = (1 + r(x-1))^3$ for $r = 0.044$ [55]. The prefactor is determined by a slight extrapolation from $x = 0.98$ to 1.0 using the $V(1\text{ bar}, 77\text{ K}, x)$ function of Schirber and Morosin [52], followed by multiplication by $c(300\text{ K})/c(77\text{ K}) = 1.00295$: $V_{0,\mathrm{PdH}} = 17.26$ Å^3/formula unit ($a_0 = 4.102$ Å). Note that this equation of state predicts systematically larger volumes (by 0.7%) or smaller hydrogen contents (by 5%) than the measurements of Tkacz and Baranowski [54]. The mismatch may reflect an uncertainty in the composition or volume measurements of Tkacz and Baranowski [54], which nonetheless appear to be the most reliable pressure-volume measurements of a *fixed* composition of $\mathrm{PdH}_{x>0.5}$. We find that the equation of state parameters cited in Tkacz et al. 1990 [56] do not fit the data in their 1993 paper [54], according to our calculations. The data from Tkacz et al. [54], along with all other data plotted in Figs. 3-4 are listed in the supplemental spreadsheet [57]. New measurements in preparation for publication may revise the value of

r to 0.0530 and $V_{0,\mathrm{PdH}}$ to 17.171 Å^3/formula unit at 85 K, which results in a 0.35% increase in volume at 300 K compared to the value assumed here. [58]

The equation of state constructed here is based on data in the pressure range 1 bar to 12 GPa, the temperature range 77 to 300 K, and the composition range $x = 0.6$ to 0.98. It should not be extrapolated far outside that range, including to $x = 0$. In the pressure range 0 to 10 GPa, it is very close to the equation of state proposed in Guigue et al. [47], in which the sample's composition is assumed to be $\mathrm{PdH_1}$ between 3 and 100 GPa (Fig. 2). A comparison of equation of state parameters between studies is shown in Table I. A comparison between the equation of state for different values of x and our data shows that $x \approx 1$ from 1.5 to 8 GPa (Fig. 2). By solving for x and plotting the result as a function of pressure in Fig. 3, we find that $x = 1 \pm 0.02$ from 2 ± 0.5 to 8 GPa. The value of x appears to saturate at 2 (± 0.5) GPa. In other words, the hydrogen content saturates at 1 ± 0.02 at 2 (± 0.5) GPa and 300 K; further compression and decompression do not change the hydrogen content of $\mathrm{PdH}_{1\pm\epsilon}$.

The conclusion that x saturates at 1 at $P_{\mathrm{PdH}} = 2$ (± 0.5) GPa is similar to the finding of Guigue et al. [47] ($P_{\mathrm{PdH}} = 1.9$ GPa) and the estimations of Baranowski and Debowska [23] ($P_{\mathrm{PdH}} > 1.2$ GPa) and of Kuzovnikov and Tkacz [46] ($P_{\mathrm{PdH}} \approx 1$ GPa). It is also consistent with the data up to 1.2 GPa of Tkacz and Baranowski [59] and of Szafranski [60] (Fig. 3).[61] There are eight tetrahedral sites and four octahedral sites per four-atom unit cell of fcc palladium. Saturation at $x = 1$ suggests that all four octahedral sites are occupied at high pressure. Nevertheless, uncertainties remain in the details of site occupancy at $x = 1$. For example, if we assume the values of r and $V_{0,\mathrm{PdH}}$ from Antonov et al. [62], we conclude that the hydrogen content of our samples saturates at $x = 0.97$ to 1.0.

The new observations of this study are that X-ray volumes are reversible upon decompression at room temperature from 4 GPa and 8 GPa (Runs 1 and 2), and do not depend on whether the sample was heated to 600 K for ~ 10 minutes. Both of these observations add to the mounting body of evidence that $\mathrm{PdH}_{1\pm\epsilon}$ is in thermodynamic equilibrium with $\mathrm{H_2}$ at room temperature and 1.5 GPa to at least 8 GPa, and possibly up to 100 GPa [45, 47]. In other words, fcc $\mathrm{PdH}_{1\pm\epsilon}$ is the most hydrogen rich equilibrium structure in the Pd-H binary system at 2 ± 0.5 to 8 GPa.

The equilibrium states documented here rule out the possibility to use the pressure-temperature routes from this study to generate non-equilibrium structures (such as those found by Syed et al. [11]) or lattice volumes (such as the dihydride found by Kuzovnikov et al. [46] or the phase separation found by Fukada et al. [35, 36]). The absence of SAVs and anomalous volumes upon resistive heating is in line with the laser-heating results of Guigue et al. [47] at ~ 0.8 GPa and ~ 3.8 GPa, and in contrast to the results from resistive heating at $P < 10$ GPa in Refs. [27–32, 35, 36]. The absence of anomalous lattice volume upon decompression in the present study shows that room temperature pressure cycling is not a promising method to increase hydrogen content of $PdH_{1\pm\epsilon}$.

On the other hand, alternative routes and rates of change through pressure-temperature space seem to result in different structures and lattice volumes. In addition to the synthesis of SAVs mentioned above, electrical data of Syed suggests new structures upon cooling at 330 K/min from 573 K to less than 50 K at 0.01 GPa [11, 12]. Also, the lowest pressure X-ray diffraction data point of PdH_x of Brownsberger et al. [45] is not consistent with the data collected here. It could be explained by extrapolation of the pressure-volume-composition equation of state to $x = 1.2$ (Fig. 2). This sample was prepared in a similar way to the samples studied here, with one significant difference: pressure was increased from 0.2 GPa to > 5 GPa within ~ 10 seconds inside the gas loading device. Overall, further work, including studies of the kinetics of hydrogen uptake at these pressures, is required to identify and characterize higher hydrogen content material.

IV. CONCLUSION

In conclusion, palladium metal becomes progressively hydrogenated when compressed in a pure H_2 medium at room temperature, reaching a ratio [H]:[Pd] ~ 1 at 2 (± 0.5) GPa. From 2 to 8 GPa, the ratio remains in the range 0.98 to 1.02 assuming an equation of state constructed from the previously reported results. Dehydrogenation upon room-temperature decompression reverses the hydrogenation process. The fcc lattice of $PdH_{1\pm\epsilon}$ is in thermodynamic equilibrium with H_2 at 2 to 8 GPa, as evidenced by the reversibility and independence of heating vs. no-heating, though further study of the hydrogen uptake kinetics and possible metastable formation of higher hydrides of Pd are warranted.

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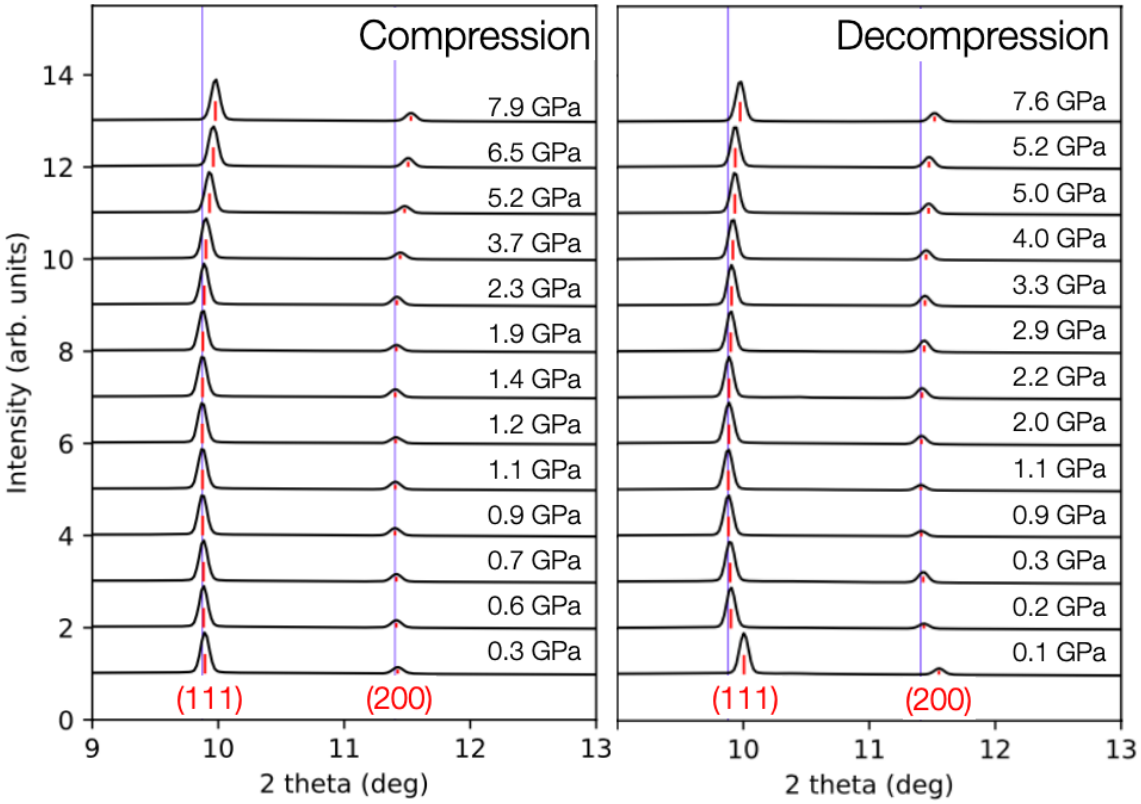

FIG. 1. Stack of room temperature X-ray diffraction patterns from PdH_x during run #2 upon compression (left) and decompression (right). The pattern at 0.3 GPa was collected before resistive heating, while all others were collected after heating. Red line segment mark the locations of the (111) and (200) diffraction peaks. Vertical blue lines mark the minimum scattering angle of each peak during compression and decompression. The X-ray wavelength is 0.4066 Å. Note that the sample is not a powder, but rather a textured Pd foil starting material that has been hydrogenated.

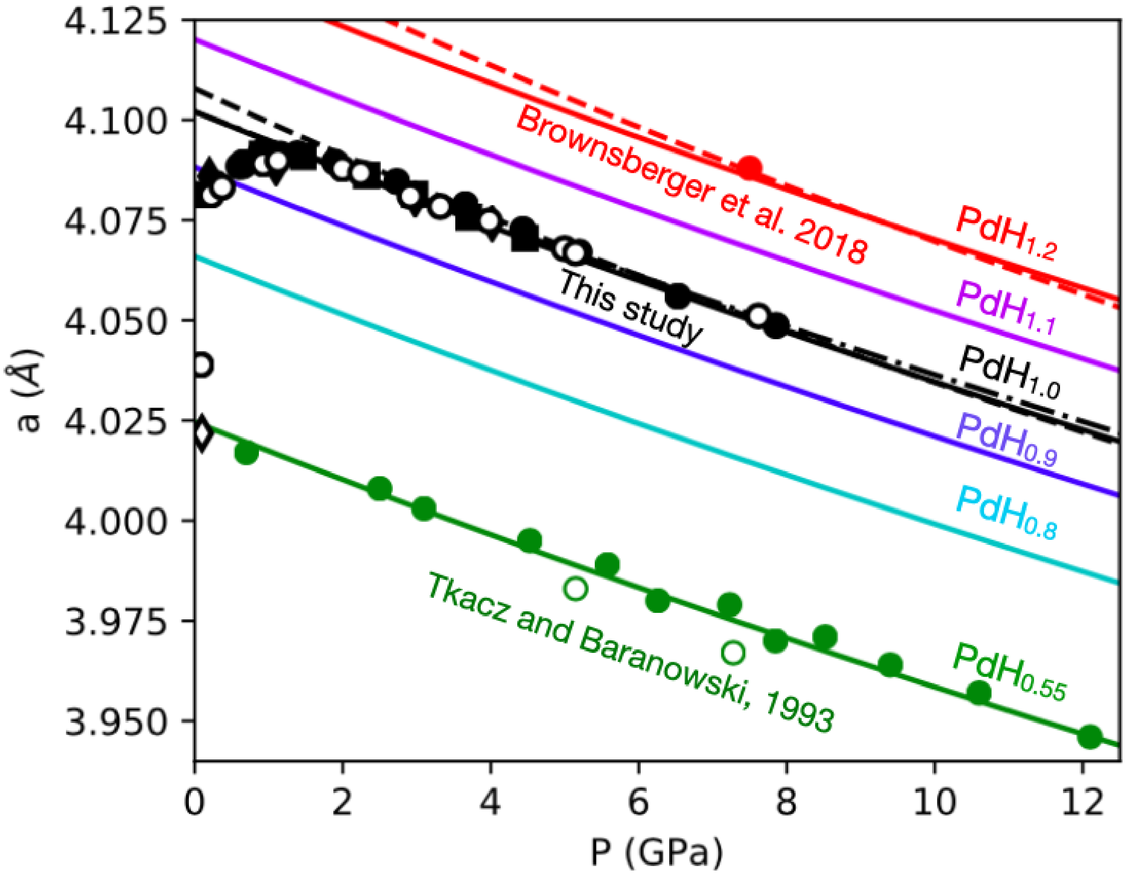

FIG. 2. Lattice parameter of PdH_x versus pressure. Data collected on compression (closed symbols) and decompression (open symbols) is overlaid on the pressure-volume-composition equation of state constructed here (solid curves), the equation of state for PdH of Guigue et al. [47] (black dashed curve), the pressure-volume equation of state of Brownsberger et al. [45] (red dashed curve), and the second order Birch-Murnaghan equation of state fitted to the volumes measured here at $P > 2$ GPa (black dash-dot). The data from Tkacz et al. [54] is shown in green circles. Black diamonds, circles, and squares indicate runs 1, 2, and 3 of Table II, respectively. The typical uncertainty in pressure is 0.1 to 0.2 GPa.

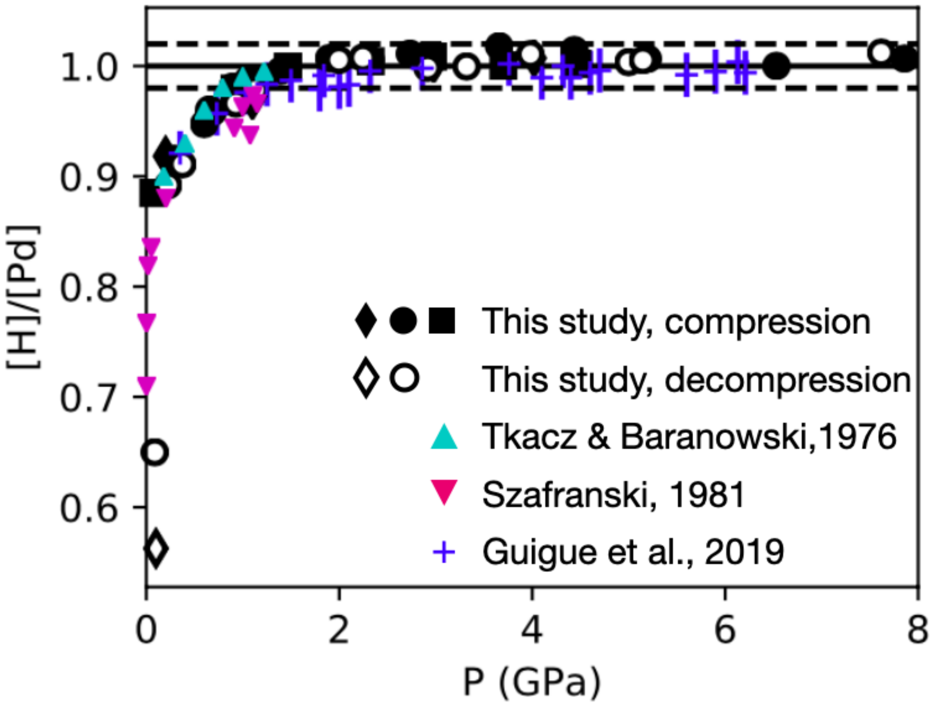

FIG. 3. Atomic ratio of H to Pd at room temperature. The ratio determined here is shown by the black symbols. Typical uncertainty in pressure is 0.1 to 0.2 GPa. Colors show ratio determined previously by mass spectrometery and weighing (Szafranski [60], pink triangles) and by piston displacement measurements (Tkacz and Baranowski [59], cyan triangles), where the highest value of x reached was $x = 0.995$. Blue crosses show ratios from Guigue et al. [47], determined by assuming [H]/[Pd] = 1.0 at $P > 3$ GPa. The height of each cross represents uncertainty. Solid and dashed black lines mark [H]/[Pd] $= 1 \pm 0.02$.

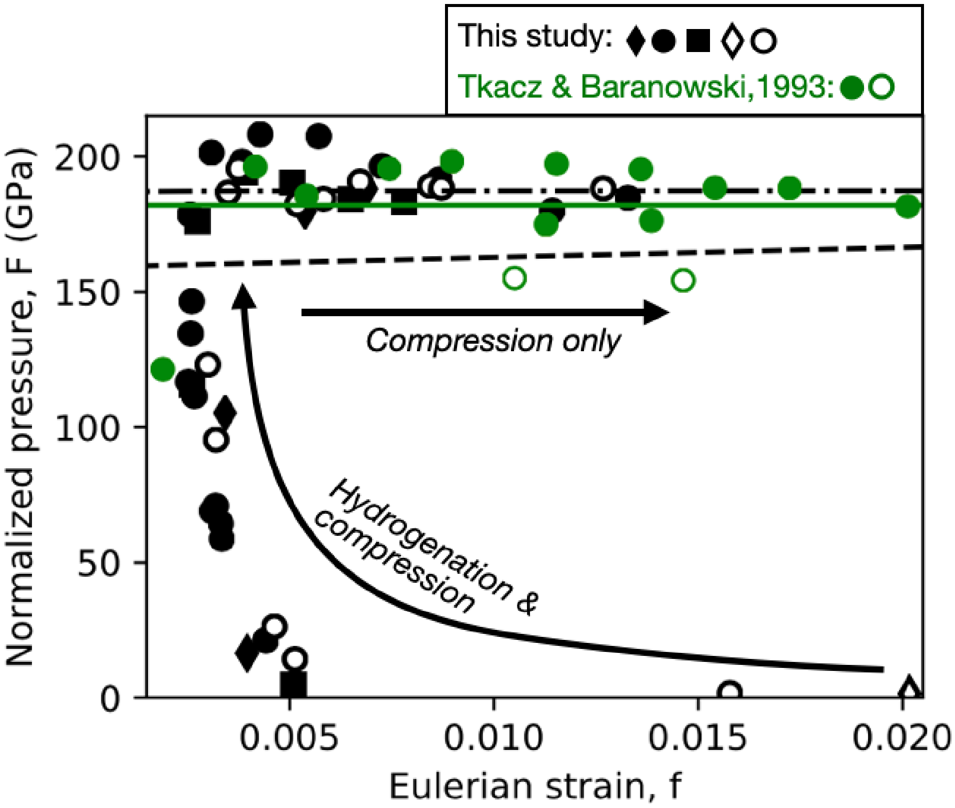

FIG. 4. Normalized pressure as a function of Eulerian strain; see Angel [63] for formulas. Volumes at ambient pressure are extrapolated from the fits from this study (V_0 = 17.257 Å/f.u.) and Tkacz and Baranowski [54] (V_0 = 16.2975 Å/f.u.). The arrows show the trajectory of data upon compression of Pd in H_2. The approximately zero slope at $F \sim 180$ GPa is consistent with a Birch-Murnaghan equations of state with $K' = 4$ for both the data from this study at $P > 2$ GPa, and the data from Tkacz and Baranowski [54]. Symbols match those of Fig. 2: data from this study (black symbols), data from Tkacz and Baranowski [54] (green circles), our Birch-Murnaghan fit to Tkacz and Baranowski (green solid line), our extrapolation to PdH (black solid curve), our Birch-Murnaghan fit to our data (black dash-dot line), the Vinet fit of Guigue et al. [47] (black dashed curve).

	EOS type	$V_{0,\mathrm{PdH}}$ (Å^3/formula unit)	K_0 (GPa)	K'	$a_{0,\mathrm{PdH}}$ (Å)
This study (constructed EOS)	Birch-Murnaghan	17.26	182 ± 18	4 (fixed)	4.102
This study (constructed EOS)	Vinet	17.26	200 ± 18	1 (fixed)	4.102
This study (fitted EOS)	Birch-Murnaghan	17.26 ± 0.08	187 ± 40	4 (fixed)	4.102
Guigue et al., (2020)	Vinet	17.33 ± 0.04	159 ± 3	5.6 ± 1.1	4.108 ± 0.003
Brownsberger et al.	Birch-Murnaghan	17.82 ± 0.05	147 ± 11	4.7 ± 0.5	4.146 ± 0.004
Brownsberger et al.	Vinet	17.83 ± 0.05	143 ± 11	5.1 ± 0.5	4.147 ± 0.004

TABLE I. Equations of state (EOS) for PdH. Values derived here are based on data up to 12 GPa, whereas equations in Guigue et al. [47] and Brownsberger et al. [45] are based on data up to $\sim$ 100 GPa. The choice to fix $K' = 4$ for Birch-Murnaghan and $K' = 1$ for Vinet equations of state is motivated by the limited range of data used in this study. We use the data up to 12 GPa of Tkacz and Baranowski [54]. The choice of $K' = 4$ is justified by the strain-independence of normalized stress in Fig. 4. Best fit values of K_0 anti-correlate with the assumed or fitted value of K'.

Run	Max P (GPa)	Decompression?	Heating?	P Scale	Endstation
1	4	yes	yes	H_2 vibron	16-BM-D
2	8	yes	yes	Au diffraction	16-ID-B
3	6	no	no	Au diffraction	16-ID-B

TABLE II. Details of high pressure runs.