| ESRF | **Experiment title:** Structural search for $PdH_x$ with x>1 up to 100 GPa | **Experiment number**: HC-3382 |
|---|---|---|
| **Beamline**: ID27 | **Date of experiment**: from: 21/10/2017 to: 24/10/2017<br>from: 14/02/2018 to: 17/02/2018 | **Date of report**: 27/02/2018 |
| **Shifts:** 12 | **Local contact(s)**: M. Mezouar | *Received at ESRF:* |

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## Report:

In 1972, the observation of superconductivity in $PdH_x$ with x~0.75 at ambient pressure, was the first demonstration of how the addition of hydrogen can greatly improve the superconducting properties of a metal [1]. PdH has also been extensively studied as an hydrogen storage material. There is currently a great interest in the study of hydrides under pressure since pressure is expected to favor the formation of polyhydrides that hold great promise as a class of high temperature superconductors

The aim of this proposal was to investigate the stable compounds in Pd-H systems under pressure. *Ab initio* calculations [3] show that $PdH_2$ could be stable in the 20-30 GPa range but that taking into account the H zero point motion contribution, the rock-salt-like PdH should be the only structure stable up to 100 GPa for the Pd-H systems. Yet, zero point motion contribution being smaller for D atoms in interstitial site, $PdD_2$ could be stable.

We therefore performed a detailed structural study of the palladium hydrides synthesized directly under pressure by laser heating mixtures of Pd+$H_2$ and Pd+$D_2$ up to 100 GPa and 50 GPa respectively. We also studied a palladium sample embedded in Ne to measure a reference equation of state so to estimate reliably the volume expansion per H atom. We have carried out five experiments at 300 K, in different pressure ranges. The sample was annealed using a YAG laser, at various pressures (see Table 1). The temperature reached was about 1300 K. The pressure was measured using either a gold volumic gauge or ruby luminescence gauge. The volume was measured using angular-dispersive x-ray diffraction. The conditions of the experiments are summarized in **Table 1**.

| Name | Sample | Culet diameter (μm) | Pressure range (GPa) | T (K) | P laser annealing (GPa) |
|---|---|---|---|---|---|
| Run 1 | Pd+$H_2$ | 300 | 0.1 - 32 | 300 | 25 |
| Run 2 | Pd+$H_2$ | 150 | 46 - 104 | 300 | 79 |
| Run 3 | Pd+$H_2$ | 150 | 36 - 86 | 300 | 85.5 |
| Run 4 | Pd+$D_2$ | 300 | 0.3 - 50 | 300 | 25, 44 |
| Run 5 | Pd+Ne | 300 | 0.7 - 62 | 300 | - |

**Table 1:** Conditions of the five experimental runs.

The measurements of *V* vs. *P* for palladium, palladium hydride and palladium deuteride at 300 K are plotted in **figure 1a**. In **figure 1b** is shown a zoom in the 0 - 5 GPa range. PdH and PdD form spontaneously, with a “loading” phase belown 1 GPa. Above 1 GPa, a 1:1 stoichiometry is reached as magnetic measurements conducted in our lab on a SQUID magnetometer confirmed [4]. A clear isotopic shift between the V(P) of PdH and PdD is observed, of about 0.7 % at ambient pressure, essentially due to the zero point motion effect of H/D in octahedral sites. We performed several laser heatings, and the volume remained unchanged. PdH is stable up to 100 GPa. PdD is observed stable up to 50 GPa. A fine analysis of these results is being made to disclose a possible fraction occupancy of tetrahedral sites in PdD.

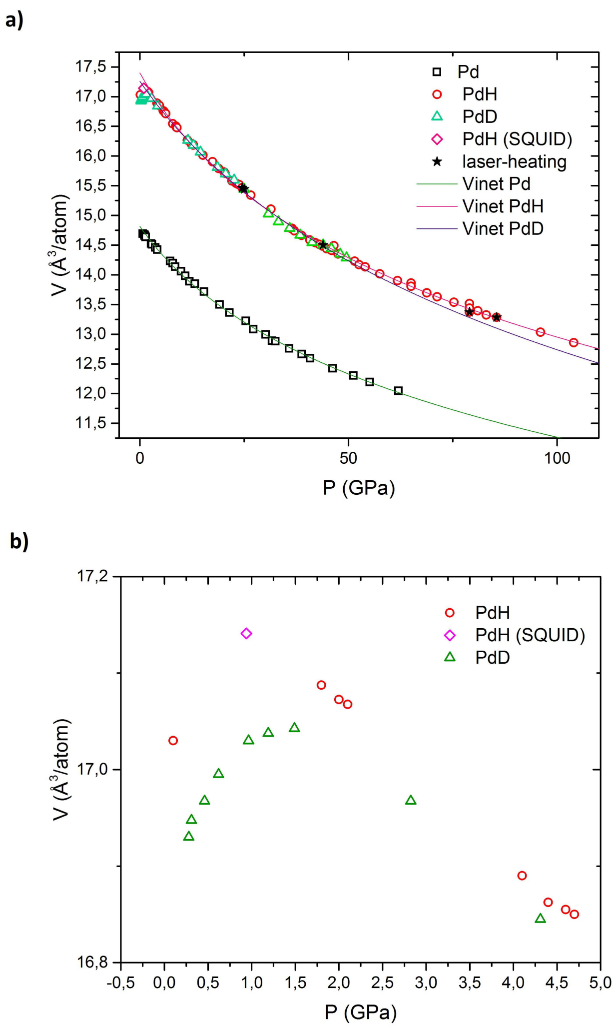


**Figure 1**:
(a) Evolution of the volume as a function of pressure for Pd, PdH and PdD together with the Vinet fits of the data. Stars show the laser heating processes. The increase in volume from Pd to PdH/PdD is about 2.5 $Å^3$ at low pressure.

(b) Zoom in the 0 – 5 GPa range of the equation of states. One can see a “loading” phase below 1 GPa were octaedral site of the Pd lattice are spontaneously filled, reaching PdH with 1:1 stoichiometry around 1 GPa (as confirmed with a SQUID magnetic measurement).

**References:**
[1] T. Skoskiewixz, Phys. Status Solidi 1 11, K123 (1972)
[2] H. M. Syed, Preprint at: https://arxiv.org/abs/1608.01774 (2016)
[3] I. Errea, Phys. Rev. Lett. 111, 177002 (2013)
[4] A. Marizy, High Pres. Res. 37:4, 465-474 (2017)