Experimental Report

24/02/2014

Proposal: **5-25-216** **Council:** 10/2012

Title: Real-time study of the hydrogenation and deuteration of palladium

This proposal is a new proposal

Researh Area: Chemistry

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Samples: palladium

Instrument	**Req. Days**	**All. Days**	**From**	**To**
D20	3	3	02/04/2013	05/04/2013

Abstract:

Palladium hydride and deuteride are known for more than 100 years and have been well investigated. Structural data at non ambient conditions, however, are scarce, real-time studies not available. We would therefore like to use our recently developed single crystal based sapphire gas pressure cell to investigate the hydrogenation as well as the deuteration of palladium. Both reactions shall be followed through the two-phase region, where alpha and beta palladium hydride (deuteride) coexist, and at higher temperatures above the critical point. These investigations will yield new structural data at non ambient conditions not available before, allow to link these structure data to the kinetics observed in these real time studies and to test the hypothesis of tetrahedral void occupancy of deuterium in the supercritical region of the phase diagram.

Real-time study of the hydrogenation and deuteration of palladium (5-25-216)

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Palladium is the archetypical example of a metal incorporating hydrogen [1]. α- and β-PdH(D)$_x$ both have a disordered arrangement of hydrogen (deuterium) atoms in a cubic closest packing of palladium atoms and are separated by a miscibility gap at room temperature [2]. The two-phase region vanishes at the critical point of T_c = 563 K (556 K), p_c = 1.9 MPa (3.9 MPa), x = 0.257. We have undertaken *in situ* neutron powder diffraction investigations with a sapphire single crystal based gas pressure cell [3], which was developed within LTP-5A-1. By increasing the deuterium pressure at 446 K the formation of both α- and β-PdD$_x$ indicates the two-phase region in accordance with the phase diagram [2]. The refined structural parameters (Fig. 1) including deuterium occupation are in good agreement with former experiments and the phase diagram [2] and provide new crystal structure data for p,T conditions not investigated before.

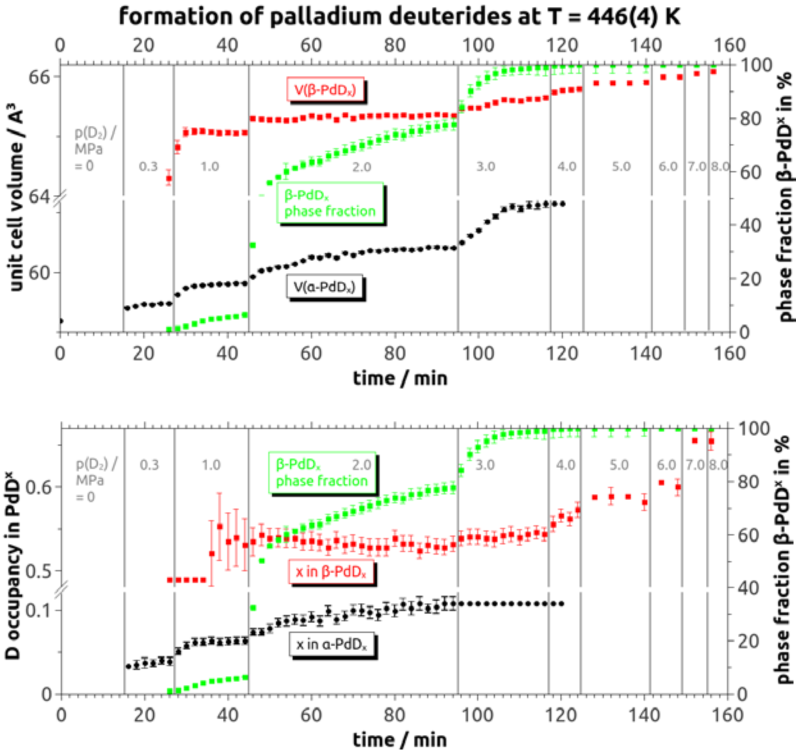

Fig. 1: Structural parameters of α- and β-PdD$_x$ as a function of time from Rietveld refinement based on *in situ* neutron powder diffraction data. Error bars represent one estimated standard uncertainty.

When deuterium is introduced at a pressure of 0.3 MPa, the α-phase forms immediately and only a few minutes later the β-phase as well. Both coexist during 96 minutes. The deuterium content of the α-phase deuterides PdD_x starts at x = 0.038(4) at a deuterium pressure of 0.3 MPa and reaches a maximum of x = 0.108(8) at 2.0 MPa. At pressures up to 1.0 MPa the formation of the β-phase is relatively slow, but speeds up considerably at 2.0 MPa, where 50% of the α-phase converts into the β-phase within only four minutes. The reaction rate then slows down and the reaction is complete after two hours with no trace of α-PdD_x reflections left. The deuterium content of the β-phase continues to grow with increasing deuterium gas pressure to a composition of β-$PdD_{0.72(3)}$ at T = 446(4) K and 8.0 MPa. Incorporation of tetrahedral voids was not observed in the course of this *in situ* study. After each pressure increase, unit cell volume and deuterium occupation of the α-phase increase slowly, while those of the β-phase do so very quickly (Fig. 1). This is probably due to the well-known fact that diffusion of hydrogen in the former is slower than in the latter [4]. This further suggests that deuterium diffusion is the time-limiting step, at least for the formation of the α-phase deuteride PdD_x.

Another deuteration experiment of palladium aimed at formation of the deuteride above the critical point. Palladium powder was again contained in a sapphire single crystal based gas pressure cell for *in situ* neutron powder diffraction [3]. A temperature of 593 K was chosen and deuterium pressure was increased stepwise. After exceeding the critical pressure formation of the β-phase began in accordance with the phase diagram [2]. The following parameters could be refined from the *in situ* neutron powder diffraction patterns at 593 K:

$p(D_2)$ / bar	a / pm	composition
41	392.7(2)	$PdD_{0.01(2)}$
60	393.9(4)	$PdD_{0.03(2)}$
81	395.6(4)	$PdD_{0.18(2)}$
110	400.3(4)	$PdD_{0.25(2)}$

The diffraction patterns show the presence of only one phase at a time, except at 81 bar, where reflections are broadened and seem to split (Fig. 2). This suggests that the two-phase region was entered despite applying a temperature well above the critical point, which may indicate temperature gradients in the pressure cell already noted before [3]. The highest deuterium concentration was reached at 110 bar deuterium gas pressure and corresponds to the composition $PdD_{0.25}$, which is precisely the one at the critical point. All deuterium uptake reactions are very fast and completed in less than 30s. This is again a strong indication of fast diffusion of deuterium in β-PdD_x. Unfortunately, the experiment had to be stopped at the highest pressure due to mechanical failure of the sapphire crystal. The planned repetition of the experiment using the natural isotopic mixture of hydrogen instead of pure deuterium failed due to repeated technical problems with the gas supply system and subsequent time constraints.

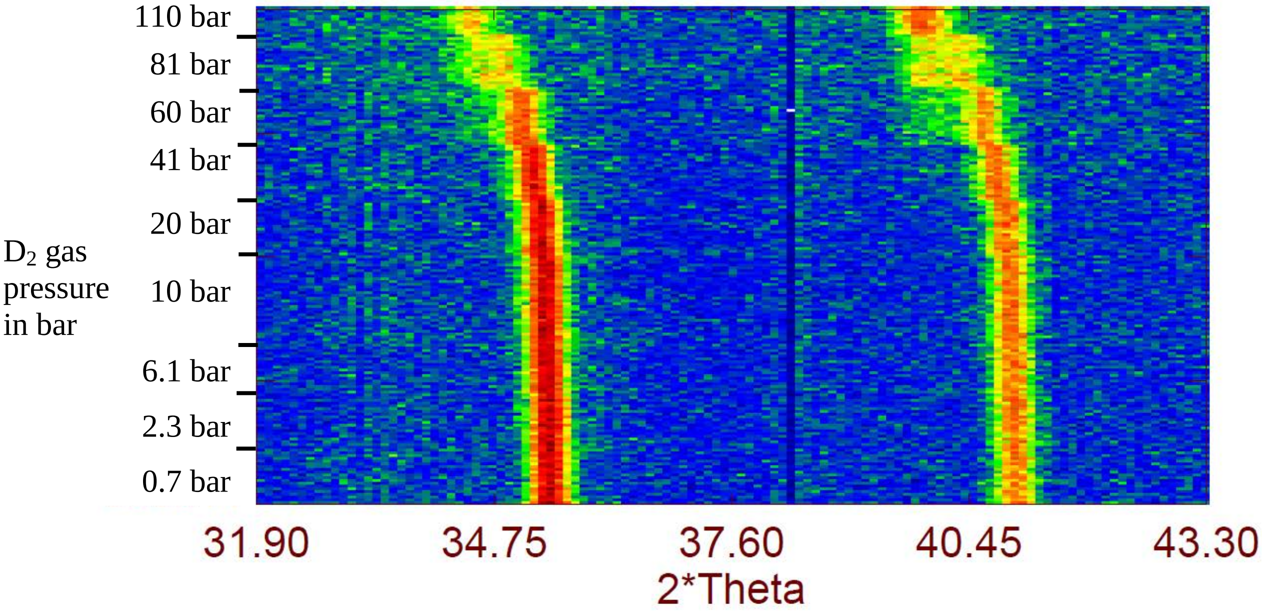

Fig. 2: (111) and (200) reflections of β-PdD_x in false colours as a function time and deuterium pressure at 650 K.

Literature

[1] T. Graham, *Philos. Trans. R. Soc. London* **1866**, *156*, 399-439

[2] T. B. Flanagan, W. A. Oates, *Annu. Rev. Mater. Sci.* **1991**, *21*, 269-304

[3] H. Kohlmann, N. Kurtzemann, T. C. Hansen, *Powder Diffr.* **2013**, *28*, 242-255

[4] E. Storms, *J. Alloys Compd.* **1998**, *268*, 89-99