Experimental report

10/10/2019

Proposal:	**5-24-613**	**Council:**	4/2018

Title: Reaction pathways of hydrogenation-dehydrogenation of InPd3 and FePd3by in situ neutron diffraction

Research area: Chemistry

This proposal is a new proposal

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Samples:
FePd3
InPd3

Instrument	Requested days	Allocated days	From	To
D20	3	3	05/10/2018	08/10/2018

Abstract:

The hydrogen-induced atomic rearrangements in intermetallic compounds MPd3 (M = In, Fe) will be studied by in situ neutron powder diffraction. A user-supplied gas-pressure cell with laser heating installed on D20 will provide the means to collect diffraction patterns as a function of temperature (up to 600 K) and deuterium gas pressure (up to 100 bar) with a time resolution of two minutes. This will allow to identify intermediates including deuterium positions in the crystal structures and provide an understanding of the underlying principle of hydrogen-induced rearrangement in intermetallics. For InPd3, the series of superstructures of the cubic-close packing (ccp) TiAl3 type - ZrAl3 type - PbTl2Pd9 type - AuCu3 type is to be monitored upon hydrogen uptake. For FePd3, the effect of atomic order (Fe/Pd, AuCu3 type and Cu type) on hydrogenation and hydrogen-induced ordering will be elucidated. These reactions are of importance in hydrogen embrittlement of materials and in catalytic processes.

Reaction pathways of hydrogenation-dehydrogenation of $InPd_3$ and $FePd_3$ by *in situ* neutron diffraction (experiment 5-24-613)

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$InPd_3$ crystallizes in ordered superstructures of the cubic close packing (ccp), the $ZrAl_3$ and the $TiAl_3$ type. Upon hydrogen uptake, a rearrangement to another ccp superstructure, the $AuCu_3$ type, occurs with hydrogen atoms occupying octahedral [Pd_6] voids [1]. The hydrogenation and dehydrogenation was followed *in situ* in this experiment on a $ZrAl_3$ type sample using deuterium in a sapphire single-crystal cell [2]. When increasing deuterium pressure at 400 K to 5.0 MPa, a new phase is formed, $InPd_3D_{<0.7}$ with a deuterium filled $ZrAl_3$ type structure. Raising temperature to 500 K leads to the cubic deuterides $InPd_3D_{\approx 0.8}$ with a cubic antiperovskite type structure [1]. Heating in vacuum leads to a decrease in deuterium content of the cubic deuterides, and upon complete deuterium release $ZrAl_3$ type $InPd_3$ is restored (Fig. 1). Due to the sluggish reaction of the $ZrAl_3$ type sample and time constraints ($FePd_3$ samples see below) the $TiAl_3$ type sample could not be measured as foreseen in the proposal text.

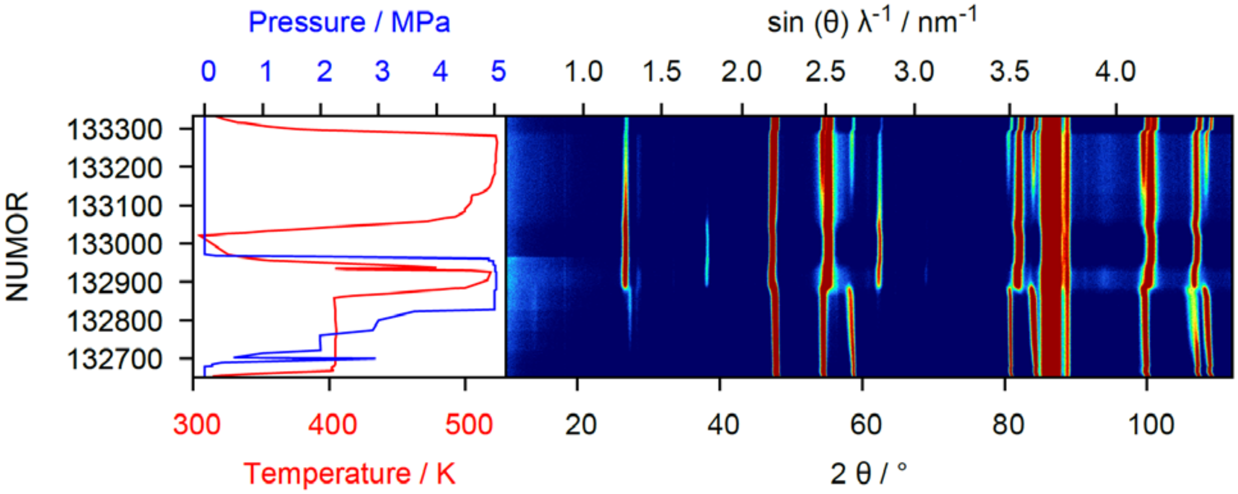

Figure 1: *In situ* neutron powder diffraction data of the deuteration of $InPd_3$ taken on diffractometer D20 at $\lambda = 1.86796(3)$ Å in a single crystal sapphire cell [2] under various deuterium pressures and temperature conditions. Intensities are in false colors, each measurement (NUMOR) with two minutes data collection time.

To study the influence of structural order in $FePd_3$ on hydrogenation properties, *in situ* neutron powder diffraction on an ordered and a disordered sample using deuterium in a sapphire single-crystal cell [2] was performed. Deuterium gas pressure was slowly increased up to 8.0 MPa, before raising the temperature to about 550 K (Fig. 2). $FePd_3$ with ordered and disordered structure showed less deuterium uptake than expected from previously executed laboratory X-ray diffraction experiments. For the disordered compound the unit cell increases only by 0.05% ($a_{\text{before}} = 3.8512(4)$ Å, $a_{\text{after}} = 3.8518(2)$ Å) and the site occupancy factor (SOF) of deuterium is refined to zero (Wyckoff position 4*b*), i. e. it does not take up a significant amount of deuterium. Furthermore, no ordering of the metal atoms is observed. The unit cell volume of ordered $FePd_3$ expanded by 0.2% ($a(FePd_3)$ = 3.85158(9) Å, $a(FePd_3D_{0.03(1)})$ = 3.85416(2) Å) during deuteration. The deuterium atoms occupy $[Pd_6]$ octahedral voids as determined by difference Fourier analysis. During the *in situ* experiment (Fig. 2) the superstructure reflections of $FePd_3$ and its deuteride are broadened due to very small magnetic domains of the ferromagnetic compound analogous to $MnPd_3$ [3]. The width of these reflections decrease when reaching the Curie temperature ($T_C(FePd_3)$ = 499.1 K [4]). Additionally, the intensities of the superstructure reflection decrease and β-PdD_x is formed. Both effects are reversible during the cooling process.

Complete serial refinements based on the *in situ* diffraction data for both $FePd_3$ and $InPd_3$ samples are in progress.

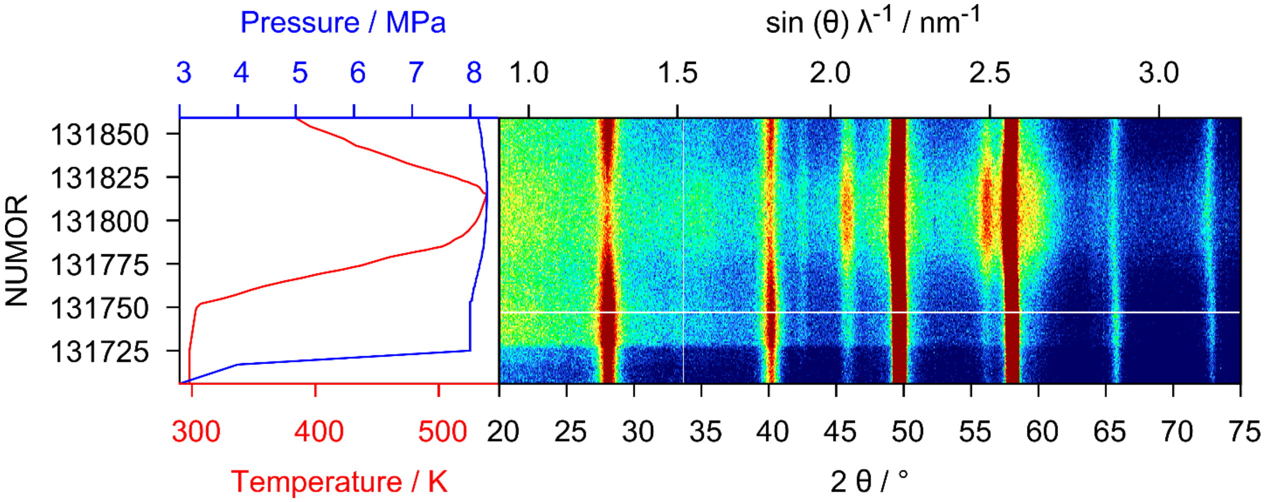

Figure 2: *In situ* neutron powder diffraction data of the deuteration of ordered $FePd_3$ taken on diffractometer D20 at λ = 1.86796(3) Å in a single crystal sapphire cell [2] under various deuterium pressures and temperature conditions. Intensities are in false colors, each measurement (NUMOR) with two minutes data collection time.

Literature

[1] H. Kohlmann, A. V. Skripov, A. V. Soloninin, T. J. Udovic, *J. Solid State Chem.* **2010**, *183*, 2461-2465

[2] A. Götze, H. Auer, R. Finger, T. C. Hansen, H. Kohlmann, *Phys. B (Amsterdam, Neth.)* **2018**, *551*, 395-400

[3] P. Önnerud, Y. Andersson, R. Tellgren, P. Nordblad, *J. Solid State Chem.* **1997**, *128*, 103-114.

[4] G. Longworth, *Phys. Rev.* **1668**, *172*, 572-776.