Experimental report

15/03/2017

Proposal:	**5-21-1103**	**Council:**	4/2016

Title: Metal-semiconductor transition andcrystal structures of ternary lanthanide hydrides

Research area: Chemistry

This proposal is a new proposal

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Samples:
$EuMg_2D_x$
$NdMg_2D_7$
$TbMg_2D_7$
Eu_2RuD_6
$YbD_{2.67}$

Instrument	Requested days	Allocated days	From	To
D20	1	1	18/06/2016	20/06/2016

Abstract:

In contrast to other Laves phases lanthanide containing $LnMg_2$ (Ln = La, Ce, Sm, Eu) show a metal-semiconductor transition upon hydrogenation and formation of $LnMg_2H_7$ and $EuMg_2H_6$. Recently we found new hydrides of Laves phases $LnMg_2$ (Ln = Nd, Eu, Tb). $NdMg_2H_7$ seems to be isotypic to $LaMg_2D_7$ according to laboratory X-ray diffraction. $EuMg_2$ forms intermediate hydrides with crystal structures similar to that of the parent hexagonal Laves phase, which are of particular interest in view of the metal-semiconductor transition. $TbMg_2$ behaves similar, but crystallizes in a monoclinic space group. In addition to these Laves phase hydrides, two further lanthanide hydrides need completion of their crystal structure; these are Eu_2RuH_6 (probably K_2PtCl_6 type) and $YbD_{2.67}$, where the ordering of deuterium atoms is under debate. All powders will be investigated at D20 at room temperature. The high neutron absorption of europium requires a short wavelength (0.8A) and the use of double-walled sample holders. All other samples will be measured at 1.87A in high-resolution mode. The $YbD_{2.67}$ sample will be measured in situ at 100 bar deuterium pressure in a user supplied gas pressure cell.

Metal semiconductor transition and crystal structure of ternary lanthanide hydrides

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$NdMg_2D_7$ and $PrMg_2D_7$

Laves phase hydrides play an important role in hydrogen storage, e. g. $ZrCr_2$ based materials for rechargeable battery application. They reversibly take up considerable amounts of hydrogen to form metallic hydrides, e. g. ZrV_2H_6 with hydrogen in tetrahedral voids of the parent crystal structure. Lanthanide (*Ln*) magnesium based Laves phases $LnMg_2$ on the other hand form ionic hydrides $LnMg_2H_7$ (*Ln* = La, Ce, Sm) or $EuMg_2H_6$ [1-3], i. e. show a metal-semiconductor transition during hydrogenation. The Laves phases $NdMg_2$ and $PrMg_2$ were deuterated at 140 bar and 95 bar deuterium pressure, respectively, and 393 K. X-Ray powder

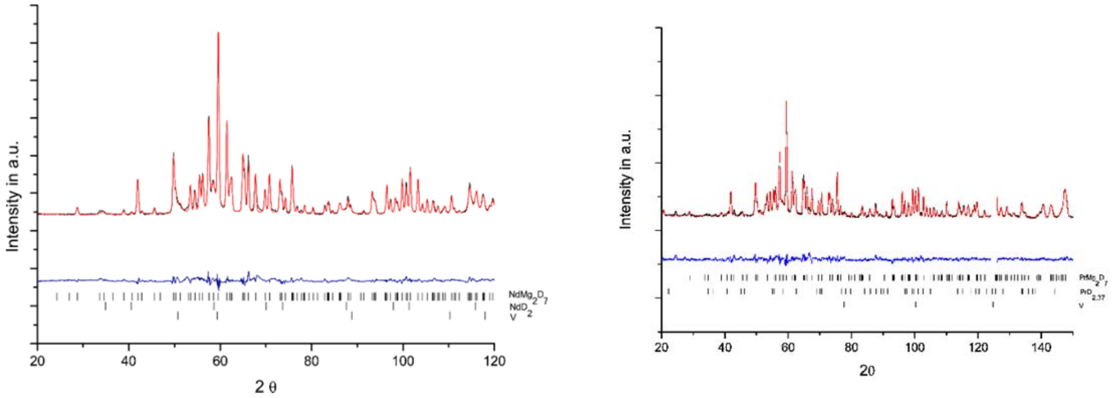

Fig. 1: Rietveld refinement of the crystal structure of $NdMg_2D_7$ (left) and $PrMg_2D_7$ (left) using neutron diffraction data (D20, ILL, Grenoble, λ = 186.78(3) pm, R_p = 3.7% / 4.5%, R_{wp} = 5.2% / 5.8%), Bragg positions from top to bottom $NdMg_2D_7$, NdD_2, V / $PrMg_2D_7$, $PrD_{2.37}$, V

Tab. 1: Crystal structure of $NdMg_2D_7$, $P4_12_12$, a = 628.14(3) pm, c = 940.33(5) pm

atom	site	x	y	z	B_{iso} / Å^2
Nd	4*a*	0.2699(5)	x	0	0.55(10)
Mg	8*b*	0.0254(6)	0.2603(7)	0.3514(4)	1.144(94)
D1	8*b*	0.0379(5)	0.0240(6)	0.1289(4)	2.25(94)
D2	8*b*	0.0796(6)	0.4336(5)	0.1803(3)	1.721(86)
D3	8*b*	0.3143(5)	0.1574(5)	0.2551(5)	2.171(94)
D4	4*a*	0.7557(7)	x	0	2.06(11)

Tab. 2: Crystal structure of $NdMg_2D_7$, $P4_12_12$, a = 630.561(17) pm, c = 943.25(3) pm

atom	site	x	y	z	B_{iso} / Å^2
Pr	4*a*	0.2674(9)	x	0	1.31(14)
Mg	8*b*	0.0255(6)	0.2605(7)	0.3487(4)	1.81(9)
D1	8*b*	0.0395(6)	0.0246(7)	0.1287(5)	2.94(8)
D2	8*b*	0.0788(6)	0.4334(6)	0.1800(4)	2.54(8)
D3	8*b*	0.3109(5)	0.1587(5)	0.2544(5)	0.74(8)
D4	4*a*	0.7584(8)	x	0	2.50(11)

Tab. 3: Selected interatomic distances in $LnMg_2D_7$ in pm (*Ln* = La [1], Ce[1], Pr [this work], Nd [this work], Sm [2]

	La [1]	Ce[1]	Pr [this work]	Nd [this work]	Sm [2]
D1-Ln	2.469(4) 2.409(4)	2.463(4) 2.362(4)	2.425(7) 2.329(7)	2.445(5) 2.303(5)	2.405(8) 2.316(8)
D1-Mg	1.921(4)	1.904(4)	1.930(6)	1.907(5)	1.853(9)
D2- Ln	2.466(4) 2.388(3)	2.437(4) 2.360(3)	2.411(7) 2.322(6)	2.406(5) 2.315(4)	2.424(9) 2.276(7)
D2-Mg	2.131(4) 1.991(3)	2.179(4) 1.990(4)	2.164(6) 1.958(6)	2.153(4) 1.972(5)	2.197(9) 1.948(9)
D3-Ln	2.554(3) 2.550(3)	2.529(3) 2.507(4)	2.517(7) 2.511(5)	2.516(5) 2.492(5)	2.468(8) 2.462(8)
D3-Mg	2.116(3) 2.032(4)	2.118(3) 2.012(4)	2.108(6) 2.003(6)	2.128(6) 1.961(6)	2.070(10) 2.049(10)
D4-Mg	2.062(3) 1.982(3)	2.027(3) 1.980(3)	2.018(6) 1.977(6)	2.007(6) 1.963(6)	1.982(8) 1.969(9)

diffraction suggested deuterides with the $LaMg_2D_7$ structure type. Neutron diffraction at ambient conditions was performed in order to locate deuterium positions. The Rietveld refinements confirmed the $LaMg_2D_7$ type structures and yielded precise structural parameters and bonding distances (Figs. 1-2, Tabs. 1-3). The latter agree well with known *Ln*-D and Mg-D distances and reflect the lanthanide contraction.

$EuMg_2D_x$ and Eu_2RuD_6

The hexagonal Laves phase $EuMg_2$ was deuterated under 120 bar and 373 K, which yielded partial formation of the ternary hydride $EuMg_2D_x$. Deuteration of a mixture of 2 EuD_2 + Ru powder yielded a multi-phase product. Neutron diffraction data were taken at a short wavelength of $\lambda = 0.8$ Å in order to minimize the enormous neutron absorption of the natural mixture of isotopes of europium [4]. Unfortunately, broad reflections and heavy overlap due to the short wavelength, multi-phase nature of the samples and probably pseudo-symmetry (in case of $EuMg_2D_x$) hampered a proper extraction of individual reflection intensities. Location of deuterium positions has not been successful so far.

YbD_x

In the previous experiment 5-24-510 a new crystal structure model for $YbD_{2.67}$ could be determined, however, refinement was not satisfactory, because the phase content in the *in situ* experiment was not sufficient. We prepared a fresh sample of $YbD_{2.67}$ in a sapphire gas pressure cell in our laboratory under the conditions determined in the previous *in situ* experiment and took neutron powder diffraction data of the so prepared sample at room temperature in the gas pressure cell under deuterium pressure. This approach does not allow for checking the success of the synthesis before the neutron diffraction measurement. Unfortunately, the sample was not of better quality than in experiment 5-24-510 as shown by the neutron diffraction data. This underlines the importance of *in situ* experiments, where a direct synthesis control is possible. We will have to extend the capabilities of our *in situ* gas pressure cells in order to better characterize the crystal structure of $YbD_{2.67}$.

Literatur

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