Experimental report

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Title: Reaction pathways to the Zintl phase hydride NdGaD1.66 by in situ neutron diffraction

Research area: Chemistry

This proposal is a new proposal

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Samples: NdGa

Instrument	Requested days	Allocated days	From	To
D20	2	2	10/11/2016	12/11/2016

Abstract:

The system NdGa-H2 shows intriguing hydrogenation behaviour with various intermediate phases. Gallium chains of the Zintl phase NdGa are fragmented by inserting hydrogen leading to (GaH)2- chains with partially occupied hydrogen positions as evidenced by ex situ neutron powder diffraction on deuterated samples. Full occupation leading to electron precise Nd3+H-(GaH)2- could not be achieved as yet, probably due to high desorption pressure. These Zintl phase hydrides are difficult to prepare and characterize by ex situ diffraction methods. Therefore time-resolved in situ neutron diffraction shall be applied to study these transient phases, determine their crystal structures and elucidate reaction pathways. In the case of NdGaH1+x (0 ≤ x ≤ 1) they further offer the possibility of attaining the fully hydrogenated phase with x = 1, which is elusive so far. A user supplied single-crystal based sapphire gas pressure cell will be used to collect neutron powder diffraction data with a time resolution of two minutes, thus mapping the complete deuteration reaction pathway of NdGa.

Reaction pathways to the Zintl-phase hydride $NdGaD_{1.66}$ by *in situ* neutron diffraction

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The hydrogenation of Zintl phases was investigated recently because of interesting bonding properties of the corresponding hydrides and their use as hydrogen storage media [1]. CrB-type Zintl phases such as *M*Si and *M*Ge (*M* = Ca, Sr, Ba) show a fascinating behaviour towards hydrogen, which occupies tetrahedral sites formed exclusively by *M* as well as sites coordinating the polyanionic silicon and germanium chains, respectively [2]. Most rare earth elements (*Ln*) form monogallides *Ln*Ga, which also crystallize in the CrB type structure. Recently, NdGa was found to absorb hydrogen and reversibly form hydrides [3].

The reaction of NdGa to $NdGaD_x$, $x \geq 1$ was monitored *in situ* at isothermal conditions (500 K) and increasing deuterium gas pressures up to 9 MPa (Fig. 1, top). Applying the reaction gas at 0.2 MPa lead to a first, quite fast reaction step, that formed $NdGaD_x$ with x already larger than 1. A slower deuterium uptake followed. A final composition of $NaGaD_{1.803(7)}$ was reached already at 500K and 4 MPa and did not change upon increasing pressure to 9 MPa and within more than 300 min. This phase could be cooled down to room temperature without structural changes. At about 300 K the sample was evacuated and did not show any deuterium release within 1 h. Heating was started again. At 350 K deuterium started to be released. The sample was heated under vacuum up to 500 K reaching a final composition of $NdGaD_{1.234(9)}$.

Structural information could be obtained by sequential Rietveld refinement. The precursor Zintl phase NdGa crystallizes in the CrB structure type. According to the Zintl-concept there are formally Ga^{3-}-anions forming linear zigzag chains. Within the whole experiment the $NdGaD_x$ structure kept an orthorhombic unit cell as already present in the parent phase and did not show any sign for a lowered symmetry. A previous work gave different structural candidates for the $NdGaD_x$ structure and suggested a monoclinic setting [3] which cannot be confirmed. The general structure of $NdGaD_x$-phases, therefore can be described as a distorted version of the deuterium free Zintl phase NdGa. It crystallizes in space group type *Cmcm* with contracted *a* and strongly elongated *b* lattice parameter, while *c* is hardly affected. Tetrahedral Nd_4-voids are fully occupied with deuterium for the whole experiment (Fig. 1, middle, red x - D-TV). Additional deuterium atoms bridge two gallium atoms and are part of the polyanionic

structure. Thus the sum formula can be rewritten as $NdGaD_{1+y}$, y < 1. The changing deuterium content of the samples only depends on the filling of Ga-chain coordinating sites (Fig. 1, middle, blue x - D-chain). During the reaction different superstructures occur (Fig. 1, bottom, colored bar), i. e. a two-fold superstructure for compositions of about $NdGaD_{1.5}$ and a threefold superstructure for about $NdGaD_{1.66}$, indicating deuterium ordering. Structure models could not be finally determined for the intermediate phases.

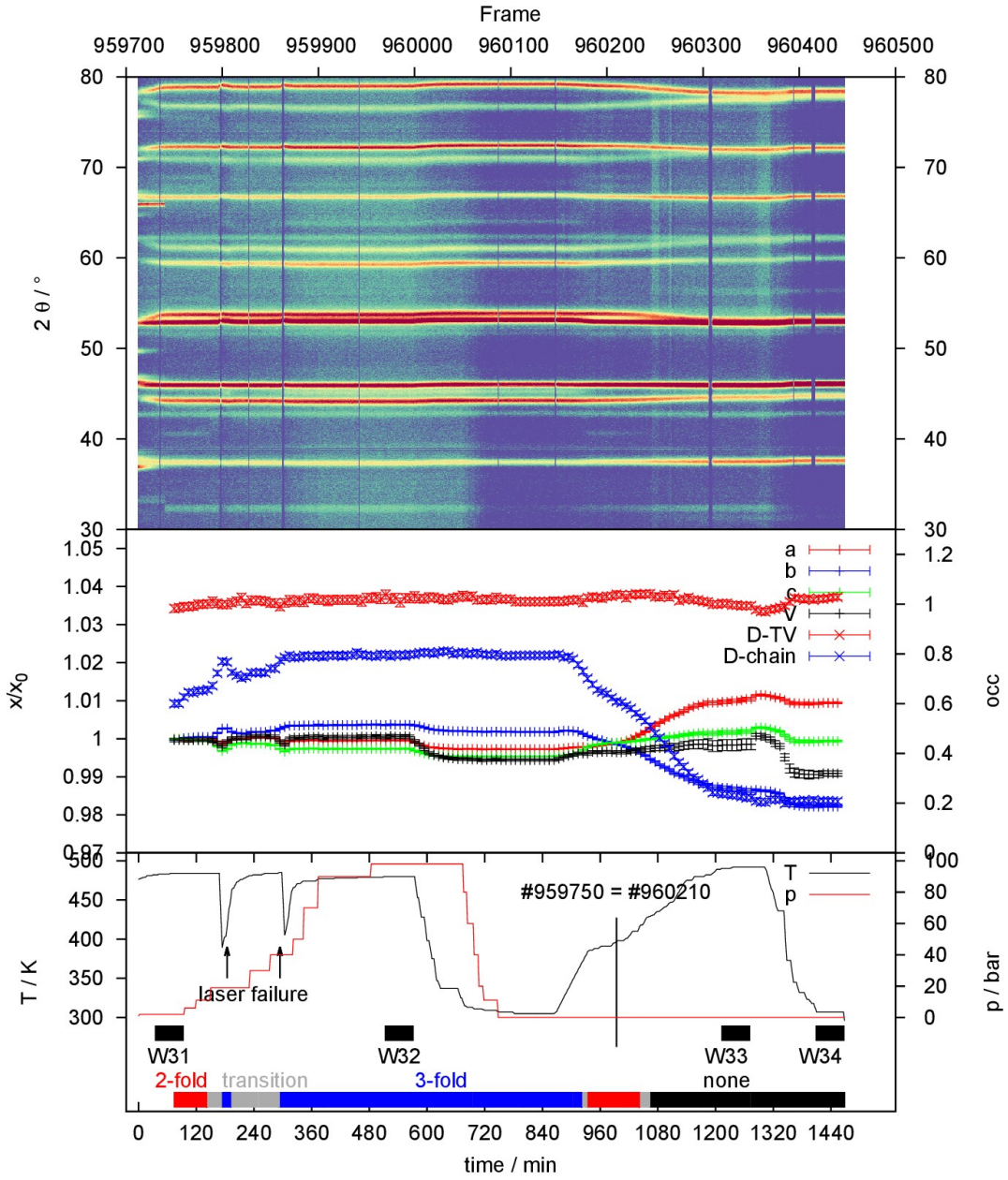

Fig 1. *In situ* diffraction (top), sequential Rietveld refinement results (middle) and T-p profile (bottom). The occupation of tetrahedral Nd_4-voids (D-TV) and the site bridging two gallium atoms (D-chian) are shown. The colored bar at the bottom gives information about the obtained super structure (always crystallographic *a* direction regarding NdGa).

Upon evacuation the superstructures are present as well. The final phase ($NdGaD_{1.234(9)}$) does not show any superstructure. Rietveld refinement of a structure model as described above shows deuterium filled Nd_4-tetrahedral voids and a gallium bridging site with 23.4(9)% occupation.

Along zig-zag chain direction d(Ga-Ga) decreases upon deuteration from 263.9(4) pm (NdGa, 298 K) to 246.3(4) pm ($NdGaD_{1.226(10)}$, 298 K). When the deuterium occupation between the chain increases, the change in d(Ga-Ga) is not significant within 3 e.s.u.: 252.1(4) pm in $NdGaD_{1.22}$ (500 K); 254.1(11)-256.9(8) pm in $NdGaD_{1.80(2)}$ (500 K, threefold superstructure). Due to the *Cmcm* model without superstructure d(Ga-D) is equidistant. There is no degree of freedom perpendicular to the chains, i.e. no free *x* parameter. The decreasing chain length can be attributed as a depopulation of π*-bands and therefore an increasing bond strength (see e.g. [4]).

The major problem with Rietveld refinement corresponds to at least one non-described impurity phase that was hardly seen by X-ray diffraction. Fortunately these phase do not change during the whole in situ experiment.

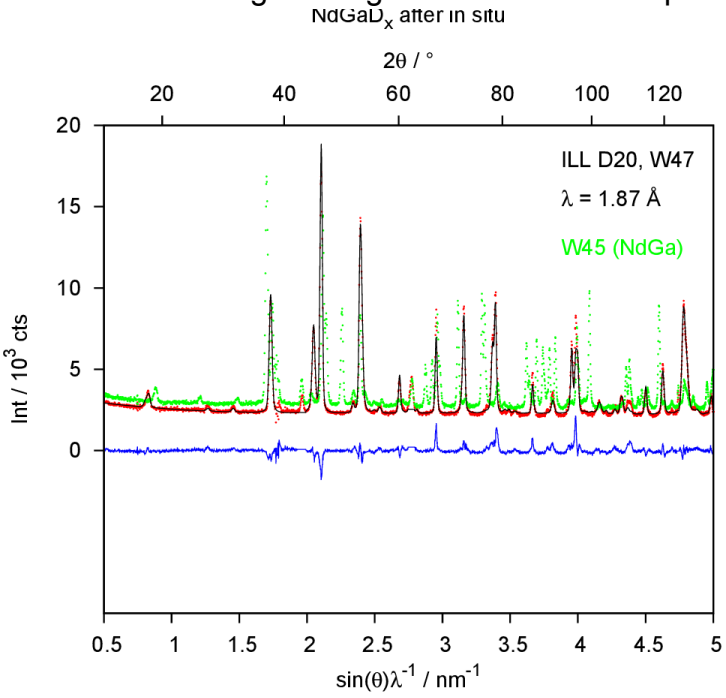

Fig 2. Rietveld refinement of the structure of $NdGaD_{1.234(9)}$ after the *in situ* experiment, measured in a vanadium container. There is still a non-described impurity phase. The original Zintl phase NdGa is superimposed. *Cmcm*, *a* = 416.16(3) pm, *b* = 1202.26(12) pm, *c* = 418.04(3) pm; R_{wp} = 19.5%, R_p = 21.0%, gof = 5.67 .

[1] U. Häussermann, *Z. Kristallogr.* **2008**, *223*, 628-635
[2] experimental report 5-22-734, ILL, 2016
[3] J. Ångström, R. Johansson, T. Sarkar, M. H. Sørby, C. Zlotea, M. S. Andersson, P. Nordblad, R. H. Scheicher, U. Häussermann and M. Sahlberg, *Inorg. Chem.* **2016**, *55*, 345-352 .
[4] H. Auer, R. Guehne, M. Bertmer, S. Weber, P. Wenderoth, T. C. Hansen, J. Haase and H. Kohlmann, *Inorg. Chem.* **2017**, *56*, 1061-1071; H. Auer, R. Schlegel, O. Oeckler, H. Kohlmann, *Angew. Chem. Int. Ed.* **2017**, DOI: 10.1002/anie.201706523.