Experimental report

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Proposal: **5-22-734** **Council:** 10/2014

Title: Reaction pathways to the Zintl phase hydrides CaSiH and MGeHx (M = Sr, Ba)

Research area: Chemistry

This proposal is a new proposal

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Samples:
CaSi
BaGe
SrGe

Instrument	Requested days	Allocated days	From	To
D20	5	5	23/07/2015	28/07/2015

Abstract:

The hydrogenation (deuteration) of the Zintl phases CaSi and MGe (M = Sr, Ba) will be followed by in situ neutron powder diffraction in a user supplied sapphire single crystal cell. For CaSi an intermediate hydride between CaSi and the fully hydrogenated (deuterated) CaSiD1.2 was found in a previous experiment, which will now be specifically addressed in order to map out its stability and determine its crystal structure including deuterium positions. For the isostructural MGe hydrogenation was not reported before and by in situ X-ray diffraction on a laboratory diffractometer it was shown, that similar intermediate and fully deuterated compounds exist as for CaSi. In situ neutron diffraction will lead to reaction pathways of the deuteration of MGe (M = Sr, Ba) and the full structural characterization of its deuterides. Determination of the crystal structures of such Zintl phase hydrides will help to better understand the fascinating crystal and bonding chemistry of this class of compounds, in which the connectivity of polyanions can be tuned by the reaction with hydrogen.

Reaction pathways to the Zintl phase hydrides CaSiH and MGeH$_x$ (M = Sr, Ba)

Experiment 5-22-734

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The hydrogenation of the CrB structure type Zintl-phases EaSi, Ea = Ca-Ba and EaGe, Ea = Sr, Ba leads to hydrogen rich phases of type $Ea_3Tt_3H_{n-\delta}$, n = 4-6. These phases show fully occupied tetrahedral Ea_4-voids and additional Tt-coordinating positions for hydrogen with partial occupation. The formation of these β-phases ($CaSiD_x$, $BaGeD_x$, $SrGeD_x$) were monitored under 50 to 100 bar deuterium pressure at elevated temperatures in a user supplied sapphire single-crystal gas pressure cell at the diffractometer D20.

CaSi was first heated to 474K before deuterium gas was introduced, which yielded an α-phase deuteride (Fig. 1) with neutron diffraction patterns similar to those of the corresponding phases of SrGe and BaGe (see below). The deuterium content could be influenced easily by changing deuterium pressure between 1 and 55 bar. Increasing the pressure finally led to a higher deuteride, which could be described in space group *Pnma* (a = 14.494(3), b = 3.8224(6), c = 11.239(2)Å) with a structure model similar to that of β-$SrGeD_{1+x}$ (see below) and that of Wu et al. [1]. Rietveld refinement of the crystal structure of this β-phase under various temperature and gas pressure conditions led to compositions in the range of $CaSiD_{1.15(1)}$ to $CaSiD_{1.48(2)}$. In contrast to Wu et al. [1], however, there are close silicon-deuterium contacts in the crystal structure indicating the possibility of covalent Si-D bonds. The resulting interatomic distance of 1.16(4)Å on the other hand is considerably shorter than expected. To clarify structural details and thus the complete picture of chemical bonding in $CaSiD_{1+x}$ further studies are necessary. In order to increase data quality with respect to the time-resolved studies presented here *ex situ* neutron diffraction patterns on $CaSiD_{1+x}$ samples at room temperature would be helpful.

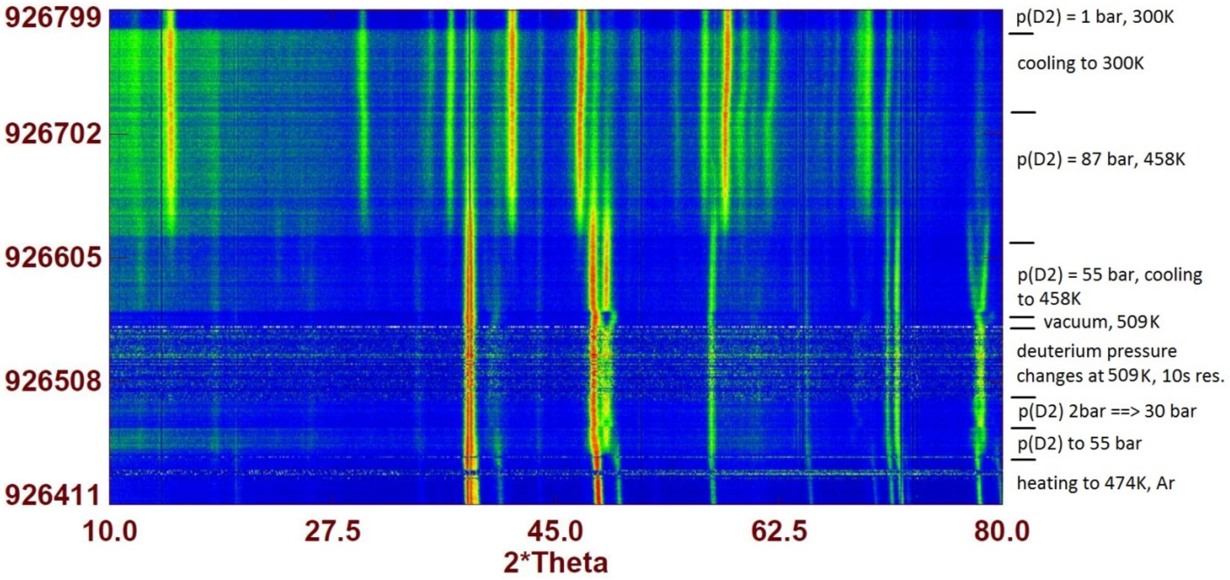

Fig. 1: *In situ* neutron powder diffraction patterns during the reaction of CaSi with deuterium gas as false colour plot showing formation and decomposition of an intermediate deuteride in the lower part and the formation of $CaSiD_{1.2}$ in the upper part (λ = 1.8673(2) Å).

The deuteration of BaGe was followed isobaric at 50bar deuterium pressure. There is a first deuterium uptake even at room temperature as can be concluded from an increased background and the occurrence of broad reflections. Rietveld refinements of its crystal structure are not satisfactory yet, but the metrical shift indicates the formation of a deuterium poor α-phase as explained below. In a subsequent step the expected deuterium rich beta-$BaGeD_x$ phase was formed. An increased pressure had no influence on the formed products.

Since the formation of the intermediate phase at room temperature gave very broad reflections, two additional experiments were performed:
In a decomposition experiment under dynamic vacuum (p = 0.1Pa) the formation of the deuterium poor α-phase could be observed again. During the decomposition of the β-phase the germanium bound deuterium is removed at first while a second phase with approximately half filled tetrahedral voids is formed. This phase subsequently loses deuterium down to 20% occupation of the tetrahedral voids. This α-phase is stable under vacuum at least up to 200°C where the experiment was stopped.

The second additional experiment was an isothermal cycling at 230°C similar to the CaSi experiment. Releasing the pressure from 50bar, at 10 bar deuterium pressure a strong phase change can be observed. Above this pressure mainly the deuterium rich β-phase is present while below the intermediate phase is formed. Changing from 2 bar deuterium pressure to vacuum another metrical shift can be monitored. During cycling from 2bar deuterium pressure to vacuum and vice versa with 10s time resolution two phases can be distinguished (Fig. 2). The phase under vacuum conditions will be called α-phase and has still 20% of the tetrahedral Ba4-voids filled (space group *Cmcm*, a = 5.0336(9), b = 12.215(2), c = 4.2734(8)Å). At 2 bar pressure the α'-phase is present. An averaged structural model could be refined and gave an occupation of about 50% for the tetrahedral voids (space group *Cmcm*, a = 4.9389(2), b = 13.2188(4), c = 4.2059(2)Å). This model ignores super structure reflections, i. e. further evaluation is necessary.

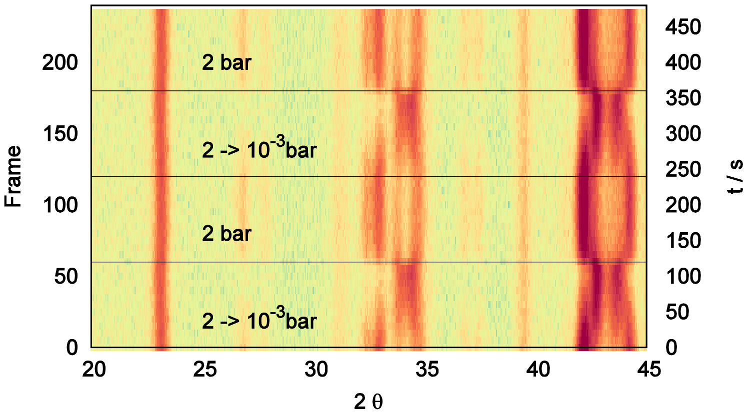

Fig. 2: *In situ* neutron powder diffraction patterns during the reaction of BaGe at low deuterium pressures as false colour plot showing the α'-phase at 2 bar and the α-phase under vacuum (λ = 1.8673(2) Å). The reaction is faster than the time resolution of 10s. The evacuation took 60s to reach the lowest pressure, which causes the impression of a slower dehydrogenation step.

The reaction of SrGe was studied at 50bar deuterium pressure under heating up to 320°C. In contrast to the BaGe-D system the formation of the deuterium rich β-phase could be shown to be a one-step reaction. *In situ* thermal analysis experiments (differential scanning calorimetry, DSC) show a reversible endothermic reaction of the β-phase under 50bar hydrogen pressure and temperatures about 300°C to occur before an irreversible decomposition at higher temperatures.

The decomposition step could be reached and yielded a hydrogen poorer α-phase that is isopointal to the hydrogen free Zintl-phase but shows an increased volume and distinct tetrahedral Sr4-voids. These are partially filled with 20% occupation (space group *Cmcm*, *a* = 4.7661(5), *b* = 11.8280(13), *c* = 4.1541(5) Å). Under cooling the β-phase was reformed alongside an additional intermediate (α'-phase). It already seems to show the super structure of the β-phase but there are still no deuterium atoms inbetween the Ge-chains. The tetrahedral voids are filled at 30-80% (space group *Cmcm*, *a* = 13.999(3), *b* = 12.507(3), *c* = 4.1126(8) Å).

Since the formation of $SrGeD_x$ was incomplete before the decomposition took place, the second experiment at a pressure of 100 bar deuterium pressure was skipped. Instead the first run was repeated with a previously prepared β-$SrGeD_x$ sample as starting material to get proper data for Rietveld refinement of the crystal structure of the intermediate phases. The above stated behavior could be confirmed (Fig. 3). Rietveld refinement of the two intermediate states was performed on these data.

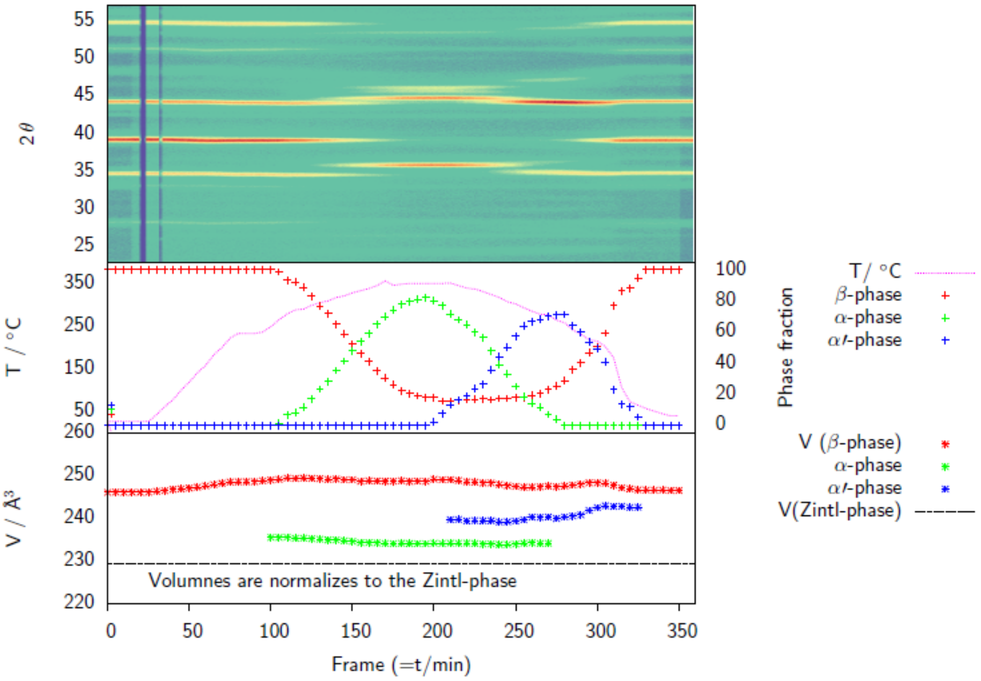

Fig. 3: *In situ* neutron powder diffraction patterns during the decomposition of β-$SrGeD_x$ under 50bar deuterium pressure and heating as false colour plot showing the α'-phase at 2 bar and the α-phase under vacuum (λ = 1.8673(2) Å). A deuterium poor α-phase is formed with 20% occupation of tetrahedral Sr4-voids. Upon cooling another α'-phase is formed with 30-80% Sr4-tetrahedra filled before the hydrogen rich β-phase reforms. The volumes are normalized to the basic structure of the deuterium free Zintl phase. The volume steps match the increased deuterium contend for the different phases

[1] H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *74*, 224101