Experimental report

19/09/2018

Proposal: 5-24-605 **Council:** 4/2017

Title: In situ investigations of the hydrogenation of CaRh2

Research area: Chemistry

This proposal is a new proposal

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Samples: CaRh2

Instrument	Requested days	Allocated days	From	To
D20	2	2	23/03/2018	26/03/2018

Abstract:

The formation of perovskite deuteride CaRhDx by two deuteration pathways with intermediate cubic CaRh2Dx or hexagonal CaRh2Dx will be followed by in situ neutron powder diffraction in a user supplied sapphire single-crystal cell at deuterium pressures up to 50 bar and temperatures up to 723 K. Rietveld analysis of diffraction data will allow the location of deuterium positions in the deuterides and the mapping of the complete reaction pathway of deuterium uptake and release.

In situ investigations of the hydrogenation of $CaRh_2$ (5-24-606)

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Several hydrides of intermetallic compounds in the system Ca-Rh are known [1,2]. Decreasing the Ca:Rh ratio from 2 (K_2PtCl_6 type in Ca_2RhH_5) towards 1 results in an increasing connectedness of RhH_6 octahedra [2]. However, the ratio of 1 was not be achieved yet, i. e. solid-state synthesis of the perovskite $CaRhH_x$ starting from calcium hydride and rhodium was not successful [2]. An alternative access to this hydride was found by hydrogenation of the cubic Laves phase $CaRh_2$ [3]. *In situ* thermal analysis (DSC) and powder X-ray diffraction indicated intermediates during this reaction. In order to locate hydrogen in the crystal structures, $CaRh_2$ was deuterated *in situ* and neutron diffraction data were collected at the diffractometer D20.

The neutron experiment was executed in a sapphire single crystal cell. Vacuum was applied at the beginning (Figure 1). The deuterium gas pressure was slowly increased up to several kPa. During this process, the unit cell volume of the cubic Laves phase expands by 0.25% (a_{start} = 7.5245(6) Å, a_2 = 7.5308(12) Å). This is a strong indication of deuterium absorption and the formed compound is referred to as *a*-$CaRh_2D_x$. A new hydride phase started to form under 20 kPa deuterium pressure. The unit cell of this *β*-phase could by indexed as orthorhombic (*Pnma*, *a* = 6.0028(3) Å, *b* = 5.6065(3) Å, *c* = 8.1589(5) Å). The crystal structure of *β*-$CaRh_2D_{3.93(5)}$ is related to the cubic Laves phase (Figures 2 and 3, Table 1). Possible deuterium sites are [Rh_4], [$CaRh_3$] and [Ca_2Rh_2] tetrahedral voids. The deuterium positions were determined by alternating refinement of deuterium positions or occupation, and subsequent Fourier analyses. Deuterium was found to occupy [Ca_2Rh_2] tetrahedral voids and distorted [Ca_3Rh_2] trigonal bipyramids (combination of two [Ca_2Rh_2] tetrahedra). A further increase in deuterium pressure up to 5 MPa does not have any influence in deuterium content. To check the reversibility of this reaction vacuum was applied and the cubic Laves phase was formed back, though, a third intermediate, *γ*-$CaRh_2D_{3.20(10)}$, was formed during dedeuteration. This *γ*-phase is isotypic to the *β*-phase but contains less deuterium noticeable by decreased lattice parameters (*a* = 5.9601(10) Å, *b* = 5.4912(2) Å, *c* = 8.0730(11) Å) [3].

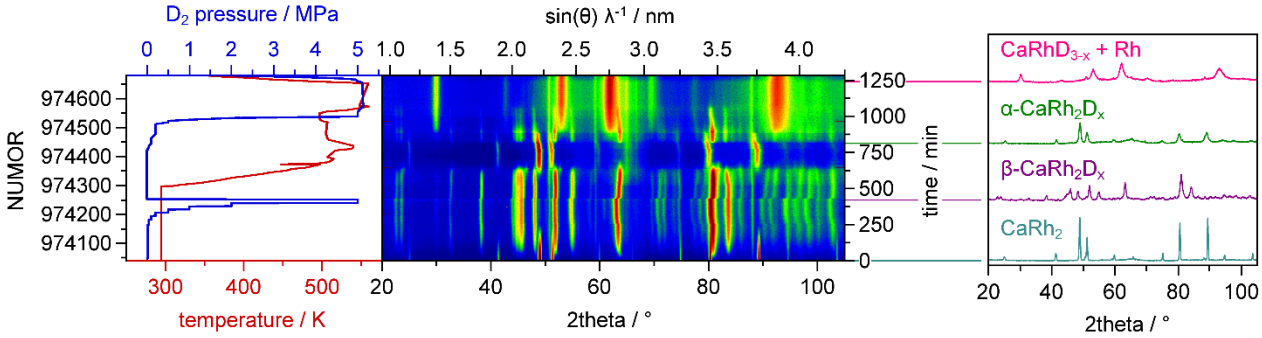

Figure 1: *In situ* neutron powder diffraction data of the deuteration of $CaRh_2$ taken on diffractometer D20 at λ = 1.8676(3) Å in a single crystal sapphire cell under various deuterium pressures and temperature conditions. Intensities are in false colors.

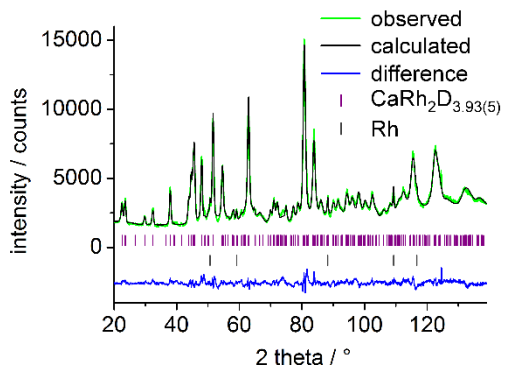

Table 1: Refined atomic parameters of *β*-$CaRh_2D_{3.93(5)}$ (*Pnma*, *a* = 6.0028(3) Å, *b* = 5.6065(3) Å, *c* = 8.1589(5) Å)

atom	Wyck.	*x*	*y*	*z*	B_{iso} (Å²)	*SOF*
Ca	4*c*	0.0711(10)	¾	0.1340(7)	0.5(1)	1
Rh1	4*b*	0	½	½	0.31(8)	1
Rh2	4*c*	0.6977(9)	¾	0.7380(5)	0.59(10)	1
D1	4*c*	0.0581(8)	¼	0.6079(7)	0.83(4)	0.737(9)
D2	8*d*	0.143(2)	0.015(3)	0.667(2)	B_{iso}(D1)	0.203(5)
D3	4*c*	0.0576(9)	¼	0.1468(6)	B_{iso}(D1)	0.949(9)
D4	8*d*	0.7538(5)	0.9906(6)	0.6039(3)	B_{iso}(D1)	0.921(9)

Figure 2: Rietveld refinement and crystal structure of *β*-$CaRh_2D_{3.93(5)}$ (D20, ILL, Grenoble, $\lambda_{neutrons}$ = 1.8676(3) Å, R_p = 0.037, χ^2 = 7.51, 0.1 MPa deuterium gas pressure, *T* = 296(1) K).

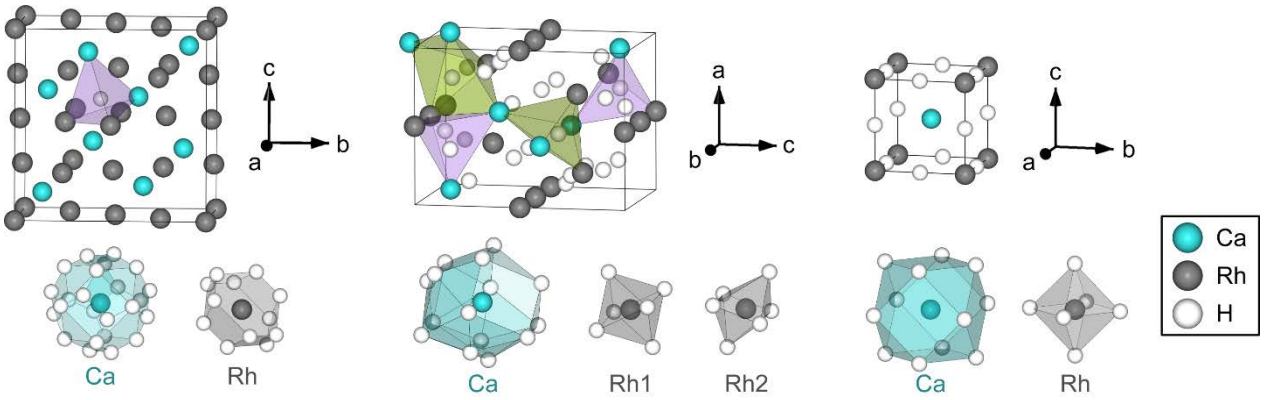

Figure 3: Crystal structures of hydrides in the Ca-Rh-system with coordination polyhedra of metal atoms (bottom). From left to right: *a*-$CaRh_2Hx$ (filled Laves phase), *β*-$CaRh_2H_x$ (orthorhombic superstructure of the Laves phase), $CaRhH_x$ (perovskite type).

In the next step the sample was heated by a laser up to 500 K under applied vacuum The subsequent deuteration was performed under almost isothermal conditions (T = 530(30) K). Again *a*-$CaRh_2Dx$ and *β*-$CaRh_2D_x$ were formed, before the decomposition to the perovskite hydride $CaRhD_x$ and rhodium took place. Crystal structure refinement yields a composition of $CaRhD_{2.93(2)}$ (Figure 4 and Table 2). Deuterium is located between two rhodium atoms forming RhH_6 octahedra (Figure 3, right). The deuterium content of the perovskite hydride is almost constant. Two different rhodium phases are observed at the end of the experiment. Rhodium as secondary phase from the synthesis of $CaRh_2$ and nano-crystalline rhodium formed by decomposition of $CaRh_2H_x$. The crystallite size is estimated to be below 1.8 nm by the Scherrer equation (determined on (111) reflection).

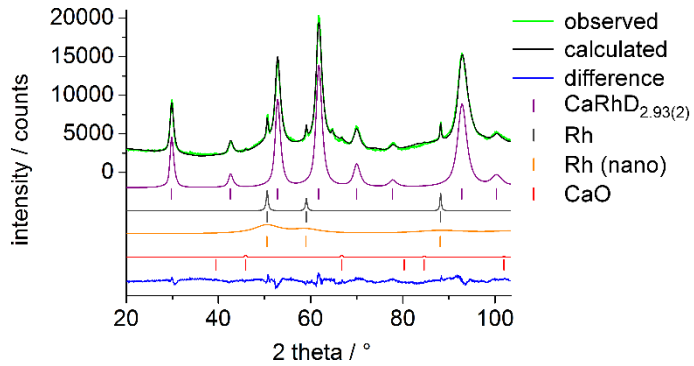

Table 2: Refined atomic parameters of $CaRhD_{2.93(2)}$ ($Pm\bar{3}m$, perovskite-type a = 3.6512(2) Å).

atom	Wyck.	x	y	z	B_{iso} (Å²)	*SOF*
Ca	1*b*	½	½	½	0.95(7)	1
Rh	1*a*	0	0	0	0.87(5)	1
D	3*d*	0	0	½	1.68(3)	0.976(6)

Figure 4: Rietveld refinement and crystal structure of $CaRhD_{2.93(2)}$ and nano-crystalline rhodium (D20, ILL, Grenoble, $\lambda_{neutrons}$ = 1.8676(3) Å, R_p = 0.036, χ^2 = 6.50, 0.1 MPa deuterium gas pressure, T = 306(2) K).

Literature

[1] Bronger, W.; Jansen, K.; Breil, L. $Ca_2RhD_{5.4}$ − Strukturbestimmung über Neutronenbeugungsexperimente, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1477−1480. DOI: 10.1002/(SICI)1521-3749(199809)624:9<1477::AID-ZAAC1477>3.0.CO;2-I

[2] W. Bronger, L. Breil, Calcium-Rhodium-Hydride – Synthese und Struktur, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1819-1822. DOI: 10.1002/(SICI)1521-3749(1998110)624:11<1819::AID-ZAAC1819>3.0.CO;2-L

[3] Götze, A.; Möllmer, J.; Kohlmann, H. From the Laves Phase $CaRh_2$ to the Perovskite $CaRhH_3$ - In Situ Investigation of Hydrogenation Intermediates $CaRh_2H_x$, *Inorg. Chem.* **2018**, *57*, 10925-10934. DOI: 10.1021/acs.inorgchem.8b01547