ESRF	**Experiment title:** In-situ X-ray Raman study of the desorption behavior of complex metal-borohydrides	**Experiment number**: HC-990
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Report: The aim of experiment HC-990 was to investigate the hydrogen desorption pathways of complex metal-borohydrides in-situ using X-ray Raman scattering together with a chemical reaction cell. This way we wanted to detect amorphous decomposition products which cannot be unambiguously identified by other methods but are of high relevance in understanding and controlling the hydrogen release process.

Hydrogen is one of the promising candidates as a clean energy carrier [Chuchard2011]. However, the storage of hydrogen is technically challenging and the search of lightweight storage media which allow the reversible hydrogen de- and resorption is of utmost relevance [Schlapbach2001]. Owing to their large gravimetric hydrogen storage capacity, borohydrides have been identified as possible hydrogen storage materials. Hence, enormous efforts were undertaken to study the hydrogen release pathways and hydrogen resorption in various borohydrides with contradicting results (For $Mg(BH_4)_2$ see e.g. [Li2008, Hanada2008, Soloveichik2009, Chong2011, Paskevicius2012]). The reason for the contradictions is due to the fact that most likely amorphous decomposition products occur both in the intermediate phases of decomposition as well as end-products after full dehydrogenation which are difficult to detect. This concerns particularly amorphous boron and $B_{12}H_{12}$ species.

We used X-ray Raman scattering (XRS) to study the boron K- and Mg L-edges of $Mg(BH_4)_2$ in-situ. The decomposition conditions were controlled by loading the sample into a chemical reaction cell [Mauron2011] under hydrogen atmosphere. XRS-spectra were measured at temperatures ranging from room temperature up to 500°C and the hydrogen release was detected simultaneously by the pressure increase within the cell. We used the direct

tomography method to get information also on the real-space behavior of the sample and to remove signal contributions from other parts of the reaction cell than the sample itself [Huotari2011]. To fingerprint the decomposition products with respect to changes of annealed $Mg(BH_4)_2$ XRS-spectra, the reference compounds amorphous and crystalline B, H_3BO_3, $MgB_{12}H_{12}$, MgH_2, MgB_2, MgO, and Mg were measured. This way a principal component analysis of both absorption edges allows to track the possible decomposition products. The temperature evolution of XRS-spectra, both for the Mg L- and B K-edge during temperature driven decomposition are presented in Fig. 1.

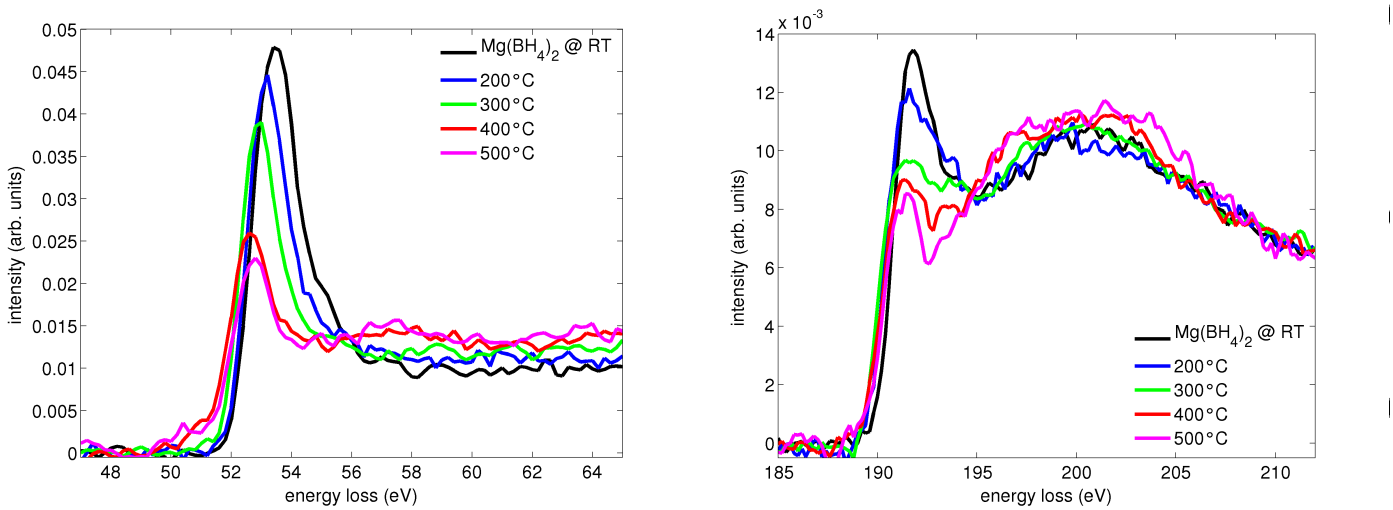

Figure 1: XRS-spectra at the Mg L-edge of $Mg(BH_4)_2$ measured in-situ in hydrogen atmosphere using the reaction cell at different decomposition temperatures (left). XRS-spectra at the B K-edge of $Mg(BH_4)_2$ at same conditions as for the Mg L-edge (right).

First analysis provides strong evidence for a significant formation of amorphous boron whereas formation of $MgB_{12}H_{12}$ is unlikely. Decomposition of MgH_2 to elemental Mg is observed and, up to 500 °C, no formation of MgB_2 occurs. Notably, in the first stages of decomposition the XRS spectra can not be modeled by a superposition of references indicating the occurrence of unknown intermediates other than $B_{12}H_{12}$ species.

The data analysis is still in progress and we aim to identify a complete reaction pathway that is in agreement with our complementary results obtained for the local environment of Mg and B species in our sample. Therefore, modeling of XRS spectra of possible intermediates is necessary and is currently in progress using atomic structure models of intermediates [Zhang2012]. Calculations of XRS spectra will then be performed based on the Bethe-Salpeter equation using the new OCEAN software [Vinson2011].

References:

[Churchard2011] A.J. Churchard, et. al., Phys. Chem. Chem. Phys. 13 16955 (2011). **[Schlapbach2001]** L. Schlapbach and A. Züttel, Nature 414, 353 (2001). **[Li2008]** H.-W. Li, K. Kikuchi, Y. Nakamori, N. Ohba, K. Miwa, S. Towata, S. Orimo, Acta. Mater. 56, 1342, (2008). **[Hanada2009]** N. Hanada, K. Chlopek, Ch. Frommen, W. Lohstroh, and M. Fichtner, J. Mater. Chem. 18, 2611 (2008). **[Soloveichik2009]** G.L. Soloveichik, Y. Gao, J. Rijssenbeek, M. Andrus, S. Kniajanski, R.C. Bowman, Jr., S. Hwang, J. Zhao, Int. J. Hydro. Ener. 34, 916 (2009). **[Chong2011]** M. Chong, A. Karkamkar, T. Autrey, S. Orimo, S. Jalisatgi, and C.M. Jensen, Chem. Commun. 47, 1330 (2011). **[Paskevicius2012]** M. Paskevicius, M.P. Pitt, C.J. Webb, D.A. Sheppard, U. Filso, E.M. Gray, and C.E. Buckley, J. Chem. Phys. C 116, 15231 (2012) **[Mauron2011]** Ph. Mauron, M. Bielmann, A. Remhof, and A. Züttel, Rev. Sci. Instrum. 82, 065108 (2011.). **[Huotari2011]** S. Huotari, T. Pylkkänen, R. Verbeni, G. Monaco, and K. Hämäläinen, Nat. Mater. 10, 489 (2011). **[Zhang2012]** Y. Zhang, E. Majzoub, V. Ozolins, and C. Wolverton, J. Chem. Phys. C 116, 10522 (2012). **[Vinson2011]** J. Vinson, J.J. Rehr, J.J. Kas, and E.L. Shirley, Phys. Rev. B 83, 115106 (2011).