

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Effect of Cobalt additives on hydrogen sorption in Magnesium Borohydride: in situ combined X-ray Absorption, X-ray Diffraction and Raman spectroscopy study		Experiment number: CH-4068
Beamline: BM01B	Date of experiment: from: 30 April to: 5 May	Date of report: 27.02.2015
Shifts: 12	Local contact(s): Dr. Paula Macarena Abdala	<i>Received at ESRF:</i>
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Report:

Experimental details

In the proposal we indicated both dehydrogenation and rehydrogenation experiments on the series of $Mg(BH_4)_2 + Co$ -based additives samples. We were not able to conduct the rehydrogenation experiments, requiring 120 bar of H_2 pressure, due to the lacks in our experimental set-up. We intended to use the high pressure in-situ cell with the sapphire capillaries tested for up to 125 bar, but it appeared that sapphire absorb strongly in the Co-K-edge energy range. Therefore the glass capillaries were used, with the H_2 (desorption) pressure of maximum 3 bar. For the measurements in Ar, the samples were placed in 1.0 mm thick glass capillaries and sealed in the glove-box with the air-tight glue. For the measurements in H_2 , the capillaries were attached to a sample holder enabling connection to the gas line. Before the measurements in H_2 , the samples were evacuated in vacuum at RT, and 3 bar H_2 pressure was set in the capillaries.

We have conducted decomposition of three samples: $Mg(BH_4)_2 + CoF_2$, $Mg(BH_4)_2 + CoF_3$, and $Mg(BH_4)_2 + CoCl_2$ in H_2 and Ar atmosphere ($CoCl_2$ only in Ar). Samples were heated at 5 K/min till 177, 220,

and 290 °C. The heating was paused at the indicated temperature steps. The decomposition was followed by X-ray diffraction, X-ray absorption and Raman scattering measurements (green laser). XRD data were collected at the RT, during heating steps, and during the isothermal steps. XAS data were collected at the isothermal steps. Raman data were obtained during all the steps, but after about 160 °C the sample became fluorescent. It might be a good idea to use the red laser with Mg(BH₄)₂.

XAS spectra of the reference compounds: CoF₂, CoF₃, CoCl₂ Co powder, CoO were also obtained. The reference powders were measured diluted with boron nitride to 2 mol% of Co_{add}. The mixtures were pressed into pellets and mounted in aluminum sample holder. To avoid contact with air, the sample holders were covered by Kapton tape adhered by air-tight grease. XAS data analysis was carried out with DEMETER software pack (ATHENA and ARTEMIS).^[1] The spectra were pre-processed in ATHENA (background subtracted, aligned, the step scans were averaged and used for final plots and fitting). Calculation of the theoretical scattering paths in the EXAFS region and fitting were performed with the FEFF6 code^[2] using ARTEMIS.

Results

In-situ PXD

Figure 1 shows the in-situ XRD data, obtained for the decomposition of Mg(BH₄)₂+CoF₂ sample in Ar and in H₂ atmosphere, and of Mg(BH₄)₂+CoCl₂ in Ar, as an example of the obtained data.

At room temperature (RT), Mg(BH₄)₂ is in γ-phase. At ~150 and ~200 °C we observed γ→ε and ε→β phase transitions, which is in accordance with literature.^[3] It appears, however, that in Mg(BH₄)₂+CoF₂ in Ar atmosphere the γ→ε phase transition started at a lower temperature. At 290 °C amorphous phases were formed which is the results of either melting or decomposition of Mg(BH₄)₂.^[3-4] For this reason, Raman spectroscopy was used to aid in identification of the amorphous (melted?) phases.

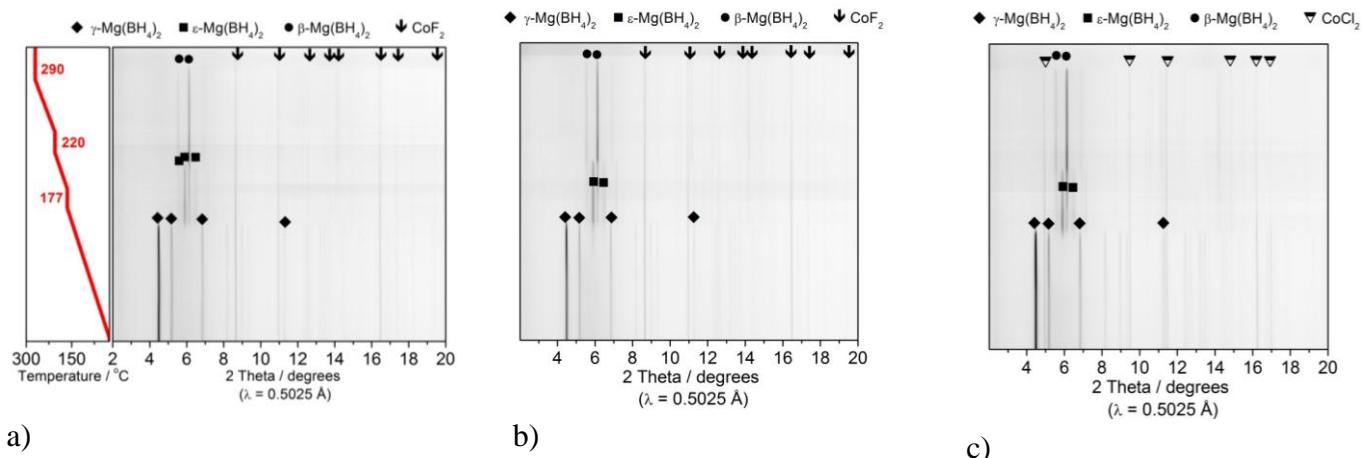


Figure 1. In-situ SR-PXD of Mg(BH₄)₂+CoF₂ decomposition in H₂ (a) and Ar (b), and Mg(BH₄)₂+CoCl₂ in Ar (c)

In situ Raman

Raman spectra of the two samples, obtained at RT, and at 170 °C, are shown on Figure 2. Unfortunately, the sample became fluorescent at the higher temperatures, and it was not possible to utilize Raman spectroscopy to identify the amorphous phases obtained at 290 °C. We suppose that the decomposition phase of Mg(BH₄)₂ is fluorescent with 532 Raman excitation wavelength. In the future measurements, red laser should be used for the samples based on Mg(BH₄)₂.

In the 2900-600 cm⁻¹ region, Mg(BH₄)₂ exhibits absorption bands corresponding to the internal vibrations of (BH₄)⁻ ions. The B–H fundamental stretching modes are centered at 2321 cm⁻¹, whereas the bending modes are located at *ca.* 1404, and 1192 cm⁻¹. Absorption due to the overtones and combinations of (BH₄)⁻ bending are observed at 2535 and 2209 cm⁻¹. Raman spectra has shown the decrease in the intensity of BH₄ stretching and bending vibrations, which can be related to decomposition of Mg(BH₄)₂. It should be noted that the

decomposition of $\gamma\text{-Mg(BH}_4\text{)}_2$ is expected to occur at $>200\text{ }^\circ\text{C}$,^[3] and this result might indicate that CoF_2 decreases decomposition temperature of the compound.

The spectra obtained at $160\text{ }^\circ\text{C}$ show new vibrations at 2496, 2413, 760, and 467 cm^{-1} , which can be related to (one of the?) decomposition phases (Figure 2a).

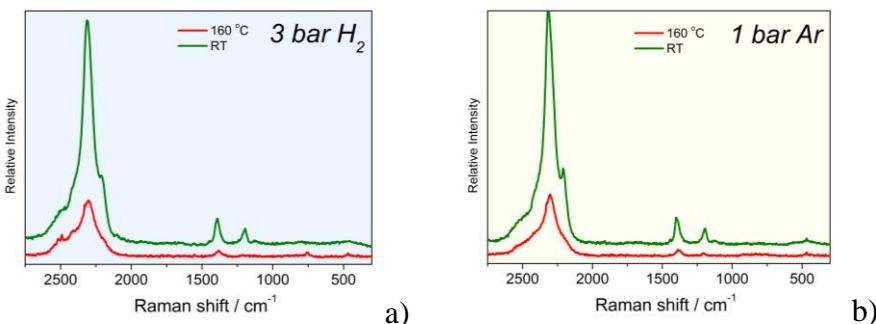


Figure 2. In-situ Raman data of $\text{Mg(BH}_4\text{)}_2\text{+CoF}_2$ decomposition in H_2 (a) and Ar (b).

$\text{Mg(BH}_4\text{)}_2\text{+CoF}_2$ sample in Ar and in H_2 atmosphere are shown in the Figure 3. They confirm that the additive reacted and was transformed to another species. The analysis of other data is in progress.

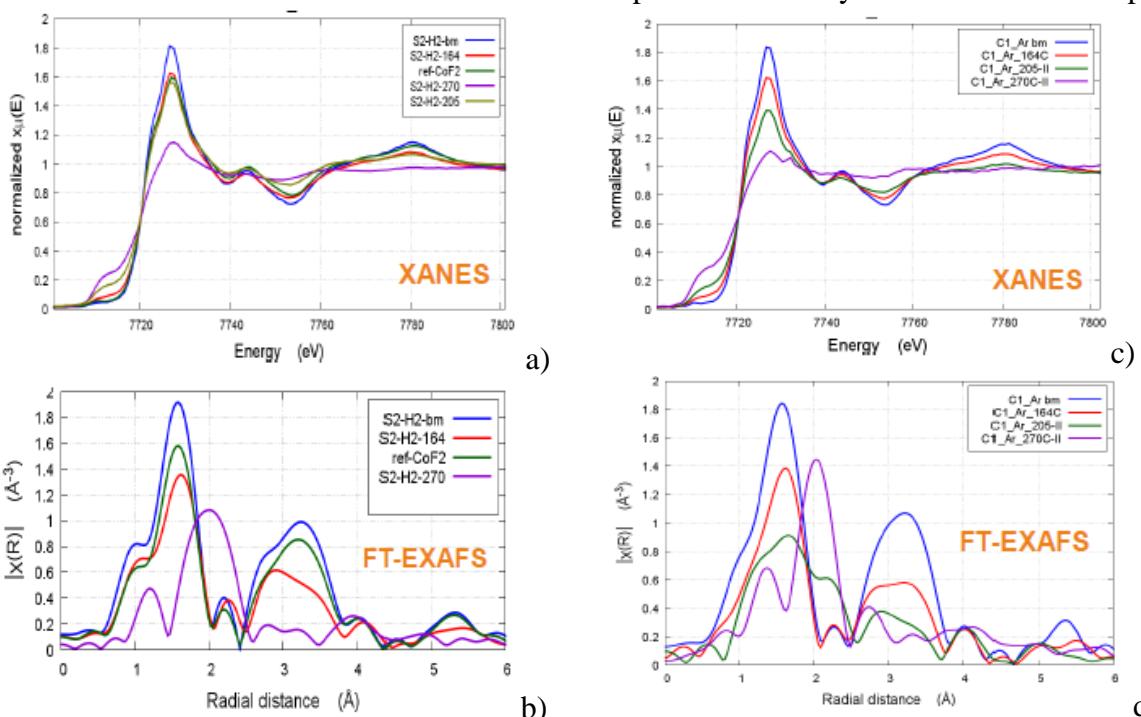


Figure 3. XANES and FT-EXAFS spectra of $\text{Mg(BH}_4\text{)}_2\text{+CoF}_2$ decomposition in H_2 (a,b) and Ar (c,d)

The results obtained in this experiment were reported at the two conferences:

- ⊕ (oral presentation) O. Zavorotynska, Ivan Saldan, Satoshi Hino, Terry Humphries, Stefano Deledda and Bjørn C. Hauback “Additives in magnesium borohydride: local structure and effect on reversibility” 14th International Symposium on the Metal-Hydrogen Systems / Manchester, UK, June 20-25 2014
- ⊕ (poster) O. Zavorotynska, M.N. Guzik, J. G. Vitillo, I. Saldan, S. Deledda, B.C. Hauback “Decomposition of Magnesium Borohydride with Cobalt Additives: An in-situ Synchrotron X-ray Study Combined with Raman Spectroscopy” SYKNØYT Users meeting, 19-20 January 2015, Stavanger, Norway

A publication is in preparation which will include the results of this experiment.

In situ XAS

The reflections in the in-situ PXD patterns due to CoF_2 and CoCl_2 additives decrease in intensity indicating transformation of the additives (Figure 1). However, no new phases, which could be related to chemically modified Co-additives, were observed.

For this reason, XAS spectroscopy at the Co k-edge was used.

In situ XAS spectra obtained on

References

- [1] B. Ravel, M. Newville, *J. Synchrotron Radiat.* **2005**, *12*, 537-541.
- [2] J. J. Rehr, R. C. Albers, *Rev. Mod. Phys.* **2000**, *72*, 621-654.
- [3] M. Paskevicius, M. P. Pitt, C. J. Webb, D. A. Sheppard, U. Filso, E. M. Gray, C. E. Buckley, *J. Phys. Chem. C* **2012**, *116*, 15231-15240.
- [4] aM. D. Riktor, M. H. Sorby, K. Chlopek, M. Fichtner, F. Buchter, A. Züttel, B. C. Hauback, *J. Mater. Chem.* **2007**, *17*, 4939-4942; bG. L. Soloveichik, Y. Gao, J. Rijssenbeek, M. Andrus, S. Kniajanski, R. C. Bowman, Jr., S.-J. Hwan, J.-C. Zhao, *Int. J. Hydrog. Energy* **2009**, *34*, 916-928.