Results of X-ray Raman Scattering experiments

In order to complement the data provided by X-ray diffraction and nuclear magnetic resonance (NMR), we performed a complementary study of the environment of calcium with X-ray Raman Spectroscopy (XRS), which yields similar spectra as soft x-ray absorption spectroscopy (XAS) but in a bulk-sensitive fashion. Details concerning the technique are available in literature [1].

The XRS experiment was performed using the 72-element X-ray Raman spectrometer on the beamline ID20/UPBL6 of the European Synchrotron Radiation Facility (ESRF) [2]. The beam was monochromated using a Si(111) double crystal and Si(311) channel-cut monochromators, and focused to a spot size of 20 x 20 µm. The spectrometer employs Si(660) analysers that reflect X-rays with a fixed photon energy of 9.69 keV with an energy resolution of 0.6 eV. Spectra were collected at room temperature. A suitable background was subtracted from the spectra and they were normalized over the whole edge intensity to a fixed area in the range 345–360 eV.

Figure S1I shows the Ca L₂,3 edges of Ca(BH₄)₂-Mg₂NiH₄ decomposed under two different conditions, namely 350°C for 150 minutes and 450°C for 42 hours. Two broad peaks are evident at the energies of 348.5 and 352 eV, corresponding to the transitions from 2p₃/₂ and 2p₁/₂ states, respectively. The spectra are rather similar but there is a small shift toward lower excitation energies with higher level of decomposition. We analysed the spectra with a multi-component fitting of these Ca L₂,3 edges performed with the shown reference compounds. This is an established method for the quantitative evaluation of phase fractions [3]. The best fit is obtained with the scenario that the Ca(BH₄)₂ decomposes according to the partial reaction: Ca(BH₄)₂ -> a CaH₂ + b CaB₆ /Ca(BH₄)₂ + c Ca-free boron compounds + d H₂.

Figure S1I: (Upper panel) Ca L₂,3 edges of Ca(BH₄)₂-Mg₂Ni₂B₂ decomposed in different thermodynamic conditions (continuous lines) and their multi component fitting (dashed lines). (Lower panel) Ca L₂,3 edges of reference materials.

Since Ca(BH₄)₂ and CaB₆ have absorption edges at the same energies, our XRS results are not able to distinguish between these components. Furthermore, our best fit is obtained when neglecting contributions of CaB₁₂H₁₂, thus supporting the results of the complementary techniques, which tend to minimize the formation of CaB₁₂H₁₂ as a stable product.
At 350°C, $a=0.78$ and $b=0.22$, providing an amount of free, elemental boron, corresponding to a stoichiometry of $c=0.68$. At 450°C, the reaction further progresses with $a=0.96$ and $b=0.04$, resulting in $c=1.76$. Calcium hydride ($\text{CaH}_2$) is the best fit for the main product and its overall stoichiometry depends on the reaction conditions. A minor fraction of the side product CaB$_6$ is clearly produced, at the decomposition of the composite material, most likely for all the reported reaction conditions as suggested by NMR.

Boron is progressively released while the reaction advances: most of it is released as MgNi$_2$B$_2$ directly and in minor amounts as CaB$_6$, CaB$_2$H$_2$ and elemental boron that are then further consumed for the formation of MgNi$_2$B$_2$. The amount of boron in the dehydrogenation products increases with the increasing time, namely at 450°C after 42 hours.

We also collected x-ray absorption near edge spectra (XANES) at the Ni K edge in order to explore the products from the perspective of the local environment of nickel atoms. We collected these XANES data on the beamline ID20/UPBL6 at the ESRF while using the previously described beamline setup together with Si-drift detector. Results are shown in Figure SI12.

![Figure SI12: Upper panel] XANES spectra of the Ni K edge of the composite Ca(BH$_4$)$_2$-MgNH$_4$ decomposed in different thermodynamic conditions and of the reference material MgNi$_2$B$_2$. (Lower panel) XANES spectra of the products of the reactions between MgNH$_4$ and B, CaB$_6$ and CaB$_2$H$_2$.

Spectra are composed of a pre-peak at the energy of 8.332 keV and of a broad, main-peak region at 8.35 keV. The former feature is due to the sum of the contributions of the dipole allowed 1s-4p transition and 1s-3d transition happening as a consequence of the partial p-type character of nickel 3d states due to their hybridization with boron 2p states [4]. The latter feature, namely the main edge, is due to the absorption process involved in the dipole-allowed transition between 1s-4p states.

Normalizing the spectra to the area in the plotted range, the pristine MgNi$_2$B$_2$ exhibits a stronger pre-peak region intensity than the decomposed samples.

We compare the spectra with those of the products of the reactions between MgNH$_4$, B, CaB$_6$ and CaB$_2$H$_2$, shown in the lower panel of figure SI12. These results are also complementary to PXRD and NMR data in the Figures 4 and 5 of the manuscript.

The reactions between MgNH$_4$ and either CaB$_6$ or CaB$_2$H$_2$ produce XANES spectra comparable to the ones of the decomposed mixture of hydrides, while after the reaction between MgNH$_4$ and B, the Ni K edge features stronger pre-edge peak and weaker EXAFS region.

From the analysis of these three reactions (detailed in Figure 4 and related paragraph in the manuscript), we know that both CaB$_6$ and CaB$_2$H$_2$ promote an almost complete transfer of boron to MgNi$_2$B$_2$ (96 and 97%, respectively), while the reaction with B transfers a fraction leaving unreacted elemental boron available (~28%) and a portion of the unknown phase.

In addition, the fraction of MgNi$_2$B$_2$ in the absorbed samples shown in figure 10 appears to suffer from a deficiency in the stoichiometry of boron.

We may conclude that such effect is mirrored in the local environment of nickel (and of its electronic structure), in particular affecting the availability of 3d low energy states in the conduction band that become available for the transition of the electron from the core level.

The difference that we see in the spectra corresponding to the reactions between Mg$_2$NiH$_4$, B, CaB$_6$ and CaB$_2$H$_2$, is comparable to the one that we observe between the spectra of the decomposed composite Ca(BH$_4$)$_2$-MgNH$_4$ and of the reference MgNi$_2$B$_2$. The weaker pre-edge features that we observe in the decomposed samples, arguably suggest that the decomposition process promotes a variable transfer of boron that happens to be more complete in the MgNi$_2$B$_2$ produced from the mixture Ca(BH$_4$)$_2$-Mg$_2$NiH$_4$ than the one in pure MgNi$_2$B$_2$.

Obtaining a quantitative description of this effect is not within the possibilities of our data, as SR-PXRD shown in Figure 6 does not exclude that the decomposition of MgNH$_4$ also produces elemental Mg and Mg$_2$Ni that can coexist for temperatures higher than 450°C.

Nevertheless, the picture presented by X-ray and XANES spectra is in agreement with the SR-PXRD and NMR results and strongly supports the conclusions of the manuscript, namely confirming the progress of the decomposition reaction as shown in equation (3) and providing strong hints of the mobility of boron within MgNi$_2$B$_2$.

References
2. S. Huotari et al., A large-solid-angle X-ray Raman scattering spectrometer at ID20 of the European Synchrotron
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