



New fundamental experimental studies on α - $\text{Mg}(\text{BH}_4)_2$ and other borohydrides

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ABSTRACT

Several new studies of $\text{Mg}(\text{BH}_4)_2$ are reported. A 1:1 LiBH_4 : $\text{Mg}(\text{BH}_4)_2$ mixture was studied by in situ synchrotron X-ray diffraction and reveals an eutectic behavior with the eutectic composition more rich in $\text{Mg}(\text{BH}_4)_2$, and the eutectic temperature lower than 456 K. No dual cation compound was observed in this experiment.

New vibrational spectra including INS data have been obtained and are compared with theoretical DFT calculations and recent NMR studies, showing good agreement.

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1. Introduction

Magnesium borohydride with a theoretical hydrogen content of 14.8% has received much interest in view of potential hydrogen storage applications [1], as its stability appears to be lower than for the alkali borohydrides. The crystal structure of $\text{Mg}(\text{BH}_4)_2$, which presents two phases at ambient pressure, is surprisingly complex [2–4]. Single crystal diffraction has shown that α - $\text{Mg}(\text{BH}_4)_2$ crystallizes in the space group $P6_122$ [4].

In this paper, we address several properties of $\text{Mg}(\text{BH}_4)_2$ and related compounds combining various experimental and theoretical methods.

2. Synthesis of $\text{Mg}(\text{BH}_4)_2$ and study of LiBH_4 : $\text{Mg}(\text{BH}_4)_2$

The preparation of $\text{Mg}(\text{BH}_4)_2$ can be performed by several methods [5–7]. We have obtained [7] highly pure (>99%) $\text{Mg}(\text{BH}_4)_2$ by recrystallization of 95% pure $\text{Mg}(\text{BH}_4)_2$ obtained from the reaction of MgH_2 and Et_3NBH_3 [5].

Deuterium–hydrogen exchange has been studied in solid α - $\text{Mg}(\text{BH}_4)_2$ [8]. The volume of the autoclave was ca 80 cm³, yielding a H/D ratio of 1/10 for the initial charge. About 95% deuterium substitution was achieved after exposing ca 0.25 g of $\text{Mg}(\text{BH}_4)_2$ for 72 h

to 40 bar of D_2 at 172 °C, with one intermediate evacuation of the gas and refill with pure D_2 .

The system LiBH_4 – $\text{Mg}(\text{BH}_4)_2$ has been studied by temperature dependent in-situ synchrotron diffraction. A 1:1 molar intimate mixture was prepared by ball milling of commercial LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ (prepared as outlined above) using a Fritsch Pulverisette. A milling period of 10 min was followed by a rest time of 5 min to avoid overheating of the sample. This cycle was repeated 35 times. Fig. 1 shows the evolution observed with increasing temperature from 293 to 500 K. The origin of the diffraction peak labelled “?” in Fig. 1 is not clear, it does not belong to any known potential compound such as Mg, MgH_2 or LiH. It is still observed after the cycling experiment. At 385 K, the LT–HT phase transition of LiBH_4 is observed (seen very clearly for $2\theta = 12.2$). At 456 K, the lines of $\text{Mg}(\text{BH}_4)_2$ disappear, while HT LiBH_4 is still seen. This behavior is probably related to the eutectic system, and signals that the eutectic composition is more rich in $\text{Mg}(\text{BH}_4)_2$, and the eutectic temperature lower than 456 K. No other compound than LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ was found after cooling (red pattern in Fig. 1). A recent study [9] reported the formation of a dual cation compound in this LiBH_4 – $\text{Mg}(\text{BH}_4)_2$ system. The DSC experiment in this study [9] on the LiBH_4 / $\text{Mg}(\text{BH}_4)_2$ mixture shows signals at 116 and 183 °C (389 and 456 K), in good agreement with the changes seen in Fig. 1.

3. Vibrational spectroscopy

Fig. 2 presents the Raman and IR spectra of α - $\text{Mg}(\text{BH}_4)_2$ and IR of α - $\text{Mg}(\text{BD}_4)_2$ obtained at room temperature. The isotopic shifts

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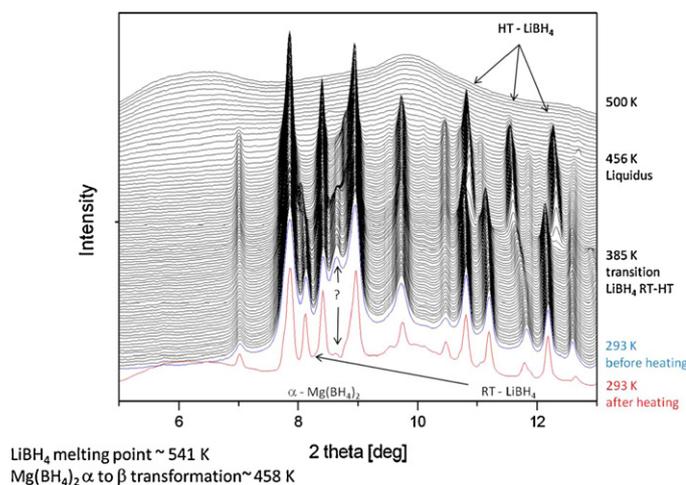


Fig. 1. In situ X-ray diffraction from room temperature (blue) to 500 K (top) of $\text{Mg}(\text{BH}_4)_2:\text{LiBH}_4$ 1:1 mixture. The lowest trace (in red) corresponds to the sample cooled to 293 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

of the different bands are shown by the arrows. It is important to note that despite the complex crystal structure with formally six different borohydride groups, the spectra look quite simple with basically one broad IR-active stretching and two IR active deformation modes. The observed frequencies correspond very well to the theoretical spectra calculated for the $P6_122$ phase [10].

The crystal structure of $\text{Mn}(\text{BH}_4)_2$ [11] is not as complex as the crystal structure of $\text{Mg}(\text{BH}_4)_2$ [4], but the two structures present some similarities. Both compounds were studied using IR, Raman [11] and new inelastic neutron scattering (INS) scattering experiments (see Fig. 3) and show similar spectra. The INS data have been recorded with MAPS at ISIS [12].

Fig. 3a shows the data for $\text{Mg}(\text{BH}_4)_2$ as obtained from the instrument. It is interesting to note that the lower frequency modes appear to show some dispersion, leading to a broadening of the bands obtained by integration over all values of momentum transfer as seen in Fig. 3b. Using a monochromator with higher resolution (with simultaneous reduction of spectral range) the second experimental trace in Fig. 3b was obtained. Between 1000 and 1500 cm^{-1} , 4 BH_4^- deformation bands are clearly resolved. These bands cor-

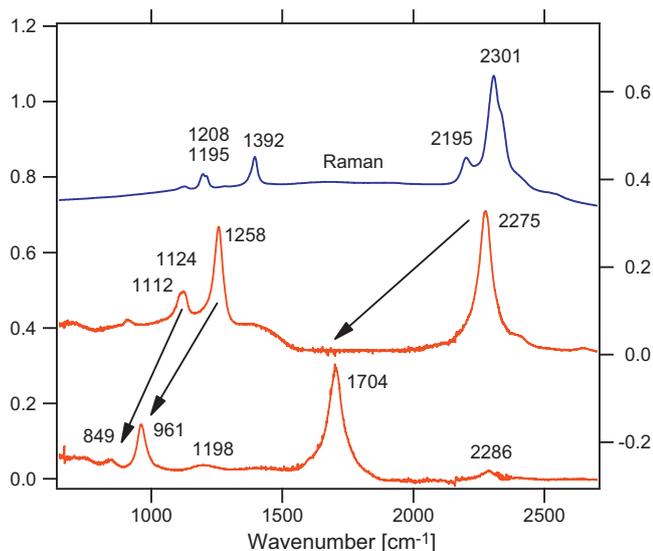


Fig. 2. Raman (top) and IR spectra of $\text{Mg}(\text{BH}_4)_2$ (center) and $\text{Mg}(\text{BD}_4)_2$ (bottom) at room temperature in the $P6_122$ phase (vertical scale shifted for clarity).

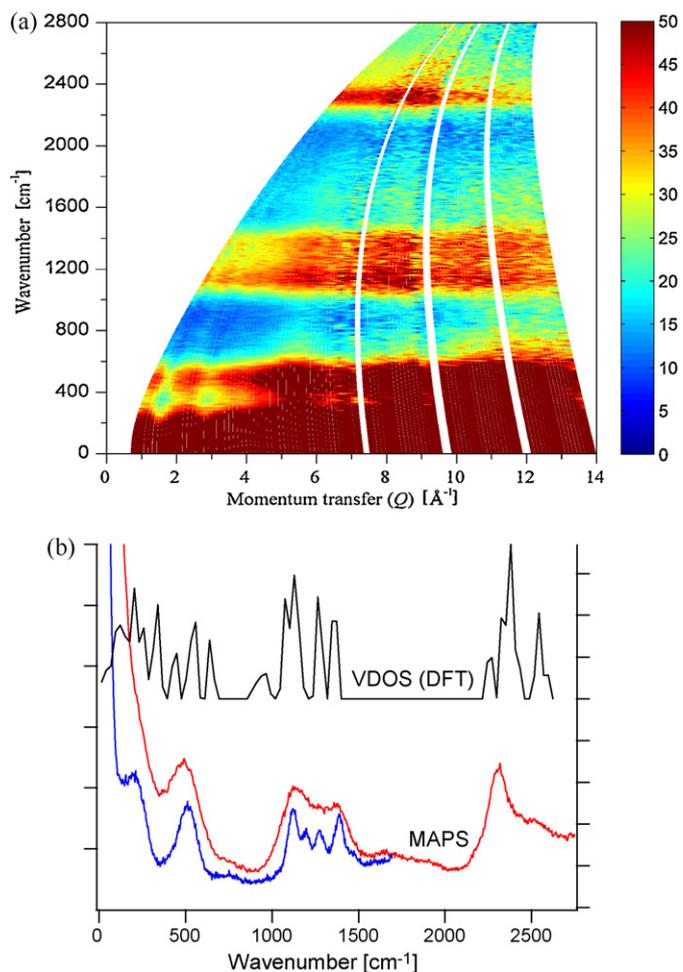


Fig. 3. INS of $\alpha\text{-Mg}(\text{BH}_4)_2$. Integrated INS signal at lower (as in part a) and higher resolution and DFT calculated VDOS for a simplified crystal structure of $\text{Mg}(\text{BH}_4)_2$ with space group $Pmc2_1$.

relate well with the two bands seen in the IR and the two other seen in the Raman spectra (at the center of the Brillouin zone), highlighting the small dispersion of these modes. Due to the complex crystal structure of $\text{Mg}(\text{BH}_4)_2$ [4], the vibrational spectra for this compound were first calculated for a simplified structure with space group $Pmc2_1$. As can be seen from Fig. 3b, there is a good agreement with the INS data for the internal BH_4^- modes (above 1000 cm^{-1}). To account correctly for the lattice mode region, the experimental structure (space group $P6_122$) must be used for the calculations which are under way.

Note that very recently Raman and INS data for $\text{Mg}(\text{BH}_4)_2$ were also reported in [13].

Skrpov et al. [14] have studied reorientational motions in $\alpha\text{-Mg}(\text{BH}_4)_2$ and obtained three different barriers with activation energies of 116 ± 6 meV, 198 ± 12 meV and 362 ± 5 meV. The value of the highest barrier, assigned to the rotation around the twofold axis perpendicular to the B–Mg line, can also be related to the highest energy librational mode (ν_{lib}) observed by Raman or INS spectra using a relation initially proposed by Gutowsky [15]:

$$V = \frac{\pi^2 I \nu_{\text{lib}}^2}{2} \left(1 + \frac{h}{2\pi^2 I \nu_{\text{lib}}} \right)^2 \quad (1)$$

where I is the moment of inertia of the BH_4^- group. Using the value of 362 meV, the value of ν_{lib} is estimated to be ca 545 cm^{-1} , in reasonable agreement with the band observed at 525 cm^{-1} observed by INS [13 and this work]. We have shown [16,17] that one can

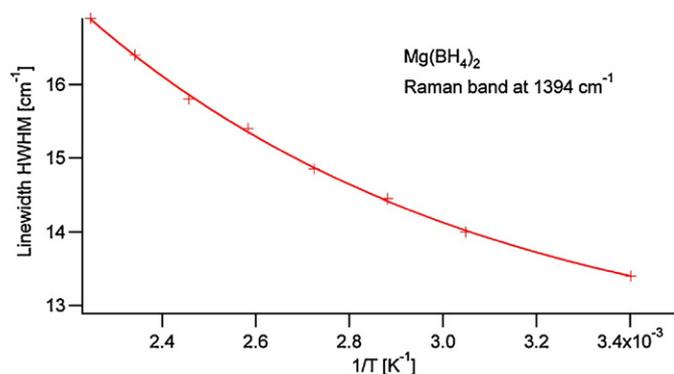


Fig. 4. Temperature dependence of the linewidth of the Raman band at 1394 cm^{-1} . The solid line is the fit based on Eq. (2).

also obtain an estimate of rotational barrier from the temperature dependence of the linewidth of the Raman active BH_4^- bending mode, using the following relation:

$$\Gamma(\omega, T) = a + ce^{-V/kT} \quad (2)$$

In $\text{Mg}(\text{BH}_4)_2$ the band at 1394 cm^{-1} corresponds to the BH_2 bending motion directed towards the Mg ion. This motion may couple to a librational motion around the Mg–B axis. Fig. 4 shows the results of a temperature dependent Raman study from 300 K to ca 450 K. The value of the barrier of reorientation estimated from this experiment is $102 \pm 6\text{ meV}$, in good agreement with the lowest value found by NMR spectroscopy [14].

4. Conclusions

We have studied the chemical and physical properties of $\alpha\text{-Mg}(\text{BH}_4)_2$. Pure $\alpha\text{-Mg}(\text{BH}_4)_2$ and $\alpha\text{-Mg}(\text{BD}_4)_2$ have been synthesized. The 1:1 LiBH_4 : $\alpha\text{-Mg}(\text{BH}_4)_2$ mixture appears to show an eutectic behavior with the eutectic composition more rich in $\text{Mg}(\text{BH}_4)_2$, and the eutectic temperature lower than 456 K. No Mg–Li borohydride (as reported previously [9]) was observed in

our experiment. The vibrational spectra show good agreement with periodic DFT calculations. This work shows also the good complementarity between NMR measurements and vibrational spectroscopy for the study of rotational barriers in borohydrides, with good numerical agreement for the different barrier heights.

Further studies including also the high temperature phase are in progress.

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