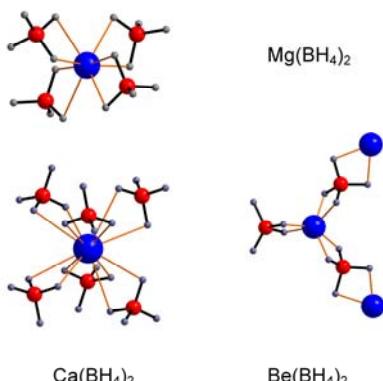


# Magnesium borohydride : synthesis and crystal structure

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**Figure 1.** Structural comparison of the  $M(BH_4)_2$  series' members.  $M$  (in blue) = Mg and Ca: 3-d framework; Be: 1-d polymer. Coordination of Mg5 is shown for  $Mg(BH_4)_2$ .

$Mg(BD_4)_2$  at 20°C:  
 $P6_1$ ,  $a = 10.3182(1)$ ,  $c = 36.9983(5)$  Å,  $V = 3411.3(1)$  Å $^3$

Five symmetry independent  $Mg^{2+}$  ions and ten symmetry-independent  $[BD_4]$  ions. The  $Mg^{2+}$  and  $[BD_4]$  ions are connected into a novel three-dimensional framework. All  $Mg^{2+}$  cations have similar atomic environments.

$BD_4$  tetrahedra as semirigid bodies with ideal tetrahedral bond angles and a common refined BD distance of 1.18(1) Å.

Each  $Mg^{2+}$  ion is surrounded by four  $[BD_4]$  tetrahedra arranged in a deformed tetrahedron ( $Mg\text{-B } 2.31(3)\text{--}2.53(2)$  Å;  $B\text{-Mg\text{-}B } 83(2)\text{--}131(2)$  deg). Each  $[BD_4]$  ion is approximately linearly coordinated by two  $Mg^{2+}$  ions ( $Mg\text{-B-Mg } 148(1)\text{--}177(2)$  deg).

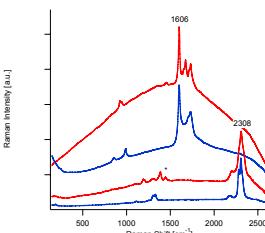
The orientation of the  $[BD_4]$  tetrahedra is such that each  $Mg^{2+}$  ion is coordinated by tetrahedral edges only ( $\mu_2\text{-D}_2$  bridges), resulting in an unusual eightfold, relatively irregular hydrogen coordination environment.

$Mg\text{-D}$  distances in the range of 1.81(4)–2.25(5) Å, with the exception of one longer distance of 2.46(8) Å.

The increase of the hydrogen coordination number from six (for  $Be^{2+}$ ) to eight (for  $Mg^{2+}$ ) and twelve (for  $Ca^{2+}$ ) suggests that cation size is one of the reasons that  $Mg(BD_4)_2$  does not adopt one of the simpler structures of its alkaline-earth analogues.

The structure of  $Mg(BD_4)_2$  differs from those of its beryllium and calcium analogues, as well as from those predicted by theory [1,2].

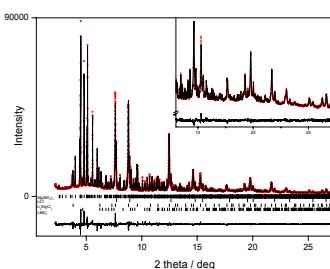
The structure is one of the most complex atom arrangements solved from powder diffraction data so far.



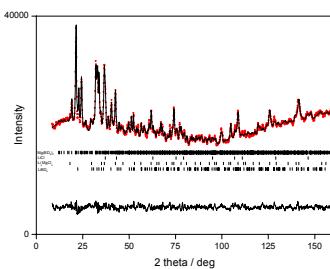
**Figure 2.** Raman spectra of  $Mg(BH(D)_4)_2$  (in red) and  $LiBH(D)_4$  (in blue). Upper curves: deuteride, lower curves: hydride. The asterisk indicates a band resulting from residual diethyl-ether.

	$LiBD_4$	$LiBH_4$	$Mg(BH_4)_2$	$Mg(BD_4)_2$
$v_1 + v_3$ B-H(D) stretching +Fermi resonance	1730 1705 1603	2321sh 2275 2301	2334sh 2283sh 2308vs	1733 1716 1674 1654 1606
$v_2 + v_4$	989 856 838sh	1316 1286 1235 1099 1090	1310 1288 1205 1190 1126w 1088w 1039w	946 924 830 802 775
Lattice modes	673 366 245	285 255 189	670 248 204 195 172	

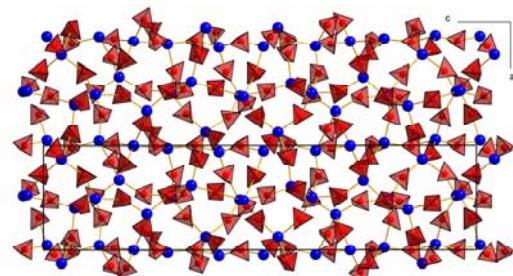
**Table 1.** Observed Raman shifts (in cm $^{-1}$ ) for lithium and magnesium borohydride at room temperature (see Figure 2) vs = very strong, sh = shoulder, w = weak.



**Figure 3.** Observed (red), calculated (black) and difference (bottom) neutron powder diffraction patterns for  $Mg(BD_4)_2$ ,  $\lambda = 0.40008$  Å. The Bragg positions for individual phases are shown with ticks.



**Figure 4.** Observed (red), calculated (black) and difference (bottom) neutron powder diffraction patterns for  $Mg(BD_4)_2$ ,  $\lambda = 1.8857$  Å. The Bragg positions for individual phases are shown with ticks.



**Figure 5.** Structure of  $Mg(BH_4)_2$  viewed along the hexagonal  $b$  axis, showing two unit cells. Red (partially transparent) are  $BD_4$  units; Mg atoms in blue. Considering the cations as A and the tetrahedral anions as B, the resulting three-dimensional framework, in which each tetrahedron  $AB_4$  shares all of its vertices with another tetrahedron, resembles the frameworks of oxides and aluminosilicates, which generally display nearly linear A-B-A fragments.

## Synthesis:

Commercial  $LiBH_4$  or  $LiBD_4$  (2 g, 91.8 mmol) and anhydrous  $MgCl_2$  (4 g, 42 mmol) were introduced into a 500-mL flask containing dry diethyl ether (300 mL). The mixture was heated under reflux for 3 days in a nitrogen atmosphere, and ether was repeatedly added to compensate for evaporation losses. The reaction mixture was allowed to cool for 1 h. Then the liquid phase was removed using a syringe equipped with a small filter and collected in a new flask. The ether was removed under vacuum ( $10^{-2}\text{--}10^{-3}$  mbar, liquid-nitrogen trap) at room temperature, leaving a white paste of solvated  $Mg(BH_4)_2$  or  $Mg(BD_4)_2$  and other compounds.

Upon careful drying under vacuum at increasing temperatures (50, 70, 90, 110, 130, and 145°C) over 3 or 10 days (in two different experiments), a dry solid was obtained. X-ray analysis revealed the presence of some  $LiCl$ ,  $Li_2MgCl_4$ , and  $LiBH_4$  or  $LiBD_4$ , in addition to the main phase  $Mg(BH_4)_2$  or  $Mg(BD_4)_2$  (yield ca. 30%). Above 150°C, the sample started to decompose.

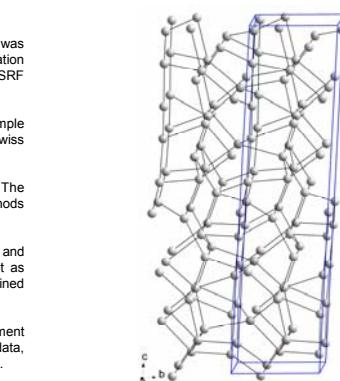
For samples heated to only 120°C, ether was detected in the Raman spectrum; these samples were not sufficiently well-crystallized for high-resolution diffraction studies.

## Raman spectra:

In the BH stretching region (around 2300 cm $^{-1}$ ), the spectra of  $Mg(BH_4)_2$  and  $LiBH_4$  are similar, while those of the corresponding deuterides are more complex.

In the bending region (1000–1400 cm $^{-1}$ ), the spectra of the hydrides and the deuterides show significant differences.

By correlating the BD stretching frequency with the BD bond length, as was done for the cubic alkali-metal borohydrides [3], a frequency of 1605 cm $^{-1}$  suggests a bond length of 1.17 Å.



**Figure 6.** Considering the cations (A) only, the  $Mg^{2+}$  network ( $Mg\cdots Mg > 4.6$  Å) resembles an amorphous state on a local level. Four-connected Mg nodes are shown.

A powder synchrotron X-ray diffraction (S) pattern for  $Mg(BD_4)_2$  was measured over 24 h at room temperature using synchrotron radiation ( $\lambda=0.400080(1)$  Å) at the Swiss–Norwegian Beam Line BM1B of the ESRF (Grenoble).

A powder neutron diffraction (N) pattern was measured for the same sample at 100°C using neutron radiation ( $\lambda=1.8857$  Å) on the HRPT at the Swiss Spallation Source (SINQ) of the PSI (Villigen).

The S data were indexed in a hexagonal cell by using Dicvol96. The structure was solved jointly from the S and N data by direct-space methods (program FOX [4]) in space group  $P6_1$ .

Five magnesium atoms and ten  $BD_4$  groups were refined jointly on the S and N data by using TOPAS Academic [5]. The  $BD_4$  tetrahedra were kept as semirigid bodies with ideal tetrahedral bond angles and a common refined BD distance.

In the final cycle, 186 parameters were refined, yielding the agreement factors of  $R_{wp}=0.048$ ,  $R_{Bragg}(\text{main phase})=0.034$ , and  $\chi^2=16$  for the S data, and of  $R_{wp}=0.018$ ,  $R_{Bragg}(\text{main phase})=0.008$ , and  $\chi^2=7.45$  for the N data.

Nine S patterns were collected over the temperature range 100–200°C to check for the phase transition reported in reference [6]. A transition to a HT phase was indeed observed at approximately 180°C. The HT phase is possibly unstable above this temperature. Its diffraction peaks were not consistent with a hypothetical cubic Cu<sub>2</sub>O-type metal substructure nor with a face-centered cubic structure ( $\sim 15.5$  Å) as reported in reference [6].

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