

## Supporting Information

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## Magnesium borohydride : synthesis and crystal structure

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Synchrotron and neutron diffraction: Synchrotron powder diffraction patterns (S) were measured at room temperature at the Swiss Norwegian Beam Line BM1B of the ESRF (Grenoble) using the Debye-Scherrer geometry and a 6-crystal (Si 111) analyser detector. A pattern used for indexing was measured on the hydride sample at a wavelength of 0.699470(1) Å. The pattern used for the structure solution and refinement was measured on the deuteride sample at a wavelength of 0.400080(1) Å during 24 hours to accumulate statistically important data even for very weak intensities. 0.5 mm glass capillaries were filled with samples in an argon glove-box and sealed with vacuum grease. The neutron powder diffraction pattern (N) was measured at--100°C on the HRPT powder diffractometer at the Swiss Spallation Source SINQ (PSI Villigen) at a wavelength of 1.8857 Å on the same deuteride sample as used for synchrotron diffraction. To reduce the absorption by the natural boron isotopes mixture the sample was placed into a double-walled vanadium container.

The synchrotron powder pattern collected on the hydride was used for indexing. All impurity phases have been identified first, and then positions of 22 remaining peaks located within 7-18° 20 range (5.72-2.28 Å d range) were extracted. Peak positions were not corrected for a small zero shift of -0.01°, obtained from calibration data using a standard silicon sample. All 22 peaks have been indexed using Dicvol96, assuming the symmetry not lower than orthorhombic and the unit cell dimensions do not exceed 40 Å, in an orthorhombic cell with a = 37.10426, b = 8.96107 and c = 5.17407 Å. Checkcell/Truecell/Celref utilities were used to find a higher metric symmetry (hexagonal). A le Bail fit and the refined zero shift of -0.0123(1)° were highly satisfactory. Refined cell parameters for the deuteride at 20°C are: a = 10.3182(1), c = 36.9983(5) Å, V=3411.3(1) Å<sup>3</sup>; for the deuteride at -100°C: a = 10.313(1), c = 36.921(9) Å, V=3400(1) Å<sup>3</sup>. The structure was solved jointly from synchrotron and neutron data by direct space methods (program  $FOX^{[23]}$ ). Although observed systematic absences suggested a  $6_1$  screw axis in the primitive hexagonal cell, the structure solution has been attempted in all possible space groups, namely P6/mmm, P6<sub>1</sub>22, P-62m, P-6m2, P6<sub>3</sub>/m, P6<sub>2</sub>22, P6<sub>1</sub>, P6<sub>2</sub>, P6<sub>3</sub>. 5-6 independent Mg atoms and 10-12 independent ideally tetrahedral BD<sub>4</sub> groups (B-D distance fixed to 1.15 Å) were optimized with respect to their position and orientation. The tasks were distributed over five personal computers, thus enabling to finish all calculation in one week. A reasonable model was obtained only in the polar and chiral space group P61 using 5 Mg atoms and 10 BD4 groups. This solution was refined jointly on synchrotron and neutron data by using the TOPAS-Academic<sup>[24]</sup> keeping the BD<sub>4</sub> tetrahedra as a semi-rigid bodies with ideal tetrahedral bond angles and a common, refined B-D distance. Apart from the Mg(BD<sub>4</sub>)<sub>2</sub> phase (~50 wt %) three impurities phases were identified in the samples: cubic LiCl (a=5.14405 Å at 20°C), cubic Li<sub>2</sub>MgCl<sub>4</sub> (a=10.4153 Å at 20°C) and orthorhombic LiBD<sub>4</sub> (a=7.1033, b=4.3834, c=6.777 Å at 20°C) with relative weight fractions of 5, 35 and 10%, respectively. The weight fraction found from refinements on the synchrotron and neutron data alone were highly consistent.

In the final refinement cycle 186 free parameters were refined: 14(N) and 12(S) background parameters, 2 zero shits (N+S), 1 receiving slit length (S), 1 air scattering parameter (S), 8 scale factors, 6 PV profile parameters for each phase and each data set (48 in total), 2 lattice parameters for the main phase for each data set (4 in total), 5 lattice parameters for the impurities in each data set (10 in total), 3 isotropic displacement parameters for the main phase in each data set (6 in total), 3 isotropic displacement parameters for the impurities for each data set (6 in total), 14 atomic coordinates, 60 position and rotation (Euler angles) parameters and 1 B-D distance for the BD<sub>4</sub> tetrahedra in the main phase. An anti-bump restraint of 1.8 Å was used for the nearest Mg-D distances. The final agreements factors are  $R_{wp} = 0.048$ ,  $R_{Bragg, main phase} = 0.034$ ,  $\chi^2 = 16$  for the synchrotron data, and  $R_{wp} = 0.018$ ,  $R_{Bragg, main phase} = 0.008$ ,  $\chi^2 = 7.45$  for the neutron data.

The refined atomic parameters for the  $Mg(BD_4)_2$  are given in Table S2, and selected interatomic distances in Table S3. Rietveld plots of synchrotron and neutron powder diffraction patterns are given in Figures S1 and S2, respectively. The uncertainties of the atomic coordinates for the boron atoms are equal to the uncertainties of the respective  $BD_4$  tetrahedron positional parameters. The uncertainties of the atomic coordinates for the deuterium atoms are not reported here, because they were not freely refined. Instead we report the uncertainties of the rotation parameters (Euler angles) of the BD<sub>4</sub> tetrahedra they vary between 1.3 and 17.2° (highest value for B5 atom).

*Crystal structure*: The hydrogen surroundings of magnesium need special attention. Due to the complexity of the structure (55 symmetry independent atoms) and the methodology used (powder diffraction) the standard uncertainties (e.s.ds) of some structural parameters are relatively high, and require more work, preferably on single crystals. The e.s.ds of the rotation parameters for the BH<sub>4</sub> tetrahedra, for example, reach 17.2°, leading to e.s.ds for the Mg-D distances of up to 0.2 Å (see deposited material). Thus, from the powder diffraction data alone we cannot completely rule out some corner ( $\mu_1$ ) and/or face ( $\mu_3$ ) Mg-BH<sub>4</sub> bonding, in addition to the edge ( $\mu_2$ ) bonding, at least at the temperatures of our structure determination (-100°C and 20°C). However, there are various reasons that make such a situation unlikely. One is related to the small spread of observed metal-boron distances. As suggested beforel<sup>[S11]</sup> these distances are relatively sensitive to the type of hydrogen bridge. In the two polymers of U(BH<sub>4</sub>)<sub>4</sub>, for example, the U-B distances for  $\mu_2$  and  $\mu_3$  bridging differ by about 0.32 to 0.34 Å.<sup>[S1,S2]</sup> Given that in Mg(BH<sub>4</sub>)<sub>2</sub> the spread between the 20 independent (and more accurate) Mg-B distances is relatively small (2.31(3) - 2.53(2) Å), a possible  $\mu_3$  and/or  $\mu_1$  hydrogen bridging is unlikely. Secondly, the Mg( $\mu_2$ -H<sub>2</sub>BH<sub>2</sub>- $\mu_2$ )Mg units in the 3-dimensional framework of Mg(BH<sub>4</sub>)<sub>2</sub> are not far from linear. Thus, a simultaneous  $\mu_2$  and  $\mu_3$  bridging of the borohydride anion such as that observed in the LT phase of LiBH<sub>4</sub><sup>[11]</sup> is geometrically hard to achieve. Finally,  $\mu_2$  bonding is the only one observed in solvates of Mg(BH<sub>4</sub>)<sub>2</sub><sup>[4]</sup> and also in its alkaline earth analogues M(BH<sub>4</sub>)<sub>2</sub> (M = Be, Ca).

If Mg(BH<sub>4</sub>)<sub>2</sub> crystallized in the cubic Cu<sub>2</sub>O-type arrangement in which [BH<sub>4</sub>]<sup>-</sup> occupies the copper and Mg<sup>2+</sup> the oxygen site (model obtained by packing optimization), it would display the same Mg atom environment (four  $\mu_2$  hydrogen bridges), and similar Mg-H distances (~1.97 Å) and H-H distances between adjacent [BH<sub>4</sub>]<sup>-</sup> anions (~2.48 Å) as the much more complex arrangement in hexagonal Mg(BH<sub>4</sub>)<sub>2</sub> (Mg-H>1.81 Å, H-H>2.33 Å). Both models have the same density (0.79 g·cm<sup>-3</sup>, that is much lower than suggested before <sup>[7]</sup>) and contain no major open pores, as expected for ionic bonding between Mg<sup>2+</sup> and [BH<sub>4</sub>]<sup>-</sup>. Yet, there are no indications that the metal atoms in Mg(BH<sub>4</sub>)<sub>2</sub> adopt the Cu<sub>2</sub>O-type structure, not even in its HT-modification. The reason for this is currently under investigation. Packing effects resulting from a subtle balance between attractive Mg-H and repulsive H-H interactions could play a role but need to be quantified by theoretical modeling.

[S1] E.R. Bernstein, W.C. Hamilton, T.A. Keiderling, S.J. la Placa, S.J. Lippard, J.J. Mayerle, *Inorg. Chem.*, 1972, 11, 3009-3016.

[S2] P. Charpin, M. Nierlich, D. Vigner, M. Lance, D. Baudry, Acta Cryst. C 1987, 43, 1465-1467.

	LiBD <sub>4</sub>	LiBH <sub>4</sub>	Mg(BH <sub>4</sub> ) <sub>2</sub>	Mg(BD <sub>4</sub> ) <sub>2</sub>
$\upsilon_1 + \upsilon_3$	1730	2321sh	2334sh	1733
	1705	2275	2283sh	1716
B-H(D) stretching	1603	2301	2308vs	1674
+ Fermi resonance				1654
				1606
υ <sub>2</sub> + υ <sub>4</sub>	989		1388	946
	856	1316	1310	924
	838sh	1286	1288	830
		1235	1205	802
			1190	775
		1099	1126w	
		1090	1088w	
			1039w	
Lattice modes	673	285	670	
	366	255	248	
	245	189	204	
			195	
			172	
	1			

**Table S1**. Observed Raman shifts (in cm<sup>-1</sup>) for lithium and magnesium borohydride at room temperature (see figures of spectra) vs = very strong, sh = shoulder, w = weak.

**Table S2**. Atomic coordinates and isotropic displacement parameters for Mg(BD<sub>4</sub>)<sub>2</sub>. Joint Rietveld refinement of synchrotron ( $\lambda$ =0.40008 Å) data at RT and neutron (1.8857 Å) data at -100°C. The uncertainties of the atomic coordinates for the deuterium atoms are not reported here, because they were not freely refined. Instead we report the uncertainties of the rotation parameters (Euler angles) of the BD<sub>4</sub> tetrahedra - they vary between 1.3 and 17.2° (for B5).

	х	У	Z
Mg1	0.0462(5)	0.5197(9)	0
Mg2	0.3341(7)	0.3837(6)	0.4536(2)
Mg3	0.5198(9)	0.4940(7)	0.1750(2)
Mg4	0.3961(5)	0.3391(5)	0.0565(1)
Mg5	0.0007(10)	0.1299(7)	-0.0798(5)
B1	0.690(5)	0.716(3)	0.299(1)
D11	0.5701	0.6207	0.2898
D12	0.7065	0.8331	0.2903
D13	0.7814	0.6972	0.2840
D14	0.7034	0.7117	0.3301
B2	0.827(4)	0.871(2)	-0.062(1)
D21	0.7929	0.9174	-0.0875
D22	0.9344	0.9697	-0.0486
D23	0.8533	0.7777	-0.0718
D24	0.7281	0.8203	-0.0413
B3	0.538(4)	0.695(3)	-0.193(1)
D31	0.4836	0.7238	-0.2184
D32	0.6073	0.8024	-0.1760
D33	0.6174	0.6527	-0.2050
D34	0.4425	0.6000	-0.1762
B4	0.009(5)	0.526(2)	-0.2216(6)
D41	-0.0992	0.4756	-0.2397
D42	0.1145	0.6049	-0.2393
D43	0.0236	0.4281	-0.2096
D44	-0.0020	0.5954	-0.1977
B5	1.007(2)	0.720(4)	0.369(1)
D51	0.8943	0.6969	0.3827
D52	0.9836	0.6776	0.3388
D53	1.0568	0.6562	0.3850
D54	1.0932	0.8495	0.3694
B6	0.473(4)	0.475(2)	0.5060(7)
D61	0.4281	0.5372	0.4876
D62	0.5973	0.5602	0.5148
D63	0.4707	0.3759	0.4896
D64	0.3975	0.4277	0.5319
B7	0.871(3)	0.288(5)	0.374(2)
D71	0.8403	0.3743	0.3616
D72	1.0025	0.3435	0.3757
D73	0.8237	0.1817	0.3549
D74	0.8189	0.2514	0.4029
B8	0.020(3)	0.464(3)	0.564(1)
D81	-0.0917	0.4222	0.5803
D82	0.0064	0.3690	0.5438
D83	0.1189	0.4916	0.5841

D84	0.0468	0.5719	0.5474
B9	0.283(3)	0.585(2)	0.3272(6)
D91	0.2724	0.6735	0.3450
D92	0.4035	0.6406	0.3142
D93	0.1925	0.5419	0.3040
D94	0.2642	0.4831	0.3454
B10	0.119(3)	0.206(2)	0.0634(8)
D101	0.0637	0.2219	0.0898
D102	0.1867	0.1460	0.0709
D103	0.1997	0.3237	0.0505
D104	0.0240	0.1320	0.0424

Note: The isotropic displacement parameters B were constrained to be identical for the same atom type:  $B_{Mg} = 1.62(7)$ ,  $B_B = 2.0(2)$ ,  $B_D = 1.0$  from synchrotron and  $B_{Mg} = 3(1)$ ,  $B_B = 0.5(5)$ ,  $B_D = 2.0(3)$  Å<sup>2</sup> from neutron data. The coordinates are not standardized to keep the BH<sub>4</sub> groups bonded also in the asymmetric unit.

**Table S3**. Selected interatomic distances (Å) for magnesium borohydride as refined jointly from synchrotron and neutron data. The results correspond to RT synchrotron data. Cut-off limits for Mg-D and Mg-B distances are 2.67 and 4.35 Å, respectively. In the calculation of Mg-D distances the uncertainties of rotation parameters (Euler angles) of the BH<sub>4</sub> tetrahedra were used.

Mg1	D92	1.9(1)	Mg4	D41	1.81(4)
	D11	1.9(1)		D62	1.84(7)
	D34	1.87(9)		D74	1.9(1)
	D84	2.0(2)		D103	2.0(1)
	D94	2.1(1)		D73	2.0(1)
	D14	2.1(1)		D102	2.2(1)
	D33	2.14(9)		D42	2.25(5)
	D82	2.2(1)		B7	2.36(3)
	B9	2.40(4)		B4	2.42(3)
	B3	2.42(4)		D64	2.46(8)
	B1	2.44(4)		B10	2.50(2)
	B8	2.49(3)		B6	2.53(2)
Mg2	D61	1.87(5)	Mg5	D22	1.84(6)
	D24	1.88(8)		D13	1.92(8)
	D81	1.9(1)		D12	2.05(8)
	D63	1.97(5)		D51	2.1(2)
	D32	2.02(9)		D101	2.15(8)
	D31	2.04(9)		D54	2.2(2)
	D23	2.05(9)		D21	2.19(6)
	D83	2.2(1)		D104	2.2(1)
	B6	2.31(3)		B1	2.41(4)
	B2	2.38(2)		B2	2.44(2)
	B8	2.38(3)		B5	2.47(5)
	B3	2.45(4)		B10	2.52(3)
Mg3	D44	1.82(4)			
	D52	1.9(2)			
	D71	1.89(9)			
	D53	2.1(2)			
	D43	2.10(4)			
	D72	2.1(1)			
	D93	2.1(1)			
	D91	2.2(1)			
	B4	2.38(2)			
	B5	2.39(5)			
	B7	2.42(4)			
	B9	2.45(4)			
В	4D	1,18(1)			

**Figure S1.** Observed (red), calculated (black) and difference (bottom) synchrotron powder diffraction patterns for Mg(BD<sub>4</sub>)<sub>2</sub>,  $\lambda$  = 0.40008 Å. The Bragg positions for individual phases are shown with ticks.



**Figure S2**. Observed (red), calculated (black) and difference (bottom) neutron powder diffraction patterns for Mg(BD<sub>4</sub>)<sub>2</sub>,  $\lambda = 1.8857$  Å. The Bragg positions for individual phases are shown with ticks.



Figure S3. Coordination of five Mg atom sites.

Mg1



Mg2



Mg3









Mg5

**Figure S4.** A novel tetrahedral framework topology in  $Mg(BH_4)_2$ . Four-connected Mg nodes are shown. Mg...Mg distances range from 4.6 to 5 Å.



**Figure S5.** Structure of  $Mg(BH_4)_2$  viewed along the hexagonal *b* axis, showing two unit cells. Red (partially transparent) tetrahedra are  $BH_4^-$  units; Mg atoms in blue.

