

A density functional study of α -Mg(BH₄)₂

Michiel J. van Setten, Gilles A. de Wijs, Maximilian Fichtner, and Geert Brocks

Optimized structures: Tables S1 and S2 give the optimized atomic positions starting from the experimental structures determined by Černý *et al.*⁴ and Her *et al.*⁵ respectively. All atoms are in the 6a Wyckoff position. The atomic positions of the two sets follow the order used in the original papers, with the first four hydrogen positions forming the tetrahedron around the first boron position etc. The two sets of positions differ by a shift along the c-axis. The Černý positions can be obtained by adding 0.55c to the relaxed Her positions. The Černý magnesium positions 1 to 5 correspond to the Her magnesium positions 4,5,1,2,3. The Černý boron positions 1 to 10 correspond to the Her 5,8,4,9,7,10,6,2,3,1 boron positions. The hydrogen atoms follow the order of the boron atoms in groups of four.

Crystal structure: The basic building block of the crystal structure consists of a MgH₈ dodecahedron, where the H atoms are shared in pairs with 4 BH₄ tetrahedra, as shown in figure 2. Each BH₄ tetrahedron forms a bridge to a neighboring MgH₈, thus generating a tetrahedral network between dodecahedra. The B and H atoms in a BH₄ tetrahedron are bonded by strong sp³ covalent bonds, implying that the BH₄ tetrahedral geometry is not easily distorted. Indeed all B-H distances are in the range 1.22-1.23 Å. The H-B-H bond angles involving 2 H atoms coordinating the same Mg atom are 115±1° and the remaining tetrahedral H-B-H angles are 107±1°, which means that the BH₄ tetrahedra are only slightly flattened. The Mg and H atoms in a MgH₈ dodecahedron are bonded by dominantly ionic bonds. Although pairwise such bonds are isotropic (they only depend upon the distance between the atoms), the sum of the attractive Mg-H and repulsive H-H Coulomb interactions gives rise to a coordination shell that has a fairly rigid structure.^{22,23} Mg-H distances show a spread of ~7%, and the nearest neighbor H-H distances along the edges of a dodecahedron a spread of ~10%, see figure 2. This introduces some flexibility in the MgH₈ geometry, but the basic dodecahedral shape remains.

In summary, the covalent bonding between H and B atoms, and the ionic bonding between H and Mg atoms fix the structure locally. Neighboring dodecahedra are connected by a BH₄ bridge. Because of the tetrahedral shape of the latter, a rotation of 90° between neighboring dodecahedra is introduced by each BH₄ bridge, which is illustrated in figures 3 and S1. Such a constraint makes it difficult to generate a tetrahedral network that has a simple structure. This can be visualized by omitting the H atoms and putting the 4 B atoms surrounding a Mg atom on

the corners of a tetrahedron as in figure S1. These MgB_4 tetrahedra are distorted and flattened with 2 B-Mg-B angles in the range $120\text{-}130^\circ$ and the remaining ones in the range $90\text{-}110^\circ$. Each B atom that is shared between neighboring MgB_4 tetrahedra then introduces a rotation around the Mg-B-Mg axis. If the tetrahedra would be perfectly regular, the rotation angle would be 90° , or $120\text{-}90 = 30^\circ$. This is stressed by the blue and red lines in figure S1. A simple structure like the Cu_2O structure can also be visualized in terms of linked tetrahedra as shown in figure S2. However, in order to obtain the zigzag chains of tetrahedra, which are vital in the Cu_2O structure, two neighboring tetrahedra then need to be rotated around the Mg-B-Mg axis by 60° , see figure S2. Simple tetrahedral networks involve rotation angles of (multiples of) 60° . The rotation angles in $\text{Mg}(\text{BH}_4)_2$ are fixed by the dodecahedron/tetrahedron geometry discussed above, and are far from 60° . This introduces considerable strain in the network, which can only be alleviated by spreading it over many sites in a large unit cell.

Table S1: Optimized atomic positions starting from the structure determined by Černý *et al.*⁴

	x	y	z
Mg1	0.0311	0.5124	0.0002
Mg2	0.3329	0.3785	0.4514
Mg3	0.5234	0.4851	0.1724
Mg4	0.3820	0.3329	0.0533
Mg5	0.0026	0.1361	0.9190
B1	0.6891	0.7101	0.2988
B2	0.8211	0.8852	0.9383
B3	0.5569	0.7052	0.8031
B4	0.0046	0.5373	0.7755
B5	0.0103	0.7081	0.3723
B6	0.4923	0.5024	0.5027
B7	0.8558	0.2923	0.3663
B8	0.0153	0.4727	0.5633
B9	0.2949	0.5867	0.3393
B10	0.1183	0.1808	0.0667
H1	0.5618	0.6349	0.2867
H2	0.7234	0.8417	0.2952
H3	0.7687	0.6723	0.2826
H4	0.7033	0.6931	0.3310
H5	0.7915	0.9509	0.9149
H6	0.9354	0.9630	0.9557
H7	0.8377	0.7894	0.9229
H8	0.7172	0.8378	0.9600
H9	0.5156	0.7281	0.7741
H10	0.6397	0.8169	0.8211
H11	0.6309	0.6455	0.7962

H12		0.4430		0.6292		0.8211
H13		0.8834		0.4662		0.7601
H14		0.1099		0.6167		0.7557
H15		0.0313		0.4440		0.7884
H16		0.9924		0.6191		0.7976
H17		0.8902		0.6785		0.3859
H18		0.9894		0.6943		0.3395
H19		0.0486		0.6251		0.3863
H20		0.1127		0.8369		0.3771
H21		0.4819		0.5718		0.4769
H22		0.6272		0.5561		0.5079
H23		0.4392		0.3676		0.4975
H24		0.4230		0.5136		0.5284
H25		0.8197		0.3700		0.3486
H26		0.9901		0.3470		0.3719
H27		0.8192		0.1782		0.3487
H28		0.7964		0.2743		0.3958
H29		0.8919		0.4184		0.5776
H30		0.0108		0.3820		0.5412
H31		0.1188		0.5006		0.5840
H32		0.0401		0.5926		0.5506
H33		0.2221		0.5482		0.3673
H34		0.4237		0.6733		0.3486
H35		0.2579		0.6545		0.3181
H36		0.2766		0.4755		0.3231
H37		0.0530		0.2111		0.0901
H38		0.2142		0.1642		0.0821
H39		0.1657		0.2842		0.0448
H40		0.0397		0.0658		0.0494

Table S2: Optimized atomic positions starting from the structure determined by Her *et al.*⁵

		x		y		z
Mg1		0.0255		0.5224		0.7893
Mg2		0.6598		0.0491		0.8377
Mg3		0.9927		0.8661		0.8705
Mg4		0.9541		0.4816		0.9498
Mg5		0.9451		0.3258		0.0684
B1		0.8147		0.9407		0.8514
B2		0.0015		0.4624		0.0131
B3		0.6975		0.2864		0.9516
B4		0.6999		0.1369		0.0880
B5		0.9749		0.6924		0.9167
B6		0.8433		0.2979		0.8189
B7		0.0107		0.7123		0.8237
B8		0.1737		0.1166		0.8892
B9		0.5200		0.9853		0.8925
B10		0.9862		0.4887		0.1194
H1		0.8313		0.0538		0.8664

H2		0.9289		0.9759		0.8341
H3		0.7108		0.8833		0.8298
H4		0.7853		0.8469		0.8751
H5		0.1067		0.4873		0.0328
H6		0.8807		0.4117		0.0286
H7		0.9894		0.3696		0.9907
H8		0.0278		0.5828		0.0006
H9		0.5686		0.2455		0.9427
H10		0.7132		0.1915		0.9679
H11		0.7379		0.3917		0.9725
H12		0.7688		0.3172		0.9235
H13		0.6208		0.1723		0.1052
H14		0.7196		0.1964		0.0584
H15		0.6457		0.0029		0.0823
H16		0.8130		0.1739		0.1059
H17		0.9327		0.5702		0.9029
H18		0.9971		0.6994		0.9493
H19		0.8750		0.7223		0.9122
H20		0.0949		0.7802		0.9027
H21		0.8171		0.1861		0.8016
H22		0.7757		0.2761		0.8473
H23		0.8078		0.3729		0.8000
H24		0.9761		0.3585		0.8269
H25		0.1086		0.8430		0.8277
H26		0.9825		0.6963		0.7913
H27		0.8925		0.6761		0.8392
H28		0.0595		0.6353		0.8363
H29		0.0593		0.0398		0.9066
H30		0.2774		0.1647		0.9108
H31		0.1577		0.2117		0.8733
H32		0.2027		0.0494		0.8662
H33		0.5725		0.1088		0.8784
H34		0.6114		0.9910		0.9145
H35		0.4938		0.8832		0.8716
H36		0.4000		0.9584		0.9054
H37		0.9080		0.4183		0.1452
H38		0.0677		0.6230		0.1247
H39		0.9044		0.4778		0.0942
H40		0.0674		0.4359		0.1136

Figure S1: *Top:* A substructure in the $\text{Mg}(\text{BH}_4)_2$ crystal illustrating MgH_8 dodecahedra (orange) linked by BH_4 tetrahedra (green) along the c-axis of the unit cell. Each dodecahedron is linked to other substructures by two more tetrahedra, thus forming a tetrahedral network. *Bottom:* the same structure visualized by omitting the H atoms and putting the 4 B atoms surrounding a Mg atom on the corners of a tetrahedron. The blue and red lines illustrate the rotation between neighboring tetrahedra, which is introduced by the BH_4 bridges. Going from left to right, the blue and red lines give a rotation out of and into the plane, respectively.

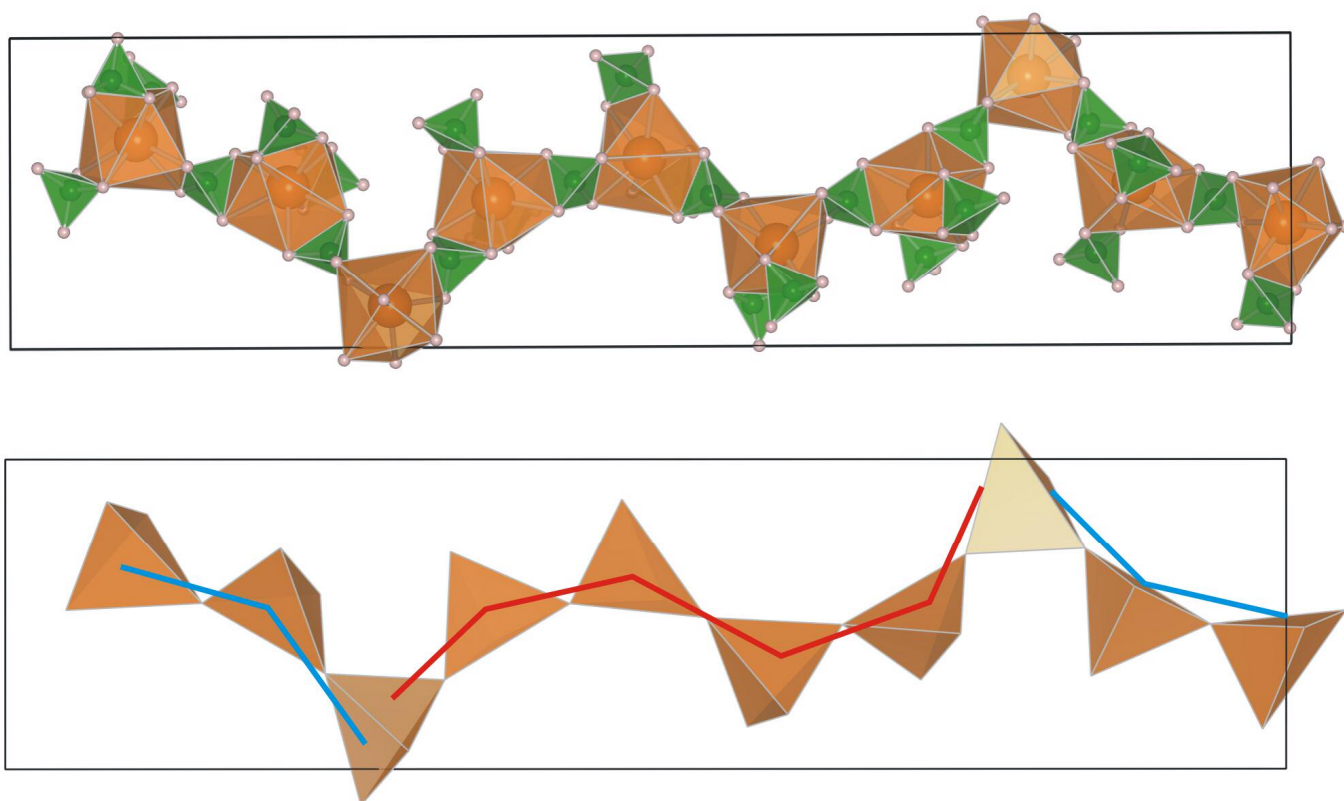


Figure S2: A substructure in the Cu_2O structure illustrating the linkage of tetrahedra.

