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Ab-initio crystal structure prediction by combining symmetry analysis representations and total energy calculations. An insight into the structure of $Mg(BH_4)_2$

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Atom type	Atomic positions in $I4_1/amd$ as well in $I\bar{4}m2$ without displacements	Symmetry allowed displacements from $I4_1/amd$ to $I\bar{4}m2$	Atomic position in $I\bar{4}m2$ from our optimization
Mg	(0, 0, 0)	Inactive	(0, 0, 0)
	(0.5, 0.5, 0.5)	Inactive	(0.5, 0.5, 0.5)
B	(0.266, 0, 0.894)	[A1, 0, B1]	(0.269, 0, 0.9)
	(0.734, 0, 0.894)	[-A1, 0, B1]	(0.731, 0, 0.9)
	(0, 0.734, 0.106)	[0, -A1, -B1]	(0, 0.731, 0.1)
	(0.5, 0.234, 0.606)	[0, -A1, -B1]	(0.5, 0.231, 0.6)
	(0.766, 0.5, 0.394)	[A1, 0, B1]	(0.769, 0.5, 0.4)
	(0.234, 0.5, 0.394)	[-A1, 0, B1]	(0.231, 0.5, 0.4)
	(0, 0.266, 0.106)	[0, A1, -B1]	(0, 0.269, 0.1)
	(0, 0.734, 0.106)	[0, -A1, -B1]	(0, 0.731, 0.1)
H1	(0.137, 0, 0.837)	[A2, 0, B2]	(0.143, 0, 0.835)
	(0.863, 0, 0.837)	[-A2, 0, B2]	(0.857, 0, 0.835)
	(0, 0.863, 0.163)	[0, -A2, -B2]	(0, 0.857, 0.165)
	(0, 0.137, 0.163)	[0, A2, -B2]	(0,0.143, 0.165)
	(0.637, 0.5, 0.337)	[A2, 0, B2]	(0.643, 0.5, 0.335)
	(0.363, 0.5, 0.337)	[-A2, 0, B2]	(0.357, 0.5, 0.335)
	(0.5, 0.363, 0.663)	[0,-A2,-B2]	(0.5, 0.357, 0.665)
	(0.5, 0.637, 0.663)	[0, A2, -B2]	(0.5, 0.643, 0.665)
H2	(0.253, 0, 0.011)	[A3, 0, B3]	(0.252, 0, 0.018)
	(0.747, 0, 0.011)	[-A3, 0, B3]	(0.748, 0, 0.018)
	(0.5, 0.753, 0.489)	[0, A3, -B3]	(0.5, 0.752, 0.482)
	(0.5, 0.247, 0.489)	[0, -A3, -B3]	(0.5, 0.248, 0.482)
	(0.753, 0.5, 0.511)	[A3, 0, B3]	(0.752, 0.5, 0.518)
	(0.247, 0.5, 0.511)	[-A3, 0, B3]	(0.248, 0.5, 0.518)
	(0, 0.253, 0.989)	[0, A3, -B3]	(0, 0.252, 0.982)
	(0, 0.747, 0.989)	[0, -A3,-B3]	(0, 0.748, 0.982)
H3	(0.375, 0.837, 0.635)	[B4, -A4, C4]	(0.375, 0.84, 0.625)

(0.625, 0.163, 0.635)	[-B4, A4, C4]	(0.625, 0.16,0.625)
(0.337, 0.875, 0.865)	[-A4, B4, -C4]	(0.34, 0.875, 0.875)
(0.663, 0.125, 0.865)	[-B4, A4, -C4]	(0.66, 0.125, 0.875)
(0.375, 0.163, 0.635)	[B4, A4, C4]	(0.375, 0.16, 0.625)
(0.625, 0.837, 0.635)	[-B4, -A4, C4]	(0.625, 0.84, 0.625)
(0.337, 0.125, 0.865)	[-A4, -B4, -C4]	(0.34, 0.125, 0.875)
(0.663, 0.875, 0.865)	[A4, B4, -C4]	(0.66, 0.875, 0.875)
(0.875, 0.337, 0.135)	[B4, -A4, C4]	(0.875, 0.34,0.125)
(0.125, 0.663, 0.135)	[-B4, A4, C4]	(0.125, 0.66, 0.125)
(0.837, 0.375, 0.365)	[-A4, B4, -C4]	(0.84, 0.375, 0.375)
(0.163, 0.625, 0.365)	[A4, -B4, -C4]	(0.16,0.625, 0.375)
(0.875, 0.663, 0.135)	[B4, A4,C4]	(0.875, 0.66, 0.125)
(0.125, 0.337, 0.135)	[-B4, -A4, C4]	(0.125, 0.34, 0.125)
(0.837, 0.625, 0.365)	[-A4, -B4, -C4]	(0.84, 0.625,0.375)
(0.163, 0.375,0.365)	[A4, B4, -C4]	(0.16, 0.375, 0.375)

TABLE I: Symmetry group correspondence $I4_1/amd \rightarrow I\bar{4}m2$. Agreement between optimized structures and the ones coming from symmetry analysis is reached for: $A1 = 0.003$, $B1 = 0.006$, $A2 = 0.006$, $B2 = -0.002$, $A3 = -0.001$, $B3 = 0.007$, $A4 = -0.03$, $B4 = 0$, $C4 = -0.01$.

	$I4_1/amd$	$I\bar{4}m2$	$F222$	$C222_1$
Mg	4a	2a	4a	4a, 4b
		2c	4c	4a, 4b
	4b	2b	4b	8c
		2d	4d	8c
B,H1,H2	16h	2x(8i)	2x(16k)	8x(8c)
H3	32i	2x(16j)	4x(16k)	16x(8c)

TABLE II. Splitting of Wyckoff positions along $I4_1/amd \rightarrow I\bar{4}m2 \rightarrow F222 \rightarrow C222_1$ group-subgroup pathway.

	$I4_1/amd$	$Fddd$	$F222$	$C222_1$
Mg	4a	8a	4a	4a, 4b
			4b	8c
	4b	8b	4c	4a, 4b
			4d	8c
B,H1,H2	16h	32h	2x(16k)	8x(8c)
H3	32i	2x(32h)	4x(16k)	16x(8c)

TABLE III. Splitting of Wyckoff positions along $I4_1/amd \rightarrow Fddd \rightarrow F222 \rightarrow C222_1$ group-subgroup pathway.

	$I4_1/amd$	$I4_122$	$F222$	$C222_1$
Mg	4a	4a	4a	4a, 4b
			4c	4a, 4b
	4b	4b	4b	8c
			4d	8c
B,H1,H2	16h	16g	2x(16k)	8x(8c)
H3	32i	2x(16g)	4x(16k)	16x(8c)

TABLE IV. Splitting of Wyckoff positions along $I4_1/amd \rightarrow I4_122 \rightarrow F222 \rightarrow C222_1$ group-subgroup pathway.

Symmetry group No	a	b	c	
$C222_1$ (No 20)	11.546	11.686	20.997	
atom	x	y	z	site
Mg	0	0	0	4a
Mg	0.25	0.25	0.125	8c
Mg	0	0.5	0.25	4b
B	0.3653	0.3669	0.0518	8c
H	0.0718	0.0671	0.5813	8c
H	0.3722	0.3721	0.4938	8c
H	0.2347	0.3927	0.1849	8c
H	0.3953	0.2301	0.1835	8c
B	0.1347	0.1330	0.0519	8c
B	0.1348	0.3670	0.1983	8c
B	0.3654	0.1331	0.1982	8c
H	0.0719	0.0668	0.0814	8c
H	0.0720	0.4331	0.1687	8c
H	0.4283	0.0670	0.1687	8c
H	0.1278	0.1278	0.4937	8c
H	0.1279	0.3723	0.2564	8c
H	0.3725	0.1279	0.2563	8c
H	0.2656	0.1076	0.1848	8c
H	0.2654	0.3926	0.0653	8c
H	0.2346	0.1076	0.0653	8c
H	0.1050	0.2700	0.1836	8c
H	0.1048	0.2300	0.0667	8c
H	0.3950	0.2698	0.0665	8c

TABLE V. Wyckoff positions of the orthorhombic structure $C222_1$ (No 20) optimized at DFT level. The lattice parameters are in Å.

Symmetry group No	a	b	c	
$F222$ (No 22)	10.278	11.361	11.946	
atom	x	y	z	site
6 Mg	0.25	0.25	0.25	4c
7 Mg	0	0	0	4a
1 B	0.1478	0.1129	0.1190	16k
2 H	0.1153	0.1479	0.0262	16k
3 H	0.0859	0.1708	0.1876	16k
4 H	0.1247	0.0093	0.1388	16k
5 H	0.2662	0.1234	0.1234	16k

TABLE VI. Wyckoff positions of the orthorhombic structure $F222$ (No 22) optimized at DFT level. The lattice parameters are in Å.

Symmetry group No	a	b	c	
$Fddd$ (No 70)	10.936	11.085	12.368	
atom	x	y	z	site
Mg	0.125	0.125	0.625	8b
Mg	0.125	0.125	0.125	8a
B	0.2662	0.0144	0.0010	32h
H	0.2167	0.2844	0.3263	32h
H	0.3771	0.0004	0.0055	32h
H	0.0267	0.2807	0.0831	32h
H	0.0018	0.1229	0.2583	32h

TABLE VII. Wyckoff positions of the orthorhombic structure $Fddd$ (No 70) optimized at DFT level. The lattice parameters are in Å.

Symmetry group No	a	b	c	
$I\bar{4}m2$ (No 119)	8.198	8.198	10.449	
atom	x	y	z	site
2 Mg	0	0.5	0.75	2d
3 Mg	0	0	0	2a
1 H	0.1608	0.1264	0.1188	16j
4 B	0.2322	0	0.1463	8i
5 H	0.3608	0	0.0860	8i
6 H	0.2455	0	0.2629	8i

TABLE VIII. Wyckoff positions of the tetragonal structure $I\bar{4}m2$ (No 119) optimized at DFT level. The lattice parameters are in Å.

Symmetry group No	a	b	c	
$I4_1/amd$ (No 141)	8.401	8.401	10.668	
atom	x	y	z	site
Mg	0	0.75	0.125	4a
Mg	0	0.25	0.375	4b
H	0.1225	0.0853	0.2593	32i
B	0	0.0155	0.2307	16h
H	0	0.6116	0.2871	16h
H	0	0.0033	0.1163	16h

TABLE IX. Wyckoff positions of the tetragonal structure $I4_1/amd$ (No 141) optimized at DFT level. The lattice parameters are in Å.

Symmetry group No	a	b	c	
$Fd\bar{3}m$ (No 227)	12.600			
atom	x	y	z	site
Mg	0.375	0.375	0.375	8b
Mg	0.125	0.125	0.125	8a
B	0.2664	0.2664	0.2664	32e
H	0.2093	0.2093	0.2093	32e
H	0.0053	0.0053	0.3580	96g

TABLE X. Wyckoff positions of the cubic structure $Fd\bar{3}m$ (No 227) optimized at DFT level. The lattice parameters are in Å.

Symmetry No	wave numbers cm^{-1}	mode
22	401.11, 409.24	rotation
	1227.31, 1228.86, 1231.08	bending
	2289.67, 2291.68	symmetric stretching
	2323.87, 2330.29, 2340.70	asymmetric stretching
ZPE = 2.180	2395.28, 2400.46, 2404.92	
70	345.89, 346.91, 347.81	rotation
	1210.57, 1213.17, 1216.15	bending
	2346.89, 2347.17, 2348.59	asymmetric stretching
ZPE = 2.169	2364.32, 2379.70, 2394.73	
119	394.90, 404.05	rotation
	1225.80 (x2), 1229.15	bending
	2286.86 (x2)	symmetric stretching
	2325.95 (x2), 2341.67	asymmetric stretching
ZPE = 2.173	2370.66 (x2), 2393.12, 2402.42	
164	149.64 (x2), 321.72, 527.09	rotation
ZPE = 2.221	2343.36 (x2), 2415.96	asymmmetric stretching
227	403.46	rotation
	1130.86(x3)	bending
	2355.83 (x3)	symmetric stretiching
ZPE = 2.019	2436.75 (x3), 2491.89 (x3)	asymmetric stretching

TABLE XI. Calculated (DFT level) wave numbers of the IR-active modes of vibration of selected structures, which IR spectra are reported in Figure 6. The zero-point energy (ZPE) is expressed in eV per formula unit.

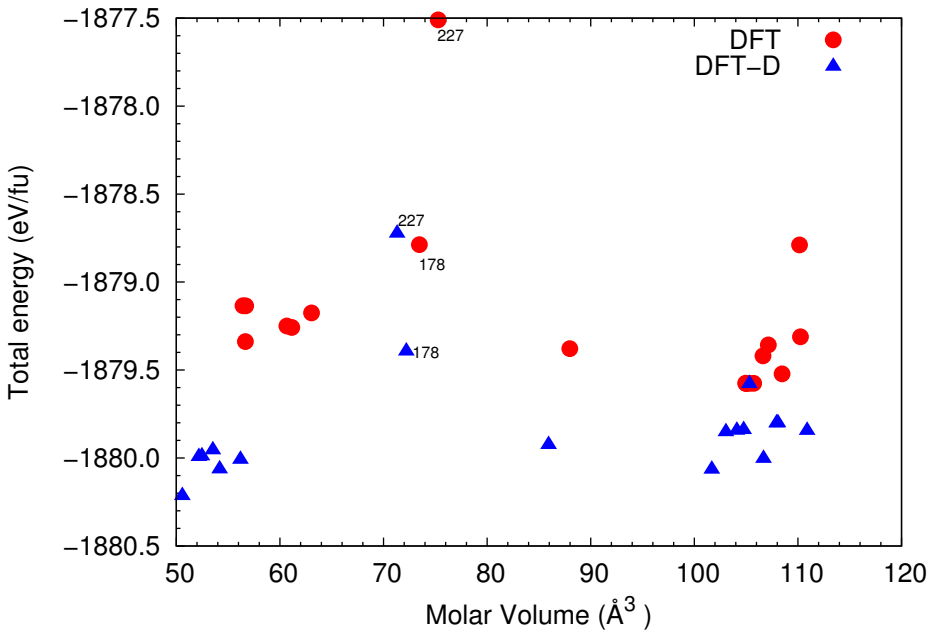

FIG. 1. The $E - V$ curve of optimized structures, calculated at DFT and DFT-D level of theory.