First-Principles Prediction of a Ground State Crystal Structure of Magnesium Borohydride

V. Ozolins,[1] E. H. Majzoub,[2] and C. Wolverton[3]

[1]*Department of Materials Science and Engineering, University of California, Los Angeles, California 90095-1595, USA*
[2]*Department of Physics and Astronomy, University of Missouri, St. Louis, Missouri 63121, USA*
[3]*Department of Materials Science & Engineering, Northwestern University, Evanston, Illinois 60208, USA*

(Received 26 October 2007; published 31 March 2008)

$Mg(BH_4)_2$ contains a large amount of hydrogen by weight and by volume, but its promise as a candidate for hydrogen storage is dependent on the currently unknown thermodynamics of H_2 release. Using first-principles density-functional theory calculations and a newly developed prototype electrostatic ground state search strategy, we predict a new $T = 0$ K ground state of $Mg(BH_4)_2$ with $I\bar{4}m2$ symmetry, which is 5 kJ/mol lower in energy than the recently proposed $P6_1$ structure. The calculated thermodynamics of H_2 release are within the range required for reversible storage.

DOI: 10.1103/PhysRevLett.100.135501 PACS numbers: 61.50.Ah, 61.66.Fn, 63.20.−e, 65.40.−b

Borohydrides with the chemical formula $X(BH_4)_n$, where X is a metal with valence n, have some of the highest gravimetric and volumetric hydrogen densities among all known materials. Unfortunately, monovalent borohydrides, such as $LiBH_4$, are unsuitable for hydrogen storage because the hydrogen is bound too strongly and its extraction requires high temperatures. Attention has shifted to multivalent borohydrides, such as $Mg(BH_4)_2$, which are expected to have lower H binding enthalpies. Recent experimental studies have found that $Mg(BH_4)_2$ releases hydrogen only at very high temperatures and is practically irreversible [1], but it remains unclear whether these limitations are kinetic or whether they are thermodynamic. If the reason is poor kinetics, then a suitable catalyst can often be found, such as Ti for $NaAlH_4$, or Ni for $Li_3BN_2H_8$ [2]. However, if the reason lies in thermodynamics, then the material is impractical for reversible hydrogen storage and any further search for catalysts is futile.

It would be desirable to accurately estimate the thermodynamic properties of new materials before substantial resources are expended on their synthesis and characterization. First-principles calculations of the total crystal binding energies using the density-functional theory (DFT) have proven to be a sufficiently accurate tool for obtaining hydride thermodynamics [3,4], but they need the crystal structure as input, which is often unavailable. After extensive efforts by several groups, the crystal structure of $Mg(BH_4)_2$ has been determined recently using x-ray diffraction on solution-grown samples [5–7]. In spite of a deceivingly simple chemical formula, the measured low-temperature (LT) structure of $Mg(BH_4)_2$ contains 330 atoms in a primitive cell of hexagonal $P6_1$ symmetry. Above 453 K, an irreversible polymorphic transformation to an orthorhombic high-temperature (HT) $Fddd$ phase has been observed [6]. The primitive cell of the HT phase contains 176 atoms. Such an unexpected structural complexity raises an important question: Could these structures have been predicted, or at least closely approximated to obtain practically useful estimates of the thermodynamic properties of $Mg(BH_4)_2$?

In this Letter, we present a comprehensive study aimed at predicting the $T = 0$ K crystal structure of $Mg(BH_4)_2$. We compare the performance of three different methods: (1) search based on the known structures of chemically similar compounds from the Inorganic Crystal Structure Database (ICSD), henceforth referred to as database searching [8], (2) simulated annealing *ab initio* molecular dynamics (SA-AIMD), and (3) a newly developed Monte Carlo method based upon rigid-ion electrostatics, called the prototype electrostatic ground state (PEGS) search [9]. We have also obtained optimized structural parameters and DFT total energies for the LT and HT phases proposed in Refs. [5,6]. The PEGS search outperforms the database searching and SA-AIMD methods and unexpectedly finds a new tetragonal ground state structure of $I\bar{4}m2$ symmetry, which is 5 kJ/mol lower than the LT structure observed in solution-grown crystals. The primitive unit cell of the $I\bar{4}m2$ structure contains only 2 f.u. (22 atoms), compared with 30 f.u. for the LT structure. Interestingly, both these structures have very similar near-neighbor environments, but dramatically different densities, suggesting that solvent molecules may play an important role in promoting the growth of the LT phase. To the best of our knowledge, the $I\bar{4}m2$ structure has not been observed in any other compounds, which demonstrates the usefulness of the PEGS approach for rapidly generating completely new crystal structure types. Using the derived $I\bar{4}m2$ structure, we obtain a $T = 25\ °C$ enthalpy of 29.3 $kJ/mol\ H_2$ for the thermodynamically favored decomposition reaction of $Mg(BH_4)_2$, corresponding to hydrogen release at $T = 20\ °C$ and $p = 1$ bar. Our results indicate that the experimentally observed high H_2 release temperatures and lack of reversibility must be due to sluggish kinetics. Therefore, this compound deserves further studies with the aim of finding effective catalysts.

First-principles DFT calculations were carried out using the Vienna *Ab Initio* Simulation Package (VASP) [10,11]. All total energies and structural parameters were obtained using the projector augmented wave (PAW) method [12] and the so-called "hard" pseudopotentials. The plane wave and augmentation energy cutoffs were 875 and 1000 eV, respectively. Brillouin zones of all structures were sampled on regular meshes with at least 128 **k** points per formula unit. Atomic positions and cell shapes were relaxed until all the forces and components of the stress tensor were below 0.01 eV/A and 0.2 kbar, respectively. Phonons were calculated using the supercell frozen phonon method (details of our implementation are given in Ref. [3]). SA-AIMD simulations were carried out using ultrasoft pseudopotentials with a 500 eV plane wave cutoff and 32 **k** points per formula unit. The generalized gradient approximation of Perdew and Wang was used to approximate the electronic exchange and correlation [13].

Database searching.—Perhaps the most popular method is to choose "reasonable" crystal structure types (the so-called "usual suspects") and find the one with the lowest total (free) energy using the DFT. This approach has been used in numerous studies of high-pressure phases [14] and metallic alloys [15]. The database searching relies heavily on the existence of an extensive collection of "good" trial structures and cannot predict new structures that have never been seen before, i.e., those that are not isostructural with compounds already observed in other systems. This is a serious limitation, since new and sometimes surprisingly complex structure types are being discovered continuously [16].

Database searching was carried out as in Ref. [8]. From the ICSD, we found a set of candidate crystal structures for compounds of stoichiometry AB_2C_8 where C = H/D, F, Cl, Br, I, and O. In total, we used a set of 93 candidate AB_2C_8 structures. DFT calculations were used to relax all structural degrees of freedom consistent with the symmetry group of the prototype structure.

The results for the five ICSD structures with the lowest total energies are shown in Fig. 1, labeled by their prototype compounds. The lowest-energy structure identified from the database searching is the $CdAl_2Cl_8$-type structure, which is monoclinic with 2 f.u. in the primitive cell. After relaxation, it was found to exhibit orthorhombic $Pmc2_1$ symmetry, in agreement with the results of an earlier DFT study by Vajeeston *et al.* [17]. The $Pmc2_1$ structure is 9.6 kJ/mol lower in energy than the $P2/c$ structure proposed by Nakamori *et al.* [18], who used intuitive guessing of structures based on simple binary ionic prototypes.

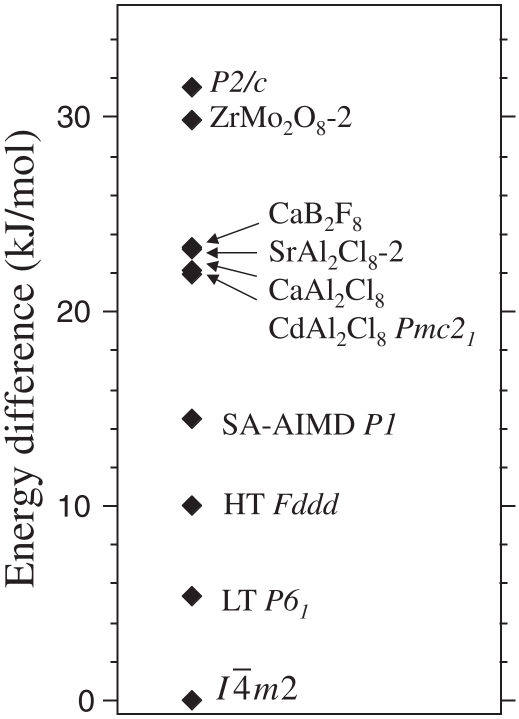

FIG. 1. DFT energies of $Mg(BH_4)_2$ crystal structures.

To ascertain the mechanical stability of the $Pmc2_1$ structure, we performed first-principles frozen phonon calculations of all Γ-point vibrational frequencies. These calculations revealed the existence of a slightly unstable (with an imaginary frequency $75i$ cm^{-1}) optical phonon mode of B_2 symmetry corresponding to coupled rotations of BH_4 tetrahedra. DFT calculations of the total energy as a function of the phonon displacement revealed an unstable double-well energy curve. Static total energy minimization starting from one of the two equivalent minima resulted in a monoclinic structure of $P2_1$ symmetry, which was 1.5 kJ/mol lower in energy than the orthorhombic $Pmc2_1$ structure. We conclude that the simple ICSD searching method fails to predict a dynamically stable structure for $Mg(BH_4)_2$. This result is quite surprising, especially when one considers that a large number (93) of prototype ICSD compounds exist at this composition. Our findings underscore the importance of (1) checking for the dynamical stability of the structures predicted from ICSD searching (which was not done in Ref. [17]), and (2) developing theoretical methods for systematically predicting new, yet unobserved crystal structure types. In what follows, we describe the performance of two such methods.

SA-AIMD.—Variable cell shape *ab initio* molecular dynamics (AIMD) based on the Parinello-Raman formalism has been used with considerable success to find new phases of materials and study the associated transformation paths [19]. In the present work, we used the simulated annealing (SA) AIMD method to optimize the geometry within a 4-formula unit orthorhombic supercell that was obtained from the $Pmc2_1$ structure by doubling its unit cell along the shortest direction [20]. An initial 10 ps long isothermal annealing run at $T = 500$ K was performed using the Nose-Hoover thermostat, followed by gradual cooling at a rate of 10 K/ps down to $T = 200$ K. The final structure (including atomic positions and cell shape) was optimized using the conjugate gradient algorithm. This approach resulted in a structure ("SA-AIMD $P1$") that was 7.4 kJ/mol lower in energy than the starting $Pmc2_1$ structure (see Fig. 1). The resulting structure had no symmetry at all ($P1$ space group), which strongly suggests that this is a low-energy structure, but not a reasonable ground state. Reheating and/or different annealing schedules could potentially lead to better structures; however, they were not pursued due to the highly demanding nature of these computations.

PEGS search.—Recently, we have proposed a method that can predict entirely new, unsuspected ground state structure types for complex ionic crystals [9]. Physically, this approach is based on the observation that complex hydrides are characterized by an arrangement of positively charged cations (e.g., Mg^{2+}) and negatively charged complex anions (e.g., BH_4^-), with strong covalent bonds within each anionic complex and predominantly electrostatic interactions between the cations and anions [9,21]. These considerations suggest that the type and symmetry of the ground state crystal structure can be determined by minimizing the total electrostatic energy for a given set of ionic charges, ionic radii, and fixed shapes of complex anions. The resulting ground states, henceforth called prototype electrostatic ground states (PEGS), are then used as input to first-principles DFT calculations to relax all structural parameters and calculate accurate total energies. The PEGS Hamiltonian includes electrostatic and soft-core interionic repulsion terms:

$$E = \sum_{i<j}\left(\frac{Z_i Z_j}{r_{ij}} + \frac{1}{r_{ij}^{12}}\right), \tag{1}$$

where the sums run over all Mg, B, and H ions, r_{ij} is the separation between ions i and j, Z_i is the ionic charge, and the second term (soft-core repulsion) is zero for nonoverlapping ions. We assume that the BH_4 complex is a perfect tetrahedron with a B–H bond length of 1.23 Å and a total ionic charge of -1 [11]. Charge balance requires that $Z_{Mg} = +2$. The distribution of the charge between H and B is determined by maximizing the correlation between the final DFT energies and the final electrostatic energies calculated for the DFT-relaxed ionic positions, assuming that in equilibrium the soft-core repulsion energy is much smaller than the electrostatic energy. The $I\bar{4}m2$ structure was found using $Z_H = -0.3$ and the ionic radii $R_{Mg} = 0.7$ and $R_H = 1.3$, close to the canonical Pauling radii. We note here that the success of our approach does not depend on the precise values of the parameters, since PEGS are determined for a range of ionic radii and charges, spanning the parametric regions corresponding to a wide range of materials. Monte Carlo simulated annealing in conjunction with distance scaling potential energy surface smoothing techniques [22] are used to minimize Eq. (1). The resulting low-energy PEGS structures are structurally relaxed using VASP and the total DFT energies are used to select the global ground state. The full technical details of the PEGS search as well as systematic tests of its performance for alkali and alkaline earth alanate compounds are given elsewhere [9].

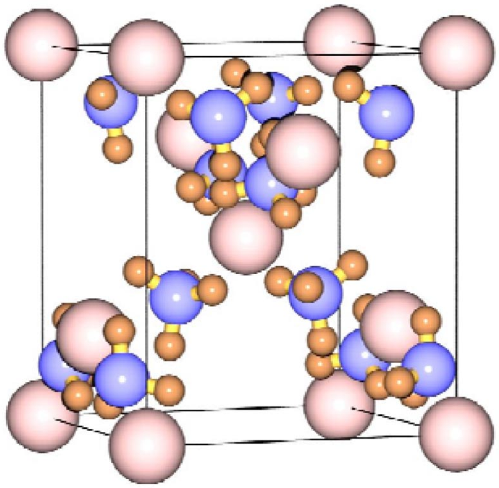

FIG. 2 (color online). Tetragonal $I\bar{4}m2$ structure of $Mg(BH_4)_2$.

For $Mg(BH_4)_2$, the PEGS approach yields a tetragonal structure of $I\bar{4}m2$ symmetry, space group 119, shown in Fig. 2. The DFT static energy of the $I\bar{4}m2$ structure is lower than all other proposed structures for $Mg(BH_4)_2$, both the previously proposed theoretical structures, as well as the experimentally determined ones. In particular, the $I\bar{4}m2$ structure is 5.4 kJ/mol lower in energy than the low-temperature $P6_1$ structure found in Refs. [5,6].

Fully relaxed DFT ionic coordinates and lattice parameters are given in Table I. The $I\bar{4}m2$ structure is characterized by a fourfold coordination of B ions around the Mg cations, at distances 2.415 and 2.411 Å for Mg1 and Mg2 ions, respectively. Furthermore, each Mg^{2+} has 8 nearest-neighbor H ions, at distances 2.023, 2.069, and 2.065 Å. B–H distances are 1.222, 1.229, and 1.223 Å for H1, H2, and H3 ions, respectively (the average B–H distance is 1.224). These bond lengths are all very similar to the those in the $P6_1$ structure, where Mg–B distances are between 2.365 and 2.417 Å, with an average value of 2.399 Å; Mg–H distances are between 1.992 and 2.129 Å, with an average value of 2.049 Å; B–H covalent bond lengths vary from 1.219 to 1.227 Å, with an average of 1.224 Å. In spite of the close structural similarities between these two struc-

TABLE I. Calculated structural parameters for the lowest-energy $I\bar{4}m2$ (space group 119) body-centered tetragonal structure of $Mg(BH_4)_2$. Lattice parameters are $a = 8.18$ and $c = 9.965$ Å.

Ion type	Wyckoff position	x	y	z
Mg1	1c	0	$\frac{1}{2}$	$\frac{1}{4}$
Mg2	1a	0	0	0
B	4i	0.7306	$\frac{1}{2}$	0.3492
H1	4i	0.2485	0	0.7275
H2	4i	0.1429	$\frac{1}{2}$	0.4157
H3	8j	0.1582	0.1266	0.8764

TABLE II. Thermodynamic data for decomposition pathways of $Mg(BH_4)_2$. T_c gives the equilibrium temperature at an H_2 pressure of 1 atm, and ΔS^0 is the standard-state reaction entropy.

Reaction products	ΔH (kJ/mol H_2)		ΔS^0 (J/mol K)	T_c (°C)
	Static	25 °C		
$\frac{1}{6}MgB_{12}H_{12} + \frac{5}{6}MgH_2 + \frac{13}{6}H_2$	48.5	29.5	100.7	20
$MgB_2 + 4H_2$	54.9	38.8	111.6	75
$\frac{1}{2}MgB_4 + \frac{1}{2}MgH_2 + \frac{7}{2}H_2$	55.9	38.7	109.7	80
$\frac{2}{7}MgB_7 + \frac{5}{7}MgH_2 + \frac{23}{7}H_2$	57.4	39.3	108.3	90
$MgH_2 + B + 3H_2$	66.9	47.3	106.9	170

tures, we find that the density of the $I\bar{4}m2$ structure is much lower than that of the LT $P6_1$ phase (0.547 versus 0.783 g/cm^3). Such a large difference between two phases with almost identical near-neighbor environments is surprising, but not unprecedented. For instance, density differences of more than 30% have been observed for other tetrahedrally coordinated crystalline compounds, such as between the BC8 [23] and clathrate [24] phases of Si. We hypothesize that interactions with solvent molecules may be responsible for the nucleation and growth of the $P6_1$ structure in solution-grown crystals, and that a structural transformation to the lower-energy $I\bar{4}m2$ structure is inhibited at ambient temperatures by the need to break interionic bonds and accommodate large volume change. We note also that the transformation from the LT to HT phase is observed to be endothermic [7], and our DFT calculations are consistent with this observation: the latter has higher energy (see Fig. 1). However, many aspects of these transformations are still unsolved [5,7], and more research is needed to fully understand the polymorphism of $Mg(BH_4)_2$. The possibility of a high-temperature stabilization of the LT phase due to the vibrational entropy cannot be excluded, but the symmetry and size of the unit cell make accurate phonon calculations a formidable challenge.

Table II gives the calculated enthalpies and entropies of dehydrogenation for $Mg(BH_4)_2$ in the $I\bar{4}m2$ structure via several competing reaction pathways. We see that the favored decomposition pathway involves $MgB_{12}H_{12}$, releasing 8.1 wt. % H_2 at room temperature [25]. In view of the relatively small energy difference between the $I\bar{4}m2$ and the LT phases (5 kJ/mol or ~1 kJ/mol H_2), the thermodynamics of hydrogen release from the LT phase is not expected to be much different from that shown in Table II. Experimentally, the decomposition of $Mg(BH_4)_2$ occurs only at temperatures above 300 °C via a complicated sequence of polymorphic and chemical transformations [6]. The data in Table II strongly suggest that this sequence is determined by kinetic factors and that $Mg(BH_4)_2$ is well suited for reversible hydrogen storage if an effective way of accelerating the kinetics can be found.

This research was supported by the U.S. Department of Energy under Grants No. DE-FG02-05ER46253, No. DE-FG02-07ER46433, and No. DE-AC04-94AL85000.

[1] H. W. Li *et al.*, Scr. Mater. **57**, 679 (2007).
[2] F. E. Pinkerton *et al.*, J. Alloys Compd. **433**, 282 (2007).
[3] C. Wolverton, V. Ozolins, and M. Asta, Phys. Rev. B **69**, 144109 (2004).
[4] L. G. Hector, Jr., *et al.*, Phys. Rev. B **76**, 014121 (2007).
[5] R. Cerny *et al.*, Angew. Chem., Int. Ed. **46**, 5765 (2007).
[6] J. H. Her *et al.*, Acta Crystallogr. Sect. B **63**, 561 (2007).
[7] K. Chlopek *et al.*, J. Mater. Chem. **17**, 3496 (2007).
[8] C. Wolverton and V. Ozolins, Phys. Rev. B **75**, 064101 (2007).
[9] E. H. Majzoub and V. Ozolins, Phys. Rev. B **77**, 104115 (2008).
[10] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[11] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[12] P. E. Blochl, Phys. Rev. B **50**, 17 953 (1994).
[13] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[14] A. Mujica *et al.*, Rev. Mod. Phys. **75**, 863 (2003).
[15] Y. Zhong *et al.*, Acta Mater. **52**, 2739 (2004).
[16] For instance, the Cambridge Crystal Structure database is growing exponentially, with the doubling time of less than one decade.
[17] P. Vajeeston *et al.*, Appl. Phys. Lett. **89**, 071906 (2006).
[18] Y. Nakamori *et al.*, Phys. Rev. B **74**, 045126 (2006).
[19] R. Martonak, A. Laio, and M. Parrinello, Phys. Rev. Lett. **90**, 075503 (2003).
[20] G. Kresse and J. Hafner, J. Phys. Condens. Matter **6**, 8245 (1994).
[21] V. Ozolins, E. H. Majzoub, and T. J. Udovic, J. Alloys Compd. **375**, 1 (2004).
[22] R. J. Wawak *et al.*, J. Phys. Chem. A **102**, 2904 (1998).
[23] J. Crain *et al.*, Phys. Rev. B **50**, 8389 (1994).
[24] J. Dong, O. F. Sankey, and G. Kern, Phys. Rev. B **60**, 950 (1999).
[25] The structure of $MgB_{12}H_{12}$ was also predicted using the PEGS search and will be detailed in a future publication.