PHYSICAL REVIEW B **79**, 212102 (2009)

Crystal structure and stability of magnesium borohydride from first principles

Xiang-Feng Zhou,[1] Quang-Rui Qian,[1] Jian Zhou,[1] Bo Xu,[2] Yongjun Tian,[2] and Hui-Tian Wang[1,3,*]
[1]*Department of Physics and Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China*
[2]*State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China*
[3]*School of Physics, Nankai University, Tianjin 300071, China*

(Received 9 February 2009; revised manuscript received 6 April 2009; published 24 June 2009)

We present a structure model for constructing $Mg(BH_4)_2$. The first-principles calculations reveal that some stable ground-state crystal structures of $Mg(BH_4)_2$ have the same or slightly lower energy than the *I*-4*m*2 structure predicted in a paper by Ozolins *et al.* [Phys. Rev. Lett. **100**, 135501 (2008)]. The possible mechanism for the anomalous stability originates from the fact that the charge transfer between different atoms is more homogeneous. The structure model can be anticipated to have potential application for predicting new stable structures of this group of homologous materials.

DOI: 10.1103/PhysRevB.79.212102 PACS number(s): 61.50.Ah, 61.66.Fn, 63.20.−e, 65.40.−b

I. INTRODUCTION

Intense theoretical and experimental effort has focused on the possibility of new hydrogen-storage materials with high storage capacity and efficiently reversible storage.[1–9] One of the approaches on hydrogen storage is in borohydrides such as $LiBH_4$. It is well known that the relatively high decomposable temperature and irreversible hydrogenation hamper practical application of these synthesized samples.[10,11] Magnesium borohydride [$Mg(BH_4)_2$] is a very promising candidate for hydrogen storage because of not only its high gravimetric storage density (14.9 wt %) but also the lower hydrogen binding enthalpy.[12–19] However, the accurate structural study on borohydrides has been limited owing to the complicated structural arrangement and the difficulty for establishing hydrogen positions by the x-ray diffraction (XRD) method.[17] For example, the $Mg(BH_4)_2$ system has the relatively complicated structures, and its low- and high-temperature phases contain 330 and 704 atoms in the unit cell and exhibit the hexagonal and orthorhombic symmetries, respectively.[16]

Based on an extensively accepted structural model [$A(BC_4)_2$ prototype] for seeking and predicting new phases for complex hydrides [including $Mg(BH_4)_2$], the *Pmc*21 structure of $Mg(BH_4)_2$ was proved to be the most stable phase among the polymorphs of $Mg(BH_4)_2$ by starting from the $Cd(AlCl_4)_2$-type structure.[16,17] By using the prototype electrostatic ground-state approach (PEGS), Ozolins *et al.* have validated the existence of a new stable body-centered tetragonal $Mg(BH_4)_2$ phase (with the *I*-4*m*2 symmetry), which is much lower in energy than the *Pmc*21 structure and more suitable for reversible hydrogen storage.[20] Very recently, Voss *et al.* predicted a new *F*222 $Mg(BH_4)_2$ structure, which has a lower energy than all the previous proposed phases of $Mg(BH_4)_2$.[21] We also found the low-energy structure of *F*222 $Mg(BH_4)_2$ by the structural model we proposed here at the same time,[22] which has been proved to have the same energy and symmetry as the structure reported in Ref. 21. Due to the structural polymorphism, the $Mg(BH_4)_2$ system deserves to further explore the underlying physics. Two important subjects are remained at least: (i) What physical origin results in the anomalous stability of the *I*-4*m*2 or *F*222 structures? (ii) Would there be other suitable structures for reversible hydrogen storage? In this work, our motivation aims at resolving two such questions with the aid of first-principles calculations, in particular, we present other metastable phases of $Mg(BH_4)_2$.

II. METHOD

The total energy has been calculated by using the *ab initio* pseudopotential density-functional method in CASTEP code[23] within the generalized gradient approximation. The ultrasoft pseudopotentials were expanded by a plane-wave basis set with the cutoff energy of 600 eV. For performing the integration in the Brillouin zone, the Monkhorst-Pack *k*-point sampling were $4\times4\times3$ for both the *I*-4*m*2 and *I*4122 structures, $3\times3\times3$ for the *F*222 structure, and $8\times4\times4$ for the *Pmc*21 structure, respectively. During the geometric optimization, no symmetry and no restriction were constrained for both the unit cell shape and the atomic positions with respect to the Brodyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme. The structural relaxation was stopped until the total energy, the maximum ionic displacement, the maximum stress, and the maximum ionic Hellmann-Feynman force were within 5×10^{-6} eV/atom, 0.01 eV/Å, 5×10^{-4} Å, and 0.02 GPa, respectively. Our calculations are for the zero-temperature ground state, due to our proposed structure has almost the same total energy as the *I*-4*m*2 $Mg(BH_4)_2$,[20] we hope the neglect of the zero-point vibrational energy would not affect present results.

III. RESULTS AND DISCUSSION

To construct the new structures of $Mg(BH_4)_2$, we propose an alternative approach starting from the prototype structures of $Zr(BH_4)_4$ with the *P*-43*m* symmetry and $Hf(BH_4)_4$ with the P23 symmetry.[24] Evidently, the $A(BH_4)_4$ model cannot be used to directly construct the structural model of $A(BH_4)_2$ due to difference in stoichiometry, where A denotes a metallic element. To resolve this problem, we add a metallic atom (surrounded by square in Fig. 1) into the body center of the unit cell of $A(BH_4)_4$ and then produce a modified structural

©2009 The American Physical Society

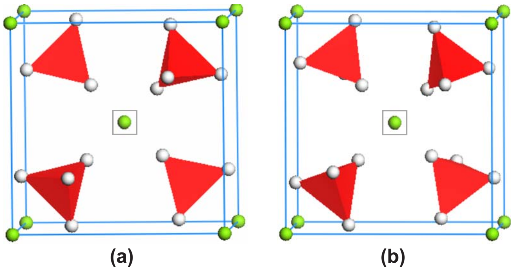

FIG. 1. (Color online) Modified prototype structures of (a) *a*-Mg$(BH_4)_2$ and (b) *b*-Mg$(BH_4)_2$. We added a metal atom (surrounded by square) to the body center of the unit cell and keep the original symmetry [*P*-43*m* for *a*-Mg$(BH_4)_2$ and *P*23 for *b*-Mg$(BH_4)_2$].

model, which nicely satisfies the requirement of stoichiometry for A$(BH_4)_2$.

Based on the modified model from the prototype of Zr$(BH_4)_4$, which is named as *a*-Mg$(BH_4)_2$ as shown in Fig. 1(a), we build up a 1×1×2 supercell along the [110] direction of *a*-Mg$(BH_4)_2$, the intention is to construct *I*-4*m*2 Mg$(BH_4)_2$. To carefully examine the similarity and difference between the *I*-4*m*2 Mg$(BH_4)_2$ and *a*-Mg$(BH_4)_2$, we give the projections of both in the (001) plane, as shown in Figs. 2(a) and 2(b). One can see that *I*-4*m*2 Mg$(BH_4)_2$ and *a*-Mg$(BH_4)_2$ are the same in the topological figure viewed along [001] direction. However, as shown in Fig. 2(c), in the projection along the [010] or [100] direction, the manner of arrangement of BH_4 units in *a*-Mg$(BH_4)_2$ forms a two-dimensional flat triangular motif. In contrast, for *I*-4*m*2 Mg$(BH_4)_2$, the projection along the [010] or [100] direction is composed of buckled hexagonal and triangular motifs, as shown in Fig. 2(d). If we remove the parts surrounded by circles [the BH_4 tetrahedrons and the closest metallic atoms, see Fig. 2(c)] from the flat triangular sheetlike BH_4 units to produce hexagonal holes. By forming a mixture of triangles and hexagons, the hexagonal holes will be buckled ones after the structural relaxation. Ultimately, the modified *a*-Mg$(BH_4)_2$ transfers to *I*-4*m*2 Mg$(BH_4)_2$.

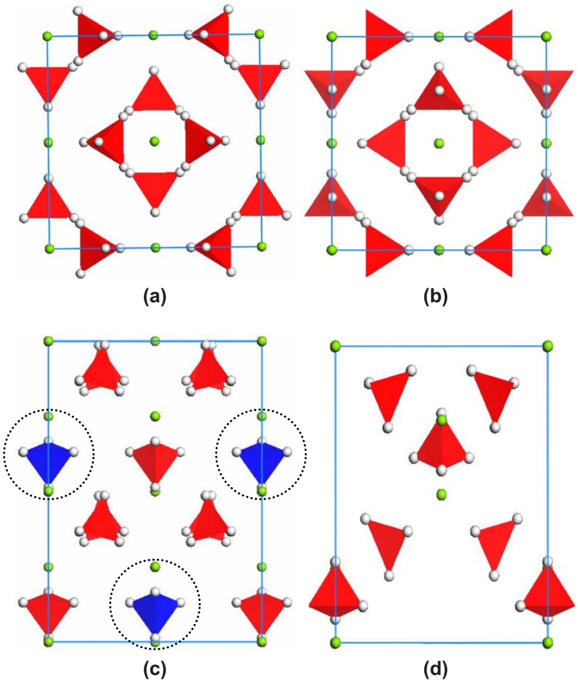

FIG. 2. (Color online) Projections of supercell in the (001) and (010) planes for *a*-Mg$(BH_4)_2$ and *I*-4*m*2 Mg$(BH_4)_2$. (a) The (001) projection of *a*-Mg$(BH_4)_2$, (b) the (001) projection of *I*-4*m*2 Mg$(BH_4)_2$, (c) the (010) projection of *a*-Mg$(BH_4)_2$, and (d) the (010) projection of *I*-4*m*2 Mg$(BH_4)_2$.

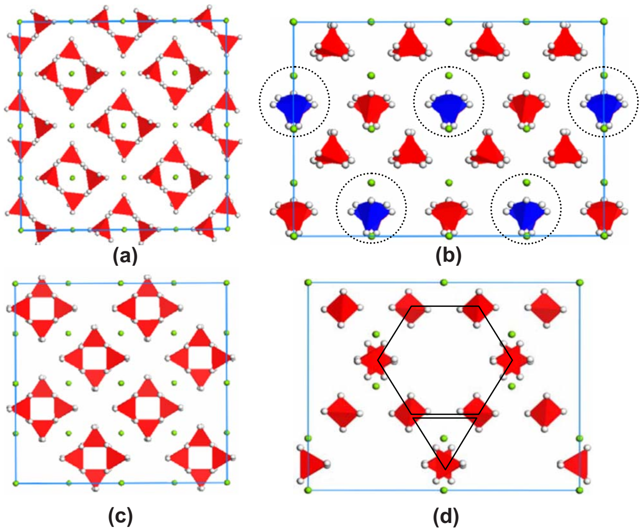

FIG. 3. (Color online) Projections along [001] and [010] directions of 2×2×2 supercell of *b*-Mg$(BH_4)_2$ and 2×2×1 supercell of *I*4122 Mg$(BH_4)_2$. (a) and (b) the (001) and (010) projections of *b*-Mg$(BH_4)_2$ as well as (c) and (d) the (001) and (010) projections of *I*4122 Mg$(BH_4)_2$, respectively. The parts (including Mg atoms and BH_4 tetrahedrons) surrounded by the dotted circles would be removed in order to search more stable structure such as *I*4122.

Due to the structural comparability between Zr$(BH_4)_4$ with the *P*-43*m* symmetry and Hf$(BH_4)_4$ with the *P*23 symmetry,[24] both are very similar in lattice constants and atomic positions (as shown in Fig. 1). We could also follow the same procedure as mentioned above to construct the modified structural model of Mg$(BH_4)_2$ from the prototype of Hf$(BH_4)_4$, which is named as *b*-Mg$(BH_4)_2$ as shown in Fig. 1(b). Starting from this modified model, we construct a 1×1×2 supercell along the [110] direction of the *b*-Mg$(BH_4)_2$. Figures 3(a) and 3(b) show the projections along the [001] and [010] directions of 2×2×2 supercell in *b*-Mg$(BH_4)_2$, respectively. From the projection of the [001] direction shown in Fig. 3(a), one can see that the four close-packed BH_4 tetrahedrons form a rhombic motif and the manner of arrangement of BH_4 units of the supercell forms the two-dimensional flat triangular motif along [100] or [010] direction. We remove the parts [including Mg atoms and the BH_4 tetrahedrons, in Fig. 3(b)] surrounded by the dotted circles, and then to produce hexagonal holes. By carefully examining the symmetry, we find that the new initial structure to exhibit the *F*23 symmetry (with the lattice parameters of $a=b=c=12.2$ Å, 88 atoms per unit cell) and contains a big novel tetrahedron composed of 16 BH_4 tetrahedrons. However, this new structure is in fact unstable. After the strict geometric relaxation, when performing the symmetry

TABLE I. Structural parameters, Mulliken charges (only the maximum and minimum values are listed for nonidentical atoms), and the total energy of the polymorphs of $Mg(BH_4)_2$. The energy difference (ΔE) makes reference to that of *Pmc*21 $Mg(BH_4)_2$.

Symmetry	*I*4122	*F*222	*I*-4*m*2	*Pmc*21
a (Å)	7.448	12.122	8.165	4.302
b (Å)	7.448	10.362	8.165	7.936
c (Å)	12.15	10.741	10.126	8.110
Mg (*e*)	+2.00	+2.00	+2.00	+2.00
B (*e*)	−0.89	−0.89	−0.89	−0.86
H (*e*)	−0.04	−0.04	−0.05	−0.12
	−0.01	−0.01	−0.01	+0.09
E_t (eV/formula)	−1262.748	−1262.748	−1262.746	−1262.547
ΔE (kJ/mol)	−19.4	−19.4	−19.2	0

search with the *find symmetry* technique that is supplied by MaterialsStudio package,[23] the ultimate relaxed structure is validated to be *I*4122 $Mg(BH_4)_2$ (find symmetry with tolerance 0.5 Å) or may also be identified as the *F*222 $Mg(BH_4)_2$ (find symmetry with tolerance 0.2 Å). Figures 3(c) and 3(d) show the projections along the [001] and [010] directions of $2\times2\times1$ supercell in *I*4122 $Mg(BH_4)_2$. It seems to form the mixture of triangles and hexagons in the projection of supercell in the (010) plane for *I*4122 $Mg(BH_4)_2$, as shown in Fig. 3(d).

We first confirm that *I*-4*m*2 $Mg(BH_4)_2$ has 0.2 eV/formula (19.2 kJ/mol) in energy lower than the orthorhombic *Pmc*21 structure,[17] which is in good agreement with the previous calculation (about 19 kJ/mol).[20] The GGA and LDA calculations have both validated that our proposed polymorphs of *I*4122 $Mg(BH_4)_2$ and *F*222 $Mg(BH_4)_2$ are almost the same or little lower in energy (0.2 KJ/mol) than that of *I*-4*m*2 $Mg(BH_4)_2$. For *I*4122 $Mg(BH_4)_2$, the lattice parameters are $a=b=7.448$ Å and $c=12.15$ Å [space group 98, see Figs. 3(c) and 3(d)], the Mg and B atoms occupy the 4a (0, 0, 0) and the 8f (0.4613, 0.25, 0.625) sites, and two nonidentical H atoms occupy the 16g (0.3629, 0.1203, 0.6195) and 16g (0.5588, 0.2421, 0.5447) sites, respectively. For *F*222 $Mg(BH_4)_2$, the lattice parameters are $a=12.122$ Å, $b=10.362$ Å, and $c=10.741$ Å [space group 22, the Mg atoms occupy the 4a (0, 0, 0) and 4c (0.25, 0.25, 0.25) sites, B atoms occupy the 16k (0.1238, 0.1461, 0.107) and four nonidentical H atoms occupy the 16k (0.1207, 0.2621, 0.1226), 16k (0.0405, 0.1037, 0.1552), 16k (0.2014, 0.0897, 0.1539), and 16k (0.1320, 0.3701, 0.5044) sites, respectively]. Compared with *I*-4*m*2 and *Pmc*21 structures, the detailed information of *I*4122 and *F*222 structures are listed in Table I. The *I*4122, *F*222, and *I*-4*m*2 phases have the similar structural characters compared with the experimentally synthesized $Mg(BH_4)_2$. For instance, each Mg atom is surrounded by four BH_4 tetrahedrons and is coordinated by tetrahedral edges only, resulting in an unusual eightfold and relatively irregular hydrogen coordination environment.[12] It is one of the reasons that these structures have the lowest energy among all the predicted structures. In contrast, each Mg atom is surrounded by six hydrogen atoms in a slightly distorted octahedral arrangement for the *Pmc*21 structure.[17] The lower coordination number of Mg-H bond gives rise to the higher total energy for the *Pmc*21 structure.

Since the charge transfer from metal cations to BH_4 anions is expected to be a key feature for the stability of borohydrides as mentioned in Ref. 24, we further explore the structural chemical environment of ions. Nakamori *et al.* found a linear relation between the stability of borohydrides and the electronegativity of different metal cations.[24] However, it is difficult to apply to the polymorphs of $A(BH_4)_2$ because $A(BH_4)_2$ isomorphs have approximately the same Pauling electronegativity. We calculate the Mulliken charges of many possible configurations, but list only four polymorphs of $Mg(BH_4)_2$ in Table I. Due to the charge transfer from Mg atoms to the neighboring B and H atoms in *I*-4*m*2 $Mg(BH_4)_2$, the Mulliken charges are determined to be +2.00*e* for all the Mg atoms, −0.89*e* for all the B atoms, and −0.05*e* and −0.01*e* for two kinds of nonidentical H atoms, respectively. It should be noted that the pseudopotential used for Mg was constructed by the electron configurations as $3s^22p^6$ states, there are eight formal ionic charges which are composed of both Mulliken charges and effective ionic charges.[25] For the *I*4122 and *F*222 phases, the calculated Mulliken charges are +2.00*e* for all the Mg atoms, −0.89*e* for all the B atoms, −0.04*e* and −0.01*e* for two kinds of nonidentical H atoms, respectively. It is obvious that there is a little difference among the *I*-4*m*2, *F*222, and *I*4122 phases in Mulliken charge, in detail, the differences in Mulliken charge among the nonidentical atoms are +0.04*e* for the H atoms in the *I*-4*m*2 phase, while only +0.03*e* for the H atoms in *I*4122 and *F*222 phase, respectively. In contrast, the differences in Mulliken charge among the nonidentical H atoms are +0.21*e* in *Pmc*21 $Mg(BH_4)_2$, respectively. Therefore, the *I*4122, *F*222, and *I*-4*m*2 phases should be the more stable structures than *Pmc*21 $Mg(BH_4)_2$, due to the homogeneous distribution of the charge transfer. Despite that the theoretically predicted structures have the similar ionic environment, the tiny differences of hydrogen coordination environment and network topology result undoubtedly in the great reduction in energy.

IV. CONCLUSION

In conclusion, we present an approach to construct the structure model of $Mg(BH_4)_2$, starting from the prototype of $A(BH_4)_4$ instead of the comprehensively used model $A(BC_4)_2$. We not only explain the stability of the *I*-4*m*2 $Mg(BH_4)_2$,[19] but also predict the new stable *I*4122 and *F*222 phases of $Mg(BH_4)_2$. The results would have importance for searching new homologous materials that may be suitable for reversible hydrogen storage, such as $Zn(BH_4)_2$ and $Ca(BH_4)_2$.[26,27] We also validated that the Mulliken charge transfer could be perhaps used to clarify the energy difference of metal borohydrides to some extent.

ACKNOWLEDGMENTS

This work is partially supported by the National Natural Science Foundation of China under Grant No. 50532020, by the 973 Program of China under Grant No. 2006CB921805 and No. 2005CB724400.

*htwang@nju.edu.cn; htwang@nankai.edu.cn

[1] L. Schlapbach and A. Züttel, Nature (London) **414**, 353 (2001).

[2] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O. Keeffe, and O. M. Yaghi, Science **300**, 1127 (2003).

[3] A. Janotti, S. B. Zhang, and S. H. Wei, Phys. Rev. Lett. **88**, 125506 (2002).

[4] Y. Zhao, Y. H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. **94**, 155504 (2005).

[5] T. Yildirim and M. R. Hartman, Phys. Rev. Lett. **95**, 215504 (2005).

[6] H. Lee, W. I. Choi, and J. Ihm, Phys. Rev. Lett. **97**, 056104 (2006).

[7] E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim, Phys. Rev. Lett. **97**, 226102 (2006).

[8] M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, and Z. Zhang, Phys. Rev. Lett. **100**, 206806 (2008).

[9] V. Ozolins, E. H. Majzoub, and C. Wolverton, J. Am. Chem. Soc. **131**, 230 (2009).

[10] Z. Łodziana and T. Vegge, Phys. Rev. Lett. **93**, 145501 (2004); **97**, 119602 (2006).

[11] N. A. Zarkevich and D. D. Johnson, Phys. Rev. Lett. **100**, 040602 (2008).

[12] R. Černý, Y. Filinchuk, H. Hagemann, and K. Yvon, Angew. Chem. Int. Ed. **46**, 5765 (2007).

[13] J. H. Her, P. W. Stephens, Y. Gao, G. L. Soloveichik, J. Rijssenbeek, M. Andus, and J. C. Zhao, Acta Crystallogr., Sect. B: Struct. Sci. **63**, 561 (2007).

[14] K. Chłopek, C. Frommen, A. Léon, O. Zabara, and M. Fichtner, J. Mater. Chem. **17**, 3496 (2007).

[15] T. Matsunaga, F. Buchter, P. Mauron, M. Bielman, Y. Nakamori, S. Orimo, N. Ohba, K. Miwa, S. Towata, and A. Züttel, J. Alloys Compd. **459**, 583 (2008).

[16] B. Dai, D. S. Sholl, and J. K. Johnson, J. Phys. Chem. C **112**, 4391 (2008).

[17] P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg, Appl. Phys. Lett. **89**, 071906 (2006).

[18] C. Wolverton and V. Ozolinš, Phys. Rev. B **75**, 064101 (2007).

[19] E. H. Majzoub and V. Ozolinš, Phys. Rev. B **77**, 104115 (2008).

[20] V. Ozolins, E. H. Majzoub, and C. Wolverton, Phys. Rev. Lett. **100**, 135501 (2008).

[21] J. Voss, J. S. Hummelshøj, Z. Lodziana, and T. Vegge, J. Phys.: Condens. Matter **21**, 012203 (2009).

[22] When our paper was under review, we learned that the same low-energy structure of $F222$ $Mg(BH_4)_2$ was independently found by J. Voss, J. S. Hummelshøj, Z. Łodziana, and T. Vegge.

[23] M. Segall, P. Lindan, M. Probert, C. Pickard, P. Hasnip, S. Clark, and M. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002); http://accelrys.com

[24] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. I. Towata, A. Züttel, and S. I. Orimo, Phys. Rev. B **74**, 045126 (2006).

[25] M. D. Segall, R. Shah, C. J. Pickard, and M. C. Payne, Phys. Rev. B **54**, 16317 (1996).

[26] P. Choudhury, V. R. Bhethanabotla, and E. Stefanakos, Phys. Rev. B **77**, 134302 (2008).

[27] E. H. Majzoub and E. Rönnebro, J. Phys. Chem. C **113**, 3352 (2009).