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First-principles prediction of phase stability and crystal structures in Li-Zn and Na-Zn mixed-metal borohydrides

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We use a combination of first-principles density functional theory (DFT) calculations and the recently developed prototype electrostatic ground state (PEGS) method to predict low-energy crystal structures and study phase stability of Li-Zn and Na-Zn mixed-metal borohydride compounds [i.e., $NaZn(BH_4)_3$, $NaZn_2(BH_4)_5$, $LiZn(BH_4)_3$, and $LiZn_2(BH_4)_5$]. We find the following: (i) DFT + PEGS successfully predicts low-energy structures in these mixed-metal borohydride systems. (ii) DFT calculations show negative mixing energies in both the Li-Zn and Na-Zn borohydride systems, consistent with the observation of mixed-metal ordering in these systems. (iii) Our DFT calculations of the recently reported experimental crystal structures of $NaZn_2(BH_4)_5$ and $NaZn(BH_4)_3$ show that the former has a negative mixing energy, while the latter has a positive mixing energy. (iv) Using the PEGS approach, we predict a new crystal structure of $NaZn(BH_4)_3$ with negative mixing energy and find that the experimental structure of $NaZn_2(BH_4)_5$ and the PEGS obtained structure of $NaZn(BH_4)_3$ lie on the ground state convex hull. (v) In the Li-Zn borohydride system, we have used the PEGS + DFT approach to predict a stable crystal structure of new, previously unobserved stoichiometry, $LiZn(BH_4)_3$. As a consequence of this predicted low-energy compound, DFT calculations of the experimentally reported structure of $LiZn_2(BH_4)_5$ show that it is unstable with respect to decomposition into $LiZn(BH_4)_3 + Zn(BH_4)_2$. (vi) In addition, we also elucidate the ground state crystal structure of $NaBH_4$, and confirm that reorientation of $(BH_4)^-$ units is the driving force behind the order-disorder phase transition in $NaBH_4$. (vii) Finally, we predict a new low-energy crystal structure of $Zn(BH_4)_2$, and illustrate its similarities with the crystal structure of $Mg(BH_4)_2$.

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I. INTRODUCTION

Light metal single-cation borohydride-based materials have received significant attention due to their high hydrogen-storage capacities. For example, $LiBH_4$, which is the prototypical material in this class, has a theoretical gravimetric storage capacity of ∼18 wt%. However, its hydrogen binding energy is also very high, which results in high endothermic hydrogen release enthalpy (−67 kJ/mol) (Ref. 1) thus limiting its practical applications. Other metal borohydrides have also found limited applicability due to various drawbacks. For instance, alkaline-earth borohydride compounds often have slow kinetics of hydrogen release and are often difficult to rehydride, whereas the transition metal borohydrides are often either unstable or decompose by releasing impurity gases, such as diborane. Unfortunately, efforts to overcome these problems have not been completely successful. Therefore, alternative borohydride-based systems, such as double-cation borohydrides formed by mixing two metal borohydrides are currently under investigation, as they may open new opportunities.

Recently, both theoretical[2–5] and experimental[6–8] studies have been performed to understand mixing of two metal borohydrides. Li *et al.*[9] mixed $LiBH_4$ with Zn-, Zr-, or Al-based borohydrides, and showed that the decomposition temperature of $LiBH_4$ could be decreased on mixing with other metal borohydrides. Recently, a theoretical study[3] using density functional theory (DFT) was performed on a large number of combinations of double-cation mixed-metal borohydride systems using template crystal structures to screen out stable mixed-metal borohydrides. One particular result of this study was that Li-Zn- and Na-Zn-based mixed-metal borohydride compounds were found to be thermodynamically stable with respect to the individual metal borohydrides. This theoretical prediction led to a more recent experimental study[6] elucidating the crystal structure and hydrogen release characteristics of 1 : 1 and 1 : 2 mixtures of $NaBH_4$ and $Zn(BH_4)_2$, i.e., $NaZn(BH_4)_3$ and $NaZn_2(BH_4)_5$ respectively, and 1 : 2 mixture of $LiBH_4$ and $Zn(BH_4)_2$ [i.e., $LiZn_2(BH_4)_5$]. These are new materials whose properties are not yet fully understood; therefore, in this work, we perform crystal structure and phase stability analysis of these three experimentally investigated materials using DFT.

The thermodynamic properties of a wide range of hydrogen-storage materials can be accurately predicted from DFT calculations.[10–17] These DFT calculations require *a priori* knowledge of the hydride crystal structures, and hence are most directly applicable for those materials that have already been structurally well characterized. In contrast, DFT becomes more difficult for new materials whose crystal structures are unknown. To overcome this limitation, a new theoretical approach for predicting crystal structures, known as prototype electrostatic ground state (PEGS),[18] has been recently developed. The PEGS approach, combined with DFT calculations has been shown to successfully predict low-energy crystal structures of alanates[18] and borohydrides.[19] More recently, it has also predicted low-energy crystal structures of mixed-metal borohydrides, $NaK(BH_4)_2$ (Ref. 2) and $LiSc(BH_4)_5$ (Ref. 5.) Here, we use this PEGS + DFT approach to predict low-energy crystal structures in the Li-Zn and Na-Zn mixed-metal borohydride systems.

Once the crystal structure of a newly discovered multicomponent compound is known, its phase stability can be determined from the energy of mixing of its components. A

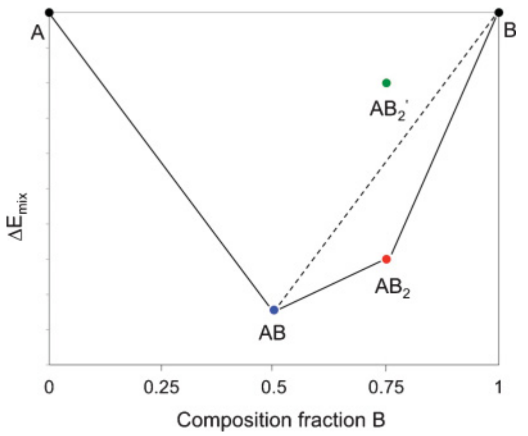

FIG. 1. (Color online) Phase stability of two compounds A and B. Points AB and AB_2 represent the mixing energy of A and B in 1 : 1 and 1 : 2 compositions, respectively. A convex hull passing through A, AB, AB_2, and B represents the stability of phases AB and AB_2. In the case of mixing energy of phase AB_2', which lies above the convex hull formed between A, AB, and B, then the phase AB_2' is unstable with respect to AB and B.

schematic illustration of the phase stability of two compounds formed between components A and B is shown in Fig. 1. When plotted in this way, the stability of a compound requires it to be on a "convex hull" (i.e., the compound should be lower in energy than the linear combination of any other phases in the system). Points AB and AB_2 in Fig. 1 represent the mixing energies of 1 : 1 and 1 : 2 compositions of A-B, respectively. The lines segments joining points A, AB, AB_2, and B represent a convex hull. This graphical construction illustrates that mixing A and B in 1 : 1 or 1 : 2 ratios would result in the formation of stable compounds represented by AB or AB_2, respectively. However, compounds whose energy lies above the convex hull are unstable, such as AB_2', which is unstable with respect to decomposition into AB and B. In this paper, we have only considered this approach for illustrating the stability of solid-state compounds with respect to other hydride phases. The decomposition of compounds for hydrogen release is not considered here.

In this paper, we use DFT calculations to examine the mixing energies and hence phase stability of borohydrides in the Li-Zn-B-H and Na-Zn-B-H systems. We consider both the recently experimentally reported mixed-metal borohydride crystal structures,[6] [i.e., $NaZn(BH_4)_3$, $NaZn_2(BH_4)_5$, and $LiZn_2(BH_4)_5$] and also perform DFT + PEGS calculations to predict new low-energy structures. The DFT energy of the experimentally reported crystal structure of $NaZn_2(BH_4)_5$ is found to lie on the convex hull, thus indicating its stability. In contrast, the DFT energies of the experimentally reported crystal structures of $NaZn(BH_4)_3$ and $LiZn_2(BH_4)_5$ lie above the convex hull, indicating their instability with respect to decomposition into $NaBH_4 + Zn(BH_4)_2$ and $LiBH_4 + Zn(BH_4)_2$. To investigate this instability, we have searched for new crystal structures in these systems using the DFT + PEGS approach. We report the existence of a stable crystal structure of $NaZn(BH_4)_3$ that lies on the convex hull. In addition, we predict the existence of a low-energy compound with 1 : 1 composition between $LiBH_4$ and $Zn(BH_4)_2$ [i.e., $LiZn(BH_4)_3$].

II. METHODOLOGY

We perform first-principles DFT calculations using the Vienna *Ab Initio* Simulation Package (VASP).[20,21] We use the generalized gradient approximation (GGA) in PW91 form[22] for the exchange and correlation. Total energies are calculated using projector-augmented wave (PAW) potentials[23] to treat interactions between ions and valence electrons. To insure highly converged calculations, we use a high plane wave energy cutoff of 800 eV for the electronic wave functions, and a $6 \times 6 \times 6$ Monkhorst-Pack k-point mesh to sample the Brillouin zone. In this work, we report only static energies at $T = 0$ K and do not consider vibrational contributions.

We use the PEGS approach[18] in conjunction with DFT to predict low-energy crystal structures of mixed-metal borohydride compounds. The PEGS Hamiltonian is a classical potential, which includes two terms: (1) a point-charge electrostatic interaction term and (2) a soft-sphere repulsion that prevents oppositely charged species from overlapping.[18] The anionic unit, $(BH_4)^-$, is treated as a rigid unit (with separate point charges on B and H atoms). The cations involved in these systems are Li^+, Na^+, and Zn^{2+}. The PEGS Hamiltonian is sufficiently simple that we can perform global optimization of a system containing a stoichiometric (initially random) arrangement of ions via an off-lattice Monte Carlo (MC)-based method. The MC-based simulated annealing is performed using a variety of different types of MC moves (i.e., change in lattice vectors, cation or anion translations, rigid rotation of the anionic unit, and swapping cation and anion location are performed). Upon the completion of simulated annealing, the system is further relaxed using a potential energy smoothing method to completely remove any atomic overlap in the system. The output from the MC minimization is a "prototype electrostatic structure," and the atomic positions, cell parameters, and volume of this structure are then fully relaxed using DFT. Since MC is a stochastic method, one requires multiple simulations to effectively explore the configurational phase-space. For each stoichiometry considered, we use ∼25–30 different MC simulations of the PEGS Hamiltonian, each distinguished by different initial random configurations. For each of the ∼25–30 different structures, the relaxed DFT energy is calculated, and the lowest-energy structure is reported as the "PEGS-predicted" structure. The DFT energy of this structure is then used in the mixing energy and convex-hull phase-stability analysis.

The input parameters for the construction of the PEGS Hamiltonian are ionic charge and radii of each element. The ionic charges can be obtained from separate DFT calculations (e.g., Bader charges[24]) and the ionic radii can be obtained from the literature values (e.g., Pauling radii). In this work, the ionic charges used for B and H are 1.56 and -0.64 e, respectively, whereas nominal charges are used for Li, Na, and Zn: $+1$, $+1$, and $+2$ e, respectively. The ionic radii used for B, H, Li, Na, and Zn are 0.183, 0.123, 0.068, 0.095, and 0.07 nm, respectively.

III. RESULTS

The stability of the mixed-metal borohydrides depends on the energy of these compounds, relative to the energies of the individual single-metal borohydrides [e.g., $LiBH_4$, $NaBH_4$, and $Zn(BH_4)_2$]. Hence, we begin by discussing these single-metal borohydrides, and subsequently discuss the mixed-metal systems. The crystal structure of $LiBH_4$ is well studied and exists in both a low-temperature and high-temperature form. We use the *Pnma* space group crystal structure of $LiBH_4$ (Ref. 25). Upon DFT relaxation of the crystal structure, the lattice parameters, a, b, and c are 7.052, 4.336, and 6.765 Å, respectively. These are within 1.7% error of the experimentally reported values, which is typical for DFT. We also obtain very good agreement between the DFT-predicted and experimentally reported atomic positions. However, the crystal structures of both $NaBH_4$ and $Zn(BH_4)_2$ are not as well established. $NaBH_4$ has been a subject of many reports[4,26–29] due to the distribution of H atoms in the structure and an order-disorder phase transition. We therefore perform calculations of the crystal structure of $NaBH_4$, finding a candidate low-energy structure that we use in our phase stability analysis of mixed-metal borohydrides. We also investigate previous crystal structures reported for $Zn(BH_4)_2$, and predict a new lower-energy crystal structure of $Zn(BH_4)_2$, based on analogies with the isovalent compound, $Mg(BH_4)_2$.

A. Single-metal borohydride systems

1. $NaBH_4$

$NaBH_4$ is an ionic compound composed of Na^+ cations and $(BH_4)^-$ anion units. It undergoes an order-disorder transition from a cubic rocksalt type crystal structure to a body-centered tetragonal (BCT) crystal structure below ∼190 K (Ref. 30). In both phases, the $(BH_4)^-$ unit consists of four H atoms that form a tetrahedra around B. In the high temperature rocksalt conventional unit cell, there are four atoms each of Na and B, and 16 H atoms. This phase has a $Fm\bar{3}m$ (#225) space group,[29] where Na and B atoms occupy 4*a* and 4*b* Wyckoff sites that are at the corners of the cubic rocksalt unit cell.[29] The H atoms randomly occupy half of the 32*f* Wyckoff sites surrounding B atoms. The low temperature BCT phase has a $P4_2/nmc$ (#137) space group in which there are two atoms each of Na and B and eight H atoms. The Na and B atoms occupy 2*a* and 2*b* Wyckoff sites, and the H atoms occupy 8*g* sites.[28] In the BCT phase, the H positions are fully determined (i.e., no partial occupancies are reported), in contrast to the random distribution in the rocksalt phase.

To calculate the lowest-energy structure of $NaBH_4$, in our DFT calculations, we start from the high temperature rocksalt crystal structure with one unit cell containing 24 atoms (four atoms each of Na and B and 16 H). The tetrahedral positions of H atoms surrounding the B atoms and the Na and B positions are taken from the experimental Wyckoff positions as given by Filinchuk and Hagemann.[29] The tetrahedron is a part of a B-centered cube that is formed by eight H atom sites, each at the corner of the cube. Out of these eight H sites, the tetrahedron is formed when only the four sites that face diagonal opposite corners of the cube are occupied by H atoms as shown in Fig. 2(a). The unoccupied four sites form another tetrahedron, but in the opposite orientation. Hence, there are two oppositely oriented tetrahedra that can be formed around a B atom. Since there are two tetrahedra orientations for each B atom, and there are four B atoms in a unit cell, we find that there are $2^4 = 16$ possible combinations of tetrahedra orientations that can exist in a unit cell. However, upon applying symmetry operations, we find that there are only three symmetry-distinct combinations of tetrahedra orientations that can exist, that is, (1) all four B atoms surrounded by the same tetrahedra orientation (we call it a 4-0 orientation), (2) three B atoms surrounded by one orientation and the fourth B by the other, (a 3-1 orientation), and (3) two pairs of B atoms surrounded by each orientation (a 2-2 orientation). These are shown in Fig. 2(b). Upon relaxing these three structures using DFT, it is found that the 2-2 structure has the lowest energy. The 3-1 structure is higher than the 2-2 structure by 1.72 kJ/mol BH_4, whereas the 4-0 structure has the highest with a difference of 5.90 kJ/mol BH_4 compared to the 2-2 structure. The space groups of the relaxed structures 2-2, 3-1, and 4-0 are found to be $P4_2/nmc$ (#137), $P\bar{4}3m$ (#215), and $F\bar{4}3m$ (#216), respectively. The lowest-energy DFT structure (i.e., the 2-2 structure) correctly reproduces the space group and the crystal structure of the low temperature phase reported by Fischer and Zuttel.[28] The relaxed 2-2 structure is, in fact, no longer a cubic rocksalt structure. Instead, it has transformed into a BCT structure with lattice parameters, $a = 4.288$ Å and $c = 5.954$ Å (see Fig. 2(c). In contrast, the 3-1 and the 4-0 structures maintain the cubic symmetry with lattice parameters, $a = b = c$ as 6.044 and 6.08 Å, respectively. These predicted lattice parameters are in very good agreement with experiment,[28] with only ∼1.5% error, which is typical for DFT. Since the 2-2 structure is the lowest-energy structure among all three, we use it in our calculations for phase-stability analysis of Na-Zn mixed-metal borohydride compounds.

We note that our calculations give an interesting insight into the order-disorder transition and may be used to roughly predict the temperature at which this transition should occur. As explained above, BH_4 tetrahedral units in this structure sit on an fcc sublattice and there are two types of orientational variants for each tetrahedron. Hence, the ordering problem in $NaBH_4$ is essentially isomorphic with a binary fcc ordering problem, which is a well-studied problem in alloy theory.[31,32] We may write the energy of this ordering problem in terms of a simple nearest-neighbor Ising model, $E = J\sum\sigma_i\sigma_j$, where σ_i are pseudospin variables with $\sigma_i = +1$ or -1 representing the two variants of BH_4 tetrahedra. J is the Ising interaction constant, and the sum is over all nearest-neighbor sites of the fcc sublattice. By considering the average of $\sigma_i\sigma_j$ over all pairs of sites in each of our three ordered structures, we can easily express these energies in terms of this Ising model: $E_{4-0} = 6J$, $E_{3-1} = 0$, $E_{2-2} = -2J$. And, we can also express the energy of a completely random distribution of the tetrahedra in the Ising model as $E_{\text{Rand}} = 0$ (since for a random distribution of $\sigma_i = +1$ and -1, with equation number of up and down spins we have the average value of $<\sigma_i\sigma_j> = 0$). From the above, we see that we can deduce the value of 2J from the energy difference between the 2-2 and 3-1 structures, which according to our DFT calculations is 1.72 kJ/mol BH_4. Hence, we can also deduce the "ordering energy," which is the energy difference between the ordered 2-2 structure and the random distribution of tetrahedral, which is also $E_{\text{ord}} = E_{2-2} - E_{\text{rand}} = -2J = -1.72$ kJ/mol BH_4. We hence can obtain a rough estimate of the order-disorder transition temperature in this system from $T_{\text{ord}} \sim E_{\text{ord}}/k_B = 210$ K, very close to the experimentally observed transition temperature of 190 K in this system.

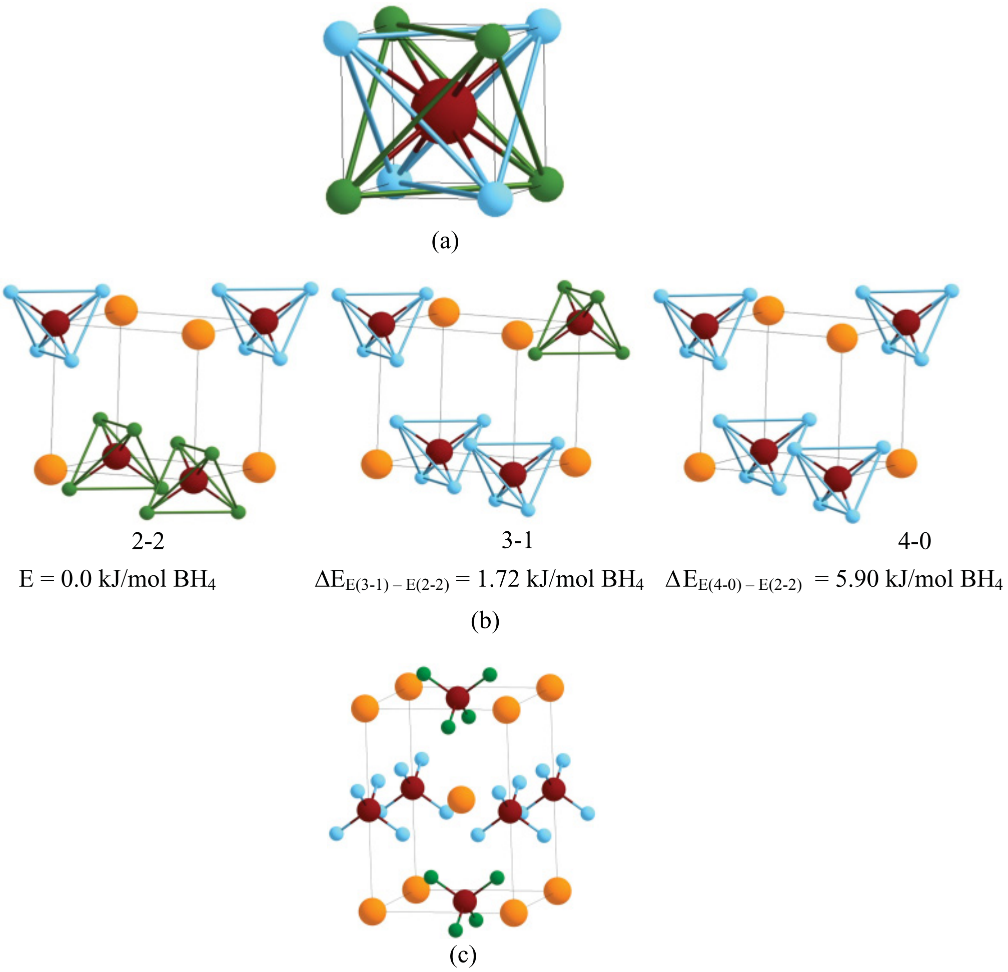

FIG. 2. (Color online) Crystal structure of $NaBH_4$. (a) Two orientations of a tetrahedra formed by four H around B in a $(BH_4)^-$ unit. (b) In a rocksalt-type structure of $NaBH_4$, there are three possible ways in which two orientations of tetrahedra can be arranged. A 4-0 arrangement in which all four tetrahedra are of same orientation, a 3-1 arrangement in which three tetrahedra are of one orientation and one of the other, and a 2-2 arrangement in which there are two pairs of tetrahedra of each orientation. The 2-2 arrangement has the lowest-energy structure, which on relaxation transforms into a bodycentered structure. A body-centered crystal structure is shown in (c). (Color scheme: B in red, Na in yellow, H in blue and green.)

2. *$Zn(BH_4)_2$*

We next turn to the crystal structure of $Zn(BH_4)_2$. The structure of $Zn(BH_4)_2$ is currently experimentally unknown, however, its crystal structure has been theoretically proposed from DFT using the *database-searching* method.[33] The database-searching method is a crystal structure search method based on predicting a lowest-energy crystal structure out of various known prototype crystal structures of chemically similar compounds with the same stoichiometry as the target compound. It has been previously shown to successfully predict low-energy crystal structures for various material systems such as $LiAlH_4$ and Li_3AlH_6 (Ref. 34), $Ca(AlH_4)_2$ (Ref. 35), and $NdAlH_6$ (Ref. 36). However, the database searching method is limited to structure types that exist in the International Crystal Structure Database, and therefore can miss new structure types. This limitation was evident in the earlier crystal structure search for $Mg(BH_4)_2$, where Ozolins *et al.*[19] found that their PEGS search predicted a lower-energy crystal structure than any other structure type available in the ICSD. Here, in the case of $Zn(BH_4)_2$, we also find (see below) that the previously proposed $Pmc2_1$ (#26) crystal structure[33] obtained from database searching is not the lowest-energy crystal structure.

Our search for a new low-energy crystal structure of $Zn(BH_4)_2$ is aided by the fact that there are commonalities between $Zn(BH_4)_2$ and $Mg(BH_4)_2$. For instance, (1) both Zn and Mg have +2 oxidation states, and (2) both Zn^{2+} and Mg^{2+} cations have similar ionic radii ($r_{Mg} = 0.065$ nm and $r_{Zn} = 0.074$ nm). Hence, both can be expected to favor similar coordination environments and could potentially possess similar crystal structures. Therefore, we discuss the recent work on the crystal structure search for $Mg(BH_4)_2$ first, and then demonstrate the similarities between the crystal structures of the two borohydrides.

The crystal structure of $Mg(BH_4)_2$ has been a subject of extensive work, both experimental and theoretical. From the database-searching approach combined with DFT calculations, Vajeeston *et al.*[37] proposed a crystal structure with space group $Pmc2_1$ (#26). Later, Cerny *et al.*[38] used x-ray and neutron diffraction experiments and found a $P6_1$ (#169)

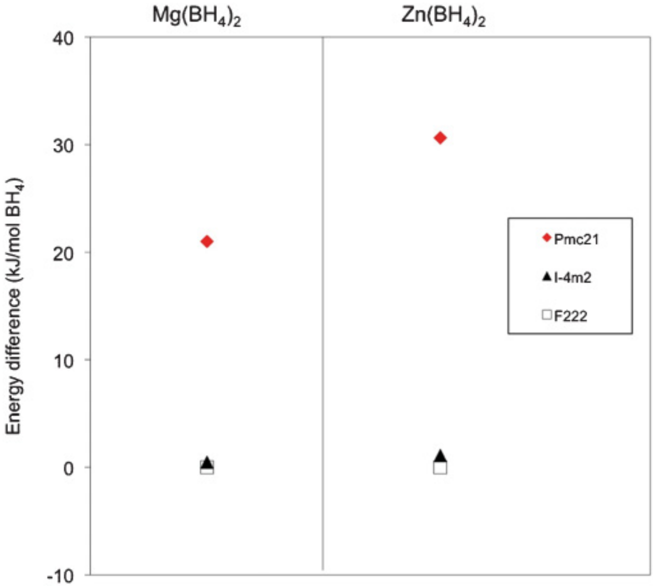

FIG. 3. (Color online) DFT energies for three different crystal structures ($Pmc2_1$, $\mathrm{I}\bar{4}\mathrm{m}2$, and $F222$) for $Mg(BH_4)_2$ and $Zn(BH_4)_2$. For both materials, $Pmc2_1$ has higher energy, whereas $\mathrm{I}\bar{4}\mathrm{m}2$ and $F222$ are the low-energy structures and are nearly degenerate. Energies are in units of kJ/mol BH_4 and are given relative to that of the lowest-energy $F222$ structure.

space group. Subsequently, Ozolins *et al.*[19] performed a crystal structure search using the PEGS + DFT method, where they found a new structure with space group $\mathrm{I}\bar{4}m2$ (#119). It was demonstrated to possess a lower energy in DFT than both the previously predicted $Pmc2_1$ structure and the experimentally obtained $P6_1$ structure. More recently, Voss *et al.*[39] have proposed a new crystal structure for $Mg(BH_4)_2$ (with space group $F222$), which is nearly degenerate to the $\mathrm{I}\bar{4}m2$ structure. In Fig. 3, we show our calculated DFT energies of the $Pmc2_1$, $\mathrm{I}\bar{4}m2$, and $F222$ crystal structures for $Mg(BH_4)_2$, which are in agreement with previous calculations. The $I\bar{4}m2$ and $F222$ structures are nearly degenerate, and the $Pmc2_1$ structure is significantly higher in energy.

In view of the recent work on $Mg(BH_4)_2$, and the commonalities between $Mg(BH_4)_2$ and $Zn(BH_4)_2$, we have used the structures proposed for $Mg(BH_4)_2$ as a guide to predict the lowest-energy crystal structure of $Zn(BH_4)_2$. We perform a comparison of the DFT energies for $Zn(BH_4)_2$ for the two recently proposed lowest-energy crystal structures of $Mg(BH_4)_2$ (i.e., $I\bar{4}m2$ and $F222$). In addition, we compare these energies to that of the $Pmc2_1$ structure.[37] The comparison of the DFT energies of the three structures is shown in Fig. 3. Interestingly, all three crystal structures follow similar energetic trends as found in $Mg(BH_4)_2$. Similar to $Mg(BH_4)_2$, we find that both $I\bar{4}m2$ and $F222$ crystal structures are significantly lower in energy than the previously proposed $Pmc2_1$. The two structures, $I\bar{4}\mathrm{m}2$ and $F222$, are nearly degenerate for $Zn(BH_4)_2$, just as was found for $Mg(BH_4)_2$. In the discussion below, we use $F222$ as the crystal structure of $Zn(BH_4)_2$ for the phase-stability analysis.[40]

We suggest that future experiments to determine the crystal structure of $Zn(BH_4)_2$ would be of considerable interest in testing our theoretical predictions. Specifically, it would be of interest to find whether there is a difference between the experimental and DFT-predicted structures of $Zn(BH_4)_2$ [just as found for $Mg(BH_4)_2$]. For $Mg(BH_4)_2$, the ground state crystal structure predicted from DFT is $I\bar{4}\mathrm{m}2$ or $F222$ (nearly degenerate), whereas that from experiments is $P6_1$. This discrepancy for $Mg(BH_4)_2$ is currently unexplained, and future experiments to see whether a similar discrepancy exists for $Zn(BH_4)_2$ would be of interest.

B. Mixed-metal borohydride systems

In this section, we examine the phase stability of $NaZn(BH)_3$, $NaZn_2(BH_4)_5$, $LiZn(BH_4)_3$, and $LiZn_2(BH_4)_5$ with respect to corresponding separate systems—$NaBH_4$, $LiBH_4$, and $Zn(BH_4)_2$ using the convex-hull framework described in the Introduction. The stability of these compounds may be described in terms of the mixing energy (ΔE_{mix}), which is the difference between the energy of a mixed-metal borohydride [e.g., $Li_{(1-x)}Zn_x(BH_4)_{1+x}$] and a composition-weighted mixture of the two single-cation borohydrides:

$$\Delta E_{\mathrm{mix}} = E_{\mathrm{Li}_{1-x}\mathrm{Zn}_x(\mathrm{BH}_4)_{1+x}} - \left[(1-x)E_{\mathrm{LiBH}_4} + xE_{\mathrm{Zn(BH}_4)_2}\right]. \tag{1}$$

To begin with, we first perform DFT relaxation of $NaZn(BH)_3$, $NaZn_2(BH_4)_5$, and $LiZn_2(BH_4)_5$ using the experimentally reported[6] crystal structures. A comparison between the DFT-obtained and the experimentally reported structural parameters for the three compounds is shown in Table I, which, in general, are in reasonably good agreement. However, some deviations are significantly larger than are typical

TABLE I. Comparison between experimental and DFT-relaxed structural parameters for $NaZn(BH_4)_3$, $NaZn(BH_4)_3$, and $LiZn_2(BH_4)_5$ in the crystal structures recently reported in Ref. 6.

	$NaZn(BH_4)_3$		$NaZn_2(BH_4)_5$		$LiZn_2(BH_4)_5$	
	Exp.	DFT	Exp.	DFT	Exp.	DFT
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Cmca$	$Cmca$
a (Å)	8.2714	8.266	9.397	9.747	8.6244	8.524
b (Å)	4.524	4.906	16.635	16.720	17.897	17.977
c (Å)	18.757	18.032	9.1359	9.257	15.4114	15.735
Beta (∞)	101.6	99.9	112.6	115.5	90	90
V (Å^3)	687.3	720.1	1318.0	1361.5	2378.7	2411.3
% Vol. diff.	4.7		3.30		1.3	

for DFT errors [e.g., ∼7% error in *b* for $NaZn(BH_4)_3$ compound where a typical error in the lattice constant from DFT is 1–2%]. Hence, we have also used the PEGS approach to predict possible new low-energy crystal structures in all of the following systems: $NaZn(BH)_3$, $NaZn_2(BH_4)_5$, $LiZn_2(BH_4)_5$, and $LiZn(BH_4)_3$. We note that for Li-Zn mixed-metal borohydrides, only the crystal structure of the 1 : 2 Li:Zn stoichiometry has been reported experimentally. In analogy with the Na-Zn system, we also use the PEGS approach to investigate the stability and the crystal structure of the 1 : 1 Li-Zn-based borohydride compound [i.e., $LiZn(BH_4)_3$]. We use the combination of experimental structures, DFT, and PEGS-predicted structures to predict both phase stability, crystal structures, and even new stable stoichiometries of the mixed-metal borohydrides systems.

1. Li-Zn mixed metal borohydride

We examine the phase stability of two stoichiometries in the Li-Zn mixed borohydride system, $LiZn_2(BH_4)_5$ and $LiZn(BH_4)_3$. We first use the PEGS approach to investigate the existence of $LiZn(BH_4)_3$ by carrying out approximately 25 crystal structure prediction simulations separately consisting of one and two formula units. Out of these structures predicted by the PEGS simulations, we find a significant number of them to possess negative DFT mixing energies. These negative mixing energies provide evidence that metal mixing is preferred relative to the single metal borohydrides in the Li-Zn system. The lowest-energy structure with mixing energy ∼−7.5 kJ/mol cation is plotted in Fig. 4. This structure contains two formula units and has a *C1* space group. The detailed crystal structure parameters are given in the Supplemental Information.

We now turn our attention to $LiZn_2(BH_4)_5$. This stoichiometry has more atoms (28 atoms in the single formula unit) than the $LiZn(BH_4)_3$ compound (17 atoms in a formula unit). The crystal structure prediction capability of PEGS becomes more limited with the increasing number of atoms. For larger systems, the calculations become more computationally expensive, and the structural degrees of freedom also increase tremendously. Consequently, a true ground state structure prediction becomes a challenging task. Since $LiZn_2(BH_4)_5$ is a more complex system with five $(BH_4)_5^-$ units, crystal structure prediction from PEGS is found to be less informative. The mixing energy of the lowest-energy structure predicted by PEGS is ∼−0.04 kJ/mol B shown in Fig. 4. We note that the experimentally reported structure has a mixing energy of ∼−3.5 kJ/mol cation, qualitatively consistent with the observation of mixed-metal ordering in this system. The experimentally observed structure has a lower energy in DFT than the lowest-energy PEGS structure found; we therefore use the experimental structure of $LiZn_2(BH_4)_5$ for further phase stability analysis.

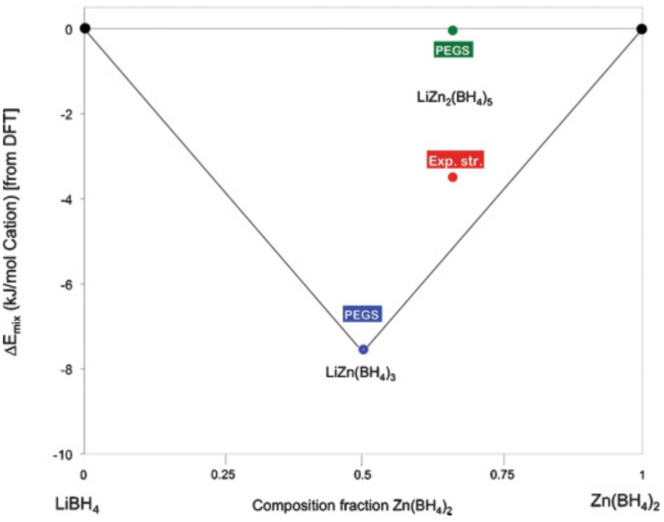

FIG. 4. (Color online) Mixing energy vs composition plot for systems involving $LiBH_4$ and $Zn(BH_4)_2$. A new phase $LiZn(BH_4)_3$ is predicted using the PEGS approach which lies on the convex hull. $LiZn_2(BH_4)_5$ is found to lie above the tie line between $LiZn(BH_4)_3$ + $Zn(BH_4)_2$, indicating that $LiZn_2(BH_4)_5$ is not a stable ground state in this system.

Now that we have low-energy structures for both stoichiometries, we use the convex-hull framework described in Fig. 1 to assess the phase stability in the Li-Zn system. Although both compounds have negative mixing energies, implying stability with respect to the single-metal borohydrides, we find that the energy of $LiZn_2(BH_4)_5$ lies above the tie-line connecting $LiZn(BH_4)_3 + Zn(BH_4)_2$ as shown in Fig. 4. Thus, while our DFT calculations show that $LiZn(BH_4)_3$ could be a stable ground state in this system, $LiZn_2(BH_4)_5$ is not. Including the vibrational contributions may affect the relative phase stabilities of both the compounds, and such calculations are currently in progress. But, in addition to further calculations, we suggest that future experiments in this system would be of considerable interest to fully understand the crystal structures and preferred stoichiometries in the Li-Zn mixed-metal borohydride system.

2. Na-Zn mixed metal borohydride

Next, we carry out a similar analysis for the Na-Zn-based system as we did for the Li-Zn above. Here, the crystal structures of both 1 : 1 and 1 : 2 compounds of the Na-Zn borohydride system [i.e., $NaZn(BH_4)_3$ and $NaZn(BH_4)_5$] are observed from experiments.[6] We calculate energetics and structural parameters of these observed structures from DFT. We also use PEGS to explore low-energy crystal structures for these two stoichiometries. Using both the experimentally observed as well as the PEGS-predicted structures, the mixing energies of the compounds are shown in Fig. 5. The mixing energy of $NaZn_2(BH_4)_5$ from the experimental and the PEGS-obtained structures are labeled as *b* and *b*', respectively. As observed above for $LiZn_2(BH_4)_5$, the large number of atoms in the formula unit of $NaZn_2(BH_4)_5$ limits the ability of the PEGS approach to fully explore the structural configuration space. In fact, the lowest-energy structure found from PEGS has a positive mixing energy, which is in contrast to the experimentally observed crystal structure with negative mixing energy of ∼−7.1 kJ/mol cation.

We next turn to the stability of $NaZn(BH_4)_3$. Somewhat surprisingly, a DFT calculation of the experimentally observed structure shows it to possess a positive mixing energy as shown in Fig. 5 labeled as *a*. This positive mixing energy is in contrast to what would be expected for a stable ground state compound, which would not only have a negative mixing energy, but

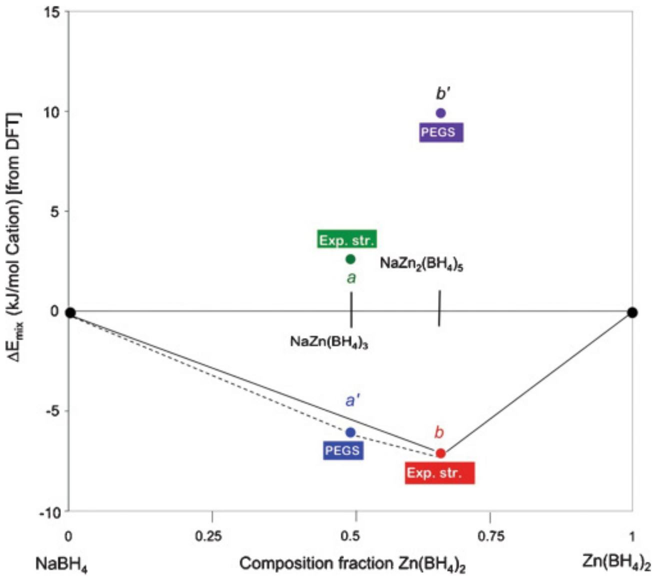

FIG. 5. (Color online) DFT mixing energies vs composition for the $NaBH_4$ – $Zn(BH_4)_2$ system. The mixing energy of the experimentally reported crystal structure of $NaZn_2(BH_4)_5$ is labeled as *b*. The crystal structure predicted by PEGS (*b*') has a positive mixing energy (see text for details). In contrast, the mixing energy of the experimentally reported structure of $NaZn(BH_4)_3$ is positive (*a*), thus indicating its instability with respect to decomposition into $NaBH_4$ + $Zn(BH_4)_2$. The PEGS approach predicts a lower-energy stable $NaZn(BH_4)_3$ structure labeled as *a*'.

would also lie on the convex hull. The experimentally observed $NaZn(BH_4)_3$ structure possesses neither of these attributes and is not a DFT ground state. In addition to the instability of this structure, we also noted in Table I that there were significant discrepancies between the observed and DFT-relaxed structural parameters. To further elucidate the phase stability of $NaZn(BH_4)_3$, we explore its crystal structure using the PEGS approach. Similarly to the $LiZn(BH_4)_3$ stoichiometry, PEGS produces multiple prototype structures that possess negative mixing energies, showing a clear tendency for stable mixing in this system. Furthermore, the lowest-energy PEGS obtained structure, represented as *a*' in Fig. 5, also lies on the convex hull. Moreover, this PEGS structure consists of only one formula unit compared to four formula units observed experimentally. The details of the crystal structure parameters are given in the Supplemental Information.[41] While we note that the predicted structure is only slightly lower in energy than $NaZn_2(BH_4)_5 + NaBH_4$, we also note that the PEGS-predicted structure is an upper bound to the true ground state energy, and structures with even lower energies are possible.

IV. CONCLUSION

In this work, we have used DFT to study the crystal structures of $NaZn(BH_4)_3$, $NaZn_2(BH_4)_5$, and $LiZn_2(BH_4)_5$ compounds determined recently from experiments. We have also performed combined PEGS and DFT calculations to predict the low-energy crystal structure of these compounds. Using this PEGS + DFT approach, we have predicted the existence of a low-energy compound with stoichiometry $LiZn(BH_4)_3$. Having obtained the low-energy crystal structures for all four compounds, we also elucidate the phase-stability of these compounds.

Our DFT calculations show that the experimentally reported crystal structure of $NaZn_2(BH_4)_5$ has a negative mixing energy, whereas $NaZn(BH_4)_3$ has a positive mixing energy. This positive mixing energy for $NaZn(BH_4)_3$ indicates an instability with respect to decomposition into $NaBH_4$ + $Zn(BH_4)_2$. Using the PEGS approach, we predict a new crystal structure of $NaZn(BH_4)_3$ with negative mixing energy. Using the convex hull approach, we find that the experimental structure of $NaZn_2(BH_4)_5$ and the PEGS-obtained structure of $NaZn(BH_4)_3$ lie on the convex hull between $NaBH_4$ and $Zn(BH_4)_2$.

In the Li-Zn borohydride system, we have used the PEGS + DFT approach to predict a stable crystal structure of $LiZn(BH_4)_3$. As a consequence of this predicted low-energy compound, DFT calculations of the experimentally reported structure of $LiZn_2(BH_4)_5$ show that it is unstable with respect to decomposition into $LiZn(BH_4)_3 + Zn(BH_4)_2$.

The number of stoichiometries that we have considered in this study are quite limited, and hence, it is possible that new compounds exist in these systems at other, currently unexplored, stoichiometries. We believe that other compositions within Li-Zn and Na-Zn systems should be explored both experimentally and theoretically. We have shown here that the PEGS approach has the capability in predicting new compounds in these systems; therefore we are continuing to work on exploring new stoichiometries in both these systems in an effort to search for more stable mixed-metal borohydride compounds.

Our work has also provided insight into the crystal structures of $NaBH_4$ and $Zn(BH_4)_2$. Our DFT calculations of NaBH4 have clarified the role of the order-disorder transition in this system in terms of the H positions of the high and low temperature phases. Our DFT calculations confirm the experimental observation of the lowtemperature crystal structure of $NaBH_4$ as the 2-2 crystal structure. We have also predicted a new low-energy crystal structure for $Zn(BH_4)_2$ and have shown a structural similarity between $Mg(BH_4)_2$ and $Zn(BH_4)_2$. We find that, just as for $Mg(BH_4)_2$, the$I\bar{4}m2$ and F222 crystal structures are the nearly degenerate lowest-energy crystal structures of $Zn(BH_4)_2$.

Note in proof: While this article was in press, we become aware of another experimental investigation of the LiZn2(BH)5 crystal structure.[42] The structure in this reference is distinct from the experimental structure cited in this paper. We are investigating the stability of this new experimental structure using DFT and have found it to be lower in energy than the experimental structure in Fig. 4 in the text. The impact of this new, lower energy structure on the conclusions of the current paper will be summarized in a forthcoming publication.

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[40] In predicting the crystal structure of $Zn(BH_4)_2$, we have not performed the PEGS calculations. However, since Mg^{2+} and Zn^{2+} are isovalent with similar ionic radii, and these two characteristics form the only two input parameters for the PEGS calculations, we would expect similar crystal structures to result from PEGS calculations of $Zn(BH_4)_2$ as was previously found for $Mg(BH_4)_2$.

[41] See supplemental material at [http://link.aps.org/supplemental/10.1103/PhysRevB.83.144111] for details of the crystal structure

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