Density functional theory based screening of ternary alkali-transition metal borohydrides: A computational material design project

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Density functional theory based screening of ternary alkali-transition metal borohydrides: A computational material design project


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We present a computational screening study of ternary metal borohydrides for reversible hydrogen storage based on density functional theory. We investigate the stability and decomposition of alloys containing 1 alkali metal atom, Li, Na, or K ($M_1$); and 1 alkali, alkaline earth or 3d/4d transition metal atom ($M_2$) plus two to five (BH$_4$)$^-$ groups, i.e., $M_1M_2$(BH$_4$)$_{2–5}$, using a number of model structures with trigonal, tetrahedral, octahedral, and free coordination of the metal borohydride complexes. Of the over 700 investigated structures, about 20 were predicted to form potentially stable alloys with promising decomposition energies. The $M_1$(Al/Mn/Fe)(BH$_4$)$_4$, (Li/Na/Zn)(BH$_4$)$_3$, and (Na/K)(Ni/Co)(BH$_4$)$_3$ alloys are found to be the most promising, followed by selected $M_1$(Nb/Rh)(BH$_4$)$_4$ alloys. © 2009 American Institute of Physics. [DOI: 10.1063/1.3148892]

I. INTRODUCTION

The development of sustainable energy solutions for the future requires new and improved materials. Specifically designed material properties are needed to solve the grand challenges in energy production, storage, and conversion. Within energy storage, hydrogen has been investigated extensively over the past decade as one of the few promising energy carriers which can provide a high energy density without resulting in CO$_2$ emission by the end user. Finding materials for efficient, reversible hydrogen storage, however, remains challenging. Here, the specific requirements of the rapidly growing transportation sector coupled with complex engineering challenges have directed research toward complex materials with extreme hydrogen storage capacities such as metal borohydrides and metal ammines. Finding materials with high reversible hydrogen content and optimal thermodynamic stability is essential if hydrogen is going to be used as a commercial fuel in the transport sector. The binary metal borohydrides have been studied extensively: the alkali based compounds, e.g., LiBH$_4$, are too thermodynamically stable, the alkaline earth compounds are kinetically too slow and practically irreversible, and the transition metal borohydrides are either unstable or irreversible. This leaves hope that mixed metal (“alloyed”) systems might provide new opportunities.

The use of computational screening techniques has proved a valuable tool in narrowing the phase space of potential candidate materials for hydrogen storage. Recent density functional theory (DFT) calculations have shown that the thermodynamic properties of even highly complex borohydride superstructures can be estimated by DFT using simple model structures, if the primary coordination polyhedra are correctly accounted for. These findings enable faster screening studies of thermodynamic stability and decomposition temperatures for, e.g., ternary and quaternary borohydride systems; not only in terms of reduced computational effort due to smaller system sizes but also with the advantage that the exact space group does not need to be known

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a priori.

In the present paper, we apply a “local coordination screening” (LCS) approach to search for novel metal borohydrides. The vast majority of the calculations were performed as part of the 2008 CAMD summer school in electronic structure theory and materials design, where more than 100 scientists combined DFT calculations, database methods, and screening techniques to investigate the structure and stability of promising ternary borohydrides. A few additional calculations were subsequently performed based on the insight gained from the initial screening.

Out of 757 investigated M₁M₂(BH₄)ₓ (M₁=alkali metal and M₂=alkali, alkaline earth or 3d/4d transition metal) compositions and structures, a total of 22 were found to form potentially stable alloys with promising decomposition energies, which should subsequently be subjected to more detailed theoretical and experimental verification.

II. COMPUTATIONAL SETUP

Groups of alloy compositions and structures were divided among different groups of scientists, each of which was responsible for its own subset of the alloy configuration space. A number of predefined structural templates and optimization procedures had been prepared to assist the groups in setting up structures and calculations for the initial optimization (see Sec. II B). This was done to ensure a sufficient accuracy in all calculations (i.e., convergence with respect to plane wave cutoff, k-point sampling, etc.).

To ensure reliability of the generated results, an automated checking procedure was enforced before a result could be included in the database (see Sec. III) to ensure the presence of the required output (total energies, lattice constants, etc.).

A. Computational parameters

The total energies and gradients were calculated within density functional theory as implemented by the software package Dacapo. A plane wave basis set with a cutoff energy of 350 eV (density grid cutoff of 700 eV) and the RPBE exchange-correlation functional were used for all calculations. Dacapo uses ultrasoft pseudopotentials for a description of the ionic cores. The coordinate optimization was implemented and performed within the atomic simulation environment. The electronic Brillouin zones were sampled with (4×4×4) k-points (spacings of ~0.05 Å⁻¹). A quasi-Newton method was used for all relaxations.

B. Configuration space and template structures

The alloys which were initially screened have the general formula M₁M₂(BH₄)ₓ, where M₁ ∈ {Li, Na, K} and x = 2−4. The x = 2 alloys were investigated for M₂ ∈ {Li, Na, K}, and x = 3, 4 for M₂ ∈ {Li, Na, K, Mg, Al, Ca, Sc−Zn, Y−Mo, Ru−Cd}.

In order to limit the total number of calculations, only template structures with tetrahedral and octahedral coordination of the (BH₄)⁻ groups to the metal atoms were used. Most metals prefer an octahedral coordination of their ligands, but for the metal borohydrides the ligand-ligand repulsion between the relatively large (BH₄)⁻ ions often forces a lower coordination number. The primary structures observed and reported in literature for the alkali and alkaline earth borohydrides are either tetrahedral (for the smallest Li and Mg) or octahedral (for the larger Na, K, and Ca), while a trigonal planar ligand arrangement is observed for Al(BH₄)₃. However, Al can also have a tetrahedral coordination as is the case of the LiAl(BH₄)₄ alloy obtained here (see Sec. V), and since the radii of the considered ions lie between the radius for K and the radius for Al, the tetrahedral and octahedral primary structures are expected to be representative.

For each alloy composition, four different template structures were used to sample the tetrahedral and octahedral primary structures in the combinations: tetrahedral/tetrahedral, octahedral/octahedral, tetrahedral/octahedral, and octahedral/tetrahedral, referring to the coordination of the (BH₄)⁻ groups to the M₁ and M₂ atoms, respectively. The coordination polyhedra were either corner sharing, edge sharing, or a combination to yield the required stoichiometric ratio of (BH₄)⁻ groups (see Fig. 1). All structures were designed to have a unit cell containing only one formula unit (see Sec. II D). It has previously been shown that these simple template structures can be within ~0.1 eV (10 kJ/mol H₂) of the true ground state energy if the local coordination is correctly accounted for; e.g., M₁M₂(BH₄)₂-tetra for LiBH₄, M₁M₂(BH₄)₄-octa for Ca(BH₄)₂, and even M₁M₂(BH₄)₄-tetra for the free energy of Mg(BH₄)₂ superstructures.

The initial optimization of the structures only relaxed the hydrogen positions and the unit cell volume while keeping the metal-boron coordination polyhedra fixed. For a given set of (M₁, M₂), the most stable structure was then used as the starting point for a calculation in which all atomic positions and the unit cell were relaxed. Even though many of the structures did not change significantly during the final relaxation, it added, in principle, an additional structure to the phase space for each set of (M₁, M₂). These are included as “other” structures in the results (Figs. 3–12) to distinguish them from the structures with fixed metal-boron coordination polyhedra, even though the original coordination polyhedra are only slightly distorted in many of them.

A number of structures were subsequently added based on the knowledge gained from the initial screening and the reference binary borohydride structures (see Secs. IV and VI). In some of these structures, the metal ions had the same valence as in the reference structures, which meant that the four x=2 templates were also applied to M₂ ∈ {Ni, Pd, Cu, Ag}, while a new template for x=5 was investigated for M₂ ∈ {Ti, Zr} in the two combinations tetrahedral/octahedral and octahedral/tetrahedral. An alternative x=3 tetragonal/trigonal template was applied to M₂ ∈ {Mg, Al, Ca, Sc−Zn, Y−Mo, Ru−Cd} to investigate possible size effects. In this structure, the M₁ ion has a tetrahedral coordination while the M₂ atom is surrounded by three (BH₄)⁻ groups in a trigonal planar arrangement (see Fig. 2). This enabled the metal-boron distances for the two metals to be optimized independently, which was not pos-
The template structures of \( M_1 M_2 (BH_4)_2 \) have been simulated and are reported herein.

In total, 757 structures have been simulated and are reported herein.

C. Group calculations

The 69 sets of \((M_1, M_2)\) combinations investigated in this study were divided among 32 groups of scientists for the initial screening. Each group followed step I of the calculational procedure outlined below for each alloy containing \( M_1 \) and \( M_2 \) and step II for the most stable resulting structure.

D. Calculational procedure

1. Step I

An initial structure was set up by calling a function that populates one of the four template structures with two supplied metal ions, e.g., Li and Sc. The function utilizes the ionic radii obtained from the calculations of binary reference borohydrides, i.e., individual metal atom borohydrides, to calculate metal-boron distances, where the ionic radius used for a \((BH_4)^-\) group depends on whether a face, edge or corner of the H-tetrahedron points toward the metal atom. In general, this ensured that the effective lattice constant and the \(c/a\) ratio were close to the optimum. The initial structure was used as the initial guess for the first iteration of the following procedure.

All hydrogen positions were relaxed until the maximum force on the atoms reached 0.05 eV/Å or, alternatively, a maximum of 50 quasi-Newton steps had been performed. The resulting structure was then contracted and expanded to 90%, 95%, 105%, and 110% of the unit cell volume by a proportional scaling of the unit cell, while keeping the B–H distances in each \((BH_4)^-\) group fixed; a single total energy calculation was performed for each volume. A Murnaghan equation-of-state was fitted to the calculated five points to estimate the optimal unit cell volume, to which the unit cell was then scaled (again while conserving B–H distances), followed by a relaxation of the hydrogen positions to a force convergence of 0.05 eV/Å.

After each iteration, an energy versus unit cell volume plot was inspected visually to decide whether the minimum had been sufficiently sampled or an additional iteration of the procedure should be performed; in the latter case, a structure resulting from the first iteration was used as the starting guess for the next iteration.
2. Step II

When all template structures for each of the $M_1$, $M_2$ alloys had been optimized in step I, the most stable structure was relaxed without constraints by repeating the procedure that first relaxes all atomic positions for a fixed cell and then the unit cell for fixed internal positions. To limit the computational time used by this algorithm, the number of iterations was limited to 5, and the number of steps per iteration was limited to 12 for the internal relaxation and 5 for the unit cell relaxation.

3. Procedure for the additional structures

For the structures calculated later, the $x=2$ structures (monovalent transition metals) followed the same procedure mentioned above, whereas only a single free optimization was performed on the extra $x=3$ and $x=5$ structures, in which all atoms were allowed to relax.

III. DATA COLLECTION AND STORAGE

Every group executed the calculation procedures for steps I and II. After each step, the validity of the results was checked by the group and the results were checked in (stored in a global location for indexing) to the common database.

A. Front end

A Python script took care of checking in all relevant files that were needed for subsequent checking. This included the calculation script and the output files containing the atoms, energies and the calculational parameters. A subversion (svn) version control system assisted to manage groups and users, storing results and assuring transaction consistency.

B. Back end

A second Python script was used to extract the relevant parameters, i.e., the total energy, unit cell volume, chemical symbols, structure, and the calculational parameters such as $k$-points, number of bands, density wave cutoff, and to select the best structure (at any given time) for every borohydride to create/update the intermediate result plots, which were accessible to all participants. Python, in combination with Matplotlib, was used to ensure a flexible user interface and to generate the plots. A special Python class managed the resulting data, consisting of approximately 5500 calculations. This class provided basic database operations such as selecting, sorting, and filtering of data and facilitated the creation of the plots considerably.

The overall construction of the database and data retrieval procedures will also facilitate screening for possible correlations between combinations of a number of different values in future projects.

IV. DATA ANALYSIS

The initial screening procedure presented here is performed to reduce the number of potential alloys for further investigation, and two simple selection criteria were set up to assess the stability of the investigated alloy structures against phase separation/disproportionation and decomposition. The stabilities were first analyzed against phase separation into the original binary borohydrides as illustrated for LiSc$\text{BH}_4$:

$$\Delta E_{\text{alloy}} = E_{\text{LiSc(BH}_4)_4} - (E_{\text{LiBH}_4} + E_{\text{Sc(BH}_4)_3}).$$

Reference energies for the 3 alkali, 2 alkaline earth, Al$\text{BH}_4$ plus 19 transition metal borohydrides were ob-
TABLE II. Structures with alloying energies $\Delta E_{\text{alloy}} < 0.0$ eV/f.u. (formula unit) and decomposition energies $\Delta E_{\text{decomp}} < 0.0$ eV/H$_2$

<table>
<thead>
<tr>
<th>wt % (kg H$_2$/kg material)</th>
<th>$\Delta E_{\text{alloy}}$ (eV/f.u.)</th>
<th>$\Delta E_{\text{decomp}}$ (eV/H$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNa(BH$_4$)$_3$</td>
<td>13.5</td>
<td>-0.020</td>
</tr>
<tr>
<td>KZn(BH$_4$)$_3$</td>
<td>8.1</td>
<td>-0.349</td>
</tr>
<tr>
<td>KAl(BH$_4$)$_3$</td>
<td>12.9</td>
<td>-0.138</td>
</tr>
<tr>
<td>NaAl(BH$_4$)$_3$</td>
<td>14.7</td>
<td>-0.279</td>
</tr>
<tr>
<td>K Cd(BH$_4$)$_3$</td>
<td>6.2</td>
<td>-0.005</td>
</tr>
<tr>
<td>NaZn(BH$_4$)$_3$</td>
<td>9.1</td>
<td>-0.358</td>
</tr>
<tr>
<td>LiAl(BH$_4$)$_3$</td>
<td>17.3</td>
<td>-0.391</td>
</tr>
<tr>
<td>KFe(BH$_4$)$_3$</td>
<td>8.7</td>
<td>-0.116</td>
</tr>
<tr>
<td>LiZn(BH$_4$)$_3$</td>
<td>10.4</td>
<td>-0.362</td>
</tr>
<tr>
<td>NaFe(BH$_4$)$_3$</td>
<td>9.8</td>
<td>-0.141</td>
</tr>
<tr>
<td>KMn(BH$_4$)$_3$</td>
<td>10.5</td>
<td>-0.148</td>
</tr>
<tr>
<td>NaNb(BH$_4$)$_3$</td>
<td>9.2</td>
<td>-0.128</td>
</tr>
<tr>
<td>KCr(BH$_4$)$_3$</td>
<td>8.5</td>
<td>-0.089</td>
</tr>
<tr>
<td>NaMn(BH$_4$)$_3$</td>
<td>11.7</td>
<td>-0.284</td>
</tr>
<tr>
<td>KNi(BH$_4$)$_3$</td>
<td>8.5</td>
<td>-0.120</td>
</tr>
<tr>
<td>LiFe(BH$_4$)$_3$</td>
<td>11.3</td>
<td>-0.141</td>
</tr>
<tr>
<td>LiNb(BH$_4$)$_3$</td>
<td>10.1</td>
<td>-0.194</td>
</tr>
<tr>
<td>NaCo(BH$_4$)$_3$</td>
<td>9.6</td>
<td>-0.143</td>
</tr>
<tr>
<td>K Rh(BH$_4$)$_3$</td>
<td>8.0</td>
<td>-0.058</td>
</tr>
<tr>
<td>LiMn(BH$_4$)$_3$</td>
<td>13.3</td>
<td>-0.358</td>
</tr>
<tr>
<td>NaNi(BH$_4$)$_3$</td>
<td>9.6</td>
<td>-0.164</td>
</tr>
<tr>
<td>NaRh(BH$_4$)$_3$</td>
<td>8.7</td>
<td>-0.033</td>
</tr>
</tbody>
</table>

TABLE III. Structures with alloying energies $0 < \Delta E_{\text{alloy}} < 0.2$ eV/f.u. (formula unit) and decomposition energies $\Delta E_{\text{decomp}} < 0.0$ eV/H$_2$

<table>
<thead>
<tr>
<th>wt % (kg H$_2$/kg material)</th>
<th>$\Delta E_{\text{alloy}}$ (eV/f.u.)</th>
<th>$\Delta E_{\text{decomp}}$ (eV/H$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNa(BH$_4$)$_3$</td>
<td>8.8</td>
<td>0.095</td>
</tr>
<tr>
<td>NaY(BH$_4$)$_3$</td>
<td>9.4</td>
<td>0.115</td>
</tr>
<tr>
<td>NaCat(BH$_4$)$_3$</td>
<td>11.2</td>
<td>0.129</td>
</tr>
<tr>
<td>LiY(BH$_4$)$_3$</td>
<td>10.4</td>
<td>0.033</td>
</tr>
<tr>
<td>LiCa(BH$_4$)$_3$</td>
<td>13.2</td>
<td>0.052</td>
</tr>
<tr>
<td>LiSc(BH$_4$)$_3$</td>
<td>14.5</td>
<td>0.143</td>
</tr>
<tr>
<td>NaCd(BH$_4$)$_3$</td>
<td>6.7</td>
<td>0.003</td>
</tr>
<tr>
<td>K Nb(BH$_4$)$_3$</td>
<td>8.4</td>
<td>0.016</td>
</tr>
<tr>
<td>NaV(BH$_4$)$_3$</td>
<td>12.1</td>
<td>0.076</td>
</tr>
<tr>
<td>NaAg(BH$_4$)$_3$</td>
<td>5.0</td>
<td>0.193</td>
</tr>
<tr>
<td>LiC d(BH$_4$)$_3$</td>
<td>7.4</td>
<td>0.102</td>
</tr>
<tr>
<td>K Cr(BH$_4$)$_3$</td>
<td>10.7</td>
<td>0.199</td>
</tr>
<tr>
<td>LiV(BH$_4$)$_3$</td>
<td>13.8</td>
<td>0.061</td>
</tr>
<tr>
<td>NaCr(BH$_4$)$_3$</td>
<td>12.0</td>
<td>0.050</td>
</tr>
<tr>
<td>K Pd(BH$_4$)$_3$</td>
<td>6.4</td>
<td>0.047</td>
</tr>
<tr>
<td>K Mo(BH$_4$)$_3$</td>
<td>8.3</td>
<td>0.185</td>
</tr>
<tr>
<td>K Ru(BH$_4$)$_3$</td>
<td>6.5</td>
<td>0.168</td>
</tr>
<tr>
<td>Na Mo(BH$_4$)$_3$</td>
<td>9.0</td>
<td>0.056</td>
</tr>
<tr>
<td>Li Cr(BH$_4$)$_3$</td>
<td>13.6</td>
<td>0.029</td>
</tr>
<tr>
<td>NaPd(BH$_4$)$_3$</td>
<td>7.0</td>
<td>0.052</td>
</tr>
</tbody>
</table>

\[ \Delta E_{\text{decomp}} = E_{\text{LiMn(BH}_4)_3} - (E_{\text{LiH}} + E_{\text{Mn}} + 3E_{\text{B}} + 5.5E_{\text{H}_2}) \]

(2)

In this definition, $\Delta E_{\text{decomp}}$ estimates the stability of the alloy against decomposition. Transition metal hydrides, metal borides, higher order boranates and diborane, which may potentially form, are thus not taken into consideration in this first screening.

The analysis is based on the ground state energies only. Although the difference in vibrational entropy between hydrogen in an alkali metal borohydride and in the gas phase is often significantly smaller than in conventional metal hydrides, the contributions to the free energy from the vibrational entropy may be significant.

A stability range of $\Delta E_{\text{alloy}} \leq 0.0$ eV/f.u. (formula unit) and $\Delta E_{\text{decomp}} \leq \{-0.5, 0.0\}$ eV/H$_2$ is used to select the most interesting alloys with $\Delta E_{\text{decomp}} \leq -0.2$ eV/H$_2$ as the target value (see Table II), but given the idealized screening criteria in Eqs. (1) and (2), alloys with only small instabilities, i.e., $\Delta E_{\text{alloy}} \leq 0.2$ eV/f.u. and $\Delta E_{\text{decomp}} \leq 0.0$ eV/H$_2$ should not be discarded a priori (see Table III).

V. RESULTS

As the first step of the stability screening, we have plotted the alloying energy against the decomposition energy of the 757 investigated alloys (see Fig. 3). Most of the alloys are found to be stable against decomposition, but the majority are found to be unstable against separation into their binary components ($\Delta E_{\text{alloy}} > 0.0$ eV/f.u.). Many are still within the 0.2 eV/f.u. boundary regime. The lithium-containing alloys (red) are less stable against decomposition than those containing sodium (blue) and potassium (green). Restricting the plot to only the most stable structure for each
energy, expected for real systems as previously observed for
choice of simple template structures; higher densities are ex-
pected around that of liquid hydrogen, which is largely due to the

\(M_1M_2\) system (see Fig. 4) seems to support this observation,
and yields a total of 22 stable alloys (see Table II). Figure 4
is dominated by alloys where (a) both metal atoms are tetra-
hedrally coordinated to the borohydride groups (\(\square\)), (b) one
is tetrahedral the other trigonal (\(\bigtriangleup\)), and (c) so-called other
(\(<\)), where all constraints have been lifted. Some octa-tetra
(\(\bigtriangleup\)) and tetra-octa (\(<\)) are also observed.

Plotting the hydrogen density of the stable alloys,
\(\Delta E_{\text{alloy}} \leq 0.0\) eV/f.u. and \(\Delta E_{\text{decomp}} \leq 0.0\) eV/H\(_2\), Fig. 5
shows that alloys containing potassium (in green) are found to
have the lowest density, followed by sodium (in blue) and lithium (in red), as expected. The overall density is found to be
around that of liquid hydrogen, which is largely due to the
choice of simple template structures; higher densities are ex-
pected for real systems as previously observed for Mg(BH\(_4\)\(_2\)).

Alloys containing Al, Mn, Fe, and Zn are found to be stable for all alkali metals screened, whereas those

\(\Delta E_{\text{decomp}}\) in Fig. 6. Here, the data from the binary reference
structures have also been included, and it is clearly seen that the
stability has been reduced significantly compared to the
highly stable binary borohydrides. Most alloys have storage
capacities above the DOE 2015 system target of 9 wt %
(Ref. 3) and several also have favorable stabilities. A number of
these ternary borohydrides have been synthesized either

\[\text{Mg(BH}_4\text{)}\] based on Co, Ni, Nb, and Rh are stable for two out of three
alkali metals. The only other stable alloys are KCd(BH\(_4\))\(_3\)
and LiNa(BH\(_4\))\(_2\) (see Table II).

The storage capacity (wt % hydrogen) of the stable alloys is plotted as a function of the decomposition energy,
\(\Delta E_{\text{decomp}}\), in Fig. 6. Here, the data from the binary reference
structures have also been included, and it is clearly seen that the
stability has been reduced significantly compared to the
highly stable binary borohydrides. Most alloys have storage
capacities above the DOE 2015 system target of 9 wt %
(Ref. 3) and several also have favorable stabilities. A number of
these ternary borohydrides have been synthesized either

\[\text{LiMg(BH}_4\text{)}\]
very recently or historically (circled in Figs. 5 and 6). Of the experimentally observed stable/metastable structures, LiSc(BH$_4$)$_4$,$^{10}$ KNa(BH$_4$)$_2$, $^{12}$ and Li$_2$Cd(BH$_4$)$_4$ (Ref. 30) show a weak preference for phase separation, but are all found to be potentially stable (see Table III); only LiK(BH$_4$)$_2$ (Ref. 33) ($\Delta E_{\text{alloy}}$ = 0.202 eV/f.u. and $\Delta E_{\text{decomp}}$ = −0.645 eV/H$_2$) and LiNi(BH$_4$)$_2$ (Ref. 30) ($\Delta E_{\text{alloy}}$ = −0.104 eV/f.u. and $\Delta E_{\text{decomp}}$ = 0.069 eV/H$_2$) fall marginally outside the selection criteria. Furthermore, LiMn(BH$_4$)$_3$ and NaMn(BH$_4$)$_3$ are found experimentally to decompose at \(-100\) and \(110\) °C, $^{34}$ and LiZn(BH$_4$)$_3$ and LiAl(BH$_4$)$_3$ are found to disproportionate at \(-130\) °C. $^{35}$ These are all structures that are located near the optimal stability in the figure (the nonshaded region).

VI. TRENDS

Given the systematic approach to the screening study it is also possible to extract information from the database about possible trends and correlations, in order to search for predictors and descriptors $^{35}$ for the design of future quaternary alloys or alloys with different cation stoichiometries.

A. 3d and 4d transition metals

The stability of the alloys, as produced by the most stable \(x=3\) and \(x=4\) initial template structures before the free relaxation, is presented for all 3d transition metals (plus Mg, Ca, and Al) in Fig. 7, and for the 4d transition metals in Fig. 8. A clear preference for the \(M_1M_2(BH_4)_4\)-tetra template is observed, which is somewhat surprising, because many of the transition metals have an oxidation state of II in the reference calculations (see Table I). This apparent discrepancy could result from partially non-ionic bonding in these structures, meaning that the coordination of the hydrogen atoms to the metal is the determining factor, not whether the metal has the “correct” valence. For instance, we find no significant energy difference between Fe$_3$(BH$_4$)$_3$ and Fe(BH$_4$)$_2$ as long as the H atoms are octahedrally coordinated to the Fe atom.

Size effects also become apparent here since the \(M_1M_2(BH_4)_4\)-tetra template is the only template structure that allows the coordination polyhedra of \(M_1\) and \(M_2\) to be relaxed independently. This is supported by the larger spacing between most of the Li, Na, and K alloy energies produced by the other template structures (see Figs. 7 and 8).

To investigate this further, the \(M_1M_2(BH_4)_3\)-tetra/tri-template was applied to all alloys, and in Figs. 9 and 10, the final alloy stabilities are presented; these also include the free relaxation and the additional \(x=2\) and \(x=5\) calculations. It is seen that the \(M_1M_2(BH_4)_3\)-tetra/tri-structures now become the most stable for a number of alloys and that the Li, Na, and K points lie closer indicating a reduction in the size effects.

There is a general agreement between valencies in the reference calculations and the alloys; divalent metals are
found to prefer a $M_1M_2(BH_4)_3$ configuration, whereas trivalent metals prefer $M_1M_2(BH_4)_3$ and the monovalent Cu and Ag prefer $M_1M_2(BH_4)_2$. Some deviations are found, but given the simple model structures used for both alloys and reference calculations, and given the fact that some of the metals are found by experiments to form ternary borohydrides in different oxidation states, the agreement is good.

The most stable alloys are found for the half-filled $d$-bands, but interesting alloys are also found for the empty and fully occupied $d$-bands with the addition of Al, where the $M_1Al(BH_4)_4$ are found to be promising (see Figs. 9 and 10).

Lithium-based alloys (red) are generally found to be the most stable, followed by sodium (blue) and potassium (green), although significant deviations are observed. This follows the observed trend for the storage capacities.

**B. Stability versus electronegativity**

A number of recent publications have shown an apparent linear correlation between the decomposition temperature and the average cation Pauling electronegativity. Although this might be expected, given the definition of Pauling’s electronegativity, it also indicates that the kinetic barriers—if any—do not appear to be particularly system dependent.

Plotting the calculated decomposition energy as a function of the average Pauling electronegativity for all alloys in their preferred $M_1M_2(BH_4)_x$, coordination (see Fig. 11) appears to support this observation. The scatter of the data points around the “line” (which would have a slope that agrees with Ref. to within 10%–15%) is, however, significant and deviations of ±0.1 eV/H$_2$ can be sufficient to shift a material from interesting to irrelevant for storage applications, or vice versa.

The stable alloys ($\Delta E_{\text{decomp}} \leq 0.0$ eV/f.u.) are seen to cluster around certain average electronegativities of 1.3–1.4 and 1.6 (see Fig. 12). The cluster around 1.3–1.4 is highly promising with $\Delta E_{\text{decomp}} \approx -0.1$ eV/H$_2$ for Mn and Nb and particularly promising for Al, Zn, and Fe with $\Delta E_{\text{decomp}} \approx -0.3$ eV/H$_2$. The Mo and Rh alloys at electronegativities around 1.6 are found to border on decomposition, but experimental work by Nikels et al. estimates the decomposition temperature of such compounds to be around 150 °C.

**VII. CONCLUSIONS**

We have analyzed the thermodynamic properties of possible alkali-transition metal borohydride systems, finding a number of candidates showing favorable properties.

The $M_1(Al/Mn/Fe)(BH_4)_x$, $(Li/Na)Zn(BH_4)_3$, and $(Na/K)(Ni/Co)(BH_4)_3$ alloys are found to be the most promising, followed by selected $M_1(Nb/Rh)(BH_4)_4$ alloys. These findings are in good agreement with experimental observations for LiFe(BH)$_3$, LiAl(BH)$_4$, (Li/Na)Mn(BH)$_3$, and others.
and (Li/Na)Zn(BH₄)₃, 39 whereas the Co, Cd, Nb, and Rh alloys still remain to be synthesized and tested. Although some structures can be observed experimentally in different metal-metal stoichiometries than those used in the screening study, e.g., the Li–Zn system, 39 the alloy systems were still identified as promising candidates in this screening study. Some of the recently stable compounds in Table III, e.g., LiSc(BH₄)₄ (Ref. 10) and KNa(BH₄)₂ (Ref. 32) have recently been found to be metastable, while LiNi(BH₄)₃ (Ref. 30) was found to be marginally unstable here. The LCS approach was found to limit the 757 potential alloys to 22 promising candidates of which ~10 are highly promising. These structures can now be pursued further, analyzing their detailed decomposition pathways, both theoretically 40 and experimentally.

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