First principles study of the crystal structure and dehydrogenation pathways of Li$_4$BN$_3$H$_{10}$

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Using density functional theory we examine the crystal structure and the finite-temperature thermodynamics of formation and dehydrogenation for the new quaternary hydride Li$_4$BN$_3$H$_{10}$. Two recent studies based on X-ray and neutron diffraction have reported three bcc crystal structures for this phase. While these structures possess identical space groups and similar lattice constants, internal coordinate differences result in bond length discrepancies as large as 0.2 Å. Geometry optimization calculations on the experimental structures reveal that the apparent discrepancies are an artifact of X-ray interactions with strong bond polarization; the relaxed structures are essentially identical. Regarding reaction energetics, the present calculations predict that the formation reaction 3 LiNH$_2$ + LiBH$_4$ $\rightarrow$ Li$_4$BN$_3$H$_{10}$ is exothermic with enthalpy $\Delta H^{\text{T=550K}}$ $\approx$ $-$11.8 kJ/(mol f.u.), consistent with reports of spontaneous Li$_4$BN$_3$H$_{10}$ formation in the literature. Calorimetry experiments have been reported for the dehydrogenation reaction, but have proven difficult to interpret. To help clarify the thermodynamics we evaluate the free energies of seventeen candidate dehydrogenation pathways over the temperature range $T$ = 0–1000 K. At temperatures where H$_2$-release has been experimentally observed ($T$ $\approx$ 520–630 K), the favored dehydrogenation reaction is Li$_4$BN$_3$H$_{10}$ $\rightarrow$ Li$_4$BN$_3$ + LiNH$_2$ + 4H$_2$, which is weakly endothermic ($\Delta H^{\text{T=550K}}$ = 12.8 kJ/(mol H$_2$)). The small calculated $\Delta H$ is consistent with the unsuccessful attempts at re-hydridation reported in the literature, and suggests that the moderately high temperatures needed for H-desorption result from slow kinetics.

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I. INTRODUCTION

Recent efforts to improve the efficiency and reduce the environmental impact of automobile transport have focused on hydrogen-based fuel cells (FC) and internal combustion engines (H$_2$ICE) as possible replacements for current technologies powered by fossil-fuels. A significant obstacle to realizing this transition is the on-board storage of hydrogen at high gravimetric and volumetric densities. To achieve the storage densities necessary for mobile applications, novel means for H-storage are necessary, and a set of targets have been established to guide the search for new storage systems. At present no known storage material or mechanism meets these targets.

One promising avenue for efficient storage of hydrogen is via solid state storage, such as in the form of complex- or metal-hydrides. Solid storage has the advantage of providing volumetric densities beyond what can be achieved with compressed H$_2$ gas or cryogenic liquid storage. However, all known hydrides suffer from one or more of the following limitations: low gravimetric densities, high H-desorption temperatures, or an inability to be easily re-hydrided. The search for new hydrides that overcome these limitations has attracted intense interest during the past 5 years.

Towards these ends, recent experiments by Pinkerton and co-workers and Aoki et al. on the H-storage properties of the quaternary Li-B-N-H system are noteworthy. By mixing lithium borohydride (LiBH$_4$) and lithium amide (LiNH$_2$), both groups have reported the formation of a new hydride phase, which when heated above 520 K released approximately 10 wt.% hydrogen. While the reported desorption temperature is somewhat too high, and reversibility has not yet been demonstrated, improvement in these areas may be possible (and has been partially demonstrated) by the addition of catalytic dopants or via novel synthetic routes, suggesting that further study of this system is warranted.

The composition of the new Li-B-N-H phase was preliminarily identified as “Li$_3$BN$_3$H$_5$,” but subsequent experiments based on single crystal X-ray diffraction and, synchrotron X-ray and neutron powder diffraction identified its true stoichiometry as Li$_4$BN$_3$H$_{10}$. Combined, these diffraction experiments identify three similar crystal structures, all sharing the bcc space group $I2_1$3 with lattice constant $a$ = 10.66–10.68 Å, but with somewhat different internal coordinates. The discrepancy in atomic positions results in N-H bond lengths that differ between structures by as much as 0.2 Å.

A careful characterization of a hydride’s crystal structure is desirable because it enables an independent, ab initio assessment of the thermodynamics of hydrogen desorption/absorption reactions. Such an assessment is of value because it can clarify the thermodynamics when calorimetry measurements yield ambiguous results, such as in situations where multiple reactions occur simultaneously (see below). A key thermodynamic property which determines the suitability of a hydride for H-storage applications is the strength of the hydrogen-host bond. The bond strength is quantified via the change in enthalpy ($\Delta H$) occurring during hydrogen uptake/release. In mobile FC applications, for example, it is desirable that the desorption reaction be endothermic ($\Delta H > 0$) with $\Delta H$ $\approx$ 20–50 kJ/(mol H$_2$). Neglecting kinetics, an enthalpy in this range would allow for H-desorption at temper-
Unfortunately, calorimetric measurements of H-desorption in Li₄BN₃H₁₀ have been difficult to interpret. (See Refs. 6 and 8, and the supplementary information accompanying Ref. 4.) Because Li₄BN₃H₁₀ melts at ~460 K, approximately 60 degrees below the onset of H-desorption, hydrogen gas evolves from the liquid state. Concurrent with H₂ release is the formation of a solid reaction product, generally involving one or more polymorphs of Li₃BN₂ along with other unidentified phases and desorption of 2-3 mol % ammonia. Measurements based on differential scanning calorimetry (DSC) and differential thermal analysis (DTA) suggest that the net heat flow during dehydrogenation is exothermic (ΔH < 0). However, it is unclear what fraction of the total thermal profile arises from the exothermic latent heat of Li₃BN₂ solidification and furthermore how H₂ and NH₃ release impacts the calorimeter response. Consequently, it has been impossible to unambiguously assess the endo- or exothermic nature of H-desorption alone. Neglecting kinetic effects, the fact that it has proven very difficult to re-hydrate Li₄BN₃H₁₀ suggests desorption is weakly endothermic, or exothermic. Regarding Li₃BN₂H₁₀ formation, several studies have reported the spontaneous formation of Li₃BN₃H₁₀ after mixing LiBH₄ with LiNH₂, even at temperatures as low as room temperature, suggesting that the formation reaction is exothermic.

In light of the discrepancy noted above regarding the crystal structure of Li₄BN₃H₁₀, and the additional ambiguity surrounding its dehydrogenation thermodynamics, we employ density functional theory (DFT) calculations in an attempt to clarify these issues. First, we determine the ground state crystal structure by performing separate geometry optimization calculations on each of the experimentally proposed crystal structures. We find that the relaxed structures are essentially identical, and have N-H bond lengths that are consistent with the structure based on neutron diffraction thus confirming the conjecture that the anomalously short N-H bond lengths observed in Ref. 11 are an artifact of X-ray measurements. Second, we evaluate the finite-temperature reaction enthalpies and free energies for the formation and dehydrogenation of Li₄BN₃H₁₀. Li₄BN₃H₁₀ formation (with respect to LiNH₂ and LiBH₄) is found to be exothermic, in agreement with experimental reports of spontaneous Li₄BN₃H₁₀ formation in the literature. For H₂-desorption we explore the thermodynamics of seventeen candidate reactions over the temperature range 0–1000 K, as there appears to be some uncertainty in determining the reaction products experimentally. At temperatures where desorption has been reported (~520–630 K), the favored reaction is predicted to be Li₄BN₃H₁₀ → Li₃BN₂ + LiNH₂ + 4 H₂, which is weakly endothermic. Moreover, the calculated free energies suggest Li₄BN₃H₁₀ is a metastable phase that should decompose via one of three temperature-dependent pathways.

**II. METHODOLOGY**

First-principles calculations were performed using a planewave method based on the PW91 generalized gradient approximation to density functional theory (VASP). The core-valence electron interaction was treated using Blöchl’s projector augmented wave (PAW) method and k-point sampling was performed on a dense Monkhorst-Pack grid with an energy convergence of better than 1 meV per supercell. (In the case of Li₄BN₃H₁₀, a 2 × 2 × 2 grid was sufficient to achieve this level of precision.) Electronic occupations were determined via a gaussian smearing algorithm with a 0.1 eV smearing width. For high-precision calculation of static zero Kelvin (omitting zero point vibrational effects) electronic energies and crystal structures we used the so-called “hard” VASP PAW potential with a planewave cutoff of 875 eV, and a geometry relaxation tolerance of better than 0.02 eV/Å. Internal atomic positions and external cell shape/volume were optimized simultaneously.

Finite-temperature thermodynamics were evaluated within the harmonic approximation. Vibrational frequencies (ωᵢ) were extracted by diagonalizing a dynamical matrix whose elements were determined via the so-called direct method. The forces generated by series of symmetry inequivalent atomic displacements about the equilibrium geometry (±0.02 Å, ±0.04 Å) were fit to cubic splines in order to extract the force constants. Because large supercells are desirable to minimize finite-size effects, and with the exception of the molecular species (H₂, N₂, NH₃) where the number of atoms per supercell is small, the dynamical matrix calculations on the solid-state phases were preformed using a softer set of PAW potentials and planewave cutoff energies ranging from 400–500 eV. A comparison of calculated structural parameters and formation energies with existing experimental and theoretical data is presented in the following section.

Once the normal-mode frequencies have been determined, finite-temperature energetics can be obtained by enthalpic (Hₘₜ) and entropic (Sₘₜ) additions to the static electron energies. Within the harmonic approximation these contributions are given by

\[ H_{\text{vib}}(T) = \sum_{i} \frac{1}{2} \hbar \omega_{i} + \hbar \omega_{i} \left( \exp\left( \frac{\hbar \omega_{i}}{k_{B} T} \right) - 1 \right)^{-1} \]  \hspace{1cm} (1)

\[ S_{\text{vib}}(T) = k_{B} \sum_{i} \frac{\hbar \omega_{i}}{k_{B} T} \exp\left( \frac{\hbar \omega_{i}}{k_{B} T} \right) - 1 - \ln \left[ 1 - \left( \exp\left( \frac{\hbar \omega_{i}}{k_{B} T} \right) \right) \right] \]  \hspace{1cm} (2)

where the sums run over vibrational frequencies (3N – 3 frequencies for solids and non-linear molecules, 3N – 5 frequencies for linear molecules), kₜ is the Boltzmann factor, and T is the absolute temperature. For the linear (non-linear) molecules an additional \( \frac{1}{2} k_{B} T (3k_{B} T) \) term is added to Eq. 1 to account for translational, rotational, and ° degrees of freedom. The zero point energy (ZPE) can be recovered from Eq. 1 in the limit \( H_{\text{vib}}(T = 0) \). The enthalpy and free energy...
of a phase can therefore be expressed as:

\[ H(T) = E + H_{\text{ vib}}(T) \]  
(3)

\[ G(T) = H(T) - S(T)T, \]  
(4)

where \( E \) is the static electronic energy of the crystal/molecule in its ground-state geometry and \( S \) represents either the standard tabulated entropy of a given molecular species in the gas phase at \( p = 1 \text{ bar} \) \( S_{0}^{\text{gas}} = 130.858 \text{ (H2), 191.789 (N2), and 192.995 J K^{-1} mol^{-1} (NH3)} \), or the vibrational entropy \( S_{\text{ vib}} \) of a solid state phase.

### III. CRYSTAL STRUCTURE

The crystal structure of Li2BN3H10 has been studied by two groups. Filinchuk and co-workers used single-crystal X-ray diffraction to identify the structures of the two largest crystal domains obtained after remelting a 2:1 mixture of LiNH2 and LiBH4. Both domains exhibited a bcc structure (space group \( I2_{1}/3 \)) with lattice constants of \( 10.67-10.68 \text{ Å} \). Chater et al.\(^{12}\) used a combination of high-resolution synchrotron X-ray and neutron diffraction to examine powder samples prepared from a wide range of LiNH2-LiBH4 compositions. They determined that although the most likely stoichiometric composition was \( 3:1 \), the Li2BN3H10 structure was able to accommodate a wide range of stoichiometries. Their best-fit crystal structure had external cell parameters similar to those reported in Ref. 11: bcc (space group \( I2_{1}/3 \)) with \( a = 10.66 \text{ Å} \). Despite the good agreement in external geometries, the structures obtained by these two studies differ markedly in their internal coordinates. Most notably, the single-crystal X-ray diffraction study\(^{11}\) found anomalously short N-H bond lengths of \( 0.83-0.86 \text{ Å} \), while neutron scattering\(^{12}\) gave lengths of \( 0.98-1.04 \text{ Å} \).

The external cell parameters obtained upon relaxing each of the three Li2BN3H10 experimental structures (as well as the structures of the other phases used in our subsequent discussion of reaction thermodynamics) are summarized in Table I. The resulting structures are bcc and share the same lattice constant, \( a = 10.60 \text{ Å} \), in good agreement with both diffraction studies.

For each of the three relaxed structures, Table I compares the calculated internal atomic coordinates with the corresponding experimental values. We note first that the average absolute deviation (\( \delta \)) between theory and experiment is smallest for the neutron structure\(^{12}\), \( \delta = 3.6 \times 10^{-3} \text{, whereas for the X-ray structures} \) \( \delta = 4.4 \times 10^{-3} \text{ and} \delta = 4.2 \times 10^{-3} \text{ for domains 1 and 2, respectively. The largest discrepancy between theory and experiment is in the positions of the N-bonded hydrogen atoms, H1 & H2, in the X-ray structure. (Note that the labeling convention for hydrogens is different in the neutron structure: here H1 & H2 refer to B-bonded hydrogens.) Secondly, while there appear to be large differences in the internal coordinates measured by Refs. 11 and 12 (Table I), after relaxation these three structures may be mapped onto one another via a series of rigid body rotations and translations. We conclude that all three experimental structures relax to essentially the same structure.

A comparison of calculated bond lengths, bond angles, and intermolecular distances is given in Table III. Overall, the relaxed structures agree best with the intramolecular lengths (i.e., within an NH2 or BH4 fragment) determined using neutron diffraction; conversely, the intermolecular distances from X-ray are closest to those in the relaxed theoretical structures. As for the intramolecular structure, as noted above, the major discrepancy between the experimental structures lies in the two N-H bond lengths, \( d(\text{N-H}) \), in the NH2 fragment. The calculated length of \( 1.027 \text{ Å} \) is in better agreement with the longer bond lengths predicted by neutron diffraction of 0.983 and 1.042 Å. Similarly, the X-ray data also underestimates B-H bond lengths in the BH4 units relative to our DFT calculations and neutron data. Calculated bond angles agree best with those from the neutron structure.
TABLE II: Calculated relaxed internal atomic positions of Li$_4$BN$_3$H$_{10}$ compared with experimental measurements from Refs. [11,12].

| Atom | Calculated | Experiment |
|------|------------|------------|
| N    | 0.117      | 0.362      | 0.402 | 0.115 | 0.359 | 0.405 |
| B    | 0.113      | 0.113      | 0.113 | 0.114 | 0.114 | 0.114 |
| Li1  | 0.281      | 0.000      | 0.250 | 0.287 | 0.000 | 0.250 |
| Li2  | 0.519      | 0.000      | 0.250 | 0.524 | 0.000 | 0.250 |
| Li3  | 0.484      | 0.484      | 0.484 | 0.483 | 0.483 | 0.483 |
| H1   | 0.195      | 0.306      | 0.393 | 0.175 | 0.310 | 0.397 |
| H2   | 0.118      | 0.415      | 0.321 | 0.115 | 0.405 | 0.339 |
| H3   | 0.003      | 0.118      | 0.147 | 0.012 | 0.119 | 0.146 |
| H4   | 0.180      | 0.180      | 0.180 | 0.172 | 0.172 | 0.172 |

TABLE III: Comparison of calculated atomic distances and angles with values determined from single-crystal X-ray diffraction (Ref. [11]) and synchrotron X-ray and neutron powder diffraction (Ref. [12]). Lengths ($d$) are given in Å, angles ($\angle$) are in degrees.

| Parameter                  | Ref. [11], domain 1 | Ref. [11], domain 2 | Ref. [12] |
|----------------------------|----------------------|----------------------|-----------|
| **Intramolecular Values**  |                      |                      |           |
| $d$(N-H) ($i$)             | 1.027                | 0.83(2)              | 1.027     | 0.84(2) | 1.027 | 0.983 |
| $d$(N-H) ($ii$)            | 1.027                | 0.859                | 1.026     | 0.852  | 1.027 | 1.042 |
| $d$(B-H) ($i$)             | 1.223                | 1.08(3)              | 1.225     | 1.11(3) | 1.224 | 1.169 |
| $d$(B-H) ($ii$) $\times$3 | 1.225                | 1.137                | 1.225     | 1.121  | 1.223 | 1.270 |
| $\angle$(H-N-H)            | 103.5                | 106.2                | 103.5     | 105.9  | 103.5 | 104.9 |
| $\angle$(H-B-H) $\times$3 ($i$) | 108.0              | 108.9                | 107.9     | 109.2  | 107.9 | 107.6 |
| $\angle$(H-B-H) $\times$3 ($ii$) | 110.9              | 111.0                | 111.0     | 109.8  | 111.0 | 111.3 |
| **Intermolecular Values**  |                      |                      |           |
| $d$(N-Li) ($i$)            | 2.071                | 2.069                | 2.069     | 2.068  | 2.070 | 2.033 |
| $d$(N-Li) ($ii$)           | 2.116                | 2.115                | 2.111     | 2.113  | 2.110 | 2.053 |
| $d$(N-Li) ($iii$)          | 2.138                | 2.117                | 2.138     | 2.119  | 2.142 | 2.094 |
| $d$(N-Li) ($iv$)           | 2.164                | 2.157                | 2.164     | 2.157  | 2.169 | 2.209 |
| $d$(B-Li) ($i$)            | 2.371                | 2.410                | 2.375     | 2.406  | 2.368 | 2.527 |
| $d$(B-Li) ($ii$) $\times$3 | 2.595                | 2.651                | 2.592     | 2.642  | 2.589 | 2.681 |

IV. REACTION ENERGETICS

In order to examine the finite-temperature thermodynamics of reactions involving Li$_4$BN$_3$H$_{10}$, it was first necessary to calculate the ground-state structures of the phases that participate in those reactions. A summary of the compounds used, their crystal structures, and a comparison of the calculated structures to experimental data is presented in Table II. In general the agreement between experiment and theory is very good.

Some of the compounds listed in Table II are known to have several polymorphs. For example, at least three polymorphs have been reported for Li$_3$BN$_2$ [31,32,37,38] including low-temperature tetragonal ($\alpha$) [31], high-temperature mon-
as a function of temperature. Due to their similar vibrational spectra, all three of these phases have been observed as dehydrogenation products for Li$_3$BN$_2$(bc) and we have performed calculations on each phase to determine its relative stability as a function of temperature. The β-Li$_3$BN$_2$ phase was found to have the lowest zero-Kelvin static energy, ≈ 2 kJ/mol(f.u.) lower than that of either the bct or α phases. The latter two phases are degenerate in energy to within 0.1 kJ/mol(f.u.). Our zero-Kelvin energetics and structures agree well with recent calculations reported by Pinkerton and Herbst.

Vibrational contributions to the energies of each Li$_3$BN$_2$ polymorph were evaluated within the harmonic approximation. For α-Li$_3$BN$_2$ a careful evaluation of the vibrational spectra yielded doubly-degenerate imaginary modes at 81 cm$^{-1}$, indicating that this phase is unstable at low temperatures. A search for alternative low-energy α-Li$_3$BN$_2$ structures was performed using molecular dynamics (md) on an enlarged (2 × 2 × 2) α-Li$_3$BN$_2$ supercell at T = 423 K for 10 ps. At 1 ps intervals the current md configuration was stored, relaxed, and the symmetry of the resulting optimized structure was determined. Four unique crystal structures were identified, with space groups (numbers): P2$_1$2$_1$2$_1$ (19), Pcen (56), Pmma (59), and Pnma (62). These structures were then relaxed within their symmetry constraints, and were found to have energies ~1 kJ/mol(f.u.) lower than the original α-Li$_3$BN$_2$ structure [which is still 1 kJ/mol(f.u.) higher in energy than β-Li$_3$BN$_2$]. In light of these results we suggest that the crystal structure of α-Li$_3$BN$_2$ be experimentally re-assessed, and we exclude this phase from our evaluation of Li$_3$BN$_2$ dehydrogenation reactions. Further information regarding our proposed structure of α-Li$_3$BN$_2$ can be found elsewhere.

Unlike α-Li$_3$BN$_2$, no imaginary modes were observed in the vibrational spectra of β or bct Li$_3$BN$_2$. Using Eqs. [1,2] Fig. 1 plots the Gibbs free energies (Eq. 3) of these phases as a function of temperature. Due to their similar vibrational contributions (Table IV), the free energies of the β and bct phases exhibit nearly identical temperature dependence. Consequently, the small ~2 kJ/mol(f.u.) difference in static energies noted above is sufficient to favor the monoclinic β phase as the ground state structure, and the bct-β energy difference remains roughly constant for T < 1000 K. Based on the vibrational instability observed in α-Li$_3$BN$_2$, and the higher free energy of bct Li$_3$BN$_2$ (relative to β-Li$_3$BN$_2$), our subsequent thermodynamic analyses are performed assuming Li$_3$BN$_2$ resides in the low-energy β structure.

The zero-point, enthalpic, and entropic contributions to the free energy of the various phases are summarized in Table IV. As a further test of our computational methodology, there we also compare our calculated ZPE to other values reported in the literature, and find good agreement. With the exception of Li, vibrational effects are found to contribute substantially to the free energies of these systems. For example, in Li$_3$BN$_2$ the ZPE exceeds 300 kJ/mol.

A comparison of formation energies for the compounds used in this study (relative to the elements in their standard states) is presented in Table V. Three reports based on DFT calculations have also recently evaluated formation energies for some of these compounds, and the present calculations are in good agreement with their findings. Furthermore, the agreement with experimental enthalpies is reasonable (generally on the order of 10%), which is representative of the accuracy obtained via density functional methods for reactions involving molecular species. As expected, the largest percentage discrepancy is for the ammonia molecule. Two general trends in the data are evident: (i) With the exception of ammonia, the DFT enthalpies ($\Delta H^{T=300K}$) are more positive than the experimental values, and (ii) the inclusion of dynamical contributions ($\Delta E \rightarrow \Delta H^{T=300K}$) results in more

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**TABLE IV: Calculated vibrational contributions (at T = 300K)** to the free energies of phases used in this study. ZPE refers to the zero point energy, given by $H_{ vib}(T = 0) \approx E_{ vib} = H_{ vib} - ZPE$ (omitting the $k_{ B }T$ molecular terms); $S_{ vib}$ is the vibrational entropy, Eq 4. Units are kJ mol$^{-1}$ for ZPE and $E_{ vib}$, and J mol$^{-1}$ K$^{-1}$ for $S_{ vib}$.

| System   | ZPE | ZPE other | $E_{ vib} = 300K$ | $S_{ vib} = 300K$ |
|----------|-----|-----------|------------------|------------------|
| H$_2$    | 25.7| 25.3$^{32}$| 26.1$^{32}$     | 0 $^{300}$       |
| N$_2$    | 14.0| 14.4$^{30}$| 0 $^{300}$       | 0 $^{300}$       |
| NH$_3$   | 87.8| 89.7$^{33}$| 0.1 $^{300}$    | 0.4 $^{300}$    |
| Li      | 3.9 | 3.9$^{34}$ | 4.3 $^{300}$    | 27.7 $^{300}$   |
| B       | 12.5| 12.2$^{35}$| 1.1 $^{300}$    | 5.3 $^{300}$    |
| BN      | 29.9| 30.9$^{36}$| 8.9 $^{300}$    | 51.6 $^{300}$   |
| LiH     | 21.7| 21.4$^{37}$| 3.5 $^{300}$    | 17.7 $^{300}$   |
| Li$_3$N | 28.0| 28.6$^{38}$| 8.9 $^{300}$    | 51.6 $^{300}$   |
| LiNH$_2$| 69.0| 69.5$^{39}$| 9.6 $^{300}$    | 52.9 $^{300}$   |
| LiBH$_4$| 107.1| 106.5$^{40}$| 10.8 $^{300}$ | 63.6 $^{300}$   |
| Li$_3$BN$_2$ | 52.2 | 15.3 $^{41}$ | 37.0 $^{300}$ | 213.4 $^{300}$ |
| Li$_3$BN$_2$H$_{10}$ | 314.4 | 314.4 | 314.4 | 314.4 |

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FIG. 1: Calculated Gibbs free energies (in kJ/mol f.u.) of monoclinic (β) and body-centered tetragonal (BCT) Li$_3$BN$_2$ as a function of temperature. The energy zero is set to the static 0 K energy of β-Li$_3$BN$_2$. 
positive formation energies.

Using the energetic contributions from Table VI in Table VII we evaluate the thermodynamics for two Li$_3$BN$_3$H$_{10}$ formation reactions. Reaction (a) considers formation from the elemental phases in their standard states, and reaction (b) corresponds to the synthesis route employed in the literature involving a mixture of LiNH$_2$ and LiBH$_4$. (We consider only the stoichiometric 3:1 ratio of LiNH$_2$ to LiBH$_4$.) The energetics of each reaction are decomposed into a sequence having increasingly more physical contributions to the reaction thermodynamics, $\Delta E \to \Delta H^{T=0\text{K}} \to \Delta H^{T=300\text{K}} \to \Delta G^{T=300\text{K}}$, which allows us to gauge the importance of these contributions in comparison to the common practice of evaluating only static zero-Kelvin energetics. $\Delta E$ refers to differences in the static zero-Kelvin energies ($E$ in Eq. 3), and $\Delta H^{T=0\text{K}}$ adds ZPE contributions to $\Delta E$. Both formation reactions in Table VII are predicted to be exothermic ($\Delta H < 0$), in agreement with reports of spontaneous dehydrogenation reactions, $\Delta H_{\text{formation}}$ are significant in reaction (a) ($\Delta E \approx \Delta H$). By examining the values presented in Table VII for the phases participating in reaction (b) (Li$_3$BN$_3$H$_{10}$, LiNH$_2$, & LiBH$_4$) we see that these terms are sizable, but that they largely cancel out. This cancellation effect can be understood by the similarities in internal bonding shared by these three phases: Li$_3$BN$_3$H$_{10}$, with its Li$^+$, BH$_4^-$, and NH$_2^-$ ions is essentially an amalgam of the structures present in LiNH$_2$ and LiBH$_4$.

Turning now to the dehydrogenation of Li$_3$BN$_3$H$_{10}$, we note first that although several dehydrogenation products have been observed in experimental studies, the precise identity and respective proportions of these phases have not yet been definitively determined. For example, Aoki et al. reported unidentified diffraction peaks after dehydrogenation at $T \approx 25^\circ$ and $35^\circ$. A technique for predicting possible decomposition pathways would be of significant value in helping to understand these reactions. However, decomposition pathways and products are difficult to predict a priori. To this end, we have scanned through the thermodynamics of a large number of candidate dehydrogenation reactions over a wide temperature range in order to identify the energetically favored products.

Calculated thermodynamics for seventeen candidate Li$_3$BN$_3$H$_{10}$ dehydrogenation reactions are listed in Table VII. In addition to the room-temperature energetics, there we also present data for $T = 460$ K, which is slightly below the melting point of pure Li$_3$BN$_3$H$_{10}$. Unlike the Li$_3$BN$_3$H$_{10}$ formation reaction, which can proceed at room temperature, dehydrogenation of Li$_3$BN$_3$H$_{10}$ has been reported only at elevated temperatures. In the case of pure Li$_3$BN$_3$H$_{10}$, dehydrogenation occurs above $\sim 520$ K, about 60 degrees above the melting temperature. However, a significant reduction in dehydrogenation temperature was observed upon the addition of a small amount of a Pt/Vulcan carbon catalyst. In this latter case hydrogen release occurred from the solid phase at $T > 390$ K. To more completely assess the dehydrogenation thermodynamics over a range of relevant temperatures, in Fig. 2 we plot the enthalpies and free energies of the candidate reactions for $T = 0\text{--}1000$ K.

Out of the seventeen reactions considered, three reactions—(i), (c), and (f)—emerge as the most-favorable reactions in distinct temperature regimes (see Fig. 2 bottom panel). For low temperatures reaction (i) is preferred, followed at increasing temperatures by reaction (c) and reaction (f). More specifically, the favored products and their respective temperature ranges of stability are:

- $0 \leq T \leq 300$ K: 2LiNH$_2$ + 2LiH + BN + 2H$_2$
- 300 K $\leq T \leq 700$ K: Li$_3$BN$_2$ + LiNH$_2$ + 4H$_2$
- 700 K $\leq T \leq 970$ K: Li$_3$BN$_2$ + LiH + $\frac{1}{2}$N$_2$ + $\frac{3}{2}$H$_2$

The relatively large entropy of the gas phase products plays an important role in determining which reaction is favored at a given temperature. Reactions yielding greater quantities of gaseous products should be favored with increasing $T$, and this is consistent with the observed trend: reaction (i), 2 mols $\to$ reaction (c), 4 mols $\to$ reaction (f), 5 mols. (It should be noted that at high temperatures—and certainly above the melting point of Li$_3$BN$_3$H$_{10}$—the harmonic approximation will no longer be valid, so we expect some decrease in accuracy with increasing $T$.)

Of the three favorable dehydrogenation reactions, only reaction (c), Li$_3$BN$_3$H$_{10}$ $\to$ Li$_3$BN$_2$ + LiNH$_2$ + 4H$_2$, takes place within the temperature range where H$_2$-desorption (from undoped Li$_3$BN$_3$H$_{10}$) has been experimentally observed ($T \sim 520\text{--}630$ K). While our prediction of Li$_3$BN$_2$ as a dehydrogenation product is consistent with experimental observa-
TABLE VI: Formation energies of Li$_3$BN$_3$H$_{10}$ [in kJ/(mol Li$_3$BN$_3$H$_{10}$)]. $\Delta E$ corresponds to the static zero Kelvin DFT energies; $\Delta H^{T=0K}$ adds the zero point energies to $\Delta E$; $\Delta H^{T=300K}$ (Eq. 3) adds finite-temperature vibrational (and molecular rotational+translational+$pV$) energies to $\Delta H^{T=0K}$; $\Delta G^{T=300K}$ (Eq. 3) includes all of the contributions to $\Delta H^{T=300K}$ and adds vibrational (solids) or tabulated (molecular) entropies.

| Rxn. No. | Reaction | $\Delta E$ | $\Delta H^{T=0K}$ | $\Delta H^{T=300K}$ | $\Delta G^{T=300K}$ |
|----------|----------|-----------|-----------------|-----------------|-----------------|
| (a)      | 4 Li + B + $\frac{3}{2}$N$_2$ + 3H$_2$ $\rightarrow$ Li$_3$BN$_3$H$_{10}$ | -806.9 | -670.2 | -708.1 | -454.6 |
| (b)      | 3 LiNH$_2$ + LiBH$_4$ $\rightarrow$ Li$_3$BN$_3$H$_{10}$ | -11.3 | -11.2 | -11.8 | -10.2 |

TABLE VII: Calculated reaction energies [$\Delta E$ in kJ/(mol H$_2$)], enthalpies [$\Delta H$ in kJ/(mol H$_2$)], and free energies [$\Delta G$ in kJ/mol products] for candidate Li$_3$BN$_3$H$_{10}$ dehydrogenation reactions.

| Rxn. No. | Reaction | $\Delta E$ | $\Delta H^{T=0K}$ | $\Delta H^{T=300K}$ | $\Delta H^{T=460K}$ | $\Delta G^{T=300K}$ | $\Delta G^{T=460K}$ |
|----------|----------|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| (c)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_3$BN$_2$ + LiNH$_2$ + 4H$_2$ | 28.2 | 5.7 | 11.2 | 12.5 | -88.8 | -161.3 |
| (d)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_3$BN$_2$ + 4LiNH + $\frac{1}{2}$N$_2$ + 4H$_2$ | 40.6 | 17.7 | 23.4 | 24.3 | -61.4 | -145.2 |
| (e)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_3$BN$_2$ + LiH + N$_2$ + 3H$_2$ | 42.6 | 17.5 | 23.5 | 24.0 | -71.6 | -148.0 |
| (f)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_3$BN$_2$ + Li + $\frac{7}{2}$N$_2$ + 5H$_2$ | 50.2 | 24.1 | 29.7 | 30.8 | -82.8 | -131.0 |
| (g)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_3$BN$_2$ + Li + NH + $\frac{7}{2}$H$_2$ | 61.9 | 37.4 | 43.5 | 44.6 | 23.0 | -82.2 |
| (h)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_3$BN$_2$ + Li + NH$_2$ + $\frac{7}{2}$H$_2$ | 60.4 | 37.5 | 44.1 | 44.7 | -10.5 | -99.2 |
| (i)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ 2LiNH + 2LiH + BN + 2H$_2$ | 6.4 | -19.4 | -16.1 | -15.4 | -90.1 | -121.2 |
| (j)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ LiNH$_2$ + Li$_2$N + BN + 4H$_2$ | 56.9 | 35.8 | 40.5 | 41.3 | 34.1 | -34.9 |
| (k)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ 4LiH + BN + 3N$_2$ + 3H$_2$ | 79.6 | 44.1 | 48.5 | 48.8 | 11.1 | -60.7 |
| (l)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ 2Li$_2$NH + BN + 4H$_2$ | 45.3 | 23.3 | 27.9 | 28.8 | -14.9 | -83.3 |
| (m)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ 2Li$_2$NH + BN + 2Li + 3H$_2$ | 60.0 | 39.5 | 45.1 | 46.2 | 32.3 | -23.6 |
| (n)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ LiNH$_2$ + Li$_2$NH + LiH + BN + 3H$_2$ | 32.3 | 9.1 | 13.2 | 14.1 | -52.5 | -102.3 |
| (o)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_2$NH + 2LiH + BN + NH$_3$ + 2H$_2$ | 55.9 | 28.5 | 32.7 | 32.1 | -35.4 | -88.9 |
| (p)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ LiNH$_2$ + 3LiH + BN + NH$_3$ + H$_2$ | 27.7 | -9.1 | -6.6 | -8.8 | 73.0 | 107.9 |
| (q)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$^+$ + LiH + BN + NH$_3$ + 3H$_2$ | 80.9 | 57.7 | 62.6 | 62.4 | 51.3 | -21.6 |
| (r)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ $\frac{3}{2}$Li$_2$NH + Li$_2$N + BN + $\frac{1}{2}$NH$_3$ + 4H$_2$ | 69.3 | 47.8 | 52.7 | 53.2 | 61.5 | -18.8 |
| (s)      | Li$_3$BN$_3$H$_{10}$ $\rightarrow$ Li$_3$BN$_2$ + $\frac{5}{2}$Li$^+$ + $\frac{5}{2}$NH$_3$ + 4H$_2$ | 48.7 | 26.0 | 31.7 | 32.5 | -35.9 | -123.6 |

FIG. 2: (Color online) Calculated enthalpies ($\Delta H$, top panel) and free energies ($\Delta G$, bottom panel) of candidate Li$_3$BN$_3$H$_{10}$ dehydrogenation reactions as a function of temperature at $p = 1$ bar. The reactions are labeled as in Table VII.
ture is raised above 520 K. Taken together, these factors suggest that the relatively high temperatures needed in practice for H2-release are a consequence of poor kinetics, not unfavorable thermodynamics.

An important distinction between our calculations and the experimental dehydrogenation of undoped Li4BN3H10 concerns the phase of Li4BN3H10 present during the dehydrogenation reaction. As mentioned above, pure Li4BN3H10 releases hydrogen from the molten state. Similarly, H2 release from other hydride phases, such as LiBH4, also occurs from the molten state.\textsuperscript{4,5} Due to the computational expense associated with obtaining precise energetics for liquids using DFT, this study, and previous studies on LiBH4\textsuperscript{41,48} have modeled the dehydrogenation reaction as a solid-state reaction. Since the enthalpy of the liquid phase will be more positive than that of the corresponding solid phase, the calculated solid-state enthalpy of reaction (c) evaluated at the melting point ($T_{mp}$), $\Delta H_{T_{mp}}$ = 12.5 kJ/(mol H2), represents an upper bound on the enthalpy for desorption from liquid Li4BN3H10. It will be possible to more precisely estimate the magnitude by which $\Delta H$ is underestimated once the latent heat of melting for Li4BN3H10 has been measured. Until such data become available, it nevertheless seems reasonable to conclude that the dehydrogenation of Li4BN3H10 is either weakly endothermic, or exothermic. This conclusion is consistent with the failed attempts at re-hydriding Li4BN3H10 reported thus far in the literature\textsuperscript{5} as a small (positive) enthalpy of dehydrogenation will result in a similarly small thermodynamic driving force for re-hydriding. On the other hand, for Li4BN3H10 doped with Pt/Vulcan carbon,\textsuperscript{5} dehydrogenation begins below $T_{mp}$. In this case our approach of modeling solid state reactions more accurately captures the true phase behavior of Li4BN3H10, neglecting the possible formation of C- or Pt-containing compounds.

V. CONCLUSION

Density functional theory calculations have been employed to study the crystal structure and the finite-temperature formation and dehydrogenation thermodynamics of Li4BN3H10. The calculations have resolved the discrepancies in hydrogen bond lengths between the separate structures determined via X-ray and neutron diffraction experiments, and suggest that the neutron data yields a slightly more accurate description of the crystal structure. All three of the reported experimental crystal structures relax to essentially the same structure.

For reaction energetics, our calculations indicate that Li4BN3H10 formation is exothermic, and that the dehydrogenation enthalpy of solid-state Li4BN3H10 is temperature-dependent: H2 release is exothermic at low temperatures, and weakly endothermic at the higher temperatures probed by recent experiments. A non-zero latent heat for Li4BN3H10 melting will reduce the dehydrogenation enthalpy from the liquid state (relative to the solid state), but the size of this effect is still to be determined. To help clarify the identity of the phases produced via dehydrogenation we have performed a computational search over 17 candidate dehydrogenation reactions, and identified three reactions having favorable thermodynamics spanning the temperature range $T = 0$–1000 K. All three of these reactions exhibit a decrease in free energy, suggesting that Li4BN3H10 is a metastable phase. For temperatures where H2-desorption has been experimentally observed, the thermodynamically-favored reaction is Li4BN3H10 $\rightarrow$ Li3BN2 + LiNH2 + 4H2, with an enthalpy of 11.2–12.8 kJ/(mol H2). The relatively small dehydriding enthalpies are consistent with the failed re-hydriding attempts reported in the literature, and suggest that hydrogen release from Li4BN3H10 is a kinetically—rather than thermodynamically—hindered process.

Note added in proof—During the review of this manuscript two new studies of Li4BN3H10 were brought to our attention.\textsuperscript{29,30} In the first study Noritake and co-workers\textsuperscript{29} performed a crystal structure analysis of Li4BN3H10 using synchrotron X-ray diffraction. While they found external structural parameters (bcc, space group $I2_13$, $a = 10.67 \, \AA$) consistent with the two reports cited previously they noted that the reported N–H bond lengths were more consistent with the neutron data of Ref.\textsuperscript{12} (and with our calculated N–H distances) than the X-ray data of Ref.\textsuperscript{11}. In the other recent study, Herbst and Hector\textsuperscript{30} examined the electronic structure and energetics of Li4BN3H10 using DFT. Our results appear to be consistent with their findings.

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More specifically, the potentials employed for evaluating zero-Kelvin energies and geometries were (in the parlance of the VASP database): Li$_2$N, B$_4$H$_6$, N$_2$H, and H$_2$H, with respective valence electron configurations of $1s^2\, 2s^1$, $2s^2 \, 2p^1$, $2s^2 \, 2p^3$, and $1s^1$. The geometry of each structure was re-optimized using the softer PAW set before the dynamical matrix calculations were performed.

Our somewhat non-standard approach of using softer potentials to determine the vibrational spectra of the solid phases, but hard (semi-core) potentials for the remaining properties (zero-Kelvin energetics, ground state geometries, and molecular vibrational spectra,) is based on three considerations: First, the softer PAW set allows for more efficient calculations with a reduced planewave cutoff energy, thus permitting larger supercells and, consequently, smaller finite-size effects in the phonon spectrum. Second, our calculated formation energies for LiH, LiNH$_2$, and Li$_2$NH at $T = 300$ K agree with the hard PAW results in Ref. 42 to within 1 kJ/mol f.u. Third, testing revealed that the hard potentials yielded molecular vibrational frequencies which were in slightly better agreement with experimental data than those obtained with the softer PAW set. For example, for N$_2$, where the differences between calculated vibrational frequencies are largest, we find 2338 cm$^{-1}$ versus 2359 cm$^{-1}$ for the experimental measurement. This slight discrepancy in frequencies has only a small impact on vibrational thermodynamic properties—for example, ZPEs calculated with both PAW sets differ by 0.7 kJ/mol f.u. at most. It therefore seems likely that an approach where all vibrational properties (solids and molecules) were evaluated using the softer potentials would also yield reasonably precise results. We thus conclude that our approach of mixing potentials gives results comparable in precision to those obtained with the hard PAW set alone, but without the associated computational expense.

The discrepancy in calculated vs. experimental enthalpy for Li$_2$NH has been noted in Ref. 42 and it has been suggested that the experimental measurement be revisited in light of the good agreement for the other Li-containing compounds: LiH, LiNH$_2$, and Li$_2$N. To our knowledge the formation enthalpy of Li$_2$NH reported in Ref. 42 has not been independently confirmed.

Due to the computational difficulty associated with treating a non-stoichiometric phase, our calculations are restricted to the stoichiometric composition “Li$_2$BN$_2$H$_6$,” whereas most experiments have focused on 2:1 LiNH$_2$ : LiBH$_4$ off-stoichiometric “Li$_2$BN$_2$H$_6$” mixtures, which have been found to minimize NH$_3$ release.