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Structural and energetic analysis of the hydrogen storage materials $LiNH_2BH_3$ and $NaNH_2BH_3$ from *ab initio* calculations

M. Ramzan,[1,*] F. Silvearv,[1] A. Blomqvist,[1] R. H. Scheicher,[1] S. Lebègue,[2] and R. Ahuja[1,3]
[1]*Department of Physics and Materials Science, Condensed Matter Theory Group, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden*
[2]*Laboratoire de Cristallographie, Résonance Magnétique et Modélisations (CRM2, UMR CNRS 7036) Institut Jean Barriol, Nancy Université, BP 239, Boulevard des Aiguillettes 54506 Vandoeuvre-lès-Nancy, France*
[3]*Department of Materials and Engineering, Applied Materials Physics, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden*

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Ammonia borane (NH_3BH_3) possesses many appealing properties as a hydrogen storage material; however, the release of trace amounts of borazine during the desorption process is troublesome. Recently, it was found that substitution of one of the H atoms in the NH_3 group by Li or Na could significantly improve the hydrogen desorption properties. The resulting lithium amidoborane ($LiNH_2BH_3$) and sodium amidoborane ($NaNH_2BH_3$) compounds have been studied by us using density-functional theory. Specifically, we have succeeded in determining the detailed crystal structures of $LiNH_2BH_3$ and $NaNH_2BH_3$, including the atomic positions in their respective unit cells. Calculated hydrogen removal energies of the hydrogen release reactions are found to be in good agreement with the experimental trend.

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Ammonia borane (NH_3BH_3) has been discussed for application as a chemical hydrogen storage material, mainly due to its favorable gravimetric and volumetric properties.[1–5] The release of hydrogen results in polymerization to $(NH_2BH_3)_n$ and eventually to $(NHBH)_n$.[1–5] This rapid polymerization poses a problem for rehydrogenation. Furthermore, the released hydrogen is contaminated with aminoborane and trace quantities of borazine.[1–5] Recently, Xiong *et al.*[6] reported that the amidoboranes $LiNH_2BH_3$ and $NaNH_2BH_3$ provide high storage capacity (10.9 and 7.5 wt %, respectively) of hydrogen at easily accessible temperatures without the unwanted corelease of borazine.[6] The production of $LiNH_2BH_3$ and $NaNH_2BH_3$ occurs in the following reactions:

$$NH_3BH_3 + LiH \rightarrow LiNH_2BH_3 + H_2\uparrow, \quad (1)$$

$$NH_3BH_3 + NaH \rightarrow NaNH_2BH_3 + H_2\uparrow. \quad (2)$$

Much remains to be understood about these materials as $LiNH_2BH_3$ and $NaNH_2BH_3$ compounds have so far not yet been studied in greater detail in the literature. In this Brief Report, we focus on the ground-state properties and crystal structures of both $LiNH_2BH_3$ and $NaNH_2BH_3$ and analyze the energetics of their respective hydrogen desorption processes from first principles.

All calculations were performed using the projector-augmented wave (PAW) method[7] as implemented in the Vienna *ab initio* simulation package (VASP) code.[8,9] The generalized gradient approximation (GGA) (Ref. 10) was used throughout. The chemically "active" electrons in the PAW calculations were $Li:2s^1$; $Na:3s^1$; $N:2s^22p^3$; $B:2s^22p^1$; and $H:1s^1$. We found that a $7\times7\times3$ *k*-point mesh generated by the Monkhorst-Pack method[11] is sufficient to achieve convergence. Specifically, the final structure for *Pbca* had its total energy converged to an accuracy of 0.001 eV.

We initiated our theoretical investigation by first determining the ground-state crystal structure of both $LiNH_2BH_3$ and $NaNH_2BH_3$ from *ab initio* calculations. The single-molecule geometries of $LiNH_2BH_3$ and $NaNH_2BH_3$ were optimized in GAUSSIAN03 (Ref. 12) using a localized basis set. The resulting atomic positions were then used to set reasonable starting values for the fractional coordinates x, y, and z of all atoms in the space group *Pbca* from which a full relaxation of the crystal structure was then carried out. Although the experiment[6] determined the space group of $LiNH_2BH_3$ with near-100% certainty, we attempted to perform a theoretical test of how stable the *Pbca* phase of $LiNH_2BH_3$ might be against competing structures and thus investigated also other possible candidate phases. In the following, we list the space groups and their respective total energy difference in eV/f.u. (f.u.=formula unit) relative to the *Pbca* phase in parentheses: *Pbcn*(0.42), *Pnma*(0.48), *Pcca*(0.86), and *Pnnm*(2.27). Based on these results, we are able to confirm that the *Pbca* structure does indeed yield the lowest total energy and is stabilized by 0.42 eV/f.u. against the second most stable phase *Pbcn*. Calculations of the vibrational spectrum at the Γ point yielded information about the possible existence of soft modes in the *Pbca* structure. No imaginary frequencies were found, suggesting that the structure is dynamically stable.

Our theoretically determined lattice parameters, $a=7.108$ Å, $b=13.945$ Å, and $c=5.150$ Å, for $LiNH_2BH_3$ are in excellent agreement with those obtained experimentally,[6] namely, $a=7.11274$ Å, $b=13.94877$ Å, and $c=5.15018$ Å. For $NaNH_2BH_3$, our theoretically determined lattice parameters are virtually identical to those obtained experimentally,[6] namely, $a=7.46931$ Å, $b=14.65483$ Å, and $c=5.65280$ Å. In Table I, we list the positions of each element within the unit cell, which contains 8 f.u. We emphasize that the symmetry relationships fulfilled by atoms with an $8c$ symmetry resulted directly from *uncon-*

TABLE I. Fractional coordinates of Li, Na, N, B, and H of $LiNH_2BH_3$ and $NaNH_2BH_3$ in the *Pbca* structure determined from *ab initio* calculations. All atoms occupy the 8*c* site.

Element	$LiNH_2BH_3$			$NaNH_2BH_3$		
	x	*y*	*z*	*x*	*y*	*z*
Li/Na	0.930	0.546	0.176	0.908	0.539	0.169
N	0.208	0.430	0.093	0.227	0.419	0.083
B	0.456	0.391	0.152	0.445	0.402	0.146
H(1)	0.246	0.503	0.032	0.264	0.490	0.025
H(2)	0.128	0.306	0.069	0.171	0.296	0.061
H(3)	0.634	0.309	0.109	0.625	0.333	0.110
H(4)	0.546	0.542	0.181	0.504	0.553	0.174
H(5)	0.401	0.297	0.224	0.395	0.310	0.214

strained relaxation. A schematic of the crystal structure of $LiNH_2BH_3$ as determined by us is shown in Fig. 1(a). The optimized geometry appears virtually identical to the structural figures provided in Ref. 6. Regarding the internal structure of the $LiNH_2BH_3$ units forming the crystal, the Li-N and N-B bond lengths are found by us to be 2.02 and 1.55 Å, respectively, in very good agreement with experimental results[6] of 1.98 and 1.56 Å, respectively. The Li-N-B bond angle is determined as 110°.

Having obtained the complete detailed information about the structure, we were able to further analyze the electronic structure of these materials. The corresponding density of states (DOS) and partial density of states (PDOS) are presented in Fig. 2. Both $LiNH_2BH_3$ and $NaNH_2BH_3$ appear to be wide band-gap insulators. The band-gap value of roughly 4 eV shown by the total DOS (upper plots of Fig. 2) should only be considered as a crude estimate due to the usual problem of standard exchange-correlation functionals [local-density approximation (LDA) or even GGA) to treat properly any quantities related to excited states. The PDOS (second to last rows of Fig. 2) is used to analyze the chemical bonding between different chemical species: a strong bonding occurs between the nitrogen atom and its two neighboring hydrogen atoms, as shown by similarities in the position of the peaks in their respective PDOS. The same analysis holds for the boron atom and the remaining three hydrogen atoms. However, the lithium and sodium PDOS show a much weaker correlation with the PDOS of the other atoms, reflecting the predominantly ionic nature of the bonding in their case, although some slight chemical bonding is likely to occur as well. This interpretation is supported by an analysis of the electron localization function (ELF) (Ref. 13) shown in Fig. 3. As can be seen from the connected ELF isosurface, NH_2 and BH_3 are covalently bound while Li is forming ionic bonds with adjacent negatively charged molecular entities.

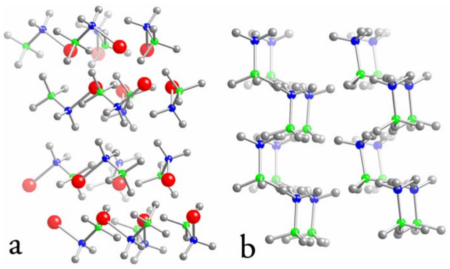

FIG. 1. (Color online) The fully relaxed crystal structures of (a) $LiNH_2BH_3$ and (b) NH_3BH_3 as obtained from our density-functional theory calculation. Li is shown as red spheres, N in blue, B in green, and H in gray.

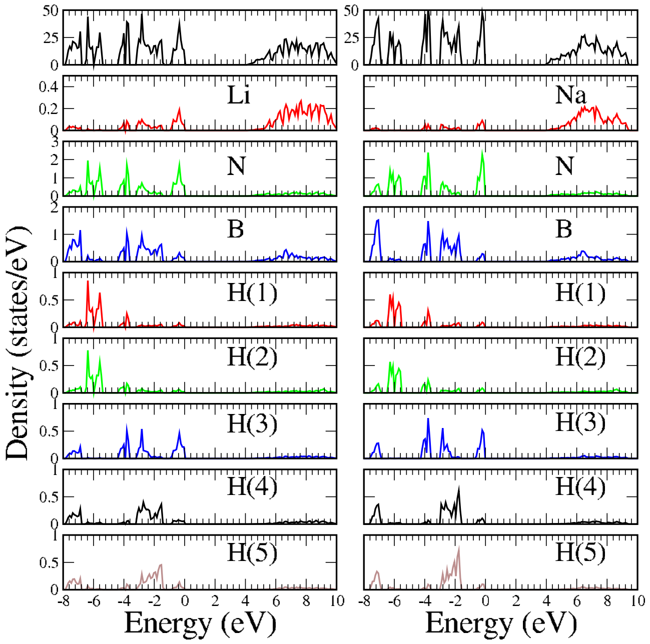

FIG. 2. (Color online) The total (first row) and partial (second to last rows) densities of states for $LiNH_2BH_3$ (left column) and $NaNH_2BH_3$ (right column). The Fermi level coincides with 0 eV.

Following Bader's theory of atoms in molecules,[14–16] we were able to analyze the charge densities of $LiNH_2BH_3$ and $NaNH_2BH_3$. Within this formalism, zero flux surfaces in the charge density are used to define each basin belonging to a particular atom. The charge assigned to this atom is then obtained by integrating the charge density over the whole basin. The corresponding charges for the two compounds investigated here are reported in Table II. The results clearly

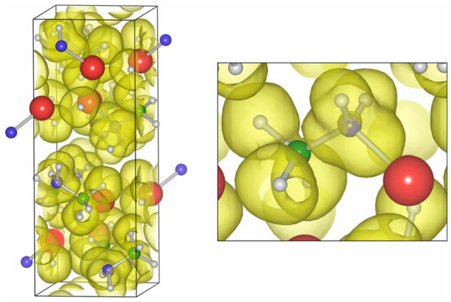

FIG. 3. (Color online) The left panel shows the calculated electron localization function for the unit cell of $LiNH_2BH_3$ plotted as yellow-colored transparent isosurfaces at a level of 0.5. The right panel presents a zoomed-in view showing more details. Li in red, N in blue, B in green, and H in gray.

TABLE II. Calculated Bader atomic charges (in units of *e*) for $LiNH_2BH_3$ and $NaNH_2BH_3$ in the *Pbca* structure.

Atom	$LiNH_2BH_3$	$NaNH_2BH_3$
Li/Na	+0.87	+0.82
N	−1.47	−1.44
B	+1.87	+1.86
H(1)	+0.36	+0.35
H(2)	+0.36	+0.36
H(3)	−0.66	−0.65
H(4)	−0.67	−0.65
H(5)	−0.65	−0.64

reveal the strong ionic character of the Li/Na-NH_2BH_3 bonds since the alkali metal ion is seen to have lost most of its electron toward the $NH_2BH_3^-$ group. The lithium and sodium atoms possess essentially the same charge, with the slight difference of 0.05 *e* being probably related to the differences in bond lengths or more generally in their respective crystal structure. Overall, only very slight differences can be noticed when comparing the atomic charges of $LiNH_2BH_3$ and $NaNH_2BH_3$. Concerning the hydrogens atoms, two groups can be clearly identified: the two hydrogen atoms, labeled H(1) and H(2) in Table II, bonded to the nitrogen atom, which have lost a significant part of their electronic charge (the charge is +0.36); and the three hydrogen atoms, labeled H(3), H(4), and H(5), bonded to the boron atom, which possess a significant negative charge (about −0.65). Therefore, the two groups of hydrogen atoms differ by a charge of approximately one electron, reflecting the different electronegativity of nitrogen and boron atoms (with charges of about −1.4 and +1.9 *e*, respectively). As we will show in the following, these differences in the charge state result in different hydrogen removal energies.

To analyze the energy that is required to remove hydrogen from the system, we constructed a 2×1×1 supercell of $LiNH_2BH_3$ for the *Pbca* space group and proceeded to take away one hydrogen atom bonded either with boron or with nitrogen. This procedure allowed us to avoid unphysical interactions between adjacent cells while determining the difference in total energy, which corresponds to the binding strength of hydrogen at the respective sites (*B* site and *N* site). We find that the binding energy for hydrogen at the *B* site is 5.63 eV and for hydrogen at the *N* site 6.02 eV. These numbers are rather similar to what we found in ammonia borane [Fig. 1(b)], namely, 5.27 eV at the *B* site and 5.81 eV at the *N* site and also follow the same trend, i.e., the N-H bonds are stronger than the B-H bonds. The similarity in the theoretical hydrogen desorption energies between $LiNH_2BH_3$ and NH_3BH_3 is in good agreement with experimental measurements[4,6] which found the hydrogen release taking place in the same temperature range (90–110 °C) for both $LiNH_2BH_3$ and NH_3BH_3.

In summary, we have presented results from our systematic first-principles study of the structural and energetic properties of $LiNH_2BH_3$ and NH_3BH_3. The space group was confirmed to be *Pbca*, and the atomic positions in the unit cell were determined by us. The lattice parameters of the crystal and the internal structure of the constituting molecular units in $LiNH_2BH_3$ are found to be in very good agreement with experiment.[6] We have calculated the hydrogen removal energies for $LiNH_2BH_3$ and NH_3BH_3 and found their near equality to be in good qualitative agreement with the similar hydrogen desorption temperatures determined experimentally for the two systems. Finally, our work opens the path to the study of related materials based on the $[NH_2BH_3]^-$ anion. In particular, calcium amidotrihydroborate $Ca(NH_2BH_3)_2$, which has been synthesized recently,[17] represents a promising candidate system for hydrogen storage as well.

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*Corresponding author; muhammad.ramzan@fysik.uu.se

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