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Theoretical investigation of intermediate phases between Li_2NH and $LiNH_2$

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Lithium imide (Li_2NH) has been considered as a promising medium for hydrogen storage with the following reaction: $LiNH_2+LiH \leftrightarrow Li_2NH+H_2$. All possible phases involved in the reaction need to be fully characterized in order to understand the right pathway connecting the two end compounds $LiNH_2$ and Li_2NH and to further improve its reaction condition to meet the requirements of practical applications. We study from first-principles calculations the possible intermediate compounds $Li_{2-x}NH_{1+x}$ between Li_2NH and $LiNH_2$. Based on the energetics results, possible intermediate phases are identified for $0<x\leq 1/4$. On the other hand, the intermediate phases are not thermodynamically favorable for $3/4\leq x<1$ with respect to phase separation into Li_2NH and $LiNH_2$. The NH and NH_2 anions coexist in the intermediate compounds, but the electronic states derived from these two units are well separated in energy. The band gap of the intermediate compounds is also smaller than that of both Li_2NH and $LiNH_2$. These signatures from the electronic structure will provide useful guidelines for experimental efforts to search for the intermediate phases.

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I. INTRODUCTION

Cycling between Li amide ($LiNH_2$) and Li imide (Li_2NH) represents a promising hydrogen storage system[1]

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2. \qquad (1)$$

This system theoretically releases 6.5 wt % hydrogen but the reaction condition is still not optimal for practical applications. Attempt to improve its reaction condition, although with some progress with the introduction of a mixed imide $Li_2Mg(NH)_2$,[2,3] has been hampered by the insufficient understanding of the reaction mechanism.[4–7] A thorough understanding of all possible phases involved in reaction in Eq. (1) is critical to the discovery of the right pathways for the reaction. David *et al.*[6] reported through x-ray diffraction studies that the sample in the hydrogenated state shows sharp Bragg peaks for the $LiNH_2$ phase, but the Bragg peaks for the Li_2NH phase of the dehydrogenated sample display an unusual broadening. This suggests that while $LiNH_2$ is the dominant phase in the hydrogenated state, phases with intermediate stoichiometry between $LiNH_2$ and Li_2NH might exist in the dehydrogenated state. More recently, an intermediate compound $Li_{1.5}NH_{1.5}$ was investigated with density-functional theory and was suggested to be a stable phase with respect to the decomposition into Li_2NH and $LiNH_2$.[8] This motivated us to perform theoretical investigations of other possible intermediate phases by first-principles calculations of the crystalline compounds with an intermediate stoichiometry $Li_{2-x}NH_{1+x}$. A careful examination of the model proposed in Ref. 8 by including the correct zero-point energy (ZPE) value shows that $Li_{1.5}NH_{1.5}$ is not stable with respect to phase separation into Li_2NH and $LiNH_2$ (this will be covered in more detail in Sec. III). Therefore, in this paper we focus on the intermediate phases in the vicinity of Li_2NH ($0<x\leq 1/4$) and $LiNH_2$ ($3/4\leq x<1$).

Li is highly ionized into Li^+ in the Li-N-H system; at the same time, electrons of H atoms also gravitate toward N atoms in the N-H bonds since hydrogen has a smaller electronegativity than nitrogen. Thus, the intermediate phases $Li_{2-x}NH_{1+x}$ can be created by swapping certain Li (H) atoms with H (Li) atoms in the end compound Li_2NH ($LiNH_2$) while the net charge of the system is kept neutral. We use the structure of Li_2NH and $LiNH_2$ as the starting point for $0<x\leq 1/4$ and $3/4\leq x<1$, respectively. Unlike $LiNH_2$ which has a well-established structure with $I\bar{4}$ (No. 82) symmetry, the ground-state structure of Li_2NH is still under debate. In some models, Li and N atoms form an antifluorite structure and H atoms randomly occupy certain symmetrical points around N.[9–11] One plausible model derived from the diffraction data moves some Li atoms from the tetrahedral sites to the octahedral sites in the antifluorite structure [see Fig. 1(a)].[12,13] Tetrahedral vacancies are created so this structure will be referred to as structure-V hereinafter. Several other structures have also been proposed that have free energies at $T=0$ a few kilojoule per mole lower than structure-V with the ZPE included.[14–16] However, these lower-energy structures do not match the diffraction data and/or the measured vibrational spectra.[16] This suggests that either some components that are missing in theoretical calculations (for example, the configurational free energy) favor structure-V at moderate temperatures or the system could be kinetically

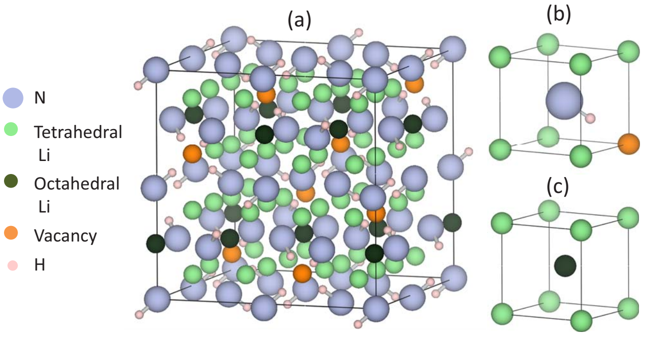

FIG. 1. (Color online) (a) The model for Li_2NH proposed in Refs. 12 and 13 that contains tetrahedral vacancies and octahedral Li atoms. (b) Local structure around an NH anion. (c) Local structure around an octahedral Li cation.

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trapped in this metastable state. Of course, there are other possibilities including the inaccuracies of the methodologies in determining the crystal structure of these materials employed in both experimental investigations and density-functional theory calculations. In this work, we use structure-V as the reference structure for Li_2NH because it matches experimental data better. In addition, structure-V connects more naturally with the intermediate phases since vacancies will be present due to the deficiency of Li in the intermediate phases.

II. COMPUTATIONAL METHODS

We have performed the calculations based on density-functional theory. The Kohn-Sham equations are solved with a plane-wave basis as implemented within the VASP package.[17,18] For the exchange-correlation functional the generalized gradient approximation in the form proposed by Perdew *et al.*[19] is used. The electron-ion interaction is described by Vanderbilt ultrasoft pseudopotentials.[20] A cut-off energy of 600 eV is used for the plane-wave basis. The total-energy converges to 10^{-5} eV in each self-consistent loop, and the structural relaxation terminates when the force on each atom is smaller than 0.01 eV/Å. A $4\times4\times4$ Monkhorst-Pack k mesh is used to carry out integrations over the Brillouin zone in structural relaxations.[21] The free energy at finite temperature is considered within the harmonic approximation.

III. RESULTS AND DISCUSSIONS

A. $Li_{2-x}NH_{1+x}$ ($0<x\leq 1/4$)

We first study $Li_{2-x}NH_{1+x}$ for $0<x\leq 1/4$ using structure-V for Li_2NH as the starting point. Two competing effects exist in this structure. On one hand, there is one vacancy among the eight tetrahedral sites that form a cube around each NH anion as shown in Fig. 1(b). With the other seven tetrahedral sites occupied by Li^+ cations, this vacancy effectively creates a local electric field that points from the center of the cube to the vacancy. Thus, the polar N-H bond prefers to point toward the vacancy to maximize the electrostatic attraction between the N-H bond and the vacancy. On the other hand, the Li cation at the octahedral site has short interatomic distances with neighboring Li cations at the tetrahedral sites [see Fig. 1(c)], thus the electrostatic repulsion among these Li atoms increases. Here, we create the intermediate compounds $Li_{2-x}NH_{1+x}$ with another pair of competing events. First, we remove part or all of the octahedral Li in structure-V (depending on the value of x), which should be energetically favorable. Then to neutralize the charge of the system, we introduce additional H atoms to bond to some of the N atoms forming NH_2 anions. This step costs energy since the single vacancy around the NH_2 unit is unable to accommodate both N-H bonds, leaving the orientation of the two N-H bonds frustrated. This method will create $Li_{2-x}NH_{1+x}$ with $0<x\leq 1/4$, since originally 1/8 of Li atoms are located at the octahedral sites in structure-V. We explicitly study two of these phases: $x=1/8$ and 1/4. We define the formation energy of $Li_{2-x}NH_{1+x}$ as

$$F=f(Li_{2-x}NH_{1+x})-(1-x)f(Li_2NH)-xf(LiNH_2), \quad (2)$$

where $f(Li_{2-x}NH_{1+x})$, $f(Li_2NH)$, and $f(LiNH_2)$ represent the free energies of $Li_{2-x}NH_{1+x}$, Li_2NH, and $LiNH_2$, respectively. The free energy of a solid includes the total energy of the electronic system and the vibrational contribution

$$f=E_{el}+f_{vib}. \quad (3)$$

The vibrational free energy in the harmonic approximation has the form

$$f_{vib}=k_BT\sum_{nk}\ln\left[2\sinh\frac{\hbar\omega_n(k)}{2k_BT}\right], \quad (4)$$

where n is the mode index for phonons with crystal momentum k. At zero temperature, f_{vib} reduces to the ZPE $E_{ZPE}=1/2\Sigma_{nk}\hbar\omega_n(k)$. To obtain the phonon dispersion $\omega_n(k)$, we have calculated the vibrational modes at the Γ point of a 128-atom supercell by diagonalizing the 384×384 force-constant matrix determined by the induced forces due to small displacements of each atom. The Brillouin zone of this large supercell is small enough that Eq. (4) can be evaluated by sampling only the Γ point. Since F defined in Eq. (2) compares the free energy of the intermediate phase with the weighted sum of $LiNH_2$ and Li_2NH under ambient pressure (the PV term is ignored), the sign of F determines whether the intermediate phase is thermodynamically stable with respect to phase separation. It is a natural choice to use the free energy of structure-V as $f(Li_2NH)$, since here we are mainly interested in predicting the possibility of creating $Li_{2-x}NH_{1+x}$ from structure-V. We follow a strategy for structural search similar to that in Ref. 12. Initially, the NH anions and tetrahedral Li atoms form a perfect cubic structure with space group $Fd\bar{3}m$ (No. 227); then we pick certain N atoms to bond to an extra H atom and assign certain 32e sites for the octahedral Li atoms. The symmetry is reduced during structural relaxation. We have investigated all inequivalent initial configurations for supercells up to 16 f.u. (64 atoms). Here only the electronic total energy is minimized in the structural relaxation. Although the inclusion of the ZPE could change the lattice constant (for example, by about 2% for LiH),[12] the change in the $T=0$ free energy is much smaller [0.1% for LiH (Ref. 12)]. The effect on F in Eq. (2) is expected to be even smaller because of the error cancellation in taking the energy difference.

Only half of the octahedral Li atoms are removed for $x=1/8$. The structure with the lowest energy has the space group Pc (No. 7) with atomic coordinates given in Table I. We show this structure in conventional cubiclike supercell together with a side view along [100] in Fig. 2(a). The N-H bond length and H-N-H bond angle in the NH_2 anion is 1.03 Å and 103.4°, respectively; both are very close to the values in $LiNH_2$ (1.03 Å and 102.7°). From the [100] side view, each octahedral Li atom is located close to an octahedral site that is a nearest neighbor to an NH_2 anion, indicating that the effect of the two energetically unfavorable elements—NH_2 and octahedral Li—is minimized when they are grouped together. The global arrangement of these local NH_2-Li pairs is not important. Several structures with differ-

TABLE I. Atomic coordinates of the structure shown in Fig. 2(a) for $Li_{2-x}NH_{1+x}$ with $x=1/8$. The structure has *Pc* (No. 7) space-group symmetry. Lattice parameters are: $a=7.07$ Å, $b=10.25$ Å, $c=7.07$ Å, $\alpha=\gamma=90°$, and $\beta=88.57°$.

Atom	*x*	*y*	*z*
Li	0.376	0.385	0.733
	0.819	0.851	0.255
	0.364	0.896	0.797
	0.872	0.387	0.268
	0.373	0.113	0.711
	0.862	0.615	0.222
	0.117	0.245	0.783
	0.107	0.123	0.501
	0.682	0.408	0.992
	0.139	0.894	0.518
	0.620	0.633	0.009
	0.120	0.369	0.494
	0.566	0.090	0.005
	0.074	0.591	0.500
	0.627	0.865	0.995
N	0.601	0.008	0.750
	0.108	0.514	0.243
	0.136	0.015	0.756
	0.632	0.506	0.243
	0.364	0.244	0.512
	0.889	0.270	0.969
	0.361	0.763	0.467
	0.871	0.744	0.010
H	0.226	0.547	0.737
	0.725	0.046	0.236
	0.523	0.564	0.747
	0.999	0.020	0.261
	0.887	0.207	0.383
	0.347	0.297	0.083
	0.849	0.793	0.577
	0.368	0.702	0.887
	0.495	0.262	0.914

ent space-group symmetries but similar NH_2-Li pairs have almost identical total energies. At $T=0$, the structure for $x=1/8$ has a negative formation energy of −8.7 meV/f.u. with the ZPE included. Figure 3(a) shows that *F* remains negative at finite temperature as high as 440 K, higher than room temperature.

For $x=1/4$, all the octahedral Li atoms are removed. Figure 2(b) gives this structure and a side view along [110]. Atomic coordinates are given in Table II. The side view along [110] shows that the NH_2 anions are also grouped into linear chains with nearest neighbors. The formation energy for this structure is −16 meV/f.u. including the ZPE at $T=0$. Temperature dependence of *F* in Fig. 3(b) shows that this structure is still stable with respect to phase separation into pure $LiNH_2$ and Li_2NH at the dehydrogenation temperature for reaction (1): ∼600 K. Moreover, *F* for the structure in Fig. 2(b) is almost double of that in Fig. 2(a), indicating a quasilinear dependence of *F* on *x* for $0<x\leq 1/4$ [see Fig. 3(b)]. This suggests that the intermediate compounds $Li_{2-x}NH_{1+x}$ could coexist for an arbitrary value of *x* within $0<x\leq 1/4$ if structure-V is the correct end structure for Li_2NH.

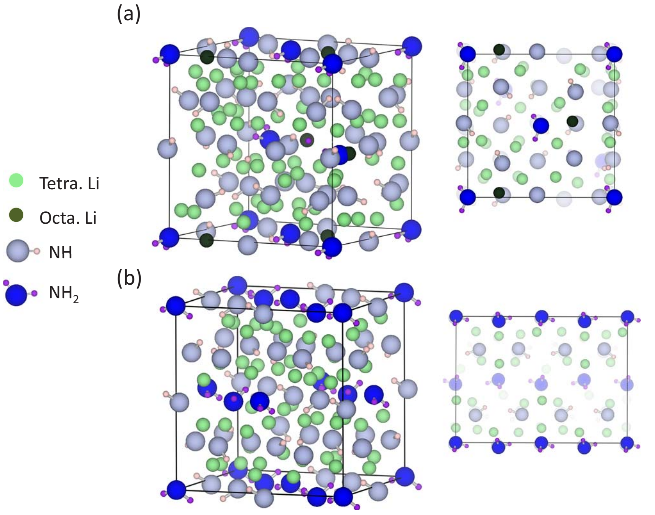

FIG. 2. (Color online) Low-energy structures of $Li_{2-x}NH_{1+x}$ for (a) $x=1/8$ and (b) $x=1/4$. The side views on the right panel are along [100] for (a) and [110] for (b). The atomic coordinates for (a) and (b) are given in Tables I and II, respectively.

Based on the above analysis of the energetics, $Li_{1.75}NH_{1.25}$ ($x=0.25$) could be first created if $LiNH_2$ and LiH is mixed at a molar ratio of 1:1, following:

$$LiNH_2 + LiH \leftrightarrow Li_{1.75}NH_{1.25} + 0.25LiH + 0.75H_2, \quad (5)$$

then, $Li_{1.75}NH_{1.25}$ further reacts with the remaining LiH and creates Li_2NH

$$Li_{1.75}NH_{1.25} + 0.25LiH \leftrightarrow Li_2NH + 0.25H_2. \quad (6)$$

The calculated reaction enthalpy for reactions in Eqs. (5) and (6) is 0.57 eV/H_2 and 0.65 eV/H_2, respectively, while the calculated reaction enthalpy for the original reaction in Eq.

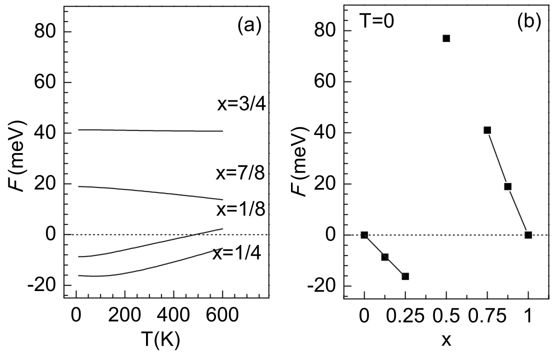

FIG. 3. (a) Formation energy of $Li_{2-x}NH_{1+x}$ in Eq. (2) as a function of (a) temperature and (b) *x* at $T=0$. The structure with the lowest formation energy for each value of *x* is used for the calculation.

TABLE II. Atomic coordinates of the structure shown in Fig. 2(b) for $Li_{2-x}NH_{1+x}$ with $x=1/4$. The structure has $Pna2_1$ (No. 33) space-group symmetry. Lattice parameters are: $a=7.15$ Å, $b=10.51$ Å, $c=7.10$ Å, and $\alpha=\beta=\gamma=90°$.

Atom	x	y	z
Li	0.010	0.105	0.409
	0.935	0.652	0.362
	0.003	0.886	0.326
	0.252	0.872	0.099
	0.233	0.649	0.164
	0.192	0.089	0.110
	0.305	0.419	0.119
N	0.999	0.770	0.594
	0.990	0.758	0.126
	0.231	0.985	0.353
	0.275	0.505	0.365
H	0.021	0.290	0.208
	0.999	0.294	0.502
	0.365	0.979	0.864
	0.158	0.547	0.874
	0.127	0.740	0.543

(1) is 0.59 eV/H_2. This two-step scheme has not been experimentally confirmed since pressure-composition isotherms of Li_2NH only show one plateau.[1] A second lower-pressure plateau at the beginning of absorption (or the end of desorption) could be missed since the data set is not fine enough at the early stage of the absorption measurements and the desorption measurements do not reach the late stage at all. Besides, contamination of samples that caused the plateau to be sloped might also play a role in missing the second plateau. Further experiments, especially in the early (late) stage of adsorption (desorption), is desirable to verify the intermediate phases close to the Li_2NH end. On the other hand, failure to establish such compounds might suggest the invalid choice of structure-V as the reference state, since the formation energy for these intermediate phases at $T=0$ will be positive (30 meV/f.u. and 14 meV/f.u. for $x=1/8$ and $x=1/4$, respectively) if a lower-energy structure such as the one proposed in Ref. 15 is used as the reference structure for Li_2NH.

The calculated volume of $Li_{2-x}NH_{1+x}$ is 64.02 Å^3/f.u. and 66.69 Å^3/f.u. for $x=1/8$ and $x=1/4$, respectively. Both are larger than that of Li_2NH (61.78 Å^3/f.u.), showing that the frustrated NH_2 anions in these intermediate compounds tend to expand the lattice. This is consistent with the broadening in the measured x-ray Bragg peaks of the dehydrogenated samples.[6] In Ref. 6, the dehydrogenated samples created at a reaction temperature of 260 °C showed disordered cubic phases of a wide and continuous stoichiometry variation. These disordered phases are expected to be stabilized by configurational entropy at high temperature, in a similar way as in the high-temperature disordered phases of $Li_2Mg(NH)_2$.[22,23] The entropy contribution to the free energy associated with many possible configurations of the frustrated NH_2 units could possibly favor a disordered arrangement. The topic of configurational entropy in the general amide/imide system remains an interesting subject for future theoretical studies.

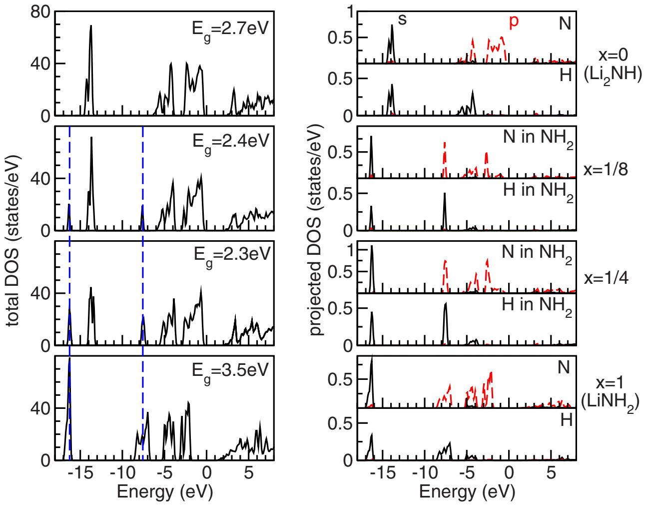

FIG. 4. (Color online) The total DOS (left) and projected DOS on N and H atoms (right) for $Li_{2-x}NH_{1+x}$ with $x=0$, 1/8, 1/4, and 1. For the two intermediate compounds, the projected DOS onto N and H atoms of NH anions is not shown, since it highly resembles that in pure Li_2NH. The energy zero is at the top of the valence bands for $x=0$, 1/8, and 1/4. The spectrum of $LiNH_2$ is shifted for comparison so that the NH_2-derived states in the intermediate compounds are aligned with the corresponding states in $LiNH_2$.

The electronic structures of the intermediate compounds are also studied. In Fig. 4, we plot the total density of states (DOS) on the left and the projected DOS onto N and H atoms on the right for $Li_{2-x}NH_{1+x}$ with $x=0$ (pure Li_2NH), 1/8, 1/4, and 1 (pure $LiNH_2$). Li makes little contribution to the electronic states below the Fermi level since it is highly ionized. For Li_2NH, the three significant regions below the Fermi level in the total DOS, from low to high energies, are mainly originated from H(s)-N(s) bonding, H(s)-N(p) bonding and the lone electron pair on the N atoms, as could be seen from the projected DOS in Fig. 4. For the intermediate compounds with $x=1/8$ and 1/4, these three regions are still the main contributions to the total DOS since the concentration of NH_2 anions is low.

However, there also exist two additional NH_2-derived peaks around $E=-16.2$ and -7.5 eV, that are well separated from the original NH-derived regions. The former is derived from H(s)-N(s) bonding and the latter has H(s)-N(p) bonding characters in the NH_2 anion. Electronic states with similar bonding characters can also be identified in $LiNH_2$. These states in $LiNH_2$ are aligned with those in the intermediate compounds as illustrated by the dashed lines in the left panel of Fig. 4, since the bonding between N and H atoms in the NH_2 anion is almost unaffected by its different environment in $LiNH_2$ and in the intermediate compounds. This is evidenced by the nearly unchanged geometrical parameters such as the bond length and the bond angle. One could see that although $LiNH_2$ has a larger gap of 3.5 eV than that of Li_2NH (2.7 eV), the conduction-band minimum for $LiNH_2$ lies below that for Li_2NH. Thus, the conduction-band minimum for the intermediate compounds is also pulled down due to the mixing of NH_2-derived states in the conduction bands, resulting in a reduced band gap of 2.4 eV (2.3 eV) for $x=1/8$ (1/4), compared with the band gap of 2.7 eV for Li_2NH.

B. $Li_{1.5}NH_{1.5}$

A structure for $x=1/2$ ($Li_{1.5}NH_{1.5}$) was proposed in Ref. 8. In this structure, N atoms are located at 4a sites of the space group $F\bar{4}3m$ (No. 216) with cubic symmetry. Li atoms partially occupy 4c and 4d sites and H atoms partially occupy 16e sites of the same space group. However, the possibility of breaking the cubic symmetry resulting from partial occupancies of certain symmetrical sites was not considered. Consequently, the final structure is in a stressed state. In addition, the Einstein model used in Ref. 8 significantly underestimated the ZPE of this structure. We have carried out further relaxation of the stress which yields a structure with a slightly lower energy. The ZPE from the full phonon spectrum is 0.59 eV/f.u., and the formation energy from Eq. (2) is 77 meV/f.u. at $T=0$ for this relaxed structure, if structure-V is used as the reference structure for Li_2NH. Given that the formation energy is positive, $Li_{1.5}NH_{1.5}$ is not a stable intermediate phase at $T=0$. In Ref. 8, an underestimated value of 0.43 eV/f.u. for the ZPE of the stressed cubic structure was used to calculate the reaction enthalpy of $1/2Li_2NH + 1/2LiNH_2 \rightarrow Li_{1.5}NH_{1.5}$. This yielded a negative value of −39 meV/f.u. for the reaction enthalpy with the structure reported in Ref. 14 (with a lower energy than structure-V) as the reference structure for Li_2NH. As mentioned above, if the most accurate value for the ZPE is used, $Li_{1.5}NH_{1.5}$ is not a favorable phase at $T=0$.

C. $Li_{2-x}NH_{1+x}$ ($3/4 \leq x < 1$)

To create the intermediate compounds $Li_{2-x}NH_{1+x}$ for $3/4 \leq x < 1$, we use the $LiNH_2$ structure as the starting point. Namely, we add certain amount of Li ions to the vacant tetrahedral sites and replace a suitable amount of NH_2 anions with NH anions in $LiNH_2$ to balance the charge. In $LiNH_2$, Li atoms only occupy half of the tetrahedral sites. The tetrahedral vacancies are arranged in such a way that each N-H bond points to a place close the midpoint of two adjacent vacancies.[23] Partially filling these vacancies with positively charged Li ions will block the space for N-H bonds both sterically and electrostatically and thus is expected to be an endothermic process. One extra Li cation can affect up to four NH_2 anions that are tetrahedrally coordinated around the extra Li. Figure 5 shows two final structures for $x=3/4$ and $x=7/8$ by enumerating all the nonequivalent positions for the extra Li cations and NH anions while preserving the $I\bar{4}$ (No. 82) space-group symmetry of $LiNH_2$ and the size of the unit cell (each unit cell contains 64 atoms for $x=3/4$ and 128 atoms for $x=7/8$). The formation energy for the structures in Figs. 5(a) and 5(b) is 41 meV/f.u. and 19 meV/f.u. with the ZPE included at $T=0$, respectively. This shows that they are unstable with respect to phase separation. Here, the choice of the structure for Li_2NH is not critical since the weight factor of Li_2NH in Eq. (2) is small. For simplicity, we keep using structure-V. Figure 3(a) shows a weak dependence of F on temperature for both structures. The added Li cations and NH anions in Figs. 5(a) and 5(b) are grouped into the same local structure shown in Fig. 5(c), where the two added Li atoms (Li1 and Li2) occupy two vertical tetrahedral vacancies, and at the same time the anions at their common nearest neighbors N1 and N2 are changed from NH_2 to NH with the remaining N-H bond well accommodated by two horizontal vacancies. Although each added Li atom still affects two other NH_2 anions that form a tetrahedron with the anions at N1 and N2, this grouping of the extra Li cations and NH anions effectively minimizes the number of affected NH_2 anions; and thus the energy for the structures in Figs. 5(a) and 5(b) is relatively low.[24] The lattice parameters of these two intermediate phases change within 1% of those of $LiNH_2$. The volume for $x=3/4$ and $x=7/8$ is 63.55 Å^3/f.u. and 63.79 Å^3/f.u., respectively, only slightly smaller than the value of 63.95 Å^3/f.u. for pure $LiNH_2$.

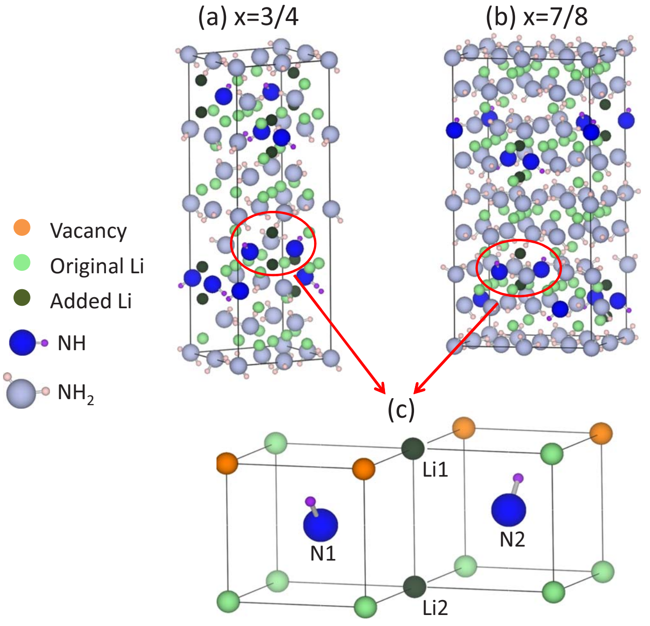

FIG. 5. (Color online) Structures with the lowest formation energy for $Li_{2-x}NH_{1+x}$ with (a) $x=3/4$ and (b) $x=7/8$. (c) is the common local structure around the extra Li cations and NH anions.

Finally, the total and projected DOSs for $Li_{2-x}NH_{1+x}$ with $x=3/4$ and 7/8 are given in Fig. 6. For the total DOS, although the electronic states similar to those in $LiNH_2$ (shown in Fig. 4) make the main contributions as expected, one can also see two extra regions indicated by the arrows. From the projected DOS onto the NH anions, it can be seen that the electronic states in these two regions are originated from the N(s)-H(s) bonding and the lone pair in the NH anions, respectively. The lone-pair states in the NH anions are higher in energy than all the NH_2-derived states below the Fermi level and define the valence-band maximum. This causes a significant drop in the band gap for these two intermediate compounds: 2.0 eV (2.3 eV) for $x=3/4$($x=7/8$), compared with the band gap for $LiNH_2$: 3.5 eV.

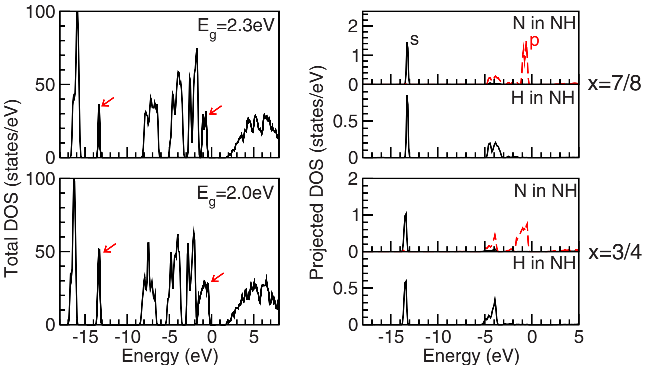

FIG. 6. (Color online) The total DOS (left) and projected DOS onto N and H atoms of NH anions (right) for $Li_{2-x}NH_{1+x}$ with $x=3/4$ and 7/8. The arrows on the left panel point to the NH-derived regions. The projected DOS onto N and H atoms of NH_2 anions is omitted, since it highly resembles that in pure $LiNH_2$.

IV. CONCLUSION

In summary, we have performed first-principles investigations of intermediate compounds $Li_{2-x}NH_{1+x}$ with $0<x\leq 1/4$, $x=1/2$, and $3/4\leq x<1$. For $0<x\leq 1/4$, $Li_{2-x}NH_{1+x}$ is created by replacing a certain amount of NH anions with NH_2 anions in pure Li_2NH and by removing at the same time a proper amount of Li to satisfy charge neutrality. When using the structure with tetrahedral vacancies as the reference structure for Li_2NH, $Li_{2-x}NH_{1+x}$ is more stable than the phase-separated mixture of Li_2NH and $LiNH_2$ for $0<x\leq 1/4$ at temperatures close to the dehydrogenation temperature of the Li-N-H system. This shows that these intermediate phases could also be present in the dehydrogenation products if the structure with tetrahedral vacancies is the right structure for Li_2NH. Similarly, $Li_{2-x}NH_{1+x}$ for $3/4\leq x<1$ is created by replacing a certain amount of NH_2 anions with NH anions in $LiNH_2$ and adding at the same time a suitable amount of Li. For these x values, $Li_{2-x}NH_{1+x}$ is unstable with respect to phase separation into $LiNH_2$ and Li_2NH. These results are consistent with the experimental fact that $LiNH_2$ is the dominant phase in the hydrogenated sample, but the Bragg peaks for the dehydrogenated Li_2NH phase exhibit unusual broadening. The NH_2- and NH-derived electronic states are well separated in energy for $Li_{2-x}NH_{1+x}$. The band gap of $Li_{2-x}NH_{1+x}$ is also smaller than that of both Li_2NH and $LiNH_2$. These electronic properties will help the experimental verification of the intermediate phases. For $x=1/2$, we do not find the structure proposed in the literature to be stable at $T=0$ after taking into account a more accurate evaluation for the zero-point energy.

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