Novel Structural Motifs in Low Energy Phases of $LiAlH_4$

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We identify a class of novel low energy phases of the hydrogen storage material $LiAlH_4$ by using the *ab initio* minima hopping crystal structure prediction method. These phases are, unlike previous predictions and known structures of similar materials, characterized by polymeric networks consisting of Al atoms interlinked with H atoms. The most stable structure is a layered ionic crystal with $P2_1/c$ symmetry, and it has lower free energy than the previously reported structure over a wide range of temperatures. Furthermore, we carry out x-ray diffraction, phonon, and GW band-structure analysis in order to characterize this phase. Its experimental synthesis would have profound implications for the study of dehydrogenation and rehydrogenation processes and the stability problem of $LiAlH_4$ for hydrogen storage applications.

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Limited fossil resources and the increasing amount of CO_2 emission have recently motivated intense research in hydrogen-based energy systems. Hydrogen has been touted as a promising alternative energy source due to its clean reaction with oxygen: The final product is water and heat, and no greenhouse gases are produced. Moreover, hydrogen can provide a high energy density (about 3 times higher than petrol) and is readily available. The key to widespread applications of hydrogen in industry and in vehicles is the development of suitable solid-state hydrogen storage materials. The goal of 6 weight percentage (wt. %) and 45 g/l of hydrogen in hydride compounds on board fuel cell vehicles has been posed by the U.S. Department of Energy in 2010. Further properties required when designing such materials are the need for an efficient hydrogen release mechanism, ideally close to $0.025\ \mathrm{g\,s^{-1}\,kW^{-1}_{fuel\ cell}}$ at temperatures preferably below 100 °C and moderate pressures, as well as on-board refueling times less than 10 min at reasonable H_2 pressures. Besides experimental synthesis of candidate materials, *ab initio* methods have been widely applied to assist in searching for novel hydrogen storage materials to satisfy the above requirements (e.g., Ref. [1]).

Complex hydrides such as alanates, which are compounds that contain aluminum, hydrogen, and a metal like sodium or lithium, have been widely discussed as promising candidates [2,3]. In this Letter, we investigate the structural diversity of $LiAlH_4$, a material that has drawn attention as a hydrogen storage material, since it contains 10.6 wt. % hydrogen [4–6]. The decomposition occurs in three steps with a theoretical release of 7.9 wt. % hydrogen at moderate temperatures in the first two steps [6,7]:

$$LiAlH_4 \rightarrow 1/3Li_3AlH_6 + 2/3Al + H_2, \tag{1}$$

$$1/3Li_3AlH_6 \rightarrow LiH + 1/3Al + 1/2H_2. \tag{2}$$

Note also that complex reactions of $LiAlH_4$ with $LiNH_2$ [8,9], $NaNH_2$ [10], and $Mg(NH_2)_2$ [11] have been investigated and were reported to desorb 5, 5.2, and 8.5 wt. % of hydrogen, respectively. Nevertheless, challenges in reversible dehydrogenation still remain [12].

Recently, the crystal structure of $LiAlH_4$ was accurately resolved by powder x-ray diffraction (XRD) and neutron diffraction experiments [13], which was followed by a detailed theoretical study of the structural, electronic, and thermodynamic properties of this phase [14]. This ternary hydride was found to crystallize in the α-$LiAlH_4$ phase which has a $P2_1/c$ symmetry. It is an ionic crystal that consists of complex AlH_4^- anions together with Li^+ cations [13,14]. Unfortunately, the phase diagram of this compound remains relatively unexplored, and several problems still exist in determining its possible polymorphs at various temperatures and pressures. In fact, although $LiAlH_4$ has been known since 1947 [4], there is still controversy regarding its thermodynamic stability. Spontaneous decomposition of $LiAlH_4$ towards Li_3AlH_6 was observed with a half-life of approximately 20 years at room temperature [15], and the first dehydrogenation step was reported to be exothermic [7]. The stability, however, seems to correlate strongly with impurities in the sample [16], and indeed several theoretical studies predict pure $LiAlH_4$ to be stable against such decomposition [14,17], although opposite claims have also been made [18,19]. Clearly, this is a particularly important problem in view of the use of this compound as a hydrogen storage material, and it could be resolved by enhancing the stability of $LiAlH_4$.

To address this issue, we investigated possible low energy structures of $LiAlH_4$ by using an efficient crystal structure prediction algorithm, the minima hopping method [20,21]. This method was designed to predict the low energy structures of a system given solely its chemical composition. The energy surface is explored by performing consecutive short molecular dynamics escape steps followed by local geometry relaxations taking into account both atomic and cell variables. The initial velocities for the molecular dynamics trajectories are chosen approximately along soft mode directions, thus allowing efficient escapes from local minima and aiming towards low energy structures. The predictive power of this approach has been demonstrated in a wide range of applications [22–27].

Several minima hopping method simulations were performed with cells containing 2 and 4 f.u. of $LiAlH_4$ starting from different input configurations. During the search process, the energies and Hellman-Feynman forces were evaluated within the projector augmented wave formalism as implemented in ABINIT [28,29]. The Perdew-Burke-Ernzerhof [30] exchange-correlation functional was used, which has been found to give reasonable results in earlier studies on lithium alanates [18,19]. The results were refined by using norm-conserving Hartwigsen-Goedecker-Hutter pseudopotentials [31] with a plane-wave cutoff energy of 2700 eV and well converged Monkhorst-Pack [32] k-point meshes, resulting in an accuracy of the total energy better than 1 meV per atom. The atomic and cell degrees of freedom were fully relaxed, such that the maximum force components were less than 0.005 eV/Å and stress components less than 0.003 GPa.

During our structural search, we discovered a whole class of novel structures with low energies. These structures consist of negatively charged polymeric networks of H and Al atoms surrounded by Li^+ ions. These AlH_4 polymers have structures similar to polymeric alane [11] and form both wires and 2D planes within the material. Surprisingly, a large number of such structures was found to be energetically more stable than the experimentally observed α-$LiAlH_4$ phase. In Table I, we show a selection of these structures, together with the corresponding space group and total energy, taking also into account the zero-point energy (ZPE) correction within the harmonic approximation [34]. The most stable structure found in our simulations belongs to the $P2_1/c$ space group. We will hereon refer to this novel, polymeric structure as p-$P2_1/c$ and continue to refer to the experimentally observed structure as α-$LiAlH_4$. The p-$P2_1/c$ phase is energetically favored over the α-$LiAlH_4$ phase by $\Delta\mathrm{E} = -111.1$ meV/f.u. and $\Delta\mathrm{E} + \Delta\mathrm{ZPE} = -63.7$ meV/f.u. To reconfirm the energetic ordering, calculations with the local density approximation (LDA) [35] and the Heyd-Scuseria-Ernzerhof hybrid functional [36–38] (as implemented in the VASP code [39]) were carried out, resulting in the following relative energies: $\Delta\mathrm{E}_{\mathrm{LDA}} = -257.7$ meV/f.u., $\Delta\mathrm{E}_{\mathrm{LDA}} + \Delta\mathrm{ZPE}_{\mathrm{LDA}} = -208.5$ meV/f.u., and $\Delta\mathrm{E}_{\mathrm{HSE06}} = -506.7$ meV/f.u. Furthermore, comparing the configurational enthalpy shows that the stability of p-$P2_1/c$ increases monotonically with respect to α-$LiAlH_4$ under pressure at least below 8 GPa.

TABLE I. Several low-lying structures are listed with the corresponding space groups. The energy differences per formula unit of $LiAlH_4$ with respect to the previously reported α-$LiAlH_4$ structure are given in the third column, and the contributions of the vibrational ZPE are added in the fourth column. All these structures can be found in the Supplemental Material [33].

Symmetry	Space group	ΔE (meV)	ΔE + ΔZPE (meV)
$P2_1/c$ (deuterium)	14	−111.1	−74.9
$P2_1/c$	14	−111.1	−63.7
$P2_1$	4	−82.6	−34.2
$Pnc2$	30	−81.9	−30.9
$P2_1/m$	11	−81.2	−32.4
$Cmmm$	65	−66.3	−15.4
$P-1$	2	−65.2	−12.2
$P2_1/c$	14	−64.4	−15.8
$P1$	1	−56.8	−4.2
$P2/c$	13	−54.1	−0.7
$P-42_1m$	113	−49.5	−1.9

The unit cell of the p-$P2_1/c$ phase is shown in Fig. 1(a). At ambient pressure, the cell parameters are given by $a = 5.162$ Å, $b = 4.279$ Å, $c = 5.084$ Å, $\alpha = \gamma = 90°$, and $\beta = 66.831°$. One Li atom occupies the crystallographic $2b$ site at $(1/2, 0, 0)$, the Al atom occupies the $2c$ site at $(0, 0, 1/2)$, and the H atoms are at the $4e$ sites with coordinates $(0.131, 0.723, 0.680)$ and $(0.316, 0.175, 0.374)$. The Li atoms as well as the Al atoms are arranged in alternating parallel planes, where the Al atoms are interlinked with half the H atoms in the cell with an Al-H distance of 1.77 Å. The rest of the H atoms are single-bonded to the Al atoms, oriented out of plane at a bond length of 1.68 Å.

We simulated the XRD and neutron diffraction patterns of the p-$P2_1/c$ structure and compared them with the experimentally observed structure (α-$LiAlH_4$) of Ref. [13]. A comparison of the XRD spectrum is shown in Fig. 1(b) (the neutron diffraction pattern can be found in the Supplemental Material [33]). As expected, the XRD (and neutron) spectra of p-$P2_1/c$ and α-$LiAlH_4$ are quite different, proving that these are two distinct phases.

To investigate the electronic structure of the p-$P2_1/c$ phase, we used the perturbative many-body GW technique [35]. To converge the band structure to better than 0.1 eV, we used a $6 \times 6 \times 6$ k-point grid (112 points in the irreducible wedge of the Brillouin zone) and 35 empty bands. These calculations [see Fig. 2(b)] reveal that the p-$P2_1/c$ structure is an indirect band-gap semiconductor with a photoemission gap of 5.0 eV and a direct gap at Z of 5.3 eV. The top valance bands are essentially composed of states of d character provided by the Al atoms and a small portion of p states of Li, while the bottom of the conduction band is formed by s states of Al and p states of Li. The charge transfer among the constituent atoms was analyzed by using the Bader charge analysis method as implemented in the ABINIT package [40]. A charge of

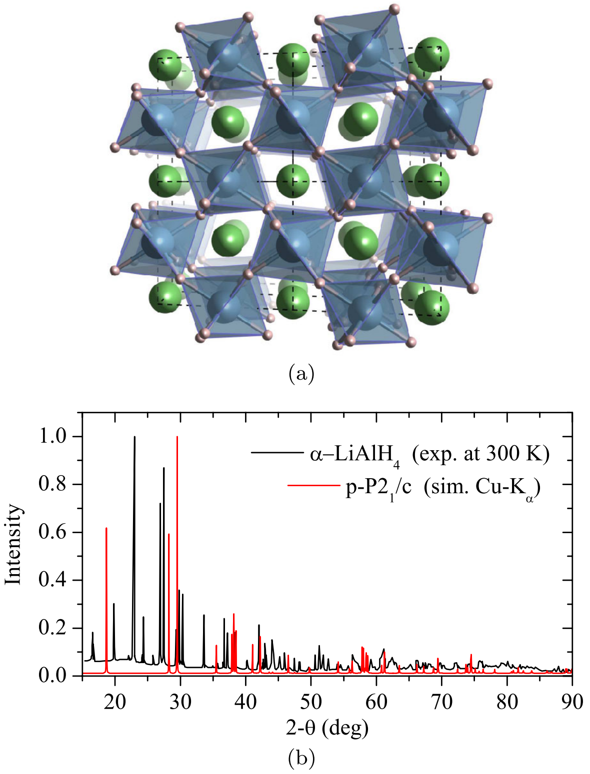

FIG. 1 (color online). (a) The crystal structure of the p-$P2_1/c$ phase shown from the top. The hydrogen atoms (small white spheres) form the corners of AlH_4 polyhedra containing aluminum atoms (in blue). The large (green) spheres represent the Li^+ ions. The arrangement of the polyhedra shows the polymeric structure of Al atoms interlinked by H atoms. In panel (b) the simulated XRD pattern of the p-$P2_1/c$ phase is compared with the experimental spectrum taken from Ref. [13].

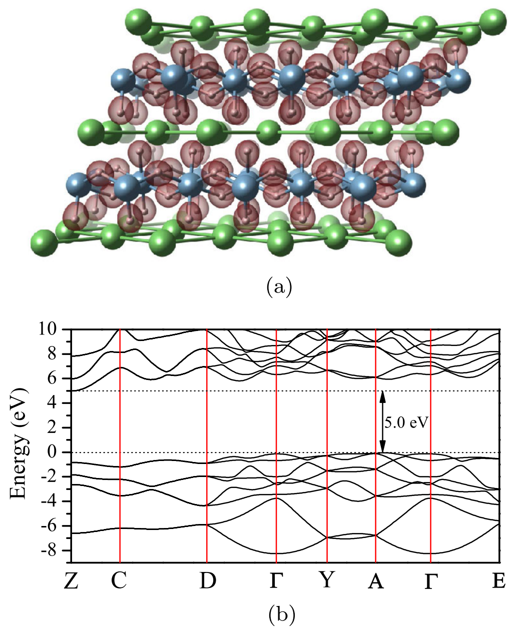

FIG. 2 (color online). Panel (a) shows the layered character of the ionic planes in the p-$P2_1/c$ phase and the isosurface of the charge density at the value of $0.06q_e$. The GW electronic band structure calculated for the p-$P2_1/c$ phase is illustrated in panel (b). The energy was shifted such that the top of the valence band has energy 0.

approximately $-0.87q_e$/atom is stripped off the Li atoms and transferred to the AlH_4^- substructure, leading to a layered ionic crystal. The electronic charge density within the p-$P2_1/c$ structure is illustrated in Fig. 2(a), clearly showing the layered ionic character of the phase.

We further investigated the dynamical stability of the p-$P2_1/c$ structure by performing calculations of the phonon dispersion. The phonon spectrum was obtained from density-functional perturbation theory [41] as implemented in ABINIT. Convergence was ensured by a $6 \times 6 \times 6$ Monkhorst-Pack k-point sampling and a $3 \times 3 \times 3$ q-point sampling for the phonon wave vectors. The longitudinal optical–transverse optical zone splittings were taken into account. However, the effect of the longitudinal optical–transverse optical zone splittings was found to be small, as previously reported for other hydride materials [42,43].

Figure 3(a) shows the phonon dispersion calculated for $LiAlD_4$. No imaginary phonon frequencies appear within the whole Brillouin zone, ensuring the dynamical stability of the structure. Replacing deuterium by hydrogen shifts up the characteristic frequencies due to the difference in the atomic masses. Figure 3(b) represents the partial phonon density of states. As expected, low frequency modes are mostly dominated by vibrations of the Al atoms, together with a smaller contribution from the Li atoms. The high energy range is predominated by the vibrations of deuterium (with frequencies around 1260 cm^{-1}) or hydrogen (around 1750 cm^{-1}).

Finally, we discuss why the experimentally observed phase is the α-$LiAlH_4$ and not the energetically lower p-$P2_1/c$ structure. An important hint comes from the observation that these structures contain very light atoms with high vibrational frequencies. One can therefore

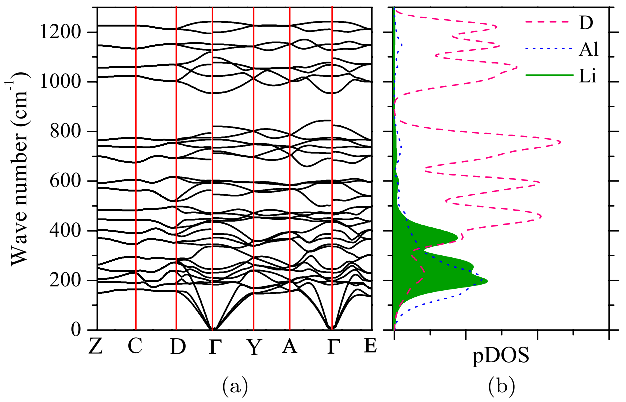

FIG. 3 (color online). (a) The $LiAD_4$ phonon band dispersion is shown, revealing the dynamical stability of the p-$P2_1/c$ structure. (b) The partial phonon density of states of $LiAD_4$ illustrating the contribution of the three atomic species.

expect that the phonon contribution to the (free) energy is large. We computed the ZPE correction within the harmonic approximation [34] for all low-lying structures listed in Table I. The correction is significant, being larger for phases containing AlH_4 polymers, since stronger covalent bonds are present compared to the softer ionic bonds of the α-$LiAlH_4$ phase. From Table I, we see that the ordering of the phases changes but that the p-$P2_1/c$ is still the lowest by 30 meV (and lower than the α-$LiAlH_4$ phase by 64 meV). Moreover, replacing hydrogen by deuterium further stabilizes the structure by around 10 meV.

The situation changes, however, at finite temperature. The temperature dependence of the free energy for the four phases with lowest energy is shown in Fig. 4 relatively to the α-$LiAlH_4$ structure. Within our approximation, the thermal expansion effects as well as the volume dependence of the ZPE are neglected since thermodynamic quantities have been reported to be fairly insensitive to these corrections [19]. Anharmonic contributions from possible molecular librations are also ignored. We can see that the p-$P2_1/c$ phase has the lowest free energy up to roughly 380 K, after which it crosses the α-$LiAlH_4$ phase. This shows that $LiAlH_4$, like many other similar layered (binary and ternary) amide-hydride systems [44], can have different polymorphs at different temperatures and pressures. These polymorphs are usually linked with the existence of cation vacancies, crystal defects, and the mechanism of the dehydrogenation or rehydrogenation process [45]. Furthermore, a direct comparison with the free-energy calculations in Refs. [18,19] shows that the p-$P2_1/c$ phase would lead to an endothermic behavior of reaction (1) at least for low temperatures. Note that one can expect a systematic error in the transition temperature due to the approximations employed in the density-functional theory and free-energy calculations.

Possible reasons for the fact that the p-$P2_1/c$ phase has not been observed yet might lie within the conventional methods to synthesize crystalline $LiAlH_4$. Originally, it was prepared from LiH and $AlCl_3$ in boiling diethyl ether [4], leading to temperatures of at least 307.8 K. In fact, temperatures might have been considerably higher and in a range where p-$P2_1/c$ becomes unstable or has a too high formation barrier. Industrial synthesis is performed through a metathesis reaction of $NaAlH_4$ with LiCl [46]. Since $NaAlH_4$ already contains complex AlH_4^- anions, its reformation and polymerization are unlikely, especially when considering the strong Coulomb repulsive forces. Using AlH_3 as a reactant and a low-temperature synthesis might be a possible pathway en route to the synthesis of the novel p-$P2_1/c$ phase. We propose the following reaction:

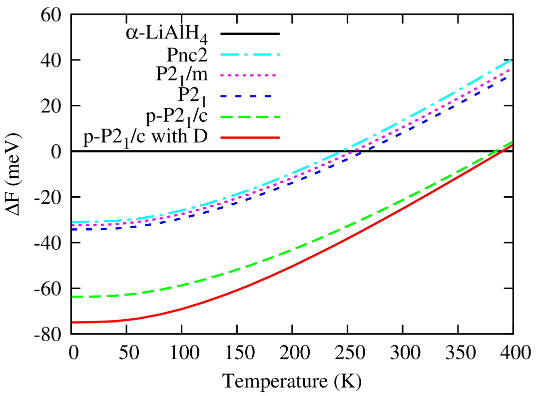

FIG. 4 (color online). The free-energy differences per formula unit of the four lowest phases are plotted with respect to α-$LiAlH_4$. The lowest curve represents the p-$P2_1/c$ structure where hydrogen was replaced by deuterium (with respect to α-$LiAlD_4$).

$$LiH + AlH_3 \rightarrow LiAlH_4. \qquad (3)$$

The reaction was studied with respect to its thermodynamic properties, by using the α-AlH_3 phase [47] with $R\bar{3}c$ symmetry, the $Fm3m$ LiH phase [48], and the novel p-$P2_1/c$ phase of $LiAlH_4$. Our calculations reveal that reaction (3) is exothermic by $\Delta E = 138.4$ meV/f.u. By taking into account the vibrational free energy, the reaction heat increases to $\Delta F_{0\,K} = 203.1$ meV/f.u. at a temperature of 0 K and $\Delta F_{298\,K} = 140.8$ meV/f.u. at a temperature of 298 K. Although these results do not guarantee the success of the above pathway, they show that it is thermodynamically accessible.

In conclusion, we performed a systematic structural search for $LiAlH_4$ and identified a class of novel structures. In contrast to other alanates and previous predictions, AlH_4 does not form complex anions but appears rather as a polymeric network. The most stable structure, p-$P2_1/c$, exhibits a layered ionic configuration and is favored at ambient pressure for temperatures up to roughly 380 K. This phase is a polar semiconductor with an indirect band gap of 5.0 eV, and by replacing hydrogen with deuterium the material can be further stabilized with respect to α-$LiAlD_4$. Moreover, it can probably be produced by using a low-temperature synthesis and by using precursors not containing complex AlH_4^- anions. As this phase is energetically more stable than α-$LiAlH_4$, there are good chances that it solves the stability problems of the latter. Furthermore, the existence of these new phases can have profound implications for the dehydrogenation and rehydrogenation process and for understanding and developing novel materials for hydrogen storage.

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