Integrated Experimental–Theoretical Investigation of the Na–Li–Al–H System

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First-principles modeling, experimental, and thermodynamic methodologies were integrated to facilitate a fundamentally guided investigation of quaternary complex hydride compounds within the bialkali Na–Li–Al–H hydrogen storage system. The integrated approach has broad utility for the discovery, understanding, and optimization of solid-state chemical systems. Density functional theory ground-state minimizations, low-temperature powder neutron diffraction, and low-temperature synchrotron X-ray diffraction were coupled to refine the crystallographic structures for various low-temperature distorted Na2LiAlH6 allotropes. Direct method lattice dynamics were used to identify a stable Na2LiAlH6 allotrope for thermodynamic property predictions. The results were interpreted to propose transformation pathways between this allotrope and the less stable cubic allotrope observed at room temperature. The calculated bialkali dissociation pressure relationships were compared with those determined from pressure-composition-isotherm experiments to validate the predicted thermodynamic properties. These predictions enabled computational thermodynamic modeling of Na2LiAlH6 and competing lower order phases within the Na–Li–Al–H system over a wide of temperature and pressure conditions. The predictions were substantiated by experimental observations of varying Na2LiAlH6 dehydrogenation behavior with temperature. The modeling was used to identify the most favorable reaction pathways and equilibrium products for H discharge/recharge in the Na–Li–Al–H system, and to design conditions that maximize the theoretical hydrogen reversibility within the Na–Li–Al–H system.

Introduction

This study will illustrate the utility of combining first-principles, experimental, and thermodynamic methodologies to tune the reversible hydrogen capacity within the Na–Li–Al–H compositional system. This integration of methodologies was inspired by the need to develop high capacity hydrogen storage media; however, the approach described herein is broadly applicable toward the discovery of new solid-state compounds and the investigation of their behavior. A quaternary phase within this system, Na2LiAlH6, has been the subject of a number of recent studies in the hydrogen storage community.1−6 A major motivation for studies of the Na–Li–Al–H system was the prospect of developing a mixed bialkali alanate phase that leveraged both the reversibility of the sodium alanates and the higher capacity of the lithium alanates.4−10 This rationale is evident from a van’t Hoff plot of the equilibrium sodium and lithium alanate dissociation pressures constructed from recent thermody-

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Figure 1. The van’t Hoff plot predicted for the first and second dissociation reactions of lithium and sodium alanate. The wt. % H$_2$ discharged and the dissociation enthalpy, $\Delta H_{\text{diss}}$, are listed for each reaction (from refs 11 and 12).

namic predictions$^{11,12}$ in Figure 1. The practical operating 1–100 bar pressure range and 25–100 °C temperature range for hydrogen storage reversible dehydrogenation and rehydrogenation on-board of a transportation vehicle was used to define an “in situ window of reversibility” in the plot. In the first reaction of the sodium alanate system, sodium aluminum tetrahydride, NaAlH$_4$, dissociates to release 3.7 wt. % molecular hydrogen, H$_2$. The predicted equilibirum dissociation pressure of this reaction traverses the in situ window of reversibility. However, the predicted equilibrium pressure for second sodium alanate dissociation reaction skims the lower left corner of the window of reversibility. Here, the more stable trisodium aluminum hexahydride, Na$_3$AlH$_6$, dissociates to release an additional 1.9 wt. % H$_2$. Since both reactions are only partially reversible in Ti-activated sodium alanate in practice,$^{12,13}$ the sodium alanate system does not meet the DOE 2006 hydrogen storage gravimetric target of 4.5 wt. % H$_2$. The lithium alanate system has a greater H$_2$ gravimetric capacity. In the first and second dissociation reactions given in Figure 1, lithium aluminum tetrahydride, LiAlH$_4$, and trilithium aluminum hexahydride, Li$_3$AlH$_6$, dissociate to release 5.3 and 2.6 wt. % H$_2$, respectively. However, as shown in Figure 1, the predicted dissociation pressures of these less stable reactions lie inaccessibly above the in situ window of reversibility. Recent modeling investigations exploring the possible increase in gravimetric capacity of the sodium alanates through lithium substitution on the sodium sublattice, or the possible lowering of the lithium alanates’ dissociation pressure through sodium substitution on the lithium sublattice, predicted that Na$_2$-LiAlH$_6$ is the sole stable phase in the Na–Li–Al–H quaternary system.$^{8–10}$ On the basis of these findings, integrated theoretical-experimental methodologies were used in this study to design the maximum theoretical hydrogen storage capacity that could be achieved with this Na$_2$LiAlH$_6$ phase within the Na–Li–Al–H system.

Methods

Experimental Synthesis and Characterization. Na$_2$LiAlD$_6$ was synthesized by ball milling LiAlD$_3$ and 2NaAlD$_3$ in a Fritsch P7 planetary ball mill with a ball to sample mass ratio of 20 and at 700 rpm for 3 h, followed by heat treatment at 180 °C and 30 bar. All operations were performed under argon in a glove box with less than 1 ppm O$_2$ and H$_2$O.

Synchrotron Radiation Powder X-Ray (SR–PXD) data at 110 K were collected at the Swiss-Norwegian beam line (station BM1B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The samples were kept in rotating 0.5 mm boron-silica-glass capillaries. Intensities were measured in steps of $\Delta(2\theta) = 0.003^\circ$. The wavelength 0.49957 Å was obtained from a channel-cut Si(111) monochromator.

Powder neutron diffraction (PND) data at 8 K were collected with the PUS instrument at the JEEP PI reactor at Kjeller, Norway. Neutrons with wavelength 1.5554 Å were obtained from a Ge-(511) focusing monochromator. The detector unit consists of two banks of seven position-sensitive $^3$He detectors, each covering 20° in 2θ (binned in steps of 0.05°). Data were collected from 10 to 130° in 2θ. The sample was placed in a rotating cylindrical vanadium sample holder with 5 mm diameter.

Rietveld refinements were carried out using the program Fullprof (version 2.80).$^{15}$ X-ray form factors and neutron scattering lengths were taken from the Fullprof library. Pseudo-Voigt profile functions were used, and the backgrounds were modeled by interpolation between manually chosen points.

First-Principles Calculations. Two methodologies were linked for the first-principles prediction of finite temperature thermodynamic properties of the solid-state phases in the Na–Li–Al–H system. These methodologies were detailed in preceding papers on the lower order phases within the Li–Al–H ternary system,$^{11}$ the Na–H binary system,$^{16}$ and the Na–Al–H ternary system.$^{12,17}$ The first methodology employed was a full structure minimization at the ground state using the density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP) version 4.6 with plane wave basis sets. The second methodology generated finite temperature thermodynamic predictions of the minimized structure using the direct method lattice dynamics approach of Parlinski et al.$^{21}$ implemented in the Materials Design Phonon direct method module interfaced with the VASP code$^{22}$ (herein referred to as the “Phonon direct method”). This study focused exclusively on the Na$_2$LiH$_4$ quaternary phase, which was predicted with geometry optimizations to be the only stable quaternary phase to exist within the Na–Li–Al–H system.$^{8–10}$ The thermodynamic predictions of lower order stable solid-state compound phases with the Na–Li–Al–H systems NaAlH$_4$, Na$_2$AlH$_6$, LiAlH$_4$, Li$_3$AlH$_6$, NaH, and LiH have already been reported.$^{11,12,16}$

The first-principles thermodynamic property predictions of these phases will be employed to make a comprehensive survey of possible reactions and competitive phase stability within the Na–Li–Al–H system.


(22) Parlinski, K. MedeA-Phonon Version 1.0 using Phonon Software 3.1; Materials Design, Inc.: Angel Fire, NM.
The Na–Li–Al–H System

This study sought to identify the most stable ground state Na2–LiAlH6 allotrope to input into the Phonon direct method for reliable thermodynamic predictions. The search for the most stable structure followed a structural analog protocol similar to that described in our paper on the Li–Al–H system\(^1\) and in subsequent studies on the biaalkali system.\(^8\)–\(^10\) Here, Na2LiAIH6 candidate structures were derived by substitution of ions into stoichiometrically equivalent analogous ternary and quaternary compounds having structures representing the widest possible range of space groups. The VASP minimizations employed the generalized gradient approximation (GGA) of Perdew and Wang,\(^2\) and the valence electrons were explicitly represented with projector augmented wave (PAW) potentials,\(^24\) using the valence configurations: Na 2s\(^2\)2p\(^3\), Li 2s\(^1\), Al 3s\(^3\)3p\(^1\), and H 1s\(^1\). The plane wave cutoff energy of 780 eV and the Gaussian smearing with an energy broadening of 0.2 eV was used. Odd-sized k-point meshes were created by a Monkhorst-Pack scheme for minimization of the primitive cells,\(^23\) using a k-mesh spacing of 0.2 Å\(^{-1}\) or smaller. The overall total energy convergence error for these parameters was well below 0.01 meV/unit cell. The convergence criterion for electronic self-consistent field convergence was 10\(^{-7}\) eV. A full minimization method was employed to allow simultaneous relaxation of ionic coordinates, unit cell size, and shape. The ground state structure was determined by minimizing the Hellmann–Feynman forces with the conjugate gradient algorithm, until all of the ionic forces were less than 0.005 eV/Å. Following convergence, the minimizations were restarted, as necessary, until no further ionic relaxation took place. A final total energy calculation with accurate precision was made using the tetrahedron smearing method with Bloechl corrections.\(^26\)

The Phonon direct method was employed to predict the lattice dynamics using the harmonic approximation on the VASP minimized Na2LiAIH6 structures that had the combination of the lowest ground state energy and the highest space group symmetry. Displacements were made on 1 \(	imes\) 1 \(	imes\) 1 supercell for the \(Fm\overline{3}m\) and \(P4/n\) Na2LiAIH6 structure (40 atoms each), and on a 2 \(	imes\) 2 \(	imes\) 1 supercell of \(P2_1/n\) Na2LiAIH6 structure (80 atoms). A 0.1 strength of condition factor was applied for translational invariance. Following the methodology described in the preceding Na–H paper,\(^16\) the integrated predicted phonon density of states was analyzed with statistical mechanical functions to determine the vibrational contribution as a function of temperature. The vibrational contribution was added to the ground state electronic energy, to approximate the Gibbs free energy as a function of temperature, \(G(T)\). The finite temperature free energy \(G(T)\) values referred to the constitutive stable element 298 K enthalpy values, are called GHSER values.\(^16\) Predicted hydride GHSER values were used in combination with established values for elemental and gaseous phases\(^27\)–\(^28\) in the Thermo-Calc program\(^29\) to calculate thermodynamic reaction energies, equilibria, and phase diagrams.

Results and Discussion

A thorough evaluation of the mixed sodium-lithium alanate system for hydrogen storage media required a thermody-
The Rietveld fit of one of the models, i.e., model II with \( \chi^2 \) of 2.07, \( 180^\circ \) Woodward, P. M.; Acta Cryst. B (32) Woodward, P. M.; Acta Cryst. B, same reliability factor. Five groups, seven of the models were eliminated. The remaining groups, looking at the unit cell size and extinctions of the space group. There are 23 tilt systems with 15 different models. By approximate atomic positions of the different tilt systems. They have given the unit cell size, space group, and very similar average Al–D distances that are close to the distances at room temperature. From PND measurements it was confirmed that the transition takes place above 110 K. Therefore, SR–PXD data at 110 K was used in an attempt to distinguish between the models. But no splittings of the cubic reflections, i.e., the reflections of the \( \text{Fm}\bar{3}m \) model, were observed. From PND and SR–PXD, it appeared that \( \text{Na}_2\text{LiAlD}_6 \) at low temperature assumed one of ordered perovskite structures in space group \( \text{Fm}\bar{3}m \) and \( \text{Pm}\bar{3}m \), average Al–D distances that are close to the distances at room temperature. From PND data, approximately the same number of atomic parameters, and very similar average Al–D distances that are close to the distances at room temperature. From PND measurements it was confirmed that the transition takes place above 110 K. Therefore, SR–PXD data at 110 K was used in an attempt to distinguish between the models. But no splittings of the cubic reflections, i.e., the reflections of the \( \text{Fm}\bar{3}m \) model, were observed. From PND and SR–PXD, it appeared that \( \text{Na}_2\text{LiAlD}_6 \) at low temperature assumed one of ordered perovskite structures in space group \( \text{C}2/c \), \( \text{P}2_1/\text{n} \), or \( \text{P}4_2/\text{n} \) described by Woodward, but it was not possible to conclude which one best described the crystal structure.

The first three tilt structures that gave the best refinement fits (cf. Table 1) were reviewed to prepare for Phonon direct method lattice dynamic simulations. First, full ground state minimizations were made of the newly identified \( \text{P}2_1/\text{n} \) model, \( \text{AlD}_6 \) and \( \text{LiD}_6 \) octahedra of different sizes, where each D corner is shared between two octahedra. \( \text{Na} \) atoms (red) are in interstitial positions surrounded by 12 D atoms.

### Table 1. Best Structural Models Tested for \( \text{Na}_2\text{LiAlD}_6 \) Powder Neutron Diffraction at 8 K

<table>
<thead>
<tr>
<th>rotation model</th>
<th>space group</th>
<th>( \chi^2 )</th>
<th>Al–D (Å)</th>
<th>no. of atomic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>I a'( b')c−</td>
<td>( \text{C}2/c )</td>
<td>2.07</td>
<td>1.768</td>
<td>11</td>
</tr>
<tr>
<td>II a'( b)−b−</td>
<td>( \text{P}2_1/\text{n} )</td>
<td>2.08</td>
<td>1.765</td>
<td>12</td>
</tr>
<tr>
<td>III a'( a)c−</td>
<td>( \text{P}4_2/\text{n} )</td>
<td>2.05</td>
<td>1.763</td>
<td>10</td>
</tr>
<tr>
<td>IV a'( b)c−</td>
<td>( \text{P}2/c )</td>
<td>1.98</td>
<td>1.770</td>
<td>22</td>
</tr>
<tr>
<td>V a'( b)c−</td>
<td>( \text{P}1 )</td>
<td></td>
<td>1.770</td>
<td>48</td>
</tr>
</tbody>
</table>

*Models based on ordered perovskite structures from Woodward, 1997, rotation mode according to Glazer, 1975; space group, \( \chi^2 \), average Al–D distance and number of atomic parameters are given.

### Figure 2. \( \text{Na}_2\text{LiAlH(D)}_6 \) powder neutron diffraction (PND) structural analyses at 8 and 295 K.

### Figure 3. Crystal structure of \( \text{Na}_2\text{LiAlH(D)}_6 \) at room temperature. \( \text{AlD}_6 \) octahedra (blue) and \( \text{LiD}_6 \) octahedra (green) form a corner-sharing network where each corner is shared between two octahedra. \( \text{Na} \) atoms (red) are in interstitial positions surrounded by 12 D atoms.

are very close to one another and are not distinguishable within the limits of accuracy for VASP ground state calculations. These results can be interpreted to imply that there may be a number of energetically equivalent crystal structures accessible at the ground state.

Phonon direct method lattice dynamic predictions were made on the highest symmetry $Fm\bar{3}m$, $P4/n$, and $P2_1/n$ minimized structures. This enabled the comparison of the phonon dispersion relations of the original refined $Fm\bar{3}m$ structure with two of the most stable, energetically equivalent simulated structures. The phonon dispersion relations for the $Fm\bar{3}m$ and $P2_1/n$ phases are shown in Figure 5a–b. Both the $Fm\bar{3}m$ and the $P4/n$ dispersion relations exhibited significant imaginary frequencies representing instabilities to transformation to other phase structures. The $Fm\bar{3}m$ structure dispersion had an unstable $T_{1g}$ acoustical mode at the $\gamma$ point. The $P4/n$ structure had two imaginary $B_{2g}$ and $A_g$ Raman-active branches. The $P2_1/n$ structure lacked imaginary dispersion frequencies and was hypothesized to be the most stable ground state phase.

These observations brought forth to question the relationship between the predicted stable $P2_1/n$ ground state structure and the experimentally observed $Fm\bar{3}m$ room-temperature structure. The first scenario postulated was that the $Fm\bar{3}m$ structure could undergo one or more second-order transformations with decreasing temperature to form the $P2_1/n$ structure. One possible pathway could be a multistep transformation of $Fm\bar{3}m$ to $P4/n$ structure, followed by transformation to the $P2_1/n$ structure. However, animation with the Medea Phonon module of the $Fm\bar{3}m$ instability at the $\Gamma$ point led to a $P1$ structure. Likewise, animation of the instabilities at the $W$, $X$, $Y$, and $L$ points led to a structures in the space groups $P2_1$, $P4/nmc$, $Pm$, and $R3$, respectively. Following an established approach for the investigation of phase transformations, the Bilbao Crystallographic Server Subgroupgraph program was used to determine whether the $P2_1$, $P4/nmc$, $Pm$, and $R3$ spacegroups and other spacegroups could be intermediate subgroups between the $Fm\bar{3}m$ spacegroup and the $P2_1/n$, $C2/c$, or $P4/n$ structures. Indeed, such a direct transformation pathway was found between the $Fm\bar{3}m$ and the $P2_1/n$ and $C2/c$ structures via the $X$ instability, through the $P4/nmc$ structure. This means that these monoclinic structures are closely related to the instability of the cubic structure, which may explain why the latter is not stable at low temperatures.

The predicted GHSER values for the $P2_1/n$ Na$_2$LiAlH$_6$ phase are compared to those for the $Fm\bar{3}m$ phase in Figure 7, where only the integrated phonon density of state values over frequencies $\leq 0$ were used to predict the $Fm\bar{3}m$ phase thermodynamic values. The $P2_1/n$ phase was predicted to be significantly more stable than the $Fm\bar{3}m$ phase at all temperatures. A crossover in the GHSER values, which would indicate a transformation from the $P2_1/n$ phase to the $Fm\bar{3}m$ phase with increasing temperature, was not predicted. A second simpler scenario relating the phase structures is even more credible. The $P2_1/n$ and other simple tilt structures.
could be actually comprised of two (or more) mirror-symmetry equivalent structures, each where the AlH₆ octahedra are tilted off-center from the Fm3m cubic structure in opposite directions. With the availability of kinetic energy with increasing temperature, the energy barriers to tilting could be overcome, and the octahedra could rapidly tautomerize between these equivalent structures. During the crystallographic analyses at elevated temperatures, these equivalent oscillations could be time-averaged to appear as the intermediate cubic structure. In order to explore this possible phenomenon, the Fm3m structure was recast in Pm3n symmetry, and a tilting pathway with three intermediate steps was constructed between the two structures. By recasting the Fm3m structure in the Pm3n symmetry, the unit cell and atom positions were as similar as possible to the n structure. The structure at any reasonable temperature may actually be the tautomer average of a number of energetically similar structures that represent different tilting of the AlH₆ octahedra (such as the most favorable structures listed in Table 2).

Thermodynamic descriptions generated from the Phonon direct method were used to evaluate compound formation and dissociation reactions within the Na−Li−Al−H system. The various mechanochemical routes reported in the literature for the synthesis of the Na₂LiAlH₆ phase²−⁵,35 are summarized in Table 3. Many of these syntheses used annealing treatments to increase the detectable yield of Na₂LiAlH₆. The predicted thermochemical equilibrium constants, K_eq, for the related Na₂LiAlH₆ synthetic reactions versus temperature

$$\text{LiH} + 2\text{NaH} + \text{AlH}_3 = \text{Na}_2\text{LiAlH}_6$$  \(\text{(1)}\)

$$\text{LiAlH}_4 + 2\text{NaH} = \text{Na}_2\text{LiAlH}_6$$  \(\text{(2)}\)

$$\text{LiH} + \text{NaH} + \text{NaAlH}_4 = \text{Na}_2\text{LiAlH}_6$$  \(\text{(3)}\)

$$1/3\text{Li}_3\text{AlH}_6 + 2/3\text{NaAlH}_4 = \text{Na}_2\text{LiAlH}_6$$  \(\text{(4)}\)

$$\text{LiAlH}_4 + 2\text{NaAlH}_4 = \text{Na}_2\text{LiAlH}_6 + 2\text{Al} + 3\text{H}_2$$  \(\text{(5)}\)

$$\text{LiH} + 2\text{NaAlH}_4 = \text{Na}_2\text{LiAlH}_6 + \text{Al} + 3\text{H}_2$$  \(\text{(6)}\)

are plotted in Figure 8. The higher the K_eq, the greater the reaction equilibrium shifts to the products. As expected, in reactions 1 and 2 with the metastable AlH₃ and LiAlH₄ precursors were predicted to have a greater Na₂LiAlH₆ yield. However, the K_eq for these reactions decreases with increasing temperature, and reaction 5 is predicted to predominate at temperatures greater than ~373 K (~100 °C). These predictions show why the reaction 5 using NaAlH₄ and LiAlH₄ precursors employed by Brinks et al.³ required a 453 K anneal to increase the Na₂LiAlH₆ fraction. These results demonstrate the potency of the predictive thermodynamic methodology for designing the best experimental conditions for synthesis of a target phase.

The thermochemical predictions provided insight into how various possible dissociation mechanisms may be interrelated with changing temperature. Hydride dissociation reactions are commonly described in terms of reaction dissociation enthalpies, ΔH_diss, determined from the slope of the Arrhenius plot of the equilibrium H₂ pressure formed upon dissociation versus the reciprocal of the equilibrium temperature, according to the van’t Hoff equation: In P_H₂ = ΔH_diss/RT + ΔS/R, where P is the equilibrium H₂ pressure at temperature T, S in the dissociation entropy, and R is the universal gas constant. The predicted ΔH_diss for Na₂LiAlH₆ and Na₃AlH₆ dissociation reactions per dissociation of 1 mole H₂

Table 3. Summary of Reported Na₂LiAlH(D)₆ Mechanochemical Syntheses

<table>
<thead>
<tr>
<th>reactants</th>
<th>anneal T (K)</th>
<th>anneal P (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH + 2NaH + AlH₃</td>
<td>373</td>
<td>200</td>
</tr>
<tr>
<td>LiAlH₄ + 2NaH</td>
<td>423</td>
<td>50</td>
</tr>
<tr>
<td>LiH + NaH + NaAlH₄</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>LiH + NaH + NaAlH₄</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>LiAlH₃ + 2NaAlH₄</td>
<td>453</td>
<td>30</td>
</tr>
<tr>
<td>LiH + 2NaAlH₄</td>
<td>453</td>
<td>80</td>
</tr>
</tbody>
</table>

The Na–Li–Al–H System

\[ \frac{2}{3}Na_2LiAlH_6 \rightarrow 4/3NaH + 2/3LiH + 2/3Al + H_2 \]  
(7)

\[ \frac{2}{3}Na_3AlH_6 \rightarrow 2NaH + 2/3Al + H_2 \]  
(8)

are compared to \( \Delta H_{\text{dis}} \) values determined from pressure composition isotherm measurements\(^5,\text{36} \) in Table 4. The predicted \( \Delta H_{\text{dis}} \) values were smaller, but were within 10 kJ/mol of the reported measured equilibrium values. A residual error of up to 10 kJ/mol in the predicted \( \Delta H_{\text{dis}} \) can impact the predicted dissociation pressure by a factor of up to 25 at 373 K.

The differences between the predicted and measured values were most likely due to the inherent inaccuracies in the ground state minimizations with the density functional exchange-correlation GGA approximation, and/or the harmonic approximation which does not account for the possible anharmonic free rotational modes of the \( AlH_6 \) octahedra. Such rotations would be described by 3 of the 27 total degrees of freedom in the \( Na_2LiAlH_6 \) structures, and thus affect a relatively small proportion of the vibrational thermodynamic contributions. An upper bound to the error from using the harmonic approximation for the rotations of the \( AlH_6 \) groups is given by assuming that they are free rotors and comparing the thermodynamic functions to those calculated for the approximately 3 THz harmonic oscillators from the harmonic approximation. The error in the enthalpy and free energy is no more than 6 kJ/mol over the temperature range considered. This is an upper bound and the actual error due to the harmonic approximation is probably considerably less.

The van’t Hoff plot for the most favorite predicted dissociation reactions are shown in Figure 9, in terms of equivalent starting amount of \( Na_2LiAlH_6 \) (not per equivalent mole of \( H_2 \) generated), for ease of comparison. The expected dehydrogenation reaction to form binary hydrides, aluminum and 3.5 wt. % \( H_2 \) [reaction 7], is predicted to be favorable at temperatures above 360 K (87 °C). The predicted dissociation curve traverses the lower left-hand corner of the window of reversibility, generating a lower dissociation pressure with respect to the dissociation reaction for the equivalent amount of \( Na_3AlH_6 \) (the comparison can be made by referring to Table 4). At temperatures below 360 K, a higher dissociation \( H_2 \) pressure and hence greater favorability is predicted for the reaction

\[ \frac{2}{3}Na_2LiAlH_6 \rightarrow 4/9Na_3AlH_6 + 2/3LiH + 2/9Al + 1/3H_2 \]  
(9)

which releases only 1.2 wt. % \( H_2 \).

Experimental observations corroborated the predicted relationship between the competing \( Na_2LiAlH_6 \) dissociation reactions 7 and 9. In situ PXD showed that for Ti-enhanced \( Na_2LiAlH_6 \) heated in vacuum at 1 K/min, \( Na_3AlH_6 \) was partially dissociated via \( Na_3AlH_6 \) before \( Na_2LiAlH_6 \) was thermally dissociated to \( NaH, LiH \) and \( Al \). The \( Na_3AlH_6 \) formed was dissociated before the remaining \( Na_2LiAlH_6 \).

Table 4. Comparison of Predicted and Measured Dissociation Energies

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H_{\text{dis}} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predicted</td>
<td>Measured</td>
</tr>
<tr>
<td>( 2/3Na_2LiAlH_6 \rightarrow 4/3NaH + 2/3LiH + 2/3Al + H_2 )</td>
<td>47.5</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2/3Na_3AlH_6 \rightarrow 2NaH + 2/3Al + H_2 )</td>
<td>44.8</td>
</tr>
</tbody>
</table>

* Reference 4.  
* Reference 5.  
* Ref 36.

reacted. The same effect was seen, but to less degree, with pure \( Na_2LiAlH_6 \). Traces of \( Na_3AlH_6 \) were seen in the diffraction diagrams at intermediate temperatures below the main dissociation of \( Na_2LiAlH_6 \). This proved experimentally that at lower temperature, \( Na_3AlH_6 \) was more stable than \( Na_2LiAlH_6 \), whereas at higher temperature \( Na_3AlH_6 \) was less stable than \( Na_2LiAlH_6 \). In addition, it showed that the metal ions had sufficient mobility for such a reaction to take place at relatively low temperature.

Phase diagram predictions were made to assess the relative stability of the different phases in the quaternary Na–Li–Al–H system with composition, temperature, and pressure. An excellent perspective was obtained from Na–Li–Al ternary sections calculated at constant \( H_2 \) activity, temperature, and pressure. Ternary sections generated with the fixed conditions (a) 100 bar, 300 K (27 °C), and \( 3.9 \times 10^{-3} \) \( H_2 \) activity and (b) 100 bar, 400 K (127 °C), and \( 1.0 \times 10^{-3} \) \( H_2 \) activity are shown in Figure 10a,b. The lines in these diagrams demarcate the regions where common sets of phases coexist. The \( Na_2LiAlH_6 \) phase is shown to coexist with the ternary alanate and the elemental hydride phases is predicted over a wide compositional range in these diagrams.

The phase equilibria were systematically surveyed over varying conditions to identify the composition, temperature, and pressure conditions for the optimum reversible hydrogen retrieval in the Na–Li–Al–H system. The optimum composition contained the elemental stoichiometry: \{2 Na:1 Li:2 Al:3 H\}.
Under the conditions of 300 K and 100 bar, this composition is predicted to form fully hydrided NaAlH₄ and LiH phases, in a ratio of 2:1. The predictions show that LiH destabilizes the dissociation of NaAlH₄ to form the more favorable Na₂LiAlH₆ phase [reaction 6], increasing the H₂ plateau pressure approximately 1 order of magnitude to 11 bar at 306 K (33°C) compared to the first dissociation reaction of pure NaAlH₄.\(^{36}\)

\[
\text{NaAlH}_4 = 1/3\text{Na}_3\text{AlH}_6 + 2/3\text{Al} + \text{H}_2 \quad (10)
\]

However, the benefits for destabilization are compromised by the extra weight of LiH which dilutes the total capacity of NaAlH₄ and the smaller amount of H₂ released in the first dissociation step: 2.6 wt. % H₂ for reaction 6 versus 3.7 wt. % H₂ for reaction 10. At temperatures higher than 360 K at 1 bar pressure, the dissociation of the Na₂LiAlH₆ phase [reaction 7] has a greater equilibrium constant than the dissociation of the equivalent amount of pure Na₃AlH₆ [reaction 8]. The amount of hydrogen released is greater in the Na₂LiAlH₆ decomposition reaction, 2.6 wt. % H₂, compared to that released in the second Na₃AlH₆ dissociation reaction, 1.9 wt. % H₂. It is envisioned that the two step dissociation process could be used to extract 5.2 wt. % H₂ reversibly from the optimum \{2Na:1Li:2Al:9H\} composition: first, degassing through reaction 6 by changing the pressure from 100 to 1 bar at room temperature, and second, degassing through reaction 7 by increasing the temperature to ≥400 K at 1 bar pressure. This reaction pathway is summarized schematically in Figure 11. In practice, often even higher temperatures and/or lower pressures are required to overcome kinetic barriers and to achieve acceptable hydrogen discharge rates. The feasibility of the forward reaction scheme has been experimentally confirmed in recent synthetic studies;\(^{35}\) however, the reversibility and kinetics of these coupled reactions await further experimental examination.

Conclusion

Combined experimental and theoretical methodologies were used to investigate the structure and transformation behavior of the Na₂LiAlH₆ phase. A low-temperature \(P2_1/n\) monoclinic structure was jointly identified through crystallographic refinement and direct method lattice dynamics to be a suitable stable ground state structure for thermodynamic property predictions. Two feasible transformation pathways were proposed to relate this structure to the less stable room temperature observed \(Fm\overline{3}m\) structure. First, the \(Fm\overline{3}m\) structure may directly transform to the \(P2_1/n\) structure along the \(X\) instability, passing through an intermediate \(P4/nmc\) structure. Second, the \(Fm\overline{3}m\) structure could actually be the time-average of a structure that rapidly oscillates between one or more pairs of mirror-symmetry perovskite distortions, formed by tilting of the AlH₆ octahedra. The thermodynamic predictions enabled the thermodynamic modeling of the Na₂-LiAlH₆ syntheses and dehydrogenation reactions, generating unique insights into competing reaction mechanisms. The calculated bialkali dissociation pressure relationships were compared with those determined from pressure-composition-isotherm experiments to validate the predicted thermodynamic properties. The predictions of varying Na₂LiAlH₆ dehydrogenation behavior with temperature were substantiated by experimental observations and were used to aid in their interpretation. Gibbs energy minimization and phase diagram predictions were then used to determine the reaction
pathways for the maximum theoretical capacity of 5.2 wt. % H$_2$ that could be achieved with the Na–Li–Al–H system.

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