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Crystal structures and pressure-induced phase transformations of LiAlH\textsubscript{4}: A first-principles study

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ABSTRACT

Given the fact that lithium aluminum hydride (LiAlH\textsubscript{4}) can exist in distinct crystalline structures under different conditions, in this study, we aim to theoretically investigate the structural properties and the pressure-induced phase transformations of its 13 closely related crystal structures by means of the density functional theory (DFT). The present study reveals that the phase transformation of LiAlH\textsubscript{4} from the most stable form (\(\alpha\)-phase) to the second most stable form (\(\beta\)-phase) occurs at approximately 3.3 GPa, corresponding to a volume collapse of \(\sim 14\%\) and a reduction of 22\% in the crystal volume. Due to the relatively higher hydrogen weight content, \(\beta\)-LiAlH\textsubscript{4} becomes a potentially attractive candidate for solid-state hydrogen storage at moderate pressures. The two most stable forms, i.e., the structures with the (i) \(P\overline{2}_1/c\) (\(\alpha\)-LiAlH\textsubscript{4}) and (ii) \(I\overline{4}1/a\) (\(\beta\)-LiAlH\textsubscript{4}) space groups, have been selected so that their structural and electronic properties can be discussed in greater detail. Our study also shows that the numerical results are greatly influenced by the choice of the DFT methods used, such as the exchange-correlation functionals and optimization schemes.

I. INTRODUCTION

Recently, there have been a number of studies devoted to developing cleaner, safer, renewable, and more efficient fuel sources due to the dramatic population growth worldwide and the rapid increase in the demand of critically limited fossil fuel. Obviously, these factors have strong negative impacts on the global environment. Among many different types of alternative fuel sources, solid-state hydrogen storage materials have become more and more attractive due to their light weight, low cost, high storage capacity, and compactness. Metal hydrides and their complexes are among those materials that hold great promise as a powerful hydrogen resource. In this work, we particularly focus on LiAlH\textsubscript{4} as a prime example of those metal hydride complexes. The central aim of this work is to study the crystal and electronic structures, stability, and pressure-induced phase transformations of LiAlH\textsubscript{4} using \textit{ab initio} calculations by means of density functional theory (DFT).

Lithium aluminum hydride, LiAlH\textsubscript{4}, is a metal hydride complex that has a considerably high hydrogen storage capacity, i.e., \(\sim 10.6\%\) by weight. It is commonly used as a strong reducing agent in chemical synthesis and a hydrogen fuel generator in the laboratory as the solid violently reacts with water, releasing flammable hydrogen gas. According to the x-ray and neutron diffraction study by Hauback and co-workers, LiAlD\textsubscript{4} crystallizes in the monoclinic-\(P2_1/c\) space group (\(\alpha\)-form) with the unit cell parameters \(a = 4.8254\), \(b = 7.8048\), and \(c = 9.8968\) Å and \(\beta = 112.268^\circ\) at 8 K. The study also shows that each of the lithium atoms in the crystal is surrounded by five neighboring deuterium atoms from (AlD\textsubscript{4})\textsuperscript{−} tetrahedral complexes in the shape of a trigonal bipyramid with Al–D distances ranging between 1.59 Å and 1.64 Å.

A number of experimental observations have found that the LiAlH\textsubscript{4} solid decomposes to Li\textsubscript{3}AlH\textsubscript{6} and LiH and then eventually forms the LiAl alloy as the temperature is slowly elevated. Additionally, previous studies have also shown that the hydrogen charge/discharge process in the LiAlH\textsubscript{4} solid is reversible.
The reversibility and thermodynamic properties of the hydrogenation and dehydrogenation processes of LiAlH₄ have been studied by the combination of thermal desorption spectroscopy, x-ray diffraction, thermogravimetry and differential thermal analyses. The studies have also pointed out that the pure LiAlH₄ solid decomposes at very high temperatures (under a moderate pressure), which is obviously not practical for real-world applications as a solid-state hydrogen fuel source. However, these poor thermodynamic properties of the solid can be significantly improved by adding some chemical additives, such as Ti, V, Ce, La, and the salts of some other transition metals.

Under different conditions, α-LiAlH₄ can transform to other phases. In 1977, Bulychev et al. experimentally studied the temperature-dependent phase transformations of α-LiAlH₄ at constant pressure. At 7 GPa, α-LiAlH₄ (monoclinic-P2₁/c) transforms to β-LiAlH₄ (tetragonal-I4₁/a) at ~250–300 °C, and it subsequently transforms to γ-LiAlH₄ (orthorhombic-Pnma) at 500 °C. In 1987, similar results were obtained by Bastide et al.¹⁸

With the same approach, one can also obtain the information of the phase transformations of the crystalline solid induced by external pressure through isothermal experiments. According to the studies by Talyzin and Sundquist¹⁹ and Chellappa et al.,¹² the pressure-induced phase transformations of LiAlH₄ have been experimentally observed using in situ Raman spectroscopy at room temperature. The studies have revealed that the α-phase transforms to the β-phase at approximately 2–4 GPa.

Vajeeston et al.¹¹ have shown that computational studies of the properties of many hydride solids using the first-principle density functional theory (DFT) play a crucial role in understanding, predicting, and developing novel solid-state hydrogen storage materials. Previously, there were a number of computational studies focusing on the crystal structures and thermodynamic properties of LiAlH₄.¹⁴–¹⁶ Vajeeston and co-workers¹⁷ have theoretically proposed that α-LiAlH₄ successively transforms to β-LiAlH₄ and γ-LiAlH₄ at 2.6 GPa and 33.8 GPa, respectively, at absolute zero. The study is in good agreement with the previous experimental observations.

The aforementioned structural transition evidence provides valuable insights that pressure can perturb the stability of the lithium aluminum hydride crystal and the existence of thermodynamically stable polymorphs pose a considerable challenge. In the present study, we aim to theoretically explore more on the extensive data set, i.e., available closely related potential phases, and pressure-induced phase transformations of the LiAlH₄ solid through means of ab initio approaches. The 13 crystal structures considered in this work are in phase with the Ama₂, Cmc₂₁, Cnmc, I₄₁/a, P₂₁/c, P₄₂₁/c, P₂₃/m, P₄/mmm, P₆₃/mc, Pm, and Pnma space groups. Furthermore, we also aim to point out the influences of the choice of the DFT methods used on the numerical results, e.g., the effects of different exchange-correlation functionals and optimization schemes.

II. COMPUTATIONAL DETAILS

The initial crystal structures of LiAlH₄ were obtained from a materials database maintained by the Materials Project,¹ except for the P₄/mmm and P₄₂₁/c structures which were brought from Ref. 16. Three existing structures of LiAlH₄ within the database, i.e., the I₄₁/a, P₂₁/c, and Pnma structures, were immediately chosen for electronic calculations. On the other hand, the other structures were selected using different parent crystal structures whose stoichiometry is identical to that of LiAlH₄, such as LiBH₄, NaAlH₄, and NaBH₄. Further details on the initial structures can be found in the supplementary material provided online.

For static total-energy calculations, the electronic wave-functions were represented by the plane-wave basis set (PAW)¹⁹ as an implementation in the Vienna Ab initio Simulation Package (VASP).³⁰ The accurate exchange and correlation energy were obtained using the generalized-gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) functionals.¹¹,²² A plane-wave energy cutoff of 650 eV was used for all the calculations. For the P₂₁/c-phase structure at equilibrium, we have used 462 k-points (11 × 6 × 7 sampling k-mesh) within the Brillouin zone (BZ). For consistency in the numerical results, we have used similar k-grid densities for the other structures. First, all of the initial crystal structures were fully relaxed using the conjugate–gradient (CG) minimization method with stopping criteria of 0.01 meV and 0.01 eV Å⁻¹ for the self-consistent electronic and ionic steps, respectively. The optimized structures are illustrated in Fig. 1. To be more precise, before constructing the volume–energy or pressure–energy profiles,

![FIG. 1. Optimized structures of LiAlH₄ with 13 different space groups: (a) Ama₂, (b) Cmc₂₁, (c) Cnmc, (d) I₄₁/a, (e) P₂₁/c, (f) P₄₂₁/c, (g) P₂₃/m, (h) P₄/mmm, (i) P₆₃/mc, (j) Pm, and (m) Pnma.](scitation.org/journal/adv)
TABLE I. Effects of exchange-correlation DFT functional on structural properties.

| Property                  | LDA     | GGA-PBE | GGA-PBESol | Experiment* |
|---------------------------|---------|---------|------------|-------------|
| Cell parameters (Å)       |         |         |            |             |
| \(a\)                     | 4.6292  | 4.8457  | 4.7055     | 4.8174      |
| \(b\)                     | 6.7487  | 7.8228  | 6.9158     | 7.8020      |
| \(c\)                     | 7.7786  | 7.8081  | 7.9212     | 7.8214      |
| \(\beta\)                 | 112.638 | 111.714 | 112.318    | 112.228     |
| Crystal volume (Å\(^3\) f.u.\(^{-1}\)) | 56.0720 | 68.7440 | 59.6171    | 68.0310     |
| Density (g cm\(^{-3}\))   |         |         |            |             |
|                           | 1.1239  | 0.9167  | 1.0570     | 0.9263      |

*From Ref. 1.

TABLE II. Optimized cell parameters, gravimetric density, and calculated total energy for LiAlH\(_4\) with 13 different space groups.

| Space group | Cell parameters (Å) | Volume (Å\(^3\) f.u.\(^{-1}\)) | Density (g cm\(^{-3}\)) | Energy (eV f.u.\(^{-1}\)) |
|-------------|---------------------|---------------------------------|--------------------------|---------------------------|
| Amm2 (40)   | \(a = 7.1956\)      | 62.6548                         | 1.0058                   | -19.9034                  |
|             | \(b = 7.0992\)      |                                 |                          |                           |
|             | \(c = 4.9061\)      |                                 |                          |                           |
| Cmc2\(_{1}\) (36) | \(a = 3.4020\)      | 54.6768                         | 1.1525                   | -20.0089                  |
|             | \(b = 13.5609\)     |                                 |                          |                           |
|             | \(c = 4.7406\)      |                                 |                          |                           |
| Cmcm (63)   | \(a = 6.4582\)      | 70.6974                         | 0.8914                   | -19.9972                  |
|             | \(b = 7.1831\)      |                                 |                          |                           |
|             | \(c = 6.0959\)      |                                 |                          |                           |
| F\(_{4}\)\(_{3}\)m (216) | \(a = 6.7668\)      | 77.4622                         | 0.8135                   | -18.8197                  |
|             | \(b = 7.1831\)      |                                 |                          |                           |
|             | \(c = 6.0959\)      |                                 |                          |                           |
| I\(_{4}\)\(_{1}/a\) (88) | \(a = 4.5758\)      | 53.4856                         | 1.1782                   | -20.0261                  |
|             | \(c = 10.2181\)     |                                 |                          |                           |
| P\(_{2}\)\(_{1}/c\) (14) | \(a = 4.8457\)      | 68.7440                         | 0.9167                   | -20.0765                  |
|             | \(b = 7.8228\)      |                                 |                          |                           |
|             | \(c = 7.8081\)      |                                 |                          |                           |
| \(\beta = 111.714\)\(^{3}\) |         |                                 |                          |                           |
| P\(_{4}\)\(_{2}\)\(_{1}/c\) (114) | \(a = 4.5338\)      | 60.4485                         | 1.0425                   | -19.8528                  |
|             | \(c = 5.8816\)      |                                 |                          |                           |
| P\(_{4}\)/\(_{2}/nm\)) (137) | \(a = 5.4192\)      | 76.6339                         | 0.8223                   | -19.5384                  |
|             | \(c = 5.2190\)      |                                 |                          |                           |
| P\(_{4}\)\(_{3}\)\(_{3}\)m (215) | \(a = 4.0630\)      | 67.0732                         | 0.9395                   | -19.7244                  |
|             | \(c = 4.4938\)      |                                 |                          |                           |
| P\(_{6}\)\(_{3}\)mc (186) | \(a = 4.9028\)      | 90.0521                         | 0.6998                   | -19.3311                  |
|             | \(c = 8.6518\)      |                                 |                          |                           |
| P\(_{m}\) (6) | \(a = 4.5772\)      | 76.6761                         | 0.8219                   | -19.7309                  |
|             | \(b = 5.0336\)      |                                 |                          |                           |
|             | \(c = 6.7073\)      |                                 |                          |                           |
| \(\beta = 97.0932\)\(^{3}\) |         |                                 |                          |                           |
| P\(_{n}\)\(_{m}\) (62) | \(a = 6.4628\)      | 58.2621                         | 1.0816                   | -19.9445                  |
|             | \(b = 5.4434\)      |                                 |                          |                           |
|             | \(c = 6.6245\)      |                                 |                          |                           |
all of the structures have already been fully optimized, i.e., without any constraints. The cell parameters and atomic coordinates at equilibrium are also listed in the supplementary material provided online. For the pressure-induced phase transitions of LiAlH₄, we have performed ionic relaxations at different constant volumes for all crystal structures in order to obtain volume–energy and volume–pressure profiles.

III. RESULTS AND DISCUSSION

A. Structural properties and stability analysis

In calculations using DFT, the level of its reliability strongly depends on how the approximations to the exchange and correlation energy as a function of the electron density are made. To choose the most suitable functional, in this work, the structural properties of the fully optimized structures of α-LiAlH₄ using three common DFT exchange-correlation functionals, i.e., the local-density approximation (LDA), the generalized-gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE), and the revised version of the GGA-PBE designed for solids (GGA-PBEsol), were first observed and compared with those from the experiment, as listed in Table I. Unlike the LDA, where the exchange-correlation energy solely depends on the electron density at a particular point, the GGA additionally includes its gradient at the point. With this extra information, GGAs are therefore expected to be more accurate in general. According to Narasimhan and de Gironcoli, the LDA tends to underestimate the lattice constants and thermal expansion coefficients of crystalline solids at all temperatures, while the GGA tends to overestimate those parameters. Compared to the GGA-PBE, the GGA-PBEsol is adjusted to more accurately reproduce the bulk properties of crystals. For densely packed crystals, e.g., metals and other non-molecular solids, the GGA-PBEsol yields better lattice parameters and other bulk properties. However, the GGA-PBEsol is found to be less accurate for molecular systems in general. Table I clearly shows that the GGA-PBE functional has the best agreement with the properties observed experimentally, while the LDA and GGA-PBEsol both significantly underestimate the crystal volume leading to the relatively high crystal densities. This can be due to the structures of LiAlH₄ containing molecule-like units, e.g., (AlH₄)⁻. Therefore, we have considered using the GGA-PBE functional for all calculations in this work.

It can be observed from Fig. 1 that all the crystalline structures of LiAlH₄ with the 13 space groups can be depicted as different arrangements of Li atoms and Al–H complexes in the crystal. In most structures, each of the Al atoms forms a tetrahedral complex with four neighbor H atoms, while those of the Cmc₂ and P4/mmm phases form octahedral complexes. The structural properties and the calculated energies of the 13 crystal models are summarized in Table II. The DFT results show the P2₁/c crystal model possesses the lowest energy. This implies that LiAlH₄ is predicted to occur naturally as a crystalline solid with the P2₁/c space group, and this is in line with the previous experimental finding. The structure with the second lowest energy is in the I4₁/a phase. Further details on the structural and electronic properties of these two most stable phases will be discussed comprehensively in this section.

Figure 2 shows the simulated x-ray powder diffraction (XRD) patterns of the optimized P2₁/c and I4₁/a structures generated using the Mercury program. The Miller plane indices for major peaks are labeled, and the intensities are in an arbitrary unit. The simulated XRD pattern of the P2₁/c phase agrees very well with the available experimental XRD pattern of LiAlH₄ at 295 K. This confirms that the optimized structure is very similar to the experimentally observed one. For the P2₁/c phase, the top three strongest XRD peaks are (110), (112), and (012), respectively, and the ratios of the intensities to the strongest peak are I(112)/I(110) = 0.7453 and I(012)/I(110) = 0.5605. For the I4₁/a phase, (103), (101), and (025) are the three strongest peaks, and their ratios are I(101)/I(103) = 0.6554 and I(025)/I(103) = 0.1871.

B. Electronic structures

The charge density plots of P2₁/c and I4₁/a, as shown in Fig. 3, can be used to roughly explore how electrons distribute throughout the crystalline structures. The regions (surfaces) of higher and lower electron densities were represented by the red and yellow (iso)surfaces, respectively. Clearly, both figures show that the electron density of the regions around Al–H complexes is relatively higher than that of the other regions far away from them, e.g., around the Li atoms. Additionally, Al–H complexes and Li atoms are very well separated from each other. The implicit meaning of these data is that in the crystals, each of the Al atoms is covalently bonded with its four neighbor H atoms forming an (AlH₄)⁻ anionic complex in the shape of a tetrahedron surrounded by Li⁺ cations, and vice
versa. For the \( P_2\frac{1}{1}/c \) structure, the tetrahedral shape of \((\text{AlH}_4)^-\) complexes is slightly distorted, i.e., the length of Al–H bonds lies between 1.62 and 1.65 Å, while an \((\text{AlH}_4)^-\) complex of the \( I_4\frac{1}{1}/a \) phase is a perfectly symmetric tetrahedron with four 1.65 Å Al–H bonds. Each of the Li atoms within the \( P_2\frac{1}{1}/c \) structure has five neighbor H atoms from the \((\text{AlH}_4)^-\) complexes, with the lengths of Li–H bonds lying between 1.86 and 1.90 Å. On the other hand, each of the Li atoms in the \( I_4\frac{1}{1}/a \) phase has eight H neighbors, with the Li–H distances ranging from 2.06 to 2.18 Å.

The band structure and density of states (DOS) plots of the \( P_2\frac{1}{1}/c \) crystal are shown in Fig. 4. For the band structure plots in this work, the suggested paths within the Brillouin zone were taken from the work of Setyawan and Curtarolo.\(^{31}\) Apart from the atomic-projected DOS, the orbital-projected DOS plots for each atomic species are also provided. All the energy values shown in the plots were normalized by the corresponding Fermi energy \((E_F)\) marked by horizontal-dotted lines. The band structure and DOS plots show that the LiAlH\(_4\) solid in the \( P_2\frac{1}{1}/c \) form has two well-separated regions of the valence band (occupied states) and the conduction band (unoccupied states) with a considerably large energy bandgap of 4.67 eV. This implies that the solid in this form exhibits a non-metallic character or it is simply said to be an insulator. Below the Fermi level, the DOS plot is divided into two regions, lower and higher valence bands, with an energy gap of \( \sim 0.84 \) eV.

The density of electronic states within the higher valence band is mainly contributed by the H-s and Al-p states, while there is only a small contribution of Li-s and -p states to this region. For the lower region, the major contribution of the DOS is from the Al-s and H-s states. In both regions, the Al-s, -p, and H-s states are energetically degenerate. Therefore, this clearly confirms the existence of the covalently bonded \((\text{AlH}_4)^-\) complexes in the crystal facilitated by the hybridization of the Al’s atomic orbitals. The DOS in the conduction band are contributed by the states of all the three atomic species.

On the other hand, Fig. 5 shows the band structure and the DOS plots for the \( I_4\frac{1}{1}/a \) phase. The plots show that the \( I_4\frac{1}{1}/a \) phase has a relatively smaller bandgap of \( \sim 3.88 \) eV. This also implies that the solid in this form is also a non-metallic solid. A remarkable difference from the plots of the \( P_2\frac{1}{1}/c \) phase is that there is no gap within the valence band below \( E_F \) which may be caused by the increase in the degree of the hybridization interaction.\(^{17}\) Similarly, the electronic states in the occupied band are contributed primarily by the H-s and Li-s states. The conduction band of the \( I_4\frac{1}{1}/a \) phase is apparently similar to that of the \( P_2\frac{1}{1}/c \) phase.

### C. Pressure-induced phase transformations

The volume–energy and pressure–energy profiles for the nine phases of LiAlH\(_4\) are shown in Fig. 6. In the plot of cell volume–energy profiles, on the right-hand side, four profiles of the \( F\frac{4}{3}m, P4_3/mmc, P4/mmm, \) and \( P6_3m \) phases are not included as they are out of the range considered. From the volume–energy profiles, the energy of a crystal structure is increased while applying external pressure to the solid (by either compressing or stretching). A major advantage of the plot is to use it to theoretically predict the phase transitions of a solid of interest that can have different crystalline

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**FIG. 4.** Band structure and density of states (DOS) plots of the \( P_2\frac{1}{1}/c \) structure.
structures. Furthermore, the pressure–energy profiles can also be used to estimate the pressure value at the transition point.

For the $P2_1/c$ phase, at equilibrium, the crystal has the volume of 68.7 Å$^3$ f.u.$^{-1}$, as also shown in Table II. As the pressure is increased, the crystal volume decreases and the energy increases. Until the crystal volume is $\sim$59 Å$^3$ f.u.$^{-1}$, the energy profile of the compressed $P2_1/c$ phase crosses the energy profile of the stretched $I4_1/a$ phase. At this point, the energy of these two structures is exactly the same, which means the phase transition is at equilibrium. Instead of having a further increase in energy as the pressure is increased, the $P2_1/c$ structure spontaneously transforms to the $I4_1/a$ phase which now has a lower energy. After reaching the transition point, the solid with the $P2_1/c$ space group is relaxed to the second most stable $I4_1/a$ form with an equilibrium crystal volume of 53.5 Å$^3$ f.u.$^{-1}$, leading to a reduction of approximately 22% in the crystal volume. It should be noted that the volume collapse at the transition point is $\sim$14%. The phase transformation from the $P2_1/c$ phase to the $I4_1/a$ phase is predicted to occur at approximately 3.3 GPa, as illustrated in the pressure–energy profile in Fig. 6.

The predicted transition pressure for the $P2_1/c \to I4_1/a$ transformation in the present work agrees very well with the previous experimental findings.$^{11,12}$ However, the calculated value is found to be larger than the value of 2.6 GPa predicted in the previous theoretical work by Vajeeston and co-workers.$^{17}$ This discrepancy may be caused by the option of the optimization process while producing volume–energy profiles. In this work, we allowed only the atomic positions to relax at a given volume while full relaxation was carried out in the other work. Theoretically, the energy optimization of a less constrained structure yields a lower energy value than that of a more fixed structure. It is worth noting that the effects of temperature are not included in these first-principles calculations.

We have also probed the effects of the three optimization options, namely, (i) no optimization, (ii) ionic relaxation, and (iii) full optimization, on the predicted numerical results, as shown in the Fig. 7. As expected, the increase in the degree of freedom while performing structural optimization leads to a more stable, lower energy structure. For option (i), no optimization, it is found that the $P2_1/c \to I4_1/a$ transformation occurs at 6.22 GPa with a corresponding $\sim$12% volume collapse at the transition point. The pressure at the transition point is much higher than that obtained from the previous findings. Therefore, this optimization option is not suitable for constructing volume–energy profiles. For options (ii) and (iii), the profiles of the $I4_1/a$ phase are not significantly different, while the profiles of the compressed $P2_1/c$ phase show a slight deviation from each other.
and all the calculations in this work. Furthermore, the optimization was used to further simulate the electronic structures of the crystal PBESol and LDA functionals. Therefore, the GGA-PBE functional closer to the experimental ones than those obtained using the GGA-functional can lead to greatly different predicted results. We have pointed out that a choice of the DFT exchange-correlation functional scheme also plays a vital role when constructing volume–energy profiles for the prediction of phase transitions. While varying the crystal volumes, allowing the cell shape and ionic positions to simultaneously relax gives predicted values that are in good agreement with those obtained by the experimental observations. However, we have found that a crystal with a given space group may change its symmetry and transform into different phase when the crystal volume is far from the equilibrium value, i.e., too large or too small. In order to avoid this, we performed ionic relaxation with only a fixed cell shape at all volumes. This strategy also yields very good results compared to the experiments. With the methods used, at absolute zero, the LiAlH$_4$ non-metallic solid in the most stable $P2_1$/$c$ phase is predicted to transform to the less stable but more compact $I4_1$/a phase at approximately 3.3 GPa with a crystal volume reduction of $\sim$22% and volume collapse of 14% at the transition point. Under moderate pressures, the theoretical results suggest that the LiAlH$_4$ solid in the $I4_1$/a phase is a better potential candidate for hydrogen storage due to its higher hydrogen content and the naturally occurring $P2_1$/$c$ phase.

SUPPLEMENTARY MATERIAL

See the supplementary material for information on the 13 initial and optimized crystal structures of LiAlH$_4$.

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