The structural stability and electronic structure of the potential hydrogen-storage material Li$_3$AlH$_6$ have been investigated up to 90 GPa using density-functional total-energy calculations. At ambient conditions Li$_3$AlH$_6$ stabilizes in space group R3. The structure consists of isolated, close-to-regular [AlH$_6$]$^3$ octahedra, which are connected via six-coordinated Li. We predict that this α phase of Li$_3$AlH$_6$ undergoes three successive structural phase transitions on application of pressure: α to β at 18.64 GPa, β to γ at 28.85 GPa, and γ to δ at 68.79 GPa. All modifications of Li$_3$AlH$_6$ should have nonmetallic character with estimated bandgaps varying between 2.72 and 4.12 eV.

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The calculated total energy vs cell-volume curves for the 14 most relevant structural arrangements are shown in Fig. 1. Among them the Mg$_3$TeO$_6$-type arrangement (designated α-Li$_3$AlH$_6$; see Fig. 1 and Table I) is found to have the lowest total energy, which is consistent with the recent experimental findings.\(^{14}\) The calculated unit-cell dimensions and positional parameters at 0 K and ambient pressure are in good agreement with room-temperature experimental findings [the calculated $a$ is within 0.3% of the experimental value whereas the larger underestimation (0.6%) in the $c$ direction is typical for the agreement obtained by density-functional calculations]. It is interesting to note that the β (Cu$_3$TeO$_6$-type) and γ (Li$_3$AlF$_6$-type) modifications are energetically very close to α-Li$_3$AlH$_6$. This indicates that synthesis under appropriate pressure and temperature conditions may be able to stabilize the β and γ modifications as metastable phases.

α-Li$_3$AlH$_6$ structure consists of isolated [AlH$_6$]$^{3-}$ octahedra. Each Li atom is connected to two corners and two edges of these [AlH$_6$]$^{3-}$ octahedra. There are two crystallographically different Al sites, both with equal Al-H distances within each octahedron, but with slightly deviating angles from the ideal 90° value. Al has eight nearest Al neighbors, in a cubic arrangement, and six more distanced neighbors placed about the faces of the cube.

In general, application of pressure will reduce the interatomic distances in a crystal structure and when the pressure exceeds a critical value a change in crystal structure occurs. The change in the structure brings about a change in the physical and chemical properties. As a result, application of pressure transforms α-Li$_3$AlH$_6$ into the β modification (with Cu$_3$TeO$_6$-type structure) at 18.64 GPa [the transition pressures are estimated from the pressure vs difference in Gibbs free-energy ($\Delta G$) curves; see Fig. 2]. The pressure induced

### Table I. Optimized structural parameters, bulk modulus $B_0$, and pressure derivative of bulk modulus ($B'_0$) for Li$_3$AlH$_6$

<table>
<thead>
<tr>
<th>Modification (structure type)</th>
<th>Unit cell dimension (Å)</th>
<th>Positional parameters</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Li$_3$AlH$_6$ ($R\bar{3}$)</td>
<td>$a = 8.0487$ (8.0712)$^a$; $c = 9.4532$ (9.513)$^a$</td>
<td>Li: 0.9334, 0.2196, 0.2804 (0.9576, 0.2260, 0.2911)$^a$; Al(1): 0.0, 0, 0; Al(2): 0, 0, 1/2; H(1): 0.8307, 0.8264, 0.0986 (0.8333, 0.8057, 0.1007)$^a$; H(2): 0.1372, 0.2014, 0.3978 (0.1582, 0.1820, 0.3900)$^a$</td>
<td>35.75</td>
<td>3.73</td>
</tr>
<tr>
<td>β-Li$_3$AlH$_6$ ($Cu_3TeO_6$: $I\bar{a}\bar{3}$)</td>
<td>$a = 8.8532$</td>
<td>Li: 0.9596, 0, 1/4; Al: 1/4, 1/4, 1/4; H: 0.3703, 0.1788, 0.3949</td>
<td>36.09</td>
<td>3.76</td>
</tr>
<tr>
<td>γ-Li$_3$AlH$_6$ ($K_3TiF_6$: $Fd\bar{3}$)</td>
<td>$a = 13.9015$</td>
<td>Li(1): 1/8, 1/8, 1/8; Li(2): 5/8, 5/8, 5/8; Li(3): 1/4, 1/4, 1/4; Li(4): 3/8, 1/8, 1/8; Al(1): 0, 0, 0; Al(2): 1/2, 1/2, 1/2; H(1): 0.1125, 0.0634, -0.0133; H(2): 0.6124, 0.5634, 0.5101</td>
<td>37.63</td>
<td>3.94</td>
</tr>
<tr>
<td>δ-Li$_3$AlH$_6$ ($Li_3AlF_6$: $Pna2_1$)</td>
<td>$a = 9.2173$; $b = 7.9755$; $c = 4.7258$</td>
<td>Li(1): 0.3798, 0.3697, 0.4991; Li(2): 0.1033, 0.4445, 0.5016; Li(3): 0.3423, 0.5601, 0.004; Al: 0.1285, 0.2436, 0; H(1): 0.2281, 0.0728, 0.1329; H(2): 0.0303, 0.2387, 0.3139; H(3): 0.2333, 0.2487, 0.6940; H(4): 0.2413, 0.3869, 0.1788; H(5): 0.0198, 0.0855, 0.8283; H(6): 0.0213, 0.3997, 0.8514</td>
<td>35.84</td>
<td>3.32</td>
</tr>
</tbody>
</table>

$^a$Experimental value from Ref. 14.
α-to-β transition of Li$_3$AlH$_6$ (see Figs. 1 and 2) involves reconstructive rearrangements (viz., bonds are broken and reestablished) of the cation and anion sublattices. β-Li$_3$AlH$_6$ is stable in a fairly narrow pressure range and converts to γ-Li$_3$AlH$_6$ (K$_3$TlF$_6$-type) at 28.85 GPa and further to δ-Li$_3$AlH$_6$ (Li$_3$AlF$_6$-type) at 68.79 GPa. α-, β-, and δ-Li$_3$AlH$_6$ have very similar equilibrium volumes (~87.76, 86.74, and 86.78 Å$^3$/f.u., respectively) and the energy difference between them is also very small (see Fig. 1). This closeness in total energy suggests that the relative appearance of these modifications will be quite sensitive to, and easily affected by, external factors such as temperature and remnant lattice stresses. Another important point is that at the α-to-β phase-transition point, the estimated volume difference is also small (Fig. 2) suggesting that α-Li$_3$AlH$_6$ has an efficiently packed structure. Similar is the process for the β-to-γ and γ-to-δ transitions (Fig. 2). For comparison it may be recapitulated that the volume discontinuity at the α-to-β transition point in LiAlH$_4$ (Ref. 23) is ~17%. The closeness in volume of the different Li$_3$AlH$_6$ modifications at the transition pressure should be a challenging task also for experimentalists.

The calculated bulk modulus $B_0$ and its pressure derivative $B_0'$, for different Li$_3$AlH$_6$ phases are given in Table I. The involved phases have almost similar bulk moduli, which is partially due to the closeness in the equilibrium volumes of the different modifications. The estimated $B_0$ for Li$_3$AlH$_6$ in the different modifications are closer to β-LiAlH$_4$ than α-LiAlH$_4$. This indicates that Li$_3$AlH$_6$ is harder than α-LiAlH$_4$ with strong bonding interactions between the constituents, which, in turn, may be the reason for the higher decomposition temperature of Li$_3$AlH$_6$ compared with α-LiAlH$_4$.

The calculated total and partial density of states (DOS) for α-Li$_3$AlH$_6$ are shown in Fig. 3. There is a finite energy gap between the valence and conduction bands in all modifications of Li$_3$AlH$_6$ (not shown for β-, γ-, and δ-Li$_3$AlH$_6$). Hence Li$_3$AlH$_6$ must be classified as nonmetallic. The estimated band gap $E_g$ is varying between ~2.72 and 4.12 eV, but no experimental values are available for comparison. The estimated $E_g$ for α-Li$_3$AlH$_6$ is ~3.52 eV, which is almost ~1 eV smaller than that in α-LiAlH$_4$, but it should be recalled that theoretically derived band gaps in semiconductors and insulators may be underestimated by 20–50% (Ref. 24) compared with experimental values. Earlier experience$^{19}$ for this type of materials shows that GGA underestimates $E_g$ by ~1.4 eV compared with experiments.$^{25}$ If we assume a similar underestimation for α-Li$_3$AlH$_6$, this compound should have an experimental gap of 4.9 eV. The calculated valence-band width is increased from 7.5 eV (in the α phase) to 12 eV (in the δ phase), which is due to the reduction in the interatomic distance upon pressure.

The partial DOS for Li shows (Fig. 3) that the $s$ and $p$ states of α-Li$_3$AlH$_6$ are energetically degenerate in the whole energy range, while Al-$s$ and -$p$ states are well separated. The energetic degeneration of the Al-$p$ and H-$s$ states together with the spatially favorable constellation of Al and

![FIG. 2. Calculated pressure vs cell-volume relation for Li$_3$AlH$_6$. The inset shows the stability of high-pressure phases of Li$_3$AlH$_6$ with respect to the equilibrium phase, transition pressures being marked by arrows at the corresponding transition points.](image1)

![FIG. 3. Calculated total and partial DOS for α-Li$_3$AlH$_6$. The Fermi level is set at zero energy and marked by the vertical dotted line; $s$ states are shaded.](image2)
H facilitates covalent bonding between Al and H, an inference that is further substantiated by the charge-density and electron localization function (ELF) analyses (Fig. 4). The charge-density distribution and ELF for $\text{AlH}_6^2-$ clearly convey that $[\text{AlH}_6]^{3-}$ forms distinct covalently bonded units in these modifications, well separated from other $[\text{AlH}_6]^{3-}$ anions and Li$^+$ cations. The high ELF along the Al-H bonds reflects its covalent character, whereas the almost negligible ELF between $[\text{AlH}_6]^{3-}$ and Li$^+$ confirms the ionic bonding. A finite electron distribution occurs between the H atoms within the $[\text{AlH}_6]^{3-}$ units, which suggests a non-negligible covalent-type of interaction present between the hydrogen atoms. The ELF analysis accordingly corroborates the traditional chemical intuition of the bonding in $\alpha$-Li$_3$AlH$_6$. The magnitude of the bond strength in $\alpha$-Li$_3$AlH$_6$ is calculated using crystal orbital Hamilton population (COHP) analysis. The calculated integrated COHP between the Al and H is 2.3 eV, which is much smaller than that in $\alpha$-LiAlH$_4$ (4.2 eV), reflecting that the interaction between Al and H in $\alpha$-Li$_3$AlH$_6$ is weaker than that in $\alpha$-LiAlH$_4$. This in turn is only natural when the coordination number is increased and the bond strength between the Al and H is decreased. A corresponding study on structural stability of sodium and potassium hexahydroaluminates is in progress, and the findings will be presented in a forthcoming paper.

In conclusion, the calculated structural parameters for $\alpha$-Li$_3$AlH$_6$ are in good agreement with the experimental findings. It is found that the ground-state structure of Li$_3$AlH$_6$ becomes unstable at higher pressure. The high-pressure modifications and equilibrium structures have almost similar equilibrium volumes, and the energy difference between the involved phases is also very small. The electronic structure shows that, in all modifications, Li$_3$AlH$_6$ has nonmetallic character.

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