

Crystal Structure and Stability of LiAlH_4 from First Principles^{*}

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Abstract: The structural stability of LiAlH_4 , a promising hydrogen storage material, under high pressure was researched using the *ab initio* pseudopotential plane wave method. It is found that the phase transition occurs at 1.6 GPa from the α - LiAlH_4 phase to the β - LiAlH_4 (space group $I2/b$) phase. This phase transition is identified as first-order in nature with volume contractions of 18%. Moreover, the analysis of the phonon dispersion curves suggests that phase transition is related to the phonon softening. Mulliken population analyses indicated that the ambient phase (α - LiAlH_4) is expected to be the most promising candidate for hydrogen storage.

Keywords: crystal structure; hydrogen storage materials; density functional theory; pressure-induced structural transition; electronic structure

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Light metal complex hydrides are promising materials for solid-state hydrogen due to their gravimetric hydrogen density^[1-5]. For example, lithium alanate (LiAlH_4) and sodium alanate (NaAlH_4) have theoretical hydrogen capacities of 10.6% and 7.5% (mass fraction), respectively. Hence, LiAlH_4 and NaAlH_4 could be viable candidates for practical usage as on-board hydrogen storage. However, a serious problem with these materials is their poor kinetics and lacking reversibility with respect to hydrogen absorption/desorption. Recent experimental evidences show that LiAlH_4 and NaAlH_4 release 7.9% and 5.6% (mass fraction) of H, respectively. This represents nearly 4 and 5 times more stored hydrogen than LaNi_5 -based alloys which are currently used in nickel-based hydride batteries. However, it is difficult to accurately identify the positions of the hydrogen atoms by the high-pressure X-ray and neutron diffraction studies. Therefore, exploration of the phase stability and structures has attracted a great deal of attention.

Under ambient conditions, LiAlH_4 crystallizes at a monoclinic structure with a space group $P2_1/c$ (denoted as α - LiAlH_4). The structure consists of AlH_4 units separated by Li^+ ions, and the hydrogen atoms are arranged around the aluminum atoms in an almost regular tetrahedral configuration. On the theoretical side, the α - LiAlH_4 structure transforms into a new tetragonal β - LiAlH_4 structure (space group $I4_1/a$) at 2.6 GPa with a 17% volume contraction^[6]. However, the neutron diffraction confirms

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that the structure of the high pressure β -LiAlH₄ has a monoclinic space group $I2/b$ ^[7]. It is determined that there is a reversible phase transition back to the α -LiAlH₄ with a slow release of pressure and cooling. Consequently, the Raman measurement confirmed that the ambient structure transform to the β -LiAlH₄ structure (space group $I2/b$) at 3 GPa^[8], as well as the previously reported transition pressure between 2.2 and 3.5 GPa^[9].

In this work, we report our results on the geometries and electronic structures of LiAlH₄ with pressure using the *ab initio* calculations. The total-energy calculations for the pressure-induced phase transition in LiAlH₄ were performed. The structural transition from α - to β -LiAlH₄ happened at 1.6 GPa. The full phonon dispersion curves were calculated, for the first time, to provide the evidence of phonon stability for pressured-induced phase transition. We also discussed the density of states and bond overlap populations about the two phases.

1 Computational Method

The calculations were performed within the density functional theory (DFT), using the Perdew-Burke-Ernzerh of generalized gradient approximation functional^[10-12]. A plane-wave norm-conserving pseudopotential method^[13] as implemented in the CASTEP code^[14] was employed. We used the plane-wave kinetic-energy cutoff of 850 eV which was shown to give excellent convergence of the total energies and structural parameters. According to the Monkhorst-Pack method, k -point spacing smaller than 0.3 nm⁻¹ was individually adjusted in reciprocal space to the size of each computational cell^[15]. The optimization was performed, all forces on atoms were converged to be less than 0.1 eV/nm and all the stress components are less than 0.02 GPa. The tolerance in the self-consistent field (SCF) calculation was set to 10⁻⁶ eV/atom. The phonon frequencies were calculated by the direct approach, which is based on the first-principles calculations of the total energy, the Hellman-Feynman forces, and the dynamical matrix as implemented in the phonon packages^[16-17]. Convergence test gave the use of 2×1×1 and 2×2×1 supercell in the phonon calculation.

2 Results and Discussions

We optimize the crystal structures allowing simultaneously variations of unit cell and atomic positions at selected pressures. The calculated lattice parameters of α -LiAlH₄ (space group $P2_1/c$) and β -LiAlH₄ (space group $I2/b$) are listed in Table 1, which also includes the experimental data for comparison^[18]. For the α -LiAlH₄ phase, the deviations between our calculated results and the experimental values are less than 2%, which is sufficiently accurate. This strongly supports the choice of the pseudopotentials and GGA approximation for the current study. The theoretical generated pressure-volume curve (see Fig. 1) shows that the α -LiAlH₄ transforms to a monoclinic phase of β -LiAlH₄ with a volume contraction ($\Delta V/V$) of 18%, which suggests that this is a first-order phase transition. The

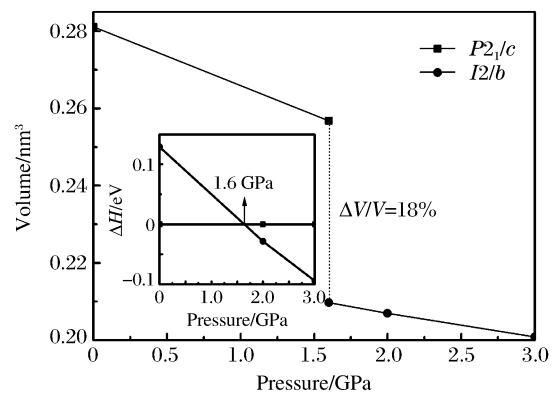


Fig. 1 Volume vs. pressure curves of α -LiAlH₄ and β -LiAlH₄ phases (Enthalpy difference (per formula unit) between α -LiAlH₄ and β -LiAlH₄ as a function of pressure is shown in the insert.)

huge volume contraction is consistent with the Raman scattering measurement and the other theoretical results^[6,8]. In order to give a clear picture of the structural transition, the difference of the enthalpy (per formula unit) between the α -LiAlH₄ and β -LiAlH₄ phases as a function of pressure is shown in the insert of Fig. 1. It can be clearly seen that the β -LiAlH₄ phase becomes energetically more favourable than the α -LiAlH₄ phase above 1.6 GPa, which is the transition pressure from α -LiAlH₄ to β -LiAlH₄.

Table 1 Optimized structural parameters, atomic position parameters for the α -LiAlH₄ and the β -LiAlH₄ structures

Phase	Unit-cell dimensions	Atom coordinates
α -LiAlH ₄ ($P2_1/c$)	$a=0.4851\text{ nm}(0.4817\text{ nm}^*)$ $b=0.7814\text{ nm}(0.7802\text{ nm}^*)$ $c=0.7732\text{ nm}(0.7821\text{ nm}^*)$	Li: (0.585, 0.459, 0.829), (0.560, 0.466, 0.827) *
		Al: (0.159, 0.204, 0.938), (0.139, 0.203, 0.930) *
		H1: (0.193, 0.102, 0.766), (0.183, 0.096, 0.763) *
		H2: (0.377, 0.371, 0.986), (0.352, 0.371, 0.975) *
		H3: (0.254, 0.082, 0.119), (0.243, 0.081, 0.115) *
		H4: (0.822, 0.268, 0.882), (0.799, 0.247, 0.872) *
β -LiAlH ₄ ($I2/b$)	$a=0.4452\text{ nm}$	Li: (0, 0, 0.125)
	$b=0.4459\text{ nm}$	Al: (0, 0, 0.625)
	$c=1.0102\text{ nm}$	H1: (0.259, 0.425, 0.542)
	$\beta=89.978^\circ$	H2: (0.324, 0.508, 0.792)

Note: “*” represents experimental data from Ref. [18].

To investigate the dynamic stability, we calculated the phonon dispersion curves along some high-symmetry lines in the Brillouin zones (BZ) and the corresponding phonon density of states (DOS) for the LiAlH₄ structure. No imaginary frequency is observed throughout the whole BZ, indicating that the two novel phases are dynamically stable in the pressure region from this study. We also calculated the phonon dispersion curves at the phase transition pressure for the α -LiAlH₄ structure in Fig. 2. For comparison, the stability of phonon dispersion curves for the α -LiAlH₄ at 0 GPa are shown in Fig. 2(a). In Fig. 2(b), it is indicated that the phase transition should not be related to the pressure-induced phonon softening. The total and partial densities of states for the two phases are shown in Fig. 3. Analysis of the calculated electronic density of state reveals that the two phases exhibit a common insulating feature with a finite energy gap. The valence band (VB) in α -LiAlH₄ phase is split into two regions. Subsequently, the two peaks combine into one broader peak in the β -LiAlH₄ phase producing the broadening of VB under high pressure. This is originated from the shortened inter-atomic distance upon squeezing, for the VB region is mainly dominated by H 1s, and Al 2s, 2p states. It shows that the H and Al atoms become the directional covalent bonds within the AlH₄ tetrahedron or AlH₄ octahedron layers. The bottom of the conduction band just above the

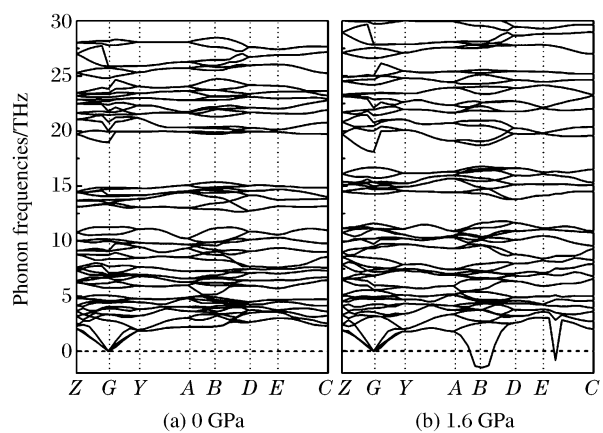


Fig. 2 Phonon dispersion relations and density of state in high-symmetry directions for the α -LiAlH₄ structure at 0 and 1.6 GPa

Fermi energy is composed of the Al $2s, 2p$, Li $1s$, and H $1s$ states, which are consistent with the ionic bonding between the Li and the AlH_4 unit. We found more mixing of the s and p states for Al atom in the $\beta\text{-LiAlH}_4$ phase. Consequently, the electronic transition from the Al- s to $-p$ state is related for the huge volume collapse during the $\alpha\text{-LiAlH}_4$ to $\beta\text{-LiAlH}_4$ phase transition.

In order to better understand the bonding interactions between H, Al and Li atoms, we studied the Mulliken charges and the bond overlap population (BOP) P on the basis of Mulliken Populations in Table 2^[19-20]. The scaled BOP (P^s) is defined in $P^s_{\text{Al(Li)}-\text{H}} = P_{\text{Al(Li)}-\text{H}}/L_{\text{Al(Li)}-\text{H}}$ with L representing the average bond length of Al—H or Li—H, respectively^[21]. It is found that the $P^s_{\text{Al-H}}$ value for the $\alpha\text{-LiAlH}_4$ phase (0.506) is smaller than that of the $\beta\text{-LiAlH}_4$ phase (0.534) as the coordination number of Al (4) stays unchanged at the $\alpha\beta$ transition. Previous studies have shown that the smaller the BOP, the lower the hydrogen desorption kinetic energy^[22]. From this point of view, the current study suggests that the activation energy of the $\alpha\text{-LiAlH}_4$ is lower than that of the $\beta\text{-LiAlH}_4$. The ambient phase of $\alpha\text{-LiAlH}_4$ is expected to be the most promising candidate for hydrogen storage.

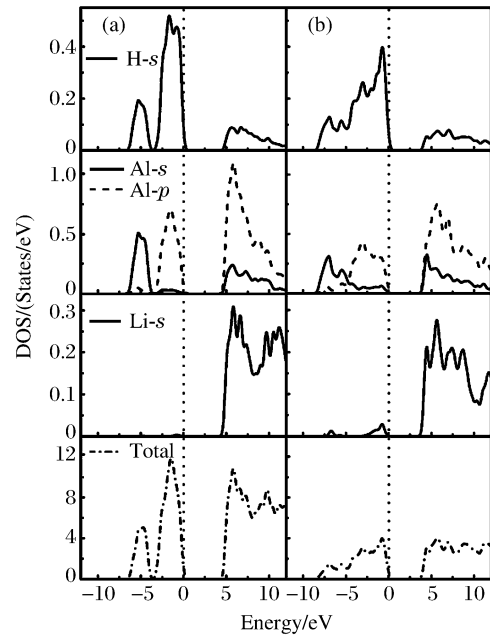


Fig. 3 Calculated total and partial electronic densities of states for $\alpha\text{-LiAlH}_4$ structure at 0 GPa (a) and $\beta\text{-LiAlH}_4$ structure at 1.6 GPa (b) respectively

Table 2 Average net charges, bond length (L) and scaled bond overlap population (P^s) between H, Al, and Li atoms in the $\alpha\text{-LiAlH}_4$ (at 0 GPa) and the $\beta\text{-LiAlH}_4$ (at 2.0 GPa) structures

Phase	Average net charge			L/nm		P^s	
	H	Al	Li	Al—H	Li—H	Al—H	Li—H
$\alpha\text{-LiAlH}_4$	-0.48	0.64	1.29	0.1615	0.1886	0.506	0.019
$\beta\text{-LiAlH}_4$	-0.46	0.55	1.28	0.1628	0.2067	0.534	-0.063

3 Conclusions

We investigated the pressure-induced phase transformations in LiAlH_4 using the first-principles based on the density functional theory with the plane-wave basis. The structural transitions from $\alpha\text{-LiAlH}_4$ to $\beta\text{-LiAlH}_4$ occurs at 1.6 GPa, accompanied with about 18% volume collapse, originating from the electronic transition of Al- s to $-p$ states. The phase transition should be related to the pressure-induced phonon softening. The BOP analysis shows that the activation energy of the $\alpha\text{-LiAlH}_4$ is smaller than that of the $\beta\text{-LiAlH}_4$. The $\alpha\text{-LiAlH}_4$ is expected to be the most promising candidate for hydrogen storage.

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LiAlH₄ 晶体结构及稳定性的第一性原理研究

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摘要: 基于密度泛函理论的第一性原理赝势平面波方法, 研究高压下三元碱金属氢化物 LiAlH₄ 的相变行为, 分析了 LiAlH₄ 高压相变的物理机制。研究表明, 在 1.6 GPa 时 LiAlH₄ 发生了相变, 从 α -LiAlH₄ 转变为空间群为 $I2/b$ 的 β -LiAlH₄, 相变时伴随 18% 的体积坍塌, 即一级相变。通过分析声子色散曲线得出, 相变与声子软化有关。Millikan 布局分析表明, 常压相 (α -LiAlH₄) 是很有潜力的储氢材料。

关键词: 晶体结构储氢材料; 密度泛函理论; 压力诱导结构转变; 电子结构

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