

Huge-pressure-induced volume collapse in LiAlH₄ and its implications to hydrogen storage

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A detailed high-pressure study on LiAlH₄ has been carried out using the *ab initio* projected augmented plane-wave method. Application of pressure transforms α - to β -LiAlH₄ (α -NaAlH₄-type structure) at 2.6 GPa with a huge volume collapse of 17%. This abnormal behavior is associated with electronic transition from Al-*s* to -*p* states. At 33.8 GPa, a β to γ transition is predicted from α -NaAlH₄-type to KGaH₄-type structure. Up to 40 GPa LiAlH₄ remains nonmetallic. The high weight percent of hydrogen, around 22% smaller equilibrium volume, and drastically different bonding behavior than α -phase indicate that β -LiAlH₄ is expected to be a potential hydrogen storage material.

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Metal hydrides which can accommodate more than 3 wt % hydrogen have been targeted in the Japanese WE-NET project MITI.¹ The parallel international cooperative project under IEA Task-12 is set up to develop storage materials which can store more than 5 wt % hydrogen. Several interstitial metal hydrides operate at around room temperature, but their reversible hydrogen storage capacity is limited to at most 2.5 wt %.² Recent interest is directed toward ternary aluminum hydrides as potential materials with enhanced storage capacity (e.g., LiAlH₄ and NaAlH₄ with 10.6 and 7.5 wt % theoretical hydrogen content, respectively) as solid-state sources for hydrogen cells (e.g., fuel reservoirs) etc. Hence, LiAlH₄ and NaAlH₄ could be viable candidates for practical usage as on-board hydrogen storage materials. However, a serious problem with these materials is poor kinetics and lacking reversibility with respect to hydrogen absorption/desorption. Improved understanding of the processes which occur in these hydrogen-containing materials during uptake and release of hydrogen are of considerable interest. Recent experimental evidences show that LiAlH₄ and NaAlH₄ after being subjected to mechano-chemical processing under ambient conditions in the presence of certain transition-metal catalysts³⁻⁶ rapidly release 7.9 and 5.6 wt % of H, respectively. This represents nearly four to five times more stored hydrogen than LaNi₅-based alloys which are presently used in nickel-based hydride batteries. The detailed crystal structure of LiAlH₄ is known, but a systematic high-pressure study has not yet been reported. A theoretical investigation of LiAlH₄ assumes importance as high-pressure x-ray and neutron diffraction studies will experience difficulties in identifying more accurate positions for the hydrogen atoms. The present study concerns the phase stability and electronic structure of LiAlH₄ using first-principles *ab initio* calculations.

LiAlH₄ crystallizes in the monoclinic α -LiAlH₄-type structure with space group $P2_1/c$ and four formula units per unit cell.⁷ Four hydrogen atoms are arranged around aluminum in an almost regular tetrahedral configuration. The structure consists of [AlH₄]⁻ units well separated by Li⁺ ions. The Al-H distances vary between 1.59 and 1.64 Å, the Li-H separations between 1.83 and 1.97 Å, and the arrangement of the lithium ions gives rise to one short Li-Li distance of ca. 3.1 Å.

Seven closely related potential structure types have been considered for the present theoretical modeling: α -LiAlH₄ (monoclinic; $P2_1/c$),⁷ α -NaAlH₄ (tetragonal; $I4_1/a$),^{8,9} β -LiBH₄ (hexagonal; $P6_3mc$),¹⁰ NaGaH₄ (orthorhombic; $Cmcm$),¹¹ NaBH₄ (cubic, $Fm3m$),¹² SrMgH₄ (orthorhombic; $Cmc2_1$),¹³ and KGaH₄ (orthorhombic; $Pnma$).¹⁴

For the total-energy calculation we have used the projected augmented plane-wave (PAW) (Ref. 15) implementation of the Vienna *ab initio* simulation package (VASP).¹⁶ The generalized-gradient approximation (GGA) (Ref. 17) was used to obtain the accurate exchange and correlation energy for a particular atomic configuration. The structures were fully relaxed for all volumes considered in the present calculations using force as well as stress minimization. Experimentally established structural data were used as input for the calculations when available. For α -LiAlH₄ we have used 500 **k** points in the whole Brillouin zone. In order to avoid ambiguities regarding the free-energy results we have always used the same energy cutoff and corresponding **k**-grid densities for convergence in all calculations. A criterion of at least 0.01 meV/atom was placed on the self-consistent convergence of the total energy, and the calculations reported here used a plane-wave cutoff of 600 eV.

In agreement with the experimental observations we found that the lowest energy configuration among the seven considered possibilities for LiAlH₄ is the already established ambient pressure/temperature α -LiAlH₄-type structure (Fig. 1). The calculated unit-cell volume and atom coordinates fit very well (within 1.5%; Table I) with the experimental findings.⁷

A similar theoretical approach has recently been applied¹⁸ successfully to reproduce the ambient-pressure and high-pressure phases for MgH₂ (and also to predict two further phases at higher pressures). In fact recent high-pressure experiments¹⁹ have reproduced the theoretically predicted pressure-induced structural transitions in MgH₂. We have identified two potential high-pressure modifications of LiAlH₄: At 2.6 GPa α -LiAlH₄ (prototype structure) transforms to β -LiAlH₄ (α -NaAlH₄ type) and a subsequent transition from β - to γ -LiAlH₄ (KGaH₄ type) is established at 33.8 GPa (Fig. 2). In order to get a clearer picture of the structural transition points we have displayed (see the inset of Fig. 2) the Gibbs free-energy difference (relative to

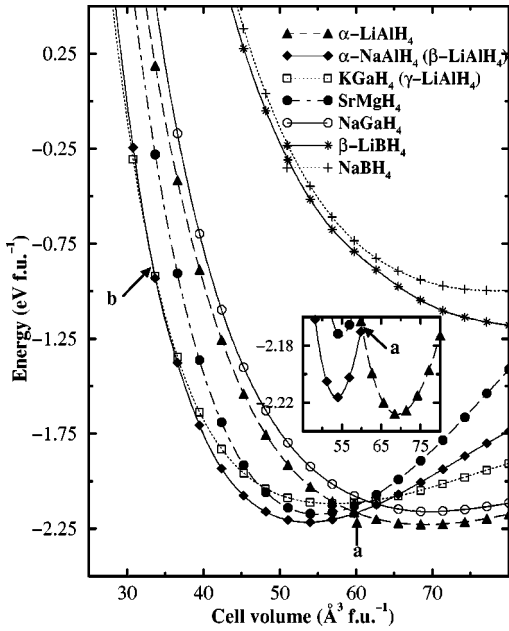


FIG. 1. Calculated cell volume vs free energy for LiAlH_4 in actual and possible structural arrangements (structure types being labeled on the illustration). Arrows make (a) $\alpha \rightarrow \beta$ and (b) $\beta \rightarrow \gamma$ transition points.

α - LiAlH_4) for the pertinent crystal structures of LiAlH_4 as a function of pressure. The experimental high-pressure/high-temperature study of Bulychev *et al.*²⁰ found that the α to β transition occurs at a static pressure of 7 GPa and a temperature of 250–300°C. When the temperature was increased to 500°C, the same study²⁰ reports that a third LiAlH_4 modification occurs. Experimental structural data for β - and γ - LiAlH_4 are not available, but the present calculated findings are included in Table I together with the available experimental parameters for α - LiAlH_4 .

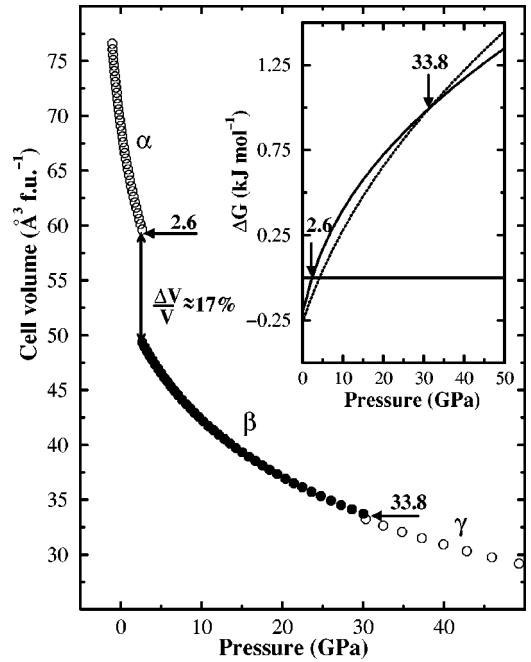


FIG. 2. Graphical representation of equation of state data for LiAlH_4 . The stabilities of the β - and γ - LiAlH_4 phases relative to α - LiAlH_4 as a function of pressure are shown in the inset. Transition points are marked with arrows and numerical pressure values (in gigapascal) are stated.

At the α to β transition point for LiAlH_4 the estimated difference in cell volume is ca. 17% (Fig. 2). The Raman scattering measurement on the high-pressure phase also indicates the presence of a large volume collapse at the transition point.²¹ Comparison on the basis of the equilibrium volumes for α - and β - LiAlH_4 shows an even larger volume difference (viz. a huge value of 22%). For example, in NaAlH_4 the calculated volume difference at the transition point between the α and β phases is less than 4%.⁹ Another

TABLE I. Optimized structural parameters, bulk modulus B_0 and its pressure derivative B'_0 for LiAlH_4 in different structural arrangements.

Phase	Unit-cell dimensions (Å)	Atom coordinates	B_0 (GPa)	B'_0
α - LiAlH_4 ($P2_1/c$)	$a = 4.8535(4.8174)^a$ $b = 7.8259(7.8020)^a$ $c = 7.8419(7.8214)^a$ $\beta = 111.878^\circ (112.228^\circ)^a$	Li : .5699, .4652, .8245 (.5603, .4656, .8266) ^a Al : .1381, .2017, .9319 (.1386, .2033, .9302) ^a H1 : .1807, .0986, .7630 (.1826, .0958, .7630) ^a H2 : .3542, .3723, .9777 (.3524, .3713, .9749) ^a H3 : .2361, .0810, .1146 (.2425, .0806, .1148) ^a H4 : .7948, .2633, .8717 (.7994, .2649, .8724) ^a	12.95	4.10
β - LiAlH_4 (α - NaAlH_4 type; $I4_1/a$)	$a = 4.6611^b (4.7312)^c$ $c = 10.5219^b (10.7161)^c$	Li : (0, 1/4, 5/8) ^{b,c} ; Al : (0, 1/4, 1/8) ^{b,c} H : (.2527, .4237, .5413) ^b (.2492, .4191, .5429) ^c	25.64	4.35
γ - LiAlH_4 (KGaH_4 type; $Pnma$)	$a = 6.4667^b (5.4421)^c$ $b = 5.3478^b (4.4843)^c$ $c = 6.5931^b (5.5225)^c$	Li : (.2428, 1/4, .2467) ^b (.2497, 1/4, .2502) ^c Al : (.5120, 1/4, .8221) ^b (.5002, 1/4, .7361) ^c H1 : (.3067, 1/4, .9617) ^b (.2815, 1/4, .9617) ^c H2 : (.7162, 1/4, .9631) ^b (.7189, 1/4, .9467) ^c H3 : (.4889, .9833, .2943) ^b (.4998, .9173, .3279) ^c	14.25	4.85

^aExperimental value from Ref. 7.

^bCalculated value at equilibrium.

^cCalculated value at transition point.

important feature of the α to β LiAlH_4 transition is the small energy difference (Fig. 1) between the involved phases (only 11.56 meV f.u.⁻¹ or 1.154 kJ mol⁻¹, which is indeed much smaller than that found for other hydrides¹⁸ and oxides²²). Hence, LiAlH_4 significantly deviates from the other isoelectronic compounds in the ABH_4 ($A=\text{Na, K, Rb, or Cs}$; $B=\text{Al or Ga}$) series.²³ It should be noted that our findings support the experimental observation of a high-pressure phase that has been stabilized at ambient pressure by quenching.²¹ The relatively small equilibrium volume of β - LiAlH_4 along with its high weight content of hydrogen imply an increased hydrogen storage capacity and therefore it would be of interest to explore the possibility of stabilizing this phase by chemical means, and perhaps also find a way to improve the kinetics of reversible hydrogen absorption/desorption because the bonding behavior of the β phase is drastically different from the α phase. It should be noted that the β - and γ - LiAlH_4 have almost the same volume at the β to γ transition point.

We have calculated the total energy for 12 different volumes for each of the modifications α , β , and γ . By fitting the total energy as a function of cell volume using the so-called universal equation of state²⁴ the bulk modulus B_0 and its pressure derivative B'_0 are obtained, but no experimental data for comparison are yet available. Among the three structures identified for LiAlH_4 as a function of pressure (Figs. 1 and 2), β - LiAlH_4 has almost twice the bulk modulus of the α and γ modifications. Comparison of the equilibrium volumes of these modifications shows that β has lower equilibrium volume than the α and γ phases and this is the main reason for its larger bulk modulus.

The density of states (DOS) of α -, β -, and γ - LiAlH_4 are shown in Fig. 3. A common feature of these three phases is their nonmetallic character with finite energy gaps (4.71, 4.25, and 3.95 eV, respectively). Measurements of resistivity as a function of pressures²⁵ suggested that the boron containing compounds LiBH_4 and NaBH_4 form new phases at higher pressures (indicated by jumps in the resistivity²⁵), whereas LiAlH_4 and RbBH_4 showed no evidence of pressure-induced phase transitions (almost linear pressure vs resistivity relationships). The present identification of two structural transitions in LiAlH_4 therefore could indicate that lacking resistivity evidence of the transitions reflects the nonmetallic nature and the similar sized band gaps of the α , β , and γ phases. However, regarding the conductivity of LiAlH_4 two other reports are also found in the literature. Alder and Christian²⁶ report that the resistivity of LiAlH_4 becomes reduced by a factor of some 10^4 at 5 GPa and Griggs *et al.*²⁷ report lacking metallic conduction in this pressure range. The latter finding complies with the presently established insulating nature of LiAlH_4 up to 40 GPa.

The DOS of α -, β -, and γ - LiAlH_4 differ noticeably mainly in the valence band (VB) region. In the total DOS of the α phase, the VB is split in two separate regions (region I: -6.2 to -4 eV, region II: -3.5 eV to E_F) with a ca. 0.4 eV gap between the two regions. Al- s states are mainly found in region I. The total DOS in region II is contributed by Al- p , H- s , Li- s , and Li- p states. In general the Al- s and - p states

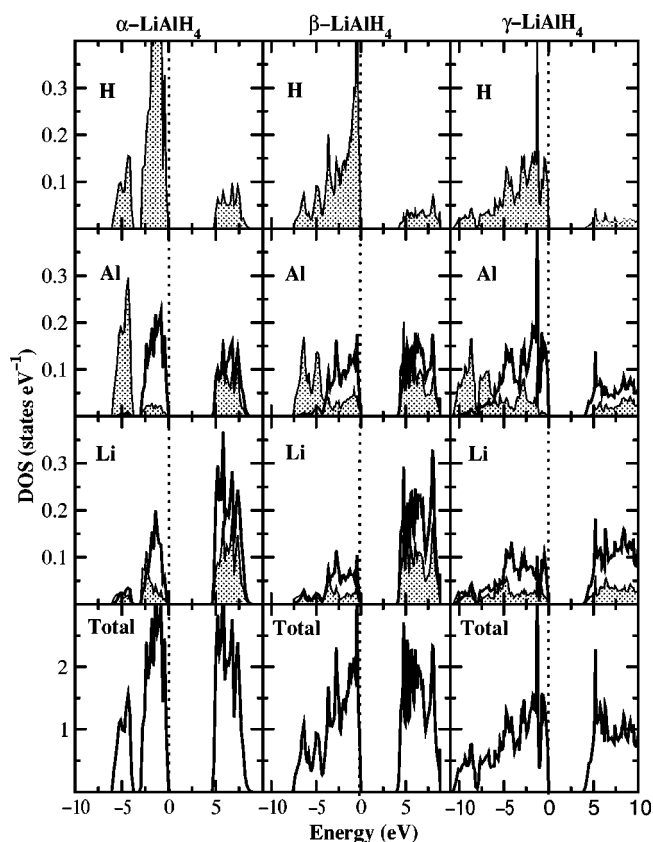


FIG. 3. Calculated density of states (DOS) for α - (at equilibrium), β - (at transition pressure; 2.6 GPa), and γ - LiAlH_4 (at transition pressure; 33.8 GPa). Fermi levels are set at zero energy and marked by dotted vertical lines; s states are shaded.

are well separated whereas the Li- s and - p states mainly appear in region II. The Al- p and H- s states are energetically degenerate in region II, which clearly facilitates the formation of the covalently bonded $[\text{AlH}_4]^-$ subunits in the crystal structure. When we go from α - LiAlH_4 to the β and γ phases the gap in the VB region disappears, which may reflect the increase in the hybridization interaction. The changes in the DOS for Li are rather insignificant between α - and β - LiAlH_4 whereas the DOS for Al are markedly different. In β - LiAlH_4 we find more mixing of the s and p states for Al. The s -to- p electronic transition within the Al atom in the β phase causes the huge volume collapse during the α to β phase transition. Moreover, on going through the β to γ transition the tetrahedral environment of Al in the β modification is changed to a strongly deformed octahedral environment in the γ modification (four H atoms at distances of 1.23–1.36 Å and two further H atoms at some 2.25 Å). The identification of AlH_6 -configured units in the γ phase is consistent with the measured infrared spectra.²⁰

The electron localization function (ELF) is a powerful tool to visualize different types of bonding in solids.²⁸ The value of ELF is limited to the range 0–1. High value of the ELF corresponds to a low Pauli kinetic energy, as can be found in covalent bonds or lone electron pairs. The ELF's for α - and β - LiAlH_4 displayed in Fig. 4 clearly convey that

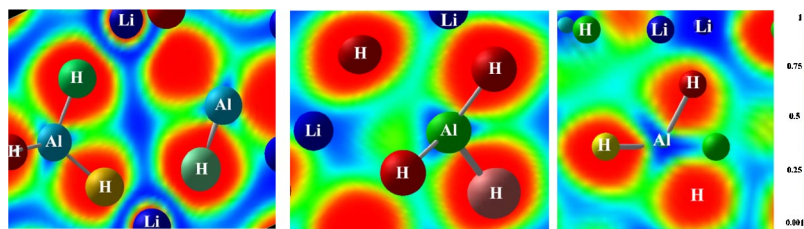


FIG. 4. (Color online) Electron localization function for α - [left picture; (100) plane], β - [middle picture; (001) plane], and γ -LiAlH₄ [right picture; (110) plane].

[AlH₄]⁻ forms distinct covalently bonded units in these modifications; well separated from other [AlH₄]⁻ anions and Li⁺ cations. The high ELF along the Al-H bonds reflects its covalent character whereas the almost negligible ELF between [AlH₄]⁻ and Li⁺ confirms the ionic bonding. The ELF analysis accordingly corroborates the traditional chemical intuition of the bonding in α - and β -LiAlH₄. The right picture of Fig. 4 mirrors the increase from four to six hydrogen atoms in the coordination around Al in γ -LiAlH₄ and emphasizes the correspondingly more composite bonding situation in this modification.

In summary, on application of pressure α -LiAlH₄ transforms to β -LiAlH₄ at 2.6 GPa and this transition is associated with a 17% volume collapse, apparently originating

from electronic transition of Al-*s* to -*p* states. Above 33.8 GPa the β phase transforms to γ -LiAlH₄ with a negligible change in volume, but with an increased coordination number of Al from four to six. The electronic density of states confirms that all these phases have nonmetallic character up to 40 GPa. The energy difference between α - and β -LiAlH₄ is small, the α to β transition pressure is relatively low, the equilibrium volume for β -LiAlH₄ is low (implying efficient storage of hydrogen), and the relative weight content of hydrogen is high, and hence, the β phase stands out as a promising candidate for hydrogen storage.

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