

Reversible phase transition in LiAlH_4 under high-pressure conditions

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The structural stability of the hydrogen storage compound LiAlH_4 was studied by Raman spectroscopy in the pressure interval 0–6 GPa. A slow phase transition from α - LiAlH_4 to a β phase was observed to occur between 2.2 and 3.5 GPa. The phase transition is reversible and a reverse transformation to α - LiAlH_4 was observed below 1.4 GPa. Analysis of Raman spectra from β - LiAlH_4 shows that they cannot be explained by the theoretically predicted α - NaAlH_4 -type structure with $I4_1/a$ symmetry.

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I. INTRODUCTION

Ternary metal hydrides have recently attracted considerable attention due to their high capacity for hydrogen storage. Recent experimental results show that LiAlH_4 and NaAlH_4 are able to release reversibly 7.9 and 5.6 wt % of hydrogen, respectively, in the presence of certain catalysts.^{1–4} Recent theoretical studies suggest that both LiAlH_4 and NaAlH_4 must undergo phase transitions with volume collapse under moderately high pressure.^{5,6} According to these predictions NaAlH_4 will transform into a new phase at 6.43 GPa,⁵ while for LiAlH_4 a phase transition is expected at an even lower pressure of 2.6 GPa.⁶ The phase transitions are associated with significant decreases in volume, especially for LiAlH_4 (about 17%). As noted by Vajeeston *et al.*,⁶ the high-pressure modification of LiAlH_4 could be a very interesting material for hydrogen storage applications if it could be stabilized upon release of pressure.

Under ambient conditions LiAlH_4 has a monoclinic structure, denoted α - LiAlH_4 , with space group $P2_1/C$ (Ref. 7) and four formula units per unit cell. 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. According to the predictions of Vajeeston *et al.*,⁶ the α - LiAlH_4 transforms above 2.6 GPa into a new tetragonal structure, β - LiAlH_4 , similar to that of the α - NaAlH_4 phase and with space group $I4_1/a$. Existing experimental data on high-pressure phase transformations of LiAlH_4 are relatively old and were obtained only using *ex situ* methods.^{8,9} A reversible phase transition at ambient temperature was impossible to observe in such experiments, but an important result from these early studies was that α - LiAlH_4 was recovered after pressure treatment up to at least 9 GPa. It should be noted that the β and γ phases reported in these early studies were observed only when high pressure was combined with high-temperature treatment. For this reason we here reserve the term β phase for the structure predicted by Vajeeston *et al.*⁶ to exist at room-temperature conditions.

To test the interesting predictions of Vajeeston *et al.*⁶ we have decided to investigate the structural stability of LiAlH_4 under pressure, and here we present the results of an *in situ* Raman study of LiAlH_4 at pressures up to 6 GPa and ambient temperature. The experiment indeed shows clear indications of a reversible phase transition in the predicted range of

pressure, but the Raman spectra observed are not fully compatible with the suggested structure of the β phase.

II. EXPERIMENTAL

LiAlH_4 of 97% purity was purchased from Merck and studied using a diamond anvil cell (DAC) with 0.6 mm flat culets. The sample was loaded into a 0.3 mm hole in the steel gasket together with a ruby chip used for pressure calibration, and a 4:1 methanol-ethanol mixture was used as pressure-transmitting medium. The initial thickness of the sample was 60 μm . An x-ray diffraction (XRD) test of the starting material showed cell parameters $a=4.83$ Å, $b=7.81$ Å, $c=7.92$ Å, and $\beta=112.34^\circ$, in good agreement with literature data for LiAlH_4 .⁷ Since the material is sensitive to moisture, the loading was performed as quickly as possible. Raman spectra of the starting material and for the sample loaded into the DAC were identical, which confirmed that the brief exposure to air during loading had not affected the sample. The pressure was increased gradually with Raman spectra recorded on every step during compression and decompression. Usually, the time of treatment at every pressure step was about 1–2 h. A Renishaw Raman 1000 spectrometer with a 514 nm excitation laser and a resolution of 2 cm^{-1} was used in these experiments. Raman spectra were recorded *in situ* through the diamond anvils (long focus 20 \times objective) during both compression and decompression, using pressure steps of 0.2–0.5 GPa.

III. RESULTS AND DISCUSSION

The Raman spectra recorded from the sample during pressurizing up to 6 GPa at room temperature are shown in Fig. 1. The Raman spectrum of LiAlH_4 at ambient conditions is dominated by peaks due to Al-H stretching vibrations found in the spectral region 1500–1900 cm^{-1} (with strong peaks at 1832 and 1753 cm^{-1} and a weak peak at 1709 cm^{-1} in our measurements) and by bending modes of Li-Al-H at 600–1000 cm^{-1} (with peaks at 923, 873, 824, 779, and 689 cm^{-1}). The spectrum recorded under ambient conditions inside the closed DAC was identical to a reference spectrum recorded directly from LiAlH_4 powder and showed good agreement with the literature data.^{10,11} Weak libration and translation modes below 500 cm^{-1} were too difficult to ob-

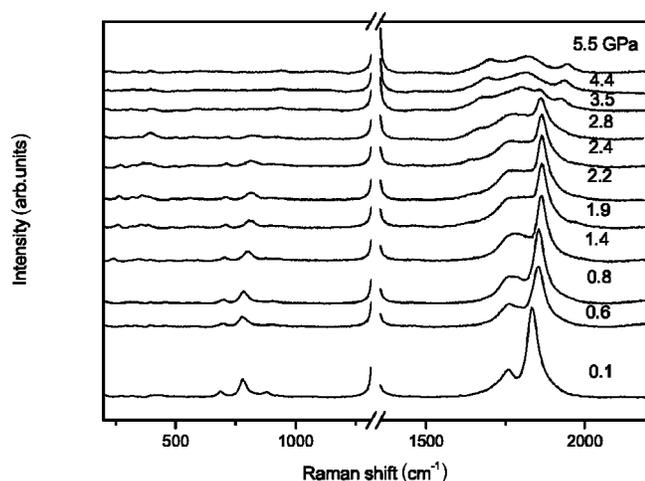


FIG. 1. Raman spectra of LiAlH_4 recorded during pressure increase up to 5.5 GPa.

serve in our DAC experiments. As can be seen in Fig. 1, upon increase of pressure, the peaks of $\alpha\text{-LiAlH}_4$ disappeared at 4.4 GPa and were replaced by peaks from a new phase which could be observed already at 2.2 GPa. A complete set of peaks indicating the simultaneous presence of two phases can be observed very clearly on the spectrum recorded at 3.5 GPa. It is possible that keeping the pressure constant for a longer time at every step would lead to a sharper and more complete transformation to the new phase, and that the coexistence of two phases over the pressure region 2.2–3.5 GPa is only due to slow transition kinetics.

The evolution of the Al-H peak positions during the pressure increase is shown in more detail in Fig. 2. The peaks for $\alpha\text{-LiAlH}_4$ showed a rather strong upshift with pressure in the beginning of the compression cycle, but above 1 GPa the peak positions become almost independent of pressure until we reached the phase transition at about 2.2 GPa.

To test that the transition was completed, the sample was finally held for 1 week at constant load, which resulted in a

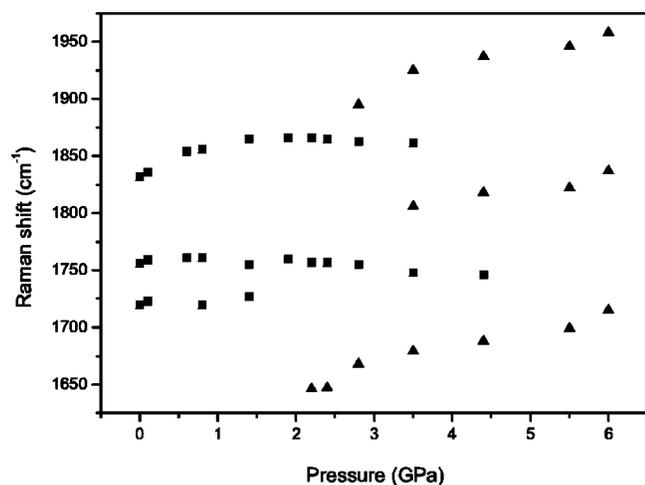


FIG. 2. Peak positions of Al-H vibrations upon pressure increase. Peaks from $\alpha\text{-LiAlH}_4$ are noted with square symbols, and peaks from $\beta\text{-LiAlH}_4$ by triangles.

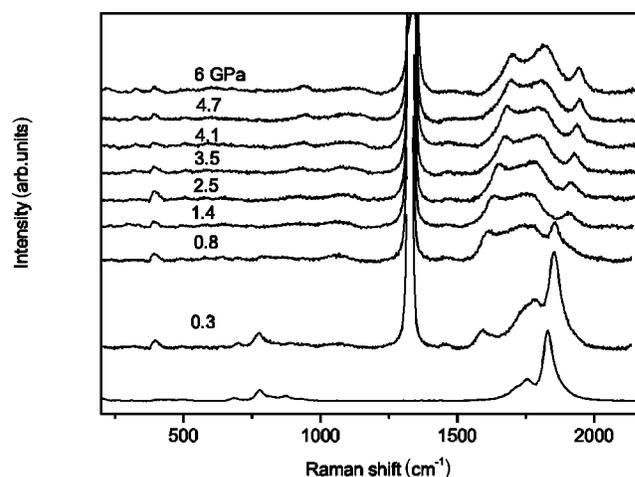


FIG. 3. Raman spectra of LiAlH_4 recorded during pressure decrease from 6 GPa. A reference spectrum recorded at ambient conditions is shown in the bottom.

slight increase of pressure from 5.5 to 6 GPa due to the mechanical relaxation of the DAC. However, the spectral change was limited to some change in the relative intensity for the peaks of the new phase.

The high-pressure modification of LiAlH_4 , which we here call $\beta\text{-LiAlH}_4$, shows three peaks of similar intensity in the region of Al-H vibrations (at 1704, 1824, and 1949 cm^{-1} at 5.5 GPa) and only one clearly visible peak at 947 cm^{-1} in the lower spectral region. It is possible that further peaks due to Li-Al-H vibrations exist but were not recognized due to their low intensity.

The Raman spectra recorded during decompression are shown in Fig. 3. It is evident from this figure that the transformation from the α to the β phase is reversible upon the decrease of pressure. Below 1.4 GPa, peaks of $\alpha\text{-LiAlH}_4$ are clearly recognizable again, and at 0.3 GPa the transformation is almost complete. At this step some air leaked into the cell and the sample was destroyed by moisture. Nevertheless, the present data are sufficient to clearly prove that the pressure-induced phase transition in LiAlH_4 is reversible upon release of pressure. All peaks from Li-Al-H bending vibrations and from Al-H vibrations in $\alpha\text{-LiAlH}_4$ can be recognized in the final Raman spectrum recorded at 0.3 GPa. Obviously, the kinetics of the reverse phase transition are also slow, which did not allow us to see a complete transformation. Figure 4 shows the pressure dependence of the peaks in the spectral region of the Al-H vibrations upon pressure decrease. Peak positions of $\beta\text{-LiAlH}_4$ shift down in frequency almost linearly with pressure during decompression to 1.4 GPa. Starting from 0.8 GPa, their intensities then drop dramatically, and at 0.3 GPa the peaks corresponding to $\alpha\text{-LiAlH}_4$ finally replace them almost completely.

The experimental results very clearly verify the theoretical prediction about a structural phase transformation under pressure at room temperature, and the observed value for the transformation pressure is in almost perfect agreement with that predicted by Vajeeston *et al.*⁶ However, closer scrutiny of the Raman spectra for the β phase, shown in Figs. 1 and 3 raises an interesting question regarding its structure. Accord-

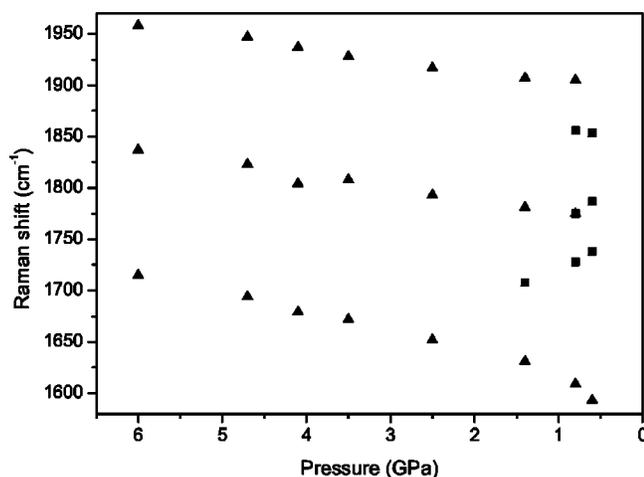


FIG. 4. Positions of peaks due to Al-H vibrations upon pressure decrease. Peaks from α -LiAlH₄ are noted with square symbols, and peaks from β -LiAlH₄ by triangles.

ing to the predictions of Vajeeston *et al.*, the β -LiAlH₄ formed above 2.6 GPa should have a structure with space group $I4_1/a$ (α -NaAlH₄ type). The structure of the original α -LiAlH₄ contains slightly deformed AlH₄ tetrahedra, and these deviations from perfect symmetry give rise to three distinct Al-H Raman peaks, as mentioned in Sec. I and observed in the experimental data. The model of Vajeeston *et al.* predicts that the structural transformation should include a transformation of the original deformed AlH₄ tetrahedra into perfectly symmetrical ones. This should modify the Raman spectrum and we note that the highly symmetrical

α -NaAlH₄ structure, which is proposed as the structural prototype for β -LiAlH₄, exhibits only *two* Al-H modes, assigned to the symmetric and antisymmetric Al-H stretch. If the high-pressure β phase of LiAlH₄ was also composed of perfectly tetrahedral AlH₄ units we would expect to find only two Al-H vibration peaks. However, the experimental data provide clear evidence for at least *three* peaks in this spectral region. This fact points towards a lower symmetry tetrahedral arrangement of AlH₄ units in β -LiAlH₄. It is likely that AlH₄ tetrahedra are deformed also in the high-pressure modification of LiAlH₄ and that the lattice structure is different from the proposed $I4_1/a$ tetragonal one. The exact structure of β -LiAlH₄ can be determined only from *in situ* high-pressure XRD studies, which are planned as a future step of the present study.

In summary, a theoretically predicted phase transition from α -LiAlH₄ to β -LiAlH₄ was observed above 2.2 GPa by *in situ* Raman spectroscopy studies. A reverse transition was observed below 1.4 GPa. The structure of the high-pressure β -LiAlH₄ is likely to be different from the predicted α -NaAlH₄ prototype with symmetric AlH₄ units, but unless a way can be found to stabilize the high-pressure phase at atmospheric pressure, the actual structure can only be determined by *in situ* high-pressure studies. The development of such a stabilization procedure might also be of interest for future hydrogen storage applications because of the predicted 17% increase in density⁶ at the transition.

ACKNOWLEDGMENT

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