Raman spectroscopy and structural transformations in hydrides under pressure

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Summary
We have investigated the structural stability of the hydrides LiAlH$_4$, NaAlH$_4$, and NaBH$_4$ under high pressure at room temperature using Raman spectroscopy. For all compounds studied we observe reversible structural phase transformations under pressure. The Raman results are not always compatible with the structures predicted by earlier theoretical calculations for the high-pressure phases, and further theoretical studies of the stability of NaBH$_4$ under pressure have been carried out.

Introduction
Light metal alanates and borohydrides, AXH$_4$ with A = Li, Na,.. and X = Al, B have recently been identified as very promising materials for use as hydrogen storage materials. The hydrogen storage capacity reaches 16% in LiBH$_4$ and hydrogen may be reversibly stored in and released from some other compounds (Bogdanovic and Schwickardi 1997). However, in spite of the large current interest in these compounds many of their properties have not been well investigated, and the pressure-temperature phase diagrams remain largely unknown.

Over the last few years, a number of calculations have been carried out on the structural properties of hydrides under high pressure. These calculations have revealed the possible existence of a number of structural phase transformations at reasonably low pressures. In particular, Vajeeston et al. (2003b) predicted that LiAlH$_4$ should have a structural transition at 2.6 GPa involving an increase in density by 17%, thus giving a significant increase in the volumetric capacity to store hydrogen. Similarly, NaAlH$_4$ has been predicted to transform into a new structure near 6.4 GPa (Vajeeston et al. 2003a) but with a smaller change in volume. Stimulated by these predictions we have investigated the lattice stabilities of LiAlH$_4$, NaAlH$_4$ and NaBH$_4$ by Raman scattering under pressure at room temperature, and for NaBH$_4$ we have complemented the experimental study by theoretical calculations of the lattice stability. As will be reported below, we find structural changes near the theoretically predicted transition pressures for all materials studied.

Experimental and theoretical methods
The high pressure studies were carried out using diamond anvil cells with 0.4 - 0.6 mm flat culets. Samples were loaded into gasket holes with half the diameter of the culets together with ruby chips for pressure calibration. While a 4:1 methanol-ethanol mixture was used as hydrostatic pressure transmitting medium in the study of LiAlH$_4$, no pressure medium was used for NaBH$_4$ and NaAlH$_4$. Raman spectra were collected using a Renishaw 1000 notch filter spectrometer using a long focus 20x microscope objective, with a 514 nm Argon ion laser for excitation. Pressure was increased and decreased in steps of 200-500 MPa, and since all materials gave high Raman scattering intensities only 1 - 2 h were usually spent at each pressure. The NaBH$_4$ and NaAlH$_4$ were loaded into the cell in a glove-box under Ar gas. In the case of NaBH$_4$ low temperature studies were also carried out in Ar at atmospheric pressure using a Linkam FDCS 196 cold stage with liquid nitrogen cooling.
Results and discussion

LiAlH₄

LiAlH₄ powder with a nominal purity of 97% was obtained from Merck. X-ray diffraction data for the material showed good agreement with literature data (Hauback et al. 2002). Because a phase transformation had been predicted to occur already at 2.6 GPa (Vajeeston et al. 2003b), pressure steps were kept as small as possible in the experiments on this material.

We show in Figure 1 a few selected Raman spectra obtained during a pressure increase from zero to 6 GPa. The figure shows the range 200 - 2400 cm⁻¹, containing bending modes for Li-Al-H at 680 - 950 cm⁻¹ and strong Al-H stretching modes at 1600 - 2000 cm⁻¹. From atmospheric pressure up to near 2 GPa the spectra obtained are very similar except for rather weak shifts with pressure, but at 1.9 GPa peaks from a new phase start to appear. On further increase of pressure the new peaks gradually grow stronger while the original peaks decrease in intensity. Peaks from the low-pressure phase can be observed over a rather wide pressure range until they finally disappear at 4.4 GPa. We have not investigated whether the wide range of coexistence is caused by slow kinetics or is an intrinsic feature of this first-order transition. The strong peaks above 1740 cm⁻¹ both show a tendency to decrease in frequency with increasing pressure close below the transition; this is most obvious for the peak at 1750 cm⁻¹ at ambient pressure, which shifts continuously downward in energy with increasing pressure from about 0.5 GPa to 4 GPa.

On decreasing pressure the new high-pressure phase was stable to below 0.8 GPa, although weak lines for the low-pressure phase appeared again already at 1.4 GPa, and at 0.3 GPa the Raman spectrum was again almost identical to the starting spectrum. More detailed experimental data have been reported by Talyzin and Sundqvist (2004).

The experiment thus verifies the prediction by Vajeeston et al. (2003b) of a transformation to a new high-pressure phase, and the new transformation also occurs at almost exactly the pressure predicted by the calculations. However, Vajeeston et al. suggest that the high-pressure phase should have a structure very similar to that of α-NaAlH₄ (symmetry I₄₁/a), with highly symmetrical AlH₄ tetrahedra. The monoclinic low-pressure phase of LiAlH₄ has

![Fig. 1. Selected Raman spectra of LiAlH₄ recorded on increasing pressure.](image-url)
slightly deformed AlH₄ tetrahedra, which should give rise to three separate Al-H stretch peaks. To get a good fit to our low-pressure spectra, we must indeed assume the presence of three such peaks. The predicted, more symmetric high-pressure structure should have fewer Raman lines in the same frequency range, but from Figure 1 it is very clear that we find at least three Al-H Raman lines also in the high pressure range. Although Raman scattering obviously cannot provide structural data, this observation suggests that the structure of the new high pressure phase needs to be investigated carefully by X-ray or neutron diffraction in order to find out whether it is indeed identical to, or different from, the structure predicted by Vajeeston et al. We plan to carry out such structural studies in the near future.

NaAlH₄

The NaAlH₄ material was obtained from Sigma-Aldrich and had a nominal purity of only 90%, but a structural check by X-ray diffraction showed no significant impurities of other phases. For this material, Vajeeston et al. (2003a) predicted a structural transition near 6.4 GPa from the tetragonal zero-pressure phase to an orthorhombic structure with symmetry Cmc₂₁. This transition is associated with a rather small change in volume, about 4%.

We show in Figure 2 selected spectra obtained on increasing the pressure from 1 atm to 8 GPa. It is evident that all spectra are very similar, but closer analysis shows that there are indications of a transformation at intermediate pressures, starting near 2 GPa and ending near 7 GPa. In Figure 2, arrows indicate the positions of peaks from the new high pressure phase, which is most clearly recognized from the splitting of peaks in low-energy collective lattice vibrations and from spectral changes in the Al-H stretch region at 1600-2100 cm⁻¹. Smaller changes can also be seen in the intermediate region of Al-H-Na bending vibrations. Again, the transformation is reversible and the original Raman spectrum is recovered below 1.5 GPa. The transition pressure found in the experiment is in reasonably good agreement with the theoretical prediction. However, the changes observed in the Raman spectra at the phase transition can probably be explained by deformation of the Al-H tetrahedra rather than by the change to an octahedral coordination of the Al atoms. Again, we plan to carry out XRD experiments in the near future to determine the actual structure of the high pressure phase.

Fig. 2. Selected Raman spectra of NaAlH₄ recorded on increasing pressure. Arrows indicate new peaks at high pressure and asterisk denotes a peak originating from the Raman spectrometer system.
$\text{NaBH}_4$

Powder with a nominal purity of 97% was obtained from Merck and the initial structure was checked against literature data (Davis and Kennards 1985) using X-ray diffraction. Because of the high sensitivity of this material to water, the diamond anvil cell was filled in a glove box under dry Ar gas and no pressure transmitting medium was added. This procedure might modify the range of transition pressures but is still preferable to using a transmitting medium with unknown effects on the material studied.

For this material many Raman modes of interest coincided with either the diamond peak or with impurity bands from the set of anvils used, and we have concentrated our study on the B-H stretching mode $\nu_1$ near 2330 cm$^{-1}$ (at zero pressure) and overtones to the bending modes falling in the neighbourhood of this (Orimo et al. 2004). Figure 3 shows Raman spectra of NaBH$_4$ at a few selected pressures in the range up to 15 GPa, obtained on increasing pressure. In the range below 7 GPa the spectra are almost identical, with the peaks shifting continuously to higher energy with increasing pressure at approximately the same rate. At 10.8 GPa new peaks begin to appear in the spectrum, at 13.5 GPa we have a two-phase material, and at 14.8 GPa only the peaks from the new high-pressure phase remain. On decompression the transformation is reversible: again, the transformation starts near 10.8 GPa and at 7 GPa we only observe the original low-pressure structure in the sample. Detailed experimental data will be reported elsewhere (Moysés Araújo et al. 2005).

Again, we cannot identify the structure of the high pressure phase from our spectroscopic data, but we can clearly see that the BH$_4$ cluster must become less symmetric in the high pressure phase, since the single strong B-H stretch mode splits into three above the transition. Such a spectrum could be consistent with an orthorhombic or a monoclinic structure. To ascertain that the high pressure phase was not identical to the known tetragonal low-pressure phase we also carried out a low-temperature experiment, in which we measured the Raman spectrum of the material from room temperature down to 77 K. The spectrum of the low-temperature phase was found to be very similar to that found at room temperature.
temperature, as would be expected for a transition which is basically of the order-disorder type (Fischer and Züttel, 2004). The new high-pressure phase is thus not identical to the tetragonal low-temperature phase of NaBH₄.

In an attempt to identify the new structure, self-consistent calculations of the cohesive energy of several possible structures were carried out in Uppsala. The methods used are described fully by Moysés Araújo et al. (2005). These calculations showed that a transformation should occur from the zero-pressure face centered cubic structure of NaBH₄ to the monoclinic structure of the low-pressure α-LiAlH₄ phase near 19 GPa. The calculated transition pressure is in quite reasonable agreement with the observed transition pressure just below 15 GPa, and we note that the Raman spectra of both the new phase and of the low-pressure α-LiAlH₄ phase show three Al-H stretch modes. The agreement between experiment and theory is thus very good, showing that the monoclinic α-LiAlH₄ structure is a very probable candidate for the structure of the high-pressure phase of NaBH₄. However, for a final identification of the high-pressure structure an in situ diffraction experiment should still be carried out.

Conclusions
Three light metal hydrides, LiAlH₄, NaAlH₄, and NaBH₄, have been studied by Raman spectroscopy under pressure at room temperature. For all of these, reversible phase transformations have been observed at pressures very close to those at which theoretical calculations have predicted that structural phase transformations should occur. In all cases the transformations were found to be reversible on pressure release, which explains why earlier ex situ studies (Bastide et al. 1987) have not indicated the presence of any structural transformations. Because these largely exploratory studies were carried out using Raman spectroscopy the actual structures of the high pressure phases have not been identified. Further in situ structural studies by X-ray diffraction are thus necessary for a full structural identification of the new phases.

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References