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Phase transitions in hydrogen storage compounds under pressure

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Abstract

Solid, hydrogen-rich compounds, such as alkali metal hydrides, MAH_4 , where M is an alkali metal and A is boron or aluminium, may be used for hydrogen storage. We briefly review recent high-pressure work in this field aimed at exploring the phase behaviour, and especially the possibility to find highly dense new structures. In particular we present experimental data on the structure, lattice dynamics, phase diagrams, and thermal properties obtained by us and others by Raman scattering, x-ray diffraction, and thermal conductivity measurements under pressure between 100 and 400 K. From these data and the results of theoretical calculations we map observed structural phases and phase transitions in the pressure–temperature plane for the materials that have so far been investigated under pressure.

1. Introduction

One of the main problems in building a future hydrogen-based energy system is to find safe methods to store large amounts of hydrogen. Light metal hydrides have recently been discussed as a possible basis for such a system because of the high weight fraction of hydrogen in these materials [1]. In particular, alkali metal borohydrides and alanates MAH_4 , where M is an alkali metal and A is boron or aluminium, respectively, have shown promising results. Although the borohydrides usually release H_2 by reaction with water, giving solid reaction products, some alanates can reversibly absorb and release hydrogen by a thermal cycle in the presence of catalysts. Interest in the high-pressure properties of these materials was kindled a few years ago when Vajeeston *et al* [2] predicted that $LiAlH_4$ should have a structural phase transition at 2.6 GPa into a phase 17% more dense, and thus with a similarly higher volumetric hydrogen storage capacity. Following this, many materials have been explored under pressure in the hope of finding ways to produce novel structures with even higher volumetric hydrogen contents. Here we review recent published work, including our own, adding new results and collecting available information on the phase diagrams of these materials.

2. Experimental details

Below we present new and recent data obtained in our laboratory by Raman spectroscopy and thermal conductivity measurements. The Raman data were all collected using a Renishaw 1000 micro-Raman spectrometer, using either an Ar⁺ ion or a HeNe laser for excitation. The spectra were obtained using a 20× or 50× long focus objective with the sample in a diamond anvil cell. In most cases the samples were loaded into the cell under argon gas in a glove box. The ruby fluorescence technique was used for the pressure measurements. Thermal conductivity measurements were carried out using the dynamic hot-wire heat pulse technique [3], with a Ni wire probe embedded in the sample. The method also provides data for the heat capacity, but with low accuracy. In some experiments differential thermal analysis was also used, with one thermocouple placed inside the sample and another one in the Teflon cell wall. For all thermal measurements a 2.5 GPa piston-cylinder device, with 45 mm inside diameter, was used.

3. Results and discussion

3.1. Borohydrides

At room temperature, the heavier borohydrides, NaBH₄, KBH₄, RbBH₄, and CsBH₄, all have the same face-centred cubic $Fm\bar{3}m$ structure containing orientationally disordered tetrahedral BH₄⁻ units [4]. On cooling, the BH₄⁻ units tend to form an orientationally ordered structure, and for the Na and K compounds this leads to phase transitions at 190 and 76 K into tetragonal phases with symmetries $P4_21c$ and $P4_2/nmc$, respectively, differing only in the relative positions of the H atoms [5]. Several studies have indicated that the Rb and Cs compounds also form lower symmetry structures at 35–44 K and 22–27 K, respectively, but these have not yet been identified [4].

Of these compounds, only NaBH₄ has so far been reasonably well investigated under pressure. The possible existence of a transition under pressure was noted long ago by Wakamori *et al* [6], but accurate data were not obtained until recently [7–11]. Raman measurements carried out in our laboratory using the methods described above showed [7, 9] very clear changes in the Raman spectrum, starting near 10.8 GPa, and indicating a structural phase change. The transformation was rather sluggish and was not complete until above 14.5 GPa. Although completely reversible, it was also associated with a sizable hysteresis such that the reverse transformation again started at 10.8 GPa but was not complete until below 7 GPa. No anomalies or sudden changes were detected in Raman spectra taken at lower (or higher) pressures, and a direct comparison between the spectra for the high-pressure phase and for the low-temperature tetragonal phase showed that the two phases were different.

An x-ray study by Sihachakr *et al* [8], on the other hand, found clear indications of another structural transformation at 6.8 GPa. This transition was later also found by Kumar and Cornelius [10], who identified it as a cubic-to-tetragonal transition starting at 6.3 GPa, and also detected a second transformation near 8.9 GPa. Above this pressure the structure was indexed as orthorhombic with symmetry $Pnma$, a structure found to be stable up to 30 GPa. Combining all these results we actually find them to be in quite good agreement, and we can use the data to find a first version of a phase diagram for NaBH₄ near room temperature. From the two sets of x-ray data we find that the orientationally disordered face-centred cubic phase is stable up to 6.3 GPa, above which the material transforms into the orientationally ordered tetragonal phase also obtained on cooling below 190 K at atmospheric pressure. This result is compatible with the fact that the transition is not observed in the Raman data, since the difference between the Raman spectra of these two phases is difficult to detect even under

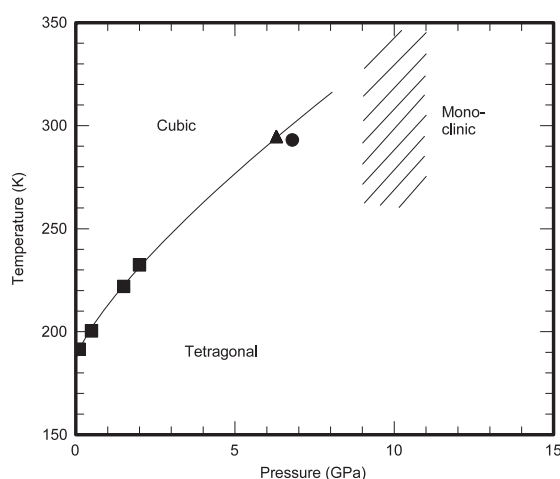


Figure 1. Low-temperature phase diagram of NaBH_4 .

ideal zero-pressure conditions [9] because of the close structural relationship between the two phases. At higher pressures, a second transition into an orthorhombic phase is indicated by both Raman [7, 9] and x-ray [10] data, starting at 10.8 and 8.9 GPa, respectively.

To obtain further information on the phase diagram, Sundqvist and Andersson [11] measured the thermal conductivity κ of NaBH_4 as a function of temperature at several pressures up to 2 GPa. As shown in figure 3, phase transitions produce very clear anomalies in the data for κ , and the low-pressure phase line could be accurately mapped up to above 230 K. The low-temperature slope of the transition boundary was 23 K GPa^{-1} , significantly smaller than found in a recent calculation [12]. Collecting all data we find the low-temperature phase diagram of NaBH_4 shown in figure 1. The phase transition boundaries are given for increasing pressure, and both transitions are associated with some hysteresis. For the cubic-to-tetragonal transition this is only about 6 K (or 0.25 GPa), but for the tetragonal-to-orthorhombic transition it is significantly larger. In the latter case we indicate a transition zone from 9 to 11 GPa, since neither the position nor the slope of the phase line is yet accurately known.

Significantly less is known about the heavier alkali metal compounds. For KBH_4 , we have recently carried out Raman scattering experiments under high pressures up to 17 GPa, using the methods described above. Our preliminary results indicate a structural phase transition which starts near 6 GPa and is completed near 8.5 GPa. We show in figure 2 Raman spectra obtained at 4.7, 7.5 and 9.7 GPa, in the low-pressure, mixed, and high-pressure phases, respectively. The transition has a hysteresis in the normal direction; on decreasing pressure it starts just below 6 GPa and is completed below 4.5 GPa. The transition involves a rather large change in lattice symmetry and is thus probably not connected with the order-disorder (cubic-tetragonal) transition in KBH_4 , but a closer analysis and an attempt to identify the structure by *in situ* x-ray diffraction and calculations is still in progress. To complete the picture for the heavy alkalis we also note that early resistance measurements on RbBH_4 [6] indicated a possible transition near 3–4 GPa, but its existence remains very uncertain.

It may be speculated that at least the low-pressure part of the structural pressure-temperature (p - T) diagrams of the four heavier alkali metal borohydrides might be similar to that shown in figure 1 for all materials, with the order-disorder (cubic-tetragonal, for the Na and K compounds) phase boundary shifting toward lower temperatures (or higher pressures) with increasing alkali metal mass, as indicated by the observed zero-pressure transition

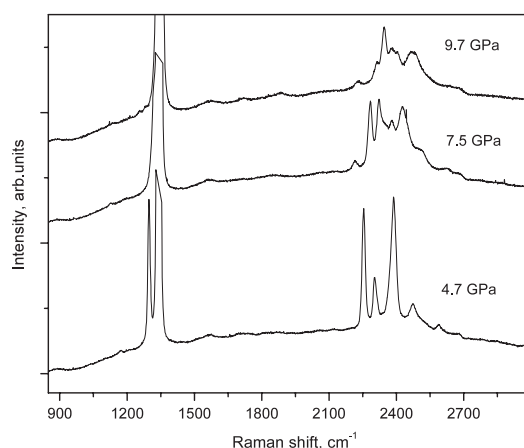


Figure 2. Experimental Raman spectra of KBH_4 at the pressures indicated.

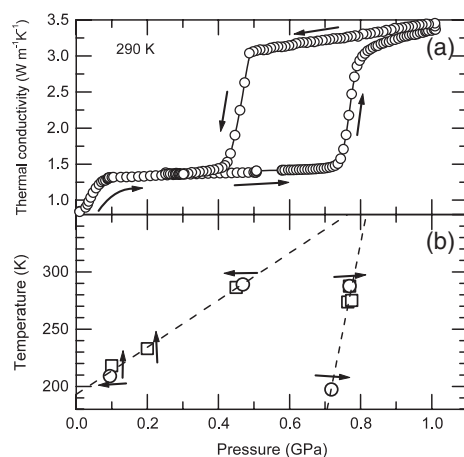


Figure 3. The upper part shows κ as a function of pressure at room temperature, and the lower part the low-temperature pressure–temperature phase diagram, both for LiBH_4 . Arrows show trajectories in the p – T plane; circles denote data obtained from measurements of κ , and squares data from DTA.

temperatures. If this is correct, the true structural parameters for the hitherto unidentified low-temperature phases of the Rb and Cs compounds might be more easily found under pressure. It is reasonable to assume that the low-temperature transition into the orientationally ordered phases is frustrated at atmospheric pressure because sufficient thermal energy is not available to complete the transition, and in such a case the transition should occur much more easily under pressure at higher temperatures. However, for these phases to exist at sufficiently high temperatures it is necessary that any transitions into higher-pressure phases occur at rather high pressures, and we note that if the slope dT/dp of the cubic-to-tetragonal phase line in KBH_4 is the same as that for NaBH_4 the tetragonal phase can never be observed at room temperature because the observed transition into a lower-symmetry phase intervenes at some low pressure. Whether there really exists a common, systematic evolution of the structures and transition pressures of the high-pressure phases of the heavy alkali borohydrides remains to be seen.

The lightest alkali metal borohydride, LiBH_4 , shows several interesting features. It contains the largest weight fraction of hydrogen, it is the only alkali metal borohydride for which the high-pressure phase diagram has been investigated in detail previously, and it also has low-pressure structures that are completely different from those of the heavier compounds discussed above. The p - T phase diagram was studied over wide ranges in T and p above room temperature by volume measurements and differential thermal analysis (DTA) by Pistorius [13]. At zero pressure, LiBH_4 has an orthorhombic structure with symmetry $Pnma$ near and below room temperature, but on heating to above 380 K it transforms into a $P6_3mc$ hexagonal lattice. As pointed out by Pistorius, the room-temperature phase is significantly less dense than a hypothetical face-centred cubic phase would be, and a pressure-induced densification should be expected. The phase diagram derived by Pistorius in the approximate range 350–825 K and 0–4.5 GPa is indeed very rich [13], containing three high-pressure phases in addition to the two known zero-pressure ones, but the lattice structures are not known for any of these. At room temperature, Pistorius only found a single phase transformation near 0.64 GPa, associated with a density increase by about 6%. The transition pressure was not very well defined because of a very strong hysteresis. A low-pressure transition was also observed by Wakamori *et al* [6].

Very recently, we have extended Pistorius' phase diagram studies to higher pressures near room temperature and to significantly lower temperatures, using the same methods as already discussed above [14]. Raman scattering studies in the range up to 9 GPa clearly showed the expected structural transformation between 0.5 and 1 GPa, but at higher pressures no clear evidence of further structural changes were observed, although minor changes in the relative intensities of some Raman peaks and small anomalies in the pressure dependence of the Raman frequencies were noted near 6 GPa. An attempt was also made to find the lattice structure by conventional x-ray diffraction, but, due to the small atomic scattering factors of the light atoms and a limited range of scattering angles available, too few reflections were observed to obtain a positive identification of the structure. Calculations have predicted a large number of possible structures [5, 15, 16]. Łodziana and Vegge [15] suggest that the high-temperature structure should be monoclinic Cc instead of hexagonal, and they predict a phase transition near 3 GPa from the room-temperature phase to this monoclinic structure. However, the observation of very clear phase transitions between the high-temperature phases and the high-pressure phases by Pistorius makes such a scenario unlikely. Vajeeston *et al* [5] propose a transition near 6.2 GPa into a tetragonal $P\bar{4}2_1c$ structure, while Frankcombe *et al* [16] suggest that transitions occur first near 1 GPa into a $P2_1c$ structure, then just above 2 GPa into the monoclinic Cc structure. In principle, our x-ray data could be fitted to both the $P2_1c$ structure and a tetragonal phase, but in neither case did the fit yield lattice parameters compatible with the compression study of Pistorius.

In the low-temperature range our thermal conductivity and DTA studies gave a very clear picture of the structural phase behaviour. Only one phase boundary was found below 2 GPa, but this boundary had a strongly temperature-dependent hysteresis, as shown in figure 3. On pressurization a transition into the high-pressure phase occurred at a weakly temperature-dependent pressure near 0.75 GPa (at 293 K). However, the reverse transformation to the normal zero-pressure phase had a quite different behaviour. Several pressure-temperature cycles carried out between 150 and 300 K revealed that the reverse phase transition line had a very steep slope, such that the transition occurred at a pressure decreasing from 0.45 GPa at room temperature to zero at 200 K. Below 200 K the high-pressure phase should be metastable at atmospheric pressure. In principle, this should make it possible to carry out detailed structural studies on this phase under atmospheric pressure at low temperatures, but at the moment we have no equipment available for this task. An extrapolation of the two phase lines to higher temperatures show that they cross very close to the two triple points found by Pistorius in his

earlier high-temperature study [13]. We conclude that at the present time the phase diagram of LiBH_4 is probably the best known phase diagram for any alkali metal borohydride, in spite of the fact that most lattice structures involved are still unknown.

3.2. Alanates

Among the alkali metal alanates, only LiAlH_4 and NaAlH_4 have so far been studied under pressure. The motivation for recent studies was the prediction by Vajeeston *et al* [2] that in LiAlH_4 a volume collapse by 17% should occur at 2.6 GPa, associated with a transition from the monoclinic $P2_1/c$ zero-pressure structure to a tetragonal $I4_1/a$ structure. At even higher pressure, near 34 GPa, a second transition into an orthorhombic $Pnma$ structure was predicted. The existence of a low-pressure transition near 2.5 GPa was indeed rapidly confirmed by us [17] in a Raman scattering experiment, although we found that the observed Raman spectra for the high-pressure phase did not match the structural predictions made. This was verified by a later neutron scattering study at pressures up to 7 GPa by Pitt *et al* [18], who found that only a small fraction of the material actually transformed into the new high-pressure structural phase at room temperature. At the slightly higher temperature of 353 K, about 37% of the sample transformed into the new high-pressure phase at 7 GPa, and the structure could be indexed as monoclinic ($I2/b$) with an atomic arrangement identical to that in the predicted tetragonal structure. In the mixed phase region the lattice structure was always distorted, and our observed Raman spectra [17] actually seem to originate from a structurally distorted form of the original zero-pressure phase. In a very recent Raman study, Chellappa *et al* [19] showed that the high-pressure phase could be pressure quenched down to about 1.2 GPa. Earlier studies by Bulychev *et al* [20] showed that a tetragonal phase was formed at 7 GPa at all temperatures between 100 and 400 °C, while an orthorhombic phase was formed at 5–600 °C at 7 GPa, as well as at 400 °C at pressures of 4–6 GPa. These high-pressure phases were sufficiently metastable to enable *ex situ* x-ray studies on the pressure-treated materials, while the samples in all recent room-temperature experiments reverted to the original structure on pressure decrease. This might indicate that the phases found by Bulychev *et al* were stabilized by hydrogen loss; however, both Bulychev *et al* [20] and Bastide *et al* [21] report transformations back to the monoclinic structure on heating at zero pressure.

Calculations on NaAlH_4 , which has a tetragonal ($I4_1/a$) zero-pressure structure, predicted a phase transition near 6.4 GPa associated with a volume change by 4% [22]. This prediction was tested by Nakano *et al* [23], who carried out both Raman and x-ray diffraction studies up to 50 GPa, using liquid He as the pressure medium. Nakano *et al* reported structural phase transitions at about 12, 20, and 30 GPa, but were unable to identify the actual structures. However, they were able to rule out the existence in this range of the actual structure suggested by Vajeeston *et al* [22], and they suggest that the phase obtained at the highest pressures was ‘amorphous-like’. In a recent experiment we have also carried out Raman scattering studies to 17 GPa [24]. Our data verify the existence of a structural transformation between 13 and 14 GPa, and we note in particular that this transformation is associated with an unusually strong pressure hysteresis. Although the transition occurs above 13 GPa on increasing pressure, once formed the new high-pressure phase is stable down to about 3 GPa before the normal low-pressure phase reappears. Raman spectra also show interesting changes in the low-pressure region 2–5 GPa [7, 24] which can possibly be associated with minor structural changes such as deformations in the AlH_4 tetrahedra, or possibly reorientations of them. To investigate whether these changes are associated with some low-temperature, low-pressure structural phase we carried out thermal conductivity measurements down to below 100 K in the range up to 2 GPa, but as shown in figure 4 the data show only the normal temperature dependence. However, close

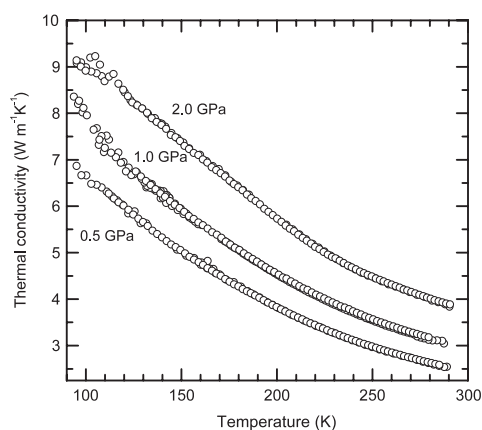


Figure 4. Thermal conductivity of NaAlH₄ as a function of temperature at the pressures indicated.

scrutiny of the data reveals unusual step anomalies in the specific heat data (not shown), which shift with pressure in a systematic way and show a hysteresis with temperature. For increasing temperatures the anomalies fall on a straight line extrapolating from 165 K at zero pressure to 4.7 GPa at 293 K. The latter point falls in the range where Raman anomalies are observed, but only careful structural studies can reveal whether these anomalies are experimental artefacts or arise from true structural changes. For completeness we add that Bulychev *et al* [20] also carried out *ex situ* studies on NaAlH₄ samples heated to various temperatures up to 600 °C near 7 GPa but found no metastable structures, in general agreement with other experiments.

For the heavy alkali metal alanates no experimental data are available, but Ravindran *et al* [25] suggest that the normal pressure structure of KAlH₄ should be stable up to above 100 GPa.

4. Conclusions

Because of the many lattice structures predicted and observed, the structural evolution of the alkali metal alanates and borohydrates under pressure is an interesting research field. Although theoretical predictions have been very important in this field, the very small energy differences between different structures make calculations somewhat uncertain, implying that experimental verification is essential. So far, reasonably detailed phase information is only available for some light compounds, and primarily for low pressures and temperature, and some interesting phase transitions with large pressure hysteresis have been identified but need to be better understood. Much thus remains to be done in this important area which may be of large future interest for hydrogen storage applications.

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