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Low-temperature phase transformation in $NaBH_4$ under pressure

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The pressure-temperature structural phase diagram of $NaBH_4$ has been mapped by thermal conductivity measurements below room temperature and up to 2 GPa. The critical transition temperature for the transformation from the low-temperature tetragonal structure to the room temperature cubic one increases from near 190 K at zero pressure to about 235 K at 2 GPa. The thermal conductivity data are consistent with the order-disorder character of the transition.

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Light metal hydrides and borohydrides are of considerable contemporary interest as potential future hydrogen storage materials,[1] but little is known about their high-pressure properties and structures. Recently, a calculation predicted[2] a structural phase transition associated with an increase in density (and thus in volumetric hydrogen storage capacity) by 17% in $LiAlH_4$ at the rather low pressure of 2.6 GPa at room temperature. Subsequent Raman studies under pressure[3] verified the existence of a reversible structural phase transition at almost exactly the predicted pressure. Since stabilization of a dense high pressure phase could be a possible way to increase storage capacity, there has been a recent surge in interest in the pressure-temperature phase diagrams of this and related materials. Similar calculations have been carried out for several compounds and a number of structural phase transformations have been predicted to occur at various pressures.[4–6]

Only a small number of experimental studies have been carried out so far, but a combined experimental and theoretical investigation of the structural properties of $NaBH_4$ was published quite recently.[6] In this study, a Raman scattering experiment showed clear signs of a reversible structural phase transformation at room temperature, starting at 10.8 GPa on increasing pressure. The transition was rather sluggish and was not completed until above 14 GPa. No structural characterization could be made, but calculations showed that the most probable high pressure structure was the monoclinic α-$LiAlH_4$ structure. The calculated transformation pressure of 19 GPa agreed reasonably well with the experimental data, and the experimental Raman spectra for the high-pressure phase were compatible with the predicted structure.

In the low-pressure range up to about 3 GPa, the Raman data showed a nonlinear dependence of the phonon energy on pressure. The reason for this anomalous behavior was not clear, but it was suggested that there might be a connection with the well-known tetragonal-to-cubic[7–9] transformation occurring in $NaBH_4$ near 190 K at atmospheric pressure. Low-temperature zero-pressure Raman studies[6] showed that the Raman signature of this transition was different from that of the transformation found above 10 GPa. Only very small changes were noted in the relevant part of the Raman spectrum at the low-temperature transition, indicating that the position of this particular transition is very difficult to detect under pressure at room temperature using this method.

Because no information was available on the pressure-temperature phase diagram of $NaBH_4$ below room temperature, we here explore the phase transition line corresponding to the tetragonal-to-cubic transformation up to 2 GPa. This transformation has been well investigated at atmospheric pressure.[7–9] On cooling below about 190 K the room temperature cubic structure, with orientationally disordered BH_4 units, transforms into a very similar tetragonal structure, where the BH_4 tetrahedra are orientationally ordered. To obtain high resolution in temperature and pressure, we have chosen to measure the thermal conductivity of the material using a fast dynamic method,[10] and we find that the tetragonal-to-cubic transition is easily observable in the measured thermal conductivity. The results clearly show that the observed nonlinearity in the Raman data[6] is not directly connected with this transition.

The $NaBH_4$ used was obtained from Fisher Scientific (general purpose grade). A Raman measurement using a Renishaw 1000 Raman spectrometer gave the spectrum shown in Fig. 1, which is in excellent agreement with literature data[11] and with data from the earlier high-pressure study.[6] The data shown were obtained using a 514 nm Ar^+ ion excitation laser. Very similar results, but with an inferior signal-to-noise ratio, were found with 782 nm excitation. The thermal conductivity measurements were carried out using the hot wire method[10] in a high-pressure cell identical to those used in our

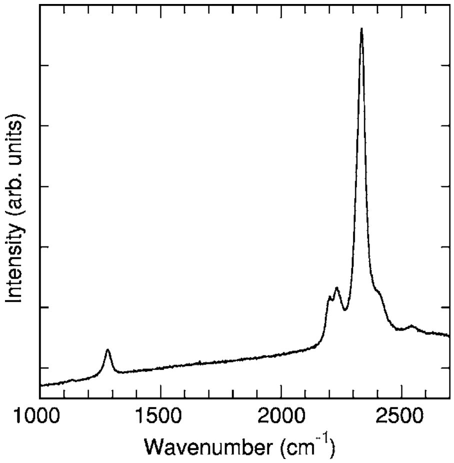

FIG. 1. Raman spectrum for $NaBH_4$ obtained using an excitation wavelength of 514 nm.

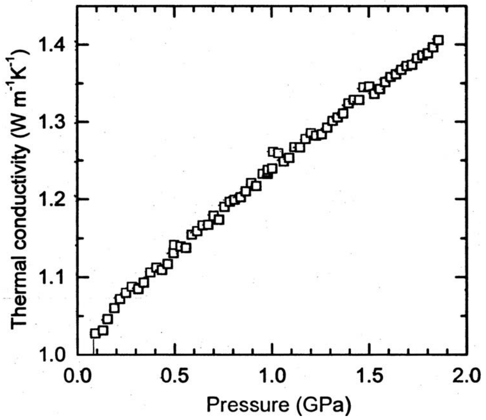

FIG. 2. Thermal conductivity of $NaBH_4$ as a function of pressure at room temperature.

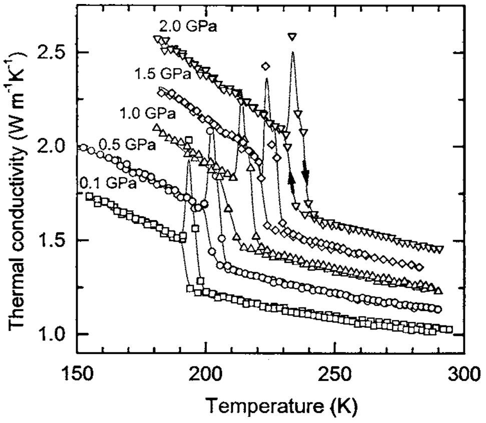

FIG. 3. Thermal conductivity of $NaBH_4$ as a function of temperature at the pressures indicated. Arrows in the dataset obtained at 2.0 GPa show the observed hysteresis behavior of the data in the transition region.

measurements[12] on C_{60}. Fine $NaBH_4$ powder was packed around a Ni probe wire in a semicircular groove in the Teflon® cell. No fluid pressure transmitting medium was used, partly because $NaBH_4$ reacts rapidly with even small traces of H_2O and partly because the method used relies on a small nonhydrostatic pressure component to promote thermal contact between the sample and the probe wire. High measurement accuracy requires that the probe wire be surrounded by a sample layer sufficiently thick that the temperature wave is not reflected noticeably by the sample-Teflon interface. The thermal conductivity of the material turned out to be somewhat too high for this requirement to be met, especially in the tetragonal phase at low temperatures. However, since the experiment was primarily designed to explore the phase diagram, the reduced accuracy for the thermal conductivity was acceptable. The high pressure was generated in an all-steel piston-and-cylinder device, 45 mm in inside diameter. The cylinder was thermally insulated with fiberglass insulation and the whole vessel was cooled directly using liquid nitrogen. The large mass of the device ensured slow cooling and heating rates and thus small temperature gradients.

The thermal conductivity κ was measured as a function of pressure at room temperature, with the results shown in Fig. 2. Below 0.1 GPa the results were strongly influenced by the initial compaction of the powder, but once the shear strength of the grains is exceeded, compaction into a homogenous sample ensures good thermal contact with the probe wire and thus reliable results. During the pressure run, isobaric measurements of the thermal conductivity as a function of temperature were made at 0.1, 0.5, 1.0, 1.5, and 2.0 GPa, with the results shown in Fig. 3. The probe wire broke during the final part of the last isobaric run. The minimum temperature was about 150 K at the two lowest pressures and 180 K above. At all pressures, the data show large, sharp step anomalies at the transitions from the low-temperature tetragonal structure to the room temperature cubic one. The peaks observed on heating are well-known artifacts of the method used, caused by probe cooling by the transition enthalpy. The transition has a well-defined, basically pressure-independent hysteresis in the transition temperature (see below). In principle, friction effects in gaskets could cause a shift in the pressure on switching from cooling to heating of the system, but the very good overlap between the thermal conductivity data obtained while increasing and decreasing the temperature, respectively, shows that such friction-induced differences are negligible.

Although the absolute accuracy for the thermal conductivity is not very high, as mentioned above, we can still give some general comments on the measured data. Figure 2 shows an increase by about 40% in the thermal conductivity to 2 GPa, and the plotted data show a fairly linear behavior as a function of pressure with a small curvature toward the pressure axis. Such behavior is normal, and the curvature is usually due to an increase in the bulk modulus with pressure. We are not aware of any published experimental data for the bulk modulus of $NaBH_4$. A graph of volume versus pressure over the range 2.5 to 6.5 GPa at room temperature is given in a recent conference abstract[13] and graphical analysis of this curve indicates rather uncertain values for the zero-pressure bulk modulus $B_0 \approx 15$ GPa and for its pressure derivative $B' \approx 5$ GPa in the cubic phase. For the tetragonal phase, values of $B_0 = 22.2$ GPa and $B' = 3.48$ were calculated in Ref. 6.[14] It is reasonable that the cubic room temperature phase should have a somewhat lower bulk modulus than the structurally better ordered low-temperature tetragonal phase,[8,9] and the two datasets are thus mutually consistent. The measured pressure coefficient of κ in the cubic phase at 0.3 GPa is approximately $d(\ln \kappa)/dp = 0.20\ \mathrm{GPa}^{-1}$. Using the uncertain experimental value for B_0, we find that the thermal conductivity κ depends on density ρ as $\mathrm{d}\ln\kappa/\mathrm{d}\ln\rho \approx 3$, which is in the range normally found for slightly disordered crystalline solids.[15]

The temperature dependence of the thermal conductivity is noticeably different in the two phases. In the tetragonal low-temperature phase, the observed temperature dependence ($\kappa \propto T^{-0.65}$) is rather close to the $\kappa \propto T^{-1}$ expected for a perfect crystalline insulator,[16] but in the high-temperature cubic phase the variation with temperature is weaker ($\kappa \propto T^{-0.45}$). This observation is compatible with the suggestion that this transition has an order-disorder character,[8,9] where the low-temperature tetragonal phase is well ordered, while

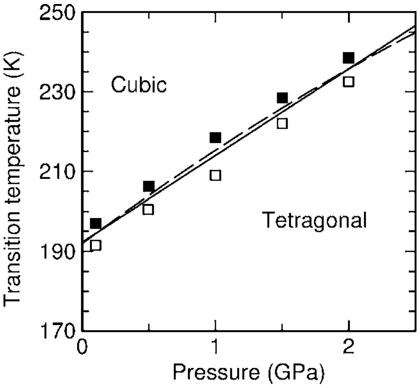

FIG. 4. Low-temperature/pressure structural phase diagram of $NaBH_4$. Open symbols indicate the temperatures at which the cubic-to-tetragonal transitions were observed on cooling while filled symbols show the reverse transition points on heating; full line and dashed (quadratic) curve were fitted to the data, as discussed in the text.

in the room-temperature structure, the BH_4 tetrahedra have some orientational freedom. The relative change in the magnitude of κ at the transition is relatively constant near 25%.

The transition temperatures were defined as the temperature at which the thermal conductivity was halfway between the (extrapolated) values for the two pure phases. Four of the five cooling cycles gave a hysteresis of (6 ± 0.5) K in the transition temperature, but the data obtained on cooling at 1 GPa (Fig. 3) differed from the other cooling curves in showing a more gradual transition from the cubic phase to the tetragonal one, resulting in a somewhat larger apparent hysteresis. All experimental points for the transition temperatures are plotted in Fig. 4, and these data define the low-temperature, low-pressure corner of the temperature-pressure phase diagram of $NaBH_4$. It is obvious from this figure that the tetragonal-to-cubic transformation is not responsible for the anomalies in the Raman frequencies versus pressure observed by Moysés Araújo *et al.*[6] at room temperature below 3 GPa. A straight line fitted to all data in Fig. 4 (full line) extrapolates to a transition pressure of 4.6 GPa at 293 K, a pressure region where no particular features were found in Raman data.[6] This agrees well with the observation[6] that the Raman spectrum shows only very small changes at this transition at atmospheric pressure. A careful look at the data in Fig. 4 shows that, except for the anomalous point at 1 GPa discussed above, they actually indicate a small downward curvature, the normal behavior for a phase boundary in a compressible material. The true room-temperature transition pressure is thus probably higher than that given by the linear extrapolation. We note that the preliminary x-ray data at room temperature referred to previously[13] also indicated a reversible structural transition at 6.8 GPa in the same material. Tentatively identifying this transition with the cubic-to-tetragonal boundary, we have fitted a quadratic function of pressure to the combined dataset to find the dashed curve in Fig. 4, in better agreement with the curvature in our data.

We have thus mapped the low-temperature part of the pressure-temperature phase diagram of $NaBH_4$ and shown that the nonlinear behavior of the Raman lines found by Moysés Araújo *et al.*[6] is not connected with the cubic-to-tetragonal transformation. A comparison with the thermal conductivity data in Fig. 2 also shows that it is very unlikely that the Raman anomaly is caused by a rapid variation of the bulk modulus with pressure, in agreement with the reasonably small values of B' given above, since such a variation would have given a similarly strong variation in $d\kappa/dp$. We speculate that the nonlinear Raman data observed by Moysés Araújo *et al.* may instead have resulted from the initial buildup of anisotropic stress in the sample during the application of pressure.

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