

High-Pressure Polymorphism as a Step towards Destabilization of LiBH_4 **

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Lithium borohydride could be an extremely efficient energy storage system containing 18.5 wt % hydrogen. However, owing to its high thermal stability, it is not yet regarded as a practical H-storage material. More experimental and theoretical efforts are required to improve the hydrogen-storage properties of this compound.^[1] Experimental investigations of light metal borohydrides such as LiBH_4 are difficult owing to the weak diffracting power of the light elements for X-ray diffraction and to considerable incoherent scattering by H and high absorption by natural B and Li for neutron diffraction. For these reasons, LiBH_4 has been extensively studied theoretically by “first-principles” methods based on density functional theory (DFT). A large amount of information has been generated, including possible crystal and electronic structures, lattice dynamics, surface properties, decomposition mechanisms, and intermediate products.^[2–9] Surprisingly, theory and experiment agreed only on the symmetry of the room-temperature, ambient-pressure polymorph of lithium borohydride. Despite the fact that the temperature-induced structural transition in LiBH_4 has been known for a long time,^[10] the experimental structural data on the high-temperature form^[11,12] have not yet been confirmed by theory. In particular, the presumed hexagonal $P6_3mc$ structure, first suggested from diffraction experiments,^[11,12] was found to have a relatively high energy and imaginary vibrational frequencies.^[4] Other calculations have also shown that the $P6_3mc$ structure is rather unstable.^[5,6]

The same problem holds for the pressure evolution of LiBH_4 ; a phase transition below 5 GPa was identified more than 30 years ago,^[13] but there is still no agreement on the structure of the high-pressure phase. Theoretical predictions

suggest a cubic NaBH_4 -type structure above 6.2 GPa,^[7,13] a monoclinic $P2_1/c$ structure at approximately 1 GPa,^[5] and a monoclinic Cc structure above 2.2 GPa^[5] (3 GPa in reference [4]). However, the most recent experimental study of LiBH_4 at pressures up to 9 GPa concludes that none of these predictions are correct,^[14] although the structure of the high-pressure polymorph itself could not be identified, owing to experimental limitations. Thus, the first efforts in understanding the material properties, both experimental and theoretical, were discouraging. Both the pressure and temperature evolution of the corresponding structure have found no consistent explanation in the framework of “first-principles” theories.

To date, only one pressure-induced phase transition, into a phase with as yet unknown crystal structure, has been observed in LiBH_4 . Inconsistent theoretical predictions and the poor quality of available experimental information motivated a new detailed diffraction study of LiBH_4 under pressure. Herein we have succeeded, using synchrotron radiation provided by the European Synchrotron Radiation Facility (ESRF), in identifying the structure of this new phase, which is characterized by an unprecedented arrangement of Li atoms relative to the BH_4 unit. We have also found a second phase transition into the previously predicted^[7,13] cubic phase of LiBH_4 , which occurs at high pressures above the reach of all previous experiments.

In agreement with previous experimental data, we find a phase transition at 1.2 GPa from the ambient-pressure polymorph (space group $Pnma$,^[11] phase I) into phase II with previously unidentified crystal symmetry. The second transformation, from phase II to phase III (see below for the structural information of both phases), starts at 10 GPa. Both the I–II and II–III transitions are of the first order. Although the first transformation (I to II) shows a remarkable volume collapse by 6.6 %, cycling the transformation with pressure steps of approximately 0.2 GPa revealed its perfect reversibility; no co-existence region was detected (within the width of a pressure step), and a hysteresis of approximately 0.4 GPa was determined. This transition has been detected previously, both by volumetric techniques (5.6 % volume drop at 68 °C)^[13] and by differential thermal analysis.^[14] The second transformation (II to III), observed for the first time in this work, starts at 10 GPa with a volume drop of 2.9 % and is not fully accomplished at the highest pressure achieved in our experiment. At a pressure of 18 GPa, about 40 vol % of phase II remained. This transformation is fully reversible; the width of the coexistence region is more than 10 GPa. We note that the complete transition to phase III could be rapidly achieved by heating the pressure cell to 500 K at about 10 GPa, thus indicating slow kinetics at room temperature.

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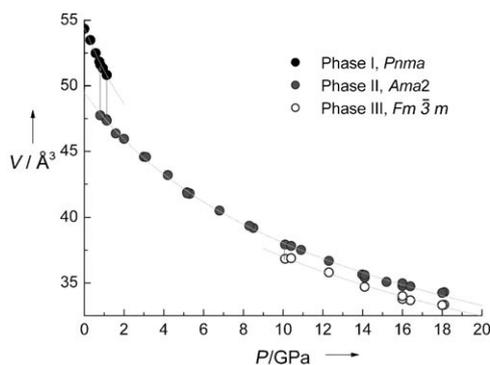


Figure 1. Variation of the volume of the LiBH_4 formula unit in the three phases at ambient temperature. The circles represent experimental data, and the lines are the best fits to the Murnaghan equation of state. Vertical lines represent phase transitions.

Figure 1 summarizes the compressibility data for all three phases of LiBH_4 , fitted using the Murnaghan equation of state [Eq. (1)], where B_0 is the bulk modulus, B_0' is the first

$$V(P) = V_0 \left(1 + B_0' \frac{P}{B_0} \right)^{-1/B_0'} \quad (1)$$

pressure derivative of the bulk modulus, and V_0 is the molar volume per formula unit at zero pressure. A fit to the experimental data for phase II yielded $V_0 = 49.49(13) \text{ \AA}^3$, $B_0 = 23.23(9) \text{ GPa}$, $B_0' = 3.51(15)$; with B_0' fixed at 3.5, we obtained $V_0 = 54.43(8) \text{ \AA}^3$, $B_0 = 14.4(5) \text{ GPa}$ for phase I and $V_0 = 47.3(9) \text{ \AA}^3$, $B_0 = 26(3) \text{ GPa}$ for phase III (Figure 1). As expected, V_0 decreases and B_0 increases from phase I through phase II and into the final high-pressure phase III. The compressibility of LiBH_4 is much higher than for binary hydrides such as the rare-earth ($B_0 = 70\text{--}145 \text{ GPa}$)^[15] and transition-metal hydrides (FeH_x , $B_0 = 120\text{--}180 \text{ GPa}$)^[16] as well as for hydrides of s- (MgH_2 , $B_0 = 45\text{--}50 \text{ GPa}$)^[17] and p-block elements (AlH_3 , $B_0 = 40 \text{ GPa}$)^[18]. However, it is comparable to the compressibility of some light complex hydrides, such as LiAlH_4 (theoretical $B_0 = 13\text{--}26 \text{ GPa}$ for three different phases)^[19] and NaBH_4 ($B_0 = 20\text{--}31 \text{ GPa}$ for two different phases).^[20] The bulk modulus for phase I is in good agreement with the theoretically predicted value $B_0 = 15.3 \text{ GPa}$ ($B_0' = 3.9$)^[8] and much smaller than that roughly estimated in a recent experimental study (ca. 45 GPa).^[14]

The crystal structure of ambient-pressure phase I ($\alpha\text{-LiBH}_4$) is orthorhombic, space group $Pnma$, $a = 7.1842(9)$, $b = 4.4431(5)$, $c = 6.811(1) \text{ \AA}$, in close agreement with previous reports.^[11] A common way of identifying the crystal structure of a new phase is to attempt to assign a known structure type to the observed diffraction pattern. In the case of phase II, however, none of the known structure types of the

ABX_4 family could be matched with our diffraction data. Therefore, we were faced with the difficult task of determining the crystal structure ab initio from high-pressure powder diffraction data (see the Experimental Section and the Supporting Information for details).

Phase II reveals a new structure type. Moreover, no isomorphous derivatives of this $Ama2$ structure exist. It is interesting that an isomorphous structure with this symmetry has only been predicted for LiHS as one of the SH^- ion ordering variants,^[21] but it has not yet been observed experimentally. A similar arrangement of structural units is observed in the tetragonal PtS structure (space group $P4_2/mmc$). However, owing to the ordering of BH_4 anions, the present structure has lower (pseudo-tetragonal) symmetry. BH_4 anions form a distorted Cu-type substructure with relatively long $\text{B}\cdots\text{B}$ distances of more than 3.75 \AA , while the Li atoms form a primitive cubic substructure ($\alpha\text{-Po}$ -type). The Li and BH_4 sublattices interpenetrate so that Li atoms occupy tetrahedral voids in the BH_4 network. Most interestingly, the BH_4 anions have a nearly square-planar coordination comprising four Li atoms, in striking contrast to phase I (tetrahedral coordination) and phase III (octahedral coordination; Figure 2). A square-planar coordination of BH_4 anions has no analogues in the crystal chemistry of metal borohydrides.^[22] To gain insight into the stability of the novel coordination of BH_4 by metal atoms, we employed DFT techniques.

We optimized the atomic positions in the structure of phase II with the help of DFT (see the Supporting Information for details), starting from the experimental lattice and structural parameters determined at 2.4 GPa. The optimized structure is in good agreement with the experimental one, its energy being lower by only 0.23 eV per LiBH_4 formula unit. In the optimized structure, the BH_4 anion fits exactly into the plane of its Li neighbors, with a deviation of the B atom from the plane of -0.06 \AA (compared with $+0.37 \text{ \AA}$ in the experimental structure), which gives us more confidence in the novel planar coordination of the BH_4 unit. Such an unusual coordination may facilitate thermal decomposition of LiBH_4 , which should have important implications for the hydrogen-storage properties of this light-weight hydride.

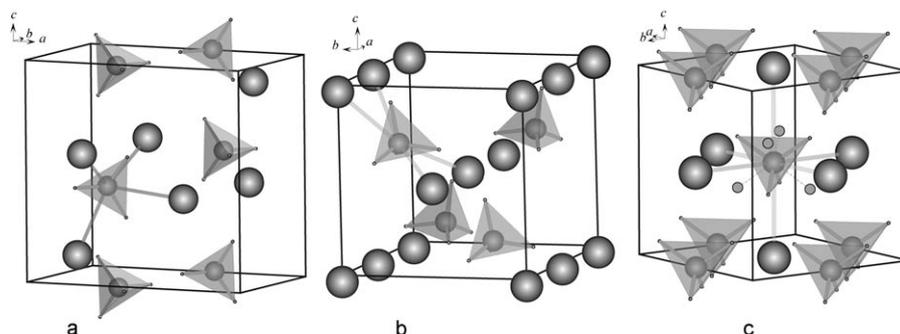


Figure 2. Crystal structures of the LiBH_4 phases observed at 0–18 GPa at ambient temperature. Coordination environment of the BH_4 tetrahedra by Li atoms is highlighted. a) Tetrahedral coordination in phase I. b) Square-planar coordination in phase II. c) Octahedral coordination in phase III; small spheres define an alternative position of the disordered BH_4 anion.

X-ray diffraction was recently shown to be a powerful tool to locate hydrogen atoms and has been applied to potential hydrogen-storage materials.^[23,24] Determination of hydrogen positions from X-ray data, especially at high pressures, is a formidable challenge.^[24] In the case of LiBH_4 , contribution of H atoms to the X-ray diffraction intensities is significant, so that their elimination from the refinement of the phase II structure would make the Bragg R factor R_B increase from 4.3% to 34.3%. This result illustrates that H atoms in LiBH_4 can be reliably determined, even from synchrotron powder data collected in a diamond anvil cell. It is important to note, however, that the B–H bond lengths are systematically underestimated, owing to the displacement of the electron cloud seen by X-rays relative to an average nuclear position (e.g. as seen by neutron diffraction and determined by DFT calculations). DFT calculations provide accurate hydrogen nuclear positions at $T=0$ K. Therefore, it should not be surprising that some of the H-atom positions as determined from DFT calculations on phase II differ by up to 0.5 Å from the experimental values determined at 293 K (see Table S1 in the Supporting Information). Also, owing to a small rotation of the BH_4 anion, the DFT-optimized Li···H separations are more regular (1.99–2.17 Å) than the experimental ones (1.90–2.50 Å), whereas the range of calculated Li···B distances (2.43–2.52 Å) is slightly narrower than in the experiment (2.35–2.66 Å). We think that both the high-pressure powder diffraction methods and DFT are not particularly sensitive to the orientation of the BH_4 anion.

The high-pressure phase III was identified by comparing experimental data with theoretical powder patterns calculated for known ABX_4 structure types. The best description of the experimental diffraction pattern has been achieved with the cubic $Fm\bar{3}m$ structure having a disordered arrangement of BH_4 anions (α - NaBH_4 -type),^[25,26] with $a=5.109(2)$ Å at 18.1 GPa. The DFT-optimized structure of phase III (an ordered variant of the structure in the space group $F\bar{4}3m$ was used in calculations) is also in good agreement with the experimental one (Table S1 in the Supporting Information), whereas the DFT-estimated pressure of 13 GPa, as obtained from the calculated tension tensor, is comparable with the experimental value (18 GPa).

For phase II, the shortest H···H distance between two neighboring BH_4 anions is 1.87 Å in the theoretically optimized model, which is even shorter than the 1.92 Å obtained from our crystallographic data at 2.4 GPa. These short contacts serve as links within chains formed by borohydride anions, as shown in Figure 3. This geometry is

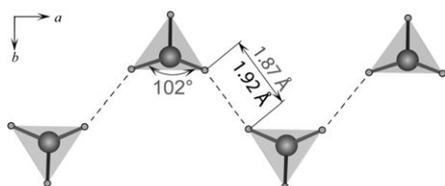


Figure 3. BH_4 anions linked by short H···H contacts into chains in the crystal structure of phase II. The experimentally determined H···H distance of 1.92 Å at 2.4 GPa is corroborated by the DFT-optimized value of 1.87 Å.

unique, and so short an H···H distance is unprecedented in metal borohydrides.^[22] For example, in the extremely complex structure of $\text{Mg}(\text{BH}_4)_2$, which contains ten independent BH_4 units, all interanionic H···H distances are longer than 2.33 Å.^[22] In phase II of LiBH_4 , the short interanionic contact H2···H3 correlates with the more acute H2–B–H3 angle of approximately 102° in the DFT-optimized structure (compared with 109.5° for ideal tetrahedral geometry; Figure 3). The H···H interactions distort the BH_4 anion, and such a distortion is believed to be step towards a decomposition of BH_4 .^[1,27]

To conclude, an old puzzle about high-pressure structures of LiBH_4 has been solved. The structure of phase II, observed between 1.2 and 10 GPa, has been determined ab initio from high-quality powder diffraction data. It shows a novel structural arrangement of spherical cations and tetrahedral anions, in which the BH_4 group has an unprecedented square-planar coordination by four Li atoms. This arrangement corresponds to an energy minimum, as found from DFT calculations. It is worth noting that the square-planar coordination of the BH_4 anion by metal atoms has neither been observed experimentally nor predicted on theoretical grounds before. Indeed, since the structure of phase II determined herein is entirely unexpected and has no analogues in the crystal chemistry of borohydrides, it comes as no surprise that the theoretical attempts to predict it were doomed to failure.^[4,5,7] This structure reveals a strikingly short H···H contact between adjacent BH_4 anions, which is likely to decrease the activation energy for hydrogen desorption.^[1,27] This new structure may show completely different hydrogen-storage properties if stabilized by chemical substitution at ambient pressure. We have also observed a new high-pressure phase III that has an even smaller volume per formula unit of $V_0=47.3(9)$ Å³, close to that predicted from geometrical considerations ($V_0 \approx 46\text{--}47$ Å³).^[13] This phase exhibits the shortest H···H contacts between BH_4 anions (1.67 Å in the optimized model). However, considering the high pressure (greater than 10 GPa) of the transition into phase III, it is less likely that this phase can be stabilized at ambient conditions.^[31]

In contrast to the cubic polymorph, phase II is a promising candidate for stabilization at ambient conditions. Talyzin et al. have shown that phase II can be quenched to ambient pressure,^[14] but it is unstable above 190 K. Given the very low pressure of the transition, we suggest that phase II may be stabilized at ambient conditions by chemical substitutions. We suggest that the internal pressure in the structure may be tuned by a partial substitution of lithium by larger cations or by substitution of some BH_4 groups by larger AlH_4 anions. The resulting LiBH_4 -based substance with $Ama2$ structure may show more favorable hydrogen-storage properties than pure LiBH_4 and may turn out to be useful for hydrogen-storage applications. We suggest the dense structure found in our high-pressure experiments to be targeted for obtaining improved hydrogen-storage materials, commonly searched for by various chemical substitutions. The experiments to stabilize it under ambient conditions are underway.

Experimental Section

High-pressure data on LiBH_4 (> 99% purity, Sigma–Aldrich) powder samples were measured at the Swiss–Norwegian Beam Lines of the ESRF. X-ray diffraction patterns were collected on the MAR345 image-plate detector. A monochromatic beam at a wavelength of $\lambda = 0.670694 \text{ \AA}$ or $\lambda = 0.701400 \text{ \AA}$ was slit-collimated down to $100 \times 100 \mu\text{m}^2$. The sample-to-detector distance and parameters of the detector were calibrated using LaB_6 NIST standard. Two-dimensional diffraction images were analyzed using the ESRF Fit2D software,^[28] yielding one-dimensional intensity versus diffraction angle patterns in the range of 3° to 40° .

Finely ground samples of LiBH_4 were loaded into a diamond anvil cell (DAC) with flat culets of diameter $600 \mu\text{m}$. To prevent a chemical reaction, all manipulations with samples were carried out in a high-purity argon atmosphere. The samples were loaded into a hole of $200 \mu\text{m}$ diameter drilled in stainless steel gaskets pre-indented to $60\text{--}80 \mu\text{m}$ thickness. Ruby provided a pressure calibration with precision of 0.1 GPa. No pressure-transmitting medium was used owing to the high reactivity of the sample material. Nevertheless, pure LiBH_4 provided good quasi-hydrostatic conditions up to 10 GPa, controlled by a small broadening of the ruby fluorescence peaks. Three experiments were performed in different but overlapping pressure ranges to obtain high-quality data suitable for structure solution and to provide good pressure sampling. Diffraction measurements were performed up to a maximum pressure of 20 GPa. The data were treated using Fullprof Suite.^[29]

A strongly pseudo-tetragonal phase II structure ($a = 6.4494(9)$, $b = 5.307(1)$, $c = 5.2919(9) \text{ \AA}$ at 2.4 GPa) has been solved in space group $P1$ by global optimization in direct space (program FOX).^[29] The true orthorhombic $Ama2$ symmetry has been uncovered using Platon software,^[30] and the structure was refined by the Rietveld method: $R_B = 4.3\%$, $R_F = 8.8\%$, $R_p = 17.2\%$, and $R_{wp} = 6.5\%$.

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