



Supporting Information

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High-pressure polymorphism as a step towards destabilization of LiBH₄

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Experimental ab initio structure determination for the LiBH₄ phase II: One of the best patterns obtained for the phase II at 2.4 GPa has been indexed using Dicvol04 software^[S1] in a tetragonal cell with $a \sim 3.75$ and $c \sim 6.45$ Å, however the structure could not be solved in any of the tetragonal space groups. It has therefore been solved by global optimization in direct space (program FOX)^[S2] in the lowest symmetry space group $P1$. Constraints on tetrahedral symmetry of the borohydride anion have been imposed, along with soft "anti-bump" restraints on Li...H distances. The true symmetry of the structure has been uncovered using Platon software,^[S3] which suggested a doubled pseudo-tetragonal cell ($a \sim 5.30$ and $c \sim 6.45$ Å) and the orthorhombic space group $Ama2$.

Atomic coordinates have been standardized by STIDY,^[S3] fixing a z -coordinate for the Li atom to zero. Using this model, the structure has been finally refined by Rietveld method with Fullprof^[S5] using 47 reflections, 11 intensity-dependent refined parameters and 8 soft restraints defining an approximately tetrahedral BH₄ geometry. During the refinement, the background was modeled by interpolated points (the highest peak-to-background ratio was about 1), but for the presentation purposes (see Fig. S1) it has been subtracted. This approach provided a very good fit to the data using a minimal set of reasonable assumptions. The refinement converged at $R_B = 4.3\%$, $R_F = 8.8\%$, $R_p = 17.2\%$, and $R_{wp} = 6.5\%$. Atomic and cell parameters are listed in Table S1, and the fit to the experimental data is shown in Fig. S1.

Experimental structure determination for the LiBH₄ phase III: The high-pressure phase III was identified by comparing experimental data with theoretical powder patterns calculated for known ABX₄ structure types. The best description of the experimental diffraction pattern has been achieved with the cubic $Fm-3m$ structural model having a disordered arrangement of BH₄ anions (α -NaBH₄-type). Our choice of the simple cubic structure was confirmed by an excellent fit to the experimental data over the whole pressure range and complementary theoretical validation. The refinement technique used is similar to the one described above for the phase II, yielding $R_B = 5.9\%$, $R_F = 7.5\%$. The essential structural parameters for the phase III at 18.1 GPa are listed in Table S1.

DFT calculations on the high-pressure structures of LiBH₄: Crystal structures of the two new polymorphs of LiBH₄ found from our diffraction experiments have been validated using *ab initio* plane-wave pseudopotential DFT method^[S6,S7] as implemented in the CASTEP package.^[S8] The generalized gradient approximation was used to account for exchange and correlation in the Perdew–Burke–Ernzerhof form,^[S9] which is known to yield more accurate structural results,^[S6] such as bond lengths, compared to the well-known local density approximation (LDA). The ionic positions have been optimized using the highly efficient Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.^[S10,S11] The use of ultrasoft pseudopotentials^[S12] for all atoms has permitted us to exercise a lower plane-wave cutoff energy of 380 eV and hence achieve a much shorter calculation time than would otherwise be possible in the case of norm-conserving pseudopotentials. A regular mesh of \mathbf{k} -points, with typical dimensions of $3 \times 3 \times 3$ in the case of phase II, was used to sample the Brillouin zone of the crystal. The accuracy of all the calculation parameters has been assessed to ensure the convergence of the final results.

Table S1. Experimental and DFT-optimized (in brackets) structural parameters for the high-pressure polymorphs of LiBH₄.

Structure	Atom	x	y	z
Own structure type	Li	0	0	0
$Ama2$, $Z = 4$	B	$\frac{1}{4}$	0.2712(4) [0.23448]	0.1730(5) [0.25048]
$a = 6.4494(9)$, $b = 5.307(1)$	H1	0.095(1) [0.09624]	0.334(1) [0.32481]	0.074(1) [0.14744]
$c = 5.2919(9)$ Å at 2.4 GPa	H2	$\frac{1}{4}$	0.0497(7) [0.00548]	0.1831(9) [0.24538]
	H3	$\frac{1}{4}$	0.351(1) [0.27944]	0.3803(8) [0.47546]
α -NaBH ₄ -type	Li	0	0	0
$Fm-3m$, $Z = 4$	B	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$a = 5.109(2)$ Å at 18.1 GPa	H ^[a]	0.37(2) [0.3655]	x	x

[a] Occupancy 0.5 in the disordered structure.

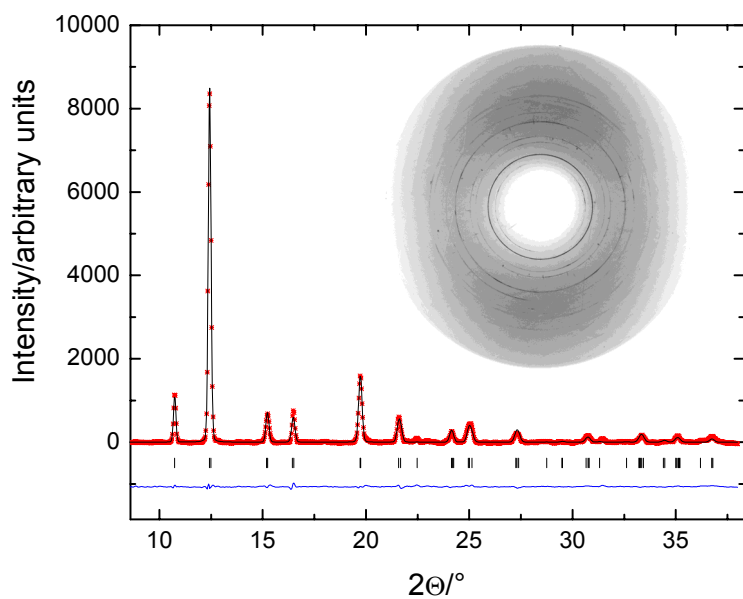


Figure S1. Background-subtracted Rietveld refinement profile for the phase II at 2.4 GPa. A raw two-dimensional image is shown in the inset ($\lambda = 0.70140$ Å), exhibiting a very clean diffraction pattern and exceptionally high integrated intensities reaching 10^8 counts per point.

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