First-principles determination of the ground-state structure of LiBH$_4$

Adem Teken, 1,* Riccarda Caputo, 2 and Andreas Züttel 2

1Informatics Institute, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey
2EMPA, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse, 129 CH-8600 Dübendorf, Switzerland

(Dated: June 11, 2010)
I. STRUCTURE

Table I summarizes the structures found for LiBH$_4$ mostly in the last decade. In the ground-state orthorhombic structure Li$^{\delta^+}$ coordinates with four [BH$_4$]$^{\delta^-}$ groups bidentately to hydrogen atoms. The six Li-H distances are: (1.909, 2.111), (2.232, 2.018), (2.022, 2.229), (2.053, 2.059) Å. Correspondently, the Li-B distances are: 2.407, 2.553, 2.557, 2.418 Å. Compared to the ground-state orthorhombic structure, the fully optimized reference structure reported by Soulié shows three shorter Li-H distances: 1.975, 1.970, 1.970 Å, where each hydrogen atom belongs to a different [BH$_4$]$^{\delta^-}$ group, and three longer Li-H distances: 2.155, 2.248, 2.516 Å.

II. SIMULATED XRD PATTERNS

We used the Reflex module, implemented in Materials Studio, to calculate the simulated X-ray diffraction patterns (XRD) of all the stable structures studied in the paper. In Figure 1, we only report the XRD patterns of the orthorhombic ground-state structure compared with the reference structure [1] and the monoclinic high-energy structure [1] compared with the hexagonal structure. The peak position in a diffraction pattern depends on the lattice parameters, therefore a shift on the X-ray intensities are expected as a function of them. In the orthorhombic phase, the interplanar spacing $d_{hkl}$ is equal to \[ \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}}. \] A more complicated dependence on the lattice parameters exists for the monoclinic and hexagonal phases, being the interplanar spacing of the monoclinic phase depending also on the lattice angles via sinusoidal functions. The lattice parameters of the monoclinic $P2/c$ high-energy structure are: $a = 11.343$ Å, $b = 6.993$ Å, $c = 8.780$ Å, $\alpha = \gamma = 90$ degrees, $\beta = 40.926$ degrees.

III. DENSITY OF STATES

Similar to the simulated XRD patterns, the density of states of the ground-state orthorhombic structure and the monoclinic high-energy structures were compared with reference structures [1] in Figure 2. The p-states reflex the different orbital overlapping in these structures.
IV. ELECTRON DENSITY DISTRIBUTION

Figure 3 shows the total electron density map projected on the (0 0 1) plane for the orthorhombic ground-state and the reference structures [1]. The isosurface at 0.28 electrons/Å³ clearly shows that in our ground-state structure electrons are spatially distributed along the $\vec{c}$-direction enabling a correlation between adjacent $[\text{BH}_4]^{\text{δ−}}$ groups.

V. HIGH TEMPERATURE PHASE

Structural details of the new high-temperature phase composed of only bidentate hydrogen-lithium coordinations (with $P2_1/c$ symmetry) and experimental hexagonal structure [1] (with $P6_3mc$ symmetry) were shown in Figure 4. After the relaxation, the $P6_3mc$ symmetry structure was further lowered by 1.137 kJ/mol [2] and it showed less imaginary modes than the reference structure. Even though there are three $[\text{BH}_4]^{\text{δ−}}$ groups in the first coordination shell of one Li$^{\text{δ+}}$ atom in both structures, a monodentate configuration observed only in the $P6_3mc$ symmetry structure along the $\vec{c}$-direction. Phonon calculations performed for the hexagonal phase showed that one of the rotational modes with negative frequency resembles to a quasi-pendulum motion of the $[\text{BH}_4]^{\text{δ−}}$ group to Li$^{\text{δ+}}$ atom. This should be due to the monodentate configuration in the hexagonal phase.

VI. THERMODYNAMIC DATA

Enthalpy of formation of the orthorhombic and high-energy structures were listed in Table II.

The temperature dependence of the enthalpy of formation is evaluated following the phonon calculations for all the compounds considered in the present work. In particular, the harmonic free energy is:

$$F(\omega) = E + \frac{1}{\beta} \int g(\omega) \log(2 \sinh(\frac{\beta \hbar \omega}{2}))d\omega$$  \hspace{1cm} (6.1)

where $E$ is total electronic energy, $\omega$ is the wave number associated to the normal modes of vibration and $g$ is the multiplicity of a mode. The lattice contribution to the heat capacity is:

$$C_v(T) = k \int \frac{(\frac{\hbar \omega}{kT})^2 e^{\frac{\hbar \omega}{kT}}}{[e^{\frac{\hbar \omega}{kT}} - 1]^2} F(\omega)d\omega$$  \hspace{1cm} (6.2)
Accordingly, the temperature contribution to enthalpy is calculated via numerical integration of the specific heat capacity over the temperature, as follows:

\[ H(T) = \int_0^T c_p dT \]  

(6.3)

Consequently, the enthalpy of formation of LiBH\(_4\) becomes:

\[ \Delta_f H(T) = \Delta_f H(0 \text{ K}) + \int_0^T \Delta c_p dT \]  

(6.4)

where \( \Delta c_p = c_p(\text{LiBH}_4) - c_p(\text{Li}) - c_p(\text{B}) - 2c_p(\text{H}_2) \). Here, \( c_p \) is the specific heat capacity at constant pressure, in particular at \( P = 0 \), at which the structures are optimized.

VII. PHONON CALCULATIONS

The phonon frequencies versus the number of normal modes were reported in Figure 5 for the ground-state and high-energy structures, compared with the reference structures. The unit cell of orthorhombic and monoclinic structures containing four formula units have 72 modes, while the hexagonal unit structure containing two formula units has 36 normal modes of vibration. The first 6 modes represent translation and rotation modes which are only negative for the hexagonal structure. The main appreciable difference between the ground-state and the reference orthorhombic structures is the frequencies in the range [300,400] of those modes involving the small angle rotation of \([\text{BH}_4]^{\delta-}\) group coordinated to the up-down motion of \( \text{Li}^{\delta+}\). The high-energy phase shows smaller values in the small frequency region, while the higher values in the high frequency region corresponds to the stretching modes of B-H bonds.


<table>
<thead>
<tr>
<th>Symmetry group (IT)</th>
<th>Lattice parameters</th>
<th>Date</th>
</tr>
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<tbody>
<tr>
<td>Pcmn (62)</td>
<td>6.81, 4.43, 7.17</td>
<td>1947 [3]</td>
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<tr>
<td>Pnma (62)</td>
<td>7.100, 4.300, 6.900</td>
<td>2005 [8]</td>
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<tr>
<td>Pnma (62)</td>
<td>7.214, 4.468, 6.877</td>
<td>2005 [9]</td>
</tr>
<tr>
<td>Pnma (62)</td>
<td>7.121, 4.406, 6.674</td>
<td>2007 [10]</td>
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<tr>
<td>Pnma (62)</td>
<td>8.484, 4.348, 5.750</td>
<td>our result</td>
</tr>
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TABLE II: Enthalpy of formation of the orthorhombic and high-energy structures, in kJ/mol. The values reported are the enthalpy of formation at T= 0 K, (∆\textsubscript{f}H(0)), the enthalpy of formation including the zero point energy, calculated as a sum over the harmonic frequencies, (∆\textsubscript{f}H(0)\textsuperscript{ZPE}), and the enthalpy of formation at T = 298 K (∆\textsubscript{f}H\textsubscript{298}).

<table>
<thead>
<tr>
<th>Structure</th>
<th>∆\textsubscript{f}H(0)</th>
<th>∆\textsubscript{f}H(0)\textsuperscript{ZPE}</th>
<th>∆\textsubscript{f}H\textsubscript{298}</th>
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<td>orthorhombic ground-state</td>
<td>-239.988</td>
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<td>-301.541</td>
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<tr>
<td>monoclinic</td>
<td>-218.724</td>
<td>-177.906</td>
<td>-190.892</td>
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<tr>
<td>hexagonal</td>
<td>-212.511</td>
<td>-177.344</td>
<td>-194.256</td>
</tr>
</tbody>
</table>
FIG. 1: (Top) Simulated XRD patterns of the ground-state orthorhombic structure compared with the reference structure [1]. (Below) Simulated XRD patterns of the monoclinic high-energy structure compared with the hexagonal structure [1].
FIG. 2: (Top) Density of states of the ground-state orthorhombic structure compared with the reference structure [1]. (Below) Density of states of the monoclinic high-energy structure compared with the hexagonal structure [1].
FIG. 3: (Top) Electron orbital relationship in the ground-state orthorhombic structure. (Below) Electron orbital relationship in the reference structure [1].
FIG. 4: (Top) $P2/c$ symmetry structure. (Below) Fully optimized $P6_3mc$ structure of Soulié et al. [1]. Representing colors: lithium, purple; boron, pink; hydrogen, white.
FIG. 5: The frequencies of the normal mode of vibration of the low- and high-energy structures.