Structural Stability of Complex Hydrides: LiBH₄ Revisited

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A systematic approach to study the phase stability of $LiBH_4$ based on *ab initio* calculations is presented. Three thermodynamically stable phases are identified and a new phase of Cc symmetry is proposed for the first time for a complex hydride. The x-ray diffraction pattern and vibrational spectra of the Cc structure agree well with recently reported experimental data on $LiBH_4$. Calculations of the free energy at finite temperatures suggest that the experimentally proposed $P6_3mc$ phase is unstable at $T > 0$ K.

The strong demand for new clean power sources has intensified the interest in materials for energy storage. In particular, intense efforts are focused on developing a storage material for the automotive industry, which allows for a reversible hydrogen storage in excess of 6.5 wt %, under ambient conditions [1]. The complex metal hydrides are one of the most promising candidates for fulfilling the storage requirements, but they are still under basic and technological research [2].

Understanding the structural properties of hydrides is the primary step toward their experimental characterization, and also a prerequisite for finding or designing materials with specific storage thermodynamics. Unfortunately, structural determination of these materials is difficult, due to the very low hydrogen scattering cross section in all diffraction methods. Structural predictions have proved successful when applied to high pressure studies of geological [3] and metallurgical materials [4]. Calculations on hydrides can accurately predict the ground state structures [5]; however, the essential question of hydride stability at finite temperatures has not been addressed previously, even though mature methods for *ab initio* free energy calculations exist [6].

In the present Letter, we present the first systematic search (not limited to previously known structures) for stable phases of a complex hydride ($LiBH_4$) at T > 0 K. By combining various methods based on *ab initio* calculations, the Helmholtz free energy $F(T)$ of the hydride is determined. We show that at high temperatures, the stable phase of $LiBH_4$ possesses the previously unresolved monoclinic Cc symmetry, with Li and B atoms aligned in a distorted Wurzite structure. The calculated x-ray diffraction (XRD) pattern, the infrared and Raman spectra are in good agreement with those reported in the literature. The present approach illustrates the importance of the free energy calculations applied to hydrides.

Complex hydrides, such as borohydrides $M(BH_4)$ and alanates $M(AlH_4)/M(AlH_6)$, have been of special interest as hydrogen storage media, since Bogdanovic and Schwickardi [7] presented reversible absorption-desorption isotherms for $NaAlH_4$ under ambient conditions using a Ti-based catalyst. Recently, Züttel *et al.* [8] showed that 13.5 wt % of hydrogen can be desorbed from $LiBH_4$. This hydride is particularly interesting since it has a gravimetric hydrogen density of 18.5% and a volumetric hydrogen density of 121 kg/m³. At low temperatures, $LiBH_4$ forms a stable structure with orthorhombic *Pnma* symmetry. Around $T = 384$ K [9] a structural transition occurs. The structure of the high temperature phase of $LiBH_4$ was recently reported [10] to belong to the hexagonal $P6_3mc$ space group, while an older report [11] claims the structure to be of a tetragonal nature. Both reports indicate an increase in hydride density at the transition point [10,11].

The structure and the lattice dynamics of $LiBH_4$ were calculated within density functional theory (DFT) [12]. We have chosen the projected augmented plane-wave [13] approach (PAW) to minimize errors [14]. In addition, the Li *s* electrons were also included in the valence band. Most of the calculations were performed with kinetic energies up to 400 eV. Final comparison of the ground state energy E_0 was done with a kinetic energy cutoff of 875 eV.

To properly describe the bonding of light atoms, the calculations were carried out within the generalized gradient approximation (GGA) using the Perdew-Wang 91 [15] exchange correlation function. The wave functions were sampled according to a Monkhorst-Pack scheme with a *k*-point mesh of spacing ≤ 0.05 Å^{-1} for all phases. For the ultimate comparison of the ground state energies a denser *k*-point grid, of spacing 0.01 Å^{-1}, was used. This procedure resulted in changes to the ground state energy of less than 0.001 eV/formula unit. The lattice dynamics was determined using the forces acting on the atoms in the supercell. The dynamical matrix is constructed from the appropriate set of displacements of the symmetry

nonequivalent atoms. The details of the *direct method* are presented elsewhere [16,17].

The candidates for the most stable high temperature structure of $LiBH_4$ include structures of closely related compounds: $P2_1/c$ (α-$LiAlH_4$) and $I4_1/a$ (α-$NaAlH_4$). These structures, known *a priori*, together with the $P6_3mc$ structure were initially tested as primary candidates for $LiBH_4$. As a preliminary step, the structural parameters of all candidate phases of $LiBH_4$ were optimized according to the calculated Hellman-Feynman forces and lattice stresses.

The lattice parameters and the ground state energy difference (ΔE_0) between the phases are presented in Table I, with the exception of the $I4_1/a$ structure, which is considerably less stable ($\Delta E_0 = 486$ meV), and thus not considered in the subsequent analysis. The lattice constants are in good agreement with experiments for the orthorhombic structure, while they differ significantly for the hexagonal one.

At finite temperatures a stable crystalline structure requires all phonon frequencies to be positive definite: $\omega^2 > 0$.

The phonon dispersion relations and phonon density of states (DOS) were initially calculated for the *Pnma*, $P6_3mc$, $P2_1/c$ phases (presented in Fig. 1). As shown in the inset in Fig. 1, a significant part of the phonon spectrum for the $P6_3mc$ phase is imaginary—which means that this structure is *unstable* at $T > 0$ K. This surprising result, considering the experimental predictions [10], triggered us to perform additional analysis. In principle, knowledge of the imaginary modes allows identification of a stable phase, but for a system with 12 such modes the elegant method based on symmetry considerations fails. Therefore, we performed a systematic search for a new possible phase of $LiBH_4$.
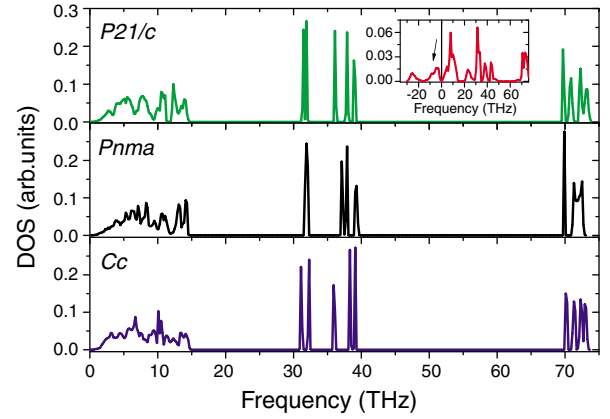

FIG. 1 (color). Total density of phonon states $g(\omega)$ for $LiBH_4$ in $P2_1/c$, *Pnma*, and *Cc* symmetries. The DOS is normalized to $\int g(\omega)d\omega = 1$. The inset shows the density of states for the $P6_3mc$ phase; the arrow points to negative (corresponding to imaginary) part of the spectrum.

A larger (48 atoms) and more symmetric supercell was used in molecular dynamics (MD) simulations to increase the correlation length. The initial atomic configuration was based on the hexagonal structure. This system was subjected to *ab initio* MD simulations with a time step of 0.4 fs. The system was rapidly heated to $T = 500$ K at a rate of 500 K/ps and subsequently cooled down to $T = 10$ K for the period of 2.5 ps. During the cooling stage, 50 snapshots of the atomic configurations were taken in the temperature range from $T = 400$ K to 50 K. For each snapshot, the symmetry of the system was determined with a precision of the atomic positions ranging from $\Delta r = 0.05$ to 0.8 Å. The two most likely crystal symmetries were found to belong to the monoclinic *Cc* and orthorhombic $Cmc2_1$ space groups. These two struc-

TABLE I. Structural parameters of $LiBH_4$. The ground state energy is given with respect to the *Pnma* phase. Internal atomic coordinates are given in the standard setting of the tables of crystallography [18], and Wyckoff positions are listed in column 4.

Symmetry	Latt. param. (Å)	ΔE_0(meV/f.u.)	Site	Internal atomic positions
Pnma	$a = 7.173$ $b = 4.434$ $c = 6.798$ [1]		$4(c)$	Li: $(0.8440, \frac{1}{4}, 0.8877)$ B: $(0.6900, \frac{1}{4}, 0.5768)$
$Z = 4$	$a = 7.179$ $b = 4.437$ $c = 6.803$ [10]	0	$4(c)$	H1: $(0.0911, \frac{1}{4}, 0.0749)$ H2: $(0.5954, \frac{1}{4}, 0.7327)$
	$a = 7.226$ $b = 4.355$ $c = 6.576$		$8(d)$	H3: $(0.2086, 0.5242, 0.4221)$
$P2_1/c$	$a = 7.267$ $b = 7.174$ $c = 7.683$		$4(e)$	Li: $(0.8673, 0.8486, 0.0439)$ B: $(0.1664, 0.6946, 0.5026)$
$Z = 4$	$\beta = 148.52°$	23	$4(e)$	H1: $(0.1013, 0.5998, 0.3204)$ H2: $(0.8902, 0.7674, 0.3295)$
$P6_3mc$	$a = 4.276$ $c = 6.948$ [10]		$2(b)$	Li: $(\frac{1}{3}, \frac{2}{3}, 0.0906)$ B: $(\frac{1}{3}, \frac{2}{3}, 0.5402)$ H1: $(\frac{1}{3}, \frac{2}{3}, 0.3616)$
$Z = 2$	$a = 4.164$ $c = 6.766$	240	$6(c)$	H2: $(0.1742, 0.3484, 0.6009)$
$Cmc2_1$	$a = 4.213$ $b = 6.953$		$4(a)$	Li: $(0, 0.6927, 0.6189)$ B: $(0, 0.6555, 0.2028)$
$Z = 4$		138	$4(a)$	H1: $(0, 0.7661, 0.0650)$ H2: $(0, 0.7537, 0.3487)$
Cc	$a = 4.131$ $b = 7.270$ $c = 6.601$		$4(a)$	Li: $(0.9541, 0.6418, 0.1562)$ B: $(0.5125, 0.1762, 0.5349)$
$Z = 4$	$\beta = 97.26°$	34	$4(a)$	H1: $(0.2088, 0.7126, 0.4157)$ H2: $(0.6667, 0.1046, 0.6850)$
			$4(a)$	H3: $(0.4000, 0.3217, 0.5866)$ H4: $(0.2970, 0.0755, 0.4541)$

tures were then reoptimized, in their symmetries, with respect to the cell parameters and the atomic positions at $T = 0$ K and the lattice dynamics were studied in the same way as before. Out of the two structures, the $Cmc2_1$ phase was ruled out from further consideration because it possesses two imaginary modes. The Cc phase is stable and the phonon density of states is presented in Fig. 1. This relatively low symmetry structure has not previously been reported for hydrides, although it possesses all the fingerprints experimentally observed in $LiBH_4$ at high temperatures [8,9].

For all stable phases, the DOS looks similar (cf. Fig. 1), however, important differences can be recognized. Three fairly separated bands can be distinguished. The modes below 15 THz are mainly due to motion of the lithium and boron framework. Between 30 and 40 THz, the first bands directly related to hydrogen (librational modes) are observed. In this frequency range the largest differences between the phases are found. The $Pnma$ band around 30 THz broadens significantly in the $P2_1/c$ phase and splits into two subbands in the Cc structure. The bands around 37 THz moves up and downward by 1 THz in the monoclinic phase, respectively. This behavior can be expected since it follows changes in the ionic framework. At high frequencies, the spectrum belongs to the internal BH_4 stretching vibrations located around 70 THz. Differences here come from distortion of the BH_4 complex, and due to symmetry, the bands are more evident in the Cc structure.

The distorted Wurzite Li/B framework has Li–B spacings between $d = 2.310$ Å and $d = 2.854$ Å, and B-Li-B angles in the range $103.18°$ to $121.92°$ in the Cc structure. The framework is more symmetric than in the low temperature $Pnma$ phase, where Li–B spacings range from $d = 2.328$ to $d = 2.519$ Å, and angles from $92.91°$ to $119.60°$. The $P2_1c$ structure can be seen as the intermediate between these two structures having Li–B spacings from $d = 2.298$ to $d = 2.920$ Å, and angles in the range
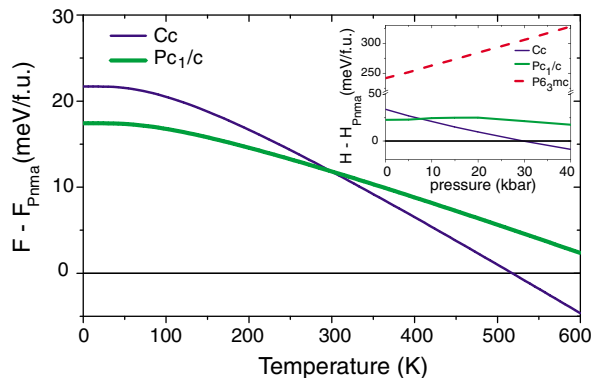
$95.38°$ to $123.76°$. The BH_4 anion is fairly rigid having an average B–H distance around 1.220 Å not changing by more than 2% between the structures. The symmetry and orientation of the BH_4 structure differs between the space groups. The H-B-H angles are in the range from $107.0°$ to $110.8°$ for the $Pnma$ structure, in the Cc structure these angles range from $107.3°$ to $111.9°$, while the $P2_1/c$ phase is the most distorted with $106.7°$ to $111.5°$. The BH_4 tetrahedra are not aligned along the z direction in Cc structure, but tilted by $\sim 8°$.

Knowledge of the vibrational spectrum allows us to calculate a free energy $\Delta F(T)$ of the system in the quasiharmonic approximation. The temperature dependence of the free energy is presented in Fig. 2. We have not found any significant anharmonic effects in the phonon spectrum and free energy.

The pressure dependence of the ground state enthalpy, shown in the inset of Fig. 2, indicates a structural change around 30 kbar, accompanied by a distortion of the angle β towards $90°$ in Cc structure is induced by a hydrostatic pressure. A pressure induced phase change for $LiBH_4$ has been reported previously [11], but no details of the resulting structure were given. The hexagonal structure is not competitive as its ground state stability decreases with increasing pressure.

The zero point energy part of the free energy is as large as $\Delta F(0) \simeq 1.12$ eV/f.u. for $Pnma$ and $\Delta F(0) \simeq 1.10$ eV/f.u. for the Cc structure. The large internal energy is related to the high frequency modes of the hydrogen vibrations and is a general property of hydrides containing many H atoms per formula unit. Therefore, a proper description of hydride thermodynamics requires taking the internal lattice energy into account. Even small changes in the vibration spectra can affect the mutual phase stability, as is the case for $LiBH_4$.

At low temperatures the $Pnma$ phase is the most stable (cf. Fig. 2), as observed experimentally. The relative stability between the phases changes upon heating in favor of the Cc structure at $T = 520$ K. At the transition point, the density of the Cc structure is 4.5% larger than

FIG. 2 (color). The difference in free energy $\Delta F = \Delta E_0 + \Delta F_{vib}$. The inset shows the pressure dependence of the ground state enthalpy $H = E_0 + pV$ with respect to the $Pnma$ phase.
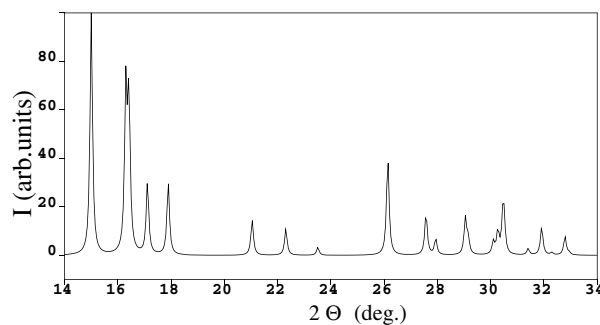

FIG. 3. The XRD diffraction pattern for $LiBH_4$ with Cc symmetry. The diffraction pattern is given for a beam wave length of $\lambda = 0.949$ Å.

Pnma, explaining the experimentally observed structural collapse [10]. The free energy of the monoclinic $P2_1/c$ phase also approaches the orthorhombic structure, and possibly falls below F_{Pnma} at higher temperatures. The calculated transition temperature is somewhat higher than experimentally observed, however, the calculations are performed on the perfect crystalline structure.

The transition between the *Pnma* and the other phases of LiBH$_4$ is of the first order. The small energy differences between the phases in the broad (p, T) range indicate that at higher temperatures, coexistence of all polymorphs of LiBH$_4$ can be observed.

A calculated X-ray diffraction pattern for the new *Cc* phase is shown in Fig. 3. The reflections between $2\Theta = 14°$ and $34°$ are in good agreement with the experiment (Ref. [10]). At high temperatures or pressures, effects related to lattice expansion could affect the observed diffraction pattern.

Raman and infrared spectroscopy are vital techniques [9,19–21] in studying borohydrides, due to the fairly localized internal modes of BH$_4$. Large unit cells result in 72 eigenmodes at the Γ point, a detailed analysis of which will be presented elsewhere [22]. Here, we focus on the comparison with the experimentally observed spectra of LiBH$_4$. The Raman modes at 38.55 and 39.45 THz [9] are located at 37.80 and 39.35 THz within the present approach. At high temperatures these bands transform into two modes at 38.45 and 39.13 THz which can be attributed to the observed band at 39.02 THz [9]. The internal BH$_4$ stretching vibrations span the range 69.87 to 72.82 THz for the low temperature phase. At high temperatures, bands narrow to the range 70.17–73.01 THz. The $P2_1/c$ phase possesses the broadest mode distribution (69.74–73.44 THz) due to the largest cation distortion.

Calculated adiabatic barriers for BH$_4$ reorientation around the C_3 axis are of the order 25 kJ/mol for the low temperature phase, increasing to 31 kJ/mol at high temperatures. Barriers for rotation around C_2 axis are higher: 106 and 85 kJ/mol, respectively. This excludes free rotation of BH$_4$, however, barriers for the monoclinic structure agree well with those proposed in Ref. [19].

There exists a well-defined electronic band gap of ~ 5 eV, which is not affected by the structural changes [22].

In conclusion, we propose that the stability of complicated hydride structures can be determined/predicted on a theoretical basis. This requires investigation of both the ground state and the lattice vibration energy, which is rather large in complex hydrides. We have calculated the structural stability of LiBH$_4$ at $T > 0$, yielding a new structure with *Cc* symmetry. The postulated structure with $P6_3mc$ symmetry turns out to be unstable at finite temperatures with respect to lattice vibrations.

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