Lightest Borohydride Probed by Synchrotron X-ray Diffraction: Experiment Calls for a New Theoretical Revision

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A combination of synchrotron X-ray diffraction techniques have been applied to resolve ambiguities between experimental and theoretical studies of $LiBH_4$ and to reveal its complex structural evolution as a function of temperature. Crystal structures of the low- and high-temperature polymorphs of $LiBH_4$ have been determined from diffraction on single-crystals. In contrast to recent theoretical conjectures, we find that the high-temperature structure is hexagonal, space group $P6_3mc$. Experimental data suggest a nearly isotropic disorder of the rigid tetrahedral BH_4 groups as one of the factors stabilizing the hexagonal structure. Tetrahedral BH_4 anions are undistorted and geometrically very similar in both polymorphs. The first order phase transition at 381 K is preceded by highly anisotropic lattice expansion and is accompanied by a negative volume change. Disorder phenomena and strong lattice anharmonicity, being ignored, lead to the failure of theoretical predictions of the structural stability of $LiBH_4$ published so far.

Introduction

Metal borohydrides have recently received increased interest owing to their potential as hydrogen storage materials. Although $LiBH_4$ contains more than 18% of hydrogen, it is so far nonreversible under practical conditions and desorbs hydrogen at rather high temperatures.[1] In order to improve its hydrogen storage properties, $LiBH_4$ has become the subject of intensive theoretical and experimental investigations.

The existence of two $LiBH_4$ polymorphs at ambient pressure has been known since 1964.[2] A phase transition at ~380 K has been detected by powder diffraction,[3,4] Raman scattering,[5,6] and calorimetry.[7] Since pure $LiBH_4$ releases hydrogen only above the temperature of the polymorphic transition, reliable structural information on the high-temperature (HT) phase would be a key for understanding the dehydrogenation process. Theoretical modeling has become a powerful tool for predicting structure and properties and substantial efforts have been made to characterize theoretically the crystal structure of lithium borohydride.[8–12] All of the models consistently find the orthorhombic *Pnma* structure to be the ground-state phase, in agreement with diffraction experiments at room temperature.[3,13,4] Thermal expansion of the orthorhombic lattice has also been analyzed in the quasi-harmonic approximation; however, the necessary experimental information is restricted to 3.5, 300 and 360 K powder diffraction data sets,[11,14,15] thus limiting a validation of computational schemes.

Strikingly, none of the calculations resulted in the hexagonal structure for the HT phase, reported from powder diffraction data.[3,4] Thus, Łodziana and Vegge,[9] using DFT and a quasi-harmonic approximation, have concluded that the high-temperature structure has a monoclinic *Cc* symmetry. The hexagonal $P6_3mc$ structure, first suggested from the diffraction experiment,[3] was found to have a relatively high energy and imaginary vibrational frequencies and therefore had been discarded.[9] Other calculations have also shown that the $P6_3mc$ structure is unstable.[8,11,12] Therefore the low-temperature $LiBH_4$ structure (LT) was used as a basis for calculations of hydrogen desorption energy,[16,8,14] theoretical prediction of chemically destabilized $LiBH_4$,[17] and first-principles study of the $LiBH_4$ decomposition path.[18] The controversy between theory and experiment could be due to an overlooked factor not modeled theoretically or due to a misinterpretation of the diffraction experiments. All conclusions published on the high-temperature $P6_3mc$ polymorph were deduced from powder diffraction,[3,4] that by its very nature may not resolve weak structural distortions and suffers from overlap of Bragg reflections. Therefore a single crystal diffraction experiment is needed for unambiguous determination of the symmetry in order to resolve the apparent contradictions between experiment and theory.

Here, we present accurate single crystal synchrotron diffraction study of both the low- and high-temperature polymorphs of $LiBH_4$, together with a powder diffraction study in 80−500 K temperature range. We confirm that the HT polymorph of $LiBH_4$ has indeed a hexagonal $P6_3mc$ structure as first proposed in ref 3 and not the monoclinic *Cc*[9] or trigonal *P*3 symmetry as proposed recently.[12] Experimental evidence for a BH_4 disorder in the HT phase is presented. We analyze the geometry of the borohydride anion, which is relevant for hydrogen desorption from $LiBH_4$,[19] and show that the tetrahedral BH_4 groups are undistorted in both polymorphs. We also show that the thermal expansion of $LiBH_4$ is highly anisotropic and deviates strongly from theoretical predictions. We also demonstrate here why and how synchrotron diffraction not only on single crystals but also on powders can provide reliable structural information on this light hydride system.

Experimental Section

Single-Crystal Diffraction. ~200 μm single crystals of LT $LiBH_4$ were extracted from a commercial sample (Aldrich) avoiding any contact with air. Selected crystals were loaded into thin-walled glass capillaries under protective oil, frozen to

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TABLE 1: Crystal Data, Details of Data Collection, and Structure Refinement for the LT and HT Phases of $LiBH_4$

polymorph	LT $LiBH_4$	HT $LiBH_4$
T (K)	225	∼535
space group	*Pnma*	$P6_3mc$
a (Å)	7.141(5)	4.3228(10)
b (Å)	4.431(3)	
c (Å)	6.748(4)	7.0368(10)
V (Å^3)	213.5(2)	113.88(4)
Z, D_c (g·cm^{-3})	4, 0.678	2, 0.635
$2\theta_{max}$ (°), completeness (%)	48.8, 99.0	47.3, 91.5
R_{int}, R_σ	0.045, 0.027	0.074, 0.025
reflns collected, unique	2161, 200	767, 80
data, restraints, parameters	200, 0, 34	80, 0, 15
final R indices, [$I > 2\sigma(I)$]	$R_1 = 0.0455$ w$R_2 = 0.1318$	$R_1 = 0.0642$ w$R_2 = 0.1874$
R indices (all data)	$R_1 = 0.0459$ w$R_2 = 0.1326$	$R_1 = 0.0683$ w$R_2 = 0.1919$
GOF on F^2	1.175	1.046
$(\Delta/\sigma)_{max}$	0.000	0.000
largest Fourier diff (e·Å^{-3})	0.11(3), −0.12(3)	0.03(1), −0.05(1)

complete oil solidification, and measured at 225 K. The temperature was controlled with an Oxford Cryostream 600. All diffraction data were collected at the Swiss-Norwegian Beam Lines (BM1A) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) using an image plate detector MAR345 and a monochromatic beam. The best crystal of LT $LiBH_4$ was measured using a wavelength of 0.71118 Å and a crystal-to-detector distance of 150 mm. Three hundred and sixty frames with an exposure time of 5 s per frame have been collected. All diffraction intensities were indexed in an orthorhombic cell and integrated using CrysAlis software.[20] The data were corrected for Lorentz factor and polarization effects. Scaling of frames for the decaying intensity of the synchrotron beam was performed using SADABS.[21]

For the HT phase it was necessary to grow and characterize crystals *in situ*, since the first-order transition from the HT to LT phase occurs upon cooling below ∼381 K, destroying the crystals of the HT phase. Thus, crystals of the HT phase were grown in a quartz capillary, repeatedly melting and cooling a powdered $LiBH_4$ sample around the melting point of 553 K. Once a crystal of ∼30 μm was grown on a wall of the capillary, a synchrotron beam was focused onto it. The best crystal of the HT phase diffracting up to 0.85 Å resolution was used for the structure determination. Diffraction data were collected at ∼535 K, slightly below the melting point of $LiBH_4$, under otherwise identical experimental conditions as for the LT phase, described above. A Cyberstar ESRF furnace and a Eurotherm temperature controller were used for these experiments. Diffraction intensities were indexed in the hexagonal cell and integrated and scaled using AutoMAR software.[22]

The structures were solved and refined using Shelx.[23] A full least-squares refinements on F^2 were performed on positional and thermal parameters of all atoms. The H-atoms were located from difference Fourier maps and refined anisotropically, without any constraints or restraints. Neutral atom scattering factors were used. Crystal data and details of data collection and structure refinement are given in Table 1.

Powder Diffraction. Two-dimensional diffraction images were collected at SNBL with MAR345 detector using 0.71118 Å synchrotron radiation and were integrated using Fit2D software[24] and calibration measurements of an NIST LaB_6 standard. Data acquisition time was ∼3 min per diffraction pattern, using a tiny amount (ca. 0.1 mm^3) of the commercial sample. Rotation of the sample during the measurement and integration of the diffraction rings provides very good powder averaging, i.e., accurate intensities. A disadvantage of having relatively weak diffraction intensities at high 2θ was largely compensated by the excellent statistics, exceeding in our experiment 10^7 counts per 2θ-step at the highest intensity peak. Uncertainties of the integrated intensities $\sigma(I)$ were calculated at each 2θ-point by applying Poisson statistics to the intensity data, considering the geometry of the detector. The procedure of $\sigma(I)$ estimation is identical to the one described in ref 25. Properly weighted, these intensities contributed to the accurate characterization of the crystal structures. In order to combine high resolution in the reciprocal and in the direct space, four data sets collected at 293 K for the LT phase at the sample-to-detector distances 100, 125, 150, and 180 mm, and two data sets collected at 382 K for the HT phase at 150 and 180 mm were used in joint Rietveld refinements by Fullprof.[26]

The data sets collected for the LT phase at 90 and 293 K were refined anisotropically for Li and isotropically for B and H, without constraints on the geometry of the BH_4 group. The HT structure at 382 K was refined anisotropically for Li and using the rigid body (TLS) formalism[27] for the BH_4 group. The B−H distance was fixed to 1.10 Å and the H−B−H angles were set to the ideally tetrahedral. Crystal data and the results of structure refinement are given in the Supporting Information.

In situ Powder Diffraction. A glass capillary with $LiBH_4$ was heated from 90 to 400 K at a rate of 20 K per hour, while synchrotron powder diffraction data were collected. Temperature was controlled with the Oxford Cryostream 700. The data were collected at SNBL using MAR345 image plate detector at a sample to detector distance 150 mm, using the radiation with $\lambda = 0.71110$ Å. The capillary was oscillated by 180° during exposure to the X-ray beam for 180 s, followed by a readout for ∼83 s. In total, 214 diffraction images were collected.

Another set of diffraction data was collected at the Materials Science beamline at SLS (PSI, Switzerland, $\lambda = 0.708349$ Å, Debye−Scherrer geometry). High resolution diffraction patterns were recorded with 25 s time sampling using the microstrip detector consisting of 15 000 Si-detector elements. Temperature was controlled using Stoe high-T attachment 0.65.3.

The unit cell parameters for the LT and HT phases of $LiBH_4$ at various temperatures were obtained from the sequential Rietveld refinement in Fullprof.[6]

Results and Discussion

The first single crystal study of LT $LiBH_4$ was done already in 1947,[28] although the structural data has not been published. Our single crystal investigation of the LT phase shows that the BH_4 group has a nearly ideal tetrahedral geometry, as theoretically predicted[9,10] and recently found in a neutron powder diffraction experiment,[4] in contrast to the strongly distorted tetrahedra reported in earlier synchrotron diffraction studies.[3,13] The observed H−B−H angles (108.8(9)−109.9(7)°) are very close to the ideal tetrahedral angle of 109.5°, while the B−H bond lengths show a narrow spread from 1.104(11) to 1.131(15) Å, thus showing that the BH_4 group is very close to the undistorted tetrahedron.

The difference between hydrogen positions measured by X-ray and neutron diffraction is well-known. Corrections for distances determined from X-ray data are tabulated for many compounds; N−H or O−H bonds serve as a good example.[29] Such corrections have never been reported for the B−H bond, that may be a reason of misinterpretation of B−H bond lengths seen by X-ray methods.[30,31] Indeed, the B−H distances presented here for the LT phase are on average by ∼0.11 Å shorter than

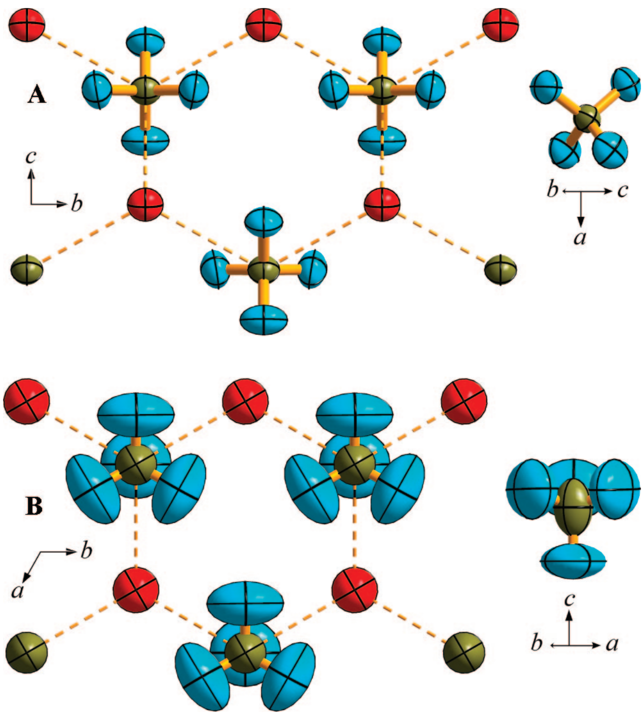

Figure 1. Six-membered Li-BH_4 rings (left) and BH_4 units (right) in $LiBH_4$ structures. Forty percent probability ellipsoids are shown. (a) The low-temperature phase at 225 K. (b) The high-temperature phase at 535 K.

those found theoretically[10] and observed by neutron diffraction at low temperature.[4] A certain part of this difference originates from a geometric effect, which is an apparent shortening of the experimental B−H bonds due to a libration of BH_4 unit; see Figure 1a. Libration-corrected B−H distances, calculated using anisotropic displacement parameters for B and H atoms and WinGX software,[32] are 0.034 Å longer than the ones directly observed by diffraction at 225 K. Therefore, the larger part of the difference between observed and expected B−H distances, of ~0.11 − 0.034 = ~0.08 Å, comes from the well-known displacement of the electron cloud (seen by X-rays) relative to an average nuclear position (seen by neutron diffraction and determined by DFT calculations). By its nature, this difference is temperature-independent. Consequently, for the direct comparison of the B−H bond lengths, derived from the synchrotron and neutron diffraction data (Table 2), 0.08 Å increment has to be added to the B−H distances determined from the synchrotron data. In order to compare H-atom positions determined from X-ray or neutron diffraction at finite temperatures with those derived from DFT calculations at $T = 0$ K, temperature-dependent libration corrections should also be applied. At low temperatures, the libration correction for the BH_4 group in borohydrides is relatively small; as follows from libration frequencies reported in ref 33, the temperature dependence of the libration shortening can be safely neglected for $T \ll (h/k_B)\omega_{lib} \approx 400$ K. We therefore estimate the corresponding correction as 0.034 Å in the LT form of $LiBH_4$ at 225 K and below. A combined correction of 0.10 Å has been recently suggested from the analysis of the available structural data for $NaBH_4$ and its hydrate at low temperatures.[34] This correction roughly accounts both for the displacement of the electron cloud on H-atoms and the effect of libration below ~200 K.

The symmetry of the HT phase has been debated both by experimentalists [35,36] and theoreticians [9,12] since its discovery.[2] To resolve this ambiguity, we have grown crystals of the HT phase and characterized them by synchrotron diffraction. It was important to do the crystal growth and characterization *in situ*, since cooling below the transition temperature of ~381 K destroys the crystals. To our knowledge, this is the first single-crystal experiment on the HT $LiBH_4$. It provides a clear evidence for the ~4 × 7 Å hexagonal cell and confirms the space group $P6_3mc$, suggested for the first time in ref 3 from powder diffraction data, but disputed later in theoretical works.[9,12] The arguments for the $P6_3mc$ symmetry are the following. All the reflections were definitely indexed in a primitive hexagonal cell. The symmetry of intensities distribution in the reciprocal space indicates that the Laue class is $6/mmm$, while the mean $|E^*E^{-1}| = 0.756$ suggests that the space group is noncentrosymmetric.[37] Analysis of systematic absences revealed an axial glide plane *c* normal to [1−10] (reflection conditions *hhl*: $h = 2n$) consistent with a possible presence of the screw axis 6_3 (systematic absences 00*l*: $l = 2n$). Considering possible twinning laws, all these observations agree only with two space groups, $P6_3mc$ and $P31c$, the latter must be twinned by merohedry. Refinement of the twinned trigonal model results in meaningless atomic displacement parameters and higher *R*-factors than for the $P6_3mc$ structure. Therefore, the hexagonal structure has finally been chosen. As in the LT phase, the BH_4 tetrahedron is nearly undistorted, in agreement with DFT calculations for the LT and hypothetical *Cc* phases,[9] and it is consistent with a strong covalent bonding within the BH_4 group and much weaker interactions between Li^+ and $[BH_4]^-$. Good statistical descriptors and nondistorted BH_4 geometry confirm the high quality of the data and the validity of the $P6_3mc$ structure. The *Cc* structure[9] and the *P*3 model[12] suggested for the HT phase can therefore be confidently rejected.

Compared to the LT polymorph, the HT structure reveals an important feature: anisotropic displacement ellipsoids show much bigger smearing of the electron density around H atoms in directions perpendicular to the B−H bonds, while atomic displacements for Li and B atoms remain small and isotropic (see Figure 1b). The shape of the atomic displacement ellipsoids indicates that the BH_4 group behaves as a rigid body, in agreement with its undistorted tetrahedral geometry. A TLS formalism, which parametrizes vibrational motions or orientational disorder of a rigid-body object by a translational (T), librational (L), and screw (S) tensors, has therefore been applied.[27] TLS analysis done with WinGX software[32] showed that the atomic anisotropic displacement parameters (ADPs) of the B and H-atoms in the HT phase at ~535 K can be very well approximated by the TLS model and indicates that the main component of the observed electron density smearing has a libration-like character. Large libration amplitudes agree with an apparent shortening of the B−H bonds to ~1.07 Å in the hexagonal phase.

Once the crystal structures of both phases had been determined on single crystals, we evaluated a more accessible technique, namely synchrotron powder diffraction, for its ability to provide accurate information on the positions of hydrogen atoms. Here we also studied $LiBH_4$ over a broad temperature range, from 80 to 500 K, using *in situ* powder diffraction and revealed its highly anisotropic thermal expansion. Cell dimensions obtained from our Rietveld refinement of 214 diffraction patterns from the image plate detector and of 43 patterns from the strip detector are shown in Figure 2, together with the data of the recent neutron powder study of $^7Li^{11}BD_4$,[4] and theoretical estimates of thermal expansion.[14]

We first comment on the volume changes with temperature. A decrease of the unit cell volume upon the LT-to-HT phase

TABLE 2: Geometry of the BH_4 Group in $LiBH_4$ Polymorphs, As Seen by Different Diffraction Techniques at Ambient Pressure

technique	T (K)	space group	B−H (Å)[a]	H−B−H (°)	ref
synchrotron diffraction on single crystals	225	*Pnma*	1.104(11)-1.131(15)	108.8(9)-109.9(7)	this work
	535	$P6_3mc$	1.05(6)-1.11(9)	108(3)-111(3)	this work
neutron powder diffraction on $^7Li^{11}BD_4$	3.5	*Pnma*	1.208(3)-1.225(6)	107.2(3)-111.7(4)	[4]
	360	*Pnma*	1.184(16)-1.217(15)	105.4(5)-111.8(8)	[4]
	400	$P6_3mc$	0.96(8)-1.02(3)	106(3)-112(3)	[4]
synchrotron powder diffraction	90	*Pnma*	1.108(8)-1.151(8)	104.9(5)-112.4(8)	this work
	293	*Pnma*	1.04(2)-1.28(1)	85.1(9)-120.1(9)	[3]
	293	*Pnma*	1.28(3)-1.44(3)	60(1)-131(1)	[13]
	293	*Pnma*	1.118(7)-1.151(11)	98.7(9)-113(1)	this work
	382	$P6_3mc$	fixed to 1.10[b]	fixed to 109.5[b]	this work
	408	$P6_3mc$	1.27(2)-1.29(2)[c]	106.4(2)-112.4(9)[c]	[3]

[a] For the direct comparison of the B−H bond lengths, derived from the synchrotron and neutron diffraction data, the 0.08 Å shift has to be applied. To compare the B−H bond lengths determined at different temperatures, the libration corrections have to be applied. [b] Geometry of the BH_4 group was fixed in order to model its thermal motion by refining the TLS tensor. [c] Restraints were applied to the B−H and H−H distances during refinement.

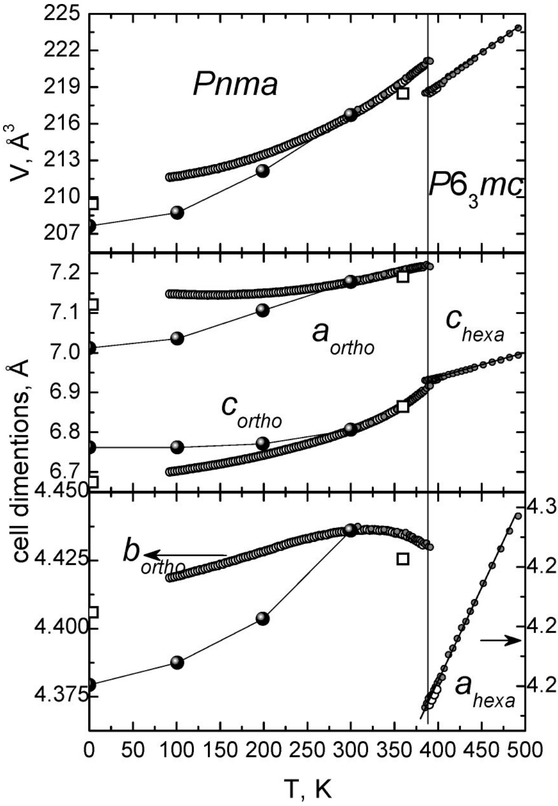

Figure 2. Unit cell volume and cell dimensions of $LiBH_4$ as a function of temperature. Open circles correspond to MAR345 data (SNBL at the ESRF), gray circles show the data collected at SLS. Big dark circles connected by lines represent results of *ab initio* calculations[14] scaled to our experimental values at 300 K, scaling coefficients are 0.887 for volume, 0.913 for *a*, and 0.917 for *b*. Open squares represent neutron powder diffraction data.[4]

transition is remarkable (Figure 2). The linear thermal expansion for the HT phase agrees with quasi-harmonic behavior of the phonon system. The HT phase remains metrically hexagonal from 381 K up to the decomposition at ~560 K. This clearly shows that the monoclinic *Cc*[9] and *P*3[12] models are not met at all temperatures. A volumetric thermal expansion coefficient is nearly constant within 300−500 K region, and equals $2.6 \cdot 10^{-4}$ K^{-1} for the LT phase and $2.9 \cdot 10^{-4}$ K^{-1} for the HT phase. These values, together with information on the symmetry, structure, and experimental bulk modulus for the LT phase,[38] provide the basis for validation of theoretical models.

Unit cell dimensions of the LT phase, in contrast, show nonlinear and highly anisotropic temperature dependence. The cell dimension *b* continuously contracts on heating from 300 K to the transition temperature. Such thermal expansion reflects an anharmonicity of the potential of the crystal binding. A softening of acoustic phonons should accompany this unusual thermal expansion, however corresponding inelastic scattering data has not been reported so far. Note that quasi-harmonic approximation, correctly predicting orthorhombic structure for the LT phase,[11] is unable to reproduce its anisotropic thermal expansion.[14] It is remarkable that the cell parameter *a* deviates from linear dependence below 200 K, shows a minimum at ~150 K and then increases on cooling (Figure 2 and the Supporting Information). According to thermal conductivity measurements, the free energy should have two minima below 180 K;[39] notably, the thermal expansion in the *a*-direction deviates from the linear behavior in the same temperature range.

Although the unit cell dimensions are reliably extracted from synchrotron powder diffraction data, sensitivity of synchrotron scattering to H-atoms may be called in question. However, for light borohyrides, the contribution from hydrogen atoms to the scattering of X-rays is substantial; it can be roughly estimated as $[\int_Q I^+(Q)dQ - \int_Q I^-(Q)dQ]/\int_Q I^+(Q)dQ$ where $I^+(I^-)$ is the scattered intensity with (without) hydrogen and integration is done over the experimental *Q*-range, while only elastic coherent scattering is considered. Having set the *Q*-range to 1−7 $Å^{-1}$ one obtains ~0.52 for neutron diffraction and ~0.26 for synchrotron diffraction,[40] the latter is far too large to be neglected. From our image plate synchrotron diffraction data, the BH_4 anion appears somewhat distorted at room temperature, but at 90 K it is nearly ideally tetrahedral, and its geometry is very close to the one determined from the single-crystal synchrotron and neutron powder diffraction data on the LT $LiBH_4$ (see Table 2 for comparison). A bias in the structural parameters obtained from powder diffraction at room temperature is partly due to the increased thermal motion of the BH_4 group, accompanied by the lattice anharmonicity. The previous synchrotron powder diffraction studies with a use of a strip detector,[3,13] measuring only a small part of Debye rings, showed strongly deformed BH_4 tetrahedron, see Table 2. Our analysis of intensity distributions along the diffraction rings suggests that the powder data obtained with 1D detector, as in the case of refs 3 and 13, suffer from a poor powder average. Our experience shows that the commercial $LiBH_4$ sample remains grainy even after thorough hand-milling in agate mortar under protective argon atmosphere. Intensity integration over the Debye rings recorded with a 2D detector provides much better average over the grains and therefore higher reliability of the refined structural parameters. From the above consideration and our experimental results (see Table 2 and the Supporting Information), we conclude that the positions of hydrogen atoms in $LiBH_4$ can be accurately determined from synchrotron powder diffraction with a help of area detectors. The good powder average provided by the 2D detector appears to be crucial in the reliable determination of H-atoms coordinates from the data collected using a small-volume powder sample. The use of the image plate detector has even recently allowed to locate hydrogen atoms in high-pressure phases of $LiBH_4$ and $NaBH_4$, both from synchrotron powder diffraction data measured in diamond anvil cells.[38,41]

Geometrical characteristics of the BH_4 group in the LT and HT polymorphs of $LiBH_4$ determined by different diffraction techniques are summarized in Table 2. Our single-crystal diffraction data show that the BH_4 group has an ideal tetrahedral geometry, with nearly equal B−H distances and regular H−B−H angles of ~109.5°. A nearly ideal tetrahedral geometry of the BH_4 group has also been found by single-crystal X-ray diffraction in other light hydrides.[34,42] Neutron powder diffraction data on the triply isotopically substituted $^{7}Li^{11}BD_4$ also show regular BH_4 tetrahedra.[4] The disordered high-temperature phase requires a considerable correction for the observed B−H distances. While at 225 K the libration-corrected B−H distances are only by 0.034 Å longer than the refined ones, this difference at 535 K is estimated (WinGX program[32]) to be about 0.10 Å. Accordingly, the B−H distances in the HT phase, corrected using the formalism of Busing and Levy,[43] are 1.08−1.18 Å long. Considering the 0.08 Å correction for the displacement of the electron cloud from the nuclear position of H-atoms, we obtain 1.16−1.26 Å as an estimate of the true B−H distances in the HT phase. These distances are much more regular than those obtained by applying the identical correction to the neutron powder diffraction data at 400 K, where the refined B−H distances of 0.96(8)−1.02(3) Å were corrected to 1.23(10)−1.56(14) Å.[4] The inaccurate distorted geometry of the BH_4 group, previously reported for the LT phase from synchrotron powder diffraction data, has been explained above by a poor powder average recorded with 1D detectors. The same arguments apply to the HT phase, studied at 408 K: although the regular geometry of the BH_4 group was achieved by using geometrical restraints, the refined B−H distances of 1.27(2)−1.29(2) Å are unrealistically long.[3] Hartman et al. showed that, in this case, the average B−H distance corrected for riding motion of H-atoms would be 1.45 Å.[4] Moreover, the atomic displacement parameters for two H-atoms vary from 0.04 to 0.81 $Å^2$,[3] while our data show that they are nearly identical ($U \sim 0.20$ $Å^2$).

Single crystal synchrotron diffraction generally yields the most accurate structural data, and this is also true for $LiBH_4$. The observed B−H distances, properly corrected for the ~0.08 Å displacement of the electron cloud from the nuclear position of H-atoms and for the riding motion of H-atoms, are in good agreement with the DFT calculations[10] and show much narrower spread than those from powder data (Table 2). Considerable deviations from the tetrahedral geometry of the BH_4 group, as for instance recently reported in ref 44 from synchrotron powder diffraction, should be explained by an experimental inaccuracy.

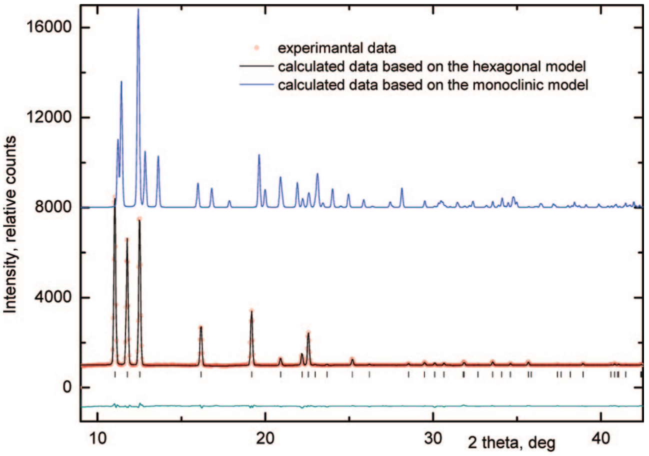

Figure 3. Rietveld fit to the experimental data ($T = 382$ K, $\lambda = 0.71118$ Å) for the HT $LiBH_4$ using $P6_3mc$ model and TLS formalism. A calculated profile for the Cc model[9] is shown for comparison.

We should note, however, that in certain metal borohydride structures, the BH_4 group can indeed be deformed, provided there exists a good structural reason of this unusual behavior, such as short H...H contacts.[38] Such deformation can reliably be detected only by DFT calculations or by diffraction on single crystals.

We used synchrotron powder diffraction data collected at 382 K, just about 2 K above the LT to HT transition, to extract additional information about atomic displacements for the BH_4 group using the TLS formalism as implemented in Fullprof.[26] A calculated profile for the Cc model of the HT phase, claimed[9] to be consistent with the experiment, and the fit of the $P6_3mc$ structure to our experimental powder data are shown in Figure 3: the inconsistency of the prediction is obvious. Refined components of the TLS tensor are $t(11) = t(22) = 0.0528(2)$, $t(33) = 0.1502(6)$ $Å^2$, $l(11) = l(22) = 0.133(3)$, $l(33) = 0.183(2)$ rad^2 and $s(12) = -s(21) = 0.089(1)$ Å·rad. The excellent fit to the data ($R_{Bragg} \sim 3\%$, see the Supporting Information for more details) using only a few parameters shows that, in agreement with single crystal data, the TLS model indeed provides a good description for the HT phase. It is remarkable that, under reasonable rigid body assumptions, even atomic displacement parameters can be extracted for the BH_4 group from powder diffraction data collected at a synchrotron source. The difference between t(33) and t(11) suggests that displacements of the BH_4 are more pronounced along the c axis than in the basal plane. The components of the libration tensor reveal that the rotation-like behavior of the BH_4 unit is nearly isotropic at 382 K. The value of s(12) indicates a considerable translation-rotation coupling. Observations made from the direct TLS fit to the powder diffraction data at 382 K qualitatively agree with those made on the ADPs with single-crystal data at ~535 K. Large displacement ellipsoids for hydrogen atoms slightly above the temperature of LT-to-HT transition indicate an abrupt increase of the libration amplitudes upon the transition.

Whereas theoretical calculations are not consistent about barriers of the BH_4 rotation in the $P6_3mc$ phase,[9,45] the observed ADPs (Figure 1) may indicate, in addition to the thermal vibrations, a rotational disorder of the BH_4 group. Considering the pronounced and nearly isotropic libration amplitudes, this disorder can occur both around the C_3 and C_2 axes of the tetrahedral anion. Strictly speaking, even precise structural data alone cannot give an answer to the question of whether the large observed libration parameters for $P6_3mc$ phase are due to a softening of the libration phonons or they result from a low-energy dynamic and/or static disorder of the BH$_4$ group. Volume decrease on heating, similar to that shown in Figure 2, has been noticed earlier for some order−disorder transitions;[46] this fact supports a disorder model for the HT phase. Pronounced broadening or unresolved splitting of Raman lines for the HT phase suggests a dynamic disorder of the BH$_4$ group[5] or lower symmetry of the HT structure.[9] Our proof of the $P6_3mc$ symmetry revives the hypothesis of dynamic disorder related to hindered rotations of rigid BH$_4$ tetrahedra within a set of relatively low energy barriers.[33]

Whatever the nature of the disorder, the corresponding entropy contribution has not been taken into account in theoretical modeling so far (recent attempts to introduce an entropy factor in molecular dynamics calculations has led to a wrong prediction of the crystal symmetry for the HT phase[12]). We consider the entropy contribution from the disorder as a factor stabilizing the hexagonal structure, which otherwise is predicted to be unstable.[9–11] A detailed study of rotational dynamics of BH$_4$ is highly desirable now in order to find a thermodynamic description of the disorder and to uncover its role in the stability of LiBH$_4$ polymorphs. Experiments probing lattice dynamics as a function of temperature are also highly desirable for understanding the very anisotropic thermal expansion presented here (Figure 3). Both disorder and anharmonicity are shown to be important components affecting structural and therefore physical properties of LiBH$_4$. Both phenomena are difficult to be accounted for in the computational schemes used so far, and therefore unrealistic theoretical predictions of structural stability and thermodynamics for LiBH$_4$ have to be revised.

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Supporting Information Available: Tables and figures giving details of the crystallographic analysis and dependence of the cell parameters versus temperature; crystal data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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