Lithium boro-hydride LiBH4 II. Raman spectroscopy

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Reference

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Lithium boro-hydride LiBH₄
II. Raman spectroscopy

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Abstract

Polycrystalline LiBH₄ has been studied by Raman spectroscopy in the temperature interval 295–412 K and the frequency range 2700–130 cm⁻¹. The Raman active modes are consistent with the presence of a (BH₄⁻) ion having a distorted tetrahedral configuration. As the temperature is increased the sudden disappearance of mode splitting points to the onset of a structural phase transition that leads to a higher local symmetry of the (BH₄⁻) tetrahedron. The transition occurs at ~384 K, is of first-order and has a hysteresis of about 8 K. A strong and discontinuous broadening of bands remaining after the transition suggests the onset of large vibrational amplitudes of the (BH₄⁻) tetrahedra about their trigonal axis.

Keywords: Hydrogen storage materials; Metal hydrides; Crystal structure; Phase transition; Optical spectroscopy

1. Introduction

In the first part of this work [1] the crystal structure of LiBH₄ has been investigated by diffraction methods both at room temperature and at 408 K. While the structure at room temperature has orthorhombic symmetry and contains an ordered array of tetrahedral (BH₄⁻) anions (point symmetry m-Cᵥ) that point along two orthogonal directions, the structure at 408 K has hexagonal symmetry and contains a partially disordered array of more symmetric (BH₄⁻) anions (point symmetry 3 m-Cᵥ) that point along one direction (c). Interestingly, one of the two hydrogen sites in the high-temperature modification shows large displacement amplitudes that suggest a dynamical disorder of the (BH₄⁻) tetrahedra about their trigonal axis. In this work the (BH₄⁻) tetrahedra and their rearrangement during the phase transition will be studied in more detail by Raman spectroscopy. For the orthorhombic room-temperature modification a Raman and infrared (IR) spectroscopy study has been reported before [2] and a full assignment of the observed modes has been given. For the high-temperature modification only partial IR data (around 2300 cm⁻¹) are available [3] which, however, have not been interpreted.

2. Experimental

Polycrystalline LiBH₄ (Alfa Aesar, purity 95%) was ground to a fine powder of white colour and filled into a Lindeman glass tube (inner diameter 1 mm) that was sealed with silicon grease. In view of the strong sensitivity of the powder to air and moisture these operations were performed in an argon-filled glove box. The capillary was placed in a brass container that was adapted to a commercial UV–visible sample holder the temperature of which was controlled by a circulating oil bath with a precision of about ±1 K. The Raman spectra were collected on a Kaiser Holospec f/1.8 spectrograph with a 50-μm slit (~3–4 cm⁻¹ resolution) that was equipped with a liquid nitrogen cooled CDD camera. The argon laser excitation source was powered at approximately 15 mW. Higher laser intensities caused excessive sample heating. The wavelength of the incident radiation was 488 nm. The instrument was calibrated with argon plasma lines as well as
with liquid CDCl₃ Raman bands. The resulting uncertainty in the measured frequency shifts was smaller than ±3 cm⁻¹. Data acquisitions were made in the frequency range 2700–130 cm⁻¹ by accumulating ten spectra of ~40 s each. The Raman spectra were further analysed by using line fitting procedures and Lorentzian line shapes with the help of the SPECTRA W program [4]. The second derivatives of the spectra confirmed the number of components used in the fitting procedures.

3. Results and discussion

3.1. Structural phase transition

Raman spectra were first collected at increasing temperature (295–412 K) and then at decreasing temperature (412–359 K). Fig. 1 shows that the spectra clearly indicate the occurrence of a structural phase transition. The transition occurs at 384±1 K on heating and 376±1 K on cooling (data not shown). The hysteresis (~8 K) suggests the transition to be of first order, in agreement with the conclusions drawn from the structure work [1]. The sample showed no sign of degradation during the heating–cooling cycle. The transition temperatures and hysteresis agree well with those reported for LiBH₄ from DTA data (381–385 K [5]) and with heat capacity data (transition temperature 386.4±1 K, hysteresis 6 K [6]). As can be seen from the temperature dependence of the peak positions in Fig. 2 three modes appear in the room-temperature modification (split stretching modes ν₂ and ν₂', and second overtone of librational mode 3ν₄ in the 1340–1240 cm⁻¹ range), while only one mode (ν₄) subsists in the high-temperature modification. The relatively sharp transition between these modes is further evidence for the first-order nature of the transition.

3.2. Assignments of the Raman scattering of the room- and high-temperature phase

The Raman assignments of the room- and high-temperature phases are consistent with the point group symmetries C₃ᵥ (space group Pnma) and C₃ᵥ (space group P6₃mc), respectively, as found by the crystallographic study [1]. Those for the room-temperature phase agree with the previously reported data at 80 K [2]. The latter as well as the vibrational spectra of NaBH₄ and KBH₄ [7] indicate that the spectra of the BH₄⁻ units can be discussed in relation to their site symmetries. Factor group splittings have not been observed so far, partly because no single crystal vibrational study has been reported. Table 1 compares the irreducible representations of the internal BH₄⁻ vibrations for the different possible site symmetries. Table 2 summarises the Raman frequencies known at present and their assignments, including those obtained from the present study. The assignments for the high-temperature phase (spectrum recorded at 412 K) are the first ones reported. A previous IR study [3] at 393–398 K showed only a very broad band at 2300 cm⁻¹ that was neither assigned nor discussed in terms of possible symmetries of LiBH₄ at this temperature.

3.2.1. Room-temperature phase

At room temperature, the point group symmetry of the BH₄⁻ ion is C₃ᵥ. Seven internal BH₄⁻ vibrations (ν₁, ν₂, ν₃, ν₂', ν₃, ν₄, ν₄') out of the nine Raman active normal vibrations are observed (Table 1). The two Raman active vibrations ν₄ and ν₄' occur at 1090 and 1099 cm⁻¹, respectively, and the two overtones 2ν₄ and 2ν₄' at 2157 and 2177 cm⁻¹, respectively. The ν₄' assignment is not in accordance with the 10ν₄ assignment given by [2] for the infrared spectrum by considering the 1⁰⁰B−1⁰⁰⁰B natural isotope shift. Indeed, the curve fitting analysis indicates that both bands have approximately the same intensity, which is contrary to the expected intensity ratio corresponding to the natural abundance of the two isotopes, as seen for instance, for BH₄⁻ diluted in alkali halides [8]. Concerning the external lattice vibrations, three Raman bands are observed out of the twelve symmetry allowed Raman active translations and the six Raman active libratory oscillations. Finally, the last vibration at 1235 cm⁻¹ corresponds to the band assigned by [2] to the second overtone 3ν₄ of a librational mode found in the spectra of alkali borohydrides. Inelastic neutron scattering experiments on LiBH₄ at 77 K showed [9] the occurrence of two peaks in the energy loss spectrum at 412 and 204 cm⁻¹ that were assigned to unresolved (full width at half height ~64 cm⁻¹) librational (412 cm⁻¹) and translational (204 cm⁻¹) modes. The value of 3×412=1236 cm⁻¹ is close to 1235 cm⁻¹ and thus confirms the initial assignment of this band.

3.2.2. High-temperature phase

Above the transition temperature the point group symmetry of the BH₄⁻ ion is increased to C₃v. Only five Raman bands ν₃, ν₂, 2ν₄, ν₁, and ν₅ are observed which are assigned to 1096, 1302, 2167, 2299 and 2355 cm⁻¹, respectively. The very broad ν₅ mode appears only by curve fitting of the region between 2100 and 2500 cm⁻¹. It is not seen in the second derivative of the spectrum because its half-width at half maximum (HWHM ~100 cm⁻¹) is very large. The published IR data for LiBH₄ in the high-temperature phase (see Fig. 3 in [3]) show a very broad band (HWHM ~150 cm⁻¹) centered at 2300 cm⁻¹. As the IR spectrum presents stronger intensities for the ν₃ than for ν₁ mode [2] it can be assigned to the two overlapping components of ν₃. No external lattice vibrations are observed in the Raman spectra of the high-temperature phase of LiBH₄. Fig. 2 shows that one of the two observed site group split components of ν₂ and ν₄ (and their overtones and combi-
nations) have disappeared from the spectra. Clearly, the disappearance of the $v_2$ mode splitting is consistent with the increased point group symmetry of the BH$_4^-$ ion in the hexagonal structure for which this mode transforms as the irreducible representation E (Table 2). For the $v_3$ as well as the $v_3$ mode a splitting into two components ($A_1 + E$) is
Table 2
Raman frequencies (cm$^{-1}$) of LiBH$_4$ at 295 and 412 K

<table>
<thead>
<tr>
<th>Assignment</th>
<th>295 K Literature [2]</th>
<th>This work</th>
<th>412 K This work</th>
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<td>-</td>
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<td>189 d</td>
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<tr>
<td>-</td>
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<td></td>
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<td>1253 d</td>
</tr>
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<td>1287 d</td>
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<td>-</td>
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</tbody>
</table>

*sh* Shoulder.

Not indicated in the literature.

Disappeared with high-temperature symmetry.

3.3. Dynamic disorder of the (BH$_4$)$^-$ tetrahedron in the high-temperature phase

Evidence for the onset of dynamic disorder of the BH$_4^-$ tetrahedron above the transition temperature can be obtained from a study of the temperature dependence of the Raman line widths during a heating and cooling cycle. As shown in Fig. 3 the line widths of the $\nu_2$ and $\nu_4$ modes increase abruptly at the phase transition during heating and decrease abruptly during cooling. Apart from the expected hysteresis the data show complete reversibility and the absence of any significant sample degradation. It is important to note that the observed bandwidths at 412 K are quite different for the internal modes $\nu_4$(HWHM=30 cm$^{-1}$), $\nu_2$(HWHM=50 cm$^{-1}$), $\nu_3$(HWHM=100 cm$^{-1}$) and $\nu_3$(HWHM=36 cm$^{-1}$). In particular, $\nu_3$ is extremely broad as can also be seen in the reported IR spectrum [3]. The disappearance of the 3$\nu_2$ band (analogous to the disappearance of the corresponding band in NaBH$_4$ at 300 K [7]) is an additional indication for the lowering of the energy barrier of a possible librational motion. Furthermore, the rate of increase of the bandwidths as a function of temperature is higher above than below the phase transition. This behaviour is a likely indication for a coupling between internal modes and librational motion as has been observed, for instance, for the NH$_2^+$ ion in...
NH\textsubscript{4}ClO\textsubscript{4} below 180 K [10]. In such a case, one expects the bandwidth (\(\Gamma\)) to vary with temperature according to the relation 

\[ \Gamma = A + B \cdot e^{-\frac{U}{kT}} \]

where \(U\) is the librational energy and \(A\) and \(B\) are constants.

Interestingly, above 180 K, the Raman bandwidths as observed for the ammonium group remain practically constant, thus indicating nearly free rotations [10]. Unfortunately, the present measurements on LiBH\textsubscript{4} do not allow one to derive reliable values for the coefficients \(A\), \(B\) and \(U\), and thus to obtain quantitative information about the dynamics of the BH\textsubscript{4}\textsuperscript{-} group. This is partly due to the difficulty in estimating accurately the widths of the rather broad bands (see Fig. 3) and partly due to the limited temperature range of the data measured. However, the available data clearly suggest the existence of a dynamic disorder of the BH\textsubscript{4}\textsuperscript{-} group that may result from large amplitude librational motions rather than from completely free rotations.

4. Conclusions

Raman spectra of LiBH\textsubscript{4} as a function of temperature confirm the onset of a first-order structural phase transition that is triggered by an order–disorder transition of the tetrahedral BH\textsubscript{4}\textsuperscript{-} groups. The data show no sign for a degradation of the sample due, for example, to a loss of hydrogen during heating–cooling cycles. The spectral changes observed at the phase transition suggest the onset of large amplitude librational motions of quasi-rigid BH\textsubscript{4}\textsuperscript{-} tetrahedra about their trigonal axis. These observations are consistent with the observations of the crystallographic study as reported in the first part of this work.

Acknowledgements

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References