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Lithium boro-hydride $LiBH_4$
II. Raman spectroscopy

S. Gomes[a], H. Hagemann[b], K. Yvon[a,*]

[a]Laboratoire de Cristallographie, Université de Genève, 24, quai E. Ansermet, CH-1211 Geneva 4, Switzerland
[b]Département de Chimie Physique, Université de Genève, 30, quai E. Ansermet, CH-1211 Geneva 4, Switzerland

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Abstract

Polycrystalline $LiBH_4$ 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 $(BH_4)^-$ 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 $(BH_4)^-$ 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 $(BH_4)^-$ 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 $LiBH_4$ 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 $(BH_4)^-$ anions (point symmetry m-C_s) that point along two orthogonal directions, the structure at 408 K has hexagonal symmetry and contains a partially disordered array of more symmetric $(BH_4)^-$ anions (point symmetry 3 m-C_{3v}) 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 $(BH_4)^-$ tetrahedra about their trigonal axis. In this work the $(BH_4)^-$ 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 $LiBH_4$ (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

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*Corresponding author.
E-mail address: klaus.yvon@cryst.unige.ch (K. Yvon).

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with liquid CD_2Cl_2 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 SPECTRAW 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 $LiBH_4$ 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 ν_2 and ν_2', and second overtone of librational mode $3\nu_L$ in the 1340–1240 cm^{-1} range), while only one mode (ν_2) 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 C_s (space group *Pnma*) and C_{3v} (space group $P6_3mc$), 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 $NaBH_4$ and KBH_4 [7] indicate that the spectra of the BH_4^- 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 BH_4^- 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 $LiBH_4$ at this temperature.

3.2.1. Room-temperature phase

At room temperature, the point group symmetry of the BH_4^- ion is C_s. Seven internal BH_4^- vibrations (ν_4, ν_4', ν_2, ν_2', ν_3, ν_1 and ν_3') out of the nine Raman active normal vibrations are observed (Table 1). The two Raman active vibrations ν_4 and ν_4' occur at 1090 and 1099 cm^{-1}, respectively, and the two overtones $2\nu_4$ and $2\nu_4'$ at 2157 and 2177 cm^{-1}, respectively. The ν_4' assignment is not in accordance with the $^{10}\nu_4$ assignment given by [2] for the infrared spectrum by considering the ^{10}B–^{11}B 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 BH_4^- 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 $3\nu_L$ of a librational mode found in the spectra of alkali borohydrides. Inelastic neutron scattering experiments on $LiBH_4$ 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 $3\times412=1236$ 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 BH_4^- ion is increased to C_{3v}. Only five Raman bands ν_4, ν_2, $2\nu_4$, ν_1 and ν_3 are observed which are assigned to 1096, 1302, 2167, 2299 and 2355 cm^{-1}, respectively. The very broad ν_3 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 $LiBH_4$ 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 ν_3 than for ν_1 mode [2] it can be assigned to the two overlapping components of ν_3.

No external lattice vibrations are observed in the Raman spectra of the high-temperature phase of $LiBH_4$. Fig. 2 shows that one of the two observed site group split components of ν_2 and ν_4 (and their overtones and combi-

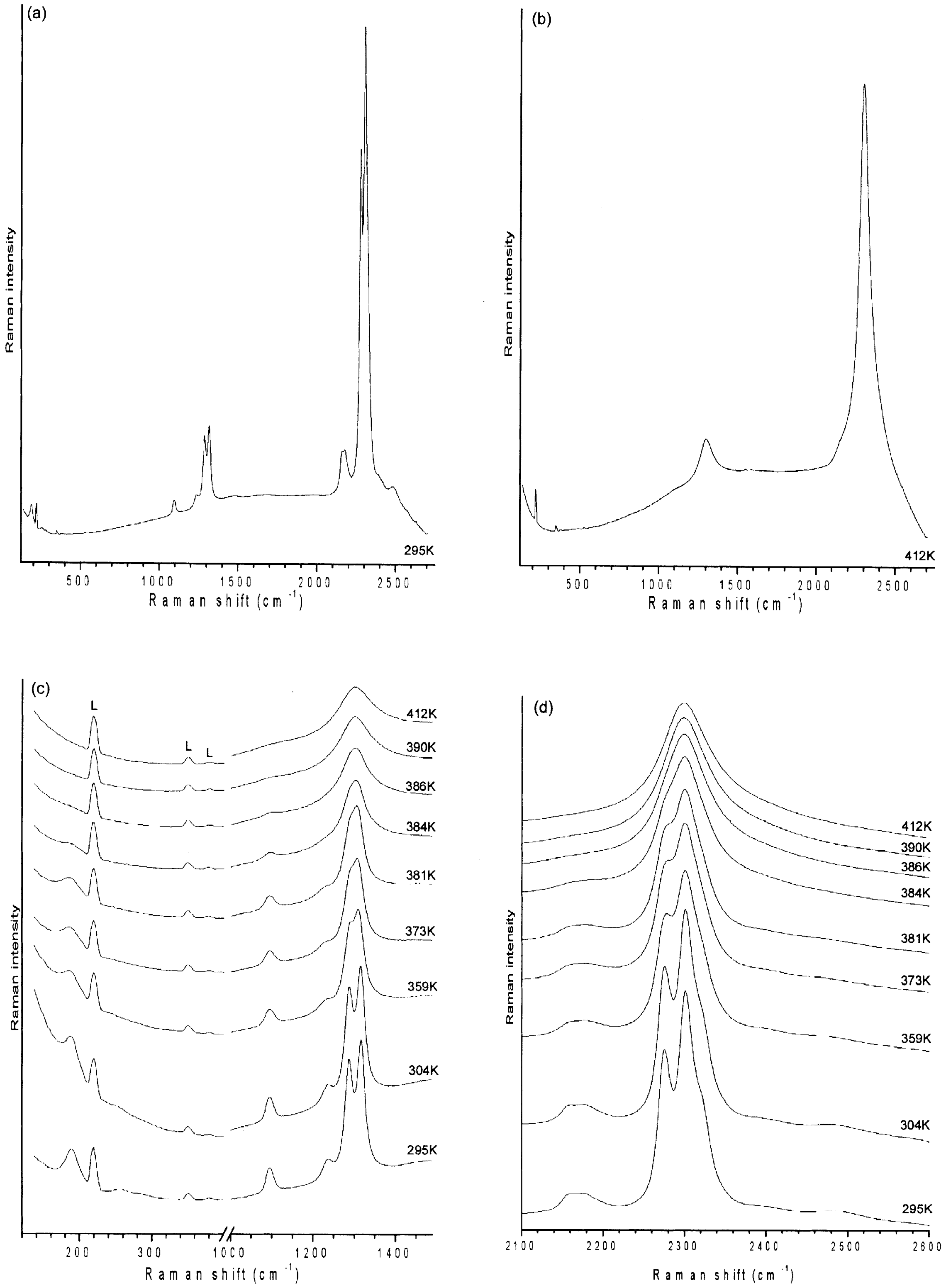

Fig. 1. Raman spectra of $LiBH_4$ at 295 K (a) and 412 K (b), and temperature-dependent Raman spectra in the ranges 120–400 and 1000–1500 cm^{-1} (c) and 2100–2600 cm^{-1} (d) at increasing temperature. Lines labelled L are laser plasma lines not belonging to the Raman spectrum.

nations) have disappeared from the spectra. Clearly, the disappearance of the ν_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 ν_4 as well as the ν_3 mode a splitting into two components ($A_1 + E$) is

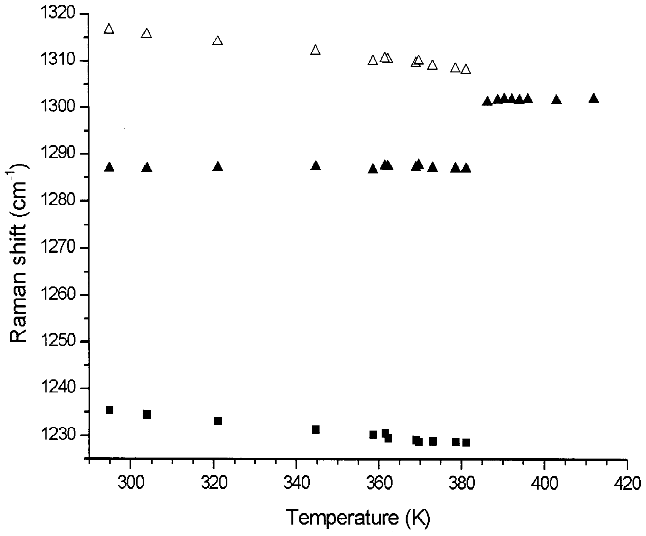

Fig. 2. Raman shift of the ν_2 (ν_2': △, ν_2: ▲) and $3\nu_L$ (■) modes versus temperature during heating.

expected but not observed. In the case of ν_4 the intensity is probably too weak (see Fig. 1), while for ν_3 strong line broadening (HWHM ≈ 100 cm^{-1}) presumably masks the second component.

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 ν_2 and ν_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 ν_1(HWHM ≈ 30 cm^{-1}), ν_2(HWHM ≈ 50 cm^{-1}), ν_3(HWHM ≈ 100 cm^{-1}) and ν_4(HWHM ≈ 36 cm^{-1}). In particular, ν_3 is extremely broad as can also be seen in the reported IR spectrum [3]. The disappearance of the $3\nu_L$ 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_4^+ ion in

Table 1
Correlation diagram for internal vibrations of tetrahedral BH_4^- ions in $LiBH_4$

Fundamental mode	Site symmetry		
	Free ion T_d	Phase 1 (*Pnma*) C_s	Phase 2 ($P6_3mc$) C_{3v}
ν_1	A_1	A'	A_1
ν_2	E	$A'+A''$	E
ν_3	T_2	$2A'+A''$	A_1+E
ν_4	T_2	$2A'+A''$	A_1+E

Table 2
Raman frequencies (cm^{-1}) of $LiBH_4$ at 295 and 412 K

Raman frequencies (cm^{-1})			Assignment
295 K		412 K	
Literature [2]	This work	This work	
–[a]	189	d[b]	External vibrations
–	255	d	
–	285	d	
–	1090	1096	ν_4
–	1099	d	
1253	1235	d	$3\nu_L$
1287	1286	1302	ν_2
1325	1316	d	
–	2157	2167	$2\nu_4$
–	2177	d	
2300	2301	2299	ν_1
2274	2275	Not observed	ν_3
2309 (sh)	2321 (sh)	2355	
–	2391	d	Combination bands
–	2491	d	
–	2572	d	

sh, Shoulder.
[a] Not indicated in the literature.
[b] Disappeared with high-temperature symmetry.

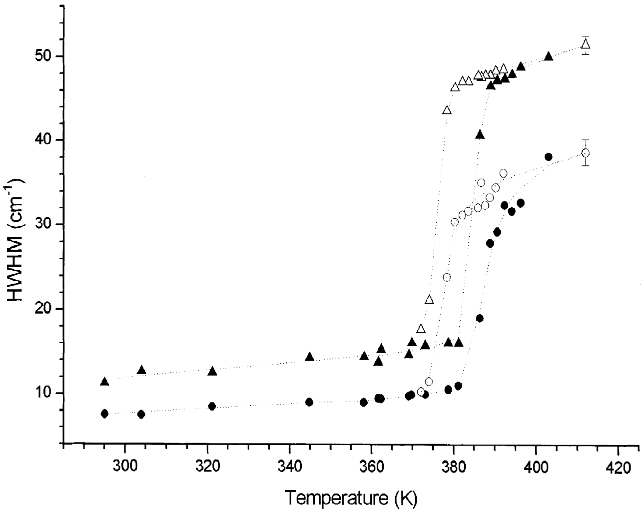

Fig. 3. Line width HWHM (half width at half maximum) as a function of temperature for the modes ν_2' (heating: ▲, cooling: △) and ν_4' (heating: ●, cooling: ○). Below the transition temperature $\bar{\nu}_2$(HWHM) = (ν_2'(HWHM) + ν_2'(HWHM))/2. Solid lines are guides to the eye.

NH_4ClO_4 below 180 K [10]. In such a case, one expects the bandwidth (Γ) 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 $LiBH_4$ 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_4^- 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_4^- group that may result from large amplitude librational motions rather than from completely free rotations.

4. Conclusions

Raman spectra of $LiBH_4$ 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_4^- 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_4^- 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.

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