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Structural and spectroscopic studies on the alkali borohydrides MBH₄ (M = Na, K, Rb, Cs)

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Abstract

Alkali borohydrides MBH₄ and their deuterides have been investigated by X-ray and neutron powder diffraction (M = K, Rb, Cs) and by infrared and Raman spectroscopy (M = Na, K, Rb, Cs). At room temperature the compounds crystallize with a cubic high temperature (HT) structure having $Fm\bar{3}m$ symmetry in which the [BH₄][−] complexes are disordered. At low temperature (LT) the potassium compound transforms into a tetragonal low temperature structure having $P4_2/nmc$ symmetry in which the [BH₄][−] complexes are ordered such as in the isotopic sodium congener. The B–H distances within the complex as measured on the deuteride at 1.5 K are 1.205(3) Å. Indications for a partial ordering in the rubidium and cesium compounds exist but are not sufficient for a full structural characterization. Infrared and Raman spectra at room temperature are fully assigned for both hydrides and deuterides, including the overtones and combination bands, the Fermi resonance type interactions and the ¹⁰B to ¹¹B splitting due to the presence of natural boron in the samples.

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Keywords: Hydrogen storage materials; Crystal structure; X-ray and neutron diffraction; Infrared and Raman spectroscopy

1. Introduction

Alkali borohydrides MBH₄ (M = alkali metal) are of interest for hydrogen storage [1]. Their solid-state structures contain relatively mobile tetrahedral [BH₄][−] units, the ordering of which tends to induce structural phase transitions. In LiBH₄, for example, a phase transition occurs at 384 K that originates from the reorientation motion of the [BH₄][−] ions as shown by synchrotron diffraction [2] and Raman spectroscopy [3]. While the disordered high temperature (HT) phase has hexagonal symmetry the ordered low temperature (LT) phase has orthorhombic symmetry [2–4]. The structure of the sodium compound NaBD₄ has been investigated by neutron diffraction [5,6]. It shows a similar transition at 190 K [7] but its HT-phase has cubic and its LT-phase tetragonal symmetry [5]. For the MBH₄ series with M = Na, K, Rb, Cs [8,9] X-ray studies have indicated the same face-centered cubic structure at room temperature thus sug-

gesting similar transitions to take place [10]. However, structure analyses for the K, Rb and Cs members have not been performed. The transition temperatures as measured by heat capacity studies were found to be 76 K for KBH₄, 44 K for RbBH₄ and 27 K for CsBH₄ [10]. A great number of spectroscopic studies have been performed on both hydrides and deuterides [3,11–17]. However, according to Memon et al. [15–17] the work published before 1982 suffers from incorrect and misleading interpretations because Fermi resonance type interactions had not been fully taken into account. Correct assignments of the spectra were later obtained from measurements on single crystals of alkali halides doped with [BH₄][−] and [BD₄][−] ions, i.e. revealing internal modes of vibration only, by taking into account the ¹⁰B to ¹¹B and ¹H to ²D isotopic dilution and the occurrence of strong Fermi resonance [15–17]. Very recently, the reorientation motions of [BH₄][−] anions in some alkali borohydrides MBH₄ have been studied by Raman spectroscopy [18]. Given the lack of reliable structural data on the HT-structures of M = Rb, Cs and the LT-structures of M = K, Rb, Cs, in particular with respect to hydrogen positions, additional structural and spectroscopic studies were desirable.

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2. Experimental

2.1. Synthesis

Hydride samples MBH₄ (M = K, Rb, Cs) were synthesized as indicated in a previous study [18]. Deuteride samples MBD₄ (M = K, Rb, Cs) were prepared in the same way. In a first step alkaline hydroxides were deuterated by repeatedly dissolving the hydroxide salts in heavy water and evaporation at room temperature under vacuum (three cycles). For NaBD₄ a commercial product (Alfa Aesar, purity 99 wt.%) was used. Isotope ¹¹B based compounds more favorable for neutron diffraction were not available. The absence of ¹H to ²D isotopic splitting in the Raman and infrared spectra suggested that the substitution of hydrogen by deuterium was close to 100% for all samples.

2.2. X-ray diffraction

All samples were analyzed by X-ray powder diffraction on a Huber Guinier Diffractometer 600 by using a monochromatic Ge(1 1 1) Cu K_{α1} radiation. The system was equipped with a closed-cycle helium Helix Model 22 Refrigerator [19]. The finely grinded powders were mixed with an internal silicon standard [20] and placed between two polyethylene terephthalate foils (Goodfellow) of 0.013 mm thickness. Measurements were performed during cooling from 300 to 10 K in the diffraction interval 10° < 2θ < 100°, with a step size of Δ2θ = 0.02°, and a counting time of 2 s per step. Cell parameters were refined by using at least 18 calibrated Bragg positions. All samples contained cubic MBH₄ (M = Na, K, Rb, Cs) and were single phase. Cell parameters for the hydrides and deuterides at room temperature and

10 K are listed in Table 1. The temperature dependence of the cell parameters is shown in Fig. 1, and the thermal expansion coefficients at 298 K as calculated from exponential fits are given in Table 1.

2.3. Neutron diffraction

The hydrogen (deuterium) positions for the K, Rb and Cs compounds were determined from neutron data as collected on deuteride samples by using the DMC [21] powder diffractometer at PSI, Villigen, equipped with a helium cryostat (ILL Orange cryostat). The following experimental conditions were used: wavelength λ = 2.5676 Å; 2θ range 20.0–99.9° for KBD₄ and RbBD₄, and 18.0–97.9° for CsBD₄; step size Δ2θ = 0.1°; temperature 295 and 1.5 K for each sample; cylindrical vanadium container (5 mm inner diameter for KBD₄ and 6 mm inner diameter for RbBD₄ and CsBD₄) filled in a He filled glove-box. Data collections were performed during 8 h at room temperature, and during 12 h at 1.5 K. The transmission factors were measured experimentally and found to be T = 0.300, 0.373, 0.296 for KBD₄, RbBD₄ and CsBD₄, respectively, while the theoretical values for the linear attenuation factors were μ = 14.65, 12.85 and 11.85 cm^{−1}, respectively. Rietveld refinements were performed by using the program FULLPROF.2k [22]. For the description of the disordered cubic HT-phase space group *Fm* $\bar{3}$ *m* rather than *F* $\bar{4}$ 3*m* was used because this allowed to reduce the number of free parameters and to avoid the use of structural constraints [5,6]. For the ordered LT-phase space group *P*4₂/*nmc* was used. The following variables were allowed to vary: 2 scale factors (MBD₄, vanadium), 5 profile parameters (Thompson-Cox-Hastings pseudo-Voigt peak shape function), 1 zero shift, 1 positional parameter

Table 1

Cell parameters for MBH₄ and MBD₄ (M = K, Rb, Cs) at 295 K and 10 K as refined from X-ray powder diffraction data

Sample	Temperature (K)	Space group	Z	Lattice parameters (Å)	Volume (Å ³)
KBH ₄	295	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 6.7306(1)	304.90(1)
	10	<i>P</i> 4 ₂ / <i>nmc</i>	2	<i>a</i> = 4.7004(2) <i>c</i> = 6.5979(3)	145.78(1)
KBD ₄	295	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 6.7074(1)	301.77(1)
	10	<i>P</i> 4 ₂ / <i>nmc</i>	2	<i>a</i> = 4.6836(1) <i>c</i> = 6.5707(2)	144.14(1)
<i>a</i> = 6.601(2) + 0.026(1) exp(^{(7/183(5))} (Å)); α ₂₉₈ = 3.2(2) × 10 ^{−4} K ^{−1} .					
RbBH ₄	295	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 7.0293(1)	347.32(1)
	10	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 6.9282(1)	332.56(1)
RbBD ₄	295	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 7.0156(1)	345.29(1)
	10	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 6.9039(1)	329.07(1)
<i>a</i> = 6.905(2) + 0.019(1) exp(^{(7/154(6))} (Å)); α ₂₉₈ = 3.6(4) × 10 ^{−4} K ^{−1} .					
CsBH ₄	295	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 7.4098(2)	406.83(2)
	10	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 7.3151(2)	391.44(2)
CsBD ₄	295	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 7.4061(2)	406.23(2)
	10	<i>Fm</i> $\bar{3}$ <i>m</i>	4	<i>a</i> = 7.2898(2)	387.39(1)
<i>a</i> = 7.300(1) + 0.013(1) exp(^{(7/132(5))} (Å)); α ₂₉₈ = 3.8(5) × 10 ^{−4} K ^{−1} .					

For the cubic HT hydride phases fits of the temperature dependence and the corresponding coefficients of thermal volume expansion at 298 K, α₂₉₈, are indicated.

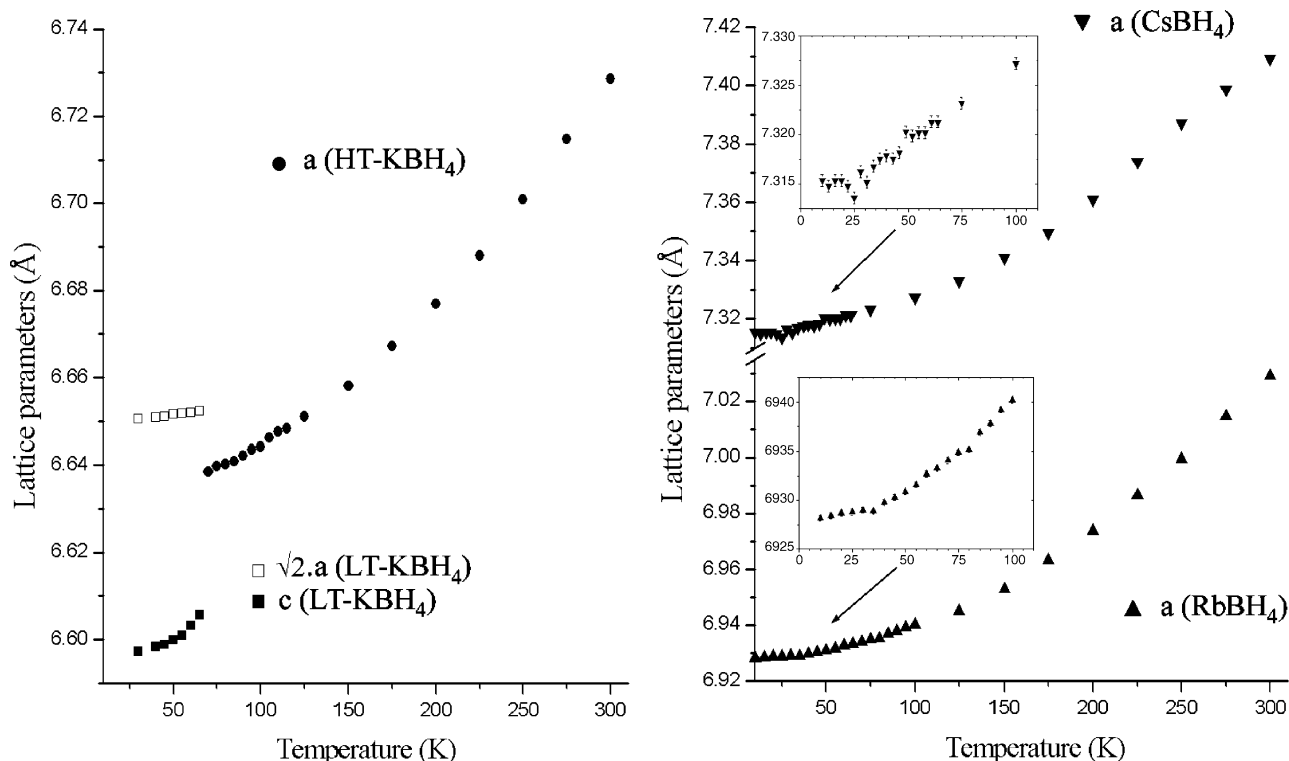


Fig. 1. Cell parameters as a function of temperature for alkali borohydrides MBH_4 ($M = K, Rb, Cs$).

for deuterium on 32f site (occupancy fixed to 1/2) for the cubic phase and 2 positional parameters for deuterium on 8g site for the tetragonal phase. Three isotropic temperature factors were refined for $M = K$ and two for $M = Rb$ and Cs , while those of boron and deuterium were constrained to be equal. The background was defined by a linear interpolation between 20 points, and cell parameters were fixed to the previously refined X-ray values. Due to a lack of diffraction evidence for a lowering of structural symmetry in $RbBD_4$ and $CsBD_4$ (see Section 3.1) the 1.5 K patterns of the latter were originally modeled by a cubic face-centred (disordered) structure in space group $Fm\bar{3}m$. Although this resulted in reasonably good fits (see Rietveld refinement indices at the end of Table 2) the true symmetry of their LT-structures was obviously lower because of the appearance of weak pseudo-cubic (100) and (110) Bragg peaks (see insets in Fig. 2) as shown by a profile matching procedure with FULLPROF.2k [22]. These peaks were stronger for the Rb than for the Cs compound. Their presence implies one of the following five space groups: $P2_13$, $Pm\bar{3}$, $P4_32$, $P4_3m$ and $Pm\bar{3}m$ of which only $P2_13$ and $P4_3m$ account for a full ordering of the $[BH_4]^-$ tetrahedra. However, attempts to solve the LT structure by using the program FOX [23] gave similar consistency indices ($R_p \sim 0.15$, $R_{wp} \sim 0.11$) for all space groups without allowing the structures to be refined in a satisfactory manner. This was attributed to the limited Q range of the neutron patterns ($0.85 \text{ \AA}^{-1} < Q < 3.75 \text{ \AA}^{-1}$) and the low counting statistics. On the other

hand, the modeling of the superstructure lines required the assumption of at least partial deuterium ordering. The refined patterns are shown in Fig. 2 and the refinement results for the face-centred cubic and the tetragonal structure models are tabulated in Table 2. Selected interatomic distances are listed in Table 3 and compared with those in the MBD_4 series ($M = Na, K, Rb, Cs$).

2.4. Raman and Infrared spectroscopy

The Raman set-up is the same as that described previously [3,18]. It consists of an Argon ion laser (488 nm excitation wavelength) and a Kaiser Optical Holospec monochromator equipped with a liquid nitrogen cooled CCD camera. The spectral resolution is ca. $3\text{--}4 \text{ cm}^{-1}$. The samples were enclosed in sealed glass capillaries with a diameter $\varnothing = 1.0 \text{ mm}$ by using an Ar filled glove-box. The FTIR spectrometer used is a Paragon 1000 (Perkin-Elmer) equipped in ATR mode with the Golden Gate Single Reflection Diamond (P/N 10 500 Graseby-Specac Series). The crystal of this apparatus is a diamond with refraction indices of 2.4 at 1000 cm^{-1} . The spectral resolution is 4 cm^{-1} and the spectral range is $500\text{--}4400 \text{ cm}^{-1}$. The powder samples to be analyzed were pressed against the crystal with a calibrated strength in an Ar filled glove-box and protected by an airtight protective polyethylene film during measurement. Both the Raman and infrared spectra were analyzed by using the line fitting procedure with Lorentzian profile of the

Table 2

Neutron refinement results for MBD₄ (M = K, Rb, Cs) at room temperature and 1.5 K; e.s.d.s in parentheses

	Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} (Å ²)	Occupancy
KBD ₄ ^a , room temperature, <i>Fm</i> $\bar{3}$ <i>m</i> , <i>Z</i> = 4, <i>a</i> = 6.7074(–) Å	K	4 <i>a</i>	0	0	0	1.6(4)	1(–)
	B	4 <i>b</i>	1/2	1/2	1/2	4.5(5)	1(–)
	D	32 <i>f</i>	0.6029(4)	<i>x</i>	<i>x</i>	3.6(4)	1/2(–)
KBD ₄ ^b , 1.5 K, <i>P</i> 4 ₂ / <i>nmc</i> , <i>Z</i> = 2, <i>a</i> = 4.6836(–) Å, <i>c</i> = 6.5707(–) Å	K	2 <i>b</i>	3/4	1/4	1/4	0.8(3)	1(–)
	B	2 <i>a</i>	3/4	1/4	3/4	1.2(3)	1(–)
	D	8 <i>g</i>	1/4	0.5400(6)	0.1440(5)	1.3(1)	1(–)
RbBD ₄ ^c , room temperature, <i>Fm</i> $\bar{3}$ <i>m</i> , <i>Z</i> = 4, <i>a</i> = 7.0156(–) Å	Rb	4 <i>a</i>	0	0	0	3.5(2)	1(–)
	B	4 <i>b</i>	1/2	1/2	1/2	5.6(4)	1(–)
	D	32 <i>f</i>	0.5993(3)	<i>x</i>	<i>x</i>	<i>B</i> _{iso} (B)	1/2(–)
RbBD ₄ ^d , 1.5 K, <i>Fm</i> $\bar{3}$ <i>m</i> , <i>Z</i> = 4, <i>a</i> = 6.9039(–) Å	Rb	4 <i>a</i>	0	0	0	2.6(2)	1(–)
	B	4 <i>b</i>	1/2	1/2	1/2	3.1(2)	1(–)
	D	32 <i>f</i>	0.6021(3)	<i>x</i>	<i>x</i>	<i>B</i> _{iso} (B)	1/2(–)
CsBD ₄ ^e , room temperature, <i>Fm</i> $\bar{3}$ <i>m</i> , <i>Z</i> = 4, <i>a</i> = 7.4061(–) Å	Cs	4 <i>a</i>	0	0	0	3.8(3)	1(–)
	B	4 <i>b</i>	1/2	1/2	1/2	7.8(5)	1(–)
	D	32 <i>f</i>	0.5948(4)	<i>x</i>	<i>x</i>	<i>B</i> _{iso} (B)	1/2(–)
CsBD ₄ ^f , 1.5 K, <i>Fm</i> $\bar{3}$ <i>m</i> , <i>Z</i> = 4, <i>a</i> = 7.2898(–) Å	Cs	4 <i>a</i>	0	0	0	1/2(2)	1(–)
	B	4 <i>b</i>	1/2	1/2	1/2	1.6(3)	1(–)
	D	32 <i>f</i>	0.5962(2)	<i>x</i>	<i>x</i>	<i>B</i> _{iso} (B)	1/2(–)

Cell parameters fixed at X-ray values.

^a Rietveld agreement indices: *R*_{wp} = 3.48%, χ^2 = 2.03, *R*_B = 2.53%.^b Rietveld agreement indices: *R*_{wp} = 3.85%, χ^2 = 2.41, *R*_B = 2.91%.^c Rietveld agreement indices: *R*_{wp} = 4.18%, χ^2 = 2.54, *R*_B = 2.20%.^d Rietveld agreement indices: *R*_{wp} = 4.50%, χ^2 = 3.08, *R*_B = 1.30%.^e Rietveld agreement indices: *R*_{wp} = 3.83%, χ^2 = 2.16, *R*_B = 1.30%.^f Rietveld agreement indices: *R*_{wp} = 4.51%, χ^2 = 2.14, *R*_B = 1.64%.

program SPECTRAW [24]. The observed infrared and Raman vibration bands are shown in Fig. 3 and their frequencies are reported in Tables 4 and 5, respectively. As can be seen in Fig. 3 both types of spectra reveal carbonate impurities coming from the starting commercial hydrated alkaline hydroxides.

Table 3

Selected interatomic distances in the MBD₄ (M = Na, K, Rb, Cs) series for low and high temperature modifications; e.s.d.s in parentheses

Sample	Modification	<i>d</i> (B–D) (Å)	<i>d</i> (M–D) (Å)	Reference
NaBD ₄	LT at 10 K	4 × 1.220(1)	4 × 2.448(1) 8 × 2.558(1)	[5]
	HT at 295 K	4 × 1.178(2)	24 ^a × 2.580(2)	[5]
KBD ₄	LT at 1.5 K	4 × 1.205(3)	4 × 2.770(3) 8 × 2.795(3)	This work
	HT at 295 K	4 × 1.196(3)	24 ^a × 2.837(3)	This work
RbBD ₄	LT at 1.5 K	4 × 1.221(2)	24 ^a × 2.922(2)	This work
	HT at 295 K	4 × 1.206(2)	24 ^a × 2.980(2)	This work
CsBD ₄	LT at 1.5 K	4 × 1.215(2)	24 ^a × 3.106(2)	This work
	HT at 295 K	4 × 1.217(3)	24 ^a × 3.161(3)	This work

^a D site occupancy 1/2.

3. Results and discussion

3.1. Structure

The room temperature structures of MBH₄ (M = K, Rb, Cs) have cubic symmetry and are isotypic with their sodium congener NaBH₄. The alkali cations and [BD₄][–] anions form a NaCl-type arrangement. Four deuterium atoms, on the average, surround boron at the corners of a boron-centered cube which is consistent with a random orientation of [BD₄][–] about $\langle 111 \rangle$ directions. At low temperature the compounds show various behaviors. The potassium compound transforms into a tetragonal LT-phase at 70–65 K, i.e. about 10 K below the temperature indicated in the literature (76 K [10]). The transition leads to an ordered structure in which the deuterium atoms surround boron in a tetrahedral configuration such as in the isotypic LT-structure of the sodium congener NaBD₄ [5]. Thus, the order-disorder phase transition is the same in both compounds in contrast to a previous study of their vibration spectra that reports anion site symmetries of T_d for the potassium and D_{2d} for the sodium congener [11]. The rubidium and cesium compounds behave differently. Their lattice appears to stay cubic over the entire temperature interval, i.e. a structural phase transition cannot be detected

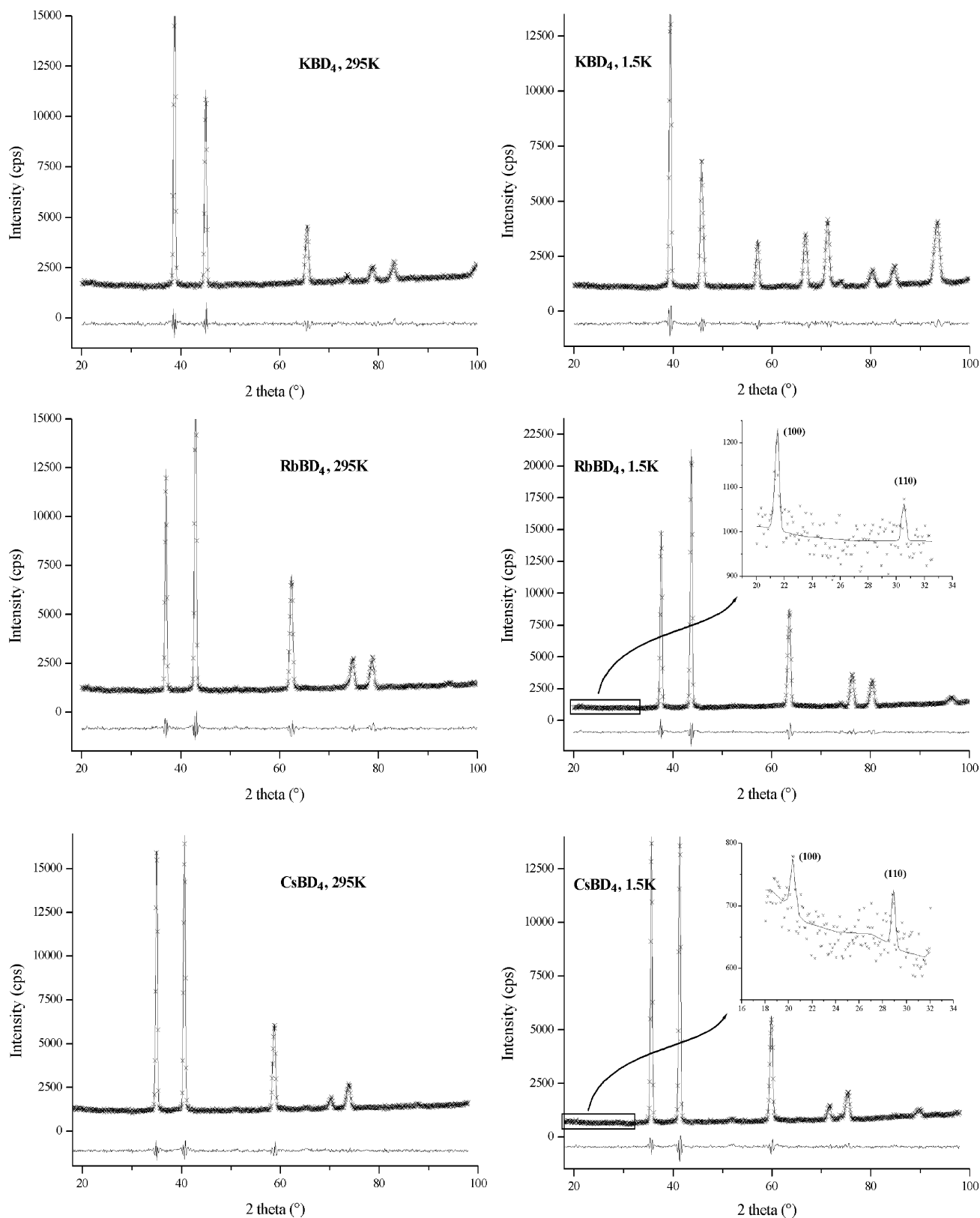


Fig. 2. Neutron diffraction patterns for alkali borodeuterides MBD₄ (M = K, Rb, Cs). Dotted lines: observed data, full lines: calculated data (top) and difference patterns (bottom). Insets for RbBD₄ and CsBD₄ at 1.5 K show the presence of pseudo-cubic (100) and (110) Bragg peaks as refined by a profile matching procedure [22].

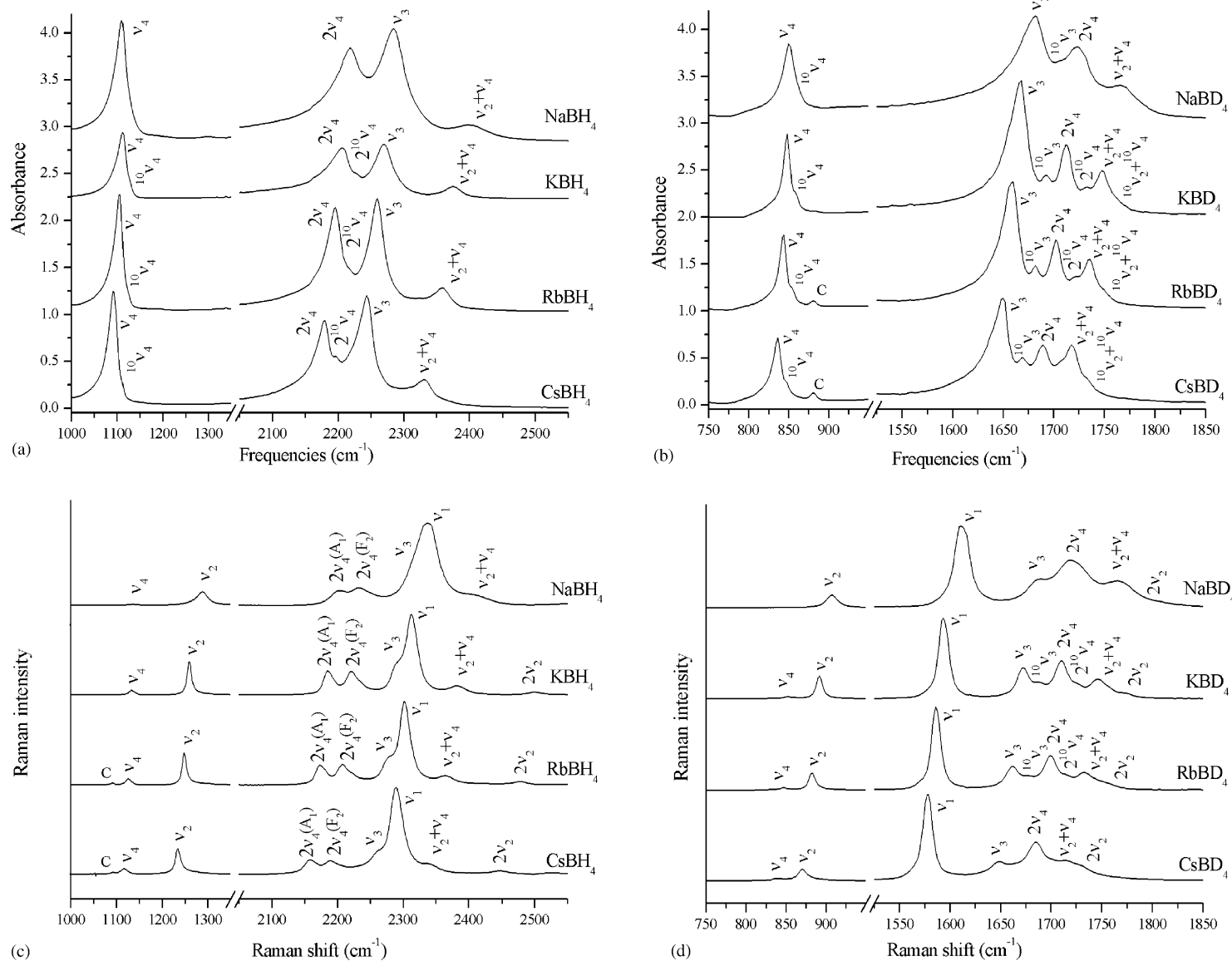


Fig. 3. Infrared (a and b), and Raman (c and d) spectra at room temperature for alkali borohydrides MBH₄ and borodeuterides MBD₄ (M = Na, K, Rb, Cs). For clarity only some of the ¹⁰B components are shown. Lines labeled C correspond to CO_3^{2-} impurities present in the starting alkaline hydroxides.

Table 4

Infrared frequencies (ω_i in cm^{-1}) at room temperature for $\text{NaBH}(\text{D})_4$, $\text{KBH}(\text{D})_4$, $\text{RbBH}(\text{D})_4$ and $\text{CsBH}(\text{D})_4$

ω_i	NaBH ₄	NaBD ₄	Ratio	KBH ₄	KBD ₄	Ratio	RbBH ₄	RbBD ₄	Ratio	CsBH ₄	CsBD ₄	Ratio
ν_4	1110	850	1.31	1112	848	1.31	1106	843	1.31	1094	836	1.31
$^{10}\nu_4$		864			860		1125	859	1.31	1111	849	1.31
$2\nu_4$	2217	1724	1.29	2208	1713	1.29	2196	1703	1.29	2179	1689	1.29
$^{10}\nu_4$				2231	1733	1.29	2225	1721	1.29	2197	1704	1.29
ν_3	2284	1681	1.36	2270	1668	1.36	2260	1659	1.36	2244	1650	1.36
$^{10}\nu_3$		1696			1693			1682			1669	
$\nu_2 + \nu_4$	2404	1769	1.36	2376	1748	1.36	2359	1736	1.36	2332	1719	1.36
$^{10}\nu_2 + ^{10}\nu_4$					1761			1750			1734	

Ratios $\omega_i^{\text{H}}/\omega_i^{\text{D}}$ are calculated when available.

with certainty. However, evidence for such a transition exists, such as the light break in slope of the cell parameters near 35 K for CsBH_4 and 22 K for RbBH_4 (see insets in Fig. 1) that are close to the reported anomalies in specific heat data (44 and 27 K, respectively [10]), and the appearance of superstructure lines in the LT neutron diffraction patterns (see insets in Fig. 2). While these data suggest at least partial deuterium ordering they do not allow a full structural characterization to be made. Clearly, diffraction data of higher resolution are needed to ascertain full order and/or a possible deviation from cubic symmetry.

As expected the cell volumes of the deuterides are smaller than those of the corresponding hydrides. The difference decreases as the alkaline radius increases ($\Delta V_{[\text{MBH}_4]} = -0.78 \text{ \AA}^3 (\text{K})$, $-0.51 \text{ \AA}^3 (\text{Rb})$, $-0.15 \text{ \AA}^3 (\text{Cs})$, see Table 1) while the coefficients of thermal expansion at room temperature, α_{298} , increase ($3.2(2) \times 10^{-4}$, $3.6(4) \times 10^{-4}$, $3.8(5) \times 10^{-4} \text{ K}^{-1}$ for KBH_4 , RbBH_4 and CsBH_4 , respectively). This suggests that anharmonicity effects increase as the alkaline network expands but become more similar between hydrides and deuterides. As to the bond distances those within the disordered $[\text{BH}_4]^-$ complexes increase as the alkaline radius increases: $\text{B}-\text{D} = 1.178(2) \text{ \AA}$ (Na), $1.196(3) \text{ \AA}$ (K), $1.206(2) \text{ \AA}$ (Rb) and $1.217(3) \text{ \AA}$ (Cs) which is expected in view of matrix effects. Simultane-

ously the M–D distances increase (see Table 3). Calculating a ‘pseudo hydrogen ionic radius’ from the formula $r(\text{H}^-) = d(\text{M}-\text{D}) - r(\text{M}^+)$ by using the ionic radius of the alkaline in 12 coordination as given by Shannon [25] (Na^+ : 1.39 \AA , K^+ : 1.64 \AA , Rb^+ : 1.72 \AA , Cs^+ : 1.88 \AA) yields $r(\text{H}^-) = 1.19 \text{ \AA}$ (NaBD_4), 1.20 \AA (KBD_4), 1.26 \AA (RbBD_4) and 1.28 \AA (CsBD_4). These values compare well with the tabulated 1.22 \AA for hydride ions in coordination four [25] as in the present compounds (H surrounded by three M and one B) while illustrating the strong dependence of M–H interactions on cation electronegativity [25].

3.2. Vibration spectra

The assignments of the infrared and Raman vibration bands (see Fig. 3 and Tables 4 and 5) are in agreement with previous spectroscopic studies [11,12,14–17]. Vibrations are present in two regions of the spectra: the bond bending region (with $\nu_2(\text{E})$ symmetric bending mode and $\nu_4(\text{F}_2)$ asymmetric bending mode) from 1050 to 1300 cm^{-1} for the hydrides and from 800 to 950 cm^{-1} for the deuterides, and the bond stretching region (with $\nu_1(\text{A}_1)$ symmetric stretching mode and $\nu_3(\text{F}_2)$ asymmetric stretching mode) from 2100 to 2500 cm^{-1} for the hydrides and from 1600 to 1800 cm^{-1} for the deuterides. The interpretation of the bond stretching

Table 5

Raman frequencies (ω_i in cm^{-1}) at room temperature from $\text{NaBH}(\text{D})_4$, $\text{KBH}(\text{D})_4$, $\text{RbBH}(\text{D})_4$ and $\text{CsBH}(\text{D})_4$

ω_i	NaBH ₄	NaBD ₄	Ratio	KBH ₄	KBD ₄	Ratio	RbBH ₄	RbBD ₄	Ratio	CsBH ₄	CsBD ₄	Ratio
ν_4	1124			1119	852	1.31	1112	847	1.31	1103	839	1.31
$^{10}\nu_4$				1126	861	1.31	1120			1111	850	1.31
ν_2	1274	908	1.40	1246	892	1.40	1234	883	1.40	1220	871	1.40
$2\nu_4(\text{A}_1)$	2197	1721	1.28	2181	1710	1.28	2166	1700	1.27	2149	1685	1.28
$^{10}\nu_4(\text{A}_1)$					1726		2175	1715	1.27	2157		
$2\nu_4(\text{F}_2)$	2231			2217			2202			2183		
$^{10}\nu_4(\text{F}_2)$				2231			2217			2194		
ν_3	2321	1686	1.38	2288	1672	1.37	2273	1662	1.37	2255	1648	1.37
$^{10}\nu_3$					1688			1678				
ν_1	2340	1609	1.45	2312	1592	1.45	2300	1586	1.45	2287	1578	1.45
$^{10}\nu_1^a$		1616			1597							
$\nu_2 + \nu_4$	2416	1769	1.37	2384	1748	1.36	2365	1733	1.36	2341	1716	1.36
$2\nu_2$	2553			2505	1774	1.41	2481	1753	1.42	2450	1732	1.41

Ratios $\omega_i^{\text{H}}/\omega_i^{\text{D}}$ are calculated when available.^a Observed ^{10}B to ^{11}B shift of the symmetric stretching ν_1 mode is due to the Fermi resonance with the $2\nu_4(\text{A}_1)$ vibration as indicated by [15].

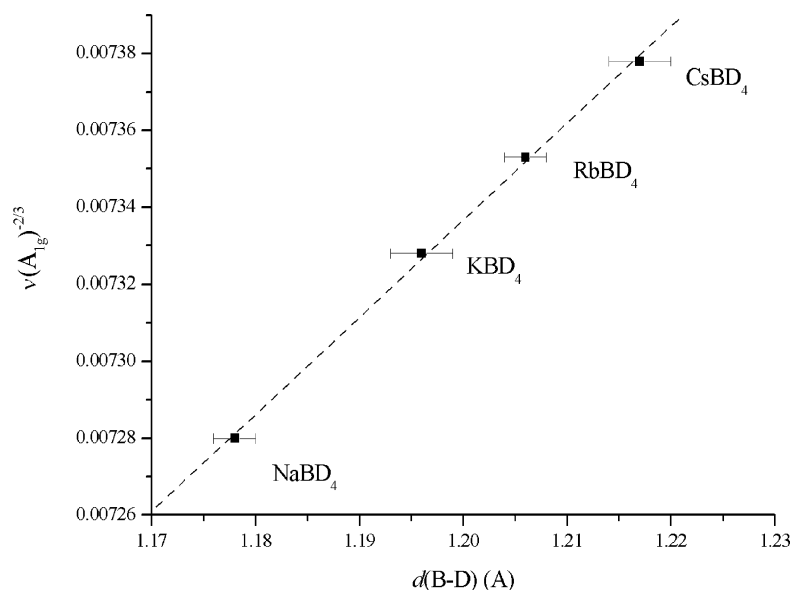


Fig. 4. Badger's rule as applied to the totally symmetric stretching mode, ν_1 , for $[\text{BD}_4]^-$ units in alkali borodeuterides MBD_4 ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) at room temperature.

region is complicated by the fact that the B–H bond bending vibrations occur at about half the bond stretching vibrations implying overtones and combinations with Fermi resonance. Because of the presence of natural boron in the samples ^{10}B to ^{11}B shifts (expected for asymmetric ν_3 and ν_4 modes) are observed in the spectra with a more intense ^{11}B component (compared to the shifted ^{10}B component) in agreement with the relative amount of the two isotopes in natural boron (19.6% of ^{10}B and 80.4% of ^{11}B). Studies by Memon et al. [15–17] on vibrational spectra of $[\text{BH}_4]^-$ and $[\text{BD}_4]^-$ groups isolated in alkali halides provide a useful guide for the assignment of these spectra. Tables 4 and 5 indicate also the ratio in frequency ($\omega_i^{\text{H}}/\omega_i^{\text{D}}$) when changing from $[\text{BH}_4]^-$ to $[\text{BD}_4]^-$ isotopic anions. The observed ratios do not vary with the alkaline and are in good agreement with theoretical values [26]. For the symmetric ν_1 and ν_2 modes the theoretical ratio is $\omega_1^{\text{H}}/\omega_1^{\text{D}} = \omega_2^{\text{H}}/\omega_2^{\text{D}} = \sqrt{2}$ to be compared with the ratios 1.45 and 1.40, respectively, as observed by Raman. These vibrations are not infrared active but the subtraction $(\nu_2 + \nu_4) - \nu_4$ allows one to calculate the ratios $\omega_2^{\text{H}}/\omega_2^{\text{D}} = 1.41$ for the sodium compound and $\omega_2^{\text{H}}/\omega_2^{\text{D}} = 1.40$ for the potassium, rubidium and cesium compounds. For the asymmetric ν_3 and ν_4 modes the relation becomes more complex as the ratio $\omega_3^{\text{H}} \times \omega_4^{\text{H}}/\omega_3^{\text{D}} \times \omega_4^{\text{D}} = 1.777$ needs to be compared with the following experimental values: 1.83 as obtained by Raman for the sodium compound by using $(\nu_2 + \nu_4) - \nu_2$ subtraction because ν_4 is not resolved in its spectra, 1.79 as obtained by Raman for the potassium, rubidium and cesium compounds, 1.77 by infrared for the sodium compound, 1.78 by infrared for the potassium and cesium compounds and 1.79 by infrared for the rubidium compound. The relatively high value of the observed ratio $\omega_1^{\text{H}}/\omega_1^{\text{D}}$ (1.45 instead of 1.41) is explained by the A_1 resonance between ν_1 and $2\nu_4(\text{A}_1)$, while the relatively high value of the observed ratio

$\omega_3^{\text{H}} \times \omega_4^{\text{H}}/\omega_3^{\text{D}} \times \omega_4^{\text{D}}$ in the case of Raman spectra of sodium compound (1.83 instead of 1.78) can be explained by the use of the $(\nu_2 + \nu_4)$ combination which participates in the F_2 resonance with ν_3 and $2\nu_4(\text{F}_2)$. The unexpected $^{10}\nu_1$ band (^{10}B to ^{11}B splitting would have to be null for the symmetric ν_1 and ν_2 modes) can be attributed to resonating mixtures between ν_1 and $2\nu_4(\text{A}_1)$ vibrations of these bands [15–17]. Finally, the spectroscopic data are in perfect agreement with the structural data at room temperature as can be seen from Badger's rule [27] represented in Fig. 4. According to this rule there exists a linear relationship between vibrational frequencies and changes in bond lengths for certain polyatomic molecules. Applying this rule to the tetrahedral molecules of the present compounds the linear relation between B–D bond lengths and the Raman shifts of the totally symmetric stretching mode, ν_1 , as expressed by the relation: $\nu_1^{-2/3} = \alpha d(\text{B-D}) - \beta$ becomes clearly apparent (see dotted line in Fig. 4). This shows that spectroscopic measurements can predict bond lengths also for this class of complex hydrides.

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