Vibrational Spectra of $Ca(BH_4)_2$

M. Fichtner,*[†] K. Chlopek,[†] M. Longhini,[‡] and H. Hagemann[‡]

Forschungszentrum Karlsruhe, Institute for Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany, and Departement de Chimie Physique, Université de Genève, 30, quai E. Ansermet, CH-1211 Geneva 4, Switzerland

Received: February 19, 2008; Revised Manuscript Received: May 20, 2008

IR and Raman data were obtained from α-, β-, and mixed (β,γ)-$Ca(BH_4)_2$ samples and from the deuterated β,γ phase mixture. The results obtained with α phase indicate that the DFT calculated values for the B−H stretching modes and the lattice vibrations are fairly close to the experimental values. The spectral behavior at temperatures around the transition to the β phase shows a continuous transition and suggests the presence of disorder caused by reorientational motions of the $[BH_4]^-$ ion in the β phase. The data indicate that there are more deformation bands observed for the mixed (β,γ) samples than for the α phase which indicates structural variations between the β and the γ phases.

Introduction

In search for new hydrogen storage materials tetrahydroborate compounds, $M(BH_4)_n$, (with M = metal cation, and n = valence of the cation) have gained considerable interest, mainly due to their high gravimetric content of H. However, only a few of the compounds exhibit thermodynamic properties that are suitable for reversible application. Among them, there are two alkaline earth compounds, $Mg(BH_4)_2$ and $Ca(BH_4)_2$.[1–4]

Recent results indicate that $Ca(BH_4)_2$ can be formed by ball milling of CaB_6 and CaH_2 and can ab- and desorb hydrogen reversibly, confirming the potential use as reversible hydrogen storage material.[5,6] α-$Ca(BH_4)_2$, obtained by desolvation of the commercial THF solvate, crystallizes in space group *Fddd*.[7] The phase transforms at about 400 K to a tetragonal structural phase with space group *P*42/*m* (No. 84) called the β-phase.[8]The structure of the β form has recently been published[9] whereas the structure of the γ form is still not known.

Table 1 summarizes the theoretical symmetry predictions for the vibrational spectra of α-Ca(BH4)2. Theoretical vibrational spectra from first principle calculations have been reported previously[7] and are compared to the experimental data in this work.

Experimental Section

α-$Ca(BH_4)_2$ was prepared by drying the commercial (Sigma-Aldrich) THF solvate $Ca(BH_4)_2 \cdot 2THF$ for 1 h at 433 K under a vacuum. Single phase β-$Ca(BH_4)_2$ was obtained by annealing α-$Ca(BH_4)_2$ for 16 h at 200 °C and quenching, or alternatively by annealing for 90 min at 250 °C and quenching. β,γ-$Ca(BH_4)_2$ was synthesized similarly to a method described in:[2] 1.920 g (0.046 mol) of CaH_2 (which was ball-milled for 1 h, at 600 rpm, in a tempered steel system) was introduced to 15.743 g (0.137 mol) of triethylamine borazane complex, $Et_3N \cdot BH_3$ (Aldrich). The mixture was heated under reflux for 2 h at 80 °C, 1 h at 95 °C, 1 h at 120 °C and finally 4 h at 140 °C. After cooling down to room temperature, 150 mL of dried and degassed *n*-hexane was introduced to the white solid. The latter was reduced to small pieces by means of a spatula. The suspension was stirred overnight, filtered under Ar, washed with *n*-hexane (3 × 20 mL) and dried at RT under vacuum, followed by drying at high temperature in vacuo (at 150 °C for 2 h, at 180 °C for 2 h, at 200 °C for 14 h). Isolated yield (with respect to CaH_2): 2.690 g (85%). Anal. Found: H, 10.68. Calcd: 11.56.

β,γ-$Ca(BD_4)_2$ was prepared from $Et_3N \cdot BD_3$ (6.161 g, 0.0522 mol) and CaD_2 (1.046 g, 0.0237 mol) (synthesis procedure in ref 10) according to the procedure described above. The deuterated compound contained up to 5% of H due to the aminoborane used. Isolated yield (with respect to CaH_2): 1.432 g (78%). The reagent $Et_3N \cdot BD_3$ was synthesized from $NaBD_4$ (Alfa Aesar, 9.500 g, 0.227 mol) and triethylamine−hydrochloride salt (Merck, 28.399 g, 0.206 mol) in diethyl ether, according to a procedure in the literature.[11] Up to five percent of H-content was registered in the final compound on the basis of the Raman spectra. Isolated yield: 20.430 g (87%).

Powder X-ray diffraction patterns (see Supporting Information) were obtained with a Philips X′PERT diffractometer, with Cu Kα radiation, 2 kW, with X′Celerator RTMS detector, automatic divergence slit. The powder was measured on an Si single crystal and sealed in the glovebox by an airtight hood made of Kapton foil, the foil being mounted out of the focus of the spectrometer.

IR spectra of $Ca(BH_4)_2$ in nujol mulls were recorded in the range of 4000−370 cm^{-1} under ambient conditions by using a Perkin-Elmer Spectrum GX FTIR spectrometer. The spectral resolution was 4 cm^{-1}. Evaluation of the data was done with the Perkin-Elmer Spectrum v. 2.00 Software. Measurements without nujol were obtained using a Specac "Golden Gate" ATR cell in a Perkin-Elmer Spectrum One instrument with a nominal resolution of 2 cm^{-1}. Several reports in the literature present IR spectra of inorganic borohydrides in KBr pellets. However, this sampling technique is not appropriate, as the BH_4^- ion and the Br^- ion have quite similar ionic radii, and partial or total ion exchange may take place. Furthermore, these spectra may also present lines originating from water (at 1630 cm^{-1}) present in the KBr powder.

Raman spectra were obtained using 3 different set-ups: the first one is an Ar ion laser (488nm) with a Kaiser Optical

---

* Corresponding author. E-mail: maximilian.fichtner@kit.edu. Telephone: +49-7247-82-5340. Fax: +49-7247-82-6368.

[†] Forschungszentrum Karlsruhe, Institute for Nanotechnology.

[‡] Departement de Chimie Physique, Université de Genève.

10.1021/jp801482b CCC: $40.75

TABLE 1: Symmetry Analysis of Vibrations in α-$Ca(BH_4)_2$ with Space Group *Fddd* (D^{24}_{2h}, No. 70)

Translational Modes of Atoms on Each Site

atom	site	
Ca	8a	D_2: $B_{1g} + B_{1u} + B_{2g} + B_{2u} + B_{3g} + B_{3u}$
B	16f	C_2^y: $Ag + A_u + 2B_{1g} + 2B_{1u} + B_{2g} + B_{2u} + 2B_{3g} + 2B_{3u}$
H_1	32f	C_1: $3A_g + 3A_u + 3B_{1g} + 3B_{1u} + 3B_{2g} + 3B_{2u} + 3B_{3g} + 3B_{3u}$
H_2	32h	C_1:$3A_g + 3A_u + 3B_{1g} + 3B_{1u} + 3B_{2g} + 3B_{2u} + 3B_{3g} + 3B_{3u}$

$\Gamma_{tot} = 7A_g + 7A_u + 9B_{1g} + 9B_{1u} + 8B_{2g} + 8B_{2u} + 9B_{3g} + 9B_{3u}$

Acoustic Modes

$\Gamma_{acoustic} = B_{1u} + B_{2u} + B_{3u}$

Librational Motions of the BH_4^- Ions

$\Gamma_{lib} = A_g + A_u + 2B_{1g} + 2B_{1u} + B_{2g} + B_{2u} + 2B_{3g} + 2B_{3u}$

Internal Vibrations of the BH_4^- Ion

free ion		
T_d	C_2	ion in crystal D_{2h}
A_1	A	$A_g + A_u + B_{2g} + B_{2u}$
E	2A	$2^*(A_g + A_u + B_{2g} + B_{2u})$
T2	A + 2B	$A_g + A_u + B_{2g} + B_{2u} + 2^*(B_{1g} + B_{1u} + B_{3g} + B_{3u})$
T2	A + 2B	$A_g + A_u + B_{2g} + B_{2u} + 2^*(B_{1g} + B_{1u} + B_{3g} + B_{3u})$

int $= 5A_g + 5A_u + 4B_{1g} + 4B_{1u} + 5B_{2g} + 5B_{2u} + 4B_{3g} + 4B_{3u}$

Optical Lattice Modes (Including Librational Modes)

$\Gamma_{ext} = 2A_g + 2A_u + 5B_{1\ g} + 4B_{1u} + 3B_{2\ g} + 2B_{2u} + 5B_{3\ g} + 4B_{3u}$

Instruments Holospec Monochromator and a liquid nitrogen cooled CCD camera, the second a Labram Raman microscope (with 532nm excitation) and finally an Ar−Kr laser (568nm) in conjunction with a Spex 1404 double monochromator and a PM detector. The samples were sealed in glass capillaries. The spectral resolution was 3−4 cm^{-1} for all experiments. High temperature spectra were obtained using the first setup in the backscattering geometry, with the sample located in a brass cylinder heated with a circulating bath thermostat.[12] Low temperature spectra were obtained using a home-built coldfinger liquid nitrogen dewar.

Results and Discussion

XRD data of the different samples can be found in the Supporting Information. Figure 1 presents vibrational spectra of α-$Ca(BH_4)_2$. Using the theoretical prediction presented in ref 7, the internal modes can be assigned as shown in Table 2. Each of the 9 internal modes expected for the local C_2 site symmetry is split into two Raman active and two Raman inactive components (see Table 1).

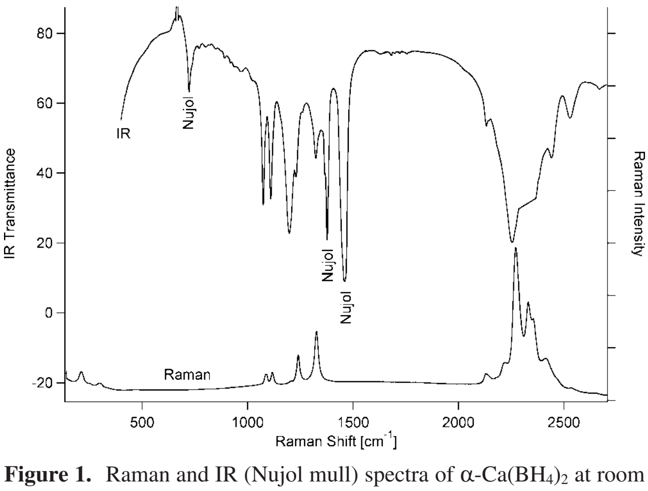

Figure 1. Raman and IR (Nujol mull) spectra of α-$Ca(BH_4)_2$ at room temperature.

The theoretical predictions for the B−H stretching modes are relatively close to the experimental values. However, the DFT calculations yield bending frequencies which are about 50 cm^{-1} below the experimental values. Figure 1 shows that the very weak Raman band at 1204 cm^{-1} has a strong IR intensity, confirming thus the assignment of this band to a component of the triply degenerate deformation mode in tetrahedral symmetry. It is interesting to note that this intensity pattern in the Raman and IR spectra of the deformation modes (between 1000 and 1400 cm^{-1}) is rather similar to the one observed for $LiBH_4$.[12]

The observed lattice vibrations agree fairly well with the calculated values (see Table 3), however, in the absence of polarized measurements, the assignments were made to the closest calculated value. Upon cooling to 80 K, the bands due to the lattice modes at 218 and 298 cm^{-1} sharpen and shift to higher frequencies by about 7 cm^{-1}, but no phase transition is observed (see Figure 2).

Upon heating α-$Ca(BH_4)_2$, one observes first significant shifts of the lattice vibrations, while the position of the internal modes

TABLE 2: Internal Vibrations of the BH_4^- Ion in α-$Ca(BH_4)_2$

				observed	
ideal symmetry T_d	local symmetry C_2	theoretical prediction[1] (cm^{-1})	theoretical prediction[1] (cm^{-1})	300K (cm^{-1})	80K (cm^{-1})
A (ϑ_1)	A	2283	2285	2273	2271
E (ϑ_2)	A	1269	1265	1327	1330
(ϑ_2)	A	1189	1191	1241	1244
T_2 (ϑ_3)	A	2368	2376	2356	2358
(ϑ_3)	B	2382	2373	2415	2426
(ϑ_3)	B	2311	2319	2332	2332
T_2 (ϑ_4)	A	1068	1059	1117	1119
(ϑ_4)	B	1164	1166	1204	1212
(ϑ_4)	B	1032	1025	1089	1093

TABLE 3: External + Librational Raman Active Modes in α-$Ca(BH_4)_2$

symmetry	theoretical prediction[7] (cm^{-1})	observed (cm^{-1})	$\Delta_{\text{obs-calc}}$ (cm^{-1})
A_g	211	218	7
A_g	492	475	−17
B_{1g}	97		
B_{1g}	156		
B_{1g}	257	252	−5
B_{1g}	298	298	0
B_{1g}	521		
B_{2g}	162		
B_{2g}	245		
B_{2g}	479		
B_{3g}	43	54	11
B_{3g}	101	111	10
B_{3g}	291	298	7
B_{3g}	339	340	1
B_{3g}	529		

do not appear to be affected. The bands at 218 and 298 cm^{-1} shift about 10 cm^{-1} to lower frequencies and broaden significantly between 294 and 450 K (see Figure 2). These temperature dependent shifts (observed between 80 and 450 K) indicate significant anharmonic behavior in the α phase. Close to the transition, the spectra (shown in figure 3 and 4) reveal a continuous transition of the α form to the high temperature phase. At high temperature, the spectra of ϑ_2 in the bending region between 1230 and 1330 cm^{1} appear to result from the superposition of somewhat sharper crystalline bands and a central much broader band. The width (fhwm) of this central band (evaluated by line fitting) is found to be 85−90 cm^{-1}, similar to the width observed for this mode in the high temperature phase of $LiBH_4$.[12] The width of the two sharper components (at 1236 and 1322 cm^{-1}) is found to be 36 and 50 cm^{-1} respectively, compared to 23 and 30 cm^{-1} for these bands in the α phase at 100 °C. The B−H stretching bands are collapsed into a broad feature, and above 150 cm^{-1}, no lattice mode is observed any more.

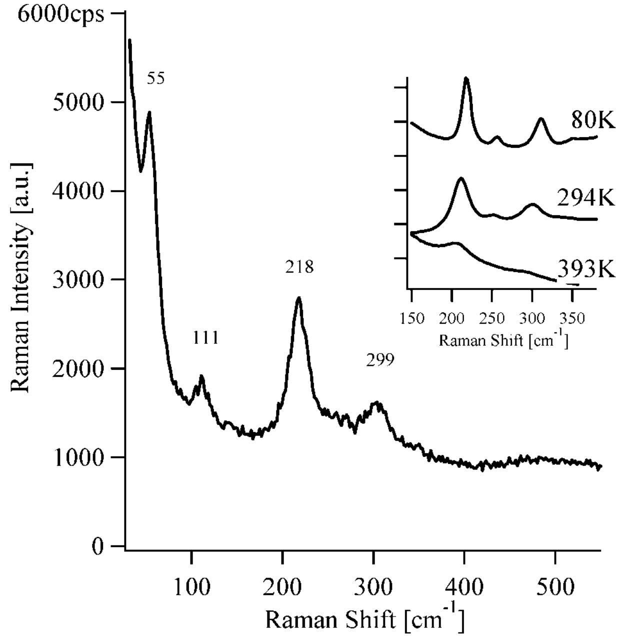

Figure 2. Low frequency Raman spectra of α-$Ca(BH_4)_2$ at room temperature. The insert shows the changes observed at different temperatures.

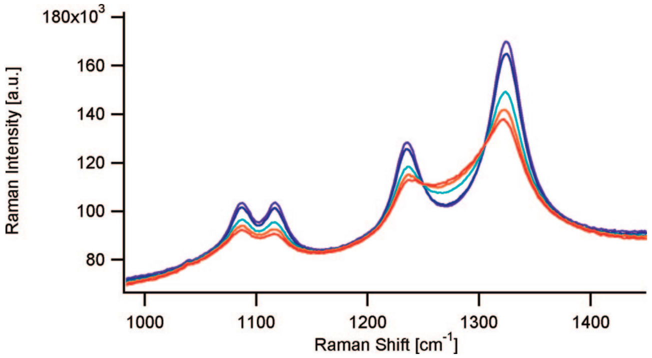

Figure 3. Raman spectra in the bending mode region around nominally 458−463 K (heating run). The spectra were taken in ca. 5 min intervals. Key: two upper curves, T = 458 K; three lower curves, T = 463 K.

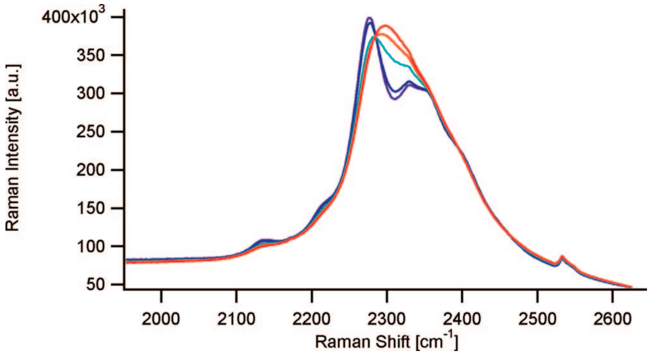

Figure 4. Raman spectra in the stretching mode region around nominally 458−463 K (heating run). (same as Figure 3) The signal around 2540 cm^{-1} is an artifact.

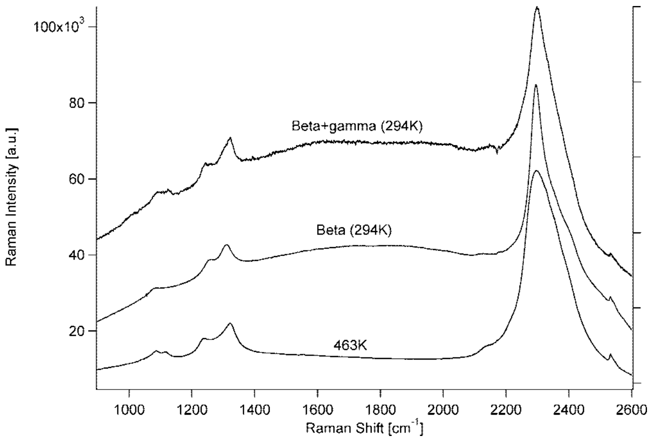

Figure 5. Raman spectra of β,γ-$Ca(BH_4)_2$, β-$Ca(BH_4)_2$ at room temperature and of α-$Ca(BH_4)_2$ heated the first time to 463K. A strong background was subtracted for the upper trace. The weak signal around 2540 cm^{-1} is an artifact.

Samples heated shortly (ca. 30 min) just above the phase transition temperature of 180 °C and cooled rapidly back to 433 K (160 °C) showed that the high temperature (β-) phase is still present. After cooling overnight in the Raman furnace to room temperature the Raman spectrum of the pure α-$Ca(BH_4)_2$ was observed. Between 180 and 200 °C, the Raman spectra evolve further, as seen mainly by the disappearance of a band near 1120 cm^{-1}. The sample cooled back to room temperature from this higher temperature yielded a mixture of α-$Ca(BH_4)_2$ and β-$Ca(BH_4)_2$, the amount of the β form increasing with increased annealing time.

The samples of the (β,γ) phase of $Ca(BH_4)_2$ yielded Raman spectra which were greatly masked by a strong luminescent

TABLE 4: Deformation Modes in cm^{-1} in the Different Phases (br = Broad, sh = Shoulder, *w* = Weak) at Room Temperature[a]

	α-Ca(BH$_4$)$_2$		β-Ca(BH$_4$)$_2$		β,γ-Ca(BH$_4$)$_2$		β,γ-Ca(BD$_4$)$_2$	
mode	IR	Raman	IR	Raman	IR	Raman	IR	Raman
ϑ_2	1325	1327	1323 w	1310	**1324**	1326 m	944	949
			1282		1285	1297	920 sh	930 w
	1229 sh	1241	1231	1254	1230 sh	1245		899
ϑ_4	1193	1204	1193		1192		905	
					1130 sh		890	
	1110	1117	1110		1110	1123	836	
					1085 sh			
	1075	1089	1074	1081 br	1074	1089	823	835

[a] Bands assigned to the γ phase are highlighted with bold characters.

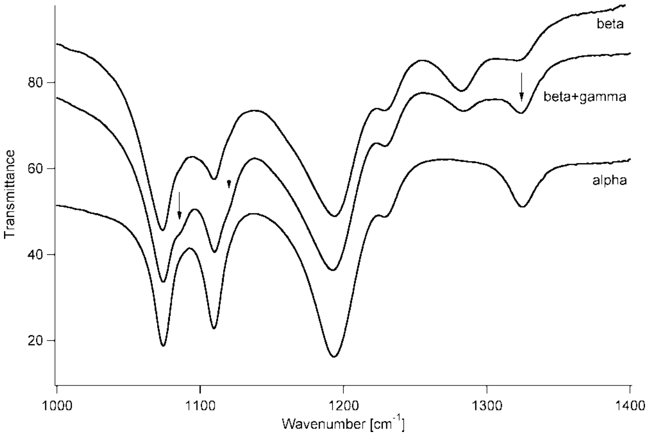

Figure 6. IR spectra in the deformation region of β-Ca(BH$_4$)$_2$, β,γ-Ca(BH$_4$)$_2$, and α-Ca(BH$_4$)$_2$ at 300K.

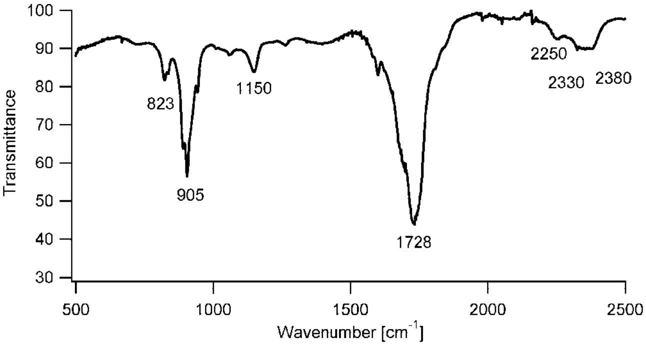

Figure 7. IR spectrum of β,γ-Ca(BD$_4$)$_2$ (neat sample in ATR cell).

background. We were not able to observe lattice vibrations for these samples. Figure 5 compares the high temperature Raman spectrum of α-Ca(BH$_4$)$_2$ heated the first time to 456 K with the room temperature spectrum of (β,γ)-Ca(BH$_4$)$_2$. These spectra look overall very similar. For the ϑ_2 region, the line widths are somewhat smaller for (β,γ)-Ca(BH$_4$)$_2$, the width of the broad central band is reduced to ca. 60 cm^{-1}. The Raman spectrum of β-Ca(BH$_4$)$_2$ at 294 K is also included for comparison. Note that for this compound, no Raman band at 1120 cm^{-1} is observed.

It is interesting to compare the Raman line width at room temperature for the α and β forms in the ϑ_2 region. For the α form, the half-width at half-maximum (hwhm) of the two bands at 1327 and 1241 cm^{-1} is found to be 11 and 8 cm^{-1} respectively. In contrast, the hwhm of the two bands at 1310 and 1254 cm^{-1} of the β form is found to be much larger, namely 26.5 and 21 cm^{-1} respectively. This spectral behavior suggests, by analogy with the behavior observed for the alkali borohydrides,[13] the presence of some disorder caused by reorientational motions of the [BH$_4$]$^-$ ion in the β phase, in agreement with recent crystallographic studies.[9]

The Raman spectra of (β,γ)-Ca(BD$_4$)$_2$ (which gave a better S/N ratio than the corresponding hydride), show between 890 and 950 cm^{-1} two rather sharp bands as well as a weaker, but not much broader band in-between. Table 4 compares for all samples studied, the observed vibrational frequencies for the ϑ_4 and ϑ_2 modes, the corresponding IR spectra are shown in figure 6, where the arrows point to features belonging to the γ phase.

The IR spectrum of β,γ-Ca(BD$_4$)$_2$ in Figure 7 shows several partly unresolved bands between 2250 and 2380 cm^{-1} which can be assigned to individual BD$_3$−H stretching modes arising from H impurities in the deuterated sample. In principle, each of these bands corresponds to a different B−H bond length, i.e. in this sample, there are at least 3 different B−H bond lengths, one being somewhat longer (weaker force constant) than the others.

Comments about Phase Transitions in Ca(BH$_4$)$_2$

The crystallographic data reported for Ca(BH$_4$)$_2$ show that, surprisingly, the unit cell volume is reduced progressively when going from the α (at 20 °C, $V = 855.03$ A) to the β (at 210 °C, $V = 210.7 \times 4 = 842.8$ Å^3) and to the γ (at 20 °C, $V = 822.7$ Å^3) phase.

In a recent paper,[14] it was shown that the $\alpha \rightarrow \beta$ phase transition is reversible, but they observed a much lower transition temperature of 130 °C (instead of ca. 180 °C in this work). However, it should be considered that their measurement was done under hydrogen pressure of 140 bar and in the presence of MgH$_2$. As the volume change for the $\alpha \rightarrow \beta$ phase transition is negative, one expects the transition temperature to decrease with increasing pressure.

The β,γ-Ca(BH$_4$)$_2$ samples studied in this work were heated for 14 h at nominally 200 °C and were obviously cooled sufficiently fast to freeze these phases at room temperature. We have obtained the pure β phase by annealing at 200 °C for 16 h. It is possible that in the first experiment, the real sample temperature was ca. 5 to 10 deg lower than in the second, accounting thus for the presence of the γ phase in that sample. Upon heating β-Ca(BH$_4$)$_2$ from room temperature to 220 °C, the Raman spectra show no significant spectral change indicative of a phase transition. Considering the observations that the transition at ca. 180 °C appears to be reversible, and that the irreversible formation of the β phase takes place between 180 and 200 °C, we cannot exclude the possible presence of an additional intermediate phase of Ca(BH$_4$)$_2$ in this temperature region.

Acknowledgment. We thank the EU-IP "NESSHy" (Contract No. 518271), the Helmholtz initiative "FuncHy" and the Swiss National Science Foundation for financial support.

Supporting Information Available: Figures showing experimental and calculated X-ray powder patterns of α-$Ca(BH_4)_2$ (Figure S1), β-$Ca(BH_4)_2$ (Figure S2), β (+γ)-$Ca(BH_4)_2$ (Figure S3) and infrared (neat sample in ATR cell) and Raman spectra of β-$Ca(BH_4)_2$ at 294 K (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Nakamori, Y.; Miwa, K.; Ninomiya, A.; Li, H.; Ohba, N.; Towata, S.; Züttel, A.; Orimo, S. *Phys. Rev. B* **2006**, *74*, 045126.

(2) Chlopek, K.; Frommen, Ch.; Léon, A.; Zabara, O.; Fichtner, M. *J. Mater. Chem.* **2007**, *17*, 3496.

(3) Her, J.-H.; Stephens, P. W. B.; Gao, Y.; Soloveichik, G. L.; Rijssenbeek, J.; Andrus, M.; Zhao, J.-C. *Acta Crystallogr. B* **2007**, *63*, 561–568.

(4) Hanada N.; Chlopek, K.; Frommen, Ch.; Lohstroh, W.; Fichtner, M. *J. Mater. Chem.* **2008,** DOI: 10.1039/b801049h.

(5) Rönnebro, E.; Majzoub, E. H. *J. Phys. Chem. B* **2007**, *111*, 12045.

(6) Kim, J.-H.; Jin, S.-A.; Shim, J.-H.; Cho, Y. W. *Scr. Mater.* **2008**, *58*, 481–483.

(7) Miwa, K.; Aoki, M.; Noritake, T.; Ohba, N.; Nakamori, Y.; Towata, S.; Züttel, A.; Orimo, S. *Phys. Rev. B* **2006**, *74*, 155122.

(8) Riktor, M. D.; Sørby, M. H.; Chlopek, K.; Fichtner, M.; Buchter, F.; Zuettel, A.; Hauback, B. C. *J. Mater. Chem.* **2007**, *17*, 4939.

(9) Buchter, F.; Lodziana, Z.; Remhof, A.; Friedrichs, O.; Borgschulte, A.; Mauron, Ph.; Zuettel, A.; Sheptyakov, D.; Barkhordarian, G.; Bormann, R.; Chlopek, K.; Fichtner, M.; Sørby, M.; Riktor, M.; Hauback, B.; Orimo, S. *J. Phys. Chem. B* **2008**, *112*, 8042–8048.

(10) Andresen, A. F.; Maeland, A. J.; Slotfeldt-Ellingsen, D. *J. Solid State Chem.* **1977**, *20*, 93.

(11) Kampel, V.; Warshawsky, A. *J. Organomet. Chem.* **1994**, *469*, 15.

(12) Gomes, S.; Hagemann, H.; Yvon, K *J. Alloys Comp.* **2002**, *346*, 206.

(13) Hagemann, H.; Gomes, S.; Renaudin, G.; Yvon, K. *J. Alloys Comp* **2004**, *363*, 129.

(14) Barkhordarian, G.; Jensen, T.; Doppiu, S.; Bosenberg, U.; Borgschulte, A.; Gremaud, R.; Cerenius, Y.; Dornheim, M.; Klassen, T.; Bormann, R. *J. Phys. Chem. C* **2008**, *112*, 2743–2749.

JP801482B