Structure of the Orthorhombic $\gamma$-Phase and Phase Transitions of Ca(BD$_4$)$_2$

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We have solved and refined the crystal structure of the orthorhombic $\gamma$-phase of Ca(BD$_4$)$_2$ by combined synchrotron X-ray powder diffraction, neutron powder diffraction, and ab initio calculations. Among five structural candidates giving the same quality of the fit of the diffraction data, the structural model with the highest symmetry and space group $Pbca$ is the most appropriate. This is supported by the implicit presence of the $Pbca$ symmetry operations in the low-symmetry space groups in both experimental and DFT calculated structures. The Ca atoms are surrounded by six BD$_4$ groups that have similar distortions as reported for the $/beta_2$-phase of Ca(BD$_4$)$_2$. On the basis of the experimental structures, free energies of the $R$, $/beta_2$, and $\gamma$-phases are calculated in the range $300 \, K < T < 620 \, K$. The phase transitions are observed in the same temperature range by means of X-ray diffraction on Ca(BD$_4$)$_2$ + MgD$_2$ and pure Ca(BD$_4$)$_2$ samples. According to the ab initio calculations, the $R$-phase is the ground state at 0 K. At room temperature, the calculated free energies of the $\alpha$-, $\beta$-, and $\gamma$-phases were found to be within $\sim 0.13 \, eV/f.u.$, in agreement with the observed coexistence of these phases. Moreover, calculations provide insight into trends for relative stabilities of $R$, $/beta_2$, and $\gamma$-phases. That is, with increasing temperature, the $/beta_2$-phase becomes more stable, while the metastable $\gamma$-phase becomes more destabilized with respect to the $\alpha$-phase.

I. Introduction

Alkali and alkaline earth complex hydrides are in the focus of current research on hydrogen storage, due to their high hydrogen content.1-4 Besides a high storage capacity, a hydrogen storage material should allow a reversible and sufficiently fast hydrogen release and uptake at temperature/pressure conditions reasonably close to the ambient ones. Ca(BH$_4$)$_2$ with a gravimetric hydrogen density of 11.5 mass % and a volumetric hydrogen density of $\sim 130 \, kg \, m^{-3}$ is one of the most promising alkaline earth complex hydrides for hydrogen storage. It has the required thermodynamical stability according to ab initio calculations,5,6 and it is reversible.7,8 However, the main drawbacks for a technical use of this compound are high formation/decomposition temperatures and pressures either due to thermodynamic or kinetic reasons. As a prerequisite to identify the mechanism of the sorption cycle or to modify the thermodynamical characteristics, it is mandatory to carefully characterize these compounds, and to understand its properties. The determination of the crystal structures and structural phase transitions are in that view fundamental steps toward a full characterization of Ca(BH$_4$)$_2$. They provide the ultimate reference for spectroscopic studies or ab initio density functional theory (DFT) calculations.
The Ca(BH₄)₂ was reported to take at least four structural polymorphs before the decomposition in a temperature range from 300 to 650 K.⁹⁻¹⁴ The polymorphs present in the samples as well as the subtle structural phase transitions between them depend on the sample synthesis.⁹⁻¹⁴ According to recent Raman and infrared spectroscopy measurements,¹⁵ no further structural transition is likely to occur upon cooling down to 80 K. An orthorhombic structural phase with space group *Fddd* (no. 70) named the α-phase⁹,¹⁰ was initially determined.³,¹² Recently, a tetragonal structural phase named the β-phase⁹,¹⁰ was solved¹² with space group *P4/mcm* (no. 84) and an orthorhombic structural phase named the γ-phase⁹,¹⁰ with space group *Pbca* (no. 61) was indexed¹² with unit cell *a* = 13.0582(3) Å, *b* = 8.3882(5) Å, and *c* = 7.5108(4) Å. A tetragonal structural phase named the α′-phase¹⁴ with space group *I42d* (no. 122) was recently reported resulting from a second order phase transition observed between the α-phase and the α′-phase.¹³,¹⁴ Lower-symmetry structural models, refined with soft restraints on the geometry of the BH₄ tetrahedra, were recently proposed for the α-phase and β-phase.¹⁴

In the present work, we have solved the crystal structure of the orthorhombic γ-phase of Ca(BD₄)₂ by combined X-ray and neutron powder diffraction on samples synthesized by a wet chemical method.¹⁶ This synthesis method yields pure Ca(BD₄)₂ samples with the orthorhombic γ-phase present in a large amount. The structure solution of the γ-phase could be carried out thanks to the previous structure determination of the α-phase and β-phase,³,¹² both present in a significant amount in the sample. Among Ca(BH₄)₂ samples synthesized by solid-gas mechanochemical or wet chemical methods, the orthorhombic γ-phase was hitherto the last one to be determined. Thus, we could use the complete structural information to perform DFT calculations of the free energy of the α-, β-, and γ-phases of Ca(BH₄)₂/Ca(BD₄)₂ and provide a qualitative picture of the thermodynamics for temperatures up to 620 K. Calculated free energies have been compared to phase transitions monitored by synchrotron radiation X-ray powder diffraction (SR-XPD) on a Ca(BD₄)₂ sample synthesized by the wet chemical method, and by laboratory source X-ray powder diffraction (XPD) on a Ca(BD₄)₂ + MgD₂ sample synthesized by the solid-gas mechanochemical reaction.⁹

The space group candidates were determined by a systematic profile matching of the data with all of the possible orthorhombic space groups, considering all six permutations of labeling of the orthorhombic symmetry directions. The profile matching was carried out using the program FullProf⁺⁺ (version 4.30). The structure solution of the γ-phase was performed by the program FOX⁺⁺ (version 1.7.6.2) using combined SR-XPD and NPD data for all of the space group candidates fitting all the indexed γ-phase peaks in the profile matching. A structure solution was found by FOX for the space group *P2₁2₁2₁* (no. 19), for the three distinct projections of the space group *Pca2₁* (no. 29), and one of the two distinct projections of the space group *Pbcn* (no. 61) (see Figure 5 and Table 4 in the Supporting Information).

The combined SR-XPD and NPD Rietveld refinement of the five structural models was carried out using FullProf. The final refinement of the best γ-phase structural model of Ca(BD₄)₂, with space group *Pbca* (see Figure 1 and details of the refined structural model in Table 1) was performed with in total 107 free parameters (including additional phases). All of the structural parameters were refined without imposing any restraints on bond lengths or angles. Details of the final refinement are provided in the Supporting Information.

The study of the coexistence and phase transitions of the α-, β-, and γ-phases of Ca(BD₄)₂ was carried out by means of X-ray diffraction data collected at selected temperature steps in the range 300 K < *T* < 620 K. We monitored the phase transitions in a sample of pure Ca(BD₄)₂ synthesized by wet chemical synthesis and in a sample of Ca(BD₄)₂ + MgD₂ synthesized by the solid-gas mechanochemical reaction. A high-resolution diffractometer was necessary to clearly separate and identify the diffraction peaks of the α-, β-, and γ-phases in the pure Ca(BD₄)₂ sample synthesized by wet chemical synthesis. On the other hand, an XPD measurement on the Ca(BD₄)₂ + MgD₂ sample was sufficient to follow the α-, β-, and γ-phases due to the largely dominant amount of the α-phase in the sample with respect to the γ-phase. The γ-phase was exhibiting an isolated peak in the diffractogram sufficiently strong to reliably track this phase. Immediately after the measurement at each temperature, the sample was quickly cooled to room temperature by removing the heating device and a diffractogram was recorded at room temperature, allowing the reversibility/metastability of the different structural phases to be followed. XPD data was collected for the Ca(BD₄)₂ + MgD₂ sample between 300 and 590 K on a Bruker D8 powder diffractometer (Cu Kα radiation). The sample was filled into a 0.7 mm diameter glass capillary, and the temperature was controlled using an MRI high-temperature capillary furnace. SR-XPD data was collected with the same procedure for the pure Ca(BD₄)₂ sample between 300 and 590 K on the high-resolution powder diffractometer of the Swiss-Norwegian beamlines (BM01B-SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The sample was filled into a 1.0 mm diameter glass capillary, the wavelength was 0.51986(2) Å, and the temperature was controlled using an Oxford Cryostream 600 blower.

**II. Methods**

**A. Experimental Section.** For the identification and indexing of the γ-phase, samples of Ca(BH₄)₂ and Ca(BD₄)₂ were synthesized by wet chemical synthesis¹⁶ at the Forschungszentrum Karlsruhe GmBH(FZK), Germany. All samples were handled exclusively in vacuum or in inert gas prior to filling into glass capillaries or vanadium sample containers used for the diffraction measurements. Details on the synthesis of the samples and indexing of the γ-phase of Ca(BH₄)₂ and Ca(BD₄)₂ are described elsewhere.¹²,¹⁶,¹⁷

For the solution and refinement of the γ-phase, SR-XPD data was collected on the sample of Ca(BD₄)₂ at 300 K on the high-resolution powder diffractometer of the material science (MS) beamline at the Swiss Light Source (SLS) at the Paul Scherrer Institute (PSI) in Villigen (Switzerland). The wavelength was 0.954872(2) Å. Neutron powder diffraction (NPD) data was collected on a Ca(BD₄)₂ sample of the same batch at 300 K. The data was collected at the high-resolution powder diffractometer for thermal neutrons¹⁵ (HRPT) at the Swiss spallation neutron source (SINQ) at the PSI. Diffraction patterns were recorded with monochromatic neutrons of a wavelength of 1.885(1) Å (see also the Supporting Information).

The wave functions were sampled according to a Monkhorst–Pack...
scheme with a \( k \)-points mesh of spacing 0.07 Å. The ground state electronic density was determined by iterative diagonalization of the Kohn–Sham Hamiltonian. All considered structures were optimized with constrained symmetry and volume of the unit cell, until the forces exerted on atoms were smaller than 0.01 eV/Å. Then, the shape and volume of the unit cell was relaxed and the relaxation procedures were repeated until self-consistency was achieved. In the last step, the symmetry constraints were removed and internal atomic positions were relaxed.

After this step, the normal-mode analysis was performed by finite displacement of the symmetry inequivalent atoms. Each ion was displaced by 0.02 Å in two opposite directions along all crystallographic axes. From the forces obtained via such calculations, the dynamical matrix was constructed and diagonalized. The diagonal elements of such a dynamical matrix represent normal modes at the gamma point. The zero point vibration energy and finite temperature properties were calculated within the harmonic approach; details are presented elsewhere.27

III. Results and Discussion

In this section, the solution of the structure and the refinement of the \( \gamma \)-phase is primarily discussed. In the second part, having the structure of the \( \gamma \)-phase in hand, the coexistence and phase transitions of the \( \alpha \)-, \( \beta \)-, and \( \gamma \)-phases observed in a temperature range of \( 300 \, K < T < 620 \, K \) are discussed together with the calculated free energy of each phase.

A. Orthorhombic \( \gamma \)-Phase Structure of Ca(BD\(_4\))\(_2\). The refinements of the orthorhombic structural model candidates identified for the hitherto unsolved orthorhombic \( \gamma \) structural phase (with corresponding space groups \( P2_12_12_1 \) (no. 19), \( Pca2_1 \) (no. 29), and \( Pbca \) (no. 61)) were carried out in two steps. Initially, the structural models were refined by imposing antibump soft restraints on the B–D interatomic distances (1.2 Å) and D–D distances (2.0 Å). These restraints are based on interatomic distances from structural results reported in the literature for alkali and alkaline earth tetrahydroborates.12,28–35 In the second step, the structural models were fully released. An equivalent quality of fit (for both neutron and X-ray pattern) was obtained for all refined structural models, and they exhibit an undistinguishable Ca and B network (see Table 4 and Figure 5 in the Supporting Information). For the refinements without restraints, in spite of the significant distortion observed for the BD\(_4\) of the space groups \( P2_12_12_1 \) and \( Pca2_1 \), the same orientation of the BD\(_4\) tetrahedra as for the restrained structural models is preserved for all candidates (see Table 4 and Figure 5 in the Supporting Information).
TABLE 1: Refined and Calculated Structural Parameters for the Ca(BD₄)₂ γ-Phase (Space Group Pnca (no. 61); Z = 8)

<table>
<thead>
<tr>
<th>site</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Biso (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/8c</td>
<td>0.6262</td>
<td>0.3791</td>
<td>0.3661</td>
<td>2.7(2)</td>
</tr>
<tr>
<td>B/18c</td>
<td>0.2254</td>
<td>0.4106</td>
<td>0.4805</td>
<td>1.6(7)</td>
</tr>
<tr>
<td>D11/8c</td>
<td>0.2647</td>
<td>0.3440</td>
<td>0.3480</td>
<td>4.9(7)</td>
</tr>
<tr>
<td>D12/8c</td>
<td>0.2658</td>
<td>0.3471</td>
<td>0.5960</td>
<td>4.9(7)</td>
</tr>
<tr>
<td>D13/8c</td>
<td>0.2370</td>
<td>0.5350</td>
<td>0.4730</td>
<td>4.9(7)</td>
</tr>
<tr>
<td>D14/8c</td>
<td>0.1367</td>
<td>0.3680</td>
<td>0.4800</td>
<td>4.9(7)</td>
</tr>
<tr>
<td>B2/8c</td>
<td>0.5030</td>
<td>0.8420</td>
<td>0.8170</td>
<td>1.6(7)</td>
</tr>
<tr>
<td>D22/8c</td>
<td>0.5240</td>
<td>0.6889</td>
<td>0.7986</td>
<td>4.9(7)</td>
</tr>
<tr>
<td>D23/8c</td>
<td>0.4006</td>
<td>0.8670</td>
<td>0.8140</td>
<td>4.9(7)</td>
</tr>
<tr>
<td>D24/8c</td>
<td>0.5420</td>
<td>0.8620</td>
<td>0.9560</td>
<td>4.9(7)</td>
</tr>
</tbody>
</table>

Calculated; a = 12.7709 Å, b = 8.1738 Å, c = 7.3328 Å

<table>
<thead>
<tr>
<th>site</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Biso (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/8c</td>
<td>0.6281</td>
<td>0.3763</td>
<td>0.3660</td>
<td></td>
</tr>
<tr>
<td>B/18c</td>
<td>0.2260</td>
<td>0.4106</td>
<td>0.4687</td>
<td></td>
</tr>
<tr>
<td>D11/8c</td>
<td>0.2719</td>
<td>0.3535</td>
<td>0.3335</td>
<td></td>
</tr>
<tr>
<td>D12/8c</td>
<td>0.2676</td>
<td>0.3565</td>
<td>0.6076</td>
<td></td>
</tr>
<tr>
<td>D13/8c</td>
<td>0.2270</td>
<td>0.5590</td>
<td>0.4620</td>
<td></td>
</tr>
<tr>
<td>D14/8c</td>
<td>0.1326</td>
<td>0.3773</td>
<td>0.4699</td>
<td></td>
</tr>
<tr>
<td>B2/8c</td>
<td>0.5030</td>
<td>0.8411</td>
<td>0.8159</td>
<td></td>
</tr>
<tr>
<td>D22/8c</td>
<td>0.5231</td>
<td>0.6961</td>
<td>0.7854</td>
<td></td>
</tr>
<tr>
<td>D23/8c</td>
<td>0.4089</td>
<td>0.8717</td>
<td>0.8090</td>
<td></td>
</tr>
<tr>
<td>D24/8c</td>
<td>0.5371</td>
<td>0.8687</td>
<td>0.9689</td>
<td></td>
</tr>
</tbody>
</table>

In order to quantitatively estimate the deviation of the low-symmetry models from the Pbca symmetry (see the Supporting Information), the symmetry determination algorithm of the software Superflip15 was applied on the refined low-symmetry structural models (P₂₁₂₁, and Pca₂₁). This algorithm analyses the scattering density for given symmetries, and provides a symmetry agreement factor for each symmetry operation compatible with the crystal lattice.30 All of the symmetry operations of the Pbca space group were found in the P₂₁₂₁ and Pca₂₁ restrained structures with the symmetry agreement factors smaller than 8% (see the Supporting Information). This is an indication that the Pbca symmetry is the appropriate one. Subsequently the same test was performed on the fully released structures. In spite of the distortions of the BD₄ geometry in the structural models with P₂₁₂₁ and Pca₂₁ space groups (see Table 4 and Figure 5 in the Supporting Information), the symmetry operations of the space group Pbca all yield agreement factors lower than 14%, a value that still indicates a strong probability of their presence in the structure. Other symmetry operations compatible with the orthorhombic symmetry yielded agreement factors larger than 40%, showing thus clearly their absence in the structure.

A further check was obtained by a series of ab initio calculations of the electronic contribution to the formation energy of the γ-phase candidates. The normal-mode frequencies calculated for all of the structural models are real, indicating their stability at finite temperatures. The optimization of structural parameters of the P₂₁₂₁ and Pca₂₁ structural models resulted in Pbca symmetry with negligible energy differences of ~3 meV/f.u. dictated by the accuracy of the calculations. This corroborates the experimental results by emphasizing that almost no difference has to be expected for this structure, whatever P₂₁₂₁, Pca₂₁, or Pbca symmetry is used for its representation.

We propose the structural candidate with the Pnca space group presented in Table 1 to be the final model. Our choice is based on the higher symmetry of the space group Pnca, the more regular refined BD₄ tetrahedra with appropriate B–D and D–D interatomic distances in this symmetry, and both experimental and theoretical strong indications that the Pbca symmetry is embedded in the lower-symmetry structural candidates.

By comparison with previous displacement parameters reported in the literature, we propose the structural candidate with the Pbca space group presented in Table 1 to be the final model. Our choice is based on the higher symmetry of the space group Pbca, the more regular refined BD₄ tetrahedra with appropriate B–D and D–D interatomic distances in this symmetry, and both experimental and theoretical strong indications that the Pbca symmetry is embedded in the lower-symmetry structural candidates.
The calculated free energy difference between $\gamma$-phase is within 0.13 eV/f.u. at room temperature (see Figure 4), this brackets the upper boundary of the interphase energy difference between the phases, and it is compatible with the ground state of Ca(BD$_4$)$_2$) and the $\gamma$-phase (discussed below) reduces further the free energy of the $\gamma$-phase. This is emphasized for Ca(BD$_4$)$_2$ by the decrease of the $\gamma$-diffraction peak measured at room temperature after heating at 440 K in Figure 3a and at 440 K in Figure 3b, the decreasing of the $\gamma$-diffraction peak, while the $\gamma$-phase the highest.

Stepwise heating of the sample shows that the $\alpha$-phase starts to transform to the $\beta$-phase at a slightly lower temperature than the $\gamma$-phase. This is emphasized for Ca(BD$_4$)$_2$ by the decrease of the $\alpha$ diffraction peak measured at room temperature after subsequent heating at 440 and 490 K in Figure 3d, while the $\gamma$ diffraction peak remains unchanged. The same behavior was observed for Ca(BD$_4$)$_2$ + MgD$_2$ in Figure 3a, where at 440 K the decreasing of the $\alpha$ diffraction peak corresponds to an increase of the $\beta$ diffraction peak, while the $\gamma$ diffraction peak remains unchanged. For Ca(BD$_4$)$_2$ + MgD$_2$, as can be seen by comparing the diffraction data at 440 K in Figure 3a and at room temperature after heating at 440 K in Figure 3b, the $\alpha$-phase reversibly transforms to the $\beta$-phase in a narrow

### Table 2: Comparison of Selected Interatomic Distance Ranges of BD$_4$ Tetrahedra and Ca–BD$_4$ Octahedra, for the Three Phases of Ca(BD$_4$)$_2$

<table>
<thead>
<tr>
<th>phase</th>
<th>$T$ (K)</th>
<th>B–D (Å)/Δ (%)</th>
<th>Ca–B (Å)/Δ (%)</th>
<th>B–B (Å)/Δ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{12}$</td>
<td>300</td>
<td>1.164(11)−1.174(11)/0.9</td>
<td>2.885(8)−2.901(1)/0.6</td>
<td>3.807(7)−4.442(2)/14.3</td>
</tr>
<tr>
<td>$\alpha_{3}^{b}$</td>
<td>300</td>
<td>1.107(30)−1.124(37)/1.5</td>
<td>2.905(2)−2.982(23)/2.6</td>
<td>3.798(6)−4.437(5)/14.4</td>
</tr>
<tr>
<td>$\alpha_{3}^{c}$</td>
<td>300</td>
<td>1.071(17)−1.123(17)/4.6</td>
<td>2.900(1)−2.921(10)/0.7</td>
<td>3.799(3)−4.439(2)/14.4</td>
</tr>
<tr>
<td>$\alpha_{3}^{d}$</td>
<td>300</td>
<td>1.229−1.240/0.9</td>
<td>2.910−2.914/0.1</td>
<td>3.822−4.474/14.6</td>
</tr>
<tr>
<td>$\beta_{12}$</td>
<td>480</td>
<td>1.02(3)−1.16(3)/12.1</td>
<td>2.930(9)−2.957(14)/0.9</td>
<td>3.91(2)−4.366(1)/10.4</td>
</tr>
<tr>
<td>$\beta_{5}$</td>
<td>300</td>
<td>0.96(3)−1.40(6)/35.1</td>
<td>2.90(2)−2.950(14)/1.7</td>
<td>3.88(2)−4.373(3)/11.2</td>
</tr>
<tr>
<td>$\beta_{5}^{12}$</td>
<td>300</td>
<td>1.217−1.227/0.8</td>
<td>2.797−2.869/2.5</td>
<td>3.794−4.303/11.8</td>
</tr>
<tr>
<td>$\gamma_{1}^{c}$</td>
<td>300</td>
<td>1.06(3)−1.24(3)/14.5</td>
<td>2.861(13)−2.972(16)/3.7</td>
<td>3.82(2)−4.618(19)/17.3</td>
</tr>
<tr>
<td>$\gamma_{1}^{d}$</td>
<td>300</td>
<td>1.17(3)−1.33(3)/12.0</td>
<td>2.769−2.921/5.2</td>
<td>3.748−4.509/16.9</td>
</tr>
</tbody>
</table>

$^a$ The difference between the two extreme values of each considered range $\Delta$ (%) is indicated. $^b$ Ca(BH$_4$)$_2$ sample. $^c$ This work ($\alpha$- and $\beta$-phases only indicative due to their little weight fraction in the studied samples). $^d$ Calculated. $^e$ Interatomic distance of the two unequivalent BD$_4$ tetrahedra in the structure.

### Table 3: Unit Cell Volume and Density of the $\alpha$-, $\beta$-, and $\gamma$-Phases of Ca(BD$_4$)$_2$

<table>
<thead>
<tr>
<th>sample</th>
<th>$T$ (K)</th>
<th>$V_o/\rho_o$ [Å$^3$/g/cm$^3$]</th>
<th>$V_f/\rho_f$ [Å$^3$/g/cm$^3$]</th>
<th>$V_{\gamma}/\rho_{\gamma}$ [Å$^3$/g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(BD$_4$)$_2$</td>
<td>300</td>
<td>857.1(1)/1.2060(1)</td>
<td>206.36(2)/1.2523(1)</td>
<td>822.7(1)/1.2565(2)</td>
</tr>
<tr>
<td>Ca(BD$_4$)$_2$ + MgD$_2$</td>
<td>300</td>
<td>855.0(1)/1.2090(1)</td>
<td>210.69(1)/1.2266(1)</td>
<td>824.1(5)/1.2544(8)</td>
</tr>
<tr>
<td>Ca(BD$_4$)$_2$ + MgD$_2$</td>
<td>480</td>
<td></td>
<td>850.9(9)/1.215(1)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Only Ca(11BD$_4$)$_2$ is considered, with the atomic mass of natural boron.
temperature range roughly between 410 and 470 K (unfortunately the same behavior could hardly be seen in the data measured on the pure Ca(BD₄)₂ sample). Above \( \sim 470 \) K (see Figure 3a), the \( \beta \)-phase becomes metastable upon cooling; i.e., when the sample is cooled down to room temperature after heating, only a part of the \( \beta \)-phase is transformed back to the energetically more favorable \( \gamma \)-phase. Above \( \sim 530 \) K, \( \gamma \)- and \( \beta \)-phases are transformed into the \( \beta \)-phase. For pure Ca(BD₄)₂, the same phase transition of the \( \gamma \)- and \( \beta \)-phases into the \( \beta \)-phase is observed up to \( \sim 590 \) K, where the whole sample is transformed into the \( \beta \)-phase. By contrast to the sample synthesized by mechanochemical reaction, the metastable \( \beta \)-phase transforms only very slowly to the \( \gamma \)-phase upon cooling. This is illustrated in Figure 3e for diffraction data of Ca(BD₄)₂ heated to 620 K and subsequently cooled down to 300 K. Immediately after having reached 300 K (the cooling rate is 0.5 K/min), no diffraction peak from the \( \gamma \)-phase could be observed; however, subsequently keeping the sample at 300 K for 1 h allowed a tiny peak corresponding to the \( \gamma \)-phase to be measured.

In first approximation (configurational entropy is not included in the quasiharmonic approach), calculations of the free energy of the phases draw partly a different equilibrium thermodynamic picture than experimentally observed. That is for temperatures below the decomposition of Ca(BD₄)₂ the \( \gamma \)-phase has the lowest free energy and the \( \beta \)-phase the highest. However, in Figure 4, the plots of the difference of the quasiharmonic free energy with respect to the \( \gamma \)-phase indicate that, with increasing temperature,
the $\beta$-phase becomes more stable with respect to the $\alpha$-phase, while the $\gamma$-phase becomes less stable with respect to the $\alpha$-phase. A direct consequence of this result is that the $\gamma$-phase is metastable at any temperature below the decomposition temperature of Ca(BD$_4$)$_2$.

For further discussion of the phase transitions, we consider the Helmholtz free energy $F$, expressed as

$$ F = U - TS $$

where $U$ is the internal energy of the system and $T$ is the temperature. The entropy $S$ can be divided into harmonic $S_h(\omega)$, anharmonic $S_a(\omega,T)$, and configurational $S_c(\xi,T)$ contributions:

$$ S = S_h(\omega) + S_a(\omega,T) + S_c(\xi,T) $$

One has to keep in mind that the quasiharmonic approach considers only the harmonic term of the entropy $S_h(\omega)$; the terms accounting for anharmonicities $S_a(\omega,T)$ and configurational $S_c(\xi,T)$ are not taken into account.

As recently reported for LiBH$_4$ and LiBD$_4$, DFT calculations in the quasiharmonic approximation can quantitatively describe the structure of light complex hydrides, provided that a significant disorder is involved (i.e., negligible $S_a(\omega,T)$ and $S_c(\xi,T)$ terms). For the $\alpha$-phase, the distortion of the BD$_4$ groups (see Table 4 in the Supporting Information) is comparable with previously reported calculations for the BD$_4$ groups in LiBD$_4$. This indicates that in the $\alpha$-phase the $S_a(\omega,T)$ and $S_c(\xi,T)$ terms are expected to be small, in agreement with the small displacement parameters reported for this phase at room temperature. Unlike calculated regular BD$_4$ geometry (see Table 4 in the Supporting Information), distortions of the BD$_4$ groups are reported experimentally for the $\gamma$-phase and $\beta$-phase (combined X-ray and neutron Rietveld refinement of models without any geometrical restraints). For the $\gamma$-phase, the larger distortions of the BD$_4$ groups reported experimentally in the present work suggest a larger nonharmonic part of entropy $S_a(\omega,T)$ than for the $\alpha$-phase. The anharmonic part results from anharmonicities of the local potential for the BD$_4$ groups. However, no significant disorder is expected in this phase, since the atomic displacement parameters of the hydrogen atoms are comparable with the ones of the $\alpha$-phase. Therefore, for the $\gamma$-phase, the configurational entropy $S_c(\xi,T)$ is likely to be negligible. The large atomic displacement parameters of the hydrogen atoms in the $\beta$-phase suggest possible disorder of the BH$_4$ orientations. For this phase, neglecting the $S_c(\xi,T)$ term (i.e., configurational entropy) may result in a significant underestimation of the entropy contribution, preventing any quantitative thermodynamical analysis involving the $\beta$-phase. Nevertheless, all phases can be qualitatively described in quasiharmonic approximation, and the description will underestimate the entropy of the $\gamma$-phase and especially the $\beta$-phase.

Accounting for the anharmonic and configurational terms will shift the free energy of the $\beta$-phase to lower values. This indicates that, upon heating, the trend (see Figure 4) between phase stabilities seen by quasiharmonic results will be enhanced, and the $\beta$-phase may eventually become more stable than the $\alpha$-phase. This would be in good agreement with the phase transition observed from the $\alpha$-phase to the $\beta$-phase. On the other hand, the free energy of $\gamma$- and $\beta$-phases may equalize upon heating (corresponding to the crossing of the two difference plots in Figure 4). This suggests that, at a certain temperature, the relative stability between the $\gamma$- and $\beta$-phases may swap, and the $\gamma$-phase becomes the least stable of the three phases. This last result explains that, once the sample is heated above the temperature of the $\gamma-\beta$ phase transition, the $\gamma$-phase never appears again upon cooling. Finally, it has to be mentioned that the time-scale difference observed for the kinetics of the $\beta-\alpha$ phase transition upon cooling between the two samples may be due to the different barriers between the energy levels of the $\alpha$-phase and $\beta$-phase. It is at the moment not possible for us to conclude if this is due to the presence of MgD$_2$ or Mg$_2$CaD$_4$ in the sample synthesized by mechnochemical reaction or if this is related to particle size effects. Kinetics effects associated to energy barriers between the metastable $\gamma$-phase and the $\alpha$- and $\beta$-phases are also likely to be responsible for the $\alpha-\beta$ phase transition occurring at a lower temperature than the $\gamma-\beta$ phase transition.

**IV. Conclusion**

We report on the solution and refinement of the orthorhombic $\gamma$-phase crystal structure of Ca(BD$_4$)$_2$ in the Pbca symmetry, determined by combined X-ray and neutron diffraction, and supported by ab initio calculations. Diffraction data were measured on a Ca(BD$_4$)$_2$ sample synthesized by the wet chemical method where the orthorhombic $\gamma$-phase is predominant. Five structural model candidates have been identified (in P2$_1$2$_1$2$_1$ symmetry, three distinct projections of the Pca2$_1$ symmetry, and Pbca symmetry) all equivalently fitting both neutron and X-ray diffraction data. All five structural models were found very similar; quantiative tests of the true symmetry of the low-symmetry models revealed that all structural models were very close to the symmetry Pbca, and therefore, the refinement in Pbca was considered to be the most appropriate one. Moreover, the structural model in space group Pbca is among the candidates the one exhibiting the most appropriate size and geometry of the BD$_4$ tetrahedra.

The free energy difference of the three phases calculated within DFT quasiharmonic formalism is of the order of $\sim 0.13$ eV/f.u. at room temperature, which is compatible with the observed phase coexistence (the $\alpha$-phase is the ground state, and the $\beta$-phase the highest energy state). The temperature-dependent free energy of the $\alpha$, $\beta$, and $\gamma$-phases was presented together with the coexistence and phase transitions of the $\alpha$, $\beta$, and $\gamma$-phases monitored at selected temperature steps by X-ray diffraction in a temperature range of 300 K $< T < 620$ K. Ca(BD$_4$)$_2$ + MgD$_2$ synthesized by solid-gas mechnochemical reaction and pure Ca(BD$_4$)$_2$ synthesized by the wet chemical method were investigated, since they exhibit a different kinetics of the phase transitions. Considering that configurational entropy is neglected, the thermodynamic picture obtained from the calculation of free energies is limited to trends on relative stabilities of the structural phases. According to ab initio calculations, with increasing temperature, the $\beta$-phase becomes more stable with respect to the $\alpha$-phase. By contrast, with increasing temperature, the $\gamma$-phase is predicted to become less stable with respect to the $\alpha$-phase. This trend provides insight on the—experimentally observed—metastability of the $\gamma$-phase, which is moreover never the most favorable structure (i.e., with the lowest free energy among the three phases) at any temperature. The observed phase coexistence also indicates the first order transformation between phases, where nonharmonic effects are crucial. The $\gamma$-phase is most probably stabilized by an energy barrier between the $\gamma$-phase and $\beta$-phase free energy levels. This barrier is possibly responsible also for the apparently kinetically hindered $\gamma-\beta$ phase transition occurring at a slightly higher temperature than the $\alpha-\beta$ phase transition. A more quantitative
theoretical study of the coexistence and phase transitions of the α-, β-, and γ-phases should in the future account for nonharmonic effects, in particular for the β-phase.

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Supporting Information Available: Description of the data collection, Rietveld refinement of the final structural model in Pbca symmetry, deviation of the low-symmetry models from Pbca symmetry, and calculations with Superflip; table showing a summary of the Rietveld refinement results of the structural model candidates; and figure showing refined Ca(BD₄)₂ γ-phase structural models and calculated structure in Pbca symmetry viewed in the (010) plane.

References and Notes

(2) Züttel, A.; Borgschulte, A.; Orimo, S. Scr. Mater. 2007, 56, 823.
(40) The symmetry agreement factor is based on a comparison between the tested density and its image obtained by transforming it by the selected symmetry operation. Similar to the R-values, the agreement factor is constructed so that a value of 0 corresponds to a perfectly symmetrical density. A value of 100% corresponds to a random density. Agreement factors smaller than ~10% reflect a very good agreement with the tested symmetry operation. Higher agreement factors but smaller than ~20% still indicate a high probability that the structure really contains the tested symmetry operation.