Cation Size and Anion Anisotropy in Structural Chemistry of Metal Borohydrides: The Peculiar Pressure Evolution of RbBH₄

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The pressure evolution of RbBH₄ has been characterized by synchrotron powder X-ray diffraction and Raman spectroscopy up to 23 GPa. Diffraction experiments at ambient temperature reveal three phase transitions, at 3.0, 10.4, and 18 GPa (at 2.6, 7.8, and ~20 GPa from Raman data), at which the space group symmetry changes in the order Fm-3m(6-4) → P4/nmm(2) → C222(1) → I-42m(4). Crystal structures and equations of state are reported for all four phases. The three high-pressure structure types are new in the crystal chemistry of borohydrides. RbBH₄ polymorphs reveal high coordination numbers (CNs) for cation and anion sites, increasing with pressure from 6 to 8, via an intermediate 4 + 4 coordination. Different arrangements of the tetrahedral BH₄ group in the Rb environment define the crystal symmetries of the RbBH₄ polymorphs. The structural evolution in the MBH₄ series is determined by the cation’s size, as it differs drastically for M = Li (CNs = 4, 6), Na (CN = 6), and Rb. Only the structure common to the whole MBH₄ family is the cubic one. Its bulk modulus linearly decreases as the ionic radius of M increases, indicating that the compressibility of the material is mainly determined by the repulsive BH₄...BH₄ interactions.

Introduction

Owing to their high gravimetric hydrogen density, metal borohydrides are seen as promising materials for energy storage. Some borohydrides desorb a large quantity of hydrogen (up to 20.8%), although the decomposition temperatures are usually high. The search for better hydrogen storage materials, with denser structures and lower binding energies, has been hampered by a lack of basic knowledge about their structural properties. However, the past few years have seen a remarkably rapid evolution of this field, and a large number of experimental and theoretical studies have recently been carried out, as summarized in several very recent reviews on crystal structures, physical properties, and phase relations in borohydrides at different P–T conditions. These experimental investigations have already revealed a surprising multitude of novel and unexpected structural phases, most of which were not predicted by calculations. The structural phases and phase diagrams of the most important light hydrides LiBH₄, NaBH₄, and the related NH₃BH₄ have already been experimentally identified and mapped. For heavier borohydrides, KBH₄ and RbBH₄, the high-pressure studies have just begun.

In the present paper we report a synchrotron X-ray diffraction study of the structural evolution of RbBH₄ under pressure at room temperature. In the range up to 23 GPa, four different structural phases are found, with transition pressures of about 3.0, 10.4, and 18 GPa. The phase transitions have also been observed by in situ Raman scattering experiments under pressure. The space group symmetry...
changes in the order $\text{Fm}-3m \rightarrow \text{P}4/\text{mm} \rightarrow \text{C}2\text{2}2 \rightarrow \text{I}-4\text{2}m$; none of the three high-pressure structure types have been observed or predicted earlier for the borohydrides. We propose that the structural properties of borohydrides are determined by the size of the alkali metal ions, and the different arrangements of the tetrahedral BH$_4$ group in the metal atom environment define the crystal symmetries of the high-pressure polymorphs. In addition to structural data, we also present experimental results for the bulk compressibility and for the individual Grüneisen parameters of the Raman-active phonon modes.

**Experimental Section**

**Synthesis.** RbBH$_4$ was prepared as previously reported by the reaction of RbOH with NaBH$_4$ in cold (ca. $-10^\circ$C) methanol. RbOH is first dissolved in CH$_3$OH and the solution is cooled. A second flask containing CH$_3$OH is precooled using a salt–ice mixture; then 1.05 equiv of NaBH$_4$ is dissolved in the cold CH$_3$OH. The two cold solutions are mixed, and the precipitate is filtered off and dried under vacuum.

The pure deuterides can also be prepared using this method, using RbOD, NaBD$_4$, and CH$_3$OD. The use of RbOH and CH$_3$OH in conjunction with NaBD$_4$ leads to the formation of some RbBD$_3$H. Thus, a mixed RbBD$_4$/RbBD$_3$H sample was obtained with three intensity-dependent parameters. The refinement was modeled as a uniaxial microstrain along [111]. Some anisotropic peak broadening developing at higher pressures was modeled by one parameter (March’s function), which appears to be nearly pressure-independent, at a value of $0.8$. Similar to the NaBH$_4$ phases, the cubic RbBH$_4$ was assumed by the analogy to the well-established structure of NaBH$_4$. The position of the H atom was fixed, and two atomic displacement parameters (for Rb and BH$_4$) were refined. Similar to the NaBH$_4$ phases, the cubic RbBH$_4$ in a DAC reveals a pronounced preferred orientation (PO). The PO along the [100] direction was modeled by one parameter (March’s function), which appears to be nearly pressure-independent, at a value of $0.8$. Some anisotropic peak broadening developing at higher pressures was modeled as a uniaxial microstrain along [111] using one refined parameter. In total, 16 reflections were fitted with three intensity-dependent parameters. The refinement with the help of Fullprof software converged at $R_B = 4.9\%$, $R_p = 3.6\%$, $R_{wp} = 0.41\%$, $R_{wp} = 0.72\%$ (not corrected for background), and $R_p = 8.7\%$, $R_{wp} = 6.4\%$ (conventional).

**Results and Discussion**

**A. Crystal Structures of RbBH$_4$ Polymorphs.** Atomic and cell parameters for the four RbBH$_4$ polymorphs are listed in Table 1. The Rietveld refinement profiles are shown in the Supporting Information (Figure S3).

**Fm-3m Phase.** The crystal structure of the ambient-pressure phase is cubic, space group $\text{Fm}-3m$ with 4 formula units in the unit cell. It has a NaCl-type arrangement of Rb cations and BH$_4$ anions, where the latter are orientationally disordered over the two positions around the inversion center. The disordered centrosymmetric structure for the cubic RbBH$_4$ was assumed by the analogy to the well-established structure of NaBH$_4$. The position of the H atom was fixed, and two atomic displacement parameters (for Rb and BH$_4$) were refined. Similar to the NaBH$_4$ phases, the cubic RbBH$_4$ in a DAC reveals a pronounced preferred orientation (PO). The PO along the [100] direction was modeled by one parameter (March’s function), which appears to be nearly pressure-independent, at a value of $0.8$. Some anisotropic peak broadening developing at higher pressures was modeled as a uniaxial microstrain along [111] using one refined parameter. In total, 16 reflections were fitted with three intensity-dependent parameters. The refinement with the help of Fullprof software converged at $R_B = 4.9\%$, $R_p = 3.6\%$, $R_{wp} = 0.41\%$, $R_{wp} = 0.72\%$ (not corrected for background), and $R_p = 8.7\%$, $R_{wp} = 6.4\%$ (conventional).

**Table 1.** Rietveld-Refined Structural Parameters for the RbBH$_4$ Polymorphs Obtained in the High-Pressure Diffraction Experiments at Room Temperature

<table>
<thead>
<tr>
<th>structure</th>
<th>atom</th>
<th>Wyckoff site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B, Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fm}-3m$, $Z = 4$</td>
<td>Rb</td>
<td>4$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.80(3)</td>
</tr>
<tr>
<td>$a = 6.96330(7)$ Å at 0.5 GPa</td>
<td>B</td>
<td>4$b$</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>7.3(3)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>32f (occ. 1/2)</td>
<td>0.410</td>
<td>x</td>
<td>x</td>
<td>9.3(3)</td>
</tr>
<tr>
<td>$\text{P}4/\text{mm}$ (choice 2), $Z = 2$</td>
<td>Rb</td>
<td>2$c$</td>
<td>1/4</td>
<td>1/4</td>
<td>0.34634(2)</td>
<td>2.69(3)</td>
</tr>
<tr>
<td>$a = 5.61216(13)$ Å</td>
<td>B</td>
<td>2$a$</td>
<td>1/4</td>
<td>3/4</td>
<td>0</td>
<td>6.0(3)</td>
</tr>
<tr>
<td>$b = 4.08873(14)$ Å at 5.5 GPa</td>
<td>H</td>
<td>8$i$</td>
<td>0.427</td>
<td>3/4</td>
<td>0.174</td>
<td>8.0(3)</td>
</tr>
<tr>
<td>$\text{C}2\text{2}2$, $Z = 2$</td>
<td>Rb</td>
<td>2$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.0(2)</td>
</tr>
<tr>
<td>$a = 5.3679(6)$, $b = 5.1343(14)$</td>
<td>B</td>
<td>2$c$</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>4.0(5)</td>
</tr>
<tr>
<td>$c = 3.9098(3)$ Å at 16.1 GPa</td>
<td>H</td>
<td>8$f$</td>
<td>0.380</td>
<td>0.121</td>
<td>0.327</td>
<td>6.0(5)</td>
</tr>
<tr>
<td>$\text{I}-4\text{2}m$, $Z = 4$</td>
<td>Rb</td>
<td>4$c$</td>
<td>0</td>
<td>0</td>
<td>0.239(4)</td>
<td>2.11(4)</td>
</tr>
<tr>
<td>$a = 5.0057(7)$</td>
<td>B</td>
<td>4$c$</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>2.4(4)</td>
</tr>
<tr>
<td>$c = 7.8161(13)$ Å at 23.5 GPa</td>
<td>H</td>
<td>16$j$</td>
<td>0.125</td>
<td>0.375</td>
<td>0.080</td>
<td>4.4(4)</td>
</tr>
</tbody>
</table>

$^a$Positions of hydrogen atoms were not refined.
**P4/nmm Phase.** A transition from the cubic to a new high-pressure phase starts at 3 GPa and completes at 3.4 GPa. First 16 diffraction peaks were indexed by Dicvol23 in a primitive tetragonal cell with a volume slightly over one-half that of the cubic structure. Analysis of systematic absences using the program ChekCell24 suggested two possible space groups: P4/n and P4/nmm. A database search suggested that this phase may be an antitype (positions of cation and anion are interchanged) of NH4Br.25 A good fit to the data confirmed this suggestion. Thus, the position of the hydrogen atom was assumed by the similarity to the NH4Br structure. A small PO along [001] was modeled by one refined parameter, which converged to 0.9635(14) at 5.5 GPa; its value is systematically smaller than 1 on compression and larger than 1 on decompression. In total, 38 reflections were fitted with four intensity-dependent parameters, including one coordinate parameter. The refinement converged at $R_B = 4.0\%$, $R_F = 3.9\%$, $R_p = 0.36\%$, $R_{wp} = 0.51\%$ (not corrected for background), and $R_p = 7.8\%$, $R_{wp} = 5.5\%$ (conventional).

**C222 Phase.** Above 10.4 GPa the P4/nmm phase starts to transform into a new phase, and this transformation completes at ~12.2 GPa. Thirteen peak positions were extracted from a data set collected at 16.1 GPa and indexed by Dicvol23 in a monoclinic cell. Although its unit cell volume allowed only one RbBH4 unit per unit cell, the structure could not be solved in any of the possible monoclinic space groups. Therefore, similar to the case of the high-pressure structure of LiBH4,6 we attempted a structure solution in the space group Cmcm. Rb and B atoms were reliably located in the special positions. The resulting atomic arrangement represents an orthorhombically distorted CsCl-type structure, and to the best of our knowledge it has no analogues, at least none that may suggest possible positions of hydrogen atoms. Our analysis shows that a fully ordered RbBH4 group can be accommodated in two subgroups of Cmcm: in Cmcm2, where nearly linear B−H···Rb fragments lead to unlikely short H···Rb contacts; and in C222, where Rb···H and H···H distances can be kept sufficiently long. Thus, we finally assumed the ordered C222 model for this phase. In the final refinement, a strong PO along [010] was modeled by one refined parameter, which converged to 1.542(10). In total, 33 reflections were fitted with five intensity-dependent parameters, including three anisotropic displacement factors for the Rb atom, yielding a reasonable displacement ellipsoid ($B_{11} = 2.42(12)$, $B_{22} = 4.75$, $B_{33} = 1.76(11)\ \AA^2$). The refinement converged at $R_B = 5.8\%$, $R_F = 5.2\%$, $R_p = 0.67\%$, $R_{wp} = 1.05\%$ (not corrected for background), and $R_p = 13.7\%$, $R_{wp} = 10.9\%$ (conventional).

**I-42m Phase.** First traces of yet another phase appear at ~17 GPa. The transition is not fully completed even at the highest pressure achieved in our experiment. However, the six most pronounced peaks were unambiguously indexed in a body-centered tetragonal cell, suggesting four RbBH4 units per unit cell. Metrically, this tetragonal structure is closely related to the C222 one, with the $a$ and $b$ parameters of the latter becoming equal and the $c$ parameter doubled. Similar to the C222 phase, the new structure also roughly resembles the CsCl-type, but a closer analysis was required to reveal a more detailed picture. The superstructure peaks 101 and 103 can be clearly observed, and they cannot be modeled in the space groups containing 4 or 4 axes: these peaks indicate a corrugated distortion of the CsCl-type, which involves a displacement of the heavy atom (Rb) along the c axis. Such displacement can be accommodated in the space group I4 and its supergroups. A good fit to the experimental data was accomplished in the space groups I4/m2 and I4/m, where the latter allows longer Rb···H distances for the ordered BH4 group. To our knowledge, this structure, like the C222 one, represents a new structure type derived from the CsCl type. A I-42m structural model well approximating the experimental data was first created in FOX26 and then refined by the Rietveld method. A PO along [100], very similar to the one in the C222 phase, was modeled by one refined parameter, which converged to 1.576(14). In total, 36 reflections were fitted with four intensity-dependent parameters, including one coordinate parameter. For the two-phase samples containing C222 and I-42m phases the atomic displacement factors for the identical atom types were constrained to be the same, thus reducing the number of parameters intrinsic to the I-42m phase to two. For the sample containing ~50% of the I-42m phase (23.5 GPa), the refinement converged at $R_B = 8.3\%$, $R_F = 6.3\%$, $R_p = 0.57\%$, $R_{wp} = 0.80\%$ (not corrected for background), and $R_p = 12.0\%$, $R_{wp} = 9.9\%$ (conventional).

**B. Pressure Evolution of the Unit Cell Dimensions.** We find three phase transitions at 3.0, 10.4, and 18 GPa, all of them of first order. Two decompression experiments showed that the first two transitions are reversible. The decompression experiment was not made for the highest pressure I-42m phase. However, since the last transition is not reconstructive, we expect it also to be reversible. The ambient-pressure Fm-3m polymorph transforms into the new P4/nmm phase with a remarkable volume collapse of 8.8% and with a small hysteresis of ~0.4 GPa. Interestingly, in a narrow pressure range, starting just below the cubic-to-tetragonal transition, we observed additional diffraction lines which do not originate from the Fm-3m and P4/nmm phases. These peaks show a maximum intensity at ~2.75 GPa ($d$-spacings: 4.015, 3.877, 2.327, and 1.996 Å). However, they always coexist with peaks of the Fm-3m or the P4/nmm phases or from both phases. Taking into account that the space group symmetry change $Fm-3m$ (number of formula units per primitive cell $Z_p = 1$) → $P4/nmm$ ($Z_p = 2$) breaks the group–subgroup relationship, this observation might be explained by the onset of an intermediate (possibly metastable) phase, which emerges during this reconstructive transition accompanied by the big volume drop.

The experimental unit cell volumes were fitted with the Murnaghan equation of state (EOS), yielding molecular volumes at zero pressure and the bulk moduli

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The pressure variation of the volume of the RbBH$_4$ formula unit at ambient temperature. The symbols represent experimental data for four different phases obtained in three independent experiments; the lines are the best fits to the Murnaghan equation of state.

(Their pressure derivatives $B'_0$ were fixed at 3.5). Figure 1 includes all reliable data points measured in three independent experiments; only the data obtained during the compression were used for the calculation of EOS.

The two transitions at higher pressures manifest small volume contractions: ~2.2% for the $P4/nmm \rightarrow C222$ transition at 10.4 GPa and ~1.1% for the $C222 \rightarrow I-42m$ transition. The latter transformation starts at ~18 GPa and is not fully accomplished until at the highest pressure achieved in our experiment: at a pressure of 23.5 GPa, about 48% of the $C222$ phase remained. Heating the sample in the DAC at 20 GPa to 100 °C and cooling to room temperature still did not produce pure $I-42m$ phase.

Compressibilities of the high-pressure phases of RbBH$_4$ are anisotropic: the $c/a$ ratio for the $P4/nmm$ phase increases linearly with pressure, from 0.7267 at 3.0 GPa to 0.7337 at 10.4 GPa. The compressibility of the $C222$ phase is even more anisotropic: along the $b$ axis the structure is nearly twice more compressible than along $a$ and $c$. However, the variation of the axial ratios from the $P4/nmm$ to the $C222$ phase is practically continuous (see Figure S4 in the Supporting Information). Some discontinuity appears on the $C222 \rightarrow I-42m$ transition: the $a$ parameter of the $I-42m$ structure is slightly smaller than the average of the $a$ and $b$ of the pseudotetragonal $C222$, while the doubled $c$ axis is slightly larger than 2$e$ of the $C222$ phase. Thus, the axial ratio for the RbBH$_4$ phases increases with pressure from 0.707 to 0.780 (Figure S4), moving away from the 1/$\sqrt{2} = 0.707$ value for the ideal NaCl and CsCl-type structures.

Table 2 lists EOS data for the alkali metal borohydrides from the literature and from the present work. Note that the true bulk modulus determined from an inelastic scattering study of the acoustic phonon dispersions is lower than the ones from high-pressure experiments in DACs.$^{21}$ The packing efficiencies of various structures are closely related with their compressibilities: for each system, a larger volume drop at a transition results in a proportional decrease in compressibility (the inverse of the bulk modulus). Among all the borohydrides, RbBH$_4$ has the largest number of pressure-driven phase transitions. The only structure common to the whole MBH$_4$ family is the cubic one (note that the $Pmna$ structure is slightly smaller than the average of the different phases obtained in three independent experiments; the lines are the best fits to the Murnaghan equation of state.

Table 2. Experimental Equation of State Parameters for Alkali Metal Borohydrides at Room Temperature

<table>
<thead>
<tr>
<th>compound</th>
<th>phase</th>
<th>$V_0$ [Å$^3$]</th>
<th>$B_0$ [GPa]</th>
<th>$B'_0$ [GPa]</th>
<th>method</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH$_4$</td>
<td>$Pmna$</td>
<td>54.43(8)</td>
<td>14.4(5)</td>
<td>3.5 (fixed)</td>
<td>XRD</td>
<td>6</td>
</tr>
<tr>
<td>$Amma_2$</td>
<td>49.49(13)</td>
<td>23.23(9)</td>
<td>3.51(15)</td>
<td>XRD</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>$Fm-3n$</td>
<td>47.3(9)</td>
<td>26(3)</td>
<td>3.5 (fixed)</td>
<td>XRD</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>$Fm-3n$</td>
<td>58.3(2)</td>
<td>19(1)</td>
<td>3.1(3)</td>
<td>XRD</td>
<td>21</td>
</tr>
<tr>
<td>KBH$_4$</td>
<td>$Fm-3n$</td>
<td>31(1)</td>
<td>3.9 (fixed)</td>
<td>XRD</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>RbBH$_4$</td>
<td>$Fm-3n$</td>
<td>87.7(2)</td>
<td>14.9(4)</td>
<td>3.5 (fixed)</td>
<td>XRD</td>
<td>this work</td>
</tr>
<tr>
<td>$P4/nmm$</td>
<td>16.8(4)</td>
<td>4 (fixed)</td>
<td>XRD</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C222$</td>
<td>73.2(18)</td>
<td>29(4)</td>
<td>3.5 (fixed)</td>
<td>XRD</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>$I-42m$</td>
<td>72</td>
<td>30</td>
<td>3.5 (fixed)</td>
<td>XRD</td>
<td>this work</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Dependence of the compressibility (inverse of the experimental bulk modulus) of the cubic MBH$_4$ phases versus the ionic radius of M (the radii are taken from ref 28 for CN = 6). The experimental uncertainties are depicted as error bars.

The ambient-pressure cubic phase is isostuctural to NaBH$_4$, where the BH$_4$ group is disordered over two positions.$^{20}$ Its partial ordering at low temperature was detected at 44 K.$^{29}$ without a reconstruction or a change of the atomic coordination numbers (CN).$^{30}$ The high-pressure structures are ordered, at least regarding the positions of the Rb and B atoms. Although hydrogen atoms cannot be

directly detected from synchrotron X-ray diffraction data in the presence of much heavier Rb, they can be located as a part of the rigid tetrahedral BH₄ group. The latter possibility is based on the tetrahedral geometry of the BH₄ group found in light metal borohydrides by accurate single-crystal X-ray diffraction.²⁸⁻³⁴ Despite an earlier controversy, it was concluded² that except for a few specific cases the BH₄ group has a nearly ideal tetrahedral geometry. This geometrical constraint, combined with the high point group symmetries of the BH₄ sites, allowed the location of the H atoms in the high-pressure RbBH₄ phases.

All four RbBH₄ phases have very simple crystal structures, each containing a single Rb, B, and H position (see Table 1). The P₄/nmm phase is an antitype to ammonium and phosphonium bromides and iodides,²⁵ while the C222 and I-42m phases represent two new structure types, which are the deformation variants of the cubic CsCl-type structure. As expected, the refined atomic displacement factors (Table 1) decrease at higher pressures, thus supporting our structural determinations.

It is interesting that the high-pressure transitions involve changes of the CN for the cation’s and anion’s sites as well as the changes in the Rb···BH₄ coordination mode. Figure 3 displays the RbBH₄ structures and the coordination polyhedra for the BH₄ group. The octahedral coordination in the ambient-pressure phase gradually transforms to a more or less distorted cubic arrangement at higher pressures. The average Rb···B distances correlate with the change of the CN: upon the first transition, CN goes from 6 to 4 + 4 and the average Rb···B distance increases by ~7% and then smoothly decreases at higher pressures. A combination of different BH₄ coordination modes together with the increase in CN leads to an increase in density by 8.8% at the cubic-to-tetragonal phase transition, in spite of the fact that the average Rb···B distance increases.

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The occurrence of the three different Rb•••BH₄ coordination modes: via a face, an edge, and a vertex of the tetrahedral anion. The BH₄ group acts with respect to the metal atom as a mono-, di-, and trihapto ligand, similar to other borohydrides and their solvates.²³ However, this is the first time that all three coordination modes are found in different polymorphic modifications of the same compound.

The CN for Rb atoms can be defined with respect to the nearest BH₄ sites and with respect to the coordinated hydrogen atoms. As can be seen from Figure 4, the first one changes regularly with increasing pressure in the sequence 6, 4 + 4, 8, 8; the second irregularly, −12, 16, 8, 8. The CNs and coordination modes are closely linked to the corresponding Rb•••B and Rb•••H distances. In the cubic phase, each Rb atom is surrounded by six η²-BH₄ groups at equal distances (η² corresponds to the coordination via a tetrahedral edge). The number of BH₄ neighbors increases to eight in the P4/nmm phase. Due to the change of the BH₄ coordination mode, the corresponding interatomic distances are segregated into four short Rb•••B of 3.05−3.2 Å (12 long Rb•••H of 2.7−3.1 Å) distances for the η²-BH₄ coordination and four long Rb•••B of 3.76−3.95 Å (four short Rb•••H of 2.6−2.7 Å) distances for the η¹-BH₄ coordination (η¹ and η² stand respectively for the coordination via a vertex and a face). The P4/nmm structure is derived from the cubic by shifting the Rb atom and the BH₄ group along the c axis of the resulting tetragonal cell. The z-coordinate for the Rb atom is the only refined coordinate in this structure. The value of z = 1/4 corresponds to the regular Rb₈ octahedra, centered by the BH₄ anion in the initial cubic structure. However, the P4/nmm phase is stable at higher z, which equals 0.34364(2) at 5.5 GPa and slightly increases with pressure. The situation with z = 0.5 would bring the structure to the CsCl type, but this value is not within the observed limits of the structural stability at room temperature. Instead, the C222 and I-42m phases appear with structures closely related to the CsCl type. Thus, the P4/nmm structure is intermediate between the NaCl and CsCl types, and the transitions occur by the mechanism of atomic displacements.

The ideal CsCl-type structure is not met in RbBH₄ owing to the better packing of the anisotropic anions and spherical cations in the distorted structures. The arrangement of the BH₄ group inside the Rb₈ cube, with η¹-BH₄ pointing the B−H bonds toward the midpoint between two Rb atoms, is likely the densest one, as it is practically the same in the higher pressure C222 and I-42m phases (Figure 3). Thus, the observed distortions of the parent CsCl-type structure are the result of an interplay between the ordered BH₄ group and its cubic Rb₈ environment. Different arrangements of the tetrahedral BH₄ group in the Rb environment result in different point group symmetries of the BH₄ anions, namely, −4m2 (D₂h) in the P4/nmm structure and 222 (D₂) in the C222 and I-42m structures, and define the crystal symmetries of the high-pressure RbBH₄ polymorphs. On the contrary, alkali metal halides, containing spherical cations and anions, show the high-symmetry cubic structures at various P−T conditions.²⁶

It is striking that the symmetry and structures of all high-pressure RbBH₄ phases differ from both those predicted theoretically (P-42c or P4/mnm)²⁷ and those (Pmna and P2/c, both with undefined structure) suggested on the basis of diffraction data.²⁸ Our study shows that the structural chemistry of RbBH₄ under pressure is not identical to that of NaBH₄, as originally proposed,²⁷ but differs drastically, revealing higher CNs (8 against 4−6 in LiBH₄²⁹ and 6 in NaN₃meye and peculiar crystal chemistry. Clearly, the larger ionic radius for the metal cation favors higher CNs, and the higher pressure defines more and more dense arrangements of the BH₄ group inside its M-atom environment. Our conclusion that the stable configurations of the BH₄•••M coordination define the crystal chemistry of metal borohydrides finds support in another example, LiBH₄. Even though the bonding between Li and BH₄ is mainly ionic, the directional Li•••BH₄ interaction results in cation−anions layers, which determine the mechanisms of transitions between the polymorphic structures.²⁸,²⁹ The stereochemical role of the anisotropic complex hydride anions has also been pointed out for the lithium amide-borohydride Li₄BN₃H₁₀.³⁰

A note on more covalent metal borohydrides is warranted. The BH₄•••M interaction involving less electropositive metals, such as Mg and Zn, appears covalent, leading to even more directed and stable BH₄•••M configurations. In such cases unexpected structural architectures appear, as doubly interpenetrated 3D frameworks in MZn₃(BH₄)₆ and a porous 3D framework in α-Mg(BH₄)₂.³¹ These structural architectures are common for the coordination polymers involving organic ligands, such as MOFs, but they were only recently observed in metal hydrides. These observations highlight the structure-forming character of the directional BH₄•••M interaction.

D. Raman Spectra. Selected Raman spectra recorded during a compression experiment from a RbBH₄ sample are shown in Figure 5. The evolution of the spectra shows three phase transitions, in agreement with X-ray diffraction data. The first phase transition is observed at around 2.5−2.7 GPa, the second phase transition at 7.5−8.2 GPa, and the third at about 19.7−21.3 GPa. The third transition (C222 → I-42m according to the XRD data) is somewhat less clear from Raman spectra due to an overall broadening of peaks and an unfortunate overlap for the region of bending modes of RbBH₄ with the broad peak from diamond anvils. The pressure dependence of the peak positions for the region up to 11 GPa is shown in Figure 6 and up to 24 GPa in Figure S5 of the Supporting Information.

Above 2000 cm⁻¹, there are strong Fermi resonances between the stretching modes (υ₁ and υ₁) with harmonics and combinations of the deformation modes (2υ₄ and υ₂ + υ₄ and 2υ₃). In particular, the bands observed at 2204 and 2240 cm⁻¹ (at 1.4 GPa) are related to Fermi

References:

resonances of $2\nu_4$ with $\nu_1$ and $\nu_3$. At the first phase transition to the $P4/nmm$ phase, the deformation modes $\nu_3$ and $\nu_4$ shift by about 30 cm$^{-1}$ to lower frequencies, while the stretching modes do not follow this trend. This results in a reduced relative intensity of the two bands relative to $2\nu_4$, and the spectra are dominated by the totally symmetrical stretch $\nu_1$. On the next phase transition (7.8 GPa), this behavior is reversed again and a complex stretching pattern is observed.

In the $P4/nmm$ phase, the borohydride ion is located on a site with $D_{2d}$ symmetry. The site group correlation table (Table 3) indicates that both bending modes $\nu_2$ and $\nu_4$ are expected to split into two components. Analysis of the symmetry of the zone center lattice vibrations (see Supporting Information) reveals no further splitting expected in the Raman spectra, as all the internal vibrations are split into g and u modes. The expected splitting is indeed observed experimentally: at 4.8 GPa, the $\nu_2$ bands are observed at 1229 and 1250 cm$^{-1}$, and the weak $\nu_4$ bands at 1117 and 1127 cm$^{-1}$. In the $C222$ phase (site symmetry $D_{2d}$), the $\nu_3$ and $\nu_4$ modes are expected to split into three components. However, only two components of the $\nu_4$ mode can be observed (at 1153 and 1183 cm$^{-1}$ at 16.8 GPa). In the highest pressure phase ($I-42d$), the site symmetry is also $D_{2d}$, and two bands are similarly observed for $\nu_4$ at 1161 and 1213 cm$^{-1}$ (at 23.7 GPa). The larger splitting suggests a stronger deformation of the BH$_4^-$ ion from the parent $T_d$ symmetry compared to the other polymorphs.

It has been shown that it is possible to relate the value of the totally symmetrical stretching mode ($\nu_1$) of the BD$_4^-$ ion to the B–D bond length using Badger’s rule in the cubic alkali borodeuterides. Recently, Racu et al. showed that Badger’s rule is valid also for the orthorhombic LiBD$_4$. This prompted us to apply this relation to the pressure-dependent data on RbBD$_4$. Experimentally, $\nu_1$ shifts from 1593.7 at ambient pressure to 1606.6 cm$^{-1}$ at 1.9 GPa. Using Badger’s rule and the results of ref 30, one can estimate a reduction of the B–D bond length by ca. 0.015(5) Å. This result indicates that the relative compression of the BD$_4^-$ ion (about 1.2%) is smaller than the compression of the unit cell (3.5%) seen from our diffraction data. A similar behavior was obtained theoretically using periodic DFT calculations under pressure for the RuH$_6^{-}$ ion in Ca$_2$RuH$_6$. Table 4 collects the observed mode Gr"uneisen parameters observed in the different phases. In the cubic $Fm-3m$ phase, the Gr"uneisen parameter for all observed bands remains similarly weak (around 0.2), indicating

![Figure 5. Raman spectra of RbBH$_4$ as a function of pressure at room temperature in the regions of phase transitions. The spectra were offset vertically for clarity. The strong peak, at ca. $\sim 1330$ cm$^{-1}$, is from the diamond anvils.](image)

![Figure 6. Pressure dependence of the Raman shift for RbBH$_4$ phases: squares represent the $Fm-3m$; triangles, $P4/nmm$; and circles, $C222$ phases.](image)

<table>
<thead>
<tr>
<th>$\nu_1$</th>
<th>$D_{2d}$</th>
<th>$D_2$</th>
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<tbody>
<tr>
<td>$v_1$</td>
<td>$A_1$</td>
<td>$A_1$</td>
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<td>$v_2$</td>
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<td>$A_1 + B_1$</td>
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<tr>
<td>$v_3$</td>
<td>$T_2$</td>
<td>$B_2 + E$</td>
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<tr>
<td>$v_4$</td>
<td>$T_2$</td>
<td>$B_2 + E$</td>
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Thus a regular compression of the BH$_4^-$ group. For RbBr, the mode Grüneisen parameters of the external translational modes were reported to be 1.67 and 2.42. The significantly smaller values of the mode Grüneisen parameters for the internal BH$_4^-$ modes shown in Table 4 confirm the observation reported above that the B–H bonds are much less compressed compared to the Rb···B distances. In the P4/nmm phase, however, a slight increase in the mode Grüneisen parameter is observed for the B–H stretching modes compared to the other bands (ca. 0.3 vs. 0.2). At higher pressures, the observation of the deformation bands is restricted by the strong diamond Raman band at 1330 cm$^{-1}$. The difference in Grüneisen parameters for the two observed components of the $\nu_4$ mode in the C222 phase reflects the increase of splitting with increasing pressure (increase of deformation). However, in the stretching mode region, the Grüneisen parameters of the combination bands and of the stretching modes are again similar (ca. 0.25), as in the cubic phase. The accuracy of the estimates of the Grüneisen parameters in the highest pressure phase is much lower due to the limited number of data points and the observed bandwidth (see Figure 5), so the values given in the table should be considered as indicative.

### Conclusions

The pressure evolution of RbBH$_4$ has been characterized up to 23 GPa by synchrotron X-ray powder diffraction and Raman spectroscopy. Diffraction experiments at ambient temperature reveal three phase transitions: the ambient pressure Fm-3m polymorph transforms at 3.0 GPa into the new P4/nmm phase with a remarkable volume collapse of 8.8%, while the two transitions at higher pressures manifest a small volume drop of 2.2% for the P4/nmm → C222 transition at 10.4 GPa and 1.1% for the C222 → I-42m transition above 18 GPa.

The P4/nmm phase is an antitype to phosphonium iodide, while the C222 and I-42m phases represent two new structure types, which are the deformation variants of the cubic CsCl-type structure. The P4/nmm structure is an intermediate between NaCl and CsCl types, and all the transitions have the mechanism of atomic displacements. The BH$_4^-$ group acts with respect to Rb atoms as a mono-, di-, and trihapto ligand. It is the first time all three BH$_4^-$···M coordination modes are found in polymorphic modifications of the same compound. Different arrangements of the tetrahedral BH$_4^-$ group in the Rb environment result in different point group symmetries of the BH$_4^-$ anions as suggested by diffraction data and confirmed by Raman spectroscopy, i.e., $-4n2$ ($D_{2d}$) in the P4/nmm structure and $222$ ($D_2$) in the C222 and I-42m structures, and define the crystal symmetries of the high-pressure RbBH$_4$ polymorphs.

Our study shows that the structural chemistry of RbBH$_4$ under pressure is not identical to that of NaBH$_4$, as originally proposed, but differs drastically, revealing higher CNs and a peculiar crystal chemistry. The larger ionic radius for the metal cation favors higher CNs, and the higher pressure yields more and more dense arrangements of the BH$_4^-$ group inside its M-atom environment. The dense packing and realization of various BH$_4^-$···M coordination modes reflect a predominantly ionic character of RbBH$_4$. The less electro-positive metals, such as Mg and Zn, form more complex structural architectures, such as an interpenetrated and a porous $^{39}$ 3D framework.

Among all the borohydrides, RbBH$_4$ has the largest number of pressure-driven phase transitions. The only structure common to the whole MBH$_4$ family is the cubic one. Our analysis reveals a practically linear dependence of the compressibility of the cubic MBH$_4$ on the ionic radius of M. We conclude that its change in the series of cubic MBH$_4$ is largely defined by the compressibility of the repulsive BH$_4^-$···BH$_4^-$ interactions.

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### Supporting Information Available

Raman spectra of RbBH$_4$/RbBD$_4$/RbBD$_3$H; Rietveld refinement profiles and pressure dependence of the axial ratios for RbBH$_4$ phases; pressure dependence of Raman shifts and symmetry of zone center vibrations in RbBH$_4$ phases; crystal data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.