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Reorientational Motion in Alkali-Metal Borohydrides: NMR Data for RbBH$_4$ and CsBH$_4$ and Systematics of the Activation Energy Variations

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Ⓢ *Supporting Information*

ABSTRACT: To study the reorientational motion of the BH$_4$ groups in RbBH$_4$ and CsBH$_4$, we have performed nuclear magnetic resonance (NMR) measurements of the ^{1}H and ^{11}B spin—lattice relaxation rates in these compounds over wide ranges of temperature (48—400 K) and resonance frequency (14—90 MHz). It is found that at low temperatures the reorientational motion in CsBH$_4$ is the fastest among all of the borohydrides studied so far. The activation energies E_a for BH$_4$ reorientations obtained from our data are 138 ± 4 meV for RbBH$_4$ and 105 ± 7 meV for CsBH$_4$. Investigating the systematics of E_a variations in alkali-metal borohydrides MBH$_4$, we have found a correlation between E_a and the relative deviation of the actual M—B distance from the sum of the ionic radii of M and BH$_4$.
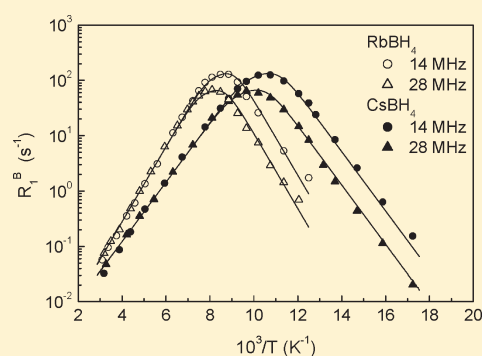
INTRODUCTION

The alkali-metal borohydrides MBH$_4$ (M = alkali metal) are considered as promising materials for hydrogen storage.[1,2] These compounds form ionic crystals consisting of M$^+$ cations and tetrahedral [BH$_4$]$^-$ anions. The volumetric and gravimetric hydrogen densities in these compounds are quite high. However, like many of the complex hydrides, the alkali-metal borohydrides are generally too stable with respect to thermal decomposition and have slow H desorption and absorption kinetics.[2,3] A search for ways of improving the hydrogen storage properties of the borohydrides is hampered by the lack of microscopic information on H dynamics and its relation to the crystal structure. A relation between the reorientational dynamics of BH$_4$ groups and the chemical bonding has been recently demonstrated for the magnesium borohydride.[4] Understanding the bonding schemes helps to elucidate the stability of borohydrides and to develop simple bonding concepts in terms of ionicity, M—BH$_4$ coordination geometries, and the cation size.[5] Thus, studies of H dynamics in borohydrides are expected to contribute to understanding the trends in the thermodynamic stability of these compounds. One of the most effective methods of investigation of atomic jump motion in solids is nuclear magnetic resonance (NMR). In favorable cases, NMR measurements of the ^{1}H spin—lattice relaxation can probe the H jump

rate τ^{-1} over the range of 8 orders of magnitude.[6] For comparison, another microscopic method of investigation of H motion — quasielastic neutron scattering (QENS) — usually allows one to trace changes in τ^{-1} over the ranges of up to 3 orders of magnitude.[7,8] The aims of the present work are to study the parameters of H jump motion in RbBH$_4$ and CsBH$_4$ by means of NMR and to look for correlations between the motional parameters and the structural features of alkali-metal borohydrides.

At ambient conditions, the structures of both RbBH$_4$ and CsBH$_4$ are cubic (space group $Fm\overline{3}m$); these structures are isomorphous to those of the high-temperature phases of NaBH$_4$ and KBH$_4$ with orientationally disordered BH$_4$ groups.[9,10] Heat capacity measurements[11] suggested phase transitions at 44 K for RbBH$_4$ and at 27 K for CsBH$_4$. However, X-ray and neutron powder diffraction studies[9] did not reveal any changes in the structure of RbBH$_4$ and CsBH$_4$ at low temperatures. The structural evolution of RbBH$_4$ under pressure at room temperature has been recently studied by synchrotron X-ray diffraction and Raman spectroscopy, and four different phases have been
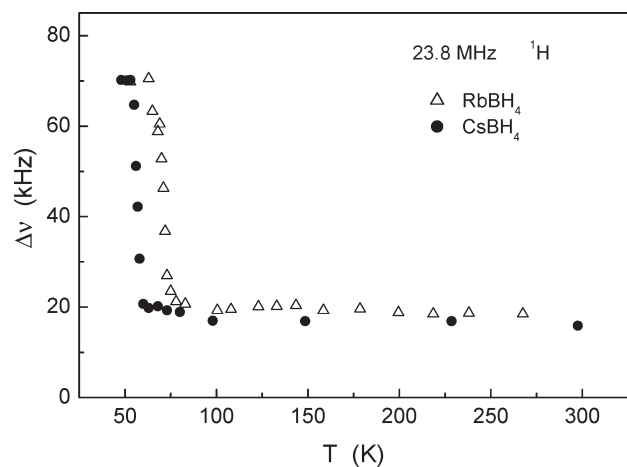
Figure 1. Temperature dependences of the width (full width at half-maximum) of the proton NMR spectra measured at 23.8 MHz for $RbBH_4$ and $CsBH_4$.

Figure 2. Proton spin–lattice relaxation rates measured at 14.5, 23.8, and 90 MHz for $RbBH_4$ as functions of the inverse temperature. The solid lines show the simultaneous fit of the standard theory to the data.

found in the pressure range up to 23 GPa.[10] The atomic jump motion in alkali-metal borohydrides has been investigated in a number of NMR[6,12−21] and QENS[7,8,22] studies. Most of these investigations are devoted to the reorientational motion of BH_4 groups in $LiBH_4$, $NaBH_4$, and KBH_4. Only one ^{11}B NMR work[15] addressed the atomic motion in $RbBH_4$ and $CsBH_4$. However, the [11]B spin–lattice relaxation measurements reported in ref 15 were performed at a single resonance frequency and over a rather narrow temperature range; these factors limit the reliability of the motional parameters derived from the experimental data. In the present work, we report the results of comprehensive ^{1}H and ^{11}B NMR measurements of the spectra and spin–lattice relaxation rates for $RbBH_4$ and $CsBH_4$ over wide ranges of temperature (48−400 K) and resonance frequency (14−90 MHz). On the basis of our results for the parameters of the reorientational motion, we discuss the systematics of the activation energy variations in alkali-metal borohydrides.

■ EXPERIMENTAL METHODS

$RbBH_4$ and $CsBH_4$ powders with a nominal purity of 98% were purchased from KatChem. X-ray diffraction measurements performed at the Swiss-Norwegian Beamlines (BM01A) of the European Synchrotron Radiation Facility (ESRF) did not reveal any impurity phases in these samples. The corresponding diffraction patterns are shown in Figures S1 and S2 of the Supporting Information. The lattice parameters found from these measurements (a = 7.02546(4) Å and 7.41326(5) Å for $RbBH_4$ and $CsBH_4$, respectively) are in reasonable agreement with the previous results.[9,10] For NMR experiments, the powdered samples were sealed in glass tubes under nitrogen gas.

NMR measurements were performed on a modernized Bruker SXP pulse spectrometer with quadrature phase detection at the frequencies $\omega/2\pi$ = 14 (or 14.5), 23.8 and 90 MHz (for ^{1}H), and 14 and 28 MHz (for [11]B). The magnetic field was provided by a 2.1 T iron-core Bruker magnet. A home-built multinuclear continuous-wave NMR magnetometer working in the range 0.32−2.15 T was used for field stabilization. For rf pulse generation, we used a home-built computer-controlled pulse programmer, the PTS frequency synthesizer (Programmed Test Sources, Inc.), and a 1 kW Kalmus wideband pulse
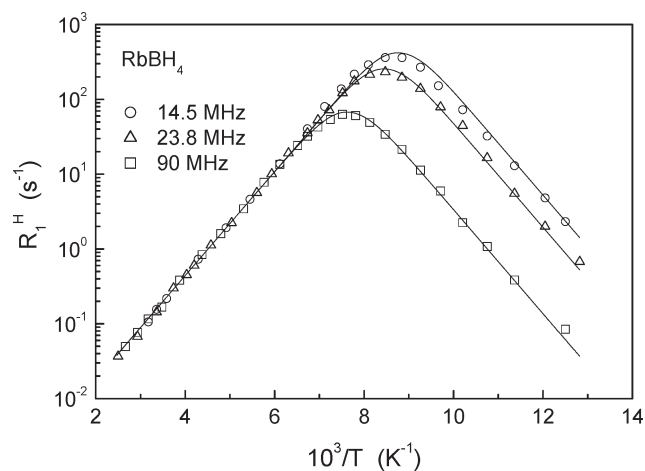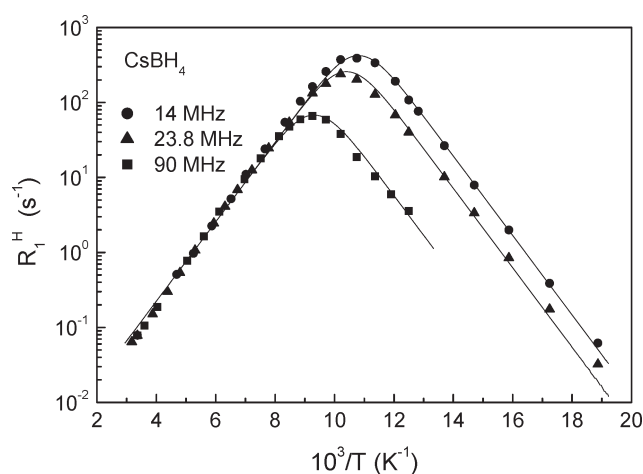
amplifier. Typical values of the $\pi/2$ pulse length were 2−3 μs for both ^{1}H and [11]B. A probehead with the sample was placed into an Oxford Instruments CF1200 continuous-flow cryostat using helium or nitrogen as a cooling agent. The sample temperature, monitored by a chromel-(Au−Fe) thermocouple, was stable to ±0.1 K. The nuclear spin–lattice relaxation rates were measured using the saturation − recovery method. NMR spectra were recorded by Fourier transforming the spin echo signals.

■ RESULTS AND DISCUSSION

1. ^{1}H and ^{11}B NMR Results for $RbBH_4$ and $CsBH_4$. The temperature dependences of the ^{1}H NMR line width (full width at half-maximum) for $RbBH_4$ and $CsBH_4$ are shown in Figure 1. For both compounds, the sharp narrowing of the proton NMR line is observed at rather low temperatures (near 55 K for $CsBH_4$ and near 70 K for $RbBH_4$). Such a narrowing indicates the excitation of H jump motion on the frequency scale of the order of 10^5 s^{-1}. This motion can be attributed to thermally activated reorientations of BH_4 groups. It should be noted that for $CsBH_4$ the sharp drop of the proton line width $\Delta\nu$ occurs at the lowest temperature among all the borohydrides studied so far; this corresponds to the fastest reorientational motion. As can be seen from Figure 1, at T > 80 K the proton line width stops decreasing being close to 18 kHz up to the highest temperature of our measurements. The substantial plateau value of $\Delta\nu$ indicates that the motion responsible for the observed line narrowing is indeed localized because such a motion leads to only partial averaging of the dipole−dipole interactions between nuclear spins.

The temperature dependences of the proton spin–lattice relaxation rates R_1^H for $RbBH_4$ measured at three resonance frequencies $\omega/2\pi$ are shown in Figure 2. The general features of the observed behavior of R_1^H are typical of the relaxation mechanism due to nuclear dipole−dipole interaction modulated by thermally activated atomic motion.[23] The proton relaxation rate exhibits the frequency-dependent peak at the temperature for which the reorientation jump rate τ^{-1} becomes nearly equal to ω. In the limit of slow motion ($\omega\tau \gg 1$), R_1^H is proportional to $\omega^{-2}\tau^{-1}$, and in the limit of fast motion ($\omega\tau \ll 1$), R_1^H is

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Figure 3. Proton spin–lattice relaxation rates measured at 14, 23.8, and 90 MHz for $CsBH_4$ as functions of the inverse temperature. The solid lines show the simultaneous fit of the standard theory to the data.

Figure 4. ^{11}B spin–lattice relaxation rates measured at 14 and 28 MHz for $RbBH_4$ and $CsBH_4$ as functions of the inverse temperature. For each of the compounds, the solid lines show the simultaneous fit of the standard theory to the data.

proportional to τ being frequency-independent. If the temperature dependence of τ follows the usual Arrhenius law,

$$\tau = \tau_0 \exp\left(E_a/k_B T\right) \qquad (1)$$

a plot of $\ln R_1^H$ vs T^{-1} is expected to be linear in the limits of both slow and fast motion with the slopes of $-E_a/k_B$ and E_a/k_B, respectively. Thus, the activation energy E_a for the reorientational motion can be obtained directly from these slopes. To evaluate the motional parameters, we have used the standard theory[23] relating R_1^H and τ and taking into account the $^1H-^{11}B$ and $^1H-^1H$ dipole–dipole interactions (eq 1 of ref 6), as well as the Arrhenius law relating τ and T (eq 1 above). The solid lines in Figure 2 show the *simultaneous* fit of the model to the data at three resonance frequencies. The motional parameters resulting from the fit are $\tau_0 = (9 \pm 2) \times 10^{-15}$ s and $E_a = 138 \pm 4$ meV. In the studied temperature range of 78–400 K, $RbBH_4$ does not exhibit any phase transitions, and the $R_1^H(T)$ data correspond to its cubic phase (space group $Fm\bar{3}m$). The value of E_a derived from our data is lower than that found for $RbBH_4$ from the ^{11}B spin–lattice relaxation measurements by Tarasov et al. (151 ± 4 meV).[15] It should be noted that the measurements of ref 15 were made over a rather narrow temperature range (145–310 K), and the relaxation rate maximum was not reached. The range of τ^{-1} variations traced by the measurements of ref 15 was about 2 orders of magnitude, whereas our $R_1^H(T)$ measurements for $RbBH_4$ probe changes in τ^{-1} over the range of 7 orders of magnitude ($\sim 10^5$ to 10^{12} s^{-1}). The fact that the dependence of R_1^H on the resonance frequency is well described by the standard model (Figure 2) indicates[6] the absence of any significant distributions of the values of the jump rate τ^{-1} in $RbBH_4$.

Figure 3 shows the temperature dependences of the proton spin–lattice relaxation rates for $CsBH_4$ measured at three resonance frequencies. Comparison of Figures 2 and 3 allows us to conclude that the behavior of R_1^H for $CsBH_4$ resembles that for $RbBH_4$; however, the $R_1^H(T)$ peak for $CsBH_4$ is shifted to lower temperatures from that for $RbBH_4$. For example, at the resonance frequency $\omega/2\pi = 23.8$ MHz, the $R_1^H(T)$ maximum is observed at 118 K for $RbBH_4$ and at 98 K for $CsBH_4$. Such a shift shows that the reorientational motion in $CsBH_4$ is faster than in $RbBH_4$, at least, at low temperatures; this is consistent with the
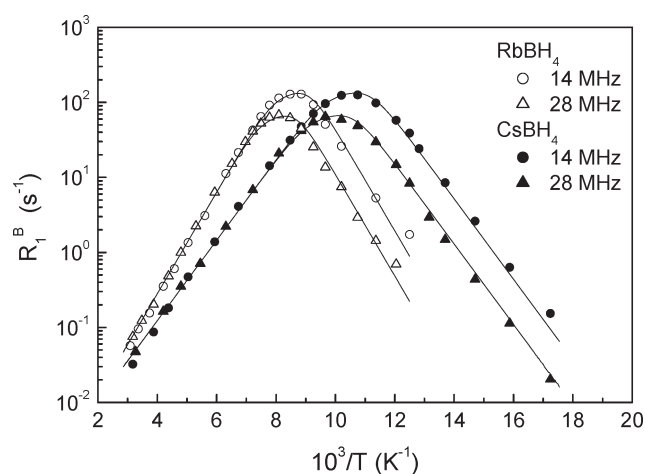
proton line width results discussed above. The $R_1^H(T)$ data for $CsBH_4$ have been analyzed in terms of the same model as those for $RbBH_4$. The solid curves in Figure 3 show the simultaneous fit of the standard theory to the data at three resonance frequencies. The motional parameters resulting from the fit are $\tau_0 = (2.1 \pm 0.9) \times 10^{-14}$ s and $E_a = 105 \pm 7$ meV. Again, this value of E_a is lower than that found for $CsBH_4$ in ref 15 (125 ± 4 meV) over a much narrower T range. As in the case of $RbBH_4$, the dependence of our R_1^H data for $CsBH_4$ on the resonance frequency is well described by the standard model (Figure 3); this is consistent with the absence of any significant distribution of τ^{-1} values.

The temperature dependences of the ^{11}B spin–lattice relaxation rates R_1^B measured at two resonance frequencies for $RbBH_4$ and $CsBH_4$ are shown in Figure 4. Comparison of Figures 2, 3, and 4 indicates that the general features of the behavior of the ^{11}B relaxation rates are similar to those of the proton relaxation rates. As in the case of other alkali-metal borohydrides,[6,17] the dominant contribution to R_1^B originates from the $^{11}B - ^1H$ dipole–dipole interaction modulated by reorientations of BH_4 groups. The solid lines in Figure 4 show the simultaneous fits of the standard theory taking into account the $^{11}B-^1H$ dipolar interactions (eq 3 of ref 6) to the $R_1^B(T)$ data at two resonance frequencies for $RbBH_4$ and $CsBH_4$. The motional parameters resulting from these fits are $\tau_0 = (1.0 \pm 0.3) \times 10^{-14}$ s and $E_a = 134 \pm 2$ meV for $RbBH_4$ and $\tau_0 = (1.6 \pm 0.4) \times 10^{-14}$ s and $E_a = 106 \pm 10$ meV for $CsBH_4$. Note that, for both compounds, the motional parameters derived from the ^{11}B relaxation data are very close to those obtained from the ^1H relaxation data. This may serve as additional evidence for the reliability of our values of the motional parameters.

2. Systematics of the Activation Energy Variations for Alkali-Metal Borohydrides. The activation energies for BH_4 reorientations obtained from NMR and QENS measurements in alkali-metal borohydrides are presented in Table 1. As can be seen from this table, the values of E_a derived by different groups are generally in reasonable agreement. For the orthorhombic phase of $LiBH_4$, NMR measurements[12,17] indicate a coexistence of two reorientational processes with different jump rates; in this case, two E_a values are shown in Table 1. For each of the compounds, the E_a values derived from the proton NMR data

Table 1. Activation Energies for BH_4 Reorientations in Alkali-Metal Borohydrides, As Derived from NMR and QENS Experiments[a]

compound	activation energy (meV)	T range (K)	method	ref
LiBH$_4$ (orthorhombic)	167 (10) and 208 (10)	107−370	NMR	12
	211 (4)	220−330	NMR	14
	180 (3)	300−375	QENS	8
	182 (3) and 251 (4)	102−384	NMR	17
NaBH$_4$ (cubic)	117 (5)	190−330	NMR	12
	154 (4)	190−310	NMR	15
	117 (1)	250−500	QENS	22
	124 (5)	200−400	QENS	7
	126 (3)	195−424	NMR	6
KBH$_4$ (cubic)	154 (4)	110−290	NMR	12
	103 (2)	300−550	QENS	8
	152 (5)	150−315	QENS	7
	161 (2)	82−424	NMR	6
RbBH$_4$ (cubic)	151 (4)	145−310	NMR	15
	138 (4)	78−400	NMR	this work
CsBH$_4$ (cubic)	125 (4)	145−310	NMR	15
	105 (7)	53−315	NMR	this work

[a] Uncertainties in the last digit of E_a are given in parentheses.

Table 2. M−B Distances, the Ionic Radii, and the Values of the Ratio δ for Alkali-Metal Borohydrides

| compound	d_{M-B} (Å)	R_M (Å)	$\delta = (R_M + R_{BH4})/d_{M-B}$
LiBH$_4$ (orthorhombic)	2.374 and 2.554	0.59	1.1036 and 1.0258
NaBH$_4$ (cubic)	3.082	1.02	0.9896
KBH$_4$ (cubic)	3.365	1.38	1.0134
RbBH$_4$ (cubic)	3.515	1.52	1.0100
CsBH$_4$ (cubic)	3.705	1.67	0.9987
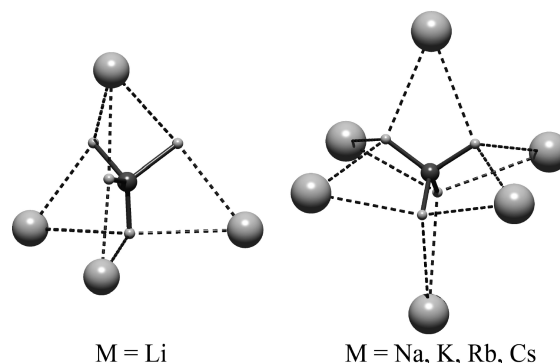
Figure 5. Coordination environments of BH_4 groups in MBH_4 phases stable at ambient conditions. The M−H bonds are shown by the bold dashed lines. For M = Li, one shorter (coordination via the BH_3 face) and three longer (coordination via the BH_2 edges) M−B distances are observed. For the heavier M, an ideal octahedral coordination via the BH_2 edges corresponds to the uniform M−B distances.

over the widest T ranges are marked by bold font. These values are considered as the most reliable. It can be seen that for the series of isomorphous cubic compounds $NaBH_4$ − KBH_4 − $RbBH_4$ − $CsBH_4$, the activation energy changes nonmonotonically as a function of the cation size: it increases from 126 meV ($NaBH_4$) to 161 meV (KBH_4), and then decreases to 138 meV ($RbBH_4$) and 105 meV ($CsBH_4$). Thus, the behavior of E_a in cubic alkali borohydrides differs from that of the order−disorder transition temperature T_0, which is known to decrease monotonically as a function of the cation size.[11] The monotonic decrease in T_0 has been attributed[11] to the decrease in the overlap energy with increasing distance between neighboring BH_4 groups. The barriers for BH_4 reorientations are believed to be determined mainly by M···H interactions;[6,24] therefore, the distances between M ions and BH_4 groups, d_{M-B}, should be of great importance. Note that the actual values of d_{M-B} in MBH_4 compounds may differ from the sum of the corresponding ionic radii, $R_M + R_{BH4}$. Table 2 presents the values of d_{M-B} for the orthorhombic (M = Li) and cubic (M = Na, K, Rb, and Cs) phases of MBH_4, the ionic radii R_M, and the values of the ratio $\delta = (R_M + R_{BH4})/d_{M-B}$. The values of d_{M-B} for the orthorhombic $LiBH_4$ phase are based on the results of the single-crystal synchrotron X-ray diffraction study[25] at 225 K. For this phase, there are two groups of Li−B distances (Figure 5): one short distance of 2.374 Å and three longer distances of 2.548−2.567 Å. The values of d_{M-B} for the cubic MBH_4 phases are based on the results of powder synchrotron X-ray diffraction studies at 293 K (ref 6 for M = Na and ref 9 for M = K, Rb, and Cs); in each case, the BH_4 group has an ideal octahedral coordination by M ions (Figure 5). The values of R_M are the "effective ionic radii", as introduced by Shannon[26] for the cases of tetracoordinated (M = Li) and hexacoordinated (M = Na, K, Rb, and Cs) ions. The ionic radius of $[BH_4]^-$ is taken as 2.03 Å.[27] The ratio δ is

the measure of a deviation of the M−B distance from the sum of the ionic radii. Its higher value indicates a stronger M···H(B) interaction, while it is equal to 1 for the case of touching ionic spheres.

Figure 6 shows the variations of both E_a and δ for alkali-metal borohydrides as functions of the ionic radius R_M. As can be seen from this figure, the behavior of E_a and δ exhibits a close correlation. The most impressive point is that such a correlation is retained for the orthorhombic $LiBH_4$ with two E_a values. As we move in Figure 6 from Cs to K, the M···H(B) interaction becomes stronger, and the value of E_a also increases. As we move further from K to a considerably smaller Na ion, the efficiency of the M···H(B) interaction drastically drops because the further shortening of the M−B distance is limited by the repulsive BH_4···BH_4 interactions. Essentially, Na ion is small compared to the cavity formed by the anionic sublattice. The weaker Na···H interaction leads to the smaller E_a. As we move further from Na to Li, the cubic structure becomes too unstable for such a small cation. The structure rearranges from the cubic to the orthorhombic one, with the accompanying change in coordination number for the metal cation from 6 to 4. The resulting Li − B distances become shorter, so that the stronger M···H(B) interactions lead to higher E_a. Note that the fcc $LiBH_4$ phase becomes stable at pressures above 10 GPa,[28] when the anionic sublattice is compressed to a much smaller size.

■ CONCLUSIONS

The analysis of the temperature and frequency dependences of the measured ^1H and ^{11}B spin−lattice relaxation rates for $RbBH_4$
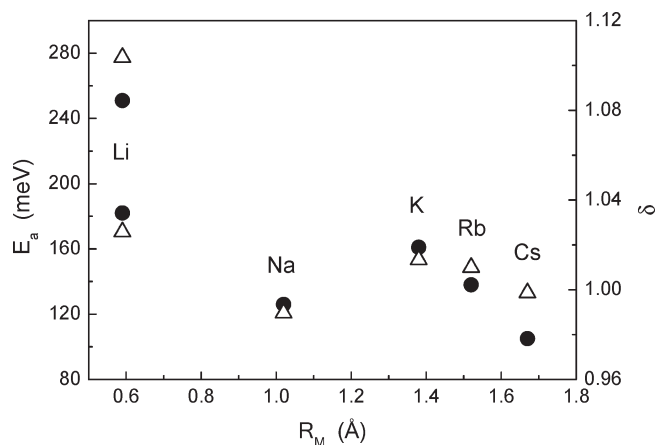
Figure 6. Activation energy for BH_4 reorientations (solid circles, left-hand scale) and the ratio $\delta = (R_M + R_{BH4})/d_{M-B}$ (open triangles, right-hand scale) as functions of the ionic radius of a metal atom in alkali-metal borohydrides.

and $CsBH_4$ has revealed the parameters of reorientational motion of BH_4 groups in these compounds. It is found that at low temperatures the reorientational motion in $CsBH_4$ is the fastest among all the borohydrides studied so far. The activation energies E_a for BH_4 reorientations obtained from our data are 138 ± 4 meV for $RbBH_4$ and 105 ± 7 meV for $CsBH_4$. For the series of isomorphous cubic borohydrides $NaBH_4 - KBH_4 - RbBH_4 - CsBH_4$, the activation energy changes nonmonotonically as a function of the cation size. Trying to understand the systematics of E_a variations in alkali-metal borohydrides MBH_4, we have found a close correlation between E_a and the ratio $\delta = (R_M + R_{BH4})/d_{M-B}$ characterizing a deviation of the $M-B$ distance from the sum of the ionic radii $R_M + R_{BH4}$. Moreover, such a correlation also remains valid for the orthorhombic $LiBH_4$ showing two values of E_a. This correlation is consistent with the idea that the barriers for BH_4 reorientations are determined mainly by $M \cdot \cdot \cdot H$ interactions.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental and refined X-ray diffraction patterns for $RbBH_4$ and $CsBH_4$ at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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