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Nuclear magnetic resonance studies of atomic motion in borohydrides

A.V. Skripov*, A.V. Soloninin, O.A. Babanova

Institute of Metal Physics, Ural Division of the Russian Academy of Sciences, Ekaterinburg 620041, Russia

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ABSTRACT

Two basic types of thermally activated atomic jump motion are known to exist in solid borohydrides: the fast reorientations of BH_4 groups and the slower translational diffusion of cations and anions. This paper reviews recent progress in nuclear magnetic resonance (NMR) studies of both these jump processes. It is shown that, for some borohydrides, NMR measurements of the nuclear spin-lattice relaxation can trace the changes in the reorientational jump rates over the range of eight orders of magnitude (10^4 to 10^{12} s^{-1}). Such a wide dynamic range leads to the high precision of the activation energies for BH_4 reorientations, as derived from the nuclear spin-lattice relaxation measurements.

1. Introduction

The alkali and alkaline-earth borohydrides $M(BH_4)_n$ (where $n = 1$ or 2 for alkali or alkaline-earth M elements, respectively) are considered as promising materials for hydrogen storage [1,2]. These compounds form ionic crystals consisting of metal cations and tetrahedral $[BH_4]^-$ anions. While the volumetric and gravimetric hydrogen densities in these compounds are high, the stability of the borohydrides with respect to thermal decomposition and the slow sorption kinetics remain the major drawbacks for their practical use. A number of methods (such as mechanical alloying, nanoconfinement, and using catalytic additives) have been suggested [3–6] to destabilize the complex hydrides and make the kinetics of dehydrogenation and rehydrogenation more favorable. Elucidation of hydrogen dynamics in borohydrides may give a key to improving their hydrogen-storage properties. This work presents a brief review of the dynamical properties of alkali and alkaline-earth borohydrides. The emphasis is put on recent experimental results obtained using nuclear magnetic resonance (NMR) measurements. NMR appears to be especially effective for studies of atomic motion in borohydrides. In contrast to transition-metal hydrides, the measured nuclear spin-lattice relaxation rates in borohydrides do not contain any significant contributions not related to atomic motion (such as the conduction-electron contribution in metallic systems). This allows us to trace the atomic jump rates in borohydrides over the range of 8 orders of magnitude (10^4 to 10^{12} s^{-1}). Another important feature of NMR studies is that different nuclei (^1H, ^{11}B, ^7Li, ^{23}Na,...) can serve as local probes of atomic motion, complementing each other. The motional parameters derived from NMR measurements will be compared to those obtained by quasielastic neutron scattering (QENS).

2. The relation between nuclear spin-lattice relaxation rates and parameters of atomic jump motion

The measured nuclear spin-lattice relaxation rate R_1 characterizes the recovery of nuclear spin magnetization after deviations of a nuclear spin system from the equilibrium state. For most of the studied borohydrides, the dominant relaxation mechanism is due to the internuclear dipole–dipole interaction modulated by atomic jump motion. The motional contribution to $R_1(T)$ shows a maximum at the temperature at which the atomic jump rate τ^{-1} becomes nearly equal to the nuclear magnetic resonance frequency ω, i.e. when $\omega\tau \approx 1$. Typical values of ω are of the order of 10^8 to 10^9 s^{-1}. In the limit of slow motion ($\omega\tau \gg 1$), R_1 is proportional to $\omega^{-2}\tau^{-1}$, and in the limit of fast motion ($\omega\tau \ll 1$), R_1 is proportional to τ being frequency-independent. If the temperature dependence of τ follows the usual Arrhenius law,

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \qquad (1)$$

the plot of $\ln R_1$ vs. T^{-1} should 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 atomic motion can be obtained directly from these slopes. Two basic types of atomic jump motion are known to exist in solid $M(BH_4)_n$ compounds: the reorientational motion of BH_4 groups and the translational diffusion of cations (M) or anions (BH_4). For the reorientational motion, the relation between R_1 and τ is available in the form of analytic expressions [7]. For the long-range diffusion, the corresponding analysis

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* Corresponding author.
E-mail address: skripov@imp.uran.ru (A.V. Skripov).

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is usually based on the Bloembergen–Purcell–Pound (BPP) model [8]. It is known [9] that, in certain cases of the long-range diffusion, the BPP model may fail to yield absolute values of τ better than a factor of 2; however, the activation energies resulting from the BPP-type analysis are quite reliable.

3. Reorientational motion of BH_4 groups

At low temperatures (80–400 K), the measured nuclear spin-lattice relaxation rates in borohydrides are usually governed by the reorientational motion of BH_4 groups. In alkali borohydrides this motion is fast enough to give rise to the $R_1(T)$ maxima in the range 120–190 K. The results of the first ^{1}H and ^{11}B relaxation rate measurements for $LiBH_4$, $NaBH_4$ and KBH_4 have been reported by Tsang and Farrar [10]. These results are consistent with the Arrhenius behavior of the jump rate $\tau^{-1}(T)$ for the reorientational motion, typical values of the activation energy being in the range of 110–210 meV. Subsequent NMR studies of the reorientational motion in alkali borohydrides [11–16] have extended the temperature and frequency ranges of the measurements and addressed the deuterium-substituted borohydrides and borohydrides of Rb and Cs. Recent studies [14,16,17] have emphasized the importance of probing the frequency dependence of R_1, in particular, in cases when a certain distribution of the jump rates τ^{-1} can be expected.

In the following, we shall discuss the results of NMR studies of the reorientational motion in borohydrides in the order of increasing complexity of the R_1 data. Fig. 1 shows the ^{1}H spin-lattice relaxation rates measured at three resonance frequencies $\omega/2\pi$ as functions of the inverse temperature for $RbBH_4$. These results provide a textbook example of the behavior of R_1 governed by a single thermally activated jump process. Our analysis is based on the standard expression [7] for the relaxation rate due to the dipole–dipole interaction modulated by atomic motion,

$$R_1^H = A_{HB}\left[\frac{\tau}{1+(\omega_H-\omega_B)^2\tau^2}+\frac{3\tau}{1+\omega_H^2\tau^2}+\frac{6\tau}{1+(\omega_H+\omega_B)^2\tau^2}\right] + A_{HH}\left[\frac{\tau}{4+\omega_H^2\tau^2}+\frac{\tau}{1+\omega_H^2\tau^2}\right], \qquad (2)$$

where ω_H and ω_B are the resonance frequencies of ^{1}H and ^{11}B, respectively, and the amplitude parameters A_{HB} and A_{HH} are proportional to the fluctuating parts of the dipolar second moment due to ^{1}H–^{11}B and ^{1}H–^{1}H interactions (the dipolar ^{1}H–^{85,87}Rb contributions to R_1^H in this system can be neglected). The solid lines in Fig. 1 show the *simultaneous* fit of Eqs. (2) and (1) 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. Note that 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 $Fm-3m$). Similar behavior of $R_1^H(T)$ at different resonance frequencies have been found for the isomorphous cubic phase of KBH_4 [16] in the T range of 82–424 K. Although KBH_4 is known to exhibit the phase transition to the ordered tetragonal phase [18], the transition temperature ($T_0 \approx 70$ K) is outside our experimental T range. For $NaBH_4$, the transition temperature is considerably higher ($T_0 \approx 190$ K), so that the $R_1^H(T)$ maximum is observed in the ordered tetragonal phase. The first-order transition from the low-T tetragonal to the high-T cubic phase of $NaBH_4$ is accompanied by the sharp change in R_1^H (corresponding to nearly an order of magnitude increase in the jump rate τ^{-1}) and by the decrease in the activation energy. The temperature dependences of the jump rates resulting from our fits for $NaBH_4$ [16], KBH_4 [16], and $RbBH_4$ are shown in Fig. 2 in the form of Arrhenius plots. The temperature ranges of the lines in this figure correspond to the actual ranges of our proton $R_1(T)$ data. As can be seen from Fig. 2, the proton spin-lattice relaxation measurements allow us to trace the changes in the jump rate of reorientations over the range of eight orders of magnitude. This unique feature of the spin-lattice relaxation measurements leads to high precision of the E_a values derived from the $R_1(T)$ data. For comparison, the ranges of τ^{-1} values traced by recent QENS experiments [19–22] for $NaBH_4$ and KBH_4 do not exceed two [19,20,22] or three [21] orders of magnitude. The main mechanism of the ^{11}B spin-lattice relaxation in alkali borohydrides is the ^{11}B–^{1}H dipole–dipole interaction modulated by reorientational motion of BH_4 groups, and the results of the ^{11}B relaxation measurements at different resonance frequencies [14,16] yield practically the same motional parameters as the ^{1}H relaxation measurements. The activation energies for BH_4 reorientations obtained from NMR and QENS measurements in $M(BH_4)_n$ are presented in Table 1. As can be seen from this table, for $NaBH_4$, KBH_4, and $RbBH_4$, the values of E_a derived by different groups are in reasonable agreement. The agreement is especially good in the case of the low-T phase of $NaBH_4$. It should be noted, however, that on the basis of the $R_1(T)$ data it is difficult to obtain unambiguous information on the type of BH_4 reorientations. In fact, the reorientational motion of a regular BH_4 tetrahedron can be represented by rotations around three 2-fold axes and four 3-fold axes; only some

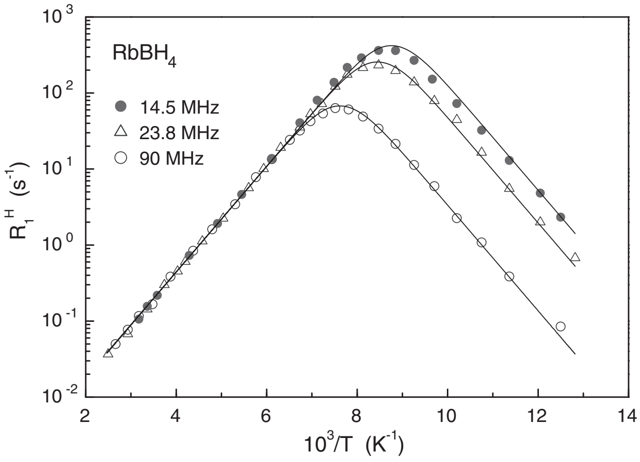

Fig. 1. Proton spin-lattice relaxation rates measured at 14.5, 23.8 and 90 MHz for $RbBH_4$ as functions of the inverse temperature. The solid lines show the simultaneous fit of the standard theory (Eqs. (2) and (1)) to the data.

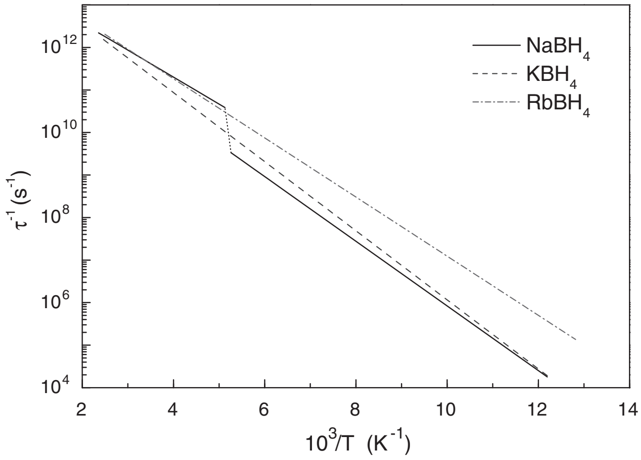

Fig. 2. Temperature dependences of the jump rates of BH_4 group reorientations, as derived from the fits to the proton spin-lattice relaxation data for $NaBH_4$, KBH_4 and $RbBH_4$.

Table 1
Activation energies for BH_4 reorientations in borohydrides, as derived from NMR and QENS experiments. Uncertainties in the last digit of E_a are given in parentheses.

Compound	Activation energy (meV)	T range (K)	Method	Reference
$LiBH_4$ (LT phase)	167 (10) and 208 (10)	107–370	NMR	[10]
	211 (4)	220–330	NMR	[12]
	180 (3)	300–375	QENS	[22]
	182 (3) and 251 (4)	102–384	NMR	[14]
$LiBH_4$ (HT phase)	69 (5)	400–540	QENS	[22]
$NaBH_4$ (LT phase)	154 (7)	97–185	NMR	[10]
	159 (4)	145–185	NMR	[13]
	140 (8)	140–184	QENS	[21]
	151 (2)	82–190	NMR	[16]
$NaBH_4$ (HT phase)	117 (5)	190–330	NMR	[10]
	154 (4)	190–310	NMR	[13]
	117 (1)	250–500	QENS	[19,20]
	124 (5)	200–400	QENS	[21]
	126 (3)	195–424	NMR	[16]
KBH_4 (HT phase)	154 (4)	110–290	NMR	[10]
	103 (2)	300–550	QENS	[22]
	152 (5)	150–315	QENS	[21]
	161 (2)	82–424	NMR	[16]
$RbBH_4$	151 (4)	145–310	NMR	[13]
	138 (4)	78–400	NMR	This work
$CsBH_4$	125 (4)	145–310	NMR	[13]
$Mg(BH_4)_2$ (LT phase)	116 (6), 198 (12), and 362 (5)	82–443	NMR	[17]

of these rotations may occur in real crystals. The spatial aspects of the reorientational motion can be effectively studied by QENS measurements of the elastic incoherent structure factor (EISF) [23]. In particular, the behavior of the EISF in $NaBH_4$ and KBH_4 is found to be consistent with combined reorientations around 2-fold and 3-fold axes [19–22].

Lithium borohydride $LiBH_4$ has an orthorhombic structure at low temperatures and undergoes a first-order phase transition to a hexagonal structure at $T_0 \approx 384$ K. The behavior of the proton spin-lattice relaxation rates in the low-T [14] and high-T [24] phases of $LiBH_4$ is shown in Fig. 3. For the low-T phase, R_1^H is governed by the reorientational motion of BH_4 groups; however, this behavior appears to be more complex than that found for $RbBH_4$, KBH_4 and $NaBH_4$. The high-temperature slope of the $R_1^H(T)$ peak for the orthorhombic phase of $LiBH_4$ is steeper than the low-temperature one. Moreover, this peak shows the inflection point near its maximum (Fig. 3) and looks like a superposition of two peaks. These features indicate a coexistence of two reorientational processes with different jump rates. Such a coexistence was first reported for $LiBH_4$ by Tsang and Farrar [10] who ascribed it to inequivalent BH_4 groups. However, structural studies [25–27] have shown that all BH_4 groups in the low-T phase of $LiBH_4$ are equivalent. Therefore, we can conclude that each BH_4 group participates in two types of reorientational motion (most probably, the rotations around 2-fold and 3-fold axes) having different rates. Bold black lines in Fig. 3 show the simultaneous fit of the 'two-peak' model to the data at three resonance frequencies; the corresponding activation energies for the two jump processes [14] are included in Table 1. The behavior of $R_1^H(T)$ in the high-T phase of $LiBH_4$ (left-hand part of Fig. 3) will be discussed in the next section.

The only alkaline-earth borohydride where the reorientational motion has been studied so far is the low-temperature hexagonal (α) phase of $Mg(BH_4)_2$. The unit cell of α-$Mg(BH_4)_2$ contains 330 atoms. Fig. 4 shows the behavior of the proton spin-lattice relaxation rates measured at three resonance frequencies for α-$Mg(BH_4)_2$. The temperature dependence of R_1^H for this compound exhibits two well-resolved maxima and can be fully described in terms of at least three reorientational processes [17] with different jump rates. Furthermore, the description of the frequency

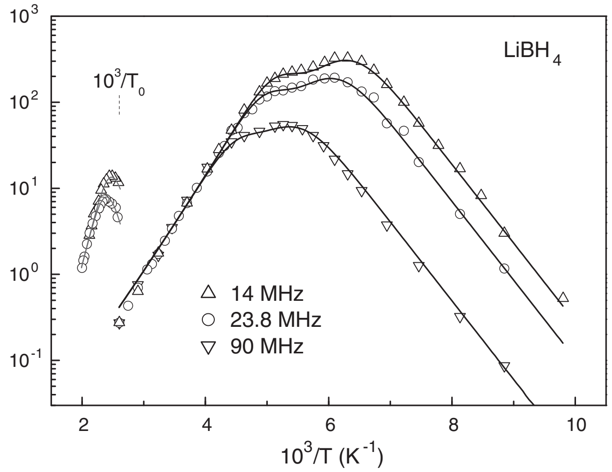

Fig. 3. Proton spin-lattice relaxation rates measured at 14, 23.8 and 90 MHz for $LiBH_4$ as functions of the inverse temperature. The vertical bar corresponds to the temperature of the structural phase transition. The bold black lines show the simultaneous fit of the 'two-peak' model for BH_4 reorientations to the data (low-T phase). The thin gray lines show the simultaneous fit of the BPP model for Li diffusion to the data (high-T phase).

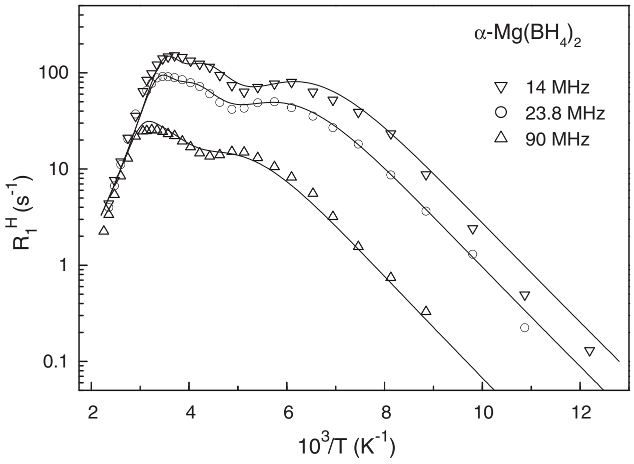

Fig. 4. Proton spin-lattice relaxation rates measured at 14, 23.8 and 90 MHz for α-$Mg(BH_4)_2$ as functions of the inverse temperature. The solid lines show the simultaneous fit of the 'three-peak' model for BH_4 reorientations to the data.

dependence of R_1^H at $T < 160$ K requires a certain distribution [17] of jump rates for the fastest process (responsible for the low-T maximum of R_1). Solid lines in Fig. 4 show the simultaneous fit of the 'three-peak' model to the data at three resonance frequencies; the corresponding activation energies for different jump processes [17] are included in Table 1. The 'three-peak' model with the same set of motional parameters also provides a good description of the ^{11}B spin-lattice relaxation data for α-Mg(BH$_4$)$_2$ [17]. As can be seen from Table 1, the highest and the lowest E_a values for α-Mg(BH$_4$)$_2$ differ by nearly a factor of 3. Although there are six crystallographically inequivalent BH$_4$ groups in α-Mg(BH$_4$)$_2$, all BH$_4$ groups have similar local environments [28], so that it is hardly possible to attribute strongly differing values of E_a to different BH$_4$ groups. The remarkable feature of the local environments of BH$_4$ groups in α-Mg(BH$_4$)$_2$ is their nearly linear coordination by two Mg atoms [17,28]. This feature suggests that the fastest jump process corresponds to the rotation around the 2-fold axis along the Mg–B–Mg line, since such a rotation does not break any Mg–H bonds. Moreover, a certain variation of the Mg–B–Mg angles for different BH$_4$ groups in α-Mg(BH$_4$)$_2$ [28] can naturally explain the distribution of the jump rates for the fastest process. The slowest jump process should be associated with the rotations around two other 2-fold axes perpendicular to the Mg–B–Mg line, since such rotations break all the Mg–H bonds. The intermediate jump process can be attributed to the rotations around 3-fold axes breaking half of the Mg–H bonds. The results for α-Mg(BH$_4$)$_2$ are consistent with the idea [16,20] that the energy barriers for BH$_4$ reorientations in borohydrides are determined primarily by the metal–H interactions.

4. Translational diffusion of Li$^+$ and (BH$_4$)$^-$ ions in the high-temperature solid phase of LiBH$_4$

The translational motion of ions in solid borohydrides has been revealed by NMR measurements only in the high-temperature (hexagonal) phase of LiBH$_4$. Matsuo et al. [29] have found that the transition from the orthorhombic to the hexagonal phase of this compound at $T_0 \approx 384$ K is accompanied by the three orders of magnitude increase in the electrical conductivity, so that the high-T phase of LiBH$_4$ can be considered as a superionic conductor. The behavior of the ^{7}Li spin-lattice relaxation rate indicates that Li ions participate in the long-range diffusion with the characteristic jump rate of about 4×10^7 s^{-1} just above T_0 and the activation energy of 0.56 eV [29]. The diffusive motion of Li ions also affects the measured ^{1}H and ^{11}B spin-lattice relaxation rates [14,15,24]. As can be seen from Fig. 3, the transition from the low-T to the high-T phase of LiBH$_4$ leads to the abrupt increase in the ^{1}H relaxation rate and to the reappearance of its frequency dependence. Near T_0, the jump rate of BH$_4$ reorientations reaches the values of the order of 10^{11} s^{-1} [14]. Since these values are much higher than the NMR frequencies, the contribution to R_1^H due to the reorientational motion becomes very small at $T \approx T_0$, and the onset of much slower process of the diffusive Li motion at $T > T_0$ provides the dominant mechanism of the proton spin-lattice relaxation in the high-T phase of LiBH$_4$. The thin gray lines in Fig. 3 show the simultaneous BPP fit to the high-T data. This fit uses the *fixed* motional parameters for Li diffusion ($\tau_0 = 1.1 \times 10^{-15}$ s and $E_a = 0.56$ eV, as found in Ref. [29]), so that the amplitude of the R_1 peak is the only fit parameter. Since the ^{1}H–^{7}Li dipole–dipole interaction in LiBH$_4$ is an order of magnitude weaker than the ^{1}H–^{1}H and ^{1}H–^{11}B interactions [14], the long-range Li diffusion modulates only a small fraction of the dipolar interactions of ^{1}H spins; therefore, the amplitude of the R_1^H peak in the high-T phase of LiBH$_4$ is considerably smaller than that in the low-T phase (see Fig. 3). It has been shown [24] that the same parameters of Li diffusion (τ_0 and E_a describing the ^{1}H relaxation data in the high-T phase of LiBH$_4$) also provide a good description of the ^{11}B and ^{7}Li relaxation rates measured for this phase at different resonance frequencies. Thus, in the temperature range 384–500 K, all the ^{1}H, ^{11}B and ^{7}Li spin-lattice relaxation data can be fully accounted for in terms of a single motional process – the translational diffusion of Li ions with the activation energy of 0.56 eV. In this temperature range, other motional processes are either too fast (BH$_4$ reorientations) or too slow (long-range hydrogen diffusion) to contribute significantly to the spin-lattice relaxation rates.

Measurements of the widths of NMR lines can probe slower atomic motions than the spin-lattice relaxation measurements. In fact, the NMR line narrowing becomes pronounced above the temperature at which the atomic jump rate exceeds the 'rigid lattice' line width [7], which for protons is typically of the order of 10^5 s^{-1}. Fig. 5(a) shows the temperature dependence of the ^{1}H NMR line width for LiBH$_4$ [24] in the range 300–500 K. The small drop in the line width just below T_0 can be attributed to the onset of translational motion of Li ions which averages out a small fraction of dipolar interactions of ^{1}H spins. However, the strong line narrowing observed above ~440 K can only be explained in terms of translational motion of hydrogen atoms [15,24]. The characteristic jump rate for the translational H motion estimated from the line narrowing [15] is about 1.5×10^5 s^{-1} at 500 K. The temperature dependence of the ^{11}B NMR line width in LiBH$_4$ [24] is shown in Fig. 5(b). It can be seen that the strong narrowing of the ^{11}B NMR line occurs in the same temperature range as that of the ^{1}H NMR line. This suggests that a common motional process is responsible for the observed narrowing of both ^{1}H and ^{11}B lines. As proposed

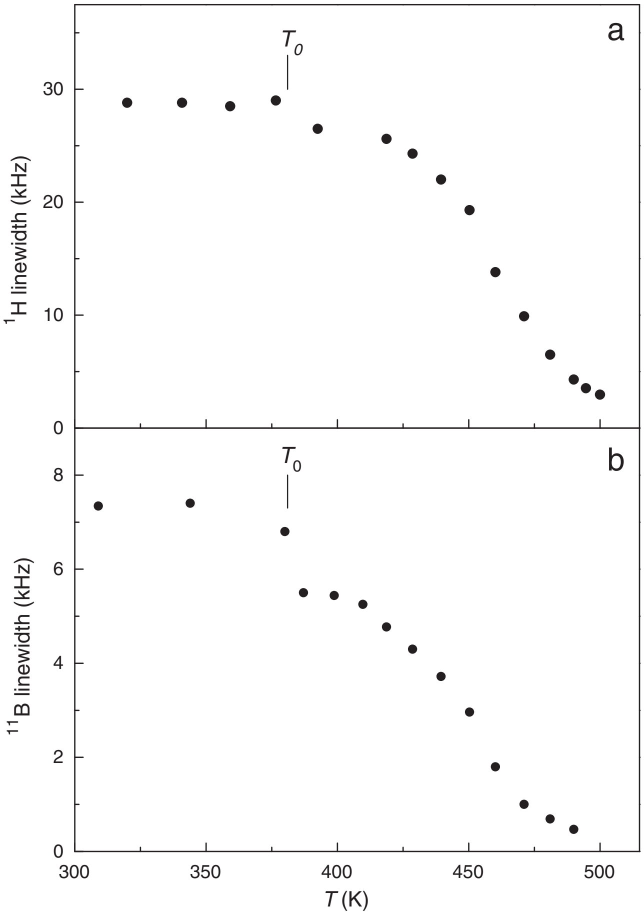

Fig. 5. Temperature dependences of the width (full width at half-maximum) of the ^{1}H NMR line (a) and the ^{11}B NMR line (b) measured at 23.8 MHz for LiBH$_4$. The vertical bar indicates the temperature of the structural phase transition.

by Corey et al. [15], such a process corresponds to translational motion of complete BH_4 units. The idea that B atoms are involved in the translational motion on the NMR time scale is supported by the observation [15,24] that the ^{11}B line width drops below the value expected for the B–B contribution to the 'rigid lattice' width. It should be noted that recent Raman scattering measurements of the H–D exchange in the high-T solid phase of $LiBH_4$ [30] have been interpreted in terms of individual hydrogen atoms moving from one BH_4 group to another. However, estimates of the local H exchange rate between BH_4 groups based on the ^{11}B NMR experiments in the liquid phase of $LiBH_4$ [31] have shown that near the melting point this rate is lower than $1\,s^{-1}$. The H exchange in solid $LiBH_4$ is expected to be at least as slow as in the melt [31]. Thus, the observed hydrogen diffusion in the high-T solid phase of $LiBH_4$ with the characteristic jump rate of $\sim 10^5\,s^{-1}$ at 500 K (see above) has a negligible contribution from the H exchange processes. The main mechanism of hydrogen diffusion in this phase should be the jump motion of intact BH_4 groups (or BH_3 groups having a hydrogen vacancy [32]).

5. Concluding remarks

This review emphasizes the potential of NMR for investigation of the dynamical properties of borohydrides. NMR measurements of the nuclear spin-lattice relaxation rates at different resonance frequencies are especially effective to detect a coexistence of several jump processes and to measure the corresponding activation energies with a high precision. While the reorientational motion of BH_4 groups in alkali borohydrides has been studied extensively, little is known about this motion in alkaline-earth borohydrides. For transition-metal borohydrides, NMR studies of atomic jump motion have not been reported so far. More work is also required to elucidate the relation between the activation energies for the reorientational motion and the structure of the environment of BH_4 groups.

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