Nuclear magnetic resonance study of Li and H diffusion in the high-temperature solid phase of LiBH$_4$

A.V. Soloninin, A.V. Skripov *, A.L. Buzlukov, A.P. Stepanov

Institute of Metal Physics, Urals Branch of the Academy of Sciences, S. Kovalevskoi 18, Ekaterinburg 620041, Russia

ABSTRACT

In order to study the atomic jump motions in the high-temperature solid phase of LiBH$_4$, we have measured the ^{1}H and ^{11}B nuclear magnetic resonance (NMR) spectra and the ^{1}H, ^{7}Li and ^{11}B spin–lattice relaxation rates in this compound over the resonance frequency range of 14–34.4 MHz. In the temperature range 384–500 K, all the spin–lattice relaxation data are satisfactorily described in terms of a thermally activated jump motion of Li ions with the pre-exponential factor $\tau_0 = 1.1 \times 10^{-15}$ s and the activation energy $E_a = 0.56$ eV. The observed frequency dependences of the spin–lattice relaxation rates in this temperature range exclude a presence of any distributions of the Li jump rate or any other jump processes on the frequency scale of 10^7–10^{10} s^{-1}. The strong narrowing of the ^{1}H and ^{11}B NMR lines above 440 K is consistent with the onset of diffusive motion of the BH$_4$ tetrahedra.

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1. Introduction

Lithium borohydride, LiBH$_4$, containing 18.4 mass% of hydrogen is considered as one of the most promising materials for hydrogen storage [1]. While LiBH$_4$ was recently shown to desorb hydrogen reversibly [2], its stability with respect to thermal decomposition and the very slow dehydriding and rehydriding kinetics [3,4] remain the major drawbacks for practical use. Diffusion of hydrogen is expected to be one of the main mechanisms affecting the kinetics of H absorption and desorption. Therefore, studies of diffusion processes in LiBH$_4$ may give a key to improving its hydrogen-storage properties.

According to the synchrotron X-ray diffraction [5–7] and neutron diffraction [8,9] measurements, at low temperatures LiBH$_4$ has an orthorhombic structure and undergoes a first-order phase transition to a hexagonal structure at $T_0 \approx 381$ K. The transition from the orthorhombic to the hexagonal phase is accompanied by the 3 orders of magnitude increase in the electrical conductivity [10], so that the high-temperature phase of LiBH$_4$ can be considered as a superionic conductor. The jump in the conductivity at T_0 is believed to originate from the structural change, since the structure of the Li sublattice in the hexagonal phase becomes favorable for long-range migration of Li ions [10]. The melting point of LiBH$_4$ is 541 K [2]. The atomic motions in LiBH$_4$ have been recently investigated by nuclear magnetic resonance (NMR) [10–12] and hydrogen-isotope exchange mea-

surements [13]. The ^{1}H and ^{11}B spin–lattice relaxation data for the low-temperature phase of LiBH$_4$ [11] are consistent with a coexistence of two types of thermally activated reorientational motion of BH$_4$ tetrahedra. For both types of the motion, the jump rates of the reorientations reach the values of the order of 10^{11} s^{-1} at T_0. Since these values are much higher than the typical NMR frequencies, the effect of the reorientations on the measured NMR parameters at $T > T_0$ should be very small, so that the nuclear spin–lattice relaxation in this temperature range is governed by the slower process of translational diffusion of Li ions [10,11]. At still higher temperatures, $T > 440$ K, the translational diffusion of hydrogen becomes observable, leading to the narrowing of NMR lines [12]. On the basis of the thermogravimetrical and Raman spectroscopy studies of H–D exchange [13], the tracer diffusion coefficient of deuterium in LiBH$_4$ is estimated to be about 7×10^{-10} cm^2/s at 523 K. However, there is a controversy concerning the mechanism of hydrogen diffusion in the high-temperature solid phase of LiBH$_4$. While the H–D exchange measurements [13] were interpreted in terms of individual hydrogen atoms moving from one BH$_4$ tetrahedron to another, the NMR measurements [12,14] gave evidence for a diffusion of complete BH$_4$ units.

The aim of the present work is to study the atomic jump motions in the high-temperature solid phase of LiBH$_4$ using ^{1}H, ^{7}Li and ^{11}B NMR measurements of the spectra and spin–lattice relaxation rates R_1. In order to characterize complex atomic motions, it is important to investigate the frequency dependences of R_1. Such an approach can be used to search for a distribution of atomic jump rates [15] or a coexistence of several types of jump motion with different rates [16]. Previous R_1 measurements in the

high-temperature phase of $LiBH_4$ were performed at a single resonance frequency (116 MHz for ^7Li [10] and 85 MHz for ^1H [12]). In the present work, we report the results of the measurements of ^1H, ^7Li and ^{11}B NMR spectra and spin–lattice relaxation rates in $LiBH_4$ over the temperature range of 309–500 K and the resonance frequency range of 14–34.4 MHz.

2. Experimental details

Polycrystalline $LiBH_4$ was purchased from Sigma-Aldrich. The same sample was used in our previous work [11]. X-ray diffraction analysis at room temperature indicated the presence of a single $LiBH_4$ phase; no diffraction peaks from impurities were detected. For NMR measurements, the powdered $LiBH_4$ sample was sealed in a glass tube under argon gas.

NMR measurements were performed on a modernized Bruker SXP pulse spectrometer with quadrature phase detection at the frequencies $\omega/2\pi = 14$, 23.8 and 34.4 MHz (for ^1H and ^7Li) and at 14 and 23.8 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 PTS500 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 all nuclei studied. The sample temperature, monitored by a copper-constantan thermocouple, was stable to ± 0.3 K. The nuclear spin–lattice relaxation rates were measured using the saturation-recovery method. In all cases the recovery of the nuclear magnetization could be satisfactorily described by a single exponential function. NMR spectra were recorded by Fourier transforming the spin echo signals.

3. Results and discussion

3.1. Spin–lattice relaxation rates

The temperature dependences of the proton spin–lattice relaxation rates, R_1^H, measured at three resonance frequencies are shown in Fig. 1. As can be seen from this figure, the transition
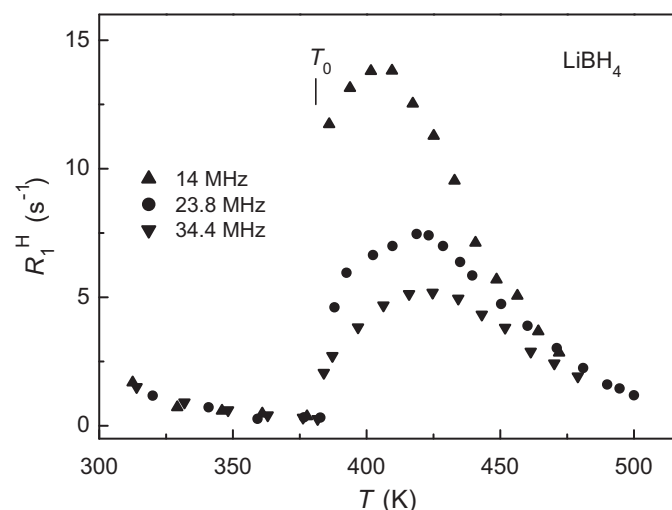
from the low-temperature (LT) orthorhombic phase to the high-temperature (HT) hexagonal phase leads to the abrupt increase in the relaxation rate and to the appearance of its frequency dependence. Such changes can be explained by the abrupt increase [10] in the mobility of Li ions above T_0. While in the LT phase the proton relaxation rate is determined by reorientational motion of the BH_4 tetrahedra [11,17], the behavior of R_1^H above T_0 is governed by the translational diffusion of Li ions [11,12]. The proton spin–lattice relaxation rates in the HT phase show a characteristic frequency-dependent peak (Fig. 1); this peak is expected to occur at the temperature at which the appropriate atomic jump rate becomes nearly equal to the resonance frequency.

The behavior of the measured spin–lattice relaxation rates for both ^7Li (Fig. 2) and ^{11}B (Fig. 3) in the HT phase resembles that found for ^1H nuclei. The results shown in Fig. 2 are also consistent with the ^7Li spin–lattice relaxation rates measured at the high resonance frequency (116 MHz) [10]. In order to discuss our relaxation rate data in more detail, we have to consider the relaxation mechanisms and to address the following questions: (1) can a single jump process of Li ion diffusion be responsible for
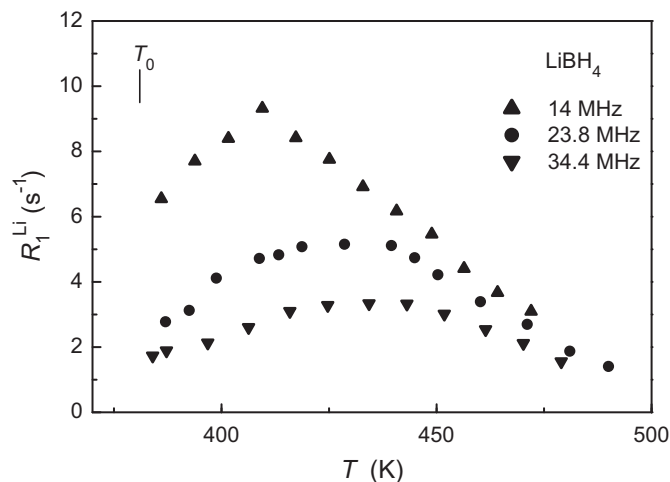

Fig. 2. The temperature dependences of the ^7Li spin–lattice relaxation rates measured at 14, 23.8 and 34.4 MHz for the high-temperature phase of $LiBH_4$.
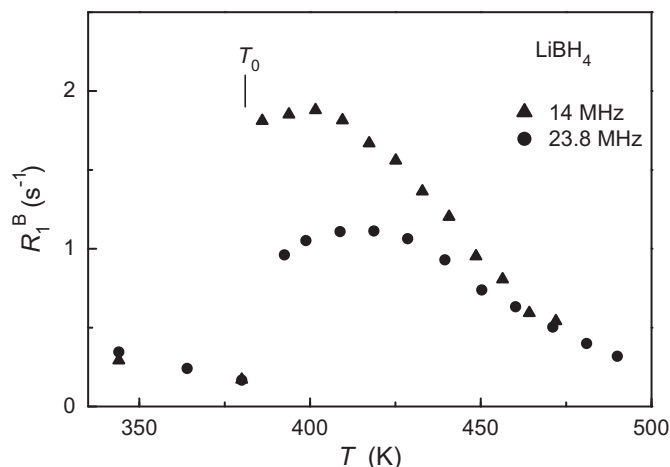

Fig. 1. The temperature dependences of the ^1H spin–lattice relaxation rates measured at 14, 23.8 and 34.4 MHz for $LiBH_4$. The vertical bar indicates the temperature of the structural phase transition.

Fig. 3. The temperature dependences of the ^{11}B spin–lattice relaxation rates measured at 14 and 23.8 MHz for $LiBH_4$. The vertical bar indicates the temperature of the structural phase transition.

all (^{1}H, ^{7}Li and ^{11}B) the spin–lattice relaxation results in the HT phase and (2) are there any distributions of the atomic jump rates governing the spin–lattice relaxation?

If Li ions are the only species moving with the jump rates which are close enough to the resonance frequency, the dominant contribution to the ^{1}H spin–lattice relaxation rate in the HT phase should originate from the H–Li dipole–dipole interaction modulated by Li diffusion. In terms of the Bloembergen–Purcell–Pound (BPP) model [18], the appropriate expression for the ^{1}H spin–lattice relaxation rate is

$$R_1^H = \frac{\Delta M_{HLi}}{2\omega}\left[\frac{y}{1+(1-b)^2y^2}+\frac{3y}{1+y^2}+\frac{6y}{1+(1+b)^2y^2}\right]. \tag{1}$$

Here $y = \omega\tau_{Li}$, τ_{Li} is the mean time interval between two successive jumps of Li ions, $b = \gamma_{Li}/\gamma_H$, γ_{Li} and γ_H are the gyromagnetic ratios for ^{7}Li and ^{1}H, respectively, and ΔM_{HLi} is the fluctuating part of the second moment of the ^{1}H NMR line due to H–Li dipolar interactions. The temperature dependence of R_1^H is determined by the temperature dependence of τ_{Li} which usually follows the Arrhenius law,

$$\tau_{Li} = \tau_0\exp(E_a/k_BT), \tag{2}$$

where E_a is the activation energy for Li diffusion. The values of the pre-exponential factor and the activation energy found from the previous ^{7}Li NMR measurements [10] are $\tau_0 = 1.1\times10^{-15}$ s and $E_a = 0.56$ eV. As the first step of our analysis, we want to verify if these parameters of Li motion can describe our proton spin–lattice relaxation data at all the resonance frequencies studied. This means that the motional parameters (τ_0 and E_a) are fixed, while the only amplitude parameter ΔM_{HLi} in Eq. (1) is varied to fit the experimental R_1^H data at three resonance frequencies simultaneously. The results of such a simultaneous fit based on Eqs. (1) and (2) with the fixed motional parameters are shown by solid curves in Fig. 4(a); the corresponding value of ΔM_{HLi} is 5.5×10^8 s^{-2}. As can be seen from Fig. 4(a), the motional parameters of Li ions give a good description of the proton spin–lattice relaxation results in the HT phase of LiBH$_4$. The 'rigid lattice' H–Li dipolar contribution to the second moment of the ^{1}H NMR line, M_{HLi}^R, calculated on the basis of the structural data [6] for the HT phase of LiBH$_4$ is 1.32×10^9 s^{-2}. The value of ΔM_{HLi} is a factor of 2.4 lower than M_{HLi}^R, which is due to the fact that a certain part of the corresponding second moment is already averaged out by the fast reorientational motion of BH$_4$ tetrahedra. A rough estimate of the H–Li second moment based on the model of 'free' rotations of the BH$_4$ groups yields $M_{HLi}^F = 5.9\times10^8$ s^{-2}.

For ^{7}Li relaxation caused by Li diffusion, we have to consider the Li–H, Li–B and Li–Li dipole–dipole interactions. Since ^{7}Li nuclei have nonzero electric quadrupole moments, one may also expect a contribution to R_1^{Li} due to the interaction between nuclear quadrupole moments and fluctuating local electric field gradients (EFGs). However, the well-resolved ^{7}Li NMR spectra in the HT phase of LiBH$_4$ consisting of the narrow central line and two sharp quadrupole satellites [10,12] suggest that Li nuclei jump between the sites with the same EFG. Thus, the quadrupole contribution to R_1^{Li} should be negligible. In order to compare the strength of the Li–H, Li–B and Li–Li dipole–dipole interactions, we can estimate the corresponding contributions to the 'rigid lattice' second moment of the ^{7}Li NMR line. Such estimates based on the structural data [6] for the HT phase of LiBH$_4$ give $M_{LiH}^R = 1.1\times10^9$ s^{-2}, $M_{LiB}^R = 1.1\times10^8$ s^{-2} and $M_{LiLi}^R = 5.4\times10^7$ s^{-2}. While the Li–H dipole–dipole interactions are evidently the dominant ones, the Li–B and Li–Li interactions are not negligible. Therefore, the BPP expression for the ^{7}Li spin–lattice relaxation rate can be
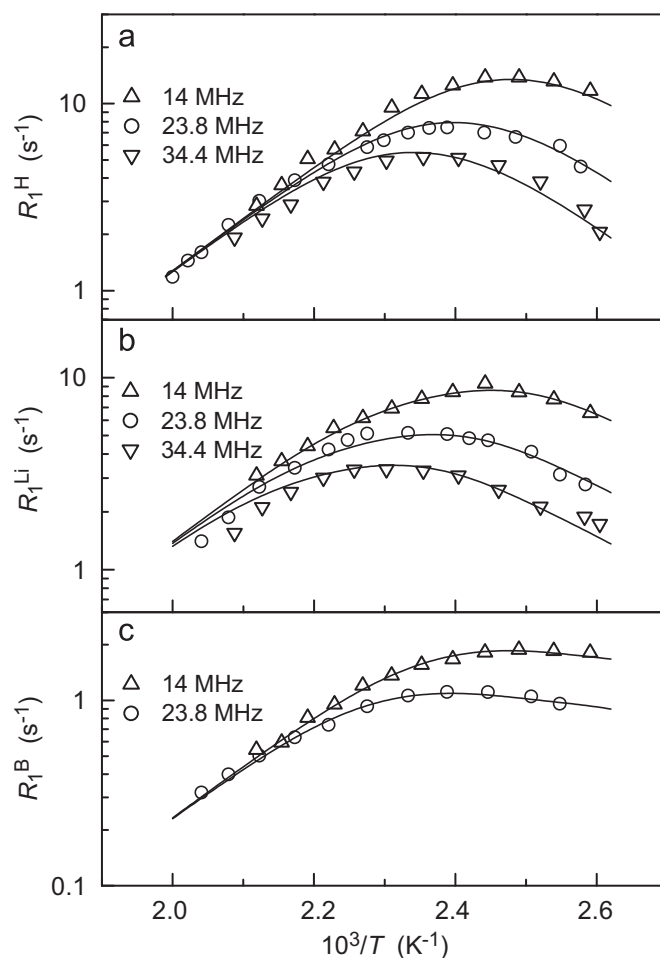

Fig. 4. The ^{1}H, ^{7}Li and ^{11}B spin–lattice relaxation rates as functions of the inverse temperature for the high-temperature phase of LiBH$_4$. The solid curves show the simultaneous BPP fits to the data with the fixed parameters of Li motion: (a) the ^{1}H relaxation data; the fit is based on Eqs. (1) and (2); (b) the ^{7}Li relaxation data; the fit is based on Eqs. (3) and (2) and (c) the ^{11}B relaxation data; the fit is based on Eqs. (4) and (2).

written as

$$\begin{aligned}R_1^{Li} = &\frac{\Delta M_{LiH}}{2\omega}\left[\frac{y}{1+(1-c)^2y^2}+\frac{3y}{1+y^2}+\frac{6y}{1+(1+c)^2y^2}\right]\\&+\frac{\Delta M_{LiB}}{2\omega}\left[\frac{y}{1+(1-d)^2y^2}+\frac{3y}{1+y^2}+\frac{6y}{1+(1+d)^2y^2}\right]\\&+\frac{4\Delta M_{LiLi}}{3\omega}\left[\frac{y}{4+y^2}+\frac{y}{1+y^2}\right]\end{aligned} \tag{3}$$

where ΔM_{LiH}, ΔM_{LiB} and ΔM_{LiLi} are the fluctuating parts of the second moments of the ^{7}Li NMR line due to the Li–H, Li–B and Li–Li dipolar interactions, respectively, $c = \gamma_H/\gamma_{Li}$, $d = \gamma_B/\gamma_{Li}$ and γ_B is the gyromagnetic ratio of ^{11}B. It should be noted that the description of the ^{7}Li spin–lattice relaxation data in Ref. [10] was based on the simplified BPP-type formula (not taking into account that the dominant contribution to R_1^{Li} originates from interactions between unlike nuclear spins). As in the case of ^{1}H relaxation, we keep the Li motional parameters fixed ($\tau_0 = 1.1\times10^{-15}$ s, $E_a = 0.56$ eV) varying only the amplitude parameters (ΔM_{LiH}, ΔM_{LiB} and ΔM_{LiLi}) to describe the observed behavior of R_1^{Li} at three resonance frequencies simultaneously. Since the Li–H, Li–B and Li–Li terms in Eq. (3) show nearly the same temperature and frequency dependences, it is difficult to determine each of the amplitude parameters independently from the fit. Therefore, we assume that

the ratios between ΔM_{LiH}, ΔM_{LiB} and ΔM_{LiLi} are nearly the same as for the respective contributions to the 'rigid lattice' second moment M_{LiH}^R, M_{LiB}^R and M_{LiLi}^R. The results of such a simultaneous fit based on Eqs. (3) and (2) with the fixed motional parameters are shown by solid curves in Fig. 4(b); the corresponding values of the amplitude parameters are $\Delta M_{LiH} = 5.5 \times 10^8\,\text{s}^{-2}$, $\Delta M_{LiB} = 5.3 \times 10^7\,\text{s}^{-2}$ and $\Delta M_{LiLi} = 2.7 \times 10^7\,\text{s}^{-2}$. A rough estimate of the Li–H second moment based on the model of 'free' rotations of the BH$_4$ groups yields $M_{LiH}^F = 6.0 \times 10^8\,\text{s}^{-2}$.

For ^{11}B spin–lattice relaxation caused by Li diffusion, we have to consider the B–Li dipole–dipole interaction and the interaction between the electric quadrupole moment of ^{11}B and the fluctuating EFGs at ^{11}B sites. The appropriate BPP expression for the ^{11}B relaxation rate can be written as

$$R_1^B = \frac{\Delta M_{BLi}}{2\omega}\left[\frac{y}{1+(1-f)^2y^2} + \frac{3y}{1+y^2} + \frac{6y}{1+(1+f)^2y^2}\right] + \frac{\Delta M_Q}{\omega}\left[\frac{y}{1+y^2} + \frac{4y}{1+4y^2}\right], \tag{4}$$

where ΔM_{BLi} is the fluctuating part of the second moment of the ^{11}B NMR line due to the B–Li dipolar interaction, $f = \gamma_{Li}/\gamma_B$, and the amplitude factor ΔM_Q is proportional to the square of the electric quadrupole moment of ^{11}B and the square of the fluctuating part of EFG at ^{11}B sites due to Li motion. Again, we try to describe the ^{11}B spin–lattice relaxation rates at two resonance frequencies keeping the same fixed Li motional parameters and varying only the amplitude parameters. The results of such a simultaneous fit based on Eqs. (4) and (2) are shown by solid curves in Fig. 4(c); the corresponding values of the amplitude parameters are $\Delta M_{BLi} = 7.1 \times 10^7\,\text{s}^{-2}$ and $\Delta M_Q = 3.0 \times 10^7\,\text{s}^{-2}$.

As can be seen from Fig. 4, all the spin–lattice relaxation data for different nuclei (^{1}H, ^{7}Li and ^{11}B) and at different resonance frequencies are satisfactorily described in terms of a single thermally activated process of Li diffusion with $\tau_0 = 1.1 \times 10^{-15}$ s and $E_a = 0.56$ eV. It should be noted that although the ^{1}H, ^{7}Li and ^{11}B spin–lattice relaxation rates are governed by the same motional process, their peaks at a given resonance frequency occur at somewhat different temperatures. This can be related to the fact that the relaxation rates for different nuclei are dominated by different terms in the BPP-type expressions. Indeed, the relaxation rate maxima predicted by Eqs. (1), (3) and (4) occur at $y = 0.92$, 0.72 and 1.33, respectively. We have not found any contributions of other motional processes (such as H diffusion) to the measured spin–lattice relaxation rates, at least up to 500 K. The presence of any considerable distribution of the jump rates τ_{Li}^{-1} can also be excluded. In fact, such a distribution would make the frequency dependence of the relaxation rate substantially weaker than that predicted by Eqs. (1), (3) and (4) [15]. The estimate of the Li jump rate at 500 K, τ_{Li}^{-1} (500 K), based on the Arrhenius relation gives $2.1 \times 10^9\,\text{s}^{-1}$. Neglecting any correlations in jump motion, the tracer diffusion coefficient of Li ions can be written as

$$D = L^2/6\tau_{Li}, \tag{5}$$

where L is the jump length. According to the structural data [6], each Li atom in the HT phase of LiBH$_4$ is coordinated by six nearest-neighbor Li atoms at a distance of 4.25 Å and six Li atoms at a distance of 4.27 Å. Assuming that the jumps occur between the nearest-neighbor Li sites, we obtain the estimate of the Li diffusion coefficient at 500 K, $D(500\,\text{K}) \approx 6.3 \times 10^{-7}\,\text{cm}^2/\text{s}$. This value is much higher than the estimated hydrogen diffusion coefficient ($7 \times 10^{-10}\,\text{cm}^2/\text{s}$ at 523 K [13]). Thus, the translational motion of H atoms remains to be much slower than that of Li atoms in the HT phase of LiBH$_4$.

3.2. Narrowing of the ^{1}H and ^{11}B NMR lines

Measurements of the widths of NMR lines can, in principle, 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' linewidth [19], which for protons is typically of the order of $10^5\,\text{s}^{-1}$. Fig. 5(a) shows the temperature dependence of the ^{1}H NMR linewidth (full width at half-maximum) in LiBH$_4$ measured at the frequency of 23.8 MHz. This temperature dependence is close to that measured previously [12] at 85 MHz. The observed proton linewidth at the low-temperature plateau ($T < T_0$) is still considerably smaller than the 'rigid lattice' linewidth [11]. This is related to the fact that the dipole–dipole interactions in this range are partially averaged by the fast reorientational motion of the BH$_4$ tetrahedra. The small drop in the linewidth just below T_0 (Fig. 5(a)) can be attributed to the onset of translational motion of Li ions. As noted previously [11], the H–Li dipolar interaction is not strong enough to cause a considerable narrowing of the ^{1}H NMR line due to Li diffusion. However, the strong line narrowing observed above ~440 K (Fig. 5(a)) can only be explained in terms of translational motion of hydrogen atoms, in agreement with the conclusions of Ref. [12]. The characteristic jump rate for the translational H motion estimated from the line narrowing [12] is about $1.5 \times 10^5\,\text{s}^{-1}$ at 500 K.
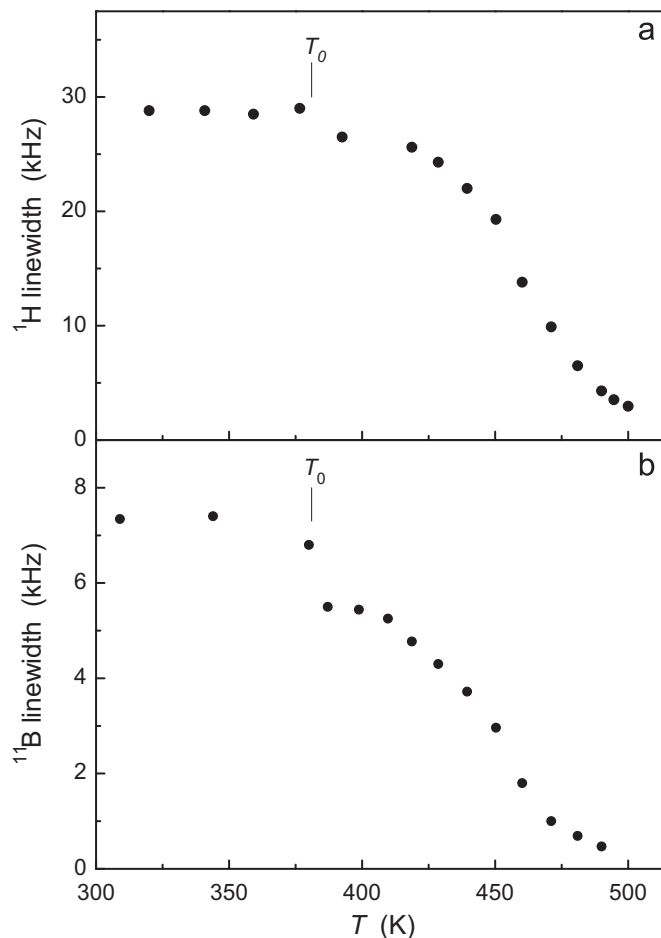

Fig. 5. The temperature dependences of the width (full width at half-maximum) of the ^{1}H NMR line (a) and the ^{11}B NMR line (b) measured at 23.8 MHz for LiBH$_4$. The vertical bar indicates the temperature of the structural phase transition.

The temperature dependence of the ^{11}B NMR linewidth (full width at half-maximum) measured at the frequency of 23.8 MHz is shown in Fig. 5(b). It can be seen from this figure 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 in the HT phase of LiBH$_4$. As proposed by Corey et al. [12], such a process may be related with the 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 [12] that the ^{11}B linewidth drops below the value expected for the B–B contribution to the 'rigid lattice' second moment. Our ^{11}B NMR results confirm this conclusion. It is likely that the onset of translational motion of the BH$_4$ units is accompanied by a transformation from the fast reorientations to the 'free' (liquid-like) rotation of the BH$_4$ tetrahedra. Such a transformation of the rotational motion of the BH$_4$ units can, in principle, be detected by quasielastic neutron scattering (QENS). For reorientations of the BH$_4$ tetrahedra, the elastic incoherent structure factor (measured by QENS on the time scale of the fast localized motion) should remain finite at high momentum transfers, whereas for free rotations it is expected to go to zero at high momentum transfers [20]. In diffraction experiments, such a transformation should be seen as an orientational disorder of the BH$_4$ tetrahedra with the associated increase in the atomic displacement parameters for H atoms. In fact, the results of both synchrotron and neutron diffraction experiments [6,8,9] have revealed that the BH$_4$ tetrahedra are extremely disordered in the HT phase of LiBH$_4$.

4. Conclusions

The analysis of the temperature and frequency dependences of our ^{1}H, ^{7}Li and ^{11}B spin–lattice relaxation rates in the high-temperature (hexagonal) phase of LiBH$_4$ has shown that in the temperature range 384–500 K all the relaxation data can be described in terms of a thermally activated jump motion of Li ions with the pre-exponential factor $\tau_0 = 1.1 \times 10^{-15}$ s and the activation energy $E_a = 0.56$ eV. In this temperature range, we have not found any distributions of the Li jump rate or any other jump processes on the frequency scale of 10^7–10^{10} s^{-1}. The slower process of hydrogen diffusion with the characteristic jump rate of about 1.5×10^5 s^{-1} at 500 K leads to the strong narrowing of the ^{1}H and ^{11}B NMR lines at $T > 440$ K. Our results support the idea [12] that the main mechanism of hydrogen diffusion in the high-temperature solid phase of LiBH$_4$ is related to the motion of complete BH$_4$ units.

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