Nuclear Magnetic Resonance Studies of BH₄ Reorientations and Li Diffusion in LiLa(BH₄)₃Cl

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ABSTRACT: To study the reorientational motion of BH₄ groups and the translational diffusion of Li⁺ ions in the novel bimetallic borohydride chloride LiLa(BH₄)₃Cl, we have measured the ¹H, ¹¹B, and ⁷Li NMR spectra and spin–lattice relaxation rates in this compound over the temperature range of 23–418 K. At low temperatures (T < 110 K), the proton spin–lattice relaxation rates are governed by fast reorientations of BH₄ groups. This reorientational process can be satisfactorily described in terms of a two-peak distribution of the activation energies with the peak Eₓ values of 41 and 50 meV. Above 200 K, the NMR data are governed by a combined effect of two types of motion occurring at the same frequency scale: Li ion diffusion and another (slower) reorientational motion of BH₄ groups. These results suggest that the Li ion jumps and the slower reorientational jumps of BH₄ groups in LiLa(BH₄)₃Cl may be correlated. The estimate of the tracer Li ion diffusion coefficient at room temperature (5.2 × 10⁻⁸ cm²/s) following from our experimental data indicates that LiLa(BH₄)₃Cl can be considered as a promising solid-state ionic conductor.

INTRODUCTION

Development of new sustainable and environment-friendly energy systems requires safe and efficient ways of energy storage. Renewable energy can be stored directly as electricity in batteries or indirectly as hydrogen in solid-state hydrides.¹ Metal borohydrides have received recent attention as promising hydrogen-storage materials²–⁴ due to their high hydrogen densities. However, practical use of the known metal borohydrides is hindered by their stability with respect to thermal decomposition and the slow hydrogen sorption kinetics.²–⁶ A number of methods (such as mechanical alloying, nanoconfinement, using catalytic additives) have been suggested⁷–¹² to destabilize borohydrides and make the kinetics of dehydrogenation and rehydrogenation more favorable. Recently, several bimetallic borohydrides and bimetallic borohydride chlorides have been synthesized, including LiSc(BH₄)₀.¹³,¹⁴ NaSc(BH₄)₀.¹⁵ KSc(BH₄)₀.¹⁶ KY(BH₄)₀.¹⁷ NaY-(BH₄)₂Cl₂.¹⁸ LiCe(BH₄)₃Cl.¹⁹,²⁰ LiLa(BH₄)₃Cl.²¹ and LiGd-(BH₄)₂Cl.²² Some of these novel compounds are found to have very unusual crystal structures and relatively low decomposition temperatures (e.g., ~260–280 °C for LiCe(BH₄)₂Cl, well below the decomposition temperature for LiBH₄ ~380 °C).

The bimetallic borohydride chloride LiLa(BH₄)₃Cl exhibits both high hydrogen density and high Li ion conductivity.²¹ Therefore, it can be considered both as a prospective hydrogen-storage material and an ionic conductor. In fact, the volumetric H density at room temperature for LiLa(BH₄)₃Cl (97.1 kg/m³) is comparable to the corresponding values for LiBH₄ (123 kg/m³) and α-MgH₂ (108 kg/m³). The gravimetric H density in LiLa(BH₄)₃Cl is 5.36 wt %. This should be compared to the corresponding values for LiBH₄ (18.4 wt %) and MgH₂ (7.6 wt %). The crystal structure of LiLa(BH₄)₃Cl is found to be cubic (space group I4̅3m) with the unit cell parameter a = 11.7955 Å.²¹ This structure is isomorphous to that for LiCe(BH₄)₂Cl²² and LiGd(BH₄)₂Cl.²² The structure contains isolated tetranuclear anionic clusters [La₄Cl₄(BH₄)₁₂]⁴⁻ with a distorted cube La₄Cl₄ core, charge-balanced by Li⁺ cations. Each La atom is coordinated by three Cl atoms and three BH₄ groups via the H₁ face, thus completing the coordination environment of an octahedron. Li⁺ ions are disordered, occupying 2/3 of the available 12d sites. At 20 °C the measured Li ion conductivity of LiLa(BH₄)₃Cl is 2.3 × 10⁻⁴ S/cm.²² Experimental studies of the relations between the crystal structure, BH₄ rotational dynamics, and Li ion mobility are expected to contribute to the search for new materials with high ionic conductivity. Microscopic information on atomic motion can be obtained from nuclear magnetic resonance (NMR) and quasielastic neutron scattering (QENS) measurements. These techniques have been used in a series of recent studies of atomic motion in alkali,²²–³³ alkaline-earth,³⁴–³⁹ and transition-metal borohydrides⁴⁰ and in Li(BH₄)₁₋ₓIₓ solid solutions.⁴¹–⁴⁴ However, hydrogen dynamics and ion mobility in bimetallic borohydride-

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based systems have not been investigated so far. The aim of the present work is to study both the reorientational motion of BH₄ groups and Li diffusion in LiLa(BH₄)₃Cl using ¹H, ¹¹B, and ⁷Li NMR measurements of the spectra and spin–lattice relaxation rates over wide ranges of temperature (23–418 K) and resonance frequency (14–90 MHz). We also discuss a possible relation between the reorientational motion and the translational diffusion in this compound. It is interesting to note that in a number of borohydride-based systems, such as the high-temperature (hexagonal) phase of LiBH₄ and LiBH₄–Li₃ solid solutions, the fast Li ion diffusion is accompanied by the very fast BH₄ reorientations. However, in the systems studied so far, these two types of motion occur at different time scales. The results of the present work suggest that in LiLa(BH₄)₃Cl the diffusive Li ion jumps and a certain type of BH₄ reorientations may be correlated since they occur at the same time scale.

## EXPERIMENTAL METHODS

The sample preparation was analogous to that described in ref 21. All preparation and manipulation procedures were performed in a glovebox with a circulation purifier maintained under an argon atmosphere with less than 1 ppm of O₂ and H₂O. The LaCl₃–LiBH₄ mixture (1:3 molar ratio) was ball-milled in a Fritsch Pulverisette 4 planetary mill in an argon atmosphere using tungsten carbide balls and vial with a 1:35 sample to balls mass ratio. To minimize sample heating, a 2 min milling period was followed by 2 min pause, and this procedure was repeated 60 times. The chemicals used were lanthanum chloride LaCl₃ (Sigma-Aldrich, 99.9%) and lithium borohydride LiBH₄ (Sigma-Aldrich, 95%). After the milling, the sample was annealed at 200 °C for 30 min under H₂ (10 bar) atmosphere. According to X-ray diffraction analysis, the resulting sample consisted of the cubic LiLa(BH₄)₃Cl (space group I₄₃m, a = 11.7955(1) Å) and LiCl. For NMR experiments, the sample was flame-sealed in a glass tube under ~500 mbar of nitrogen gas.

NMR measurements were performed on a pulse spectrometer with quadrature phase detection at the frequencies ω/2π = 14, 28, and 90 MHz for ¹H and 28 MHz for both ¹¹B and ⁷Li. 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 wide-band pulse amplifier. Typical values of the π/2 pulse length were 2–3 μs for all nuclei studied. A probe head with the sample was placed into an Oxford Instruments CF1200 continuous-flow cryostat using helium or nitrogen as a cooling agent. The sample temperature in the range 23–418 K, monitored by a chromel–Al₉Fe 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 solid echo signals (pulse sequence π/2−τ−π−π/2).

## RESULTS AND DISCUSSION

The behavior of the proton spin–lattice relaxation rates measured at three resonance frequencies for LiLa(BH₄)₃Cl is shown in Figure 1. As can be seen from this figure, the temperature dependences of the ¹H spin–lattice relaxation rate exhibit two peaks. Both peaks are frequency-dependent, which is typical of the relaxation mechanism due to the nuclear dipole–dipole interaction modulated by atomic motion. For this mechanism, the R₁(H)(T) maximum is expected to occur at the temperature at which the atomic jump rate τ⁻¹ becomes nearly equal to the resonance frequency ω. On the basis of previous structural studies, we can conclude that LiLa(BH₄)₃Cl has no polymorphic transitions in the temperature range investigated here. Thus, the presence of two well-separated R₁(H)(T) peaks indicates a coexistence of at least two types of atomic motion with strongly differing characteristic jump rates. The amplitude of each of the peaks is determined by the strength of the corresponding fluctuating part of the dipole–dipole interaction. For the borohydrides studied previously, the large R₁(H)(T) peaks were found to originate from reorientational motion of BH₄ groups, while smaller high-temperature R₁(H)(T) peaks observed in some of them were attributed to slower translational motion of Li ions.

### Low-Temperature Region

We shall start our analysis with a discussion of the behavior of the proton spin–lattice relaxation rates in the region of the low-temperature peak. For LiLa(BH₄)₃Cl, this behavior resembles that found for Li(BH₄)₂·I₃ solid solutions. In both cases, the proton relaxation rate maximum is observed below 80 K; this indicates that the atomic motion responsible for the R₁(H)(T) maximum is very fast. In fact, the R₁(H)(T) maximum for LiLa(BH₄)₃Cl at ω/2π = 14 MHz is observed near 58 K, i.e., the jump rate τ⁻¹ reaches the value of ω ~ 10⁸ s⁻¹ already at this temperature. Comparing the R₁(H)(T) data for LiLa(BH₄)₃Cl with those for other borohydride-based systems, we can conclude that the low-temperature proton relaxation rate peak originates from the reorientational motion of BH₄ groups. As it will be discussed below, this conclusion is consistent with the behavior of the ¹H NMR line width. To estimate the relative strength of the ¹H→¹⁵B, ¹H→¹¹B, ¹H→⁷Li, ¹H→⁷Li, ¹H→¹³La, and ¹H→¹⁹FCl dipole–dipole interactions, we have calculated the corresponding contributions to the “rigid lattice” second moment of the ¹H NMR line on the basis of the structural data for LiLa(BH₄)₃Cl taking into account internuclear distances of up to 4 Å. The resulting rigid lattice contributions are M⁻¹ₖB =
1.66 \times 10^{10} \text{ s}^{-2}, M_{HH}^{R} = 1.77 \times 10^{10} \text{ s}^{-2}, M_{HH}^{R} = 5.7 \times 10^{8} \text{ s}^{-2},
M_{HL}^{R} = 1.5 \times 10^{8} \text{ s}^{-1}, \text{ and } M_{HL}^{R} = 3.4 \times 10^{6} \text{ s}^{-2}. \text{ Thus, the dominant contributions originate from the H–B and H–H interactions, while the contributions of other dipole–dipole interactions can be neglected.}

According to the standard theory\textsuperscript{45} of nuclear spin–lattice relaxation due to atomic motion, in the limit of slow motion (\(\omega \tau \gg 1\)), \(R_{i}^{H}\) should be proportional to \(\omega^{-2} \tau^{-1}\), and in the limit of fast motion (\(\omega \tau \ll 1\)), \(R_{i}^{H}\) should be proportional to \(\tau\) being frequency-independent. If the temperature dependence of the jump rate \(\tau^{-1}\) is governed by the Arrhenius law with the activation energy \(E_{a}\)

\[
\tau^{-1} = \tau_{0}^{-1} \exp(-E_{a}/k_{B}T)
\]

(1)
a plot of \(\ln R_{i}^{H}\) vs \(T^{-1}\) should be linear in the limits of both slow and fast motion with the slopes \(-E_{a}/k_{B}\) and \(E_{a}/k_{B}\), respectively. As can be seen from Figure 1, the behavior of the measured proton spin–lattice relaxation rate in the region of the low-temperature peak deviates significantly from this simple picture. First, the observed high-temperature slope of the log \(R_{i}^{H}\) vs \(T^{-1}\) plot is considerably steeper than the low-temperature slope. Second, the experimental frequency dependence of \(R_{i}^{H}\) at the low-temperature slope is much weaker than the expected \(\omega^{-2}\) dependence. These features are consistent with the presence of a broad distribution of \(H\) jump rates.\textsuperscript{46}

Such a distribution in LiLa(BH\(_4\))Cl can be expected, since Li ions in this compound randomly occupy 2/3 of 12d sites, so that the local environment of a BH\(_4\) group changes from one group to another. For disordered solids, the simplest approach to the description of a jump rate distribution is based on the model with a Gaussian distribution of the activation energies. Furthermore, the relaxation data shown in Figure 1 exhibit a “shoulder” near 45 K, this suggests a coexistence of at least two low-temperature processes with different average jump rates. Therefore, for the description of the low-temperature \(R_{i}^{H}\) data we will use the two-peak model where the subscript \(i\) (\(i = 1, 2\)) denotes the two jump processes, and \(i = 1\) corresponds to the faster motion. For this model

\[
R_{i}^{H} = R_{i1}^{H} + R_{i2}^{H}
\]

(2)
where \(R_{i}^{H}\) is expressed as

\[
R_{i}^{H} = \int R_{i}^{H}(E_{a})G(E_{a}, E_{a}, \Delta E_{a}) \, dE_{a}
\]

(3)
Here \(G(E_{a}, E_{a}, \Delta E_{a})\) is a Gaussian distribution function centered at \(E_{a}\) with the dispersion \(\Delta E_{a}\) and \(R_{i}^{H}(E_{a})\) is given by the standard theory\textsuperscript{45}

\[
R_{i}^{H}(E_{a}) = \frac{\Delta M_{HH}^{R} \tau_{i}}{2} \left[ \frac{1}{1 + (\omega_{H} - \omega_{B})^{2} \tau_{i}^{2}} + \frac{3}{1 + \omega_{H}^{2} \tau_{i}^{2}} \right] + \frac{6}{1 + (\omega_{H} + \omega_{B})^{2} \tau_{i}^{2}} + \frac{\Delta M_{HH}^{R} \tau_{i}}{3} \left[ \frac{1}{1 + \omega_{H}^{2} \tau_{i}^{2}} + \frac{1}{1 + \omega_{H}^{2} \tau_{i}^{2}} \right]
\]

(4)
where the equation analogous to eq 1 relates the jump rates \(\tau_{i}^{-1}\) and the corresponding activation energies \(E_{a}, \omega_{H}\) and \(\omega_{B}\) are the resonance frequencies of \(^{1}H\) and \(^{11}B\), respectively, and \(\Delta M_{HH}^{R}\) and \(\Delta M_{HH}^{R}\) are the parts of the dipolar second moment due to \(^{1}H–^{11}B\) and \(^{1}H–^{1}H\) interactions that are caused to fluctuate by the ith type of reorientational motion. It should be noted that usually the equations similar to eq 4 are written in terms of correlation times \(\tau_{c}\) not in terms of the residence times \(\tau_{i}\). However, the relation between \(\tau_{c}\) and \(\tau_{i}\) may differ for different interacting nuclear spins. When one of the interacting spins is immobile, \(\tau_{c} = \tau_{i}\), while for independently moving spins, \(\tau_{c} = \tau_{i}/2\). A somewhat unusual form of the H–H term in eq 4 originates from the fact that here we have explicitly assumed that \(\tau_{c} = \tau_{i}/2\), which is true for most of the H–H interactions in our system. The parameters of the model are \(\Delta M_{HH}^{R}\) and \(\Delta M_{HH}^{R}\) close to each other. Therefore, for parametrization of the \(R_{i}^{H}\) data we will assume that \(\Delta M_{HH}^{R} = \Delta M_{HH}^{R} = \Delta M\). The results of the simultaneous fit of the two-peak model (eqs 2, 3, 4 and the analogue of eq 1) to the experimental data in the range 23–110 K are shown by solid curves in Figure 1. As can be seen from this figure, the experimental data at three resonance frequencies are satisfactorily described by a single set of parameters. The values of the amplitude parameters resulting from this fit are \(\Delta M_{1} = 2.3 \times 10^{9} \text{ s}^{-2}\) and \(\Delta M_{2} = 5.1 \times 10^{6} \text{ s}^{-2}\), and the corresponding motional parameters are \(\tau_{01} = (5.1 \pm 0.9) \times 10^{-14} \text{ s}, E_{a1} = 41 \pm 5 \text{ meV}, \Delta E_{a1} = 7 \pm 2 \text{ meV}, \) and \(\tau_{02} = (5.5 \pm 0.8) \times 10^{-15} \text{ s}, E_{a2} = 50 \pm 3 \text{ meV}, \Delta E_{a2} = 6 \pm 2 \text{ meV}.\) It should be noted that the values of \(E_{a1}\) and \(E_{a2}\) for LiLa(BH\(_4\))Cl are close to the activation energies for the faster reorientational process in LiBH\(_4\)–LiI solid solutions.\textsuperscript{43}

The local environment of the BH\(_4\) group in LiLa(BH\(_4\))Cl is schematically shown in Figure 2. The BH\(_4\) tetrahedron is coordinated by a single La atom via the face and by three Li sites via the edges. However, only two-thirds of the available Li sites are randomly occupied by Li ions. Figure 2 corresponds to the most probable configuration with two nearest-neighbor Li ions, but it should be kept in mind that the actual number of the nearest-neighbor Li ions may vary from one BH\(_4\) group to another. This local environment suggests that the most probable “easy” reorientation axis is the threefold axis directed along the La–B line. In fact, the rotation of the BH\(_4\) group

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Schematic view of the coordination environment of a BH\(_4\) group in LiLa(BH\(_4\))Cl. The B–H bonds are shown by yellow bars, and the La–H and Li–H bonds are shown by dashed yellow lines. Only two of three nearest-neighbor Li sites are shown; since two-thirds of the available Li sites are randomly occupied by Li ions, this corresponds to the most probable configuration. The local threefold axis of the BH\(_4\) group is oriented vertically. The solid black lines with arrows show the proposed fast reorientational process, and the dashed black line with arrows is associated with the slower exchange process.}
\end{figure}
around this threefold axis does not break any La–H bonds, and, since the apical H atom does not move, it breaks only one-half of the Li–H bonds. While the low values of $E_{\Delta \text{H}}$ and $E_{\Delta \text{E}}$ indicate that the Li–H bonds are weak, the motion of BH$_4$ groups in LiLa(BH$_4$)$_3$Cl around the threefold axes cannot be considered as a “free” rotation. In fact, neutron diffraction measurements for the related LiCe(BD$_4$)$_3$Cl compound have not revealed any anomalously large displacements of D atoms from their crystallographic sites. It seems reasonable to assume that the two jump processes contributing to the low-temperature $R_{\text{f}}^1(T)$ peak correspond to the threefold reorientations of BH$_4$ groups having two or one nearest-neighbor Li ions; the former case should then be ascribed to the slower process, and the latter one to the faster process.

Figure 3 shows the temperature dependence of the $^1$H NMR line width $\Delta \nu_{\text{H}}$ (full width at half-maximum) measured at 28 MHz. In the range 28–100 K, the line width remains nearly constant. However, the value of $\Delta \nu_{\text{H}}$ in this range ($\approx 36$ kHz) appears to be considerably smaller than the expected line width for the rigid lattice ($\approx 70$ kHz). This suggests that a partial line narrowing occurs even at temperatures as low as 28 K. In agreement with the proton spin–lattice relaxation data, such a behavior of $\Delta \nu_{\text{H}}$ indicates that the fast atomic motion in LiLa(BH$_4$)$_3$Cl survives down to very low temperatures. A substantial line narrowing is expected when the atomic jump rate $\tau^{-1}$ becomes nearly equal to the rigid lattice line width $\Delta \nu_{\text{H}}$ (in our case, this value is of the order of $10^5$ s$^{-1}$). However, localized H motion (such as BH$_4$ reorientations) leads to only partial averaging of the dipole–dipole interactions, so that $\Delta \nu_{\text{H}}$ remains finite even at jump rates much higher than $10^5$ s$^{-1}$. Thus, the $\Delta \nu_{\text{H}}(T)$ plateau in the range 28–100 K (Figure 3) is consistent with the localized character of the low-temperature H jump motion. Similar plateaus in the temperature dependences of the proton NMR line widths were observed for other borohydrides showing BH$_4$ reorientations. The value of $\Delta \nu_{\text{H}}$ at the plateau is determined by the strength of dipole–dipole interactions, which are not averaged out by a particular type of localized motion. It should be noted that for LiLa(BH$_4$)$_3$Cl the value of $\Delta \nu_{\text{H}}$ at the low-temperature plateau is larger than the corresponding values for other studied borohydrides. This means that the low-temperature reorientational motion in LiLa(BH$_4$)$_3$Cl averages out a relatively small fraction of the rigid lattice dipole–dipole interactions. Such a feature supports our assumption that the low-temperature reorientational motion in LiLa(BH$_4$)$_3$Cl corresponds to rotations around a single threefold axis, since this type of motion does not lead to complete averaging of the dipolar interactions even within the BH$_4$ group. As can be seen from Figure 3, at $T > 130$ K the proton line width decreases and reaches the new plateau. This behavior will be discussed in the next section.

**High-Temperature Region.** The expanded view of the $R_{\text{f}}^1(T)$ data in the region of the high-temperature peak is shown in Figure 4. General features of the observed behavior of $R_{\text{f}}^1(T)$ in this range are typical of the peak originating from some kind of atomic motion. Can this peak result from the translational diffusion of Li ions? To answer this question, we first discuss the behavior of the $^7$Li NMR line width, $\Delta \nu_{\text{Li}}$.

Figure 5 shows the measured temperature dependence of the width of the central $^7$Li NMR line for LiLa(BH$_4$)$_3$Cl. The observed strong narrowing of this line above 200 K is consistent with the onset of Li jump motion at the frequency scale of $\approx 10^3$ s$^{-1}$. The value of $\Delta \nu_{\text{Li}}$ in the region of the high-temperature plateau ($0.38$ kHz) is considerably smaller than the expected line width ($\approx 1.4$ kHz) for the $^7$Li–$^7$Li dipolar...
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contribution to the rigid lattice second moment. Therefore, the
$^7$Li--$^7$Li dipole–dipole interaction is averaged out in the region
of the high-temperature plateau; this can occur only in the case
of long-range diffusion of Li ions. For the same motional
process, the spin–lattice relaxation rate maximum is expected
to appear at higher temperatures than the drop of the line
width; thus, the position of the high-temperature $R_1^H(T)$ peak
($\sim 250$ K at 14 MHz) shows that this peak may originate from
Li diffusion. However, as we shall see, the amplitude of this peak
is too high to result solely from Li diffusion. Indeed, the
estimate of the $^1$H--$^7$Li contribution to the rigid-lattice dipolar
second moment of the $^1$H NMR line gives $5.7 \times 10^4$ s$^{-2}$ (see
above). The full modulation of this $^1$H--$^7$Li interaction due to
Li diffusion would result in the maximum $R_1^H$ value of 15 s$^{-1}$
at 14 MHz. The measured maximum $R_1^H$ value for the high-
temperature peak (89 s$^{-1}$ at 14 MHz) is considerably higher
than that estimated for the case of Li diffusion. Note that for
the proton relaxation peak resulting solely from Li diffusion in
the high-temperature phase of LiBH$_4$, the maximum $R_1^H$ value
is 13.8 s$^{-1}$ at 14 MHz. Thus, we can conclude that the high-
temperature $R_1^H(T)$ peak in LiLa(BH$_4$)$_3$Cl originates from a
combined effect of at least two motional processes occurring
at the same frequency scale: Li ion diffusion and another process
that involves H jumps. The latter process should give the
dominant contribution to the amplitude of the high-temper-
ature $R_1^H(T)$ peak. Since the proton NMR line width $\Delta v_{1H}$
remains rather large up to 400 K (see Figure 3), we can exclude
the possibility of long-range diffusion of H-containing species in
the studied temperature range. Therefore, the process involving
H jumps should be attributed to some kind of BH$_4^-$
reorientations. In the following, we will refer to it as the
slower reorientational process; this means that its characteristic
jump rate $\tau_0^{-1}(T)$ is several orders of magnitude lower than
both $\tau_1^{-1}(T)$ and $\tau_2^{-1}(T)$ in the range of the high-temperature
$R_1^H(T)$ peak. Most probably, the slower reorientations are those
leading to exchange between H atoms in the La-coordinated
plane of the BH$_4$ tetrahedron and the remaining apical H atom.
On the basis of quasielastic neutron scattering measure-
ments, an exchange has been identified as the slower
reorientational process in the high-temperature phase of LiBH$_4$
and in the LiBH$_4$--LiI solid solution. This process is
schematically shown by the dashed line with arrows in Figure
2. The relevant physical picture implies that each BH$_4^-$
group performs many reorientational jumps around the
threefold axis before the occurrence of an exchange between
one of the moving H atoms and the static apical H atom.

To the best of our knowledge, this is the first time that an ion
diffusion and reorientational motion occurring at the same
frequency scale are found in BH$_4^-$-based systems. However,
similar observations were reported for a number of
orthophosphate-based ionic conductors, such as Na$_3$PO$_4$.
For these compounds, there is a strong evidence of dynamic
coupling between the anion rotation and cation diffusion, as
discussed in terms of the “paddle-wheel” mechanism. It is
likely that, in the case of LiLa(BH$_4$)$_3$Cl, the slower BH$_4^-$
reorientations and Li jumps may also be correlated. On the
basis of our data, it is impossible to conclude unambiguously
which type of motion (reorientations or Li jumps) is the
primary driving force. However, in the framework of the
paddle-wheel mechanism, the reorientational motion is
believed to initiate cation jumps. In our case, one may also
assume that a certain tumbling of the BH$_4$ tetrahedron
initiates

a jump of the adjacent Li ion to the nearest-neighbor vacant
site.

For parametrization of the proton spin–lattice relaxation
results in the region of the high-temperature $R_1^H(T)$ peak, we
have used the simplest model that is consistent with general
features of the data, i.e., the one-peak model with a Gaussian
distribution of the activation energies. Since the high-temper-
ature $R_1^H(T)$ peak is dominated by slower reorientational
process, we introduce the H jump rate $\tau_1^{-1}$ for this process
with the corresponding pre-exponential factor $R_{1P}$, the average
activation energy $E_{a3}^H$, and the distribution width $\Delta E_{a3}^H$.
The model is described by eqs 3 and 4 and the analogue of eq 1.
The results of the simultaneous fit of this model to the $R_1^H(T)$
data at three resonance frequencies in the range 189–418 K are
shown by solid lines in Figure 4. The motional parameters
resulting from the fit are $\tau_0 = (2.1 \pm 0.6) \times 10^{-14}$ s, $E_{a3}^H = 264 \pm 8$ meV, and $\Delta E_{a3} = 31 \pm 5$ meV. While this model
satisfactorily describes the main features of the data over broad
ranges of temperature and the resonance frequency, the fit is
not perfect. This may be related to the fact that the model does
not explicitly take into account the diffusive Li jumps, the mean
rate of which, $\tau_1^{-1}$, may not coincide exactly with $\tau_1^{-1}$.

The $^{11}$B and $^7$Li spin–lattice relaxation measurements have
been performed in the high-temperature region at the
frequency of 28 MHz. For both nuclei, the recovery of the
nuclear magnetization deviates from a single-exponential
behavior, and the recovery curves can be reasonably
approximated by a sum of two-exponential functions. For $^{11}$B,
the two-exponential relaxation was found in some borohy-
drides, such a behavior may be ascribed to nonzero electric
quadrupole moment of this nucleus. For $^7$Li, an additional
complication may arise from the presence of LiCl in our sample
(see the Experimental Methods section). However, the $^7$Li
spin–lattice relaxation times for pure LiCl are very long;
therefore, this additional phase is not expected to give any
significant contributions on the time scale of our $^7$Li NMR
experiments. For both $^{11}$B and $^7$Li, the observed two-
exponential relaxation is dominated by the faster relaxation
component $R_{1P}$. The temperature dependences of the faster
components of the $^{11}$B and $^7$Li spin–lattice relaxation rates are
shown in Figure 6. The behavior of $R_{1F}$ for $^{11}$B resembles that
of the $^1$H spin–lattice relaxation rate in this range (Figure 4).
As in the case of the $^1$H relaxation, the maximum $R_{1F}$ value for

![Figure 6. Fast components of the $^7$Li and $^{11}$B spin–lattice relaxation rates measured at 28 MHz for LiLa(BH$_4$)$_3$Cl as functions of the inverse temperature. The data are shown in the temperature range 189–418 K.](image-url)
\^1B (~86 s\(^{-1}\)) appears to be much larger than that resulting solely from Li diffusion. For comparison, the maximum \(^{11}\)B spin–lattice relaxation rate resulting from Li diffusion in the high-temperature phase of LiBH\(_4\) is 1.1 s\(^{-1}\) at 23.8 MHz.\(^{25}\) Thus, the observed peak of the \(^{11}\)B spin–lattice relaxation rate in LiLa(BH\(_4\))\(_3\)Cl should be dominated by some reorientational process. For the \(^7\)Li relaxation rate peak, the situation is more complex. Because of the relative weakness of the \(^7\)Li–\(^1\)H dipole–dipole interactions, the effect of BH\(_4\) reorientations on the \(^7\)Li relaxation rate is moderate, so that the maximum \(R_{1\text{f}}\) value for \(^7\)Li (~18.9 s\(^{-1}\)) is only a factor of 3–4 larger than that expected for Li jumps alone. In fact, the maximum \(^7\)Li spin–lattice relaxation rate resulting from Li diffusion in the high-temperature phase of LiBH\(_4\) is 5.2 s\(^{-1}\) at 23.8 MHz.\(^{25}\) Therefore, the effects of Li jump motion should be more pronounced in the \(^7\)Li relaxation results than in the \(^1\)H and \(^{11}\)B relaxation data. It should also be noted that the \(R_{1\text{f}}\) maximum for \(^7\)Li is shifted to somewhat higher temperature from the corresponding maxima for the \(^1\)H and \(^{11}\)B relaxation rates. We have not tried to fit the \(^1\)H and \(^7\)Li spin–lattice relaxation data in the region of the peak. However, a rough estimate of the activation energy \(E_1\) for Li diffusion can be obtained using the high-temperature slope of the \(^7\)Li spin–lattice relaxation rate peak. Such an estimate yields \(E_1 \approx 0.30\) eV. This value is close to \(E_1\) for the slower reorientational process in LiLa(BH\(_4\))\(_3\)Cl (see above). For comparison, the activation energy for Li diffusion in the high-temperature phase of LiBH\(_4\) is considerably higher (0.56 eV\(^{22,25}\) and 0.54 eV\(^{30}\)).

Our data show that the diffusive mobility of Li ions in LiLa(BH\(_4\))\(_3\)Cl is very high. This is supported by the fact that the strong narrowing of the \(^7\)Li NMR line occurs already at \(T \approx 220\) K. For most of the studied solid Li ion conductors (such as Li\(_3\)N, Li\(_4\)TiS\(_2\), LiNbO\(_3\), Li aluminosilicates\(^{50,51}\)), the line narrowing is observed at higher temperatures. A rough estimate of the Li jump rate \(r_\text{Li}\) for LiLa(BH\(_4\))\(_3\)Cl can be obtained at the temperature of the \(R_{1\text{f}}\) maximum (~297 K at 28 MHz). Such an estimate yields \(r_\text{Li} \approx 1.8 \times 10^9\) s\(^{-1}\). The sublattice of 12d sites partially occupied by Li ions in LiLa(BH\(_4\))\(_3\)Cl is shown in Figure 7. It is interesting to note that this sublattice is isomorphic to the sublattice of tetrahedral interstitial sites in body-centered cubic metals, where H atoms partially occupying these sites show very high diffusive mobility.\(^{52}\)

The distance \(L\) between the nearest-neighbor 12d sites in LiLa(BH\(_4\))\(_3\)Cl is 4.17 Å. Neglecting any correlations in jump motion, the tracer diffusion coefficient of Li ions can be estimated as \(D(297\text{ K}) = L^2 r_\text{Li}^{-1}(297\text{ K})/6 \approx 5.2 \times 10^{-8}\) cm\(^2\)/s.

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\[ \sigma = nD(\sigma_0) / k_B T \]

where \(n\) is the number of charge carriers per unit volume and \(\sigma_0\) is the electrical charge of the carrier. Using the lattice parameter of LiLa(BH\(_4\))\(_3\)Cl\(^{25}\) and taking into account that Li ions occupy two-thirds of the available 12d sites, we find that \(n = 4.88 \times 10^{21}\) cm\(^{-3}\) and \(\sigma(297\text{ K}) \approx 2 \times 10^{-3}\) S/cm. This estimate shows that LiLa(BH\(_4\))\(_3\)Cl has a potential to be among the best solid Li ion conductors.\(^{53}\) The measured room-temperature conductivity of LiLa(BH\(_4\))\(_3\)Cl (2.3 \times 10^{-2}\) S/cm\(^{32}\) is an order of magnitude lower. This can be attributed to the fact that the conductivity measurements\(^{21}\) were performed on pellets containing LiLa(BH\(_4\))\(_3\)Cl and nonconducting LiCl, so that the theoretical carrier density could not be reached.

As a final remark, we would like to note that the results of our limited NMR measurements for the related Ce-based compound LiCe(BH\(_4\))\(_3\)Cl are also consistent with high diffusive mobility of Li ions in this compound. In particular, the drop of the measured \(^7\)Li NMR line width in LiCe(BH\(_4\))\(_3\)Cl (Figure S1 of the Supporting Information) occurs at nearly the same temperatures as in LiLa(BH\(_4\))\(_3\)Cl. However, a full characterization of atomic motions in LiCe(BH\(_4\))\(_3\)Cl using NMR has proved to be impossible because of the presence of localized electron spin moments on Ce. The measured proton spin–lattice relaxation rate in LiCe(BH\(_4\))\(_3\)Cl (Figure S2 of the Supporting Information) is dominated by the strong interaction between nuclear spins and these localized electron spin moments; this leads to very high proton spin–lattice relaxation rates without any peaks.

**CONCLUSIONS**

The analysis of the temperature and frequency dependences of the measured proton spin–lattice relaxation rate for LiLa(BH\(_4\))\(_3\)Cl has revealed a very fast reorientational motion of BH\(_4\) groups in this compound. The most probable value of the jump rate for this fast reorientational process is found to reach \(10^8\) s\(^{-1}\) at 58 K. Our \(^1\)H spin–lattice relaxation rate results in the low-temperature region are satisfactorily described by a two-peak distribution of the activation energies with the peak values of 41 and 50 meV. Above 200 K, BH\(_4\) reorientations for this process become too fast to be probed by NMR. Our data in the high-temperature region are governed by another (slower) motional process giving rise to the sharp drop in the \(^7\)Li NMR line width near 220 K and to the \(^1\)H, \(^{11}\)B, and \(^7\)Li spin–lattice relaxation rate peaks in the range 250–300 K. While the behavior of the \(^7\)Li NMR line width unambiguously indicates the onset of translational diffusion of Li ions, the amplitude of the observed high-temperature peak of the \(^1\)H spin–lattice relaxation rate is found to be too high to result solely from Li diffusion. This means that the high-temperature relaxation rate peaks originate from a combined effect of two types of motion occurring at the same frequency scale: Li ion diffusion and a slower reorientational motion of BH\(_4\) groups. Such a result suggests that these two types of motion may be correlated, so that certain BH\(_4\) reorientations facilitate Li ion jumps. The

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**Figure 7.** Sublattice of 12d sites, two-thirds of which are randomly occupied by Li ions in LiLa(BH\(_4\))\(_3\)Cl. The dashed lines show possible diffusion paths within the unit cell.
estimates of the activation energy for Li diffusion and the tracer Li ion diffusion coefficient at room temperature give the values of 0.30 eV and 5.2 \times 10^{-8} \text{ cm}^2/\text{s}, respectively. These values indicate that LiLa(BH_4)_3Cl can be considered as a promising solid Li ion conductor.

ASSOCIATED CONTENT

Supporting Information
Results of the 7Li and 1H NMR measurements for the related Ce-based compound LiCe(BH_4)_3Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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