Li jump process in $h$-Li$_{0.7}$TiS$_2$ studied by two-time $^7$Li spin-alignment echo NMR and comparison with results on two-dimensional diffusion from nuclear magnetic relaxation

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$^7$Li spin-alignment NMR is used to trace ultraslow diffusion of Li$^+$ in the layered Li conductor Li$_x$TiS$_2$ ($x=0.7$). Two-time correlation functions were recorded for fixed evolution times as a function of mixing time at temperatures within the $^7$Li rigid-lattice regime. The corresponding decay rates were identified as Li jump rates $\tau^{-1}$ ranging from $10^{-1}$ to $10^3$ s$^{-1}$ between temperatures $T=148$ K and 213 K. The jump rates obtained directly from spin-alignment echo NMR and those from diffusion induced maxima of spin-lattice relaxation peaks, monitored in the laboratory as well as in the rotating frame, are consistent with each other and follow an Arrhenius law with an activation energy of 0.41(1) eV and a preexponential factor of $6.3(1) \times 10^{12}$ s$^{-1}$. Altogether, a solitary Li diffusion process was found between 148 and 510 K. Li diffusion was investigated in a dynamic range of about 10 orders of magnitude, i.e., $0.1 \ll \tau^{-1} \ll 7.8 \times 10^9$ s$^{-1}$. Additionally, the analysis of final-state echo amplitudes of the two-time correlation functions revealed information about the Li diffusion pathway in Li$_{0.7}$TiS$_2$. Obviously, a two-site jump process is present, i.e., besides the regularly occupied octahedral sites also the vacant tetrahedral ones within the van der Waals gap are involved in the overall two-dimensional diffusion process.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) is a well-known powerful tool for the investigation of structure and dynamics in condensed matter. Especially, it is highly suitable to study cation dynamics in fast Li ion conducting materials which are required for the design of new secondary Li batteries in everyday use.1–7 Moreover, in recent years many studies have focused attention on lithium conductors because of their potential application in electrochromic displays8 as well as in chemical sensors, see, e.g., Refs. 9 and 10.

Layered lithium titanium disulfide, Li$_x$TiS$_2$, is one of the first materials which were used as an electrode material in a rechargeable Li ion battery.11,12 For this reason, it is one of the best investigated intercalation compounds at all.13,14 Although Li diffusion in Li$_x$TiS$_2$ was studied in previous years by others using $^7$Li NMR relaxation experiments,15–19 a comprehensive study about the cation dynamics, especially in the regime of ultraslow Li motions which are not accessible by standard measurements, is still missing. Unfortunately, the standard tracer technique is not applicable to study Li dynamics due to the lack of a suitable radioactive Li isotope. Therefore, it is a necessity in general that $^7$Li NMR methods are steadily developed to overcome this disadvantage. It is the aim of the present paper to show that newly developed20,21 but not yet well-established $^7$Li spin-alignment echo (SAE) NMR, i.e., the recording of Jeener-Broekaert echoes22 of spin-3/2 nuclei, can be used to probe directly Li jump rates with values in the kilohertz to subhertz regime. Such extremely slow Li motions are not or only hardly accessible by other NMR methods. Directly means here that no theoretical model was necessary to convert the measured echo decay rates into microscopic Li jump rates. By applying the SAE technique, it is possible to enlarge the experimental time window for studying $^7$Li jumps because the well-known $^7$Li relaxation NMR methods probe Li jump rates on much shorter time scales.20

Here, we report on the measurement of ultraslow translational $^7$Li jumps on the millisecond to second time scale by static stimulated-echo NMR spectroscopy in polycrystalline hexagonal Li$_{0.7}$TiS$_2$ at temperatures where no significant motional narrowing of the NMR linewidth has set in. The results are compared with those from various relaxation NMR experiments23 probing much faster Li jump rates. Under certain conditions, also relaxation NMR allows the model-independent determination of jump rates, however, at much higher temperatures and in a more restricted way than it is possible via SAE NMR. The combination of different $^7$Li NMR techniques allowed the direct measurement of a solitary Li diffusion process in Li$_{0.7}$TiS$_2$ over a dynamic range of about 10 decades. Li$_{0.7}$TiS$_2$ served as a model substance for this comprehensive and unprecedented investigation of two-dimensional Li diffusion by $^7$Li two-time SAE NMR spectroscopy. $^7$Li NMR relaxation data will be analyzed with respect to the two-dimensional (2D) nature of Li diffusion in Li$_x$TiS$_2$. Furthermore, first measurements of the alignment-echo final states containing information about the diffusion pathway21,24–26 in h-Li$_{0.7}$TiS$_2$ are discussed. The present paper details and greatly extending a preliminary letter version.

II. LITHIUM TITANIUM DISULFIDE

TiS$_2$ exists in two modifications, a layered and a cubic one.28,29 The hexagonal ($h$) as well as the cubic polymorph are known as fast lithium ion conductors.30,31 However, at room temperature, Li diffusion in the layered modification is about ten times faster than in the cubic one.31–33 Li ions can be easily inserted into the van der Waals gap of the layered host TiS$_2$ (CdI$_2$-type structure, space group $P\bar{3}m1$) electro-
Between the TiS$_2$ layers, small Li cations show the positions of S anions coordinating Ti cations octahedrally. The tetrahedral site (2d), highlighted by bold lines, may be a transition structure during the Li hopping process between two octahedral positions. An Li cation temporarily visiting the tetrahedral site is marked with a cross.

![Diagram of Li hopping process](https://example.com/diagram)

FIG. 1. Structure of h-Li$_x$TiS$_2$ ($P$	ext{3}$_1$m1). Small gray circles show the positions of S anions coordinating Ti cations octahedrally. Between the TiS$_2$ layers, small Li cations (white circles) can be intercalated. Li cations preferentially occupy octahedral sites (1b). The tetrahedral site (2d), highlighted by bold lines, may be a transition structure during the Li hopping process between two octahedral positions. An Li cation temporarily visiting the tetrahedral site is marked with a cross.

The low-dimensionality of the Li diffusion process was unambiguously shown for the compound with $x=0.7$ by $^7$Li solid state NMR spin-lattice relaxation rate measurements. $^7$Li, TiS$_2$ is one of only a few examples where the 2D nature of cation diffusion was probed by frequency and temperature dependent measurements, see, e.g., Ref. 35 for an analogous $^1$H NMR relaxation study of proton diffusion in polycrystalline ZrBe$_2$H$_4$. Li$^+$ ions in h-Li$_x$TiS$_2$ reside preferentially in octahedral sites between the TiS$_2$ layers (see Fig. 1). In compositions with $x<1$, the cations are highly mobile due to vacant octahedral sites (1b) within the van der Waals gap. It has been suggested that the tetrahedral site (2d) is involved in the Li diffusion process as a transition structure for Li$^+$ hopping between two 1b positions. The same diffusion pathway was recently postulated for isostructured Li$_x$TiSe$_2$ (see Refs. 38–40).

III. ACCESSIBLE TIME SCALES BY NMR

With classical NMR relaxation methods, different time scales of local ionic motions are accessible (Fig. 2). Experimentally, the easiest way to get access to microscopic Li diffusion parameters like jump rates and energy barriers is the measurement of the diffusion induced $^7$Li NMR spin-lattice relaxation rate $T_{1\text{diff}}^{-1}$ (see Ref. 23). $T_{1\text{diff}}^{-1}$ as a function of inverse temperature $1/T$ will go through a maximum at $\omega_0 \approx 1/\tau$, identifying $1/\tau$ as the jump rate of the hopping ion. $T_{1\text{diff}}^{-1}$ will vary rapidly on either side of this maximum. The low-$T$ flank of the peak might be affected by correlation effects, leading to a decrease of the corresponding slope. The high-$T$ slope is influenced only when the dimensionality of the diffusion process is lower than 3. Whereas $T_{1\text{diff}}^{-1}$ is sensitive to diffusive motion with jump rates in the region of the frequency $\omega_0/2\pi$, which in practice may be varied from about 10 MHz to several hundred megahertz, slower ionic motions can be probed by recording diffusion induced spin-lattice relaxation rates $T_{1\text{diff}}^{-1}$ in the rotating frame. $T_{1\text{diff}}^{-1}$ vs $1/T$ shows a maximum at $\omega_0 \approx 1/\tau$, i.e., at lower temperature, because $\omega_0/2\pi$, which is the locking frequency, is much smaller than $\omega_0/2\pi$ and lies typically in the kilohertz range. While there have been several papers reporting jump rates over a large dynamic range (see, e.g., Refs. 44, 46, and 47), these have been evaluated using various models for the shapes of the relaxation peaks. However, in the present case, the jump rates were determined independently of a specific model, i.e., solely from the frequency dependent positions (on the temperature scale) of the maxima of the corresponding relaxation rate peaks. In addition to $T_{1\text{diff}}^{-1}$ and $T_{1\text{diff}}^{-1}$ measurements, also solid echo NMR spectroscopy, i.e., the analysis of changes of $^7$Li NMR line shapes or the measurement of the $^7$Li NMR spin-spin relaxation rate $T_{2\text{NMR}}^{-1}$, reveals information about ionic motions in the kilohertz range depending on the modulation of interactions between the nucleus and the surrounding magnetic and/or electric fields through the dynamic process. In the case of $^7$Li, jump rates between $10^4$ and $10^3$ s$^{-1}$ are usually accessible.

Ionic motions on the ultraslow time scale, i.e., in the hertz to subhertz range, are hardly accessible by recording line shapes or spin-spin relaxation times because such extremely slow motions with jump rates smaller than $10^3$ s$^{-1}$ have no or only a marginal effect on the line shape. Up to now, only few multidimensional NMR experiments have been applied on solid ion conductors to enlighten very slow motions of $^6$Li and $^7$Li ions, respectively. For the first time, 2D exchange NMR [rotor synchronized magic angle spinning (MAS) NMR] was carried out by Xu and Stebbins to observe $^7$Li hopping dynamics among multiple crystallographic sites in polycrystalline Li$_4$SiO$_4$. Recently, details of Li diffusivity in LiMn$_2$O$_3$ were probed directly by 2D $^7$Li MAS NMR by Verhoeven et al. This work was followed by 2D NMR investigations on Li$_2$MnN$_4$ by Cabana et al. as well as on monoclinic Li$_2$V$_2$(PO$_4$)$_3$ by Cahill et al. Quite recently, van Wüllen et al. used cross-polarized $^6$Li-$^7$Li MAS-NMR to...
study Li dynamics in the hexaaluminate \( \text{Li}_2\text{TaO}_6 \) (Ref. 52) as well as in the garnet \( \text{Li}_3\text{La}_2\text{Nb}_2\text{O}_{12} \).53

In addition or alternatively to exchange NMR, the measurement of multiple-time correlation functions can be used to investigate directly ultraslow translational as well as rotational motions. SAE NMR spectroscopy of deuterons \(^2\text{H}\) with spin quantum number \( I = 1 \) was originally developed by Spiess and coworkers.54,55 The method proved to be a successful tool for the study of deuteron dynamics. Furthermore, it provides detailed information about the type of molecular motion.24–26 Quite recently, static SAE NMR spectroscopy was also applied to quaternary nuclei with a spin–quantum number \( I \) of 3/2. First, Tang et al.20,56,57 recorded \(^9\text{Be}\) NMR spin-alignment echoes to study ultraslow ionic motions in a metallic beryllium containing glass in order to reveal the prevailing diffusion mechanism in this material. The method was then used by Böhmer and co-workers58,59 to investigate ultraslow Li motions in crystalline \( \text{Li}_3\text{Sc}_2\text{PO}_6 \) and \( \text{Li}_3\text{In}_2\text{PO}_4 \). In that work, ultraslow motions of the \(^7\text{Li}\) nucleus were studied by recording two-time translational correlation functions for the first time. Moreover, spin-alignment NMR spectroscopy was used to characterize lithium diffusion in a number of dielectric materials such as \( \beta \)-eucryptite,60,61 the glass ceramic Zerodur M (Schott),62 as well as in glassy and crystalline \( \beta \)-spodumene.61,63 Besides an early account on hexagonal \( \text{Li}_2\text{Ti}_5\text{S}_2 \),54 we also reported on first SAE NMR measurements on cubic \( \text{Li}_{0.6}\text{Ti}_5\text{S}_2 \).31 Furthermore, we have used the \(^7\text{Li}\) spin-alignment technique to study extremely slow Li dynamics in a series of single crystal, polycrystalline, as well as amorphous Li conductors such as \( \text{Li}_3\text{N} \),52,65 \( \text{Li}_2\text{SiO}_4 \),66 \( \text{Li}_3\text{Ti}_5\text{O}_{12} \),67 and \( \text{LiNbO}_3 \).68

It is worth mentioning in this context that \(^{109}\text{Ag}\) stimulated echo NMR two- and four-time correlation functions were recorded recently to investigate silver dynamics in glasses of the compositions \((\text{AgI})_x(\text{AgPO}_3)_y(1-x)\)69–72 \((\text{AgI})_x(\text{Ag}_2\text{O}-\text{B}_2\text{O}_3)_y(1-x)\),73 as well as in several other Ag compounds.74,75 In contrast to spin-1 and spin-3/2 nuclei, in the case of the nonquadrupolar \(^{109}\text{Ag}\) nucleus with \( I = 1/2 \) chemical shift interactions are used to differentiate between the ions.

IV. SPIN-ALIGNMENT ECHO NMR

The principle idea of spin-alignment echo NMR spectroscopy is similar to that of 2D exchange NMR. Whereas by means of the latter one chemical shift interactions are considered, SAE NMR takes advantage of interactions between the quadrupole moment of the nucleus and the electric field gradient (EFG) tensor at its site. In exchange NMR, magnetization is produced that is labeled by chemical shift interactions due to magnetically nonequivalent crystallographic sites where the nuclei reside. The magnetization is stored so that exchange can occur before it is sampled. If there is exchange, i.e., if hopping of the ions between magnetically distinct sites occurs, the magnetization is now labeled with a different shift frequency and shows up as crosspeak, i.e., off-diagonal intensity, in a 2D plot. The quadrupole interaction, which is used in \(^7\text{Li}\) SAE NMR instead of chemical shift interactions in usual exchange NMR, is described by the Hamiltonian

\[
\hat{H}_q = \frac{1}{42IJ(I-1)}(3I_\perp^2 - I^2)(3\cos^2 \theta - 1 - \eta_q \sin^2 \theta \cos 2\phi),
\]

Here, \( e \) and \( eq \) are the proton charge and the principle component of the electric field gradient tensor, respectively. \( Q \) is the electric quadrupole moment of the nucleus. The angles \( \theta \) and \( \phi \) specify the orientation of the external field \( B_0 \) in the principle axis system of the EFG tensor at the nucleus site. \( I_\perp \) and \( I_\parallel \) are the nuclear spin operators and \( \gamma \) is the magnetic gyromagnetic ratio of the respective nucleus. \( \eta_q \) is the asymmetry parameter of the quadrupole interaction.

The quadrupole interaction alters the Zeeman frequency \( \omega_0 \) toward \( \omega_0 \pm \omega_Q \). The corresponding quadrupole frequency is given by

\[
\omega_Q = \pm \delta \pi/2[3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos(2\phi)],
\]

with the quadrupole coupling constant \( \delta = e^2qQ/\hbar \), where \( \hbar \) is Planck’s constant.

Provided electrically inequivalent sites are visited on a given diffusion pathway by the jumping ion, the information about the dynamic process is coded in terms of a change in the angular quadrupole frequency \( \omega_Q \). The spin-alignment technique allows the measurement of a single-particle correlation function yielding information about dynamic as well as geometric parameters of the hopping process.

The pulse sequence used to sample alignment echoes is based on the Jeener-Broekaert (JB) experiment,22

\[
(90^\circ)_t - t_p - (45^\circ)_t - t_m - (45^\circ)_t - t - t_{acquisition}.
\]

The phase \( \phi \) of the third pulse is arbitrary. In the ideal case, the first two pulses generate longitudinal pure quadrupole spin order. To avoid as much as possible the preparation of, e.g., dipolar simultaneously with quadrupolar order, proper pulse phasing is necessary and in the case of \(^7\text{Li}\) the preparation time usually has to be chosen short; values smaller than 20 \( \mu \)s are typical. However, this choice depends on the strength of the specific interactions. Here, sin-sin two-time correlation functions were recorded for various preparation times \( t_p \) ranging from 5 to 150 \( \mu \)s. The third or reading pulse of the JB-sequence transforms spin alignment back into an observable transverse coherent magnetization leading to an echo at \( t = t_p \).

The amplitude of the spin-alignment echo is given by

\[
S_z(t_p, t_m) = \frac{2}{5}\bar{m}(\omega_Q(t_m = 0)t_p \sin[\omega_Q(t_m)t_p]).
\]

Here, \( \langle \cdots \rangle \) denotes the powder average. The decay of stimulated echo amplitudes \( S_z(t_p, t_m) \) for fixed \( t_p \) and as a function of \( t_m \) is in general due to two processes, i.e., (i) individual jumps of the ions and (ii) spin-lattice relaxation. The first one will affect the echo formation when the ions jump between sites with different quadrupole frequencies. Thus, as mentioned above, in a stimulated-echo experiment, the frequency change from the initial value \( \omega_Q(t_m = 0) \) to the final one \( \omega_Q(t_m) \), experienced by the jumping ion, opens a way for a
direct measurement of the correlation time $\tau$. Simulta-
neously, the second process gives rise to a decay of quadrupole order and, thus, to an additional decrease of the alignment echo amplitude. This means that the experimental time window to investigate ionic motions is limited by spin-lattice relaxation and one has to choose $t_m$ to be smaller than $T_1$. The evolution time $t_p$, however, refers to intervals of processing magnetization and is limited to be less than the spin-spin-relaxation time $T_2$, which is about 100 $\mu$s for $h$-Li$_{0.7}$TiS$_2$ in the rigid lattice regime ($T<240$ K). In $h$-Li$_{0.7}$TiS$_2$, the spin-lattice relaxation time $T_1$ is of the order of several seconds below room temperature. Hopping correlation times, however, are expected to be of the order of seconds to milliseconds in this temperature range. Thus, it should be possible to distinguish between the two processes easily. In fact, the measured decay curves reveal two separable regimes, one which is due to ionic motion and a second one arising from non-diffusive spin-lattice relaxation effects.

Especially in the case of $^7$Li being subject to relatively strong homonuclear dipole-dipole interactions as compared to, e.g., $^6$Be, the complete suppression of dipolar ($D$) order showing up simultaneously with quadrupolar ($Q$) order is difficult to realize. 59,60,63,66 This is because the two corresponding time constants $\tau_{SAE,D}$ and $\tau_{SAE,Q}$ determining the echo decay will be of the same order of magnitude. The decay of dipolar order, if present, will be slightly faster than the single-particle process. Whereas pure spin-alignment NMR leads directly to a single-particle correlation function, the decay of dipolar order is described by at least a two-particle correlation function. The impact of homonuclear dipolar interactions on two-time correlation functions, especially its effect on final state amplitudes, was considered recently by simple modeling. 60 Thereby, it was shown that, as a function of $t_p$, in spin-alignment spectra of coupled $^7$Li nuclei central components will show up with apparent phases differing from those of the satellite contributions.

V. EXPERIMENT

Polycrystalline $h$-Li$_{0.7}$TiS$_2$ had been prepared by Schöllhorn and Payer starting from TiS$_2$, which was obtained via standard solid state chemistry procedures. A mixture of titanium and sulfur powders in the ratio 1:2.1 was heated at 870 K for about 2 weeks in an evacuated quartz tube. Excess sulfur was removed at 420 K under vacuum. Li was intercalated at room temperature in inert gas atmosphere using n-butyl lithium. The sample was characterized by x-ray diffraction and $^7$Li NMR spectroscopy. Further details of sample preparation, especially for the host material $h$-TiS$_2$, are reported elsewhere. 27,77 The final product was sealed in a quartz tube under vacuum. It is fully homogenized concerning the Li distribution between the TiS$_2$ layers. The same sample was used before as a model substance in a comparative NMR relaxation study of hexagonal and cubic Li$_{0.7}$TiS$_2$. 30

Spin-alignment echoes as well as spin-lattice ($T_{1}^{-1}$) and spin-spin relaxation rates ($T_{2}^{-1}$) were recorded at radio frequencies ranging from 39 to 155 MHz. The results are compared with spin-lattice relaxation data in the laboratory frame ($T_{1}^{-1}$) which had been measured by our group before in the frequency range from 10 to 39 MHz. 30,77,78 Furthermore, the new results from multiple-time NMR are compared with spin-lattice relaxation rates in the rotating frame ($T_{1\text{rot}}^{-1}$), which had been measured at effective locking frequencies $\omega_{\text{eff}}/2\pi=2.1$, 5.2, and 10 kHz on the same sample by our group earlier. 30,77 The latter ones were acquired using the well-known spin-lock technique introduced by Redfield 43 and first applied by Ailion and Slichter 44 and Look and Lowe. 45

Spin-alignment data and relaxation rates at 155 MHz were collected with a Bruker MSL 400 spectrometer connected to a shimmmed Oxford cryomagnet at a fixed field of 9.4 T with a high homogeneity of the external magnetic field $B_0$. All the measurements at lower magnetic fields $B_0$ were carried out with a modified Bruker MSL 100 console in connection with a field-variable (0–8 T) Oxford cryomagnet. 79

$^7$Li spin-alignment echoes as a function of mixing time $t_m$ (10 $\mu$s $\leq t_m \leq$ 100 s) and for various evolution times $t_p$ were measured using the three pulse Jeener-Broekaert sequence (see above). The recycle delay was at least 5$T_1$. The 90° pulse length was about 4.5 $\mu$s ensuring a nonselective excitation of both the central and satellite transitions. Appropriate phase cycling 21,59 was employed in order to pick out the correct coherence pathway and to eliminate unwanted coherences as well as to decrease the effects of pulse imperfections. Spin-lattice relaxation rates $T_{1}^{-1}$ were acquired using the well-known classical NMR methods such as the saturation recovery and/or the inversion recovery experiment. 80 Both methods yielded the same results. Spin-spin relaxation times $T_{2}$ were obtained by the solid echo technique 60 44° $-t_e-90°-t$ with 10 $\mu$s $\leq t_e \leq$ 100 $\mu$s.

VI. RESULTS AND DISCUSSION

A. $^7$Li spin-alignment echo NMR

1. Two-time correlation functions

Two-time sin-sin correlation functions $S_2(t_p,t_m)$ vs mixing time $t_m$ ranging from 10 $\mu$s to 100 s were recorded for fixed evolution times $t_p$ between 140 and 220 K. In Fig. 3, a typical decay of normalized $^7$Li alignment echo amplitudes $S_2(t_p,t_m,t)$ sampled at $t=t_p=15$ $\mu$s and $T=193$ K is shown. The correlation function was measured at a Larmor frequency of $\omega_0/2\pi=155$ MHz. The echo decay proceeds in two clearly distinguishable steps in the whole investigated temperature range. The first step leading to a finite plateau value $S_\alpha$ at intermediate mixing times represents directly ionic jumps between electrically inequivalent sites in $h$-Li$_{0.7}$TiS$_2$. The second step leading from the plateau value to $S_\alpha=0$ reflects an echo decay simply induced by longitudinal relaxation because the time constant of this decay step $T_{1\text{SAE}}$ and its temperature behavior (140–220 K) is very similar to the spin-lattice relaxation time $T_1$ measured independently by standard NMR relaxation experiments such as the inversion or saturation recovery techniques. Additionally, according to the magnetization transients of the corresponding $^7$Li NMR relaxation experiments the second $S_\alpha$ step shows a purely exponential decay, whereas the first decay
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FIG. 3. Decay of the spin-alignment echo amplitudes $S_2$ of h-Li$_{0.7}$TiS$_2$ at 193 K as a function of mixing time $t_m$ (10 $\mu$s $\leq t_m \leq 100$ s) at a Larmor frequency of 155 MHz. The echoes were sampled at $t_p=15$ $\mu$s. The decay is due to two processes: (i) ultraslow Li motions with a jump rate $\tau_{SAE}^{-1}$ of about 100 s$^{-1}$. The second decay step is induced by spin-lattice relaxation. The decay constant $T_{1SAE} = 11.4(3)$ s is equal to that measured independently by a saturation recovery experiment, $T_1 = 11.8(1)$ s.

The step has to be described with a slightly stretched exponential function,

$$S_2(t_p, t_m) = (1 - S_0) \exp \left( -\frac{t_m}{\tau_{SAE}} \right)^\alpha + S_0 \exp \left( -\frac{t_m}{T_{1SAE}} \right) + S_{0\infty},$$

A fit according to Eq. (4) is represented by the solid line in Fig. 3. In this example, the two-time constants are $\tau_{SAE} = 1.01(1) \times 10^{-2}$ s and $T_{1SAE} = 11.4(3)$ s, respectively. The stretching exponent $\alpha$ is 0.8(1) at 193 K. It will be shown below that $\tau_{SAE}$ is identical to the motional correlation time $\tau$ of the hopping process in Li$_{0.7}$TiS$_2$.

Interestingly, the relatively high plateau value $S_0$ of about 0.3 at 193 K, although recorded at short $t_p$, already indicates that only a small number of electrically inequivalent sites are involved in the Li diffusion process in h-Li$_{0.7}$TiS$_2$. In general, the (normalized) final state correlation $S_0(t_p \to \infty)$ can be regarded from the perspective of neutron scattering as a generalized elastic incoherent structure factor (EISF). The amplitude of $S_0(t_p)$ is expected to be independent of $t_m$ for large $t_p$, whereas $S_0 = f(t_p)$ and $S_0(t_p \to \infty)$ depends on the type of translation (as well as reorientation) process. For an $N$-site jump process, EISF is expected to equal $1/N$ if the $N$ Li sites equally participate in the diffusion process. Regarding the crystal structure of hexagonal Li$_{0.7}$TiS$_2$, only two available and crystallographically inequivalent sites for Li$^+$ between the van der Waals layers can be identified (see Fig. 1). The ions reside preferentially in octahedral sites ($1b$) characterized by a quadrupole coupling constant $\delta_0$ of about $\delta_0 = 14$ kHz (293 K) as obtained from the satellite positions of the $^7$Li NMR spectra. The quadrupole coupling constant $\delta_0$ of the tetrahedral site ($2d$) is experimentally difficult to measure because of the very low occupation of the $2d$ sites by lithium ions although the number of tetrahedral sites is three times larger than the number of available octahedral positions. From density functional calculations, the coupling constant was found to be larger by about a factor of 3 than that of the octahedral site. It was suggested that the second position is a transition structure of the diffusion process (see above). Assuming that the Li ion passes the tetrahedral site while jumping from an octahedral site to a vacant one ($1b \to 2d \to 1b'$), the associated fluctuations of $\omega_Q$ would lead to an echo decay with a final state amplitude $S_0$ of 1/2. In order to measure $S_0(t_p \to \infty)$, we have recorded two-time correlation functions vs evolution times up to about 150 $\mu$s (Fig. 4). The decay constant $\tau_{SAE}$, as well as that of the second decay step $T_{1SAE}$, is independent of $t_p$ as can be seen from the second correlation curves in Fig. 4. The fact that $\tau_{SAE}$ being obtained at the relatively short evolution time $t_p = 10$ $\mu$s is identical to those values found at longer times $t_p$ means that already at short $t_p$ all Li jumps are detected. Additionally, this fact reveals that the involved quadrupole frequencies differ largely from each other (as also found by the calculations in Ref. 82, see above) because with the choice of $t_p$ the sensitivity to changes in $\omega_Q$ is set. The larger $t_p$, the better small changes in $\omega_Q(t_m)$ can be detected because the difference of the associated phases $\sin[\omega_Q(0)t_p] \sin[\omega_Q(t_m)t_p]$ will become better visible with increasing $t_p$ if $\omega_Q(0)t_p = \omega_Q(t_m)t_p$. Simultaneously, a possible $\tau_{SAE}^{-1}(t_p)$ dependence should be accompanied by a decrease of the final state amplitude $S_0$ with increasing $t_p$. This is not the case here. In Fig. 5, the $S_0$ values from the correlation functions in Fig. 4 are shown vs $t_p$. For $t_p$ values above 100 $\mu$s, a limiting value of 1/2 is reached pointing out the presence of the above mentioned two-site jump process in hexagonal h-Li$_{0.7}$TiS$_2$. Obviously, Li sites with quite different quadrupole frequencies are involved which can be identified as the octahedral and tetrahedral positions between the TiS$_2$ layers. The results of Figs. 4 and 5 hold also for other temperatures.

It has to be mentioned that, especially for spin-3/2 probes, the final state amplitude may be additionally affected...
by the number of effectively dipolarly coupled $^7$Li spins. The more spins are effectively coupled the smaller would be the plateau value. The dipole-dipole interaction is much weaker than the quadrupole interaction in $h$-$Li_{0.7}TiS_2$. Dipolar contributions are increasingly stored the larger $t_p$ is chosen. Thus, one could imagine that with increasing $t_p$, the plateau values continually decrease also because of dipole-dipole contributions. As this is not observed here, we conclude that the separation of quadrupolar from dipolar order is sufficiently good in $h$-$Li_{0.7}TiS_2$ so that dipolar interactions do not play an important role in echo formation. In fact, the central line in the corresponding $^7$Li spin-alignment spectra is almost fully suppressed.

2. Comparison with results from relaxation NMR below 220 K

In Fig. 6, the SAE NMR decay rates $\tau_{\text{SAE}}^{-1}$ recorded at different external magnetic fields and evolution times $t_p = 10$ $\mu$s and $t_p = 15$ $\mu$s are shown in an Arrhenius plot in contrast with the $T_1$ and $T_2$ results below 400 K. It is helpful to check the dependence on $B_0$ in order to find out if $\tau_{\text{SAE}}$ can really be identified with the motional correlation time $\tau$ which is expected to be independent of the Larmor frequency $\omega_0/2\pi$. In the present case, $\tau_{\text{SAE}} \neq f(\omega_0)$ is fulfilled between 10.0 and 155 MHz, being the frequency range covered here. Any field dependence of $\tau_{\text{SAE}}$ would give rise to the assumption that the $S_2$ decay is additionally influenced by spin-lattice relaxation which depends, when induced by diffusion, on the applied Larmor frequency used to measure the longitudinal recovery of the magnetization. Additionally, this possibility can be ruled out in the present case because a clear separation of $\tau_{\text{SAE}}^{-1}$ from longitudinal relaxation effects was already possible via the discrimination of the two time constants describing the $S_2$ curves. The characteristic rates $T_{1,\text{SAE}}^{-1}$ of the second decay step are nearly identical to the independently measured $T_{1,\text{NMR}}^{-1}$ $^7$Li NMR relaxation rates, i.e., we have $T_{1,\text{SAE}}^{-1} \approx T_{1,\text{NMR}}^{-1}$. Moreover, $T_1$ and $\tau_{\text{SAE}}$ can be clearly differentiated via their completely different temperature behavior. The $\tau_{\text{SAE}}^{-1}$ rates show a strong dependence on $T$ yielding an activation energy of slow Li jump processes of 0.37(1) eV. In contrast to that, $^7$Li NMR longitudinal relaxation ($T_1^{-1}$) is not induced by Li diffusion in this low-temperature range at all. The characteristic frequency dependent diffusion induced rate peak $T_{1,\text{SAE}}^{-1}(1/T)$, recorded at, e.g., $\omega_0/2\pi \approx 77.7$ MHz, shows up above 400 K (see Fig. 10 and see the data point at the highest temperature). Thus, the spin-lattice relaxation rates shown in Fig. 6 reflect a nondiffusive relaxation background, i.e., $T_{1,\text{SAE}}^{-1} \neq T_{1,\text{bg}}$ (see Sec. VI B 2 for a possible explanation of this background contribution).

In addition to the influence of longitudinal relaxation on $\tau_{\text{SAE}}$ that of spin-spin-relaxation ($T_{2,\text{SAE}}^{-1}$) should also be considered. As shown in Fig. 6, below 220 K spin-spin relaxation rates are independent of $T [d/(\ln T_2)/d(1/(k_B T)] = 0$], whereas $\tau_{\text{SAE}}$ strongly depends on $T$. A value of the order of $T_{2,\text{SAE}}^{-1} = 10^3$ s$^{-1}$ is in good agreement with earlier results reported in the literature for $h$-$Li_{0.7}TiS_2$. In this so-called “rigid-lattice regime,” the Li jump rate is far away from the value of the inverse line width ($\Delta \omega^2$) $\tau^2 \gg 1$, ($\Delta \omega^2$ being the dipolar second moment) and $\tau_{\text{SAE}}^{-1}$ is not affected by transverse relaxation ($T_2^{-1}$). At about 240 K, motional averaging of local magnetic fields sets in and, therefore, the width of the corresponding resonance line starts to narrow. Accordingly, the $T_2^{-1}$ rates decrease. Roughly speaking, motional narrowing starts when the jump rate reaches a value of the order $10^3$ s$^{-1}$. This is in good agreement with the $\tau_{\text{SAE}}^{-1}$ values: At about 220 K, we obtained a Li residence time $\tau_{\text{SAE}}$ of about 1 ms.

As expected, in the rigid-lattice regime, i.e., below $T = 220$ K in the case of $h$-$Li_{0.7}TiS_2$, neither the measurement of $T_2^{-1}$ nor that of $T_1^{-1}$ is helpful to detect extremely slow Li
jumps. However, by applying $^7$Li spin-alignment echo NMR to temperatures below 220 K, it was possible to trace extremely slow ionic jumps covering a dynamic range of about four decades, i.e., $10^{-4} \leq \tau_{SAE} \leq 10^3 \text{ s}^{-1}$.

B. Diffusion induced relaxation NMR: Comparison with results from stimulated echoes

1. Spin-spin relaxation

Temperature dependent spin-spin relaxation data $T_2^{-1}$ recorded at $\omega_0/2\pi=77.7$ MHz are shown in Fig. 6 (see above). Below 220 K, spin-spin relaxation rates are temperature independent and are of the order of $10^4 \text{ s}^{-1}$ as expected for $^7$Li. After the beginning of motional narrowing at about 240 K, the rates become smaller reaching a value of $T_2^{-1}=10^2 \text{ s}^{-1}$ at 350 K. The corresponding activation energy $E_A$ is larger than the value of the slope $d(\ln T_2)/d(1/(k_BT))=0.25(2) \text{ eV}$ of the $T_2^{-1}$ values above 250 K. Taking into account the dimensionality ($d=2$) of the Li diffusion process in $h$-Li$_{0.7}$TiS$_2$, according to Ref. 83, the following relation holds:

$$
\frac{d \ln T_2}{d(1/(k_BT))} = -E_A \left(1 + \frac{E_A}{k_BT} + \frac{1}{2} \ln(\Delta \omega^2 \tau_0^2)\right).
$$

Here, $\Delta \omega^2$ is the dipolar second moment and $\tau_0^{-1}$ the pre-exponential factor of the corresponding Arrhenius relation $\tau^{-1}=\tau_0^{-1} \exp(-E_A/(k_BT))$. Taking $\tau_0^{-1}=6.3(1) \times 10^{12} \text{ s}^{-1}$ from the result to be presented in Sec. VI C, an activation energy $E_A=0.36(2) \text{ eV}$ is estimated in close agreement with the value obtained from SAE NMR and from spin-lattice relaxation in the laboratory and rotating frame [see Secs. VI A 2 and VI B (below)].

Extrapolating the spin-spin relaxation rates measured at $\omega_0/2\pi=77.7$ MHz to temperatures higher than 500 K where the corresponding $T_2^{-1}$ maximum shows up ("extreme narrowing case" $\omega_0 \tau \approx 1$), it is found that the $T_2^{-1}$ rates are much larger than the $T_1^{-1}$ rates at the same temperature. Contrary to the standard behavior $T_2^{-1} \approx T_1^{-1}$ for $\omega_0 \tau \approx 1$ (see, e.g., Ref. 23), $T_1/T_2 > 1$ occurs and is expected because of the anomalously large secular (independent of $\omega_0$) contribution to $T_2^{-1}$ for low dimensions ($d=1$ or 2). 83

2. $^7$Li NMR spin-lattice relaxation in the laboratory and rotating reference frame

Transitions between energy levels of the spin system may be induced by internal magnetic or electric fluctuating fields. Longitudinal NMR relaxation will be effectively induced by atomic diffusion when the spectral density function $J(\omega)$ has components at the transition frequencies. $J(\omega)$ is a function of the correlation rate $\tau_\tau^{-1}$, being directly related to the jump rate $\tau^{-1}$ of the atomic diffusion process, and thus a function of inverse temperature $T$, because

$$
\tau^{-1} \equiv \tau_\tau^{-1} = \tau_0^{-1} \exp(-E_A/(k_BT)).
$$

$J(\omega)$ is the Fourier transform of the correlation function $G(t)$ containing the temporal information about the diffusion process characterized by $\tau$. At a certain temperature and a given frequency $\omega_0$, $T_1^{-1}$ will be maximal indicating that $\tau$ reaches the range of the inverse Larmor frequency, i.e., $\tau \omega_0 \approx 1$. Thus, $T_1^{-1}$ measurements are sensitive to ionic motions with jump rates of the order of the Larmor frequency applied, i.e., in the megahertz range. For $\omega_0 \tau \ll 1$ and $\omega_0 \tau \gg 1$, longitudinal relaxation is much less effective, which is why diffusion induced spin-lattice relaxation has been looked at as an "internal resonance" phenomenon. 23 The resulting diffusion induced relaxation maxima with its characteristic flanks on the low-$\omega_0 \tau \approx 1$ and high-temperature sides ($\omega_0 \tau \ll 1$) are often expected to appear at high temperatures for Li conductors with moderate cation diffusivity. The measurement of relaxation rate peaks at various frequencies $\omega_0/2\pi$ offers the possibility to shift the maxima to higher and lower values of $T$ and, therefore, to scan $\tau^{-1}=1/(1/T)$, i.e., to obtain pairs of variables ($\tau^{-1}, 1/T$) fulfilling Eq. (6).

$^7$Li spin-lattice relaxation rates $T_1^{-1}$ of $h$-Li$_{0.7}$TiS$_2$ at a relatively low Larmor frequency of 10.0 MHz are shown as a function of inverse temperature in Fig. 7. Data were partly taken from Ref. 30. The characteristic relaxation rate maximum shows up around $T=415$ K. Below 250 K, Li jump rates in $h$-Li$_{0.7}$TiS$_2$ are too small ($\omega_0 \tau \gg 1$) to affect longitudinal relaxation at this frequency significantly. In this temperature range, Li diffusion is not the origin of spin-lattice relaxation. Instead, it is caused by other types of background relaxation mechanisms due to spin fluctuations of paramagnetic impurities and lattice vibrations and/or due to coupling of the $^7$Li nuclei with conduction electrons. Therefore, the effective background rate is given by a superposition of the different relaxation rates with their characteristic temperature (and frequency) dependencies,
with \( a, b, c, \ldots \) being the respective weighting factors. Here, the resulting effective (and weaker than activated) temperature dependence of \( T_{1 \text{bg}}^{-1} \) can be all in all described by a power law \( T_{1 \text{bg}}^{-1} \propto T^k \), with \( k=1.56(2) \) (see Fig. 7). Presumably, in \( h\)-Li\(_{0.7}\)TiS\(_2\) relaxation via coupling with conduction electrons plays a more important role than the other mechanisms. Irrespective of the exact nature of background relaxation here, to obtain the pure diffusion induced rate \( T_{1 \text{diff}}^{-1} \), the background relaxation has to be extrapolated to higher temperatures (dashed dotted line in Fig. 7) and subtracted from the overall rate \( T_1^{-1} \). For this correction procedure (see Fig. 7), the power law was fitted to the relaxation rates between 160 and 250 K and after that extrapolated to about 900 K. Interestingly, above 750 K, the same relaxation background as observed at low \( T \) shows up again and coincides with the performed fit. This indicates a proper ansatz for fitting and extrapolation. This analysis shows clearly that the background relaxation rate is superimposed by an Li diffusion induced spin-lattice relaxation rate peak. Comparing the slopes of the low-\( T \) flanks of the overall \( T_1^{-1} \) and purely diffusion induced rates \( T_{1 \text{diff}}^{-1} \) recorded at 10.0 MHz (Fig. 7), the activation energy increases from 0.23(2) to 0.37(2) eV. This illustrates the influence of the background contribution to \( T_1^{-1} \) and demonstrates clearly that it has to be considered for a meaningful data analysis. The value of \( E_A=0.37(2) \) eV at 10.0 MHz is in perfect agreement with the corresponding activation energy obtained from stimulated echo NMR at much lower temperatures.

Careful background correction is particularly important at higher Larmor frequencies. Increasing \( \omega_0/2\pi \) to values up to 77.7 MHz shifts the position of the rate peak \( T_{1 \text{diff}}^{-1}(1/T) \) toward higher temperatures. Simultaneously, the \( T_1^{-1} \) rate decreases, whereas the background contribution to \( T_1^{-1} \) is nearly unchanged. Therefore, at the highest frequencies, the high-\( T \) and low-\( T \) flanks of the rate maximum are no longer well detectable because \( T_{1 \text{diff}}^{-1}(1/T) \) becomes much smaller than \( T_{1 \text{bg}}^{-1}(1/T) \). As a consequence, a reliable separation of diffusion induced contributions from the overall spin-lattice relaxation rates \( T_1^{-1} \) at frequencies higher than 77.7 MHz is no longer possible. At 155 MHz, for example, the diffusion induced rate maximum is too shallow in order to be clearly distinguishable from the relaxation background. This circumstance marks the upper limit of measuring jump rates by \( ^7\)Li relaxation NMR in the present case. For the NMR relaxation measurements in the laboratory frame, the most reliable results were obtained at Larmor frequencies between 10 and 77.7 MHz, whereas for those performed in the rotating frame, the background effects are expected to show no or only a weak influence on \( T_{1 \text{diff}}^{-1} \) recorded near the rate maximum.

In Fig. 8, typical rotating frame spin-lattice relaxation rates \( T_{1 \text{diff}}^{-1}(1/T) \) are displayed. The data were recorded at a locking frequency of \( \omega_{0}/2\pi=5.2 \) kHz using an external magnetic field \( B_0 \) corresponding to \( \omega_{0}/2\pi=77.7 \) MHz. Additionally, in Fig. 8, the purely diffusion induced rates \( T_{1 \text{diff}}^{-1}(1/T) \) at \( \omega_{0}/2\pi=10.0 \) MHz are shown. As expected, the absolute rates \( T_{1 \text{diff}}^{-1} \) are much higher than those recorded in the laboratory frame in the same temperature range. Background relaxation rates were similar in both cases. Thus, for the rotating frame data, a background correction has no influence on the rates \( T_{1 \text{diff}}^{-1} \) even at higher temperatures, i.e., \( T_{1 \text{diff}}^{-1} \approx T_{1 \text{bg}}^{-1} \). Whereas the maximum of the laboratory frame relaxation peak \( T_{1 \text{diff}}^{-1}(1/T) \) recorded at 10.0 MHz shows up at around 415 K, the diffusion induced maxima of the corresponding peaks in the rotating reference frame, being similar in shape to the \( T_{1 \text{diff}}^{-1}(1/T) \) peak, are shifted toward lower temperatures due to the much smaller locking frequency \( \omega_0/2\pi \) compared to \( \omega_{0}/2\pi \).

For comparison, Li jump rates obtained from the first decay step of the two-time correlation functions \( S_2(t_\tau) \) are shown in Fig. 8, too. Without any detailed analysis of the diffusion induced relaxation rate peaks, the parallel trend of the low-temperature flanks of the rate peaks compared to the temperature behavior of the spin-alignment decay rates indicates already that all three techniques probe the same Li hopping process in Li\(_{0.7}\)TiS\(_2\). Fitting just the low-\( T \) flank of the relaxation peaks according to an Arrhenius relation yields \( E_{A \text{low}}=0.37(2) \) eV for \( T_{1 \text{diff}}^{-1}(1/T) \) (see above) and \( \Delta E_A=0.37(1) \) eV for \( T_{1 \text{diff}}^{-1}(1/T) \). For comparison, \( E_{SAE}^{1/2} \) is 0.37(1) eV. Similar results for \( E_{SAE}^{1/2} \) were obtained from spin-lattice relaxation NMR measurements performed at other frequencies, e.g., \( \omega_0/2\pi=27, 38, \) and 77.7 MHz, and at \( \omega_0/2\pi=2.1 \) kHz as well as 10 kHz. As expected for an ideal 2D ionic conductor (see next section) the \( T_{1 \text{diff}}^{-1}(1/T) \) rate peaks are not symmetric and show a reduced slope on the high-\( T \) side. Fitting both flanks using an Arrhenius relation reveals that the activation energy...
the high-T side $E_A^{\text{high}}$ is only $0.29(1)$ eV at 5.2 kHz. This is about $0.78E_A^{\text{low}}$, which is in good agreement with the expression introduced by Richards [see Eq. (9), next section] for the spectral density function of 2D diffusion revealing that the high-temperature slope is about $0.77E_A$.

3. Spectral density for a two-dimensional ionic conductor

The spectral density $J(\omega, \tau)$, determining the frequency and temperature dependence of the relaxation rate $T_{1\text{diff}}^{-1}$ for three-dimensional (3D) translational diffusion is given by the well-known phenomenological expression introduced by Bloembergen-Parcell-Pound (BPP),

$$J(\omega, \tau) \propto \frac{\tau}{1 + \omega^2 \tau^2}. \quad (8)$$

Standard BPP behavior relies on a single Lorentzian spectral density $J(\omega, \tau)$ according to a single exponentially decaying correlation function $G(t)$ resulting in a symmetric $T_{1\text{diff}}^{-1}(1/T)$ peak. The BPP model and other theoretical approaches show the same dependencies of $J(\omega, \tau)$ in the low-temperature limit [$\omega \tau \gg 1, J(\omega, \tau) \propto \tau^{-1} \omega^{-2}$] and in the high-temperature limit [$\omega \tau \ll 1, J(\omega, \tau) \propto \tau$].

In contrast to 3D diffusion, the characteristic $T_{1\text{diff}}^{-1}(1/T)$ peak in the case of two-dimensional (2D) diffusion is not symmetric. Instead, the high-T flank reveals a lower slope compared to that in the low-temperature range. Additionally, a logarithmic frequency dependence of the relaxation rates on the high-temperature side shows up, whereas for 3D systems, no frequency dependence is expected. In order to describe the temperature and frequency dependence of the NMR relaxation rates for a 2D system such as $h$-Li$_{10.7}$TiS$_2$, the two limiting cases for low [$\omega \tau \gg 1, J(\omega, \tau) \propto \omega^{-2} \tau^{-1}$ (see low-T BPP limit)] and high temperatures [$\omega \tau \ll 1, J(\omega, \tau) \propto \tau \ln(1/\omega \tau)$] are combined by Richards in the empirical expression,

$$J(\omega, \tau) \propto \tau \ln \left(1 + \frac{1}{(\omega \tau)^\beta}\right). \quad (9)$$

In a good approximation, the frequency and temperature dependencies of $T_{1\text{diff}}^{-1}$ are then described by a single function $J(\omega_0, \tau)$. Equation (9) leads to asymmetric diffusion induced relaxation rate peaks with the high-T slope ($\omega \tau \ll 1$) being reduced by about 25% compared to that in the limit $\omega \tau \gg 1$. $eta$ expresses the frequency dependence of the relaxation rate. $\beta=2$ is expected for BPP behavior. Taking into account correlation effects resulting from Coulomb interactions of the hopping ions and/or structural disorder, an exponent $\beta<2$ is expected resulting in a smaller slope of the low-T side, i.e., in the limit $\omega \tau \gg 1$. Values of $\beta<2$ can be explained by various relaxation models developed for 3D systems by Funke and by Ngai, for example.

Fits according to Richards’ expression [Eq. (9)] are shown in Fig. 8 for two relaxation rate peaks $T_{1\text{diff}}^{-1}(1/T)$ and $T_{1\text{diff}}^{-1}(1/T)$ recorded at 10.0 and 5.2 kHz, respectively. The $T_{1\text{diff}}$ fits for $\beta=2$ yield activation energies $E_A$ between 0.35 and 0.38 eV (see Table I). These values are in very good agreement with those which were obtained by fitting just the

<table>
<thead>
<tr>
<th>$\omega_0/2\pi$ (kHz)</th>
<th>$E_A$ (eV)</th>
<th>$\tau_0^{-1}$ (s$^{-1}$)</th>
<th>$\beta$ ≤ 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>0.35(1)</td>
<td>$2(1) \times 10^{11}$</td>
<td>2.0</td>
</tr>
<tr>
<td>5.2</td>
<td>0.35(1)</td>
<td>$3(1) \times 10^{11}$</td>
<td>2.0</td>
</tr>
<tr>
<td>10.0</td>
<td>0.38(1)</td>
<td>$2(1) \times 10^{12}$</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table I. Results from fits according to the Richards expression [Eq. (9)]. The fit of the $T_{1\text{diff}}^{-1}(1/T)$ data at 5.2 kHz is exemplary shown in Fig. 8. $\beta$ was always restricted to be equal to or smaller than 2.

In a good approximation, the frequency and temperature dependence of the relaxation rate peaks in the rotating frame local magnetic fields $B_{1\text{loc}}$ have to be taken into account. This is because of the much lower locking field $B_1$ compared to the external magnetic field $B_0$ being effective for $T_1$ relaxation in the laboratory frame ($B_1 \ll B_0$). Consequently, $\omega_0$ was replaced by

$$\omega_{\text{eff}} = \gamma \sqrt{B_1^2 + B_{1\text{loc}}^2},$$

where $B_{1\text{loc}}$ was estimated by a spin-echo experiment to be about $B_{1\text{loc}}/(\sqrt{3})=0.76(2) \times 10^{-4}$ T. The magnetogyric ratio of a $^7$Li nucleus.

The corresponding fits to the peaks $T_{1\text{diff}}^{-1}(1/T)$ measured in the laboratory frame yield similar results as obtained in the rotating frame experiments. For instance, the fit in Fig. 8 shown for $\omega_0/2\pi=10.0$ MHz is determined by $E_A =0.34(2)$ eV and $\tau_0^{-1}=2(1) \times 10^{12}$ s$^{-1}$ if $\beta$ is restricted to be smaller than or equal to 2. Without restrictions $\beta$ turned out to be 2.01(1), i.e., slightly above 2, once again with no influence on $E_A$ and $\tau_0^{-1}$. In Table II, the results for the activation energies from the different methods are summarized. Values of $E_A$ obtained by fitting just the low-T flanks of the corresponding rate peaks are also included.

Besides the analysis of the temperature behavior of the relaxation rate, the parameter $\beta$ is directly obtainable by recording $T_{1\text{diff}}^{-1}$ at different magnetic fields for which $\omega \tau \gg 1$ holds. $^7$Li spin-lattice relaxation rates measured at different angular frequencies $\omega_0=\nu_0/2\pi$ and various temperatures on the lower-T flank of the corresponding relaxation peaks are shown in Fig. 9. Between $\nu_0=10$ and 39 MHz, $\beta=2$ is found confirming the value obtained from the temperature analysis of $T_{1\text{diff}}^{-1}$. At higher frequencies, i.e., at 77.7 and 155 MHz, the corresponding rates have a larger error because of the more difficult separation of background relaxation effects (see above). For this reason, the data at these frequencies were not taken into account in Fig. 9.

Whereas $\beta=2$ is found for $\omega_0/\tau \gg 1$, the diffusion induced relaxation rates of $h$-Li$_{10.7}$TiS$_2$ in the laboratory as well as in the rotating frame reveal a logarithmic frequency dependence if $\omega_{0,1} \tau \gg 1$, i.e., on the high-T flank of the rate
TABLE II. Comparison of activation energies $E_A$ and preexponential factors $\tau_0^{-1}$ for polycrystalline $h$-Li$_{0.7}$TiS$_2$ in various sub-ranges of temperature obtained from different NMR methods.

<table>
<thead>
<tr>
<th>NMR method</th>
<th>$E_A$ (eV)</th>
<th>$\tau_0^{-1}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE$^a$</td>
<td>0.37(1)</td>
<td>1 $(1 \times 10^{12})$</td>
</tr>
<tr>
<td>$T_0^c$</td>
<td>0.36(2)</td>
<td>1 $(1 \times 10^{12})$</td>
</tr>
<tr>
<td>Low-T flank</td>
<td>2D Richards fit$^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$140 $< T < 220$ K (rigid-lattice regime)

$^b$250 $< T < 360$ K.

$^c$Fits according to Eq. (9) (see Fig. 8 for temperature ranges); the exponent $\beta$ was restricted to be smaller than or equal to 2 (see text for further details).

Peaks$^{30}$ Thus, besides the temperature dependence of $T_{1\text{diff}}^{-1}$ and $T_{1\text{Larmor}}^{-1}$ the 2D nature of Li diffusion in $h$-Li$_{0.7}$TiS$_2$ is confirmed also via the frequency dependence of the spin-lattice relaxation rates. To our knowledge, the layered polymorph of lithium titanium disulfide is the only Li conductor for which the two dimensionality of cation diffusion is probed in this way by frequency and temperature dependent $^7$Li relaxation NMR, so far.

C. Comparison of Li jump rates from $^7$Li SAE and relaxation NMR: Li diffusion pathway in Li$_{0.7}$TiS$_2$

In Fig. 10, the jump rates directly obtained from stimulated-echo decays at $T_f=15$ $\mu$s are shown together with those read out from the various diffusion induced spin-lattice relaxation rate peaks$^{30}$. Thus, besides the temperature dependence of $T_{1\text{diff}}^{-1}$ and $T_{1\text{Larmor}}^{-1}$, the 2D nature of Li diffusion in $h$-Li$_{0.7}$TiS$_2$ is confirmed also via the frequency dependence of the spin-lattice relaxation rates. To our knowledge, the layered polymorph of lithium titanium disulfide is the only Li conductor for which the two dimensionality of cation diffusion is probed in this way by frequency and temperature dependent $^7$Li relaxation NMR, so far.

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FIG. 9. Frequency dependence (low-temperature flank) of the diffusion induced relaxation rate. $\beta=2$ indicates that $T_{1\text{diff}}^{-1}$ in $h$-Li$_{0.7}$TiS$_2$ follows simple BPP behavior in the case $\omega_0\tau\gg 1$. Relaxation rates were recorded at various temperatures in the range $\omega_0\tau\gg 1$.

FIG. 10. Li jump rates of the 2D conductor $h$-Li$_{0.7}$TiS$_2$ vs reciprocal temperature. The $\tau_{SLR}^{-1}$ rates were measured directly by means of $^7$Li SAE NMR, whereas the rates $\tau_{SLR}^{-1}$ (\$) and $\tau_{SLR}^{-1}$ (*) were deduced from the maxima positions of the corresponding rate peaks $T_{1\text{diff}}(1/T)$ and $T_{1\text{Larmor}}(1/T)$, respectively (see partly Fig. 8). $T_{1\text{diff}}^{-1}$ relaxation peaks were recorded at 10, 19.2, 27.9, and 77.7 MHz. The $\tau_{SLR}$ rates were obtained from NMR spin-lattice relaxation experiments in the rotating frame at $\omega_0=(2\pi=2.1, 5.2, \text{and } 10$ kHz, respectively. The solid line corresponds to $E_A=0.41(1)$ eV and $\tau_0^{-1}=6.3(1) \times 10^{12}$ s$^{-1}$.
FIG. 11. (Color online) Li diffusion pathway in h-Li$_{0.7}$Ti$_2$S$_2$ as probed by $^7$Li spin-alignment echo NMR ($1b\rightarrow 2d\rightarrow 1b'$). The involvement of tetrahedral sites ($2d$) in the $Li^+$ jump process is energetically favored compared to direct hopping between the (electrically equivalent) octahedral sites $1b$. Squares denote vacant Li positions.

means of relaxation NMR, all Li jump processes are measured. The perfect consistency of the data points in Fig. 10 shows that $^7$Li SAE NMR does not detect only a subset of the total number of Li jumps in h-Li$_{0.7}$Ti$_2$S$_2$. Consequently, one has to conclude that the jump process probed by SAE NMR ($1b\rightarrow 2d\rightarrow 1b'$, see Fig. 11) is the only mechanism relevant in the whole temperature range covered here. Direct hopping between two octahedral sites ($1b\rightarrow 1b'$) seems to be not important for the overall cation transport. The jump distance of this process is about 3.64 Å and, thus, much larger than that for the corresponding tetrahedral-octahedral two-site process with a value of about 2.14 Å.

Quantum chemical calculations by Bredow confirm these results. For Li$_{2/3}$Ti$_2$S$_2$ an activation energy of 0.37 eV for the ($1b\rightarrow 2d\rightarrow 1b'$) pathway was calculated which is in perfect agreement with the experimental result presented here. The calculations have shown that direct hopping between two octahedral sites ($1b\rightarrow 1b'$) is not favored. Quite recently, theoretical calculations by Ramírez et al. on Li$_x$TiSe$_2$ were performed. Li$_x$TiSe$_2$ crystallizes in the same space group as Li$_2$TiS$_2$. Ramírez et al. have shown that in the isostructured Se analogue the tetrahedral-octahedral diffusion pathway is also the most probable Li migration path. Similar results were found recently by first-principles calculations for Li diffusion in Li$_x$CoO$_2$ which has a layered structure similar to that of Li$_2$TiS$_2$. Van der Ven et al. have shown that also in Li$_x$CoO$_2$ with $x<1$ the diffusion pathway involving tetrahedral sites is energetically favored compared to direct hopping between electrically equivalent octahedral sites. Similar results were obtained by Catti using $ab$ initio Hartree-Fock methods. However, van der Ven et al. have found also that the latter migration path becomes more important at higher Li content. Our recent studies on a sample with $x=1.0$ indicate that this seems to be valid also for the Li$_x$TiS$_2$ system. Interestingly, the activation energy for the tetrahedral-octahedral jump process is reduced to 0.26(1) eV for the Li$_{0.8}$Ti$_2$S$_2$ sample. Van der Ven et al. have found the same trend for $Li_xCoO_2$. Their explanation for the Li$_x$CoO$_2$ system may hold qualitatively also for the Li$_x$TiS$_2$ case: A larger electron density on the sulfur ions results in better shielding between a migrating Li$^+$ and the transition metal ion leading to a reduction of the activation barrier.

Quite recently, we have demonstrated that for polycrystalline Li$_x$Ti$_2$O$_{12}$ (Ref. 67), as well as for Li$_x$BiO$_6$, the activation energy obtained from $^7$Li spin-alignment echo NMR is similar to that which is probed by dc-conductivity measurements. This similarity was also found for the interlayer Li diffusion process in single-crystalline Li$_x$N$_2$, as well as for the cation transport in Ag ion conductors where the dynamic properties were probed by multiple-time $^{109}$Ag stimulated echo NMR. The activation energy for single-crystalline h-Li$_{0.7}$Ti$_2$S$_2$ obtained from electrochemical methods is about 0.4 eV. This value is remarkably similar to those probed by $^7$Li SAE NMR here. Further conductivity measurements on polycrystalline h-Li$_{0.7}$Ti$_2$S$_2$ samples are to be performed in our laboratory. Interestingly, in the present case, $E_A$ from the low-$T$ flanks of the NMR relaxation rate peaks agrees very well with the value from SAE NMR. This result is not self-evident. In a lot of cases significant differences between activation energies from low-$T$ spin-lattice relaxation NMR and conductivity (as well as spin-alignment NMR) may be expected. This difference is mainly due to the fact that both types of experiments probe ionic motion on different length and, thus, time scales. With dc-conductivity measurements, long-range diffusion parameters are probed, whereas spin-lattice relaxation NMR rates (in the laboratory frame) are sensitive to Li diffusion on a much shorter time scale (see Sec. III). Short- and long-range diffusion parameters can be considerably different, especially for structurally disordered materials with a complex potential landscape for cation migration. Additionally, the small activation energies deduced from the low-$T$ flanks ($\omega T \gg 1$) of the spin-lattice relaxation rate peaks are influenced by other aspects such as strongly localized hopping of the charge carriers, or even unsuccessful attempts of the ions at jumping to a new site. These influences result in apparently low hopping barriers and higher jump rates than expected. Moreover, correlation effects due to Coloumb interactions of the moving particles will affect the slope of $T_1^{-1}$ in the limit ($\omega T \gg 1$). Long-range diffusion parameters are accessible by NMR relaxation only, if the high-$T$ flank ($\omega T \ll 1$) is accessible and if the structure of the material allows 3D diffusion. For a 2D ionic conductor such as Li$_2$TiS$_2$, the slope of the high-$T$ flank is influenced by the dimensionality of the transport process (see above) and, thus, the slope of the high-$T$ flank cannot be transformed into $E_A$ characterizing long-range diffusion without a suitable model. Here, the nice agreement between $E_A$ from relaxation NMR on the one hand and from SAE NMR on the other hand demonstrates that in Li$_{0.7}$Ti$_2$S$_2$ no difference between short- and long-range diffusions exists. This results is by no means trivial. It may be expected only for a crystallographically simple structured low-defective material having a well defined as well as regular potential landscape for Li diffusion. This situation seems to be valid in the present case.

Thus, a single diffusion mechanism was probed over a large dynamic range, interestingly irrespective of the method applied. The energetically favored octahedra-tetrahedra-octahedra jump process ($1b\rightarrow 2d\rightarrow 1b'$) turned out to be the
elementary step responsible for long-range Li$^+$ diffusion in Li$_{0.7}$TiS$_2$ which is known to be two-dimensional from the NMR relaxation studies.

**VII. CONCLUSION**

Recording stimulated echoes for spin-3/2 spins proves to be a rather new and powerful tool for the investigation of extremely slow ionic exchange processes in crystalline ionic conductors. Here, the method was applied to the $^7$Li nucleus. Ultraslow Li jumps were probed within the rigid lattice regime of the 2D lithium ion conductor $h$-Li$_{0.7}$TiS$_2$. In the rigid lattice range, neither the measurement of $T_1^\text{SAE}$ nor that of $T_1$ are helpful for the investigation of such slow Li jumps. Even with spin-lattice relaxation NMR measurements in the rotating frame jump rates smaller than $10^4$ s$^{-1}$ are not accessible in the present case. However, extremely small $^7$Li jump rates are directly obtainable via the $^7$Li spin-alignment echo decay measured as a function of mixing time which was varied over more than six decades. In this way jump rates with values down to 0.1 s$^{-1}$ were detectable over a dynamic range of about four decades. The corresponding correlation functions showed a two-step decay behavior. Therefore, an accurate separation of jump rates from the influence of longitudinal spin-lattice relaxation effects was possible. The data from spin-alignment echo NMR experiments fit remarkably well to those values extracted from the diffusion induced spin-lattice relaxation rate maxima recorded in the laboratory and rotating reference frame, respectively. The $^7$Li NMR relaxation measurements as well as the $^7$Li spin-alignment data probe one and the same diffusion process with an activation energy of about 0.4 eV. Altogether, by using this combination of NMR techniques, a solitary Li diffusion process in $h$-Li$_{0.7}$TiS$_2$ was precisely measured over a dynamic range of about ten decades. Final state amplitudes of the $^7$Li SAE NMR two-time correlation functions reveal that octahedra-tetrahedra-octahedra jumps within the van der Waals gap between the TiS$_2$ layers are responsible for Li diffusion. The two-site jump process is identified as the elementary step of long-range 2D Li diffusion in $h$-Li$_{0.7}$TiS$_2$.

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