Lithium motion in the anode material LiC$_6$ as seen via time-domain $^7$Li NMR

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Since the commercialization of rechargeable lithium-ion energy storage systems in the early 1990s, graphite intercalation compounds (GICs) have served as the number one negative electrode material in most of today’s batteries. During charging the performance of a battery is closely tied with facile Li insertion into the graphite host structure. So far, only occasionally time-domain nuclear magnetic resonance (NMR) measurements have been reported to study Li self-diffusion parameters in GICs. Here, we used several NMR techniques to enlighten Li hopping motions from an atomic-scale point of view. Li self-diffusion in the stage-1 GIC LiC$_6$ has been studied comparatively by temperature-variable spin-spin relaxation NMR as well as (rotating frame) spin-lattice relaxation NMR. The data collected yield information on both the relevant activation energies and jump rates, which can directly be transformed into Li self-diffusion coefficients. At room temperature the Li self-diffusion coefficient turns out to be $10^{-15}$ m$^2$ s$^{-1}$, thus, slightly lower than that for layer-structured cathode materials such as Li$_4$Ti$_5$O$_{12}$.

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I. INTRODUCTION

The stage-1 graphite intercalation compound, LiC$_6$, belongs to one of the most fascinating application-oriented materials which is widely used as an anode in secondary lithium-ion batteries.$^{1–3}$ Most of the various electronic devices of our daily life such as notebooks or cell phones rely on the insertion and deinsertion of lithium ions into graphite-based negative electrodes.$^4$ In particular, the charge/discharge performance and thus the rate capability of an anode is closely related to self-diffusion of lithium ions inside the crystalline host. Moreover, if models are to succeed in simulation of the electrochemical processes in batteries, precisely measured data such as diffusion parameters are required.

Surprisingly, only a few studies can be found in the literature which directly deal with the in-depth investigation of Li diffusion parameters in crystalline, phase-pure LiC$_6$. Despite the relatively simple, but fascinating, structure of LiC$_6$ research is yet far away from drawing a comprehensive picture on diffusive Li motion. Apart from earlier studies$^5$ applying quasielastic neutron scattering (QENS)$^6$ or taking advantage of $\beta$-radiation detected nuclear magnetic resonance ($\beta$-NMR) measurements of spin-polarized $^9$Li ($t_{1/2} = 0.8$ s) nuclei produced in situ by polarized neutron capture,$^7$–$^9$ classical NMR measurements$^6$–$^{12}$ on the stable Li isotope $^7$Li have rarely been utilized for this purpose. En passant, the results obtained from $^7$Li pulsed NMR as yet turned out to be less conclusive with respect to Li diffusion parameters.$^{13}$ This is because mainly spin-lattice relaxation (SLR) measurements in the so-called laboratory frame of reference have been performed. Compared to other time-domain NMR techniques, those measurements are sensitive to Li jump rates with values in the MHz range.$^{10}$ However, in order to probe Li motional processes in the temperature range where the structurally ordered LiC$_6$ phase does exist, i.e., at ambient temperature, alternative NMR techniques have to be applied which are able to access much slower Li motions. For example, this is possible by recording SLR rates $R_1$ in the rotating ($\varphi$) frame of reference via the so-called spin-lock technique introduced by Ailion and Slichter.$^{11,12,15–18}$ If $^7$Li SLR takes solely place in the presence of a controllable magnetic field with resonance frequencies on the order of a few kHz instead of some MHz,$^{19}$ the desirable diffusion-induced rate peak $R_1(1/T)$ shows up at much lower temperatures $T$.$^{11,18}$ In general, the peak entails valuable information on both short-range and long-range motions$^{9,13,18}$ as well as correlation effects.$^{20,21}$

Here, layer-structured LiC$_6$ (see Fig. 1) served as an excellent model system to probe Li dynamics with spatially confined migration pathways; it is the most prominent anode host material with applications in energy storage technology. The stage-1 compound consists of commensurate layers of carbon and lithium; Li resides in the central site below and above each third hexagon formed by C atoms. The stacking sequence is $A_{\alpha}A_{\alpha}$ with a periodicity of 3.71 Å; A denotes the graphite basal plane and $\alpha$ the intercalate layer. The carbon host structure of LiC$_6$ allows in-plane jump diffusion and, because of the open channels parallel to the hexagonal $c$...
axis and the small size of the Li ion, it has been argued that also diffusion normal to the graphite plane cannot be ruled out a priori as in the case of the heavy alkalis. In the present contribution, the results from various $^7$Li NMR measurements investigating both (local electronic) structure and Li ion dynamics of polycrystalline LiC$_6$ will be presented and compared with those deduced from previous $\beta$-NMR and QENS studies, in particular. While $\beta$-NMR results were obtained on highly oriented pyrolytic graphite (HOPG) at temperatures around 373 K, results from QENS being sensitive to Li correlation times in the ns to ps range, were collected at much higher $T$, i.e., in a range with sufficiently fast Li motion.

II. EXPERIMENT

The synthesis procedure to obtain polycrystalline stage-1 LiC$_6$, shining like gold, is described in the classical paper by Guérard and Hérol. After preparation, the sample (approximately 300 mg) was sealed in a quartz ampoule (3 cm in length, 5 mm in diameter) and stored for several months at room temperature; we anticipate almost full lithium homogenization, i.e., a homogenous distribution of the Li ions between the layers. The sample consists of LiC$_6$ crystallites with diameters less than 500 $\mu$m. Phase purity was checked by x-ray powder diffraction (XRPD). XRPD revealed a small volume fraction of the stage-2 compound LiC$_{12}$ formed. By x-ray powder diffraction (XRPD) and compared with those deduced from previous measurements presented below. 

$^7$Li NMR measurements were carried out using two different high-performance digital Bruker Avance III spectrometers in connection with shimmed cryomagnets with nominal magnetic fields of 7 T and 11 T, respectively. This corresponds to $^7$Li Larmor frequencies of $\approx 116$ MHz and $\approx 194$ MHz, respectively. Both a commercial high-temperature probe (Bruker Biospin) and a probe designed for temperatures ranging from 203 K to 450 K; here, a Eurotherm temperature controller in combination with a type T thermocouple was used.

$^7$Li NMR SLR rates $1/T_1 = R_1$ were acquired with the saturation recovery pulse sequence $10 \times \pi/2 - \tau_d - \pi/2 - \text{acq.}$ An initial pulse train, consisting of ten $\pi/2$ pulses separated by 80 $\mu$s, was used to destroy any longitudinal magnetization $M_0$ prior to recording its temperature and frequency dependent recovery as a function of the delay time $\tau_d$. Rotating-frame $^7$Li NMR SLR rates $1/T_{1\rho} = R_{1\rho}$ were recorded with the spin-lock technique, $\pi/2 \rho(t_{\text{lock}}) - \text{acq.}$ The corresponding (angular) locking frequency $\omega_{\text{lock}}$ was chosen to be as low as possible. Here, $\omega_{\text{lock}}/2\pi \approx 10$ kHz was used and the duration of the locking pulse $t_{\text{lock}}$ was varied from 100 $\mu$s to 100 ms. Note that the recycle delay for the SLR experiments was set to at least 5 $\times \tau_d/R_1$ in order to guarantee full longitudinal relaxation between each scan. Both $R_1$ and $R_{1\rho}$ were obtained by parameterizing the magnetic transients $M_t(t_{\text{lock}})$ and $M_{\rho}(t_{\text{lock}})$, respectively, by stretched exponentials (see below): $M_t(t_{\text{lock}}) \propto 1 - \exp[-(t/T_1)^q]$ and $M_{\rho}(t_{\text{lock}}) \propto \exp[-(t_{\text{lock}}/T_{1\rho})^q]$, respectively.

In addition, temperature-variable $^7$Li NMR spin-spin relaxation (SSR) rates $1/T_2 = R_2$ were recorded by taking advantage of a (two-pulse) solid-echo pulse sequence, that had been optimized for spin-3/2 nuclei such as $^7$Li. $t_{\text{echo}}$ in $\pi/2 - \tau - \text{echo} - (64\tau)^+ - \text{acq.}$ denotes the variable interpulse delay. The transients obtained can be satisfactorily described with single exponentials. Static $^7$Li NMR spectra were either obtained after Fourier transformation (FT) of the free induction decay, which were recorded by nonselective irradiation with a single $\pi/2$ pulse, or by FT of the solid echo beginning from the top of the signal.

III. RESULTS AND DISCUSSION

A. NMR spectra and motional narrowing

Before discussing our SLR NMR results in detail, we call the reader’s attention to the static $^7$Li NMR spectra shown in Fig. 2 which were recorded at different temperatures $T$. Let us first discuss the central line of the spectrum which is also determined by a distinct powder pattern because of electric

![Graph showing static $^7$Li NMR spectra](image-url)
quadrupolar interactions (see below). At sufficiently low $T$, Li$^+$ translational motion is slow compared to the spectral width determined by the central transition. This results in dipolarly broadened NMR spectra. Motion-induced averaging of dipolar interactions causes line narrowing at elevated $T$ [see Fig. 3(a)]. Expectedly, its overall width (full width at half maximum) in the rigid-lattice regime mainly is determined by the central transition. This results in a single pattern is observed. From the inner quadrupole splitting (the outer ones are marked in Fig. 2 by vertically drawn arrows) the site-specific quadrupole coupling constant $C_q = 2 \Delta \nu_{q}$ can be estimated; see the NMR spectrum recorded at 228 K (Fig. 2). Assuming axial symmetry ($\eta = 0$), as expected from the crystal structure, the quadrupole splitting $\Delta \nu_{q}$ is given by $\Delta \nu_{q} = |e^2 q Q/(2h)|[3 \cos^2(\theta) - 1]$ where $\theta$ denotes the angle between the $c$ axis and the external magnetic field (in the principal axis system). $e$ is the elemental charge, $q$ represents the EFG at the Li site, $Q$ is the quadrupole moment of $^7$Li, and $h$ denotes Planck’s constant. At the position of the 90° singularities we obtain $\Delta \nu_{q} = |e^2 q Q/(2h)|$ leading to $2 \Delta \nu_{q} = |e^2 q Q/h| = |C_q|$. This yields 46.2 kHz for the quadrupole coupling constant at 295 K. Note once again that the values given in Fig. 2, and those shown as a function of $T$ in Fig. 3 as well, were obtained for an axially oriented EFG with respect to the principal axis system. The absolute values are consistent with those from $^7$Li-NMR and $^6$Li-$\beta$-NMR measurements in the literature. As an example, Letellier et al. found $\Delta \nu_{q} = 22.6$ kHz at ambient temperature which is in good agreement with our value (23.1 kHz). Using an oriented sample, Roth et al. report a value of 22 kHz; in an early work of Conard et al. a splitting of 24 kHz is found. LiC$_{12}$, LiC$_{18}$, LiC$_{27}$, and LiC$_{36}$ show smaller quadrupole splittings $\Delta \nu_{q}$ ranging from 17 to 19 kHz.

It is worth noting that the decrease of the quadrupole splitting $\Delta \nu_{q}$ with increasing $T$ cannot simply be ascribed to changes of the lattice parameters. Owing to the narrower temperature range covered we were not able to reveal the $T^{3/2}$ dependence found by $\beta$-NMR on an oriented LiC$_6$ sample. Here, $\Delta \nu_{q}$ (200 K $< T < 450$ K) changes linearly with $T$.  

![Figure 3](image.png)
B. Diffusion-induced relaxation NMR

1. $^7$Li SLR NMR in the laboratory and rotating frame of reference

In the Arrhenius presentation of Fig. 4(a) an overview of the $^7$Li NMR relaxation rates measured is given. At first we will briefly discuss the SLR NMR rates recorded at 116 MHz and 194 MHz, i.e., in the laboratory frame of reference. At low temperatures $R_1$ seems to be independent of the Larmor frequency applied. Combined with a linear dependence of $R_1$ on temperature, this is expected for SLR being mainly induced by coupling of the Li spins with conduction electrons. Indeed, a power-law fit

$$R_1 \propto T^\kappa,$$  

indicated by the dotted line shown in Fig. 4(a), yields $\kappa = 1.1(1)$. This can be even better illustrated by plotting $R_1$ vs $T$: The dashed line in Fig. 4(b) represents ideal linear behavior according to $R_1 = s/T^\kappa$ with $\kappa = 1$. The inset uses the representation $\log_{10}(R_1) vs \log_{10}(T)$ to calculate $\kappa$ in the low-temperature regime with a linear fit. The latter yields $s_1 = 2.9(3) \times 10^{-4} \text{s}^{-1} \text{K}^{-1}$ and $\kappa = 1.12(4)$ (cf. the power-law analysis shown above). The product $T_\rho \rho$ turns out to be approximately $650 \pm 15 \text{s} \cdot \text{K}$, which is in very good agreement with the $^7$Li NMR result reported by Estrade et al.\textsuperscript{14} (600 $\pm 120 \text{s} \cdot \text{K}$).

Above 300 K the rates $R_1$ increasingly deviate from $R_1 = S_0 T$ which points to the influence of other relaxation mechanisms owing to Li$^+$ hopping processes or (anharmonic) lattice vibrations. A two-phonon Raman process would give $R_1 \propto T^2$ at temperatures $T$ larger or similar to the Debye temperature $\Theta$. In order to separate such background effects from diffusion-induced processes, we extrapolated the power-law fit of Fig. 4(a) to higher temperatures and subtracted the rates from the overall ones measured; i.e.,

$$R_{1,\text{corr}} = R_1 - R_{1,e}$$

with $R_{1,e} \approx S_0 T^\kappa$. If we assume that the background-corrected rates obtained are mainly influenced by Li hopping, an activation energy can be roughly estimated. Note that the rates were recorded in the regime $\omega_0 T \gg 1$: i.e., the activation energy $E_{\text{act},T}$ should be characteristic of short-range (or localized) Li motions in LiC$_6$. These might include translational processes in LiC$_6$ with a short jump distance.\textsuperscript{5} Here, we obtain $0.25(2) \text{eV}$ which is very similar to the result previously estimated from NMR line narrowing.\textsuperscript{14}

Ion dynamics proceeding on a longer length scale, however, can only be probed when the so-called high-$T$ flank of the diffusion-induced rate peak is reached. In the present case, this needs very high temperatures. Fortunately, the spin-lock technique can be used which is per se sensitive to slower Li motions covering a longer time scale. Therefore, we recorded diffusion-induced SLR NMR rate peaks at frequencies $\omega_0$ on the order of some kHz instead of using $\omega_0$ with values in the MHz range. Doing so, by formally replacing $\omega_0$ with $\omega_0$ the SLR NMR rate peak shifts towards lower temperature so that both the maximum and the high-$T$ flank become accessible. The corresponding rates $R_{1,\omega}$, which have been extracted from the stretched magnetization transients recorded, are shown in Fig. 4(a) as a function of the inverse temperature. At low temperatures, that is, below 250 K, they are increasingly governed by nondiffusive background effects. Note that the ratio $R_{1,\omega}/R_1$ turns out to be approximately 1.5 orders of magnitude. Thus, besides interactions of the Li spins with conduction electrons in the case of $R_1$ measurements (see above), the low-$T$ $R_{1,\omega}$ rates seem to be influenced by additional processes (see below). For comparison, the corresponding stretching factors of the various transients measured are shown in Fig. 4(c). In Fig. 5 selected magnetization transients of the $R_{1,\omega}$ NMR measurements are shown.

Finally, with increasing $T$ the overall rates $R_{1,\omega}$ pass through a maximum located at $T = 314 \text{K}$. At even higher...
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For comparison the stretching factor around 0.7 [see Fig. 4(c)].

Diffusion-induced rate peak shown above. Solid lines show fits of temperature-variable magnetization transients yielding 0.57(2) eV and \( \beta \).

Line represents the 2D fit by means of Eq. (6). The dashed-dotted line shows the 2D fit by means of Eq. (6). The dashed-dotted line includes the pre-exponential factor \( \tau_0^{-1} \) and the activation energy \( E_a \) determining long-range Li diffusion

\[
\tau_c^{-1} \approx \tau_1^{-1} = \tau_0^{-1} \exp(-E_a/k_BT); \quad (5)
\]

\( k_B \) denotes Boltzmann’s constant. Here, the best fit yields \( \kappa' \approx 2.0(4) \), thus indicating that lattice vibrations become the main origin of background relaxation (see above). The parameter \( \beta \) reflects any asymmetry of the rate peak \( R_{1ω}(1/T) \) which may arise from correlation effects such as structural disorder and/or Coulomb interactions. In general, uncorrelated motion should result in a symmetric NMR rate peak; any correlation effects, for comparison, are expected to reduce the slope on the low-T side compared to the situation in the limit \( \omega_1 \tau \ll 1 \), that is, the high-T regime. In the present case we found \( \beta = 1.7(2) \); thus, the diffusion-induced rate peak, indicated by the dashed-dotted line in Fig. 4(a), is slightly asymmetric.

The activation energy \( E_a \) turned out to be 0.57(2) eV; the prefactor \( \tau_c^{-1} \) is approximately \( 1.6 \times 10^{14} \) s⁻¹. The latter is in very good agreement with values typically expected for phonon frequencies. Moreover, \( E_a \approx 0.57 \) eV is consistent with the prediction of Freiländer et al. The value obtained from Eq. (3) also equals the activation energy which can be directly obtained from the high-T side of the rate peak. Moreover, in the limit \( \omega_1 \tau \gg 1 \), where \( J(\omega_1, \tau) \propto \omega^{-\beta} \tau^{1-\beta} \) holds, the corresponding slope yields \( E_a, \text{low} = 0.42(2) \) eV. In the present case, \( E_a, \text{low} \) and \( E_a \) obey the relation \( E_a, \text{low} = (\beta - 1)E_a \). Note that the same result is obtained when Eq. (3) is restricted to the first term: \( R_{1ω, \text{diff}} \propto J(\omega_1) \).

It is worth noting that \( J(\omega) \) in Eq. (4) represents a spectral density function which describes diffusive motion in three dimensions (3D). Frequency-dependent \( \beta \)-NMR measurements, however, indicate a low-dimensional diffusion process in LiC₆. Additionally, at temperatures higher than 630 K, a 2D motional process was claimed based on QENS measurements. Therefore, we also tried to analyze our SLR NMR data with a semiempirical spectral density function for 2D diffusion. In concrete terms, we used the expression by Richards, which is based on a function introduced by Avogadro and Villa taking account of a logarithmic frequency dependence in the high-temperature limit \( \omega_0(1) \tau_c \ll 1 \). Following Kückler et al., who first incorporated the effect of correlation via the parameter \( \beta \) also for 2D diffusion, it reads

\[
R_{1ω, \text{2D}} = R_{1ω, \text{diff}} + R_{1ω, \text{bg}} \\
\approx C_0 \tau_c \ln[1 + (1/(\omega_1 \tau_c)^\beta)] + B'T^\kappa'. \quad (6)
\]

This ansatz worked well for other layer-structured materials showing 2D diffusion. The fit, indicated in Fig. 5 by the dashed line, yields \( B \approx B' \) and \( \kappa' \approx \kappa '' \). Moreover, \( E_a^{2D} \) is given by approximately 0.62 eV and, thus, at least comparable to the result obtained by Eqs. (3) and (4). However, in the present case, the prefactor \( \tau_c^{-1} \) turns out to be unusually high; it would be approximately \( 1.8 \times 10^{16} \) s⁻¹. This is by about two orders of magnitude larger than that obtained from the modified-BPP fit used to describe the temperature dependence of the NMR rates (vide supra). Hence, based on the results obtained it seems that the semiempirical Richards model (represented by the dashed line in Fig. 5) is less appropriate to
describe Li dynamics in LiC₆. Certainly, this fact might also be explained by nonnegligible Li hopping processes taking place via defects perpendicular to the layers, that is, channel-like diffusion, influencing the NMR response of a pure 2D process.

2. ⁷Li NMR spin-spin relaxation

The results obtained from SLR NMR are corroborated by the analysis of complementary spin-spin relaxation (SSR) data. In agreement with the results of Eqs. (3) and (4), temperature-variable SSR measurement yield an activation energy of 0.53(2) eV. This value can be extracted from the rates measured as follows. Below 285 K, that is, in the so-called rigid lattice regime, \( R^{-1}_2 \) is almost independent of temperature and amounts to approximately 125 µs. Owing to averaging of dipole-dipole interactions, because of increasing of the Li⁺ hopping, the rates significantly start to decrease indicating long-range Li translational motion. Interestingly, at 400 K hopping, the rates significantly start to decrease indicating that the gray area indicates the temperature range covered by Li⁺ diffusion-induced \( R_{1o} \) measurements. From the Arrhenius line indicated a prefactor \( τ_0^{-1} \) can be estimated (±1 × 10⁻⁴ s⁻¹) which is consistent with that obtained from the analysis of the \( R_{1o}(1/T) \) NMR peak with a BPP-type expression (vide supra).

Besides \( R_{1o} \) measurements also \( R_2 \) (and motional line narrowing as well) is suitable to estimate Li jump rates. At the temperature where the rates \( R_2 \) start to decrease \( T \approx 294 \) K; see Fig. 4(a) the Li jump rate is expected to be on the order of \( τ^{-1} \approx 2πR_2 \) with \( R_2^{-1} \approx 140 \) µs being the rigid-lattice SLR NMR rate. This yields \( τ = 22 \) µs. Even slower motions can be estimated from the onset of motional line narrowing; in the present case NMR central narrowing as well) is suitable to estimate Li jump rates.

C. Li jump rates and self-diffusion coefficients

Considering the maximum of the \( R_{1o}(1/T) \) peak probed, it is possible to precisely determine the mean Li jump rate irrespective of the spectral density function \( J \) chosen to parametrize the data. At \( T = 314 \) K, that is the temperature where the peak shows up [see Fig. 5(a)], for SLR NMR in the rotating frame of reference the condition \( ω_1τ_c \approx 0.5 \) holds.⁹ Identifying \( τ_c \) with the motional residence time of an Li spin and inserting \( ω_1 = 2π \times 10(1) \) kHz, we obtain \( τ_c \approx τ = 8 \) µs. According to the Einstein-Smoluchowki equation,⁴⁶

\[
D_{dd} = a^2/(2d \cdot τ), \tag{7}
\]

this corresponds to \( D_{dd}(314 K) \approx 1.9 \times 10^{-11} \) cm² s⁻¹ and \( D_{dd}(314 K) \approx 1.3 \times 10^{-11} \) cm² s⁻¹. Here, we used \( a \approx 3 \) Å as a good approximation for a mean jump distance and calculated the diffusion coefficient for both spatially restricted and nonrestricted motion, i.e., for \( d = 2 \) or \( d = 3 \), whereby \( d \) represents the dimensionality of the diffusion process.

In Fig. 6(a) the jump rate determined by means of the Li⁺ diffusion-induced \( R_{1o}(1/T) \) peak rate is shown in an Arrhenius plot and compared with those values which can be estimated from (analogous) ⁸Li β-NMR measurements of Freiländer et al.⁷ Although ⁸Li NMR was carried out on oriented (HOPG) LiC₆ samples good agreement is found. For comparison, the solid line represents an Arrhenius line characterized by an activation energy of 0.55 eV, which represents the mean value when the results from \( R_{1o} \) and \( R_2 \) are considered. The rate and an underestimation of the activation energy; see, e.g., Refs. 32 and 33. For comparison, activation barriers ranging from 0.1 and 0.3 eV have been calculated for different types of interstitially diffusion mechanisms in LiC₆.²²

Finally, considering the rates shown in Fig. 6(a), at room temperature (293 K) the Li jump rate turns out to be \( 4.5 \times 10^4 \) s⁻¹. This corresponds to a self-diffusion coefficient on the order of \( 5 \times 10^{-12} \) cm² s⁻¹ at 293 K. Decreasing the temperature from 293 to 268 K (≈5°C), Li self-diffusivity is slowed down by a factor of 10. Such key figures are crucial for the safe and efficient operation of graphite-based ion batteries. In particular, at freezing temperatures the performance of a battery is then additionally limited and controlled to a large extent by slow Li diffusion within the host material. It is noteworthy that room-temperature self-diffusion coefficients ranging from 10⁻¹⁰ m² s⁻¹ to 10⁻⁸ m² s⁻¹, as found for LiC₆ here, are comparable to those recently obtained by NMR also for layer-structured cathode materials such as Li₄SₓTiS₂.¹⁰ Thus, regarding Li self-diffusion in fully intercalated stage-1 LiC₆, Li ion mobility does not exceed that of conventional cathode materials.
Strictly speaking, the results presented here should not be mixed with chemical diffusion coefficients which have been experimentally probed via (solid-state) electrochemical macroscopic method as well as calculated \( (4 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}, E_0 \approx 0.4 \text{ eV}) \) recently for 2D (in-plane) Li\(^+\) motion in LiC\(_6\).\(^{45}\) Interestingly, the results of the theoretical work by Toyoura \textit{et al.}\(^{45}\) on ordered LiC\(_6\) agree well with the present findings. Activation barriers for Li migration, which were calculated separately for the vacancy and interstitial Li migration process, turned out to be approximately 0.5 eV; see also Ref. 22. The corresponding (in-plane) diffusion coefficients are \( 10^{-14} \text{ m}^2 \text{ s}^{-1} \) and \( 10^{-15} \text{ m}^2 \text{ s}^{-1} \), respectively. Apart from this good agreement, the present results are in line with those from earlier experimental studies; see, e.g., Ref. 48 for an overview of Li (chemical) diffusion coefficients determined for various carbon anode materials. Note that by the application of NMR spectroscopy we were able to study Li ion dynamics separately from electron dynamics in mixed conducting LiC\(_6\). While the latter influences the SLR NMR rates recorded at low temperatures, with increasing \( T \) diffusive motions significantly govern spin-lattice relaxation while other interactions relatively lose ground. These show up once again at temperatures higher than 400 K.

As a last comparison, in Fig. 6(b) data from the QENS study of Mageil \textit{et al.},\(^5\) pointing to an in-plane 2D jump-type diffusion mechanism, are included. The self-diffusion coefficients deduced from QENS have been roughly converted into jump rates according to Eq. (7). Here, we used both \( a \approx 4.26 \text{ Å} \) as found by QENS for the 2D diffusion process and \( a \approx 3 \text{ Å} \), which is a good approximation for the average of possible jump distances. Considering the error limits and the narrow temperature range covered by the earlier study,\(^5\) in our opinion, a relatively good agreement is found with the results obtained from NMR. The solid line is to guide the eye and refers to an Arrhenius law with \( E_0 = 0.54 \text{ eV} \) and \( \tau_0^{-1} = 5 \times 10^{13} \text{ s}^{-1} \) which is very similar to that shown in Fig. 6(a). To sum up, over a relatively broad dynamic range a single Arrhenius relation seems to be appropriate to describe Li diffusion in ordered LiC\(_6\).

IV. CONCLUSIONS AND OUTLOOK

Spin-lattice relaxation NMR using the stable isotope \(^7\text{Li}\) was applied to probe room-temperature Li dynamic parameters in polycrystalline, mixed conducting LiC\(_6\) being the most widely used anode material. As deduced from atomic-scale NMR measurements Li hopping in the bulk is characterized by an activation energy of approximately 0.55 eV and an Li self-diffusion coefficient of \( 10^{-15} \text{ m}^2 \text{ s}^{-1} \) (295 K), thus, comparable to Li self-diffusivity in layer-structured transition metal sulfides and oxides serving as positive electrodes in lithium-ion batteries. The results obtained from the different NMR techniques employed are in good agreement with previous studies\(^7,8\) using \(^7\text{Li}\) NMR to probe diffusion parameters at elevated temperatures. Most importantly, the jump rates can be well approximated with a single Arrhenius law which is determined by an activation energy of approximately 0.55 eV and a pre-factor on the order of typical phonon frequencies, viz., \( 10^{14} \text{ s}^{-1} \). On that note the present study updates our knowledge on Li self-diffusion in LiC\(_6\). It is noteworthy that the activation energy probed by NMR is in fair agreement with calculated barrier heights \((\approx 0.5 \text{ eV})\) by Toyoura \textit{et al.}\(^{45}\) for both the in-plane vacancy and interstitial Li migration mechanism. Even the
chemical diffusion coefficients reported by Toyoura et al.\textsuperscript{45} (viz., $10^{-14} \text{m}^2 \text{s}^{-1}$ and $10^{-15} \text{m}^2 \text{s}^{-1}$) for the interstitial and vacancy mechanism, respectively) agree with the present findings.

Considering solely $^7$Li NMR rates, it is difficult to judge whether the diffusion process probed is strictly governed by 2D diffusion. The present results are in very good agreement with those probed by orientation-dependent and frequency-dependent SLR.\textsuperscript{14H. Estrade, J. Conard, P. Lauginie, P. Heitjans, F. Fujara, W. Buttl, G. Kiese, H. Ackermann, and D. Guérard, Physica B 99, 531 (1980).} The $\beta$-NMR results indeed gave strong evidence for low-dimensional lithium diffusion.\textsuperscript{7,8} Fair agreement is also found with results from QENS probing in-plane diffusion in the ordered phase of LiC$_6$.\textsuperscript{5} Recent theoretical investigations also strongly point to high lithium-ion diffusivity in the direction parallel to the graphene layers and to much slower interlayer hopping, that is, motion across the basal plane.\textsuperscript{47}

However, though there are convincing reasons to claim even microscopic Li diffusion as purely low-dimensional in LiC$_6$, the semiempirical SLR NMR model introduced by Richards for 2D motion seem to be less adequate to satisfactorily describe the temperature dependence of the $^7$Li NMR $R_{1\nu}(1/T)$ rate peak probed here. The applicability of a modified BPP-type relaxation model, see, e.g., the previous work by Küchler et al.,\textsuperscript{44} might indicate a small, but nonnegligible, influence of interlayer hopping process on the diffusion-induced SLR NMR rates.

To shed further light on the Li dynamics in LiC$_6$, the application of NMR techniques being able to directly record motional correlation functions might be beneficial. For instance, considering the temperature range below 300 K, this should be possible via the generation of Jeener-Broekaert NMR echoes\textsuperscript{49} with the so-called spin-alignment echo (SAE) technique.\textsuperscript{50-53} In general, SAE (or stimulated echo) NMR is sensitive to extremely slow translational and rotational jump processes.\textsuperscript{54-60}

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