Lithium Ion Dynamics in $\text{Li}_2\text{S}+\text{GeS}_2+\text{GeO}_2$ Glasses Studied Using ^7Li NMR Field-Cycling Relaxometry and Line-Shape Analysis

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A B S T R A C T

We use ^7Li NMR to study the ionic jump motion in ternary $0.5\text{Li}_2\text{S} + 0.5[(1-x)\text{GeS}_2 + x\text{GeO}_2]$ glassy lithium ion conductors. Exploring the “mixed glass former effect” in this system led to the assumption of a homogeneous and random variation of diffusion barriers in this system. We exploit that combining traditional line-shape analysis with novel field-cycling relaxometry, it is possible to measure the spectral density of the ionic jump motion in broad frequency and temperature ranges and, thus, to determine the distribution of activation energies. Two models are employed to parameterize the ^7Li NMR data, namely, the multi-exponential autocorrelation function model and the power-law waiting times model. Careful evaluation of both of these models indicates a broadly inhomogeneous energy landscape for both the single ($x = 0.0$) and the mixed ($x = 0.1$) network former glasses. The multi-exponential autocorrelation function model can be well described by a Gaussian distribution of activation barriers. Applicability of the methods used and their sensitivity to microscopic details of ionic motion are discussed.

1. Introduction

The ionic conductivity of lithium sulfide containing glasses can reach values as high as and even higher than $10^{-3} (\Omega \text{ cm})^{-1}$ at room temperature [1], which makes them attractive as electrolytes for new all solid state Li-ion batteries. Seeking to combine the high conductivity with improved chemical stability under application conditions, Kim et al. [2] have explored the ternary glass system $0.5\text{Li}_2\text{S} + 0.5[(1-x)\text{GeS}_2 + x\text{GeO}_2]$, with a variable GeO_2 fraction x . Mixing two types of network formers, herein GeS_2 and GeO_2 , has been known to have a positive effect on the ionic conductivity. Specifically, the addition of 10 mol % of GeO_2 was found to increase the conductivity by the factor of four compared to a pure sulfide glass, while for higher fractions of GeO_2 the Li-ion conductivity eventually decreases below the original value of the pure $0.5\text{Li}_2\text{S} + 0.5\text{GeS}_2$ glass [2]. A like dependence of the ionic conductivity on glass composition was observed in various other mixed oxy-sulfide ternary systems (see refs. in [3; 4; 5]). This increase of the conductivity above the base value at a certain fraction of mixing of the glass formers is referred to as the “mixed glass former effect”.

Understanding this effect is hindered by a diversity of factors contributing to the ionic conductivity in those systems. Kim et al. emphasized that in the case of the $\text{Li}_2\text{S}+\text{GeS}_2+\text{GeO}_2$ system, one could take advantage of a simple substitution of oxygen for sulfur and analyze the effect “on the basis of purely structural (mobility) changes” [2]. An accurate model was developed [2] that relates the increase of the conductivity in this system to a reduction of the mechanical strain energy required for Li^+ diffusion caused by the addition of the smaller oxygen anion. Further, Schuch et al. [4] developed an appropriate model, called “mixed barrier model”, which described the mixed glass former effect in terms of reduced energy barriers for the mobile ions conducting in a mixed-former environment (i.e., sites containing both network former units).

An ansatz in the mixed barrier model was to suppose a random variation of barrier heights. The concept of the activation barrier distribution has been long employed in NMR and dielectric/impedance spectroscopy of ion-conducting glasses to describe the non-exponential relaxation as well as unique temperature and frequency dependences of the relaxation rates. Svare et al. [6] analyzed nuclear spin-lattice relaxation (NSLR) in lithium sulfide glasses in terms of a Gaussian barrier distribution and used the NMR determined distribution of activation energies (DAE) to fully calculate the corresponding ionic conductivity in these same glasses. A similar Gaussian DAE but with a low-barrier tail was employed in [7] to derive information on the microscopic lithium ion dynamics as a function of glass composition.

A DAE is naturally related to dynamic heterogeneity, *i.e.* dynamically distinguishable sub-ensembles of ions, which can be probed, among other methods, by measuring time correlation

functions of fluctuating local fields. However, to ascertain whether the existence of dynamic heterogeneity is a real effect or merely a theoretical concept, it is insufficient to observe two-time correlation functions, which are accessible from the majority of experimental methods, but it is necessary to analyze higher-order correlation functions. Thus, NMR measurements of three- and four-time correlation functions indicated that dynamic heterogeneity is a key feature of the ionic hopping motion in various solid electrolytes [8; 9; 10; 11; 12; 13].

Essentially, the NSLR measurements of a DAE rely on the modeling of the correlation function, or equivalently, the spectral density function, $J(\omega)$, of fluctuations responsible for relaxation. One or more of the model's parameters are then considered temperature dependent and subject to fitting for variable-temperature data. In the above examples [6; 7], such a parameter was a correlation time, $\tau_c(T)$, defined in the framework of the Bloembergen-Purcell-Pound (BPP) model. A direct measurement of the frequency dependence of $J(\omega)$ is not as practical as the fixed frequency variable-temperature measurements for the technical difficulty of varying the frequency using standard NMR equipment where typically a different magnet is used for each frequency. Indeed, the extensive T_1 measurements for many lithium ion conducting glasses by Martin et al. were only performed at four frequencies spanning the modest frequency range of 4 MHz to 40 MHz. Recently, we demonstrated that ^7Li field-cycling (FC) approaches allow us to continuously vary the resonance frequency, providing direct access to the spectral density of ionic dynamics in a broad range of 10^5 - 10^9 s $^{-1}$ [14].

Measuring the spectral density as a function of frequency has certain advantage compared to the fixed frequency variable temperature measurements. The shape of $J(\omega)$ for ion conductors relies strongly on the mechanism for the ionic motion (see *e.g.* [15]). Given $J(\omega)$, one can therefore infer essential features of ionic dynamics directly from the experiment. For comparison, the NSLR times obtained from conventional measurements as a function of temperature, $T_1(T)$, depend on the temperature evolution of both the correlation time and the shape of the spectral density, which are difficult to disentangle.

To take this advantage, we use ^7Li FC NMR to measure $J(\omega)$ in the glass system $0.5\text{Li}_2\text{S} + 0.5[(1-x)\text{GeS}_2 + x\text{GeO}_2]$. These experiments are accompanied by regular high-field ^7Li NMR line-shape and spin-lattice relaxation measurements at variable temperature. To investigate the mixed glass former effect, we compare results for the mixed GeS_2 - GeO_2 glass with the highest conductivity of the series ($x = 0.1$) [16] with that for the pure GeS_2 glass ($x = 0.0$). Unlike dc conductivity, the ^7Li NMR data are dominated by local jumps of single lithium ions, thus providing, in principle, access to the energy landscape on length scales that are smaller than the expected percolation threshold of the dc ionic conductivity. In our analysis, we pay special attention to the general aspects of modeling the non-exponential ionic correlation functions, a common problem for

studies of ion transport in glasses, including conductivity, dielectric and mechanical approaches, and to the accompanying difficulties in relating the model's parameters to the energy landscape.

2. Effects of lithium ionic motion on ^7Li line-shape and spin-lattice relaxation results

The quadrupole coupling constant amounts to ca. 50 kHz in lithium compounds [17], which makes the quadrupole interaction dominant in a typical ^7Li NMR spectrum. It is indeed the case for the studied glasses whose static spectral pattern is mainly determined by the quadrupole interaction, giving rise to a characteristic central peak and a satellite contribution (see below). The effect of the magnetic dipole-dipole coupling is only to broaden those spectral components.

Similarly, ^7Li NSLR is dominated by the fluctuating quadrupolar interaction ω_Q of the nucleus with the electric field gradient (EFG) imposed by the surrounding charge density, while other factors, including the magnetic dipole-dipole coupling, are weak. We consider the case where the ω_Q fluctuation is introduced by the translational motion of a Li^+ ion as it relocates (conducts) between different electrical charge environments within the glass network. The effect of such discrete ionic jumps on the NSLR depends on the distribution of jump rates. When the rates are high such that many individual jumps occur during the Larmor period ω_0^{-1} , the NSLR can be related to a continuous diffusion [18]. On the other hand, when individual ion jumps modulate the local field at a frequency comparable with or lower than ω_0 , the NSLR is analyzed on the basis of hopping models [19]. In either continuous diffusion or hopping models, single-particle movements are considered to describe the observable ^7Li NSLR.

In ^7Li NSLR, the double exponential relaxation of the $I = 3/2$ is usually negligible [8]. Then, the quadrupolar ^7Li NSLR rate of an isotropic system is given by

$$R_1 = C[J_2(\omega_0) + 4J_2(2\omega_0)], \quad (1)$$

where $J_2(\omega_0)$ is the spectral density of the quadrupolar fluctuation evaluated at the Larmor frequency ω_0 . $J_2(\omega_0)$ is obtained from the Fourier transform of the autocorrelation function (ACF) $F_2(t)$ characterizing the ω_Q fluctuation in the time domain. The widely-used BPP model implies an exponentially decaying ACF and, hence, a Lorentzian spectral density,

$$J_2(\omega_0) = \frac{\tau_c}{1 + (\omega_0\tau_c)^2} \quad (2)$$

The single exponential ACF is, however, rarely observed in lithium ion conductors [12].

Eq. (1) represents an average relaxation rate, $R_1 = \langle 1/T_1 \rangle$, since its derivation involves ensemble averaging [20]. It determines the initial slope of a relaxation function, which in general is a multi-exponential function due to a distribution of a local dynamics. The particular case of mono-

exponential NSLR observed in our experiments suggests that the ion exchange between dynamically distinguishable environments is fast on the T_1 timescale. The dynamical heterogeneity that can be determined from the frequency and temperature dependence of R_1 is therefore related to ionic motion on time scales shorter than $1/R_1$.

The ω_Q fluctuation manifests itself also in motional narrowing of the ^7Li NMR spectrum. The temperature dependence of the spectral line shape relies on the same ionic dynamics as NSLR and, as such, corresponds to the same ACF. A change in the line shape is anticipated when the correlation time τ_c is comparable to the reciprocal of a static spectrum width, $\Delta\omega$. In the fast motion limit, $\Delta\omega\tau_c \ll 1$, the spectral width is reduced to an averaged value. While the spectrum narrows towards a Lorentzian line when essentially all possible values of ω_Q are experienced by the nucleus upon motion, the spectrum takes on an anisotropic form of a finite width otherwise [12]. In references [21; 22], the narrowing of a Gaussian rigid-limit spectrum has been calculated as a function of $\Delta\omega\tau_c$ for two particular forms of ACF, namely a Gaussian ACF and an exponential ACF. For a dynamically heterogeneous system possessing a sufficiently broad τ_c distribution, fast ($\Delta\omega\tau_c \ll 1$) and slow ($\Delta\omega\tau_c \gg 1$) ions coexist at suitable temperatures. Then, the former species produces a narrowed Lorentzian spectrum, while the latter usually causes a broad Gaussian spectrum. Thus, the line can be modeled as a weighted superposition of the dynamics of these two ion populations (phases), slow and fast (Fig. 1). This is even more the case since one expects a strong T_2 -attenuation for transition correlation times around the mobility threshold $\tau_c^{-1} \sim \Delta\omega$. The two-phase spectral model allows one to introduce the distribution of correlation times, $G(\tau_c)$, via a Gaussian's fraction W_{Gauss} as

$$W_{\text{Gauss}} = \int_{1/\Delta\omega}^{\infty} G(\tau_c) d\tau_c \quad (3)$$

or likewise, via a Lorentzian's fraction as shown in [9; 23].

3. Sample preparation

Vitreous GeS_2 was prepared by mixing and reacting stoichiometric amounts of germanium (Cerac, 99.999%) and sulfur (Cerac, 99.999%) in an evacuated silica tube. The silica tube was rotated at ~ 5 r.p.m. at an angle of $\sim 10^\circ$ in a tube furnace and heated at $1^\circ\text{C}/\text{min}$ to 900°C , held for ~ 8 h and then quenched in air.

Ternary $\text{Li}_2\text{S} + \text{GeS}_2 + \text{GeO}_2$ glasses were prepared by melting stoichiometric amounts of Li_2S (Cerac, 99.999%), GeS_2 , and GeO_2 (Cerac, 99.999%) starting materials. They were mixed and then placed in a covered vitreous carbon crucible and heated for 5 to 10 min between 900 and 1000°C inside a hermetically sealed tube furnace attached to the side of a nitrogen-filled glove box (< 0.1

ppm O₂ and < 0.5 ppm H₂O). The molten samples were poured onto a brass mold held at 30 to 50 °C below the glass transition temperature (~300 °C), allowed to anneal for 1 h, and then cooled to room temperature at a rate of 1 °C/min.

4. NMR Experiments

⁷Li FC measurements were carried out on a home-built FC relaxometer [24] with the magnetic field varied between 60 μT and 1.5 T, corresponding to the ⁷Li Larmor frequency range 100 kHz to 12 MHz. We should mention that measurements at lower fields are possible, but then the Zeeman interaction becomes comparable to or even smaller than the fluctuating quadrupolar coupling ($\omega_Q \sim 50$ kHz, see the ⁷Li line shape), thereby making the usual perturbation-theory treatment inapplicable for NSLR analysis. The sample's temperature was controlled between 200 and 450 K using either an air/nitrogen gas flow system or an oven integrated in the probe head.

⁷Li NMR spectra were recorded on two home-built spectrometers operating at 4.7 and 8.5 T ($\omega_0 = 2\pi \times 76$ MHz and $2\pi \times 140$ MHz, respectively), employing the pulse sequence $90_x^\circ - \Delta - 64_y^\circ - \Delta - acq$ with $\Delta = 20$ μs. NSLR rates were measured using the saturation-recovery method together with the above pulse sequence for signal detection. The temperature variation on the 4.7 T spectrometer was provided by a liquid nitrogen cryostat in the range 100 to 400 K, and on the 8.5 T spectrometer by an air blowing system within 250 to 400 K.

5. Results

5.1. Spin-lattice relaxation

The saturation-recovery curves recorded on the high-field spectrometers are well fit to a mono-exponential function over the entire temperature interval. The resulting NSLR rates are plotted for the studied 0.5Li₂S + 0.5[(1-x)GeS₂ + xGeO₂] glasses in Fig. 2. For both $x=0.0$ and $x=0.1$, the monotonic decrease of R_1 with $1/T$ indicates that the Li-ion dynamics are slow on the time scale of the inverse Larmor frequency at the studied temperatures, which corresponds to the low-temperature regime in the NSLR nomenclature. The temperature dependence of R_1 gradually vanishes with $1/T$, in noticeable contrast to the low-temperature asymptote of the BPP model, where the slope of $\log(R_1)$ versus $1/T$ is constant, as given by the activation energy E_a for the Arrhenius form of $\tau_c(T)$.

The relatively weak temperature dependence of R_1 at lower temperatures has been observed in a number of ionic conductors, including lithium sulfide doped glasses [25; 26; 27; 28]. Considering that the fluctuating electric fields responsible for the ⁷Li relaxation are produced by

ionic diffusion through the glass structure at high temperatures, the change in the temperature dependence of R_1 at lower temperatures suggests a crossover to another NSLR mechanism, which is possibly related to two-level systems [29] or (as yet unknown) impurities [30], e.g., paramagnetic impurities [31], although no such impurities were purposefully added to the studied glasses. In Section 6.1 we will also refer to these arguments when addressing a weak dependence of R_1 on frequency at low temperatures.

In the following, we exploit the capabilities of ^7Li FC NMR in the study of Li^+ ion dynamics as a function of frequency, temperature, and composition in the glass series, $0.5\text{Li}_2\text{S} + 0.5[(1-x)\text{GeS}_2 + x\text{GeO}_2]$. Figure 3 (a, b) shows the temperature dependence of R_1 obtained from FC measurements for small Larmor frequencies ω_0 over the temperature range of 200–450 K. Maxima in $R_1(T)$ are observed up to $\omega_0 = 2\pi \times 5$ MHz, while such maxima are not found at higher Larmor frequencies, including the above high-field NSLR measurements with cryomagnets, see Fig. 2. Knowing the temperature T_{max} of the R_1 maximum and employing the condition $\tau_c(T_{\text{max}}) = 0.616 \omega_0^{-1}$ from the BPP model of NSLR, temperature-dependent correlation times can be determined. In Fig. 3 (c), we see that the correlation times for the $x = 0.1$ glass are higher than that for the $x = 0$ glass, but an Arrhenius law with an activation energy of $E_a = 0.44$ eV well describes the data for both glasses. We note that, for this analysis of the maximum positions, T_{max} , use of the BPP model is not critical as other shapes of the spectral density do not yield different activation energies, but only slightly shifted values of the correlation times, as long as there are no serious changes of the shape with temperature. The present activation energy is somewhat larger, but still comparable to $E_a = 0.37$ eV from dc conductivity measurements by Kim et al. [2]. In principle, the E_a values derived from NSLR and ionic conductivity can differ (for a relevant discussion, see [32; 33]).

The frequency-dependence of the NSLR is shown in Fig. 4. The data are presented in the form of an “NMR susceptibility”, χ''_{NMR} , defined as $\chi''_{\text{NMR}} = \omega_0 R_1$, for an easier comparison with electrical measurements [34]. The shape of $\chi''_{\text{NMR}}(\omega_0)$ deviates substantially from that expected in the BPP case with a single-exponential correlation function, see Eq. (2). In particular, the characteristic $\omega_0^{\pm 1}$ slopes are not observed on the low- and high-frequency sides of $\chi''_{\text{NMR}}(\omega_0)$, respectively. Over the accessible frequency range, the respective slopes are considerably less steep, indicating a broad susceptibility peak that shifts through the experimental time window. Specifically, the high-frequency and low-frequency flanks of the peak are probed at the higher and lower temperatures of the studied range, respectively. Below, we treat the broadening of $\chi''_{\text{NMR}}(\omega_0)$ compared to the BPP model in terms of a distribution of correlation times arising from a DAE.

In Fig. 4 (c) we see that χ''_{NMR} is quite similar for the two glasses, $x = 0.0$ and $x = 0.1$. A

difference between the two is apparent only at 450 K, where χ''_{NMR} in the $x = 0.1$ glass is $\sim 10\%$ higher than for the $x = 0.0$ glass, the character of the frequency dependence being retained. These findings indicate that local dynamics of an average lithium ion is comparable in both glasses.

5.2. Line-shape analysis

Figure 5 shows variable-temperature ^7Li NMR spectra of the samples with $x = 0$ and $x = 0.1$. As a consequence of the fact that, in first order, one of the allowed NMR transitions of the $I=3/2$ nucleus is not affected by the quadrupolar interaction, whereas the others are [12], the spectra exhibit a narrow central transition (CT) line and a broad satellite transition (ST) component, which are better seen in the inserts to the figure. The ST component shows no structure, indicating a random variation of the EFG parameters at the many lithium ionic positions. The low-temperature spectra of the two glass samples are identical, demonstrating that the samples are indistinguishable in this aspect. In both samples, the spectra retain a rigid-limit line width up to 200 K, followed by a motional narrowing, which continues over the rest of the studied temperature range up to 400 K.

We consider that the gradual narrowing of the spectra is a manifestation of a correlation time distribution, $G(\tau_c)$, as suggested by the broad susceptibility peaks $\chi''_{\text{NMR}}(\omega_0)$. We therefore utilize the two-phase spectrum model (Section 2) to describe the ^7Li spectra as a sum

$$S(\omega, T) = S_{CT}(\omega)W_{\text{Gauss}, CT}(T) + S_{ST}(\omega)W_{\text{Gauss}, ST}(T) + S_L(\omega)(1 - W_{\text{Gauss}, CT}(T) - W_{\text{Gauss}, ST}(T)) \quad (4)$$

Here S_{CT} and S_{ST} are the CT and ST components represented by Gaussian lines of temperature-independent widths $\Delta\omega_{CT}$ and $\Delta\omega_{ST}$ as determined from low-temperature spectra; $W_{\text{Gauss}, CT}$ and $W_{\text{Gauss}, ST}$ are their weights; and S_L is a motionally narrowed Lorentzian component. To reduce the number of free fit parameters, we use one rather than two Lorentzian lines corresponding to the CT and ST components, respectively. Figure 6 illustrates the spectral decomposition, where we use a logarithmic amplitude scale to demonstrate the good quality of the resulting fits. The so-obtained fractions, $W_{\text{Gauss}, CT}$ and $W_{\text{Gauss}, ST}$, are plotted in Fig. 7. We see that $W_{\text{Gauss}, CT}$ vanishes at lower temperatures than $W_{\text{Gauss}, ST}$ (300 K vs. 400–450 K), in accord with different mobility thresholds for the CT and ST contributions ($\Delta\omega_{CT} \ll \Delta\omega_{ST}$). In the next section, we will analyze $W_{\text{Gauss}, ST}$ in terms of a distribution $G(\tau_c)$, according to Eq. (3).

6. Data analysis

6.1. The multi-exponential ACF model

The broadening of $\chi''_{\text{NMR}}(\omega_0)$ compared to the case of a single-exponential ACF can always

be reproduced by summation of individual Lorentzian spectra, provided that an appropriate τ_c distribution is used [35]. A key issue is whether such a distribution arises from a heterogeneous dynamics, e.g., when different values τ_c can be ascribed to sub-ensembles of sites explored by a tagged ion, or it is merely a multi-exponential representation of an intrinsically non-exponential dynamic process in a homogeneous medium. Again, since the observed NSLR is described by a single T_1 time constant, a relevant heterogeneity must not exceed the length scale covered by the ion on the time scale of $\sim T_1$, but be distinguishable on the time scale of τ_c .

The applicability of the τ_c distribution model depends, therefore, on whether the random process $\omega_Q(t)$ can be described by a multi-exponential ACF. The existence of such dynamical heterogeneity is supported by the observation of distributions of mean waiting times in molecular dynamics simulations [36; 37; 38]. A similar approach, namely, superposing uncorrelated relaxation components, has been used in dielectric spectroscopy to describe a non-Debye dielectric relaxation. This certainly also motivates one to consider the multi-Lorentzian form for $J_2(\omega_0)$, especially in the context of comparison of NMR data with measurements of the electric susceptibility [39].

Thus, assuming a superposition of Lorentzian functions for the spectral density of the fluctuating quadrupolar interaction, we write instead of Eq. (2):

$$J_2(\omega_0) = \int_0^\infty \tau_c (1 + \omega_0^2 \tau_c^2)^{-1} G(\tau_c) d\tau_c, \quad (5)$$

where $G(\tau_c)$ is a τ_c distribution. Assuming thermally activated ion hops, $G(\tau_c)$ is specified via the DAE, $g(E_a)$, according to the Arrhenius relation:

$$\tau_c = \tau_0 e^{E_a/k_B T} \quad (6)$$

Following [7], we assume a Gaussian distribution for E_a :

$$g(E_a) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(E_a - \langle E_a \rangle)^2}{2\sigma^2}} \quad (7)$$

Substituting Eqs. (6) and (7) into Eq. (5) gives a model function to fit for the FC data $R_1(\omega_0, T)$. As $J_2(\omega_0) \approx J_2(2\omega_0)$ for broad distributions $G(\tau_c)$, we replace the two spectral densities in Eq. (1) by Eq. (5) as the only function of ω_0 .

We employ a trust-region Levenberg-Marquardt-type algorithm for simultaneous fitting in frequency and temperature domains. The mean activation energy $\langle E_a \rangle$ and the variance σ^2 in Eq. (7) as well as the constant C in Eq. (1) serve as free parameters, while τ_0 is fixed at $2.7 \times 10^{-12} \sqrt{E_a/k_B}$ s as suggested in [7]. For both the single and the mixed network former glasses, a good fit is obtained with *single* sets of parameters within the temperature range 300 to 450 K and the

frequency range 100 kHz to 12 MHz, see Fig. 4 (a,b). Thus, a Gaussian distribution of activation energies well describes the NMR susceptibility of the lithium ionic jump motion in the studied $0.5\text{Li}_2\text{S} + 0.5[(1-x)\text{GeS}_2 + x\text{GeO}_2]$ glasses in broad ranges of frequency and temperature, implying a substantial broadening of the corresponding distribution $G(\tau_c)$ upon cooling.

The respective best-fit parameters are given in Table 1. The $\langle E_a \rangle$ values are comparable to the activation energies obtained from the R_1 maxima of the variable-temperature FC measurements, see Fig. 3 (c). The variance σ of the DAE is high, indicating a broad inhomogeneity of the energy landscape and, thus, a pronounced heterogeneity of the ionic jump dynamics. Further, the constant C is expected to be of the same order of magnitude as the second moment $\langle \Delta\omega_Q \rangle^2$ of the ^7Li NMR spectral components involved in the stochastic process of site exchange, that is, of the order of 10^{11} - 10^{12} (rad/s)² (see Figs. 5 and 6). While the fit results in Table 1 are considerably smaller than that expectation, they are consistent with C values reported in the literature [7; 27; 40].

Fitting Eq. (5) to the relaxation data below 300 K results in progressively lower values of C and $\langle E_a \rangle$. As outlined in Section 5.1, we explain this disagreement by the argument that the lithium ionic diffusion ceases to govern ^7Li NSLR at sufficiently low temperatures. It is worth noting that the present Gaussian DAE model with the Arrhenius form of $\tau_c(T)$ is able to reproduce the concavity of the low-temperature flank of $\log(R_1)$ versus $1/T$, but it does not fit for the data (see the red lines in Fig. 2). Re-fitting the model specifically for the variable-temperature measurements yields unreasonably high C and σ values, and the fit for the low-temperature data points is still very poor (see the black lines in Fig. 2). These findings are not surprising when accepting a change in the ^7Li NSLR mechanism upon cooling.

Finally, we employ the Gaussian DAE parameters from Table 1 to compute the rigid-limit fraction $W_{\text{Gauss}, ST}$ of the ST spectral component from Eq. (3) without a free parameter. As shown by the solid lines in Fig. 7, the parameters from the spin-lattice relaxation analysis reproduce the width of the Gaussian-to-Lorentzian line shape transition and, with some underestimation, its median temperature for both glass compositions. The latter deviation may arise from a finite width of this transition, which is not accounted for in the present analysis. Thus, both ^7Li NMR techniques yield consistent results for the lithium ionic jump motion. We do not analyze the motional narrowing of the CT component, because its width does not reflect the strength and fluctuation of the quadrupolar interaction, but of the dipolar interaction so that multi-particle correlation functions become relevant.

The multi-exponential ACF model does not specify what sub-ensembles of sites explored by the hopping lithium ion correspond to particular τ_c values in the τ_c distribution. The i -th structural element of dynamic heterogeneity that is represented by $\tau_{c,i}$ may extend over length scales covered by an ion in a time somewhere between a typical mean waiting time and the time scale set by the

inverse spectral width, $1/\Delta\omega \approx 3 \mu\text{s}$. As a consequence of such uncertainty in the heterogeneity length scale, it is difficult to discuss the associated barrier distribution in terms of the glass network structure.

6.2. The power-law waiting times model

Although a Gaussian barrier distribution well describes our spin-lattice relaxation and line-shape data, the above analysis does not exclude other origins of the non-exponential correlation functions of the lithium ionic hopping motion. Therefore, we also consider a power-law waiting time model, which leads to a spectral density of the Cole-Cole type. It comes from the theory of a random walk in a random potential energy landscape and considers a random variation of barrier heights on the length scale of individual ion positions in the glass network [41; 42]. The Cole-Cole spectral density is given by [43]:

$$J_{CC}(\omega) = \frac{4\omega^{\alpha-1}\tau_{CC}^{\alpha}\sin(\alpha\pi/2)}{4 + 4(\omega\tau_{CC})^{\alpha}\cos(\alpha\pi/2) + (\omega\tau_{CC})^{2\alpha}} \quad (8)$$

We note that the spectral density $J_{CC}(\omega)$ in Eq. (8) is characterized by a single time parameter τ_{CC} , in contrast to the multi-exponential ACF model. A non-exponentiality of the dynamical process is introduced and controlled via the width parameter α .

Figure 8 (a) shows results of fitting of J_{CC} to NSLR data above 300 K in the $x = 0$ glass. The fit well interpolates the NMR susceptibility and yields a linear dependence of $\log \tau_{CC}$ on $1/T$ with an activation energy of 0.30 eV, see Fig. 8 (b). This value is somewhat smaller, but still comparable to that from the dc conductivity (0.39 eV) [2]. The width parameter α does not show a clear temperature dependence and has an average value of 0.51. Similar results are obtained for the $x = 0.1$ composition (not shown). Hence, a Cole-Cole spectral density associated with a power-law waiting time model is also well suited to describe the present ^7Li FC data for $0.5\text{Li}_2\text{S} + 0.5[(1-x)\text{GeS}_2 + x\text{GeO}_2]$ glasses.

6.3. Samples comparison

The present measurements show no considerable difference between the $x = 0.0$ and $x = 0.1$ glasses, neither in their NSLR behavior (Fig. 4) nor in their line narrowing (Fig. 7). The respective best-fit parameters of the Gaussian barrier model (Table 1) are too close to be correlated with the difference in the glass composition. Differences between the datasets of the two glasses appear only in the height of the $R_1(\omega)$ maximum at sufficiently high temperatures and in the position of the $R_1(T)$ maximum at sufficiently low frequencies. The latter analysis yields shorter correlation times

for $x = 0.0$ than for $x = 0.1$, see Fig. 3 (c), which is unexpected based on the results from the conductivity measurements by Kim et al. [2]. Specifically, the lithium ionic conductivity of the $x = 0.1$ glass was found to be approximately 4 times higher than that of the $x = 0.0$ glass. The respective activation energies were reported to be 0.37 eV and 0.39 eV, with the 0.02 eV difference exceeding the experimental error.

The finding that the present analyses and a conductivity study [16] lead to different conclusions about the dependence of the lithium ionic dynamics on the glass composition can be interpreted as follows. We accept that ^7Li NMR probes site exchange of individual lithium ions at room temperature and above. We also assume that the addition of GeO_2 only lowers local barriers for ionic jumps without changing the very character of the ionic relocation. Then, according to the mixed barrier model [4], only one of ten random hops of a lithium ion, on average, occurs over a lowered barrier in a mixed environment or, equivalently, only one out of ten lithium ions exhibits an enhanced jump rate at a given time. Thus, there are mild effects on the anyway broad distribution $G(\tau_c)$, which is probed in ^7Li NMR, while the presence of few sites with a lowered barrier may provide for a new percolation path with substantially lower energy for the dc ionic conductivity, as discussed in more detail in previous studies [7,16].

7. Discussion and Conclusion

The ^7Li FC NMR measurements show, in the most direct manner, that NSLR in the studied $0.5\text{Li}_2\text{S} + 0.5[(1-x)\text{GeS}_2 + x\text{GeO}_2]$ glasses is not consistent with the BPP model for exponential correlation functions of ionic dynamics. We take this fact as a signature of a random activation barrier variation over the glass structure. Therefore, the relaxation rate dispersion $R_1(\omega_0)$ provides access to the barrier distribution. We parameterized $R_1(\omega_0)$ using a weighted superposition of Lorentzian spectral densities of uncorrelated exponential processes. We refer to it as the multi-exponential ACF model with local τ_c values. This model allows for a one-to-one relation between a particular correlation time, $\tau_{c,i}$, in the ACF and the activation barrier's height, $E_{a,i}$, according to the Arrhenius equation. We found that the experimental $R_1(\omega_0)$ over wide frequency and temperature ranges are well described by a Gaussian distribution of E_a with a single set of the mean value $\langle E_a \rangle$ and the standard deviation σ (Table 1). ^7Li NSLR ceases to be governed by thermally activated hopping of lithium ions below 300 K, limiting the operating range of ^7Li FC NMR approaches to ion conduction in the studied glasses.

Likewise, ^7Li NMR line-shape analysis revealed a strong non-exponentiality of the ionic relaxation. Specifically, the ^7Li NMR spectra are a superposition of motional-narrowed and rigid-lattice line shapes over wide temperature ranges, indicating a coexistence of fast and slow lithium

ions on the time scale of the experiment. Such coexistence is expected when a disordered energy landscape results in a very broad distribution of correlation times $G(\tau_c)$ so that fast and slow ions from this distribution exhibit $\tau_c \ll 1/\Delta\omega$ and $\tau_c \gg 1/\Delta\omega$, respectively. A variation of temperature results in a shift of $G(\tau_c)$ so that the fractions of fast and slow ions and, consequently, the relative intensities of the motional-narrowed and rigid-lattice line shapes vary continuously. Calculating the temperature dependence of the relative intensity based on the barrier distribution determined from ^7Li FC NMR, we obtained good agreement with the experimental line-shape results, with some expected deviations due to negligence of effects from ions with $\tau_c \approx 1/\Delta\omega$. Hence, a Gaussian distribution of activation energies consistently describes the ^7Li spin-relaxation and line-shape results. In harmony with this finding, NMR multi-time correlation functions indicated that the non-exponentiality of the ionic hopping motion is in large part due to strong dynamic heterogeneity for various solid electrolytes [8; 9; 10; 11; 12; 13].

For the studied glass compositions, $x = 0.0$ and $x = 0.1$, the obtained Gaussian distribution of activation energies is characterized by a mean value $\langle E_a \rangle = 0.48\text{-}0.49$ eV and a standard deviation $\sigma = 0.09\text{-}0.10$ eV. Due to the nearly identical results for both glasses, we cannot draw conclusions about the effect of the GeO_2 addition on the barrier distribution on microscopic length scales. The observed value of $\langle E_a \rangle$ is somewhat larger than the activation energies of 0.39 eV and 0.37 eV reported in a conductivity study for the glass compositions $x = 0.0$ and $x = 0.1$, respectively [2]. Most probably, this difference can be attributed to the fact that faster ions from a distribution and, thus, lower barriers govern the ionic conductivity, as was discussed in more detail in previous work [7]. The large value of the standard deviation σ indicates that the energy landscape exhibits substantial disorder on the microscopic length scale, resulting in a strong heterogeneity of ionic dynamics. For example, the obtained Gaussian distribution of activation energies translates into a log-Gaussian distribution of correlation times with a full width at half maximum of about 6 orders of magnitude near 300 K. As a consequence of such pronounced diversity of the dynamics, a moderate speedup of some fraction of ions due to reduced energy barriers in a mixed-former environment can remain unobserved in ^7Li NMR, as the method receives equal contributions from all ions of the distribution, while such excess of short correlation times can explain the reported enhancement of the ionic conductivity by a factor of 4 in the mixed oxy-sulfide glass [2].

Although a Gaussian barrier distribution well describes the present ^7Li NMR results, other origins of the strongly non-exponential lithium ionic relaxation cannot be excluded. Therefore, we also considered a power-law waiting times model, which leads to a Cole-Cole spectral density of fluctuations associated with the ionic hopping motion. We found that this model also well describes the susceptibilities χ''_{NMR} of the studied glasses. Thus, it is not possible to discriminate between log-

Gaussian and Cole-Cole shapes of χ''_{NMR} based on the present data. Still, the ^7Li FC NMR experiments clearly show that the susceptibility peaks of the lithium ionic hopping motion are to a great extent symmetric on a logarithmic frequency axis, ruling out models of ionic transport that produce highly asymmetric shapes, e.g., a Cole-Davidson shape. Hence, the novel ^7Li FC NMR technique provides valuable information about lithium ion dynamics in solid electrolytes through direct measurements of the spectral density of the dynamical process.

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Table 1

Best-fit parameters of the multi-exponential ACF model with a Gaussian DAE. The NMR constant C is introduced in Eq. (1), while the mean $\langle E_a \rangle$ and the variance σ^2 are defined in Eq. (7).

Sample	$C, (\text{rad/s})^2$	$\langle E_a \rangle, \text{eV}$	σ, eV
$x = 0.0$	6.7×10^9	0.49	0.10
$x = 0.1$	7.6×10^9	0.48	0.09

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Figure captions

Fig. 1. Illustration of the two-phase spectrum model by the example of a log-Gaussian distribution of correlation times. At the low temperature T_{low} , most correlation times are longer than the mobility threshold of spectral narrowing, $1/\Delta\omega$, where $\Delta\omega$ is a static spectrum width. The spectrum is dominated by a rigid-lattice (Gaussian) component, its fraction being measured by the blue and red areas in the figure. At the high temperature T_{high} , the distribution shifts towards shorter correlation times such that only a small fraction of the Gaussian components is retained (the red area) while the majority of spins contribute now to a motional-narrowed (Lorentzian) component.

Fig. 2. ^7Li nuclear spin-lattice relaxation rate R_1 as a function of inverse temperature for the glasses with $x = 0.0$ (a) and $x = 0.1$ (b), measured at $B_0 = 4.7$ T (filled symbols) and 8.5 T (open symbols). The solid lines represent fits based on the multi-exponential ACF model with a Gaussian distribution of activation barriers. The black lines show the fit of the model for the variable-temperature data points above 300 K, while the red lines are those based on the model's parameters obtained from the frequency-dependent FC NMR measurements.

Fig. 3. (a, b): The temperature dependence of R_1 for the glasses with $x = 0.0$ (a) and $x = 0.1$ (b) in the FC measurements. The solid lines are guides to eye to track maxima of $R_1(T)$. The maxima are observable up to $\omega_0 = 2\pi \times 5$ MHz. (c): Correlation time τ_c of the BPP model versus the inverse temperature as estimated from the relationship $\tau_c(T_{\text{max}}) = 0.616 \omega_0^{-1}$, where T_{max} is the temperature at which R_1 maxima are observed. The straight lines are Arrhenius laws with $E_a = 0.44$ eV.

Fig. 4. (a, b): The NMR susceptibility $\chi''_{\text{NMR}}(\omega_0) = \omega_0 R_1(\omega_0)$ for the $x = 0.0$ (a) and $x = 0.1$ (b) glasses at various temperatures. The solid lines are the best fit of a multi-exponential ACF model with a Gaussian distribution of activation barriers. The dashed line shows the high-frequency asymptote for the BPP model with an exponential correlation function. (c): Comparison of χ''_{NMR} for the $x = 0.0$ and $x = 0.1$ glasses at three temperatures.

Fig. 5. Variable-temperature ^7Li NMR solid-echo spectra of the $x = 0.0$ (a) and $x = 0.1$ (b) glasses.

Fig. 6. Typical examples of the ^7Li NMR spectrum decomposition into a 3.7 kHz wide Gaussian, a 57.2 kHz wide Gaussian, and a Lorentzian of variable width for the $x = 0.0$ glass.

Fig. 7. Contribution of the Gaussian to the central ($W_{\text{Gauss, CT}}$) and satellite ($W_{\text{Gauss, ST}}$) transition lines of the ^7Li NMR spectra according to the spectral decomposition in Eq. (4), for the $x = 0.0$ (a) and $x=0.1$ (b) glasses. The solid lines are computed from Eq. (7) assuming the Gaussian distribution of activation barriers with the parameters obtained from FC relaxometry (Table 1).

Fig. 8. (a): An example of the Cole-Cole fit to FC data for the $x = 0.0$ glass. (b): The temperature dependence of the Cole-Cole correlation time τ_{CC} together with an Arrhenius law with an activation energy of $E_a = 0.30$ eV.