Tracking Ions the Direct Way: Long-Range Li$^+$ Dynamics in the Thio-LISICON Family Li$_4$MCh$_4$ (M = Sn, Ge; Ch = S, Se) as Probed by $^7$Li NMR relaxation and $^7$Li Spin-Alignment Echo NMR

Katharina Hogrefe,$^a$ Nicolò Minafra,$^b$ Wolfgang G. Zeier,$^b$ and H. Martin R. Wilkening$^a$*

$^a$Institute of Chemistry and Technology of Materials, Graz University of Technology (NAWI Graz), Stremayrgasse 9, A-8010 Graz, Austria.

$^b$Institute of Inorganic and Analytical Chemistry, University of Münster, Correnstrasse 30, D-48149 Münster, Germany.

*wilkening@tugraz.at (corresponding author)

Further information on data analysis, $^6$Li MAS NMR and $^7$Li NMR spectra as well as on $S$,$^7$Li SAE NMR correlation functions.

$^7$Li NMR line widths analysis. We applied two different approaches to analyze the motionally narrowing curve to derive activation energies for the Li hopping process. Hendrickson and Bray introduced a phenomenological expression for the temperature dependence of the line width for materials with a distribution of relaxation times.$^1$

$$
\Delta \nu(T) = \Delta \nu_0 \left[1 + \left( - \frac{E_{\text{a, HB}}}{k_B T} \right) \exp\left( \frac{E_{\text{a, HB}}}{k_B T} \right) \right]^{-1} + \nu_\infty
$$

$\Delta \nu(T)$ is the temperature dependent line width, $\Delta \nu_0$ is the temperature-independent line width at very low temperatures, $\nu_\infty$ accounts for the small contribution by temperature-independent broadening effects, $k_B$ is the Boltzmann constant in eV/K, $T$ the temperature and $E_{\text{a, HB}}$ the respective activation energy. The constant $B$ describes to which extent the averaging by ionic motion of locally varying magnetic fields can be correlated to the range of ionic motion. Accordingly, $B$ is also an indicator for the number of thermally activated ions.$^1$

Another relation between the line width evolution with temperature actually origins from BPP$^2$ and was reformulated to the well-known and used expression by Gutowsky et al.$^3$ Abragam formulates the equation as follows.$^4$

$$
\Delta \nu^2(T) = \Delta \nu_0^2 + \frac{2}{\pi} \arctan \left[ a \Delta \nu(T) r_\infty \exp \left[ - \frac{E_{\text{a, A}}}{k_B T} \right] \right]^{-1} + \Delta \nu_\infty^2
$$

This equation resembles the expression by Hendrickson and Bray in many variables. $\Delta \nu_0^2$ is the second moment of the final rigid lattice line width, the factor $a$ is a fitting coefficient and $\tau_0$ the pre-factor in the Arrhenius relation of the temperature-dependent correlation time.

SAE NMR. Figure S1 shows $^7$Li NMR lines of the four compounds investigated; the bottom of the spectra is magnified to illustrate the evolution of the quadrupole powder patterns with increasing temperature.
Figure S1. Magnification of the $^7$Li NMR spectra of Li$_4$SnS$_4$, Li$_4$GeS$_4$, Li$_4$GeSe$_4$ and Li$_4$SnSe$_4$ measured at (a) 253 K, (b) 313 K, (c) 353 K and (d) 433 K to illustrate the quadrupole satellites resulting from the interaction of the $^7$Li quadrupole moment with non-vanishing electric field gradients at the nuclear site. Arrows point to singularities from which the quadrupole coupling constants were estimated assuming axially symmetric, motionally averaged electric field gradients.

$^6$Li MAS NMR. We fitted the $^6$Li MAS NMR signal of Li$_4$SnS$_4$ by two Gaussian functions to derive the area ratio of the two contributions to the spectrum. The corresponding fit is shown in Figure S2. We derived an area ratio of 17.3 : 82.7 for the small signal compared to the larger one. Kaib et al. observed an area ratio of 27 : 73 and assigned the smaller signal to the octahedral Li-sites in Li$_4$SnS$_4$. Recently published data from neutron diffraction shows that 31% of the Li-ions occupy octahedral-sites. Correlating this to our results, the area fraction of the smaller signal in MAS NMR is too small to account for all these octahedral sites. Considering, however, only the Li$_4$ octahedral site with 11.5% to 12.5% of the total Li-content, a far better agreement is found. Another fact that is in favour of this argument is the sole appearance of the small $^6$Li MAS NMR signal in the spectrum of Li$_4$SnS$_4$. For the other compounds we observed no such signal in MAS NMR even though all four structures include octahedral sites. The unique feature in Li$_4$SnS$_4$ is the Li$_4$ position, which might give a hint for the explanation of the two contributions to the $^6$Li MAS NMR spectrum.

Figure S2. Gaussian fit of the $^6$Li MAS NMR signal of Li$_4$SnS$_4$. Solid lines represent experimental data and the overall fit result. Dashed and dotted lines illustrate the separate peak and background contributions, respectively. The residual error line is shown in the lower part of the graph. The area ratio of the two signals is 17.3 : 82.7 in respect of a 100 % total peak area.
In Figure S3a and Figure S3b the different origins leading to the damping of the $^7$Li SAE NMR two-time correlation functions $S_2$ of Li$_4$SnS$_4$ are shown. In Figure S3a we see the evolution of $S_2$ with temperature, in Figure S3b the influence of varying $t_p$ is illustrated for two different evolution times. Note that for different temperatures the decay rate $1/\tau_{SAE}$ changes whereas the final amplitudes $S_\infty$ remain rather constant. In contrast, with increasing $t_p$ the amplitude $S_\infty$ decreases while the decay rate $1/\tau_{SAE}$ is largely unaffected by $t_p$ if varied from 15 µs to 30 µs. The same $1/\tau_{SAE}$ rates are also obtained for longer $t_p$ reaching 100 µs.

In Figure S3c we present the decay of the echo amplitude $S_2$ recorded at 253 K and compare it with the magnetization transient obtained from an independent $T_1$ experiment carried out at the same temperature. For $S_2$ the two decay steps are characterized by the time constants $\tau_{SAE}$ directly probing slow Li$^+$ jumps, and $T_{1,SAE}$, which is influenced by quadrupole longitudinal relaxation. With regard to the scaling on the x-axis we see that $T_{1,SAE}$ proceeds on the same time scale as $T_1$.

**Figure S3.** (a) $^7$Li SAE NMR two-time correlation functions $S_2(t_p = 15 \mu s, t_m)$ for Li$_4$SnS$_4$ measured at 116 MHz and temperatures ranging from 213 K to 293 K. The values show the stretching factors $\gamma$ of the exponential decays (solid lines). (b) Two-time correlation functions $S_2$ for Li$_4$SnS$_4$ with variable preparation time $t_p=15 \mu s$ and 30 µs measured at ambient temperature. (c) Echo amplitude of the $S_2$ decay curve recorded 116 MHz and 253 K in comparison with the normalized recovery of the longitudinal magnetization with increasing delay time. Solid lines represent exponential fit functions; the dashed lines in (c) illustrate the two contributions to the $S_2$ decay curve.

**References**

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