^{7}Li Ion Diffusion in Isotope-diluted Glassy $Li_2Si_3O_7$ – The Generation of pure Spin-3/2 Spin-alignment NMR Echoes

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Solid-state diffusion plays one of the most important roles in materials science. In particular, the precise measurement of ion dynamics in materials with structural disorder is of great interest. Spin-alignment echo (SAE) nuclear magnetic resonance (NMR), being comparable to exchange spectroscopy, turned out to be a powerful method to probe (ultra-)slow Li dynamics even in amorphous materials [1–3]. However, ^{7}Li Jeener-Broekaert echoes can be influenced by the simultaneous generation of dipolar with quadrupolar order. In many cases, the first can be suppressed by choosing proper evolution times t_p of less than 20 µs [4, 5].

Here, glassy $Li_2Si_3O_7$ served as a suitable model system to study the positive influence of isotope dilution on ^{7}Li SAE NMR, *i.e.*, the reduction of homonuclear dipole-dipole interactions through spatial separation of the spin-3/2 probe nuclei. Two samples, one with 100% ^{7}Li and the other one with 5% ^{7}7Li (95% ^{6}Li), were investigated by ^{7}Li NMR line-shape analysis, spin-lattice relaxation NMR as well as mixing-time and preparation-time dependent ^{7}Li SAE NMR using a 32-fold phase cycle. Jeener-Broekaert echoes and their Fourier transforms show that at suffciently short t_p the interfering dipolar interactions can be completely suppressed in that sample for which the proportion of ^{7}Li was greatly reduced by substitution with ^{6}Li. The so-obtained diffusion parameters are compared with results deduced from broadband conductivity spectroscopy.

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[1] Studying Li Dynamics in a Gas-Phase Synthesized Amorphous Oxide by NMR and Impedance Spectroscopy, V. Epp, C. Brüning, M. Binnewies, P. Heitjans, M. Wilkening, Z. Phys. Chem. 226 (2012) 513.

[2] Atomic-scale Measurement of Ultraslow Li Motions in Glassy $LiAlSi_2O_6$ by two-time ^{6}Li Spin-alignment Echo NMR Correlation Spectroscopy, M. Wilkening, A. Kuhn, P. Heitjans, Phys. Rev. B 78 (2008) 054303.

[3] From Micro to Macro: Access to Long-Range Li^+ Diffusion Parameters in Solids via Microscopic ^{6,7}Li Spin-Alignment Echo NMR Spectroscopy, M. Wilkening, P. Heitjans, Chem. Phys. Chem. 13 (2012) 53.

[4] Alignment Echo of Spin-3/2 ^{9}Be Nuclei: Detection of Ultraslow Motion, X.-P. Tang and Y. Wu, J. Magn. Res. 133 (1998) 155.

[5] Ion Dynamics in Solid Electrolytes: NMR Reveals the Elementary Steps of Li^+ Hopping in the Garnet $Li_{6.5}La_3Zr_{1.75}Mo_{0.25}O_{12}$, P. Bottke, D. Rettenwander, W. Schmidt, G. Amthauer, M. Wilkening, Chem. Mater. 27 (2015) 6571.