Investigation of the Li-ion conduction behavior in the $Li_{10}GeP_2S_{12}$ solid electrolyte by two-dimensional T1–spin alignment echo correlation NMR

M.C. Paulus[1,2], M.F. Graf[1,2], P.P.R.M.L. Harks[3], A. Paulus[1], P.P.M. Schleker[1,4], P.H.L. Notten[1,3], R.-A. Eichel[1,5], J. Granwehr[1,2]

[1]Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung (IEK-9), D-52425 Jülich, Germany

[2]RWTH Aachen University, Institut für Technische und Makromolekulare Chemie (ITMC), D-52074 Aachen, Germany

[3]Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands

[4]Max-Planck-Institute for Chemical Energy Conversions, Mülheim an der Ruhr, Germany

[5]RWTH Aachen University, Institut für Physikalische Chemie (IPC), D-52074 Aachen, Germany

Motivation

- All-solid-state batteries promise higher cycle life and safety
- Problem: Relatively slow Li ion migration
- $Li_{10}GeP_2S_{12}$ fastest known **solid electrolyte** material
- Little information about different Li migration mechanisms and structural features in the real powder sample

➡ Investigate slow, rate-limiting transport mechanisms by a combination of spin-lattice relaxation and spin alignment echo correlation[2,3]

$Li_{10}GeP_2S_{12}$

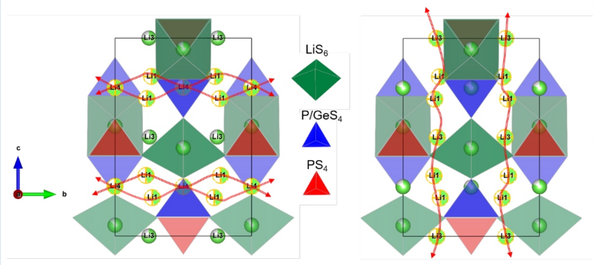


Figure 1: Structure of LGPS and coordination polyhedron GeS4, PS4 and LiS6. Red arrows illustrate the Lithium pathways in the ab plane (left structure) and in the channels along the c direction (right structure).

- Space group: $P4_2/nmc$
- Ion conductivity of up to 12 mS/cm at 27 °C[4]
- Fast migration through channels along *c*
- Interchannel migration over 4*c* position
- Poor knowledge about migration through different crystallite domains and grain boundaries

Experimental Setup

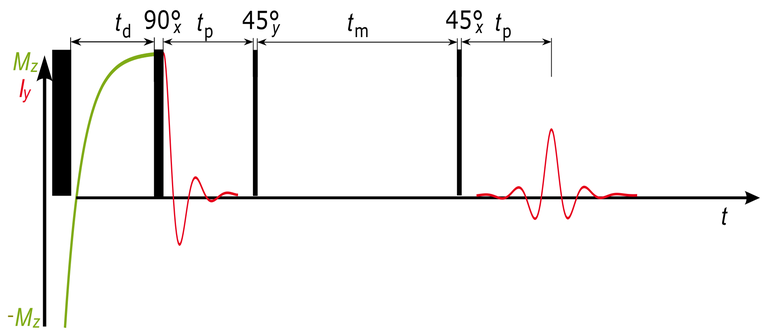


Figure 2: Inversion recovery delay with the variable time t_d followed by the Jeener and Broekaert [4] three pulse sequence with the variable mixing time t_m between the two 45° pulses and the constant evolution time t_p

- Jeener-Broekaert pulse sequence[5] (figure 2) with preceding inversion recovery scheme formed the 2D experiment
- Delay time t_d and mixing time t_m logarithmically scaled from 10^{-5} s to 10^{1} s, with 16 increment steps for t_d and 32 steps for t_m
- Processing of the obtained multidimensional data (echo maxima and spectral dimension) with algorithm for **discrete Laplace Inversion**[6] without non-negativity constraint

➡ Negative relaxation contributions are not ruled out in point of possible **exchange processes** on NMR time scale during experiment

Results

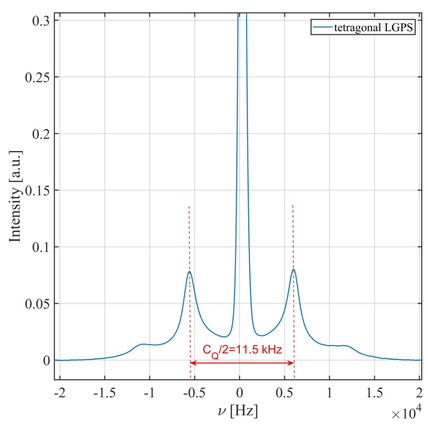


Figure 3: Static 7Li NMR spectrum of LGPS, showing spin-3/2 powder Pake-like patterns with quadrupolar coupling constants

Static spectrum of LGPS (figure 3) shows spin 3/2 pake pattern despite of the high known Li mobility in the material

Estimated quadrupole coupling constant from residual quadrupole interaction C_Q = 23 kHz

2D spin lattice - spin alignment correlation map (figure 4):

- Region A:
  - SAE decay rate below $1/T_{1Q}$ (τ_c can be quantified!)
  - Response from spins with different structural surrounding compared to B
- Region B:
  - SAE decay rate overlaps $1/T_{1Q}$, relaxation rate of pure quadrupolar order
  - No direct information about Li mobility accessible
  - Contains distribution maximum
- Region C:
  - Low amount of phosphour rich side phase, indicated by long spin lattice relaxation and the broadened spectrum
- Region D:
  - Negative components of the distribution indicate exchange of Li from region A during T_1 to region B during t_m

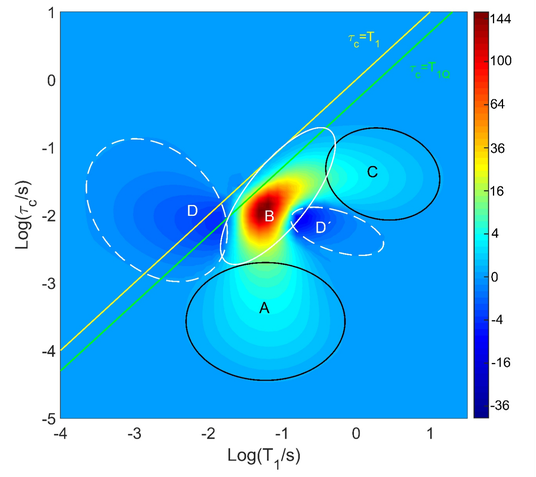
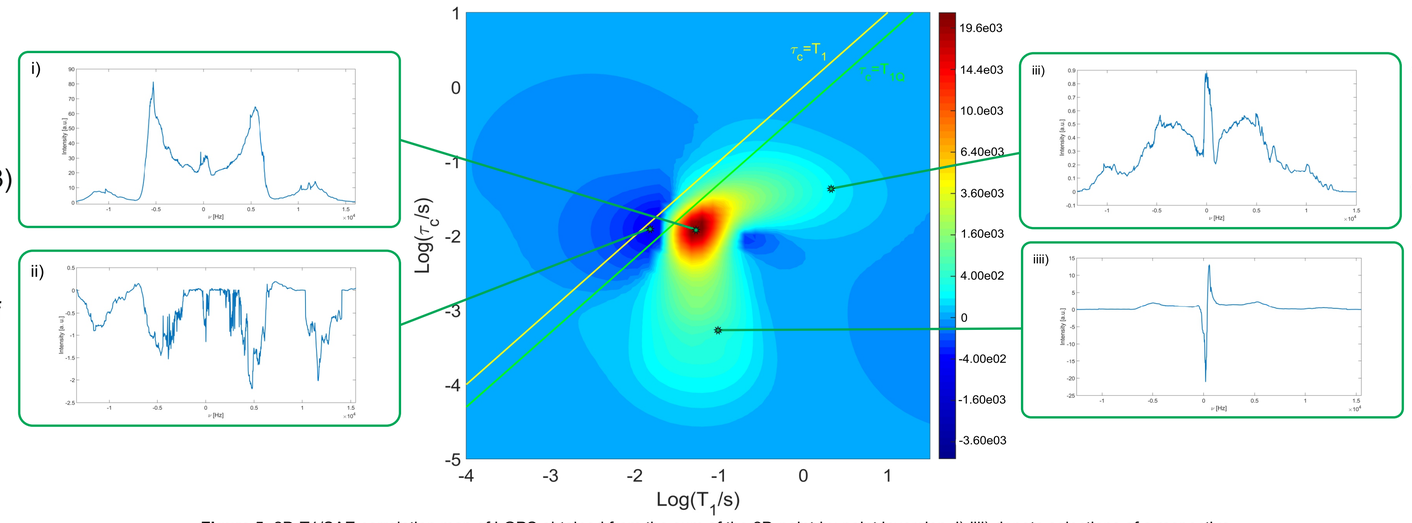


Figure 4: 2D-T_1/SAE correlation map of LGPS, recorded at room temperature. Regions of different longitudinal relaxation (T_1) and Li-migration (τ_c) behavior of LGPS are labeled A–D. The parts in the distribution encircled by dashed ellipsoids have negativ signs. The yellow solid line marks data points with τ_c=T_1 and the green solid line marks $T_{1Q,f}$=τ_c/2

- SAE powder pattern with dominant satellites and weak central component
- Quadrupolar coupling constant almost similar to the static ^{7}Li spectrum (figure 3)
- Almost zero intensity between inner and outer satellites as well as at both sides of the small central component
- Evidence for an orientation dependent spin-lattice relaxation



- Broader shaped features and narrower quadrupole splitting than spectrum i)
- Predominantely orthorombic LGPS
- Powder Pake-pattern with approximately identical splitting compared to spectrum i)
- Dispersive Lorentzian central component

Figure 5: 2D-T1/SAE correlation map of LGPS obtained from the sum of the 2D-point-by-point inversion. i)-iiii) denote selections of a respective spectrum from the areas A -D. The yellow solid line marks data points with τ_c=T_1 and the green solid line marks $T_{1Q,f}$=τ_c/2

Acknowledge:
The authors would like to thank Peter Jakes (IEK-9, Forschungszentrum Jülich) and Simone Köcher (IEK-9, Forschungszentrum Jülich and TU München) for fruitful discussions and support of the project. Funding from the Ministry of Innovation, Science and Research (MIWF) of the State of North Rhine-Westphalia through project "Ionic conductors for efficient energy storage" is gratefully acknowledged. Simulations were performed with computing resources granted by RWTH Aachen University under project *rwth0204*.

References:
[1]M.C. Paulus et al. (2018), "Investigation of the Li-ion conduction behavior in the Li10GeP2S12 solid electrolyte by two-dimensional T1–spin alignment echo correlation NMR", Journal of Magnetic Resonance (*In Press*).
[2]Böhmer, R. (2000). "Multiple-Time Correlation Functions in Spin-3/2 Solid-State NMR Spectroscopy." Journal of Magnetic Resonance 147(1): 78-88.
[3]Qi, F., et al. (2002). "Stimulated-Echo NMR Spectroscopy of 9Be and 7Li in Solids: Method and Application to Ion Conductors." Solid State Nuclear Magnetic Resonance 22(4): 484-500.
[4]Kamaya, Noriaki, et al. "A lithium superionic conductor." *Nature materials* 10.9 (2011): 682-686.
[5]Jeener, J. and P. Broekaert, *Nuclear Magnetic Resonance in Solids: Thermodynamic Effects of a Pair of rf Pulses.* Physical Review, 1967. **157**(2): p. 232-240.
[6]Granwehr, Josef, and Peter J. Roberts. "Inverse Laplace transform of multidimensional relaxation data without non-negativity constraint." *Journal of Chemical Theory and Computation* 8.10 (2012): 3473-3482.