^{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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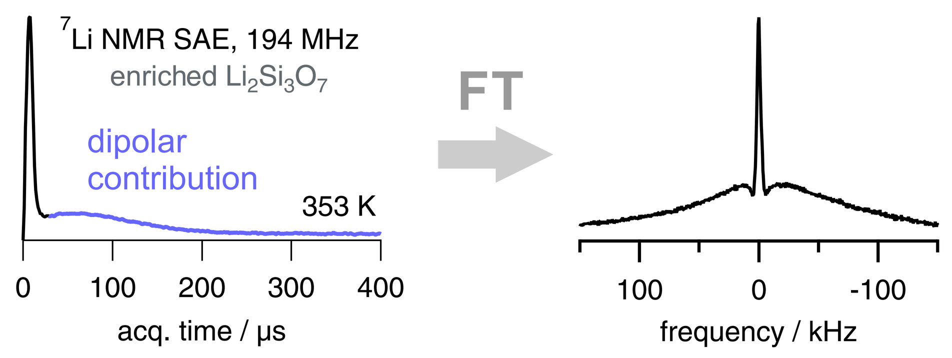
Introduction

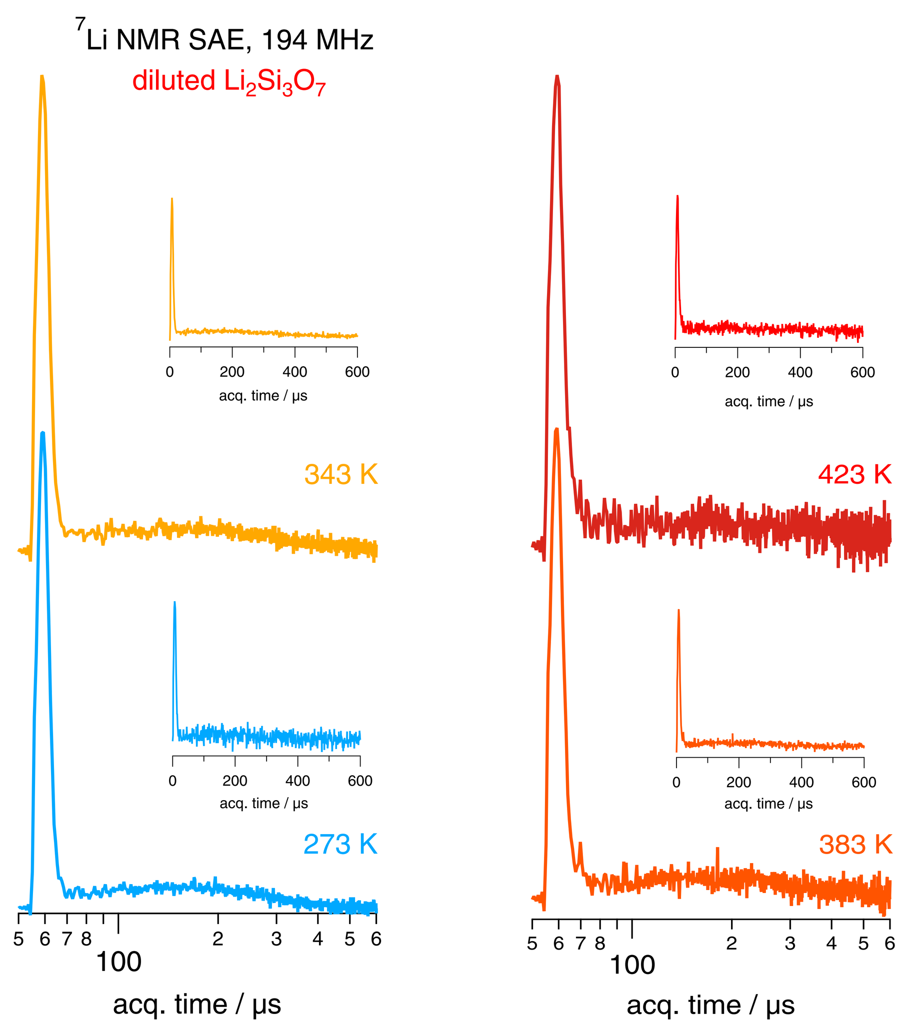
- **^{7}Li spin-alignment echo (SAE) NMR** is sensitive to **extremely slow cation exchange** processes and gives access to diffusion parameters from a microscopic point of view [1].
- Up to now, ^{6,7}Li SAE NMR spectroscopy has been applied to **crystalline** as well as structurally **amorphous** (glassy) Li conductors [2].
- Technique was first developed to study (i) ^{2}H (spin-1 nucleus) **dynamics** and (ii) **geometric aspects** of diffusion processes; later on, it was adapted to the study of spin-3/2 nuclei (e.g., investigations of ultra-slow jump processes of ^{9}Be and ^{7}Li) [3].
- Here, glassy $Li_2Si_3O_7$ served as a suitable model system to study the **effect of (interfering (?)) homonuclear dipole-dipole interactions** on echo formation, echo decay and, thus, on the SAE NMR decay rates.
- Accordingly, two samples were studied, one with **5% ^{7}Li** (95% ^{6}Li) [sample 2] and the other one with **100% ^{7}Li** [sample 1].

Results

Spin-alignment echoes and spectra

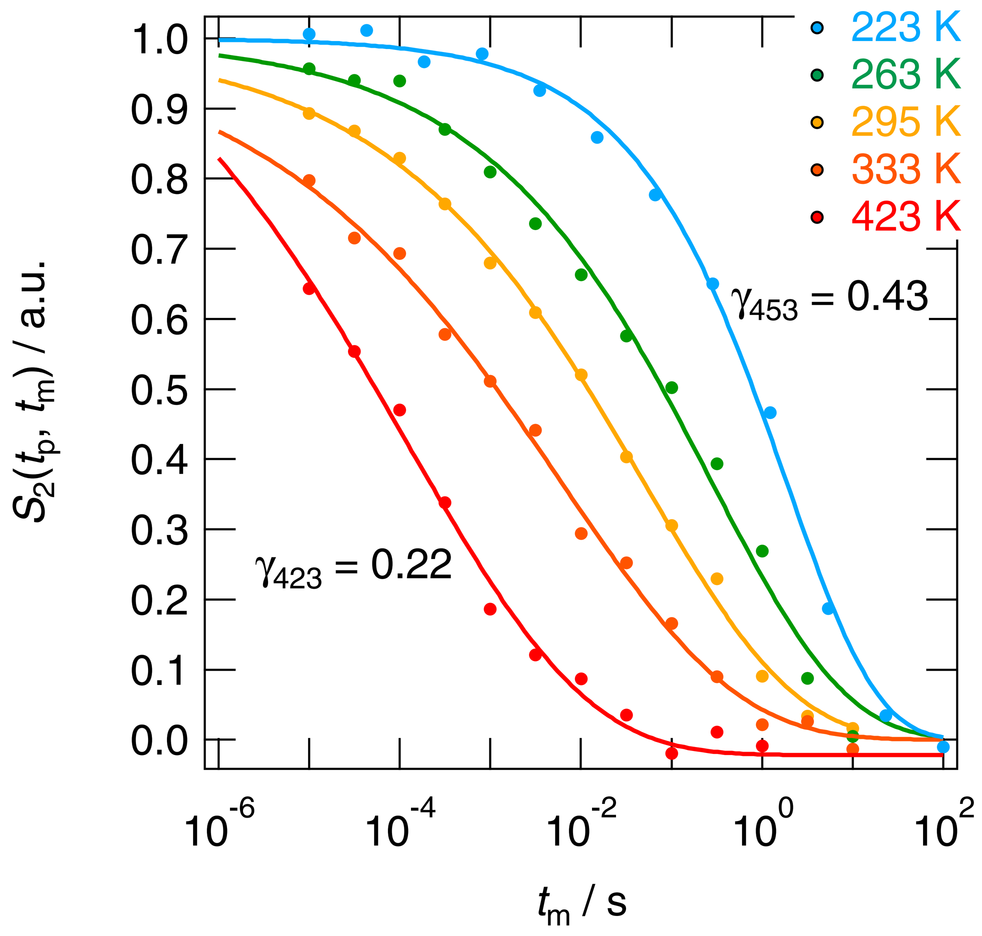


- Jeener-Broekaert echo of spin-3/2 (^{7}Li) and its Fourier transform: the enriched sample



- echoes were recorded at fixed preparation and mixing time t_p = 15 µs, t_m = 10 µs
- diluted sample: dipolar interaction can be **suppressed** to the greatest possible extent

SAE decay curves (5% ^{7}Li)

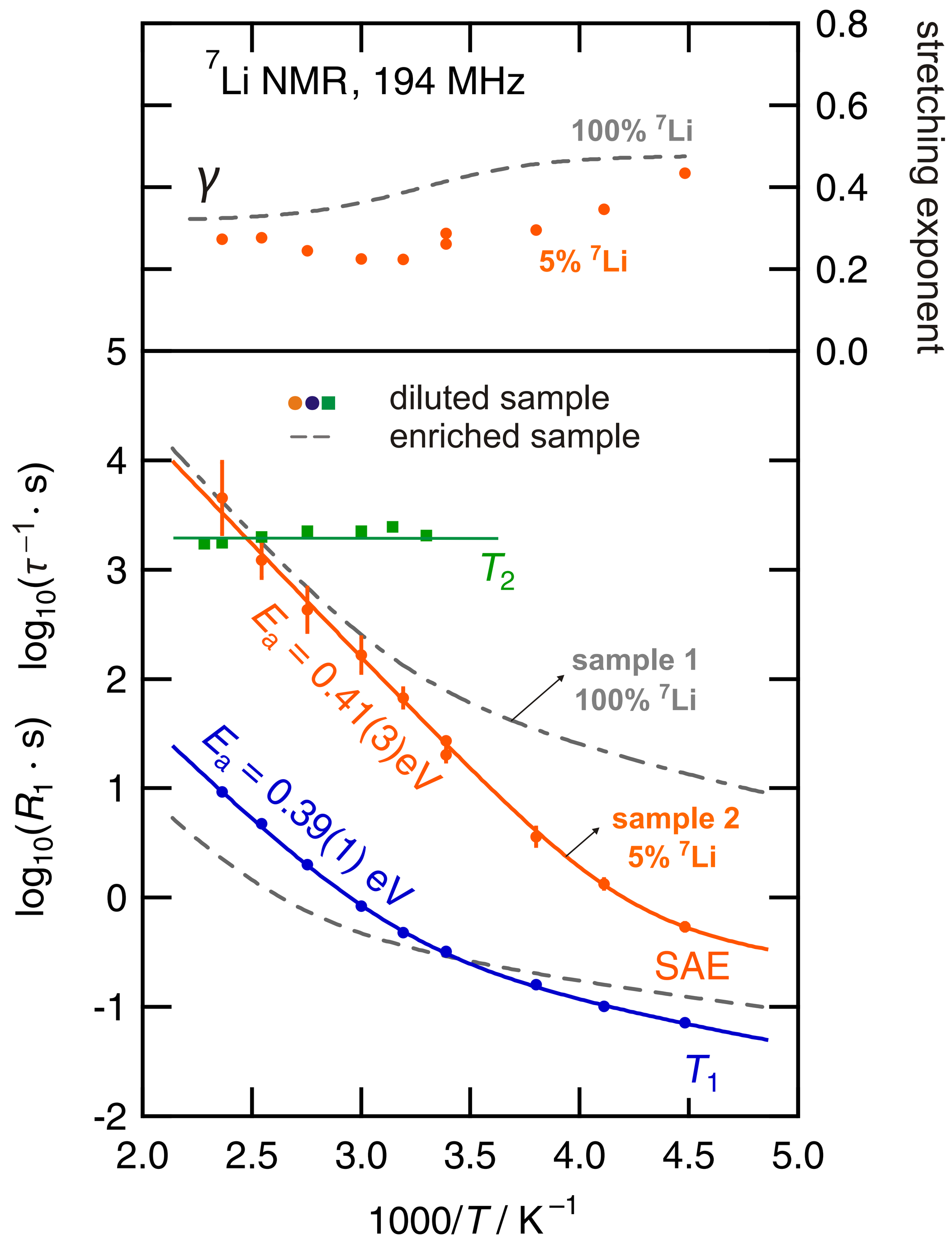


- temperature dependent decay of ^{7}Li SAE amplitudes $S_2(t_p, t_m)$ of diluted $Li_2Si_3O_7$ as a function of mixing time t_m
- data were measured at fixed preparation time t_p = 15 µs and at 194 MHz
- the solid lines are fits according to a stretched exponential

$$S_2(t_p,t_m) \propto \exp[-(t_m/\tau)^{\gamma}] \text{ with } \tau = f(T)$$

- with increasing T the inflexion point shifts towards shorter t_m due to increasing Li diffusivity

Arrhenius plot; stretching factors



- SAE decay rates and $1/T_1$ rates are both Arrhenius activated at elevated T
- enriched and diluted sample reveal the **same activation energy** of about **0.4 eV**
- γ even **lower** for the diluted sample (2) compared to that with 100% ^{7}Li (sample 1)

Conclusions & Outlook

- Jeener-Broekaert echoes show that at sufficiently short t_p interfering dipolar interactions can be (almost) completely suppressed in that sample for which the proportion of ^{7}Li was greatly reduced by substitution with ^{6}Li
- at sufficiently high temperatures (that is the diffusion-induced regime) the SAE decay rates and the activation energies probed are equal for the enriched and the diluted sample; the lower non-diffusive background rates of sample 2 are due to eliminated dipolarly controlled Li-Li interactions; this extends the T range to study diffusion-induced SAE rates.
- the γ values of sample 2 are quite small, *i.e.*, surprisingly, dipole-dipole interactions increase the value of γ, rather than decrease it.

References

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