Multinuclear Solid-State NMR Study of Local Structure and Dynamics in $Li_{0.7}Nb_3S_4$

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Solid-state nuclear magnetic resonance (NMR) spectroscopy is capable of giving insights into the diffusivity of, *e.g.*, Li ions on the microscopic scale. Standard methods of solid-state NMR such as lineshape analyses and spin-lattice relaxation measurements have repeatedly been applied also to sulfides, *e.g.*, Li_xTiS_2. Besides Li_xTiS_2 which was studied by NMR both in its hexagonal and cubic modification [1-4], measurements on layer-structured $Li_{0.7}NbS_2$ were also done [5].

The present work focuses on channel-structured $Li_{0.7}Nb_3S_4$ [6], where, among others, the question of the dimensionality of the diffusion pathway arises. Insights into the local structure are given by ^{6}Li, ^{7}Li, ^{33}S and ^{93}Nb NMR spectra. ^{6}Li and ^{7}Li NMR spectra show one mobile Li species as it could be expected from the crystal structure. Li ion dynamics are investigated by means of ^{7}Li NMR spin-lattice relaxation (SLR) and spin-alignment echo (SAE) decay measurements. Results from SLR NMR in the rotating frame of reference $T_{1\rho}$ (Fig. 1) and SAE yield Li jump rates over several decades. The Arrhenius parameters, *i.e.* the pre-exponential factor and the activation energy, obtained from the fit show that the Li diffusivity is much slower in $Li_{0.7}Nb_3S_4$ than in $Li_{0.7}NbS_2$ [5].

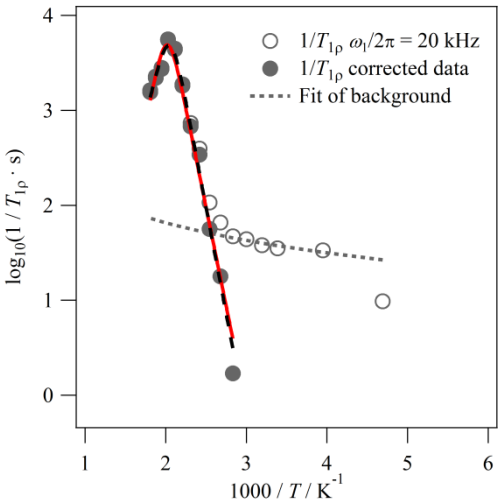

Fig. 1: ^{7}Li NMR SLR rate $1/T_{1\rho}$ ($\omega_1/2\pi$ = 20 kHz) in $Li_{0.7}Nb_3S_4$ vs. inverse temperature. The SLR background rate follows a power law. The diffusion-induced SLR rate peak shows up at $T \approx 500$ K.

References

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