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Extreme mobility: Low-temperature NMR probes highly diffusive Li^+ ions in argyrodite-type Li_6PSe_5Cl and Li_6PS_5Br

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Lithium argyrodites represent a new class of crystalline solids exhibiting a very high Li^+ conductivity and a negligible electronic conductivity [1, 2]. This makes them ideally suited to act as electrolytes in highly stable and reliable all-solid-state lithium-ion batteries. In general, the use of a solid electrolyte inherently resolves a large majority of the safety issues associated with this technology.

The accurate characterization of Li dynamics in crystalline solids helps identify the most promising candidates so that subsequent research can focus on the improvement of their overall properties for battery applications. Here, Li diffusion parameters in a series of Li-argyrodites have been comprehensively studied by using a range of complementary time-domain NMR techniques. In particular, these include the acquisition of diffusion-induced NMR spin-lattice relaxation (SLR) rates in both the laboratory (R_1) and in the rotating ($R_{1\rho}$) frame of reference [3, 4].

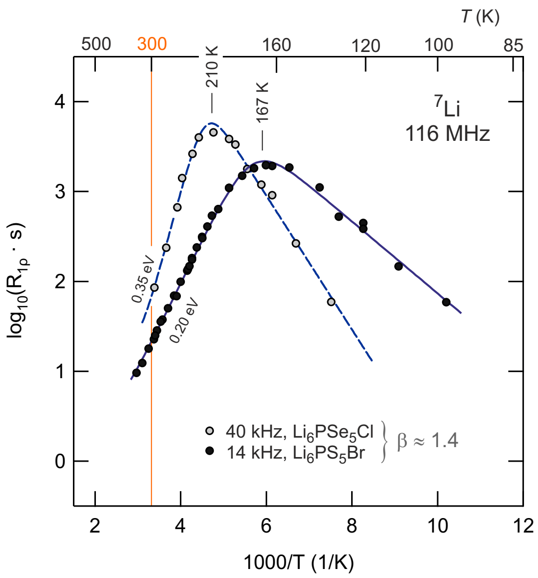

Figure 1: Arrhenius plot of the ^{7}Li SLR NMR rates recorded with the spin-lock technique in the rotating frame of reference at frequencies of 14 kHz and 40 kHz, respectively; taken from Ref. [4]. The parameter β $(1 < \beta \leq 2)$ indicates the deviation from ideal BPP-type behaviour [5] which would be reflected by $\beta = 2$.

Most importantly, for the Cl- and Br-containing compounds, Li_6PSe_5Cl and Li_6PS_5Br, extremely fast Li exchange processes are found. This manifests in diffusion-induced (laboratory frame) SLR NMR rate peaks showing up at temperatures as low as 260 K while the corresponding rate peaks measured in the rotating frame of reference are shifted towards much lower temperatures (see figure and Ref. [4]). From a quantitative point of view, at ambient temperature the Li jump rate in polycrystalline Li_6PS_5Br is of the order of 10^9 s^{-1} which corresponds to an Li ion conductivity in the order of 10^{-2} S/cm, thus, indicating ultrafast translational motion of the charge carriers.

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