From Ultrafast to Extremely Slow Li Ion Dynamics in (Nano-)crystalline Solids — Dimensionality Effects and Structural Disorder

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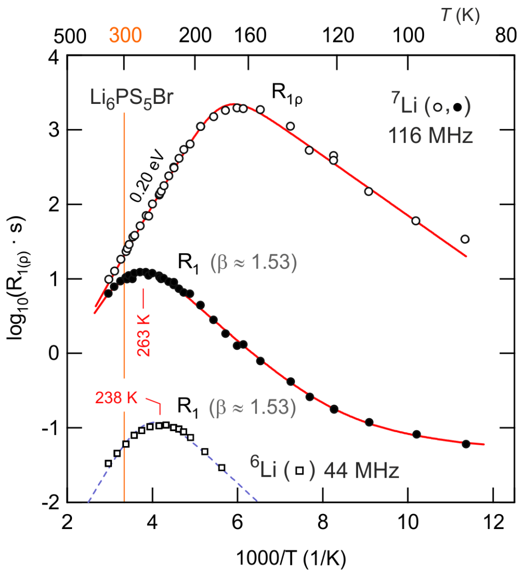
The study of diffusion processes of small ions, such as lithium, sodium or even fluorine, in crystalline and amorphous solids has a long tradition in materials science. Although many studies have been published over the past years, motivated either by fundamental interest or driven because of applications behind, the sophistication of existing techniques as well as the development of new ones still guarantees that solid state diffusion is a vital and well recognized research area.

One of the main objectives within the Research Unit 1277 is to investigate Li ion dynamics over a broad dynamic range complementarily with NMR echo and relaxation techniques as well as conductivity spectroscopy. The ongoing studies focus on *(i)* spatially confined Li^+ diffusion in crystalline solids [1] and *(ii)* ion dynamics in nanocrystalline oxides and sulfides [2]. In particular, materials offering extremely fast translational diffusion [3] or ultraslow Li hopping processes [4] are extensively studied. The NMR methods of choice that are applied in *molife* mainly include frequency and temperature dependent relaxation measurements, 2D exchange spectroscopy and stimulated echo analyses preferably using both the ^{6}Li (spin-1) and ^{7}Li (spin-3/2) isotope. The present talk will spotlight NMR results obtained over the last couple of years.



As an example, extremely fast Li ion dynamics in polycrystalline agryrodite-type Li_6PS_5Br as made visible via ^{7}Li NMR spin-lattice relaxation in both the lab frame (R_1, 116 MHz) and the rotating frame of reference ($R_{1\rho}$, 20 kHz) being two methods of the large portfolio of techniques frequently used in *molife*, data taken from ref. [3]. The R_1 rate maximum showing up at 263 K points to ultrafast Li diffusion characterized by a mean residence time being in the order of 1 ns. This corresponds to a liquid-like Li diffusion behavior with ion conductivities in the order of 10^{-3} to 10^{-2} S/cm. Our findings are corroborated by additional ^{6}Li NMR experiments carried out at 44 MHz. The vertical line marks ambient temperature.

References

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