diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Ultraslow Cation Diffusion in Li Intercalated Cubic TiS_2

Martin Wilkening, Paul Heitjans

Universität Hannover, Institut für Physikalische Chemie und Elektrochemie,
Callinstr. 3-3*a*, 30167 Hannover, Germany, E-Mail: martin.wilkening@gmx.net

1. Introduction

The Li intercalated polymorphs of titanium disulfide – the trigonal (layered) and the cubic modification – form a unique model system for comparison of Li self-diffusion in two and three dimensions, respectively, within two host structures of the same composition [1].

Slow Li^+ transport in cubic Li_xTiS_2 ($x = 0.6$) was probed by ^7Li stimulated echo NMR spectroscopy (see, e. g., [2,3]) and compared with results obtained by recording diffusion induced maxima of the NMR spin-lattice relaxation rate $1/T_{1\rho}$ in the rotating frame. Both methods are sensitive to very slow Li jumps. Whereas $1/T_{1\rho}$-measurements are useful to detect Li jumps with rates between 10^4 to 10^5 s^{-1}, ultraslow Li motions down to the sub-Hz range are *directly* accessible by the stimulated echo NMR technique. Furthermore, the data is compared with results on Li diffusion in the layered, trigonal modification $Li_{0.7}TiS_2$ [4].

2. Experimental

Spin-lattice relaxation rates $1/T_{1\rho}$ were measured with a modified Bruker MSL 100 spectrometer at different locking frequencies (2 - 10 kHz) in the temperature range between 250 K to 500 K. Spin-alignment echoes (SAE), i. e. Jeener-Broekaert echoes [5], at a radio frequency of 155 MHz for ^7Li were recorded at fixed evolution time t_p and variable mixing time t_m (10^{-5} - 10^1 s) below 250 K using a Bruker MSL 400 spectrometer. For the sample preparation see Ref. [1].

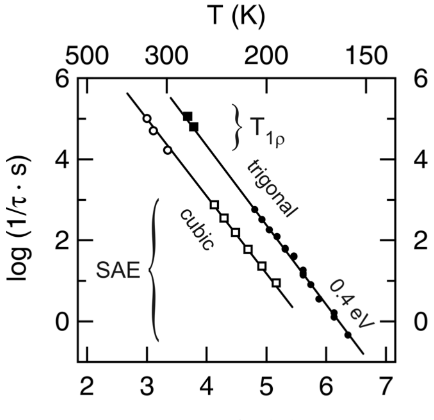

Fig. 1: Arrhenius plot of slow Li jump rates in cubic $Li_{0.6}TiS_2$ and trigonal $Li_{0.7}TiS_2$. In both cases the Li transport process is thermally activated with ≈ 0.4 eV.

3. Results

Li jump rates obtained by $T_{1\rho}$- and SAE-NMR for Li intercalated cubic TiS_2 are shown vs reciprocal temperature in Fig. 1. For comparison our results for the trigonal modification $Li_{0.7}TiS_2$ are shown, too. In both cases the same activation energy of about 0.4 eV for the diffusion process is obtained. This result is not surprising comparing the crystal structures of the two polymorphs. In cubic as well as in trigonal TiS_2 the Li^+ ions preferentially occupy octahedral positions. According to the spin-alignment measurements they use the same diffusion pathways which are supposed to be formed by face sharing octahedral and tetrahedral sites [6], so that the same activation energy is obtained in each case. Interatomic distances of octahedral and tetrahedral sites are very similar for Li contents x between 0.6 and 0.7 in both modifications. Obviously, the dimensionality of the transport process, studied in Ref. [1] via the frequency dependence of the spin-lattice relaxation rate, has no influence on the local energy barriers probed here. However, the jump rates in the cubic modification are about one order of magnitude lower than in the layered counterpart (cf. Fig. 1).

4. Conclusion

The Li diffusion process in cubic $Li_{0.6}TiS_2$ was investigated by two different ^{7}Li NMR techniques. Very slow Li jump rates with values ranging from 10 - 10^5 s^{-1} were measured by spin-alignment and $1/T_{1\rho}$ relaxation NMR. The results are compared with NMR data of an analogous study on Li^+ transport in layered $Li_{0.7}TiS_2$.

References

[1] W. Küchler, P. Heitjans, R. Schöllhorn, and A. Payer, Solid State Ion. 70/71 (1994) 434.

[2] F. Qi, G. Diezemann, H. Böhm, J. Lambert, and R. Böhmer J. Magn. Res. 169 (2004) 225.

[3] M. Wilkening and P. Heitjans, Defect and Diff. Forum 237-240 (2005) 1182.

[4] M. Wilkening and P. Heitjans, in preparation.

[5] J. Jeener and P. Broekaert, Phys. Rev. 157 (1967) 232.

[6] P.G. Bruce and M.Y. Saidi, Electrochimica Acta 36 (1991) 569.