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Li Diffusion in LiAlO$_2$ Single Crystals Studied with NMR Spectroscopy

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1. Introduction

γ-LiAlO$_2$ crystallizes in the tetragonal space group P4$_1$2$_1$2. A unit cell of this crystal contains four formula units and has lattice parameters a = (5.1687 ± 0.0005) Å and c = (6.2679 ± 0.0006) Å [1]. There are four crystallographically equivalent sites for the Li as well as for the Al atoms which, however, can be discriminated by NMR via the orientation of a single crystal with respect to an external magnetic field. LiAlO$_2$ is used as substrate material for epitaxial growth of III-V-semiconductors like GaN [2]. The stability of such systems during processing and operation will depend on lithium diffusion in the substrate and from the substrate into the semiconducting films. Furthermore, LiAlO$_2$ is used as coating in Li electrodes [3] and as additive in composite Li electrolytes [4]. LiAlO$_2$ is also considered as candidate material for tritium breeder or fusion reactors. In that case tritium release and diffusion will depend on lithium diffusion in this material. Therefore molecular dynamics simulation had been carried out which predicted a Li diffusion coefficient of $6 \cdot 10^{-11}$ m^2/s at 700 K and an activation energy of 0.5 eV [5]. First NMR measurements were performed on powder samples to determine quadrupole coupling constants and chemical shifts of ^{27}Al [6] and spin-lattice relaxation of ^{7}Li [7].

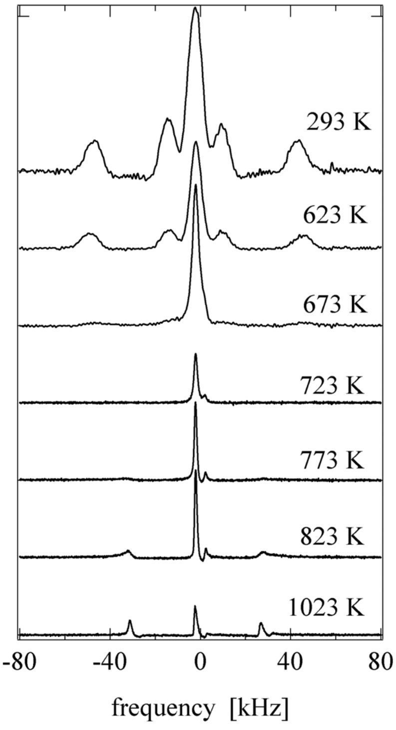

Fig. 1: ^{7}Li lineshapes for various temperatures measured at a frequency of 77 MHz on a LiAlO$_2$ single crystal with the magnetic field aligned parallel to the [110] direction.

2. Experimental results

We have studied Li diffusion in LiAlO$_2$ single crystals using solid state NMR spectroscopy. The ^{7}Li and ^{27}Al NMR spectra at room temperature show well-resolved quadrupolar splitting. Its dependence on the orientation of the crystal with respect to the magnetic field allowed us to determine the electric field gradient (EFG) tensors and thus the local symmetry at the sites of the Li and Al nuclei. The results for these EFG tensors show good agreement with quantum chemical calculations [8].

As shown in Fig. 1, temperature dependent measurements of the ^{7}Li NMR spectrum for the magnetic field aligned parallel to the [110] direction between 300 and 1100 K reveal coalescence of the quadrupole satellites at about 700 K. Motional narrowing of the central transition starts at 600 K. Both results yield at, e.g., 700 K a hopping rate of some thousands s^{-1}. With a jump length equal to the nearest neighbor Li distance (about 3 Å) a diffusion coefficient of about 10^{-16} m^2/s is obtained, which is much smaller than the predicted value from molecular dynamics simulation (see above). Furthermore, we performed measurements of the ^{7}Li spin-lattice relaxation rate at temperatures between 700 and 1000 K. It shows Arrhenius behaviour with an activation energy of 0.7 eV in agreement with an earlier result [7]. Comparison with conductivity results [9] indicates strongly correlated motion of the Li ions.

3. Conclusion

Different NMR techniques have been applied to study the Li diffusion in γ-$LiAlO_2$. In particular, by the use of single crystalline material it was possible to employ the coalescence of the quadrupole satellites at high temperatures to investigate the hopping between crystallographically equivalent sites.

References

[1] M. Marezio, Acta Cryst. 19 (1965) 396-400.
[2] P. Waltereit, O. Brandt, K. H. Ploog, Appl. Phys. Lett. 75 (1999) 2029-2031.
[3] H. Cao, B. Xia, Y. Zhang, N. Xu, Solid State Ionics 176 (2005) 911-914.
[4] M. A. K. L. Dissanayake, Ionics 10 (2004) 221-225.
[5] J.-P. Jacobs, M. A. San Miguel, L. J. Alvarez, P. B. Giral, J. Nucl. Mater. 232 (1996) 131-137.
[6] D. Müller, W. Gessner, G. Scheler, Polyhedron 2 (1983) 1195-1198.
[7] T. Matsuo, H. Ohno, K. Noda, S. Konishi, H. Yoshida, H. Watanabe, J. Chem. Soc., Faraday Trans. II 79 (1983) 1205.
[8] T. Bredow, private communication.
[9] B. Roling, private communication.