Slowly but Surely—Pathways of Ultraslow Lithium Diffusion in γ-$LiAlO_2$

Dennis Wiedemann,[1] Suliman Nakhal,[1] Stefan Zander,[2] Martin Lerch[1]

[1]Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin
[2]Helmholtz-Zentrum Berlin, Abteilung Kristallographie, Hahn-Meitner-Platz 1, 14109 Berlin

Corresponding author: Dennis Wiedemann, E-Mail: dennis.wiedemann@chem.tu-berlin.de

The ultraslow lithium-ion conductor γ-$LiAlO_2$ is used as substrate for epitaxial growth of III-V semiconductors, as coating material, and as additive in electrolytes. Our research on this material aims at gaining insight into the most basic principles of lithium diffusion in solids.
In γ-$LiAlO_2$, the metal ions are tetrahedrally coordinated by oxygen; each LiO_4 shares an edge with an AlO_4 tetrahedron. These pairs are connected *via* common vertices to form a 3D network, in which the lithium ions may diffuse (as suggested by ^{7}Li-NMR and conductivity measurements).[1]
Rietveld refinements of powder neutron-diffractograms acquired up to 1500 °C allowed modelling of Debye-Waller factors including anharmonic terms for the lithium ion. Probability-density functions (PDFs) and one-particle potentials (OPPs) were derived.
At high temperatures, the PDF sprawls through two tetrahedron boundaries into octahedral voids that form channels along the principal axes (see Fig. 1). The OPP landscape shows an activation energy of 1.25 eV for the diffusion into channels and barriers of ca. 1.5 eV/1.7 eV for undulated paths along <100>/[001]. Direct jumps between two neighboring lithium sites are forbidden.
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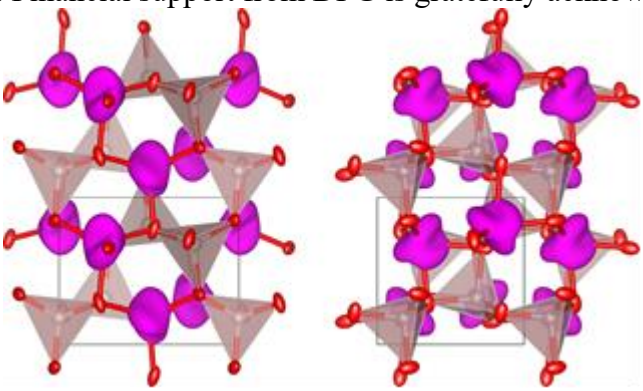

Figure 1: Crystal structure of γ-$LiAlO_2$ at 1202 °C (left: view along [01;$\bar{}$0], right: view along [001]). Pink: lithium as isosurface plot of PDF, brown: aluminium, red: oxygen as ellipsoids for 50 % probability.

References

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