Spontaneous defect formation as the origin of the superionic transition in antifluorite structures

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Solid-state electrolytes offer prospects for improved safety and higher energy density [1] compared to conventional liquid-electrolyte batteries. A key challenge in designing efficient solid electrolytes is understanding Li-ion transport mechanisms across different temperature regimes. Although Li-ion diffusion is often described by concerted-motion mechanisms [2], such descriptions can overlook defect-mediated transport. While many materials display Arrhenius-type diffusion behavior, several promising ionic conductors exhibit superionic transitions, in which diffusion properties change abruptly. Indeed, previous work on Li_3N has shown that Li-ion transport can couple to continuous phase transitions driven by spontaneous defect formation [3], suggesting a more complex picture than purely concerted motion. To explore this further, we simulated two antifluorite-type materials, Li_2O [4] and Li_2S, using an Allegro machine-learning force field [5] trained on Density Functional Theory (DFT) data selected using on-the-fly [6] molecular dynamics as implemented in VASP. Both Li_2O and Li_2S display continuous phase transitions in their heat capacities, coinciding with a non-Arrhenius behavior of the Li-ion self-diffusion coefficient. In Li_2O, this non-Arrhenius behavior correlates strongly with spontaneous Frenkel defect formation, like in the case of Li_3N. This suggests that at high temperatures, defect-assisted transport becomes dominant: interstitial Li-ions can displace lattice Li-ions, reducing the defect formation energy, the diffusion activation energy and enhancing diffusion. In contrast, Li_2S shows significantly weaker correlation, with only a small difference in defect formation energy between its normal and superionic state, despite exhibiting a pronounced superionic-like transport. The stronger electronic screening in Li_2S [7], arising from the more polarizable sulfur anion, likely reduces interactions between diffusing and lattice Li-ions and suppresses a decrease in defect formation energy at elevated temperatures. As a result, Li_2S appears to follow a superionic transitions mechanism that does not rely on defect formation to the same extent as in Li_2O. Overall, our results indicate that high-temperature Li-ion transport in Li_2O (and Li_3N) is dominated by defect-assisted diffusion, whereas Li_2S follows an alternative superionic transition pathway.

References

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Figures

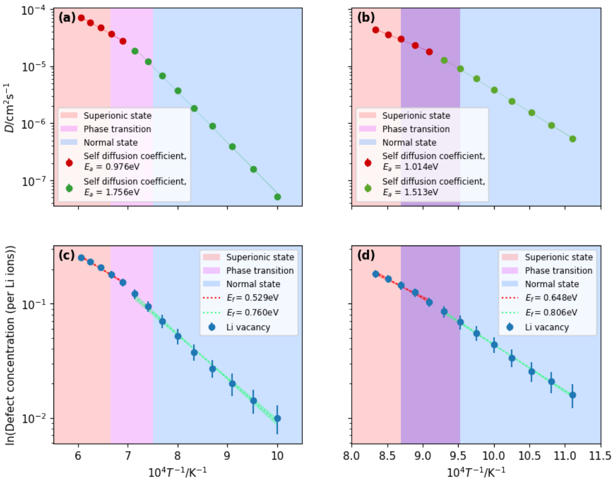

Figure 1. Arrhenius plot of Li_2O and Li_2S as a function of temperature. Phase transitions were identified from the visible peak in the heat-capacity curve. (a) Li-ion diffusion in Li_2O. (b) Li-ion diffusion in Li_2S. (c) Li-vacancy formation in Li_2O. (d) Li-vacancy formation in Li_2S.