Role of Disorder in Defect Energetics of Solid-State Electrolytes: A First-Principles Perspective

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Point defects critically govern ionic transport and electrochemical performance in solid-state electrolytes (SSEs). In this work, we present a combined first-principles and data-driven framework to investigate defect formation energetics in halide-based SSEs, with a focus on Li_2MgCl_4 as a cost-effective, earth-abundant material. Li_2MgCl_4 crystallises in the inverse spinel structure with inherent cation disorder, which complicates computational analysis.

Using density functional theory (DFT), we systematically calculate defect formation energies under varying chemical environments and compare ordered and disordered configurations. Our results show that local disorder strongly modifies defect energetics by altering coordination environments, leading to significant variations in defect stability and concentrations. Key defects, including lithium vacancies, interstitials, and antisites, exhibit environment-dependent behavior, highlighting the importance of incorporating disorder in defect modeling. We further explore extrinsic doping strategies and demonstrate how site preference and charge states depend sensitively on local environment. This work provides defect-informed design principles for optimizing SSE performance and highlights the critical role of disorder in functional materials discovery.