Accessing the effect of local order on the order-disorder phase transition in chalcopyrites

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Disordered crystalline materials have shown their potential for improved ion transport in solid electrolytes [1], enhanced solubility of disordered solid drug formulations [2], and reduced thermal conductivity in thermoelectric materials [3]. An important obstacle for the study and design of disordered crystalline materials is the lack of a unique representation of the disorder. Instead, order-disorder phase transitions and local order in nominally disordered phases complicates design. Thus, to accurately model thermodynamics and synthesizability of the disordered crystalline materials, effects of temperature, entropy and local order must be considered.

While the cluster expansion method along with Monte Carlo simulations provide accurate descriptions on the order-disorder transition temperatures and other thermodynamic properties, it requires high computational cost [4]. An alternative approach often used in simulating metal alloys is the special quasi-random structure method, which assumes perfectly random disorder and performs well for metallic alloys [5]. However, our work shows that the special quasi-random structure method falls short for order-disorder transitions in heterovalent, inorganic crystals, such as $CuInS_2$, and $ZnSnP_2$ with the chalcopyrite structure, due to the lack of short-range order in the formulation. Here, we provide an analysis of the effect of local cation ordering in the high temperature phases on the thermodynamic properties of chalcopyrite crystals, and show that these are essential for understanding order-disorder transitions. Thus, we establish the importance of treating short-range order when developing high-throughput computational screening methods of disordered materials.

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