Extreme phonon anharmonicity leading to superionic diffusion and ultralow thermal conductivity in Argyrodite Ag_8SnSe_6

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The superionic state is a novel state of matter between the ordered crystalline and disordered liquid or molten states. Due to their good electrical properties and ultra-low lattice thermal conductivity, superionic materials are an excellent class of thermoelectric materials and have great application prospects in energy conversion [1]. Studying the underlying mechanism of its ultra-low lattice thermal conductivity is an important frontier topic in condensed matter physics and materials science. Currently, researchers have proposed many different explanations, such as selective breakdown of phonon quasi-particles or liquid-like phonon, but there is a lack of exact experimental support [2, 3]. On the other hand, due to their strong ion transport properties, superionic materials have also attracted much attention in energy storage as excellent solid electrolytes [4]. Nonetheless, a deep understanding of the lattice dynamics across the superionic phase transition remains elusive.

In this work, we systematically studied the microstructure, ion diffusion, and lattice dynamics of Ag_8SnSe_6, an argyrodite-type compound, through single crystal growth, synchrotron X-ray and neutron scattering techniques as well as machine-learned molecular dynamics simulations [5]. We identify a critical interplay of the vibrational dynamics of mobile Ag and a host framework that controls the overdamping of low-energy Ag-dominated phonons into a quasi-elastic response, enabling superionicity. Concomitantly, the persistence of long-wavelength transverse acoustic phonons across the superionic transition challenges a proposed 'liquid-like thermal conduction' picture. Rather, a striking thermal broadening of low-energy phonons, starting even below 50 K, reveals extreme phonon anharmonicity and weak bonding as underlying features of the potential energy surface responsible for the ultralow thermal conductivity and fast diffusion. Our results provide fundamental insights into the complex atomic dynamics in superionic materials for energy conversion and storage.

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