

Strong anharmonicity at the origin of anomalous thermal conductivity in $\text{Cs}_2\text{NaYbCl}_6$

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INTRODUCTION

Double halide perovskites have gained attention in recent years due to their potential applications in thermoelectric and energy-related devices [1], [2], [3]. In particular, it was recently found that specific perovskites exhibit anomalous dependence on temperature of thermal conductivity that deviates from the standard phonon-dominated behavior $\kappa(T) \sim T^{-1}$, as well as negative thermal expansion coefficients [4]. This deviation has been attributed to several factors such as structural disorder, lattice defects, and grain boundary scattering [5], [6].

Among double halide perovskites, rare earth-based perovskites (as $\text{Cs}_2\text{YbNaCl}_6$) have shown particularly interesting properties. The possibility to tune the electronic bandgap [7] combined with the intrinsically low thermal conductivities ($1 - 10 \text{ W m}^{-1} \text{ K}^{-1}$) make these systems very promising for thermoelectric applications.

METHODS

We perform a full ab-initio study of the (i) structural, (ii) electronic and (iii) lattice dynamical properties of $\text{Cs}_2\text{YbNaCl}_6$ by using the QuantumEspresso software suite [8], [9]. Ultrasoft pseudopotential (USPP), PBE functional and a plane wave basis set with an energy cut-off of 45Ry are adopted to describe the conventional cubic cell (40 atoms) used in this study.

The lattice dynamical properties, i.e. the phonon dispersion curves and the phonon lifetimes, are calculated using the finite-displacement (*frozen-phonon*) methodology as implemented in the AlamoDe software package [10]. Fourth-order anharmonicity is eventually included using the Self-Consistent Phonon approach (SCPH) [11]. The thermal conductivity $\kappa(T)$ is calculated by solving the Boltzmann Transport Equation in the Relaxation Time Approximation (BTE-RTA).

RESULTS

To validate the computational setup used to modelize the double perovskite structure, a series of benchmark calculations was conducted. The lattice parameter served as the figure of merit, and we achieved a remarkable agreement with the experiment within a margin of 0.6%. We then calculated the harmonic and anharmonic interatomic force constants to determine the phonon dispersion curves and lifetimes, respectively. Our observations revealed that when only cubic anharmonicity is considered to describe phonon scattering processes, the thermal conductivity at 300 K resulted in $0.25 \text{ W m}^{-1} \text{ K}^{-1}$, significantly underestimating the corresponding experimental value of $\kappa^{\text{exp}} = 0.55 \text{ W m}^{-1} \text{ K}^{-1}$. In contrast, when we included fourth-order anharmonicity using the SCPH method, we were able to (i) resolve the underestimation and (ii) explain the anomalous trend of $\kappa(T)$ observed in the experiment. Specifically, we attribute the failure of $T^{-\alpha}$ law in describing $\kappa(T)$ to an unusual increase in the phonon group velocity and lifetimes for $500\text{K} \leq T \leq 800\text{K}$.

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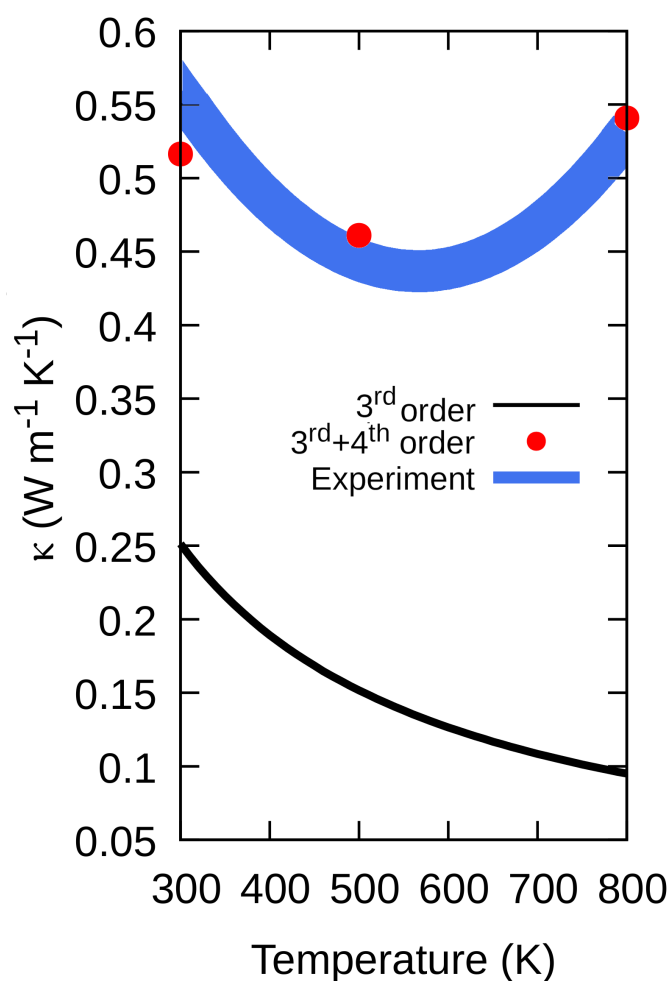


Fig. 1. $\text{Cs}_2\text{NaYbCl}_6$ thermal conductivity κ as a function of the temperature. The black line shows the theoretical prediction of $\kappa(T)$ based solely on cubic anharmonicity. The conspicuous underestimation of the anomalous experimental trend (blue band) is eventually resolved by the inclusion of fourth-order anharmonicity (red points)

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