Low Thermal Conductance Generated by van Der Waals Interaction

Masato OHNISHI

Department of Mechanical Engineering,

The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Clathrate compounds are promising candidates for thermoelectric materials in terms of the "electron-crystal phonon-glass" concept. Clathrate compounds are composed of guest atoms encapsulated in cagelike structures. It is expected that electrons can transport in the framework with much less scattering rate than that for phonons because of guest atoms leading to significant phonon scattering. Particularly, in type-I clathrate compounds, guest atoms vibrate in a strong anharmonic potential because they are composed of a Weaire-Phelan structure, which divides a space with the maximum volume with the same cross-sectional area (Fig. 1(a)). In this study, we have studies type-I $Ba_8Ga_{16}X_{30}$ (BGX, X = Si, Ge, Sn) to gain insights of the effect of phonon anharmonicity on heat transport.

Phonon properties were calculated with the self-consistent phonon (SCP) theory [1] and unified theory [2]. The SCP theory is used to consider effects of forth-order anharmonic potential and to obtain temperature-dependent harmonic interatomic force constants (IFCs). Using the unified theory, one can consider the coherent contribution, that of interbranch tunneling, to heat transport as well as the population contribution, which is considered also in the context of Peierls Boltzmann transport theory. We have employed ALAMODE package [1] to perform the above approaches and VASP to calculate forces on atoms.

While phonon dispersion have imaginary (negative) frequencies when guest atoms have negative harmonic potential at low temperatures, negative frequencies became positive at finite temperatures, as shown in Fig. 1(b). For type-I BGSn, harmonic potential was positive above 100 K, and

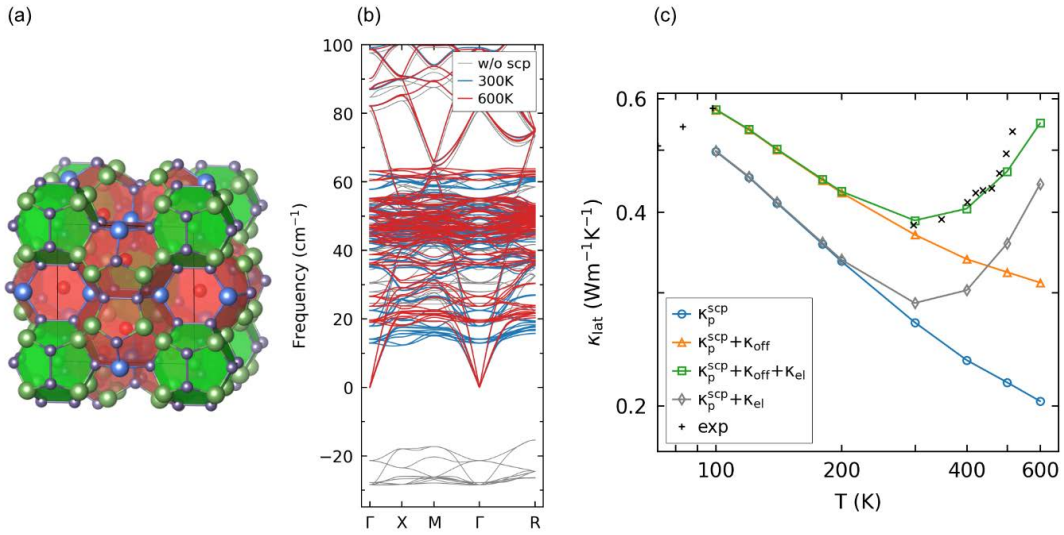

Fig. 1 Phonon properties of type-I clathrate compounds. (a) Crystal structures of type-I clathrate. (b) Phonon dispersion of $Ba_8Ga_{16}Sn_{30}$ (BGSn) without considering renormalization (grey), at 300 K (blue), and at 600 K (red). (c) Temperature-dependent thermal conductivities of BGSn. Population (blue), coherent (orange), and electron (green and red) contributions were considered.

thermal conductivities could be calculated at this temperature range. The calculated thermal conductivities including all the contributions (population, coherent, and electron contributions) were in good agreement with experimental data, as shown in Fig. 1(c). To gain insights into the effect of phonon anharmonicity, we have also analyzed mode dependent phonon properties at high temperatures in details (> 100 K). While a unique temperature-dependence of type-I clathrate at low temperatures (≈ 10 K) have been widely studies, we have revealed intriguing phonon properties at high temperatures in type-I clathrate [3].

References

[1] T. Tadano and S. Tsuneyuki, J. Phys. Soc. Jpn. 87, 041015 (2018).

[2] M. Simoncelli et al., Nat. Phys. 395, 1 (2019).

[3] M. Ohnishi et al., arXiv:2103.00413.