Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material for

Anharmonic Phonon Frequency and Ultralow Lattice Thermal Conductivity in β-Cu_2Se Liquid-like Thermoelectrics

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S1. Quartic Anharmonic Term

To apply the self-consistent phonon theory (SCPH), the anharmonicity up to the fourth order, i.e., $H = H_0+U_3+U_4$, where H_0 is the ground-state Hamiltonian, U_3 is the cubic term and U_4 is the quartic term, is considered. U_n is the nth-order contribution to the potential energy surface as a function of atomic displacement, defined as[1]

$$U_n = \frac{1}{n!}\left(\frac{\hbar}{2}\right)^{\frac{n}{2}} \sum_{\{q\}} \Delta(q_1 + \cdots + q_n) \frac{\Phi(q_1;\cdots;q_n)}{\sqrt{\omega_{q_1} \cdots \omega_{q_n}}} \times A_{q_1} \cdots A_{q_n}, * \text{ MERGEFORMAT}$$

(S1)

Where A is the displacement vector, and the function Δ becomes 1 if q is an integral multiple of the reciprocal vector $\boldsymbol{G}$ and is 0 otherwise. The reciprocal representation of the nth-order interatomic force constants (IFCs) Φ is defined by[1]

$$\Phi(q_1;\cdots;q_n) = N^{1-\frac{n}{2}} \sum_{\{\kappa,\mu\}} (M_{\kappa_1} \cdots M_{\kappa_n})^{\frac{-1}{2}} e_{\mu_1}(\kappa_1;q_1) \cdots e_{\mu_n}(\kappa_n;q_n) \times \sum_{l_2,\cdots,l_n} \Phi_{\mu_1 \cdots \mu_n}(0\kappa_1;\cdots;l_n\kappa_n) e^{i(q_2 r(l_2)+\cdots+q_n r(l_n))}. *$$

MERGEFORMAT (S2)

where M is the mass of the atom, $\Phi_{\mu_1 \cdots \mu_n}$ is the real-space IFCs for the atom κ in the lth cell along the μ direction. With the high-order anharmonic IFCs, the corresponding phonon self-energy and anharmonic phonon frequency can be renormalized.

S2. Phonon Disperse Relation

Due to the existence of liquid-like behaviors, the commonly adopted harmonic approximation will fail, resulting in the large imaginary phonon modes. In Fig. S1, the harmonic phonon dispersion

relation of β-Cu_2Se is presented. a large number of imaginary phonon modes in the first Brillouin zone is observed, indicating the existence of strong anharmonicity. We also apply the TDEP method to calculate the anharmonic phonon frequencies at finite temperatures and compare them with the harmonic phonon dispersion, as shown in Fig. S2. Though extracting the phonon frequencies from the molecular dynamics, imaginary phonon frequencies still exist.

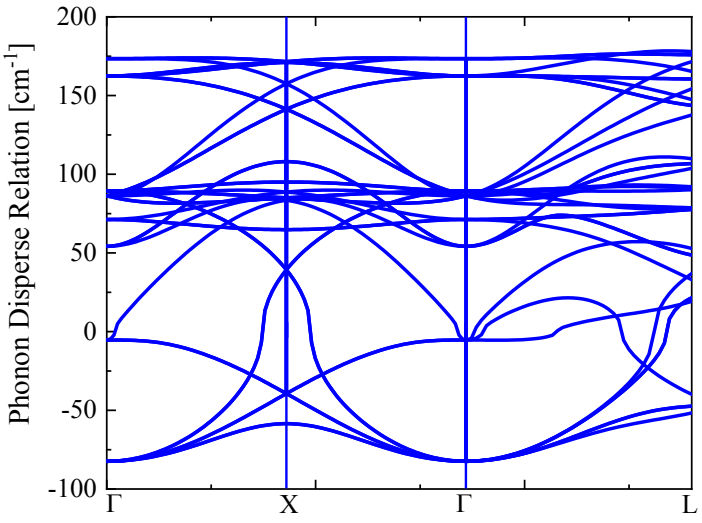

Fig. S1. The harmonic phonon dispersion of β-Cu_2Se at 0 K.

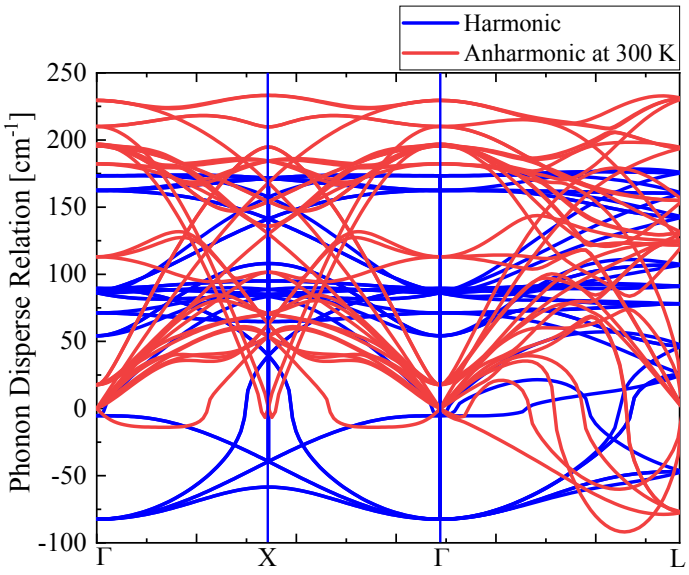

Fig. S2. The harmonic and anharmonic (TDEP, at 300 K) phonon dispersions of β-Cu_2Se.

The Grüneisen parameter is the physical quantity which suggests the anharmonicity in the solids.[2] In Fig. S3, the mode-dependent Grüneisen parameter of β-Cu_2Se is calculated using the SCPH method and it shows that strong anharmonicity exists along the L-Γ high-symmetry line.

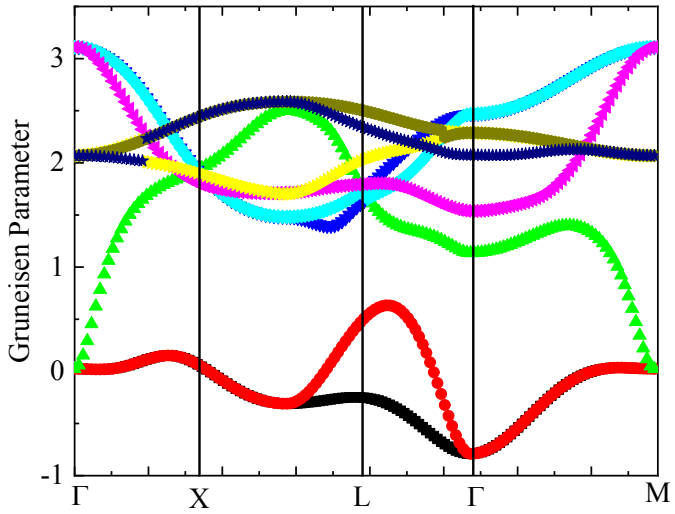

Fig. S3. The mode-dependent Grüneisen parameter of β-Cu_2Se calculated using SCPH method.

S2. Anharmonic Phonon Scattering

In Fig. S4, the cumulative lattice thermal conductivity as a function of phonon frequency is presented. It shows that low-lying phonon frequencies below 32 cm^{-1} contribute little to the total thermal transport. To get more details about the anharmonic scattering, the scattering phase space of β-Cu_2Se within the three-phonon scattering scheme is calculated. Fig. S5 shows that the absorption process where two phonons with lower energy collide into a high-energy phonon dominates the anharmonic scattering for heat-carrying phonons.

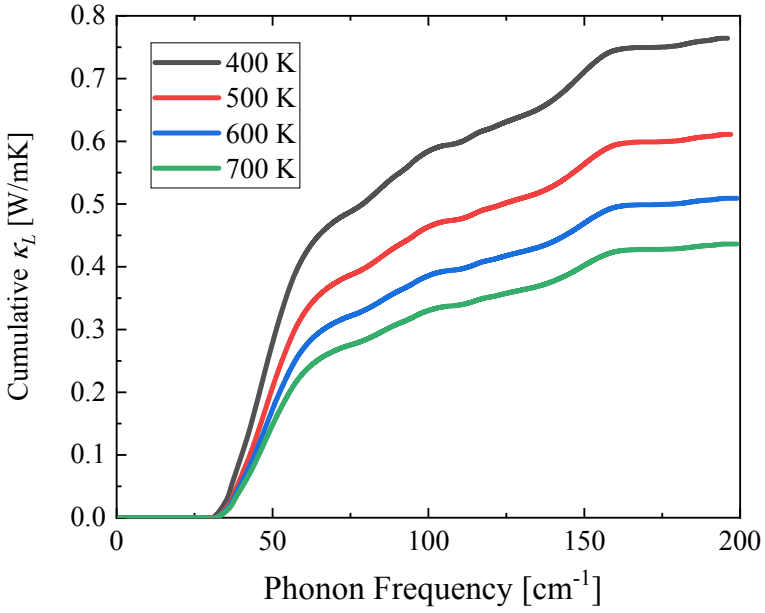

Fig. S4. The cumulative lattice thermal conductivity as a function of phonon frequency.

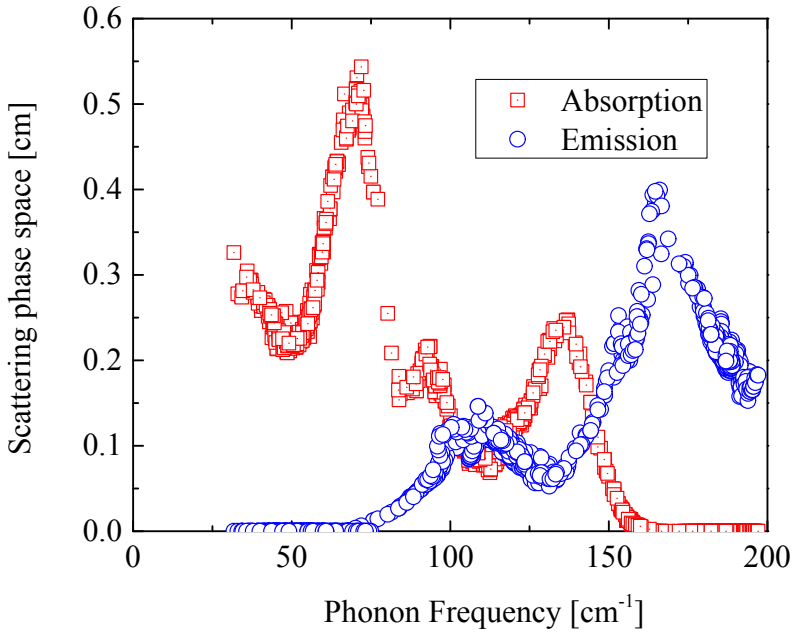

Fig. S5. The scattering phase space of β-Cu_2Se at 400 K.

S3. Convergence Test

We also perform the convergence test on the anharmonic phonon dispersion and lattice thermal conductivity as a function of q-mesh, as shown in Figs. S6 and S7.

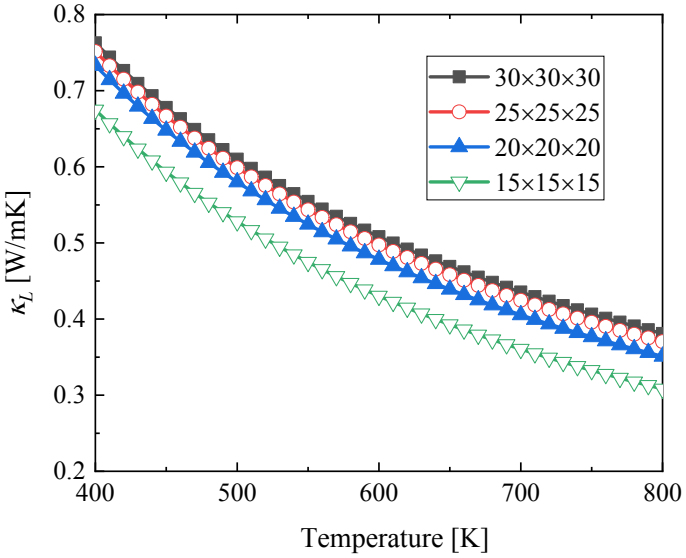

Fig. S6. The convergence test of lattice thermal conductivity as a function of *q*-mesh.

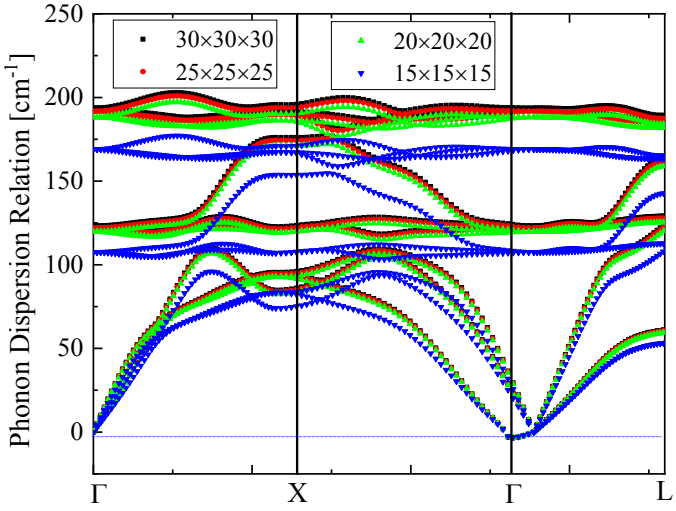

Fig. S7. The convergence test of anharmonic phonon frequency at 400 K as a function of *q*-mesh.

References

1. T. Tadano and S. Tsuneyuki, Phy. Rev. B **92** (5), 054301 (2015).

2. J. M. Ziman, *Principles of the Theory of Solids*. (Cambridge University Press, 1972).