Lattice heat conduction analysis of thermoelectric materials from first-principles

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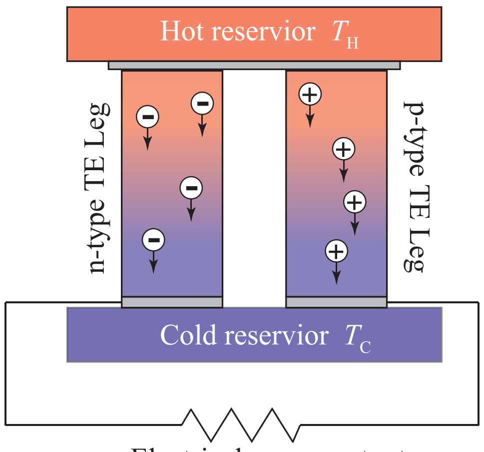
Background and Objective

✓ Thermoelectric (TE) energy conversion efficiency[1]

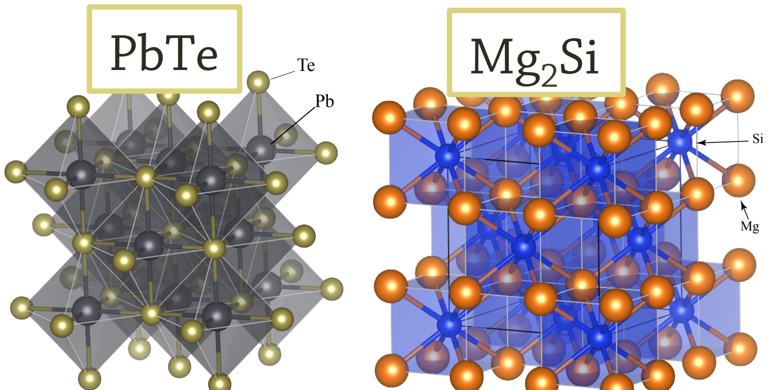


$$\eta = \frac{\Delta T}{T_H} \times \frac{\sqrt{ZT-1}-1}{\sqrt{ZT-1}+T_H/T_C}$$

- Dimensionless figure of merit[1]

$$ZT = \frac{S^2\sigma}{\kappa_{el}+\kappa_{lat}}T$$

S: Seebeck coefficient
σ: Carrier conductivity
κ : Thermal conductivity
T : Temperature



Thermoelectric materials at
Intermediate temperature range

Objective

Performing first-principles calculations, we investigate the lattice heat conduction in these two materials, accurately.

Method: Outline

First-principles calculations + Real-space displacement method[1]

Interatomic Force Constants (IFCs)

$$V = V_0 + \sum_{i,\alpha} \Pi_i^{\alpha} u_i^{\alpha} + \frac{1}{2} \sum_{ij,\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \frac{1}{3!} \sum_{ijk,\alpha\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_j^{\beta} u_k^{\gamma} + \frac{1}{4!} \sum_{ijkl,\alpha\beta\gamma\delta} X_{ijkl}^{\alpha\beta\gamma\delta} u_i^{\alpha} u_j^{\beta} u_k^{\gamma} u_l^{\delta}$$

Harmonic term

Anharmonic terms

Anharmonic Lattice Dynamics (ALD)

Boltzmann Transport Equation
with single-mode relaxation time approx.
(Considering only 3-phonon scatterings)

Molecular Dynamics (MD)

$$m\ddot{u}_i^{\alpha} = F_i^{\alpha} = -\sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^{\beta} - \frac{1}{2} \sum_{jk,\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^{\beta} u_k^{\gamma} - \frac{1}{3!} \sum_{jkl,\beta\gamma\delta} X_{ijkl}^{\alpha\beta\gamma\delta} u_j^{\beta} u_k^{\gamma} u_l^{\delta}$$

Phonon gas model

$$\kappa_{\mathrm{lat}} = \frac{1}{3\Omega} \sum_{\mathbf{q}s} C(\mathbf{q}s) v_g^2(\mathbf{q}s) \tau(\mathbf{q}s)$$

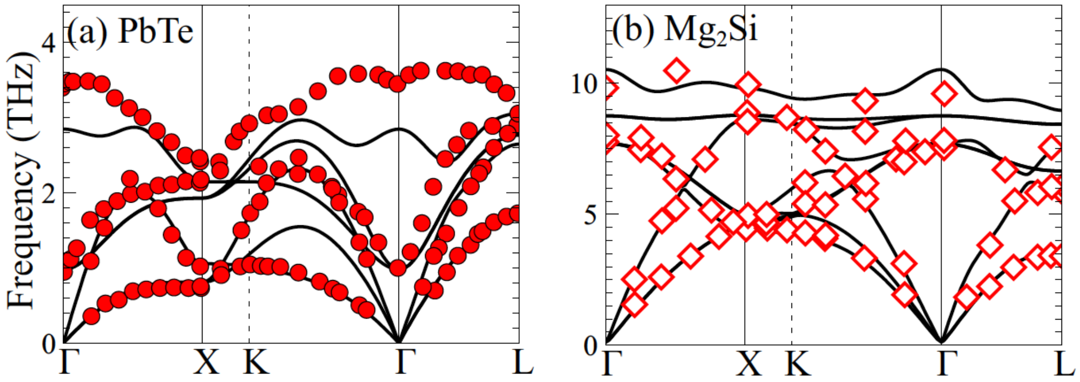
Green-Kubo formula

$$\kappa_{\mathrm{lat}} = \frac{1}{3\Omega k_B T^2} \times \int_0^{\infty} \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle dt$$

Lattice thermal conductivity

Method: Anharmonic lattice dynamics

✓ Lattice Dynamics (LD): Harmonic theory (Harmonic IFCs)



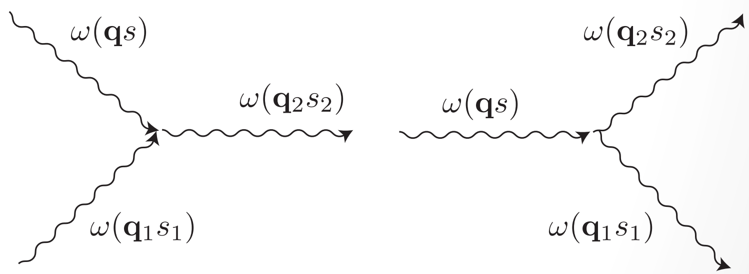
- Mode heat capacity $C(\mathbf{q}s)$
- Group velocity $v_g(\mathbf{q}s)$

✓ Phonon relaxation time from perturbation theory (Cubic IFCs)

- Fermi's golden rule[(2)]:
  Transition probability of 3-phonon scattering

$$P_i^f = \frac{2\pi}{\hbar} \left|\langle f|V_3|i\rangle\right|^2 \delta(\varepsilon_i - \varepsilon_f)$$

Scattering process I (case I) Scattering process II (case II)

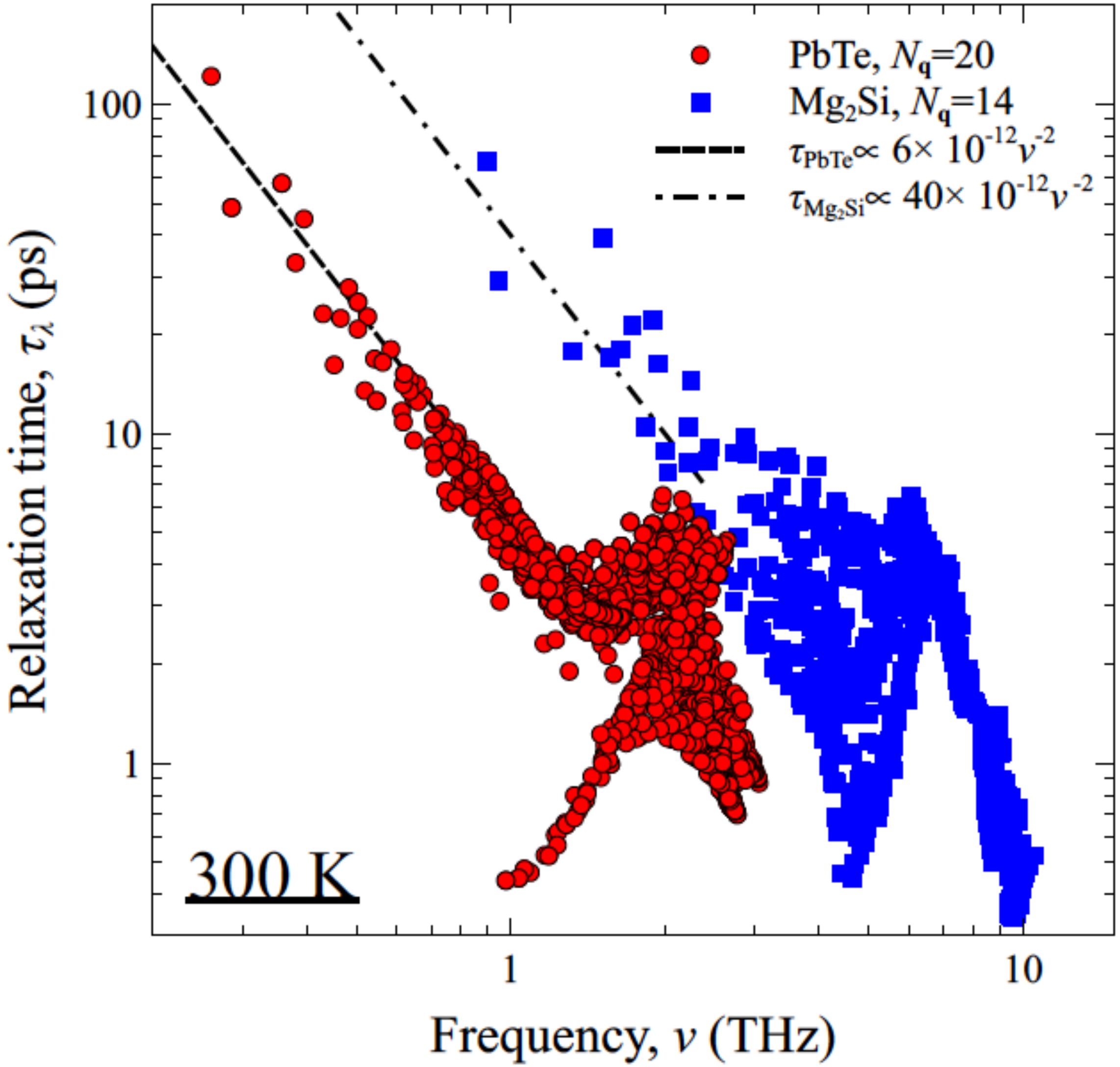


✓ Phonon gas model[(2)]

$$\kappa_{\rm lat} = \frac{1}{3\Omega} \sum_{\mathbf{q}s} C(\mathbf{q}s) v_g^2(\mathbf{q}s) \tau(\mathbf{q}s)$$

(1) K. Esfarjani, *et al.*, Phys. Rev. B **84**, 085204 (2011).
(2) G. P. Srivastava, *The Physics of Phonons* (1990).
(3)
(3) M. T. Hutchings, *et al.*, Solid State Ionics **28**, 1208 (1988).

Results: phonon relaxation time



Results: Lattice thermal conductivity