Supporting Information

Tang et al. 10.1073/pnas.0907194107

SI Text

Phonon Scattering Rate. Fermi's Golden Rule states that transition rate Γ_i^f from an initial state Φ_i to a final state Φ_f under perturbation δH is $\Gamma_i^f = \langle \Phi_f | \delta H | \Phi_i \rangle$. In the present study, we consider two types of perturbation on a harmonic crystalline system—isotope mass disorder and intrinsic third-order lattice anharmonicity.

Within the single mode excitation approximation, the phonon scattering rate due to mass disorder is static (i.e., temperature independent), and is shown as (1):

$$\Gamma_{\text{iso}}(\vec{q},i) = \frac{2\pi}{\hbar}\left(\frac{\hbar\omega(\vec{q},i)}{2}\right)^2 \frac{V_o}{8\pi^3} \times \sum_{i=1}^{3n}\int_{BZ} d\vec{q}' \left[(\delta(\hbar\omega(\vec{q},i) - \hbar\omega(\vec{q}',i') \times \sum_k g_k |\vec{e}_k^*(\vec{q},i)\cdot\vec{e}_k(\vec{q}',i')|^2 \right], \quad \text{[S1]}$$

where $g_k = \sum_n f_n(k)(1 - m_n(k)/\bar{m}(k))^2$, $\hbar$ is the Plank constant, $f_n(k)$ is the fraction of n-th isotope of atom k that has mass $m_n(k)$, and $\bar{m}$ is the average mass of atom k. $\omega(\vec{q},i)$ and $\vec{e}(\vec{q},i)$ are the phonon frequency and polarization vector of the phonon mode $(\vec{q},i)$, respectively.

The phonon scattering rate induced by the third-order lattice anharmonicity is expressed as the following:

$$\Gamma_{\text{anh}}(\vec{q},i) = \frac{V_o}{8\pi^3}\iint_{BZ} d\vec{q}' d\vec{q}'' \times \sum_{i'}\sum_{i''}\left\{ ((n(\vec{q}'',i'') - n(\vec{q}',i'))S^{\vec{q}''i''}_{\vec{q}i,\vec{q}'i'} - \frac{1}{2}((n(\vec{q}',i') + n(\vec{q}'',i'') + 1)S^{\vec{q}'i',\vec{q}''i''}_{\vec{q}i} \right\}, \quad \text{[S2]}$$

Where,

$$S^{\vec{q}''i''}_{\vec{q}i,\vec{q}'i'} = \frac{h^2\delta(\hbar\omega(\vec{q},i) + \hbar\omega(\vec{q}',i') - \hbar\omega(\vec{q}'',i''))\delta_{\vec{q}+\vec{q}-\vec{q}'',\vec{g}}}{24^2\pi\omega(\vec{q},i)\omega(\vec{q}',i')\omega(\vec{q}'',i'')} \times \left| \sum_{lmn}\sum_{\alpha\beta\gamma} \frac{A^{lmn}_{\alpha\beta\gamma}(\vec{q},\vec{q}',\vec{q}'')e^l_\alpha(\vec{q}',i)e^m_\beta(\vec{q}',i')e^n_\gamma(\vec{q}'',i'')}{\sqrt{m_l m_m m_n}} \right|^2$$

and

$$S^{\vec{q}'i',\vec{q}''i''}_{\vec{q}i} = \frac{h^2\delta(\hbar\omega(\vec{q},i) + \hbar\omega(\vec{q}',i') - \hbar\omega(\vec{q}'',i''))\delta_{\vec{q}-\vec{q}'-\vec{q}'',\vec{g}}}{24^2\pi\omega(\vec{q},i)\omega(\vec{q}',i')\omega(\vec{q}'',i'')} \times \left| \sum_{lmn}\sum_{\alpha\beta\gamma} \frac{A^{lmn}_{\alpha\beta\gamma}(\vec{q},\vec{q}',\vec{q}'')e^l_\alpha(\vec{q},i)e^m_\beta(\vec{q}',i')e^n_\gamma(\vec{q}'',i'')}{\sqrt{m_l m_m m_n}} \right|^2$$

$n(\vec{q},i) = \frac{1}{e^{\hbar\omega(\vec{q},i)/k_BT}-1}$ is the Bose–Einstein distribution function, m is the mass, ω is the phonon frequency, and $A^{lmn}_{\alpha\beta\gamma}(\vec{q},\vec{q}',\vec{q}'')$ is the third-order lattice anharmonicity tensor in the reciprocal space. We have developed an efficient real-space supercell numerical algorithm to calculate the third-order lattice anharmonicity tensors by using first-principles methods. Computational details and the results of density/pressure dependence of lattice anharmonicity in MgO can be found in our previous study (2).

The overall transition rate of a phonon mode $\Gamma(\vec{q},i)$ is approximated as the sum of $\Gamma_{\text{iso}}(\vec{q},i)$ and $\Gamma_{\text{anh}}(\vec{q},i)$ (Matthiessen's rule) that are evaluated based on first-principles calculated phonon frequencies, phonon polarization vectors as well as the third-order lattice anharmonicity tensors. A $16\times16\times16$ grid sampling provides numerically converged results for the two-atom unit cell of MgO crystals. Direct calculation of phonon lifetime is carried out only for those phonon modes at the irreducible $\vec{q}$-point in the first Brillouin zone, and the rest are reconstructed with group theory based on the crystal symmetry.

1. Tamura S (1983) Isotope scattering of dispersive phonons in Ge. *Phys Rev B* 27:858–866.
2. Tang X, Dong J (2009) Pressure dependence of harmonic and anharmonic lattice dynamics in MgO: A first-principles calculation and implications for lattice thermal conductivity. *Phys Earth Planet In* 174:33–38.