Lattice Thermal Conductivity of PbTe Materials Driven near Soft Mode Phase Transition

Ronan Murphy,
Éamonn Murray, Stephen Fahy, and
Ivana Savić

Tyndall National Institute, Cork, Ireland

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Outline

- Materials near soft mode phase transitions as efficient thermoelectric materials
- Modelling of lattice thermal conductivity from first principles
- Our strategy: reduce the lattice thermal conductivity of PbTe by driving it closer to phase transition via strain or alloying

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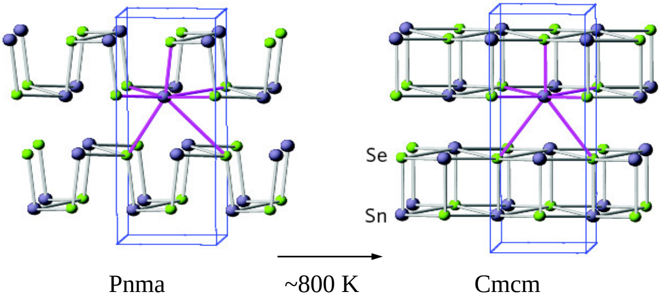
High ZT of materials near soft mode phase transitions

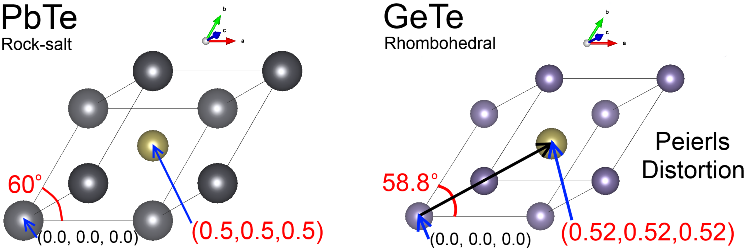
SnSe: **ultralow lattice thermal conductivity κ_{latt}** and record ZT.



Nature **508**, 373 (2014); Nature Phys. **11**, 1063 (2015)

Incipient soft optical mode phase transition in PbTe

PbTe is **near a transition from rocksalt to rhombohedral phase:**

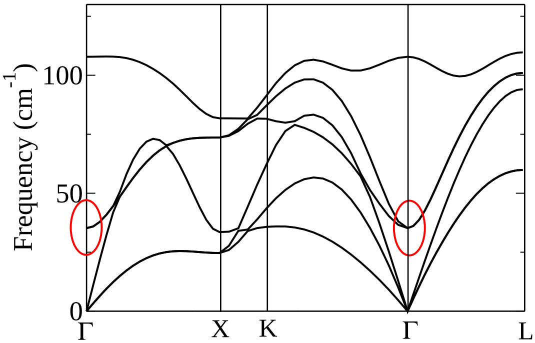


Te atomic displacement along [111] =

transverse optical (TO) mode at zone center

Soft optical phonon in PbTe

Nature Mater. **10**, 614 (2011); PRB 85, 184303 (2012)

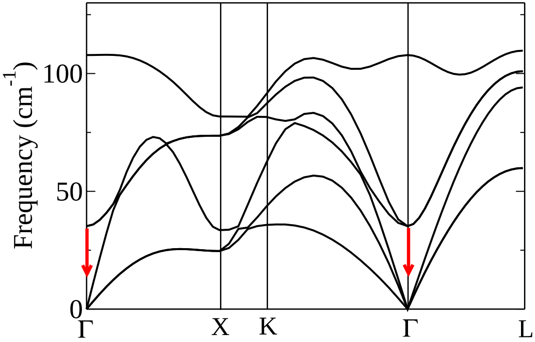


Soft TO modes ⇒ **strong acoustic-TO coupling** ⇒ **low κ_{latt}**

$$d(\log\omega)/d(\log V) = Vd\omega/\omega dV \to \infty \text{ when } \omega \to 0.$$

Our proposal to increase ZT of PbTe

Use strain or alloying to **make TO mode much softer** &
decrease lattice thermal conductivity.



R. Murphy, É. Murray, S. Fahy, and I. Savić, PRB 93, 104304 (2016); PRB 95, 144302 (2017)

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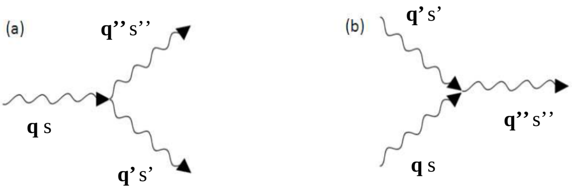
Lattice thermal conductivity from first principles

Boltzmann transport equation in the relaxation time approximation:

$$\kappa_{\mathrm{latt}} = \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q},s} \frac{\partial f_{\mathrm{BE}}}{\partial T} v_{\mathbf{q},s}^2 \tau_{\mathbf{q},s},$$

$\omega_{\mathbf{q},s}$ - phonon frequencies, $v_{\mathbf{q},s} = \partial\omega_{\mathbf{q},s}/\partial\mathbf{q}$ - group velocities,

$\tau_{\mathbf{q},s}$ - phonon lifetimes due to **three-phonon scattering** and mass disorder.



We use **density functional theory (DFT)** to calculate all these quantities.

Lattice thermal conductivity from first principles

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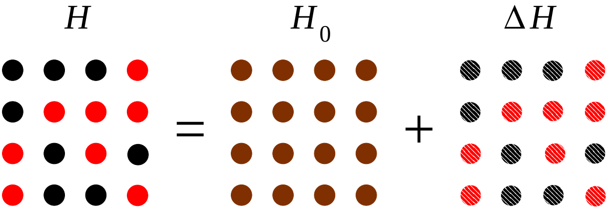

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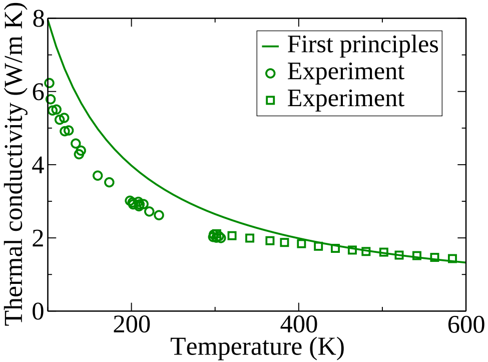
Lattice thermal conductivity of PbTe



Good agreement between our calculations and experiments.

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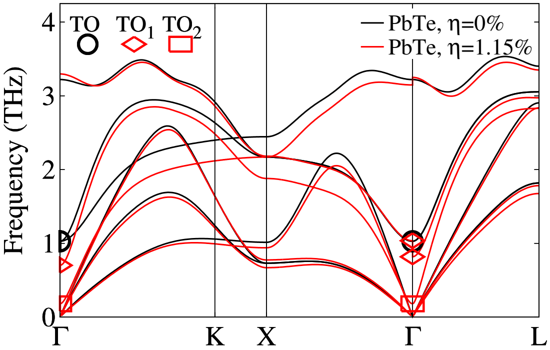
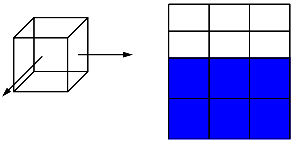
Does driving PbTe to the phase transition reduce the lattice thermal conductivity?

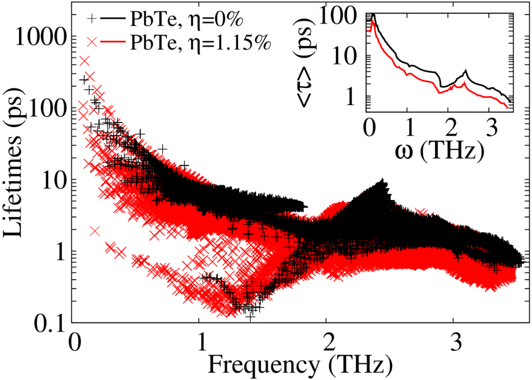
Induce **softening of TO mode at Γ** by varying strain:





Tensile (001) strain: $\eta = (a_{\parallel} - a_0)/a_0 = +1.15\%$

Phonon lifetimes reduction due to strain



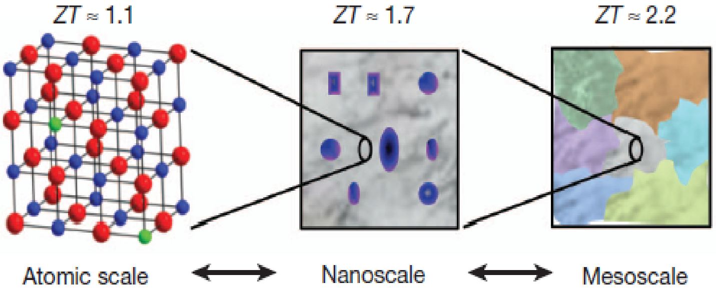
The anharmonic interaction between TO and acoustic modes increases ⇒

Phonon lifetimes are reduced at all frequencies by a factor of 2!

Blocking phonon propagation across the spectrum

Structuring across multiple length scales in PbTe:

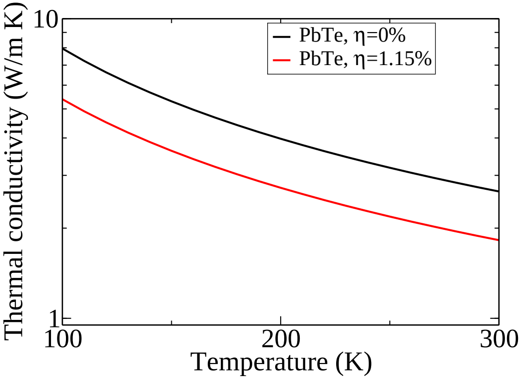
K. Biswas *et al.*, Nature **489**, 414 (2012)

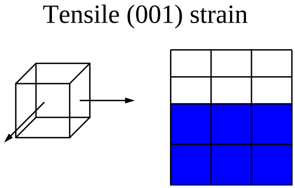


high frequencies mid frequencies low frequencies

Our strategy achieves the same effect!

Computational proof of our concept





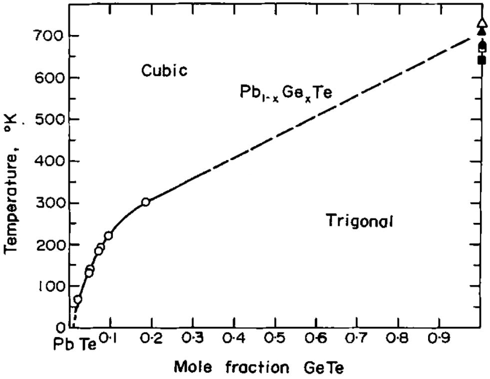
Strain reduces out-of-plane κ_{latt} of PbTe by a factor of 1.5.

R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 93, 104304 (2016)

Driving PbTe to the phase transition via alloying with GeTe

Rocksalt-rhombohedral phase transition in $Pb_{1-x}Ge_xTe$ alloys

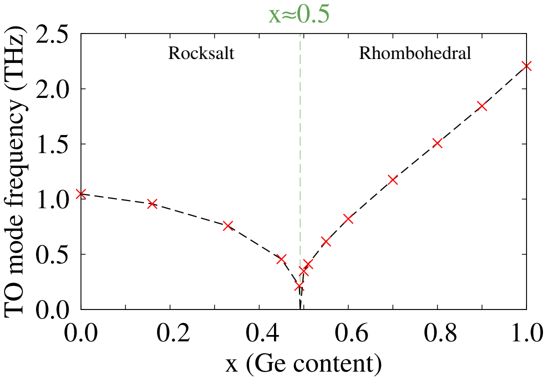
as a function of composition and temperature:



D. K. Hohnke *et al.*, J. Phys. Chem. Solids 33, 2053 (1972)

Soft TO mode in $Pb_{1-x}Ge_xTe$

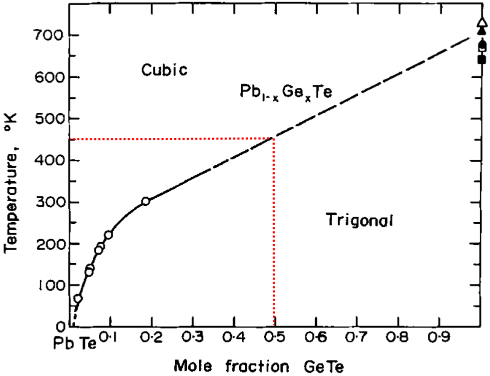
Our model cannot describe phase transition induced by temperature.



But we can qualitatively model the phase transition by varying *x*!

Applicability of our approach

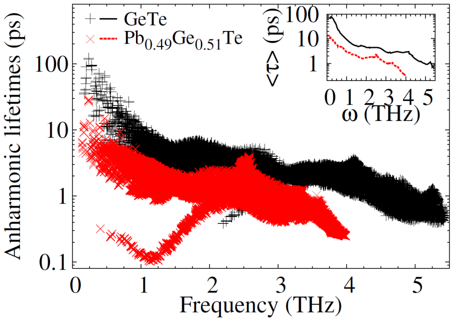
Around transition temperature for $x = 0.5$: $\sim$ **450 K**



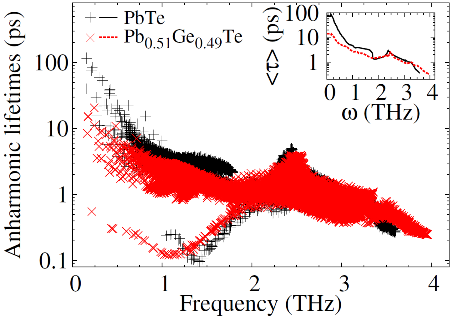
D. K. Hohnke *et al.*, J. Phys. Chem. Solids 33, 2053 (1972)

Anharmonic lifetimes (no mass disorder)

Rhombohedral phase:



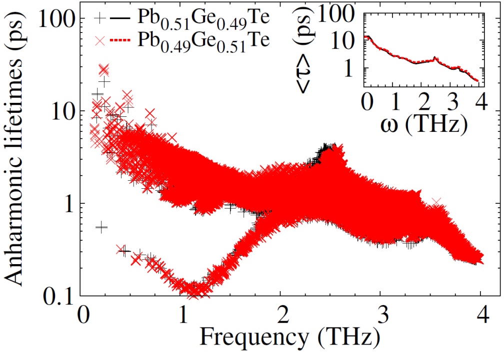
Rocksalt phase:



Minimized at the phase transition in both phases

due to the maximized acoustic-TO anharmonic coupling.

Anharmonic lifetimes at the transition

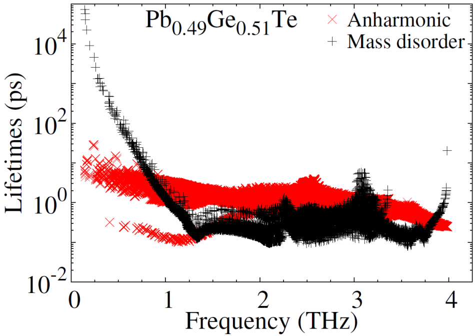


Nearly identical for the rocksalt and rhombohedral compositions

due to 2nd order phase transition.

Anharmonic lifetimes & mass disorder at the transition

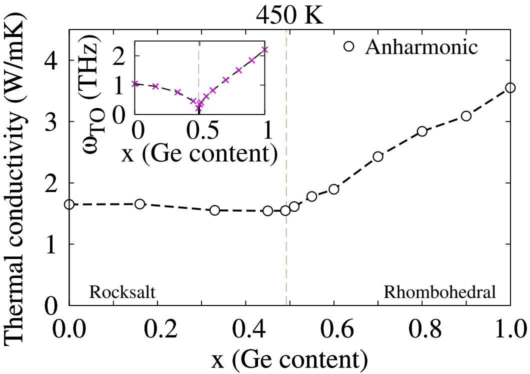
$$\tau^{-1}_{\text{total}} = \tau^{-1}_{\text{anharmonic}} + \tau^{-1}_{\text{mass disorder}}$$



Mass disorder strongly scatters high-frequency phonons:

phonons effectively scattered in the entire frequency spectrum!

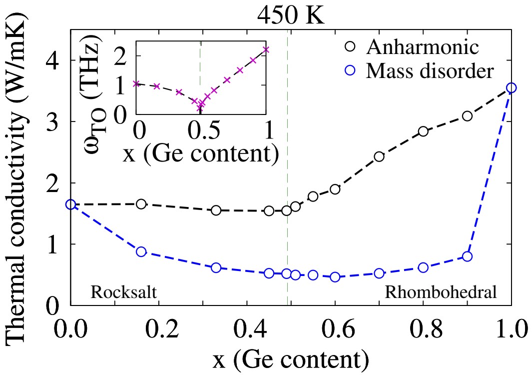
Anharmonic thermal conductivity (no mass disorder)

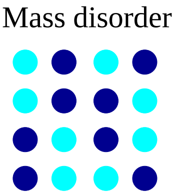


Anharmonic κ_{latt} is **minimal and continuous at the phase transition.**

R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B 95, 144302 (2017)

Total thermal conductivity (with mass disorder)





Soft TO modes and mass disorder combined lead to very low κ_{latt}:

Minimum κ_{latt} is ~3 ($\sim$ 7) times lower than PbTe (GeTe).

Summary and conclusions

- Driving PbTe closer to the phase transition will considerably reduce its lattice thermal conductivity.
- The proposed concept is general, and it would be applicable to other materials close to soft optical mode transitions.
- Materials with soft modes are promising candidates for low lattice thermal conductivity and potentially high ZT.

Phys. Rev. B 95, 144302 (2017); Phys. Rev. B 93, 104304 (2016)

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