Tailoring the lattice thermal conductivity of materials for thermoelectric applications

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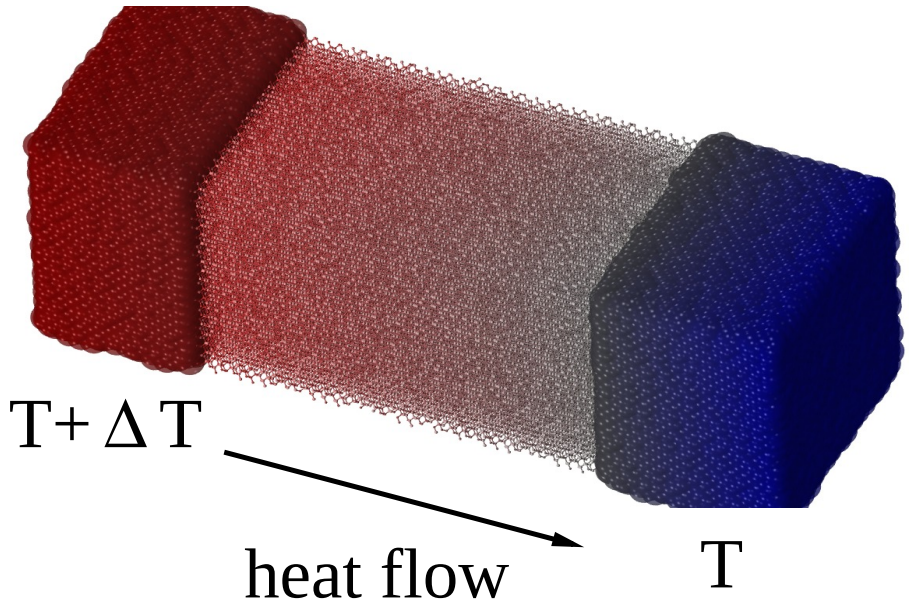
Tyndall National Institute, Cork, Ireland

ICT-Energy Training Day,
Bristol, UK, September 14, 2015

Basic problem

How is energy (heat) transported in a semiconducting material due to the temperature gradient?



Fourier law: $\mathbf{J} = -\kappa \nabla T$; $\mathbf{J}$ - heat current, κ - thermal conductivity

Outline

- Thermoelectric energy conversion for ICT applications
- Basic concepts related to lattice thermal conductivity
- Strategies to design the lattice thermal conductivity of:
  - Bulk crystalline materials
  - Bulk materials with atomic scale disorder
  - Nanostructured materials
- Summary and outlook

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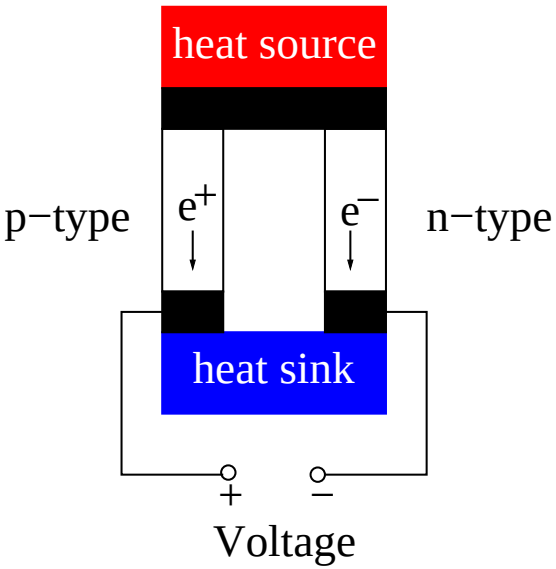
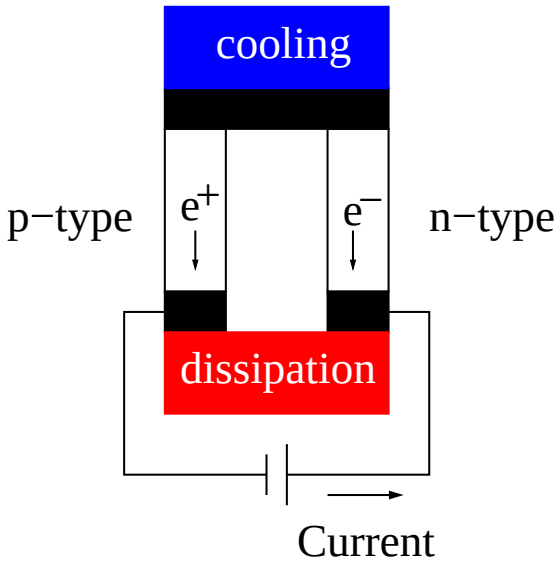
Relevance for ICT-Energy

Thermoelectric energy conversion

transform heat into electricity



transform electricity into heat



Thermoelectric figure of merit:

$$ZT = \sigma S^2 T/\kappa$$

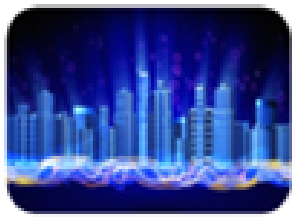
- σ - electrical conductivity
- S - Seebeck coefficient
- T - temperature

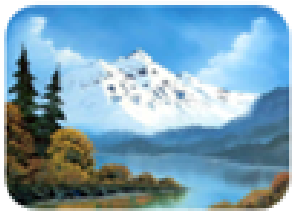
We need materials with low κ!

Thermoelectric energy conversion in ICT

Powering autonomous wireless sensor networks

Wireless sensors applications:

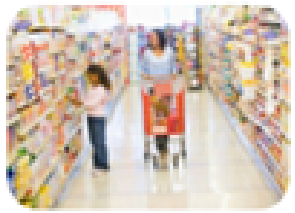

smart cities


smart environment

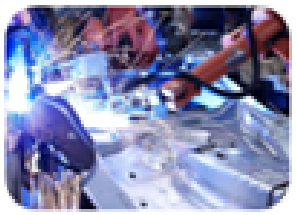

smart water


smart metering


security


retail


logistics


industrial control


smart agriculture

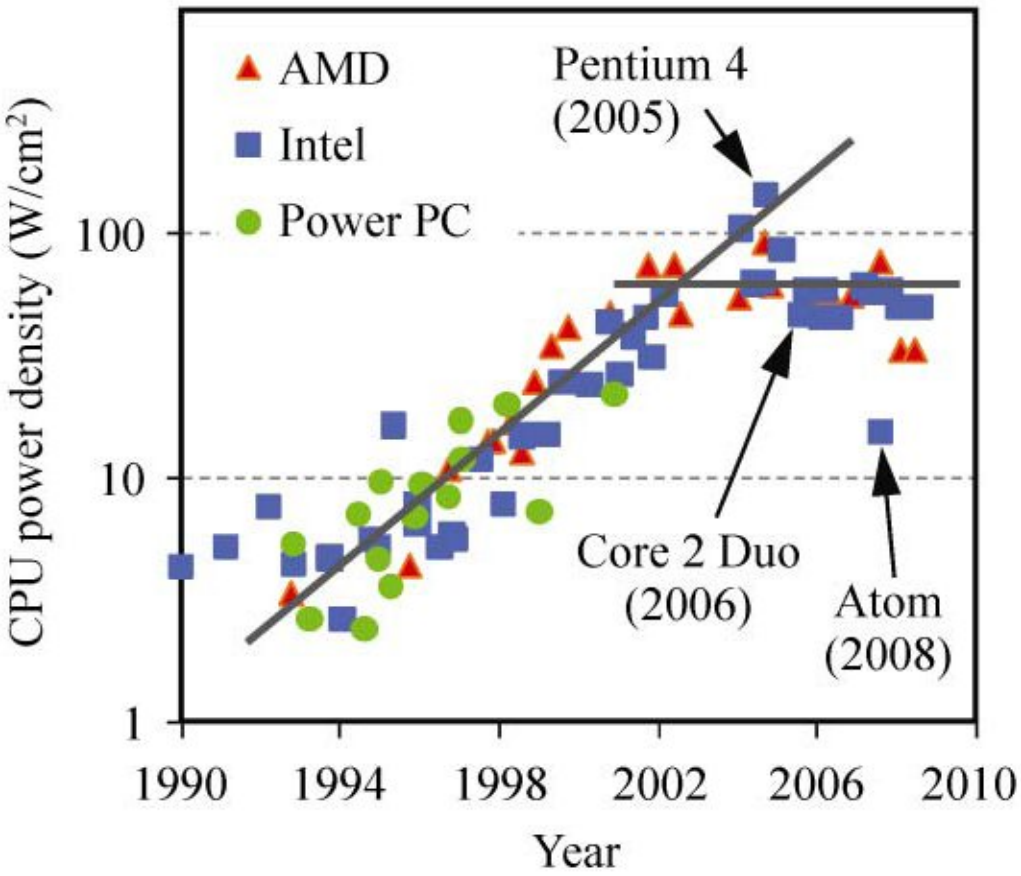

smart farming


automation


eHealth

Thermoelectric energy conversion in ICT

Active solid state cooling



E. Pop, Nano Res. **3**, 147 (2010)

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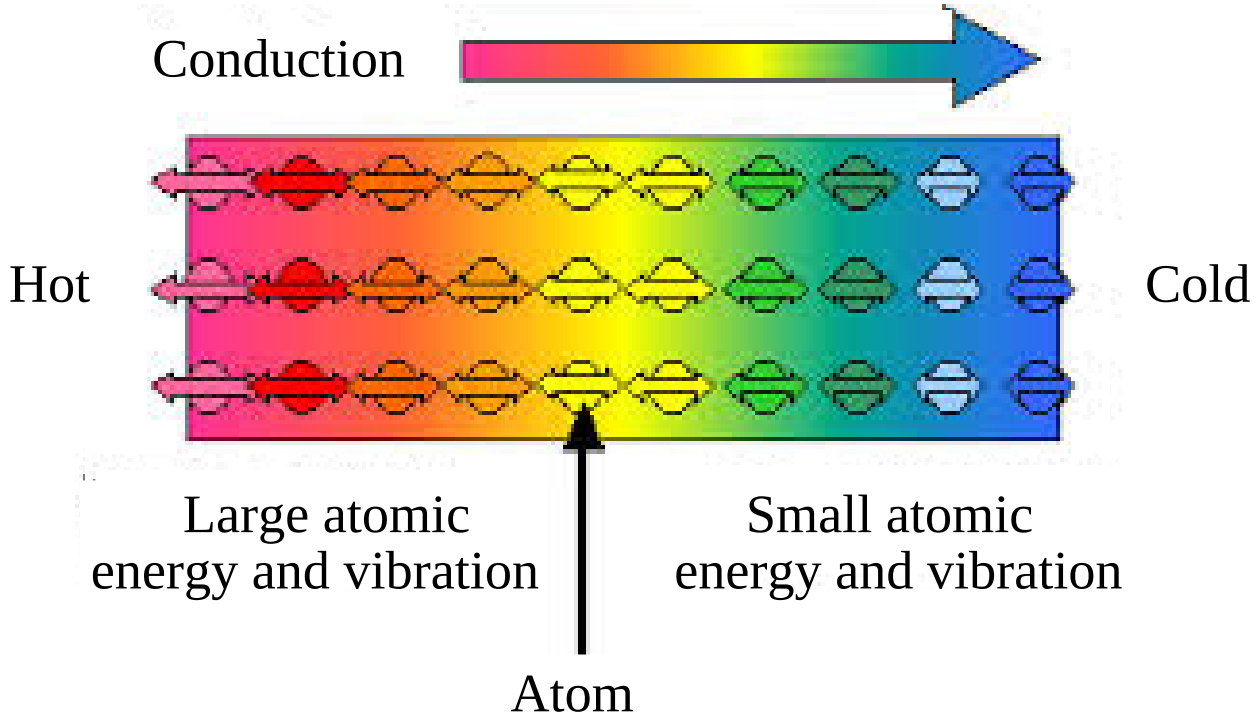
Lattice heat conduction

Heat is transported by vibrations of atoms around equilibrium positions (and also by electrons).

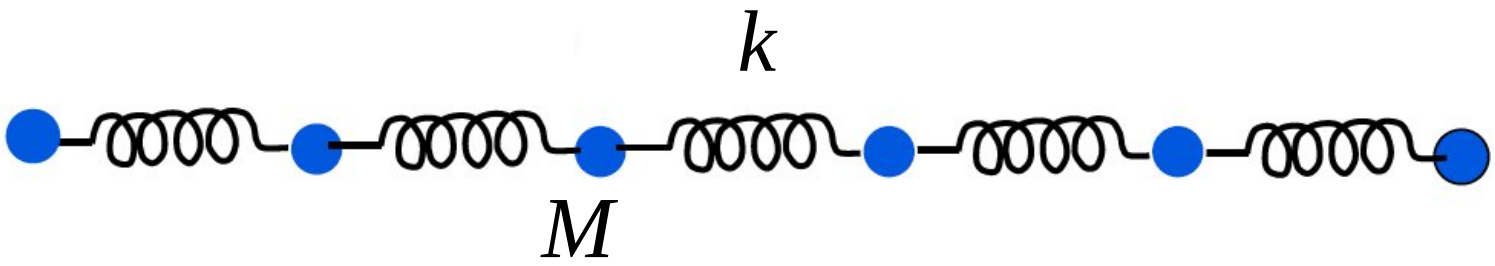


$$ZT = \sigma S^2 T/(\kappa_{\text{elec}} + \kappa_{\text{latt}}) \Rightarrow$$

κ_{latt} can be tailored separately from electronic properties!

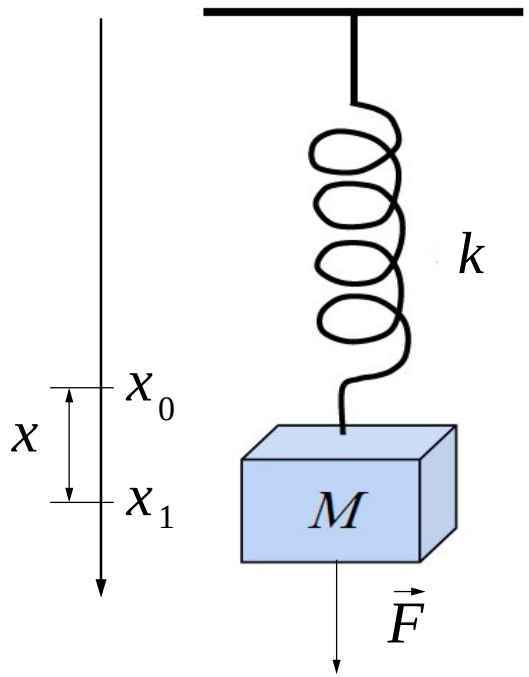
Lattice vibrations

This problem is analogous to that of coupled harmonic oscillators.

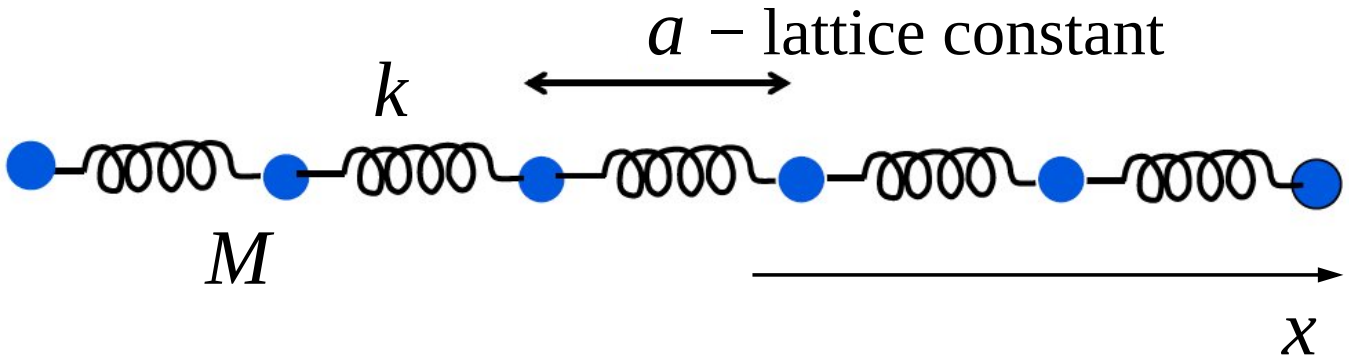


Single oscillator:

- Mass: M
- Restoring force: $F = -kx$
- Distance from equilibrium: x
- Spring constant: k
- Frequency: $\omega^2 = \frac{k}{M}$
- Energy: $U = \frac{1}{2}kx^2$



Lattice vibrations and concept of phonons



Atomic displacements from equilibrium:

$\vec{u} \sim \exp(qx - \omega t) \cdot \vec{e}_u$ – phonon modes

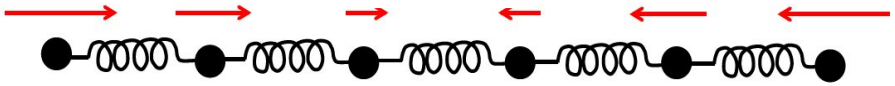
- $\vec{q} = 2\pi/\lambda \cdot \vec{e}_x$ - wave vector
- λ - wavelength
- $\vec{e}_x$ - propagation direction
- $\vec{e}_u = \vec{e}_x$ - longitudinal
- $\vec{e}_u = \vec{e}_y$ - transverse
- $\vec{e}_u = \vec{e}_z$ - transverse

Phonon dispersion: $\omega(q) = \sqrt{\frac{2k}{M}(1 - \cos(qa))}$

Phonons in diatomic materials

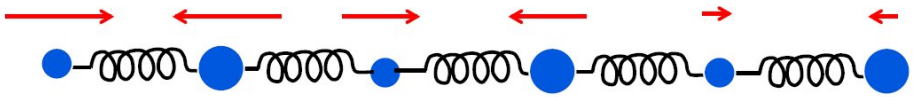
Any physical property related to lattice vibrations can be described using the concept of phonon modes.

longitudinal acoustic (LA)

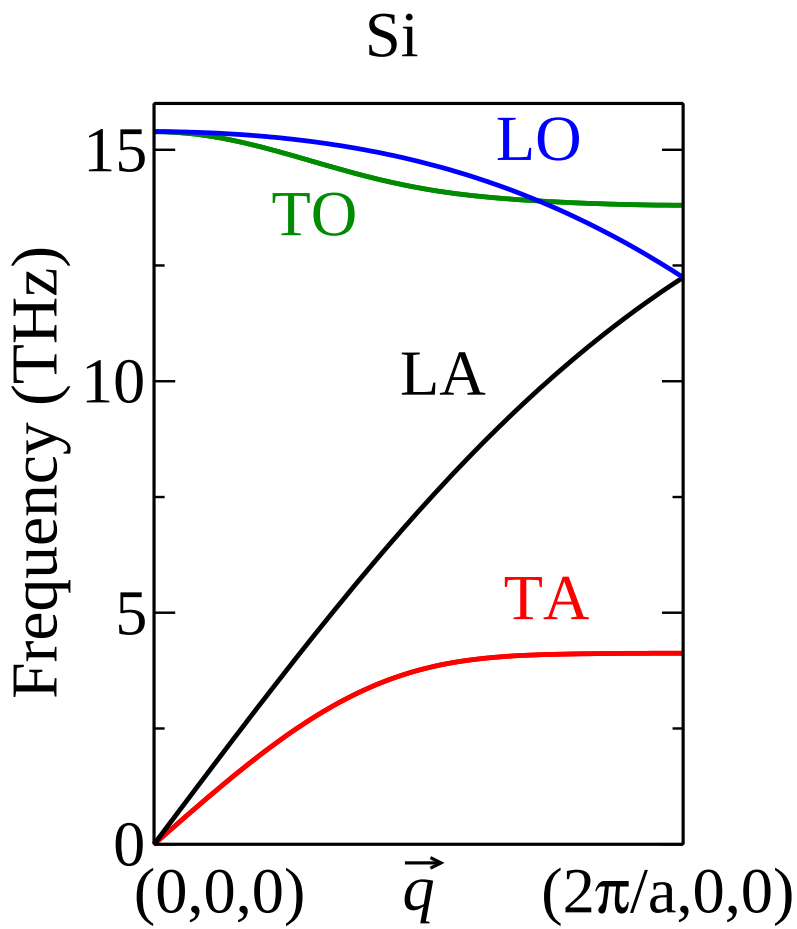


transverse acoustic (TA)

longitudinal optic (LO)

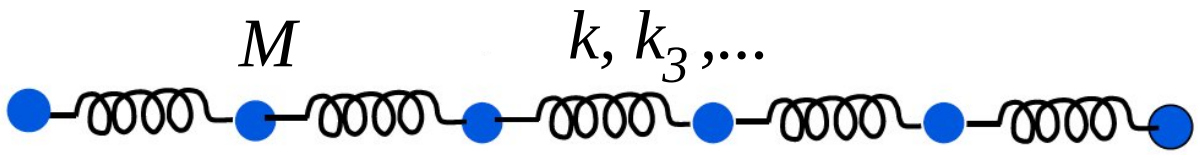


transverse optic (TO)

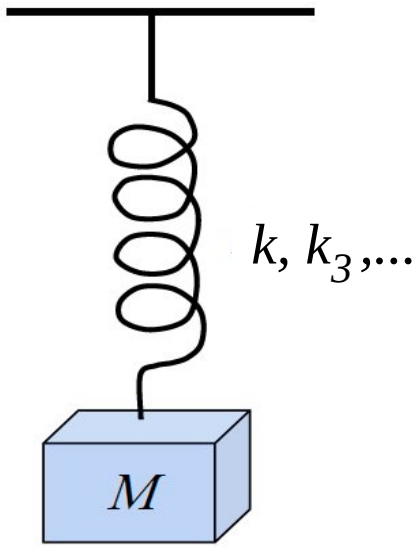


Phonon interactions with other phonons

Coupled anharmonic oscillators:

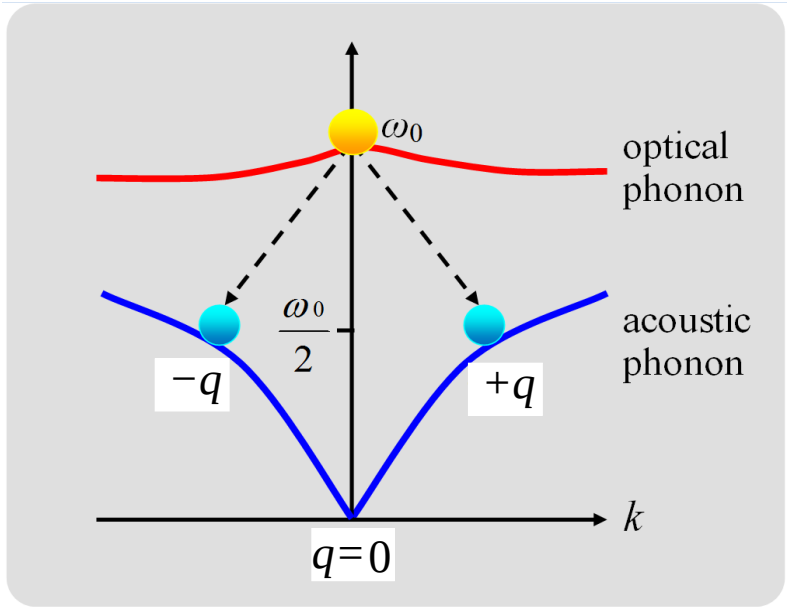


Single oscillator:



$$U = \frac{1}{2}kx^2 + \frac{1}{6}k_3x^3 + ...$$

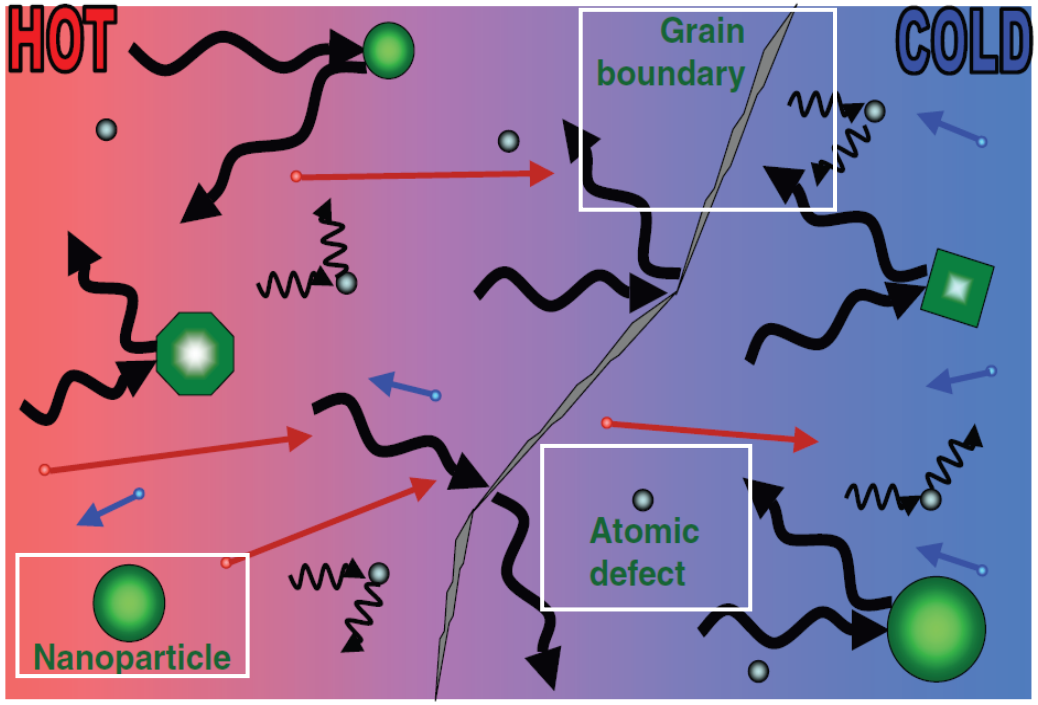
Phonon-phonon interaction



Dominant in bulk crystalline materials

Phonon interactions with crystal imperfections

Scattering due to atomic scale defects and interfaces.



C. J. Vineis *et al.*, Adv. Mat. **22**, 3970 (2010)

Dominant in alloys and nanostructures

Lattice thermal conductivity

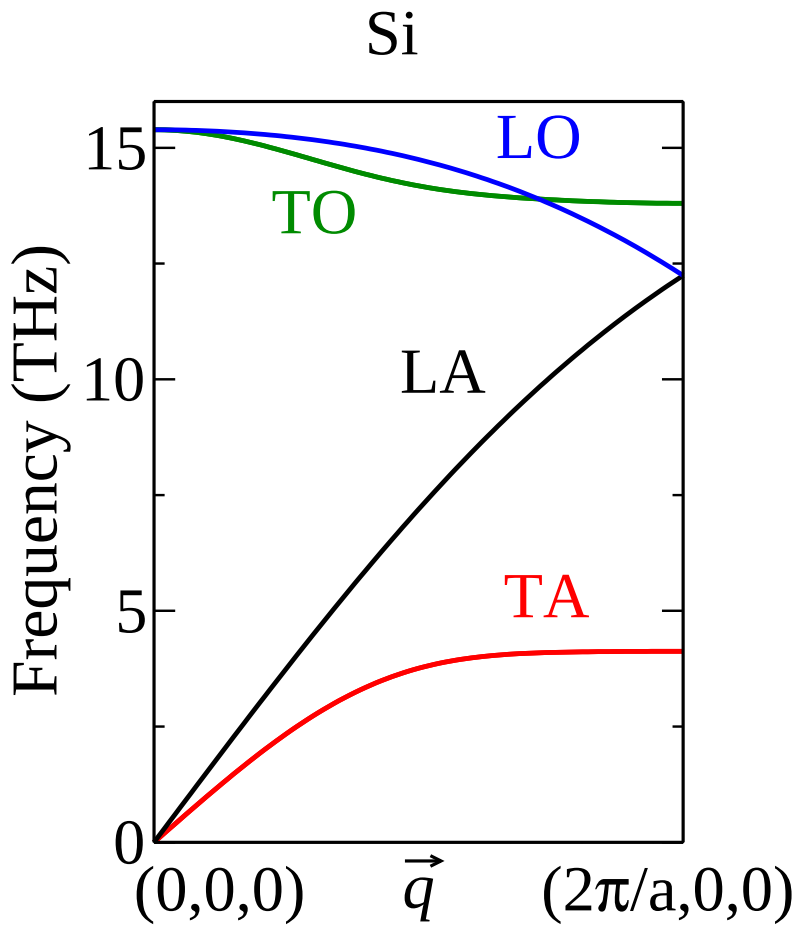
$$\kappa_{\text{latt}} = \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q},s} \frac{\partial n_{\mathbf{q},s}}{\partial T} v^2_{\mathbf{q},s} \tau_{\mathbf{q},s}$$

- $\mathbf{q}$ - phonon wave vector; s - phonon mode (TA,LA,TO,LO)
- $\omega_{\mathbf{q},s}$ - phonon frequencies
- $n_{\mathbf{q},s} = \frac{1}{\exp(\hbar\omega_{\mathbf{q},s}/k_B T)-1}$ - phonon occupations
- $v_{\mathbf{q},s} = \partial\omega_{\mathbf{q},s}/\partial\mathbf{q}$ - group velocities
- $\tau_{\mathbf{q},s}$ - phonon lifetimes due to phonon interactions

By manipulating $\omega_{\mathbf{q},s}$ and $\tau_{\mathbf{q},s}$, we can tailor their κ_{latt}!

Lattice thermal conductivity and acoustic phonons

- $\kappa_{\text{latt}} = \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q},s} \frac{\partial n_{\mathbf{q},s}}{\partial T} v^2_{\mathbf{q},s} \tau_{\mathbf{q},s}$
- $v_{\mathbf{q},s} = \partial\omega_{\mathbf{q},s}/\partial\mathbf{q}$ - group velocities
- $v_{\mathbf{q},\text{LA/TA}} \gg v_{\mathbf{q},\text{LO/TO}}$
- Heat is carried mainly by acoustic modes in most materials.



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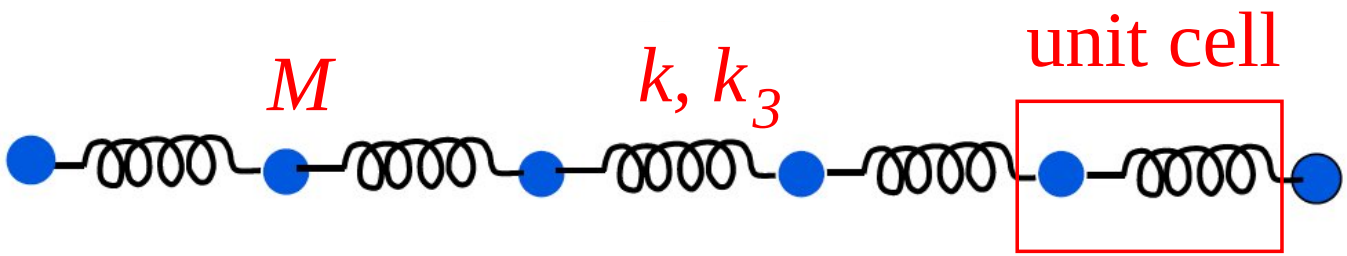
Low lattice thermal conductivity in bulk materials



Energy: $U \approx \frac{1}{2}kx^2 + \frac{1}{6}k_3x^3$

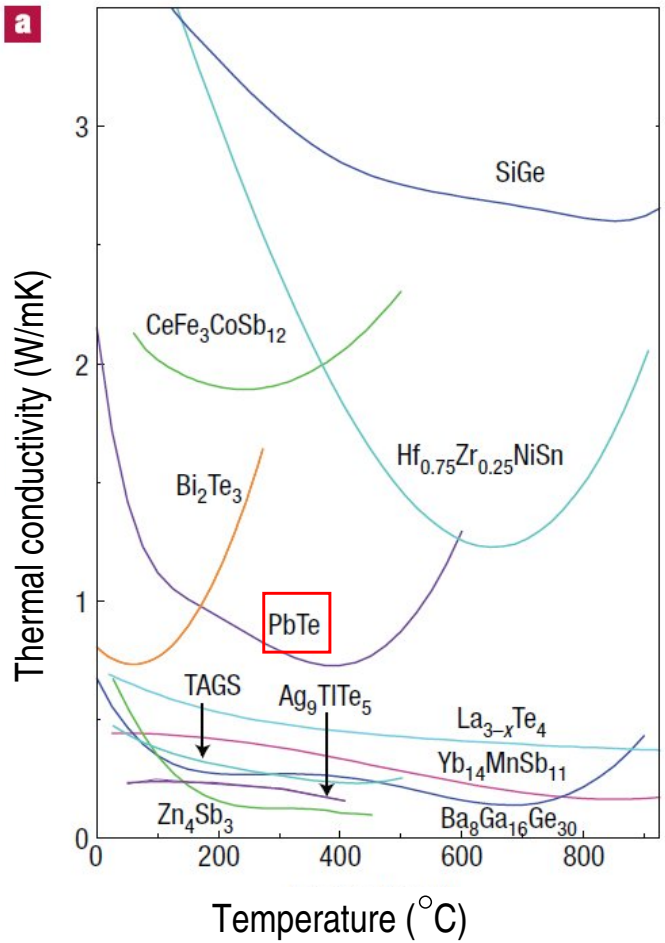
Conventional guidelines from the analysis of acoustic modes only:

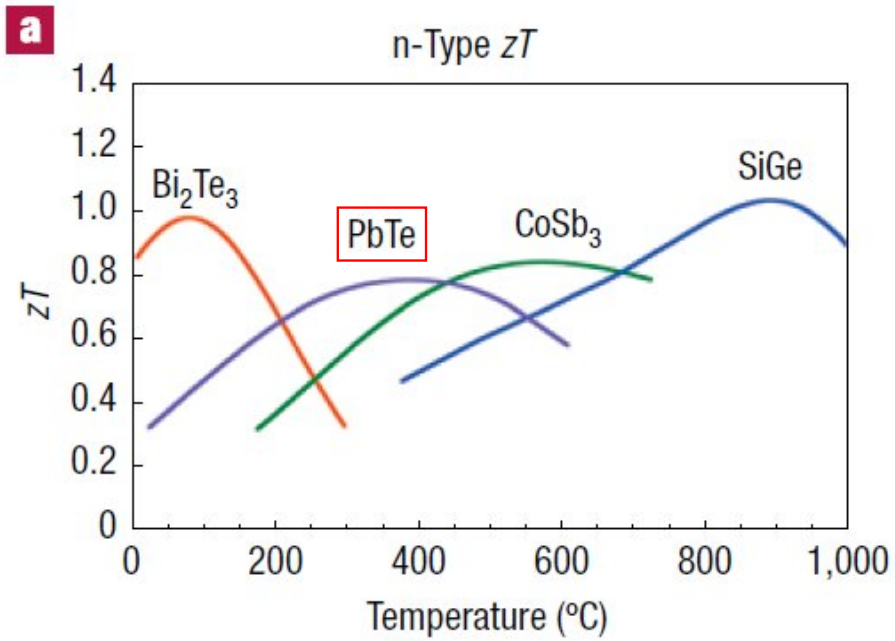
- Large number of atoms in the unit cell.
- High average atomic mass.
- Weak interatomic bonding (small k).
- High anharmonicity (large k_3).

G. A. Slack, J. Phys. Chem. Solids **34**, 321 (1973)

PbTe - partial exception to the conventional guidelines

- One of the best bulk thermoelectrics at ~ 700 K due to low κ_{latt}.
- Used for waste heat recovery applications.



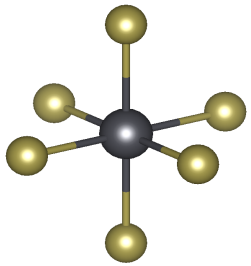


G. J. Snyder and E. S. Toberer, Nature Mater. **7**, 105 (2008)

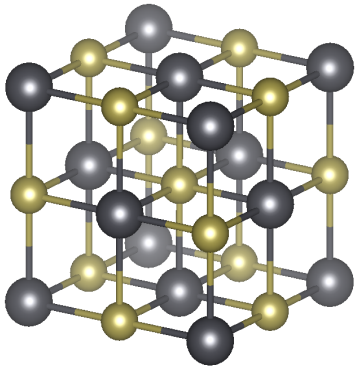
PbTe - partial exception to the conventional guidelines

IV	V	VI
	P	S
Ge	As	Se
Sn	Sb	Te
Pb	Bi	

octahedral bond



rock–salt structure

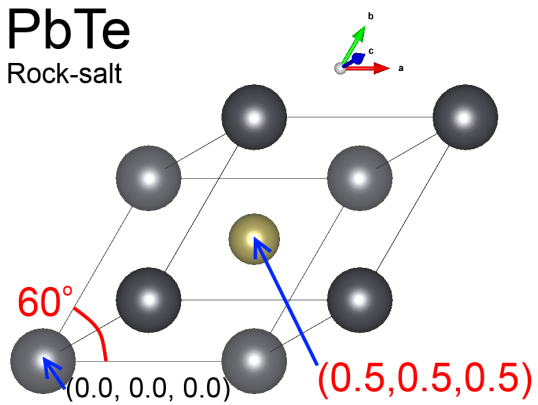


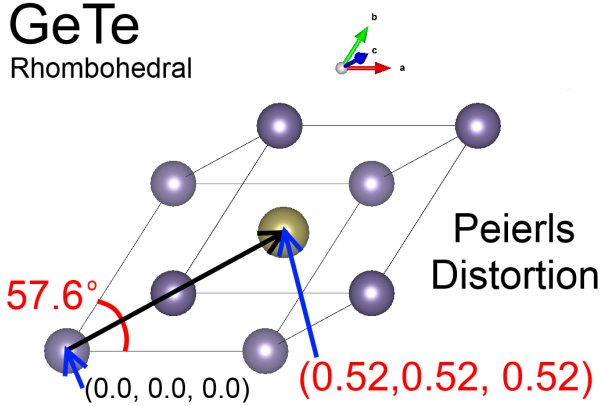
- High average atomic mass (Pb - 207.2, Te - 127.6).
- Unusually low κ_{latt} for a material with a small unit cell (2 atoms):

Material	Si	Ge	Bi	PbTe
κ (W/mK) at 300 K	155	65	8	2

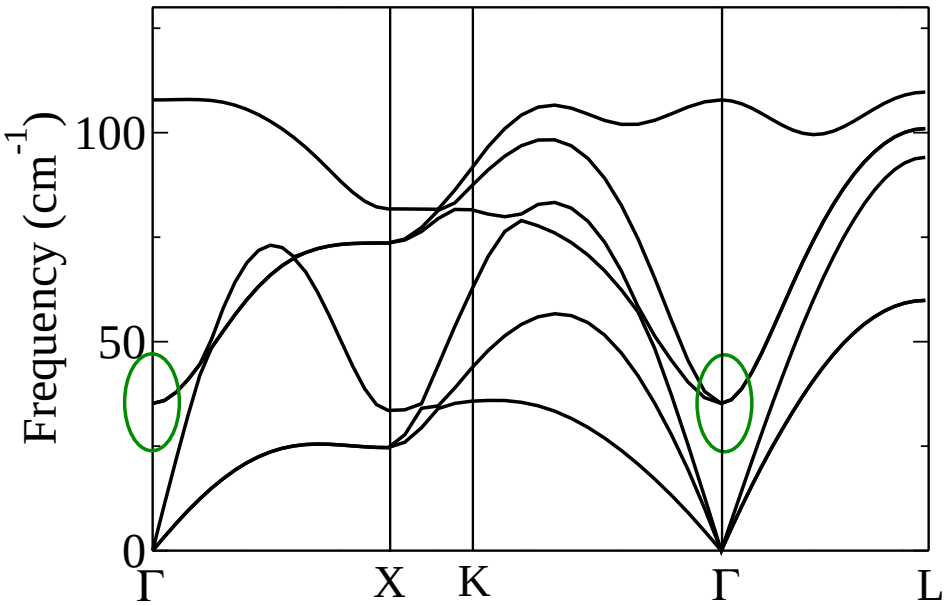
PbTe - partial exception to the conventional guidelines

Close to the phase transition to a rhombohedral structure:





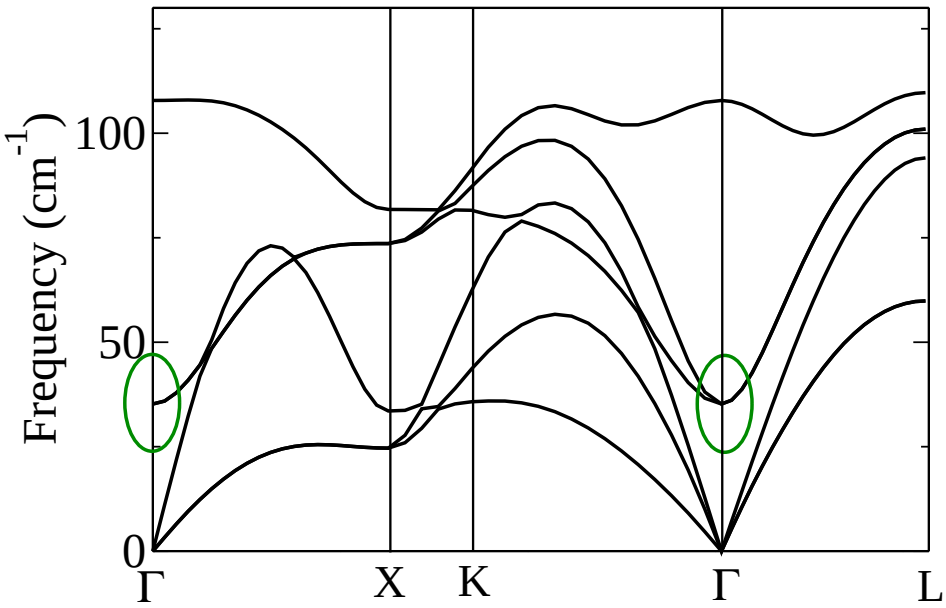
Soft transverse optical (TO) modes:



PbTe - partial exception to the conventional guidelines

- Weak bonding and high anharmonicity for TO modes, but not for heat carrying acoustic modes!
- The main effect: soft TO modes interact strongly with acoustic modes.
- Low phonon lifetimes and lattice thermal conductivity.

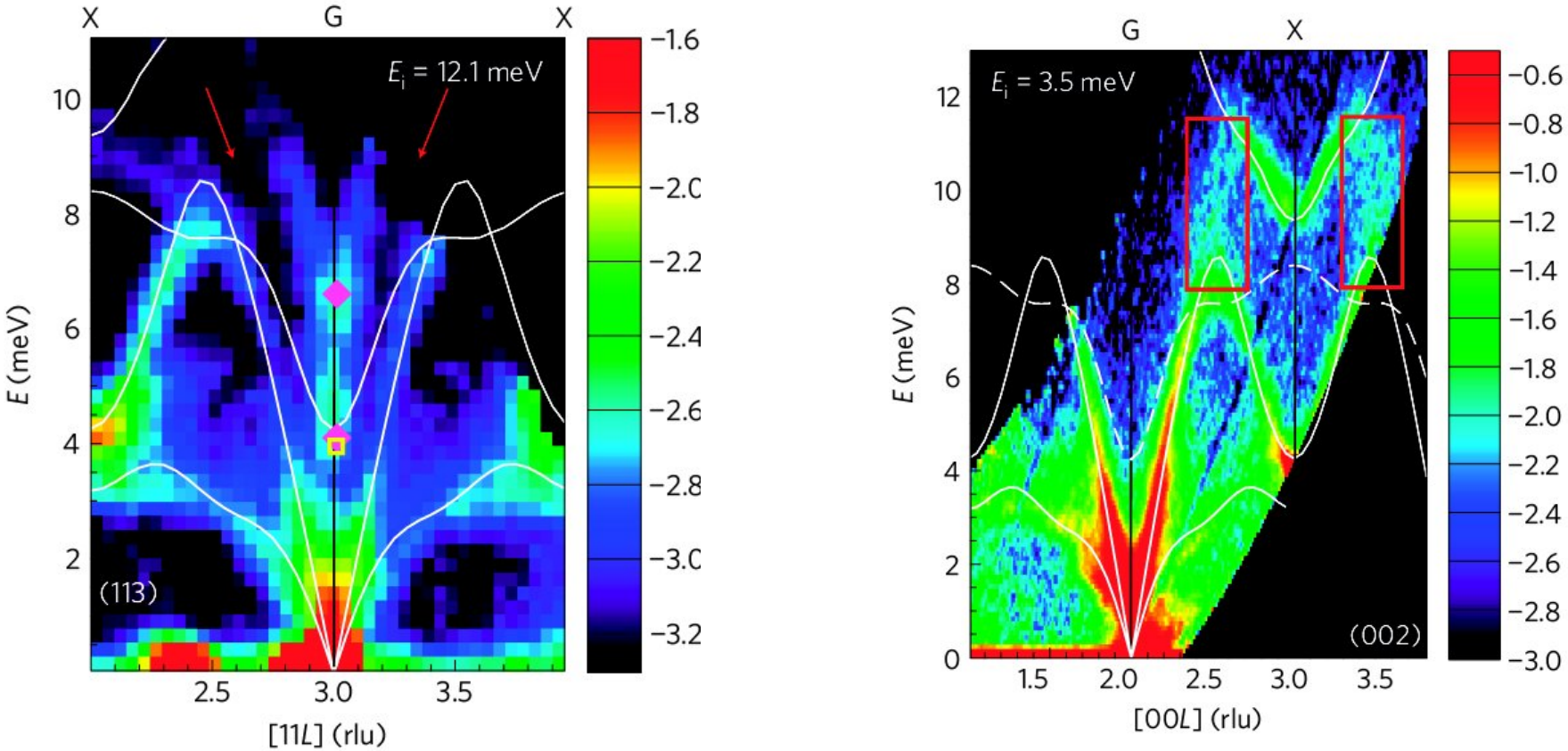
Soft transverse optical (TO) modes:



Conventional guidelines do not provide the full picture!

Experimental evidence of strong acoustic-optical interaction in PbTe

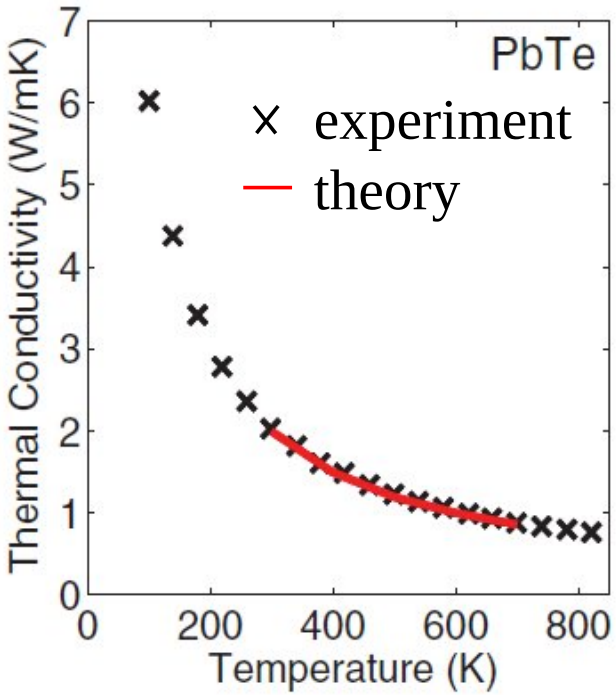
Detailed information on phonon dynamics using new experimental techniques/instrumentation:

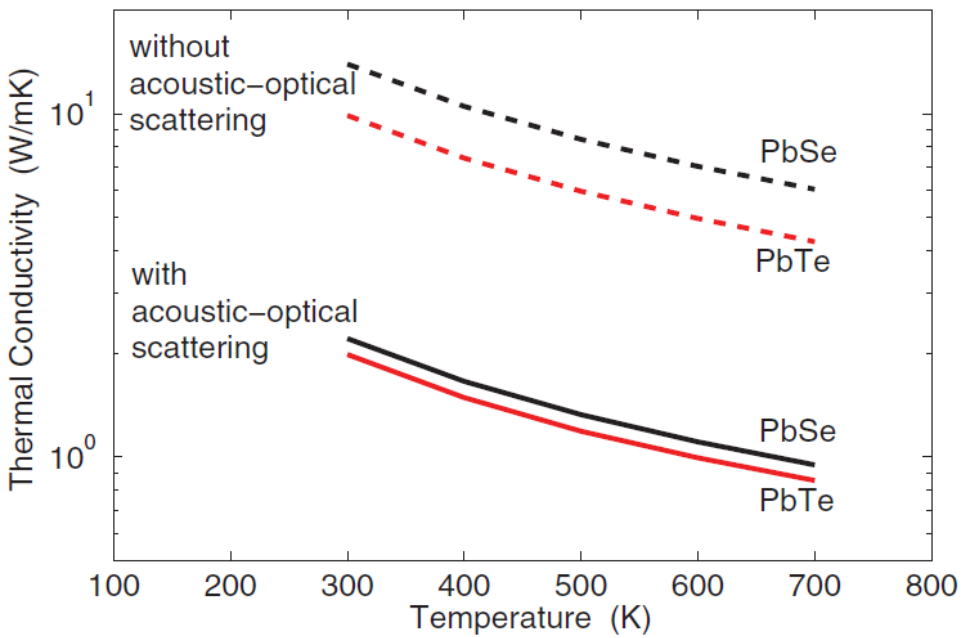


O. Delaire *et al.*, Nature Mater. **10**, 614 (2011)

Theoretical evidence of strong acoustic-optical interaction in PbTe

Detailed information on phonon dynamics using new quantitative theories:



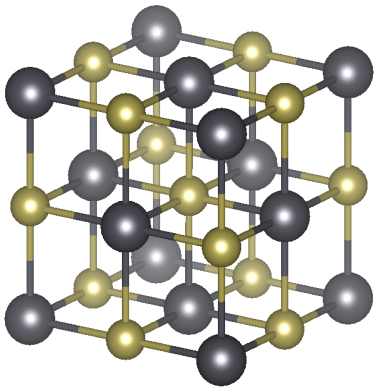


Z. Tian *et al.*, PRB **85**, 184303 (2012)

First principles approach to calculate lattice thermal conductivity

Energy: $U \approx \frac{1}{2}kx^2 + \frac{1}{6}k_3x^3$

No fitting parameters, atomic structure is the only input!



→ quantum physics → k, k_3 → quantum, classical & statistical physics → $\omega, \tau, \kappa_{latt}$

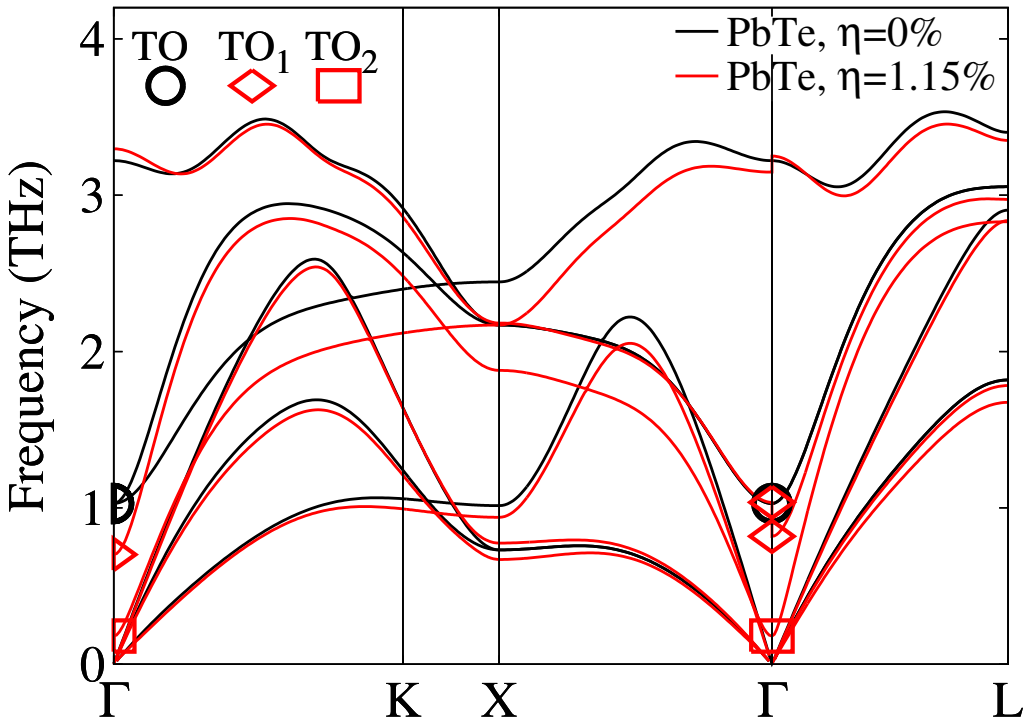
Usually very good agreement with experiments.

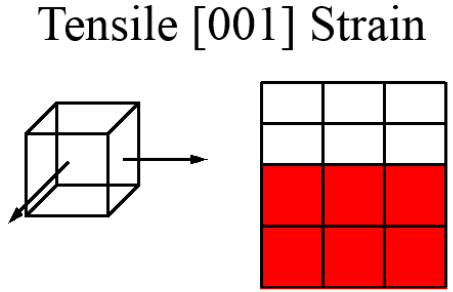
D. A. Broido *et al.*, APL **91**, 231922 (2007)

Increasing acoustic-optical phonon interaction to reduce κ_{latt} of PbTe

Drive PbTe closer to the phase transition e.g. via strain

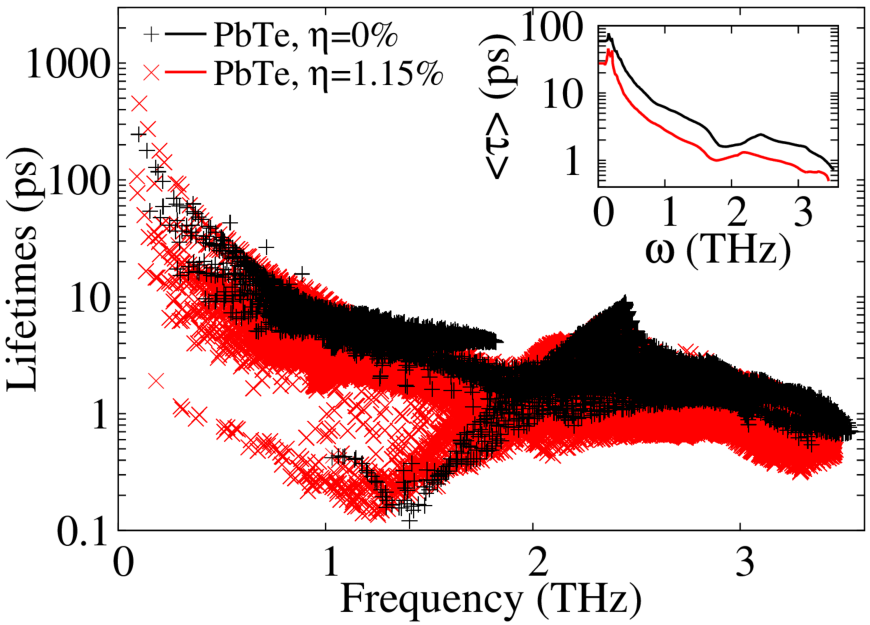
$\Rightarrow$ softening of TO modes.

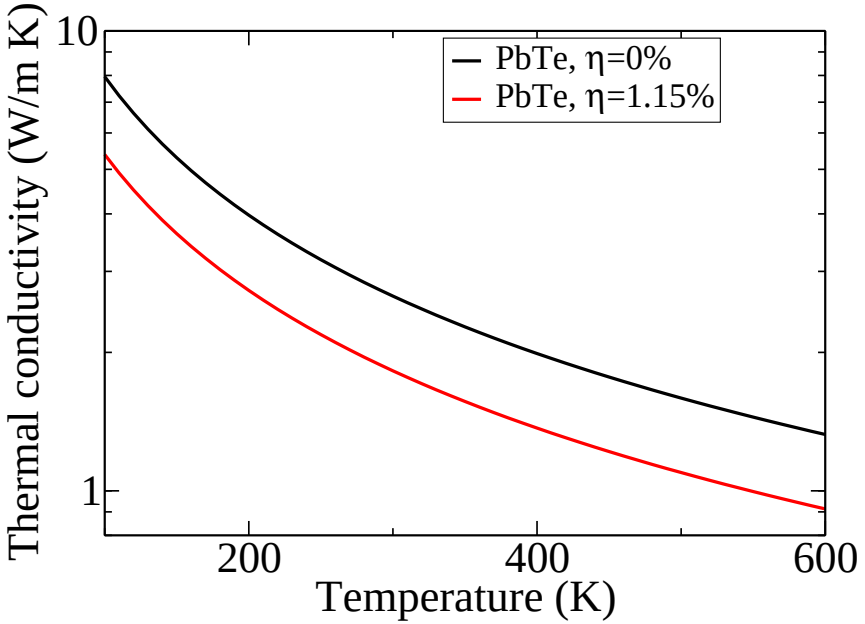




Tensile [001] strain: $\eta = (a_{\parallel} - a_0)/a_0 = +1.15\%$.

Increasing acoustic-optical phonon interaction to reduce κ_{latt} of PbTe



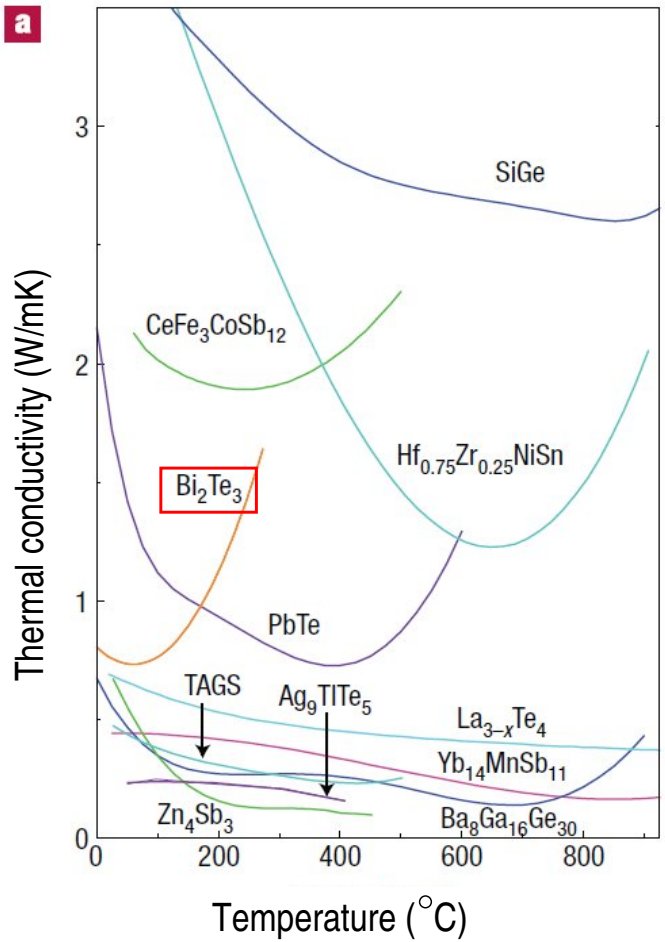


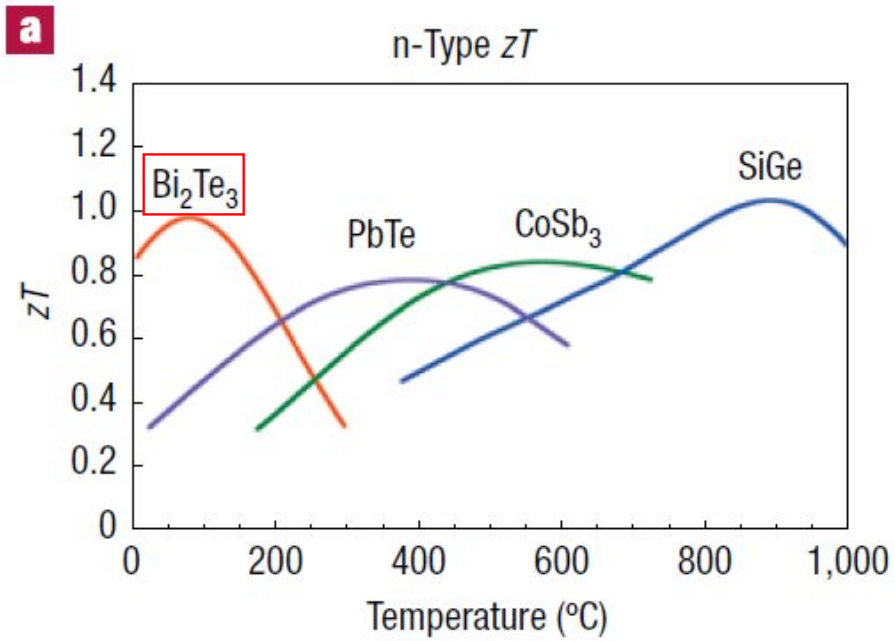
- Phonon lifetimes are reduced at all frequencies.
- κ_{latt} of strained PbTe is reduced by a factor of 1.5 compared to PbTe.

R. Murphy, É. Murray, S. Fahy, and I. Savić, submitted

Bi_2Te_3 - another efficient thermoelectric material

- The best bulk thermoelectric at ~ 300 K due to low κ_{latt}.
- Used for environmental heat harvesting and solid state cooling.

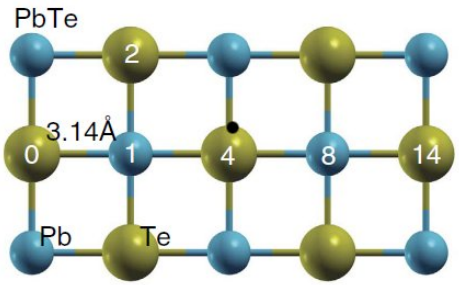


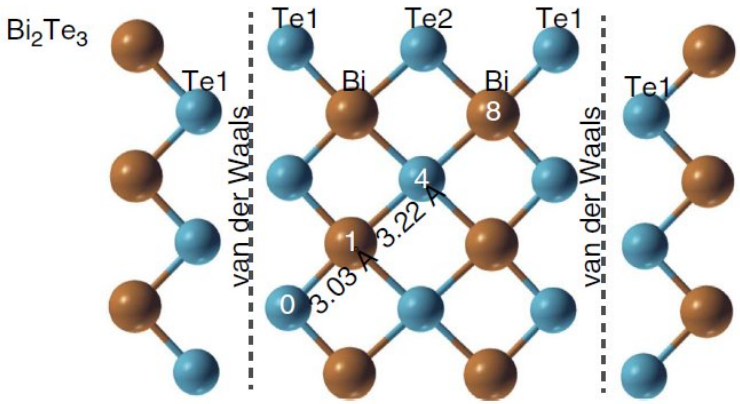


G. J. Snyder and E. S. Toberer, Nature Mater. **7**, 105 (2008)

Low lattice thermal conductivity of Bi_2Te_3

Bi_2Te_3 is structurally related to PbTe:





Nature Comm. **5**, 3525 (2014)

Very low κ_{latt} can be explained by conventional guidelines:

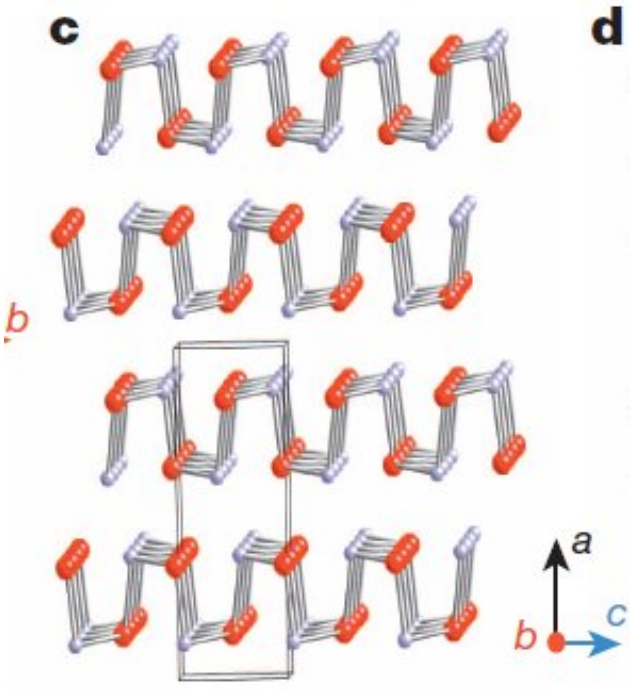
- High average atomic mass
- Complex unit cell (5 atoms)
- Weak bonding
- High anharmonicity

Coventional design rules are very useful nevertheless.

PRB **90**, 134309 (2014)

SnSe - new record thermoelectric material

IV-VI compound like PbTe:



A factor of $2-3$ lower κ_{latt} than that of PbTe despite much lighter atoms.

Low κ_{latt} values can be explained by other conventional rules:

- Complex unit cell (8 atoms)
- Weak bonding
- High anharmonicity

$ZT \sim 2.6$ at 900 K: the highest reported ZT in any material!

L. D. Zhao *et al.*, Nature **508**, 373 (2015)

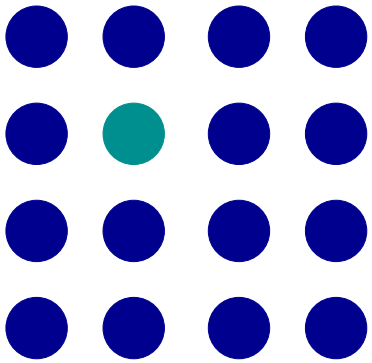
Outline

- Thermoelectric energy conversion for ICT applications
- Basic concepts related to lattice thermal conductivity
- Strategies to design the lattice thermal conductivity of:
  - Bulk crystalline materials
  - Bulk materials with atomic scale disorder
  - Nanostructured materials
- Summary and outlook

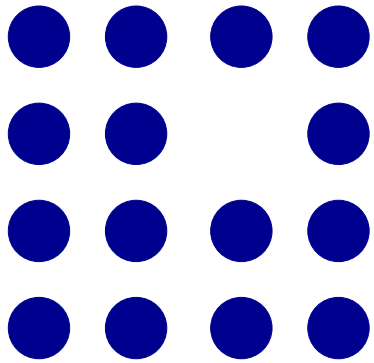
Bulk materials with atomic scale disorder

A few types of atomic scale defects in materials:

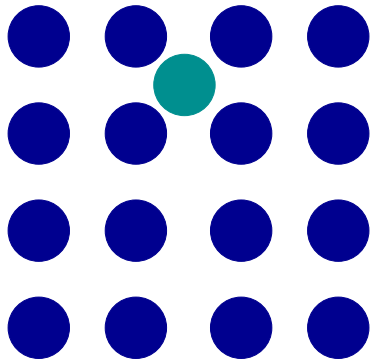
substitutional impurity



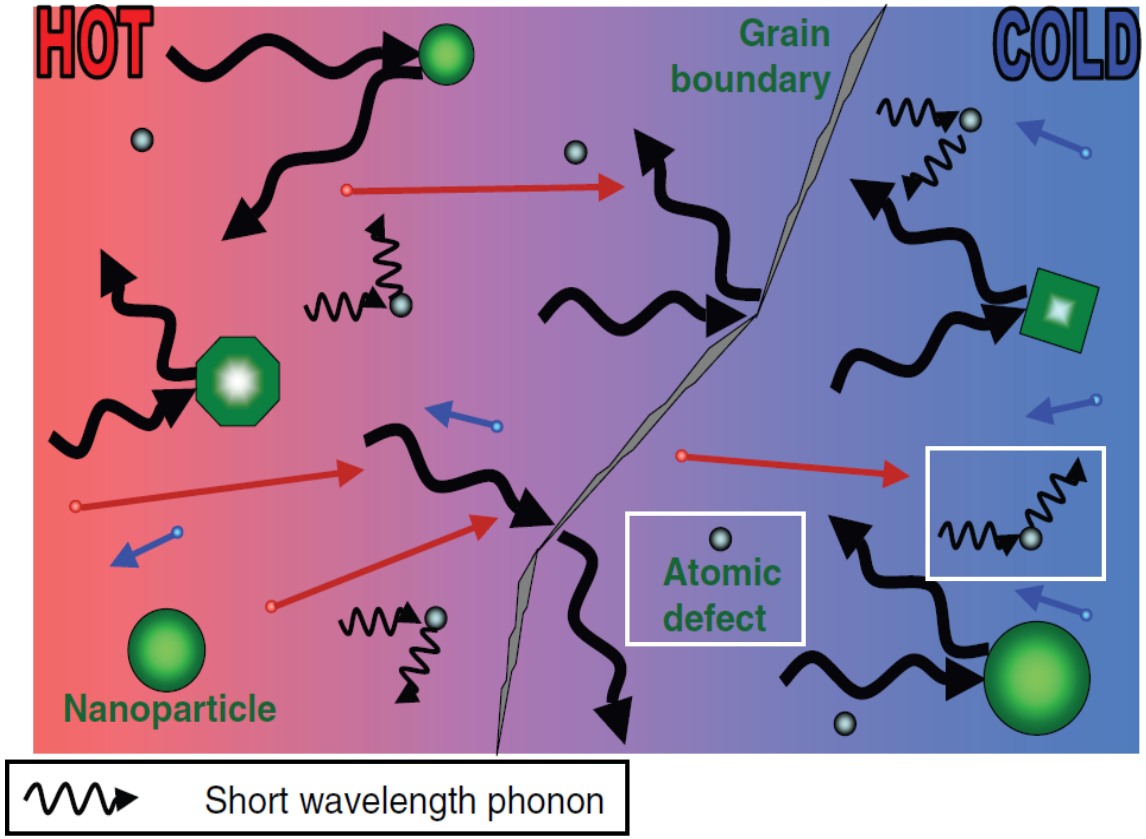
vacancy



interstitial impurity



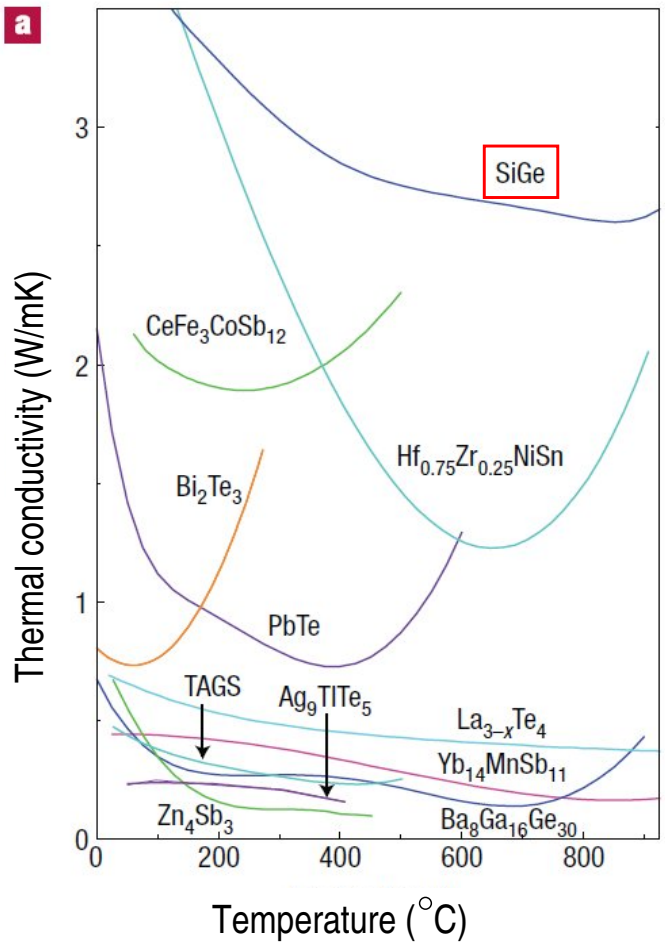
Bulk materials with atomic scale disorder

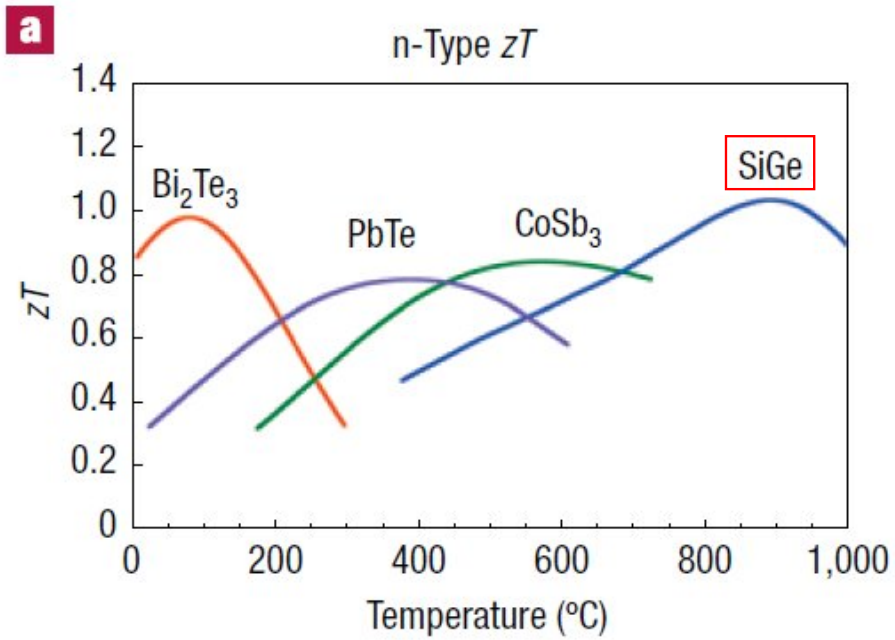


Atomic scale defects scatter short-wavelength phonons.

Si_xGe_{1-x} alloys

- One of the best thermoelectrics at ~ 900 K due to fairly low κ_{latt}.
- Used for power generation in space missions.

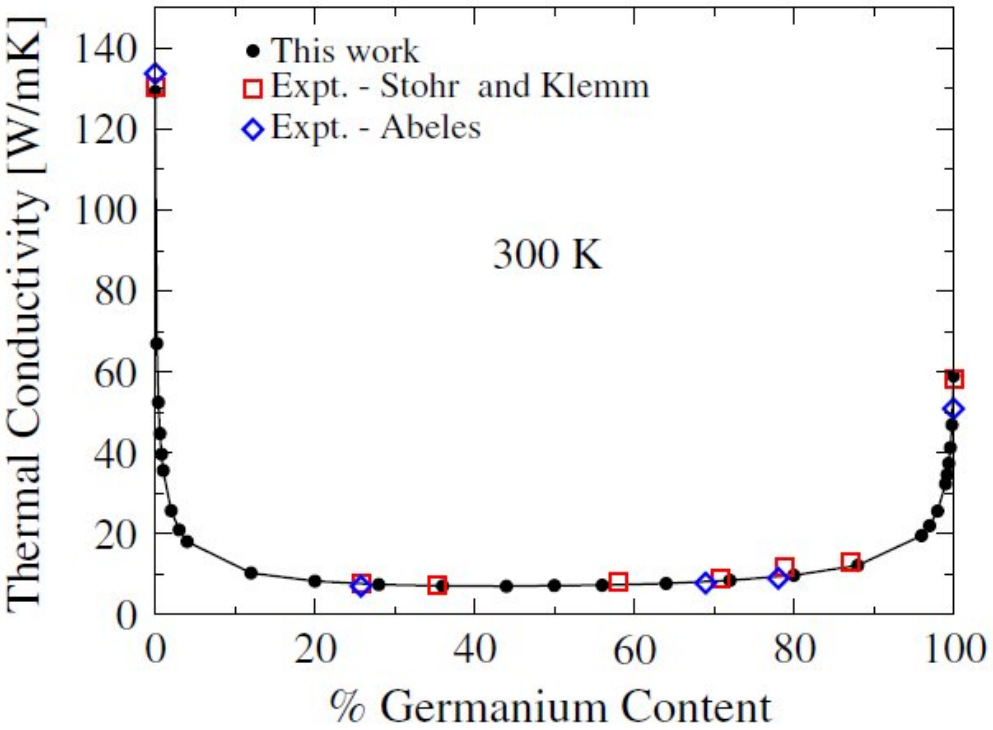




G. J. Snyder and E. S. Toberer,
Nature Mater. **7**, 105 (2008)

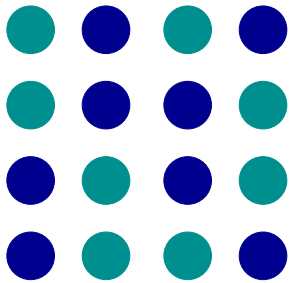
Si_xGe_{1-x} alloys

Mass disorder strongly reduces the lattice thermal conductivity of SiGe alloys with respect to Si and Ge.



Atomic mass:
Si - 28.1, Ge - 72.6

Mass disorder



J. Garg *et al.*, PRL **106**, 045901 (2011)

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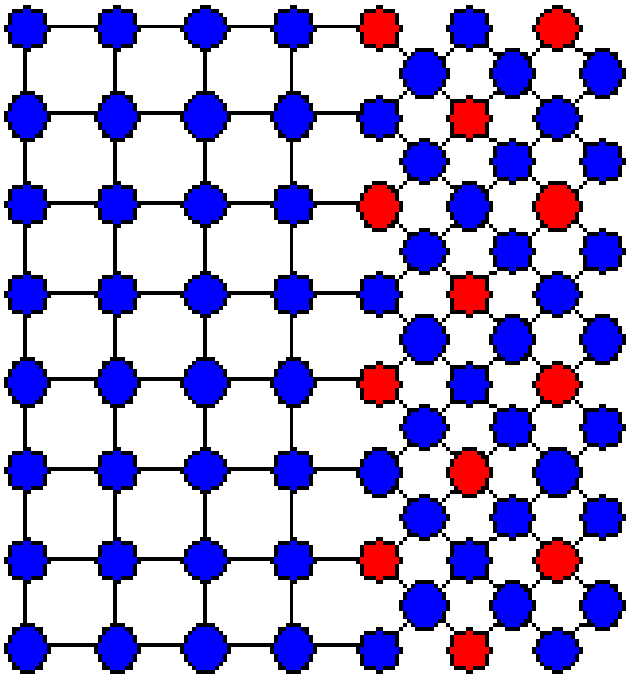
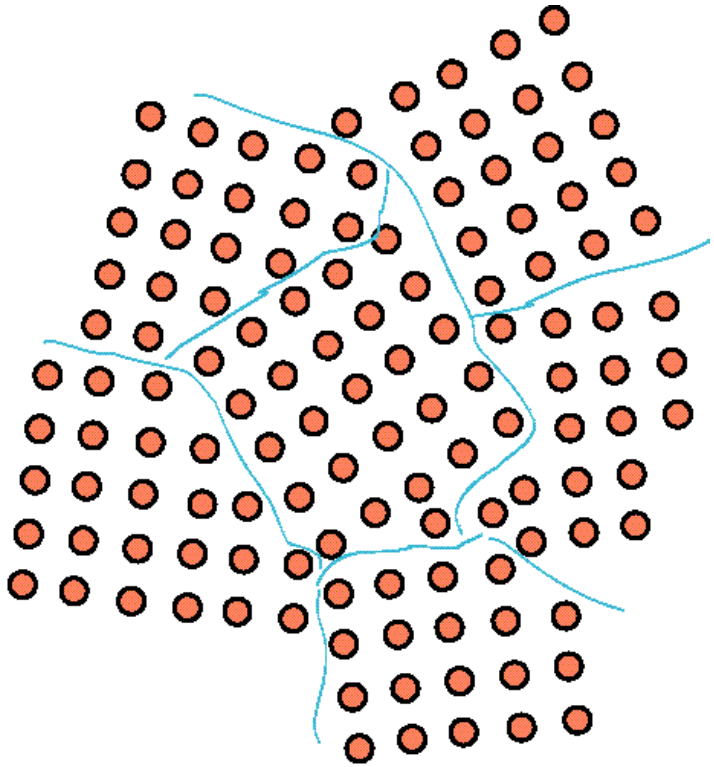
Nanostructured materials

A few types of interfaces:

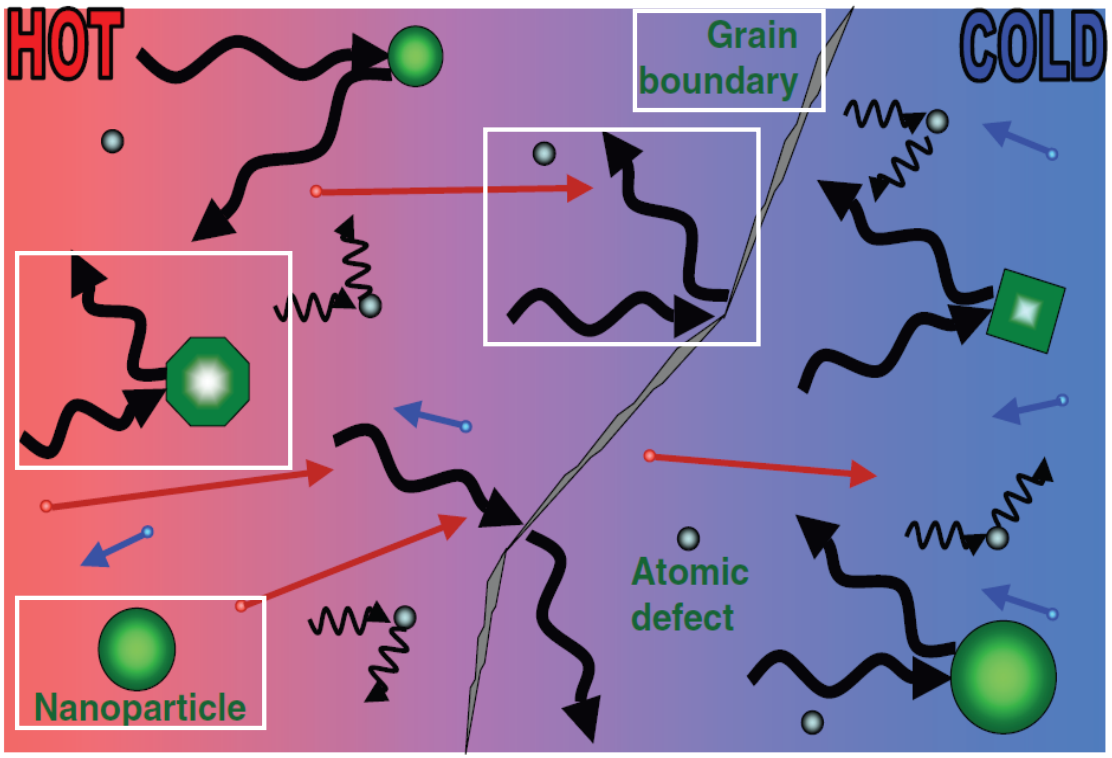
Between different materials



Between different crystal orientations (grain boundaries):



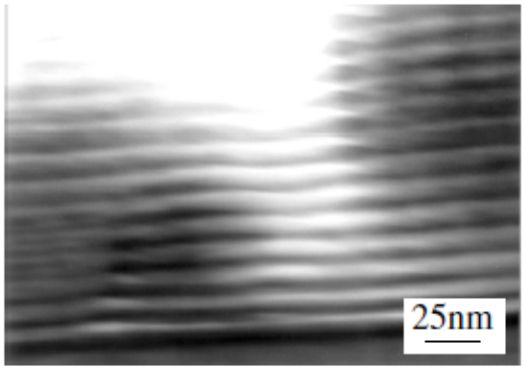
Nanostructured materials

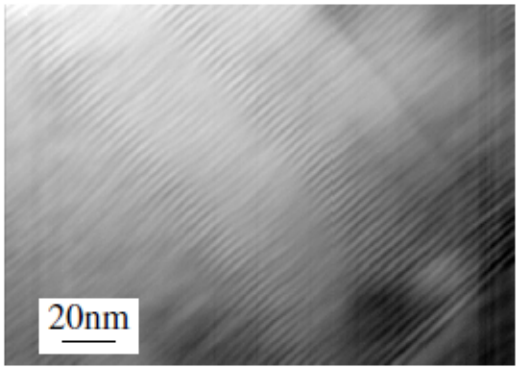


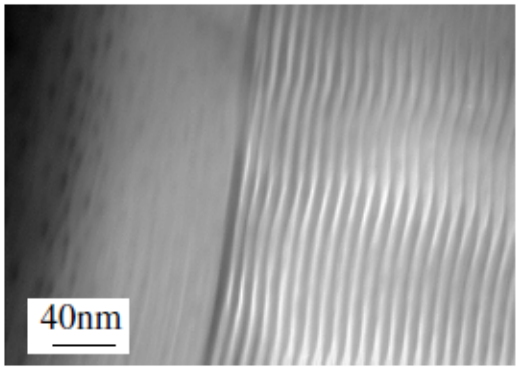
Interfaces scatter mid/long-wavelength phonons.

Proof-of-concept: thin film superlattices

Considerably reduced κ_{latt} with respect to bulk due to interfaces







- Si/Ge superlattices grown by MBE.

  Superlatt. Microstruct. **28**, 199 (2000)
- Bi_2Te_3/Sb_2Te_3 superlattices grown by MOVPE.

  Nature **413**, 597 (2001)
- PbTe/PbSe quantum dot superlattices grown by MBE.

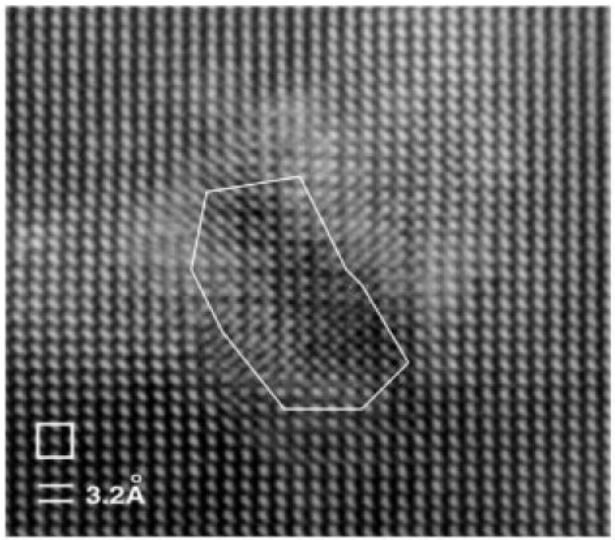
  Science **297**, 2229 (2002)

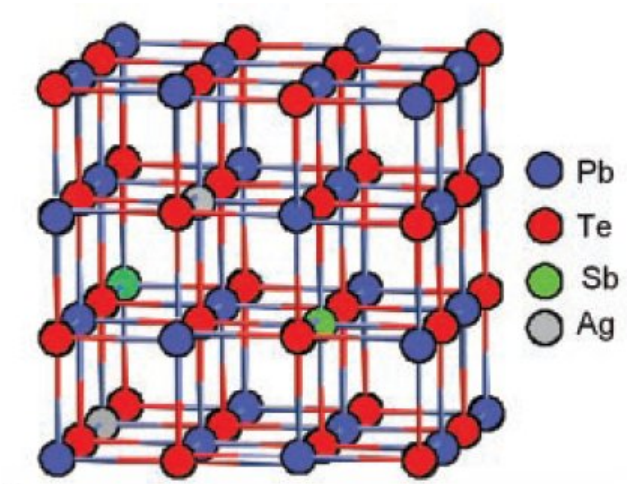
Bulk nanostructured materials

Self-formed nanoscale inclusions driven by phase segregation

Example: $AgPb_{18}SbTe_{20}$

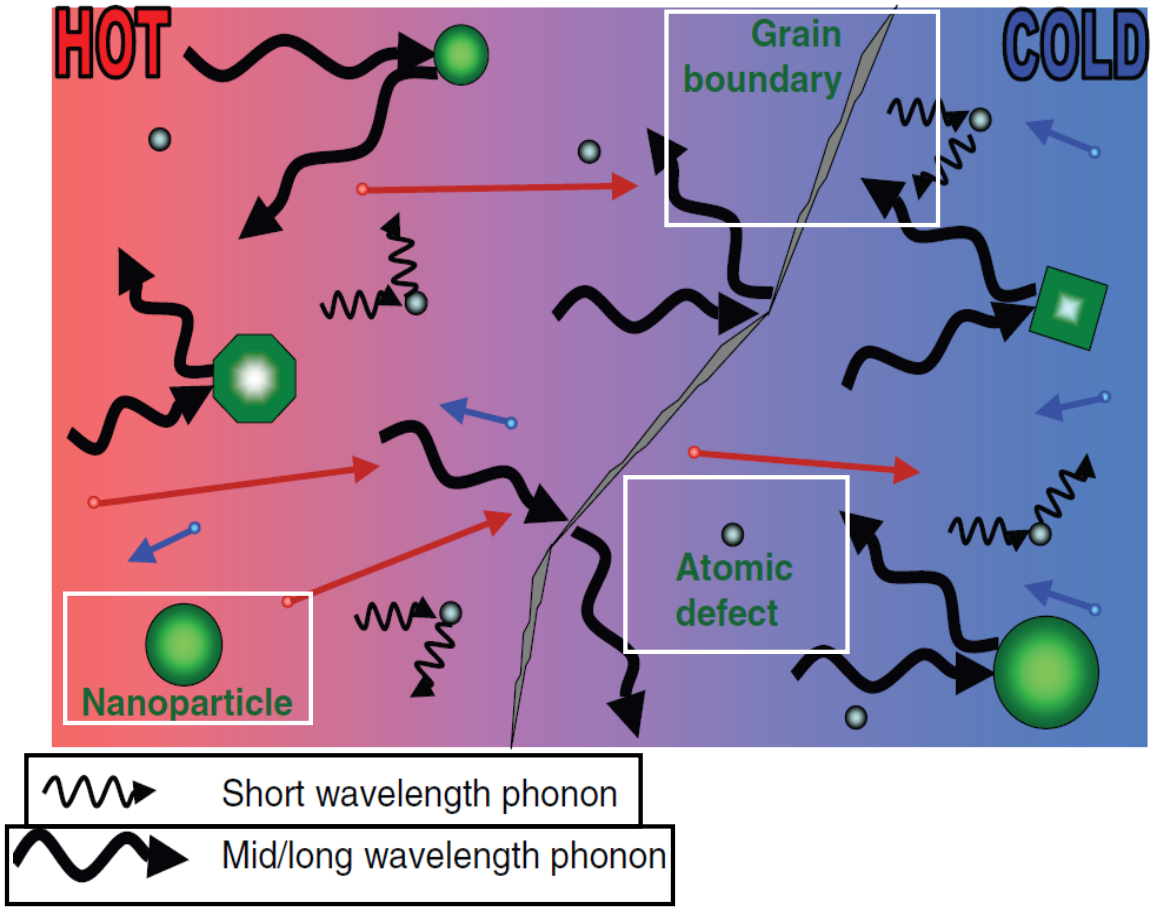
κ_{latt} is $4-5$ times smaller than that of PbTe due to nanoparticles





Science **303**, 818 (2004); Chem. Mater. **22**, 648 (2010)

Complex nanostructured materials

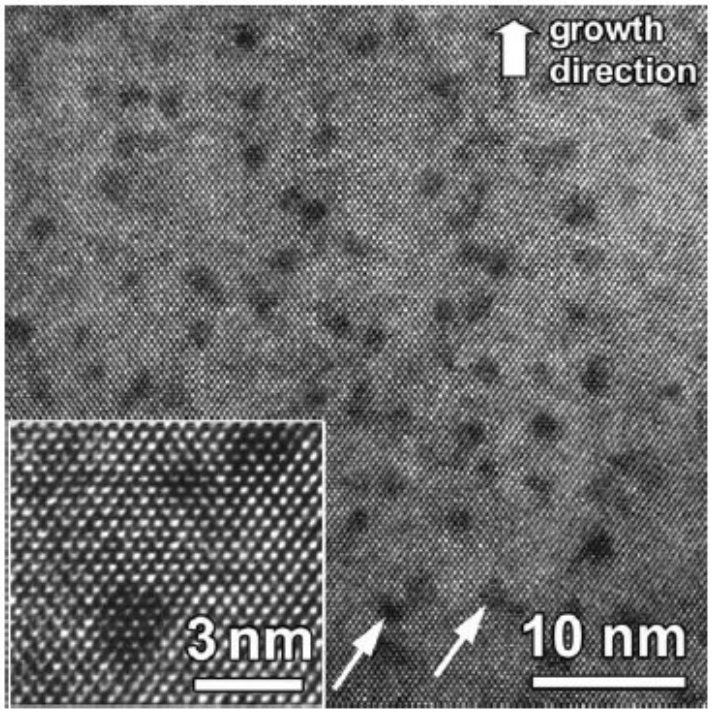


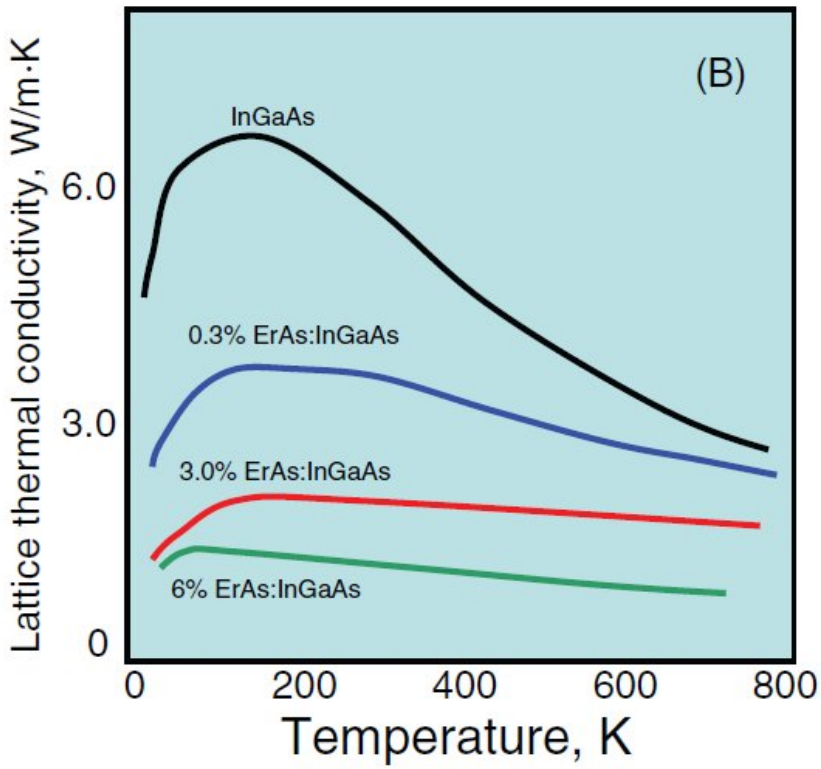
Combine atomic scale defects with interfaces $\Rightarrow$

scatter short- and mid/long-wavelength phonons simultaneously.

Nanoparticles embedded in alloys

ErAs nanoparticles in a InGaAs matrix lead to significantly reduced κ_{latt} with respect to InGaAs.





APL **87**, 112102 (2005); PRL **96**, 045901 (2006)

Bulk nanocomposites

Assembly of nanosized particles by ball-milling and hot-pressing of alloys.

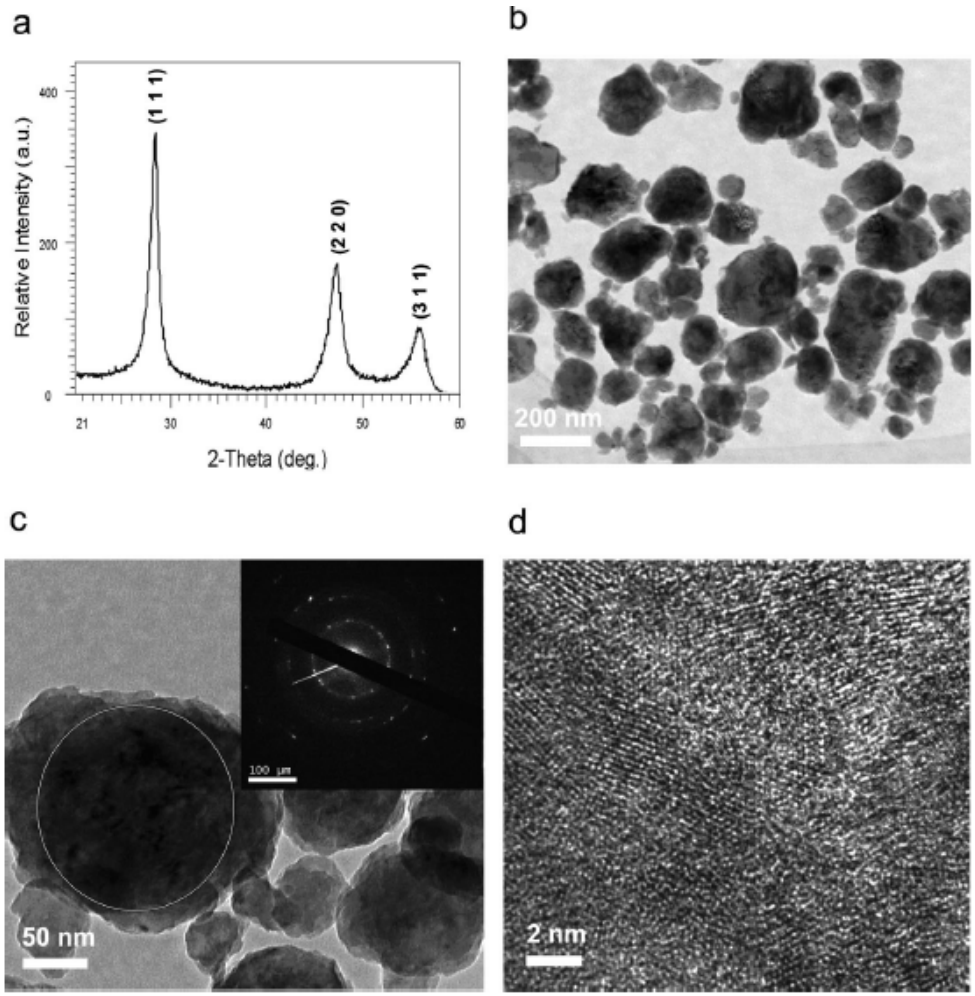
Very low κ_{latt} due to interfaces and alloy disorder.

- $(Bi,Sb)_2Te_3$ alloys:

  Science **320**, 634 (2008)

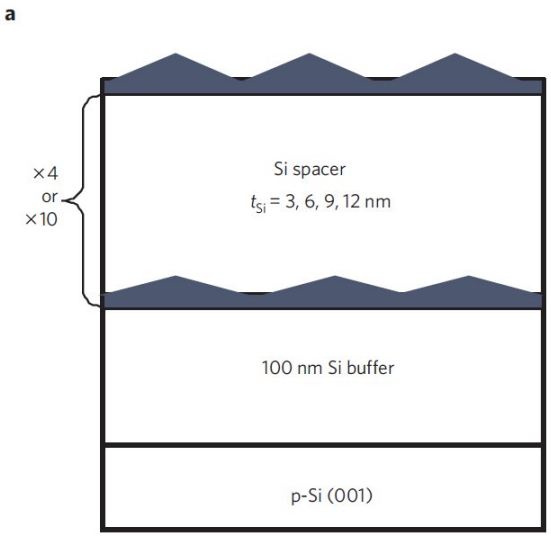
- SiGe alloys:

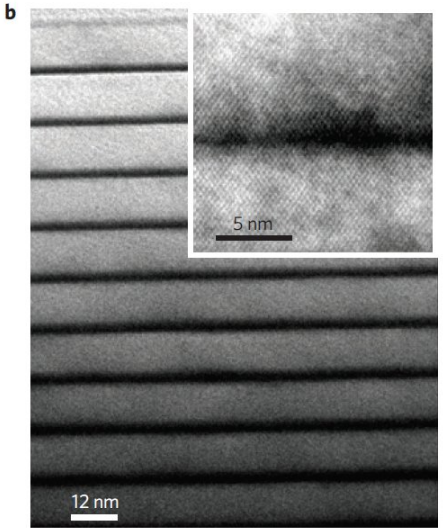
  Nano Lett. **8**, 4670 (2008)

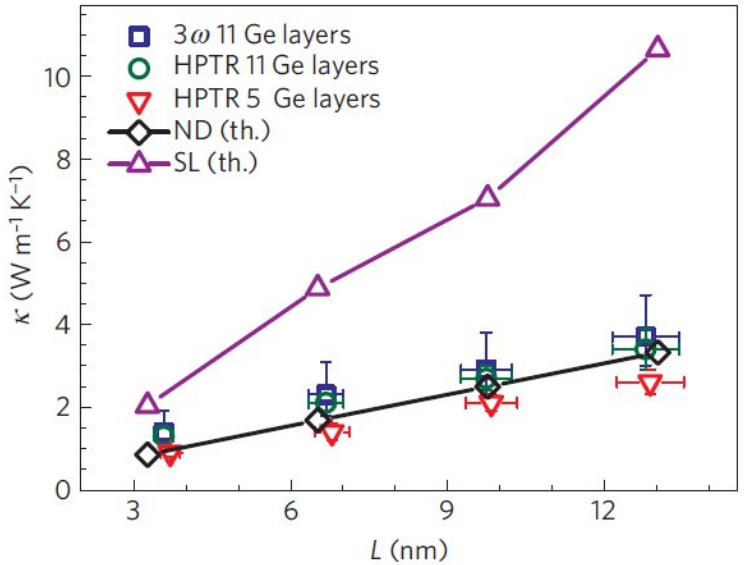


SiGe nanodots in a Si matrix

Another combination of nanostructuring and alloy disorder leads to very low κ_{latt} values.

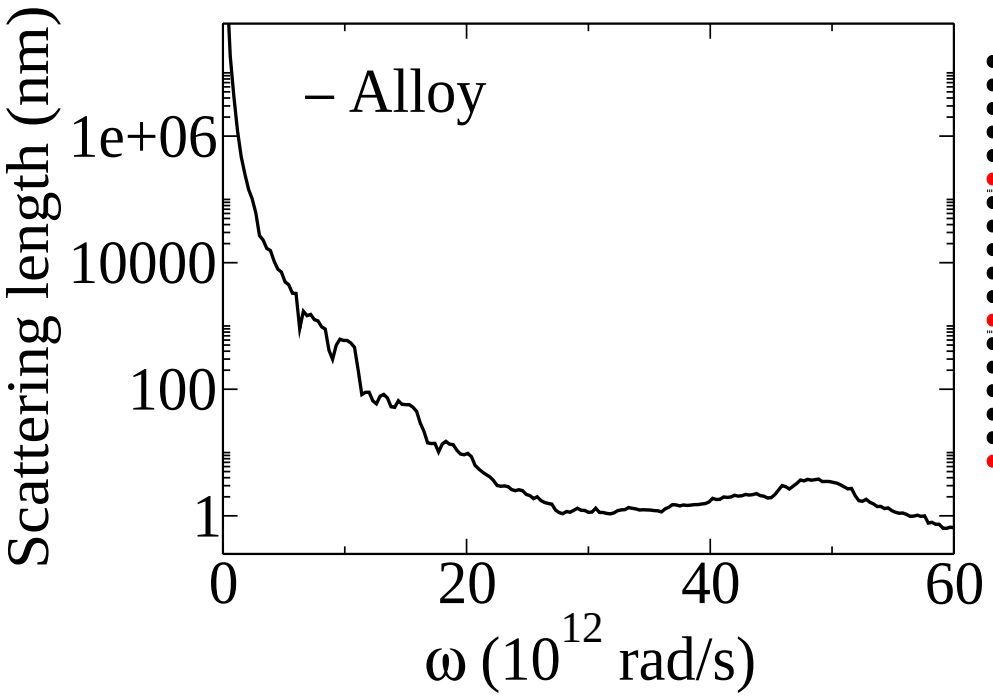


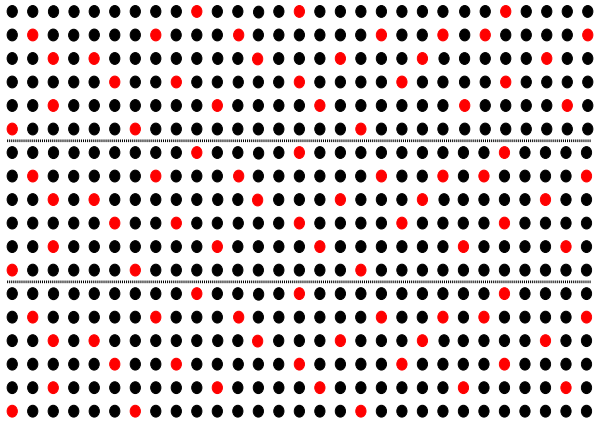




G. Pernot, M. Stoffel, I. Savić *et al*, Nature Mat. **9**, 491 (2010)

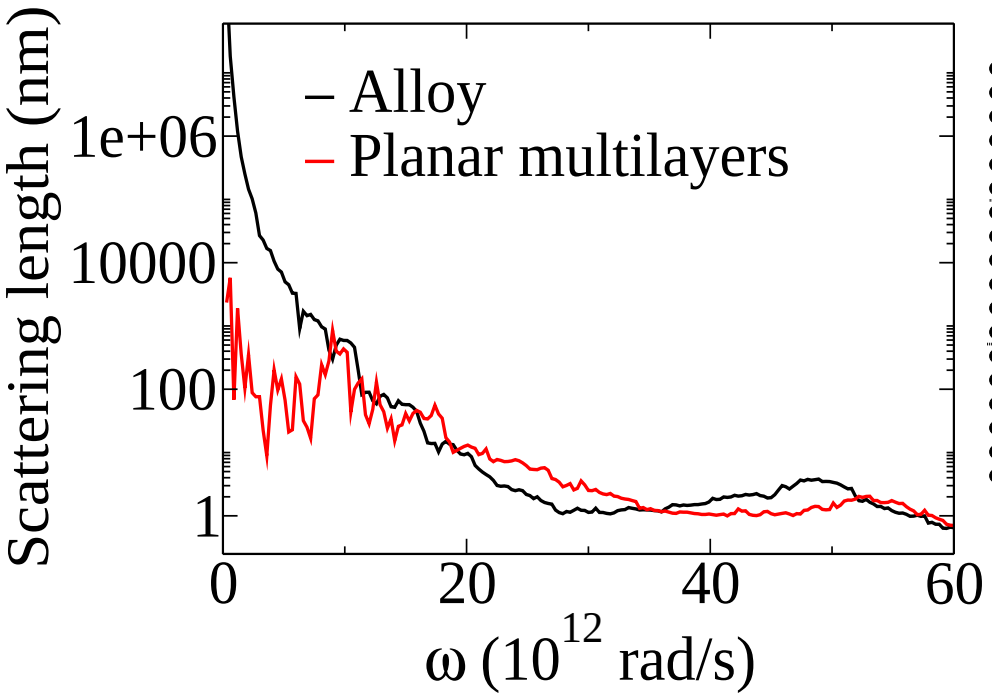
SiGe nanodots in a Si matrix

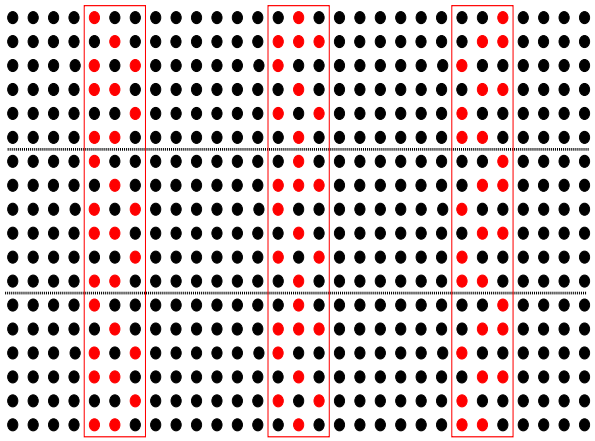




- Planar multilayers: interfaces scatter mid-to-low frequency phonons.
- Nanodot multilayers: nanodots scatter mid-to-low frequency phonons even more strongly.

SiGe nanodots in a Si matrix





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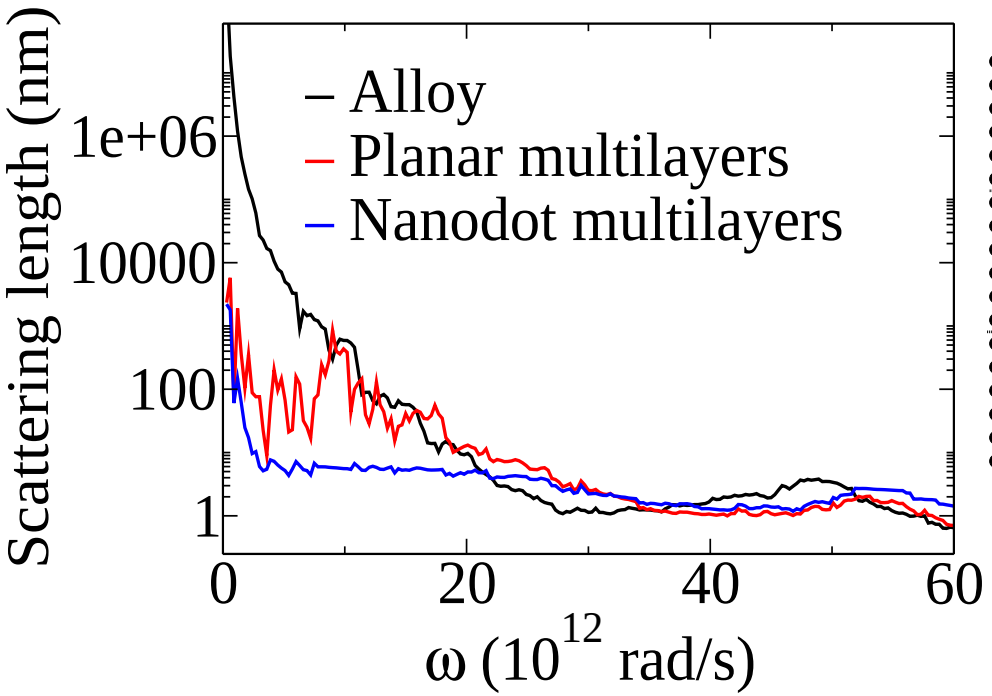
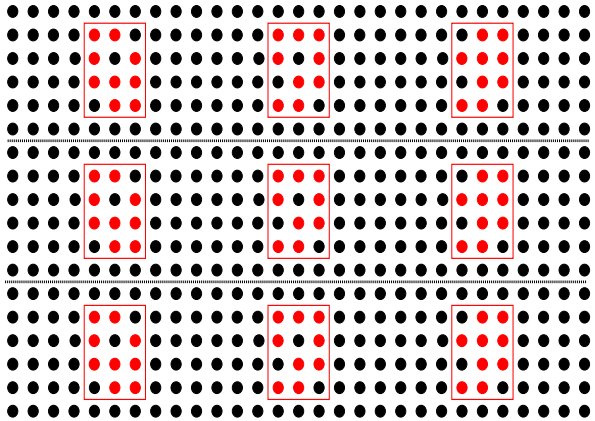


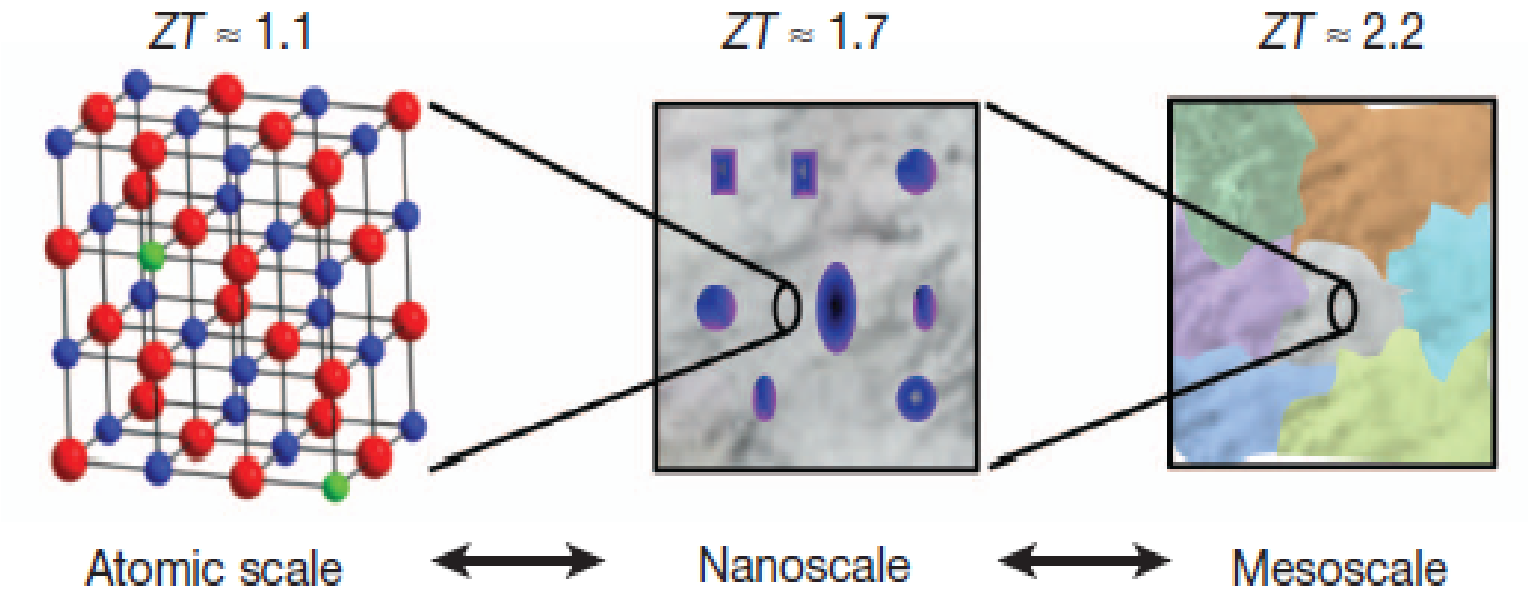


- Planar multilayers: interfaces scatter mid-to-low frequency phonons.
- Nanodot multilayers: nanodots scatter mid-to-low frequency phonons even more strongly.

Structuring across multiple length scales

Combining all the mechanisms that scatter different wavelength phonons:

PbTe with Na dopants, SrTe nanoparticles and grain boundaries.

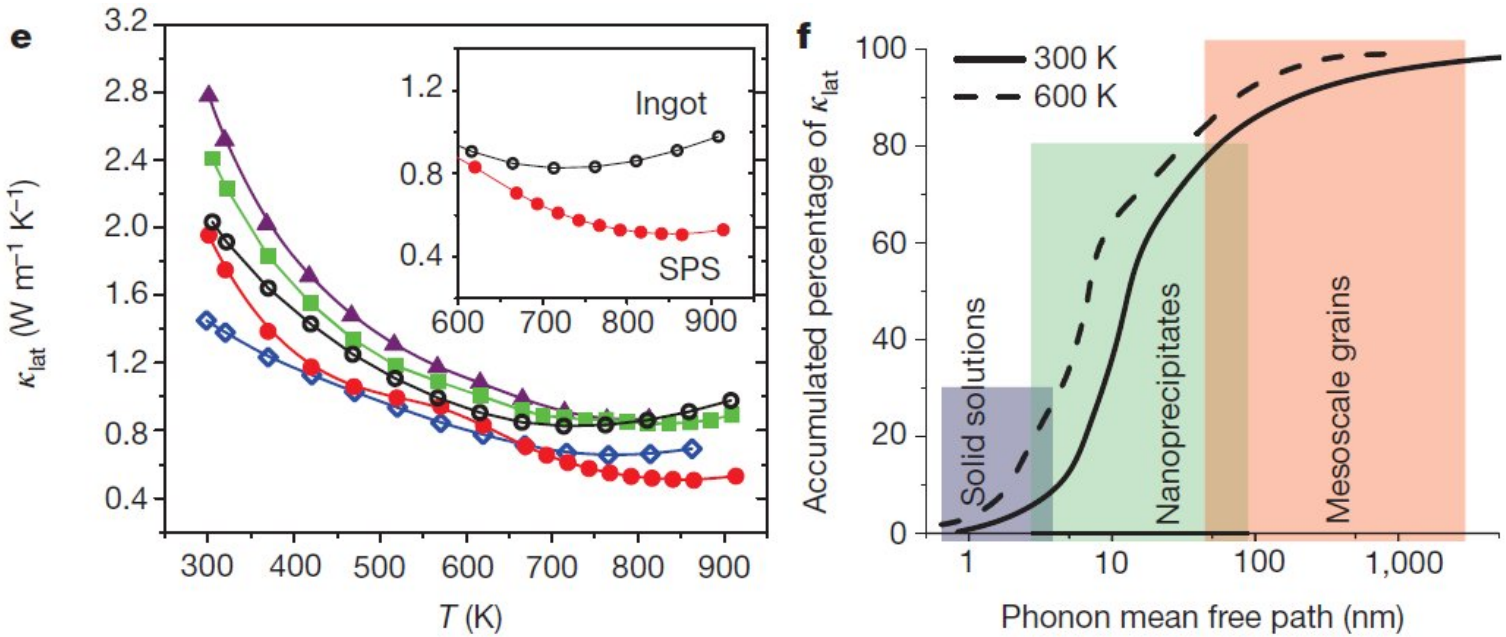


short wavelengths mid wavelengths long wavelengths

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

Structuring across multiple length scales

κ_{latt} is by a factor of $2-3$ lower than that of PbTe
due to point defects, nanoparticles and grain boundaries.



Record ZT value at the time: $ZT \sim 2.2$ at 900 K.

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

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Summary

- Thermoelectric materials are promising candidates for power generation and solid state cooling in ICT.
- Low lattice thermal conductivity is required for efficient thermoelectric energy conversion.
- New bulk materials with low lattice thermal conductivity are being discovered, guided by both conventional and unconventional design rules.
- Introducing atomic scale crystal imperfections and interfaces usually leads to considerably lower lattice thermal conductivity than that of bulk materials.

Outlook

- To achieve efficient thermoelectric conversion, we need new strategies to simultaneously suppress lattice thermal conductivity and preserve electronic thermoelectric properties.

- We need new experimental and theoretical methods, and more intense interaction among them, to understand the problem of coupled electrons and lattice vibrations.

- We need not only more efficient, but also cheaper and environment-friendly thermoelectric materials.