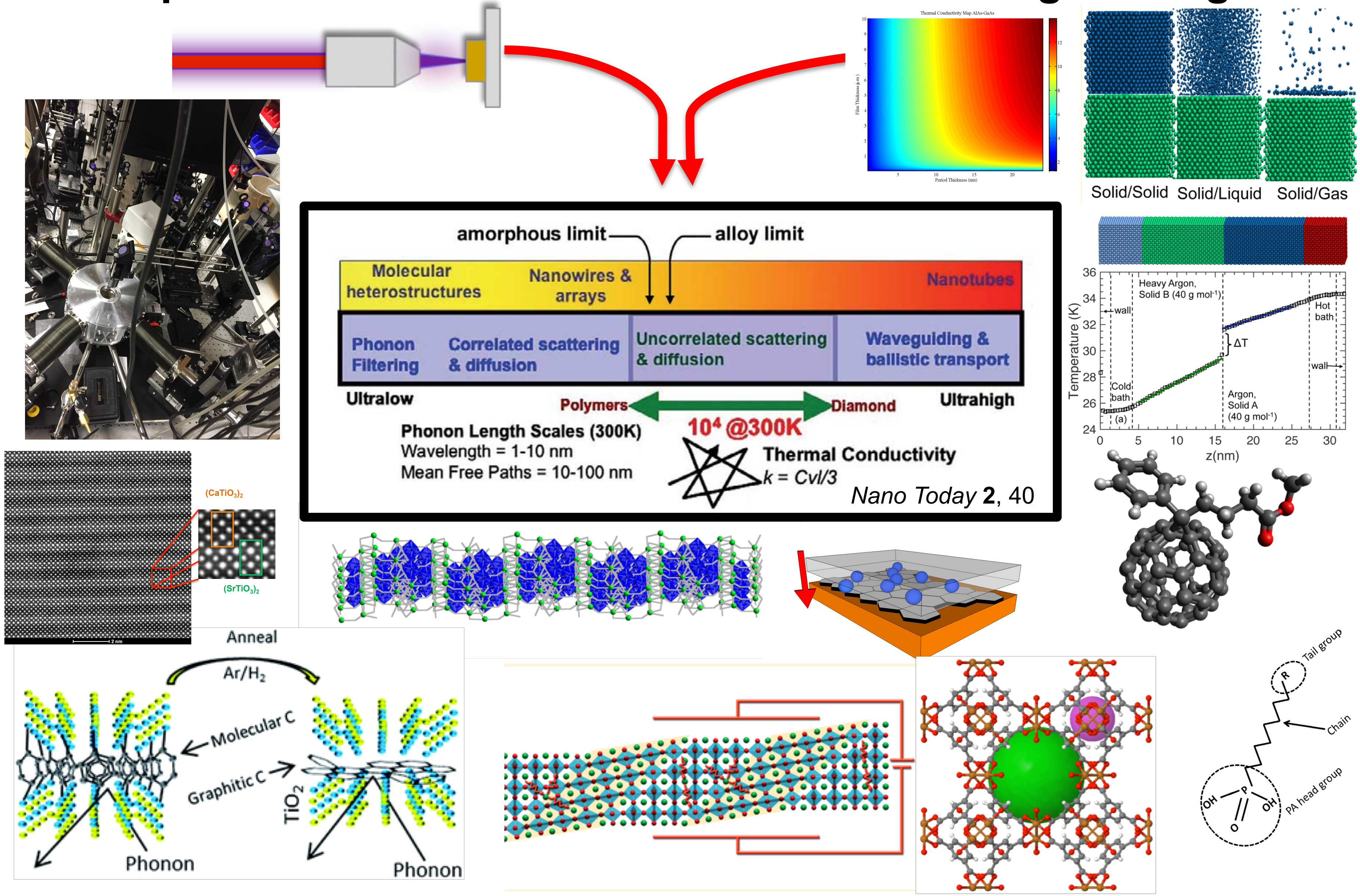
School of Engineering & Applied Science
University of Virginia

Actively and passively controlling the phonon thermal conductivity of materials

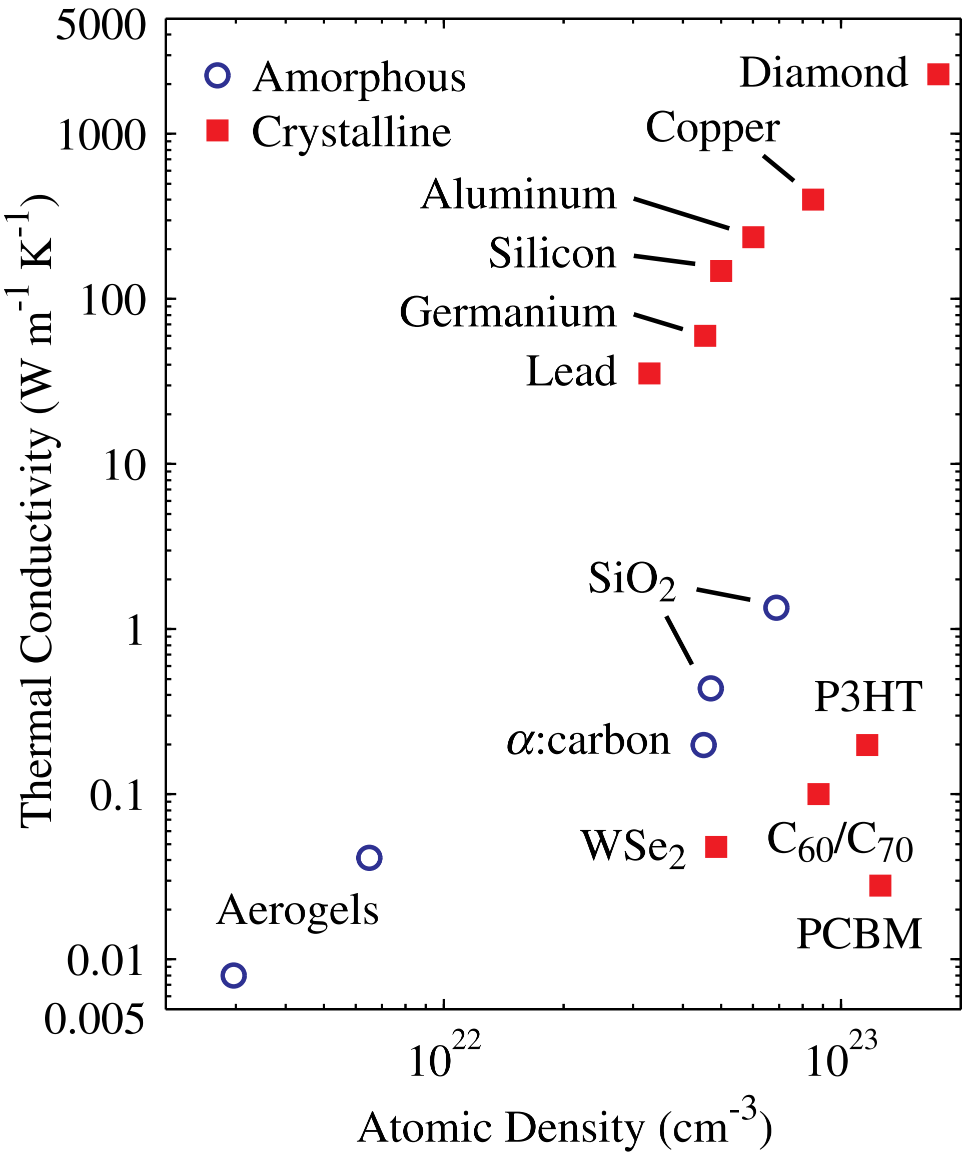
Patrick E. Hopkins
Professor
Dept. Mech. & Aero. Eng.
Dept. Mat. Sci. & Eng.
Dept. Physics
University of Virginia
phopkins@virginia.edu
patrickehopkins.com

My group – ExSiTE Lab

Experiments and Simulations in Thermal Engineering



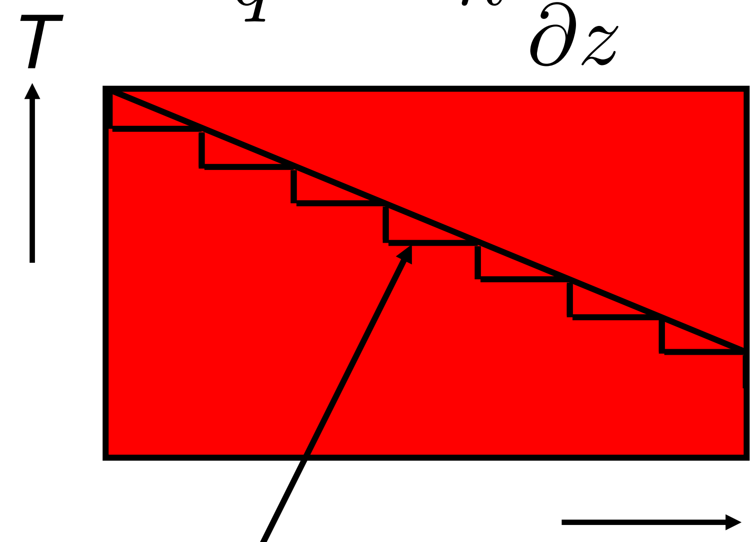
Thermal conductivity of materials – Macro/Microscopic



PRL **110**, 015902 (2013)

The Fourier Law

$$q = -\kappa \frac{\partial T}{\partial z}$$



λ = Mean free path

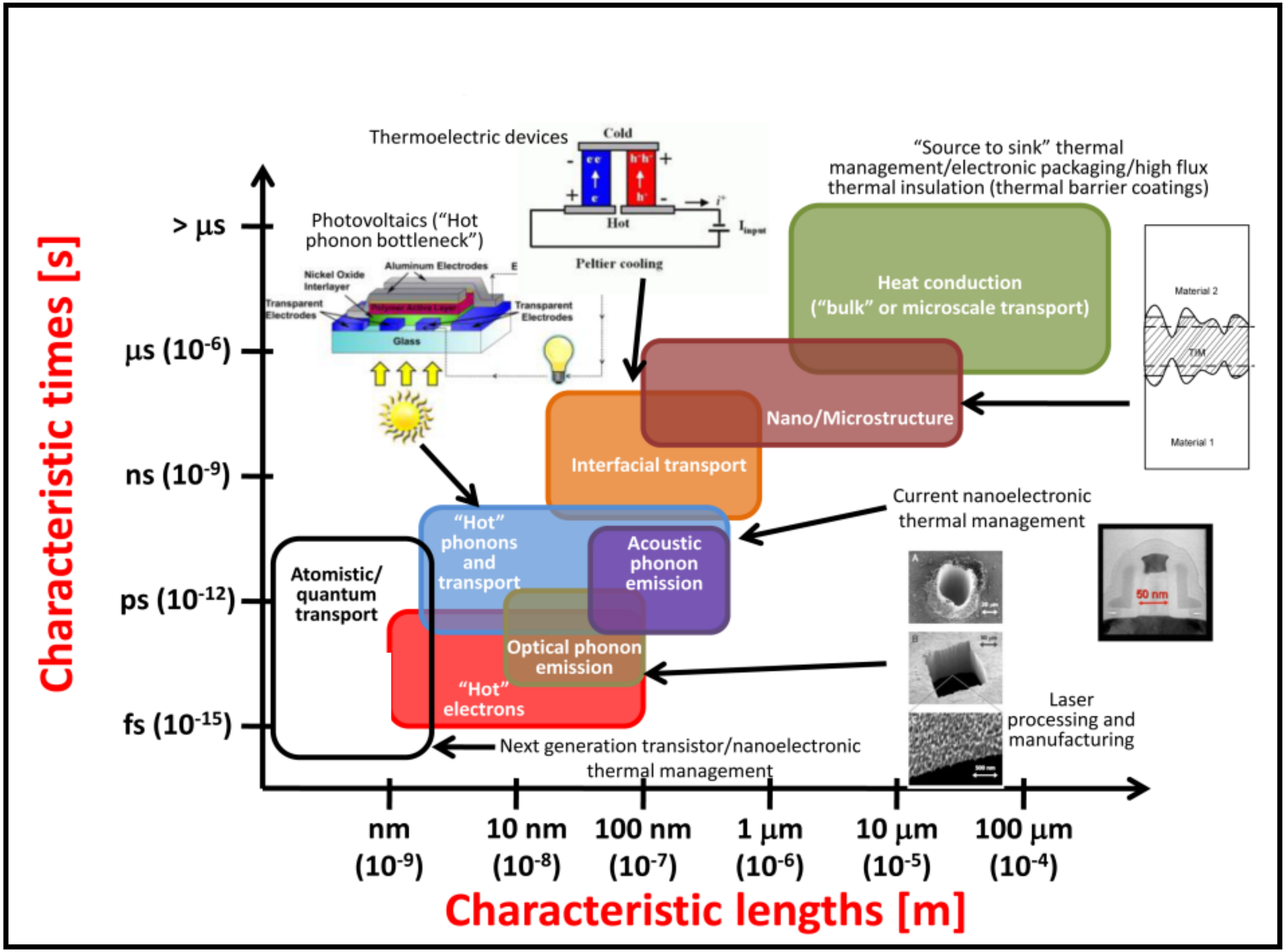
$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

Heat capacity

Velocity

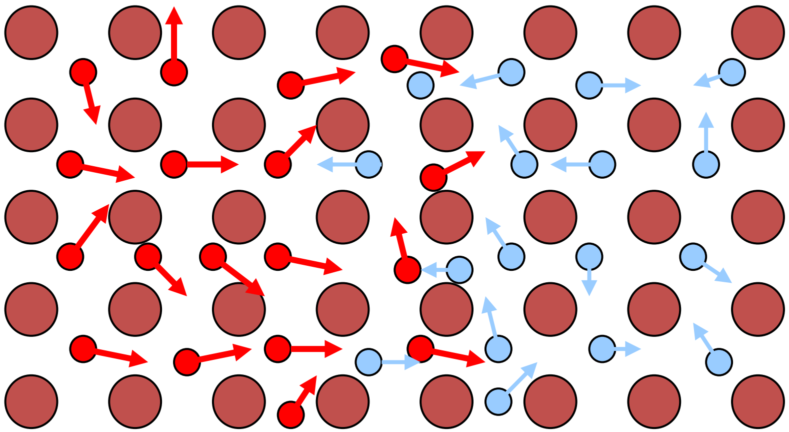
My group – ExSiTE Lab

Engineering energy transport, conversion and storage in materials over multiple time and length scales

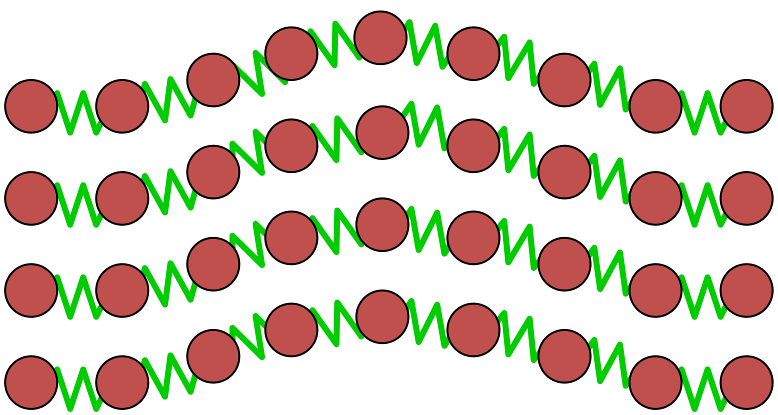


Thermal conductivity of materials - nanoscopic

Diffusion of "hot" electrons



Phonon propagation



Metals:

Free electrons are the dominant energy carriers in metals, ballistic velocity ~10^6 m/s

Electron carrier density:
in metals ~10^{23} cm^{-3}
in semiconductors ~10^{18} cm^{-3}

atom

"hot" free electron

"cold" free electron

Semiconductors:

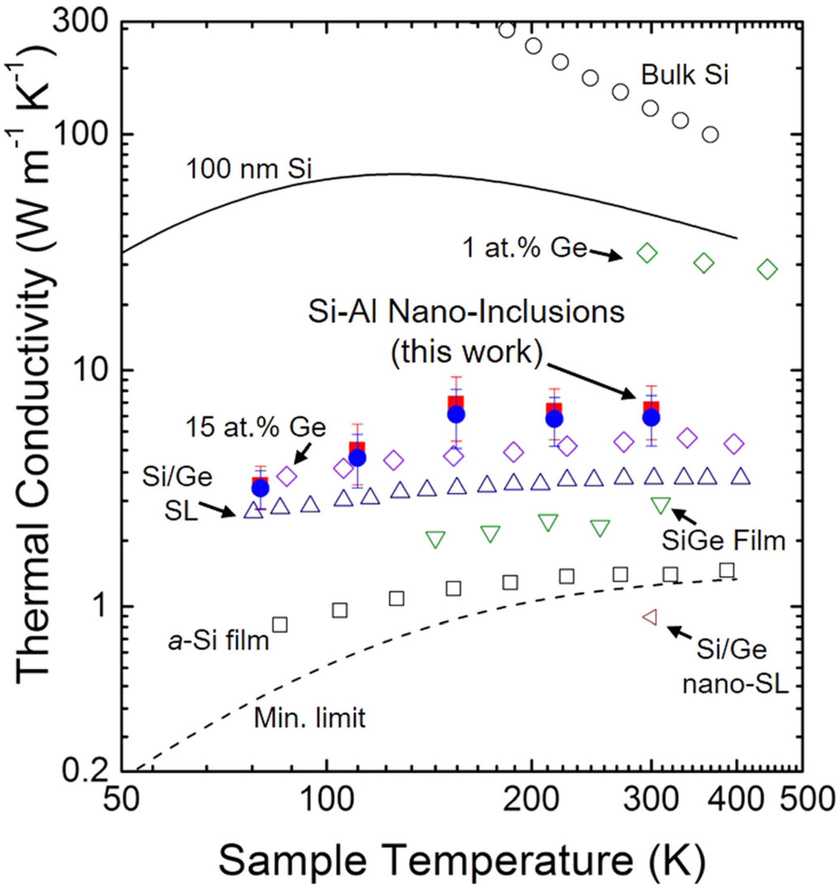
Phonons (lattice vibrations) are the dominant energy carriers in semiconductors, velocity ~10^3 m/s

$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

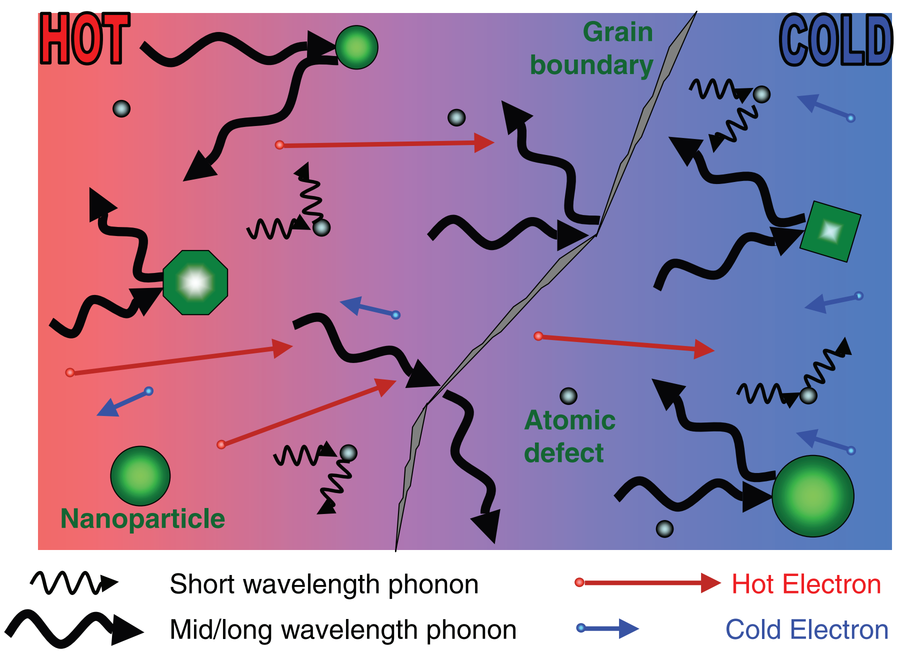
Thermal conductivity of nanostructures

Nanoscale heat transfer

Well controlled and prescribed inclusions, defects, or interfaces to *permanently* change thermal conductivity

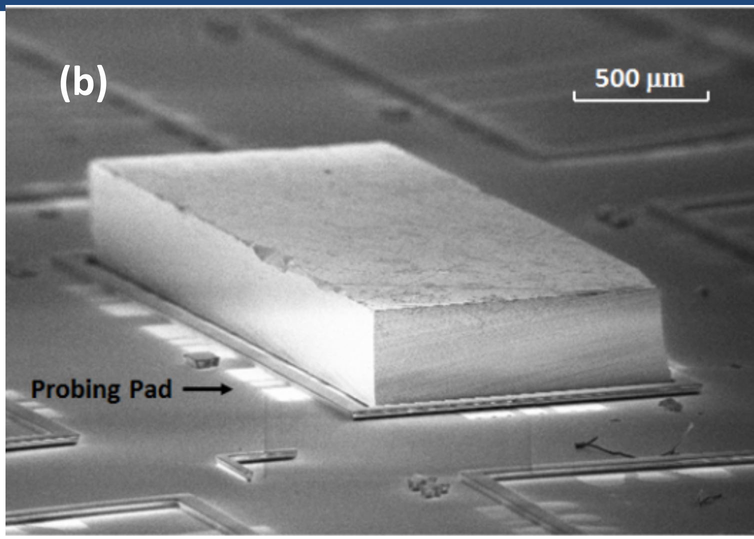


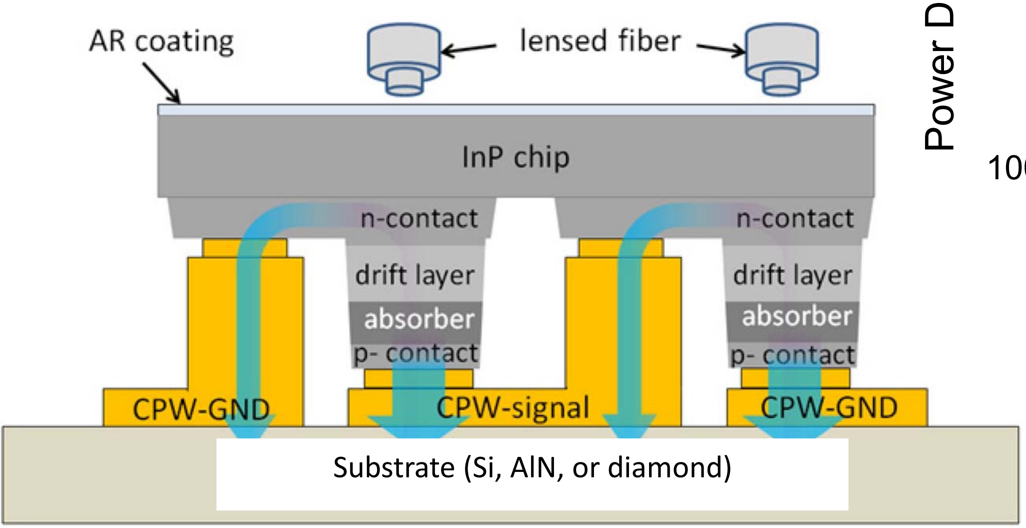
APL **112**, 213103



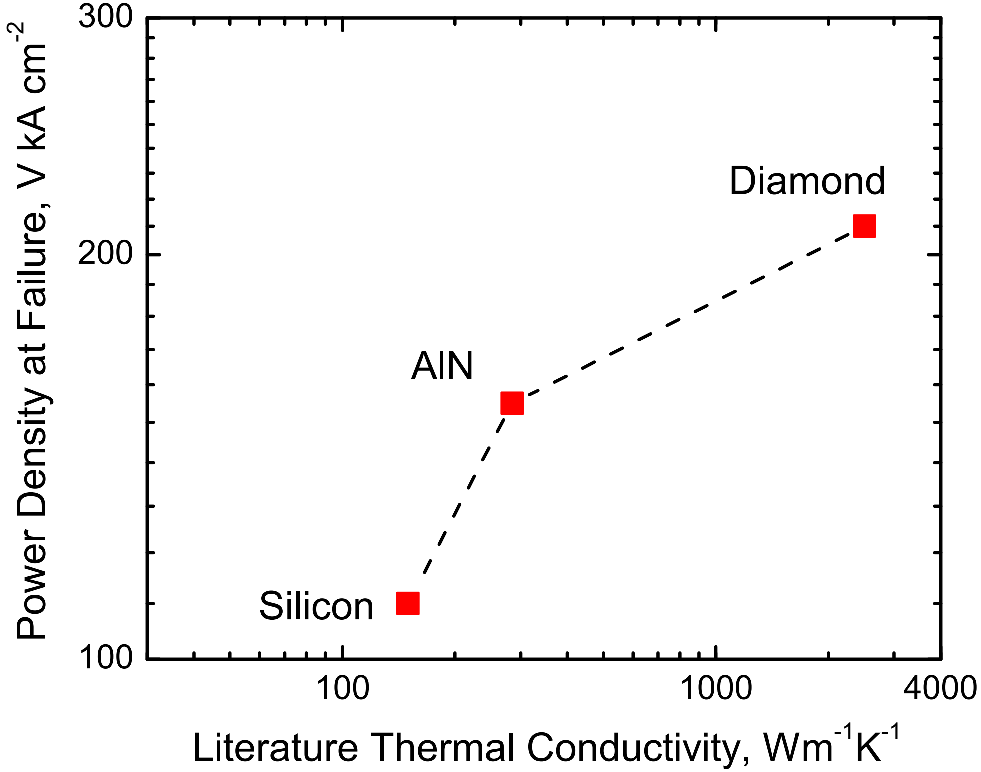
Adv. Mat. **22**, 3970

An example: High power device thermal management





(c)



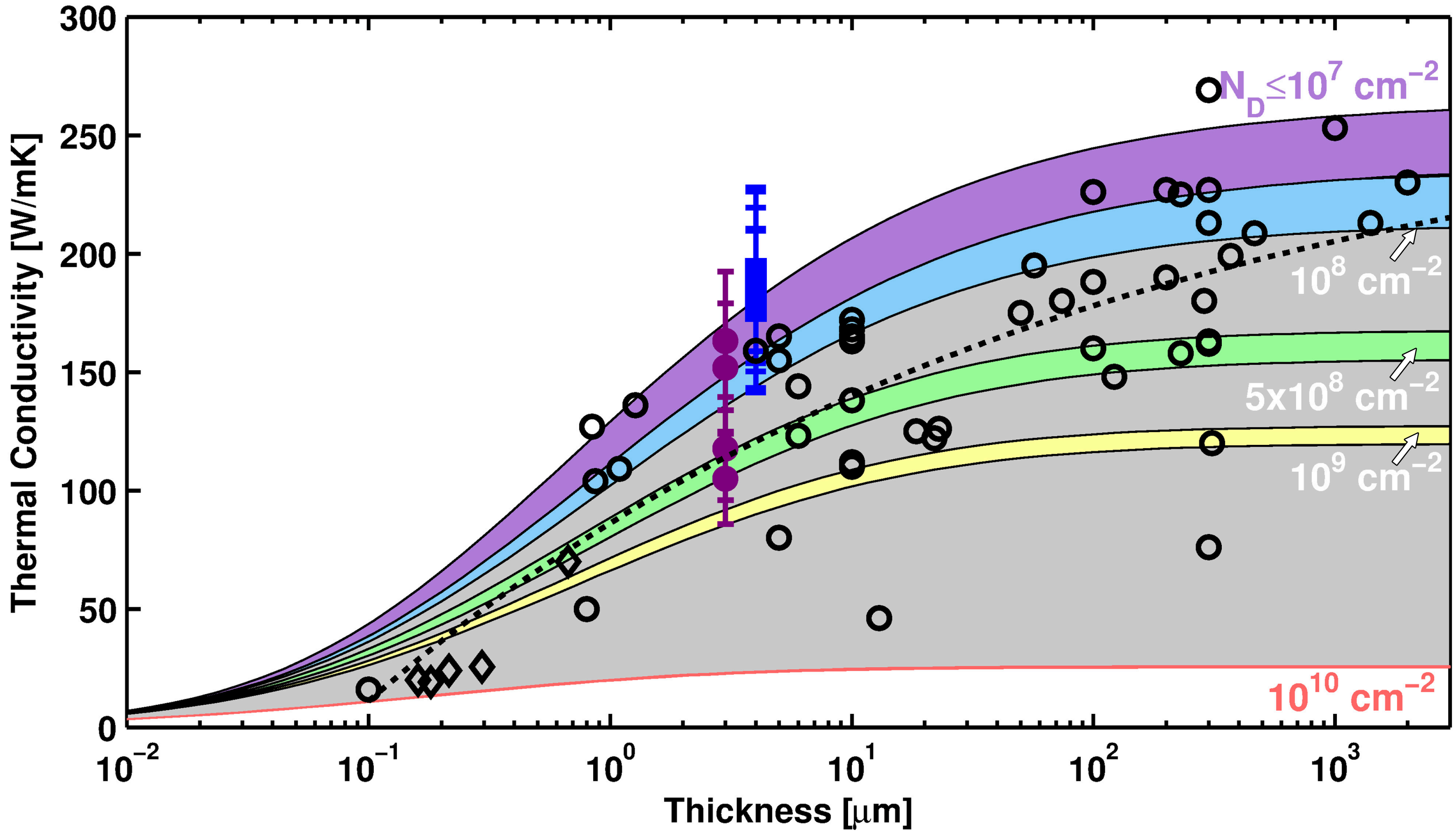
Collaboration with Joe Campbell (UVA)

J. Lightwave Technology **35**, 4242 (2017)

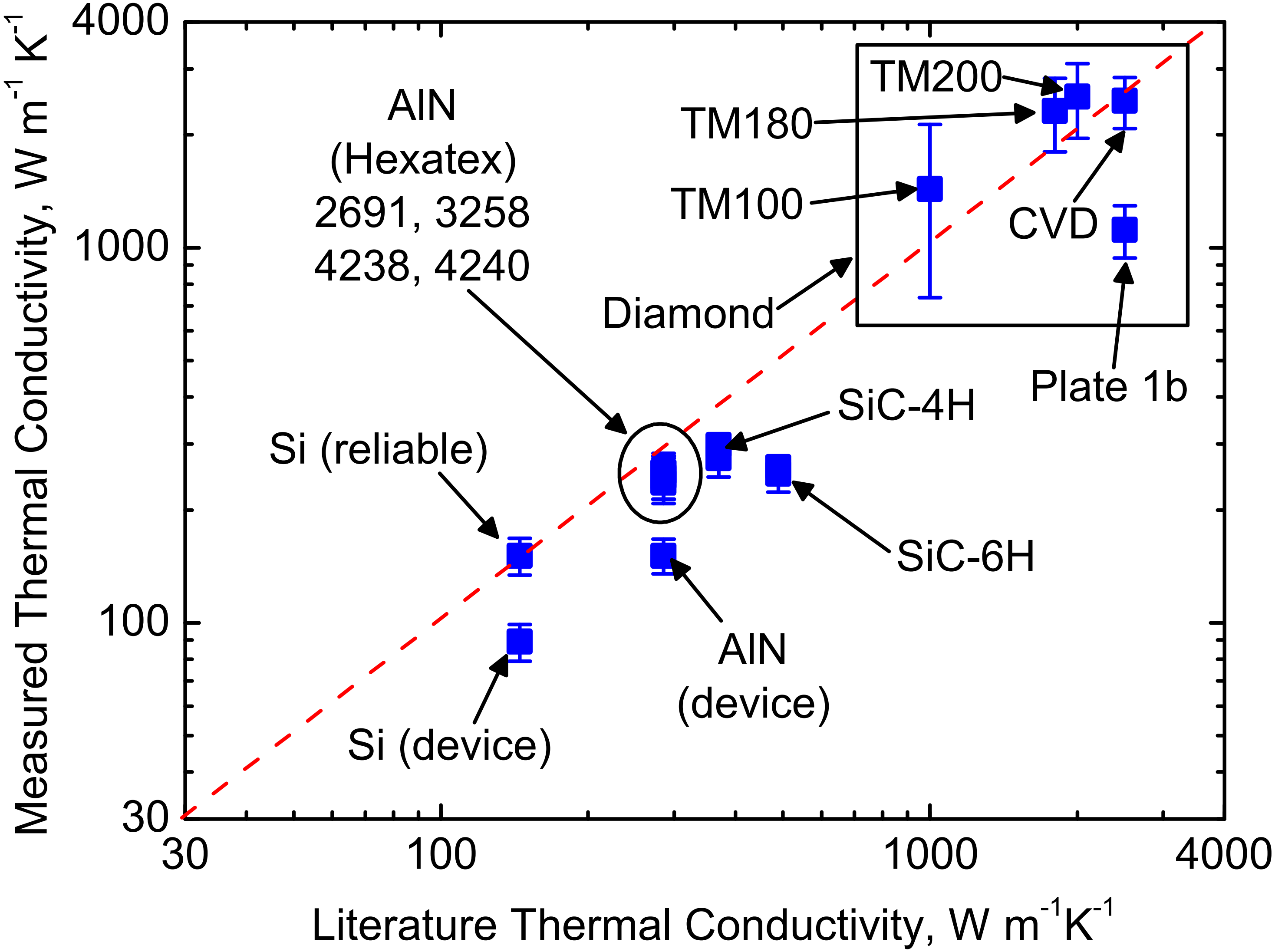
Thermal conductivity of materials – nanoscopic

$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$

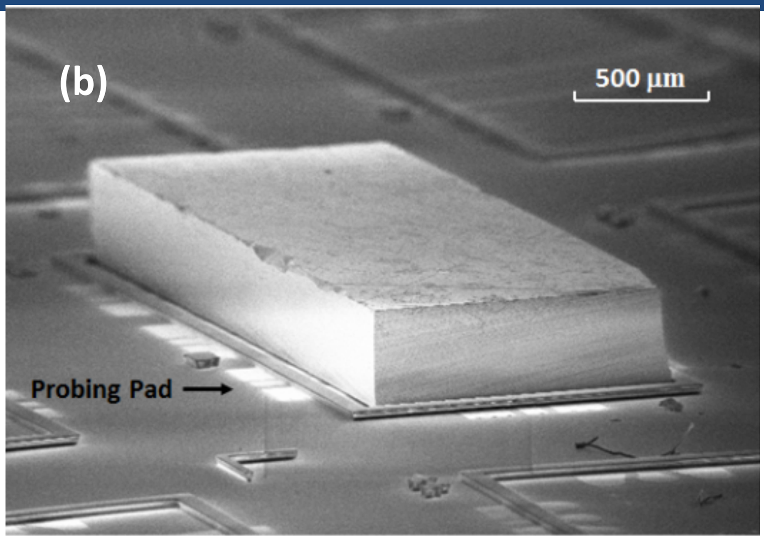
The case of GaN: Collaboration with Thomas Beechem (SNL)
J. Appl. Phys. **120**, 095104

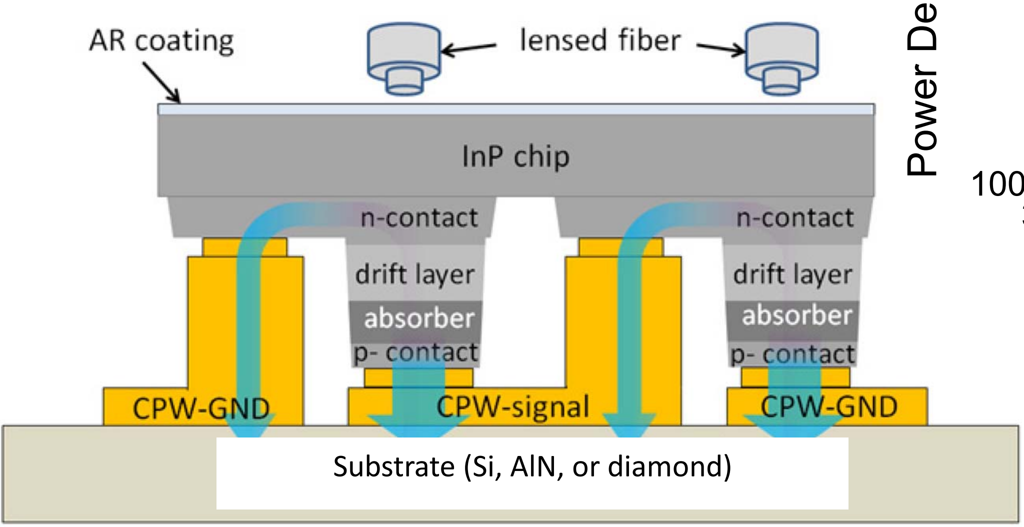


Example: thermal conductivity of common high κ substrates

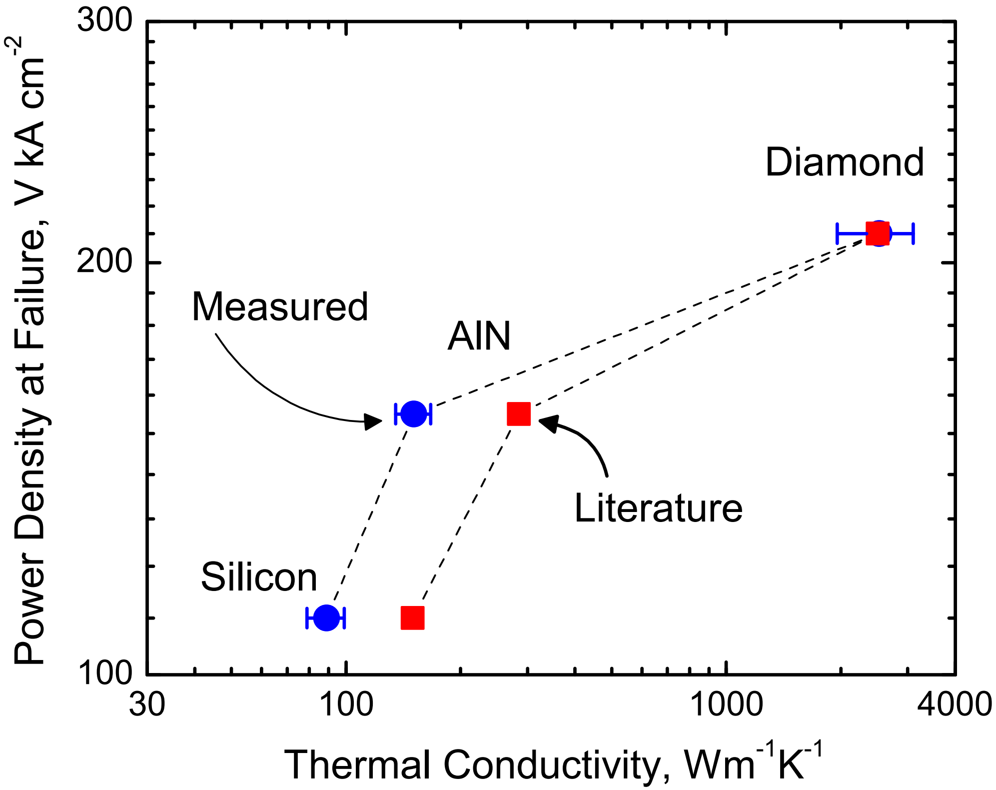


High power device thermal management – substrate effects





(c)



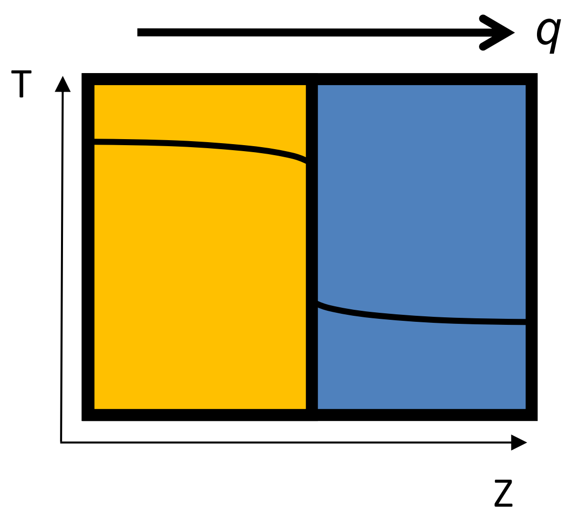
Still does not scale with heat sink thermal conductivity

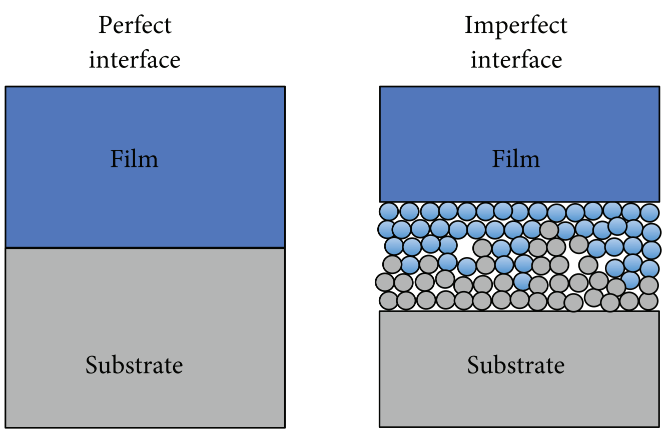
Collaboration with Joe Campbell (UVA)

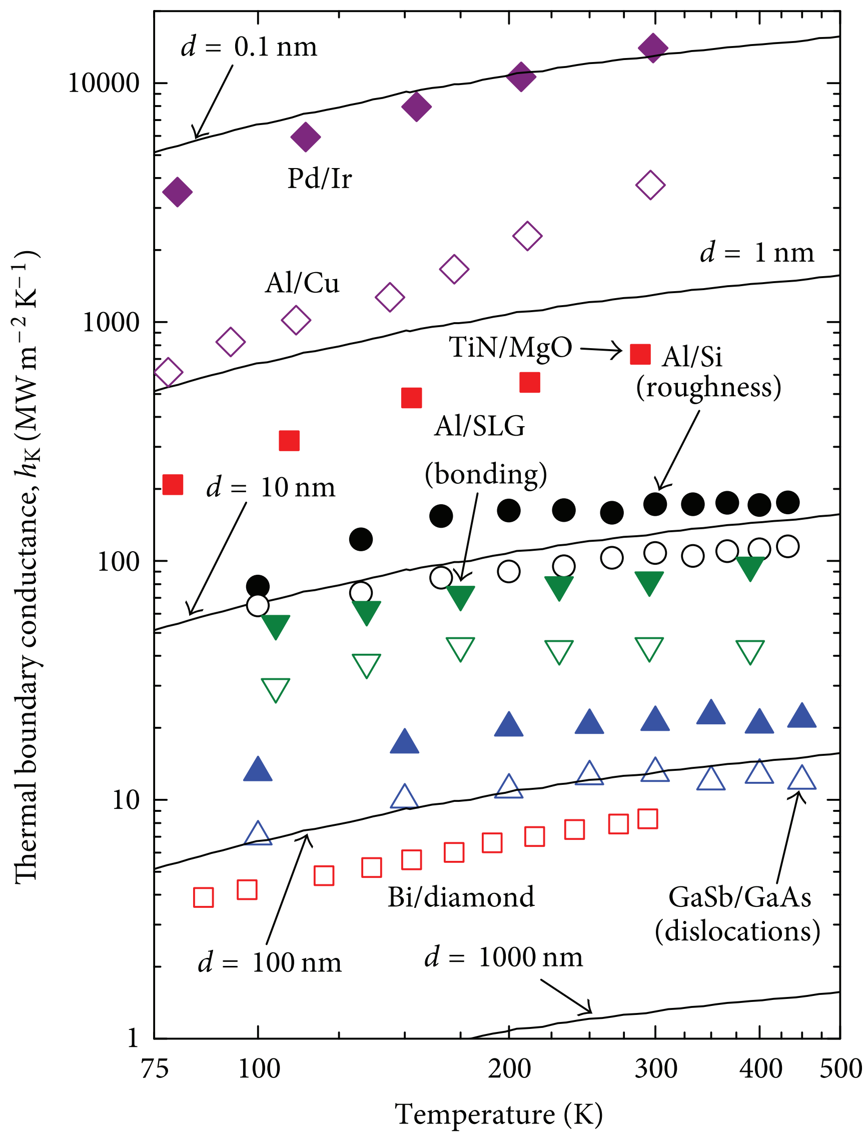
J. Lightwave Technology **35**, 4242 (2017)

Thermal boundary conductance – nanoscale resistances

$$q = h_K \Delta T = \frac{1}{R_K} \Delta T$$

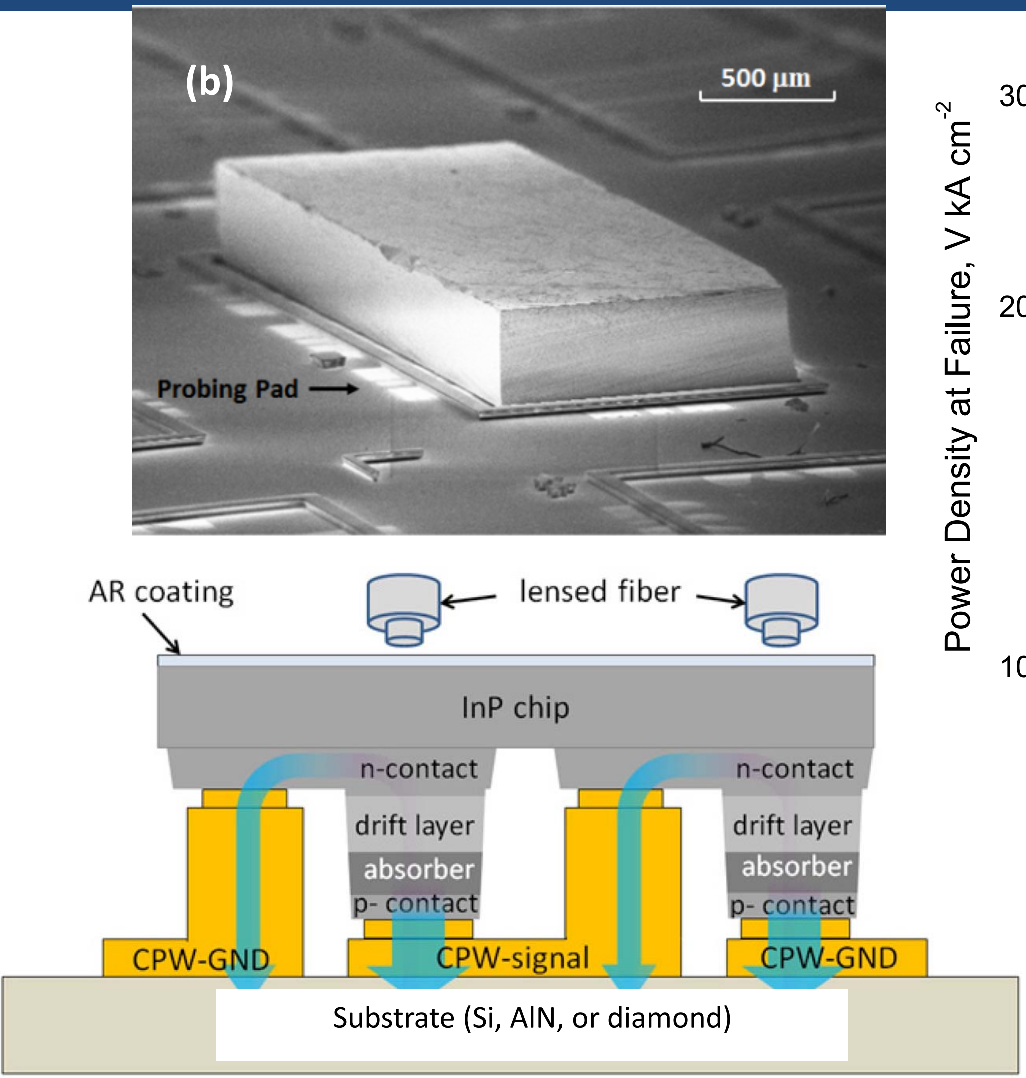




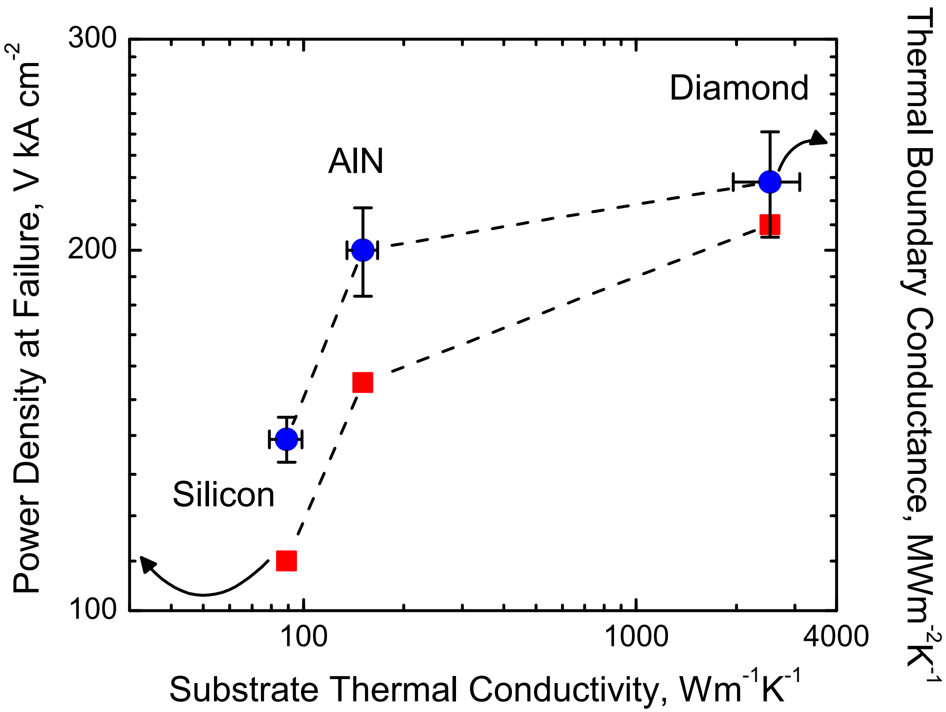


ISRN Mech. Eng. **2013**, 682586

High power device thermal management - nanoscale



(c)



TBC plays direct role in power density at failure

Collaboration with Joe Campbell (UVA)

J. Lightwave Technology **35**, 4242 (2017)

Outline

Static control of phonon transport

Defects/interfaces to permanently change κ

Dynamic control of phonon transport

Thermal conductivity switch – can we *reversibly* change κ with an external stimulus?

Outline

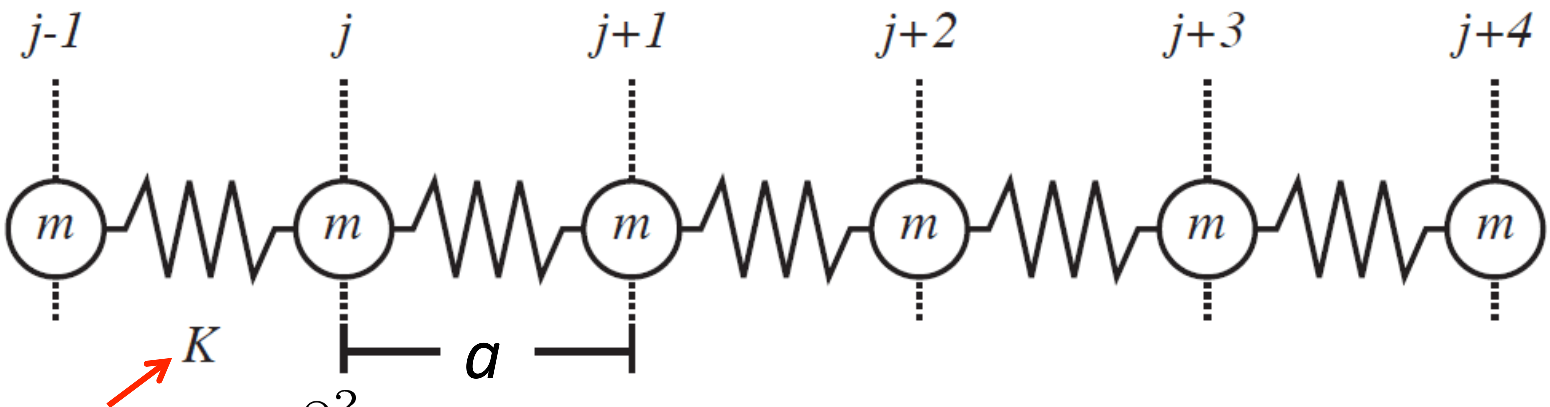
Static control of phonon transport

Defects/interfaces to permanently change κ

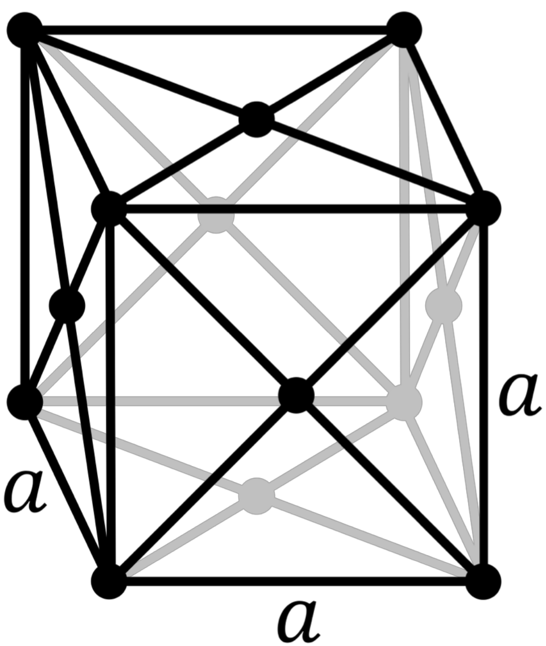
- Spectral phonon transport effects on thermal conductivity
  - When is a defect/interface "viewed" as a defect/interface from the phonon's point of view

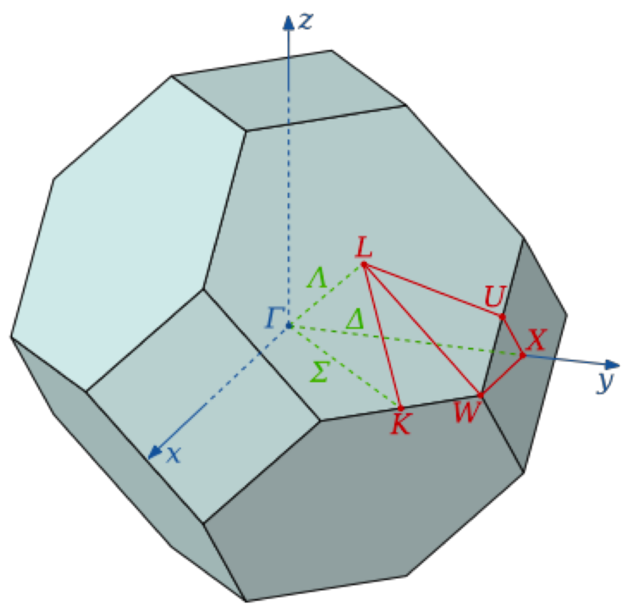
- Thermal conductivity of superlattices
  - Spectral phonon effects in superlattices
    - Long vs. short wavelength phonon transport
  - Wave vs. particle effects
    - When does a superlattice become a new material in the phonon's view?

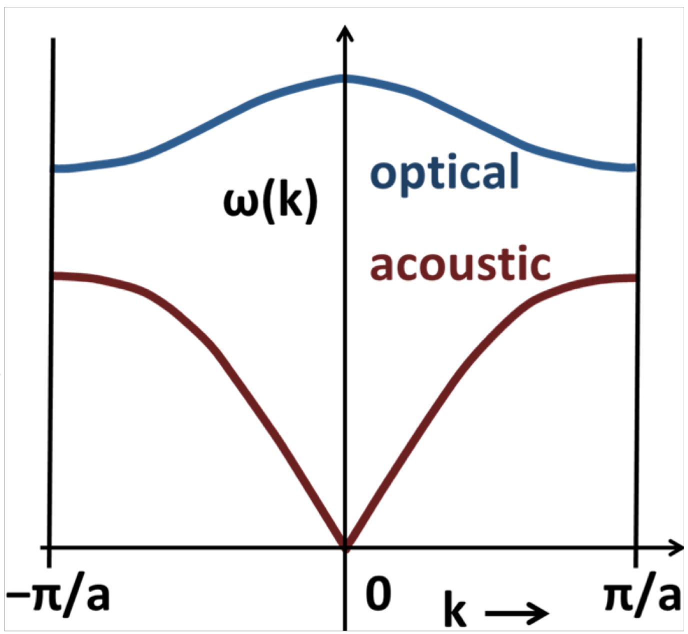
The spectrum of phonons



$$K = -\frac{\partial^2 u}{\partial x^2}$$





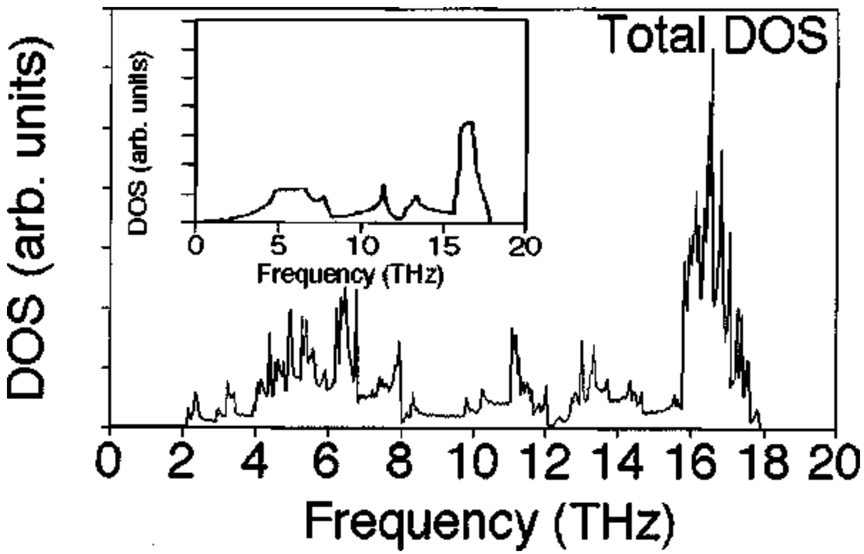


Wikipedia

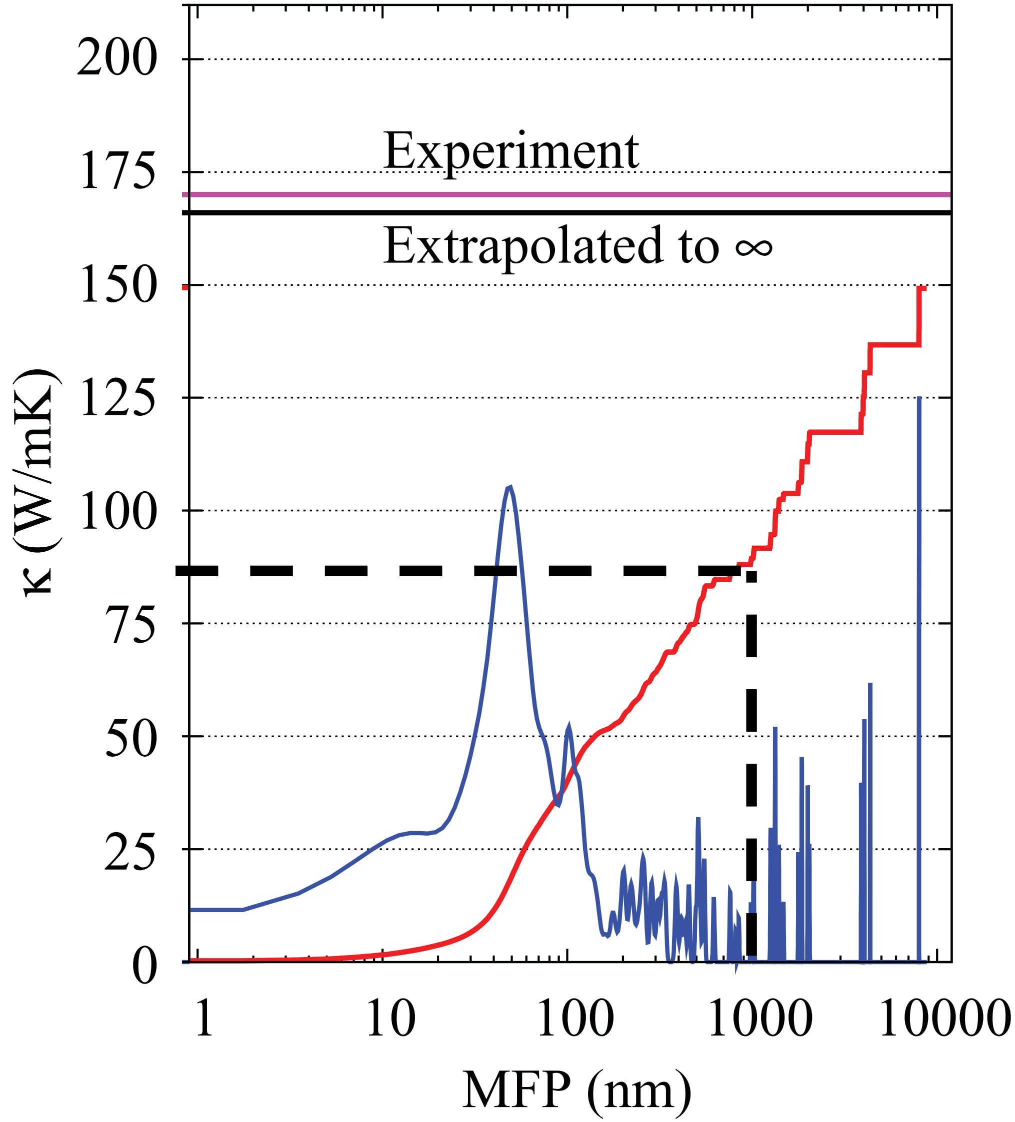
Spectral phonon transport – The "bandwidth" of phonons

$$\kappa = \int_\omega C_\omega v_\omega \lambda_\omega \, \mathrm{d}\omega$$

50% of heat in Si carried by phonons with MFP's ~1 μm and less



Schelling, Phillpot, Keblinski
J. Appl. Phys. **95**, 6082



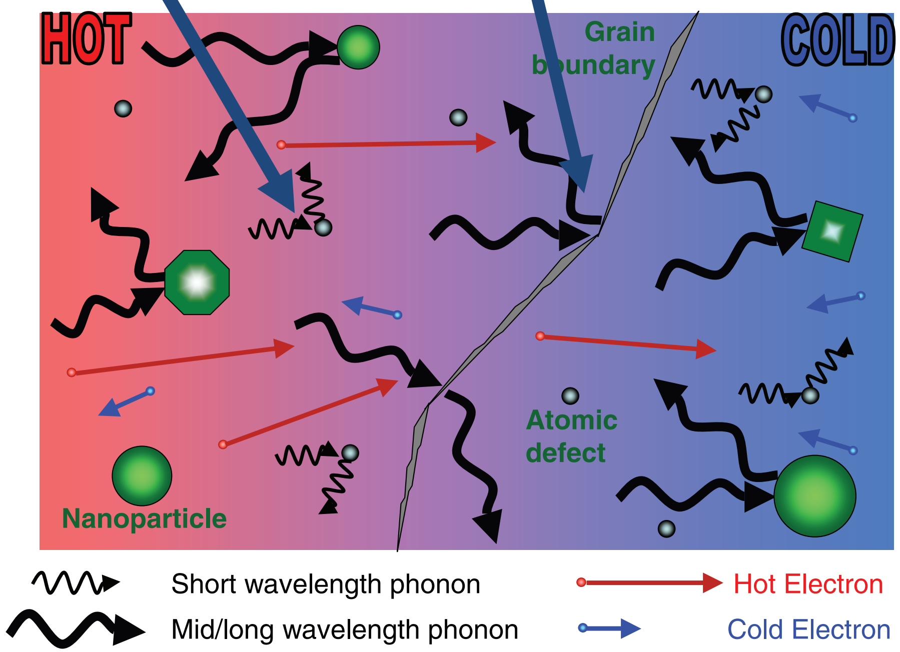
Phys. Rev. B **84**, 085204

Spectral phonon transport – The "bandwidth" of phonons

How do defects play a role?

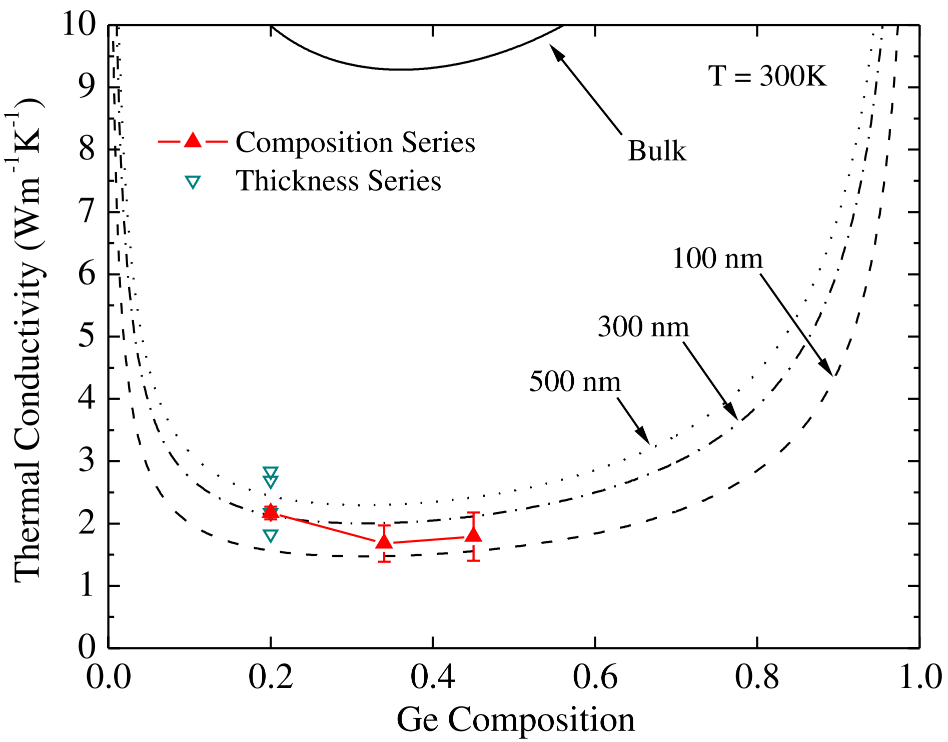
Short wave point defects

Long wave Boundaries



Adv. Mat. **22**, 3970

Thermal conductivity $Si_{1-x}Ge_x$ alloys



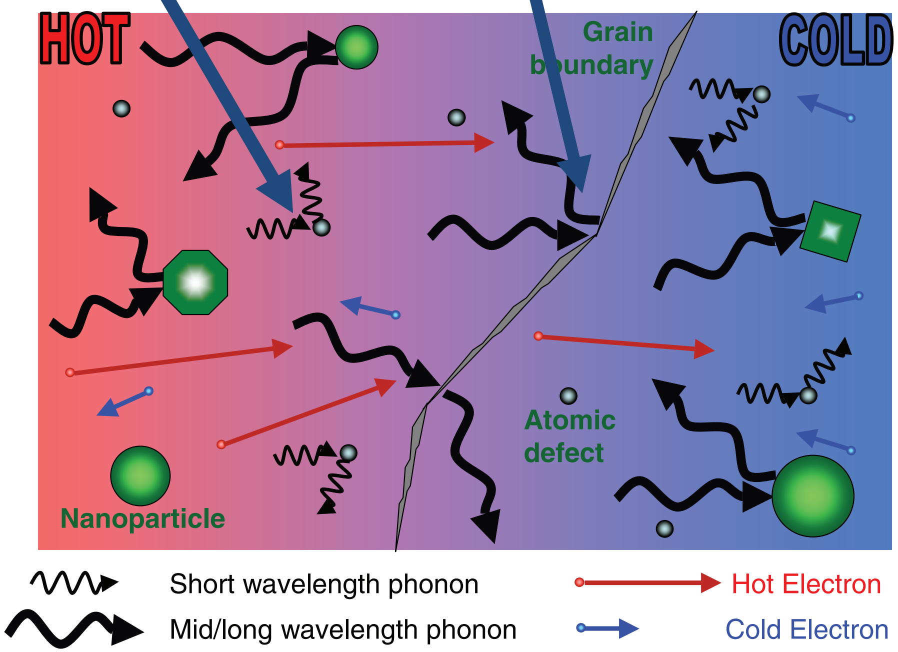
Phys. Rev. Lett. **109**, 195901

Spectral phonon transport – The “bandwidth” of phonons

How do defects play a role?

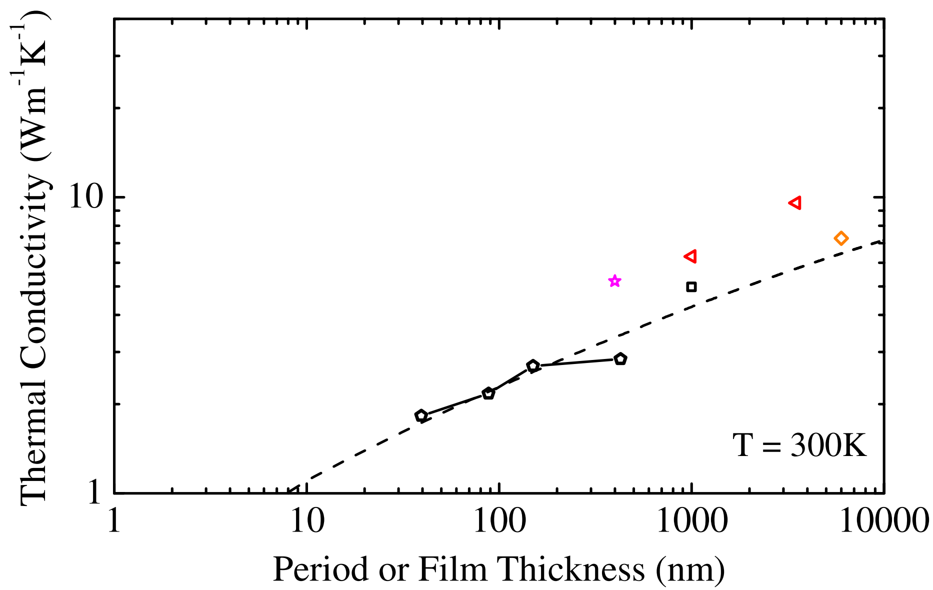
Short wave
point defects

Long wave
Boundaries



Adv. Mat. **22**, 3970

Thermal conductivity $Si_{1-x}Ge_x$ alloys



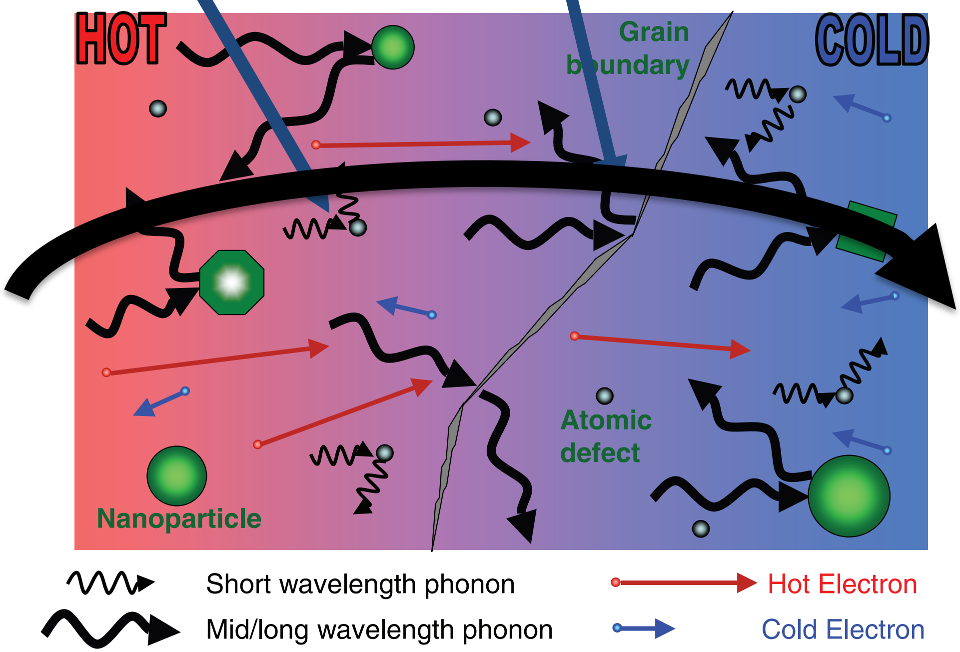
Phys. Rev. Lett. **109**, 195901

How do defects play a role?

How about long, long wavelength phonons??

Short wave
point defects

Long wave
Boundaries

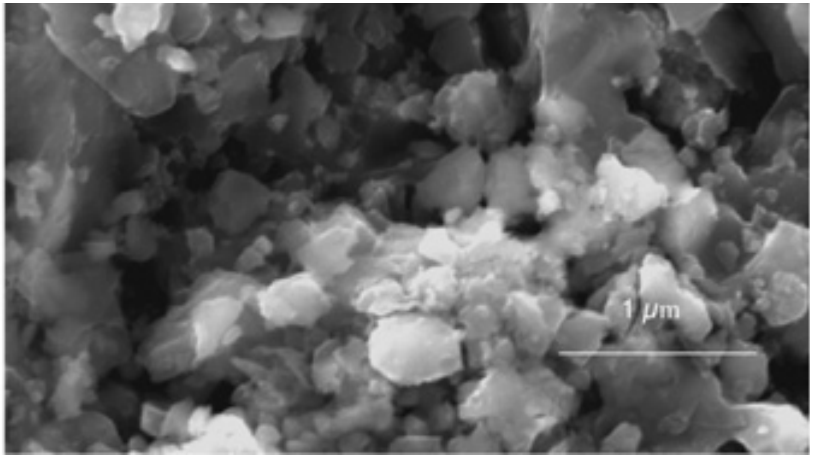


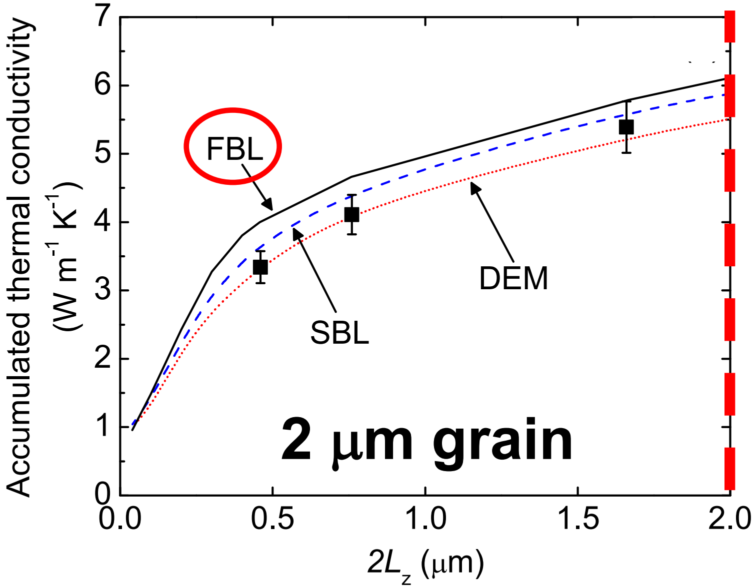
Adv. Mat. **22**, 3970

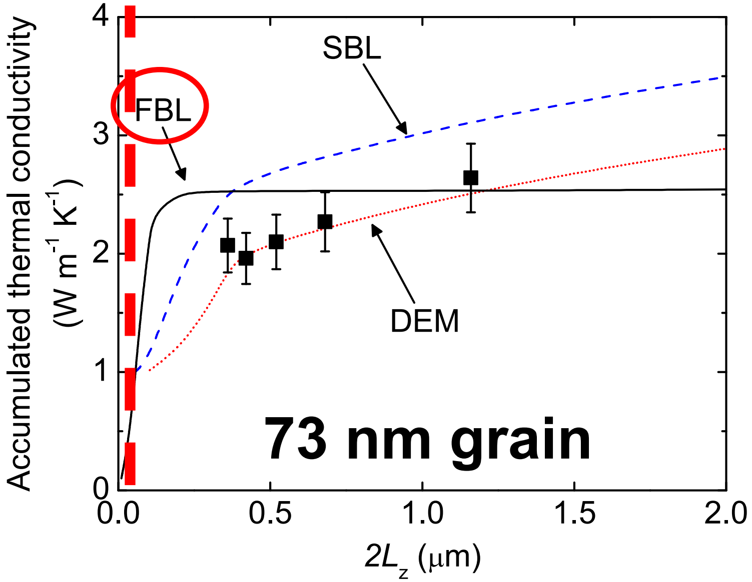
What happens when phonon wavelengths are much greater than boundaries/interfaces?

Spectral phonon transport – Nanograined alloys

Nanograined $Si_{80}Ge_{20}$







Phonons with wavelengths much larger than grain size do not scatter at grain boundaries

Appl. Phys. Lett. **11**, 131902

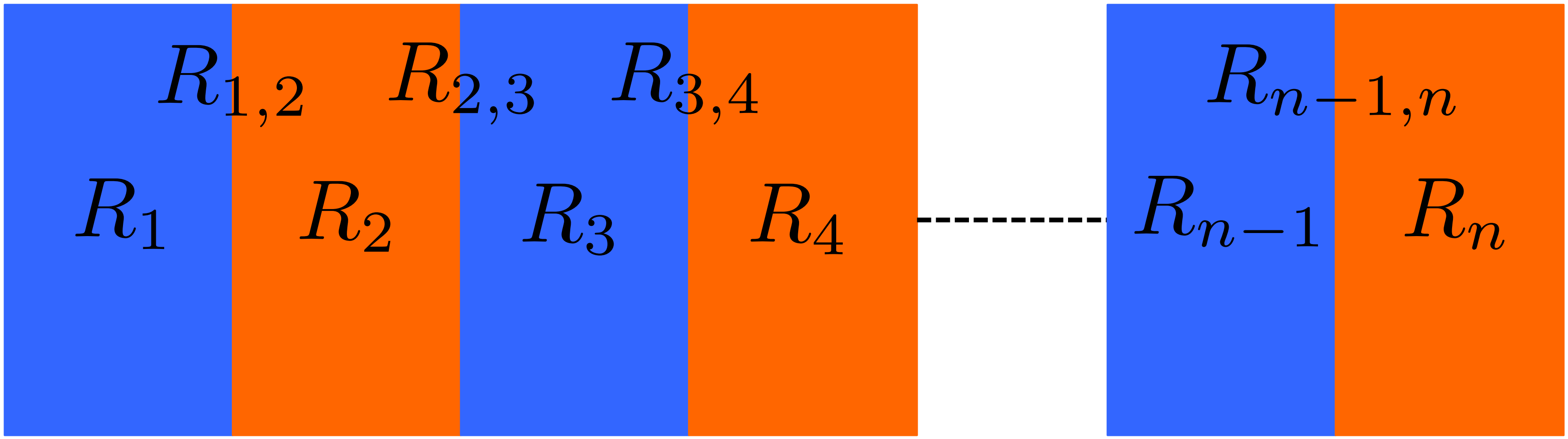
Outline

Static control of phonon transport

Defects/interfaces to permanently change κ

- Spectral phonon transport effects on thermal conductivity
  - When is a defect/interface "viewed" as a defect/interface from the phonon's point of view
- Thermal conductivity of superlattices
  - Spectral phonon effects in superlattices
    - Long vs. short wavelength phonon transport
  - Wave vs. particle effects
    - When does a superlattice become a new material in the phonon's view?

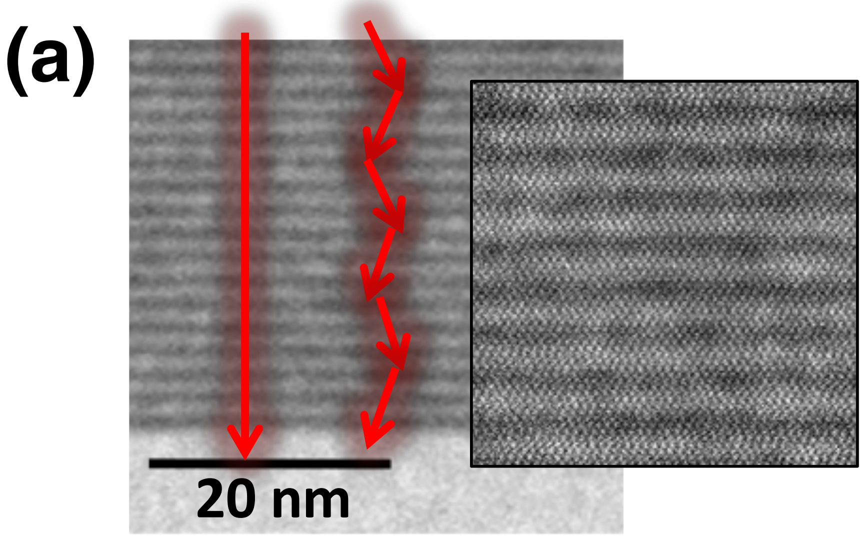
The traditional view of phonon transport in superlattices



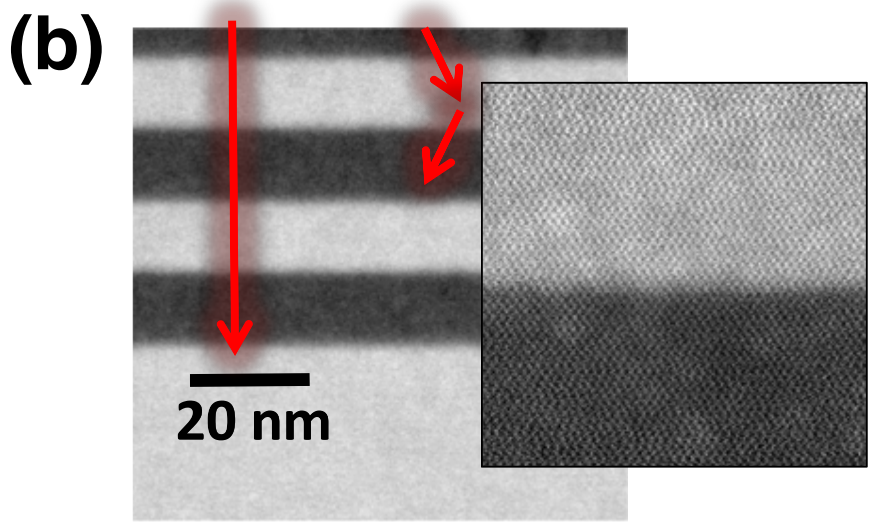
$$1/\kappa \propto 1/h = \sum_n R_j$$

Phonons scatter at every interface, and thus each interface offers a resistance to the overall thermal conductivity

The traditional view of phonon transport in superlattices



d_{SL} = 2 nm

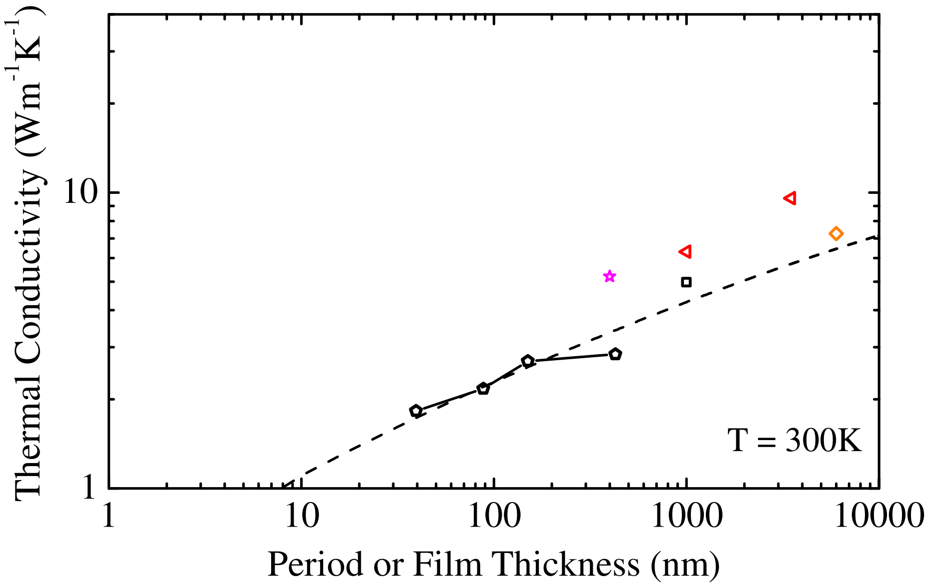


d_{SL} = 24 nm

But remember what we learned in alloys: do the phonons with longer wavelengths "see" the interfaces?

What size effects matter in superlattices?

Thermal conductivity $Si_{1-x}Ge_x$ alloys

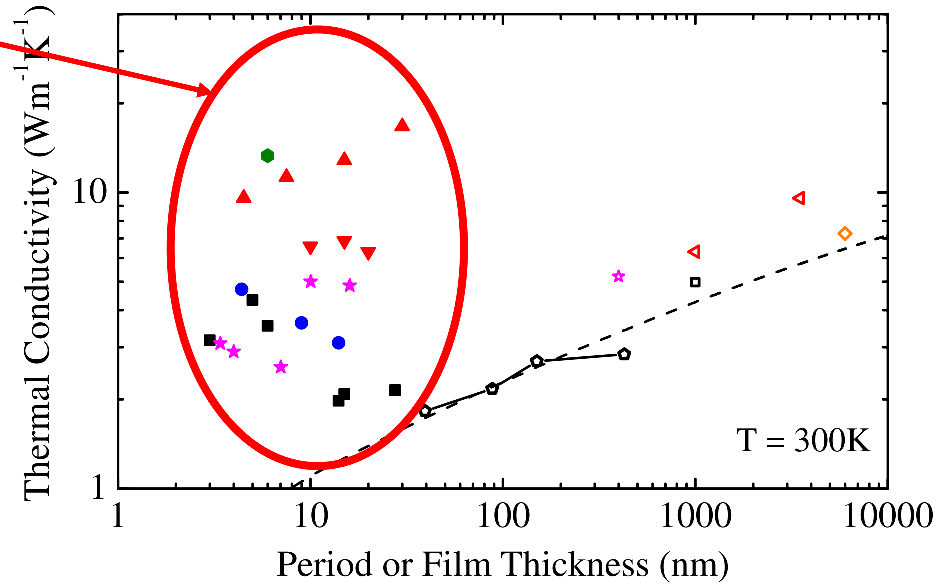


Phys. Rev. Lett. **109**, 195901

What size effects matter in superlattices?

Superlattices vs. period thickness

Thermal conductivity $Si_{1-x}Ge_x$ alloys

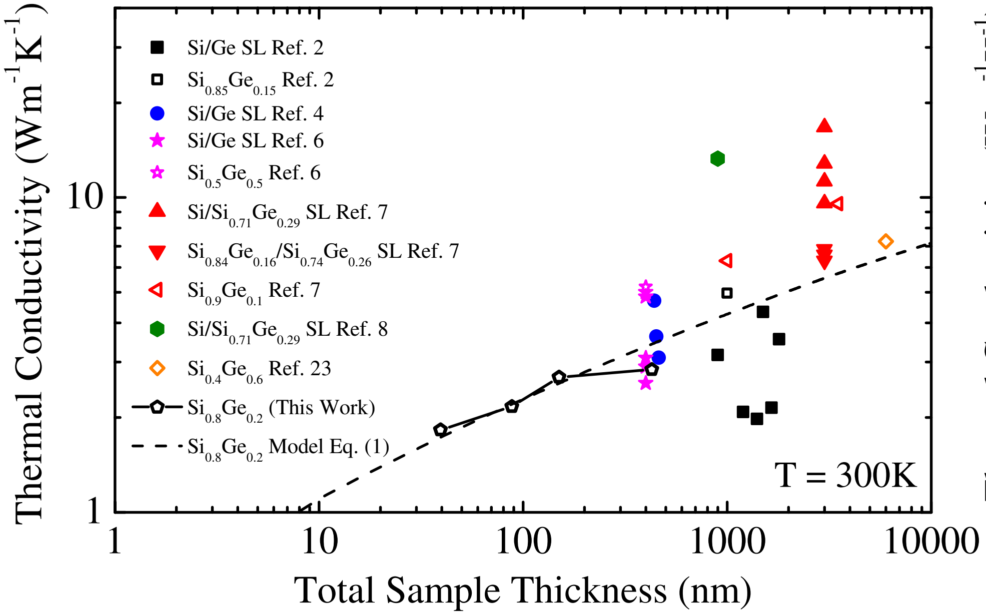


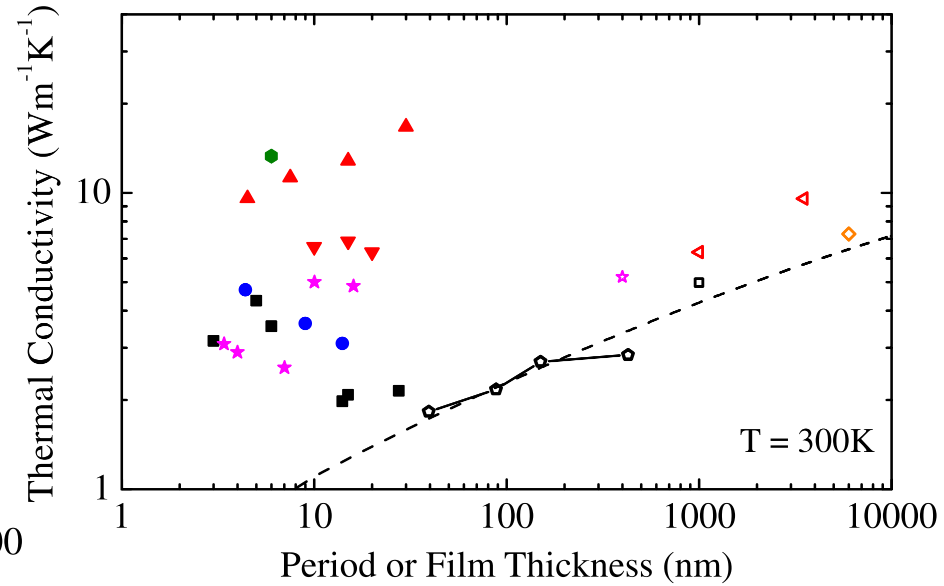
Phys. Rev. Lett. **109**, 195901

What size effects matter in superlattices?

Superlattices vs. total sample thickness

Thermal conductivity $Si_{1-x}Ge_x$ alloys





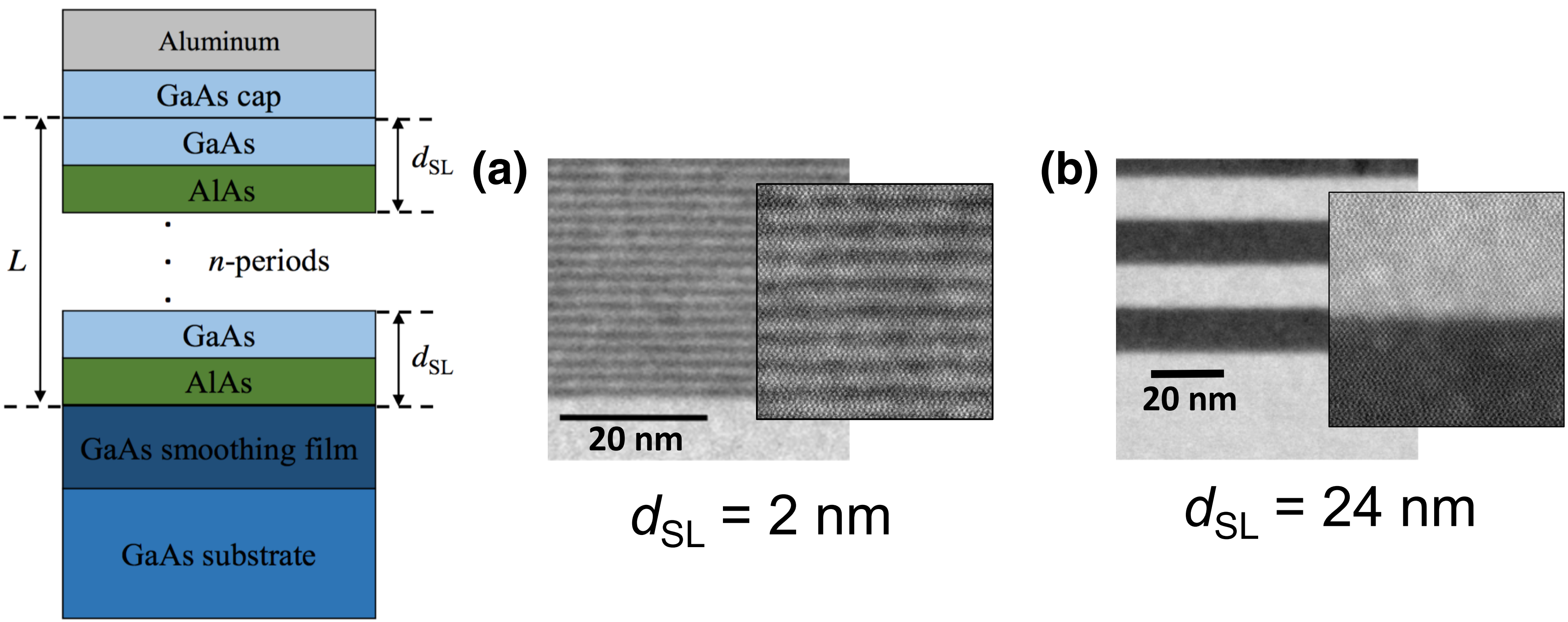
Phys. Rev. Lett. **109**, 195901

Total thickness vs. period thickness in SLs: what matters?

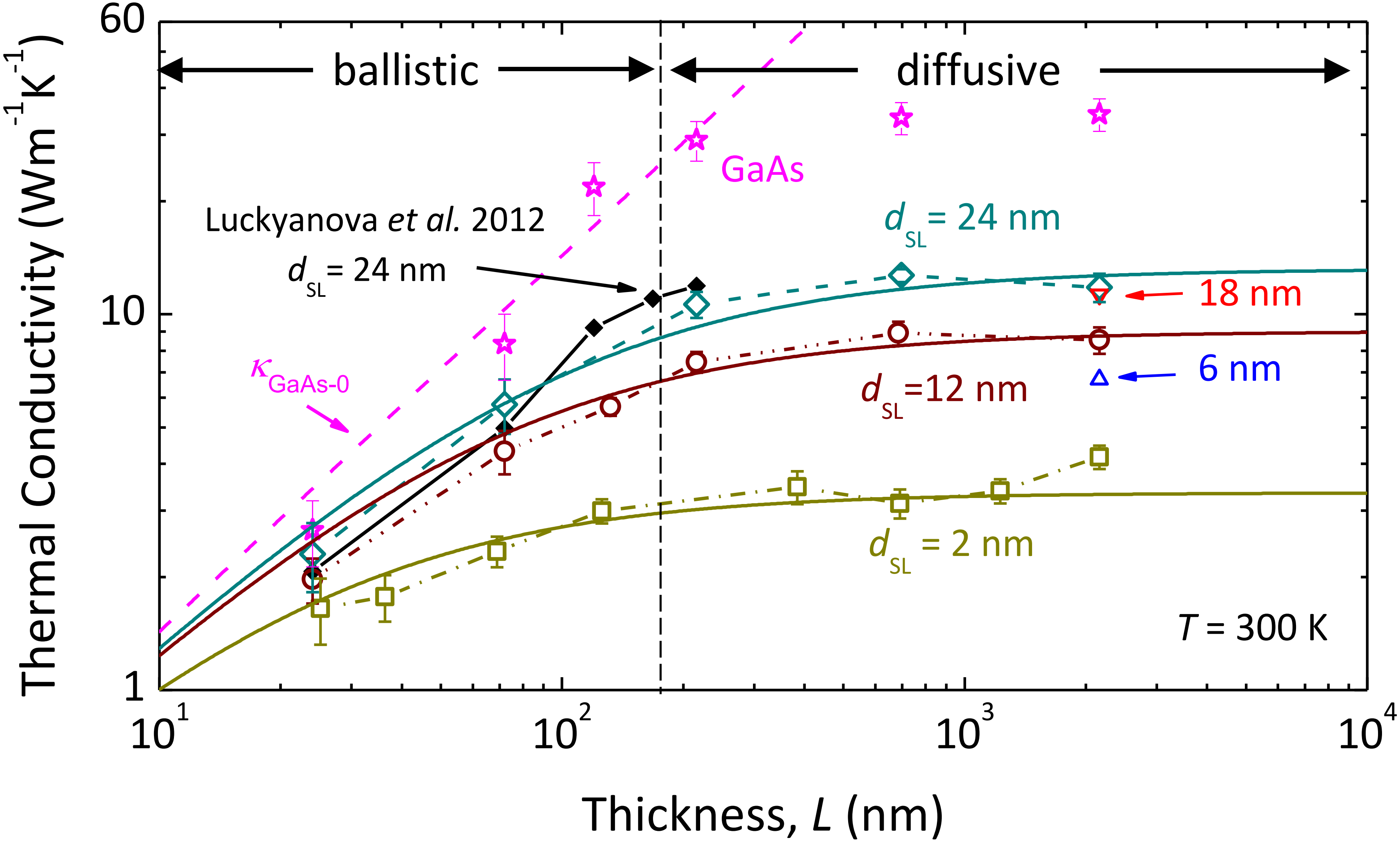
PHYSICAL REVIEW B **97**, 085306 (2018)

Interplay between total thickness and period thickness in the phonon thermal conductivity of superlattices from the nanoscale to the microscale: Coherent versus incoherent phonon transport

Ramez Cheaito,[1] Carlos A. Polanco,[2] Sadhvikas Addamane,[3] Jingjie Zhang,[2] Avik W. Ghosh,[2]
Ganesh Balakrishnan,[3] and Patrick E. Hopkins[1,4,5,*]



Thermal conductivity of GaAs/AlAs SLs

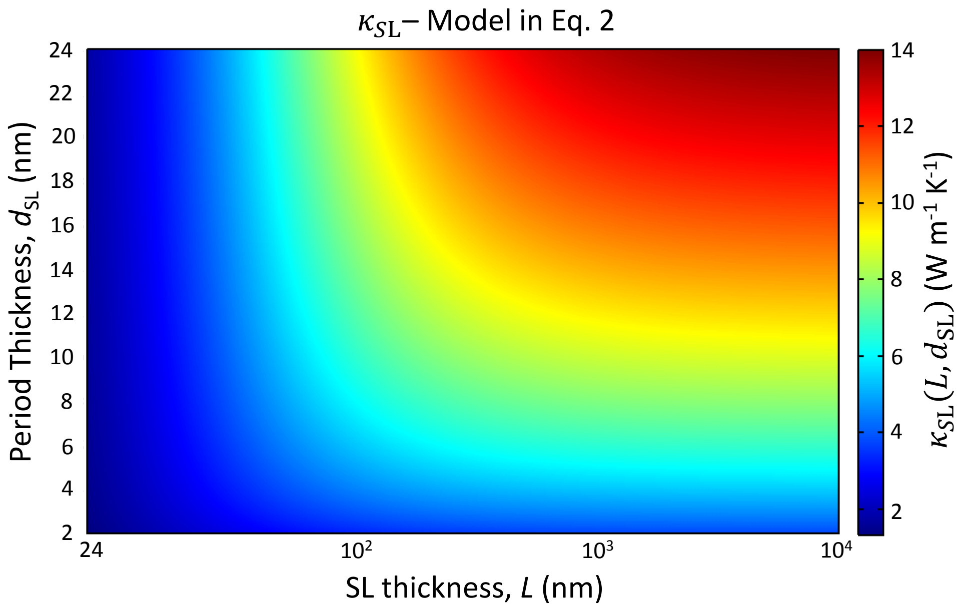


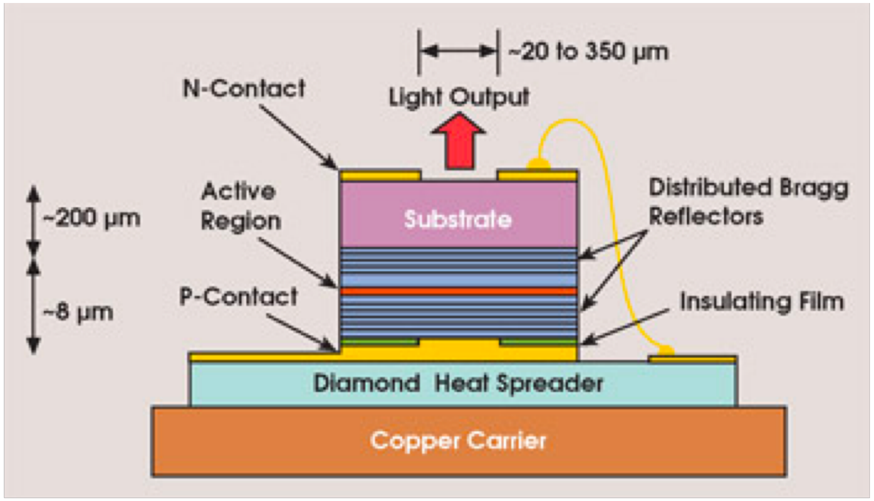
Phys. Rev. B **97**, 085306

Designing the thermal conductivity of SLs

Can use two length scales to control the thermal conductivity of SLs

Want to more efficiently remove heat from SL? Make it larger, but can keep periodicity the same (important for VCSELs)

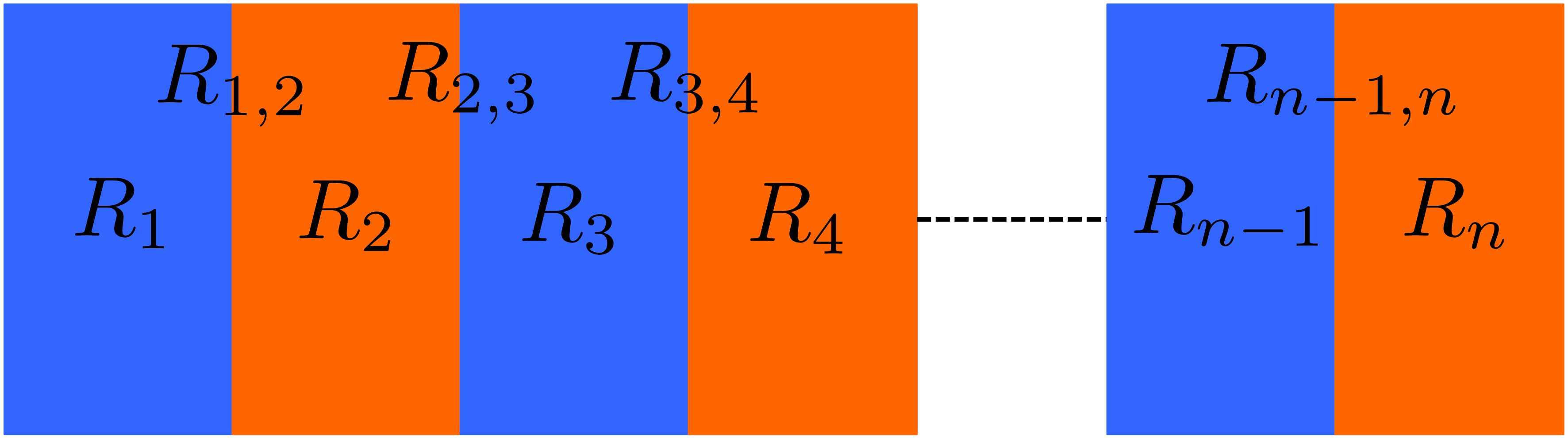




Phys. Rev. B **97**, 085306

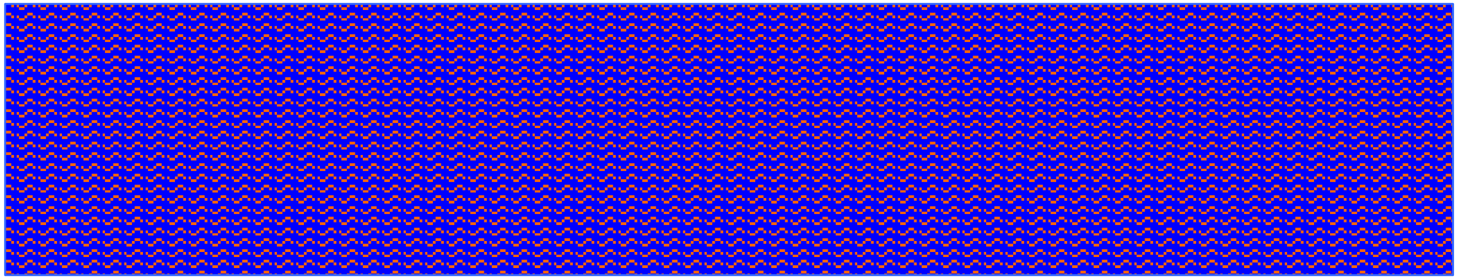
Photonics.com

Incoherent/particle picture of phonon transport in SLs



$$1/\kappa \propto 1/h = \sum_n R_j$$

What if layers are "linked"? – coherent transport

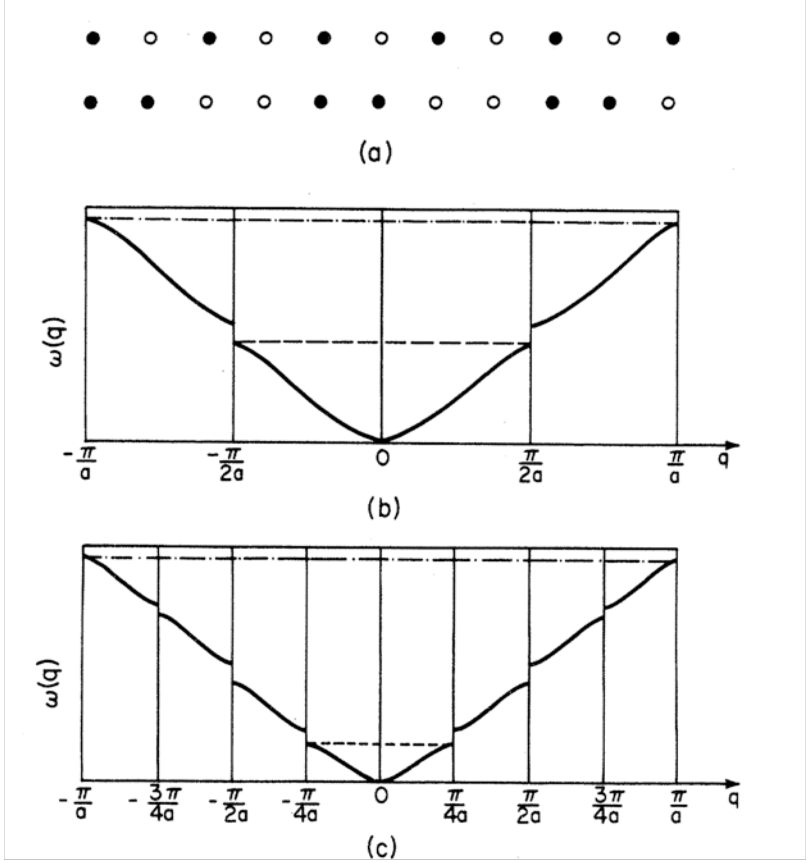


The minimum thermal conductivity of superlattices

PHYSICAL REVIEW B VOLUME 25, NUMBER 6 15 MARCH 1982

Thermal conductivity of superlattices

Shang Yuan Ren* and John D. Dow
Department of Physics and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 21 September 1981)

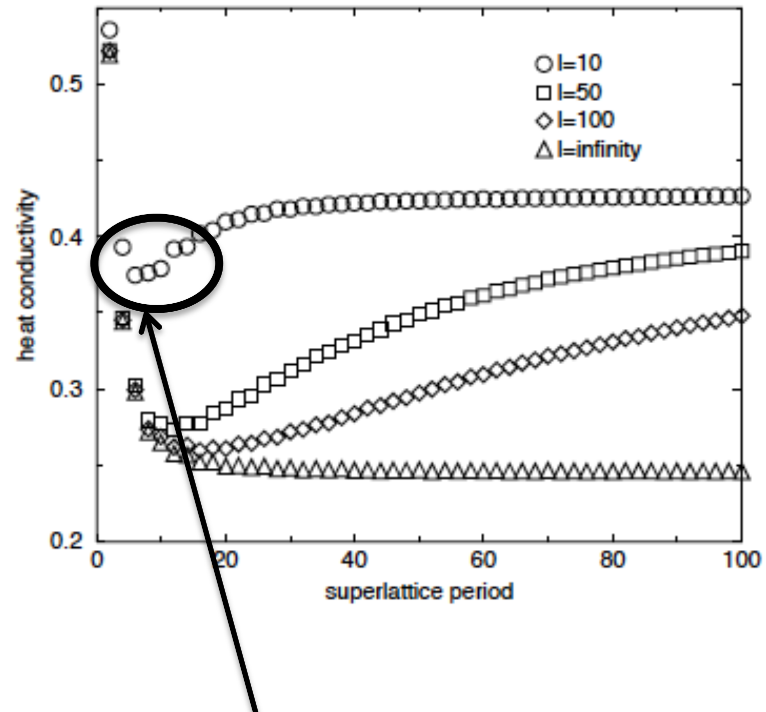


Interfacial periodicity can lead to “mini-band” formation

VOLUME 84, NUMBER 5 PHYSICAL REVIEW LETTERS 31 JANUARY 2000

Minimum Thermal Conductivity of Superlattices

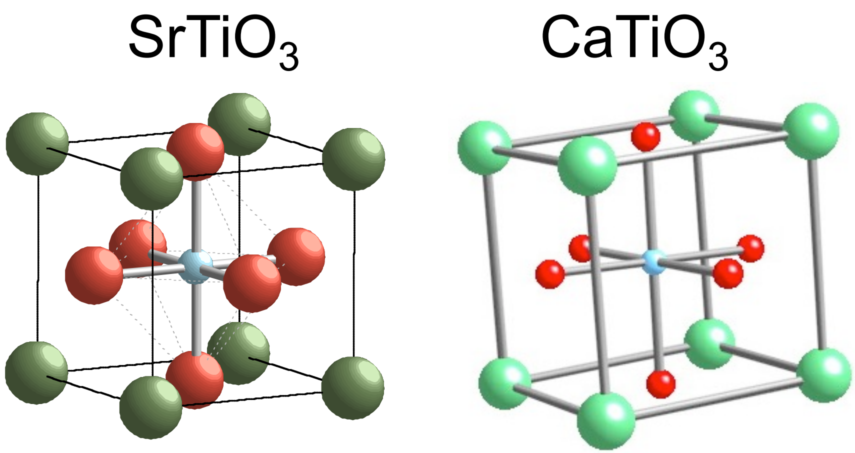
M. V. Simkin and G. D. Mahan
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200 and Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831
(Received 23 July 1999)



Mini-band formation leads to a minimum in the superlattice thermal conductivity

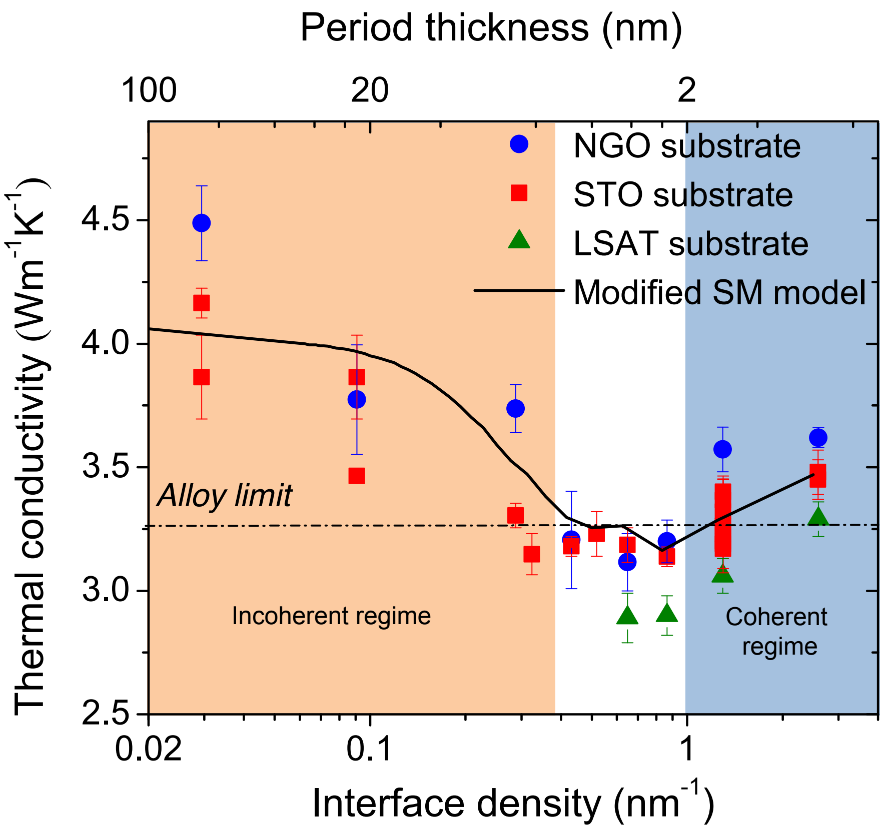
Experimental evidence of minimum thermal conductivity

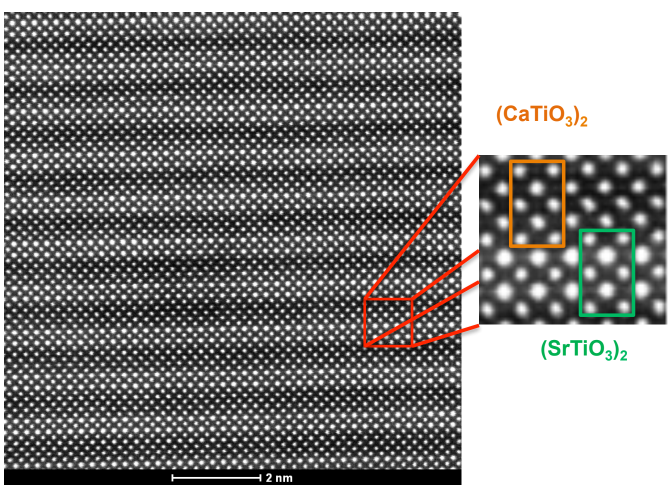
Nature Materials **13**, 168 (2013)



(a = 3.905 Å)
ρ = 5.1 g/cc
v_m = 5.41 km/s

(a_{pc} = 3.81 Å)
ρ = 3.75 g/cc
v_m = 5.71 km/s

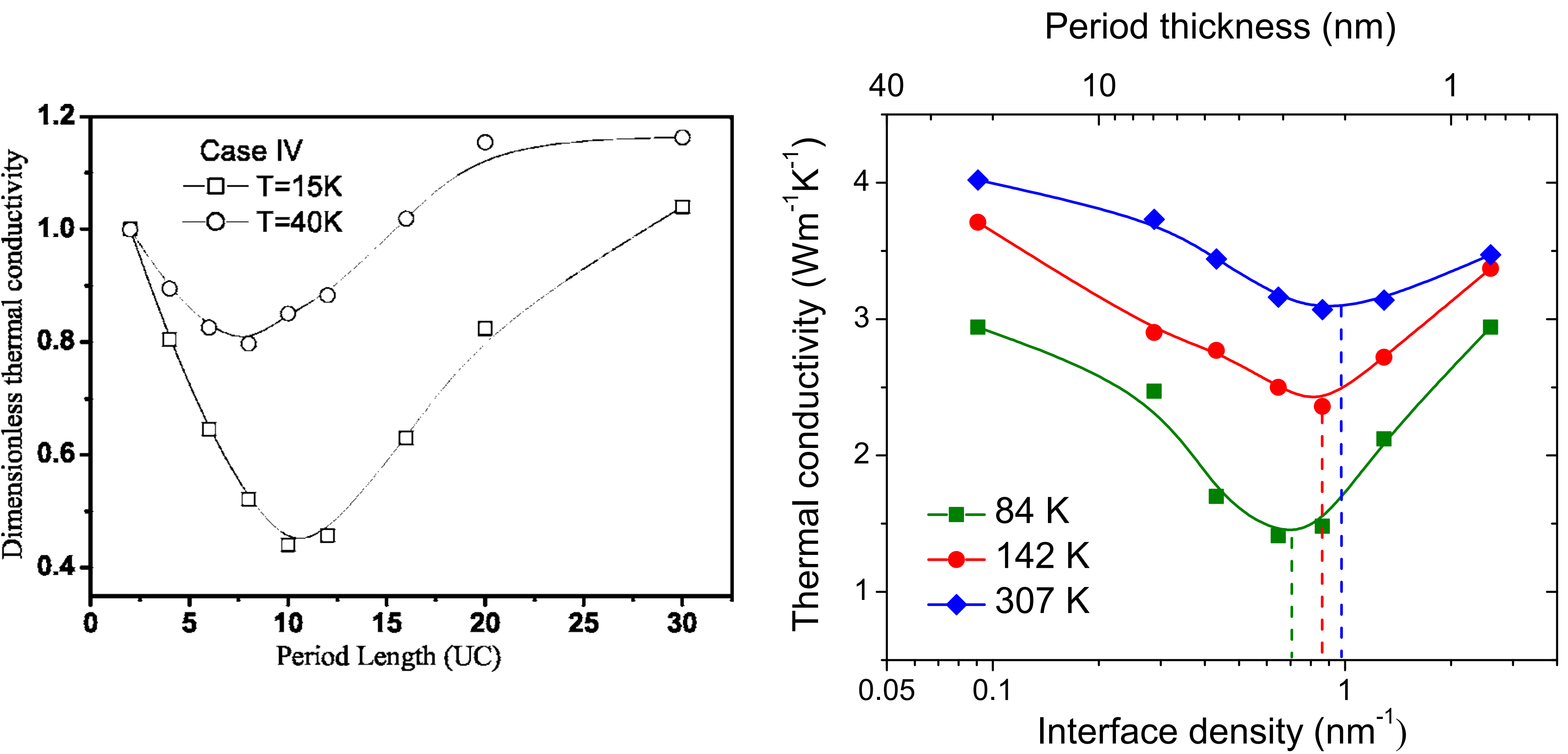




Growth PLD:
J. Ravichandran
A. Yadav
R. Ramesh
A. Majumdar

Experimental evidence of minimum thermal conductivity

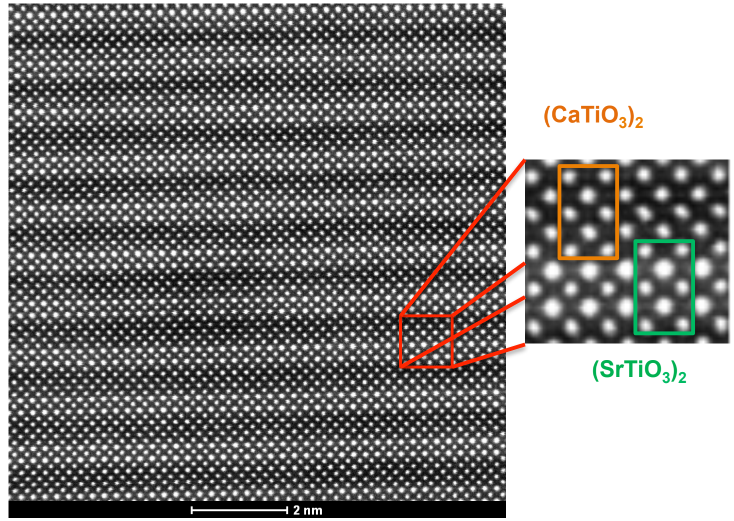
- More pronounced minimum at low T, thermal conductivity measurements show trends of mini-band formation
- MD simulation (left), mini-band = phonon bandgap (PRB **72**, 174302)



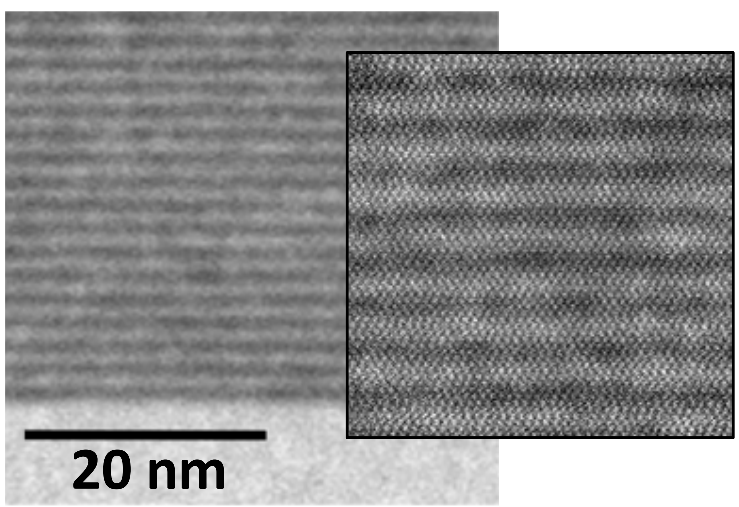
SL design to manipulate coherent phonon transport

Nature Materials **13**, 168 (2013)

Resolving unique phonon transport in SLs: interfaces matter

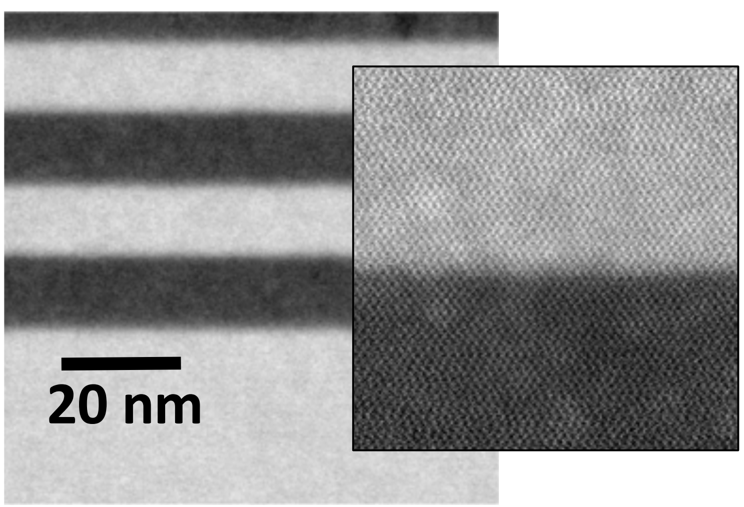


(a)



d_{SL} = 2 nm

(b)



d_{SL} = 24 nm

Outline

Static control of phonon transport

Defects/interfaces to permanently change κ

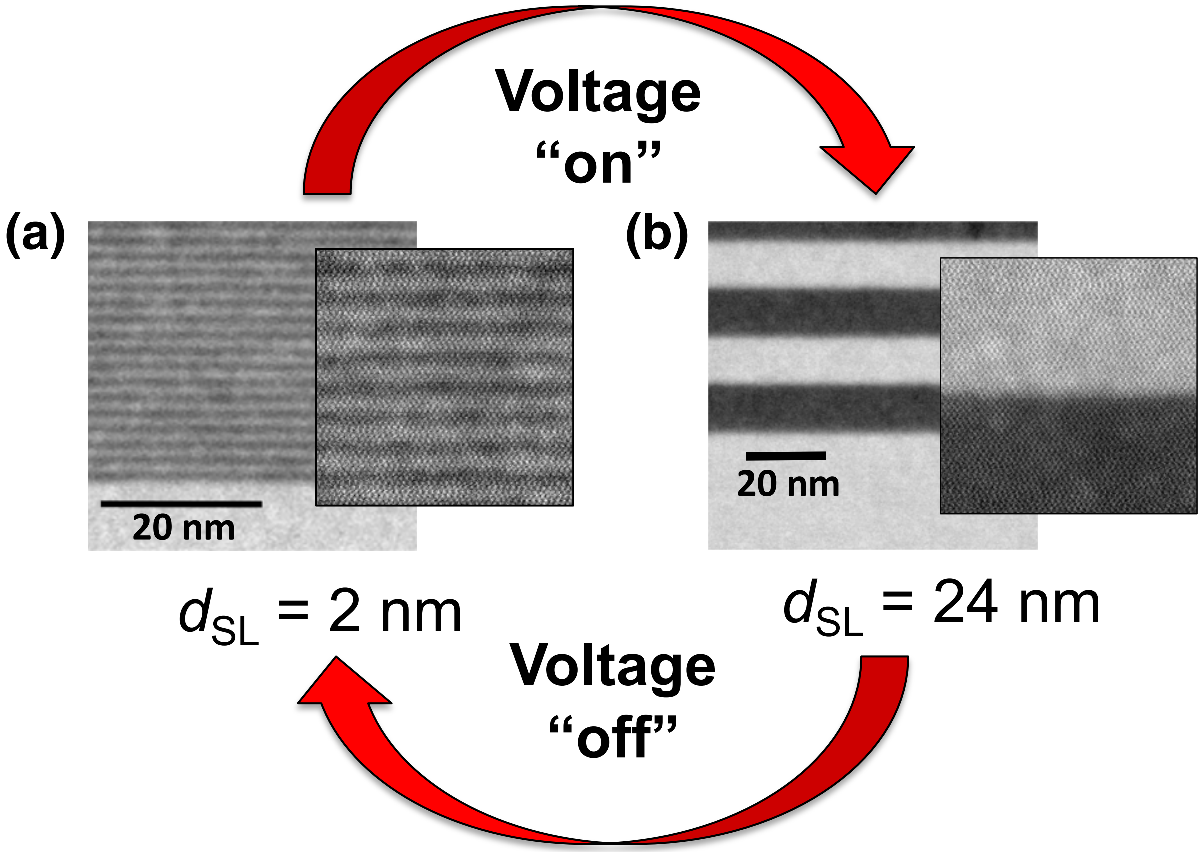
Dynamic control of phonon transport

Thermal conductivity switch – can we *reversibly* change κ with an external stimulus?

Can we use an external stimulus to change mean free path?

Thought experiment: can we dynamically and reversibly change the density of defects/interfaces?

$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$



Ok…can't really do this with these SLs….but, lets consider materials where this voltage control of defects can happen

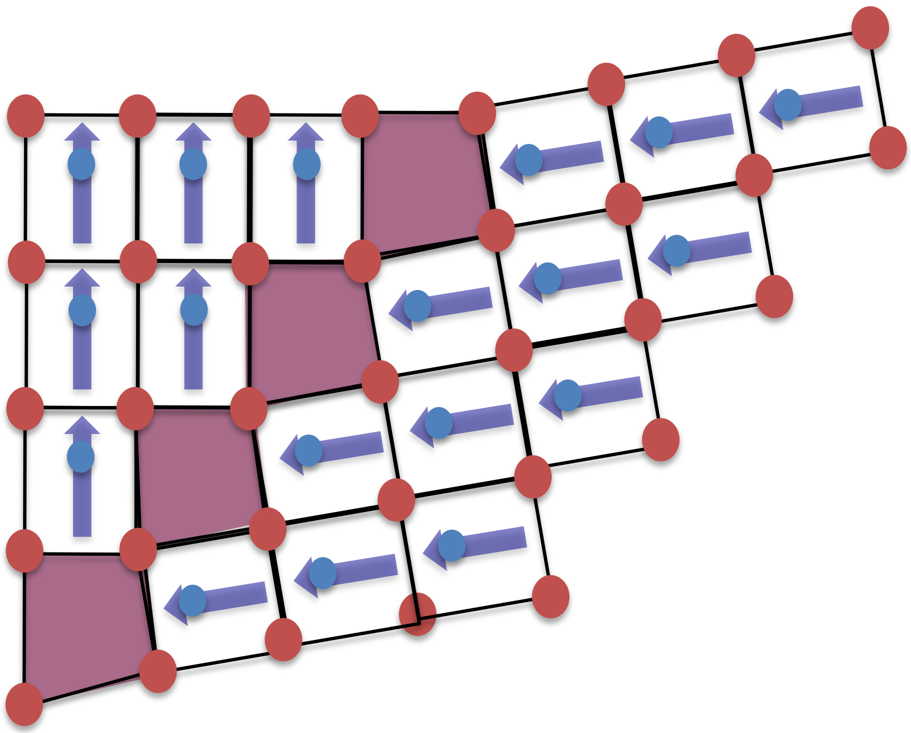
FERROELECTRICS

Mobile coherent interfaces: ferroelastic domain boundaries

- Strain and orientation changes across coherent interfaces are known to affect thermal conduction

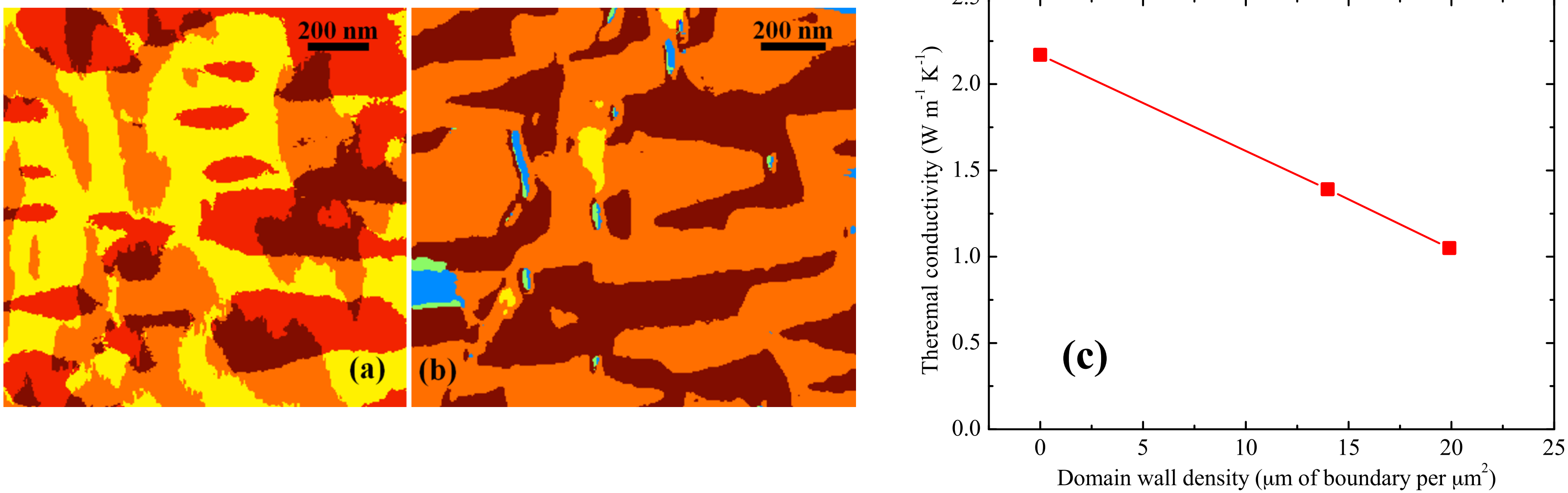
- These two features both exist at ferroelastic domain walls

- We would therefore anticipate that ***domain boundaries can scatter phonons***



Coherent interfaces: ferroelastic domain boundaries

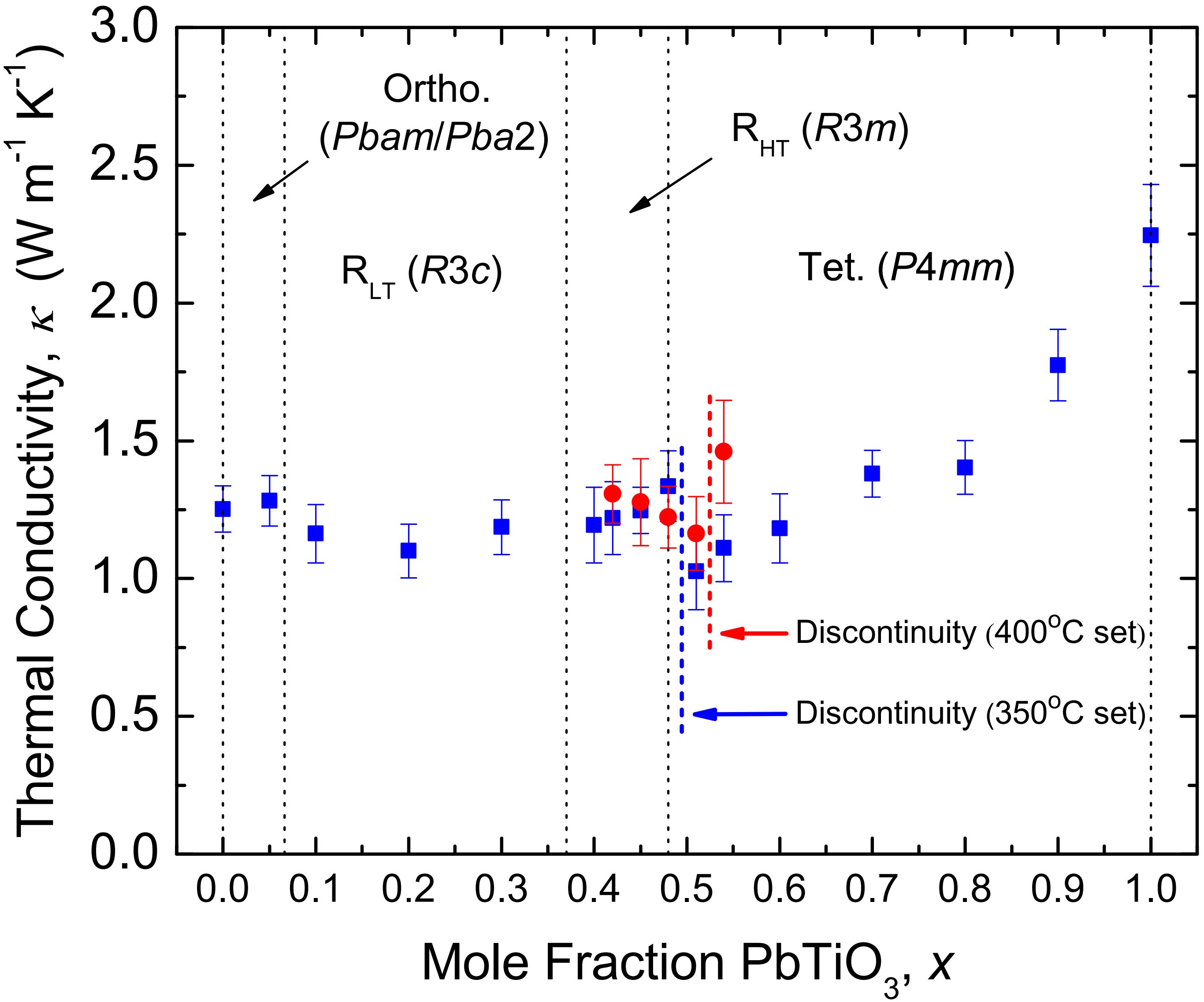
4-variants **2-variants**



- Ferroelastic domain walls scatter phonons and influence thermal conductivity in thin films and at room temperature
- With proper experimental design, domain boundaries can move based on electric fields

Appl. Phys. Lett. **102**, 121903 (2013)

More evidence of ferroelectric domain boundaries in PZT

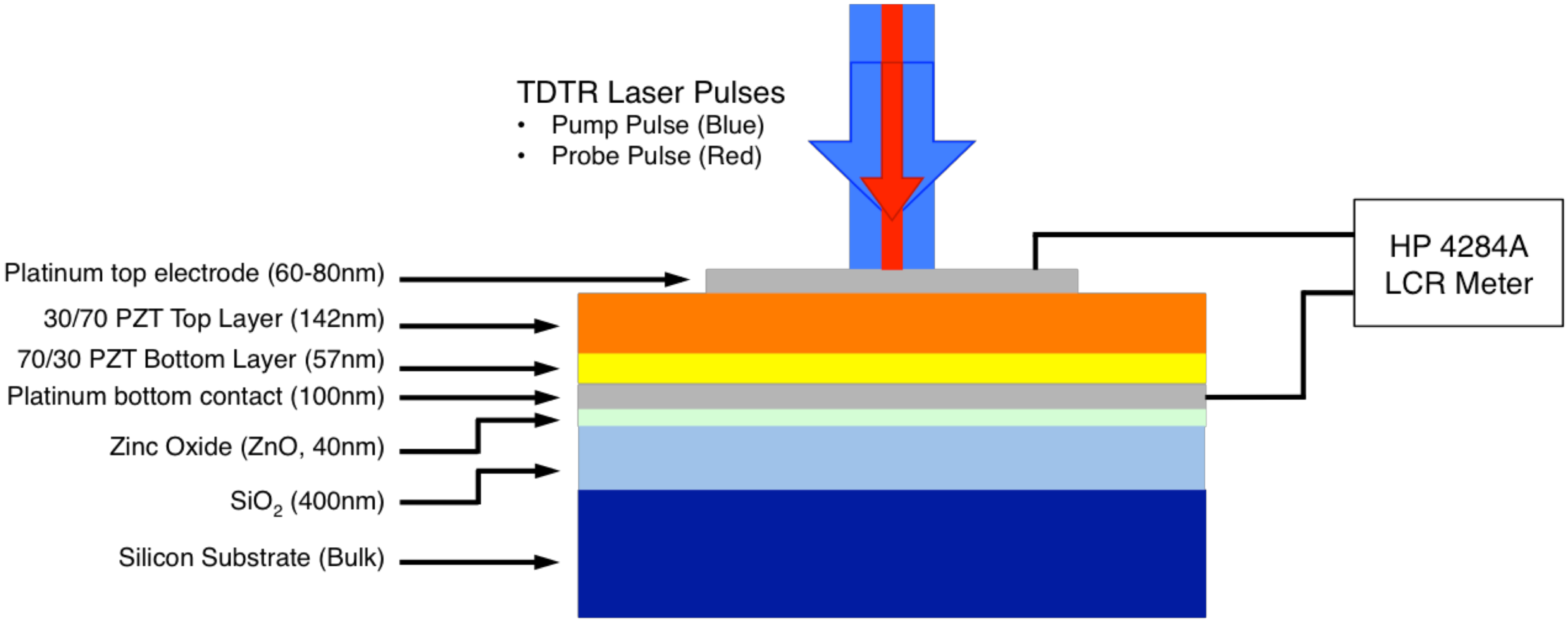


J. Appl. Phys. **121**, 205104 (2017)

Electrically switching thermal conductivity of PZT

Lead Zirconate Titanate, PZT = $PbZr_xTi_{1-x}O_3$

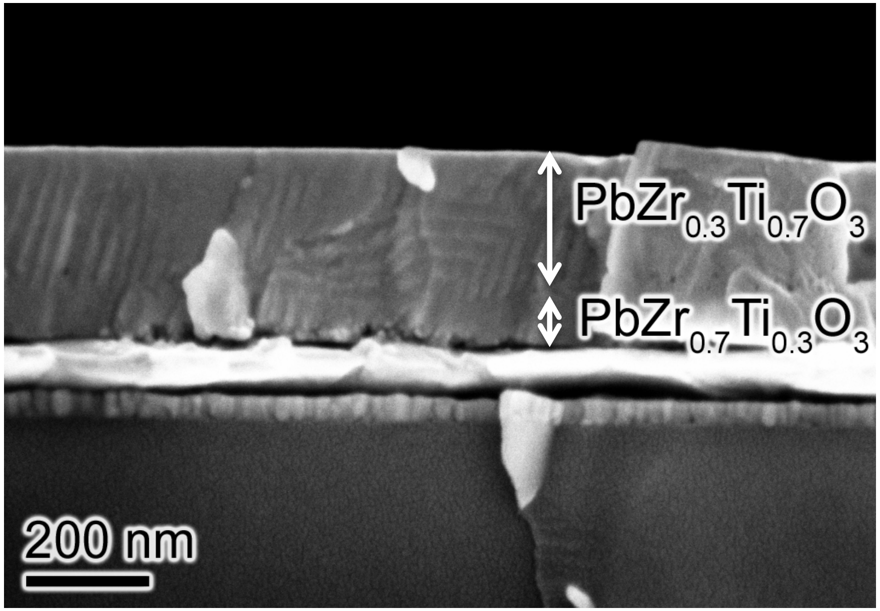
- PZT bilayer can have highly mobile ferroelastic domain walls
- Prepared bilayer films via CSD on $Pt/ZnO/SiO_2/Si$ (J. Ihlefeld, UVA)

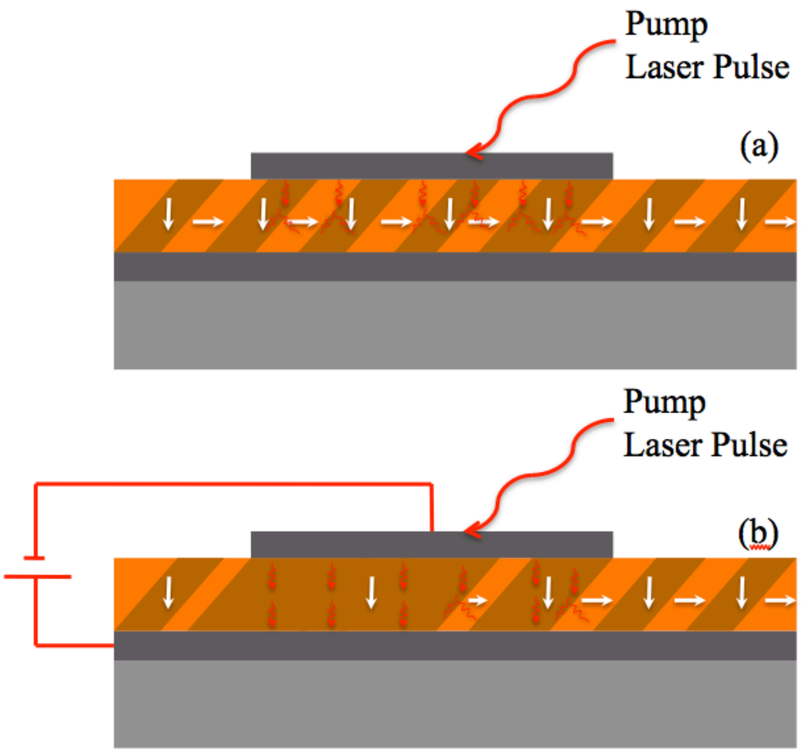


Electrically switching thermal conductivity of PZT

Lead Zirconate Titanate, PZT = $PbZr_xTi_{1-x}O_3$

- PZT bilayer can have highly mobile ferroelastic domain walls
- Prepared bilayer films via CSD on $Pt/ZnO/SiO_2/Si$ (J. Ihlefeld, SNL)

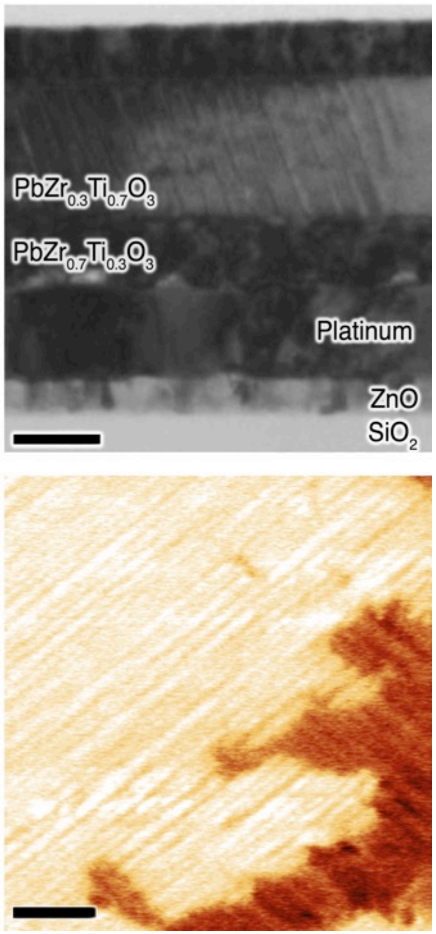




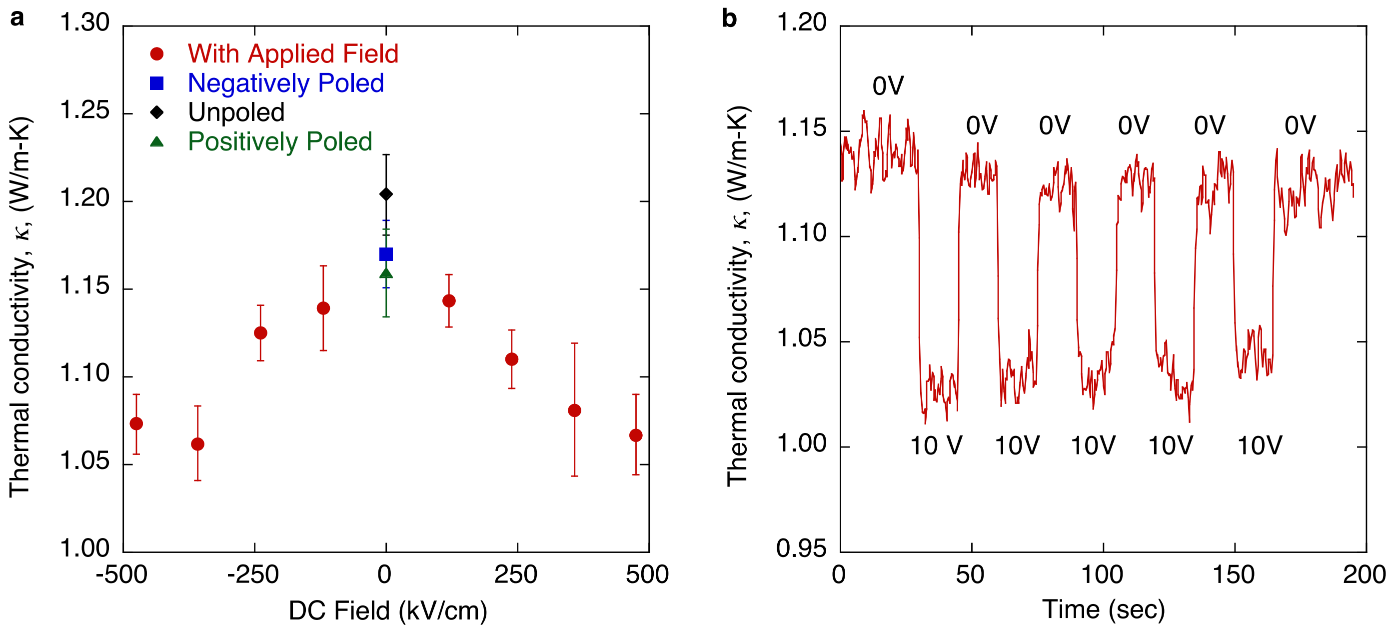
Electrically switching thermal conductivity of PZT

a

b



Domain structure becomes ***more*** complex under applied fields (*PRB* **81**, 174118 (2010))

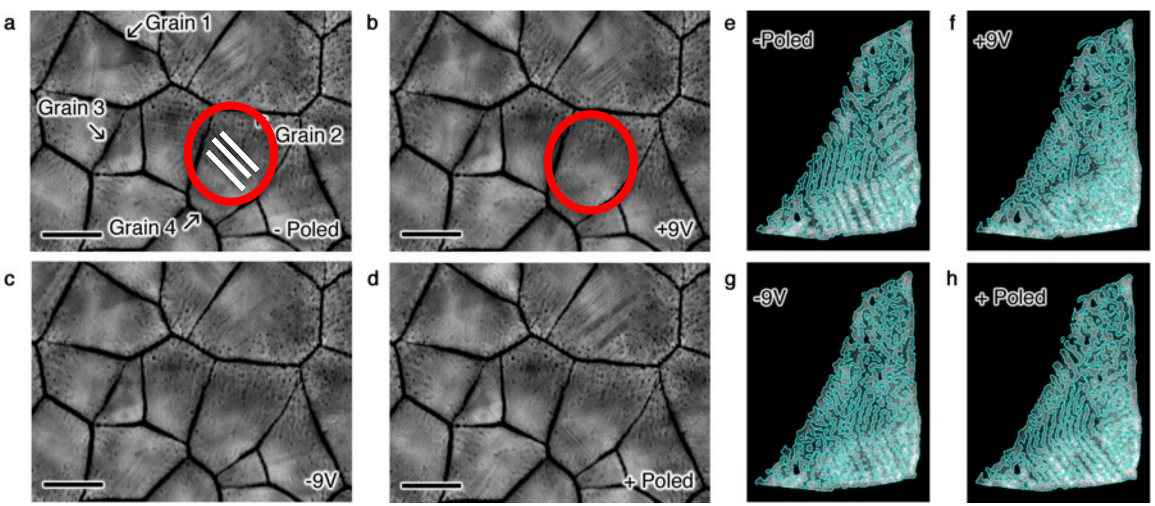


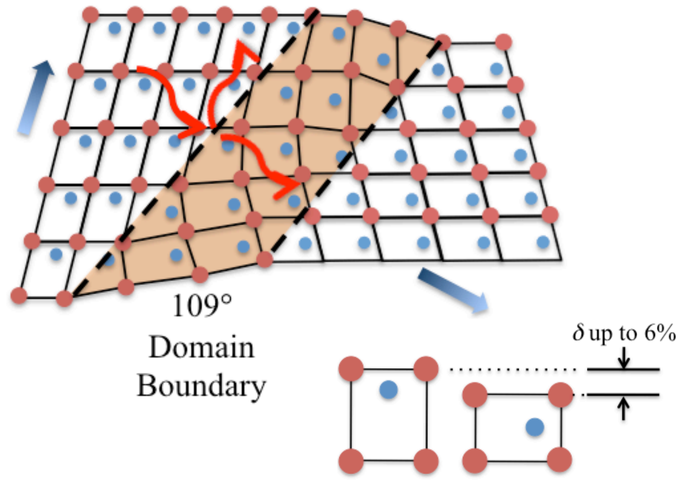
NANO LETTERS
DOI: 10.1021/nl504505t
Letter
Nano Lett. 2015, 15, 1791−1795
pubs.acs.org/NanoLett

Room-Temperature Voltage Tunable Phonon Thermal Conductivity via Reconfigurable Interfaces in Ferroelectric Thin Films

Jon F. Ihlefeld,*,[†] Brian M. Foley,[‡] David A. Scrymgeour,[†] Joseph R. Michael,[†] Bonnie B. McKenzie,[†] Douglas L. Medlin,[§] Margeaux Wallace,[∥] Susan Trolier-McKinstry,[∥] and Patrick E. Hopkins*,[‡]

Electrically switching thermal conductivity of PZT





NANO LETTERS
DOI: 10.1021/nl504505t
Letter
Nano Lett. 2015, 15, 1791−1795
pubs.acs.org/NanoLett

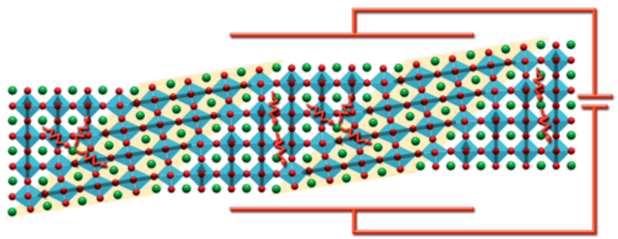
Room-Temperature Voltage Tunable Phonon Thermal Conductivity via Reconfigurable Interfaces in Ferroelectric Thin Films

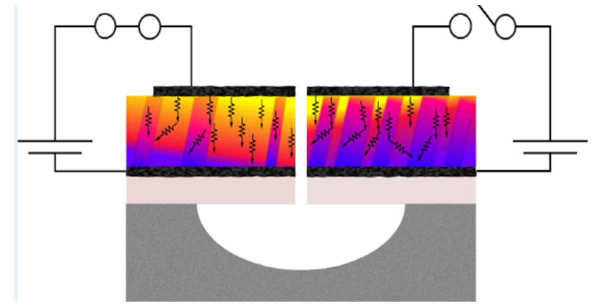
Jon F. Ihlefeld,*[†] Brian M. Foley,[‡] David A. Scrymgeour,[†] Joseph R. Michael,[†] Bonnie B. McKenzie,[†] Douglas L. Medlin,[§] Margeaux Wallace,[∥] Susan Trolier-McKinstry,[∥] and Patrick E. Hopkins*[‡]

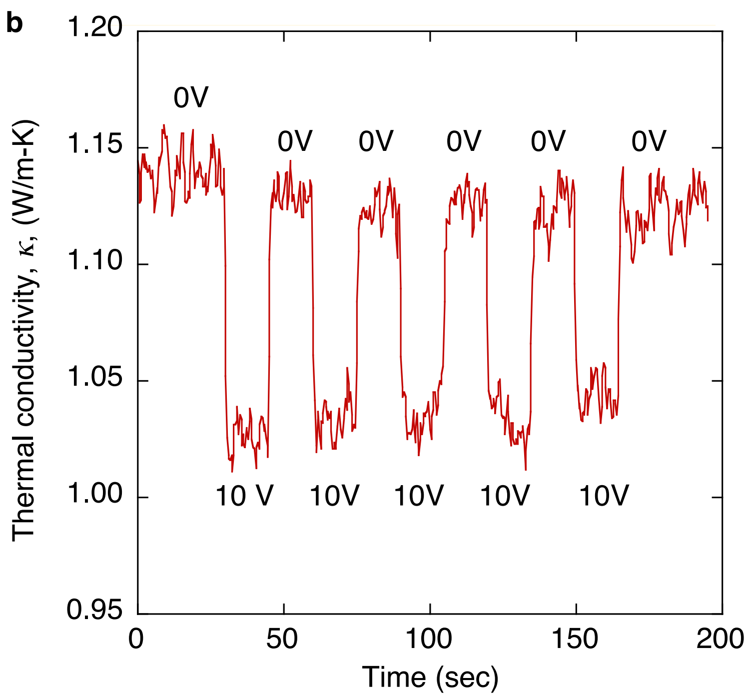
Controlling thermal conductivity - Dynamic

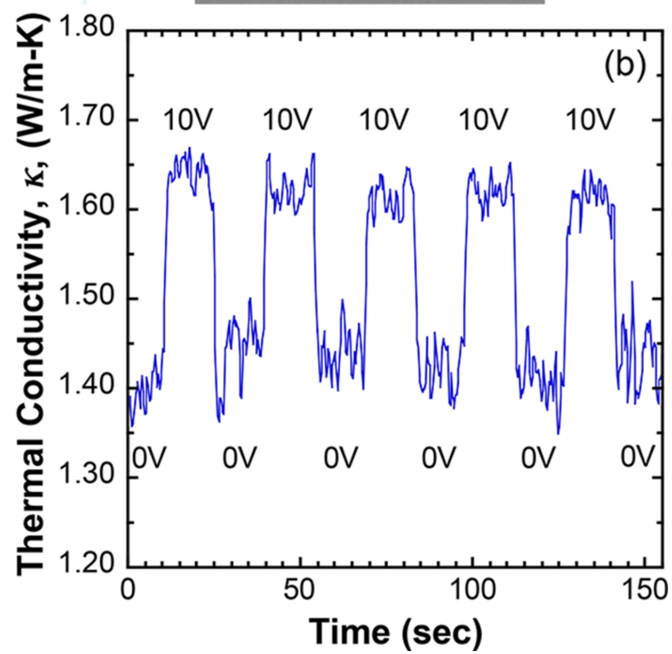
The thermal conductivity switch

Field controlled ferroelastic domain mobility in PZT









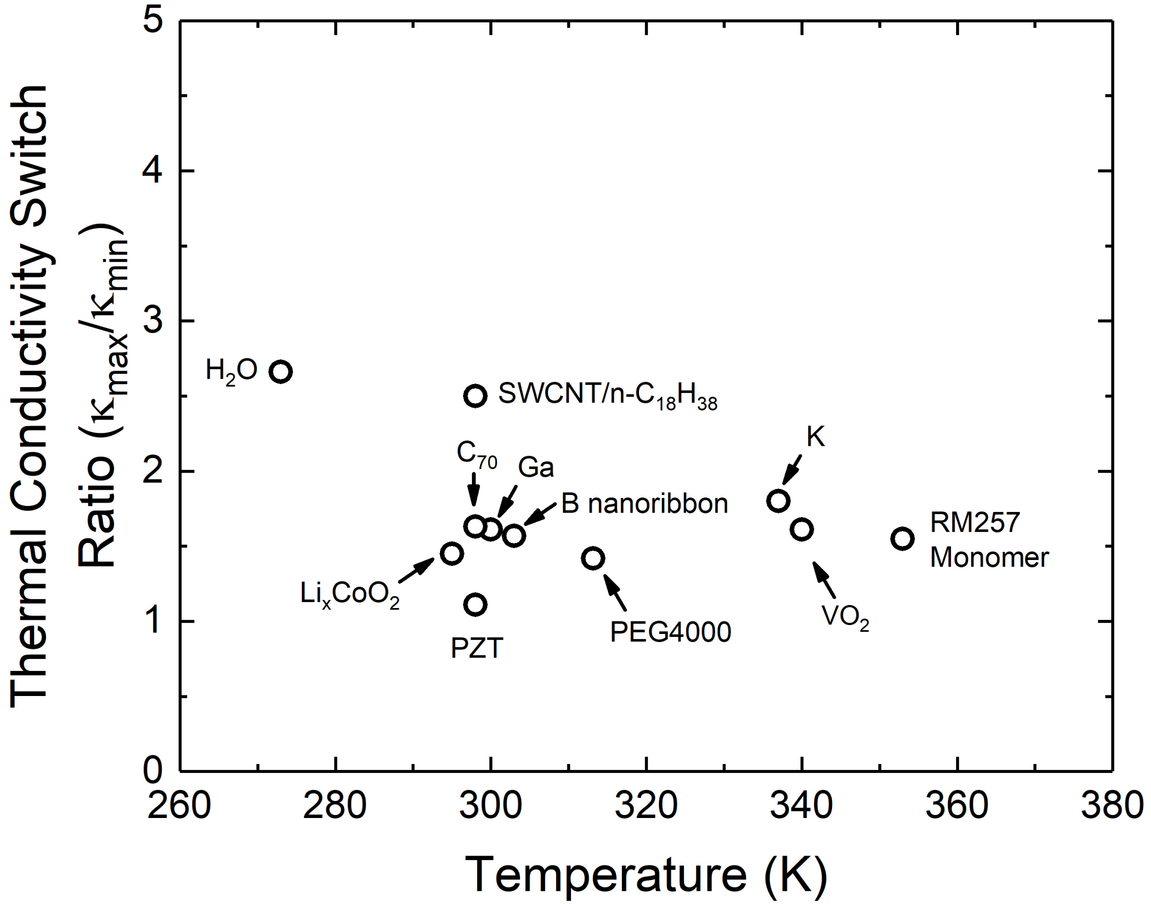
Nano Letters **15**, 1791 (2015)

Appl. Mat. & Int. **10**, 25493 (2018)

Controlling thermal conductivity - Dynamic

The thermal conductivity switch

State of the art around biologically relevant temperatures

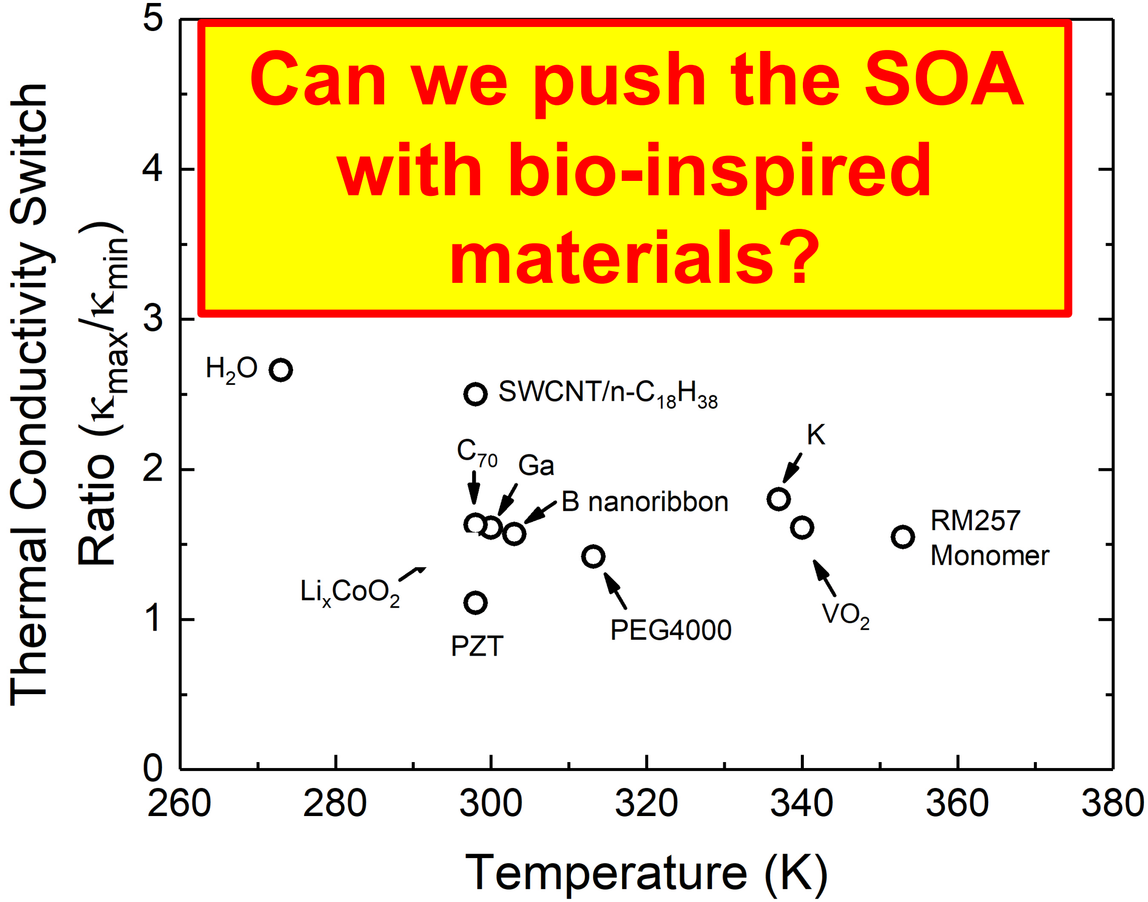


Nature Nanotechnology **13**, 959 (2018)

Controlling thermal conductivity - Dynamic

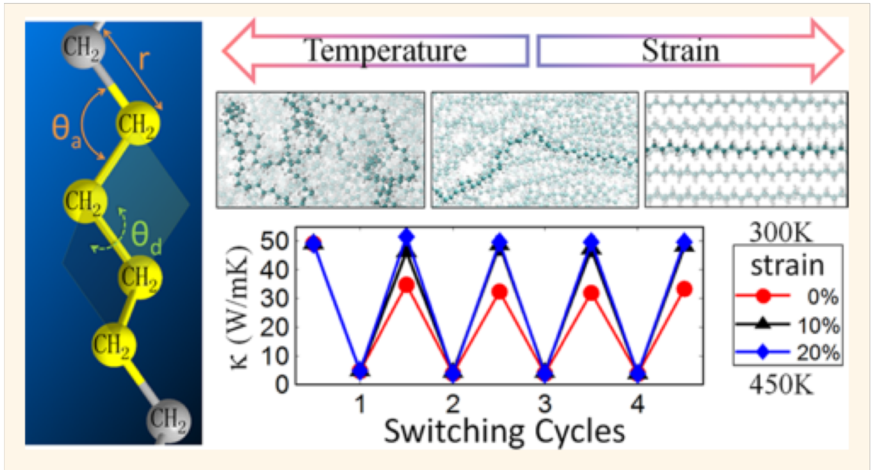
The thermal conductivity switch

State of the art around biologically relevant temperatures



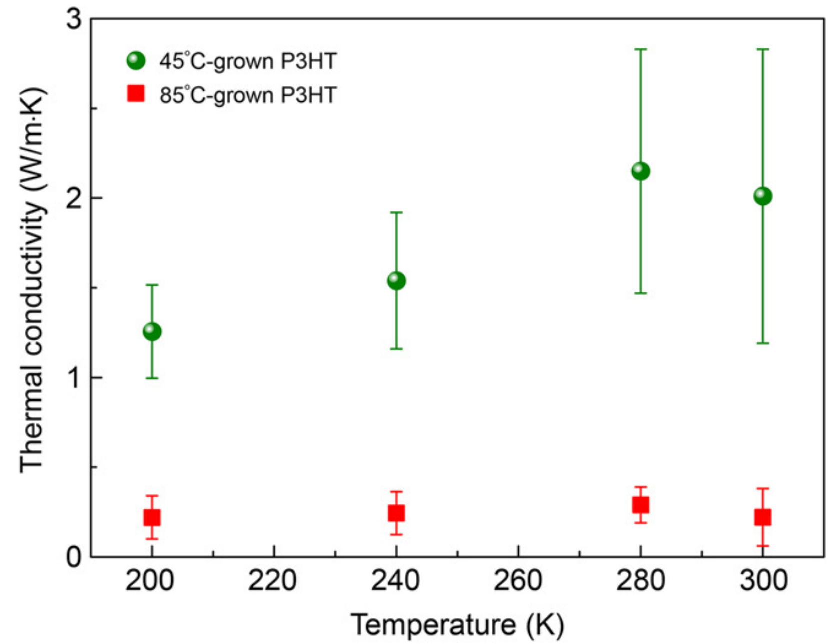
Nature Nanotechnology **13**, 959 (2018)

Heat transfer and thermal conductivity in polymers



ACS Nano **7**, 7592

Polyethylene predicted to vary thermal conductivity by a **factor of 12**

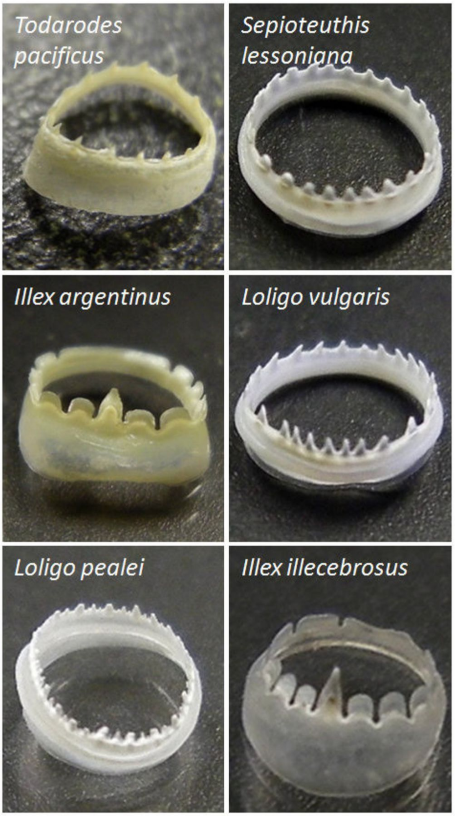


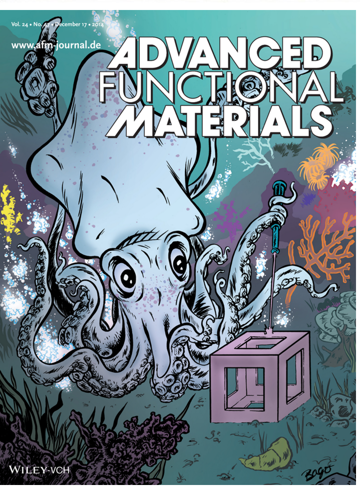
Science Advances ***4***, eaar3031

Increased inter- and intramolecular bonding has been shown to **create polymers with ~10x higher κ than conventional polymers**

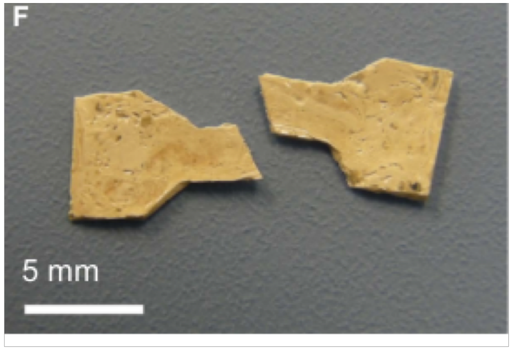
Strain, chain alignment and crystallinity lead to large changes in polymer thermal conductivity (static)

Squid ring teeth proteins – Prof. Melik Demirel (Penn State)

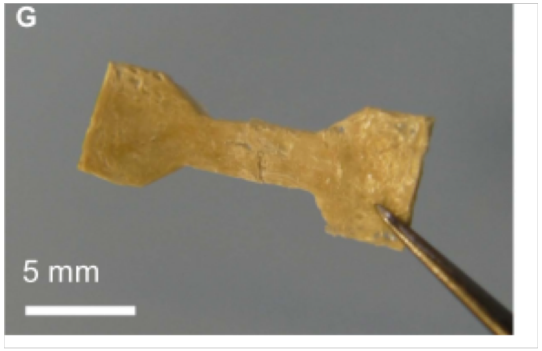




Adv. Func. Mat. **24**, 7393 (M. Demirel)

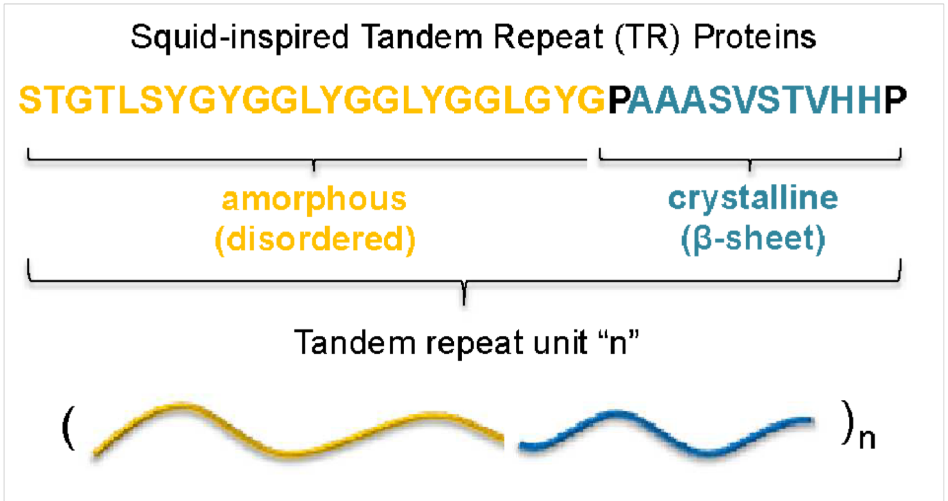


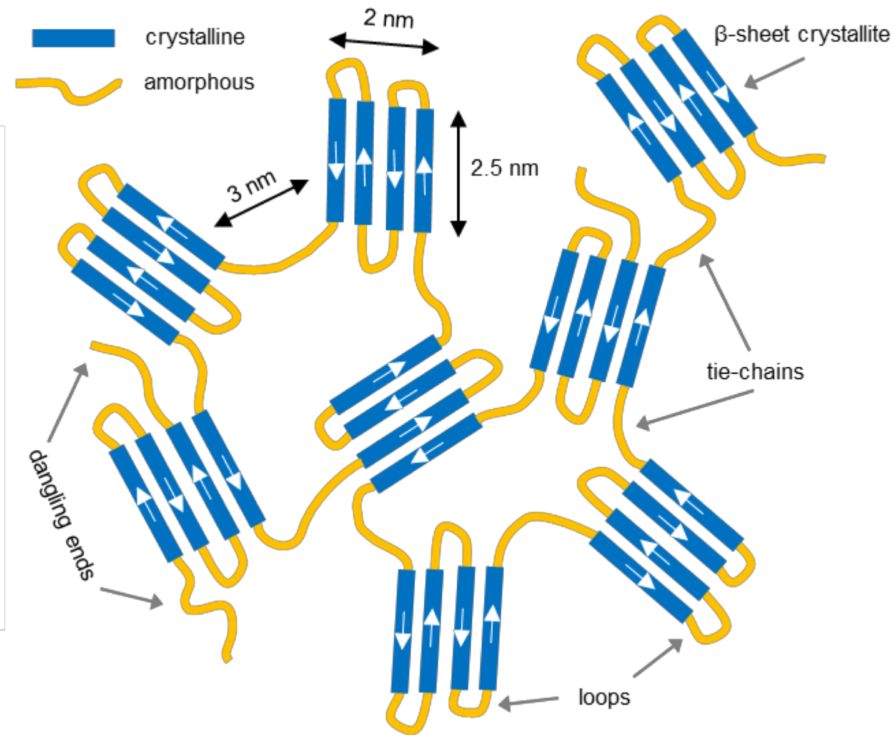
Add water!



Self healing when hydrated (with a little bit of heat)

Squid ring teeth proteins – Prof. Melik Demirel (Penn State)

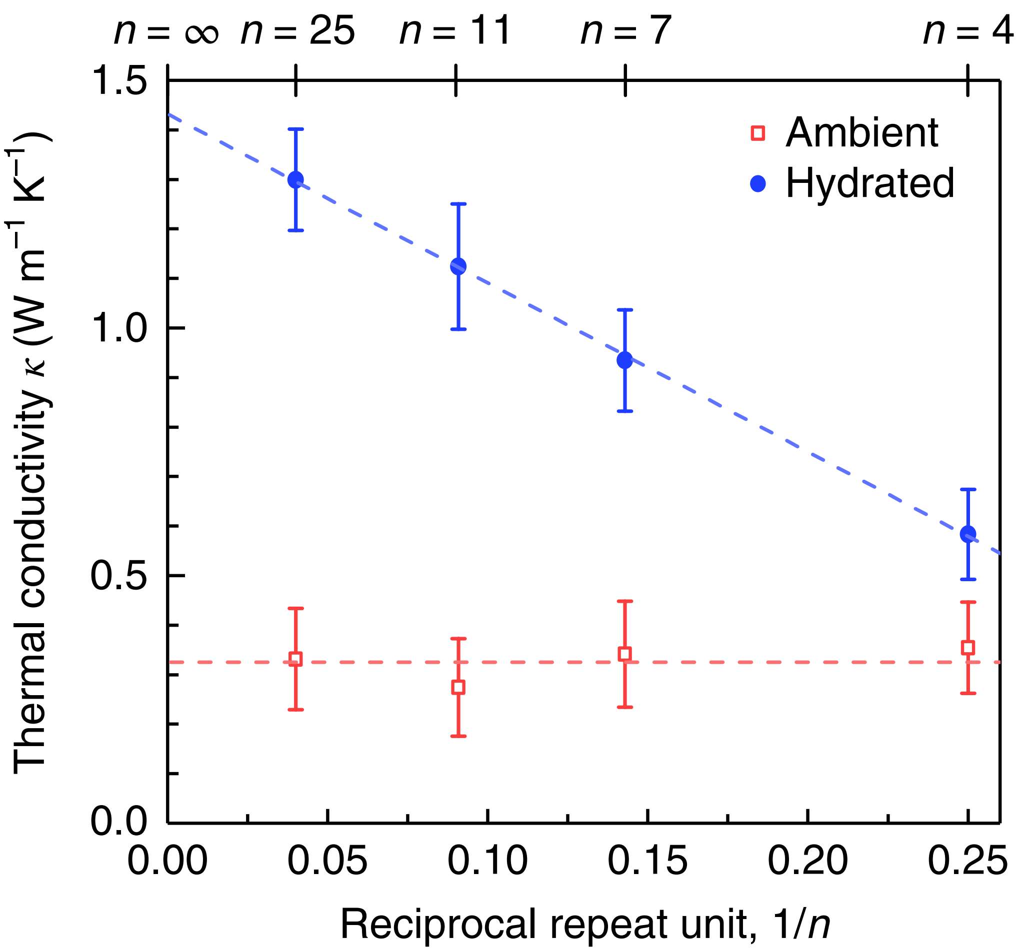




- Can we tune the thermal conductivity buy changing the molecular structure? (static)
- Can we dynamically control the thermal conductivity with hydration? (dynamic thermal conductivity switch)

Nature Nanotechnology **13**, 959 (2018)

Results – Programmable thermal conductivity



κ ambient

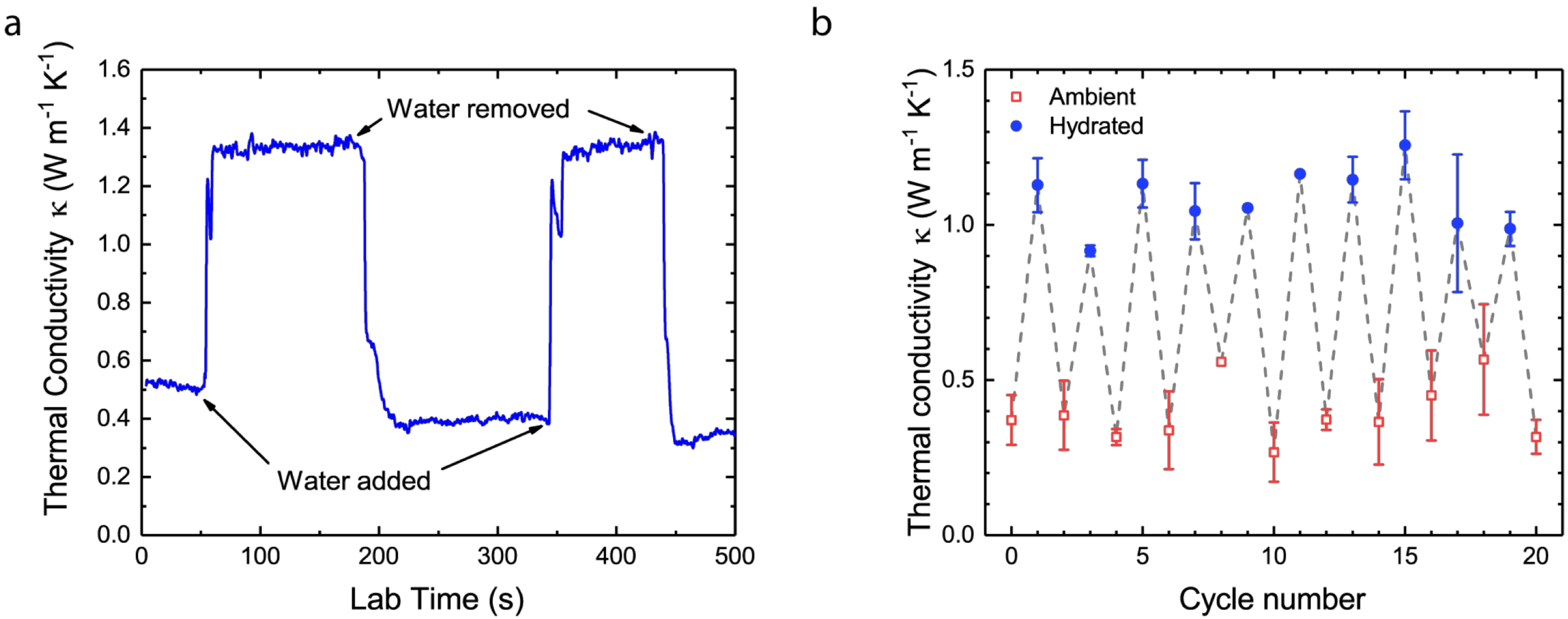
- No dependence on *n*
- Typical κ for polymer/protein
- Disorder dominates

κ hydrated

- Linear dependent on 1/n
- Up to 4X increase in κ compared to ambient

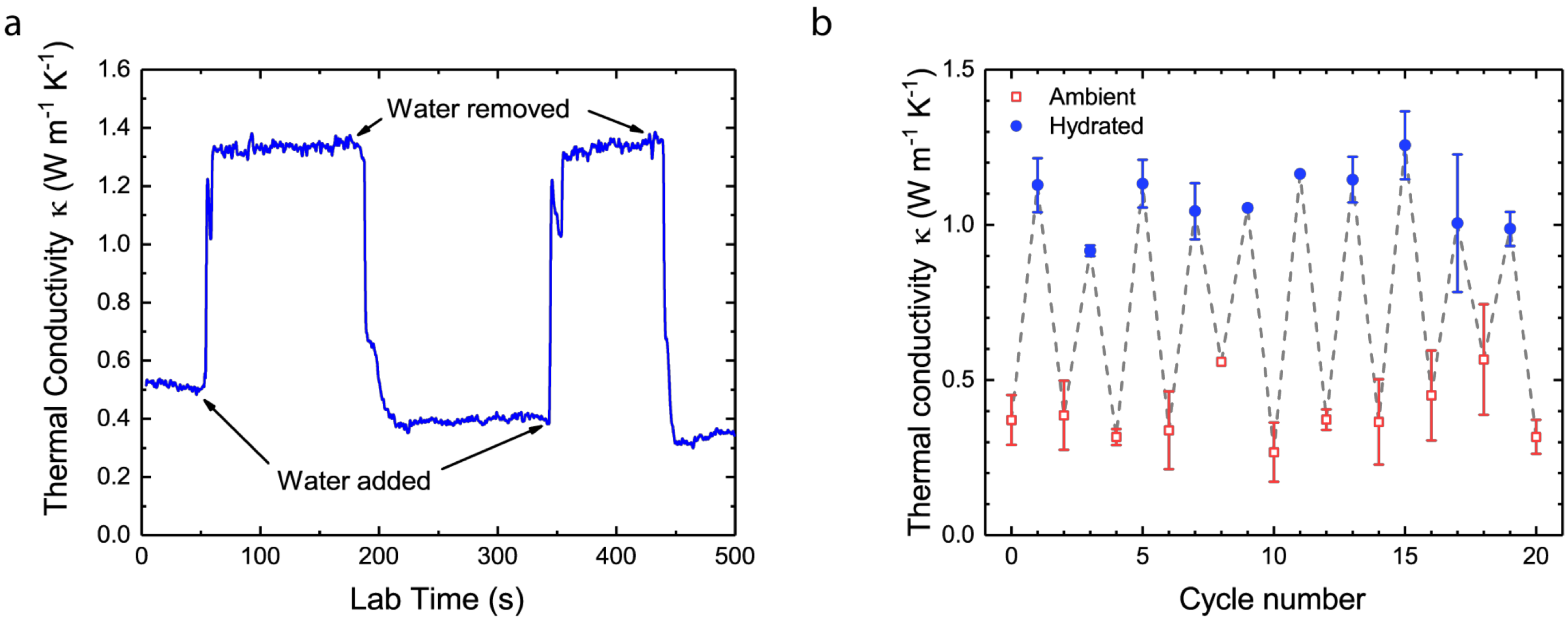
Nature Nanotechnology **13**, 959 (2018)

Results – Switchable thermal conductivity



Nature Nanotechnology **13**, 959 (2018)

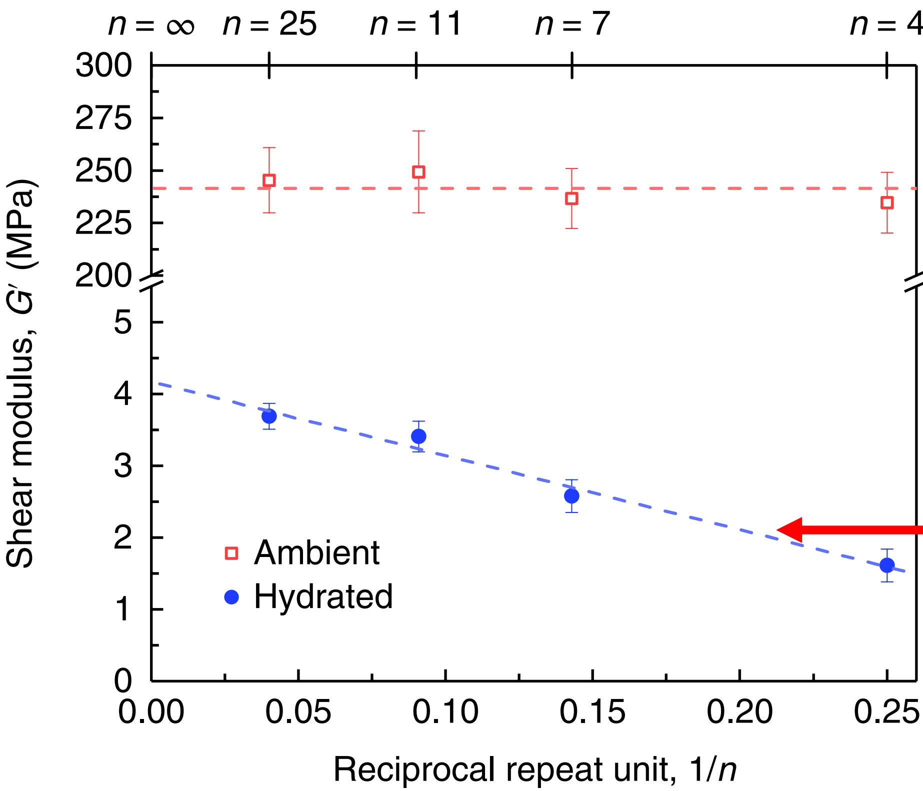
Results – Switchable thermal conductivity



But why???

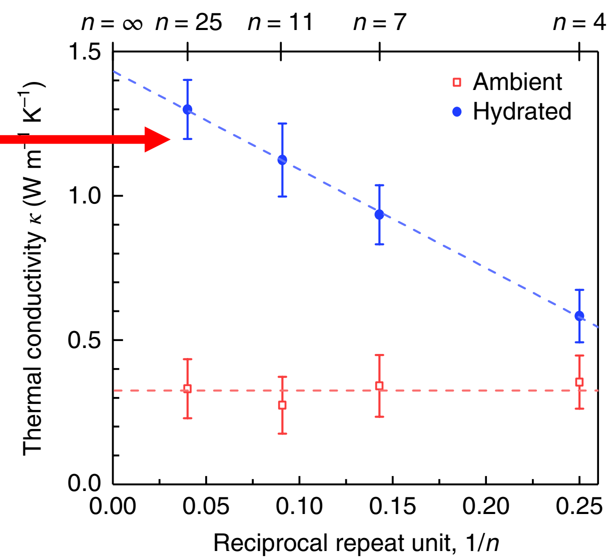
Nature Nanotechnology **13**, 959 (2018)

Results – Rheology



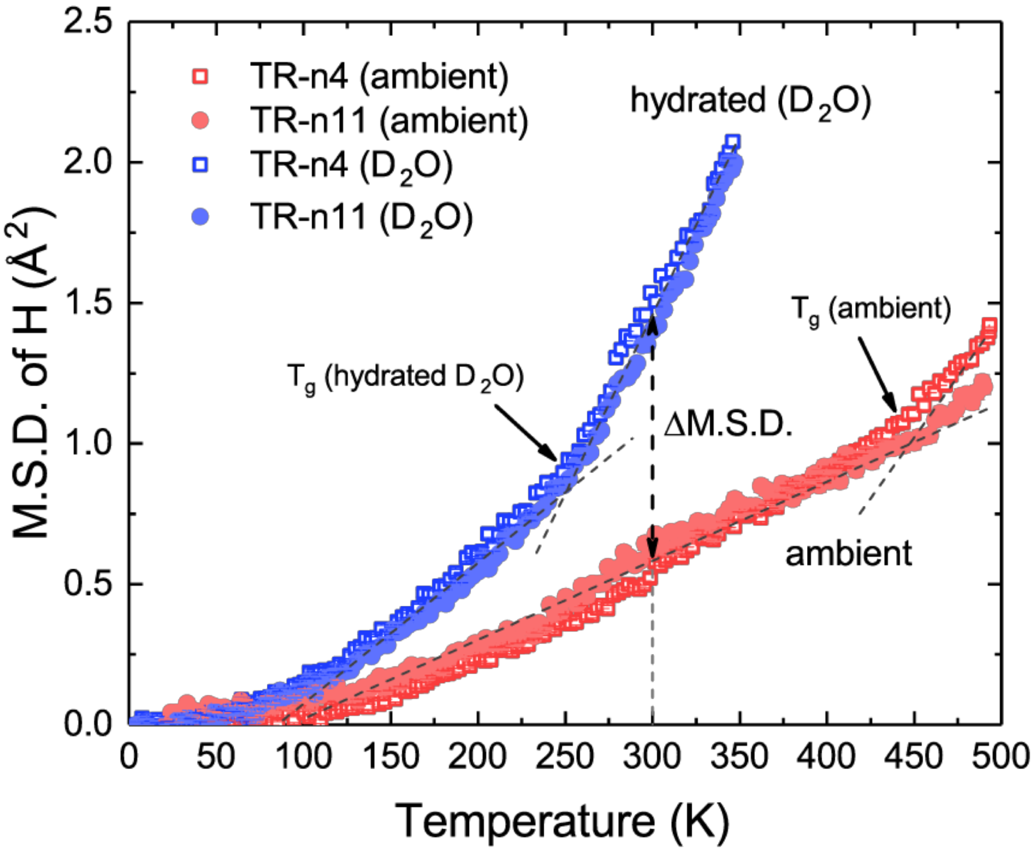
$\kappa \sim G'$

- Diamond = Strong bonds = high κ
- Polymers = weak bonds = low κ
- κ trends with $G'(1/n)$
- **Why does κ increase with hydration?**



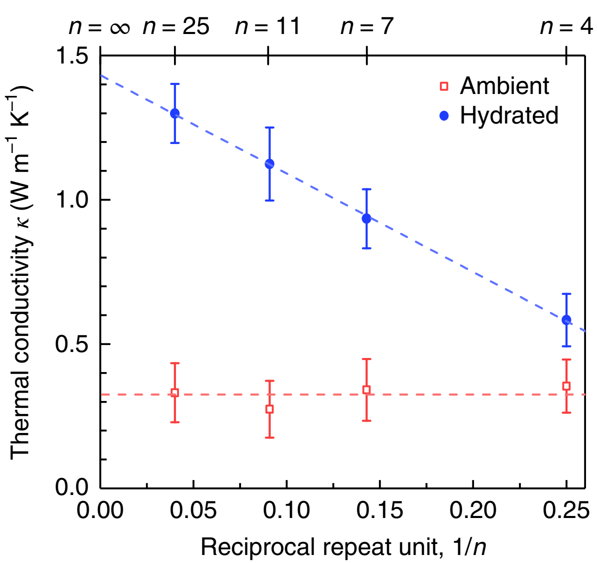
Nature Nanotechnology **13**, 959 (2018)

Results – Neutron scattering (NIST)



<u>$\kappa \sim$ MSD</u>

- QENS in ambient and hydrated environments
- Hydration increases mean square displacement of hydrogen atoms in network



Nature Nanotechnology **13**, 959 (2018)

Mechanisms of thermal conductivity switching

Thermal conductivity of crystalline/ordered solids

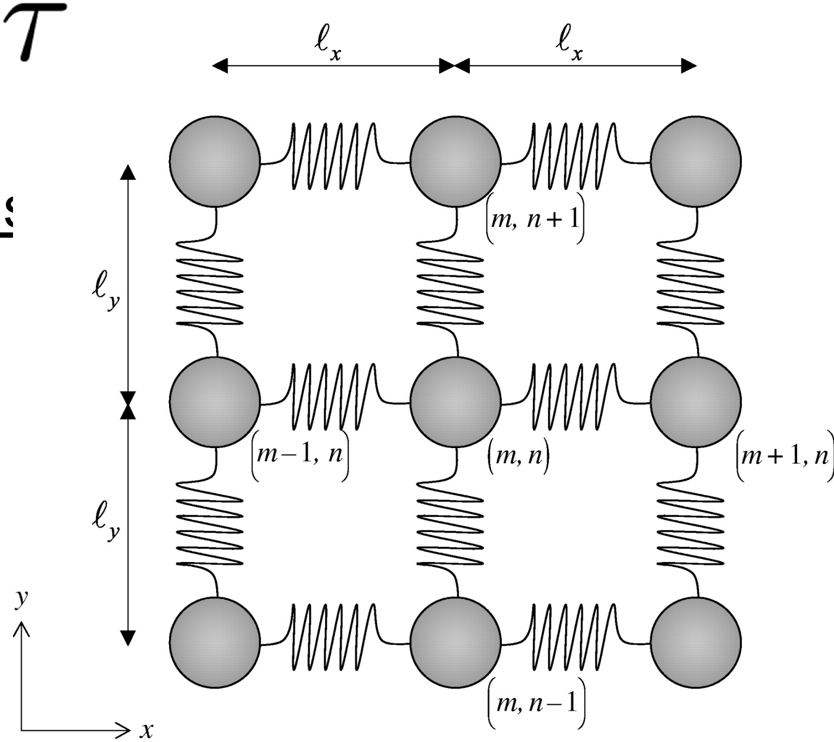
$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$

Thermal conductivity of disordered solids

$$\kappa_{\text{Diffuson}} \propto \sum C_\omega D_\omega$$

$$D_\omega = \text{Mode Diffusivity}$$

$$D_\omega \propto \text{MSD} \times G'^2$$



Nature Nanotechnology **13**, 959 (2018)

Mechanisms of thermal conductivity switching

Competing effects

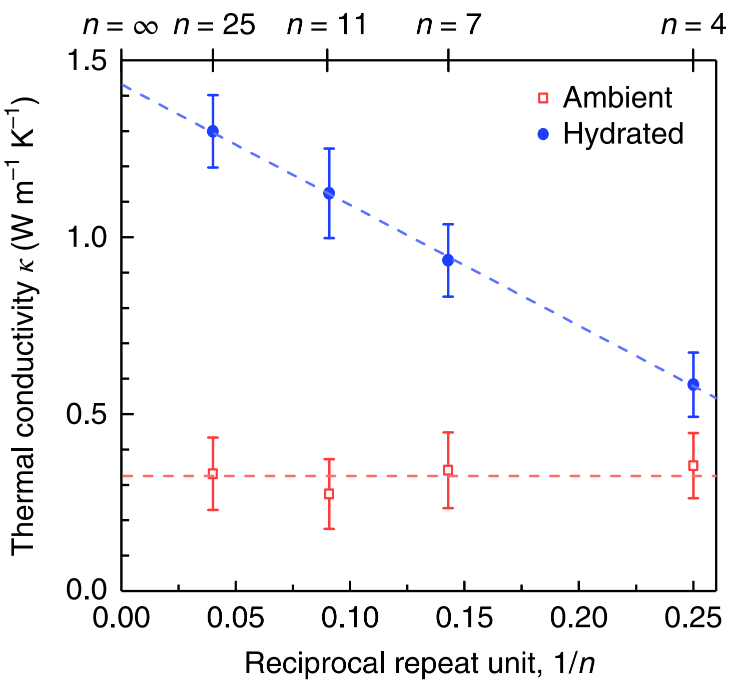
- **Increase in κ due to increase in MSD**
- **Decrease in κ (trend in 1/*n*) due to decrease in *G*'**

Thermal conductivity of disordered solids

$$\kappa_{\mathrm{Diffuson}} \propto \sum C_\omega D_\omega$$

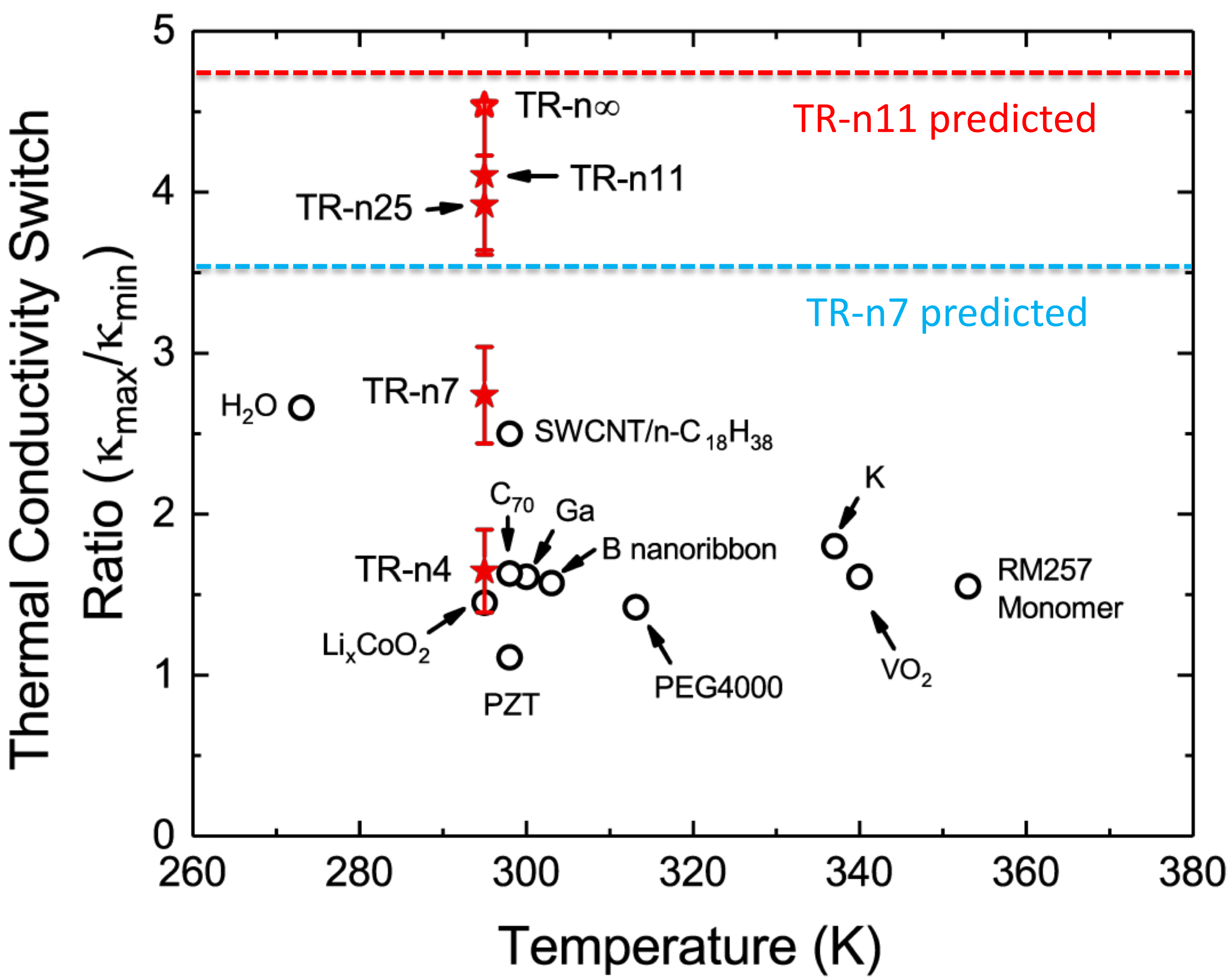
$$D_\omega = \mathrm{Mode\,Diffusivity}$$

$$D_\omega \propto \mathrm{MSD} \times G'^2$$



Nature Nanotechnology **13**, 959 (2018)

Redefining the SOA of κ switches with SRT



Nature Nanotechnology **13**, 959 (2018)

Summary

Engineering defects can be used to statically and dynamically control thermal conductivity