Current understanding and unsolved problems in thermal transport at the nanoscale

David G. Cahill
Department of Materials Science and Engineering,
Materials Research Laboratory,
Department of Mechanical Sciences and Engineering

University of Illinois at Urbana-Champaign

Special thanks to Yee Kan Koh, Wen-Pin Hsieh, Greg Hohensee, Richard Wilson, Dongyao Li, Dong-Wook Oh, Mark Losego, Jonglo Park, Xiaojia Wang, Xu Xie, Qiye Zheng, and Jungwoo Shin

ILLINOIS

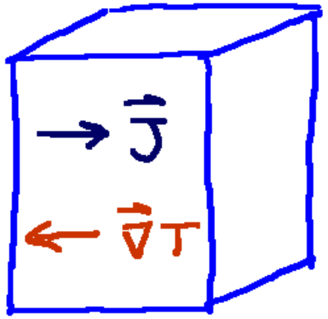
Outline

- Introduction to transport coefficients, nanoscale thermal transport.
- Big picture: how should we prioritize our work? How do we pick a “puzzle” or “problem” to study?
- How low can we go?
  - minimum and ultralow thermal conductivity
  - thermal conductance of weak interfaces.
- How high can we go and can we make use of that high thermal conductivity on small length scales?
  - deviations from Fourier transport in high thermal conductivity crystals.
  - heat conduction by magnons
- Search for thermally functional materials.

Thermal transport coefficients

- Thermal conductivity Λ is a property of the continuum

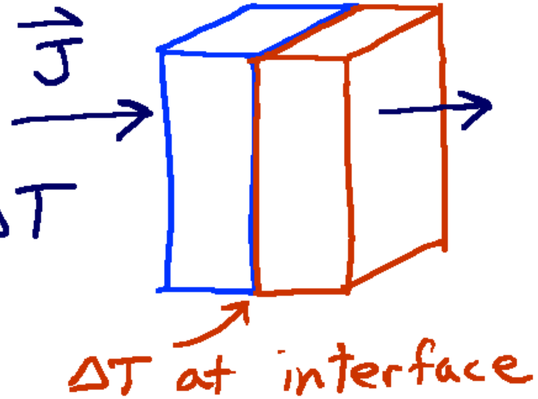
$$\vec{J} = -\Lambda \vec{\nabla} T$$



$$\Lambda = \frac{1}{3 V k_B T^2} \int_0^\infty \langle \vec{j}(t) \cdot \vec{j}(0) \rangle \, dt$$

- Thermal conductance (per unit area) *G* is a property of an interface

$$J = G \Delta T$$



$$G = \frac{1}{A k_B T^2} \int_0^\infty \langle q(t) q(0) \rangle \, dt$$

Thermal transport coefficients

- Thermal conductivity Λ appears in the diffusion equation

$$C\frac{dT}{dt} = \Lambda\nabla^2 T$$

C = heat capacity per unit volume

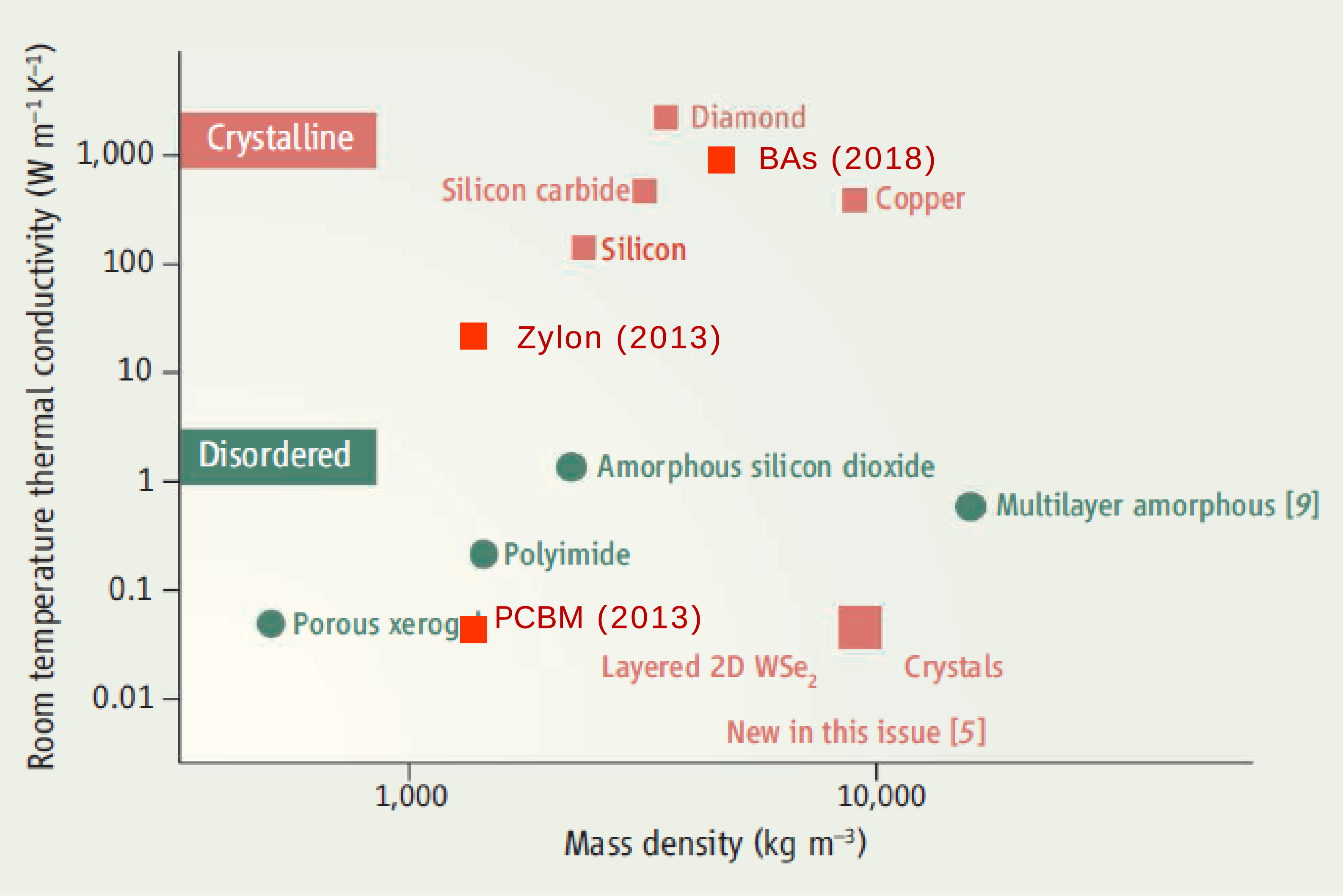
Diffusivity $D = \frac{\Lambda}{C}$ Effusivity $\varepsilon = \sqrt{\Lambda C}$

- Interface thermal conductance G is a radiative boundary condition

$$G\left(T_+ - T_-\right) = \Lambda \left.\frac{dT}{dz}\right|_{z=0}$$

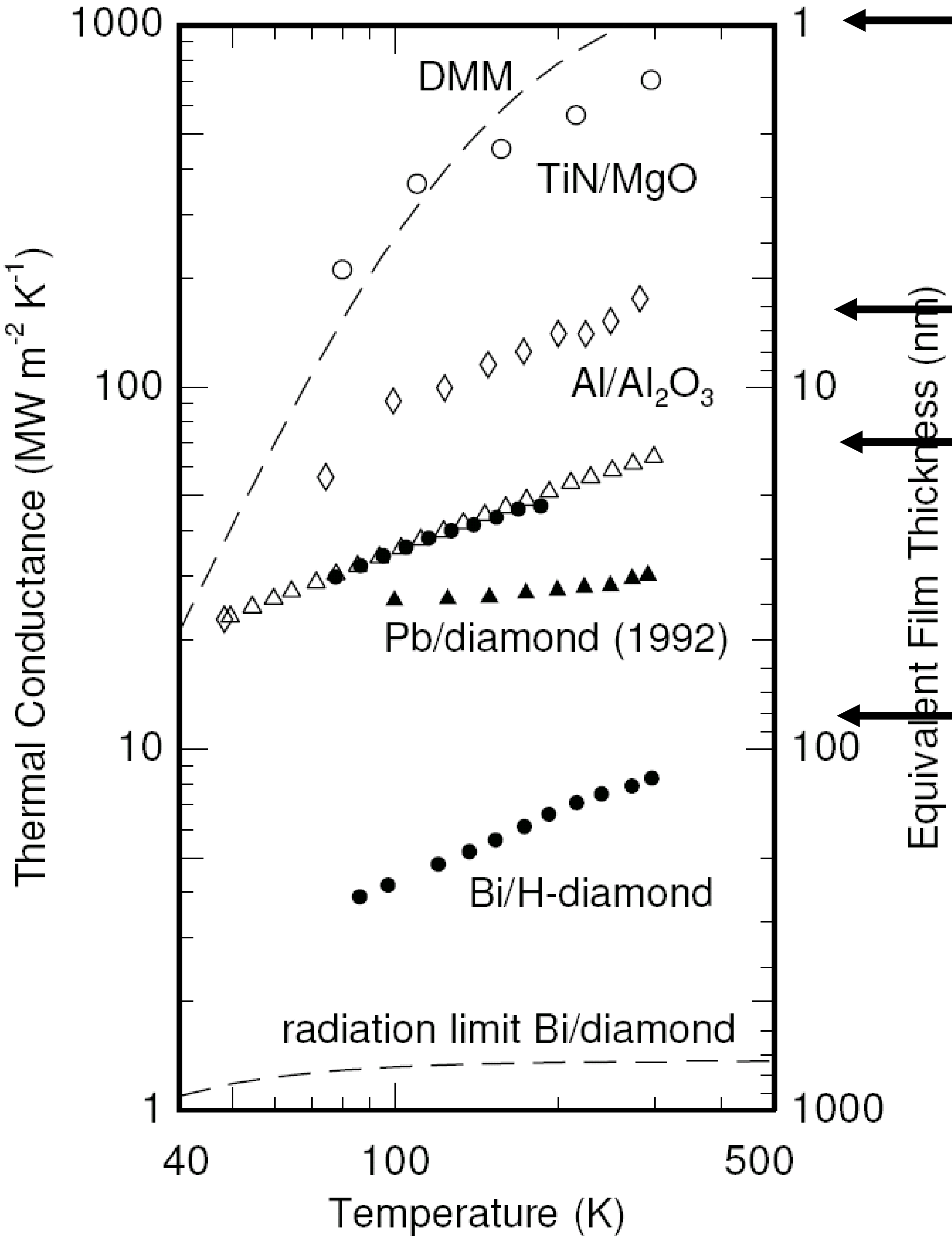
Kapitza length $L_K = \frac{\Lambda}{G}$

Thermal conductivities of dense solids span a range of 40,000 at room temperature



Adapted from Goodson, *Science* (2007)

Interface conductance spans a factor of ~100 at room temperature



Al/MgO at 60 GPa

Dalton, *Sci Rep* (2013)

hydrophilic/H_2O

Park, *JPCC* (2016)

hydrophobic/H_2O

Huxtable, *Nat Comm* (2003)

nanotube/alkane

monolayer MoS_2/SiO_2

Yalon, Nanolett (2017)

Lyeo and Cahill, *PRB* (2006)

Heat capacity per unit volume of solids spans only a factor of 4 at room temperature

Material	C (J cm^{-3} K^{-1})
water	4.18
Ni	3.95
Al	2.42
Diamond	1.78
Polymer (PMMA)	1.8
PbTe	1.2

$$G \sim Cv$$

$$\Lambda \sim Cvl$$

What are the important scientific questions to ask and answer in thermal transport at the nanoscale?

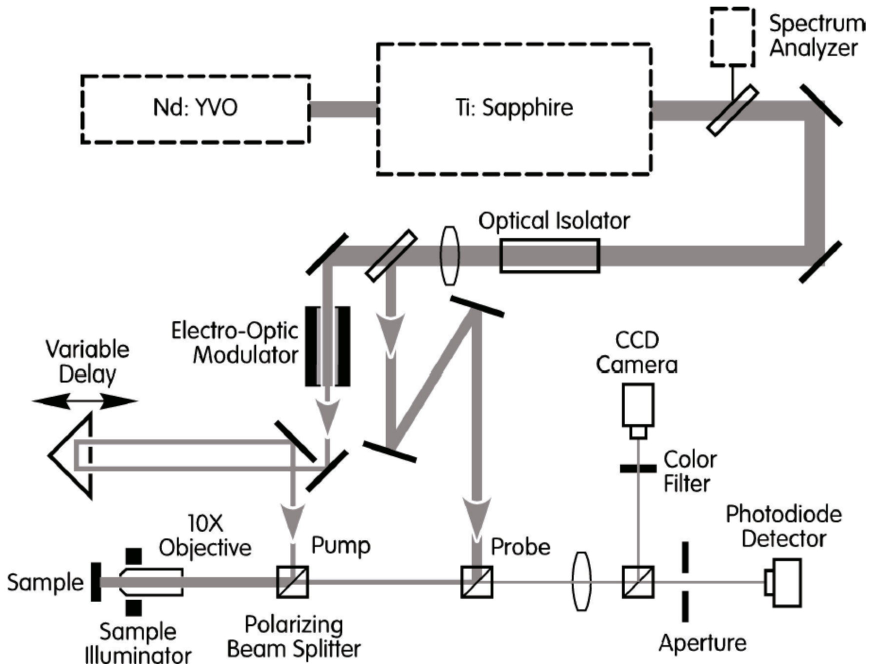
- Ultimately we want to ask what could bring **revolutionary** change to the field.
- Two categories of scientific revolutions (Galison and Kuhn)

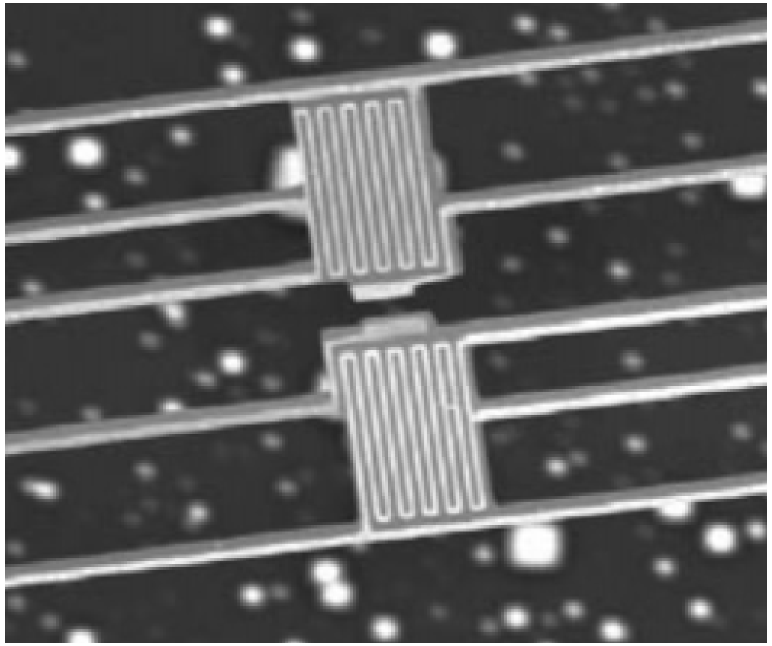
Acknowledge G. Whitesides Priestley award address, 2007, similar talk at APS Kavli "mesoscale physics" session in 2012.

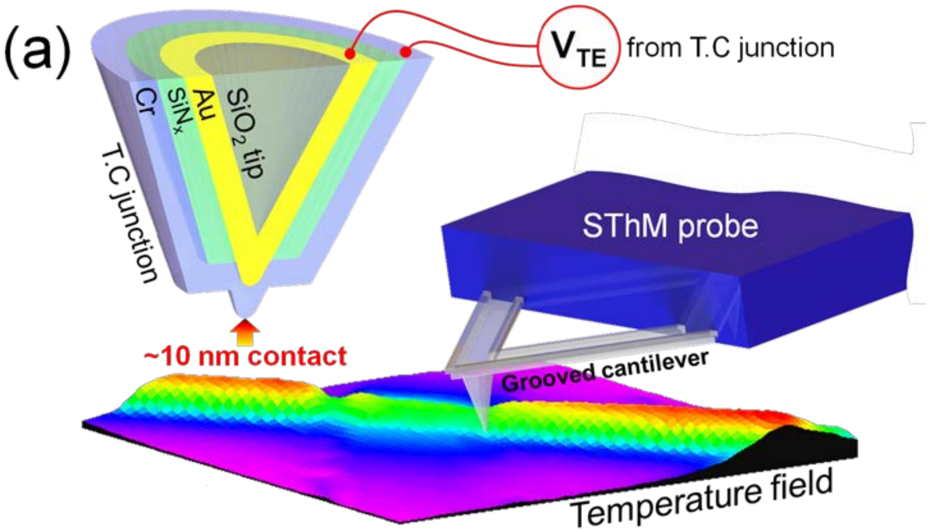
Scientific Revolution Type I (Galison)

- New techniques enable scientific revolutions
  - STM, then AFM, nucleated nanoscience
  - PCR made molecular genetics possible
  - NMR revolutionized organic synthesis
- Not in the same league but the nanothermal field has done well: TDTR, micro-fabricated test platforms, cantilever-based probes have completely changed what we can do.

TDTR, MEMS-based, scanning thermal probe







Scientific Revolution Type I

- Where are the next revolutionary tools?
  - Greater time/space/excitation-type/energy/momentum resolution?
- Certainly an important endeavor, but what theory or model do we want to probe or test?
- Fishing is often underappreciated but we need to fish in productive waters.

Scientific Revolution Type II (Kuhn)

- Revolutions occur only when there is no way out; when current theories are incompatible with experimental evidence.
  - Thermal sciences have led to revolutions before: "Ultraviolet catastrophe" and Einstein heat capacity of solids led to quantum mechanics
- Harder to declare success in the nanothermal field. What theories or "conventional wisdoms" have been overturned?
  - Thermal phonons in roughened Si nanostructures but experiments appear to be flawed.
  - High thermal conductivity of liquid suspensions of spherical nanoparticles (so called nanofluids) was due to some combination of aggregation and bad measurements.

Scientific activities (Kuhn)

- “Normal science” is driven by “puzzles”.
  - This is what most of us do, most of the time: further develop an existing scientific paradigm.
  - Whitesides puts it more pointedly:
    - ✓the answer is already known before the work starts;
    - ✓the answer is not important;
    - ✓the interest lies largely in the elegance of the solution.
  - But he goes on (to paraphrase Kuhn):
    - ✓normal science is essential and required to select specific scientific puzzles for the intense cultivation that makes clear the fundamental limitations of science and that occasionally leads to scientific revolution.

Scientific activities (Kuhn)

- Scientific “discovery” is driven by “problems”.
  - Whitesides’ take on this:
    - ✓larger scale questions in which the answer does matter;
    - ✓in which the strategy to a solution is not known;
    - ✓in which it is not even known that there is a solution.
  - What problems do we have in nanoscale thermal science?
    - ✓How can close can we approach the perfect thermal insulator?
    - ✓What are upper and lower limits to the thermal conductivity of a polymer?
    - ✓What physics of materials can provide a high-contrast solid-state heat switch or thermal regulator?

Suggested homework problem in scientific communication

- Solving puzzles is critical to science. How is your puzzle holding back the field and how is the solution to your puzzle going to allow the field to advance?
- Given the context of your experience and interests, if you were freed from the constraints of money and existing techniques (the proverbial empty lab filled with nothing but money), what problem would you study and why is that problem important?
- Structure your answer as an elevator speech (on the order of 1 min or 150 words), send to d-cahill@illinois.edu if you want feedback.

Can we beat the amorphous limit of the thermal conductivity Λ_{min}

- Einstein (1911): random walk of thermal energy
- Not good for crystals: Debye (1914)
- but does work for amorphous solids, Birch and Clark (1940); Kittel (1948)
- and crystals with strong atomic-scale disorder, Slack (1979); Cahill and Pohl (1988).

High T limit

$$\Lambda_{min} = 0.40 k_B n^{2/3} (v_\ell + 2v_t)$$

Einstein (1911)

- coupled the Einstein oscillators to 26 neighbors
- heat transport as a random walk of thermal energy between atoms; time scale of ½ vibrational period
- did not realize waves (phonons) are the normal modes of a crystal

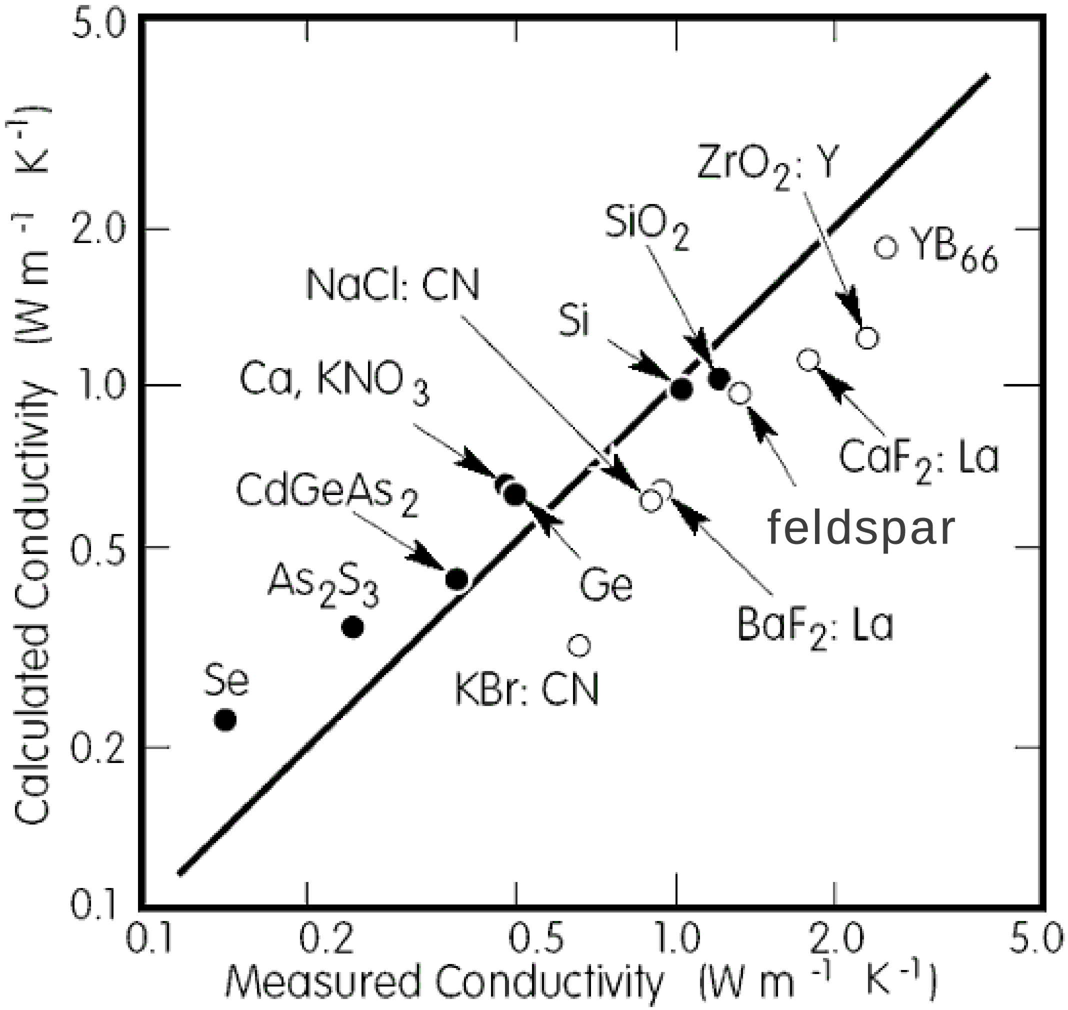
2. *Elementare Betrachtungen über die thermische Molekularbewegung in festen Körpern;* *von A. Einstein.*

In einer früheren Arbeit[1]) habe ich dargelegt, daß zwischen dem Strahlungsgesetz und dem Gesetz der spezifischen Wärme fester Körper (Abweichung vom Dulong-Petitschen Gesetz) ein Zusammenhang existieren müsse[2]). Die Untersuchungen Nernsts und seiner Schüler haben nun ergeben, daß die spezifische Wärme zwar im ganzen das aus der Strahlungstheorie gefolgerte Verhalten zeigt, daß aber das wahre Gesetz der spezifischen Wärme von dem theoretisch gefundenen systematisch abweicht. Es ist ein erstes Ziel dieser Arbeit, zu zeigen, daß diese Abweichungen darin ihren Grund haben, daß die Schwingungen der Moleküle weit davon entfernt sind, *monochromatische* Schwingungen zu sein. Die thermische Kapazität eines Atoms eines festen Körpers ist nicht gleich der eines schwach gedämpften, sondern ähnlich der eines stark gedämpften Oszillators im Strahlungsfelde. Der Abfall der spezifischen Wärme nach Null hin bei abnehmender Temperatur erfolgt deshalb weniger rasch, als er nach der früheren Theorie erfolgen sollte; der Körper verhält sich ähnlich wie ein Gemisch von Resonatoren, deren Eigenfrequenzen über ein gewisses Gebiet verteilt sind. Des weiteren wird gezeigt, daß sowohl Lindemanns Formel, als auch meine Formel zur Berechnung der Eigenfrequenz ν der Atome durch Dimensionalbetrachtung abgeleitet werden können, insbesondere auch die Größenordnung der in diesen Formeln auftretenden Zahlen-

1) A. Einstein, Ann. d. Phys. 22. p. 184. 1907.

2) Die Wärmebewegung in festen Körpern wurde dabei aufgefaßt als in monochromatischen Schwingungen der Atome bestehend. Vgl. hierzu § 2 dieser Arbeit.

Works well for homogeneous disordered materials

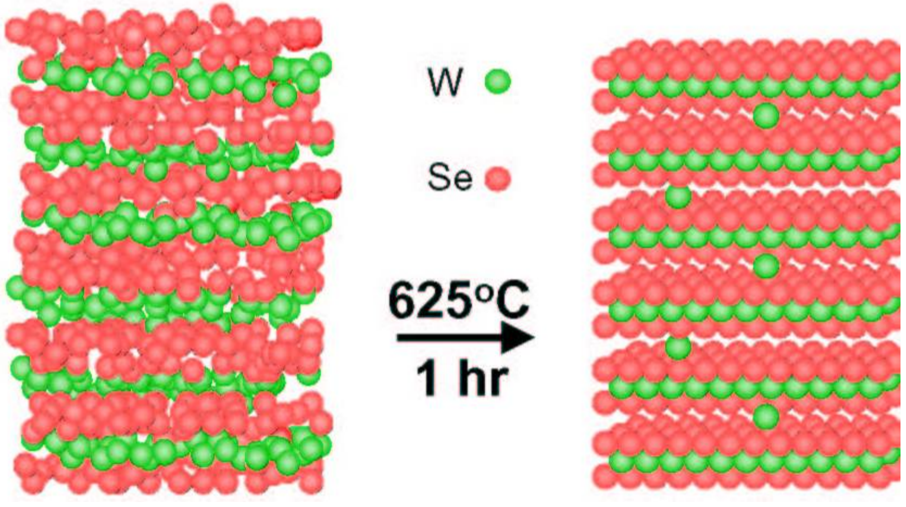


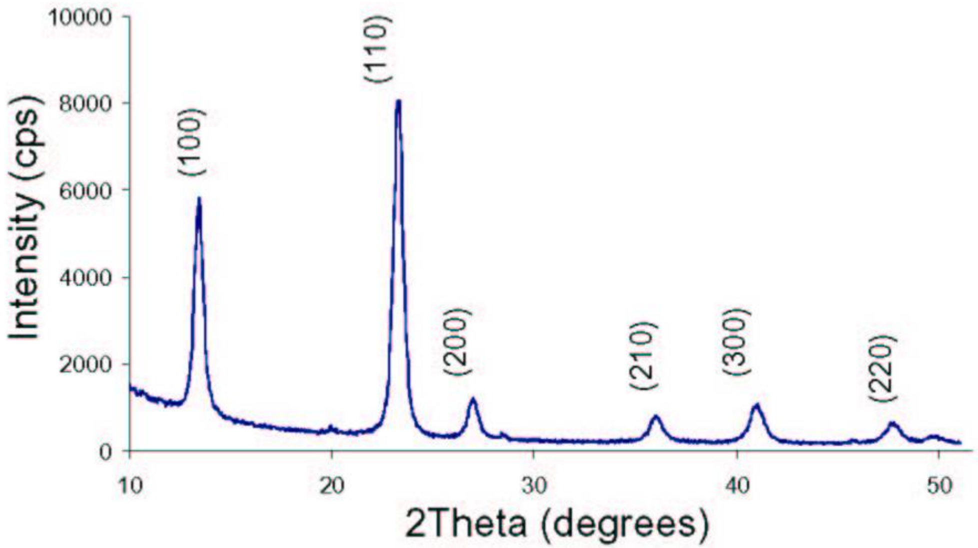
- ● amorphous
- ○ disordered crystal

Cahill, *PRB* (1992)

Layered disordered crystals: WSe_2 by "modulated elemental reactants"

- Deposit W and Se layers at room temperature on Si substrates
- Anneal to remove excess Se and improve crystallinity
- Characterize by RBS, x-ray diffraction (lab sources and Advanced Photon Source) and TEM

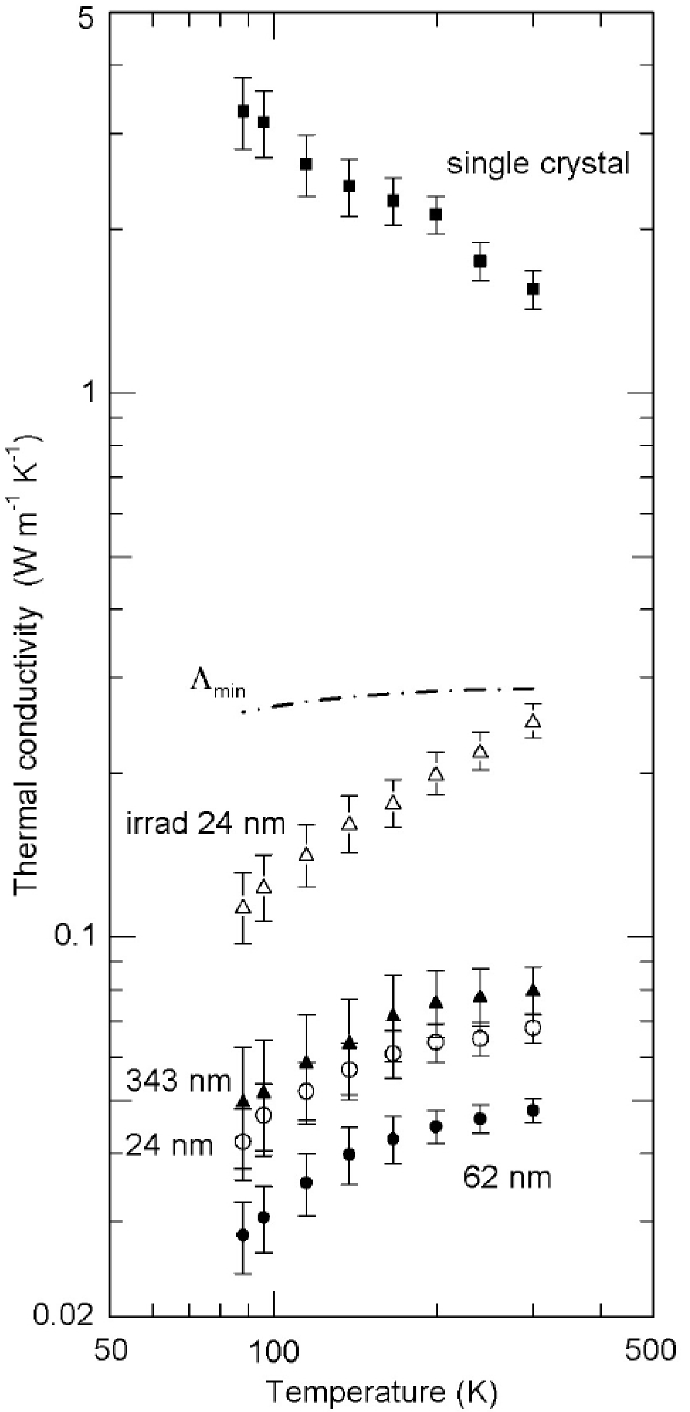




Chiritescu, *Science* (2007)

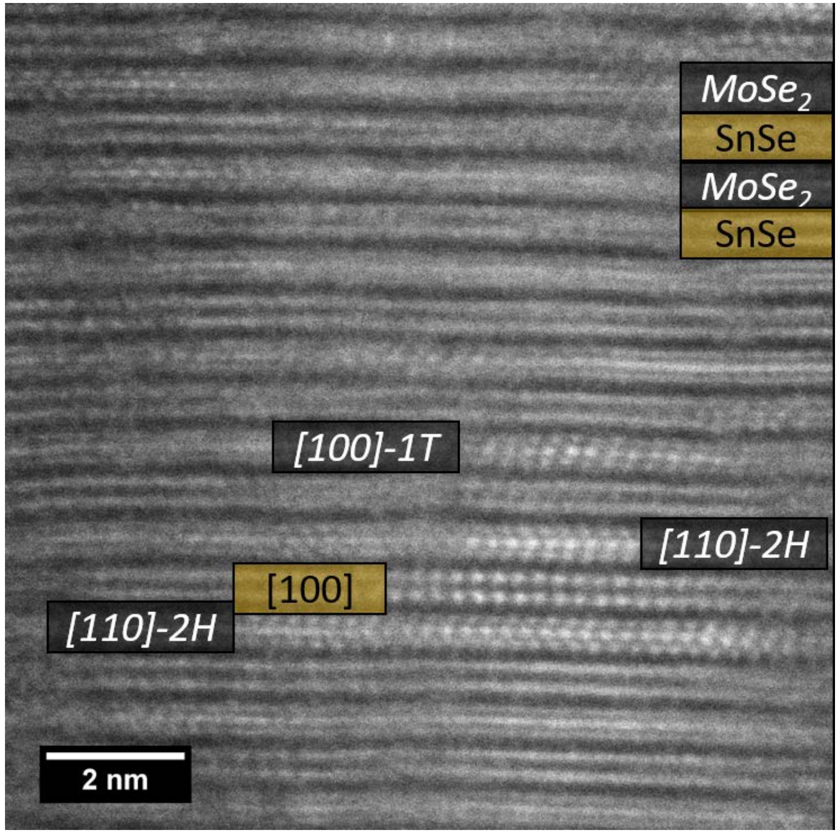
Thermal conductivity of WSe_2

- 60 nm film has the lowest thermal conductivity ever observed in a fully dense solid. Only twice the thermal conductivity of air.
- A factor of 6 less than the calculated amorphous limit for this material.



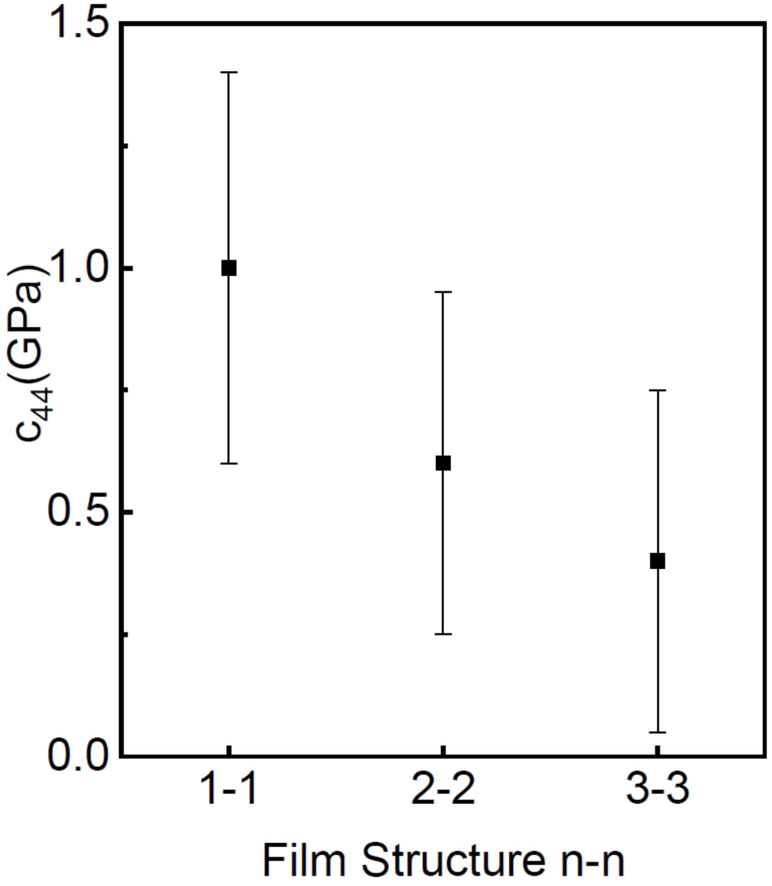
Recent realization that the shear modulus of a "disordered layered crystal" is very small, ~1 GPa

- Scanning TEM image of $[SnSe]_n[MoSe2]_m$

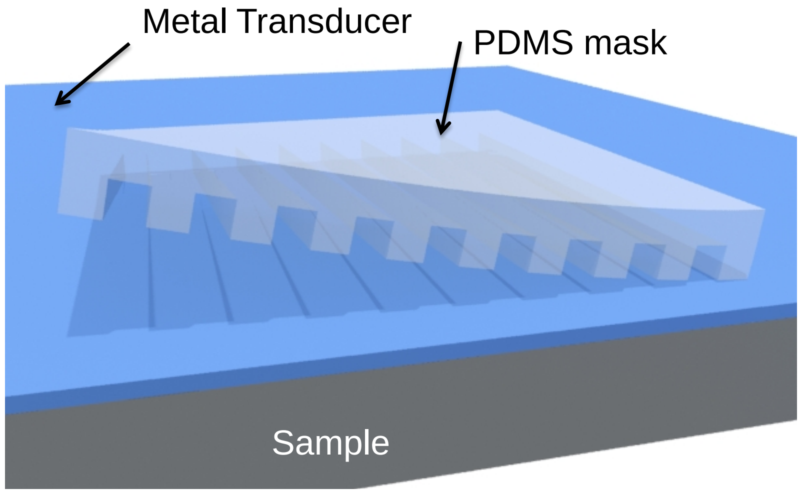


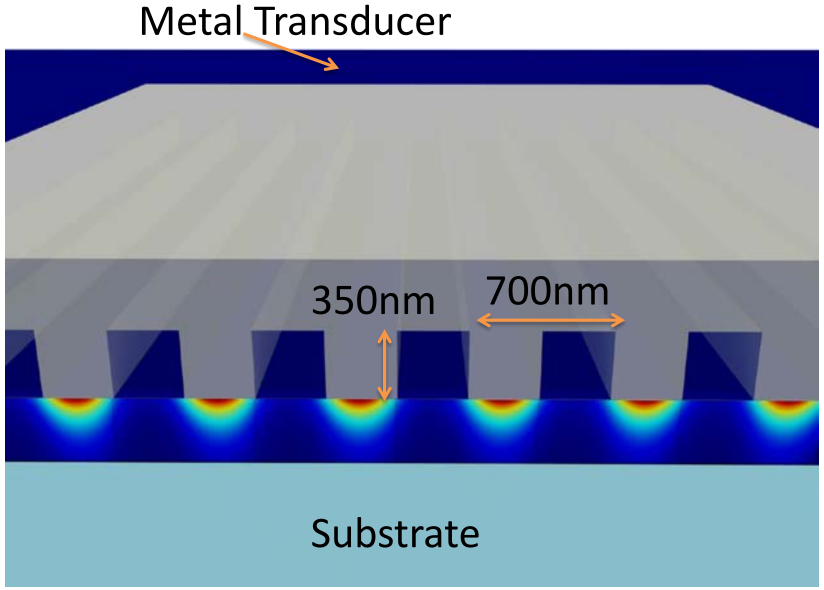
Li, *submitted* (2019)

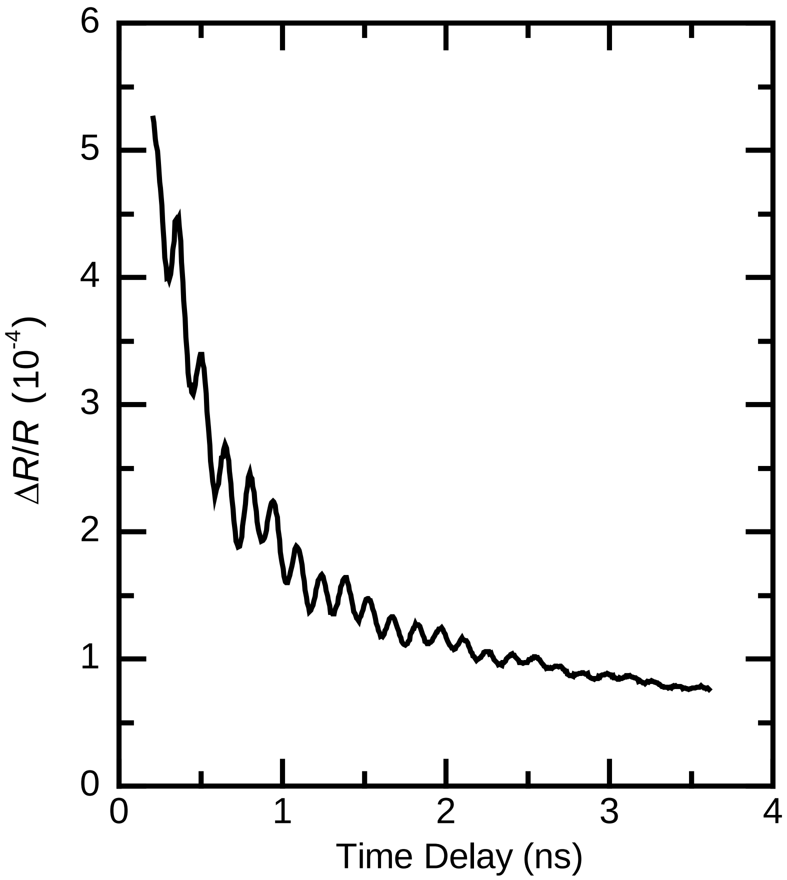
- Shear modulus measured by surface acoustic wave velocity



Measure surface acoustic wave velocity using elastomeric phase shift mask

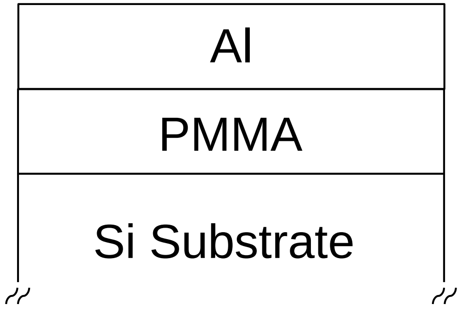






Li *et al.*, J. Appl. Phys. (2013)

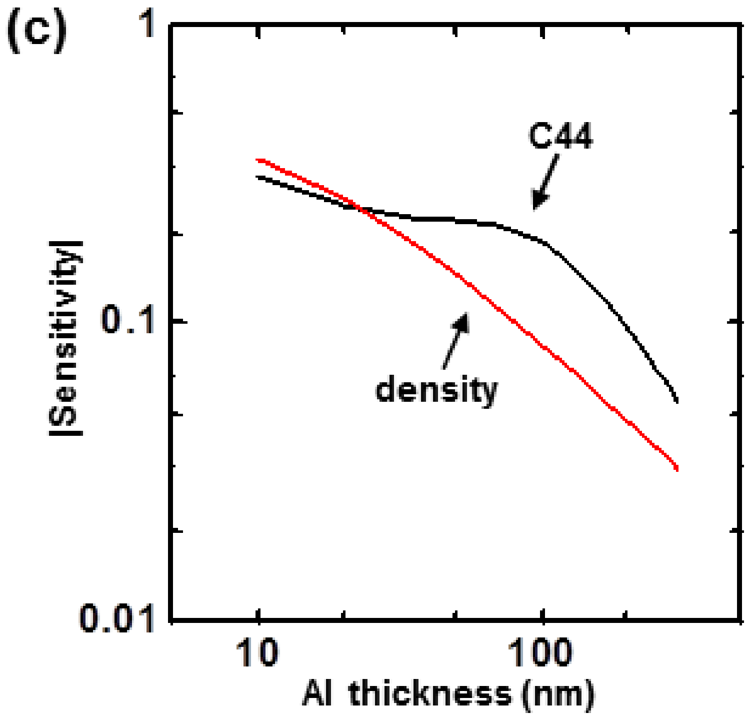
Experimental details: need to optimize thickness of sample and metal transducer



- Example sensitivity calculations for Al/PMMA(100nm)/Si

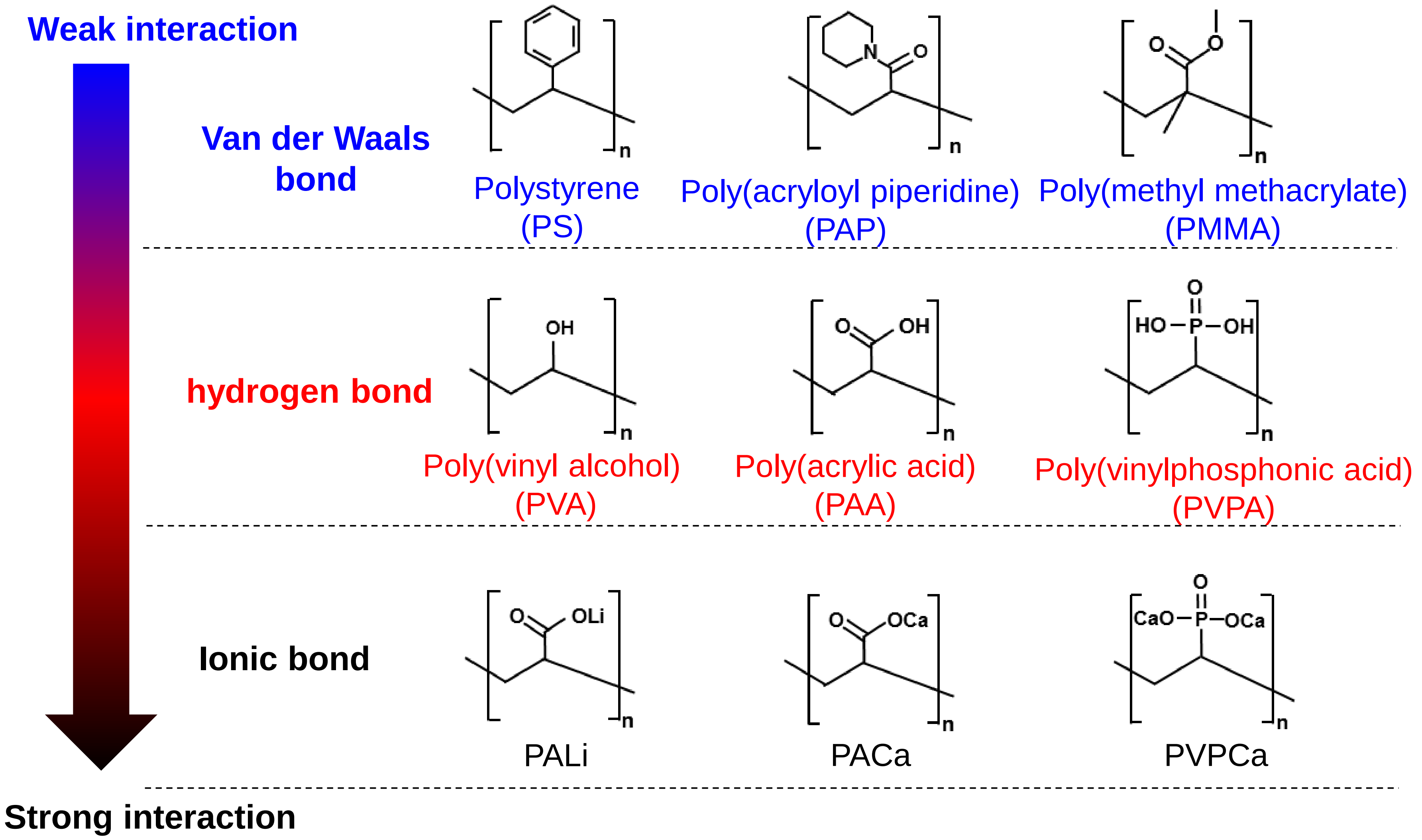
$$S = \frac{c_{44}}{v_{SAW}} \frac{\partial v_{SAW}}{\partial c_{44}}$$

- Approach fails if the Al transducer is too thin or if the PMMA layer is too thick.



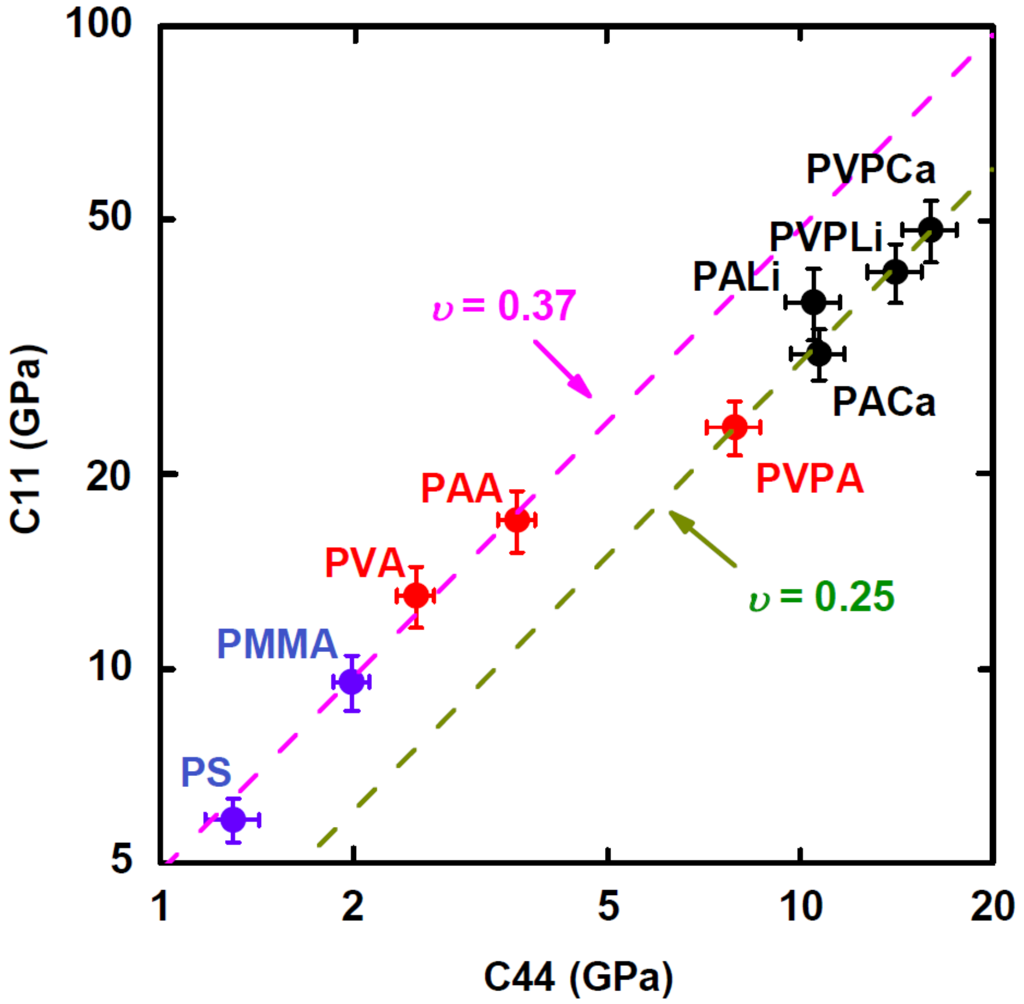
Xie *et al.*, Macromolecules (2016)

Switch to organic materials: minimum and ultralow thermal conductivity in amorphous macromolecular solids.

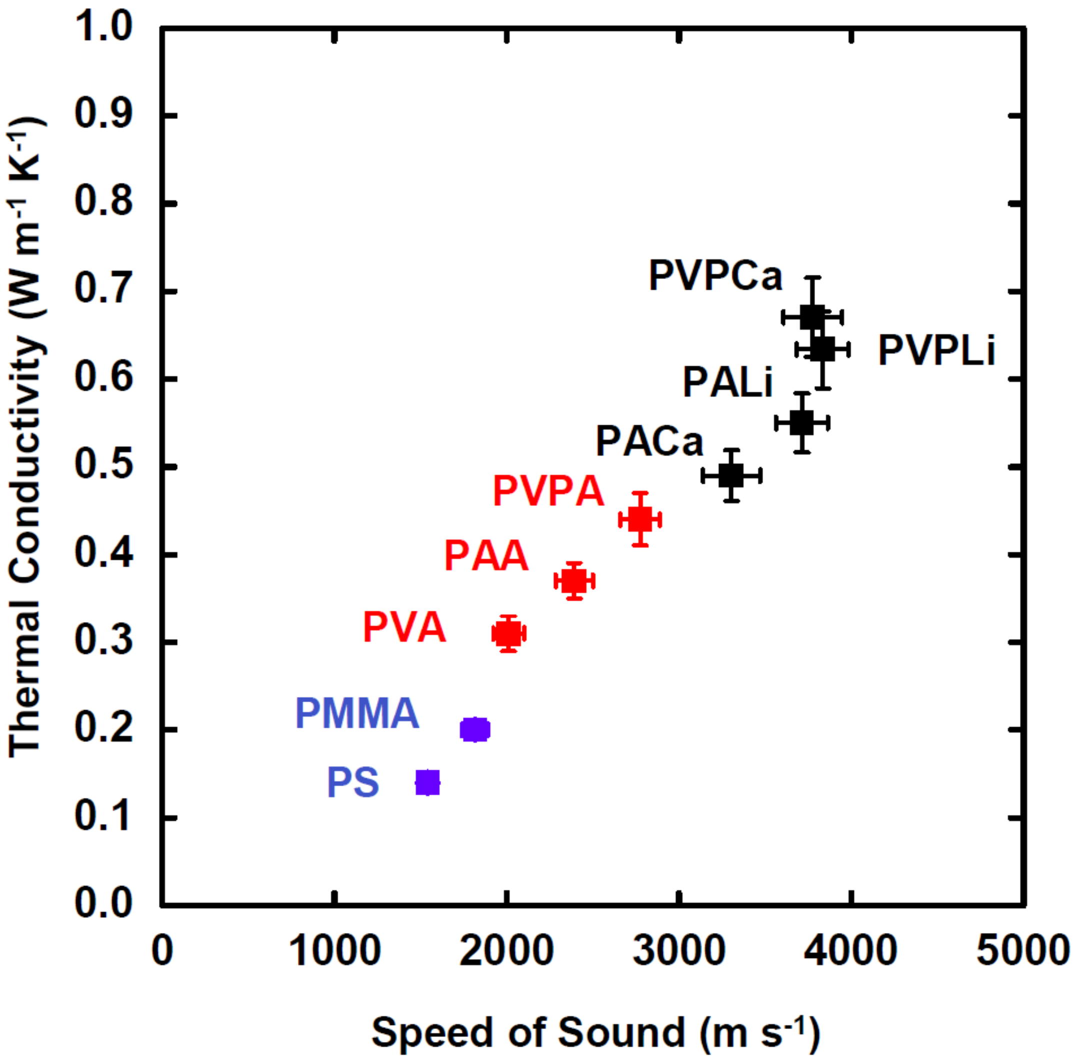


Elastic constants span an order of magnitude. Transition in Poisson ratio?

- Poisson ratio is $\nu \approx 0.37$ for polymers with small elastic constants and $\nu \approx 0.25$ for polymers with large elastic constants.



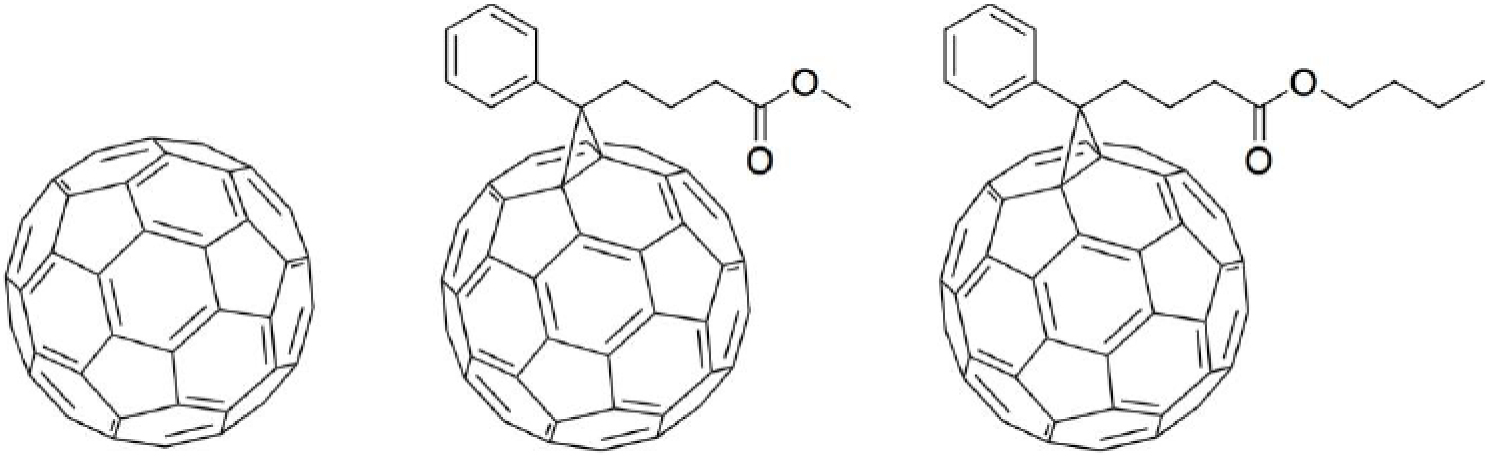
Model of minimum thermal conductivity predicts a linear correlation with average speed of sound



Xie *et al.*, Phys. Rev. B (2017)

Fullerene derivatives have “ultralow” thermal conductivity, i.e., conductivity well below the conventional lower-limit

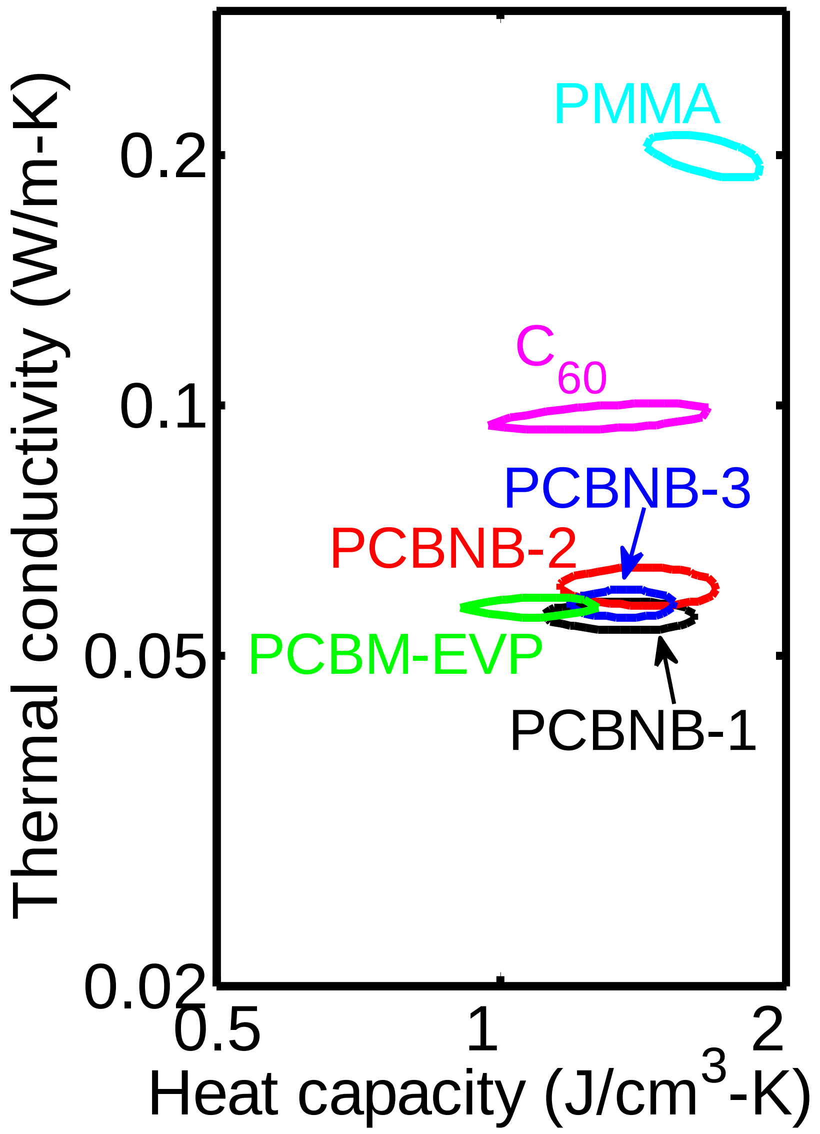
- Duda et al. (2013) reported 0.03 W m^{-1} K^{-1}.
- We find all samples are in the range 0.05 to 0.06 W m^{-1} K^{-1}.



C60 PCBM PCBNB

Wang *et al*., PRB (2013)

Fit two parameters (C and Λ) to multiple data sets (modulation frequency, thickness)



- Assume heat capacity C doesn't depend on thickness but allow thermal conductivity to vary with thickness.

Wang *et al.*, PRB (2013)

Summary of ultralow thermal conductivity

- Working to understand and extend the lower limits of thermal conduction in disordered-layered crystals and molecular materials.
- Fullerene derivatives and turbostratic WSe_2 are comparably, 0.05 W m^{-1} K^{-1}, although the physics is completely different.
- Where should we search for molecular materials with even lower thermal conductivity?
  - Larger fraction of localized vibrational states?
  - Intrinsic porosity at the nanoscale to reduce the heat capacity per unit volume?

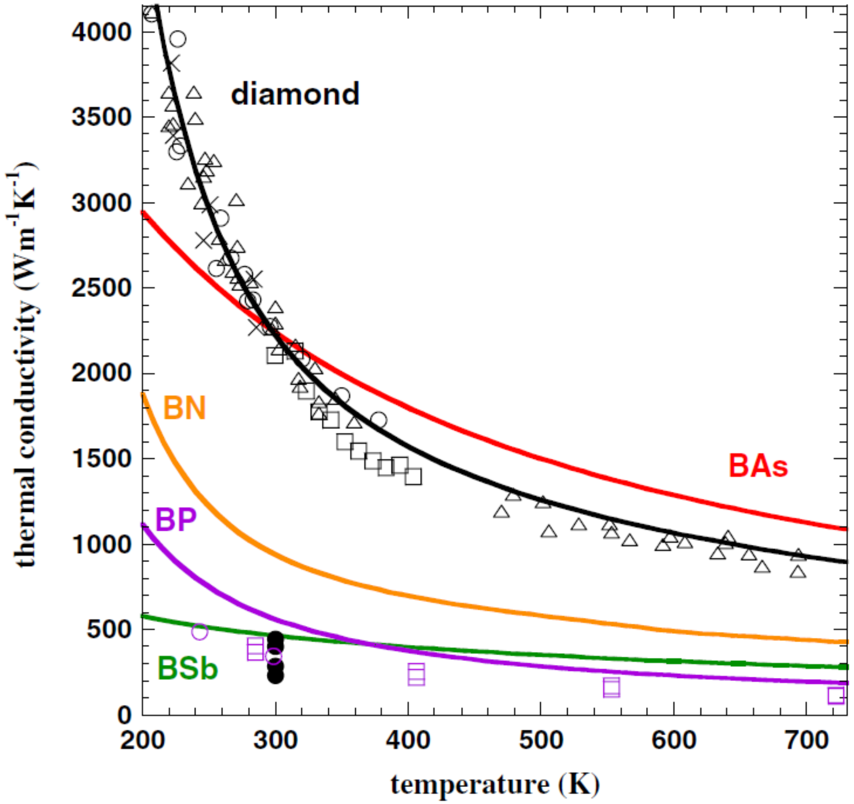
New (past decade) capabilities for calculations of thermal conductivity of crystals from 1st principles

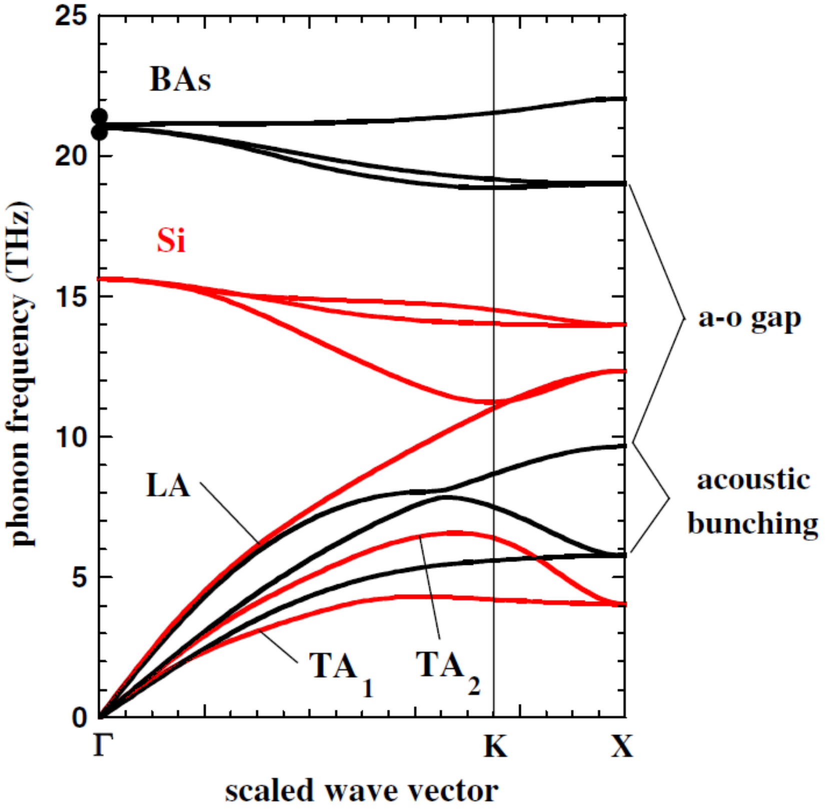
Selected for a Viewpoint in *Physics*

PRL **111,** 025901 (2013) PHYSICAL REVIEW LETTERS week ending 12 JULY 2013

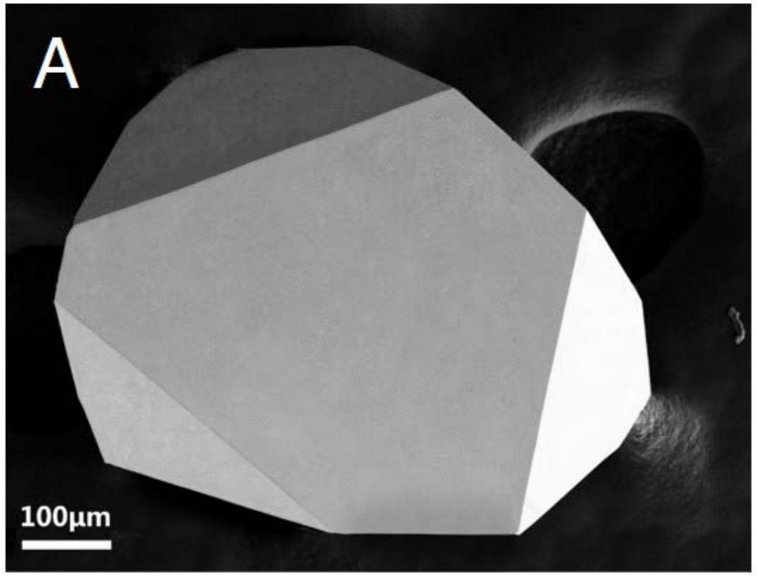
First-Principles Determination of Ultrahigh Thermal Conductivity of Boron Arsenide: A Competitor for Diamond?

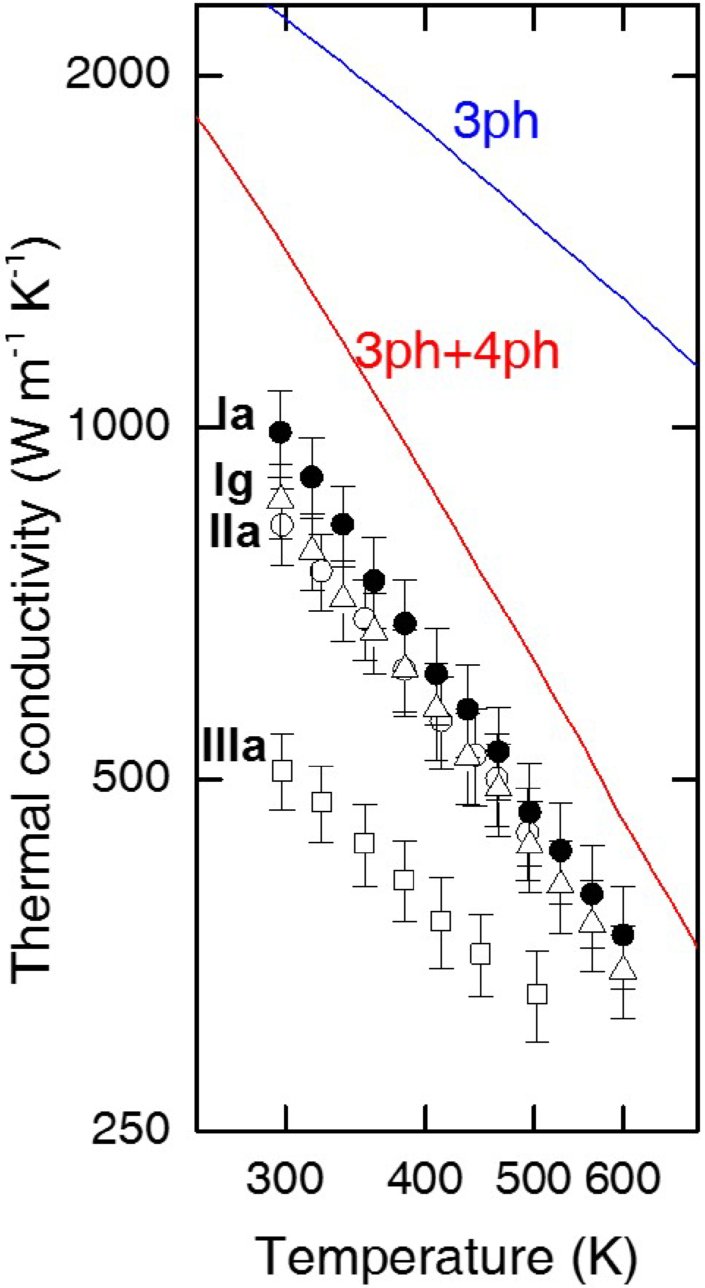
L. Lindsay,[1] D. A. Broido,[2] and T. L. Reinecke[1]





Thermal conductivity of BAs is limited by four-phonon scattering





Li, Zheng *et al.*, *Science* (2018)

In crystals, heat is carried by phonons with a broad distribution of mean-free-paths

- Simplest case of thermal conductivity where resistive scattering dominates.

$$\Lambda = \frac{1}{3}\int_0^{\omega_c} c(\omega)v_g^2(\omega)\tau(\omega)d\omega$$

$c(\omega)$ = heat capacity of phonon mode

$v_g(\omega)$ = phonon group velocity

$\tau(\omega)$ = scattering time

ω_c = cut-off frequency

Make a “Klemens-like” calculation

- Assume linear dispersion for $\omega<\omega_c$ and $\tau^{-1} \propto \omega^2 T$

$$\Lambda = \frac{A}{T}\int_0^{\omega_c} d\omega = \frac{A}{T}\omega_c$$

- Convert to an integral over mean-free-path $l = \frac{B}{\omega^2 T}$

$$\Lambda = \frac{A\sqrt{B}}{2T^{3/2}}\int_{l_c}^{\infty} \frac{1}{l^{3/2}} dl$$

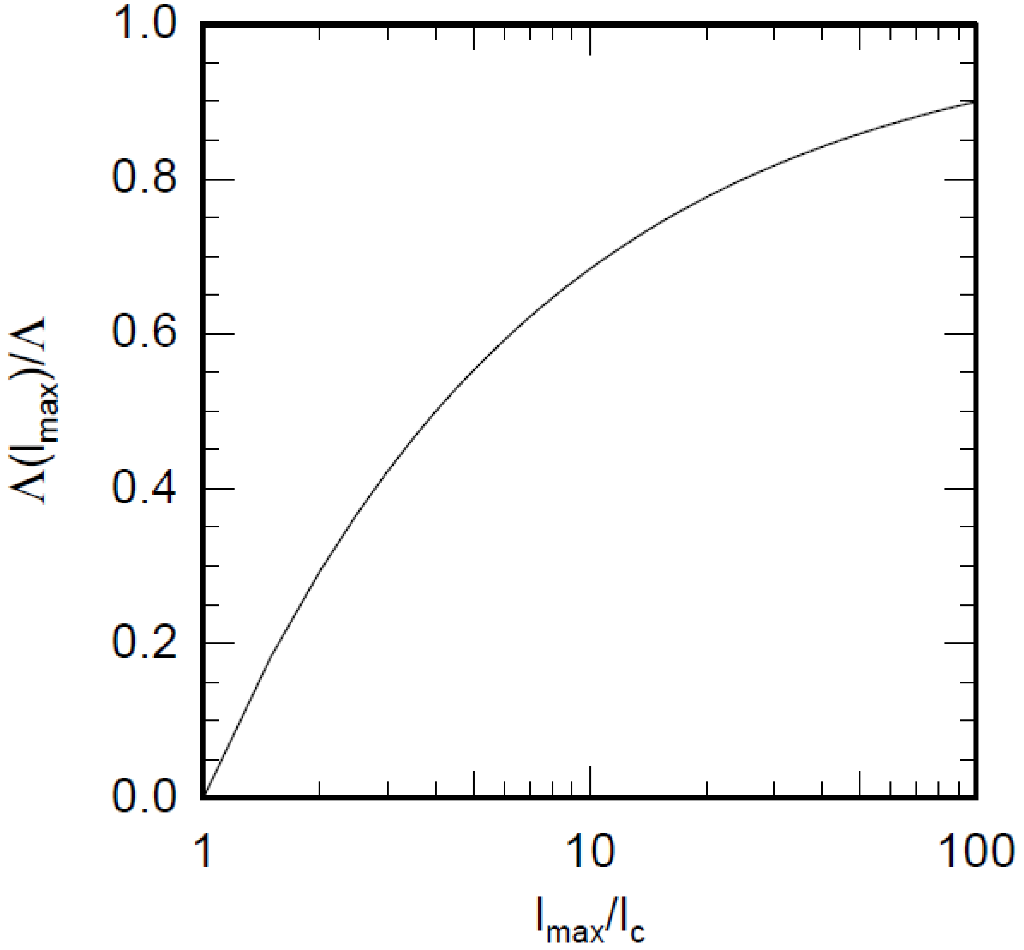
$$\frac{\Lambda(l_{\max})}{\Lambda} = 1 - \left(\frac{l_c}{l_{\max}}\right)^{1/2}$$

ℓ_c is the mean-free-path at the cut-off frequency

ℓ_{max} is the maximum mean-free-path that contributes to Λ

Heat is carried by phonons with a broad distribution of mean-free-paths

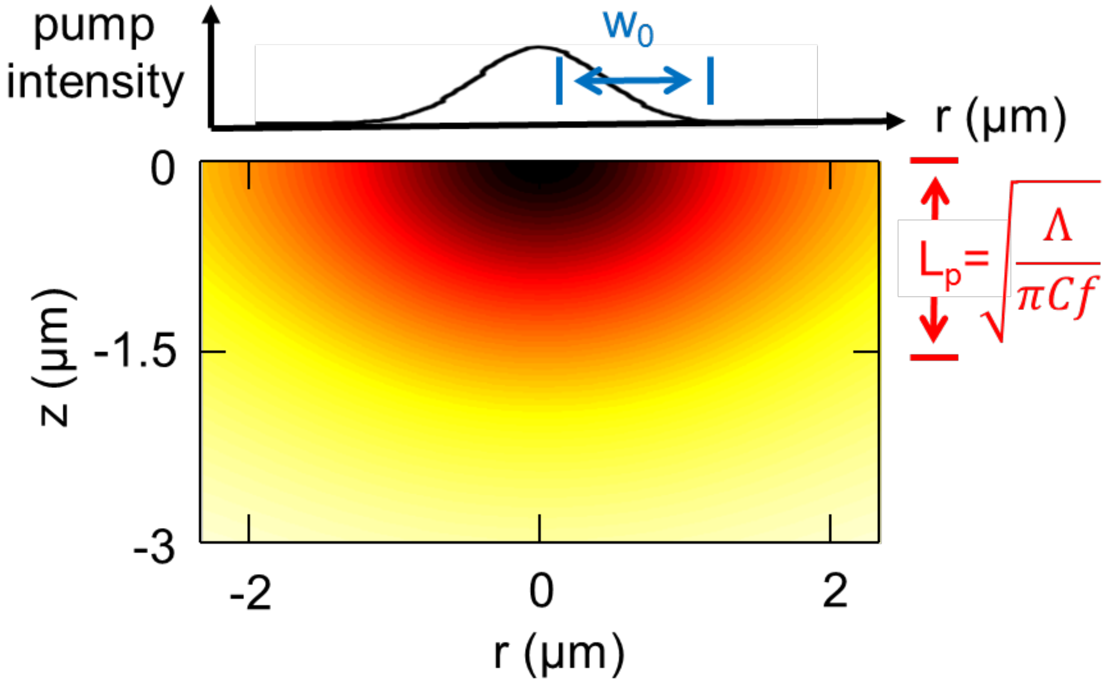
- Phonon scattering by charge carriers or boundaries will narrow the distribution.
- Alloying and point defects will broaden the distribution.
- Relaxational damping will eventually be a limiting factor.
- Details are probably important (scattering rates, normal processes, dispersion…)



TDTR and phonon mean-free-path spectroscopy

- Time-domain thermoreflectance (TDTR) is a powerful method.
  - When is Fourier's law an adequate description and when does it fail?
  - Answer depends on the details of the sample, the dimensionality of the heat conduction, and the transport properties of the metal/sample interface.
- Bring it to the next level: If we can quantitatively understand the failure of the Fourier's law, can we use that information to characterize the distribution of phonon-mean free paths?
  - The metal/sample interface complicates the problem and the answer depends on the details of the sample.

TDTR and phonon mean-free-path spectroscopy



L_P = thermal penetration depth

f = heating frequency

w_0 = laser spot size

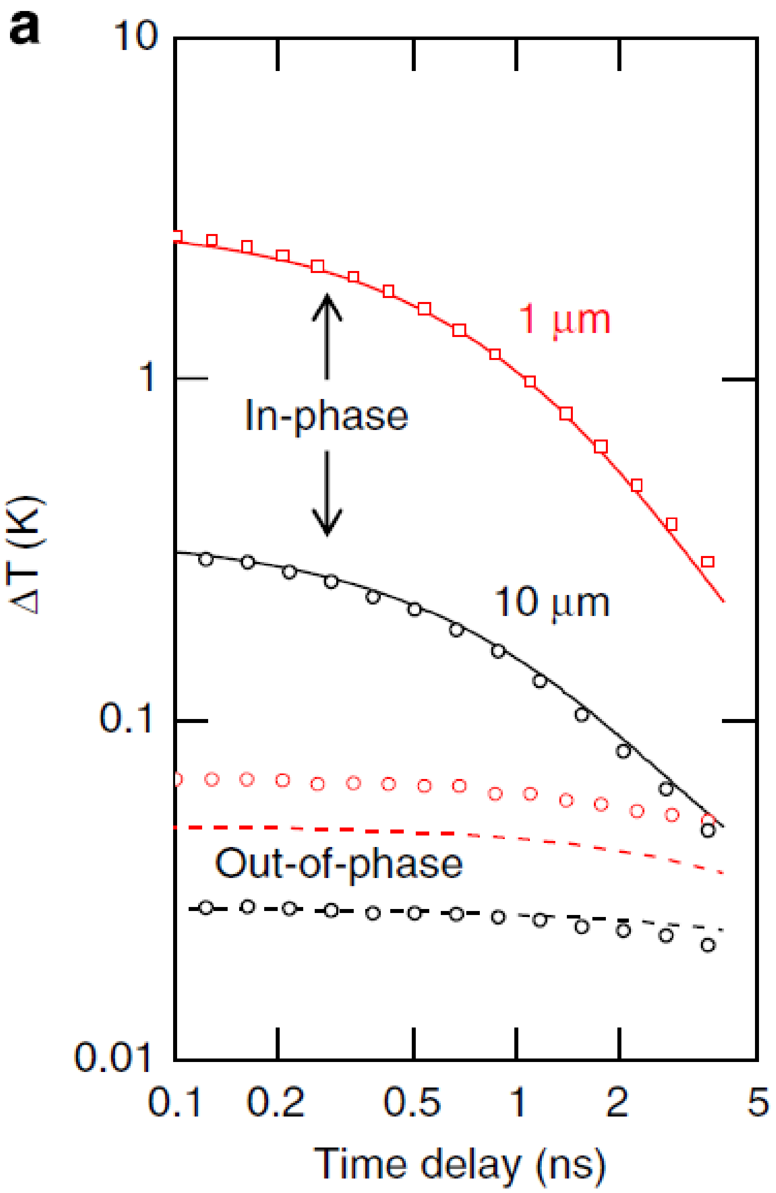
Fourier theory has been observed to fail in TDTR measurements of

semiconductor alloys as a function of f
Y. K. Koh, D. G. Cahill
PRB **76,** 075207 (2008)

silicon below 100 K as a function of w_0
A. Minnich *et al.*
PRL **107,** 095901 (2011)

Why does Fourier theory fail with frequency in semiconductor alloys but fail with spot-size in Si at cryogenic temperatures?

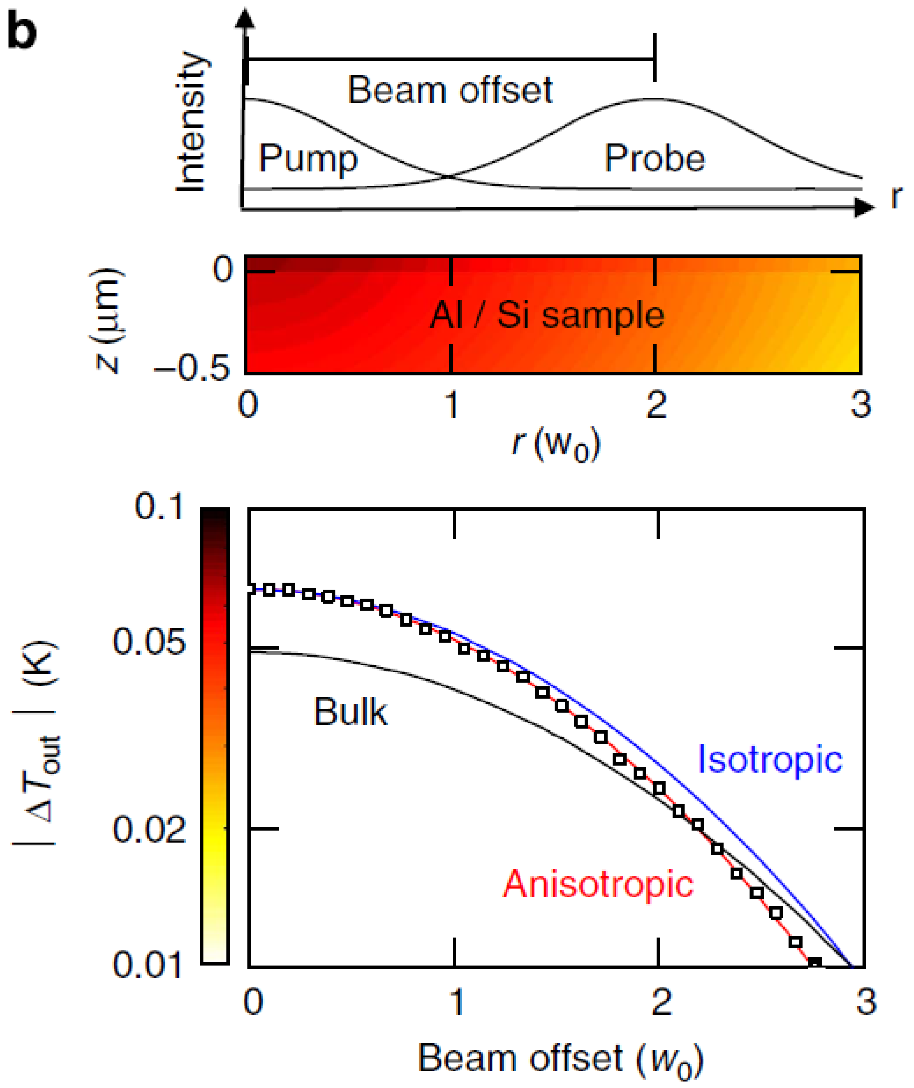
I. Anisotropic apparent thermal conductivity of Si



- Conventional TDTR with overlapping pump and probe
- Dependence on spot size is only seen in the out-of-phase signal
- Change in apparent thermal conductivity is from 140 to 105 W m^{-1} K^{-1} assuming isotropic transport.

Wilson, *Nature Commun.* (2014)

I. Anisotropic apparent thermal conductivity of Si



- Beam-offset TDTR cannot be fit with a single value of the apparent thermal conductivity.
- Anisotropic apparent thermal conductivity

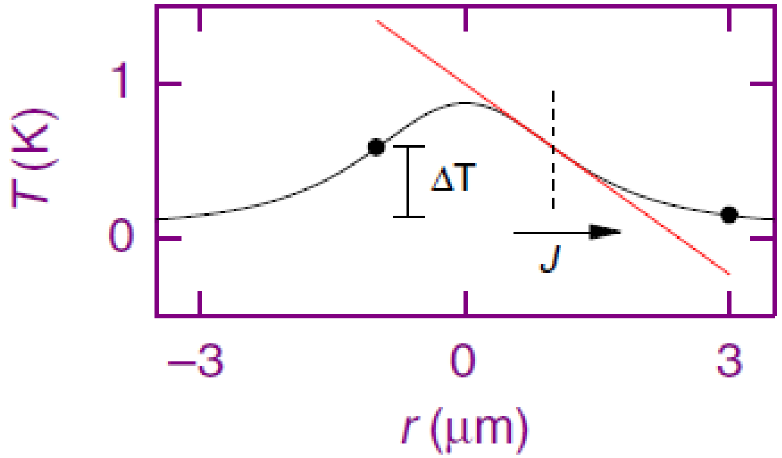
$$\Lambda_r = 80 \text{ W m}^{-1} \text{ K}^{-1}$$

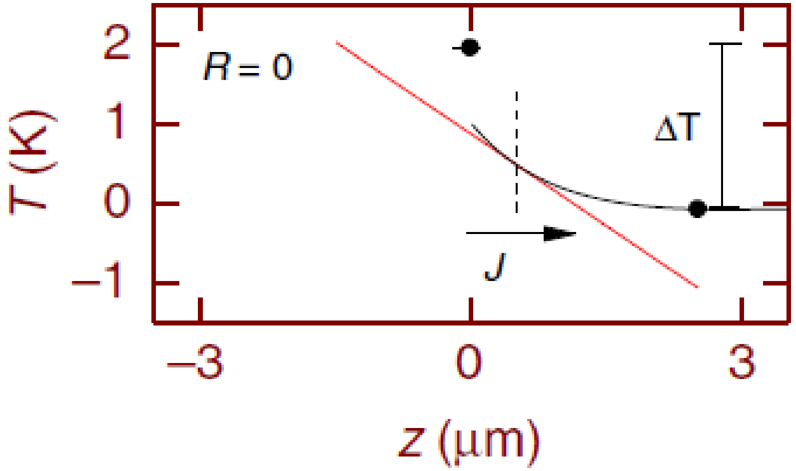
$$\Lambda_z = 140 \text{ W m}^{-1} \text{ K}^{-1}$$

I. Anisotropic apparent thermal conductivity of Si

- Is it physically reasonable that a cubic crystal can have an anisotropic apparent thermal conductivity?
  - No, if all of the heat carriers are diffusive on the length scales of the temperature excursions
  - Yes, if ballistic carriers are significant and there is an interface
- Consider the temperature profiles near the laser spot in the r and z directions

$J \propto \Delta T \neq -2\ell\nabla T$

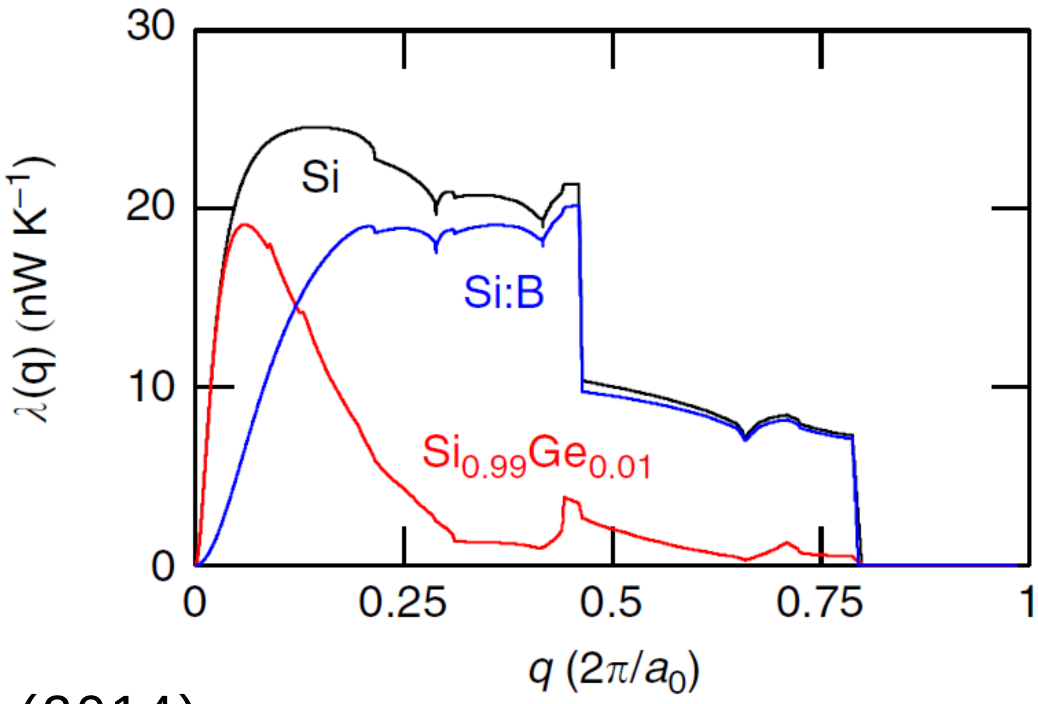




II. Manipulate the spectrum of heat carriers using B and Ge doping of Si.

- B preferentially scatters low frequency phonons (phonon/hole scattering)
- Ge preferentially scatters high frequency phonons (phonon Rayleigh scattering)

$$\Lambda = \int \lambda(q)dq$$

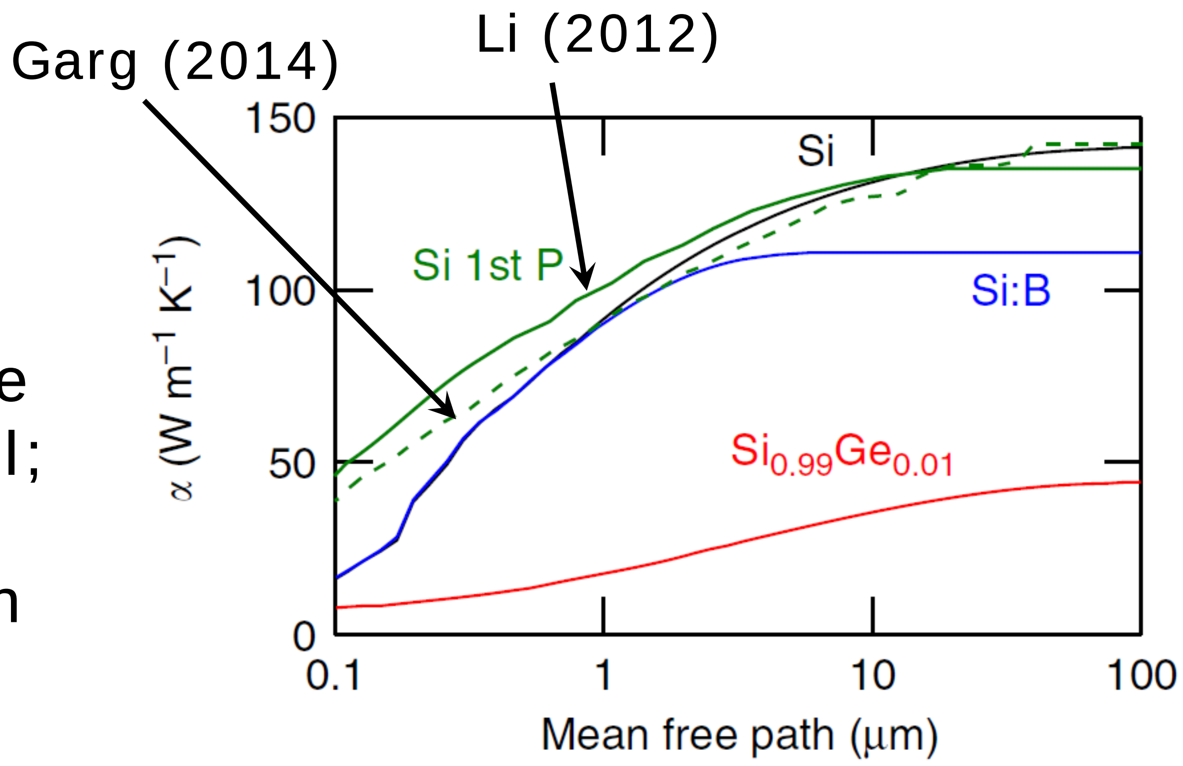


Wilson, *Nature Commun.* (2014)

II. Manipulate the spectrum of heat carriers using B and Ge doping of Si.

$$\Lambda = \int \alpha(l)dl$$

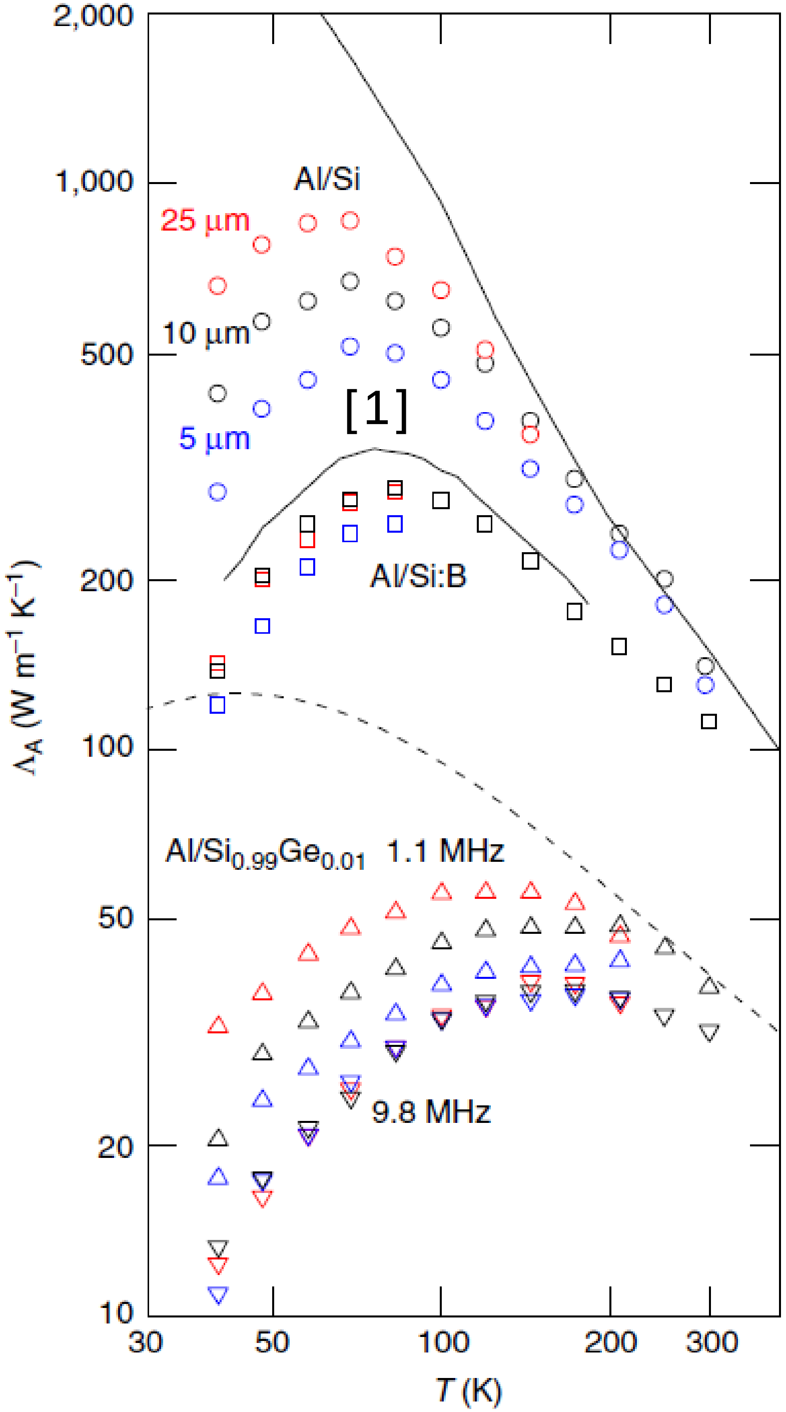
- We are using a simple relaxation time model; approximates the accumulation function of Si predicted by 1st principle calculations reasonably well



...and vary temperature

- Differences are more dramatic at low temperatures
  - Fourier law is a good description for Si:B down to 50 K
  - Failure of Fourier's law increases as the distribution of phonon mean-free-paths becomes broader, i.e., from Si:B to Si to SiGe
  - Low thermal diffusivity of high frequency phonons creates greater frequency dependence.

[1] Asheghi (2011)



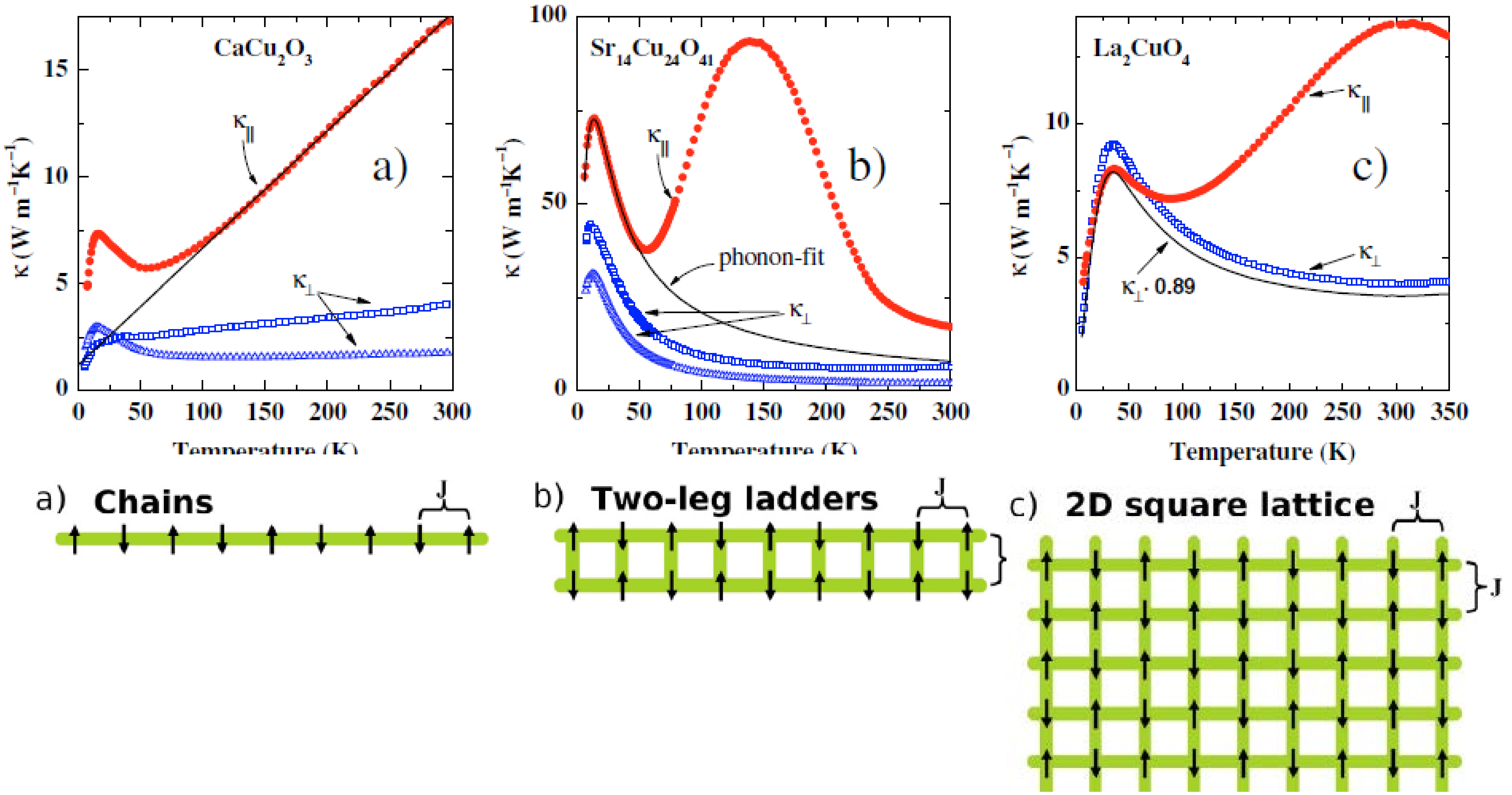
Take-home messages:

- Failure of Fourier's law in micro- and nano-scale heat transport.
  - More significant failures in the radial, as opposed to the through thickness direction.
  - More significant failures when the thermal diffusivity of the high frequency phonons is small
  - More significant failures when the thermal conductivity accumulation function is broad.
- Phonon mean-free-path spectroscopy by varying thermal penetration depth?
  - Essentially correct when the thermal diffusivity of the high frequency phonons is small and the accumulation function is broad.

Take-home messages:

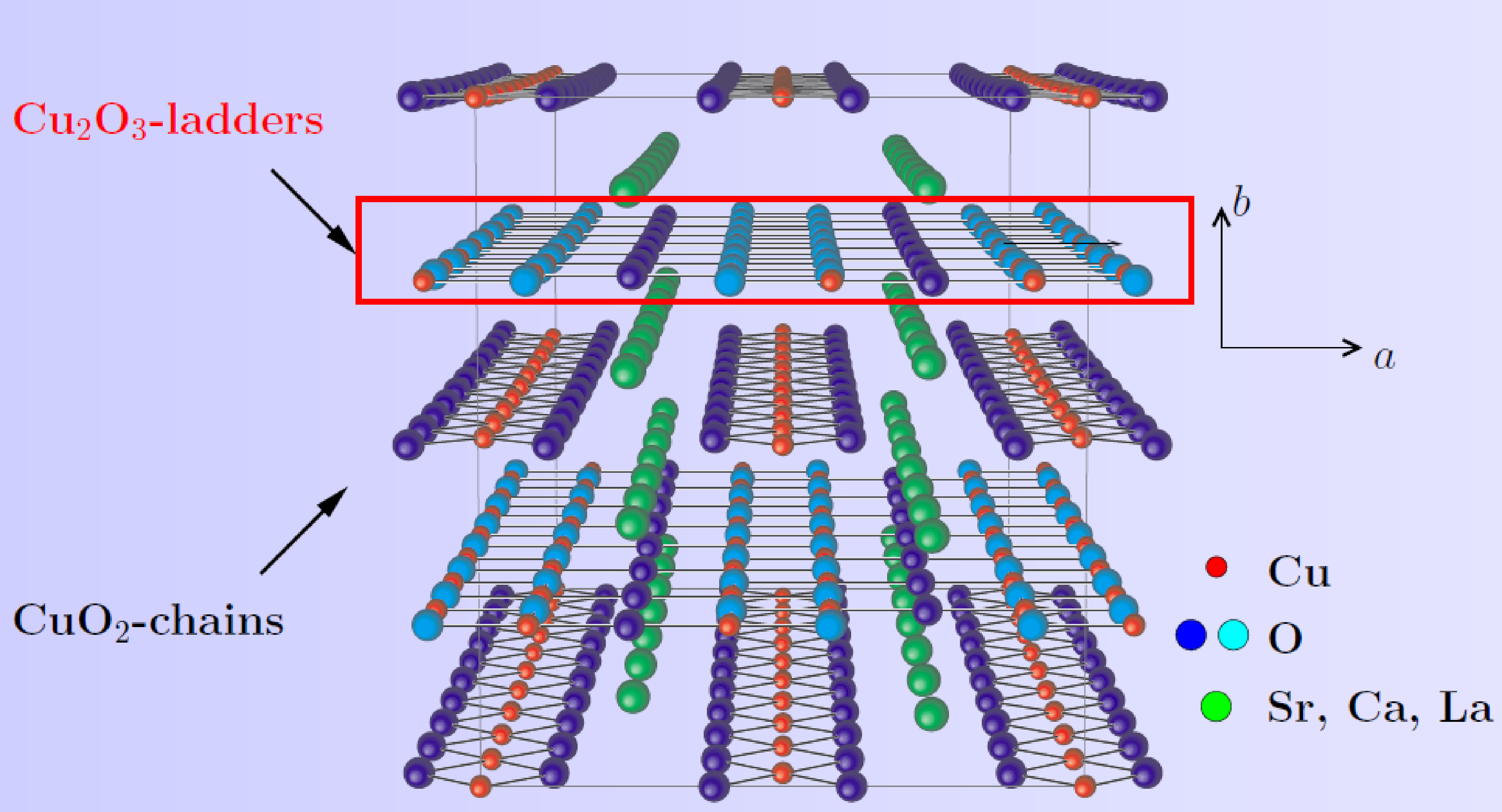
- Can the apparent thermal conductivity be reliably mapped to thermal conductivity accumulation function?
  - Probably "yes" when the accumulation function is relatively broad. But the interface matters.
  - Probably insufficient sensitivity if the accumulation function is narrow; see, e.g., the null result for Si:B at low temperatures
  - See MIT work on thermal gratings for experiments that avoid the interface problem.
  - See work by Minnich and co-workers for detailed analysis of TDTR experiments including the interface.

Diversity of anti-ferromagnetic order in copper-oxides



Hess (2007)

Magnon-phonon couplng and magnon thermal conductivity in the spin ladder $Ca_9La_5Cu_{24}O_{41}$

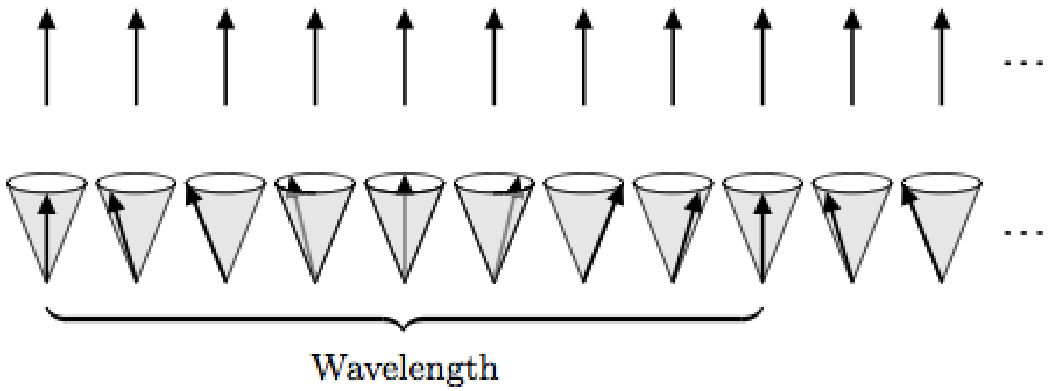


McCarron *et al.*, Mat. Res. Bull. (1988)

colorized graphic by Heidrich-Meisner (2005)

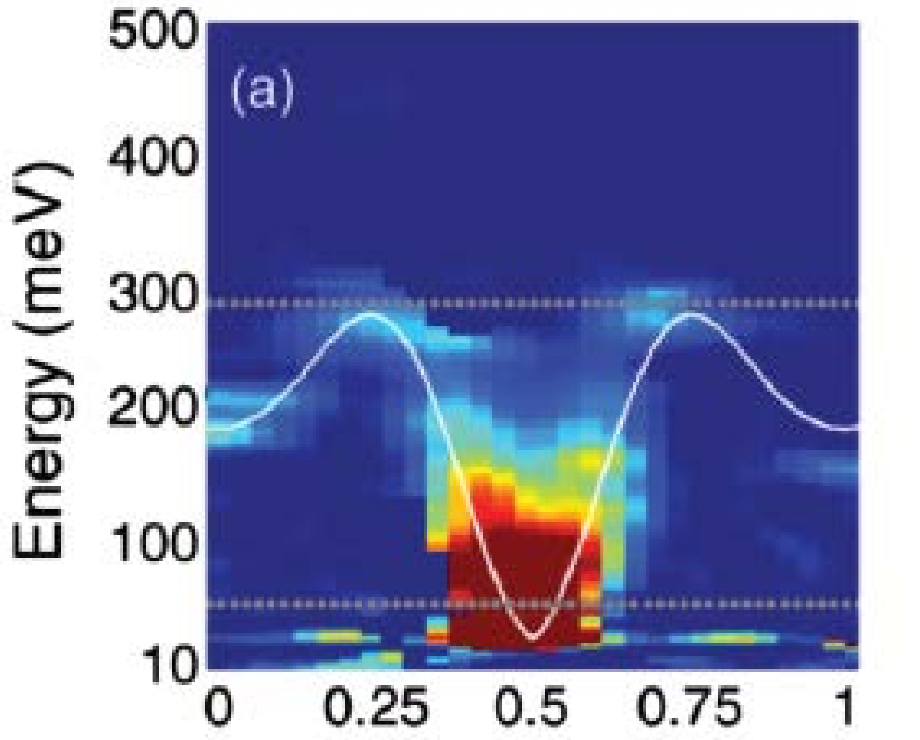
Spin waves are intrinsically quantum mechanical so hard to think about in classical analogies

Ferromagnetic ground state



Thermally-excited spin-wave state

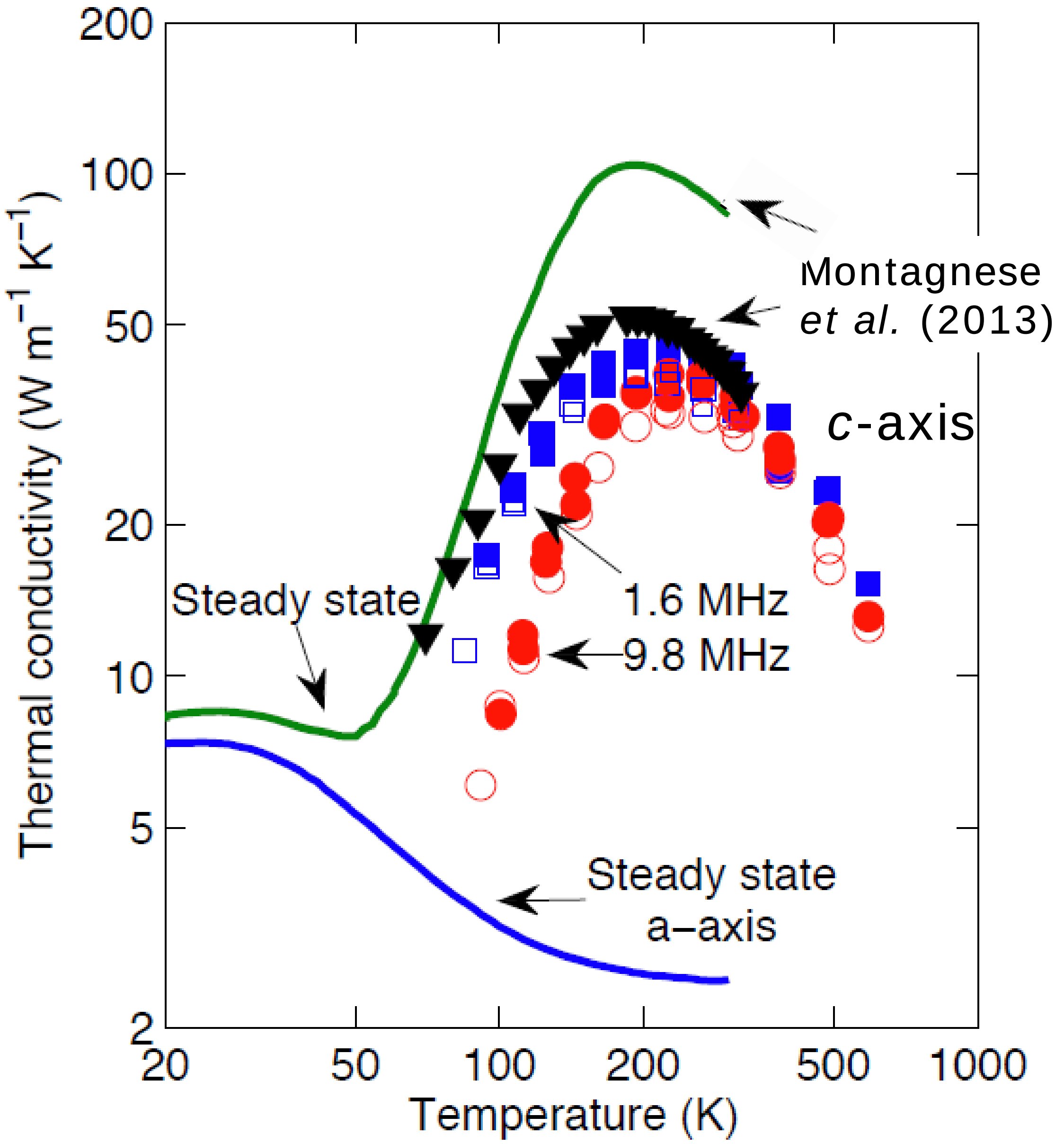
Magnon dispersion in $Sr_{14}Cu_{24}O_{41}$



Notbohm, *PRL* 2007
(inelastic neutron scattering)

http://www.physics.usyd.edu.au/~sflammia/Courses/StatMech/advanced/4/a4.html

Frequency dependent spin-wave thermal conductivity in $Ca_9La_5Cu_{24}O_{41}$

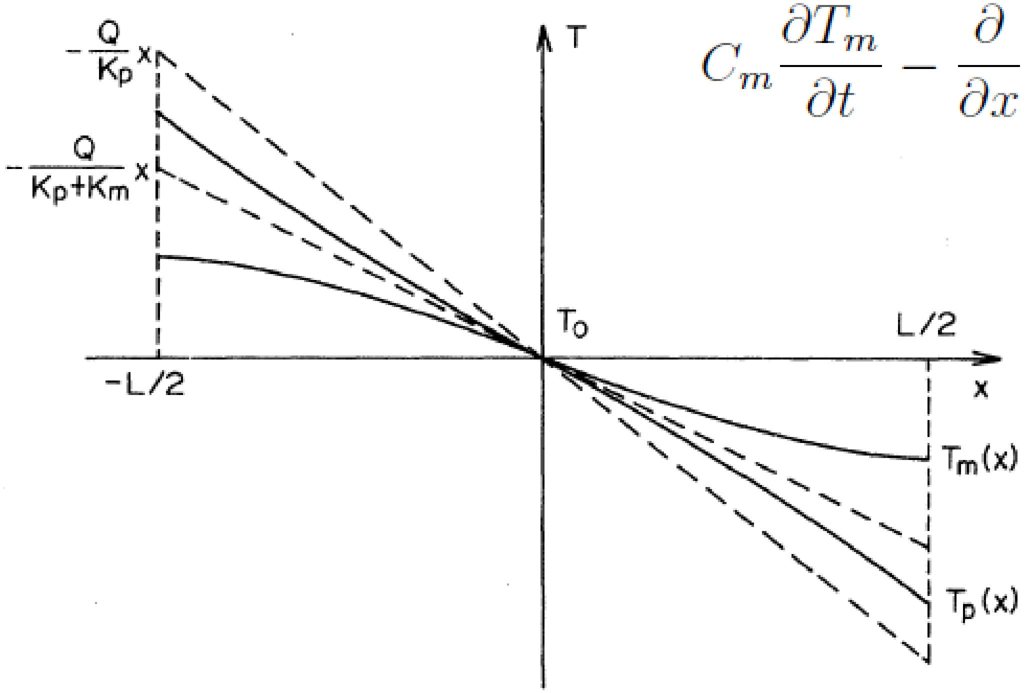


Use a two-channel model: magnons and phonons

- Sanders and Walton (1977) analyzed the steady-state situation for the context of conventional thermal conductivity measurements. Only phonons can carry heat through the ends of the sample.

$$C_p \frac{\partial T_p}{\partial t} - \frac{\partial}{\partial x}\left(\Lambda_p \frac{\partial T_p}{\partial x}\right) + g(T_p - T_m) = 0$$

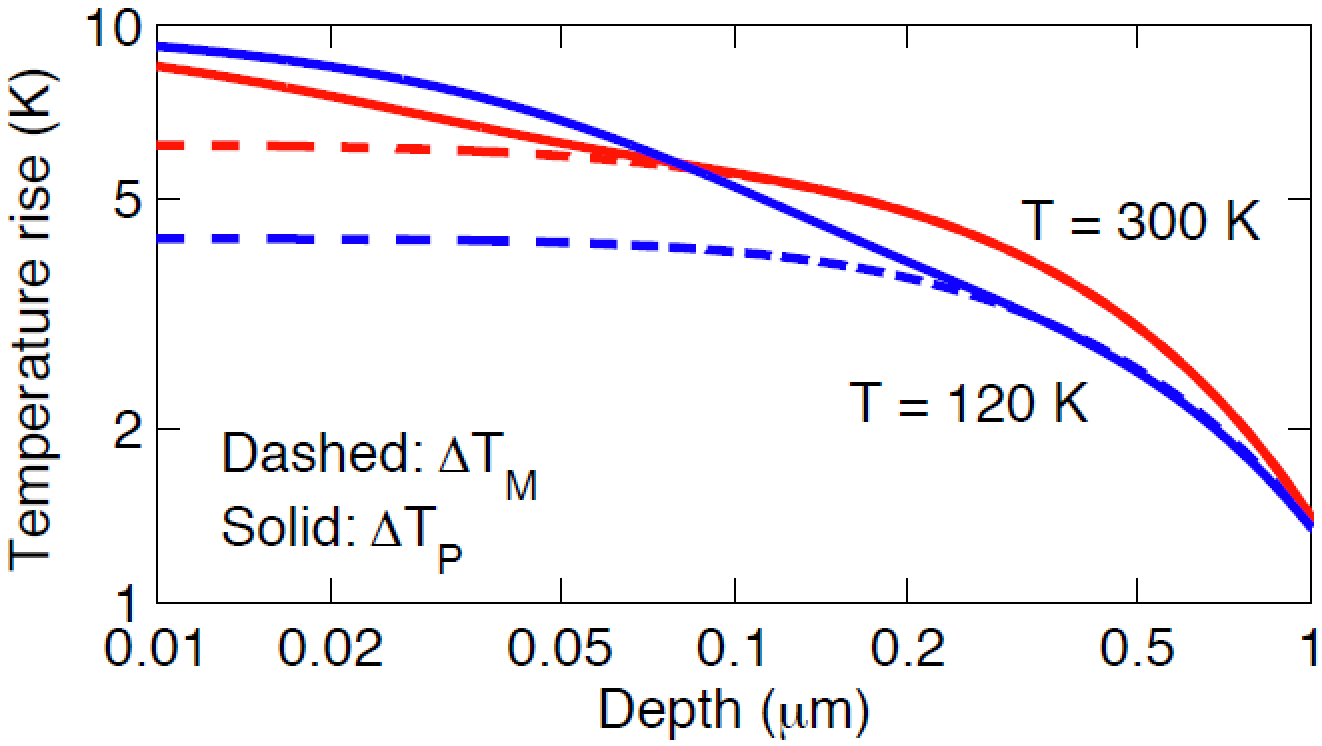
$$C_m \frac{\partial T_m}{\partial t} - \frac{\partial}{\partial x}\left(\Lambda_m \frac{\partial T_m}{\partial x}\right) + g(T_m - T_p) = 0.$$



Solution for TDTR experiments: Wilson *et al.*, PRB (2013).

Use a two-channel model: magnons and phonons

- Model calculations for 10 MHz TDTR experiment. The coupling parameter g is adjusted to get the best fit to the frequency dependent data

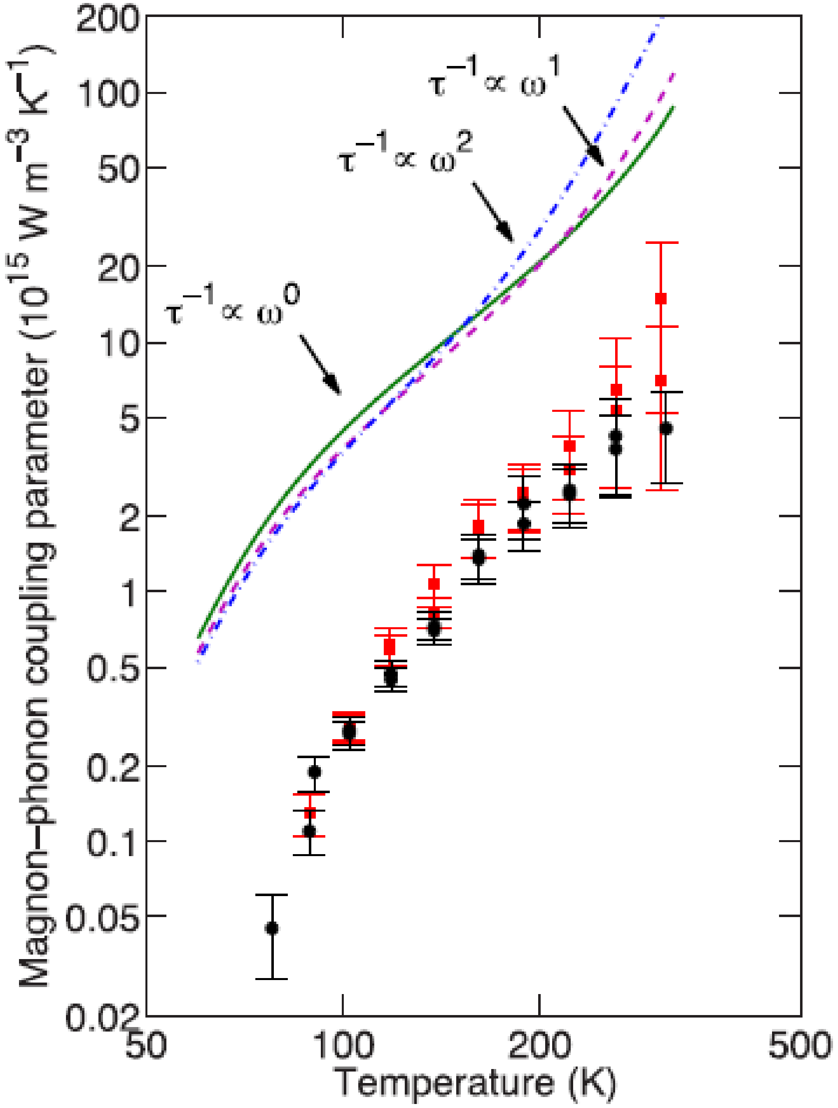


Hohensee *et al*., PRB (2014)

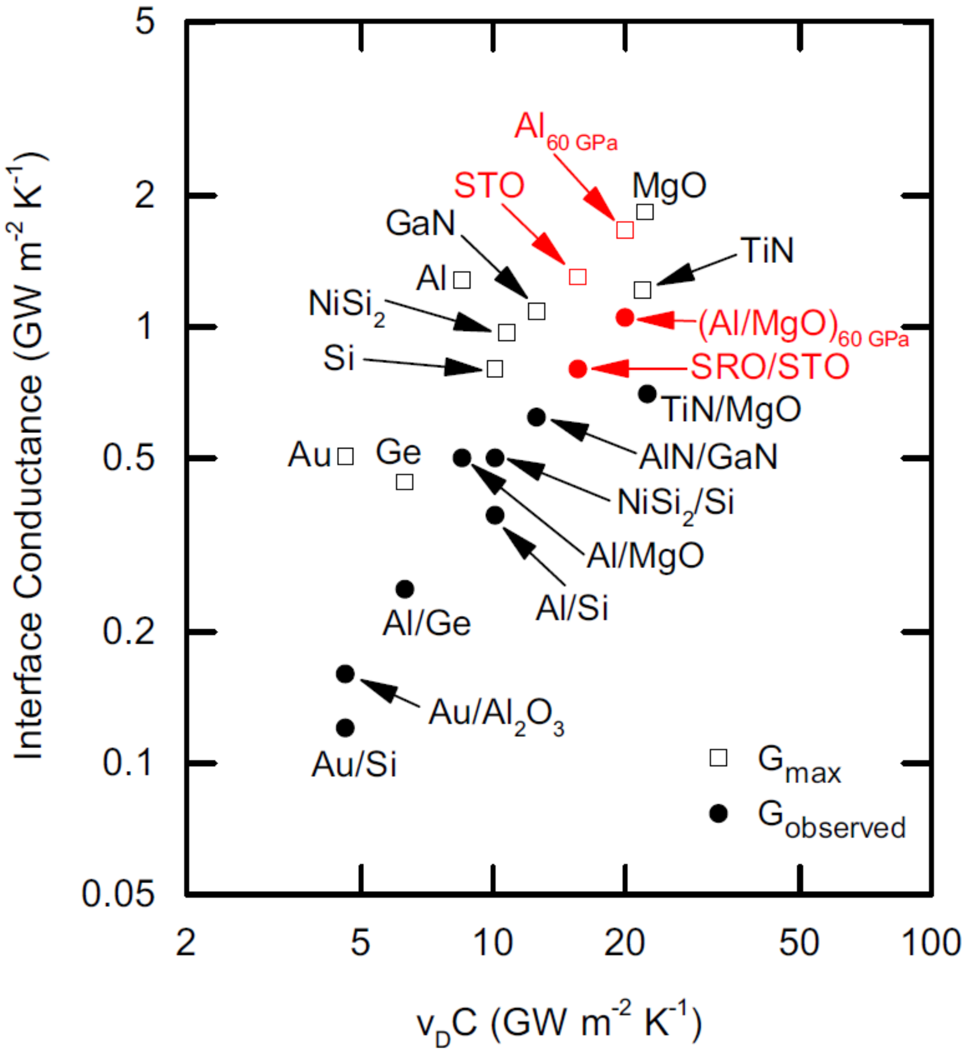
Magnon-phonon coupling parameter is strongly *T*-dependent

- $g \sim 10^{15}$ W m^{-3} K^{-1} near the peak in the thermal conductivity. (30 times smaller than g for electron-phonon coupling in Au.)
- Does this coupling (and therefore magnon-phonon scattering) determine the thermal conductivity near the peak?
- Is "two temperatures" too crude of a model to capture the physics?

PRB **89**, 024422 (2014)



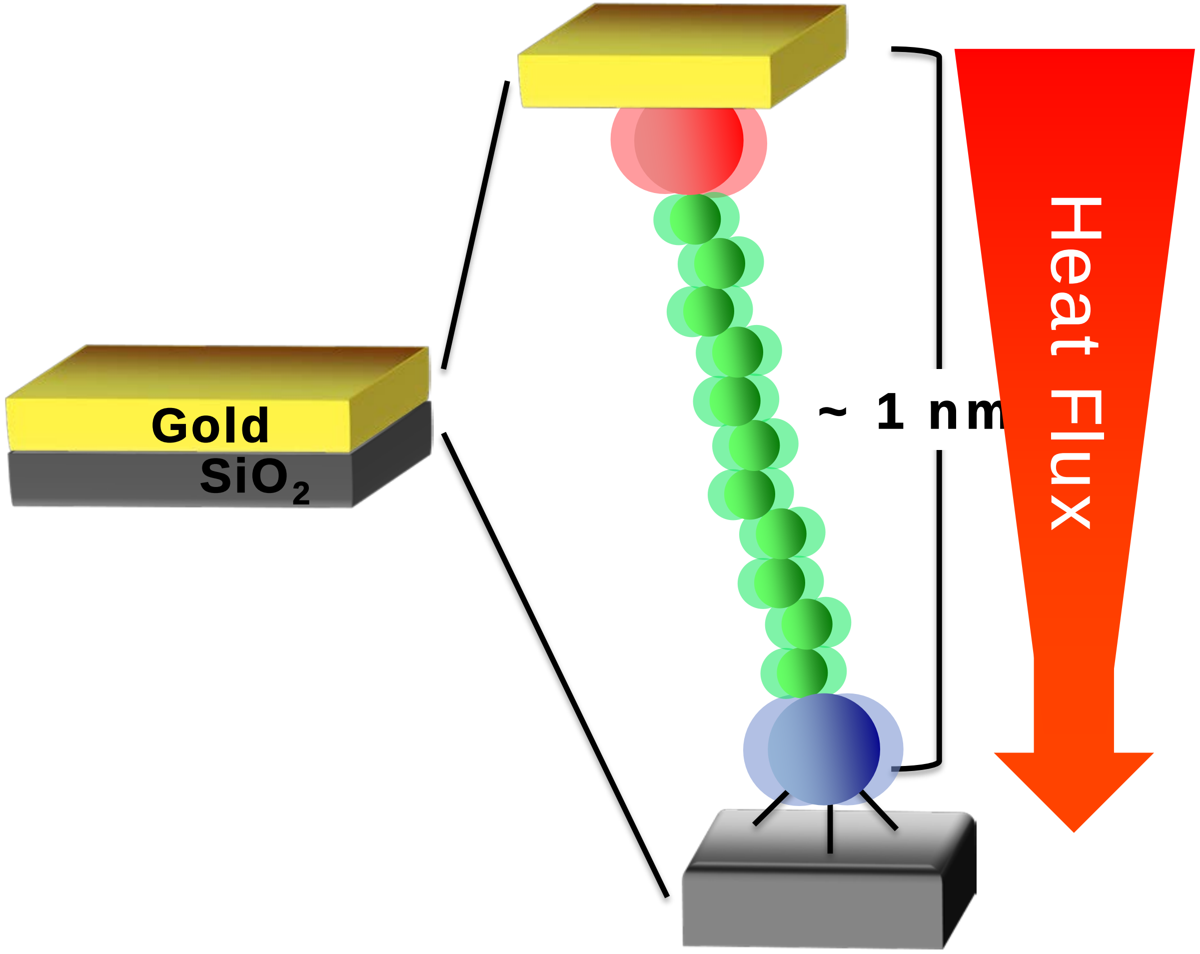
Strongly bonded interfaces typically behave as expected: the thermal conductance is ~40% of the maximum possible value



$$G_{\max} = \frac{1}{4}\sum_{j}\int c_{\omega} v_{\omega} d\omega_{j}$$

Wilson, *Phys Rev B* (2015)

I. Systematically vary the interface bonding with self-assembled monolayers with controlled chemistry



1. Can we modify the thermal conductance of an interface by introducing a molecular layer?

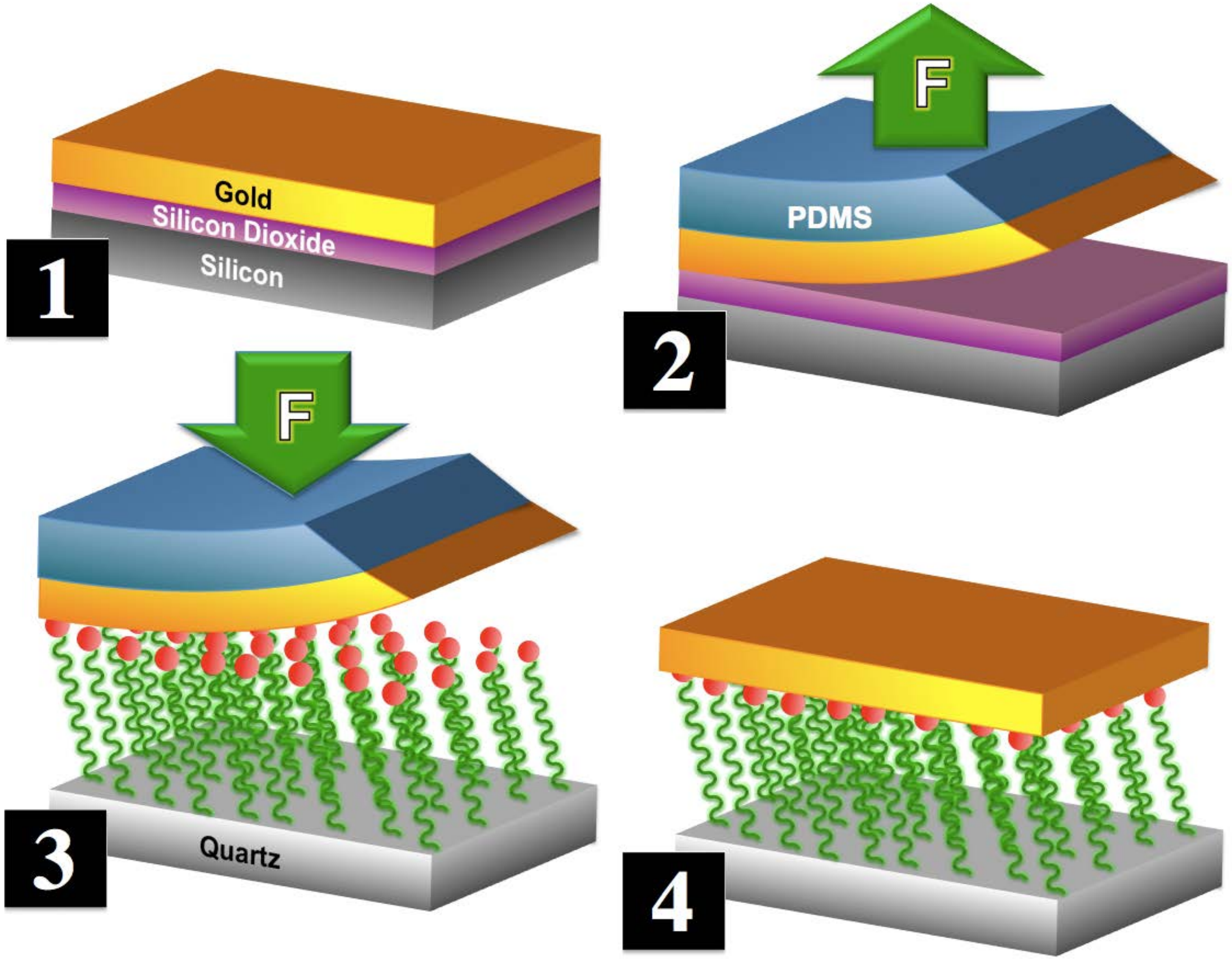
2. What parameters matter?

-Bonding?

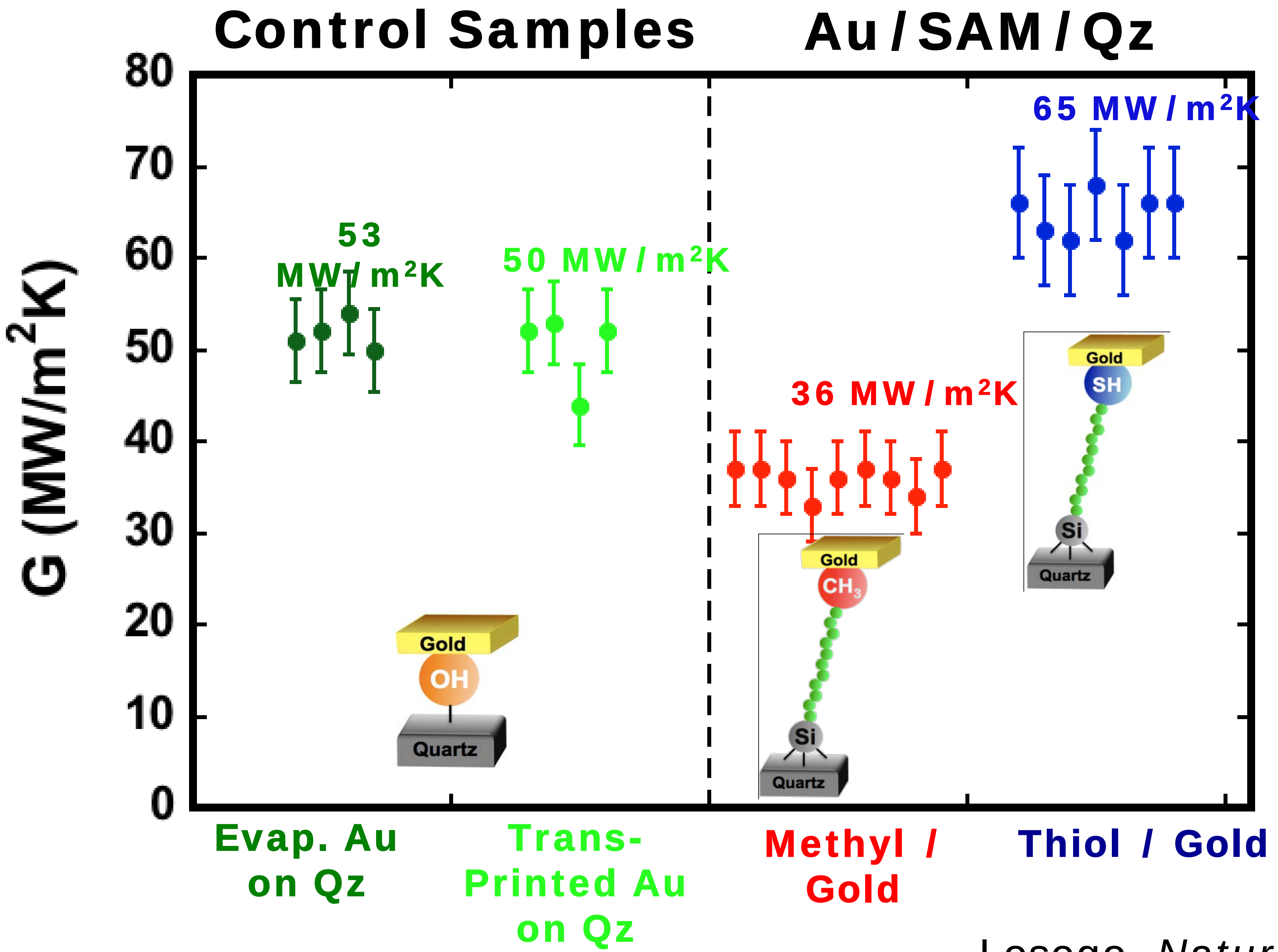
-Chain Length?

Losego, *Nature Materials* (2012)

Transfer printing of Au film to SAM-coated quartz



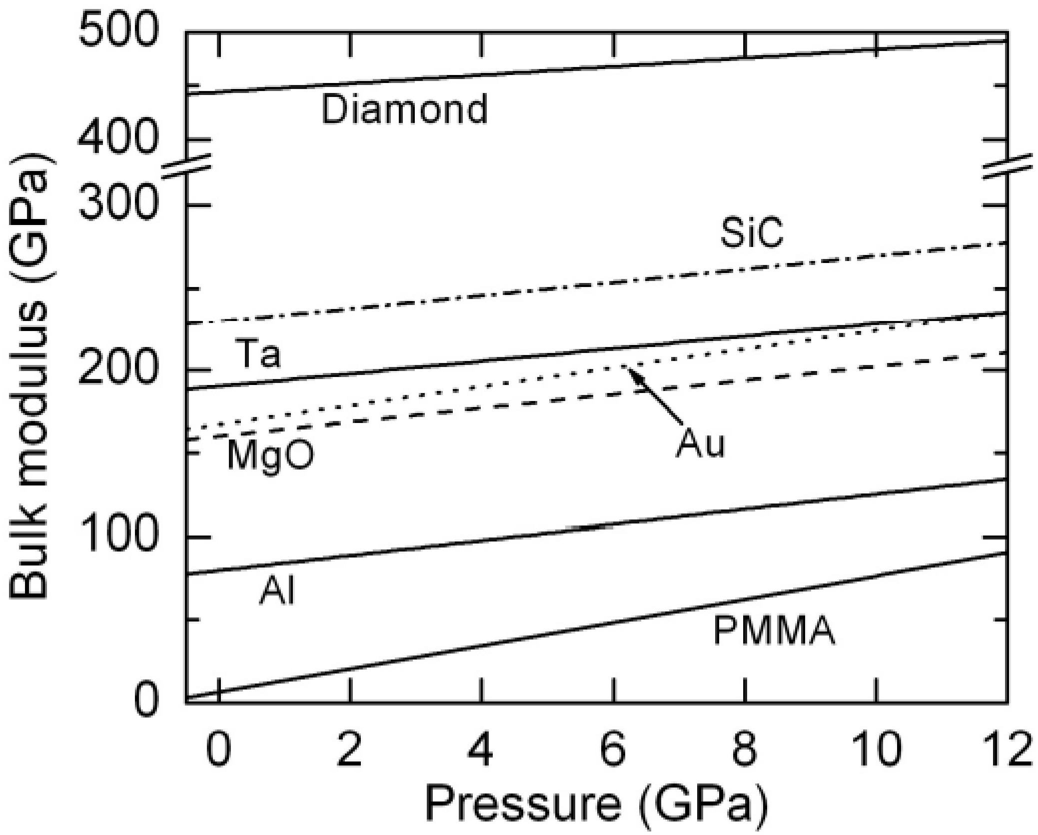
Interfacial bonding controls conductance G



Losego, *Nature Materials* (2012)

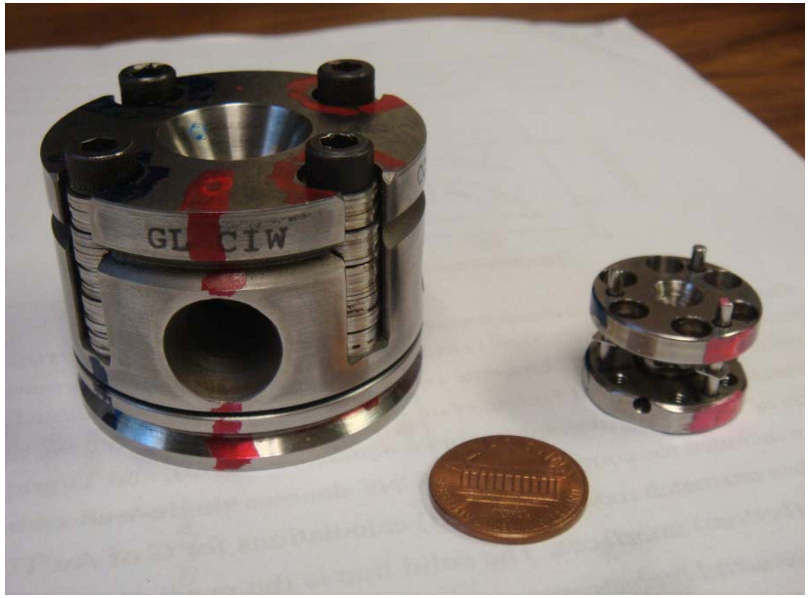
II. Systematically vary interface bonding with high hydrostatic pressure

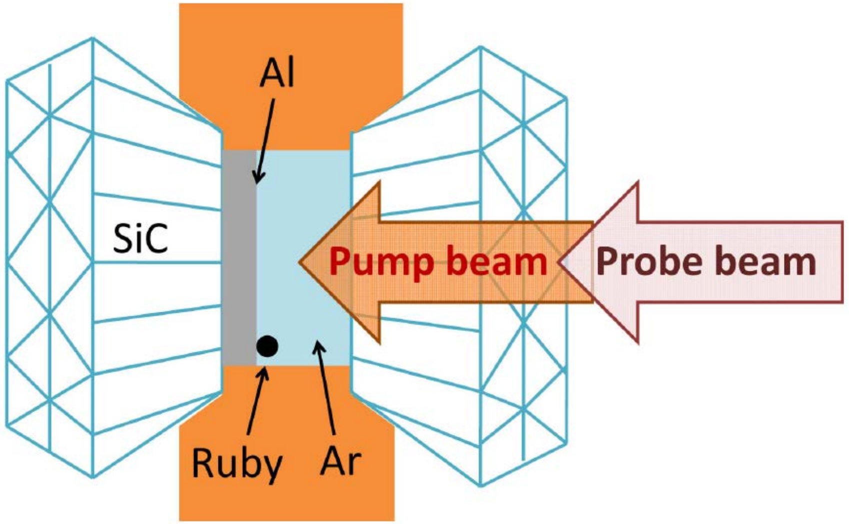
- Elastic constants and phonon spectra of typical materials do not change much between 0 <P <10 GPa.
- But weak interface bonds are expected to be highly anharmonic (more like PMMA than diamond)



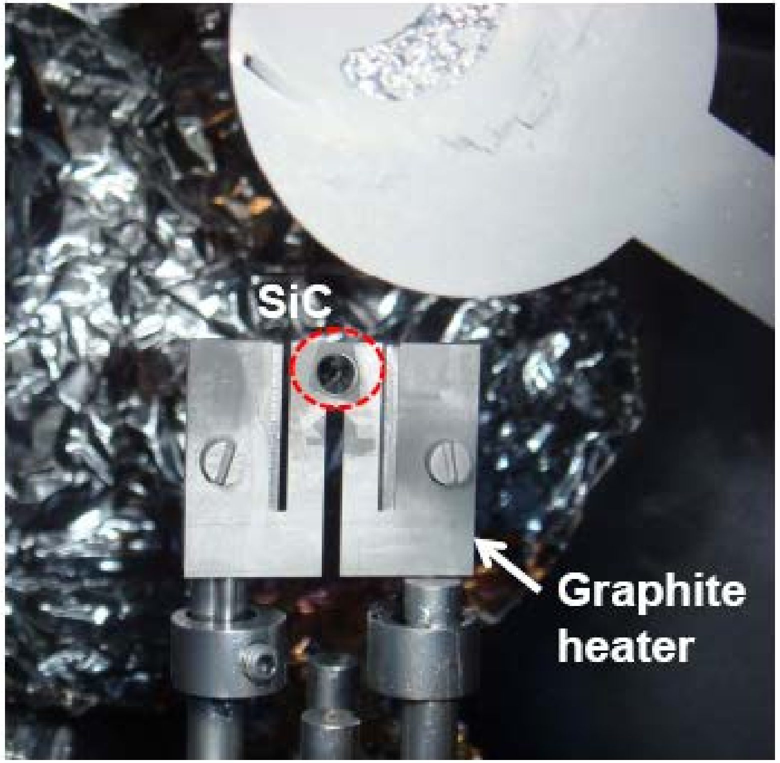
TDTR is all optical method: adaptable to “extreme” environments such as high pressure

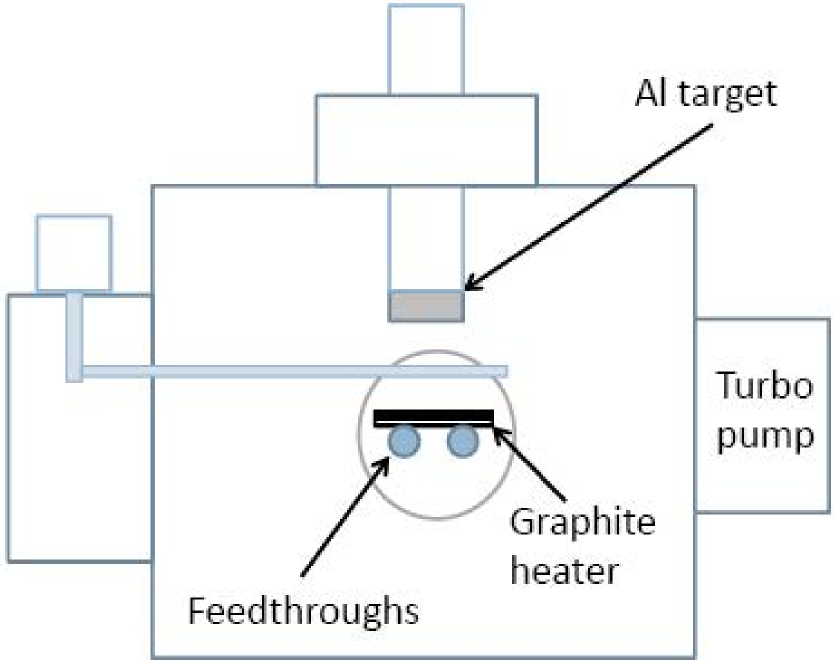
Diamond anvil cell





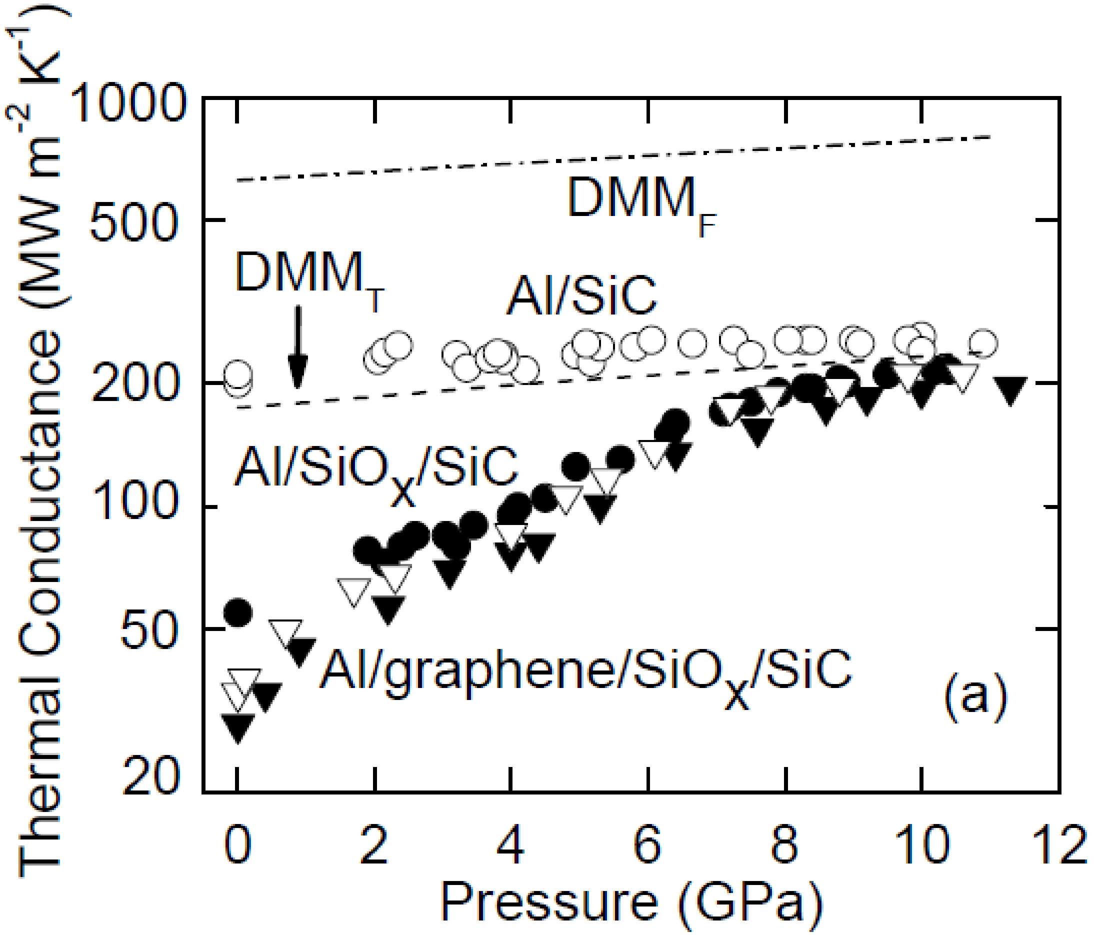
Clean SiC anvil at high temperatures and deposit Al film *in-situ* by sputtering





Compare clean interface with a layer of CVD graphene inserted at the interface

- Clean interface has the weak pressure dependence expected from diffuse-mismatch (DMM) calculations.
- Insert graphene: low conductance and strong pressure dependence.
- At P>8 GPa, “weak” interface becomes “strong” and conductance is high.



Hsieh, *PRB* (2011)

Summary for interface conductance

- Strongly-bonded interfaces, similar materials
  - Conductance is high magnitude is understood
  - With semiconductor alloys, deviations are from a "radiative boundary condition" are significant
- Strongly bonded interfaces, dissimilar materials
  - Role of electron and phonon coupling across the interface is still being discussed. No conclusive evidence that this is significant however.
- Weakly-bonded interfaces
  - Phenomenology is established. Microscopic descriptions are not.
  - What is the spectrum of vibrations that carry heat?

Final topic: Thermally functional materials

- Passive function
  - Thermal regulator: abrupt increase in thermal conductivity with increasing temperature
    - Analogy with voltage regulator. Impedance is infinite until a threshold voltage is reached; then impedance is zero.
    - Combine with materials with abrupt decrease in thermal conductivity to form effective thermal rectifiers.
- Active function
  - Thermal switch: thermal conductivity changes with application of external field or stimulus.

Materials discovery versus engineering

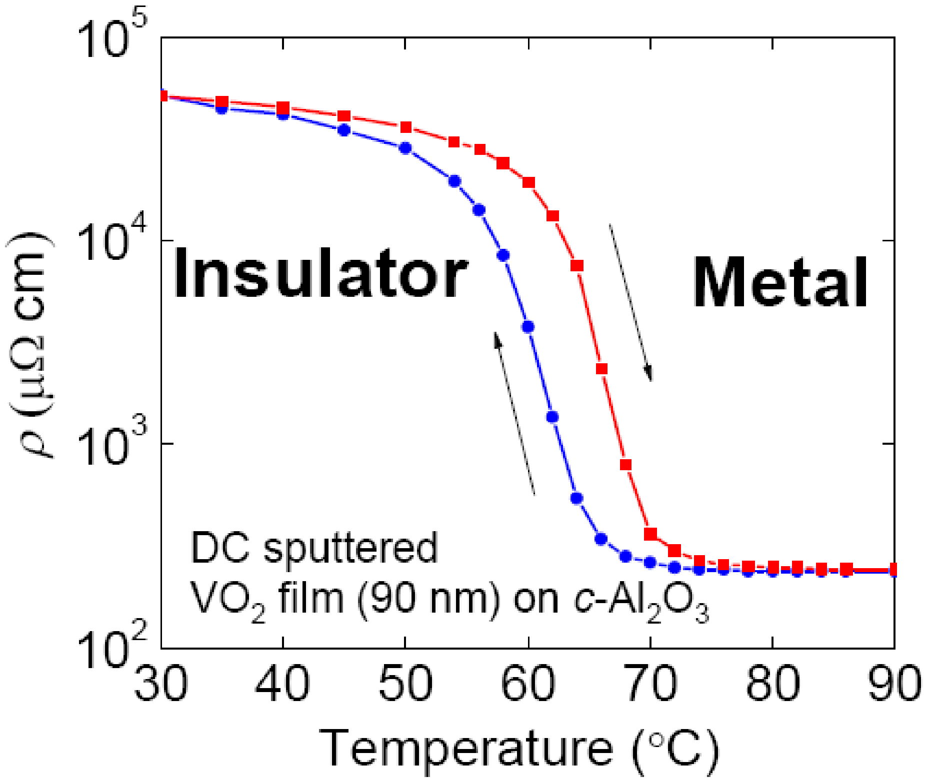
- Engineer a new device system using existing materials.
- Discover materials with new function or improved performance.
- Use time-domain thermoreflectance to efficiently explore the behavior of a wide-variety of materials in bulk and thin film forms as a function of temperature and applied fields.

Materials discovery for passive control

- Need reversibility, high contrast, and tunable threshold temperature.
- Insulator-to-metal transitions, e.g., VO_2.
  - Many examples but all I am aware of are “correlated electron metals” where the metallic state resistivity is above 300 $\mu\Omega$-cm.
  - Translates to electronic thermal conductivity <2 W m^{-1} K^{-1} at room temperature (scales linearly with absolute temperature).
  - Minimum phonon thermal conductivity is typically on the order of 1 W m^{-1} K^{-1} so best-case contrast is $(2+1)/1 = 3$.

VO_2 is a model material for insulator-to-metal transitions

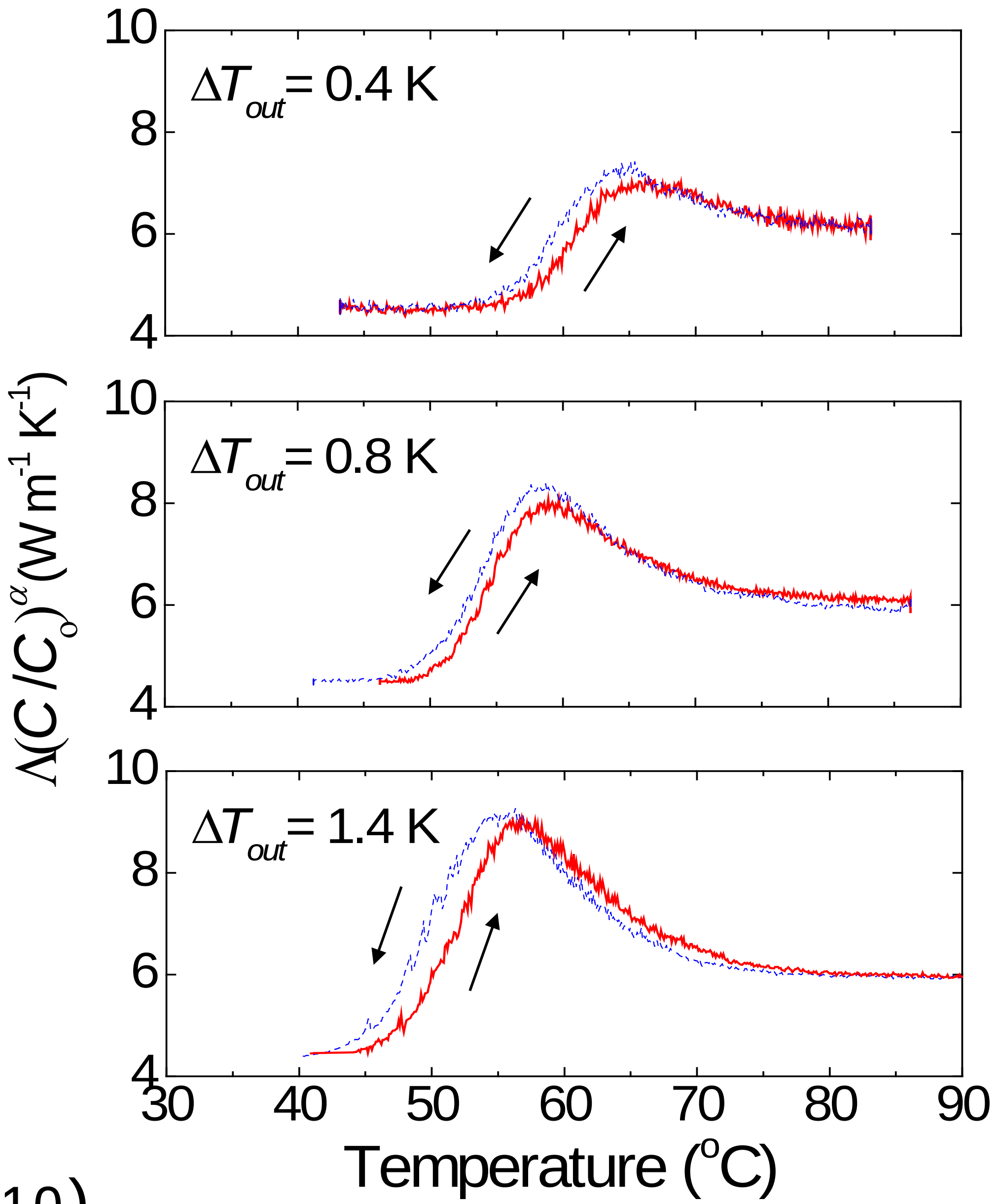
- Crystalline structure changes from monoclinic (I) to tetragonal (M) (ΔH=51.5 J/g)
- Hysteresis behavior (width ~ 5 °C)
- ρ_{el} ~ 300 $\mu\Omega$ cm corresponds to ~ 3 W/mK



Oh, *APL* (2010)

Reduced phonon thermal conductivity in films: VO_2/sapphire

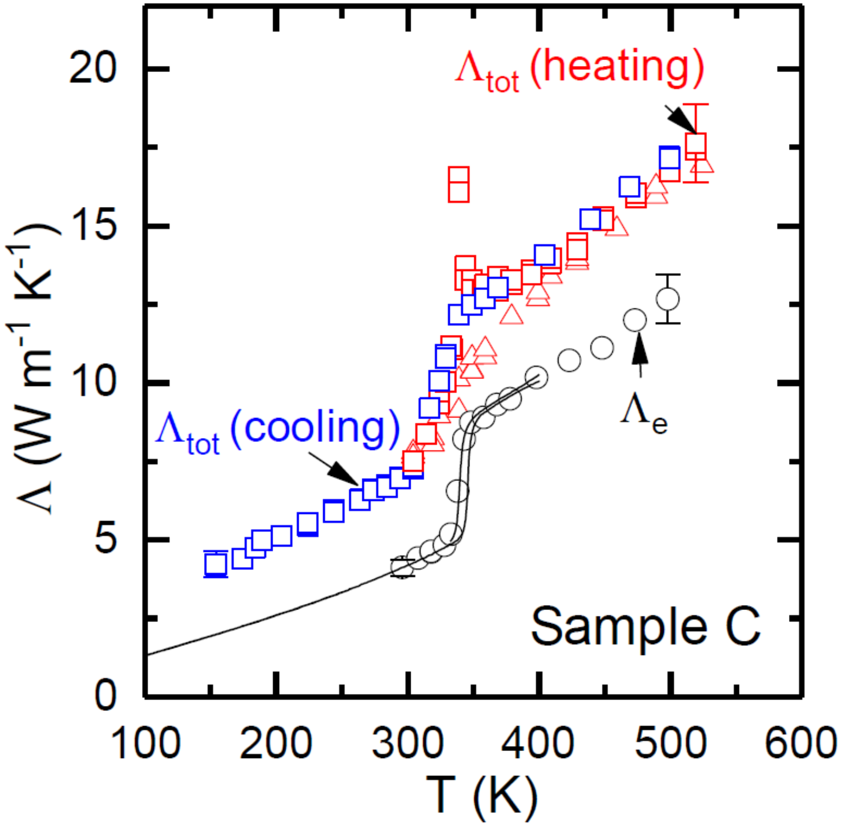
- Change across the transition is observed presumably due to point defects that suppress phonon thermal conductivity.
- Large 10 MHz temperature oscillations in the TDTR experiment activate latent heat contributions to the heat capacity
- Contrast in thermal conductivity is only 50%. Need larger contrast between "off" and "on"



Oh, *APL* (2010)

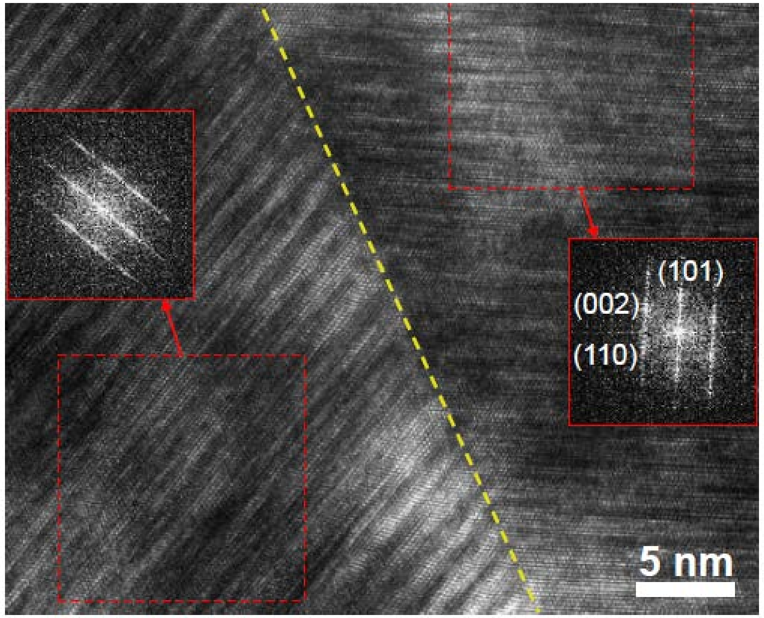
Look for larger contrast in metals, e.g., shape-memory materials

- Previous work on $Mn_{50}Ni_{50-x}In_x$ (14<x<15) motivated by potential applications in magnetically-actuated mechanical devices and magneto-caloric energy conversion



Zheng, *Adv Eng Mat* (2019)

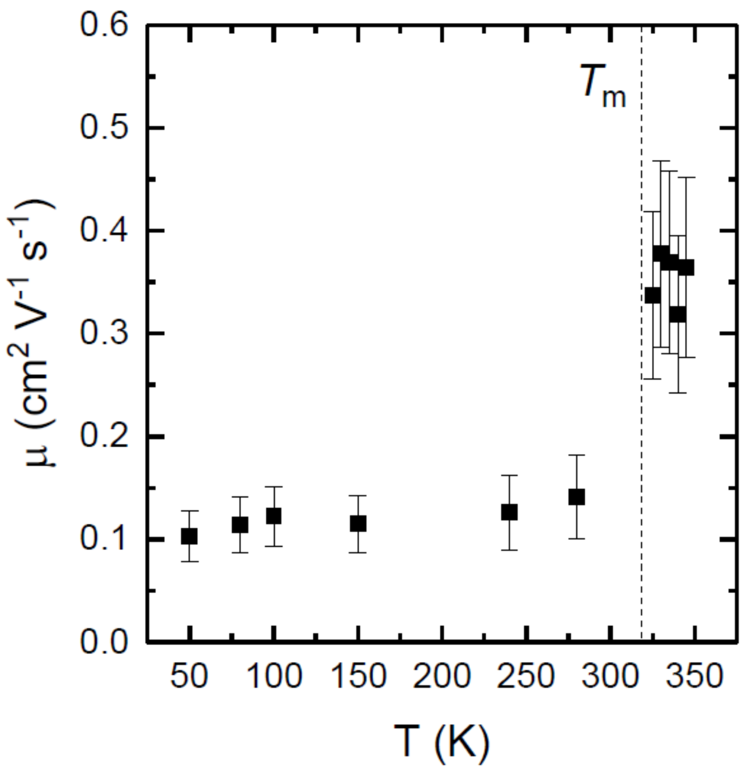
TEM image of martensite phase

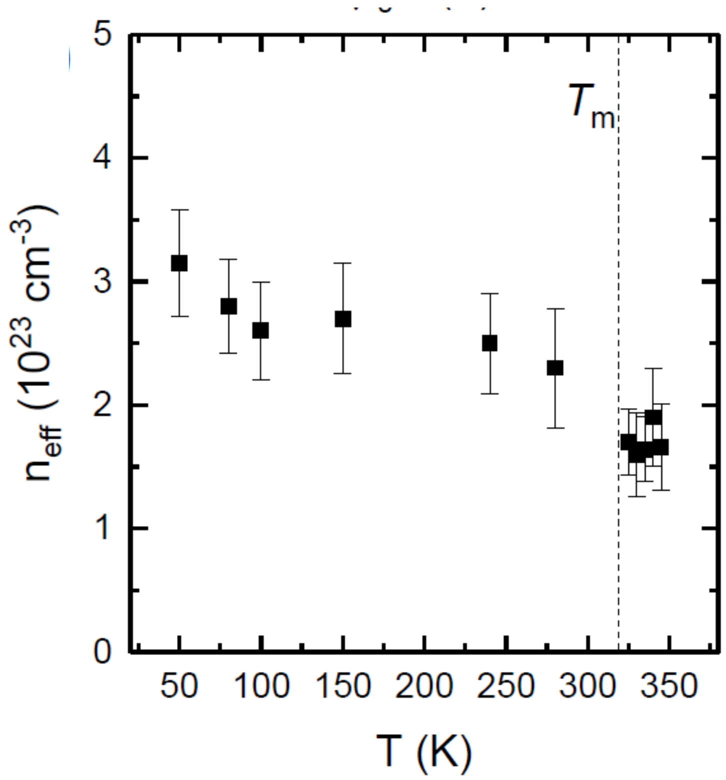


Can we find materials with higher contrast?

- Hall effect measurements show that large increase in mobility is opposed by small decrease in carrier density

- Is change in mobility intrinsic to the crystal structure or extrinsic due to high density of twins in the martensite phase?





Zheng, *Adv Eng Mat* (2019)

Materials discovery for active control

- Electrochemical processes, e.g., Li_xCoO_2 and Li_xMoS_2
  - Many well-studied examples developed for batteries, switchable windows.
  - Just starting to explore contrast in thermal conductivity
  - Challenge: Solid state diffusion is typically slow.

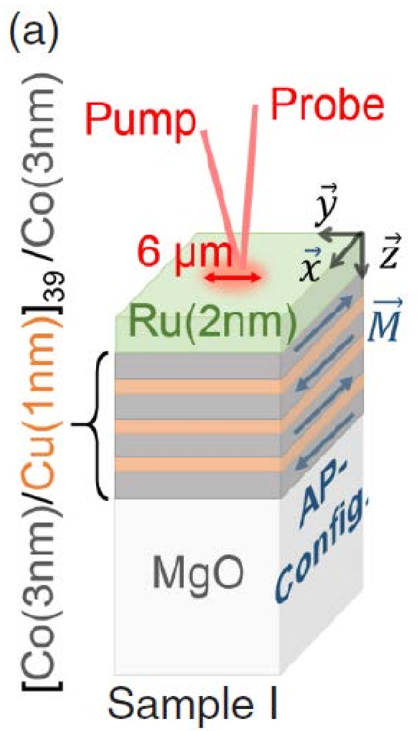
Cho *et al*., Nat. Commun. (2014)

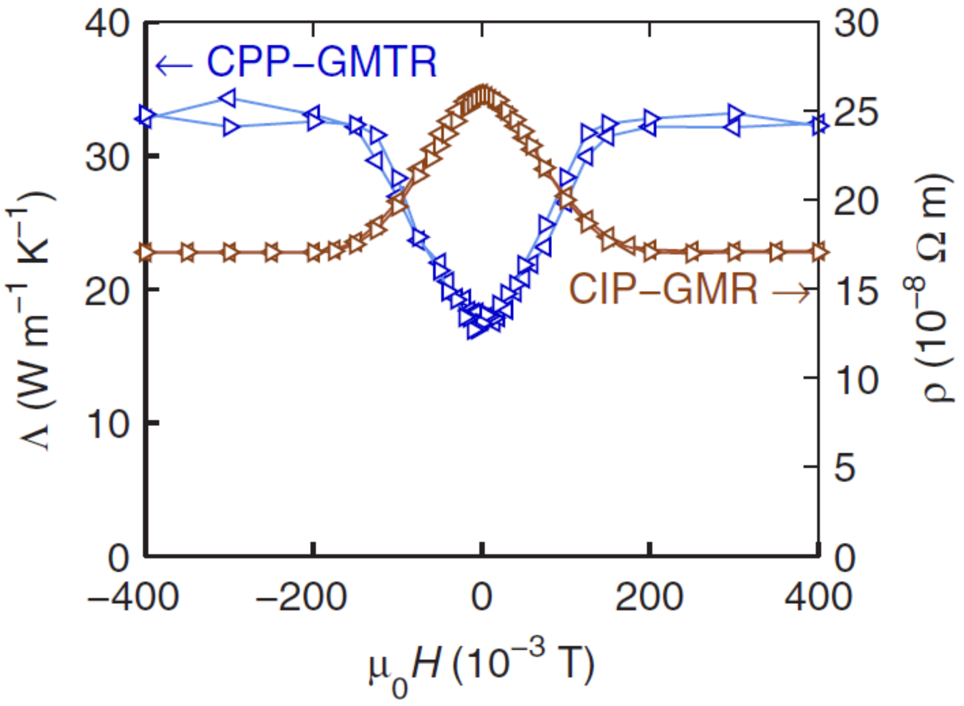
Zhu *et al*., Nat. Commun. (2016)

Sood *et al*., Nat. Commun. (2018)

Materials discovery for active control

- Where else should we be looking?
- Contrast in magnetic materials, “giant magneto-thermal resistance” is currently limited to ≈2.

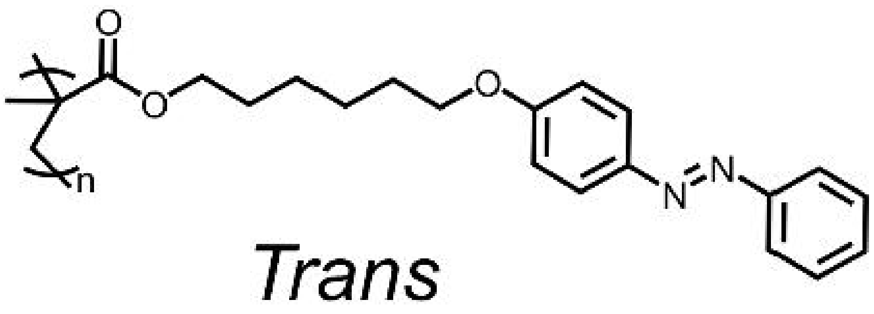


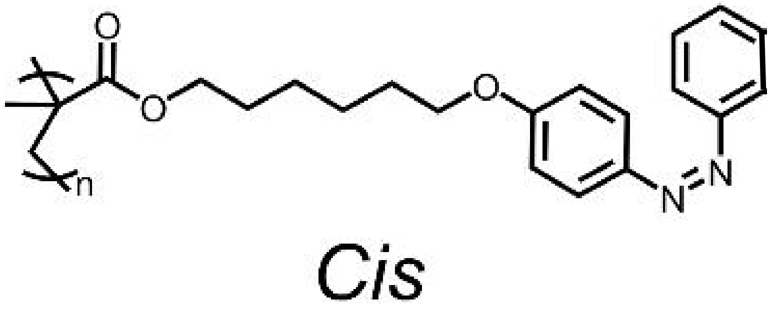


Kimling, *PRB* (2015)

Light-activated isomerization (azo-polymer)

- UV light converts *trans* to *cis* conformation
- Visible light (or thermal relaxation to equilibrium) converts *cis* to *trans*



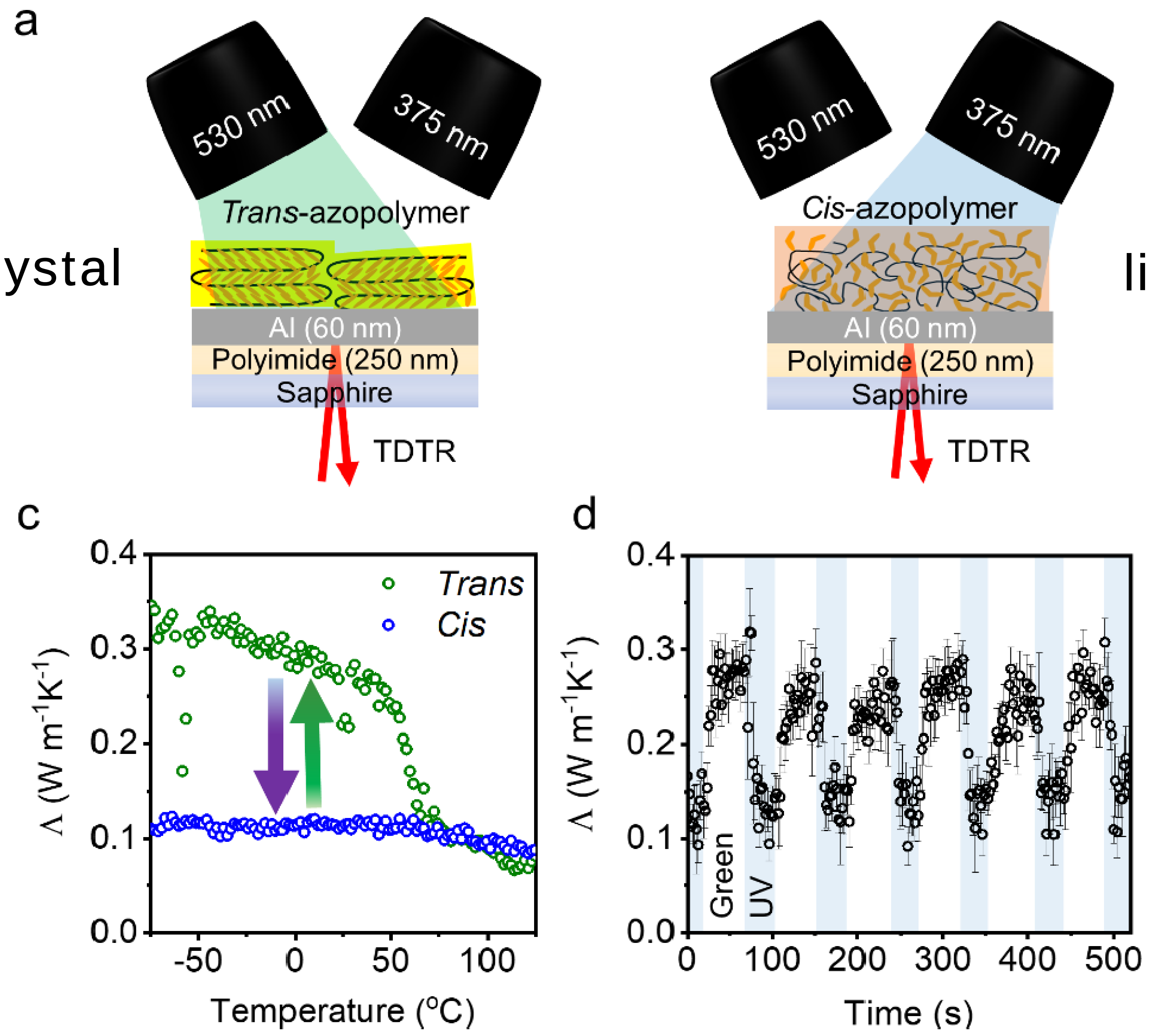


Shin, *PNAS* (2019)

Light-activated isomerization (azo-polymer)

crystal

liquid



Shin, *PNAS* (2019)

Concluding comments

- Many compelling “puzzles” and “problems” in the field of nanoscale thermal transport
- Conventional wisdom on the lower limit to the thermal conductivity of solid materials was wrong. Race to the bottom in both inorganic and organic materials.
- Deviations from Fourier behavior at room temperature in high thermal conductivity crystals on length scales ~1 μm. Particularly strong effects in Si because of the broad distribution of phonon mean-free-paths.
- Weak bonding at an interface strongly suppresses thermal conductance. Progress is being made in understanding the spectrum of heat carriers.
- Many materials can potentially provide a thermal regulating or thermal switching function but higher contrasts are needed for applications.