Ultralow thermal conductivity and the thermal conductance of interfaces

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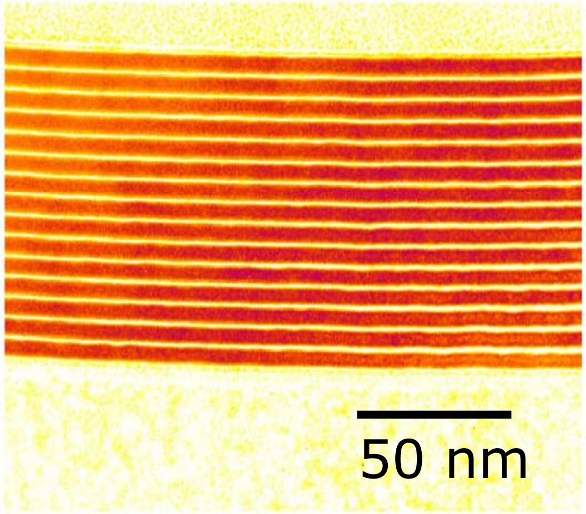
Outline

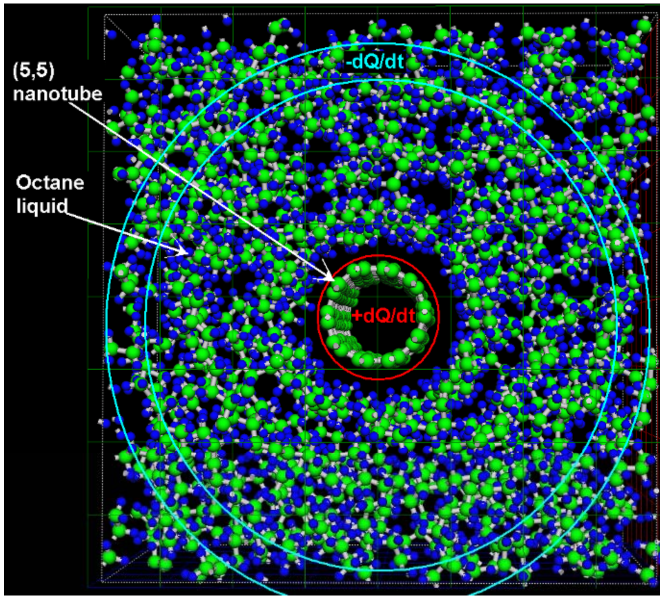
- Thermal conductivity and interface thermal conductance.
- Advances in time-domain thermoreflectance.
- Amorphous limit to the thermal conductivity of materials.
- Ultralow thermal conductivity: beating the amorphous limit in disordered layered crystals.
- On-going work on understanding and extending the physics.

Interfaces are critical at the nanoscale

- Low thermal conductivity in nanostructured materials
  - improved thermoelectric energy conversion
  - improved thermal barriers

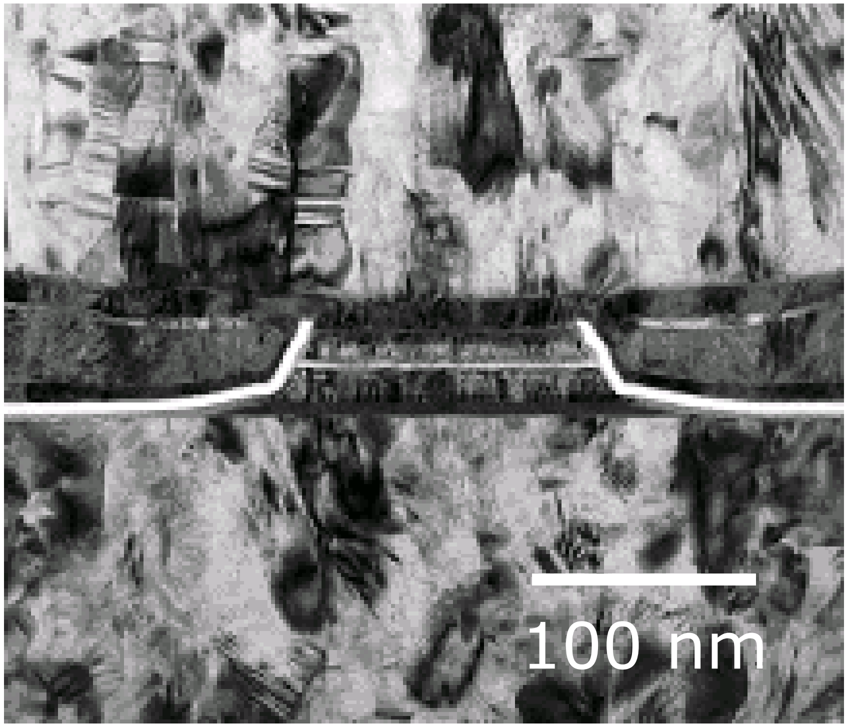


- High thermal conductivity composites and suspensions



Interfaces are critical at the nanoscale

- High power density devices
  - solid state lighting
  - high speed and power electronics
  - nanoscale sensors

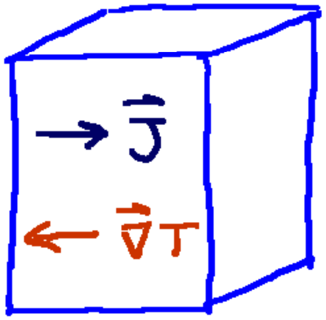


TEM micrograph of tunneling magnetoresistive sensor (view from “air bearing side") M. Kautzky (Seagate)

Thermal conductivity and interface thermal conductance

- Thermal conductivity Λ is a property of the continuum

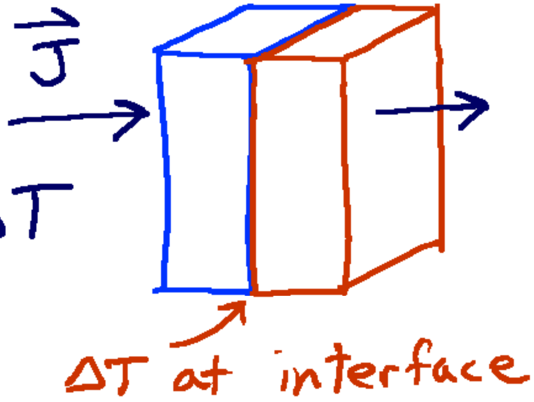
$$\vec{J} = -\Lambda \vec{\nabla} T$$



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

- 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 conductivity and interface thermal conductance

- Both properties are difficult to understand and control because they are integral properties.
- For example, simplest case of thermal conductivity where resistive scattering dominates

$$\Lambda = 1/3 \int C(\omega)\ v(\omega)\ \ell(\omega)\ d\omega$$

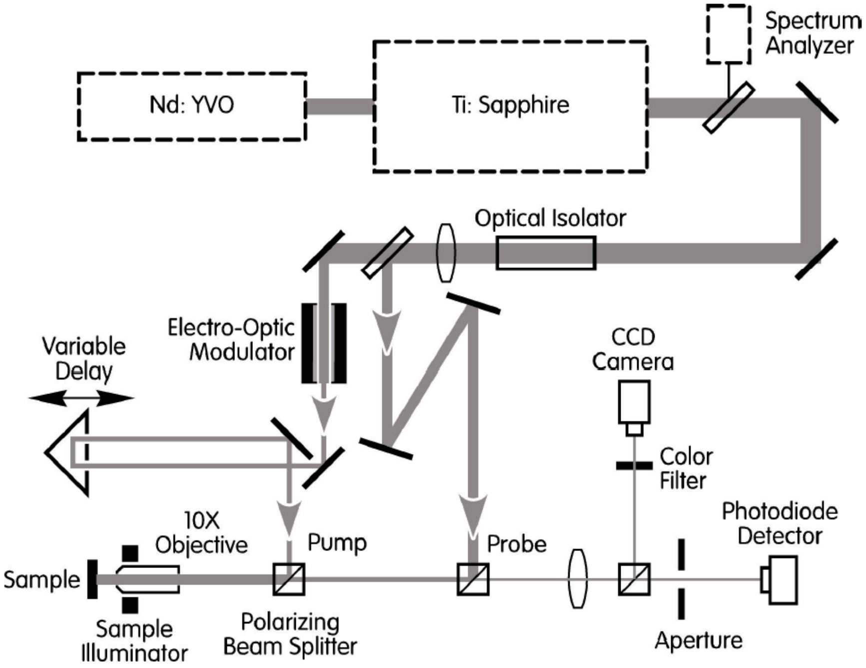
$C(\omega)$ = heat capacity of phonon mode

$v(\omega)$ = group velocity

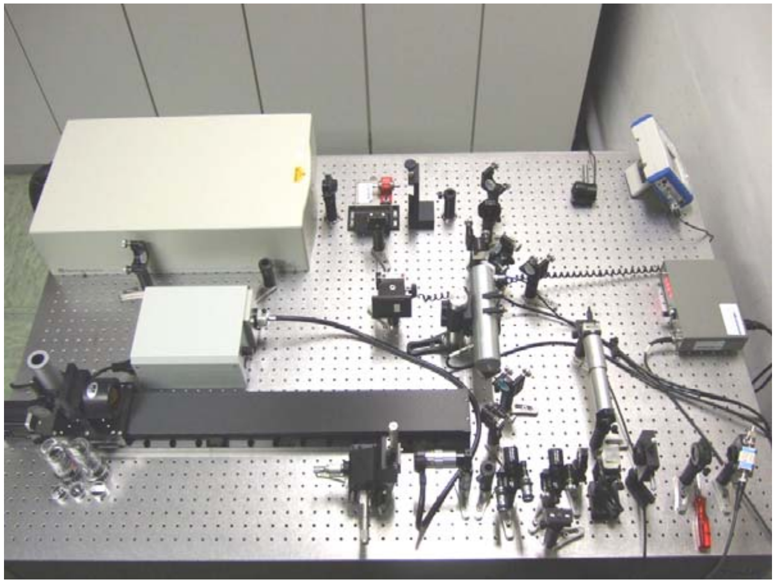
$\ell(\omega)$ = mean-free-path

Time domain thermoreflectance since 2003

- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering

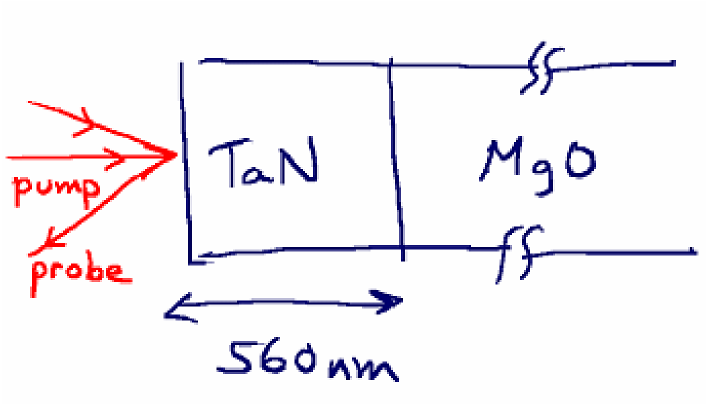


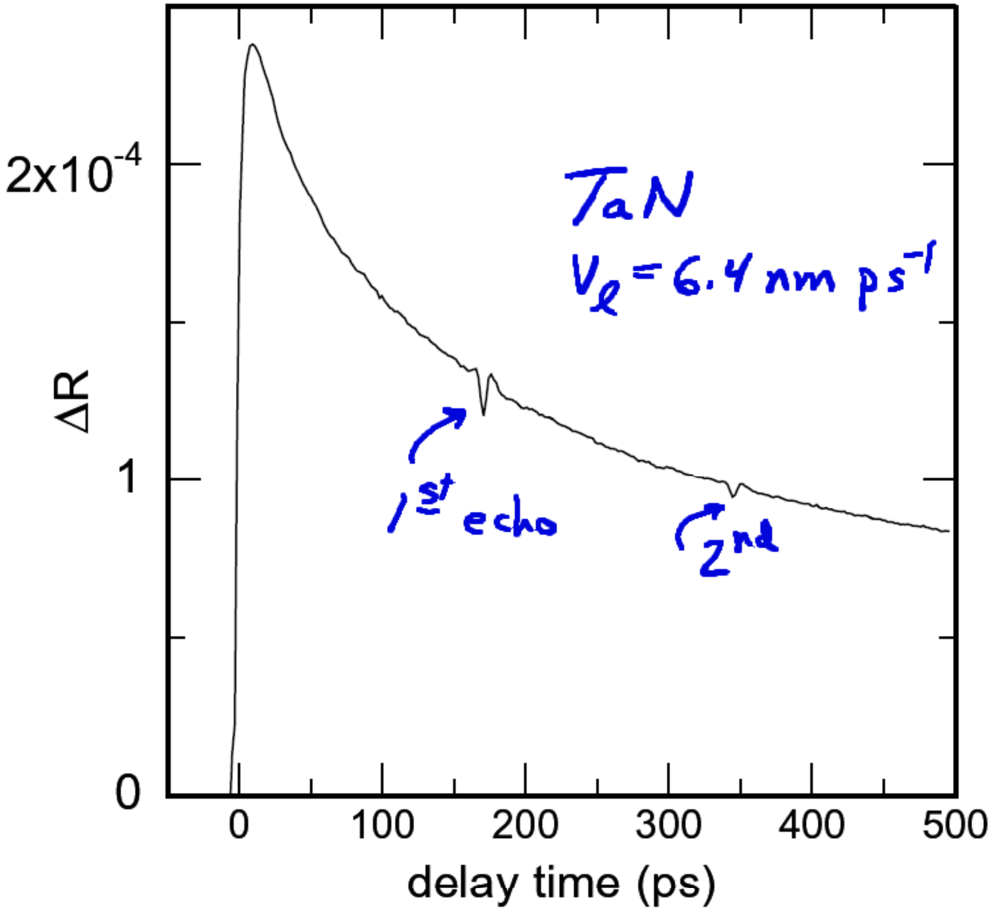
Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008



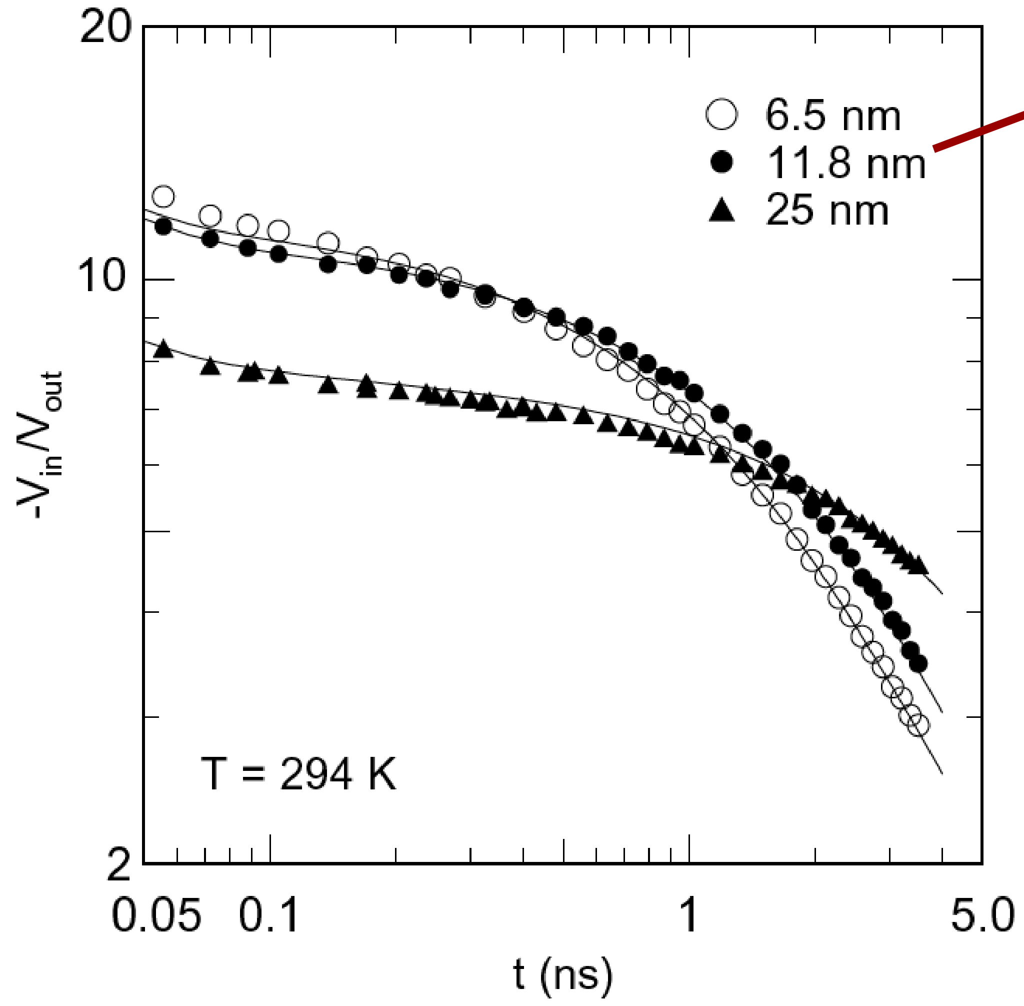
psec acoustics and time-domain thermoreflectance

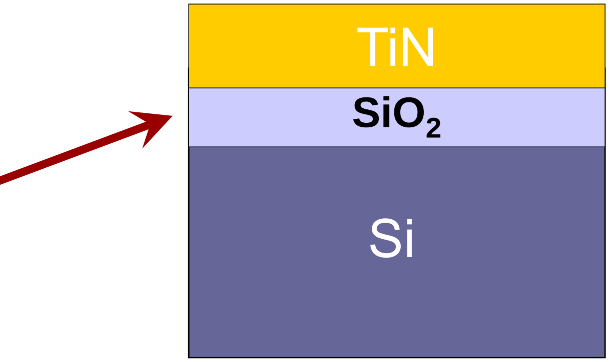
- Optical constants and reflectivity depend on strain and temperature
- Strain echoes give acoustic properties or film thickness
- Thermoreflectance gives thermal properties





Time-domain Thermoreflectance (TDTR) data for TiN/SiO_2/Si



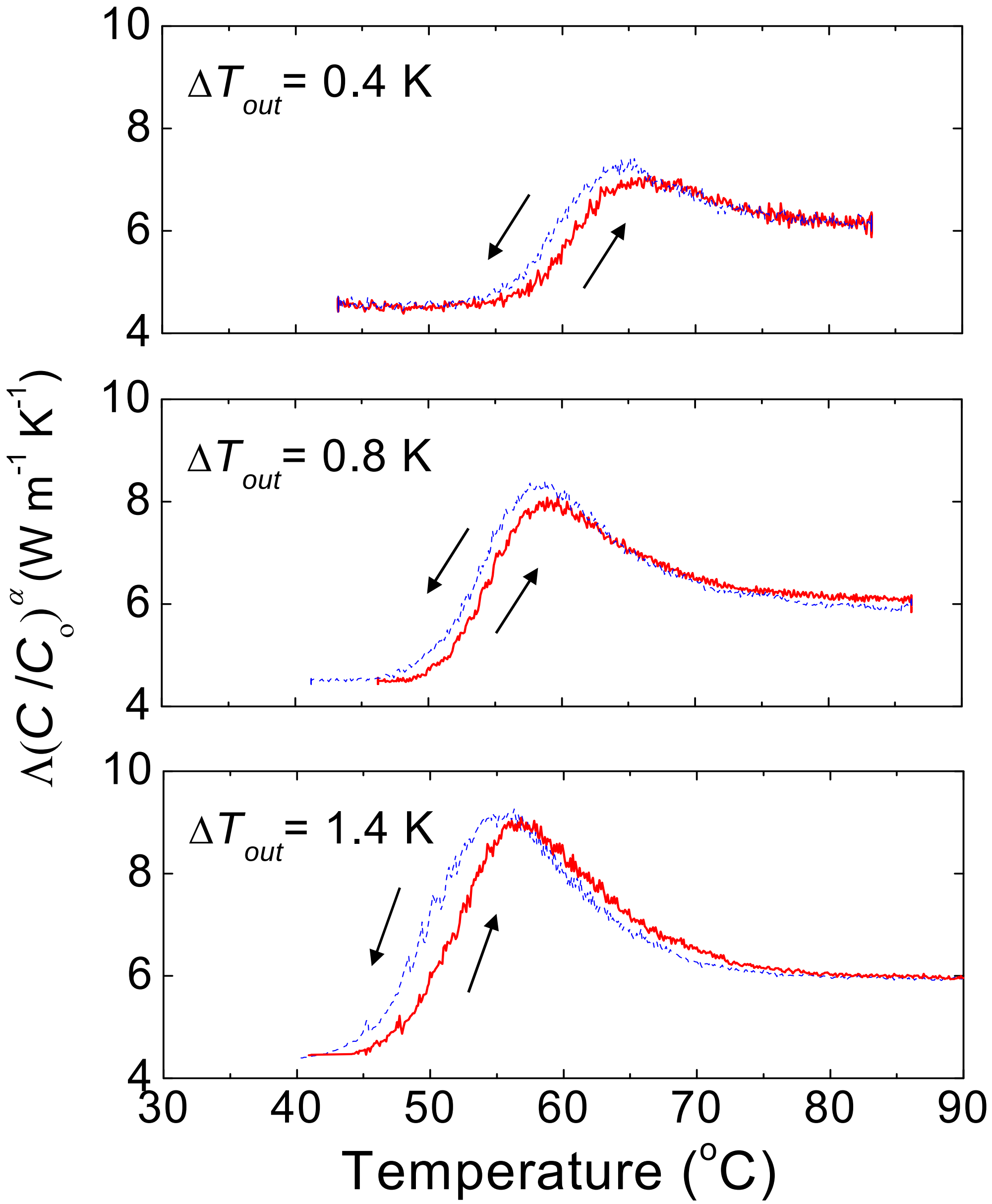


- reflectivity of a metal depends on temperature
- one free parameter: the “effective” thermal conductivity of the thermally grown SiO_2 layer (interfaces not modeled separately)

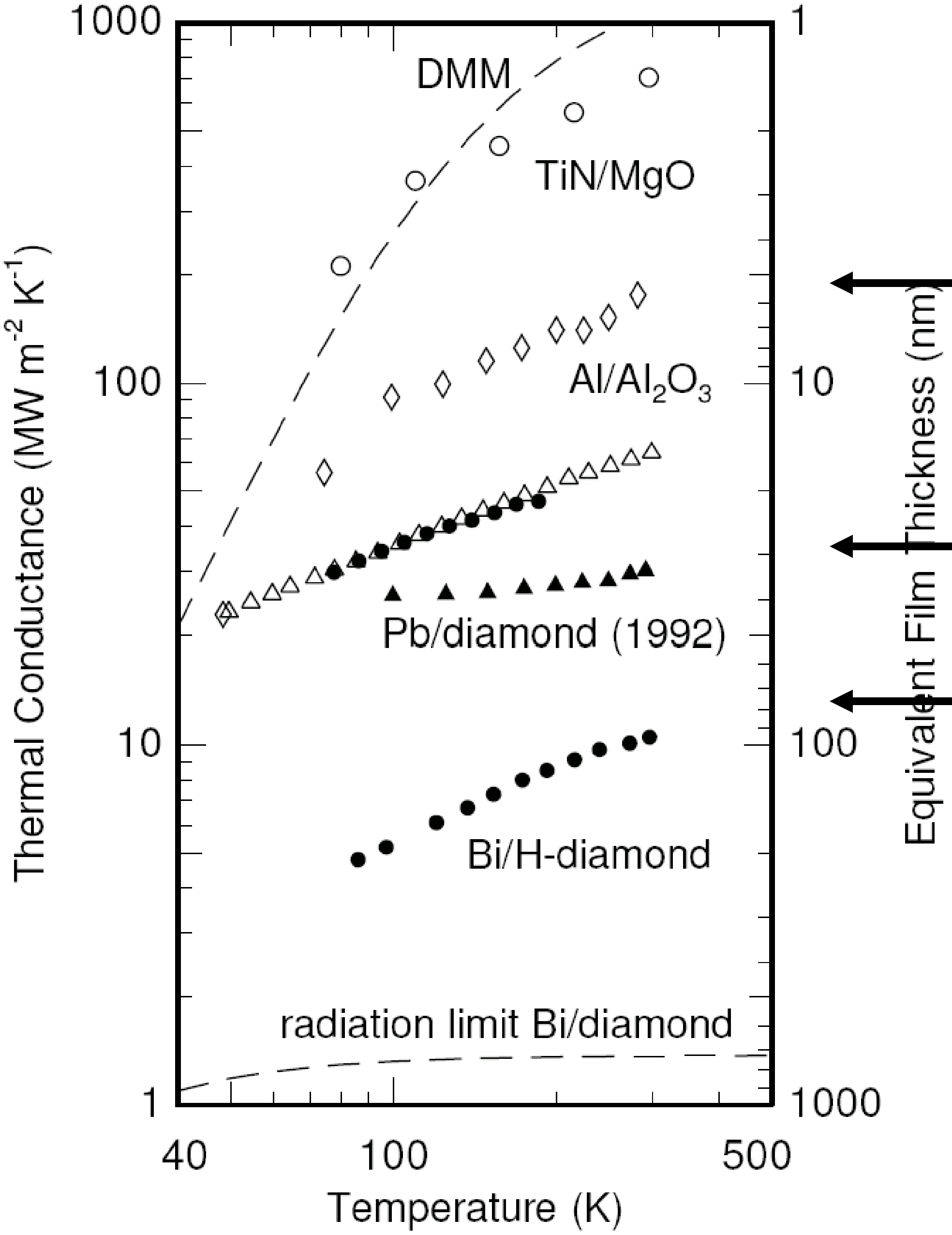
Our first steps in a search for a solid-state heat switch…

Epitaxial VO_2/sapphire

- Large temperature oscillations activate latent heat contributions to the heat capacity
- Contrast in thermal conductivity is only 50%. Need larger contrast between "off" and "on"



Interface thermal conductance: Factor of 60 range at room temperature



← W/Al_2O_3

Au/water

← $PMMA/Al_2O_3$

← nanotube/alkane

$L = \Lambda/G$

$\Lambda = 1\ W\ m^{-1}\ K^{-1}$

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

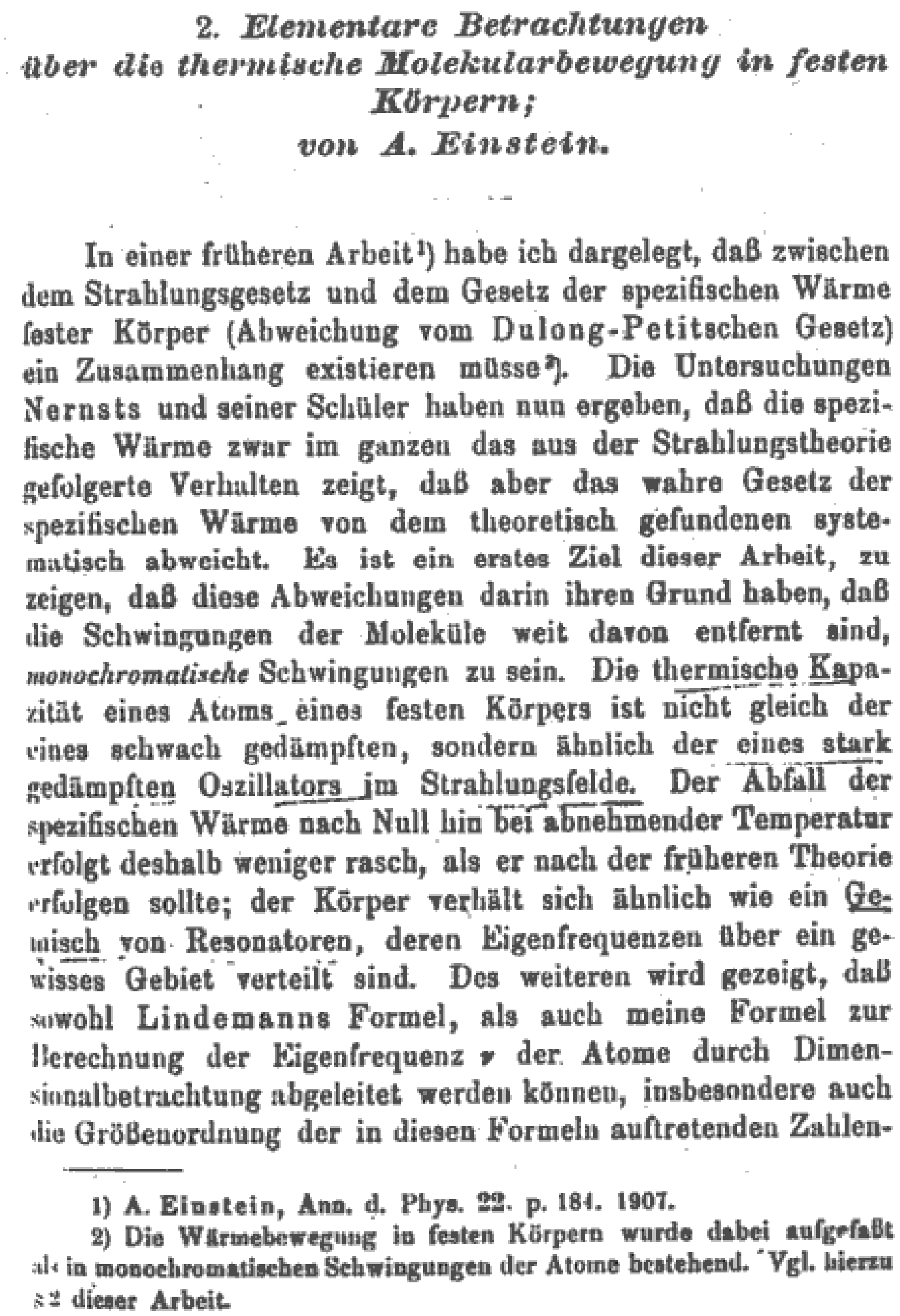
- Einstein (1911): random walk of thermal energy
- Not good for crystals: Debye (1914)
- but does work for amorphous solids, Birch and Clark (1940); Kittel (1948)
- and crystals with strong atomic-scale disorder, Slack (1979); Cahill and Pohl (1988).

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 Arbeit1) habe ich dargelegt, daß zwischen dem Strahlungsgesetz und dem Gesetz der spezifischen Wärme fester Körper (Abweichung vom Dulong-Petitschen Gesetz) ein Zusammenhang existieren müsse2). 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-

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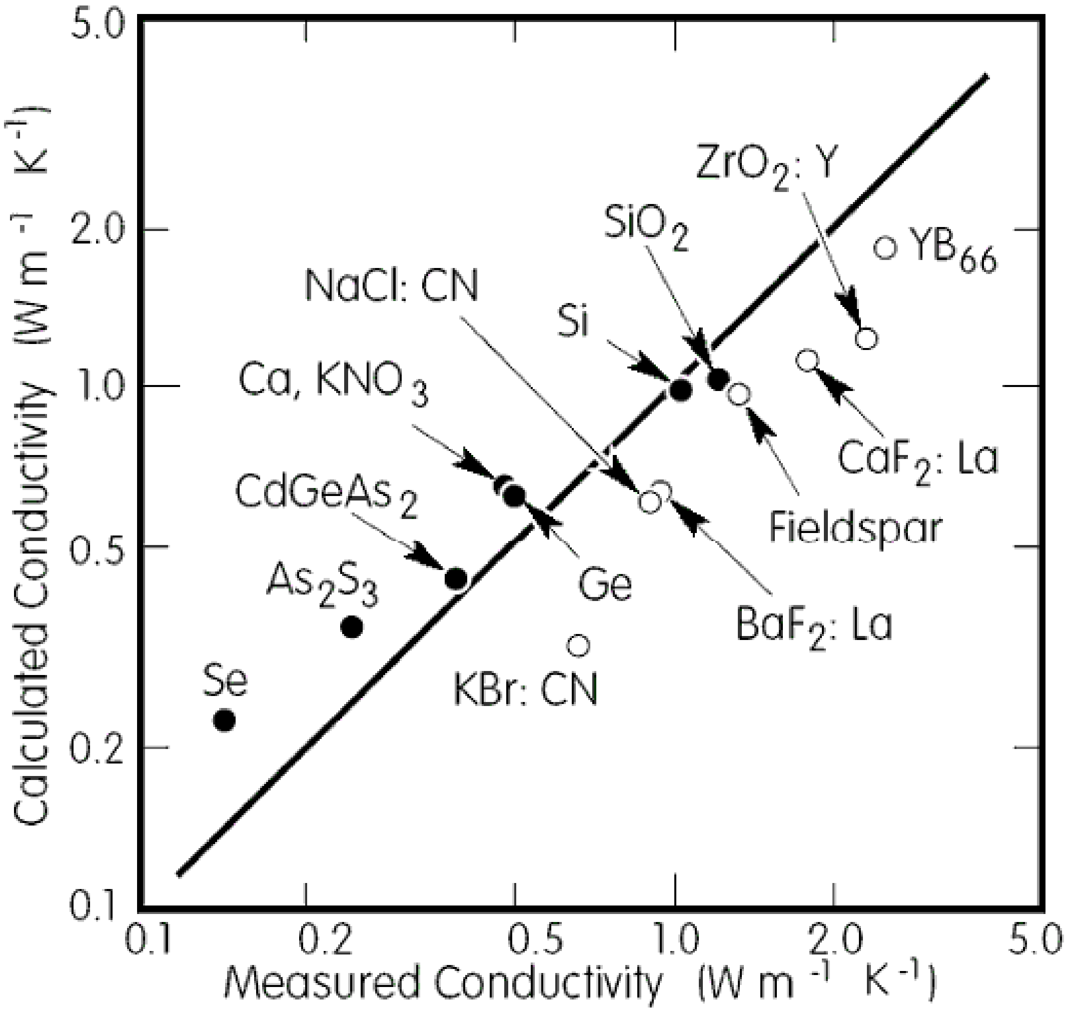
1) A. Einstein, Ann. d. Phys. 22. p. 184. 1907.

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

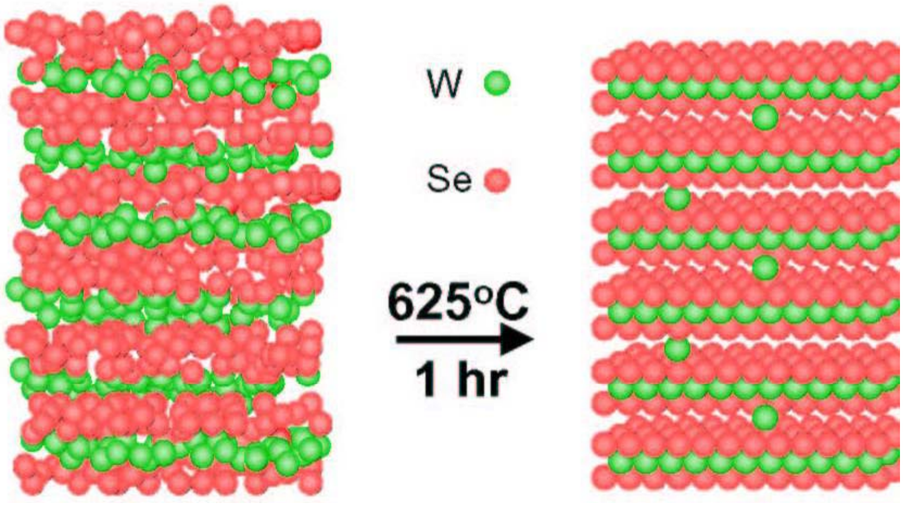
Works well for homogeneous disordered materials

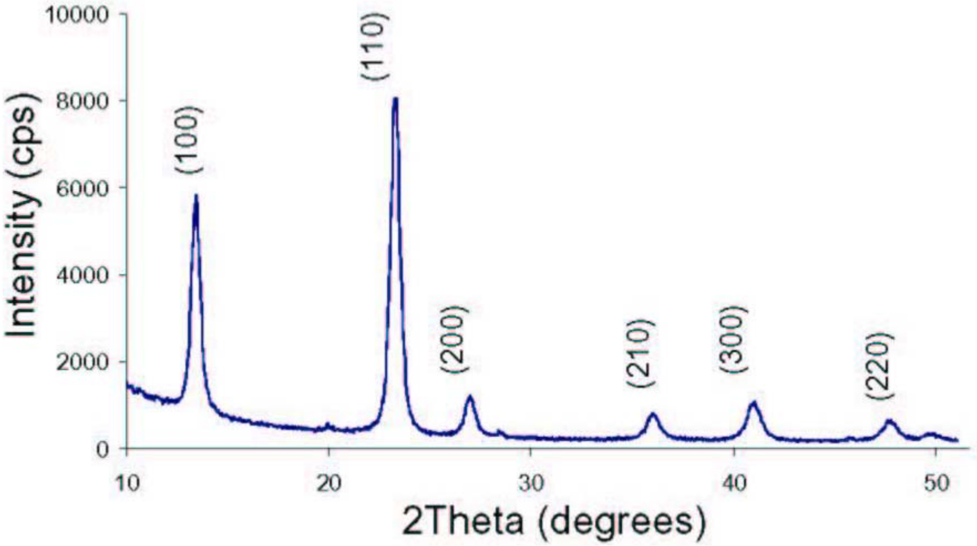


- ● amorphous
- ○ disordered crystal

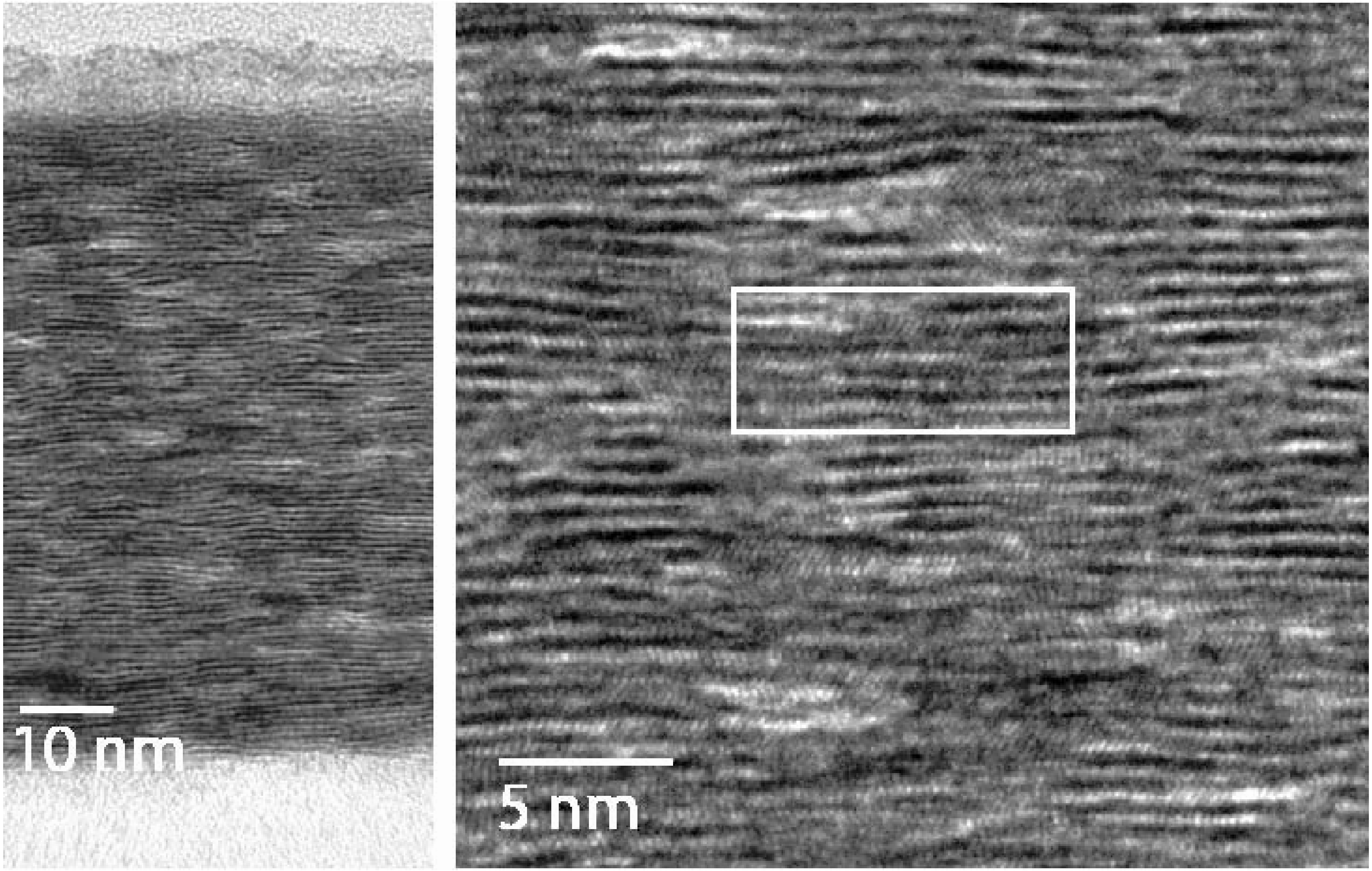
Layered disordered crystals: WSe_2 by "modulated elemental reactants"

- 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





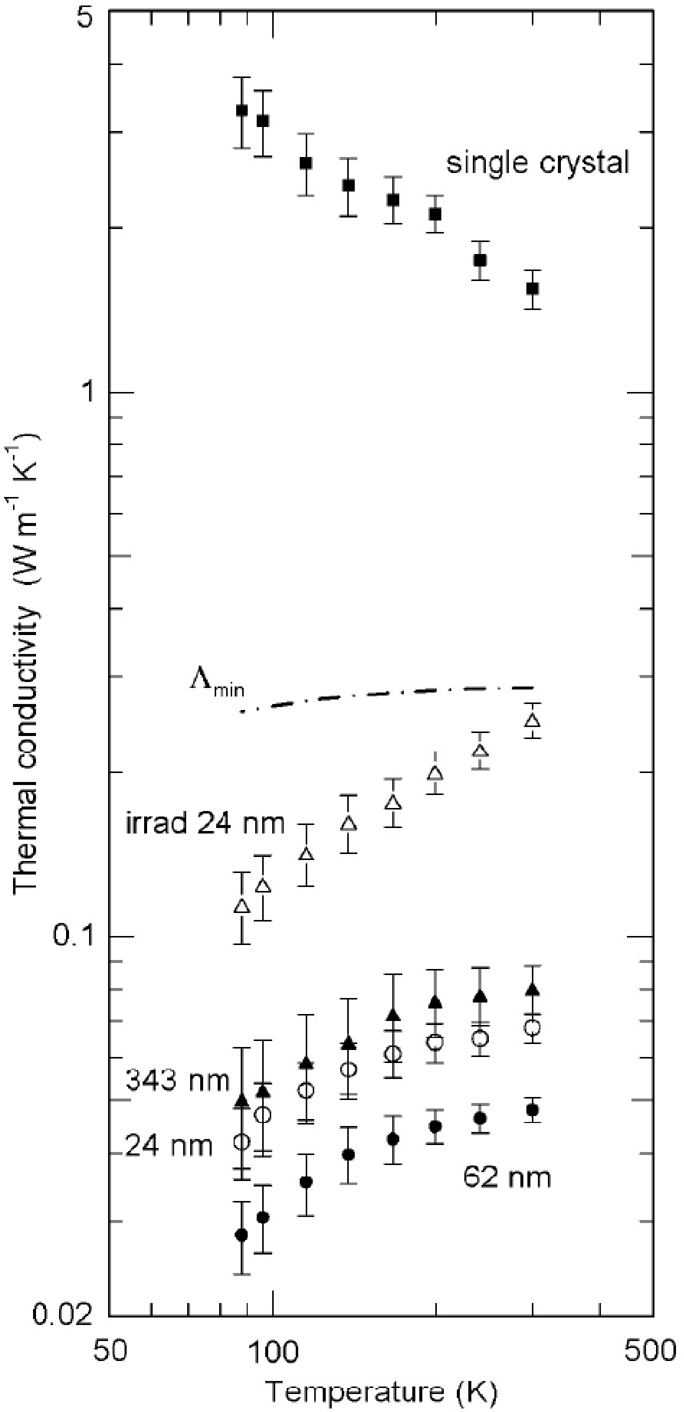
Cross-sectional TEM of 60 nm thick WSe_2



Seongwon Kim and Jian Min Zuo

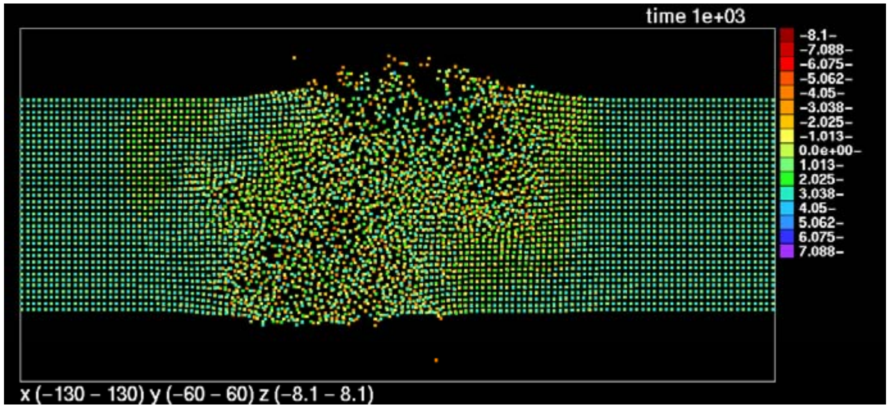
Thermal conductivity of WSe_2

- 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.

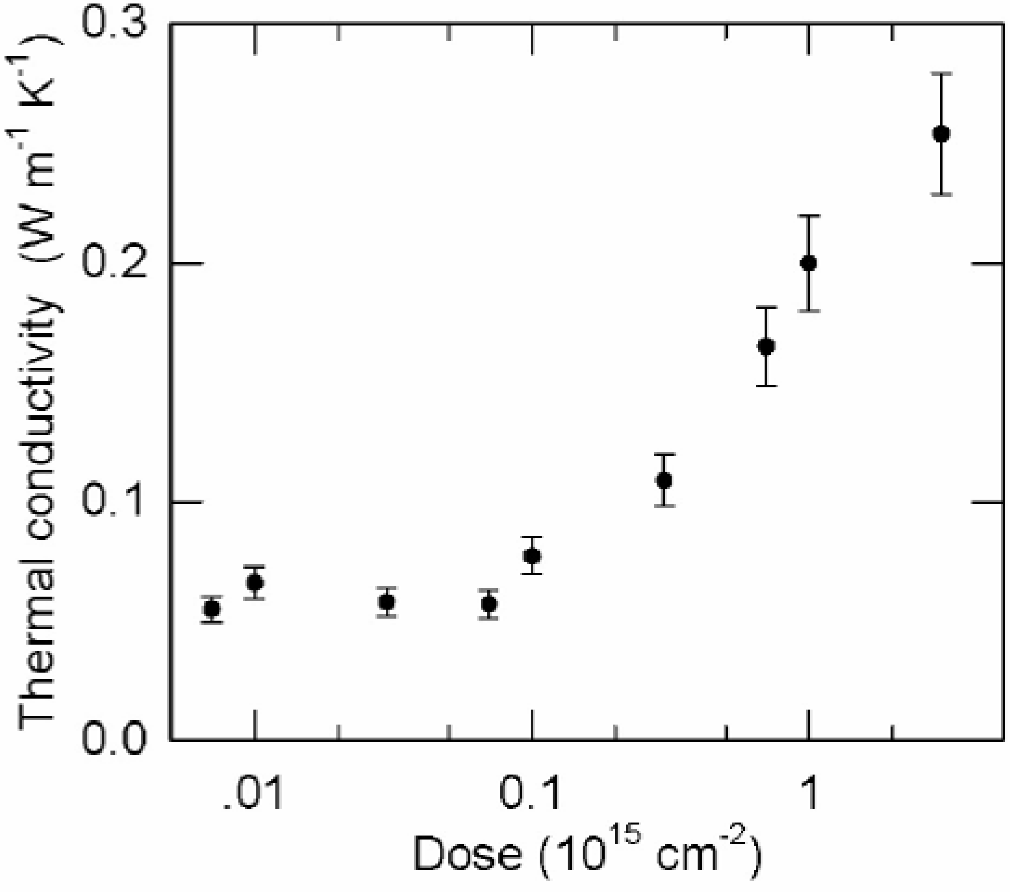


Ion irradiation of WSe_2

MD simulation of 1 MeV Kr impact on Au

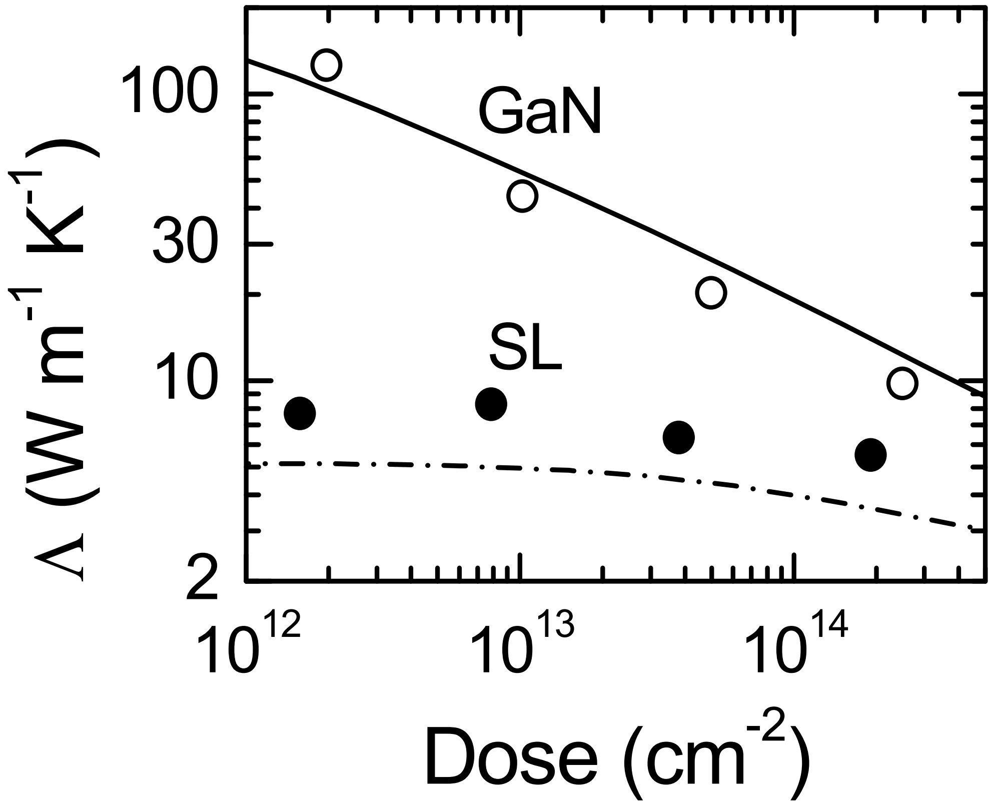


- Heavy ion irradiation (1 MeV Kr^+) of 24 nm WSe_2 film.
- Novel behavior: ion damage causes the thermal conductivity to *increase.*



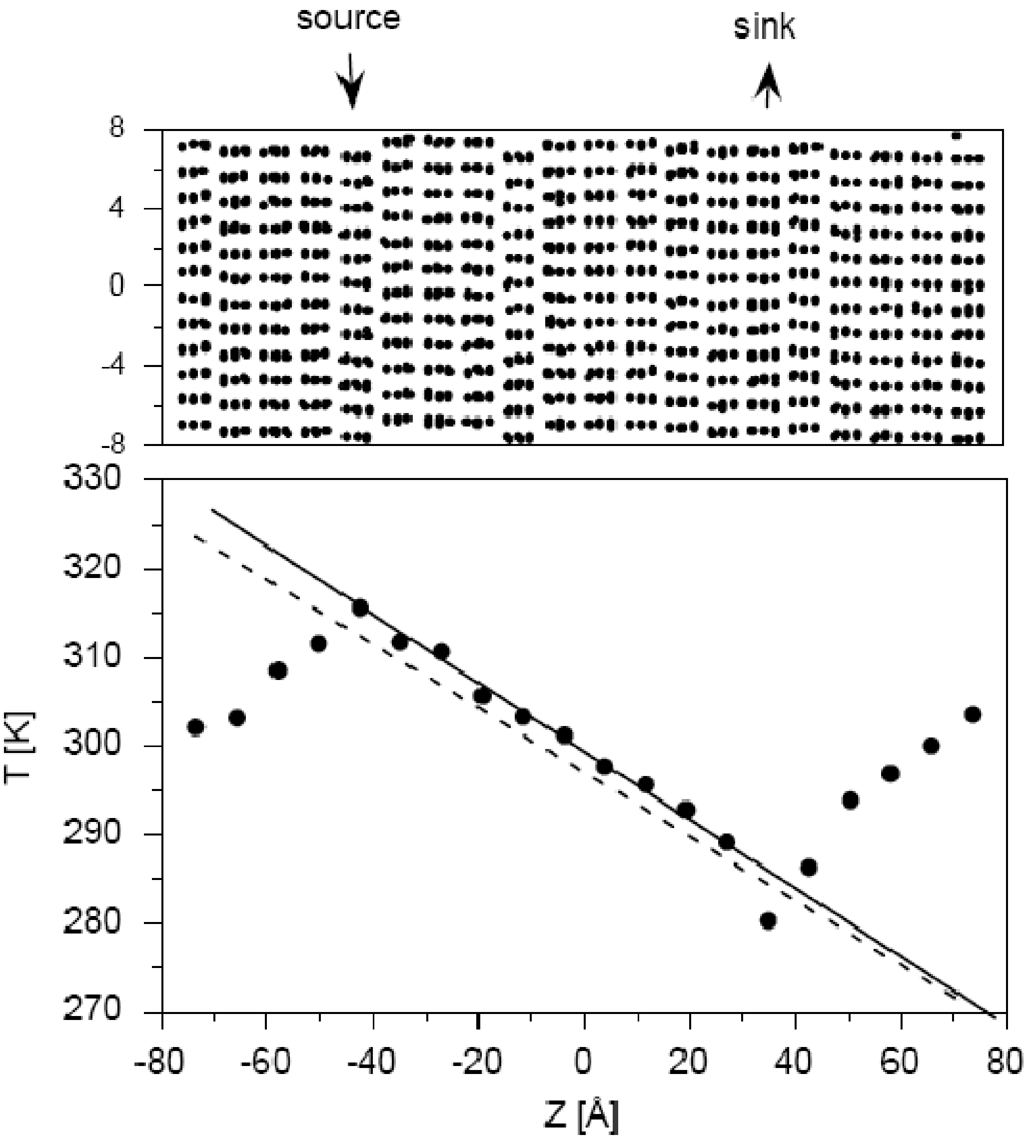
Digression: ion bombardment of a superlattice (with Y. Cao and D. Jena)

- 2.3 MeV Ar ion irradiation of GaN and $(AlN)_{4\ nm}$-$(GaN)_{5\ nm}$
- Lines are Debye-Callaway models assuming phonon Rayleigh scattering scales linearly with ion dose.
- Fit gives $\Gamma = 1$ at an ion dose of 10^{14} cm^{-2}



Molecular dynamics simulation

- MD work by Bodapati and Keblinski (RPI)
- Original LJ model of WSe$_2$ gives 0.06 W/m-K independent of length-scale
- Conclusion: physics is general, not specific to some detail of the WSe$_2$ bonding or microstructure

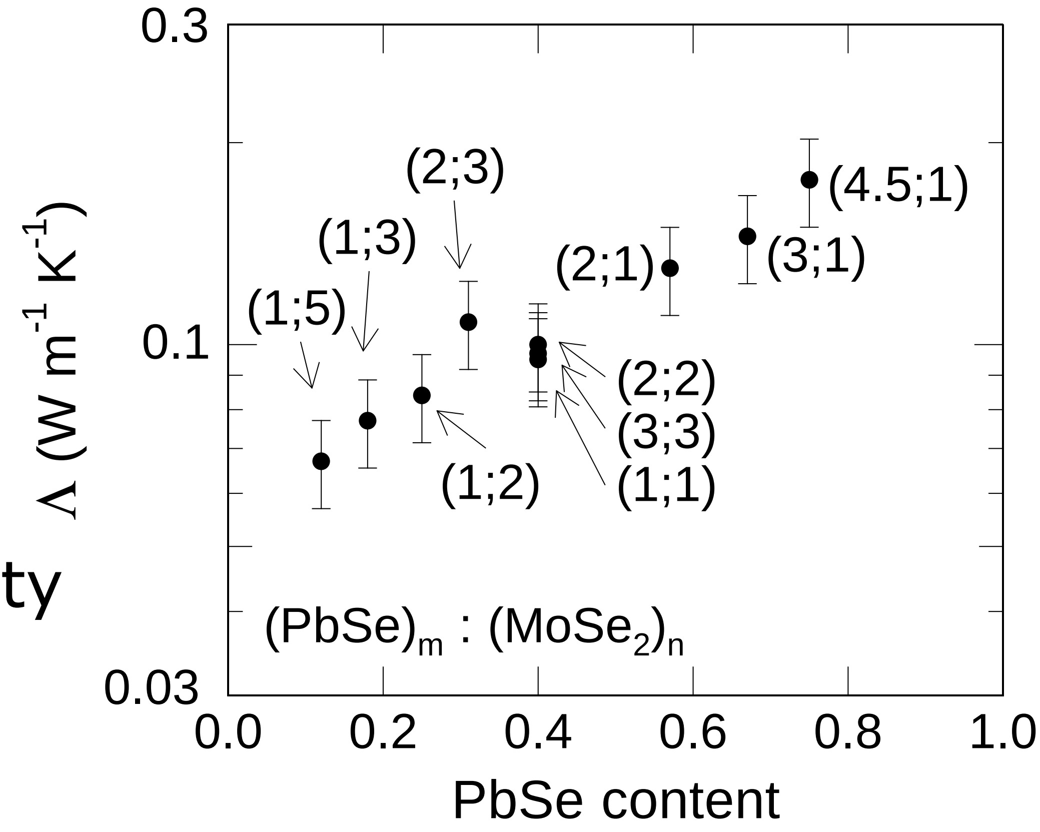


Conclusions from theoretical work (Hu and Keblinski, unpublished)

- Analysis of the participation ratio: phonon localization is not significant.
- Analysis of mode polarization: incoherent grain boundaries create diffusive but non-propagating vibrational modes. (stacking faults are not sufficient)
- Key to ultralow thermal conductivity is disorder in combination with anisotropy, i.e., an "anisotropic glass".
- Interface resistance between 2D crystalline sheets? Lowering of the effective density of states for modes diffusing perpendicular to the sheets?

Back to experiment: Can we lower the conductivity even further?

- Synthesize misfit layered compounds by elemental reactants method (Johnson and co-workers)
  - WSe_2/PbSe
  - $MoSe_2$/PbSe
- Interface density does not matter. Conductivity determined by composition not interface density.



Summary (to this point) and questions

- Incredibly low thermal conductivity (far below the amorphous limit) in the disordered, layered crystal WSe_2.
  - Combination of disorder (random stacking of sheets) and anisotropy (large differences in vibrations within and across the sheets) appears to be the key.
  - How far can we push this using other types of interfaces?
  - Can we reproduce this physics in materials with good electrical conductivity for thermoelectric energy conversion?
  - Can we reproduce this physics in refractory oxides for thermal barriers?

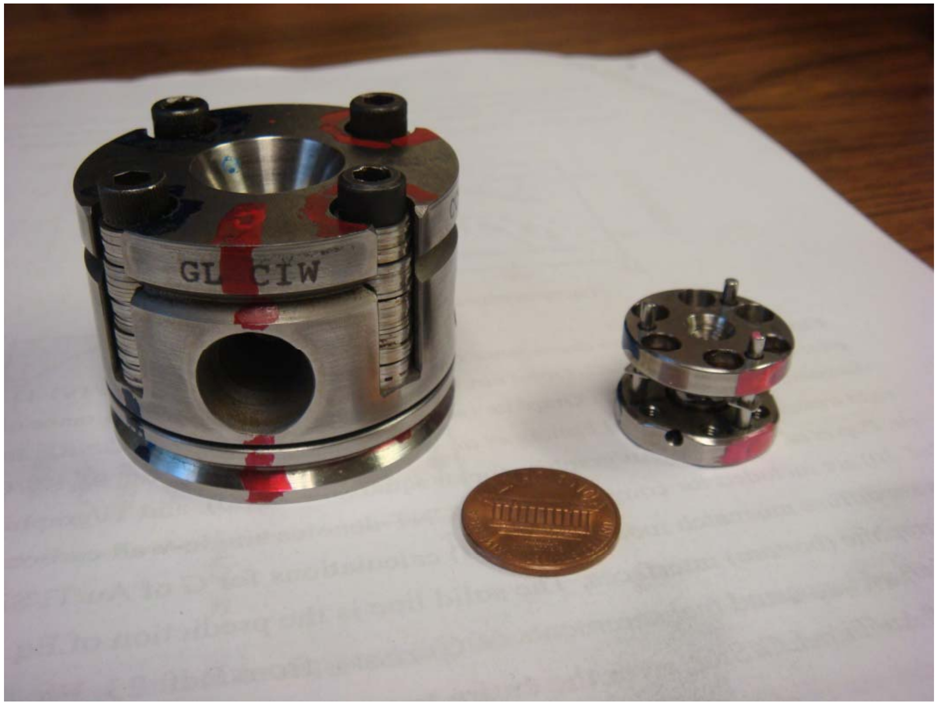
I. Is anisotropy a key factor?

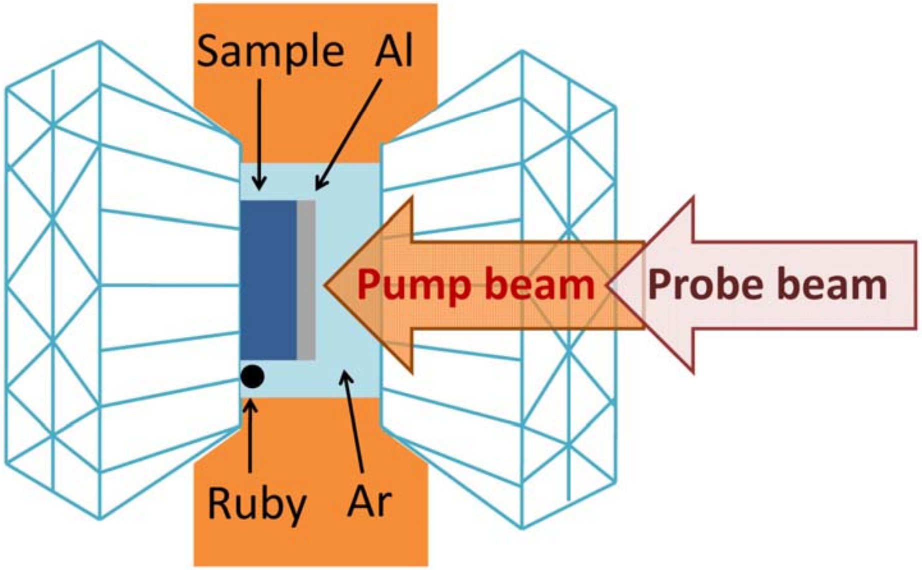
- Use “pressure tuning” to modify anisotropy
  - Mica as demonstration (not disordered)
- Low thermal conductivity in Dion Jacobson layered oxide
  - 60% of minimum thermal conductivity,
  - suppression is consistent with anisotropy but source of disorder is unknown at this time

Use pressure as a variable

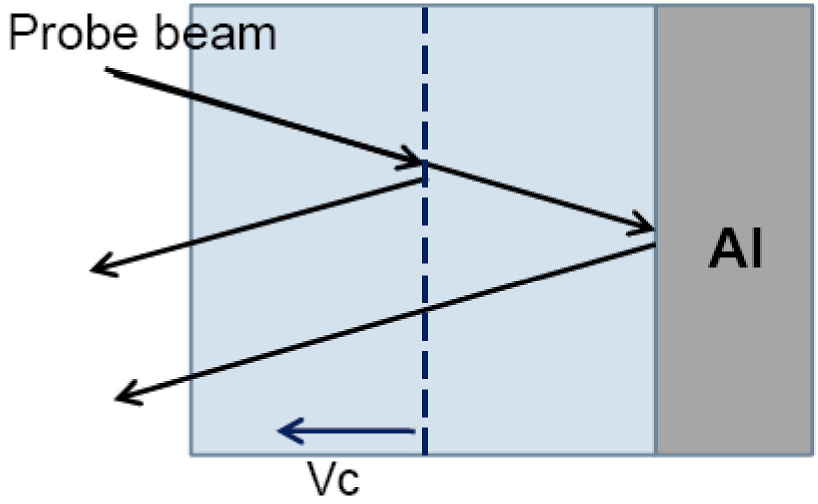
- Muscovite mica is a layered (but not disordered) crystal
- Elastic anisotropy is a factor 3; thermal conductivity anisotropy is a factor of 8

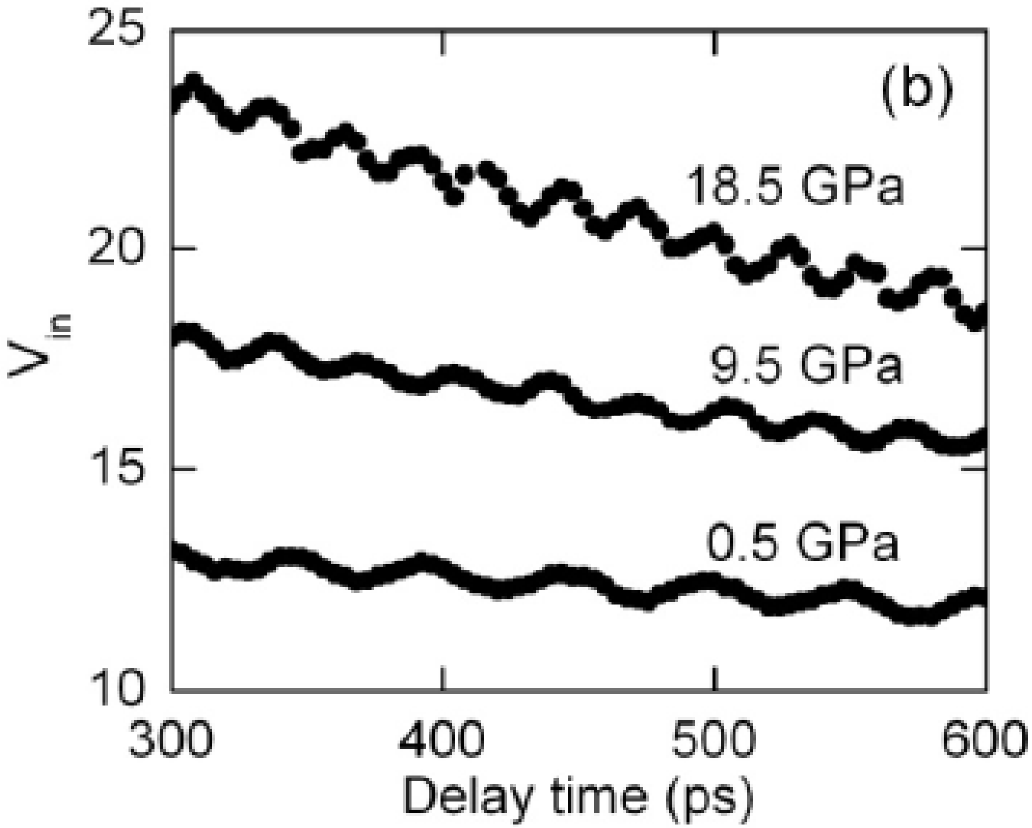
Diamond anvil cell





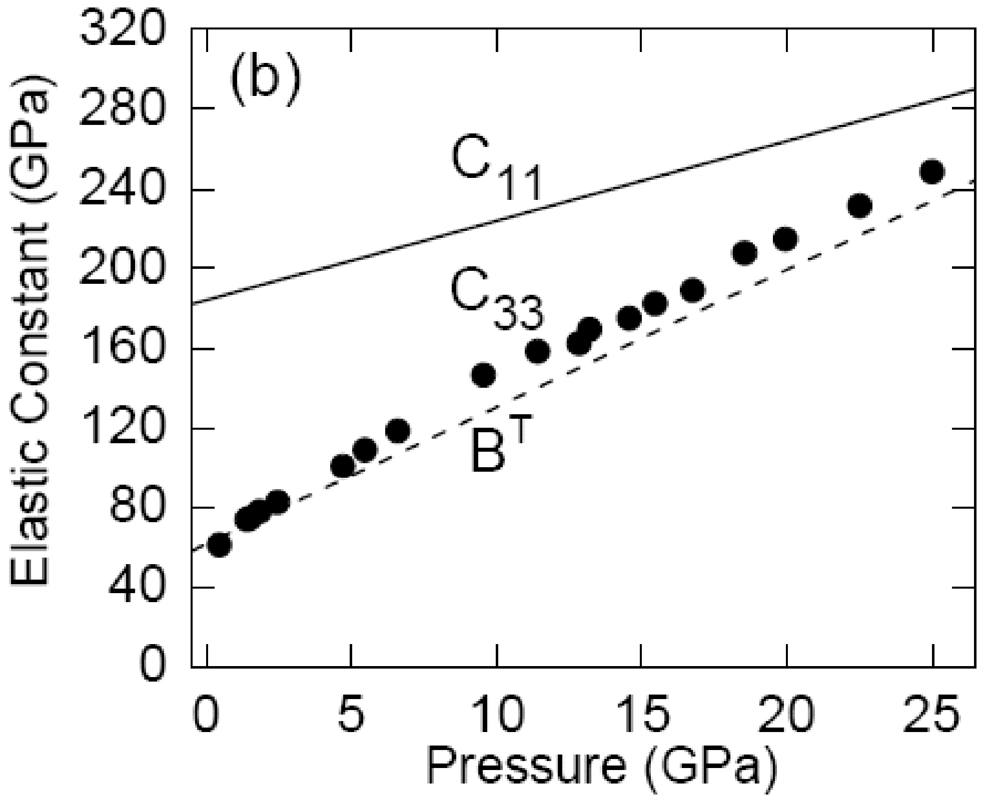
Time-domain stimulated Brillouin scattering (picosecond interferometry)





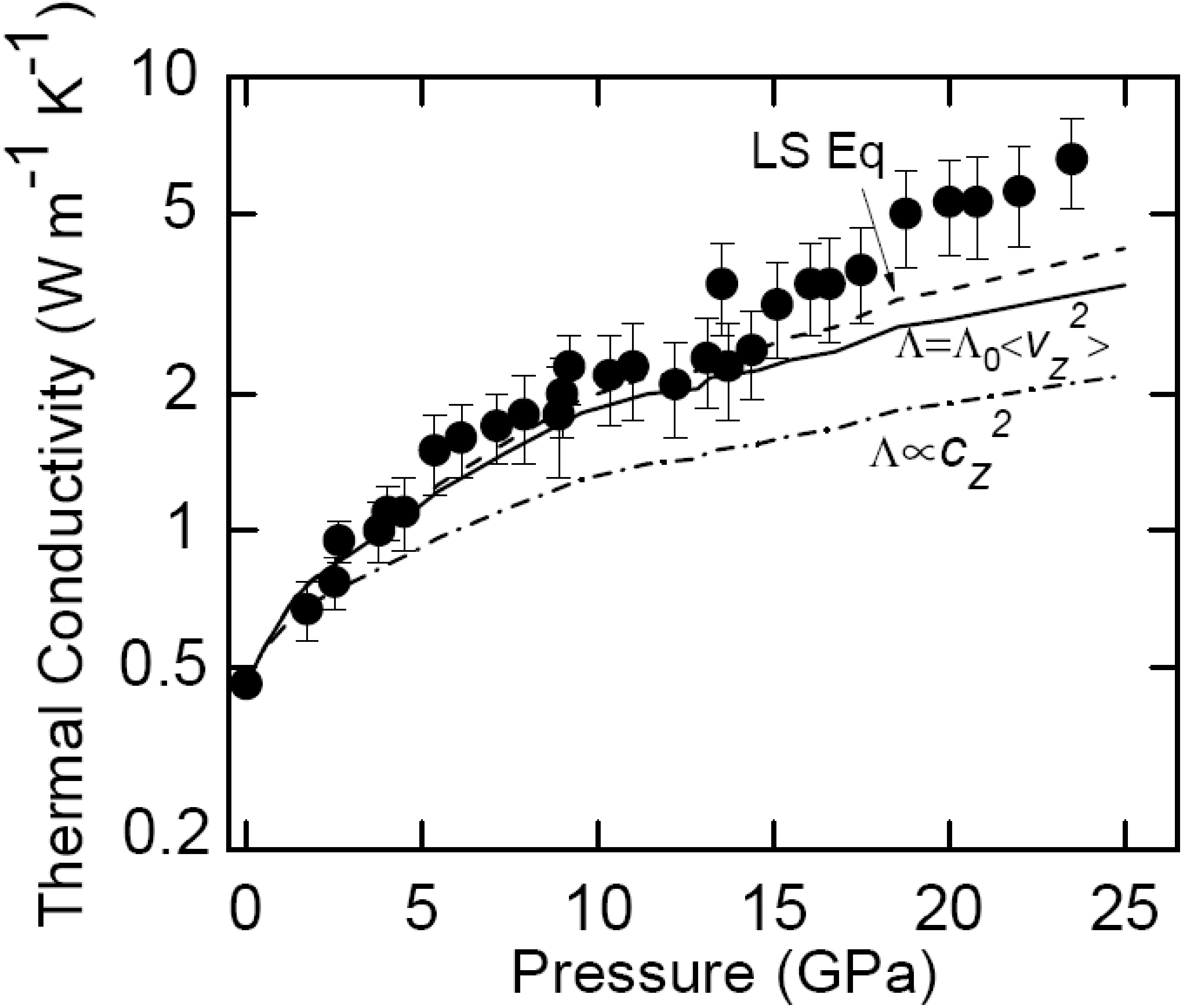
Pressure tuning of elastic anisotropy

- Cross-plane elastic constants are more anharmonic and stiffen more rapidly with pressure
- C_{33} (cross-plane) measured by picosecond interferometry (time domain Brillouin scattering); Gruenisen constant is $\gamma \approx 4$.



Hsieh, Chen, Li, Cahill, Keblinski, PRB (2009)

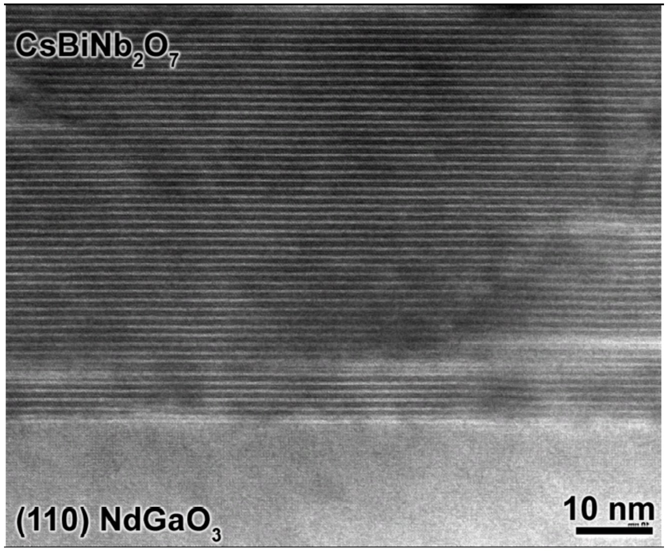
Pressure tuning of thermal conductivity of mica



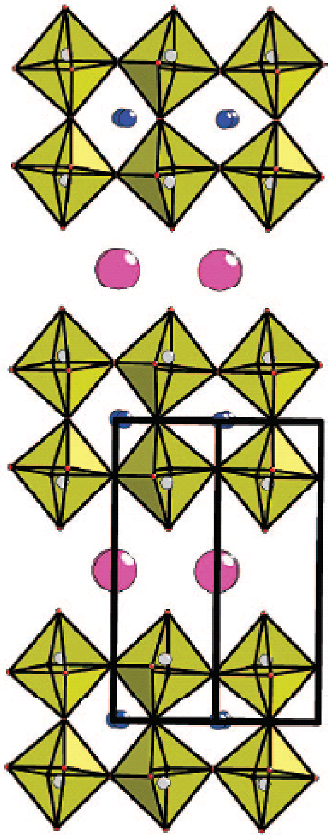
Hsieh, Chen, Li, Cahill, Keblinski, PRB (200

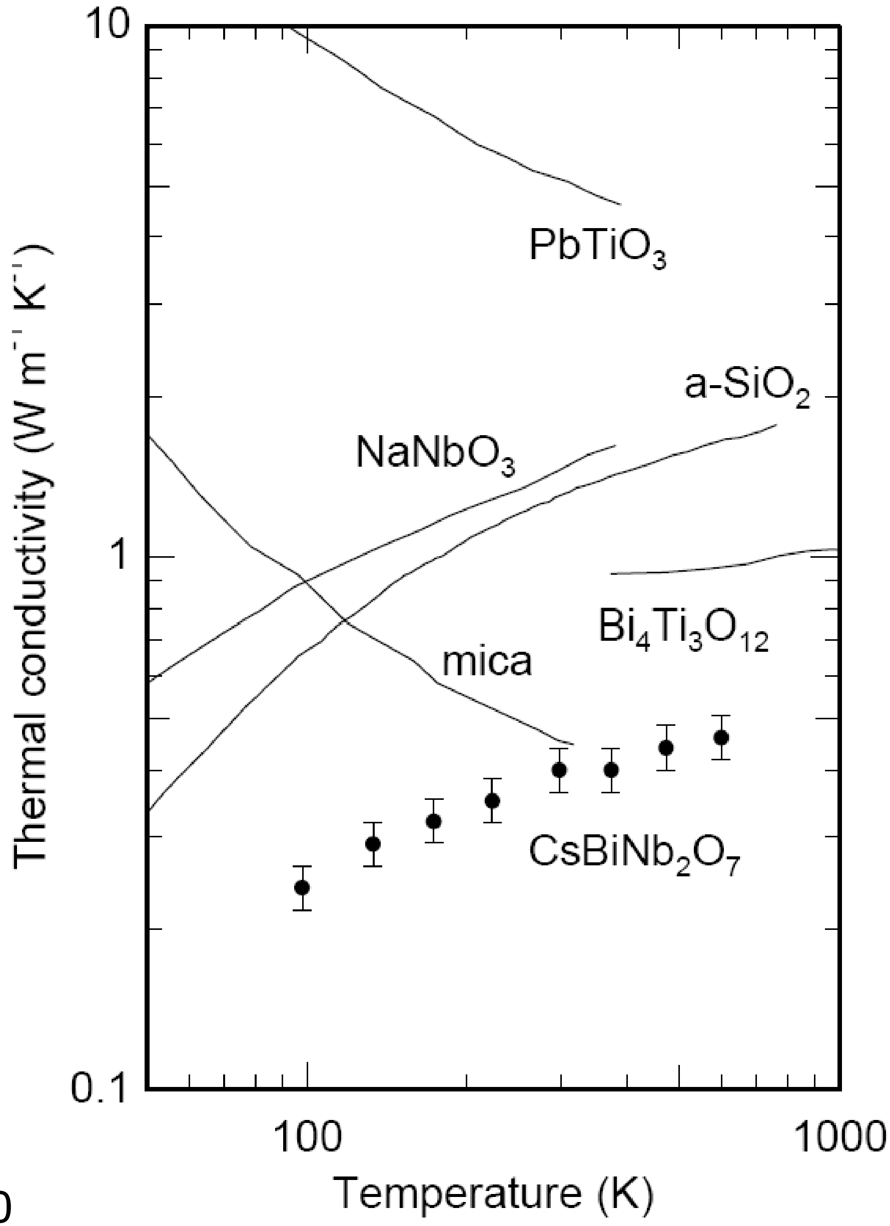
Low thermal conductivity in a layered oxide

70 nm film grown by pulsed laser deposition



$CsBiNb_2O_7$





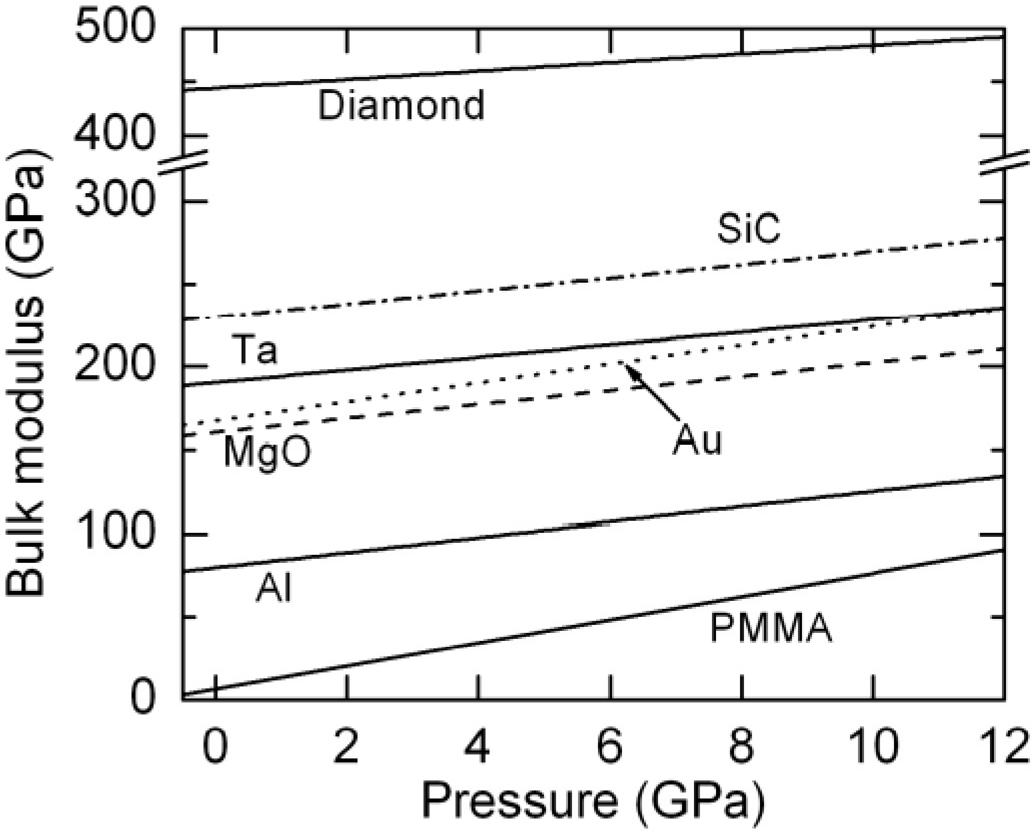
Cahill, Melville, Schlom, Zurbuchen, APL 2010

II. What can pressure dependence tell us about thermal conductance of interfaces?

- "Classical" models (DMM, AMM) for interface thermal conductance do not include physics of the interface itself: phonon transport is only a function of the properties of the two solids.

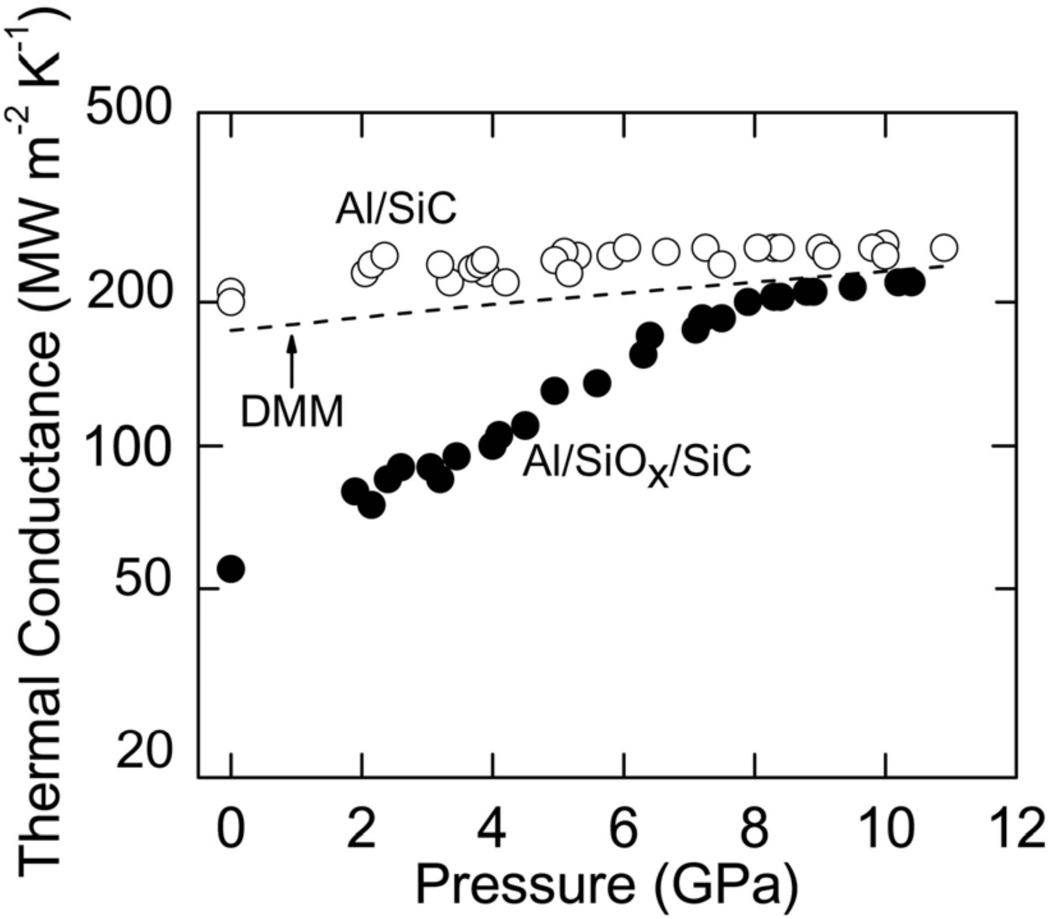
- Elastic constants and phonon spectrum of typical materials do not change much between 0 and 10 GPa.

- But interface bonding might be weak and highly anharmonic



II. What can pressure dependence tell us about thermal conductance of interfaces?

- Work in progress.
  a) Al deposited on native oxide of SiC
  b) Al deposited *in-situ* on SiC cleaned in high vacuum at 1000°C



Big picture summary

- Powerful experimental tools for probing “nanoscale thermal transport”
  - Measuring thermal conductivity of novel, thin layer materials, is no longer (in most cases) a reseach project in itself; can focus on the materials and the physics.
- Conventional wisdom about the lower limit of the thermal conductivity of dense (non-porous) solids is not correct.
  - Compelling “race to the bottom” to find even lower conductivity solids
- Pressure dependence is providing a new “knob” to turn for experiments on heat transport at the nanoscale