

Pushing the boundaries of the thermal conductivity of materials

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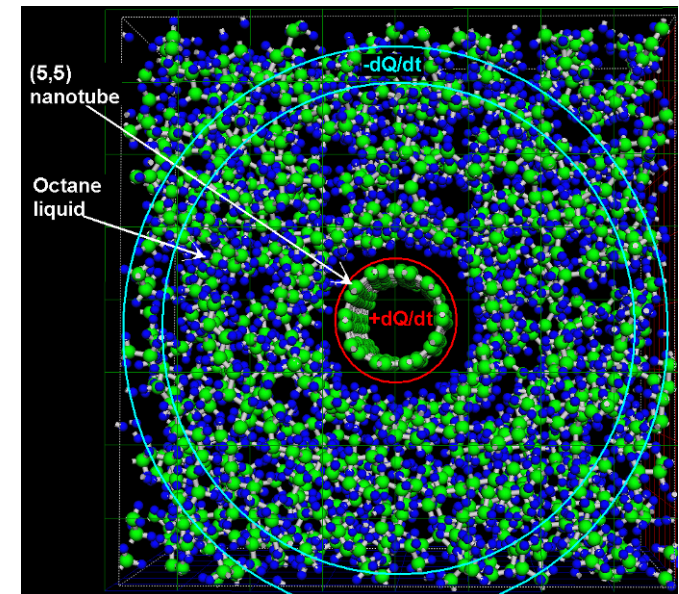
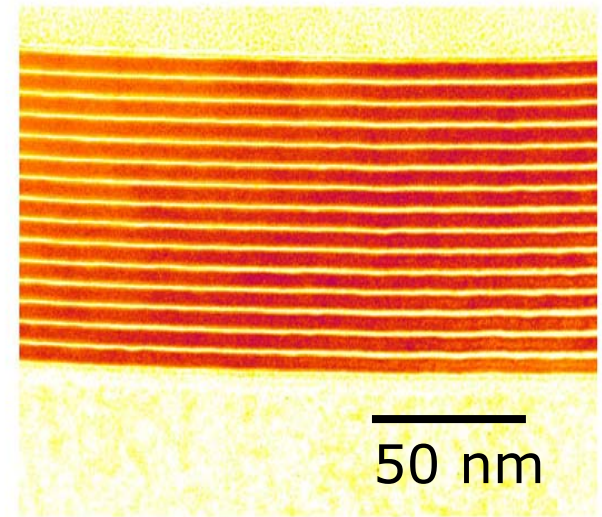
Outline

- 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 nanolaminates and disordered layered crystals.

Interfaces are critical at the nanoscale

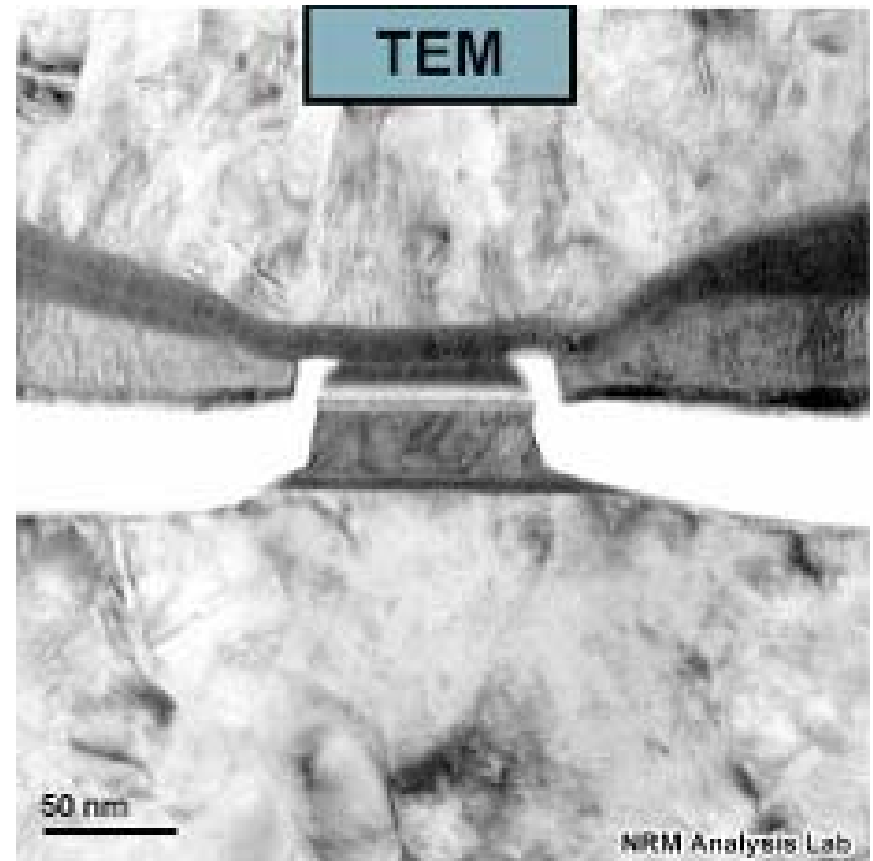
- Low thermal conductivity in nanostructured materials
 - improved thermoelectric energy conversion
 - improved thermal barriers

- High thermal conductivity composites and suspensions



Interfaces are critical at the nanoscale

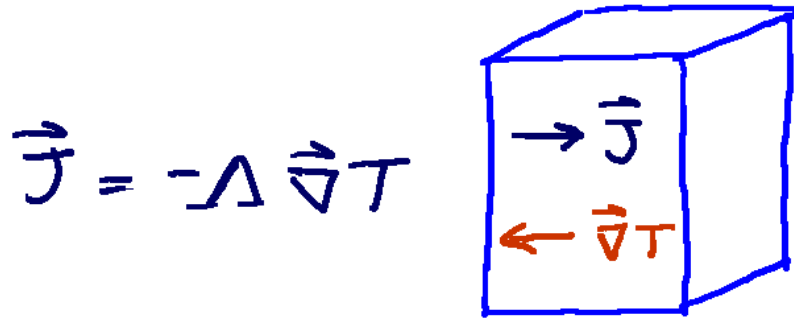
- High power density devices
 - solid state lighting
 - high speed and power electronics
 - nanoscale sensors



Micrograph of tunneling magnetoresistive sensor for 120 GB drives, M. Kautzky (Seagate)

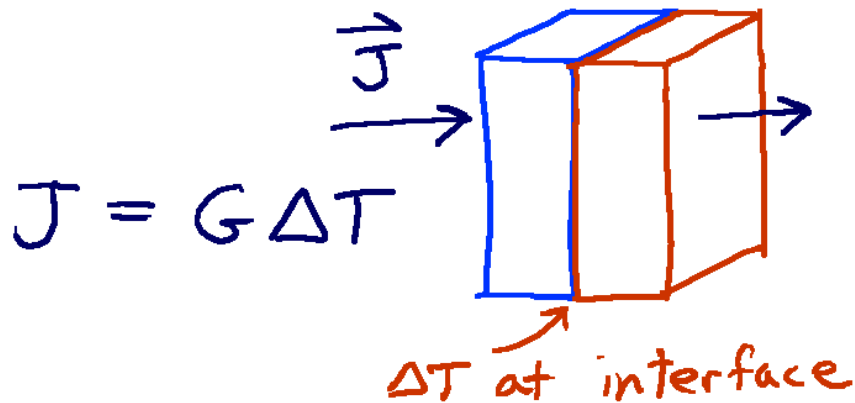
Thermal conductivity and interface thermal conductance

- Thermal conductivity Λ is a property of the continuum



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

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



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

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

Brief introduction to thermoelectric materials

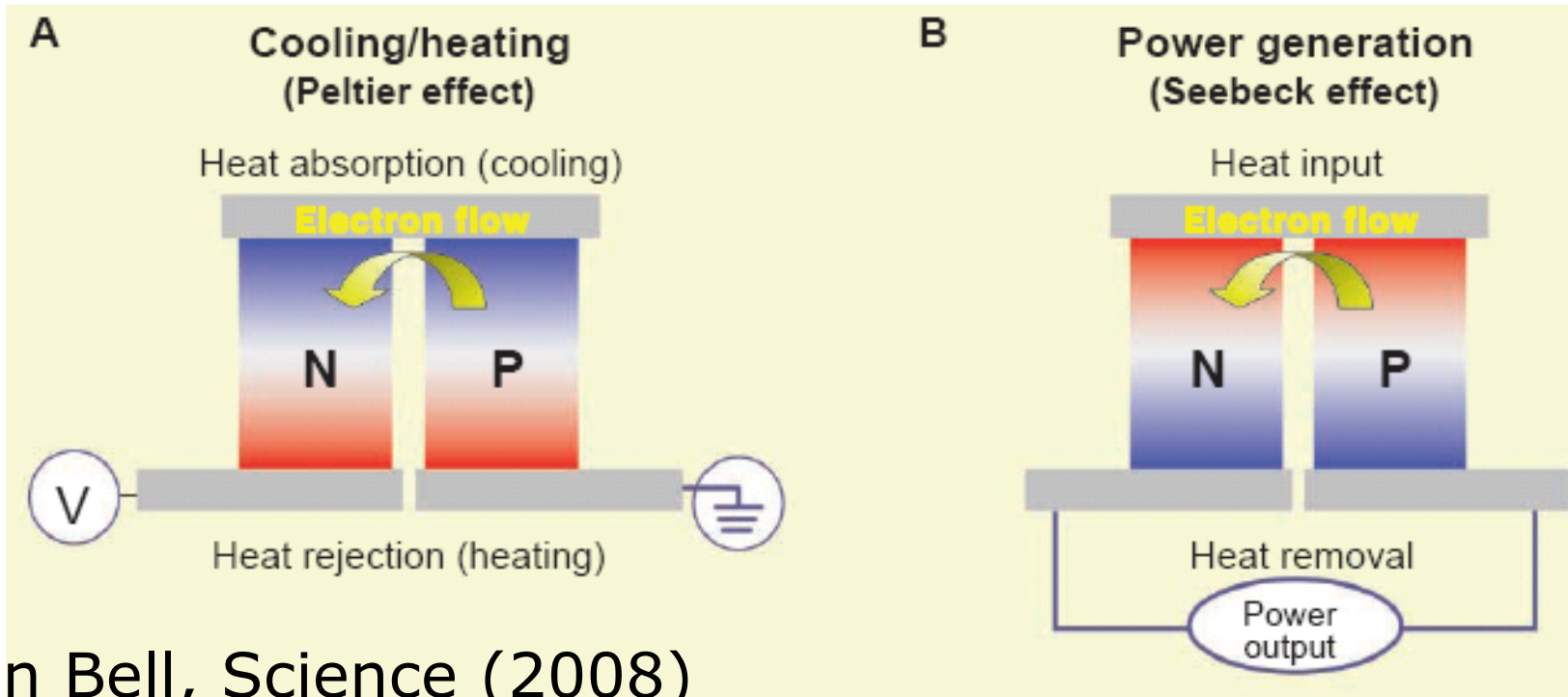
- Solid-state heat pump; thermal efficiency governed by the “figure of merit” ZT

$$ZT = \frac{S^2 \sigma T}{\Lambda}$$

S = Seebeck coefficient

σ = electrical conductivity

Λ = thermal conductivity



Lon Bell, Science (2008)

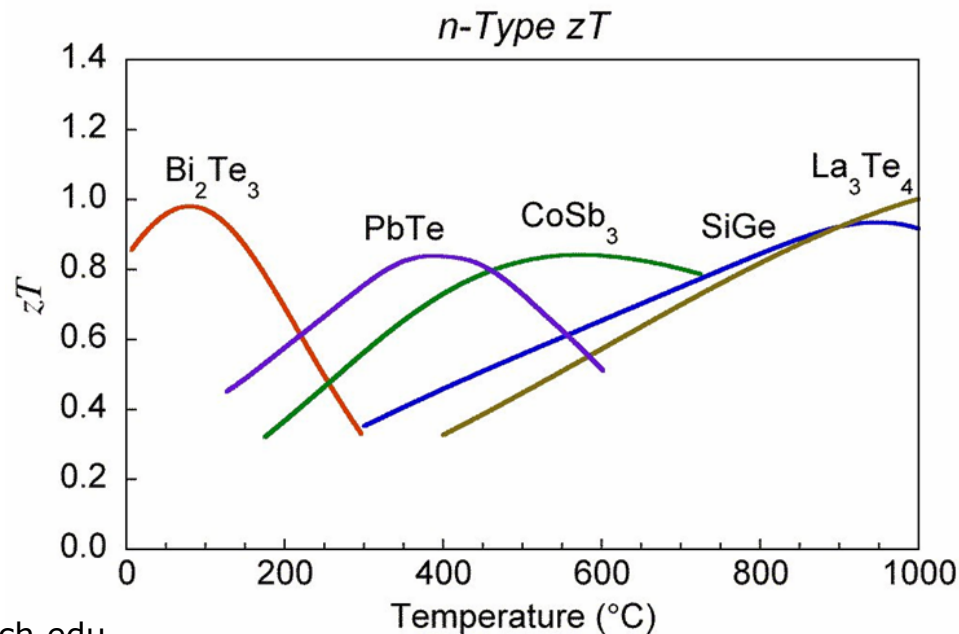
Brief introduction to thermoelectric materials

- ... or write ZT in a more obviously dimensionless form...

$$\Lambda = \Lambda_{\text{lattice}} + \Lambda_{\text{electronic}}$$

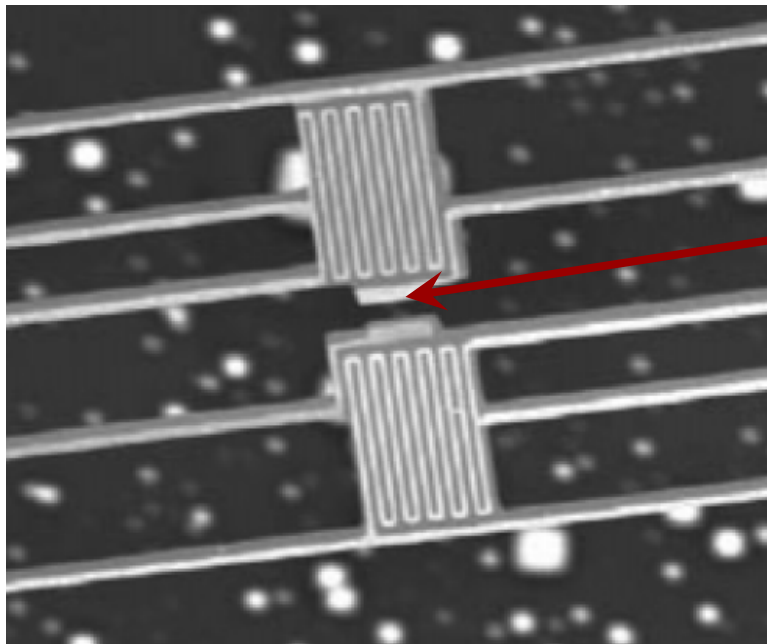
$$\Lambda_{\text{electronic}} = L\sigma T$$

$$ZT = \left(\frac{S^2}{L} \right) \frac{1}{1 + \left(\Lambda_{\text{lattice}} / \Lambda_{\text{electronic}} \right)}$$

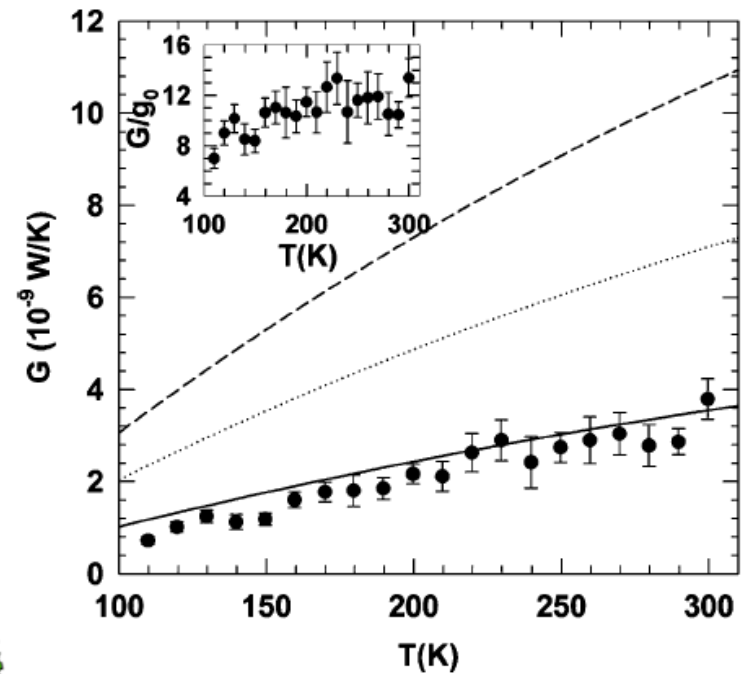
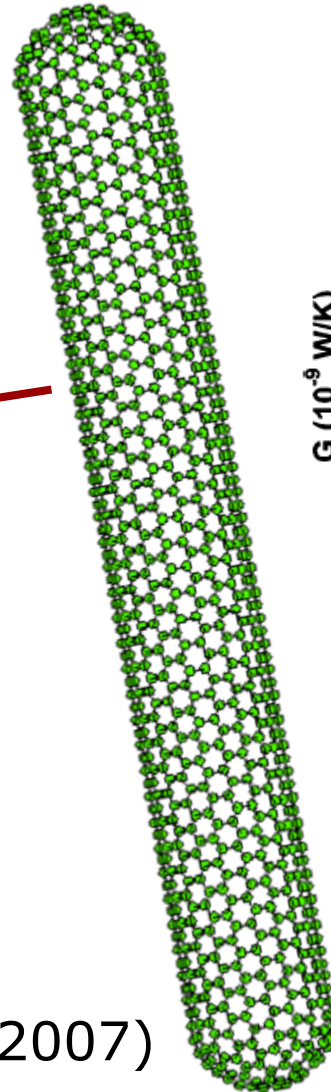


Carbon nanotubes

- Evidence for the highest thermal conductivity any material (higher conductivity than diamond)

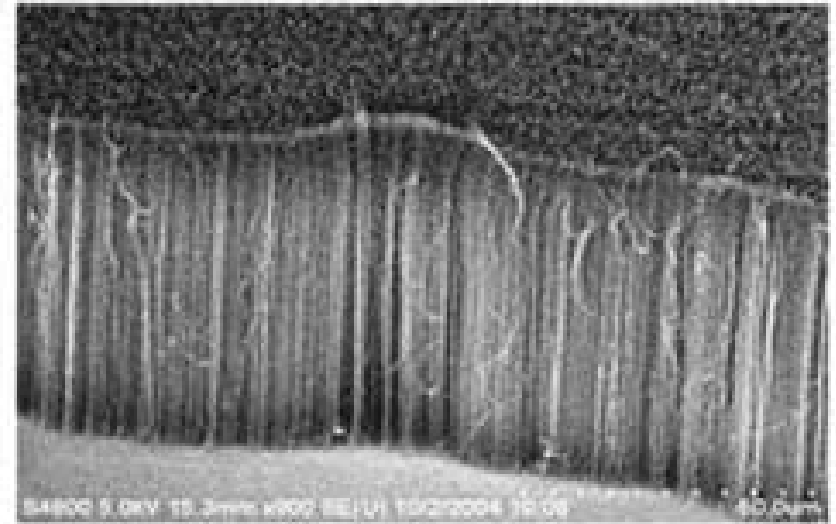


Maruyama (2007)

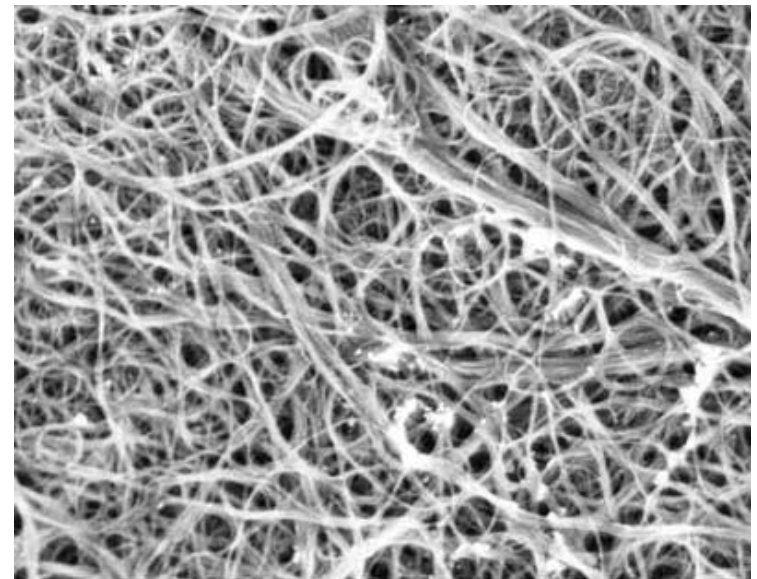


Yu et al. (2005)

- Much work world-wide:
 - thermal interface materials
 - so-called "nanofluids" (suspensions in liquids)
 - polymer composites and coatings



Oriented carbon nanotube array.



Lehman (2005)

Critical aspect ratio of a fiber composite

- Isotropic fiber composite with high conductivity fibers (and infinite interface conductance)

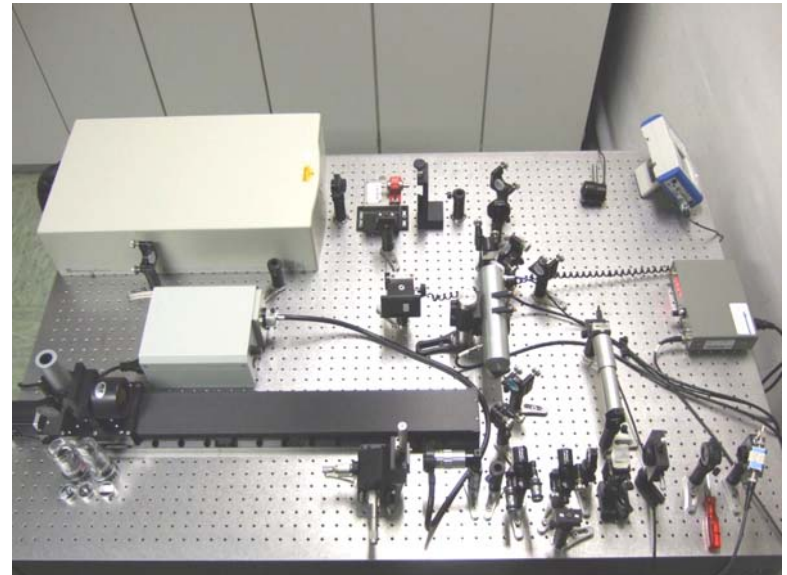
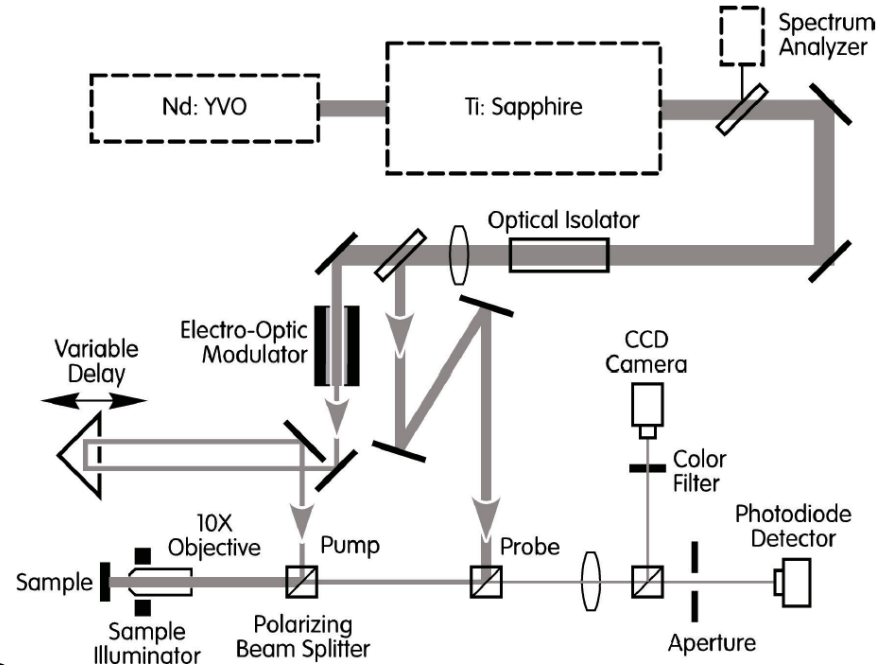
$$\Lambda_c = \frac{1}{3} V_f \Lambda_{NT}$$

- But this conductivity is obtained only if the aspect ratio of the fiber is high

$$3 \left(\frac{\Lambda_{NT}}{rG} \right)^{1/2} \approx 2000$$

Time domain thermoreflectance since 2003

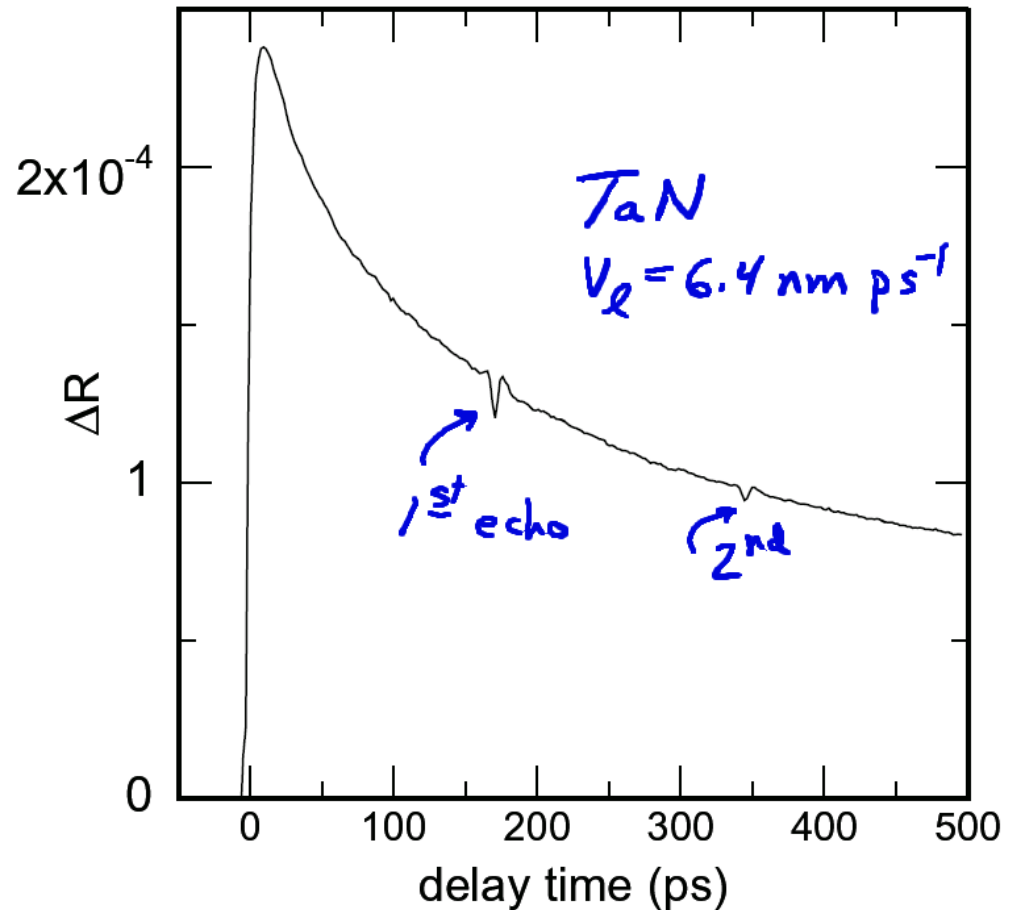
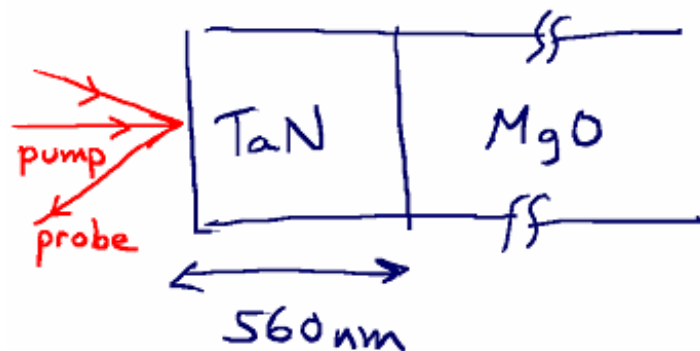
- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering



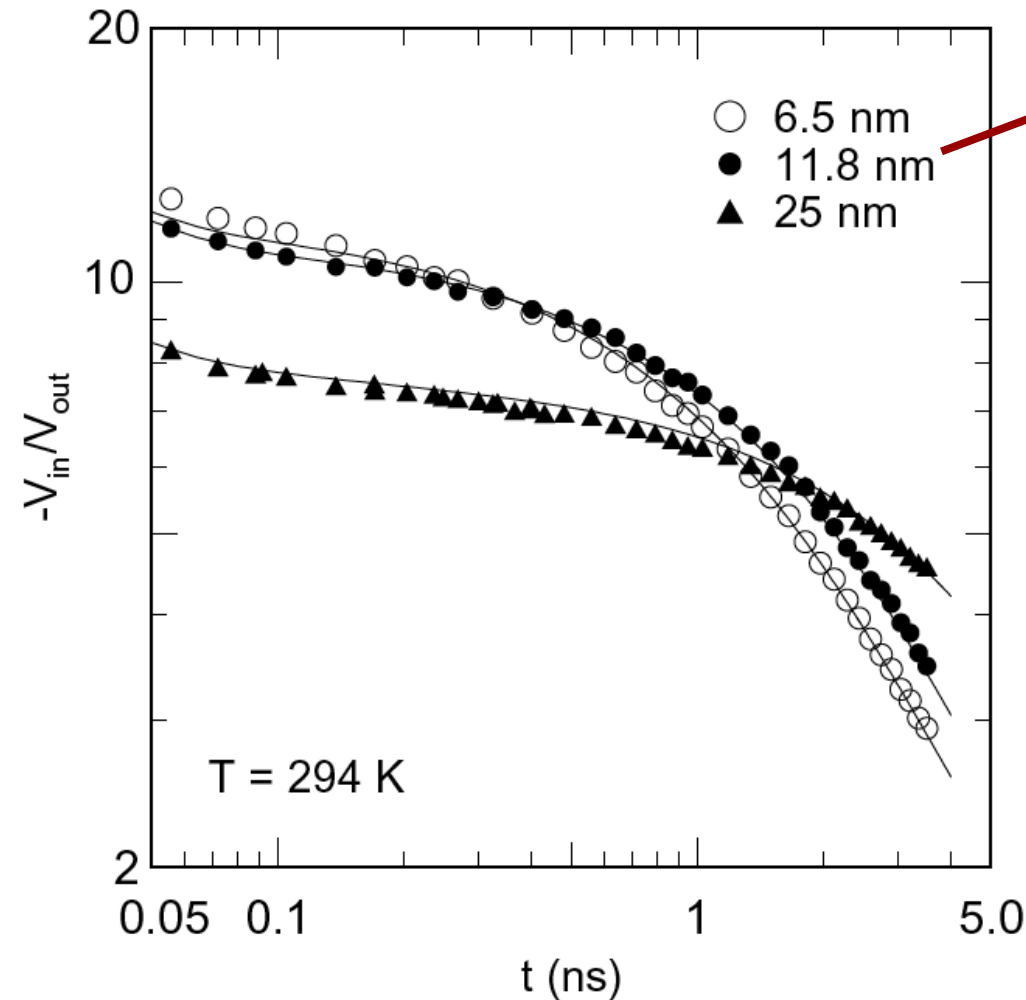
Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

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



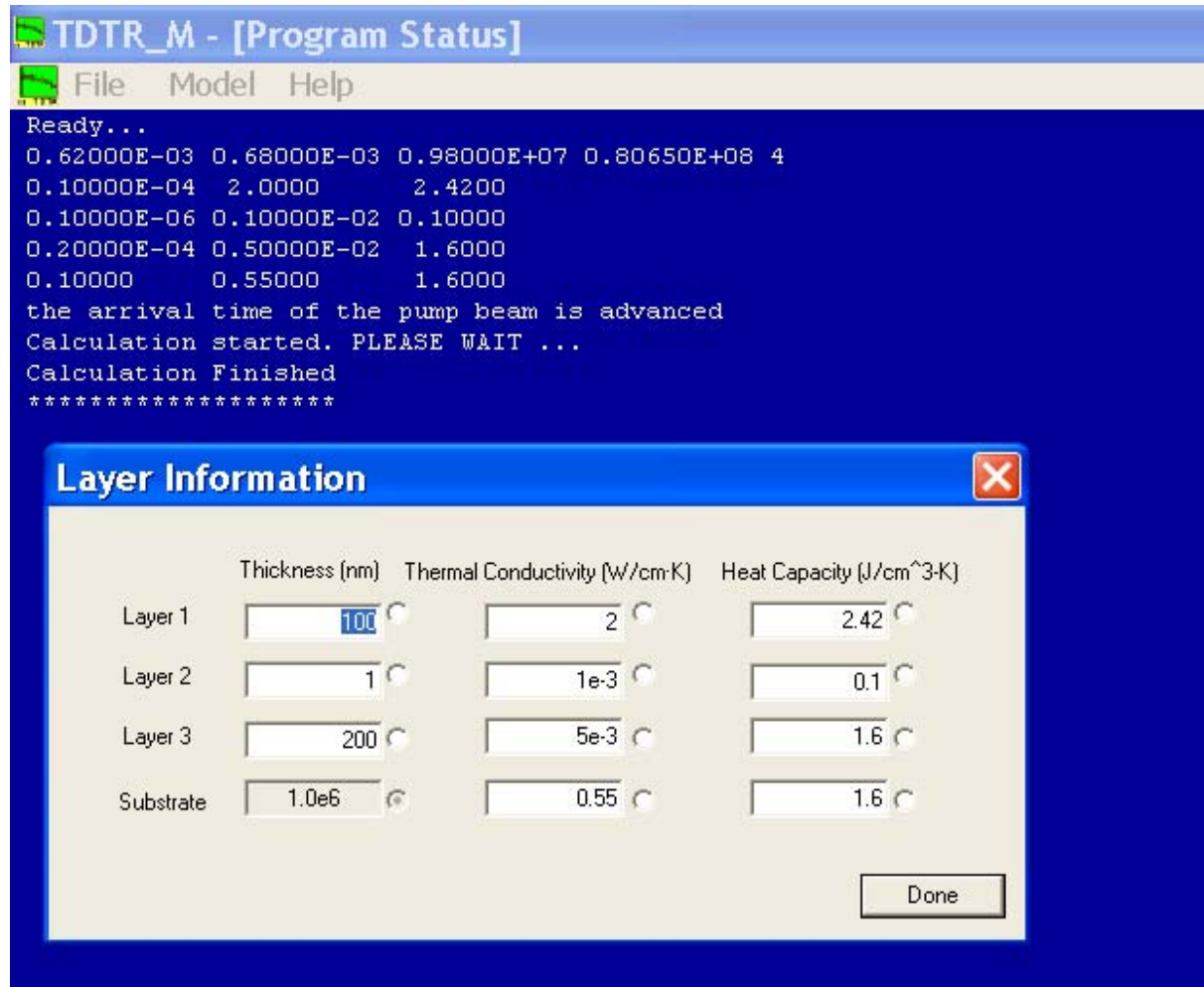
Time-domain Thermoreflectance (TDTR) data for TiN/SiO₂/Si



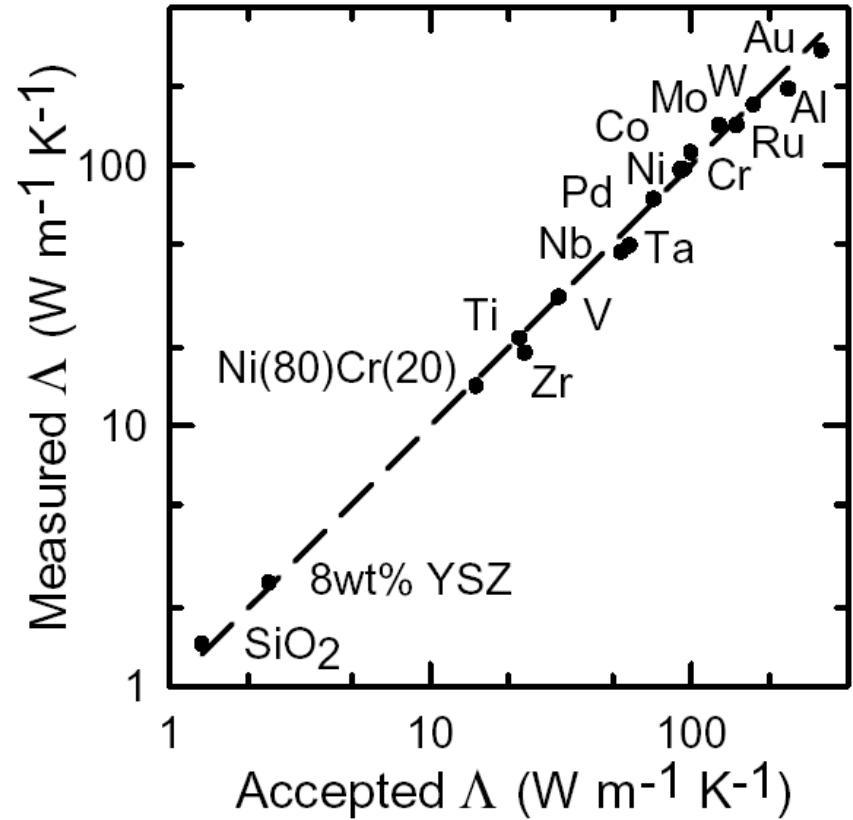
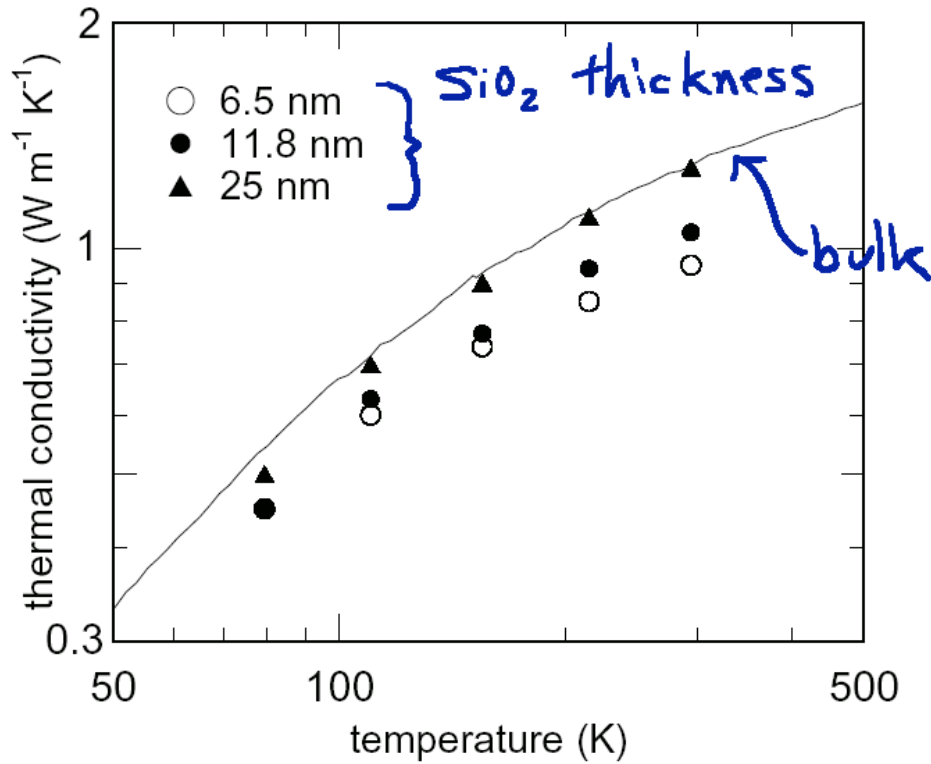
- reflectivity of a metal depends on temperature
- one free parameter: the “effective” thermal conductivity of the thermally grown SiO₂ layer (interfaces not modeled separately)

Windows software

author: Catalin Chiritescu,
users.mrl.uiuc.edu/cahill/tcdata/tdtr_m.zip

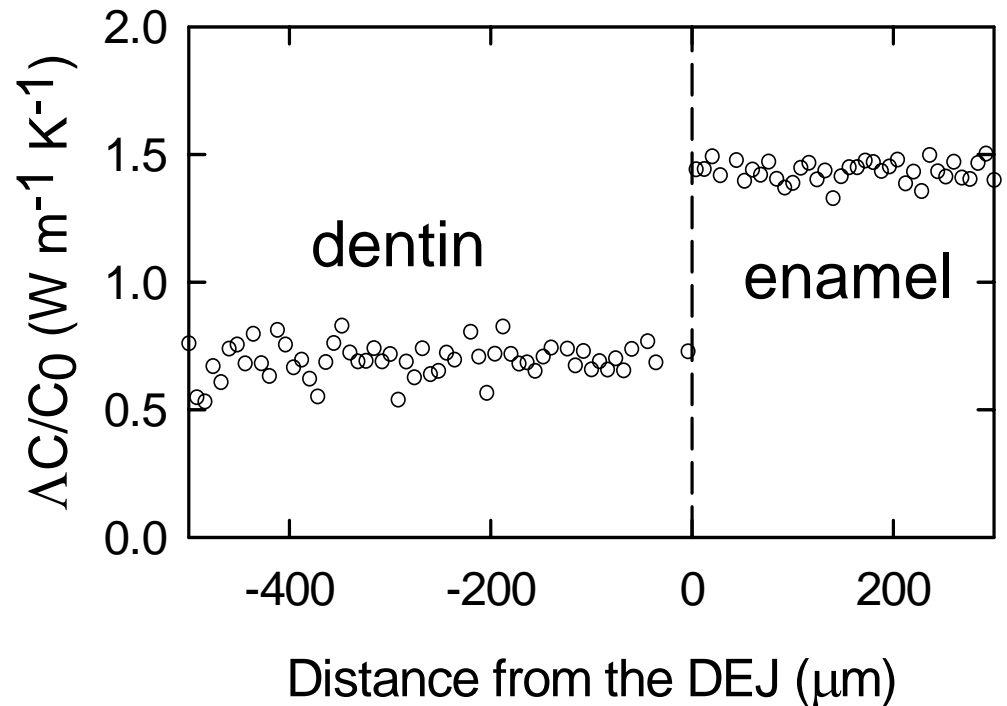
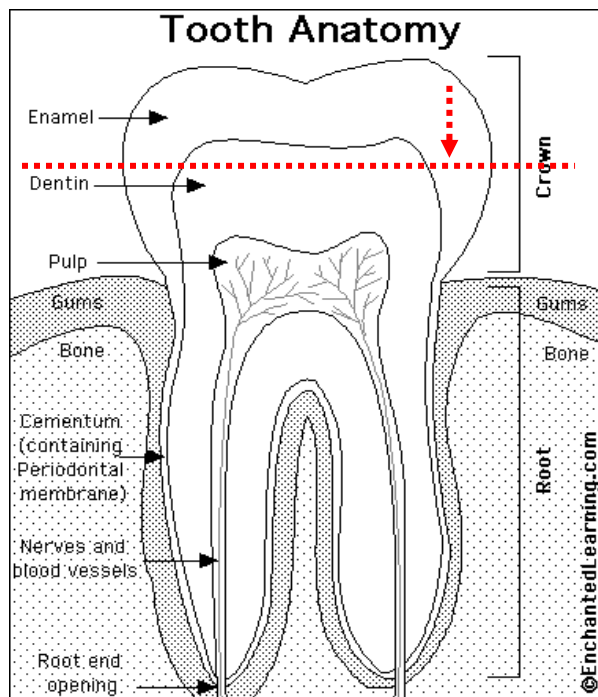
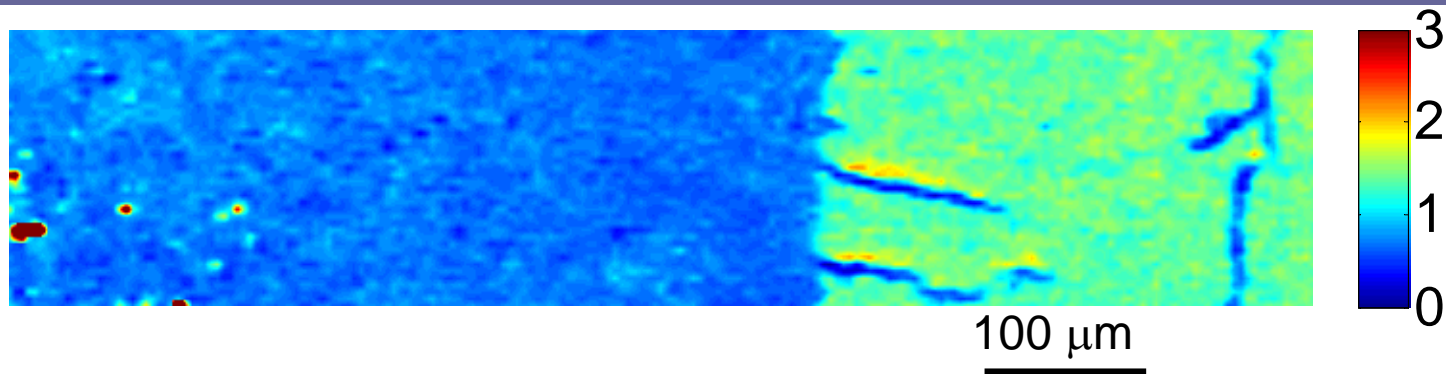


TDTR: Flexible, convenient, and accurate



- ...with 3 micron resolution...

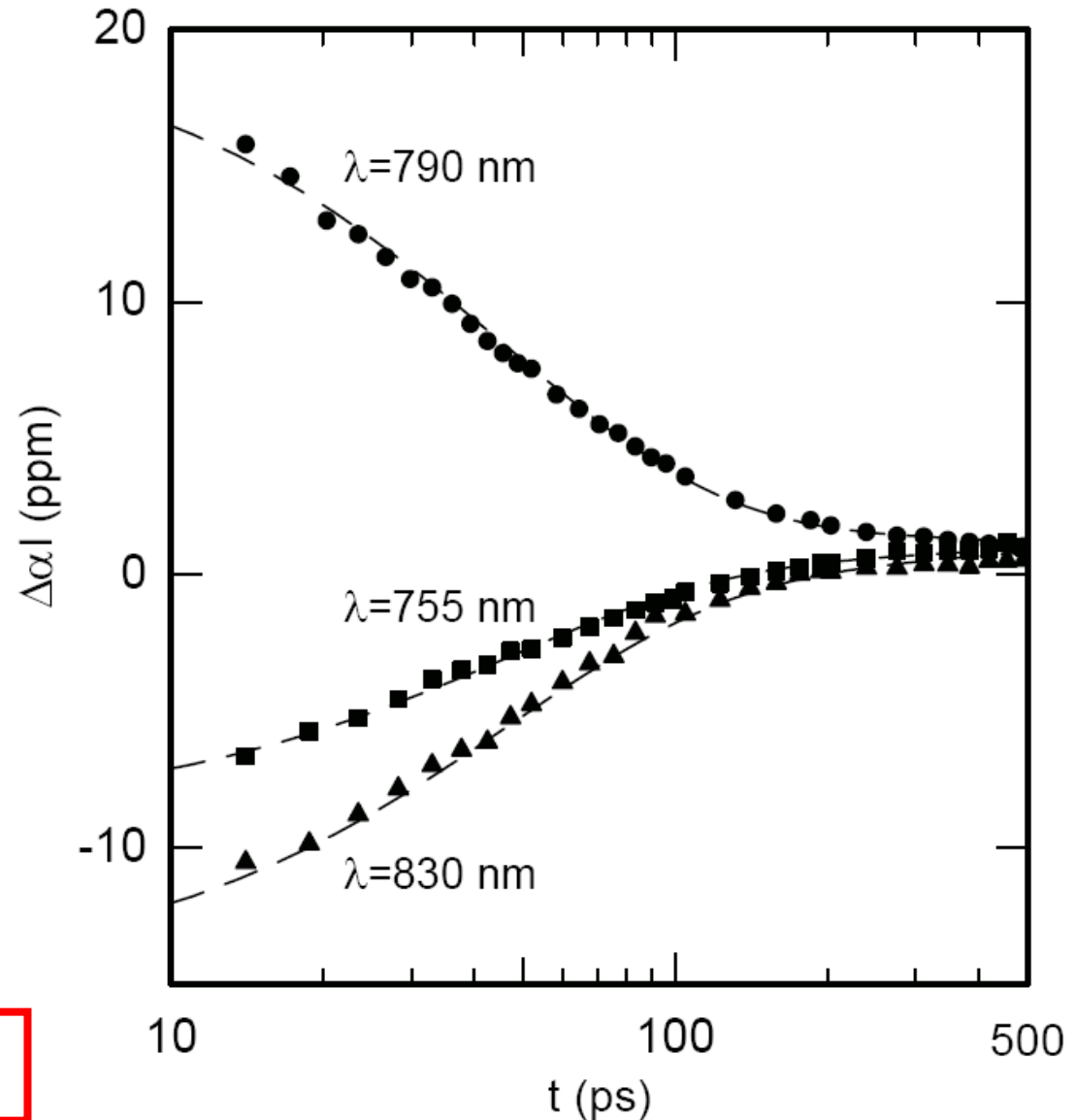
Thermal conductivity map of a human tooth



Nanotubes in surfactant in water

- Optical absorption depends on temperature of the nanotube
- Assume heat capacity is comparable to graphite
- Cooling rate (RC time constant) gives interface conductance

$$G = 12 \text{ MW m}^{-2} \text{ K}^{-1}$$



Critical aspect ratio of a fiber composite

- Isotropic fiber composite with high conductivity fibers (and infinite interface conductance)

$$\Lambda_c = \frac{1}{3} V_f \Lambda_{NT}$$

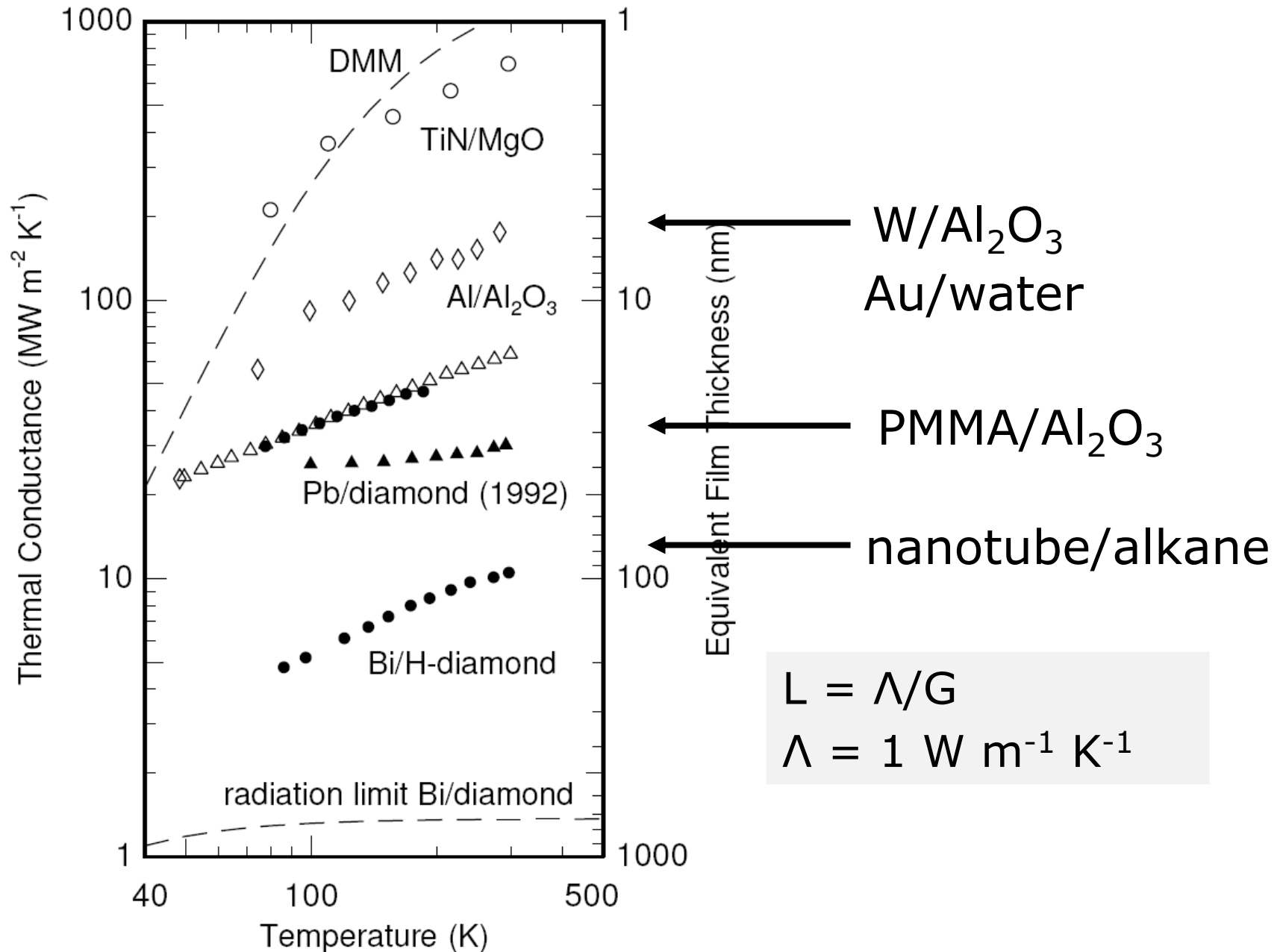
- But this conductivity is obtained only if the aspect ratio of the fiber is high

$$3 \left(\frac{\Lambda_{NT}}{rG} \right)^{1/2} \approx 2000$$

- Troubling question: Did we measure the relevant value of the conductance?

"heat capacity G" vs. "heat conduction G"

Interface thermal conductance: Factor of 60 range at room temperature



Can we beat the amorphous limit of the thermal conductivity Δ_{\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

$$\Delta_{\min} = 0.40 k_B n^{2/3} (v_l + 2v_t)$$

- coupled the Einstein oscillators to 26 neighbors
- heat transport as a random walk of thermal energy between atoms; time scale of $\frac{1}{2}$ vibrational period
- did not realize waves (phonons) are the normal modes of a crystal

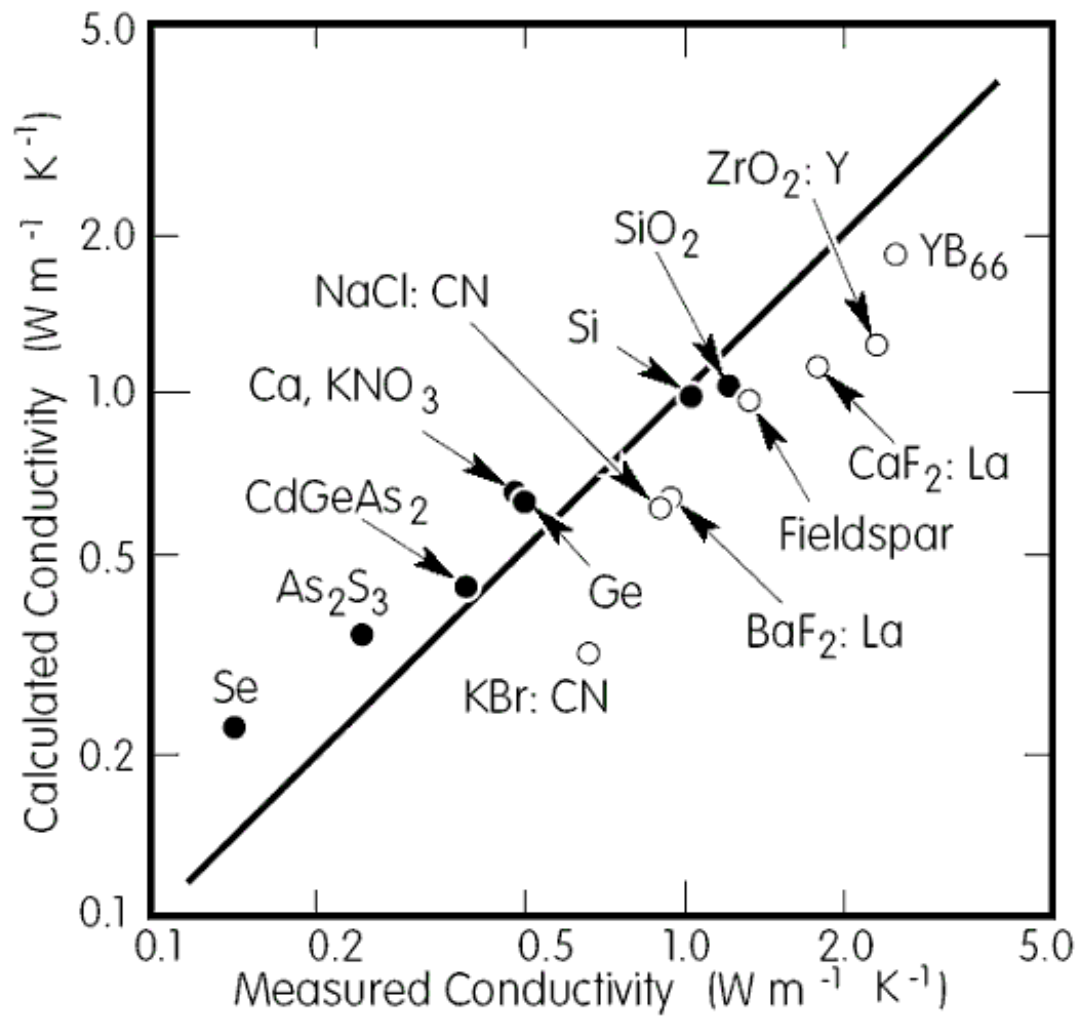
2. *Elementare Betrachtungen*
über die thermische Molekularbewegung in festen
Körpern;
von *A. Einstein.*

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 Dimensional Betrachtung abgeleitet werden können, insbesondere auch die Größenordnung der in diesen Formeln auftretenden Zahlen-

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

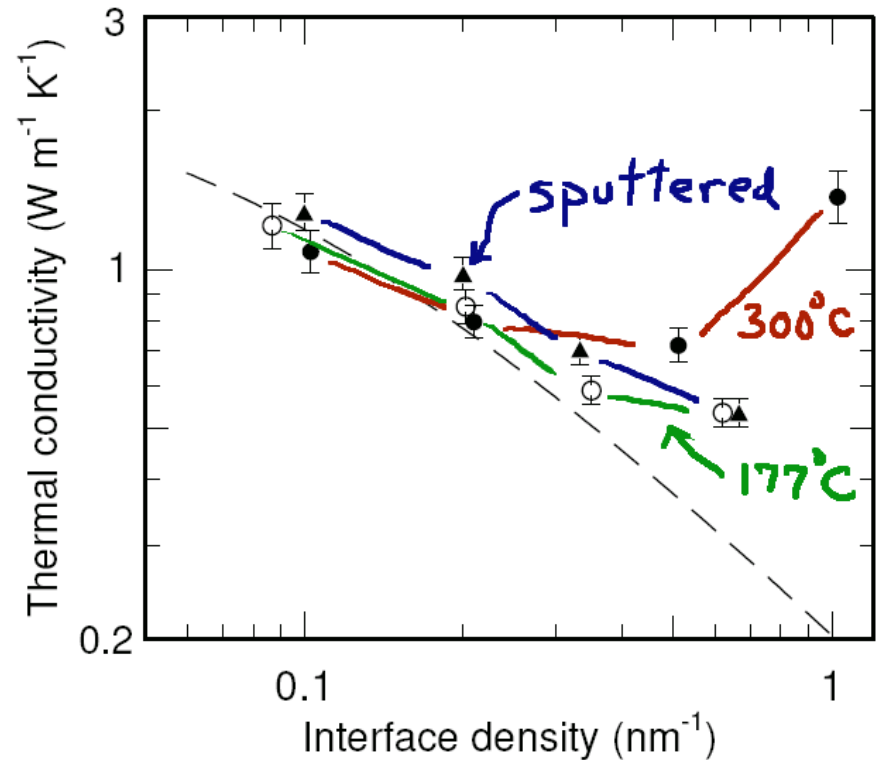
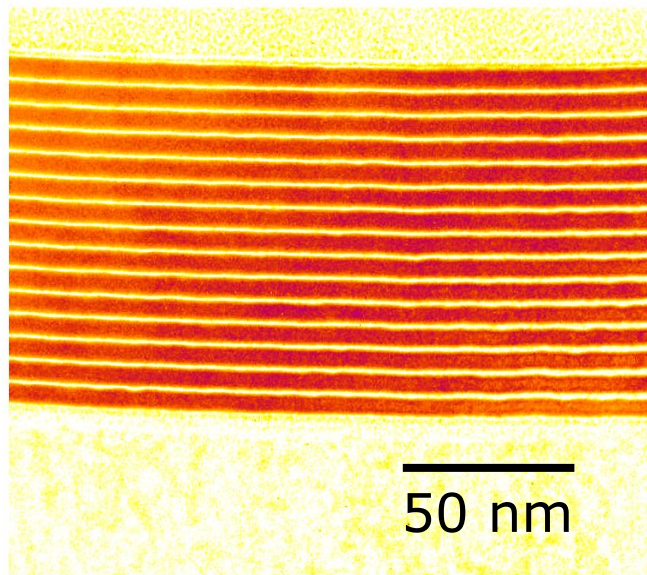
2) Die Wärmebewegung in festen Körpern wurde dabei aufgefaßt als in monochromatischen Schwingungen der Atome bestehend. Vgl. hierzu S. 2 dieser Arbeit.

Works well for homogeneous disordered materials



- amorphous
- disordered crystal

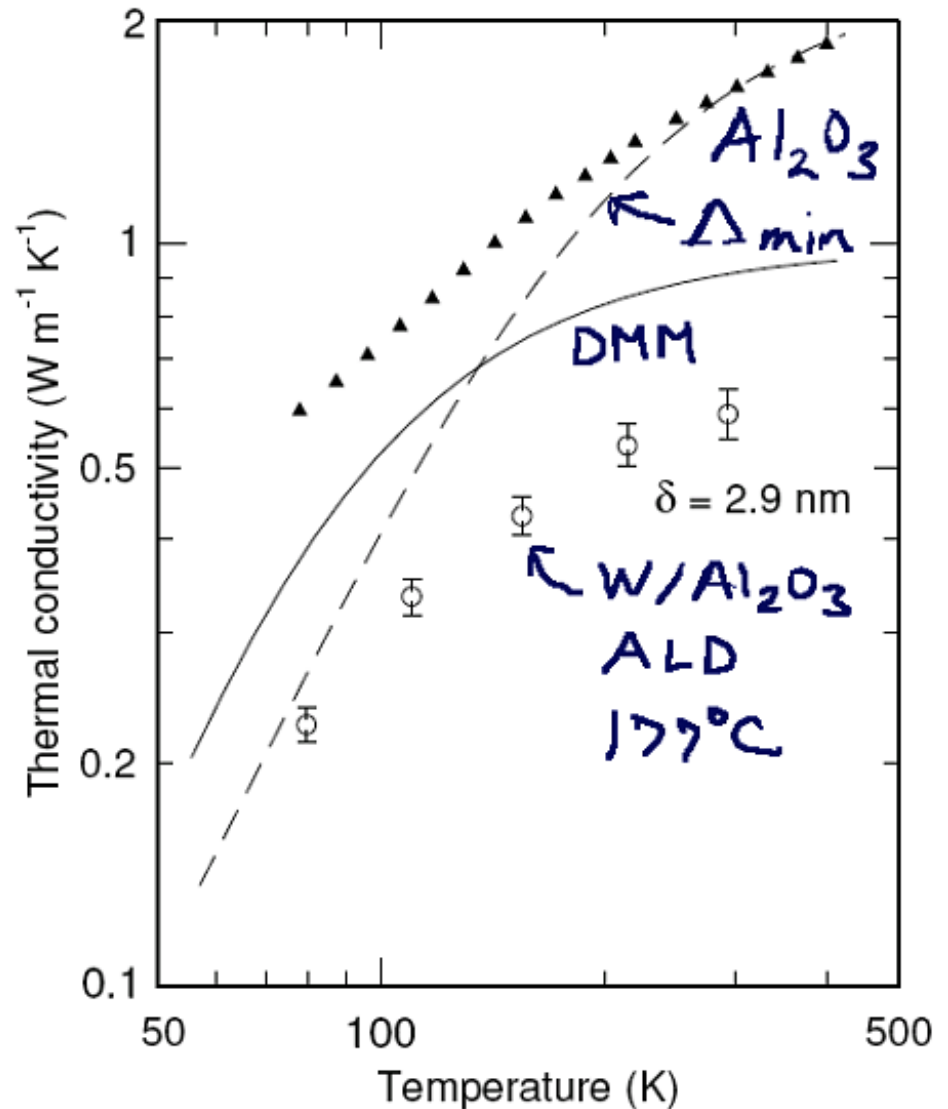
Ultralow thermal conductivity in W/Al₂O₃ nanolaminates (Costescu, 2004)



- Thermal conductance of interfaces between dissimilar materials can produce thermal conductivities below the amorphous limit.

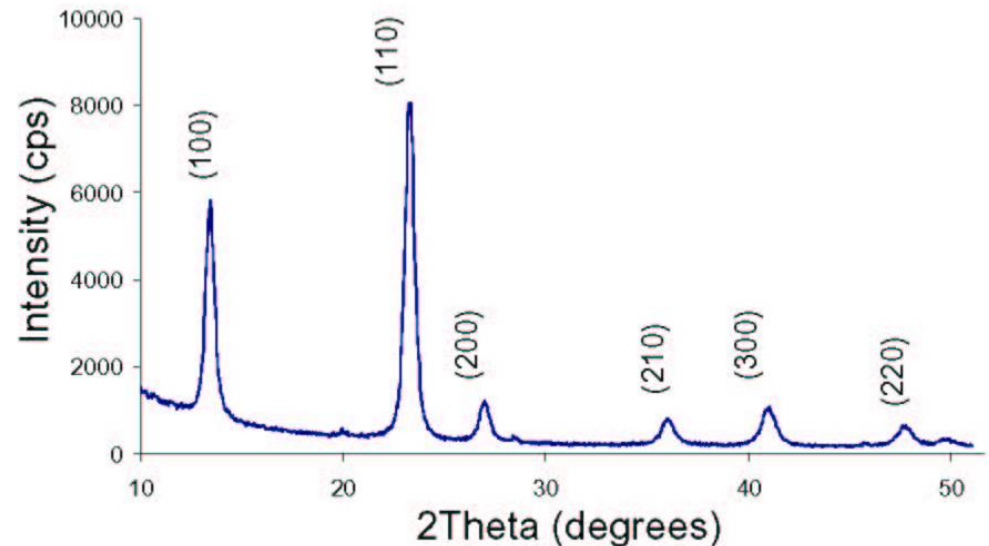
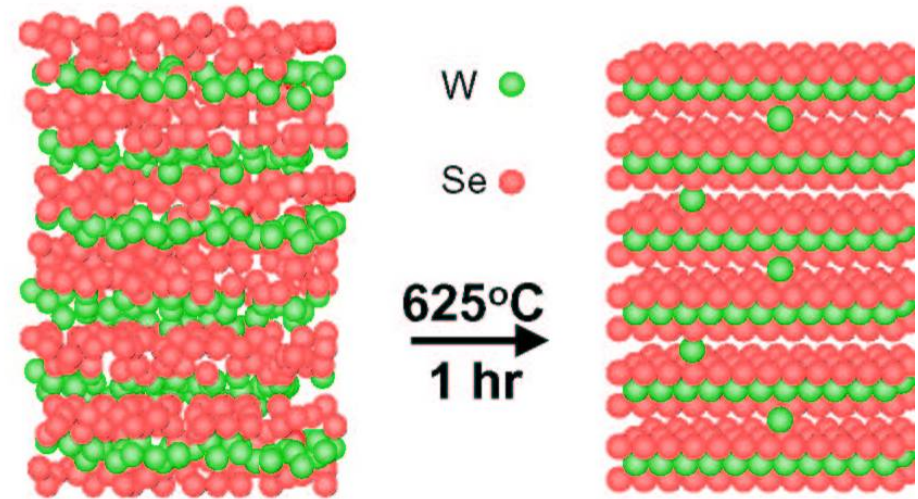
W/Al₂O₃ nanolaminates

- ultra-low conductivity in nanoscale metal/ceramic multilayers
- data close to theoretical prediction of the diffuse-mismatch model (DMM) times layer spacing

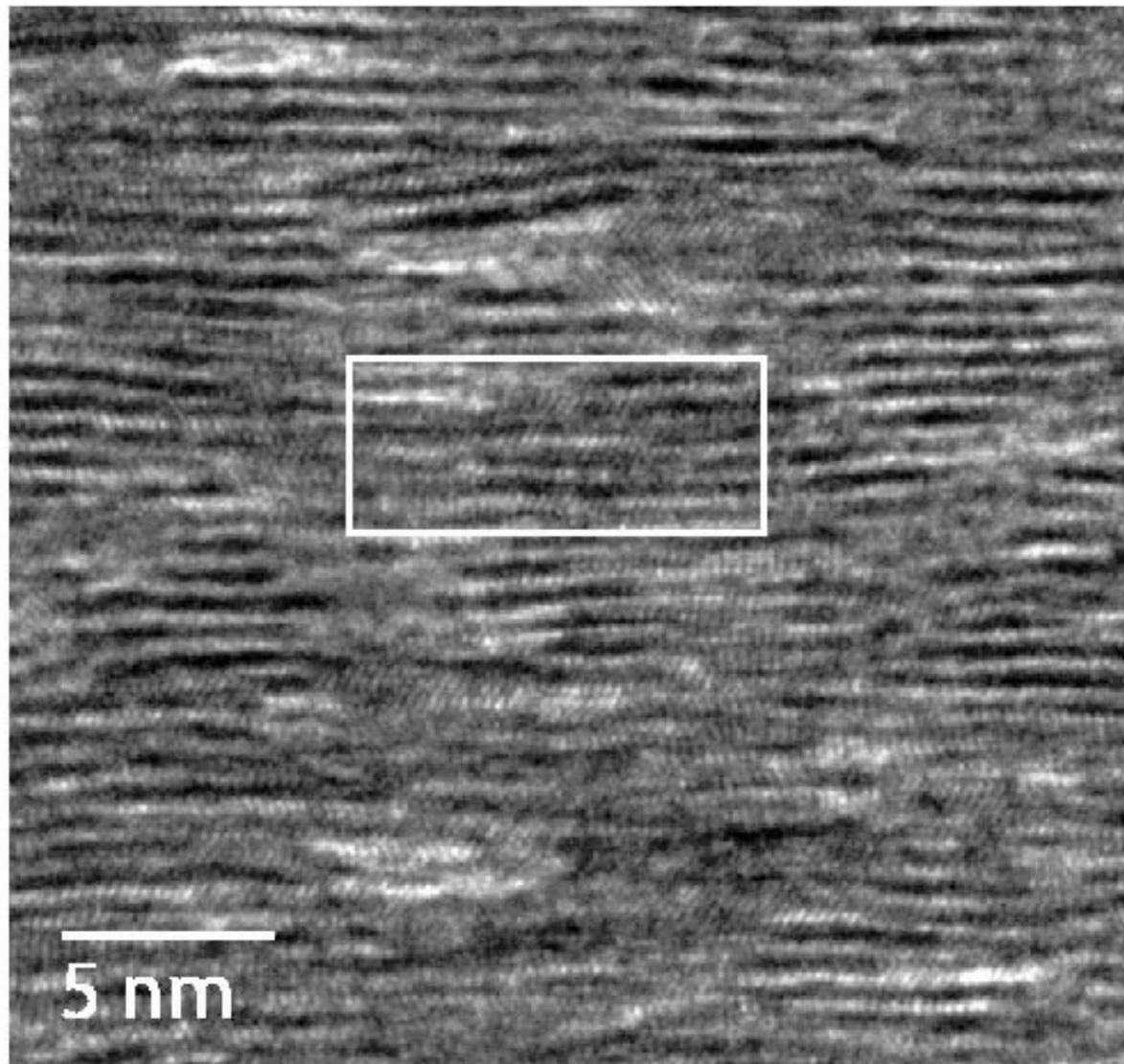
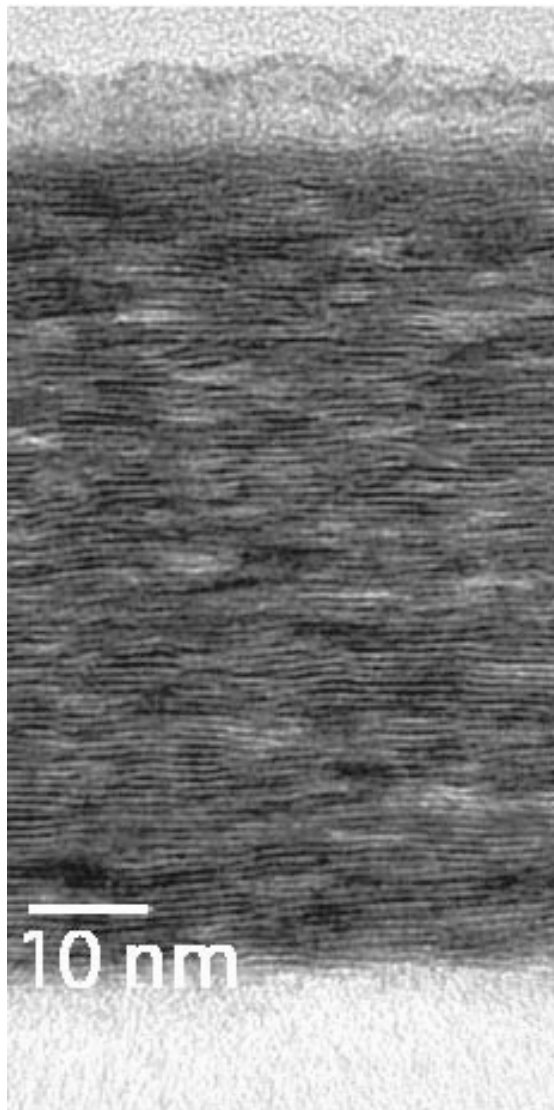


Layered disordered crystals: WSe₂ by “modulated elemental reactants”

- 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



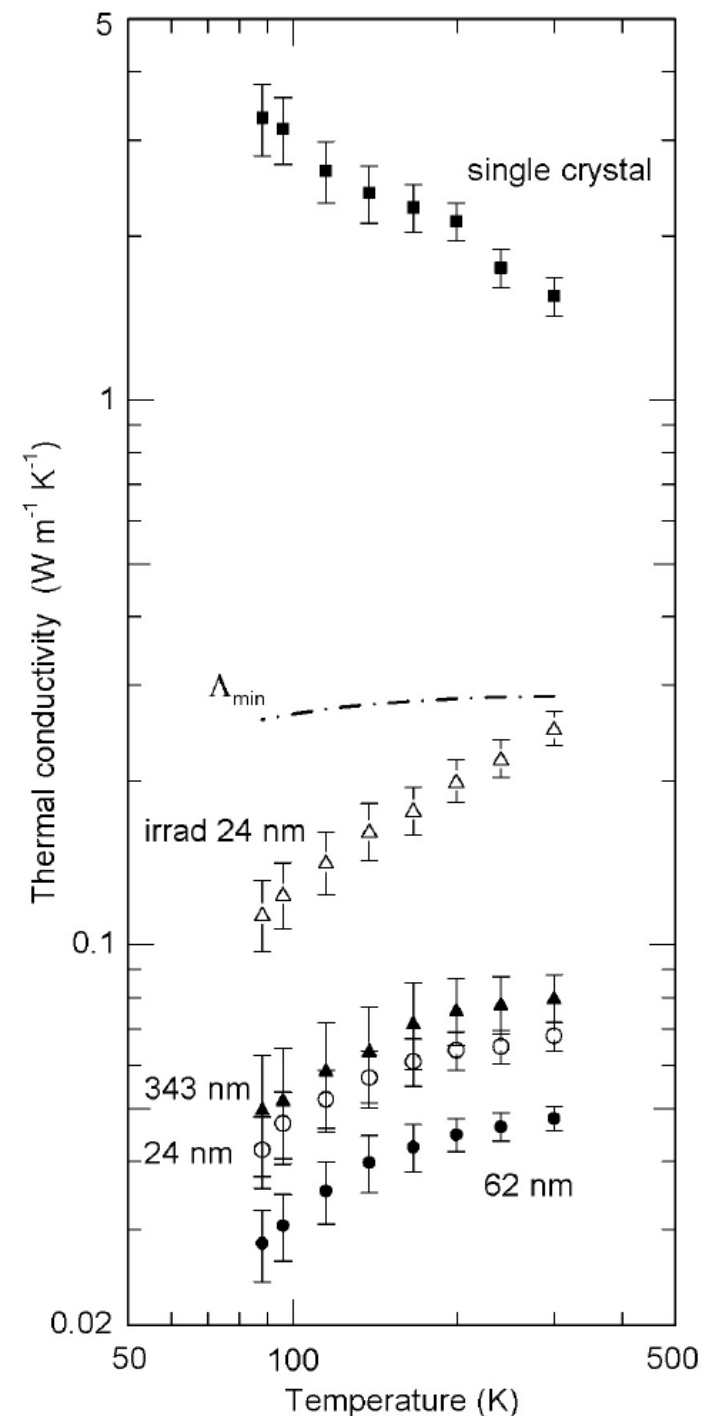
Cross-sectional TEM of 60 nm thick WSe_2



Seongwon Kim and Jian Min Zuo

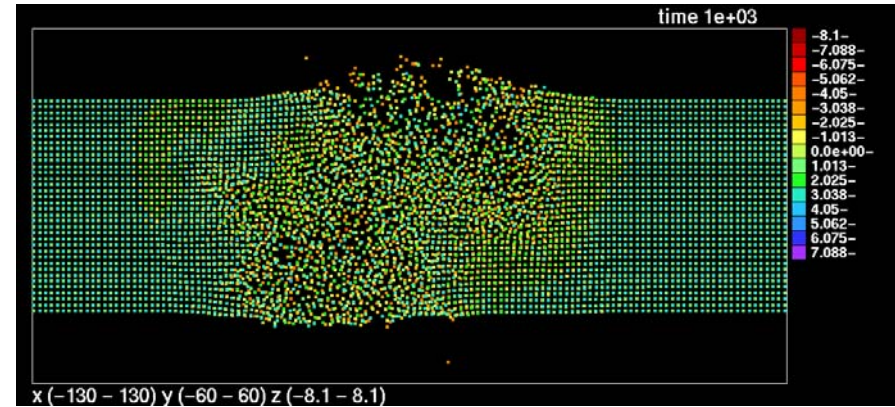
Thermal conductivity of WSe_2

- 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.

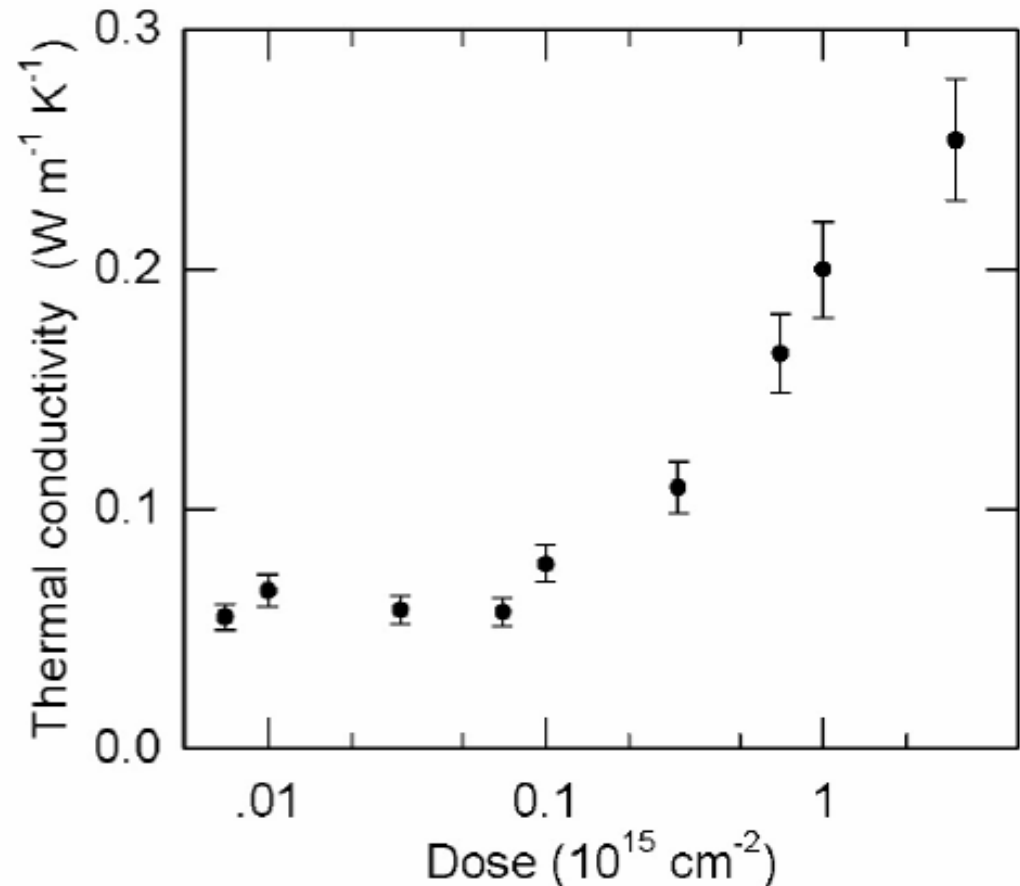


Ion irradiation of WSe₂

MD simulation of 1 MeV Kr impact on Au

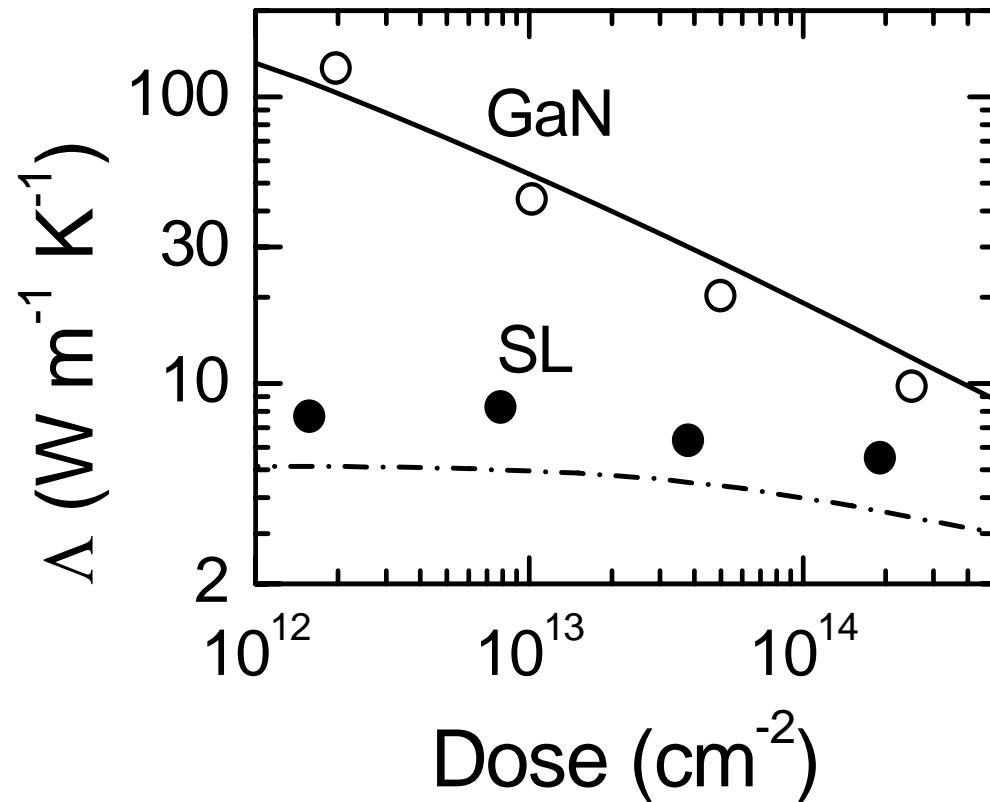


- Heavy ion irradiation (1 MeV Kr⁺) of 24 nm WSe₂ film.
- Novel behavior: ion damage causes the thermal conductivity to *increase*.



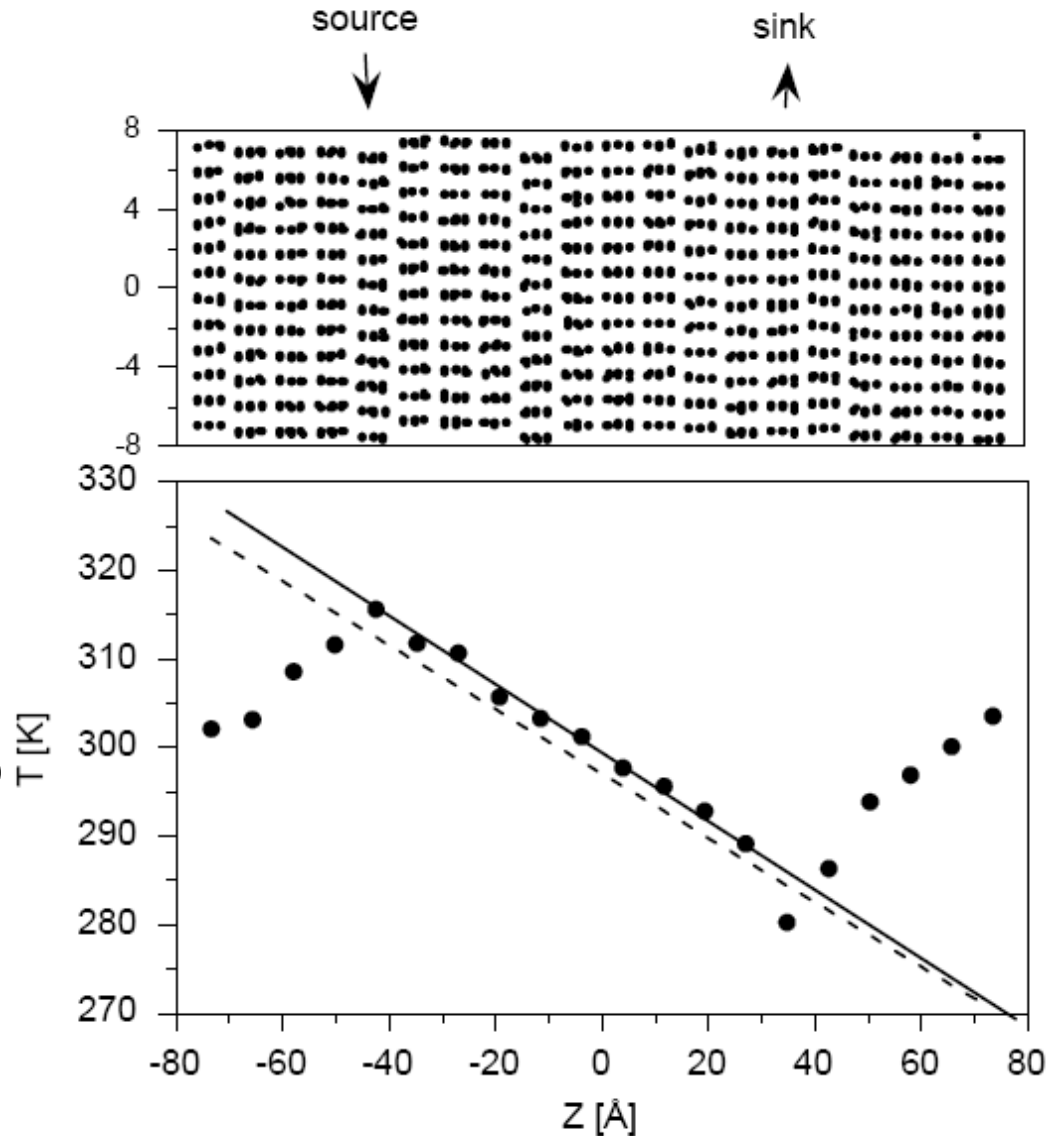
Digression: ion bombardment of a superlattice (with Y. Cao and D. Jena)

- 2.3 MeV Ar ion irradiation of GaN and $(\text{AlN})_{4 \text{ nm}}-(\text{GaN})_{5 \text{ nm}}$
- 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

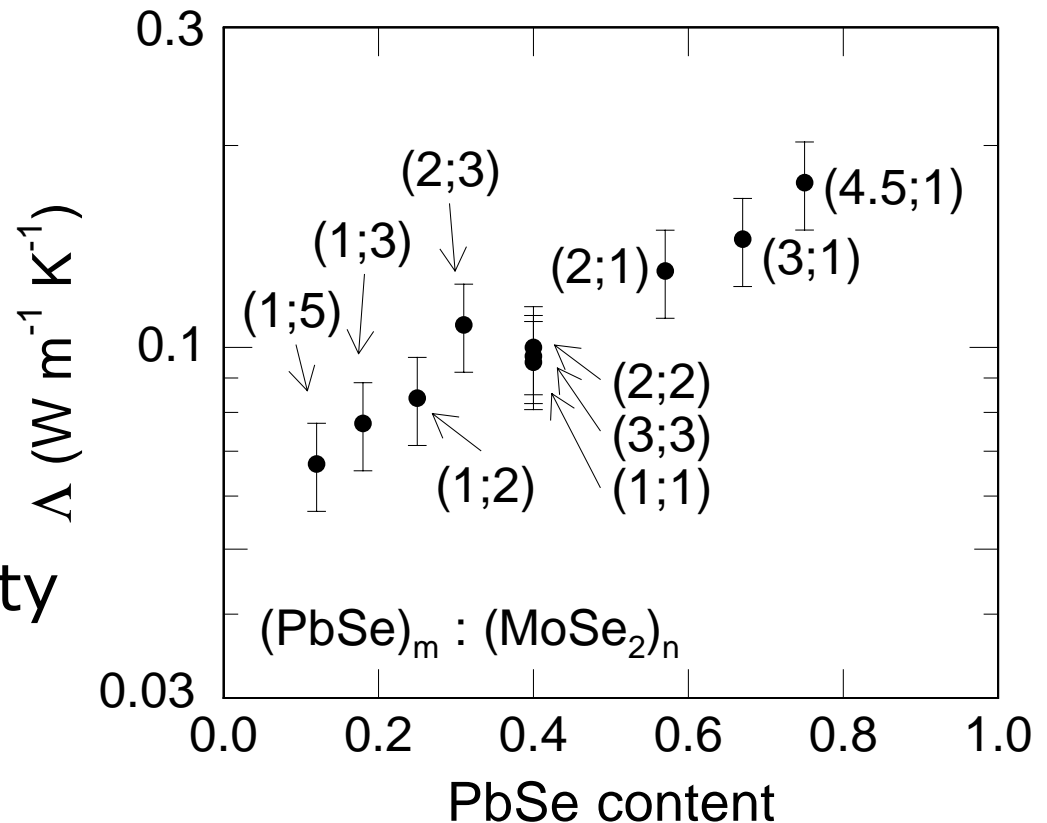


Conclusions from theoretical work (Hu and Keblinski, unpublished)

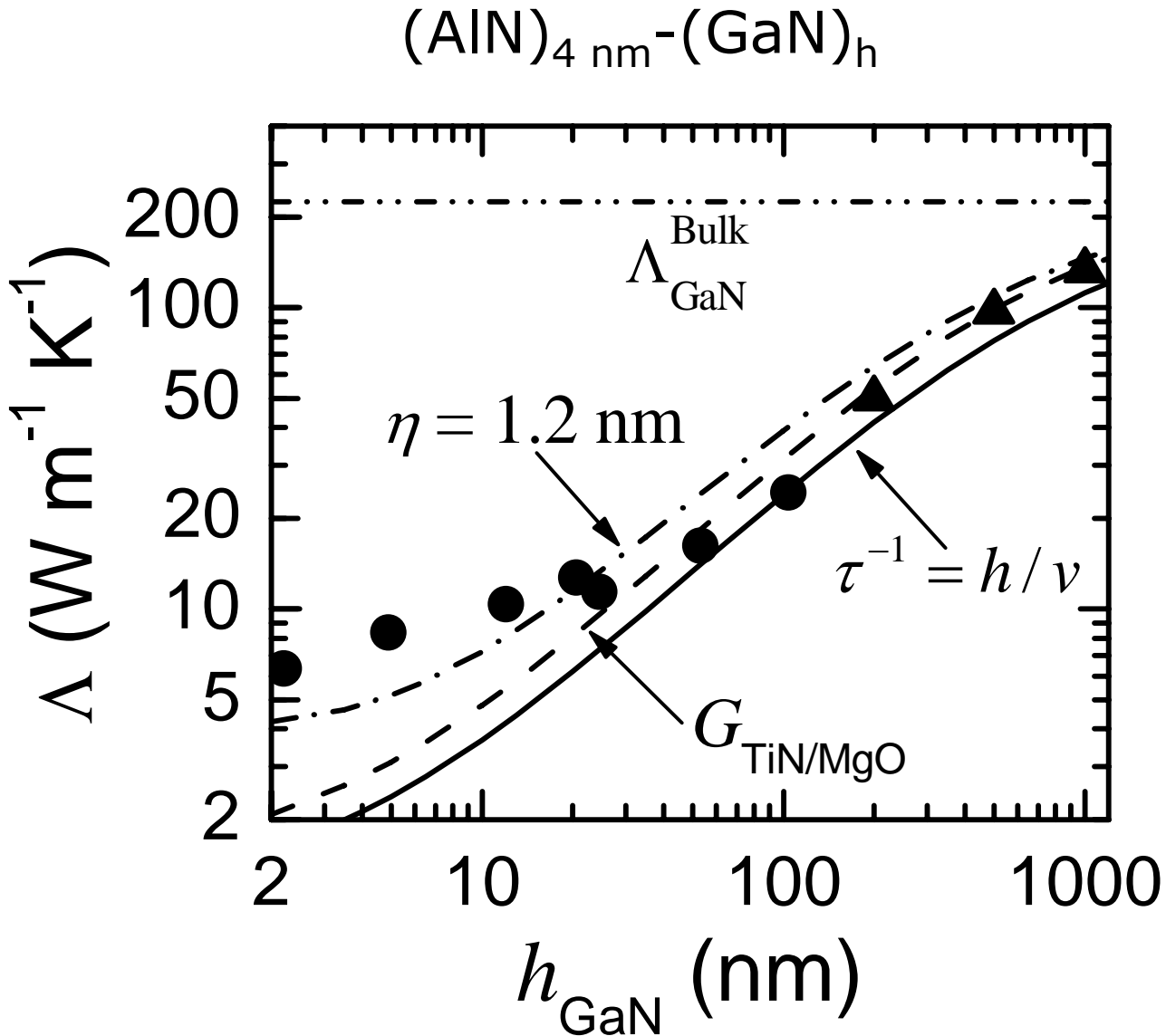
- Analysis of the **participation ratio**: phonon localization is not significant.
- Analysis of **mode polarization**: incoherent grain boundaries create diffusive but non-propagating vibrational modes. (stacking faults are not sufficient)
- Key to ultralow thermal conductivity is disorder in combination 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/PbTe
 - $\text{MoSe}_2/\text{PbTe}$
- Interface density does not matter. Conductivity determined by composition not interface density.



Contrast with typical behavior of a superlattice (with Y. Cao and D. Jena)



Conclusions

- Difficult to take advantage of superlative properties of carbon nanotubes because of "thermally weak" interfaces.
- Can beat the amorphous limit to the thermal conductivity with high densities of interfaces.
- 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
 - 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?