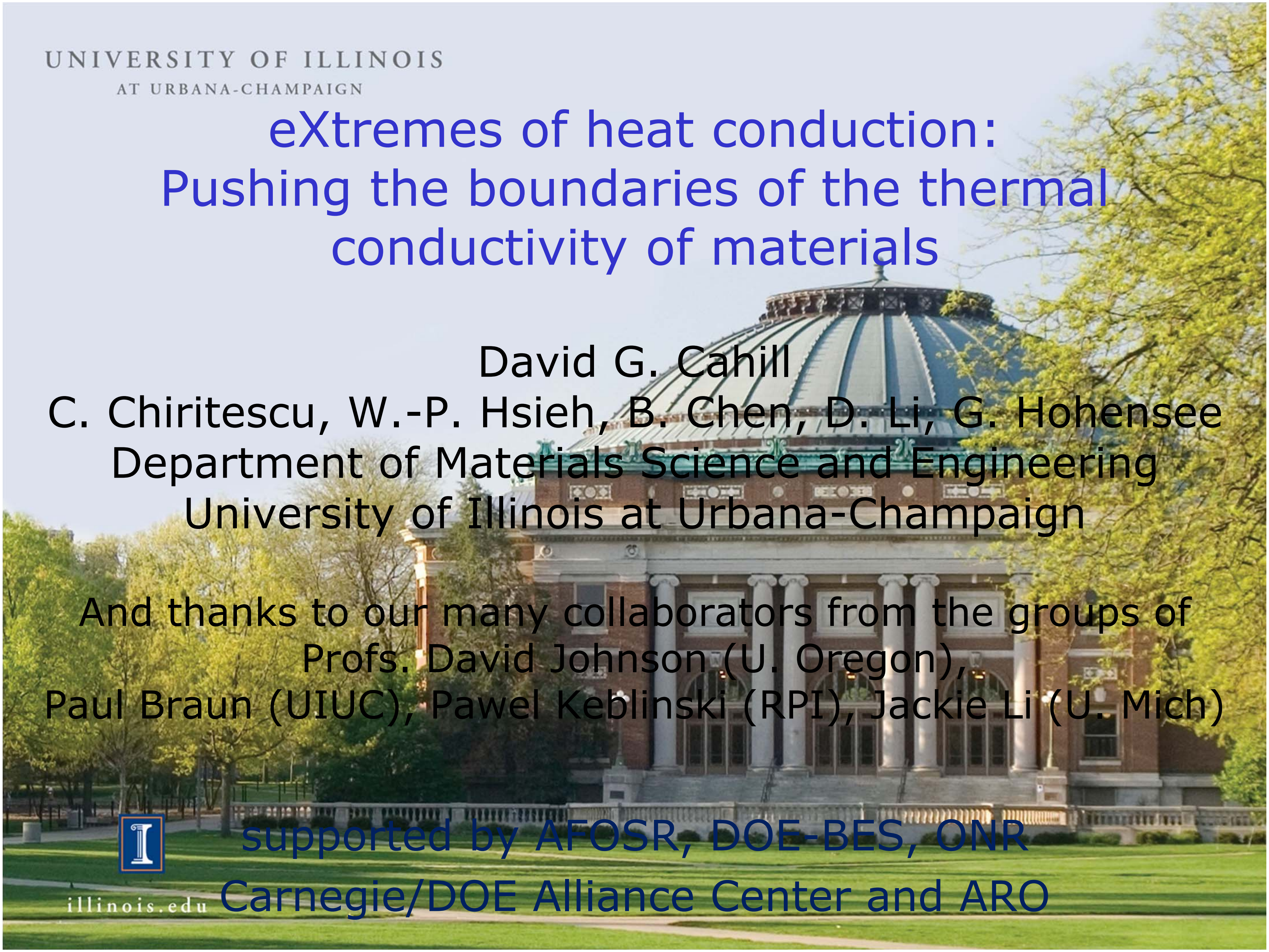

UNIVERSITY OF ILLINOIS
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eXtremes of heat conduction: Pushing the boundaries of the thermal conductivity of materials

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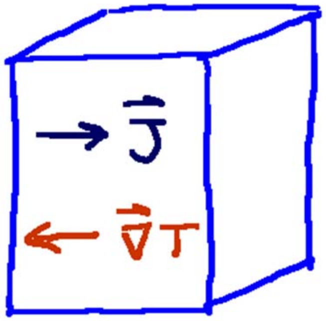
Outline

- Thermal conductivity and interface thermal conductance.
- eXtremes of thermal conductivity:
  - High conductivity nanotubes, graphene, and polyethelene
  - Ultralow conductivity disordered layered crystals
  - High pressures: ice VII at 20 GPa
  - High conductivity spin waves in one-dimensional quantum spin systems

Thermal conductivity and interface thermal conductance

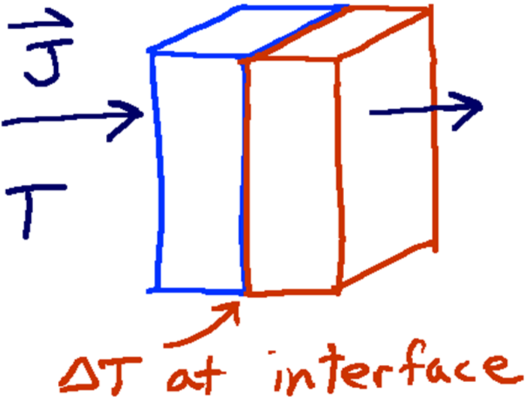
- Thermal conductivity Λ is a property of the continuum

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

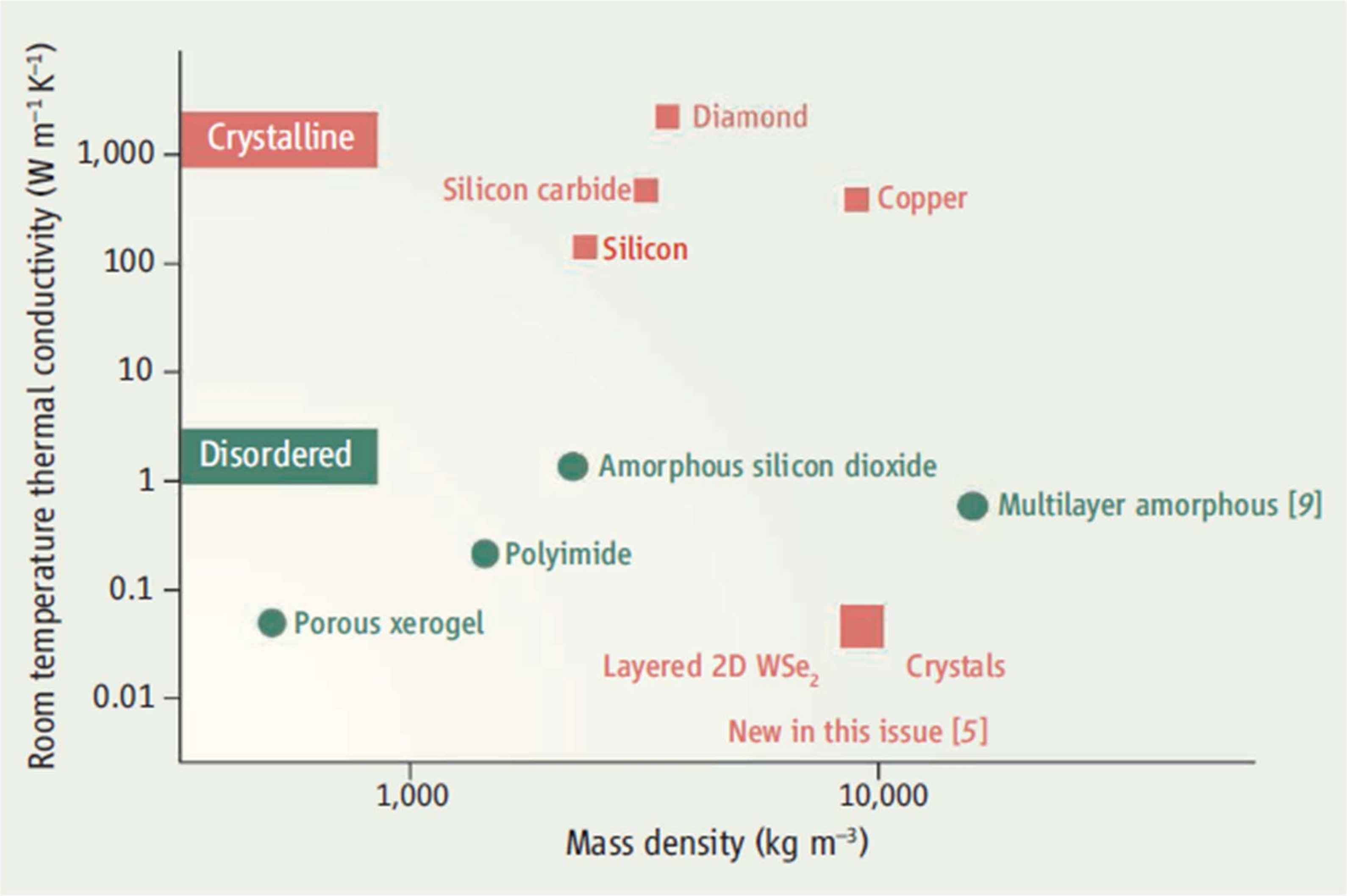


- Thermal conductance (per unit area) *G* is a property of an interface

$$J = G \Delta T$$

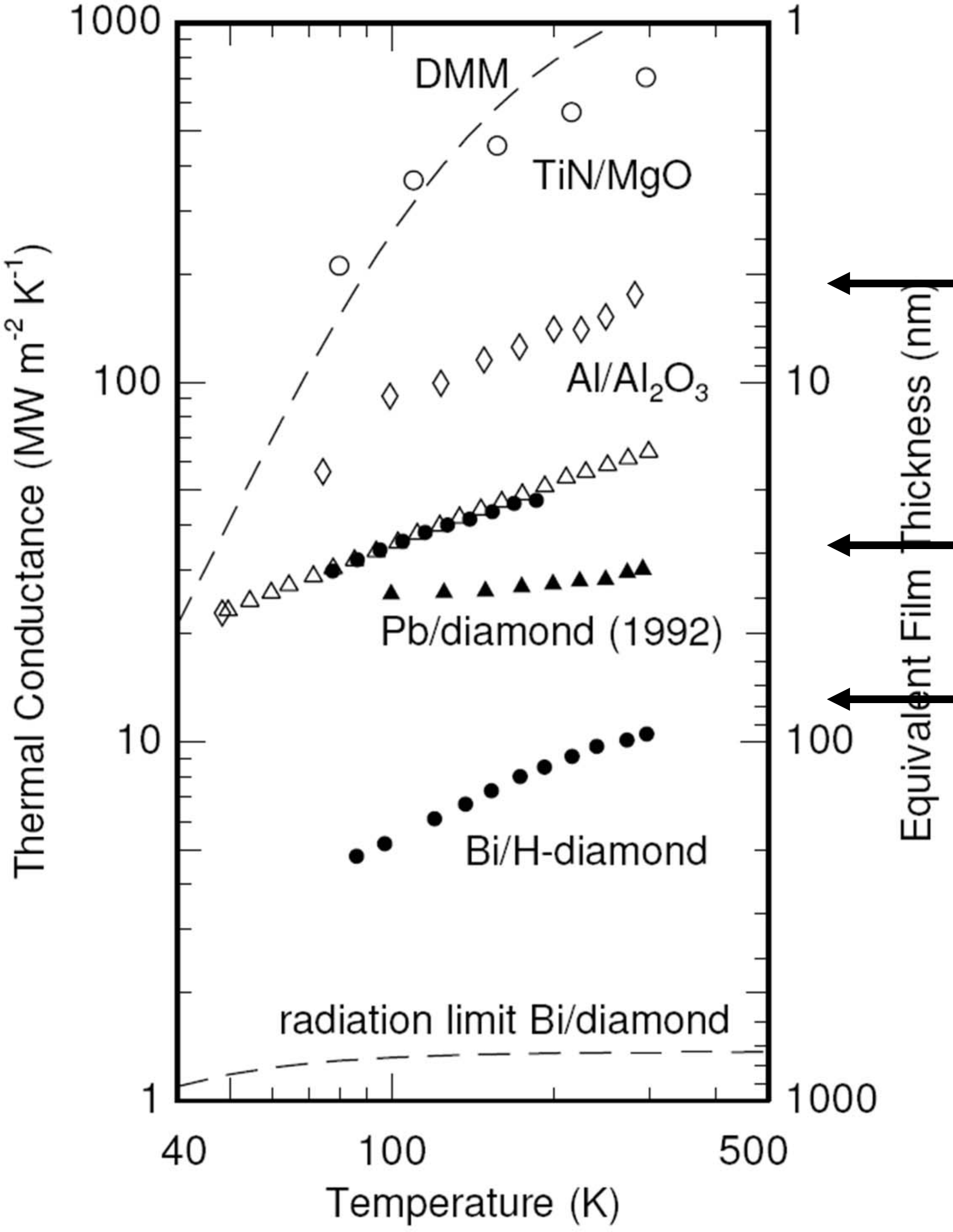


Thermal conductivities span a range of 40,000 at room temperature



Goodson, *Science* (2004)

Interface thermal conductance: Factor of 60 range at room temperature



W/Al_2O_3

Au/water

$PMMA/Al_2O_3$

nanotube/alkane

$L = \Lambda/G$

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

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

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

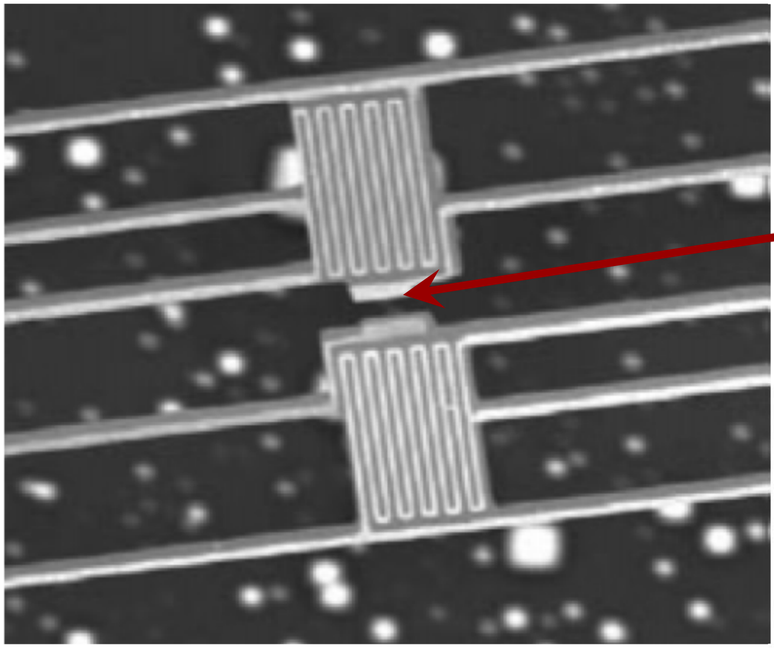
$C(\omega)$ = heat capacity of phonon mode

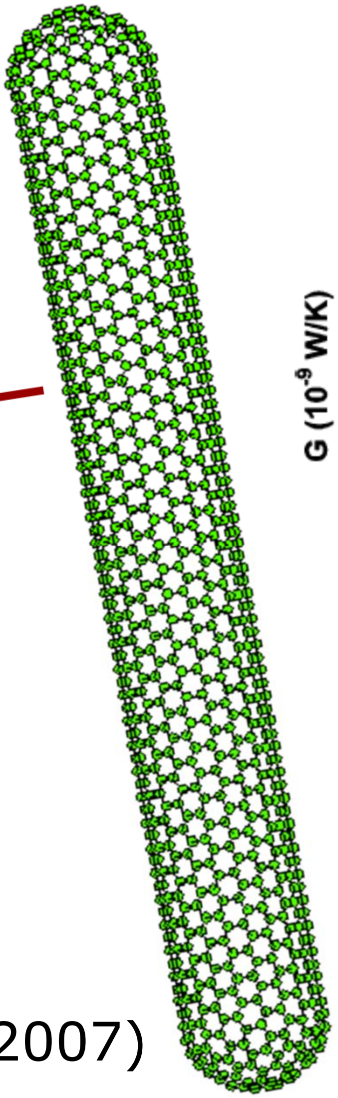
$v(\omega)$ = group velocity

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

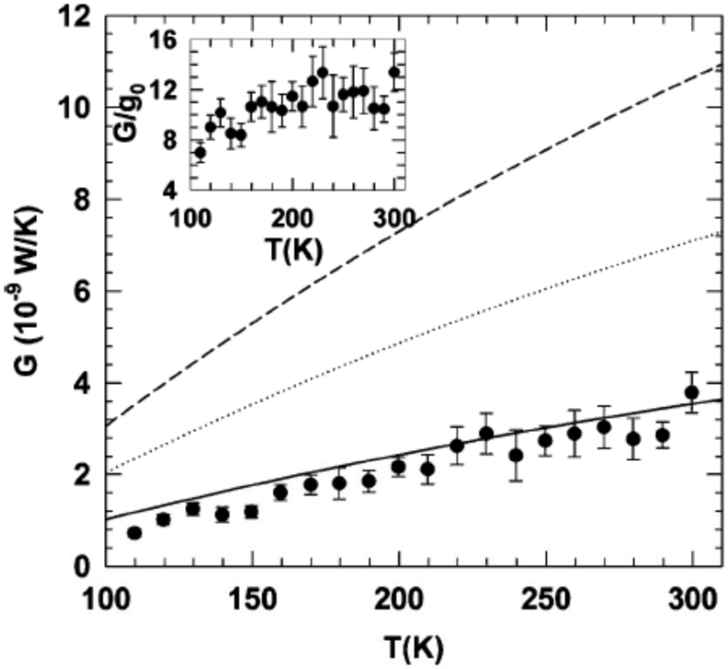
Carbon nanotubes

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





Maruyama (2007)

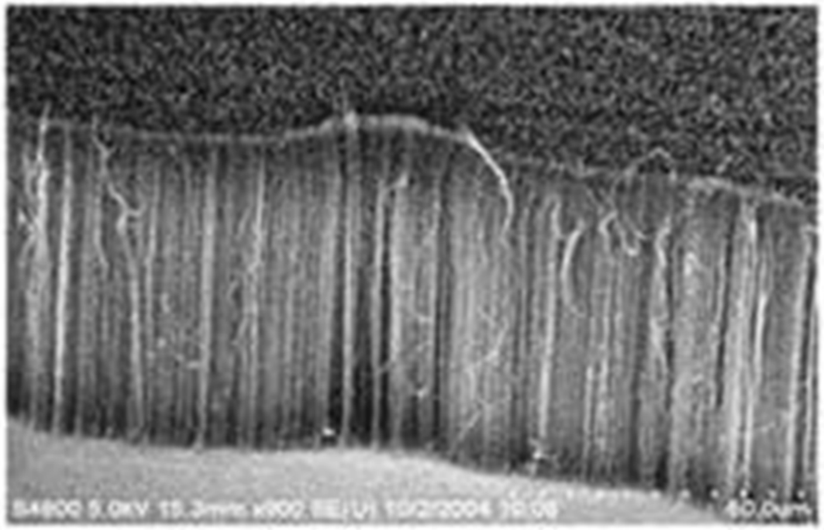


Yu et al. (2005)

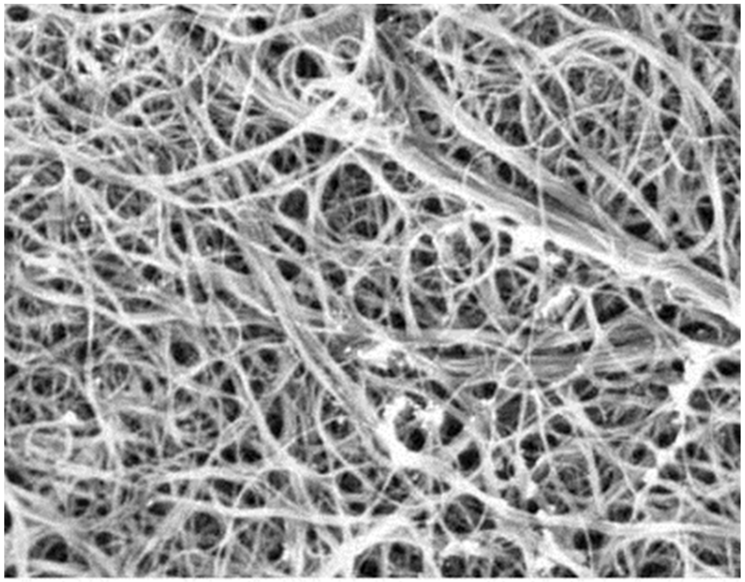
Can we make use of this?

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

Fischer (2007)



Oriented carbon nanotube array.



Lehman (2005)

Critical aspect ratio of a fiber composite

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

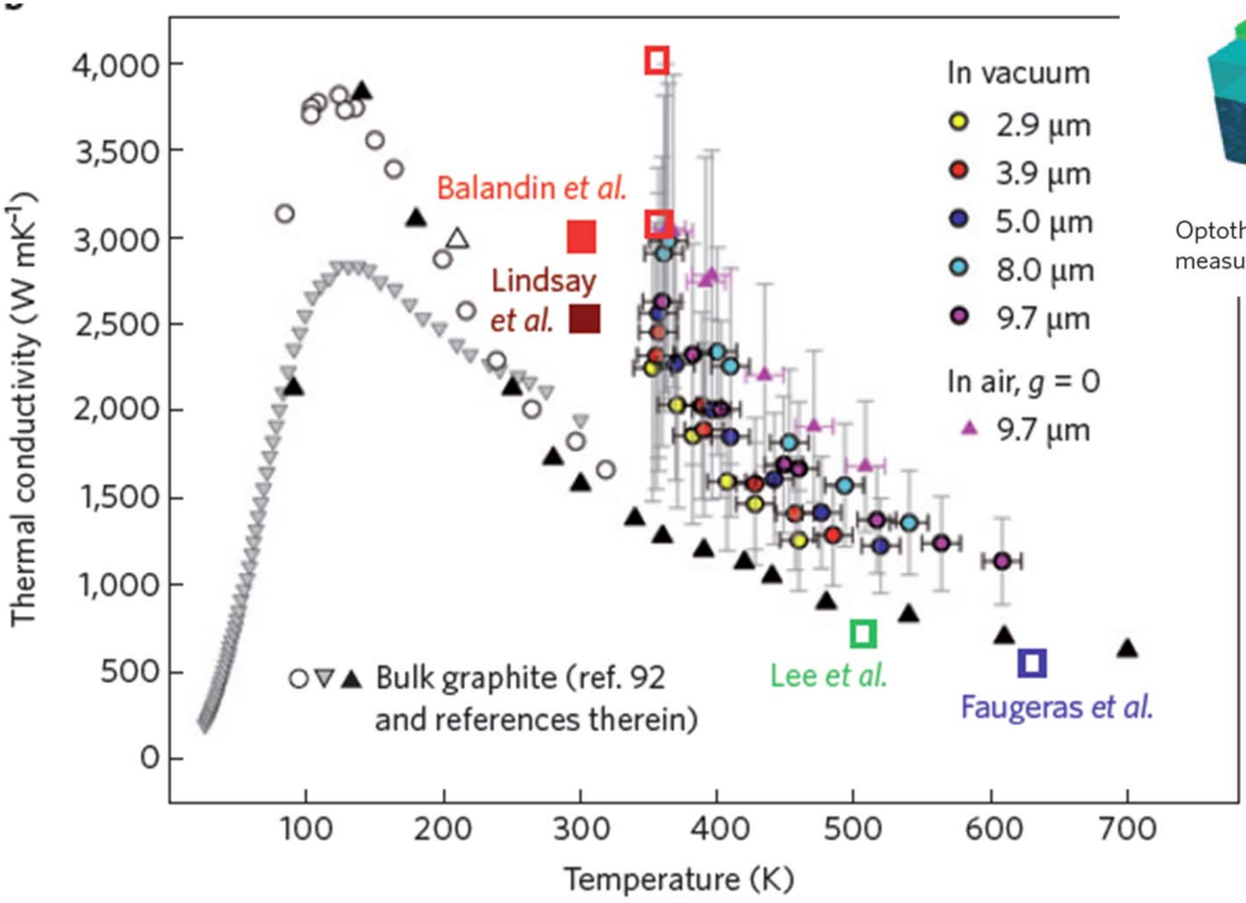
$$\Lambda_c = \frac{1}{3} V_f \Lambda_{NT}$$

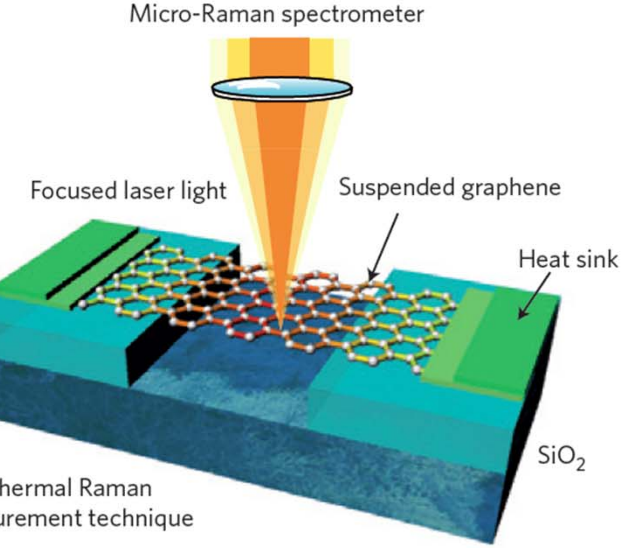
- But this conductivity if obtained only if the aspect ratio of the fiber is high

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

Two-dimensional fillers should be advantageous

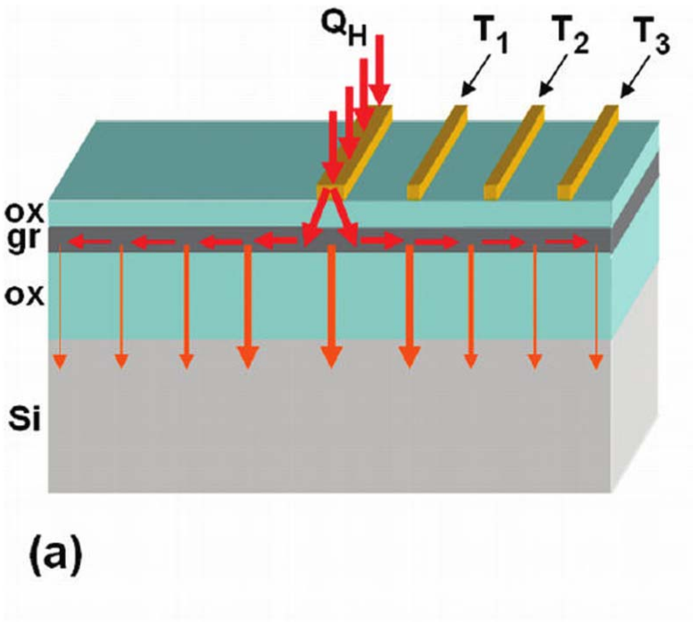
- High conductivity of suspended graphene

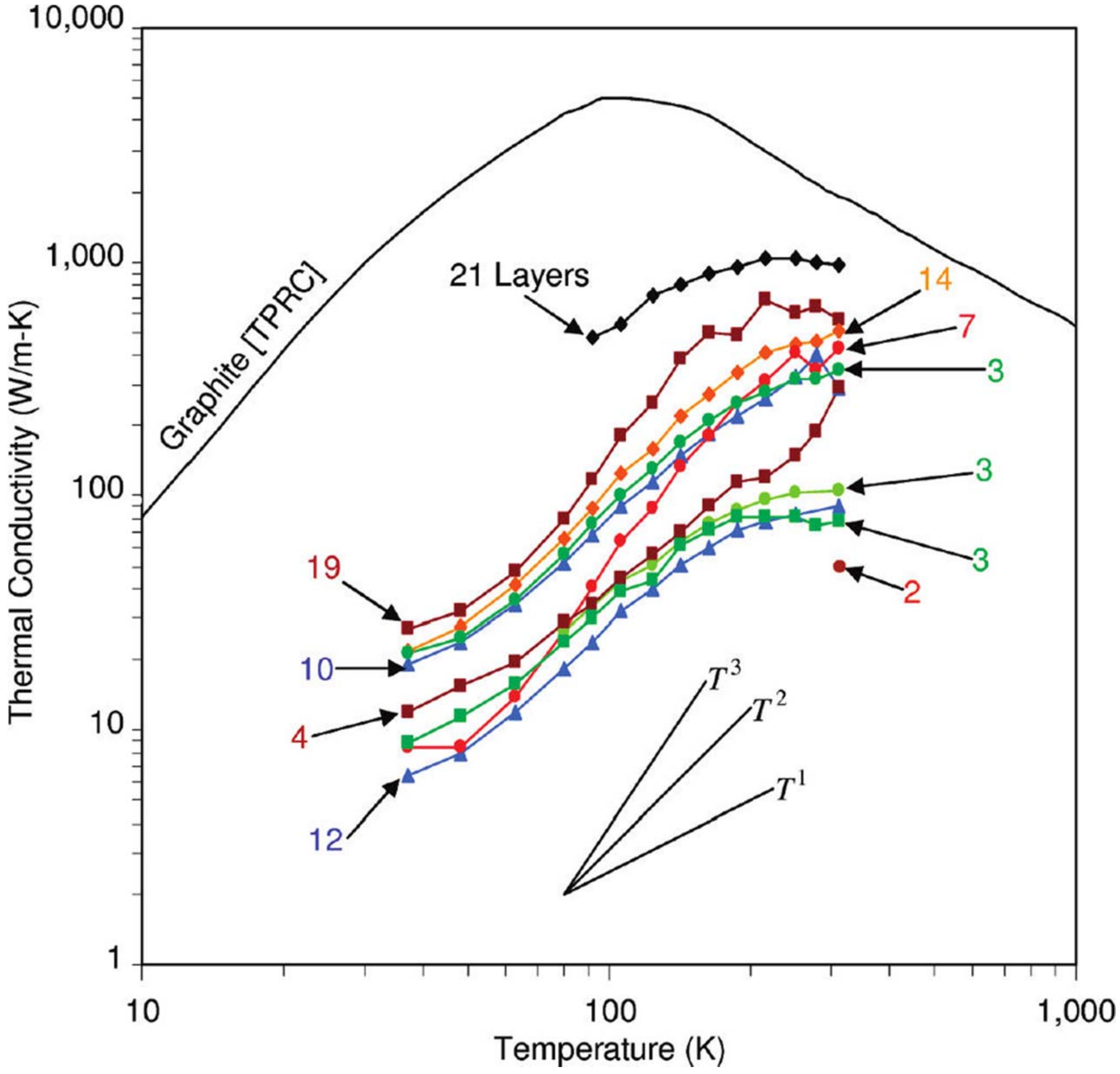




Balandin, Nature Materials (2011)

Significant reduction in conductivity for supported or "encased" graphene





Jang *et al*., Nano Lett. (2010)

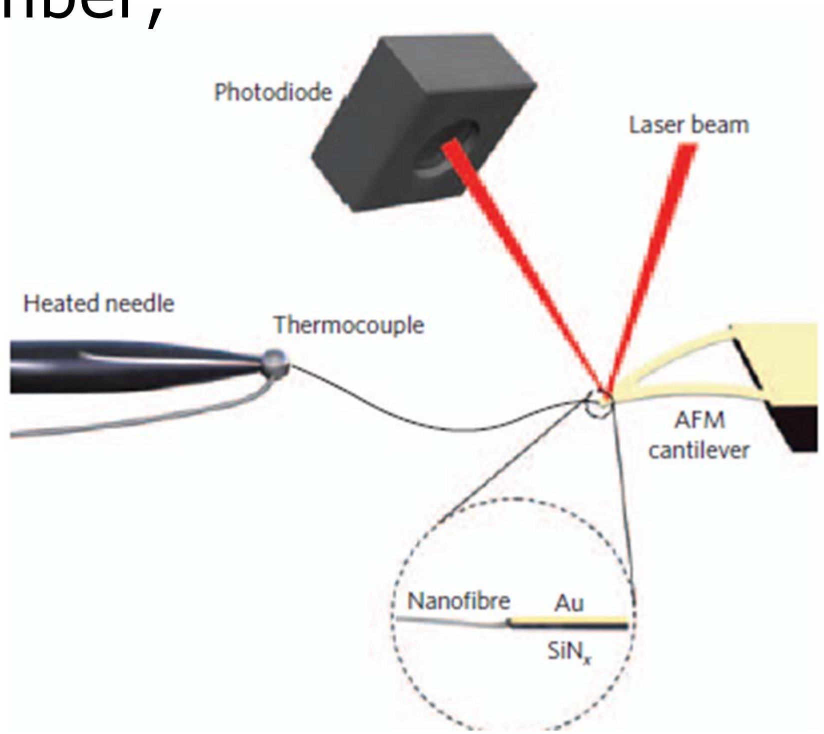
What are the limits to the conductivity of molecular structures?

- Fujishiro *et al*., Jpn. J. Appl. Phys. (1997) Dyneema polyethylene fibers

  60 W/m-K

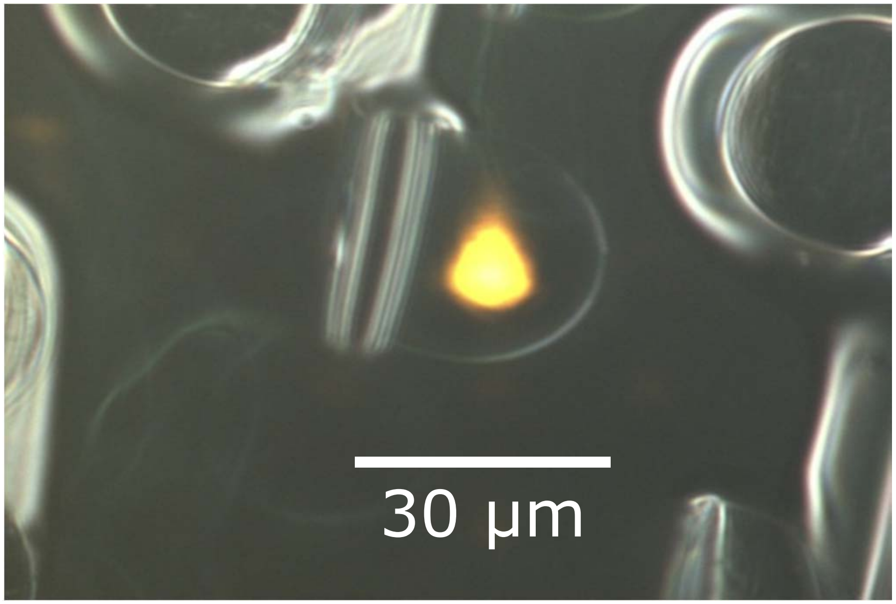
- Shen *et al*., Nature Nanotechnol. (2010) individual polyethylene nanofiber,

  100 W/m-K



High throughput measurements of polymer fibers by time-domain thermoreflectance

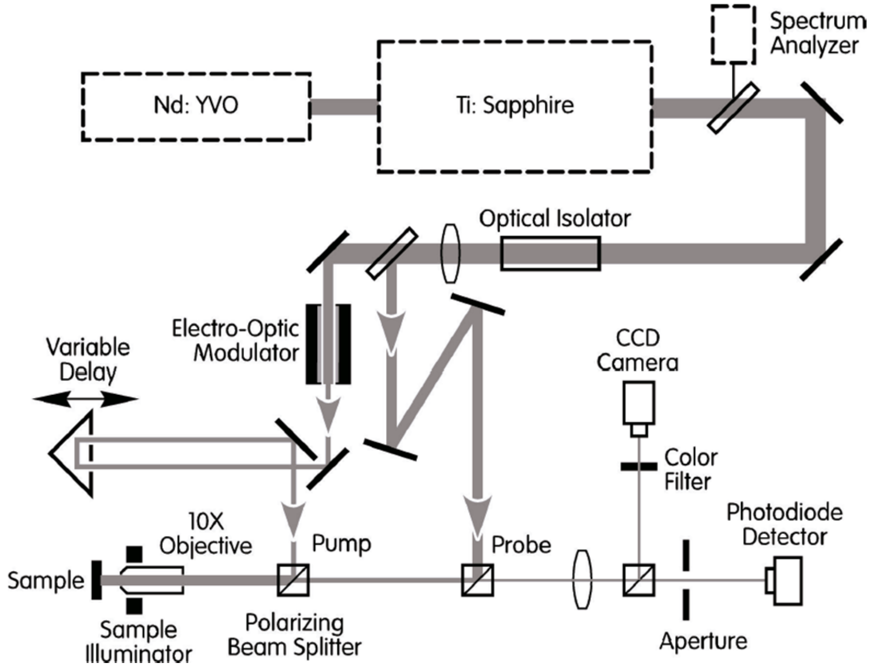
- Dyneema polyethylene fiber sold as “Samson Rope”
- Embed in epoxy and section with microtome to 500 nm thickness.
- Thermal conductivity varies but many fibers are ≈6 W/m-K

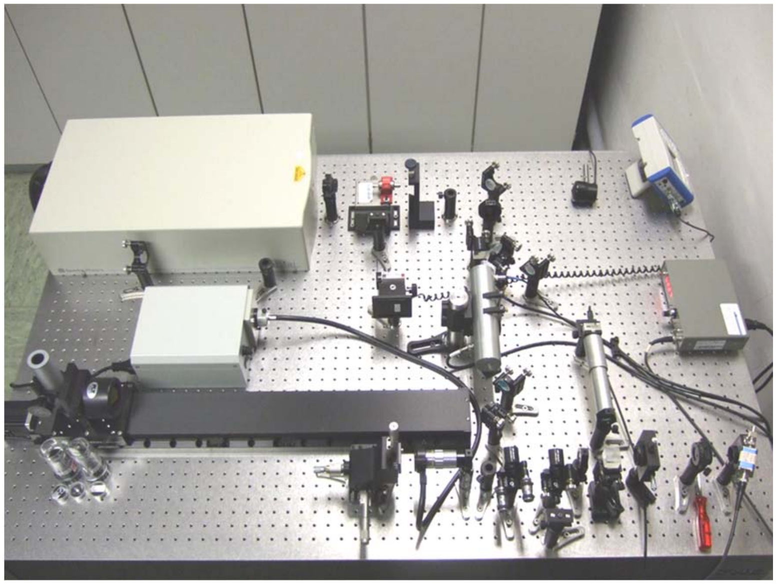


Li *et al.*, unpublished

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

Nothing new—use thermal waves to measure thermal transport—but nanoscale requires ultrafast

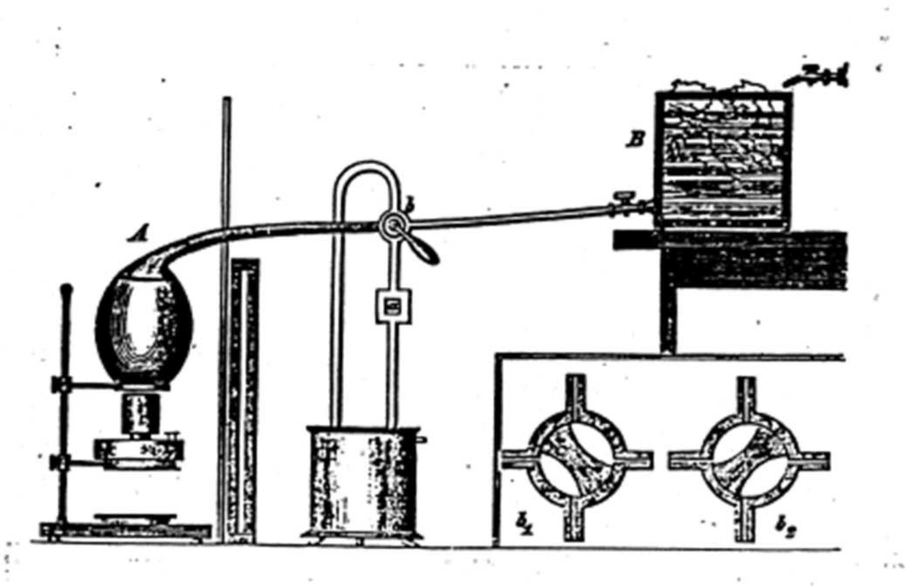
- For D=0.01 cm^2/sec heat diffuses…
    - 1 m in 1 month
    - 1 mm in 1 sec
    - 30 nm in 1 nsec

Ångstöm (1861) used fixed temperature boundary conditions:

$$T(x=0) = 0°\mathrm{C} \quad \text{for} \quad 0 < t < \Gamma/2$$

$$T(x=0) = 100°\mathrm{C} \quad \text{for} \quad \Gamma/2 < t < \Gamma$$

where Γ is the period of the temperature oscillations produced by alternating flow of ice water and steam.



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

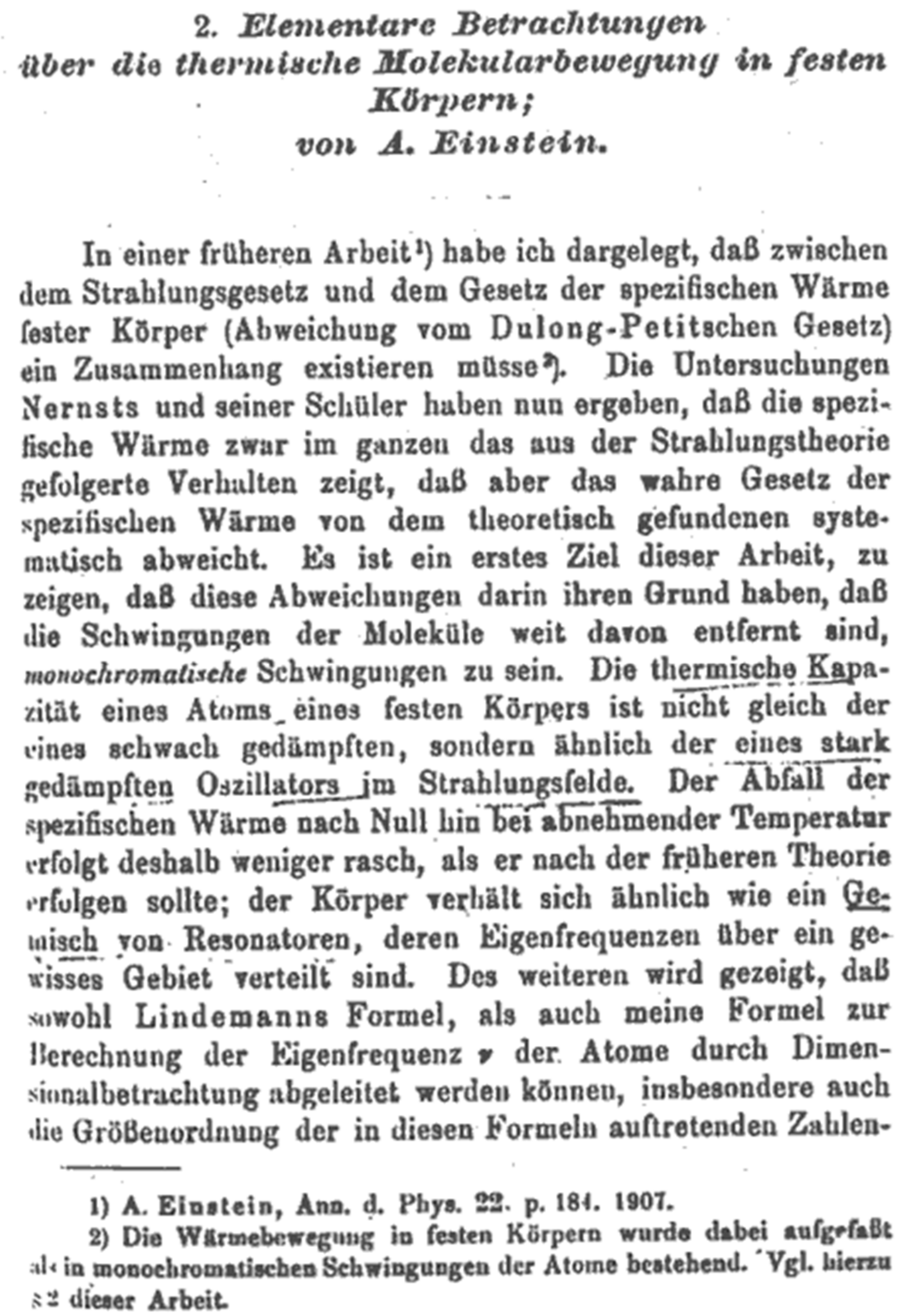
- Einstein (1911): random walk of thermal energy
- Not good for crystals: Debye (1914)
- but does work for amorphous solids, Birch and Clark (1940); Kittel (1948)
- and crystals with strong atomic-scale disorder, Slack (1979); Cahill and Pohl (1988).

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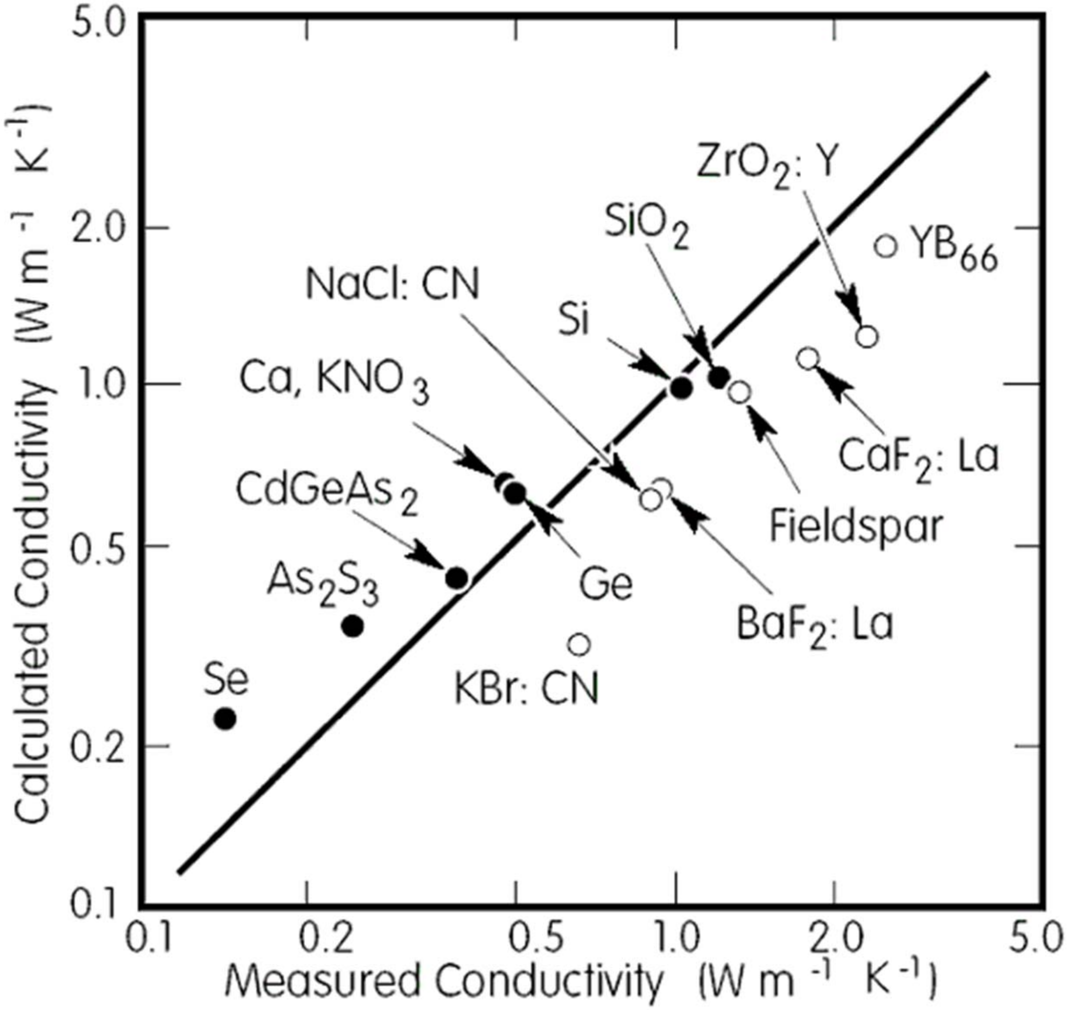
1) A. Einstein, Ann. d. Phys. 22. p. 184. 1907.

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

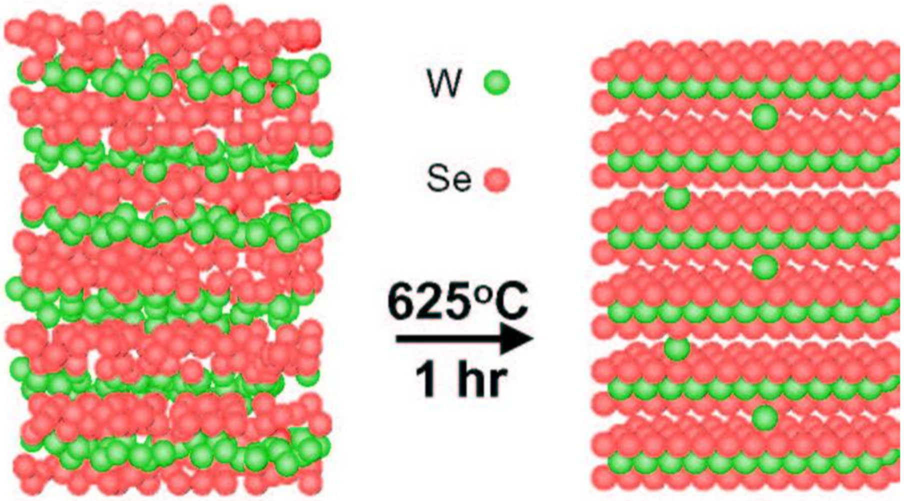
Works well for homogeneous disordered materials

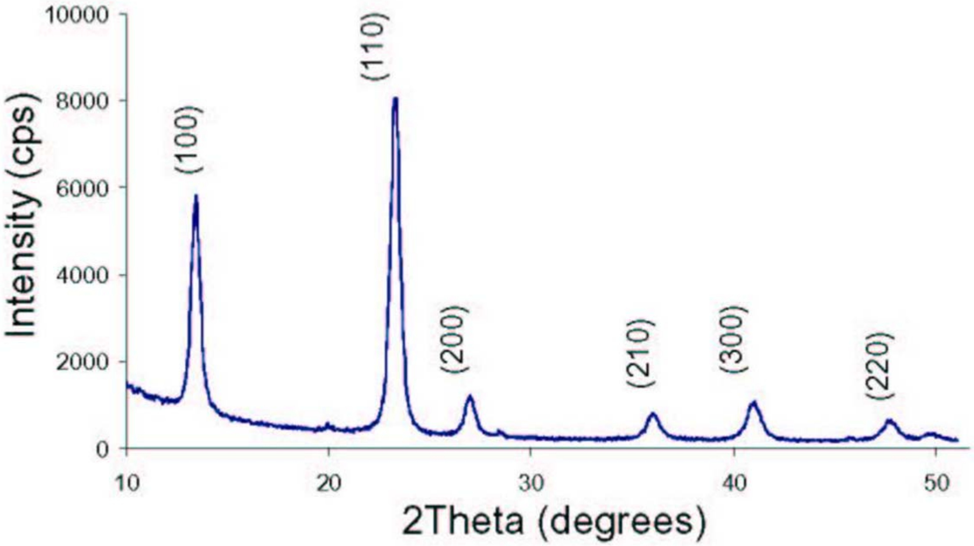


- ● amorphous
- ○ disordered crystal

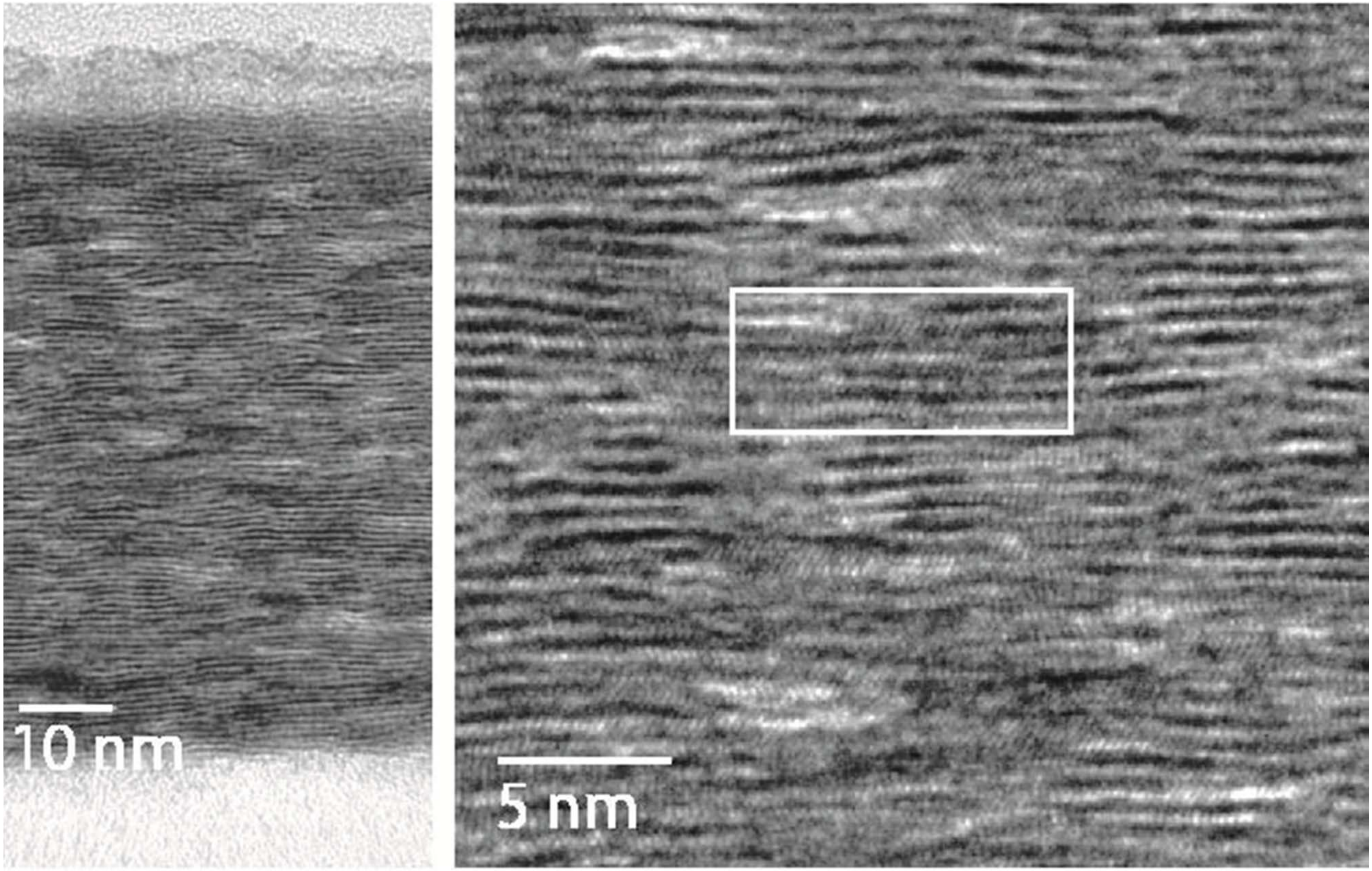
Layered disordered crystals: WSe_2 by "modulated elemental reactants"

- 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





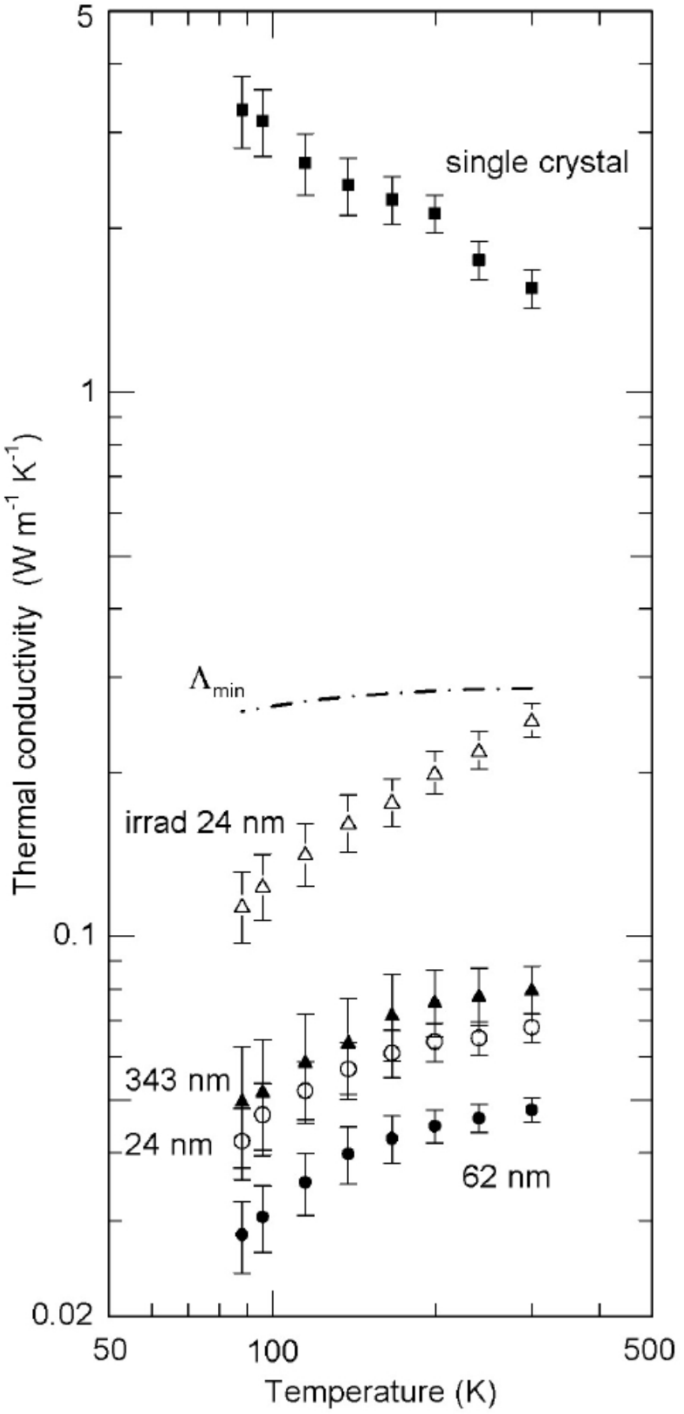
Cross-sectional TEM of 60 nm thick WSe_2



Seongwon Kim and Jian Min Zuo

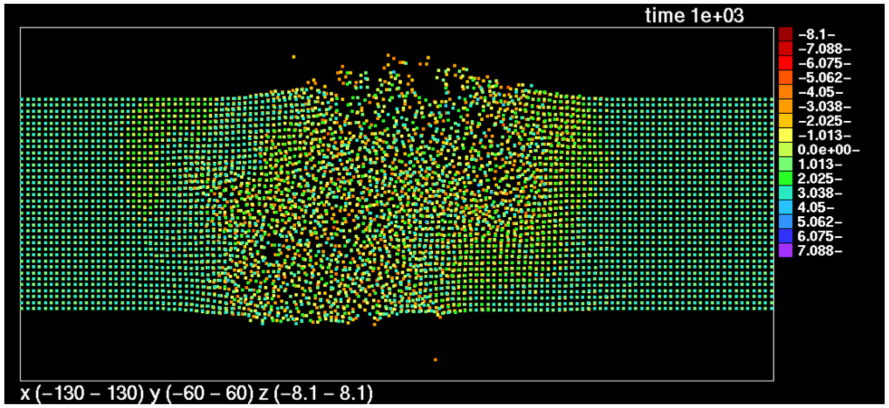
Thermal conductivity of WSe_2

- 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.

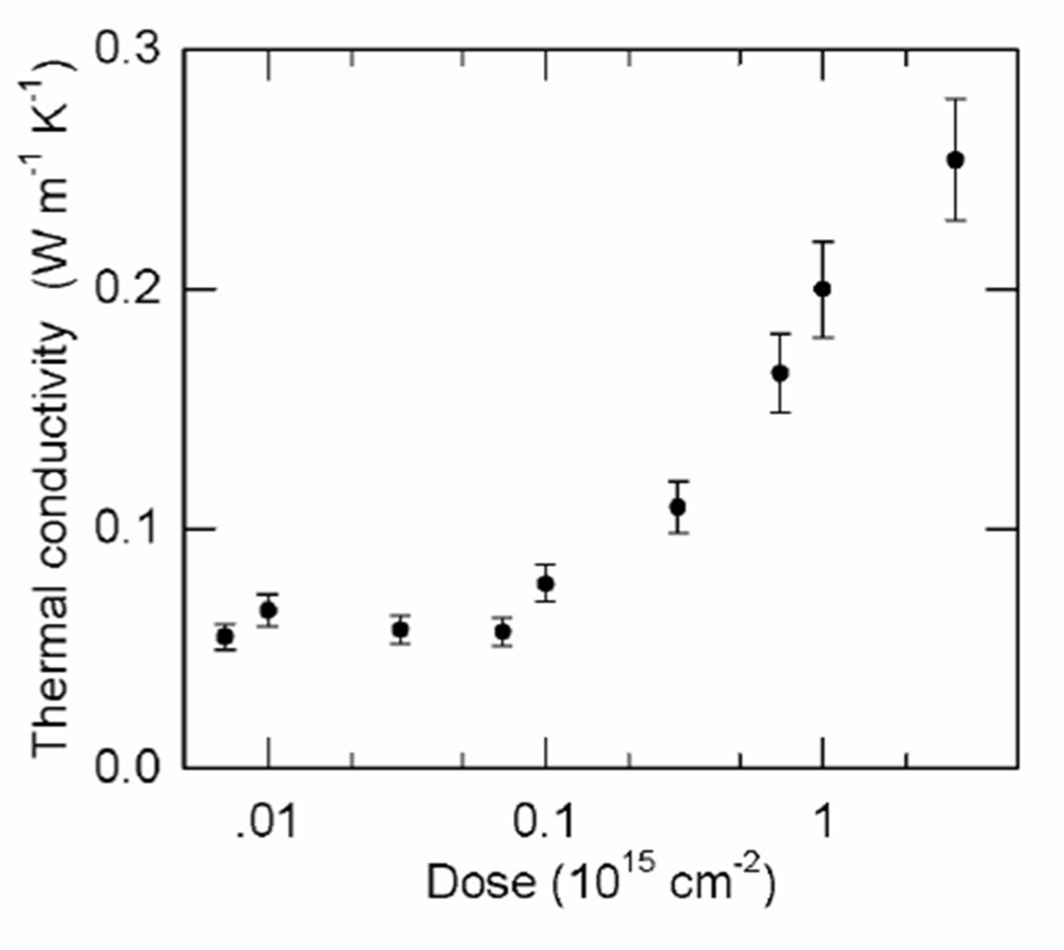


Ion irradiation of WSe_2

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.*



Extreme pressure provides a powerful method for probing the physics of heat conduction

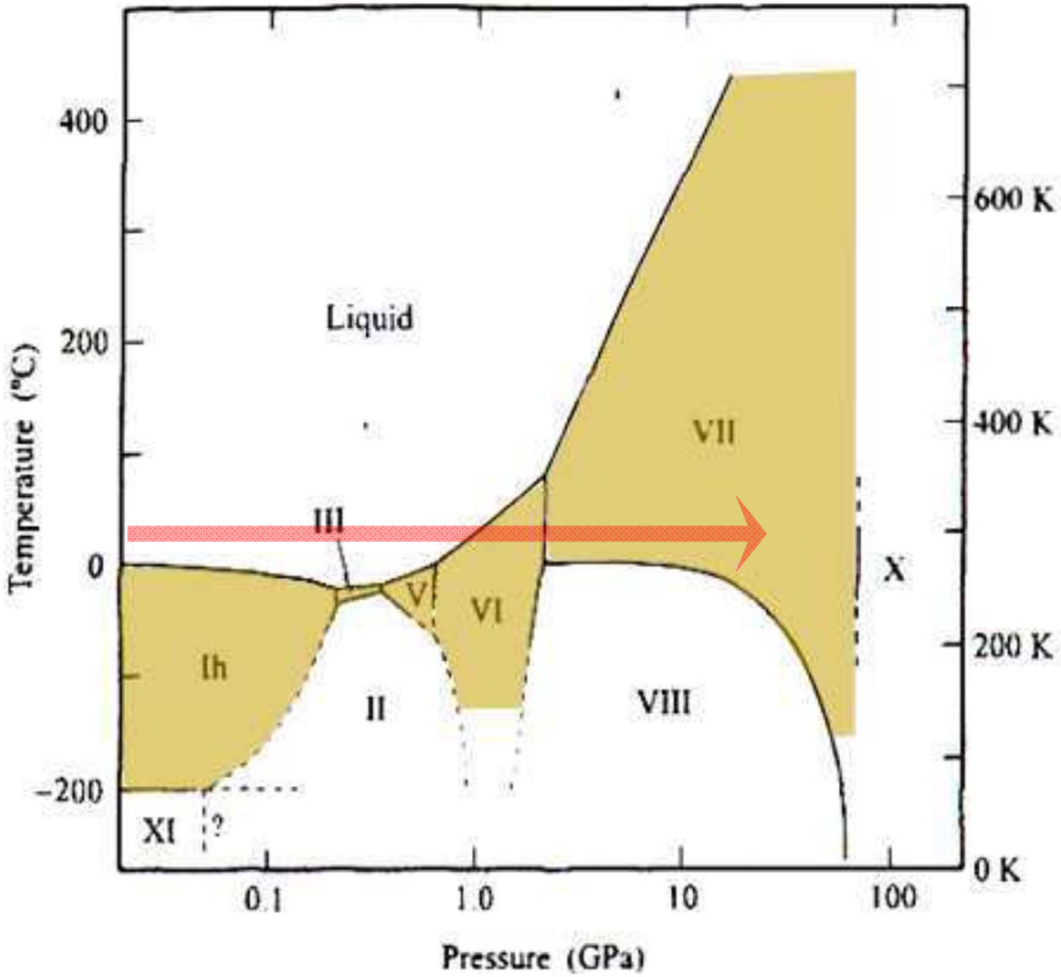
- Use high pressure (gem anvil cells) to modify phonon densities of states and lifetimes
- Measure the change in thermal conductivity by time-domain thermoreflectance (TDTR)
- Test classic models for heat conduction by phonons at high compression
  - Leibfried-Schlömann (LS) equation for perfect crystals
  - **water ice VII** is compressed by 33% at P=22 GPa.

Water ice has a remarkably rich phase diagram

1 atm=bar

1 bar=100 kPa

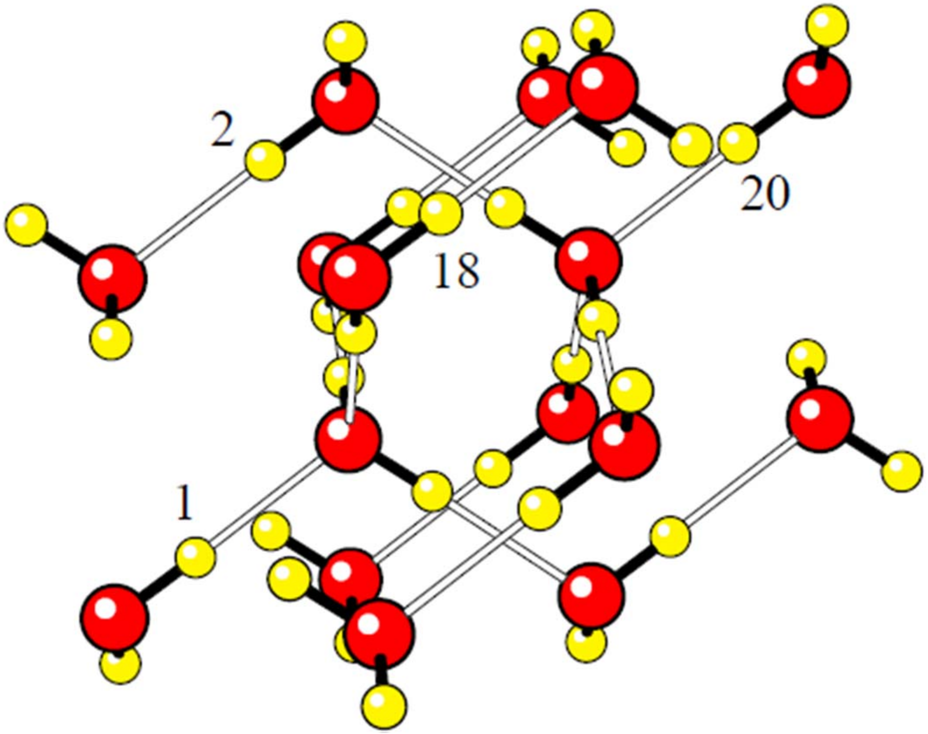
1 Mbar=100 GPa



Petrenko and Whitworth (1999)

Ice VII, cubic with two interpenetrating but not interconnected bcc sub-lattices

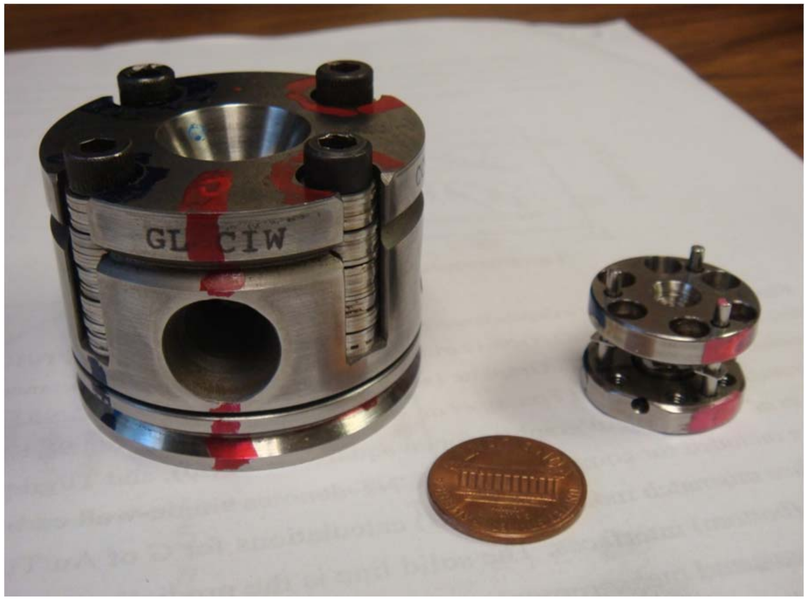
- Hydrogen-bonding in ice VII is disordered
- Ice VIII is the proton ordered form
- Ice X is thought to be "polymeric": H-bond is symmetric

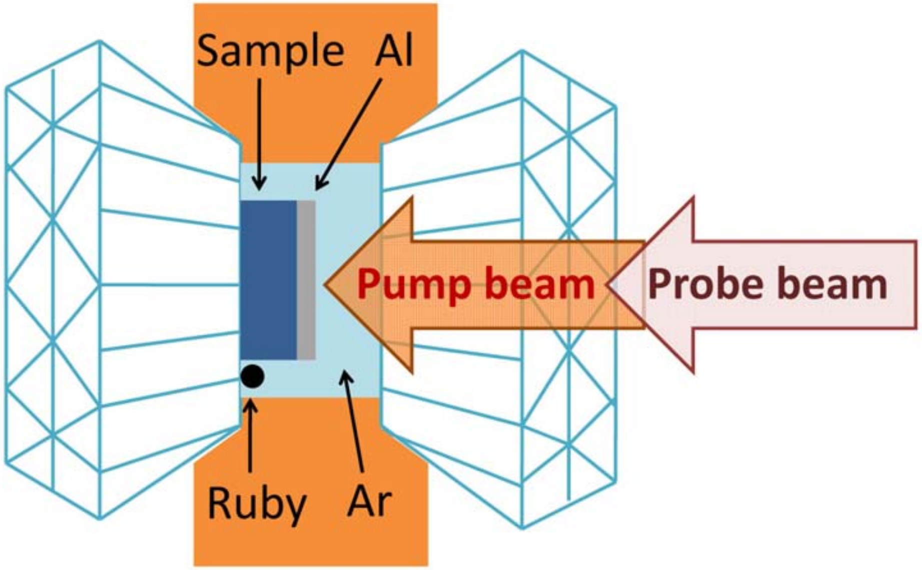


C.J. Knight, *Ph.D. thesis* (2009)

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

Diamond anvil cell





Measuring thermal conductivity of water ice VII

- Experimental details are complicated

1. coat thin mica substrate with Al
2. measure mica with Ar pressure medium
3. use published MD simulation of Ar thermal conductivity to analyze the data for mica
4. measure again with H_2O as the pressure medium
5. use density functional theory to calculate changes in H_2O heat capacity per unit volume
6. analyze the data
7. repeat...

For good crystals, accepted theory is complicated but should be correct if optical phonons are not too important

- Leibfried-Schlömann equation
  - acoustic phonons dominant heat carriers
  - three phonon anharmonic scattering between acoustic modes controls phonon mean-free-path

$$\Lambda = f\,\frac{V^{1/3}\omega_D^3}{\gamma^2 T}$$

$V =$ molecular volume

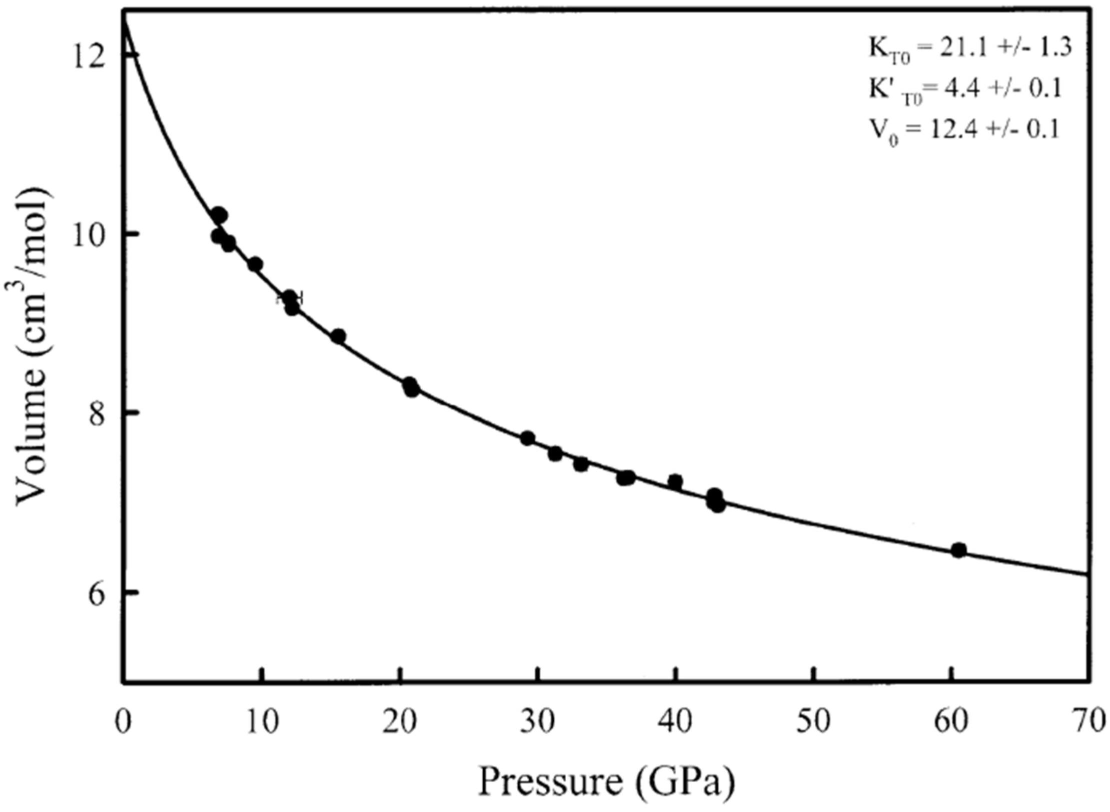
$\omega =$ Debye frequency

$\gamma =$ Grüneisen parameter

Derive changes in Debye frequency ω_D and Grüneisen parameter γ from equation of state.

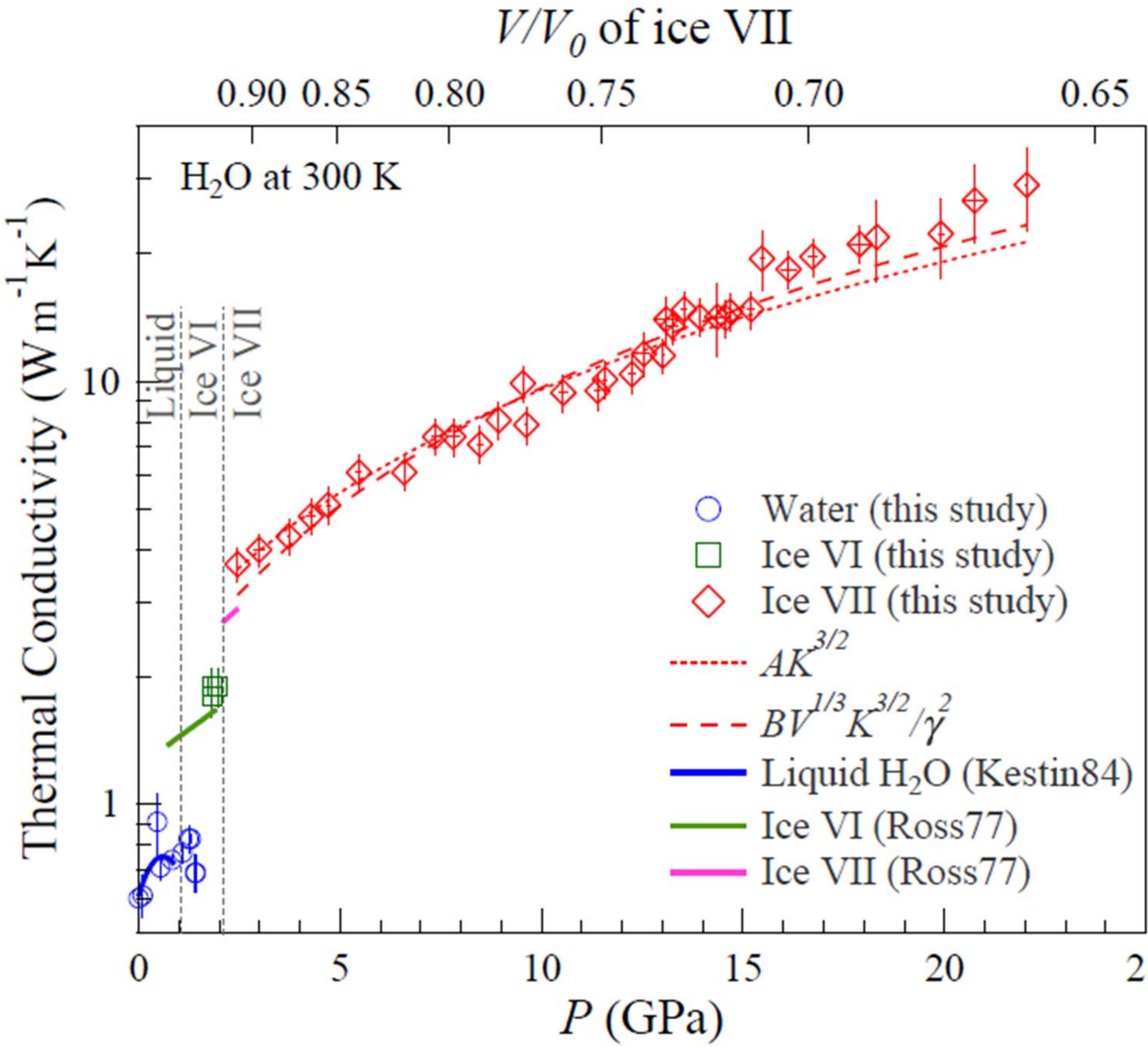
- Data for V(P) are fit to a model (e.g., Birch-Murnaghan)
- Assume ω_D scales with $K^{1/2}$
- γ is derived from a second derivative of the *V*(*P*) curve.

V(*P*) of ice VII by synchrotron x-ray diffraction



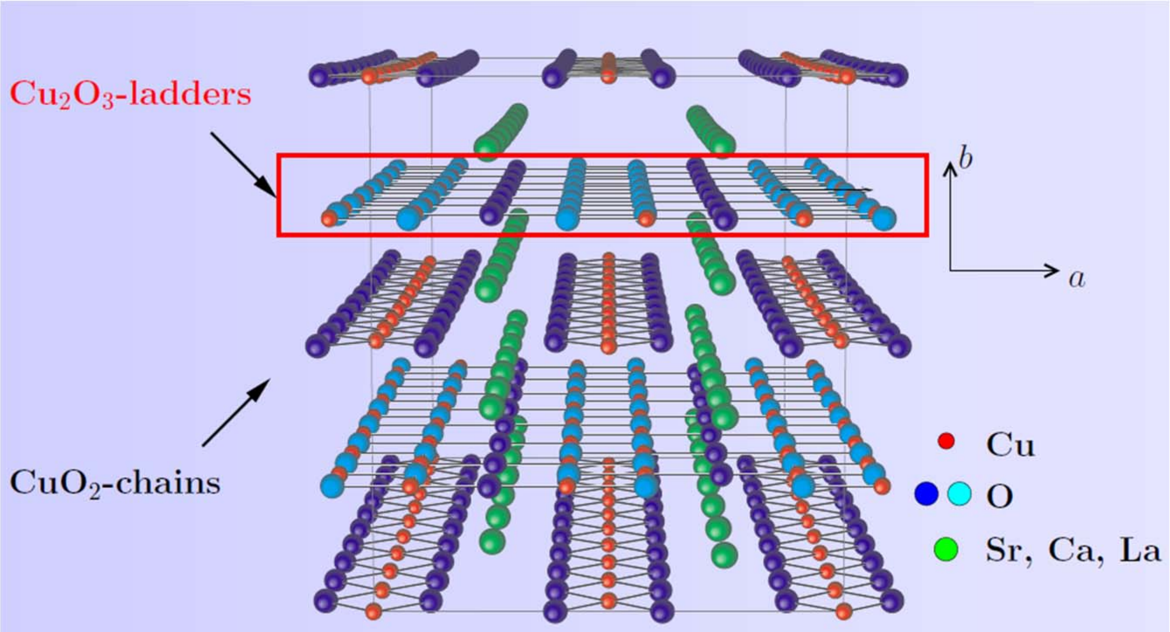
Frank *et al*., Geochimica et Cosmochimica Acta, 2004

Good agreement with LS equation over wide range of compression



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

- Electrons and phonons are usually all we care about
- Extremely high spin-wave conductivity in one-dimensional copper-oxide spin-ladders (Hess et al., 2001)
- Ultimate limits to this channel of heat conduction are not known

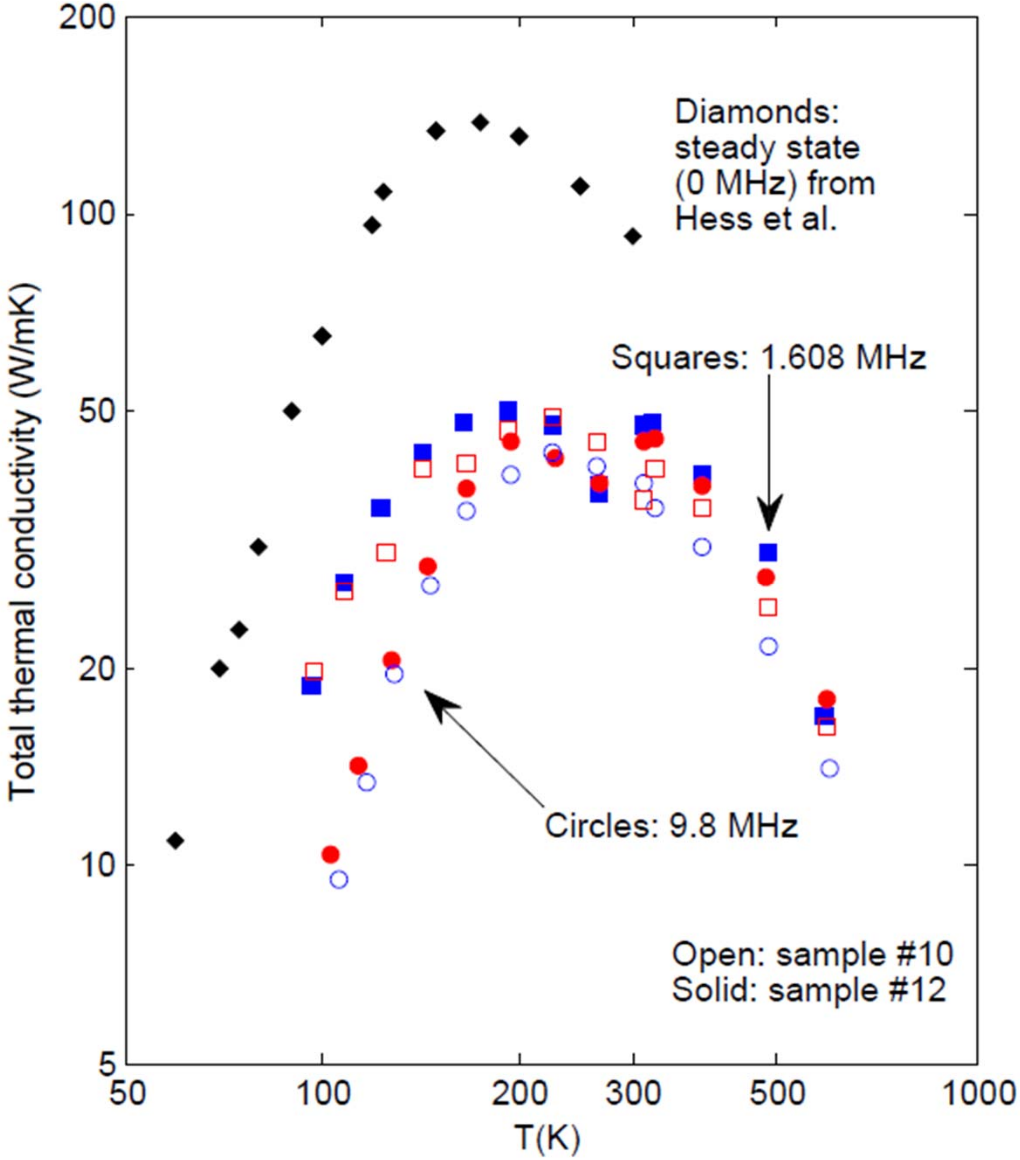


McCarron *et al.*, Mat. Res. Bull. (1988)

colorized graphic by Heidrich-Meisner (2005)

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

- Work in progress: use TDTR frequency dependence to probe magnon-phonon coupling



Hohensee *et al.*, unpublished

Big picture summary

- Ultrahigh thermal conductivity in carbon nanotubes and graphene
  - Difficult to make use of because nano is not always good: interfaces suppress conductivity and weak coupling to matrix limits performance of composites
- Time-domain thermal reflectance enables experiments (high spatial resolution, high pressure, ion irradiation damage) that were impossible a decade ago
  - Measurement of novel materials is no longer (in most cases) a research 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