Thermal unobtainiums?
The perfect thermal conductor and the perfect thermal insulator

David G. Cahill

Materials Research Lab and Department of Materials Science and Engineering, U. of Illinois

Gratefully acknowledge support from ONR and AFOSR

Outline—toward perfect thermal conductors

- Conventional conduction of heat in solids by phonons and electrons
  - phonon scattering mechanisms in dielectric crystals
  - metals
- Examples of unconventional heat conduction
  - Poiseuille flow of heat
  - ambipolar heat conduction
- Heat conduction in Bose condensates
  - electronic superconductors
  - superfluid helium
  - Bose condensate of magnons

Outline—toward perfect thermal insulators

- Einstein and minimum thermal conductivity
- Localization of lattice vibrations by disorder
- Beating the minimum with anisotropic disordered materials: disordered layered crystals

Conclude with some thoughts on promising, high-risk, research directions

Gas kinetic equation is a good place to start

$$\Lambda = \frac{1}{3}\int_0^\infty \frac{\mathrm{d}C}{\mathrm{d}\omega} v(\omega) l(\omega)\,\mathrm{d}\omega$$

- Anharmonicity (high T limit)

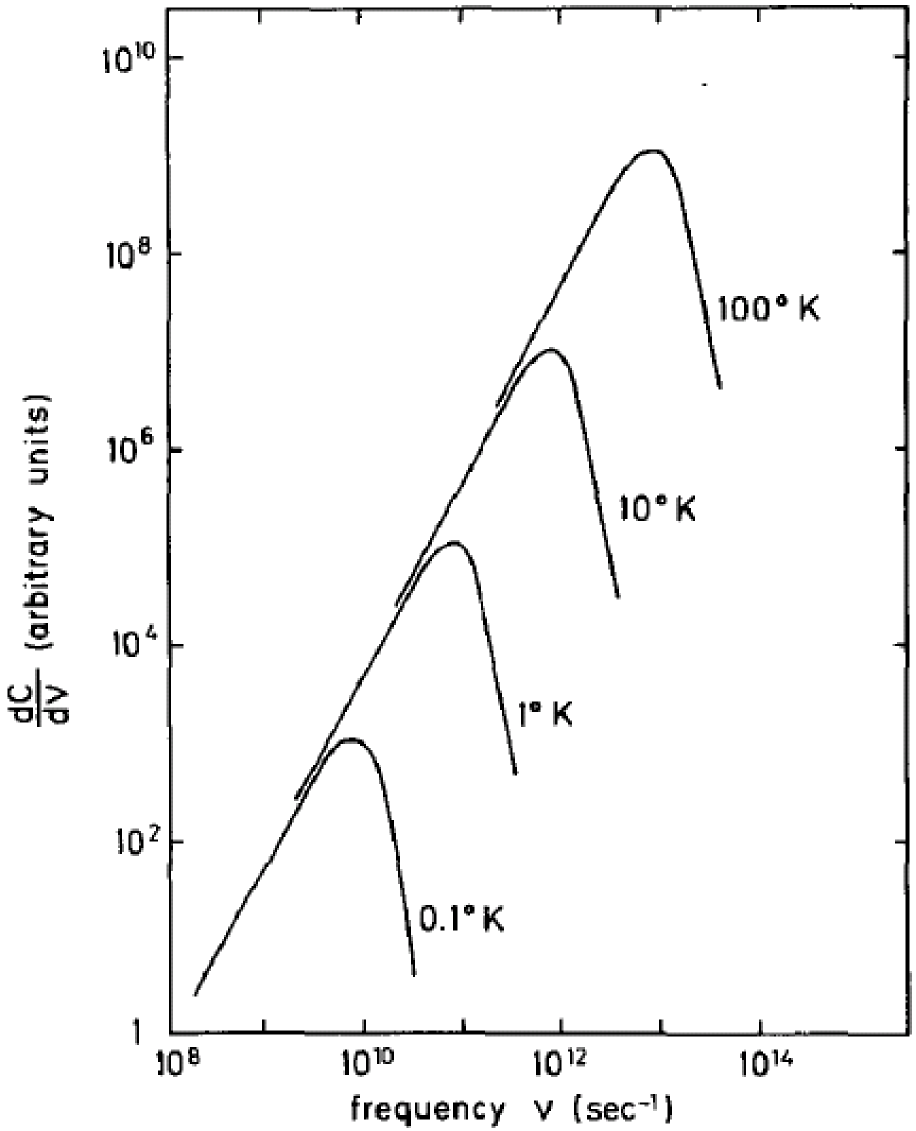
$$\tau^{-1} \propto \omega^2 T$$

- Point defect scattering

$$\tau^{-1} \propto \omega^4$$

- Boundary scattering

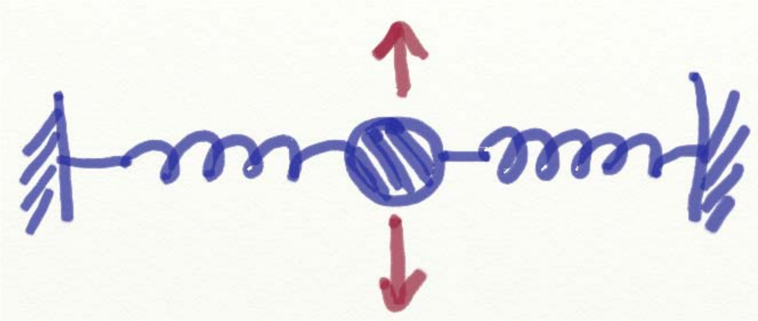
$$\tau^{-1} \propto 1/d$$

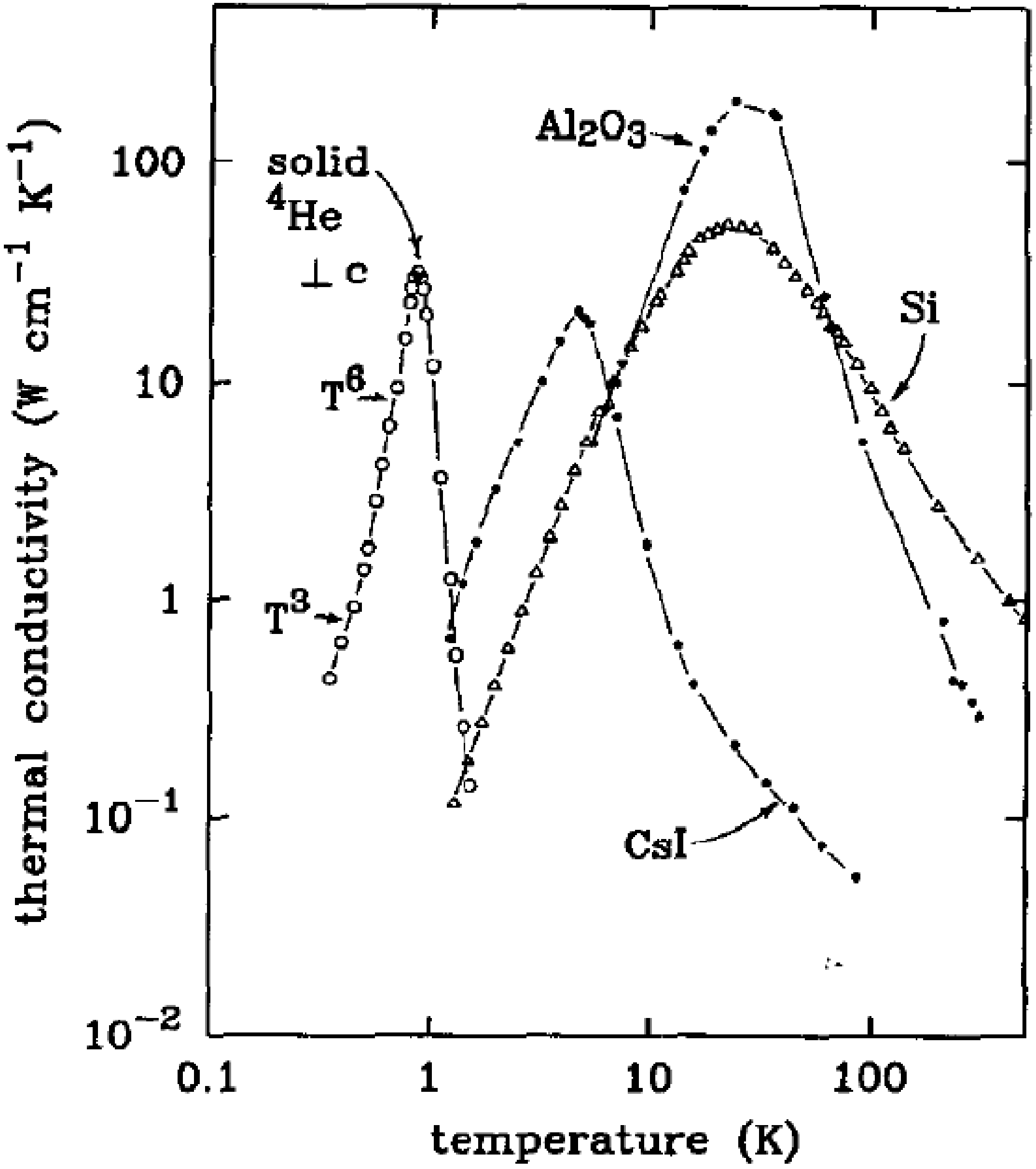


Cahill and Pohl, Ann. Rev. Phys. Chem. **39**, 93 (1988)

Peak occurs at T ~ Θ_{Debye} /30 in typical crystals

- Anharmonicity controls conductivity near room temperature.
  - – *k* is not a perfect quantum number
- Not possible (?) to eliminate anharmonicities even in a computer model.





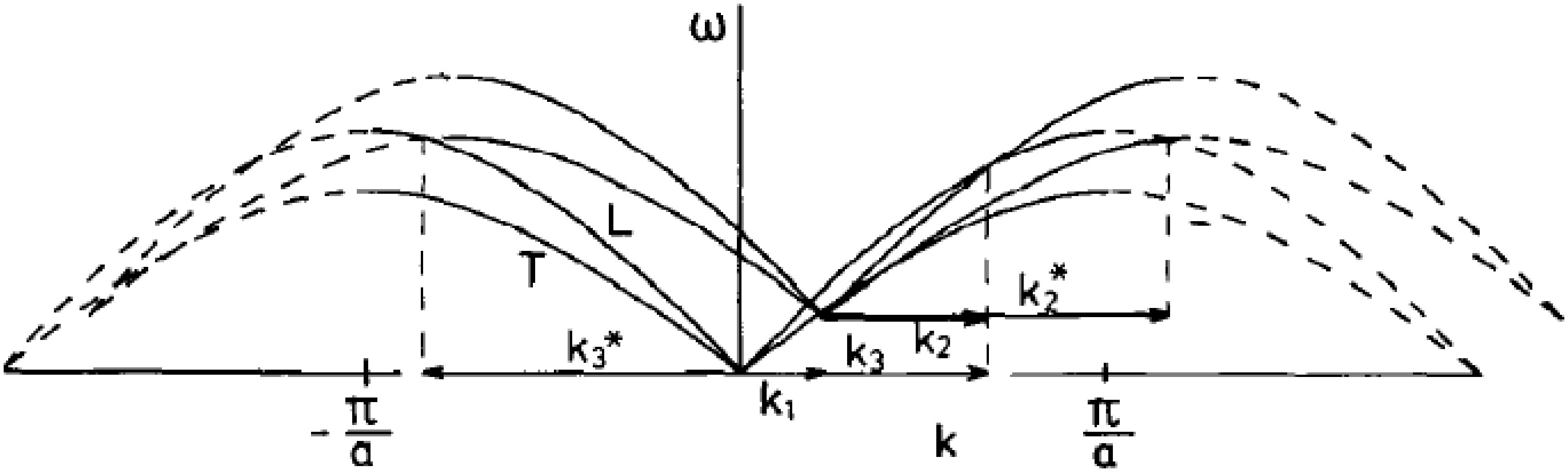
Thermal resistance is created by Umklapp scattering (U-process)

- Illustration gives examples of:

  N-process T+L → L

  U-process T+T → L

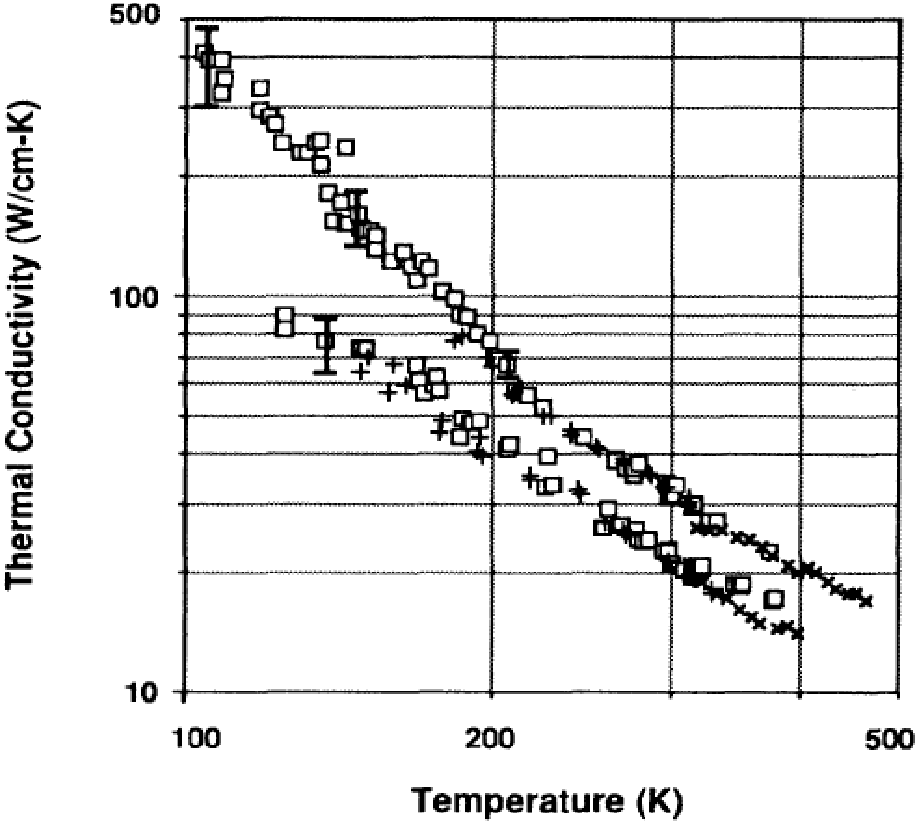
- Considerations of symmetry and dimensionality are subtle and complex, see Herring Phys. Rev. (1954).

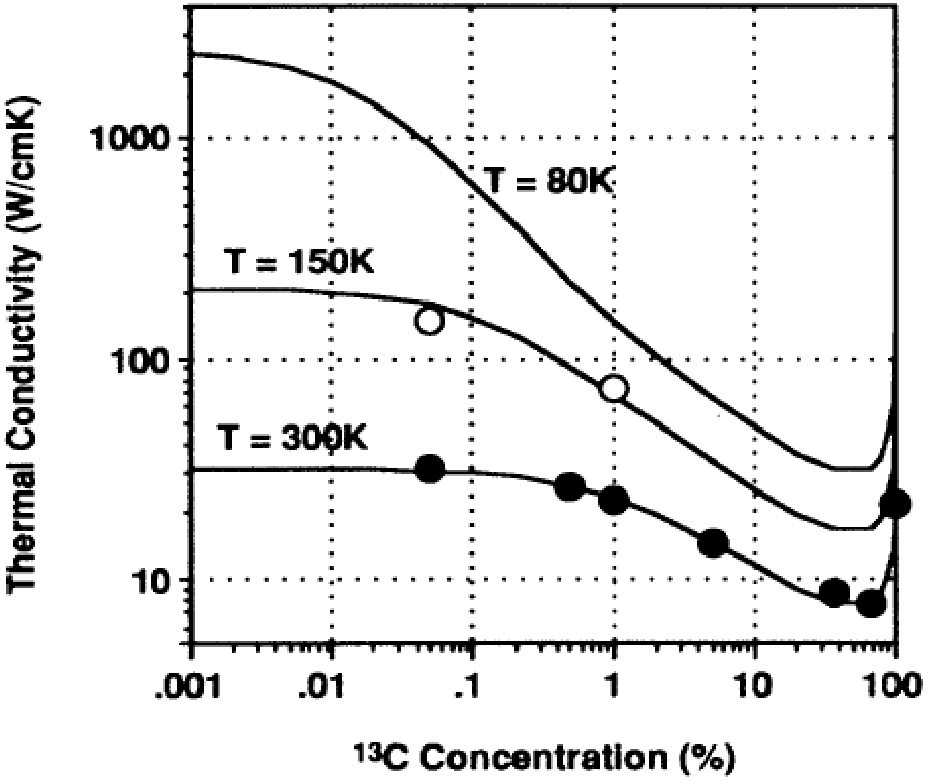


Peierls, Ann. Phys. **3**, 1055 (1929)

Isotopes contribute to thermal resistance

- Isotopically pure diamond has highest thermal conductivity of any material

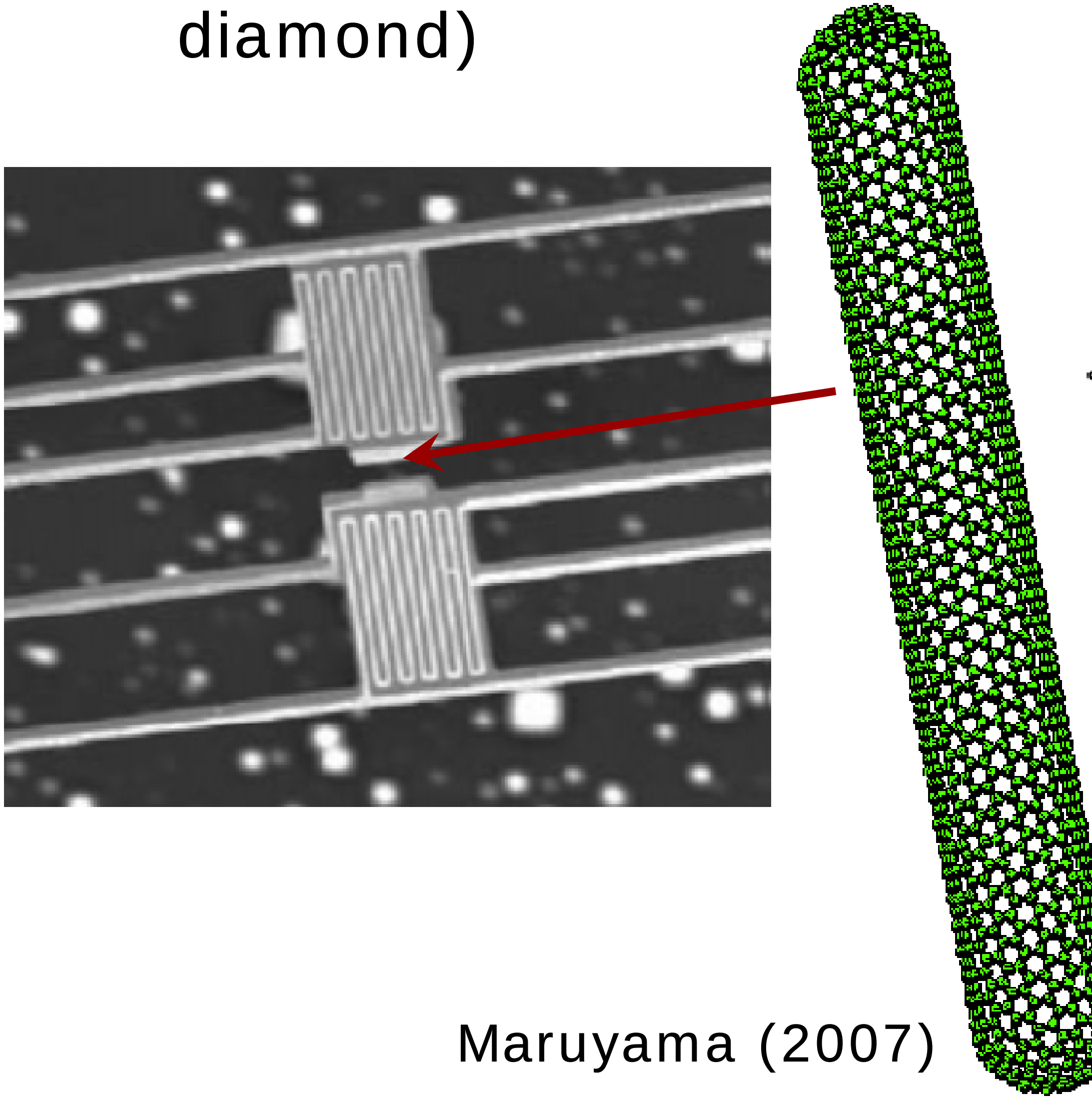




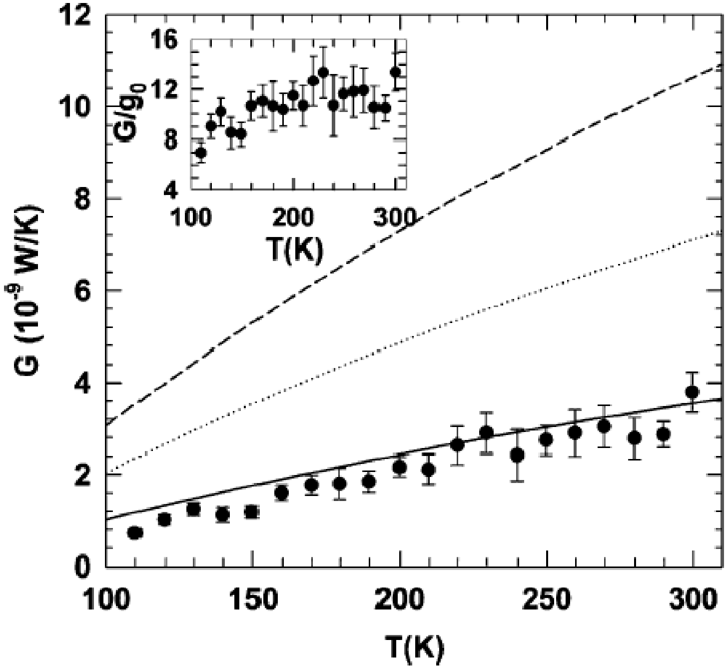
Wei *et al*., PRL **70**, 3764 (1993)

Carbon nanotubes

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



Maruyama (2007)

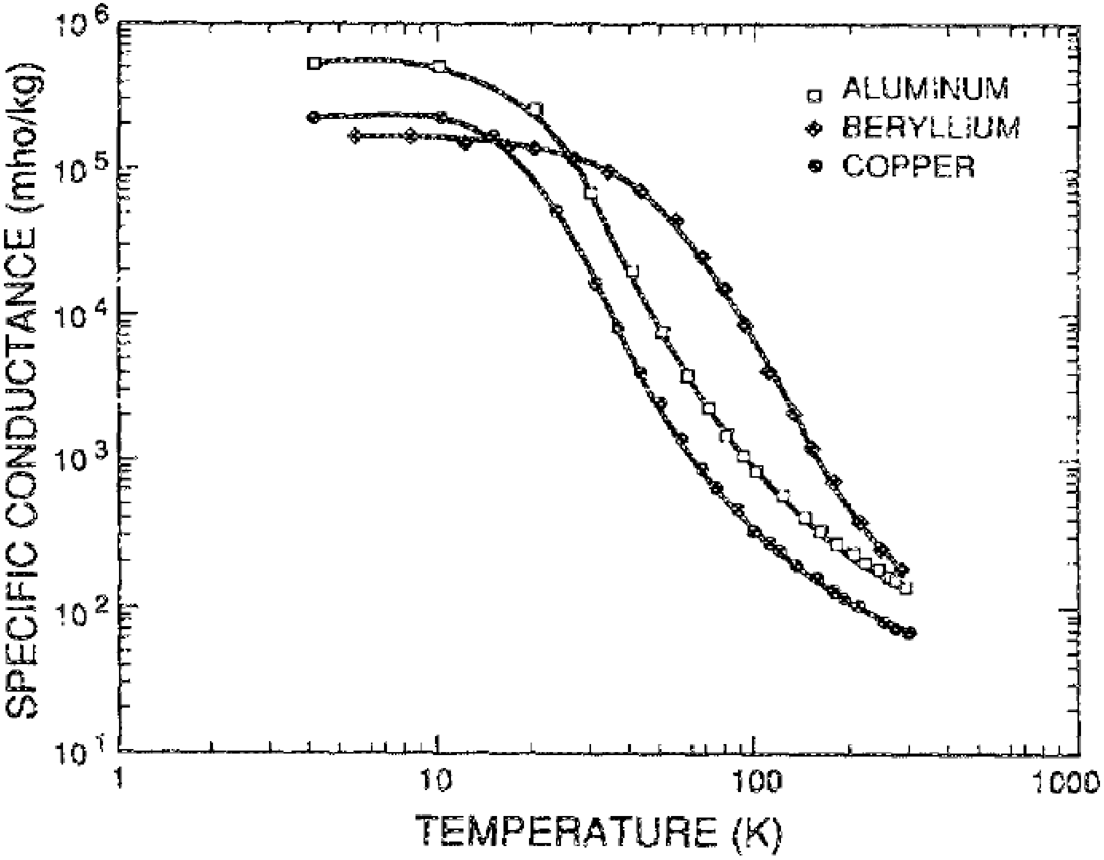


Yu et al. (2005)

High Debye temperature also produces high conductivity in metals

- Phonons disrupt the periodicity of the lattice
  - k is not a good quantum number
- Pure metals have high conductivity at low temperatures

$$\Lambda = L\sigma T$$



Mueller *et al*., APL **57**, 240 (1990)

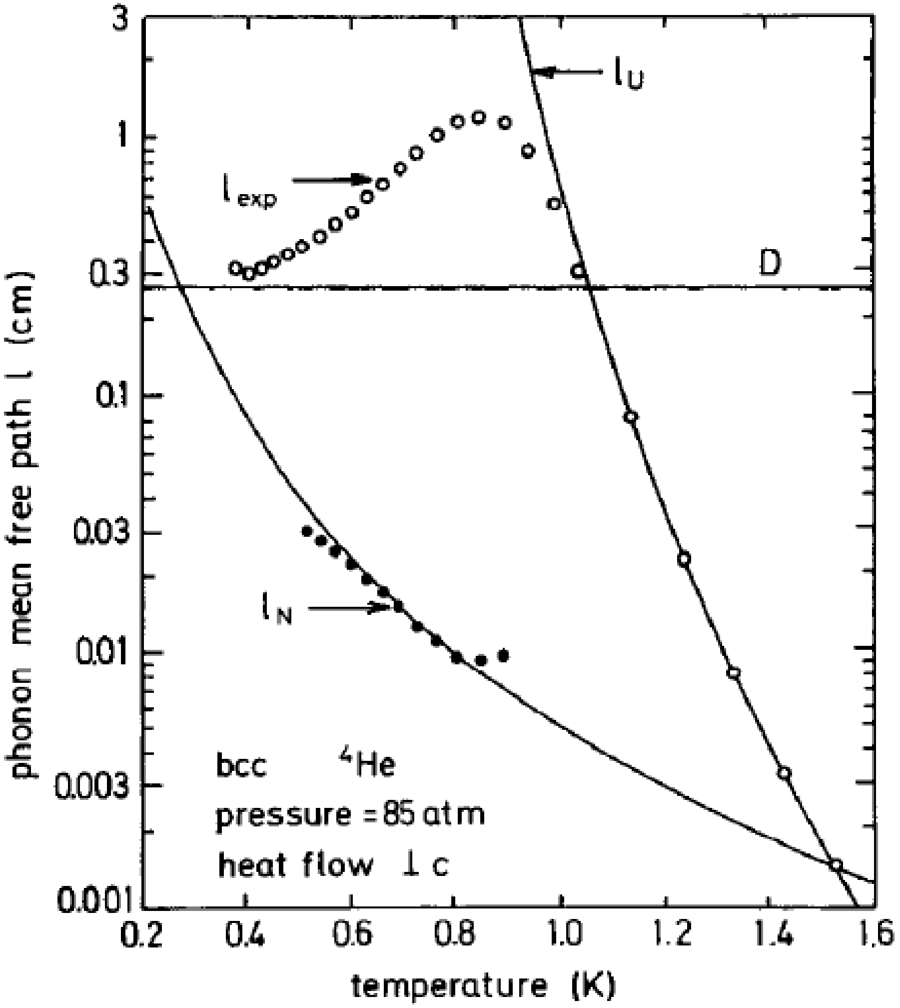
Unconventional heat conduction: Poiseuille flow of phonons

- Counter-intuitive: strong N-processes screen the interacting phonon gas from the boundaries of the crystal.
- Requires

$$l_U \gg r$$
$$l_N \ll r$$

$$\Lambda = \frac{1}{3}\frac{5}{8}C_v v \frac{r^2}{l_N},$$

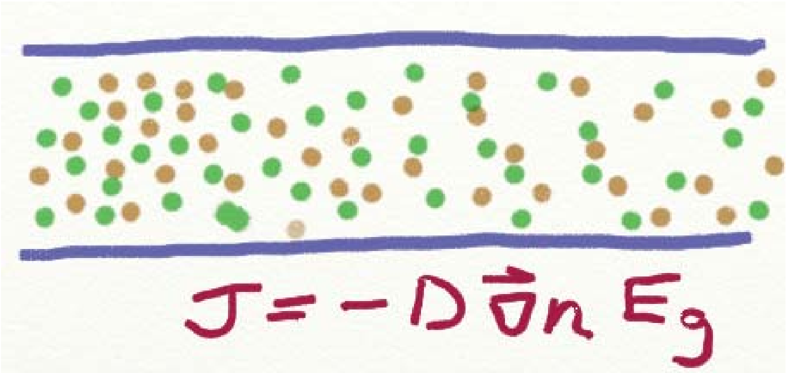
Limited to He crystals(?)



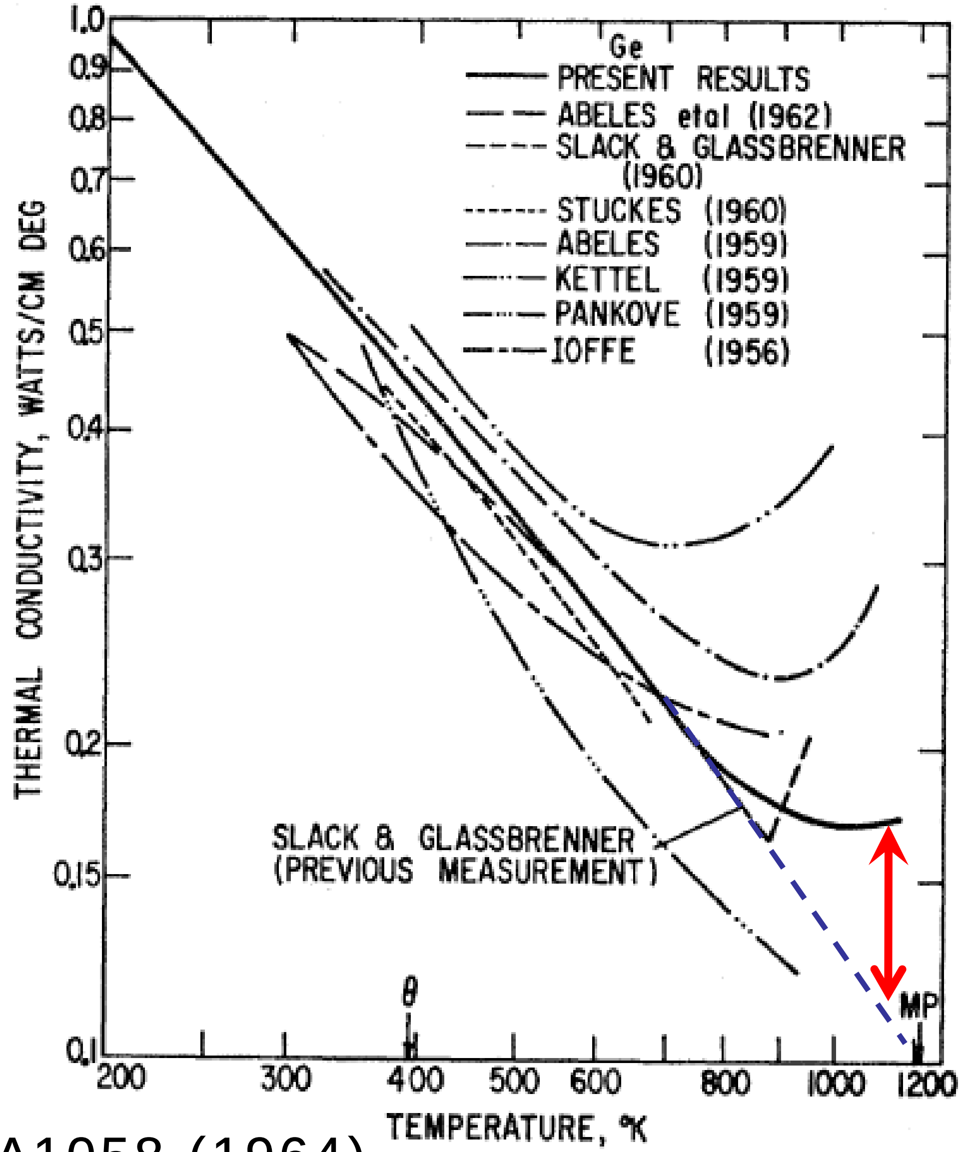
Hogan, Guyer, and Fairbank, PR 185, 356 (1969)

Ambipolar diffusion contributes to heat conduction.

- In an intrinsic semiconductor, e-h pairs diffuse from hot-to-cold, driven by the concentration gradient.
- Each pair carriers the band-bap energy (but no charge).



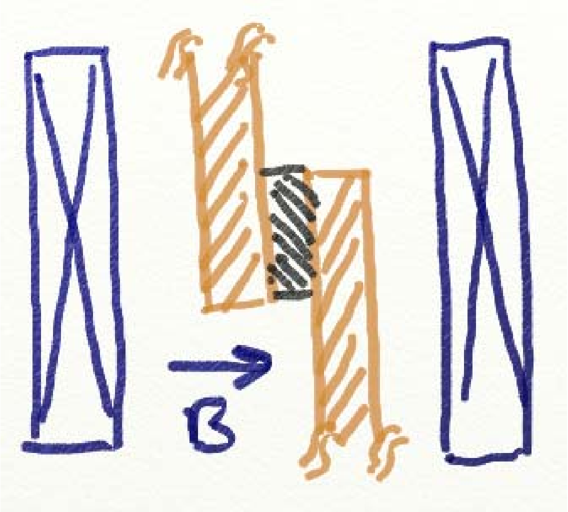
$J = -D \vec{\nabla} n E_g$

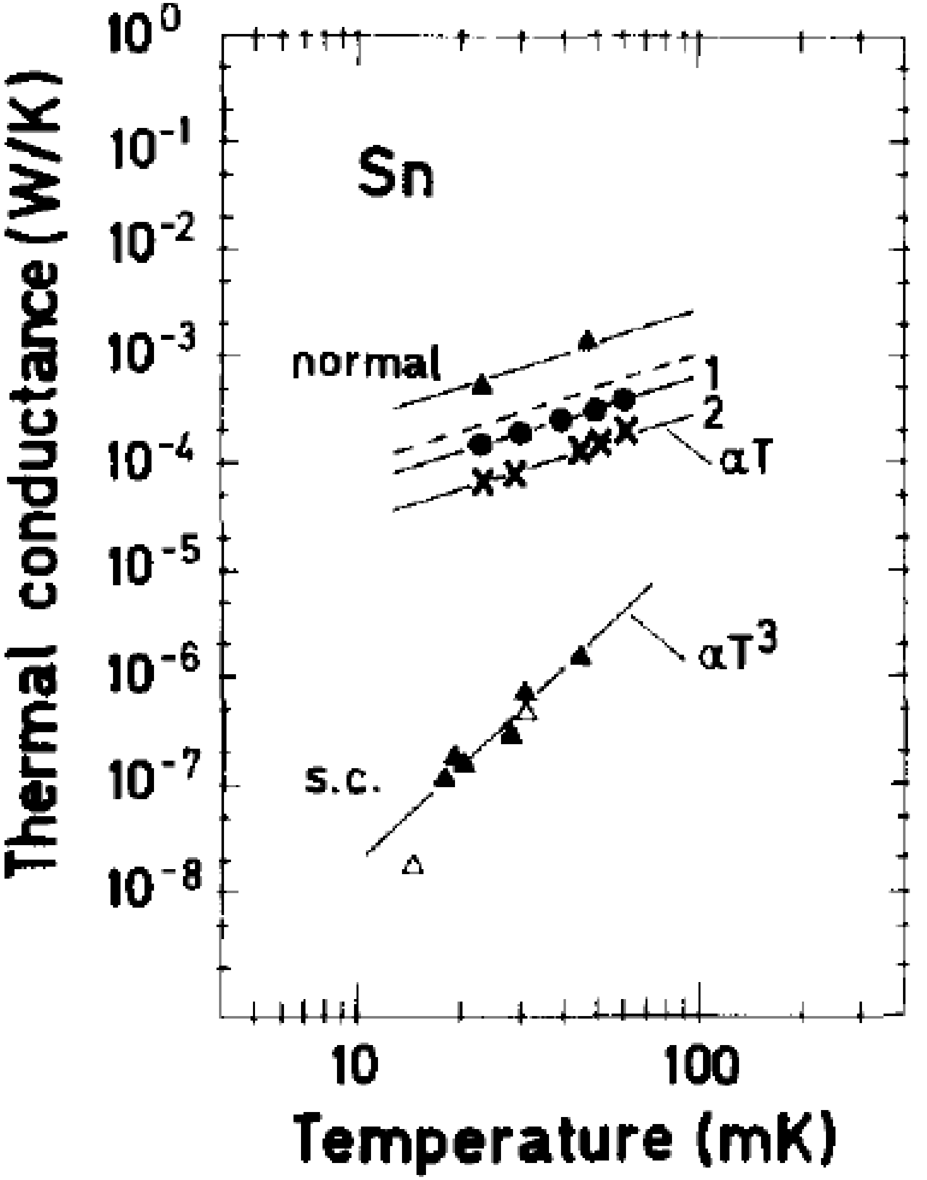


Glassbrenner and Slack, PR **134**, A1058 (1964)

Superconductors are an effective heat switch

- Strong magnetic fields quenches superconductivity.
- Normal electrons carry heat but Cooper pairs do not.

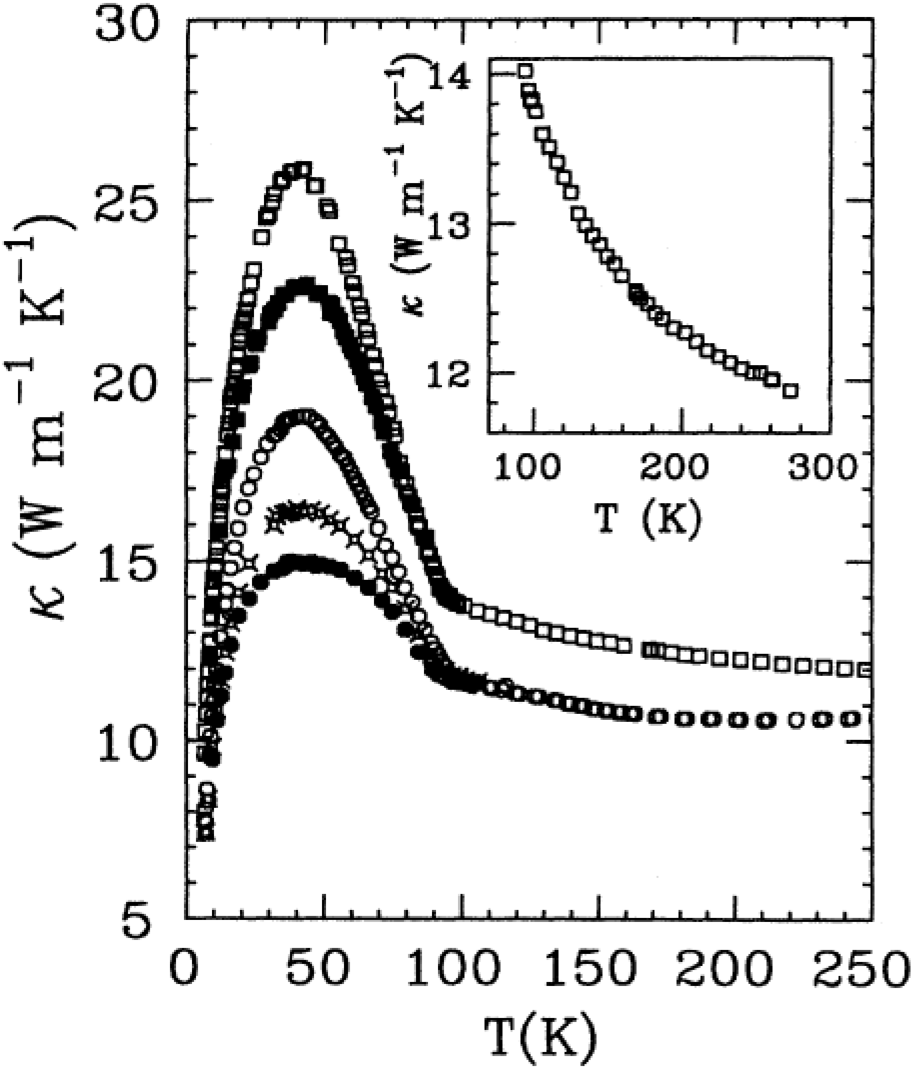




Schubert, RSI **55**, 1486 (1984)

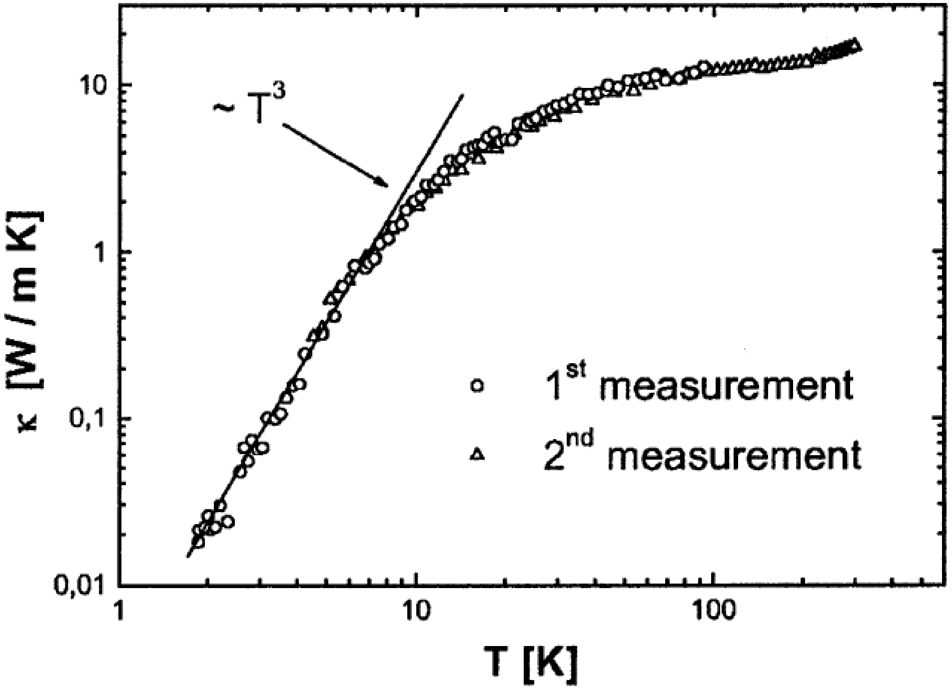
But unconventional metals show a variety of behavior

YBCO B-field dependence



Peacor, Cohn, Uher, PRB **43**, 8721 (1991)

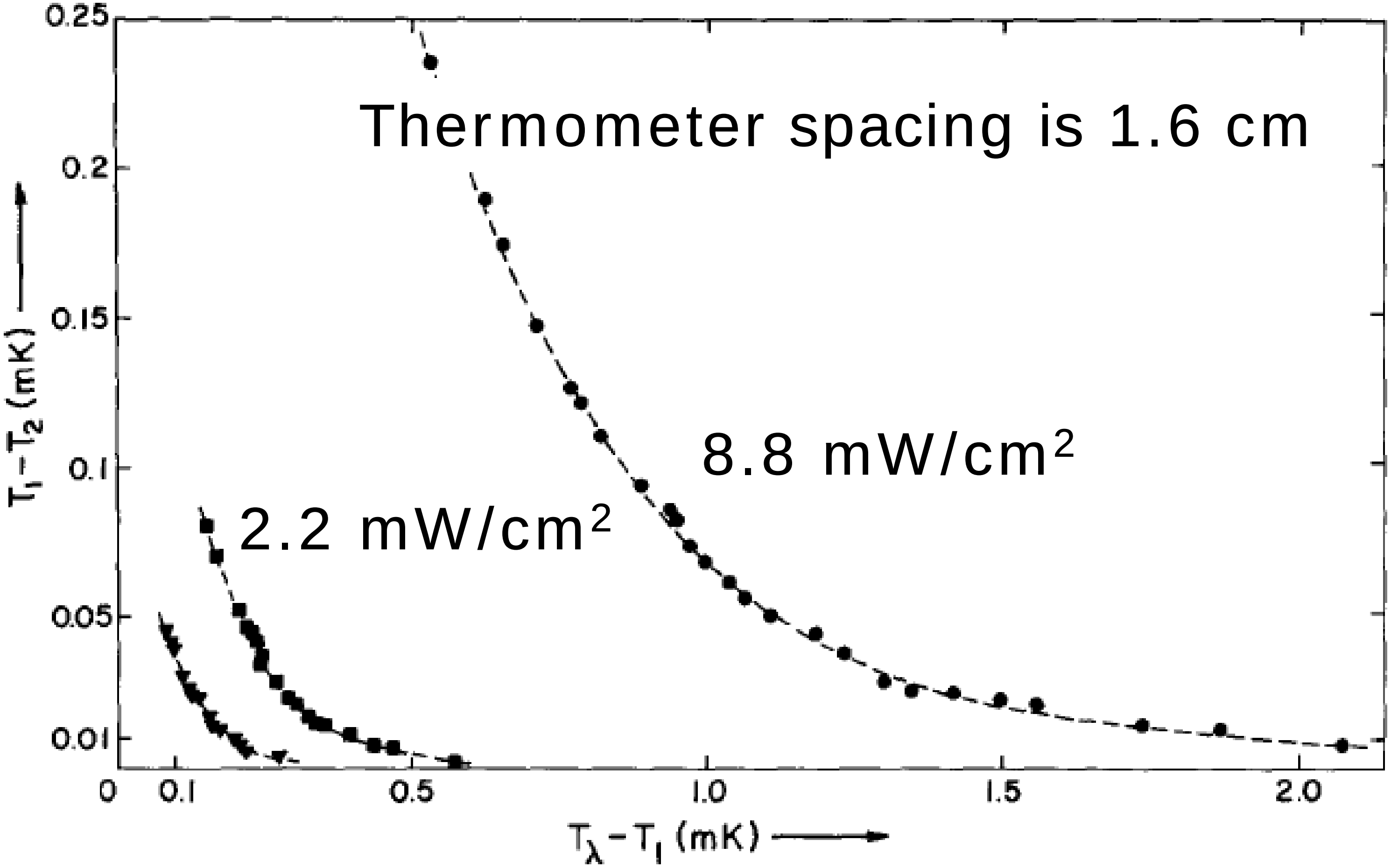
MgB$_2$



Schneider *et al.*,
Physica C **363**, 6 (2001)

Superfluid He near T_c has a conductivity comparable to Si at room temperature

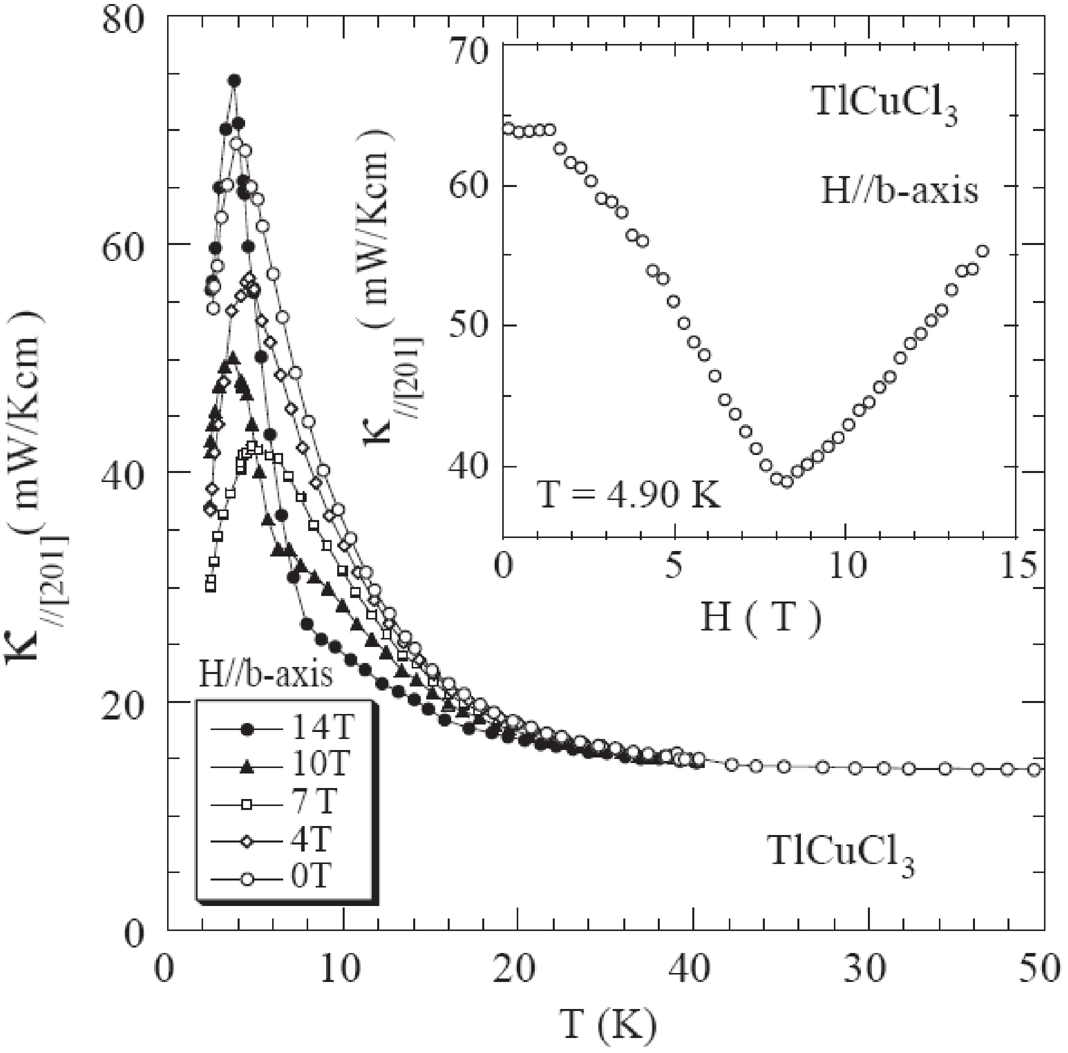
- Counter-flow of normal fluid and superfluid



Leiderer and Pobell, JLTP **3**, 577 (1970).

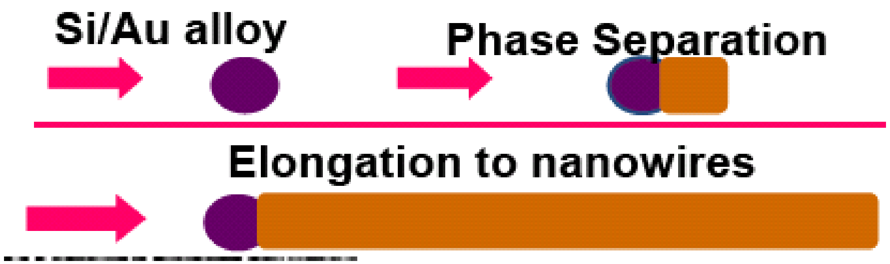
Could a solid-state Bose condensate show this superfluid behavior?

- magnons (quantized spin waves) are bosons.
- Do magnons Bose condense in an applied field?



Kudo et al., JMMM **272**, 214 (2004)

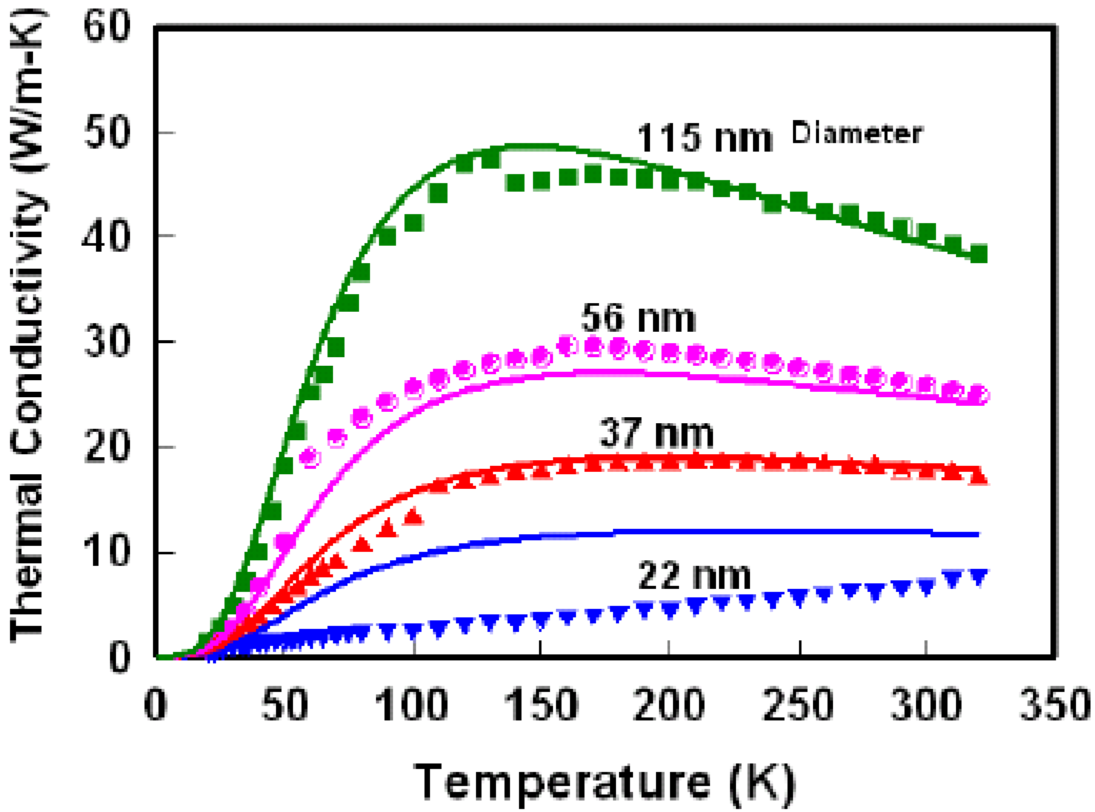
Produce low conductivity with nanoscale boundary scattering

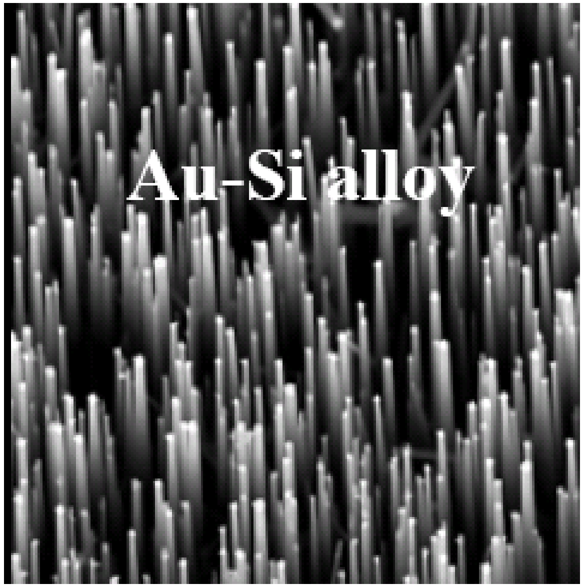


Si/Au alloy

Phase Separation

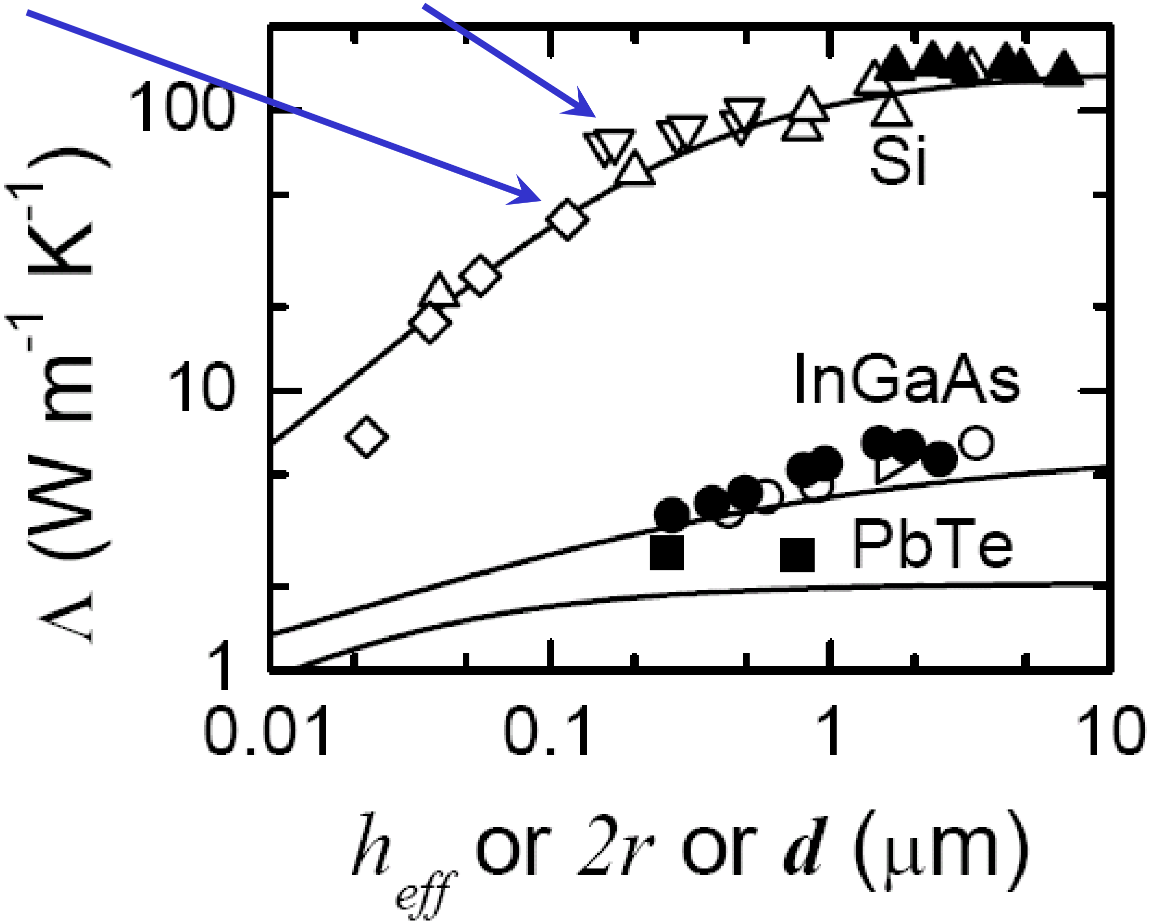
Elongation to nanowires





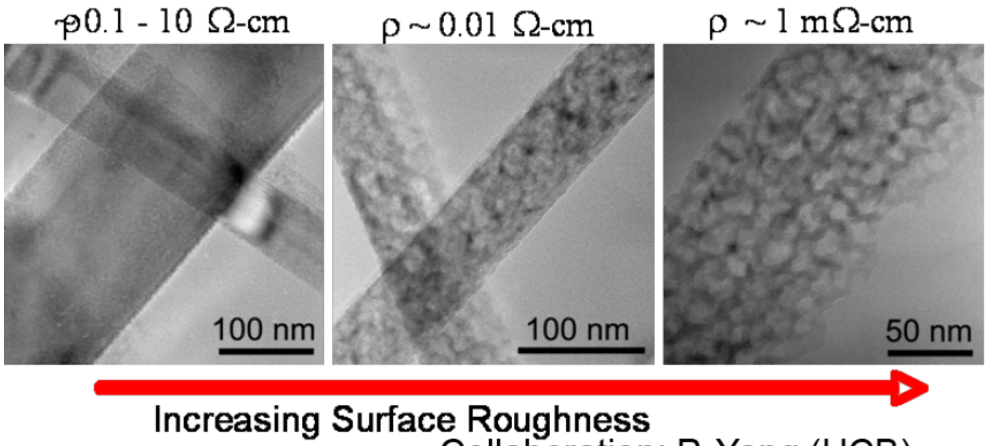
Nanoscale boundary scattering reduces the thermal conductivity

- Debye-Callaway-Morelli model
- Length-scale that reduces Λ by x2
    - Si: 300 nm
    - InGaAs: 200 nm
    - PbTe (predicted) 15 nm

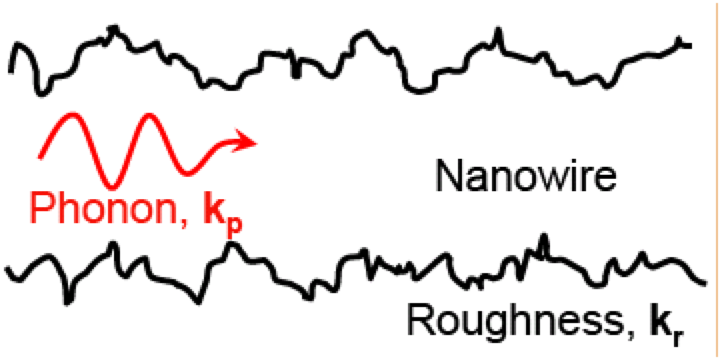

Compilation of data for Si nanowires and thin films

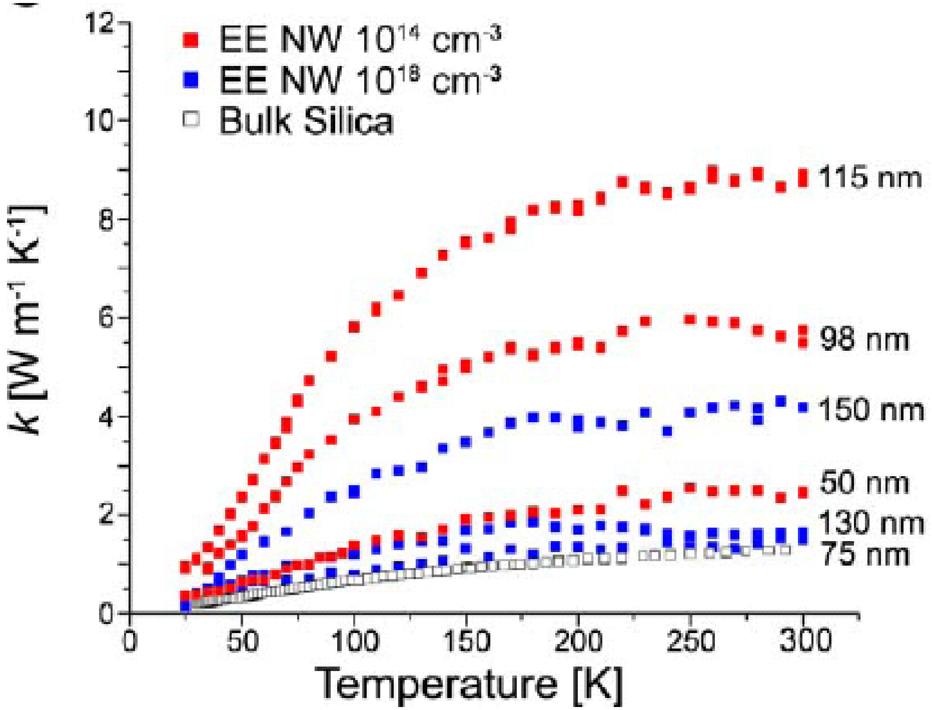
Koh and Cahill, unpublished

Etched (rough) nanowires show anomalously low conductivity



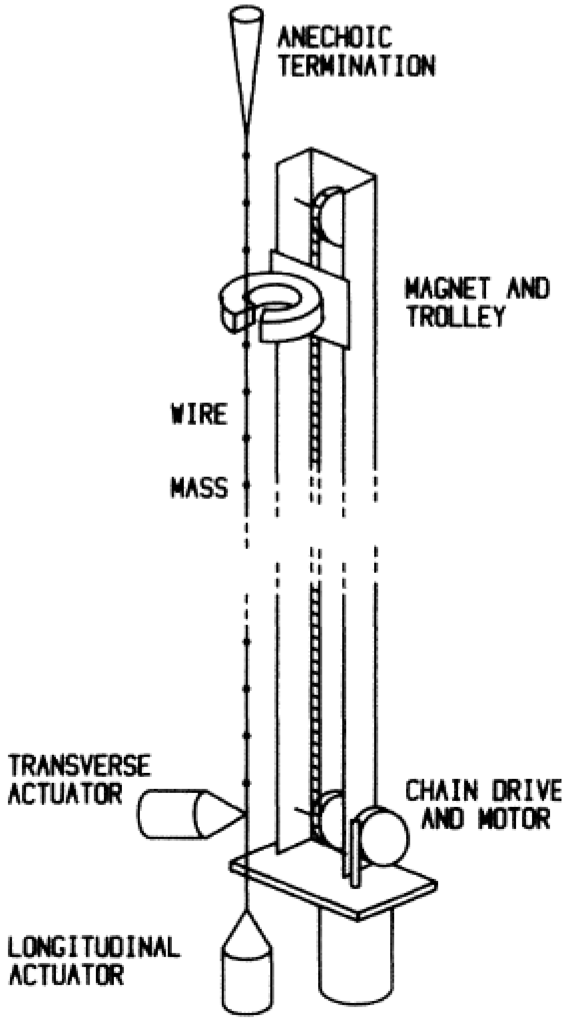
Collaboration: P. Yang (UCB)

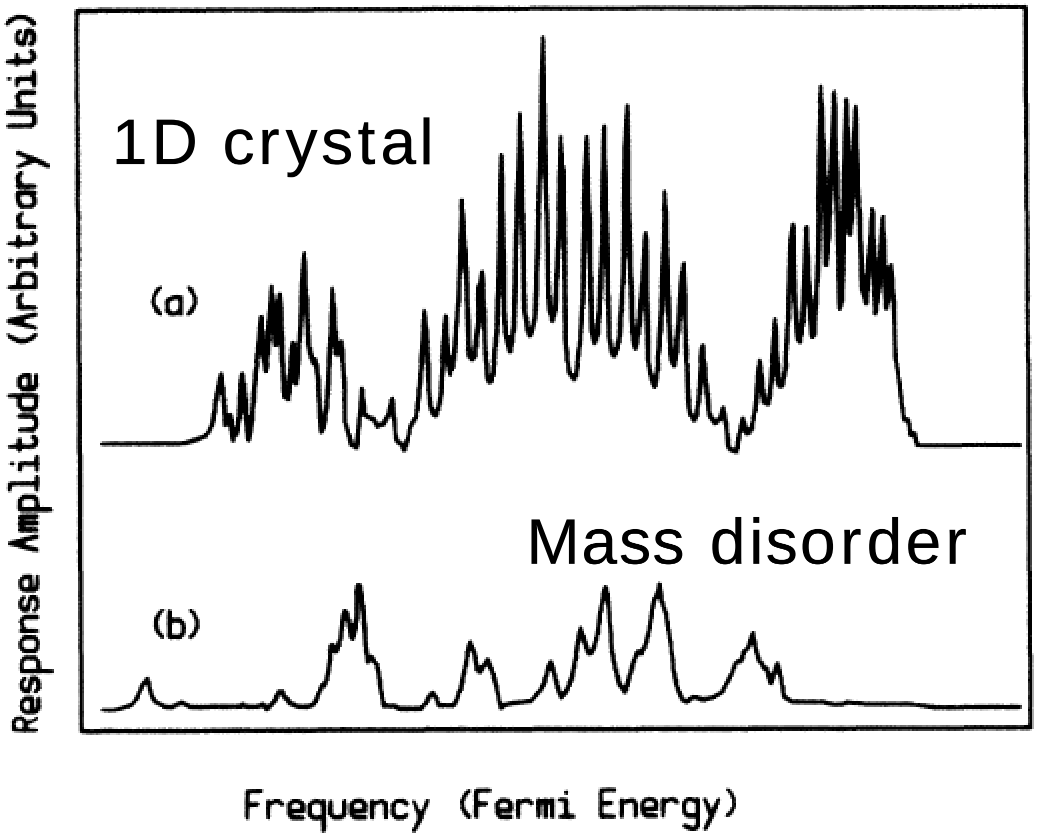




Hochbaum, Chen, Delgado, Liang, Garnett, Najarian, Majumdar, Yang, *Nature* (2008)

Disorder creates localization in 1D

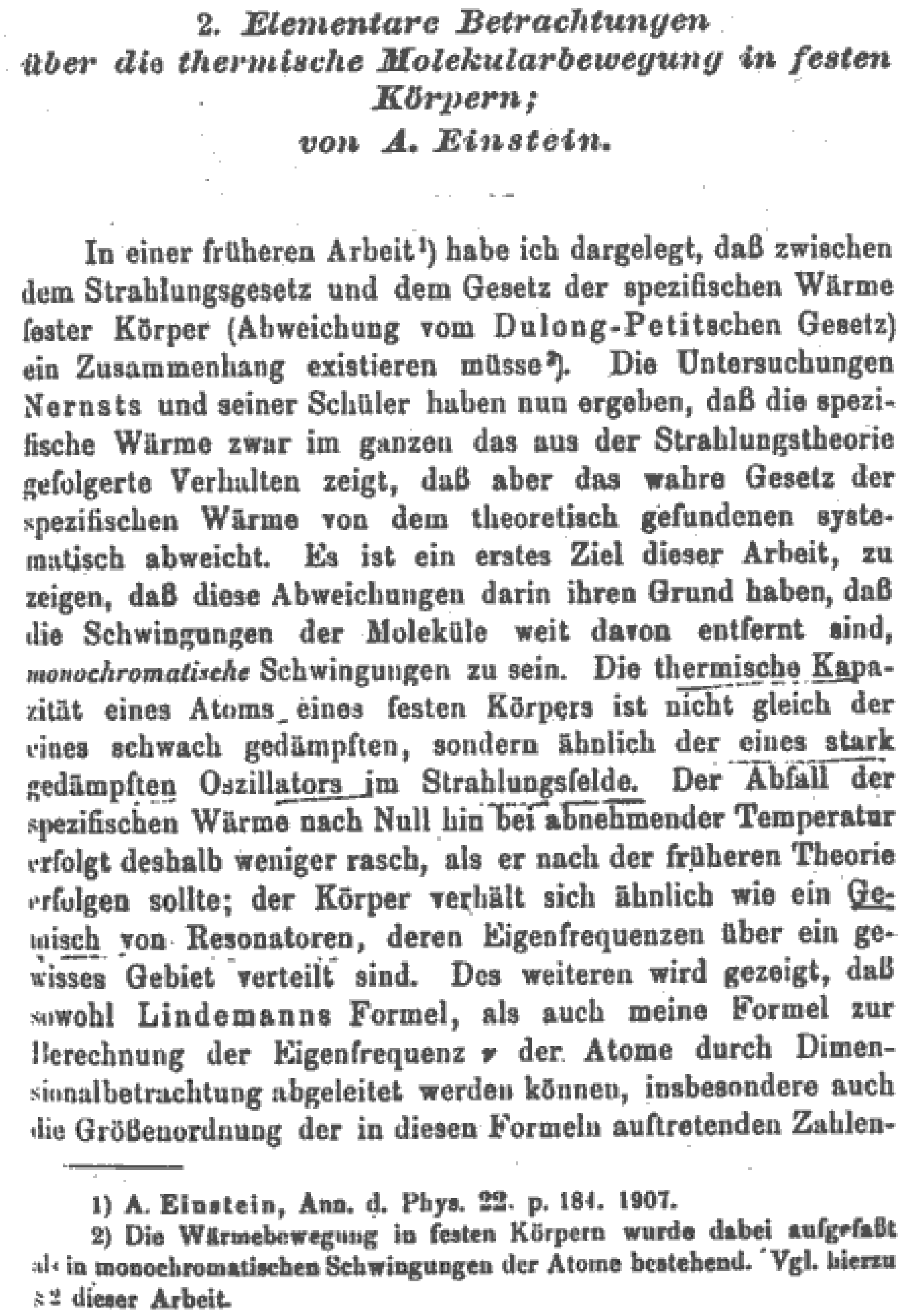




He and Maynard, PRL **57**, 3171 (1986)

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-

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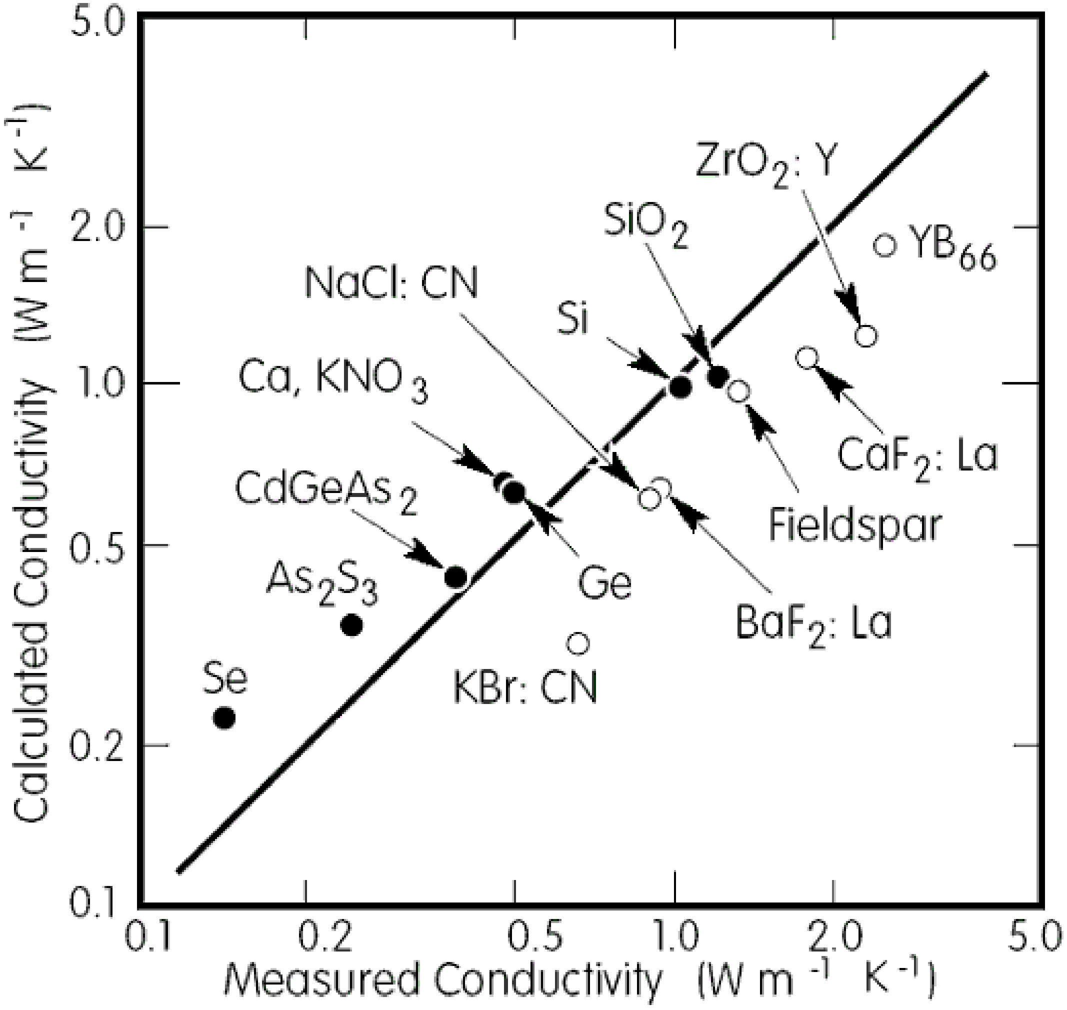
[1]) A. Einstein, Ann. d. Phys. 22. p. 184. 1907.

[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

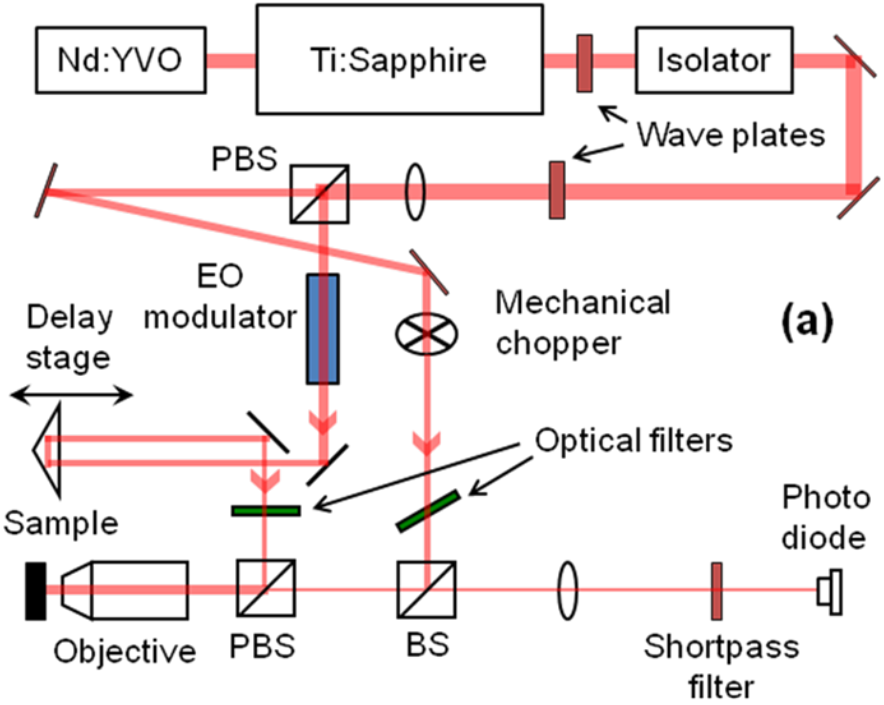


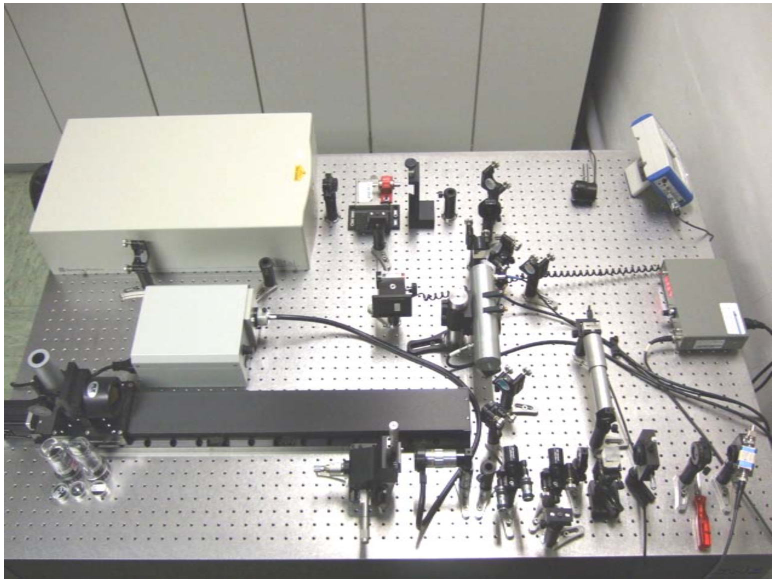
- ● amorphous
- ○ disordered crystal

Cahill, Watson, and Pohl, PRB (1991)

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, see Kang *et al*., RSI (2008)

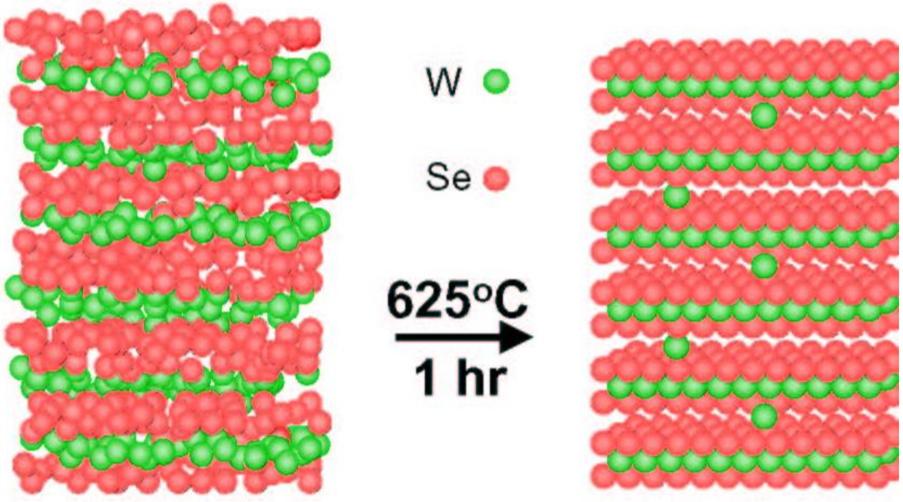


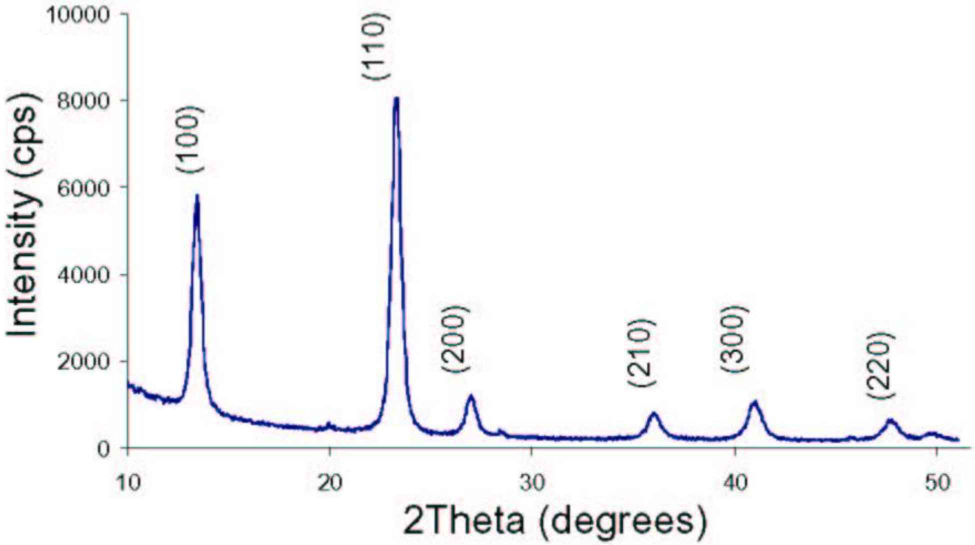


Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

Layered disordered crystals: WSe_2 by “modulated elemental reactants”

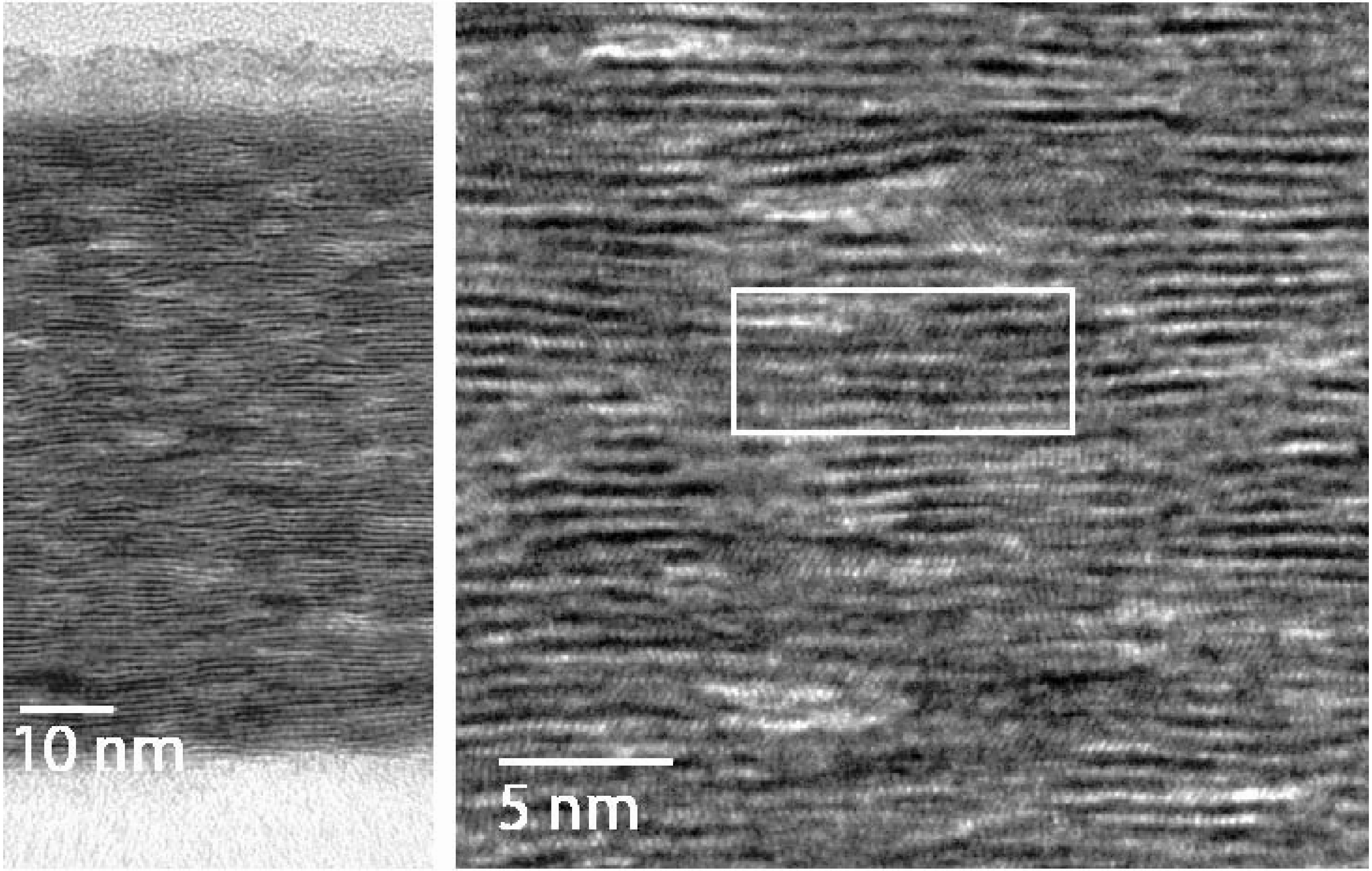
- Deposit W and Se layers at room temperature on Si substrates
- Anneal to remove excess Se and improve crystallinity
- Characterize by RBS, x-ray diffraction (lab sources and Advanced Photon Source) and TEM





D. Johnson and co-workers

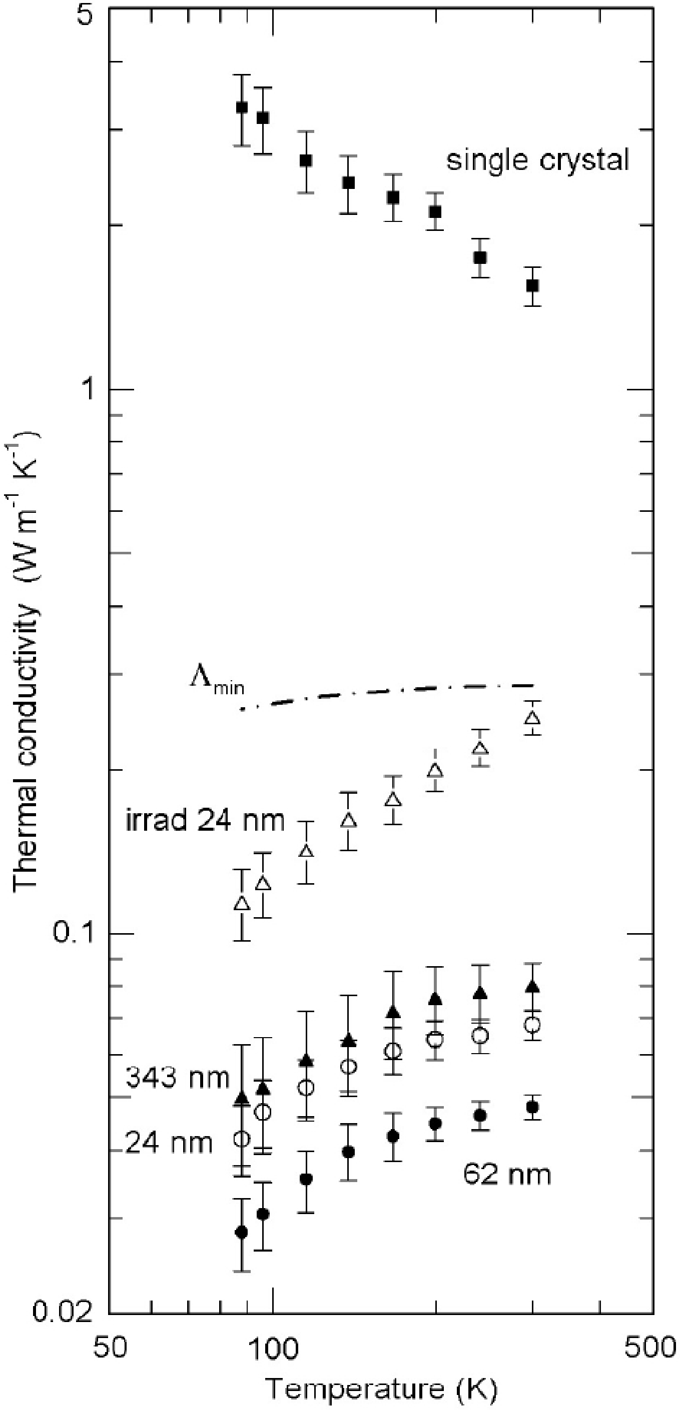
Cross-sectional TEM of 60 nm thick WSe_2



Kim, Zuo *et al.*, JMR (2008)

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.



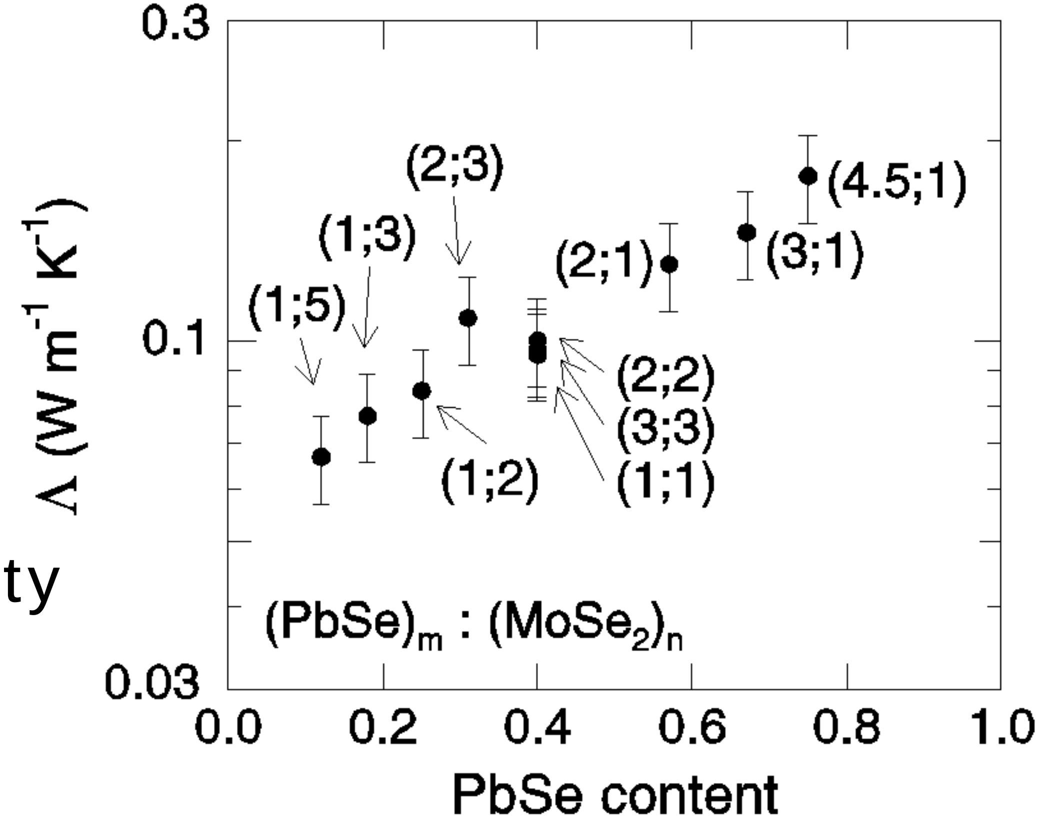
Chiritescu *et al*., Science **315**, 351 (2007)

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
  - $MoSe_2$/PbTe
- Interface density does not matter. Conductivity determined by composition not interface density.



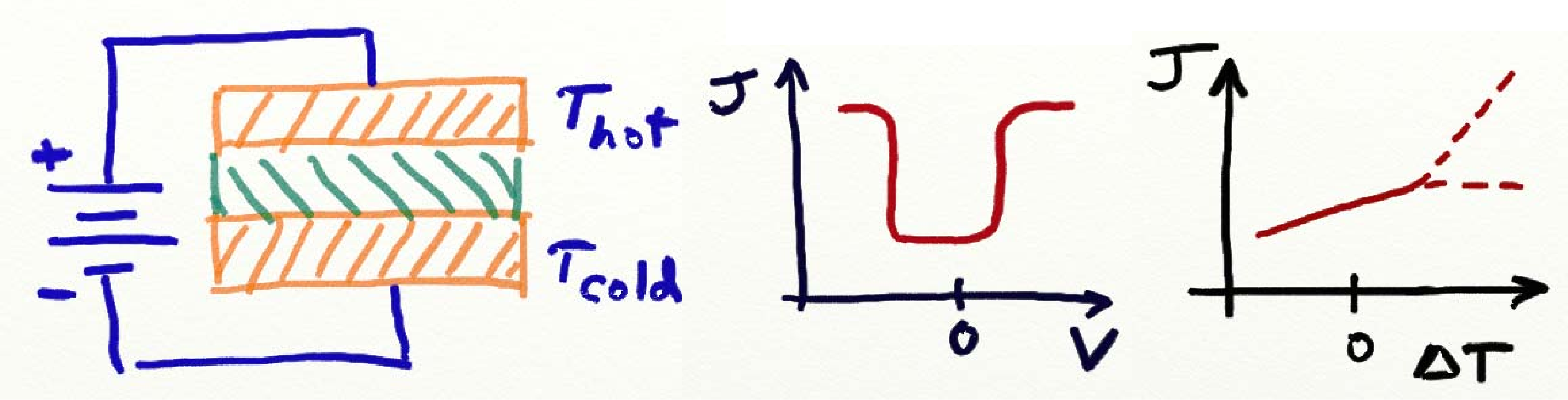
Chiritescu *et al*., JAP (2008)

Conclusions and research directions

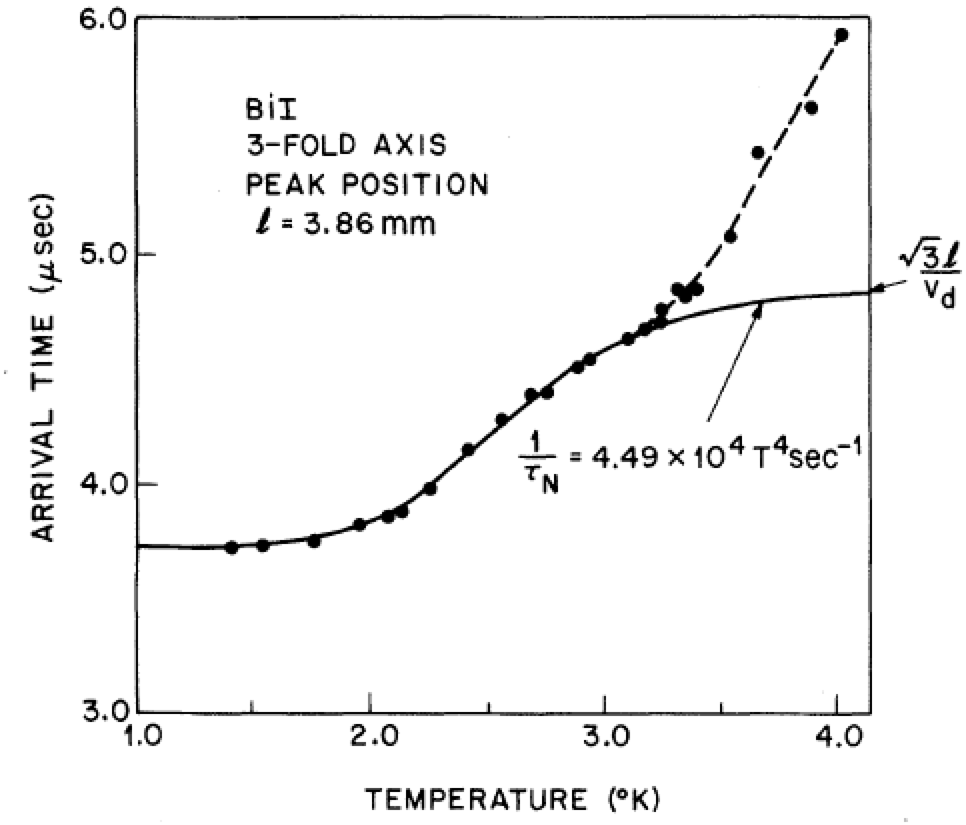
- Hard for me to see a promising path toward "ultrahigh" thermal conductivity (conductivity higher than diamond at room temperature)
- But we could think outside-the-box about...
  - design of molecular structure to provide ultrahigh conductivity polymers
  - searching for superfluid-type heat conduction in solid-state Bose condensates
- Ultralow conductivity (conductivity lower than accepted minimum) has been demonstrated.
  - extend and ehance this physics for thermal barriers and thermoelectrics
  - need to understand the physics of rough nanowires; localization in 1D?

Research directions

- Passive and active control of heat conduction
  - Thermal regulator, thermal switch, thermal rectifier
  - Phase transformations are (to me) most promising route
  - Applications for passive temperature control; electrocaloric cooling; thermal protection



Extras slides start here



V. Narayanamurti and R. C. Dynes, PRL 28, 1461, (1972).