UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

Failure of Fourier's law in measurements of thermal conductivity by time-domain thermoreflectance

David G. Cahill and R. B. Wilson

Department of Materials Science and Engineering

Materials Research Laboratory

University of Illinois at Urbana-Champaign

Wilson and Cahill, *Nature Communications* (2014)

supported by AFOSR

illinois.edu

Outline

Motivation

I. Anisotropy of the apparent thermal conductivity in a TDTR measurement of Si

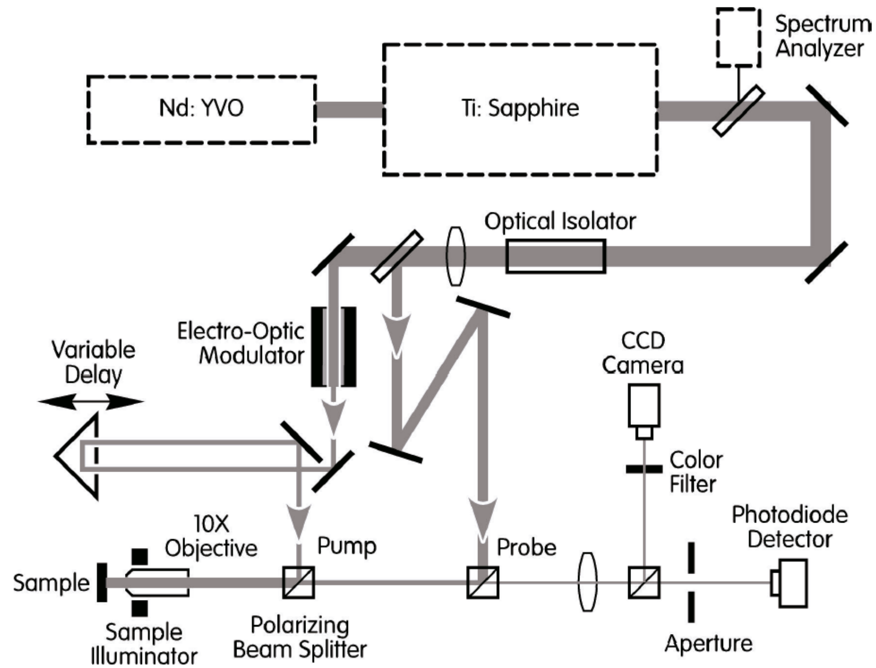
II. Manipulate the spectrum of heat carriers using B and Ge doping of Si

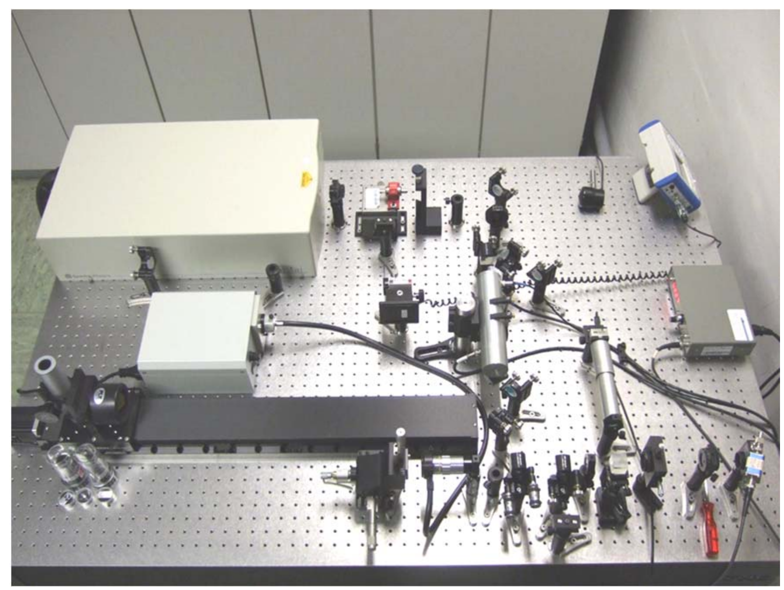
III. Consequences for TDTR measurements of interface thermal conductance

Conclusions

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



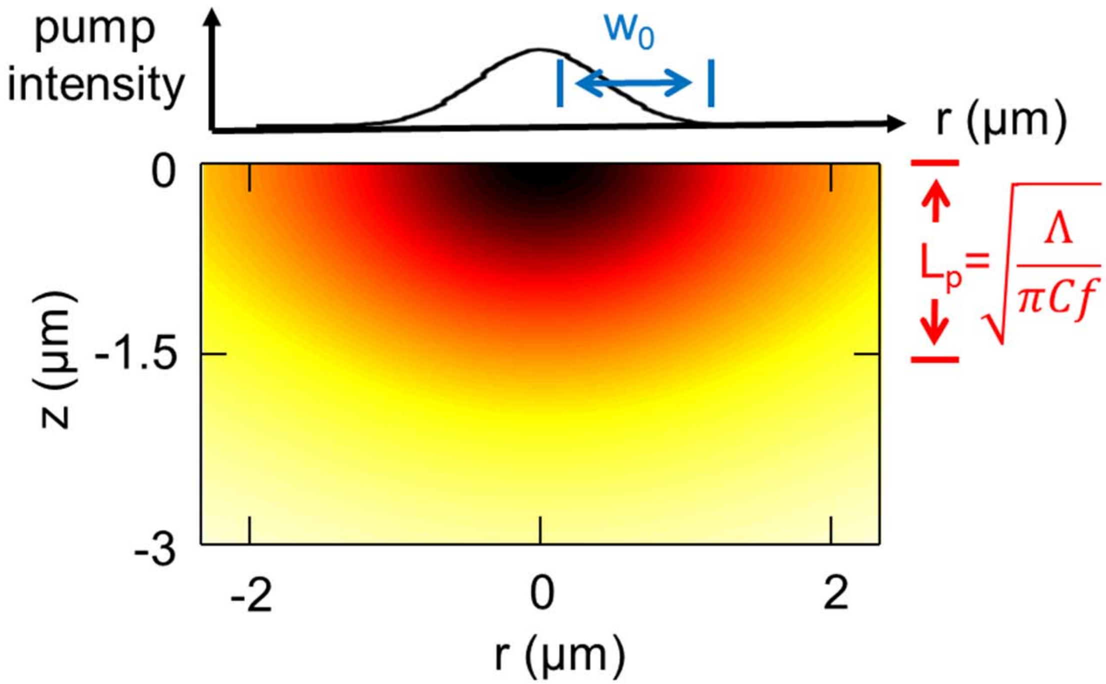


Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

TDTR and phonon mean-free-path spectroscopy

- Time-domain thermoreflectance (TDTR) is a powerful method but we do not deeply understand what we are measuring.
  - 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

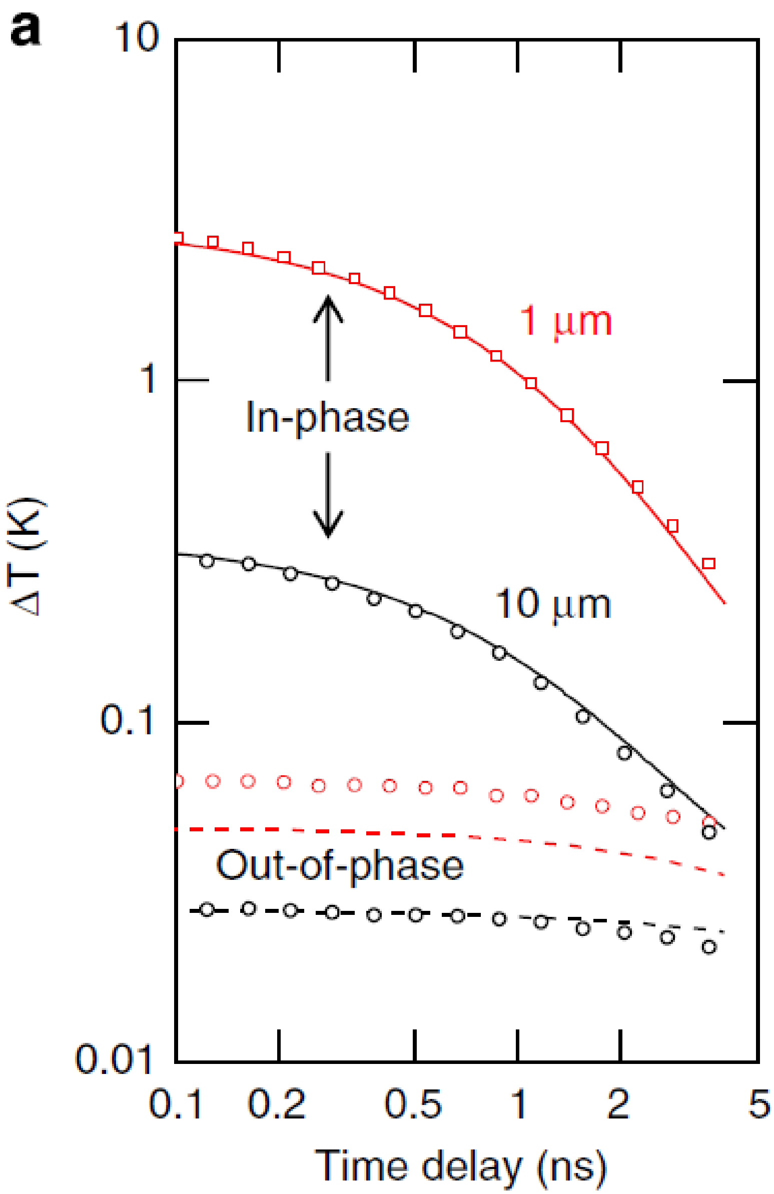
Fourier theory has been observed to fail in TDTR measurements of

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)

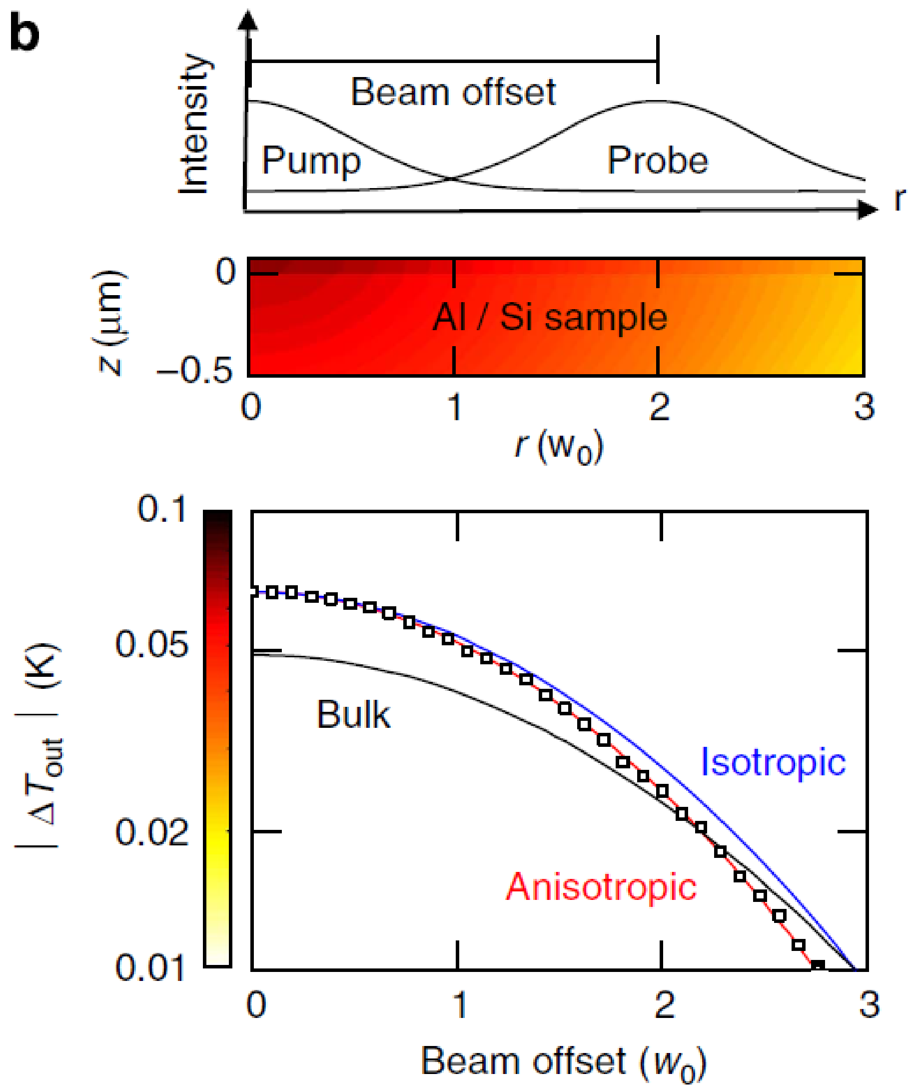
Why does Fourier theory fail with frequency in semiconductor alloys but fail with spot-size in Si at cryogenic temperatures?

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.

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

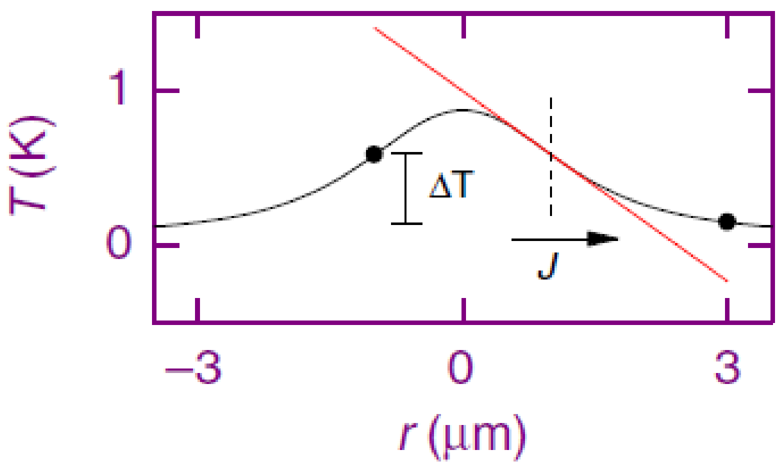
$$\Lambda_r = 80 \text{ W m}^{-1} \text{ K}^{-1}$$

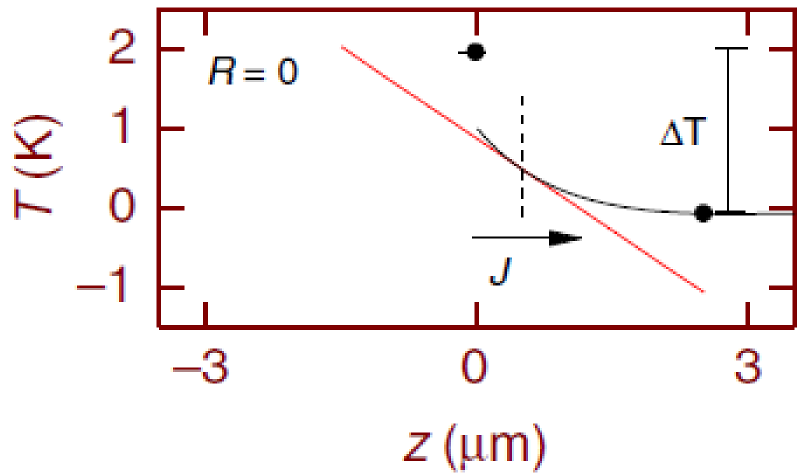
$$\Lambda_z = 140 \text{ W m}^{-1} \text{ K}^{-1}$$

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

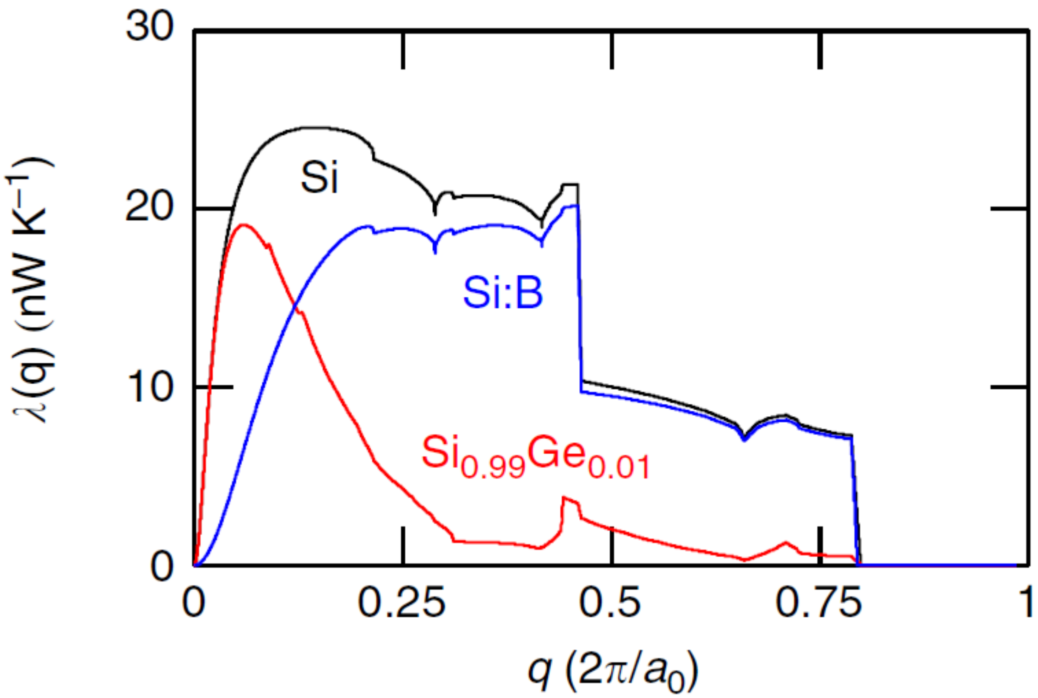
$J \propto \Delta T \neq -2\ell \nabla T$





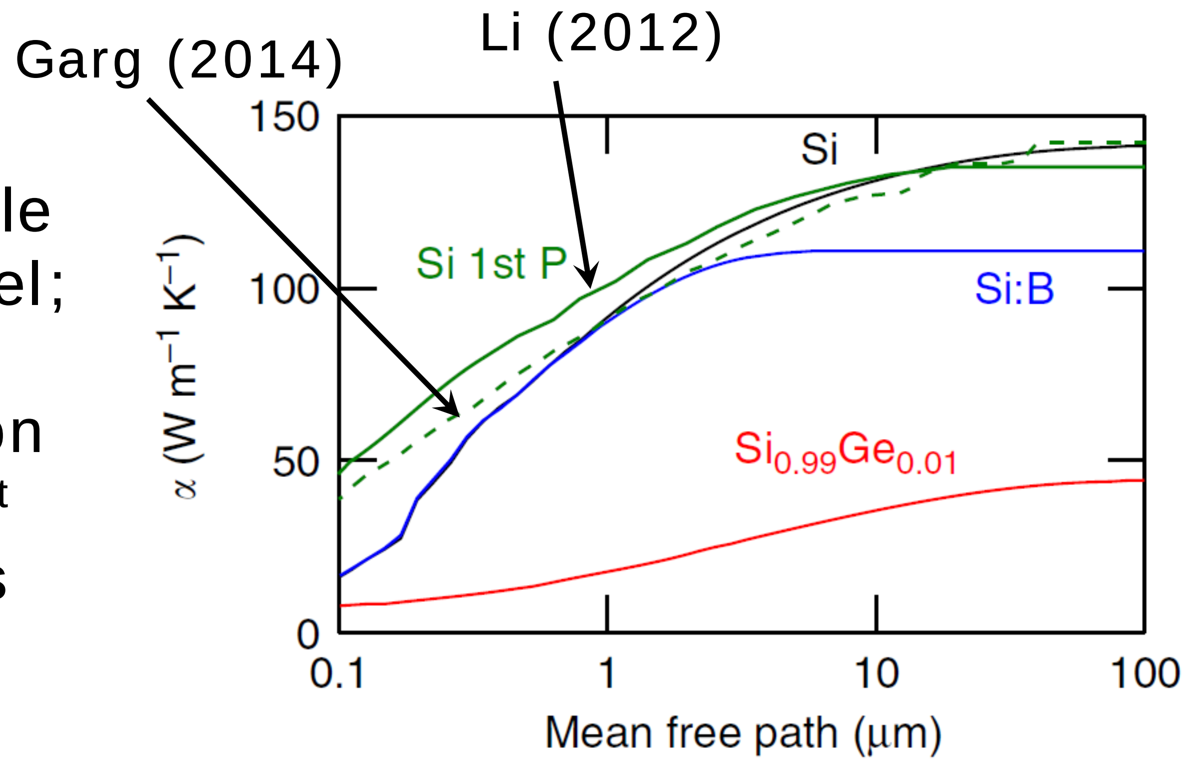
II. Manipulate the spectrum of heat carriers using B and Ge doping of Si.

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

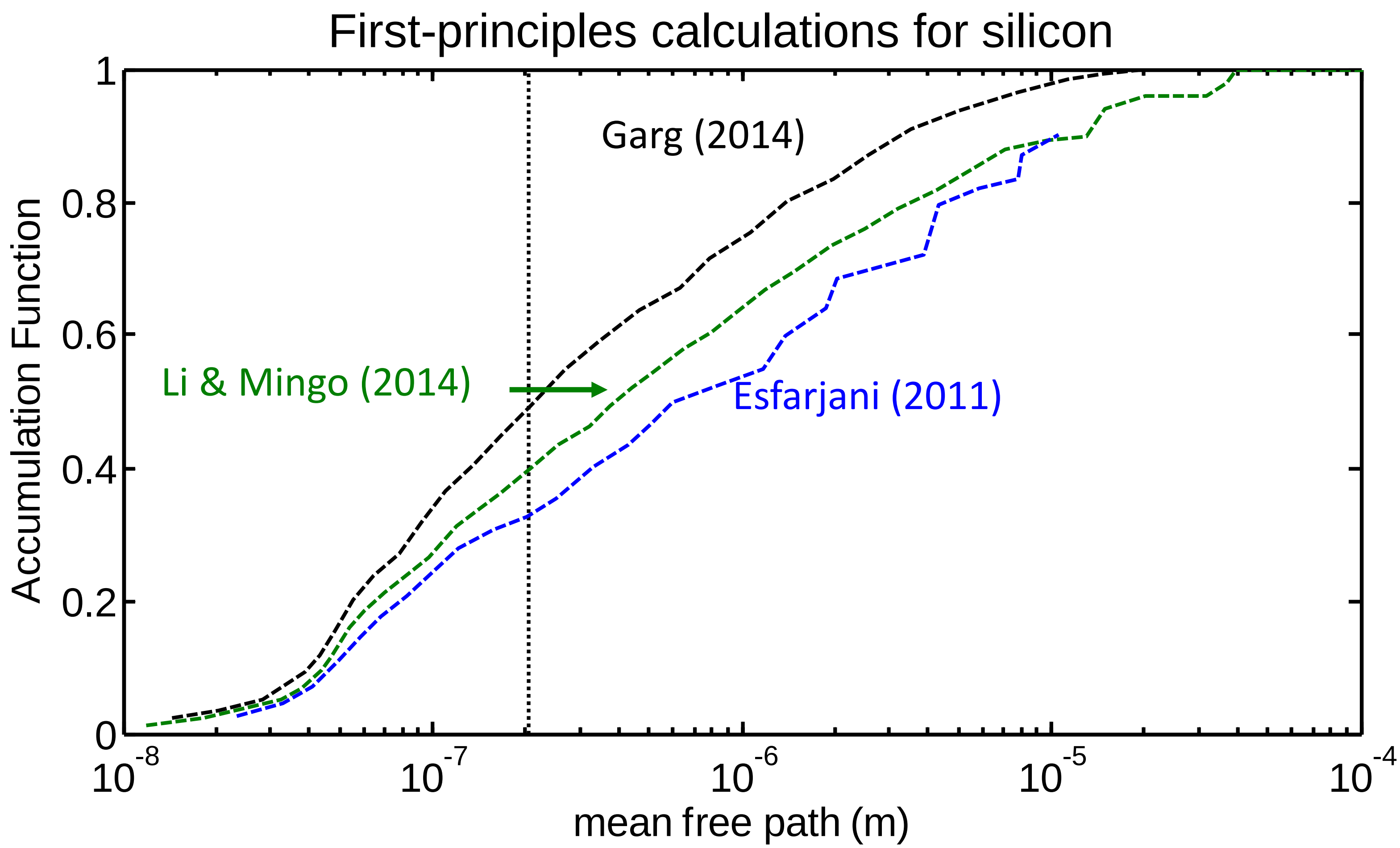


II. Manipulate the spectrum of heat carriers using B and Ge doping of Si.

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

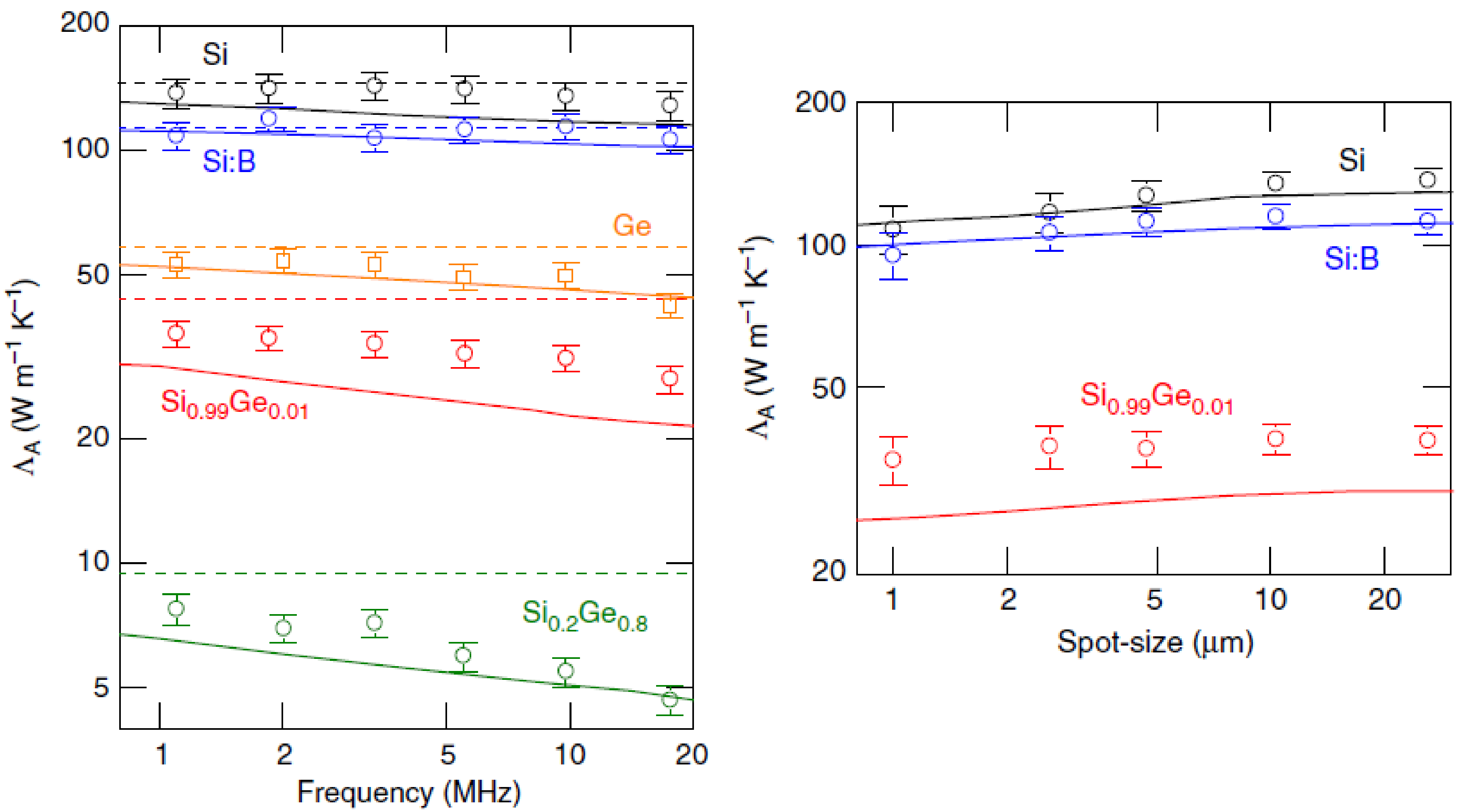


Digression: Differences between the 1st principles calculations are significant



Vary phonons, modulation frequency, spot size

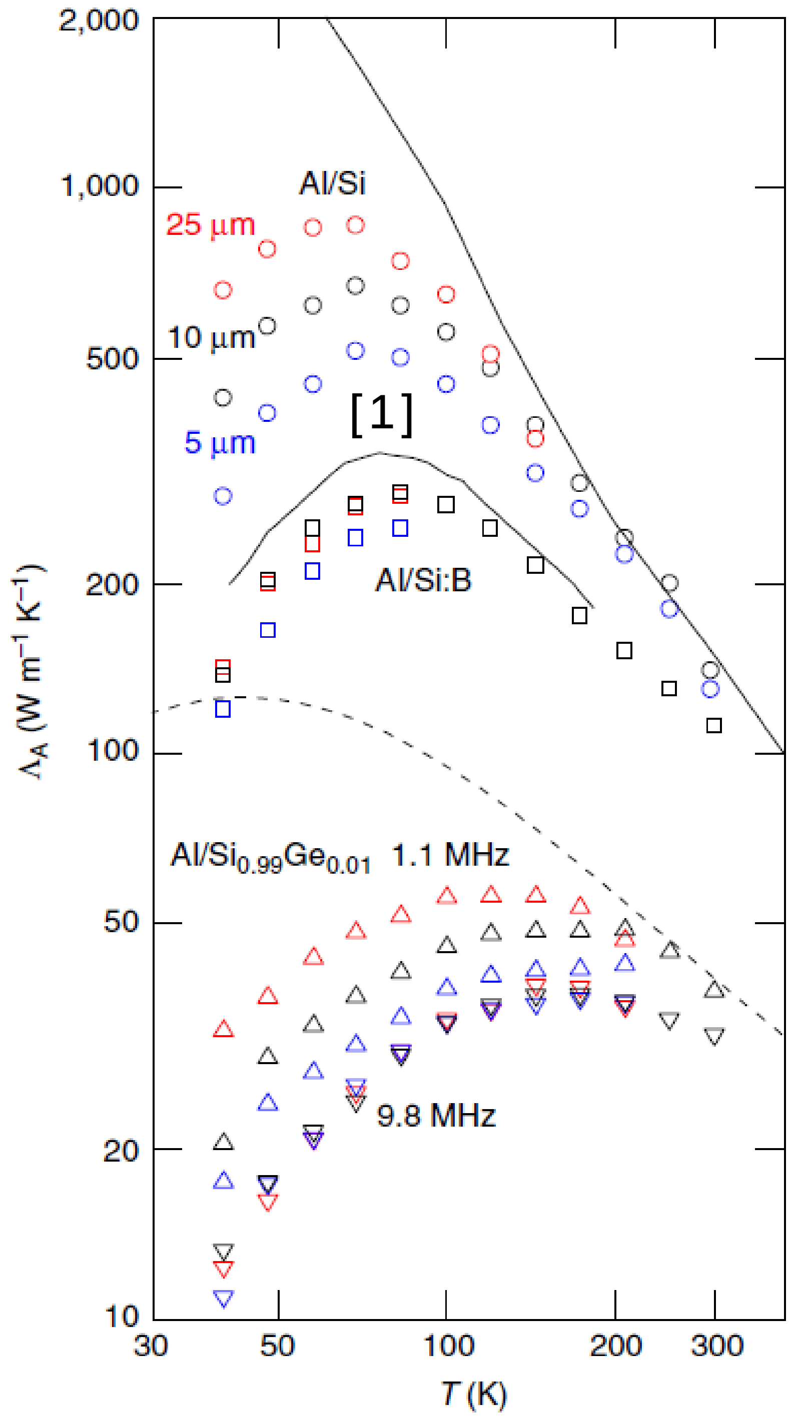
- Low thermal diffusivity of the high frequency phonons is key factor in the failure of Fourier's law in TDTR



...and vary temperature

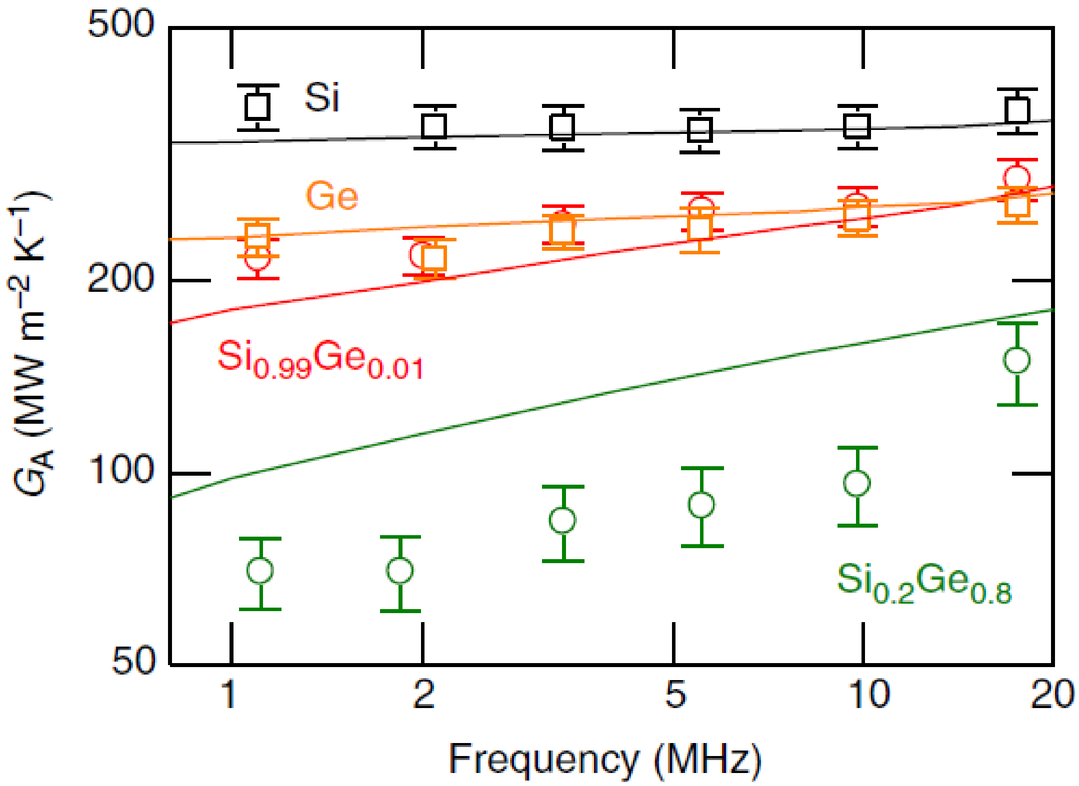
- Differences are more dramatic at low temperatures
  - Fourier law is a good description for Si:B down to 50 K
  - Failure of Fourier's law increases as the distribution of phonon mean-free-paths becomes broader, i.e., from Si:B to Si to SiGe
  - Low thermal diffusivity of high frequency phonons creates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

[1] Asheghi (2011)



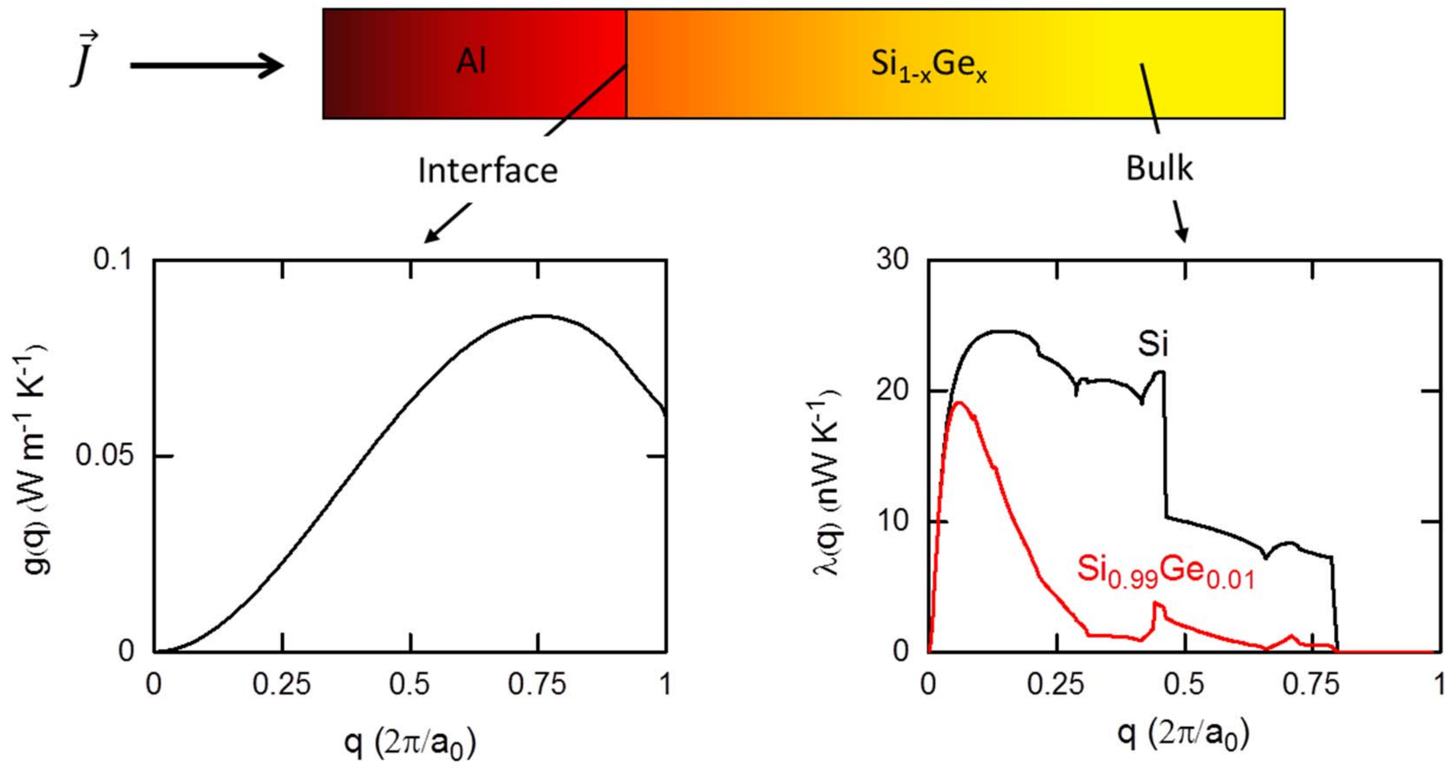
III. Consequences for measurements of interface thermal conductance

- When the thermal diffusivity of the high frequency phonons is small, the apparent interface conductance is reduced and also depends on frequency.
- Radiative boundary condition is not a good description.



III. Consequences for measurements of interface thermal conductance

Different phonons carry heat across the interface than carry heat in the solid



$$G = \frac{1}{4}\int c(q)\mathrm{v}(q)t(q)\mathrm{v}(q)dq$$

$$\Lambda = \int \frac{1}{3}c(q)\mathrm{v}(q)^2\tau(q)\mathrm{v}(q)dq$$

A spatial mismatch exists in the spectral distribution of the heat-current.

III. Consequences for measurements of interface thermal conductance

- For materials with low thermal diffusivity high frequency phonons, the non-equilibrium region created by this mismatch appears in the TDTR measurement as
  - a small interface conductance a low modulation frequency.
  - a reduced thermal conductivity at high modulation frequencies.
- The frequency dependence of the thermal conductivity depends on the transport properties of the interface.

Take-home messages:

- TDTR is surprisingly robust. Even when mean-free-paths are comparable to thermal diffusion lengths, deviations from solutions based on Fourier's law are typically minor.
  – 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 we reliably map the apparent thermal conductivity 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