UNIVERSITY OF ILLINOIS
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Time domain thermoreflectance 2.0: Advanced techniques

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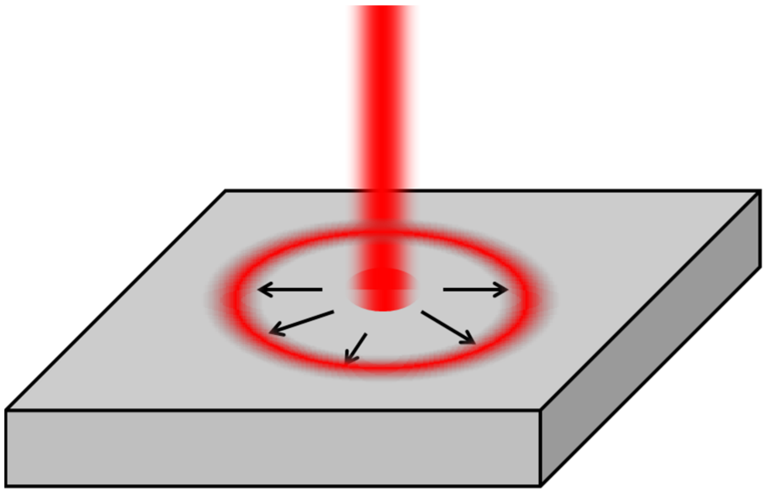
Outline

- Measurement of lateral heat flow: thin metal films, anisotropic crystals
- Non-equilibrium between excitations: electron-phonon, magnon-phonon, phonon-phonon
- Alternatives to conventional thermoreflectance for ultrafast thermometry
  - Transient absorption using plasmon resonances in Au nanostructures
  - Time-resolved magneto-optic Kerr effect (TR-MOKE) of thin film perpendicular magnets.

Lateral heat flow

- TDTR is typically only sensitive to heat flow normal to the surface because the spot radius is large compared to the thermal penetration depth, i.e., $|q| w_0 \gg 1$
- Points toward using low modulation frequency and small spot sizes but there are tough limits
  - Repetition time of laser is τ_{rep}=12.5 ns. If $f \tau_{rep} \ll 1$ sensitivity can suffer
  - Need to avoid clipping of probe so hard to get w_0<1 μm.
- Can we improve the experiment by offsetting the pump and probe? Yes, in some cases.
- Sensitivity can also be enhanced if the layer under study is thermally thin and placed on a low thermal conductivity substrate

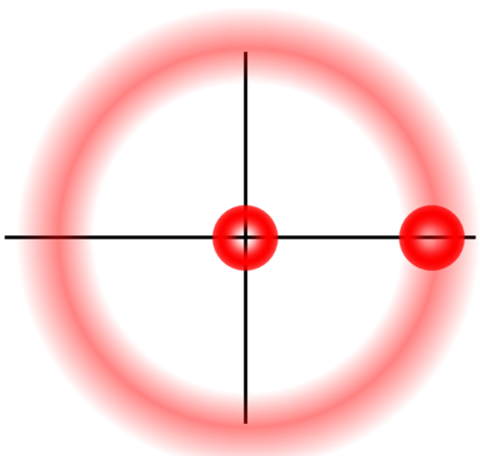
In-plane thermal conductivity using TDTR with offset laser beams



$$\Delta T(f) = \frac{2\pi}{A_S}\int_0^\infty G(f,k)P(k)S(k)k\,dk$$

↑

The only difference from normal TDTR!



$$\frac{2A_S}{\pi w_S^2}\exp\left(-\frac{2\left[(x-x_0)^2+y^2\right]}{w_S^2}\right) \Leftrightarrow \left(\frac{2A_S}{\pi w_S^2}\right)\exp\left(-\frac{2(r^2+x_0^2)}{w_S^2}\right)I_0\left(\frac{4x_0 r}{w_S^2}\right)$$

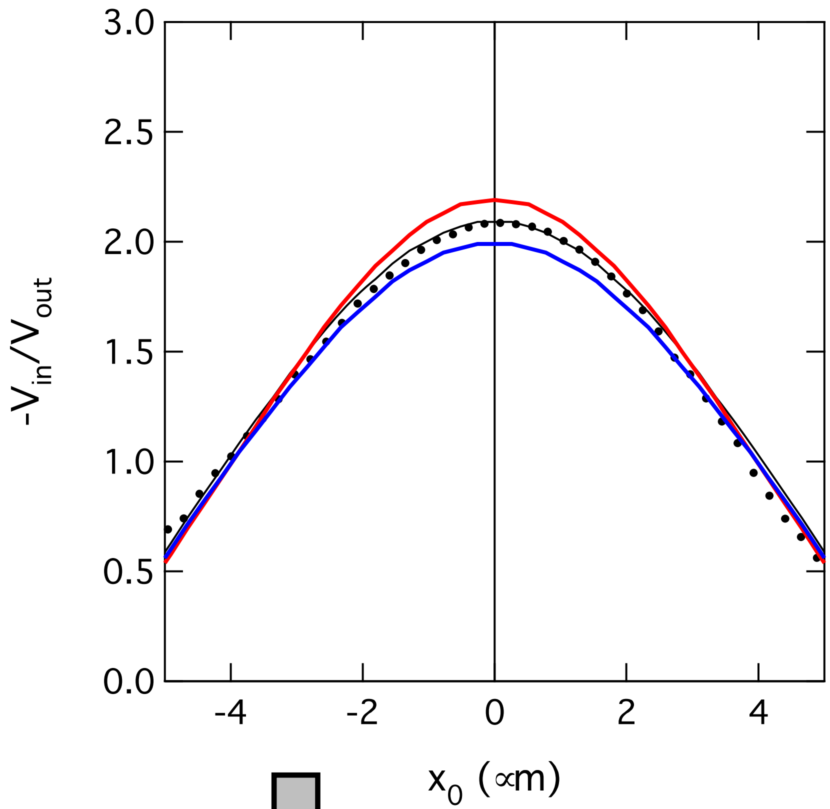
Offset Gaussian Intensity

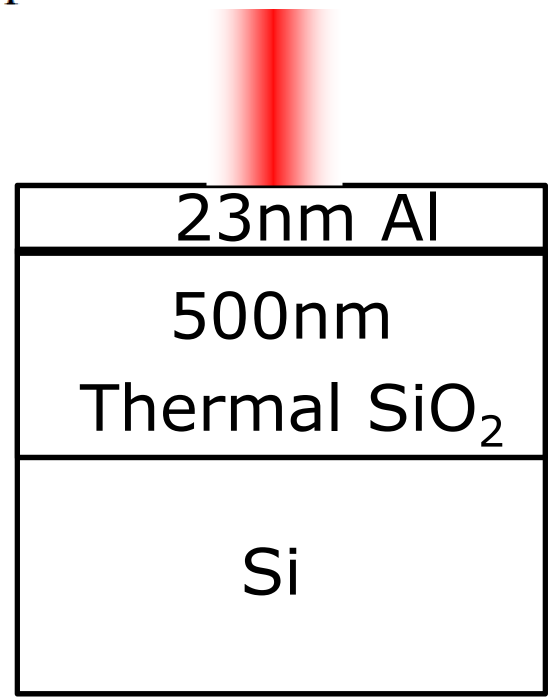
Distributed Ring Intensity

J.P. Feser, D.G. Cahill, Rev. Sci. Instr., 83, 104901 (2012).

For Al, electronic thermal conductivity should dominate; measured Λ is in agreement with W-F

$f = 1.6$ MHz, $w_0 = 2.5$ μm, and $t = 1000$ ps





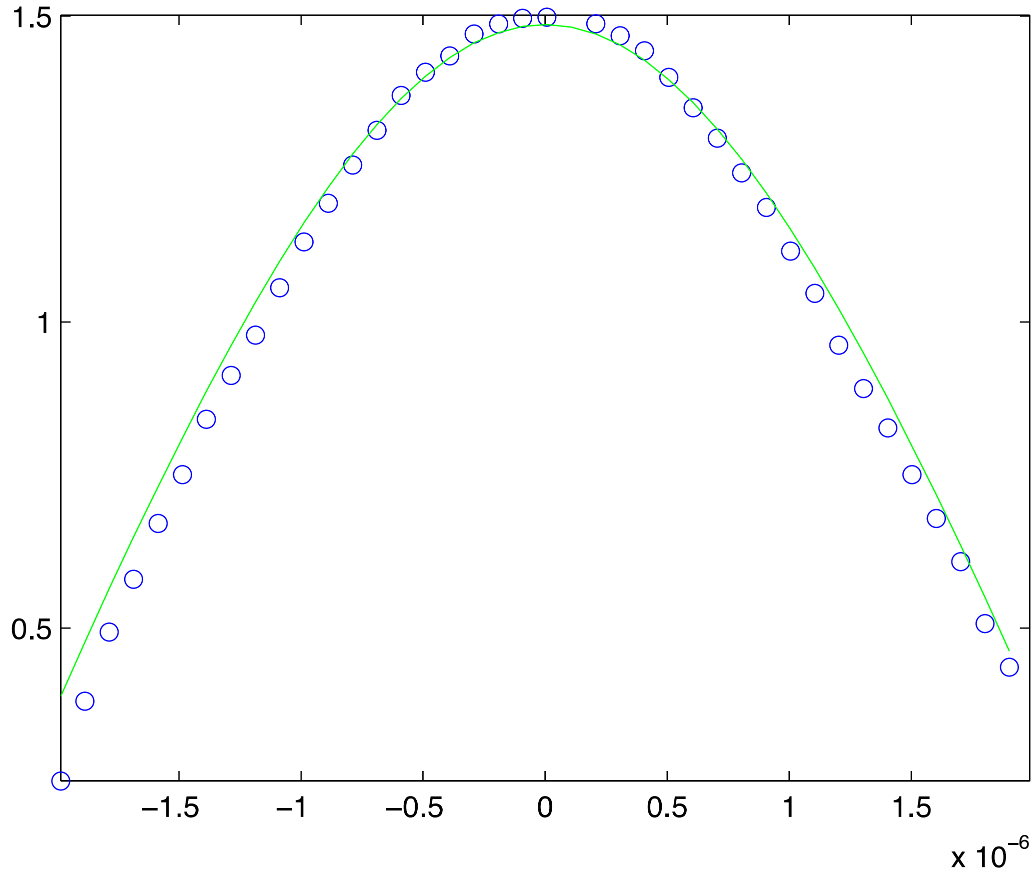
$$\Lambda_{||} = 120 \text{ W/m-K } (\Lambda_{W-F} = 132 \text{ W/m-K})$$

Pushing the sensitivity requires smaller spot size and a low thermal conductivity substrate

- In most cases, the relevant parameter is the lateral conductance of the film $h\Lambda$, h layer thickness, Λ in-plane thermal conductivity

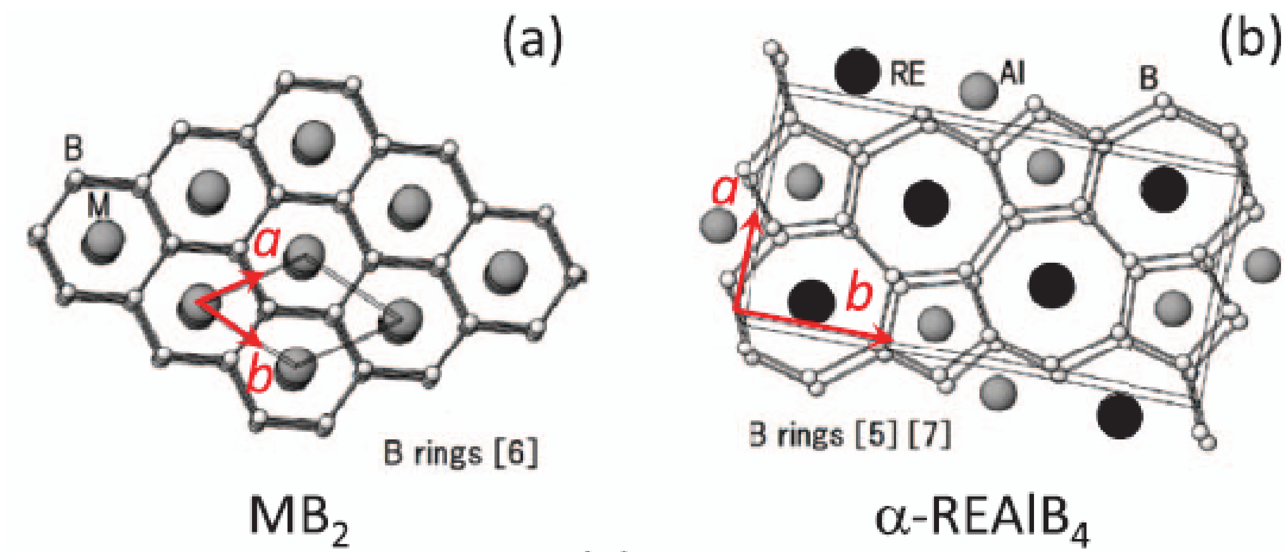
V(32 nm)/BK7
w_0 = 1.05 μm

Λ = 14.5 W m^{-1} K^{-1}
Λ_{el}= 15.0 W m^{-1} K^{-1}



Thermal conductivity of hexagonal borides

- Collaboration with T. Mori (NIMS)
- Compare AlB_2 (metallic) and $TmAlB_4$ (semi-metal)
- Cleave small crystals (flakes) along the basal plane

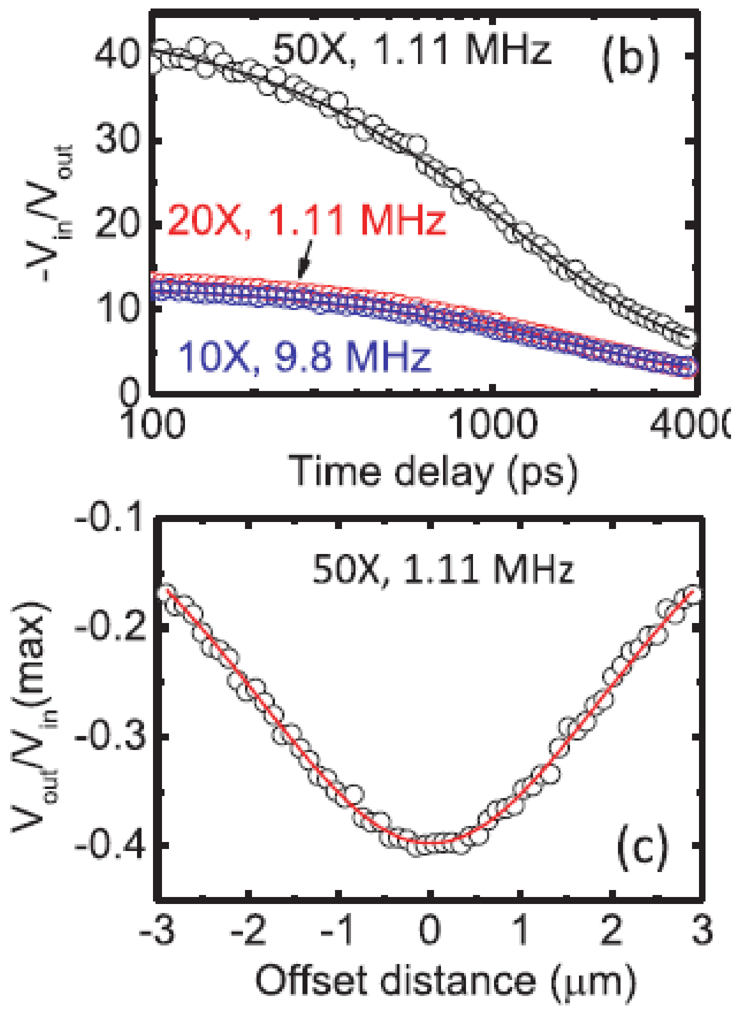


Wang *et al.*, APL Mater. (2014)

Thermal conductivity of hexagonal borides

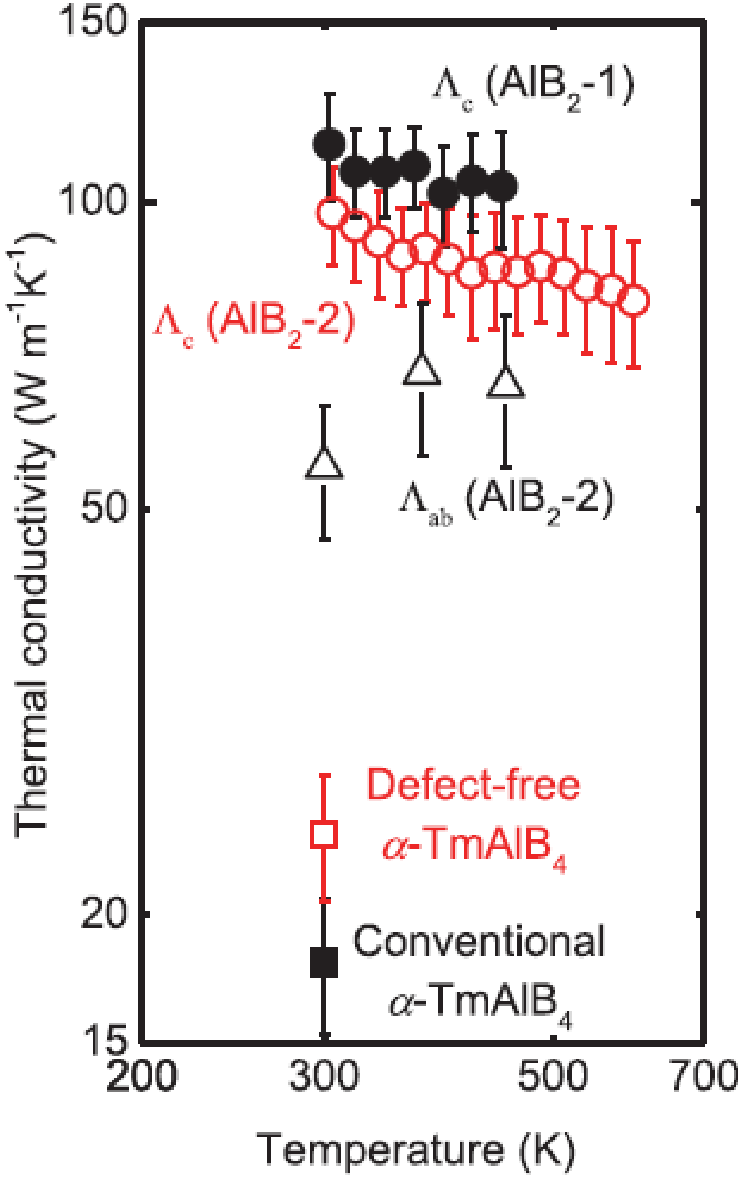
- Vary spot size, modulation frequency
- Beam offset experiment at t=-50 ps. This method of normalize minimizes error propagation.

AlB_2

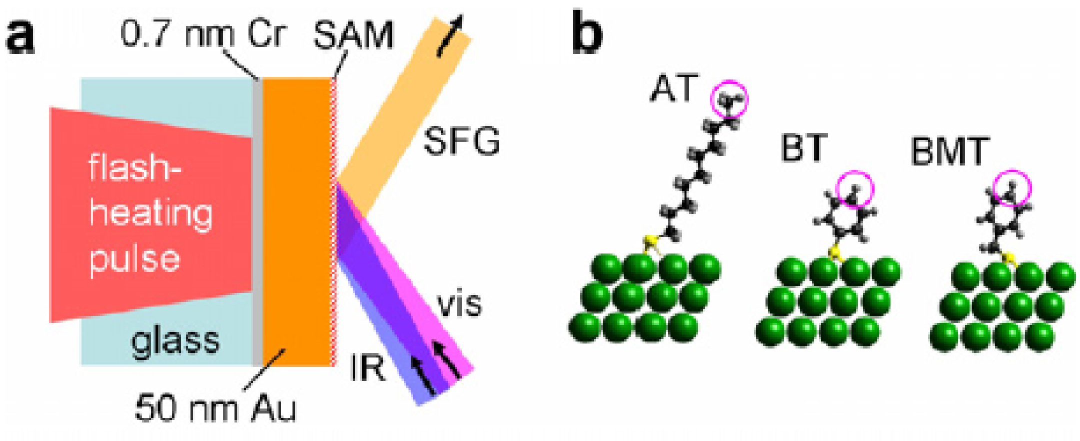


Thermal conductivity of hexagonal borides

- Could AlB_2 be used as an earth-abundant high thermal conductivity filler for composites?
- Probably not: in-plane thermal conductivity is not exceptional high.



Can we indirectly heat a Au layer through contact with a transition metal on ultrafast time scales?



- Au provides well-defined chemistry for studies of molecular layers, however
  - Optical absorption is small so challenging to produce large temperature excursions with a laser oscillator.
  - hot-electron effects are a problem if we heat Au with amplified laser pulses.

Wang, Dlott *et al*., Chem. Phys. (2008)

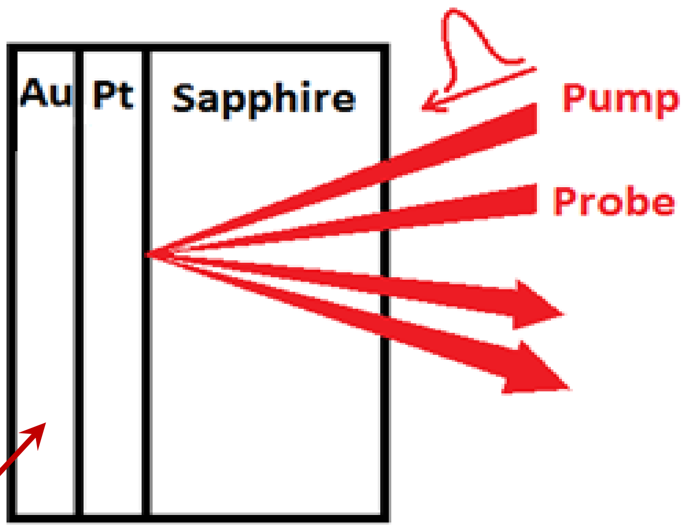
Unfortunately, heating of the Au layer is slow because of weak electron-phonon coupling in Au

- Electronic thermal conductance of Pt/Au interface is large
  - *estimate* G_{ee}>10 GW m^{-2} K^{-1}
- Effective conductance between Au electrons and Au phonons is **not** large.

g = electron-phonon coupling parameter (3×10^{16} W m^{-3} K^{-1})

h = Au thickness (20 nm)

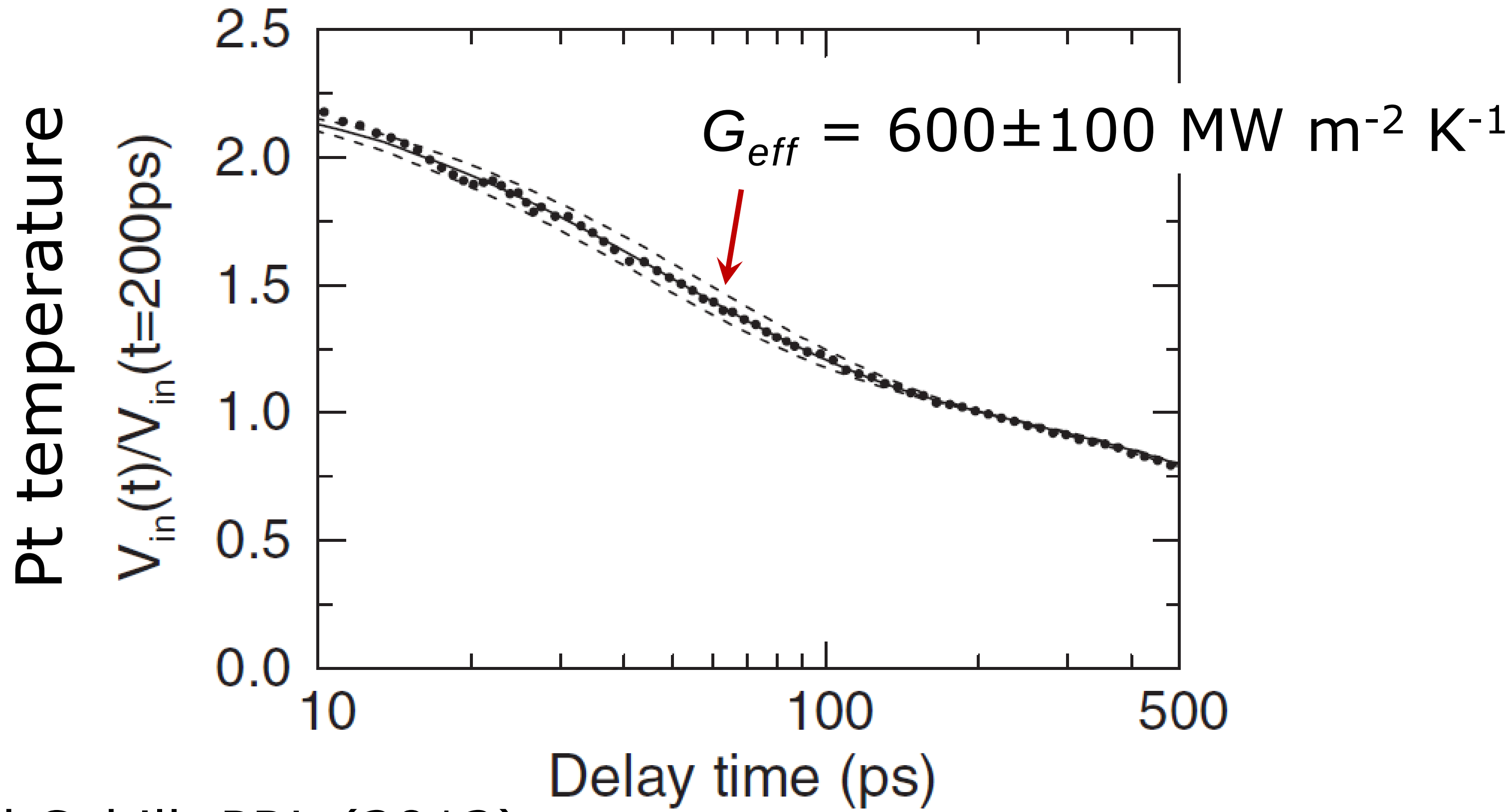
$G_{eff} = gh$ = 600 MW m^{-2} K^{-1}



Unfortunately, heating of the Au layer is slow because of weak electron-phonon coupling in Au

- Characteristic time scale for the heating of the Au phonons

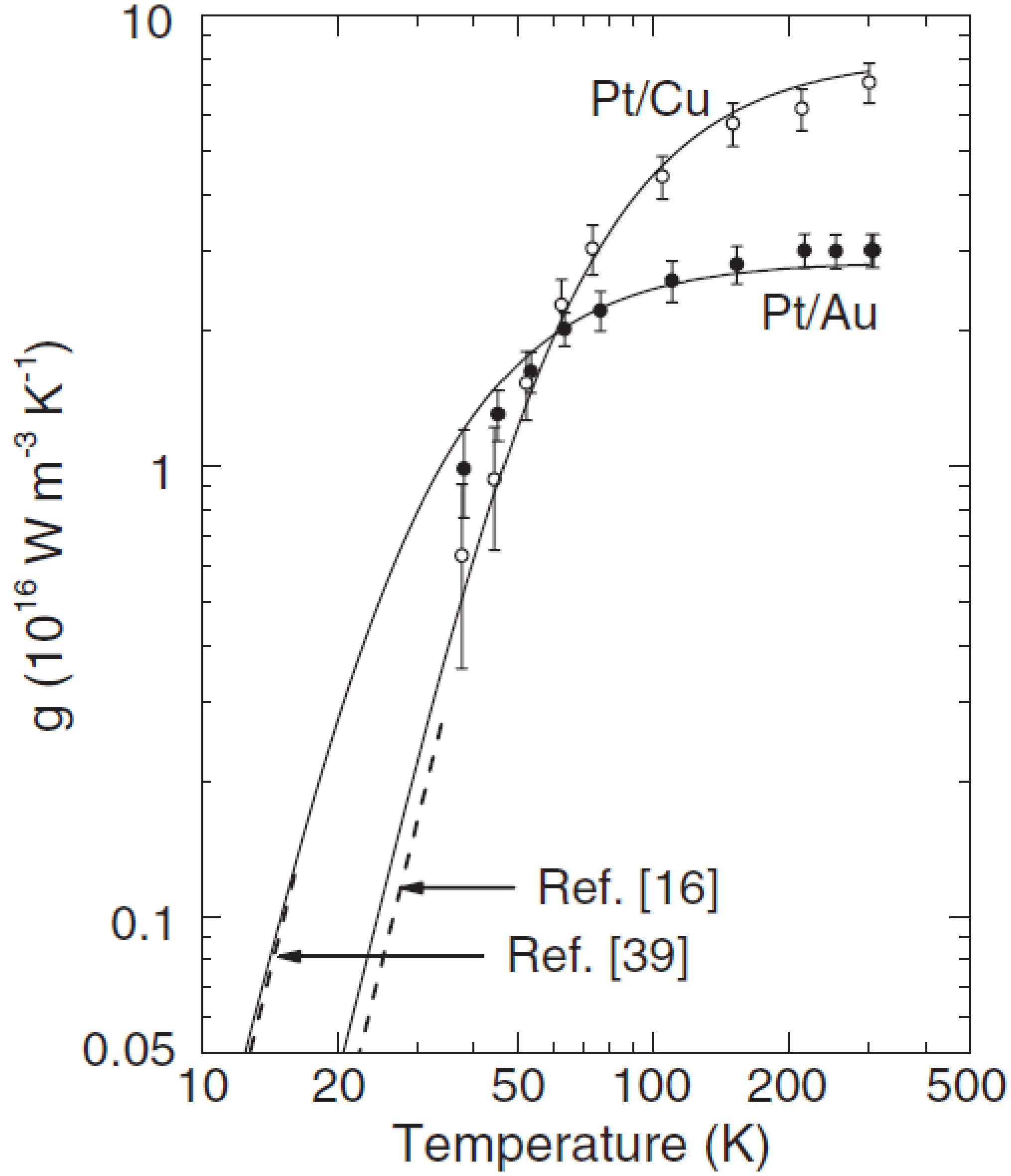
$$\tau = \frac{C}{g} \approx 80 \text{ ps}$$



Wang and Cahill, PRL (2012)

Make lemonade out of lemons: lousy way to heat Au but excellent way to measure *g*

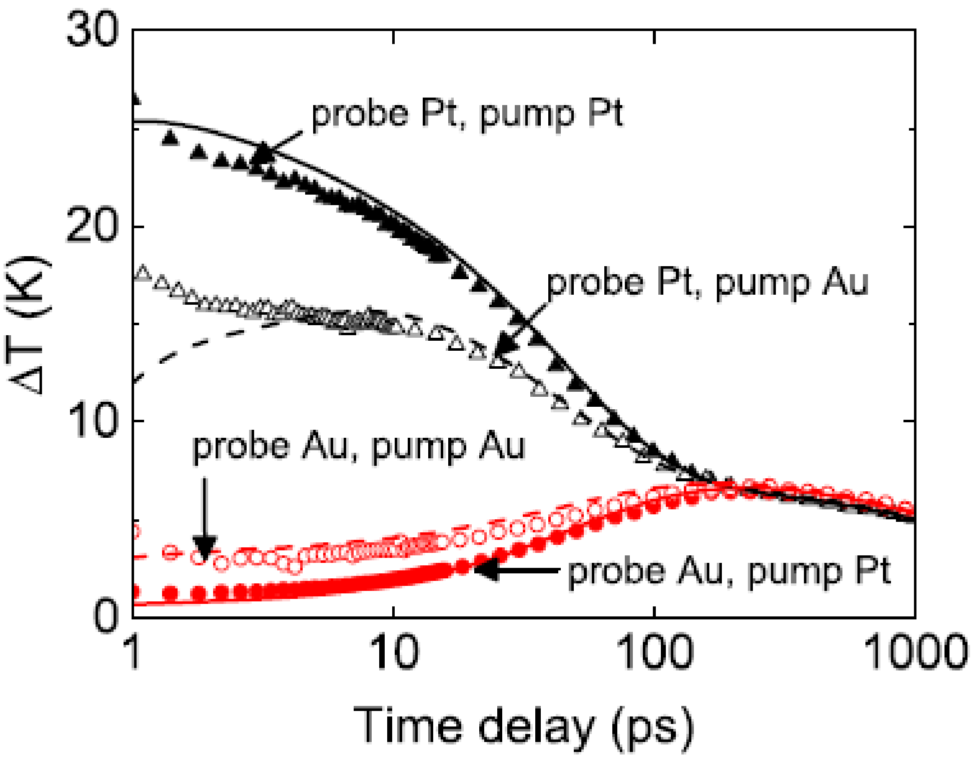
- Solid lines are the predictions of the original Kaganov "two-temperature" model of 1957
- Dashed lines are T^4 extrapolations of low temperature physics experiments.



Extend the story: pump and probe Au/Pt bilayer from different sides

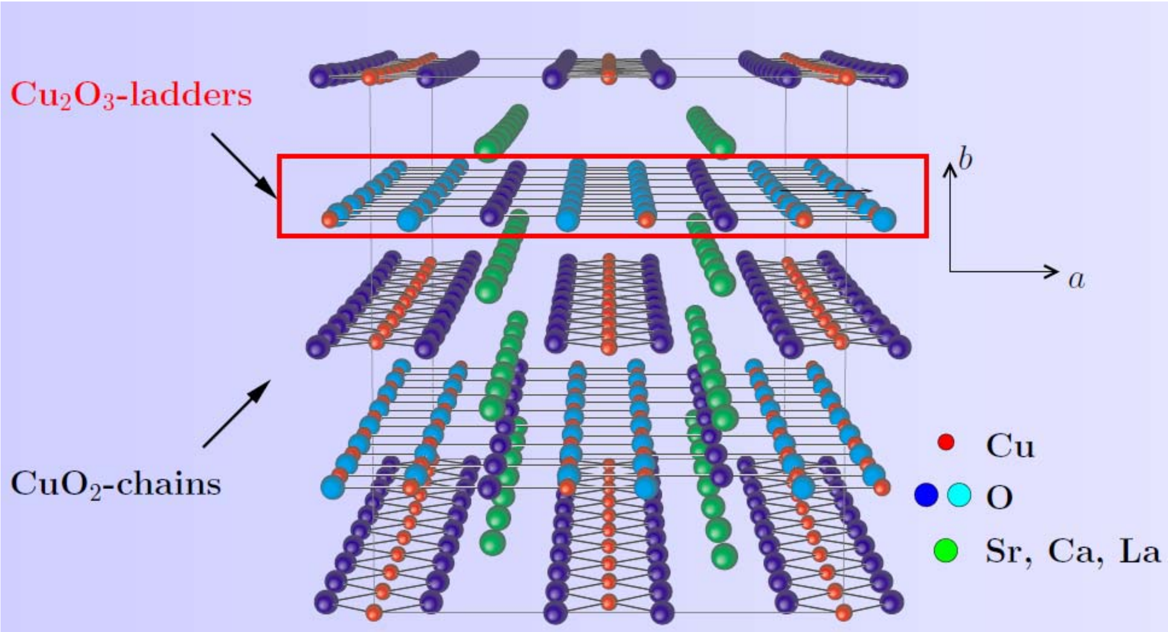
Data and transmission line modeling of Pt (23 nm)/Au(58 nm)

- Attempt to measure the Au/Pt electronic interface conductance
- Increase Au thickness to 60 nm to increase heat flux from Pt to Au
- Can only set a lower limit G_{ee}>5 MW m^{-2} K^{-1}



Choi *et al.*, PRB (2014)

Magnon-phonon couplng and magnon thermal conductivity in the spin ladder $Ca_9La_5Cu_{24}O_{41}$



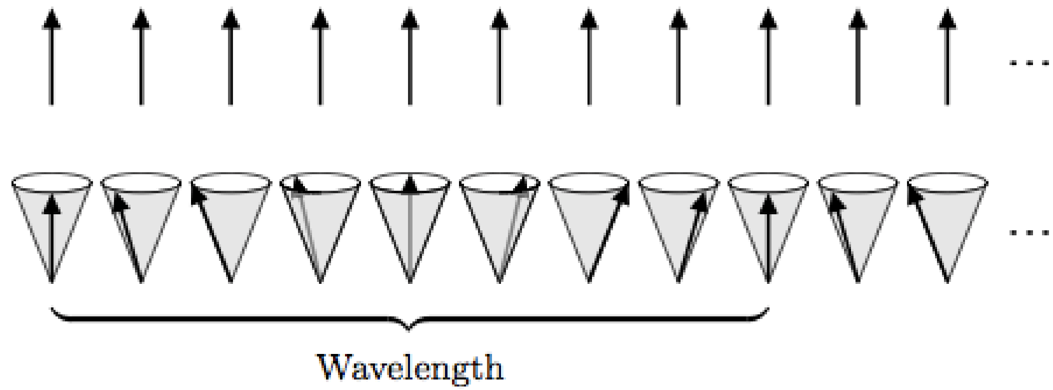
McCarron *et al.*, Mat. Res. Bull. (1988)

colorized graphic by Heidrich-Meisner (2005)

Spin waves are intrinsically quantum mechanical so hard to think about in classical analogies

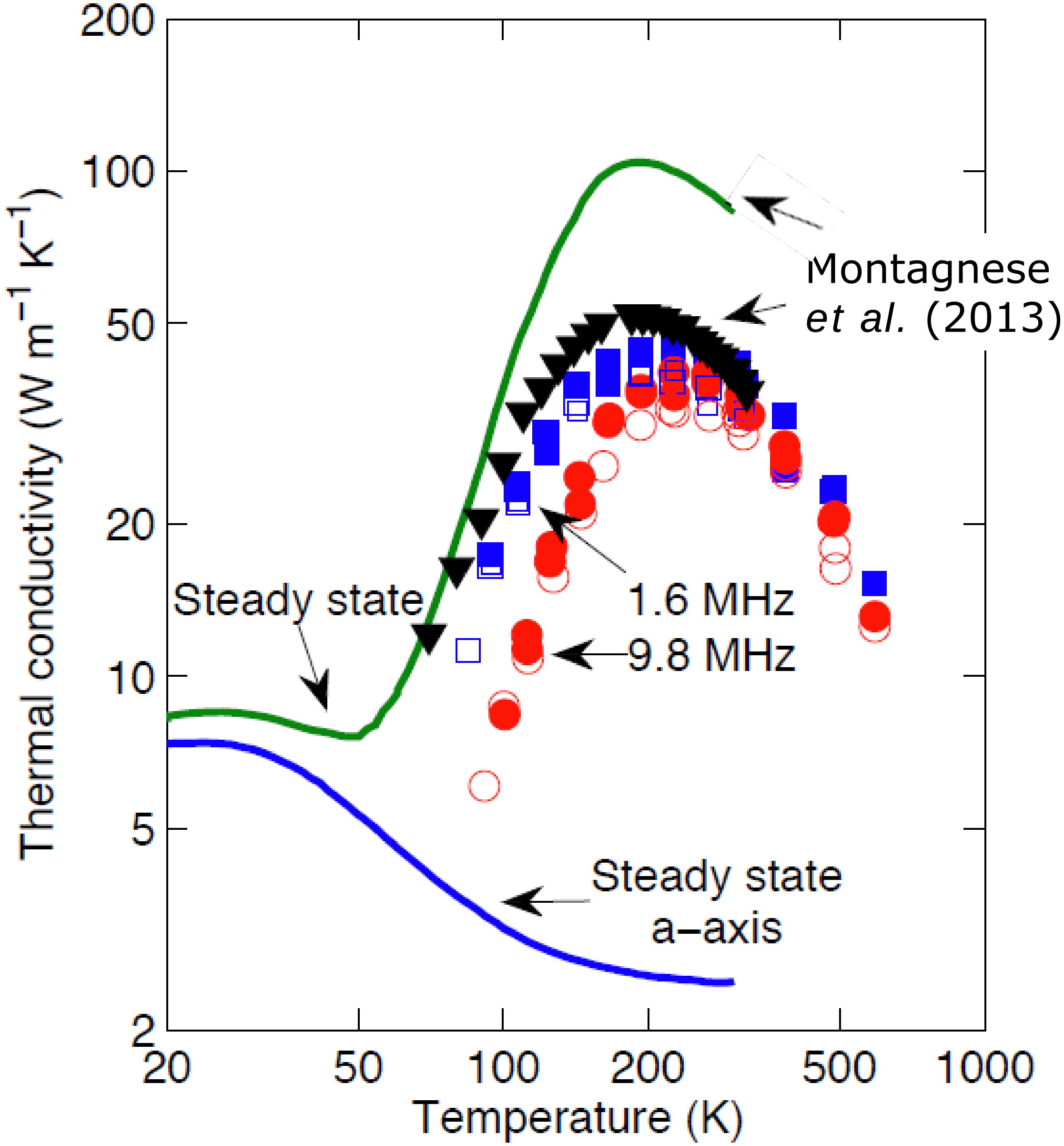
Ferromagnetic ground state

Thermally-excited spin-wave state



http://www.physics.usyd.edu.au/~sflammia/Courses/StatMech/advanced/4/a4.html

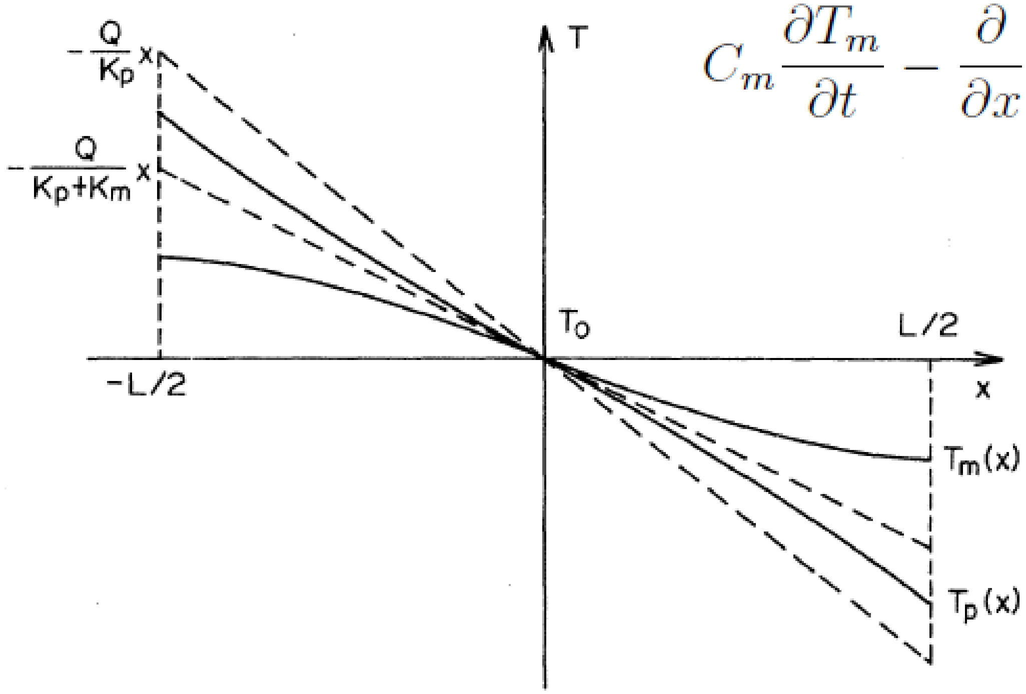
Frequency dependent spin-wave thermal conductivity in $Ca_9La_5Cu_{24}O_{41}$



Use a two-channel model: magnons and phonons

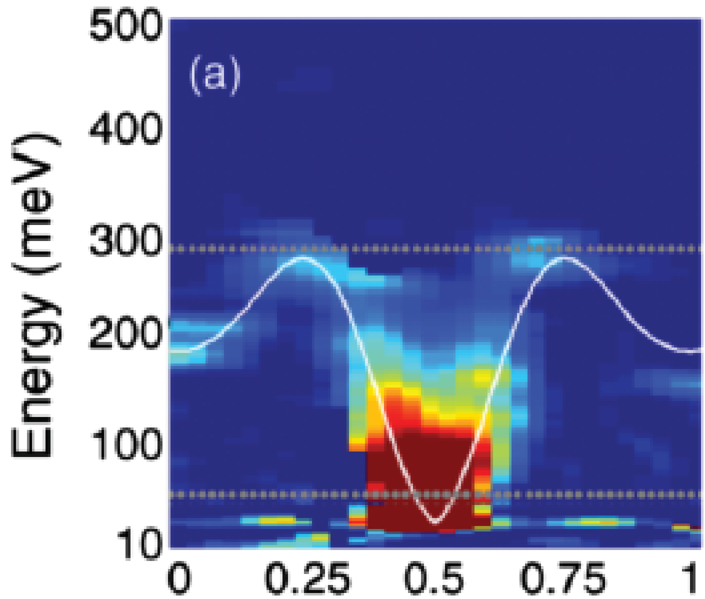
- Sanders and Walton (1977) analyzed the steady-state situation for the context of conventional thermal conductivity measurements. Only phonons can carry heat through the ends of the sample.

$$C_p \frac{\partial T_p}{\partial t} - \frac{\partial}{\partial x}\left(\Lambda_p \frac{\partial T_p}{\partial x}\right) + g(T_p - T_m) = 0$$
$$C_m \frac{\partial T_m}{\partial t} - \frac{\partial}{\partial x}\left(\Lambda_m \frac{\partial T_m}{\partial x}\right) + g(T_m - T_p) = 0.$$

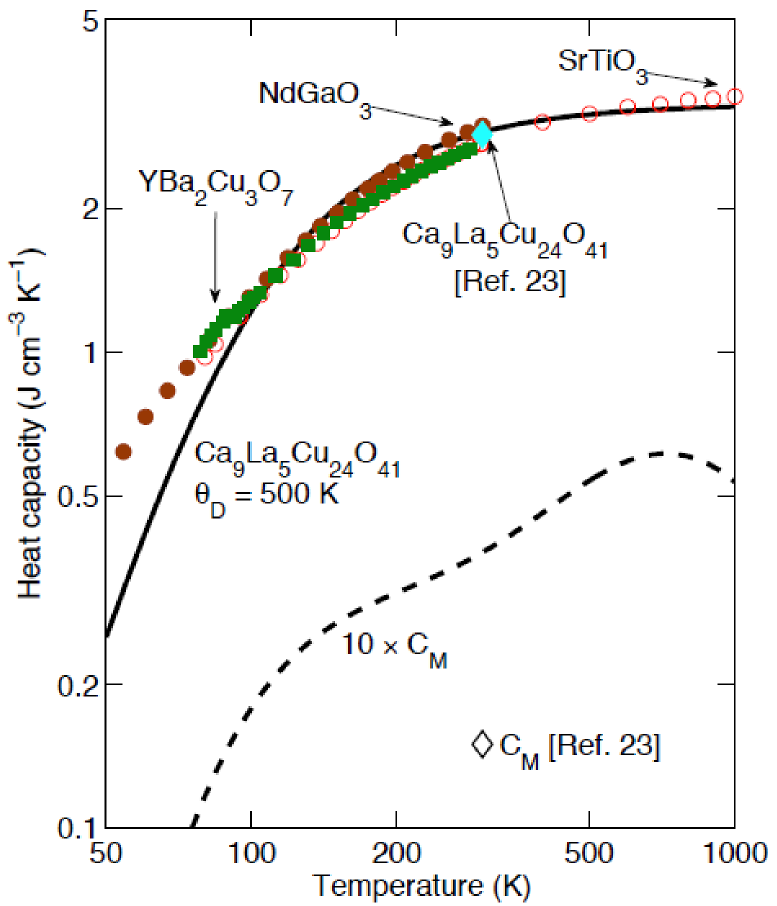


Need to fix as many parameters as possible

- Use magnon dispersion to estimate magnon heat capacity.
- Lattice and magnon thermal conductivity from Montagnese *et al*. (2013)



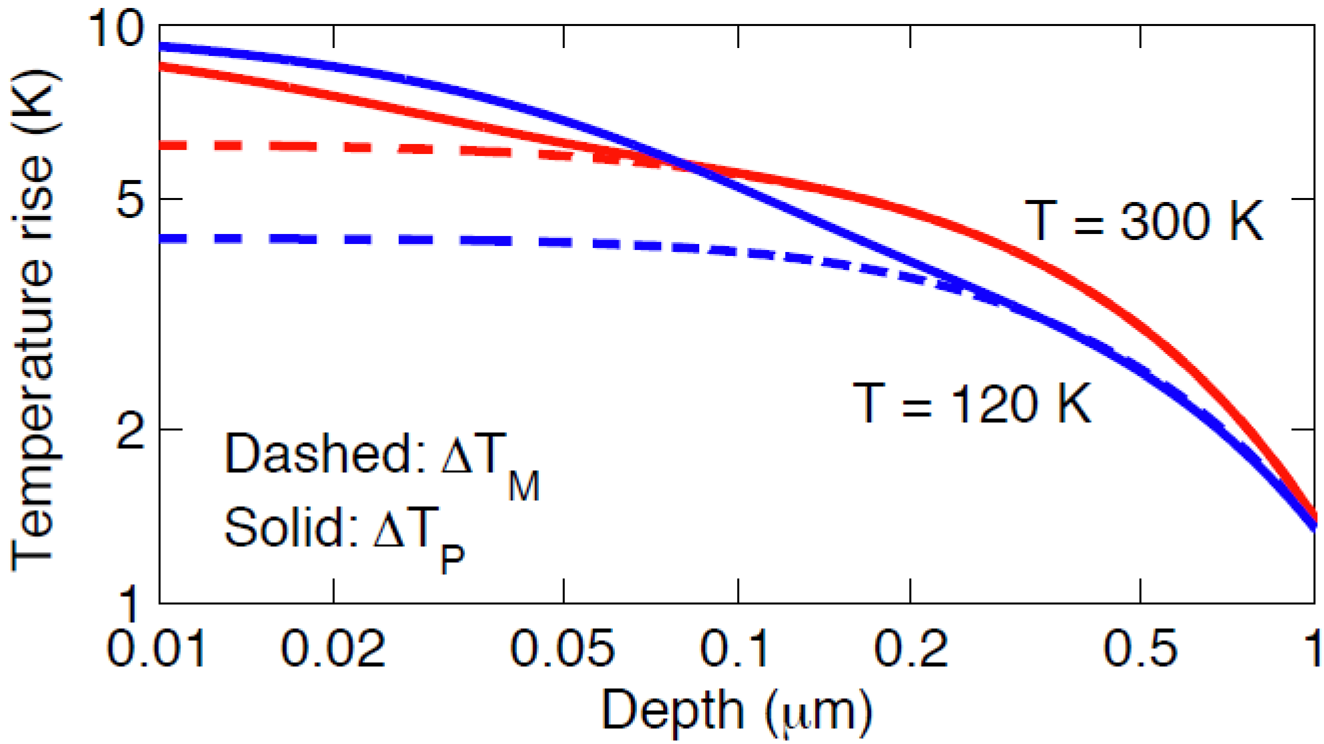
Notbohm, PRL 2007
(inelastic neutron scattering)



Hohensee *et al*., PRB (2014)

Use a two-channel model: magnons and phonons

- Model calculations for 10 MHz TDTR experiment. The coupling parameter g is adjust to get the best fit to the frequency dependent data

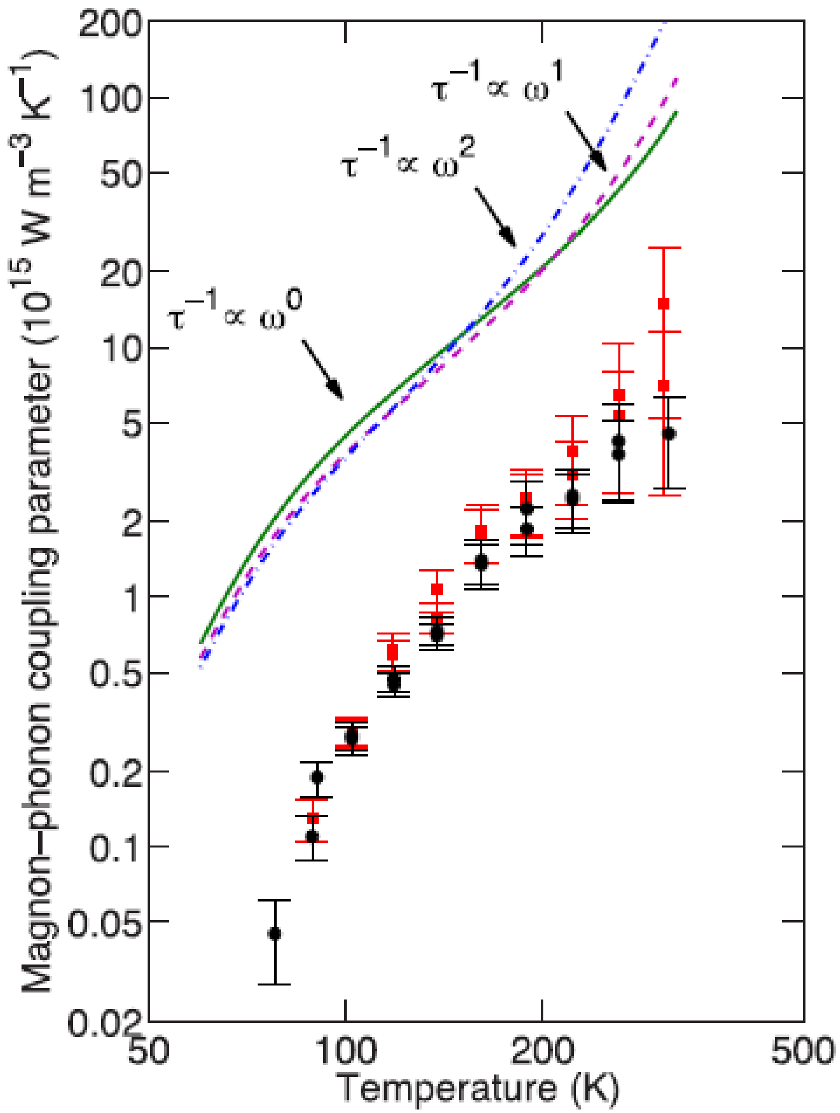


Hohensee *et al*., PRB (2014)

Magnon-phonon coupling parameter is strongly *T*-dependent

- $g \sim 10^{15}$ W m^{-3} K^{-1} near the peak in the thermal conductivity. (30 times smaller than g for electron-phonon coupling in Au.)
- Does this coupling (and therefore magnon-phonon scattering) determine the thermal conductivity near the peak?
- Is "two temperatures" too crude of a model to capture the physics?

PRB **89**, 024422 (2014)



More detail: Two-channel modeling of TDTR data

- Solution for one-dimension; can generalize to three-dimensions, see appendix of Wilson et al., PRB (2013)

$$\begin{bmatrix} T_1 \\ T_2 \end{bmatrix} = [X] \begin{bmatrix} B_1^- e^{-\lambda_1 z} + B_1^+ e^{\lambda_1 z} \\ B_2^- e^{-\lambda_2 z} + B_2^+ e^{\lambda_2 z} \end{bmatrix},$$

where λ^2 are the eigenvalues of the characteristic matrix

$$\begin{bmatrix} \alpha_1 & -g/\Lambda_1 \\ -g/\Lambda_2 & \alpha_2 \end{bmatrix}$$

and $[X]$ is the associated eigenvector matrix

$$[X] = \begin{bmatrix} v_1 & v_2 \\ u_1 & u_2 \end{bmatrix}.$$

$$\begin{bmatrix} B_1^- \\ B_2^- \end{bmatrix} = [Y]^{-1} \begin{bmatrix} q_1 \\ q_2 \end{bmatrix},$$

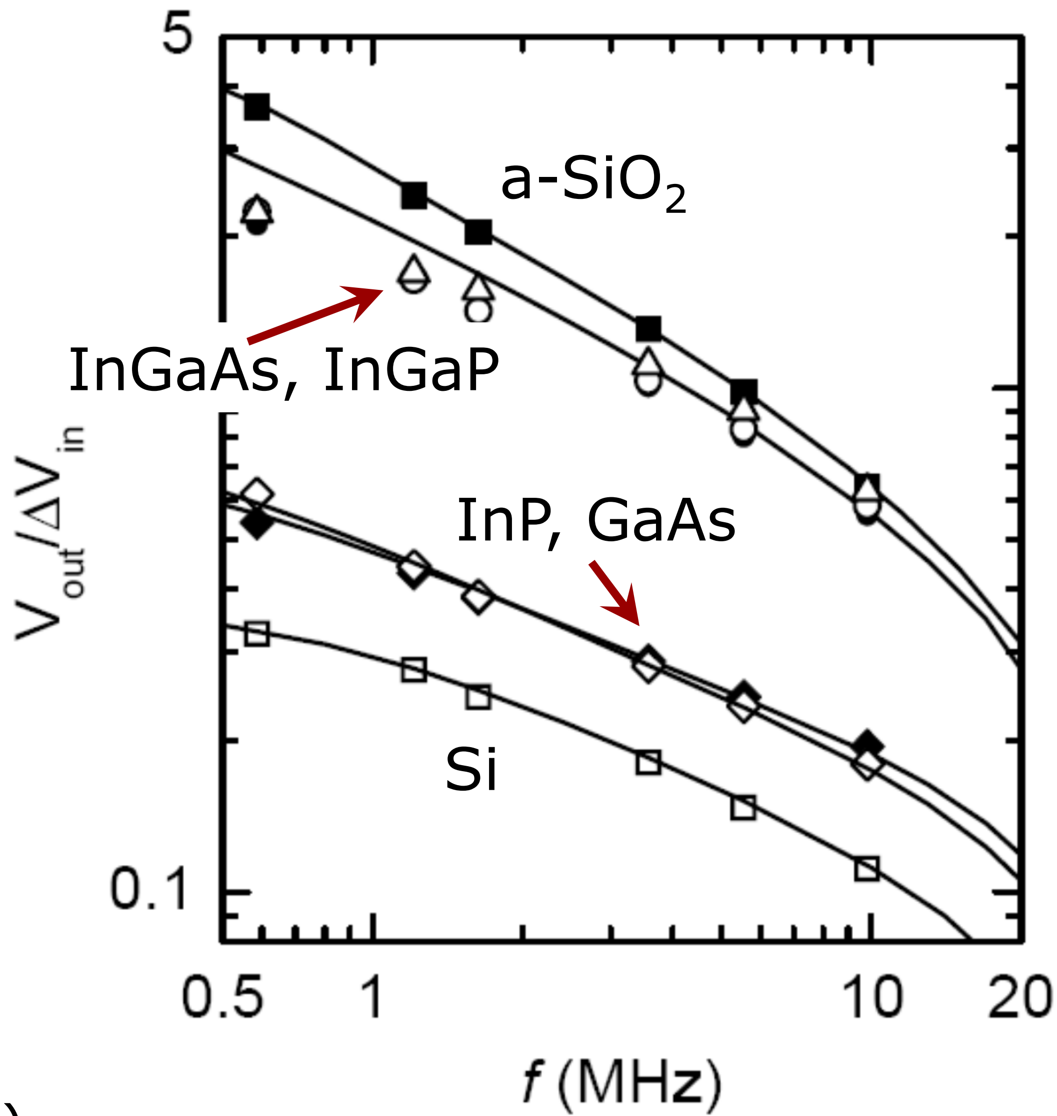
where

$$[Y] = \begin{bmatrix} \Lambda_1 & 0 \\ 0 & \Lambda_2 \end{bmatrix} [X] \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}.$$

Wilson *et al*., PRB (2013)

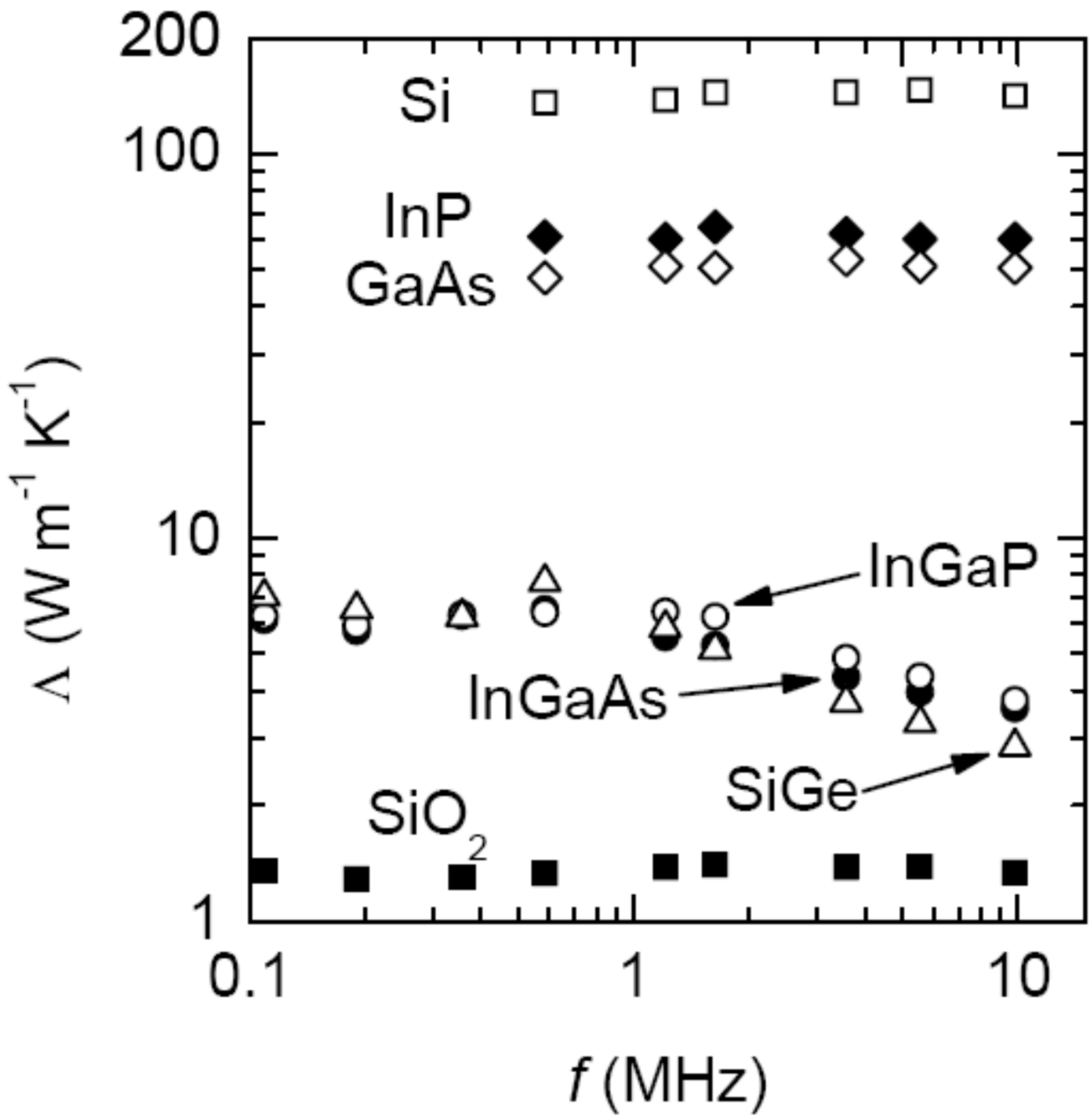
Phonon-phonon non-equilibrium effects in TDTR first reported in 2007

- fix delay time and vary modulation frequency *f.*
- semiconductor alloys show deviation from fit using a single value of the thermal conductivity
- Change in V_{in} doesn't depend on *f.* V_{out} mostly depends on $(f \Lambda C)^{-1/2}$



Koh and Cahill, PRB (2007)

Same data but allow Λ to vary with frequency *f*



How can thermal conductivity be frequency dependent at only a few MHz?

- $2\pi f\tau << 1$ for phonons that carry significant heat. For dominant phonons, τ ~100 ps, and $2\pi f\tau$ ~ 10^{-3}.
- But the thermal penetration depth d is not small compared to the dominant mean-free-path ℓ_{dom}.

$$d = \sqrt{\Lambda / \pi C f}$$

- Ansatz: phonons with $\ell(\omega) > d$ do not contribute to the heat transport in this experiment.
- True only if the "single-relaxation-time approximate" fails strongly. For single relaxation time τ, $\ell << d$ because $f\tau << 1$.

For non-equilibrium, add effusivity instead of conductivity

- Consider a "two-fluid" model with

$$\Lambda_1 \approx \Lambda_2$$

$$C_1 >> C_2$$

- Equilibrium,

$$(\Lambda C)^{1/2} = [(\Lambda_1 + \Lambda_2)(C_1 + C_2)]^{1/2}$$

- Out-of-equilibrium,

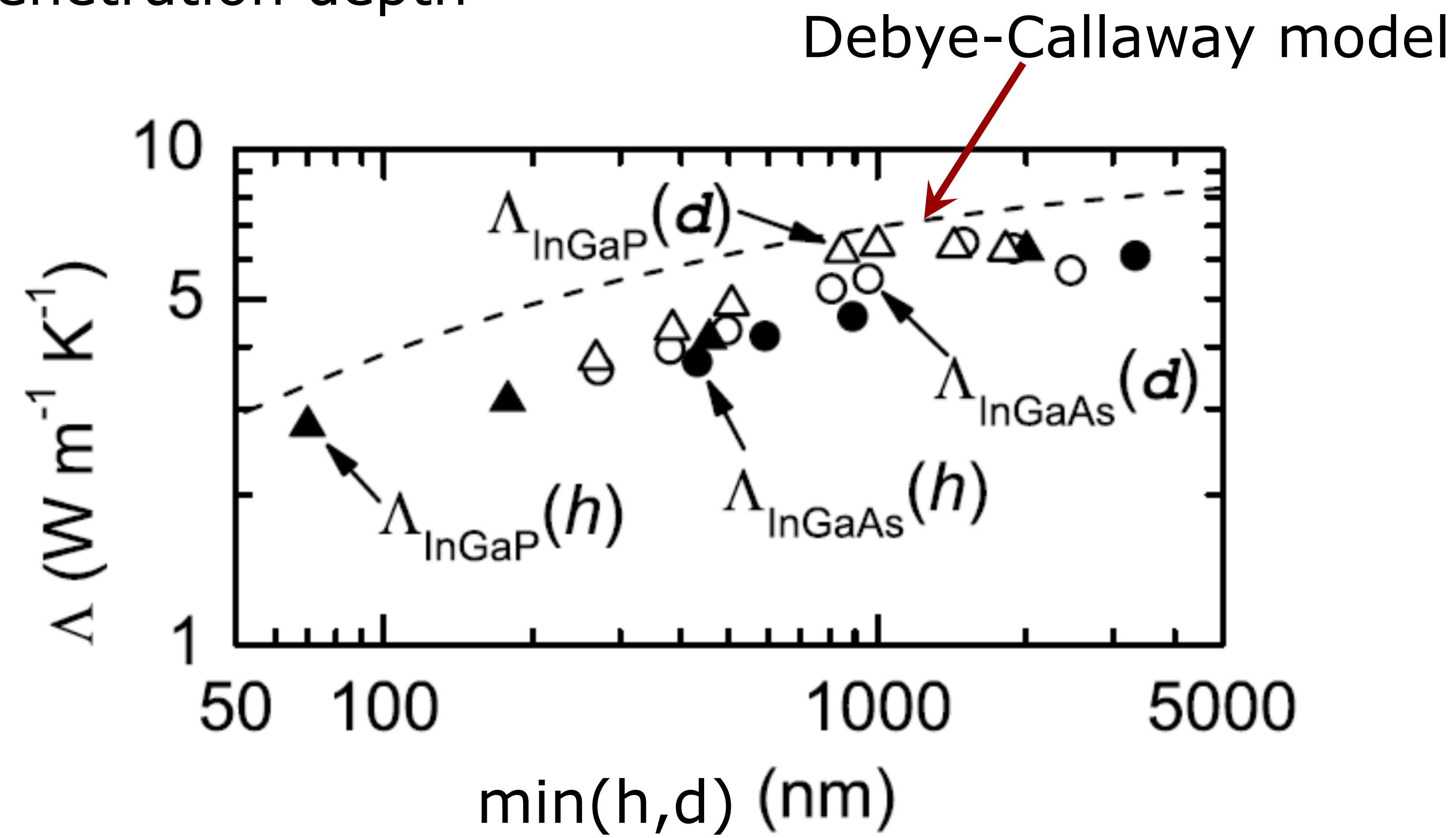
$$(\Lambda C)^{1/2} = (\Lambda_1 C_1)^{1/2} + (\Lambda_2 C_2)^{1/2}$$

$$\approx (\Lambda_1 C_1)^{1/2}$$

Frequency and thickness dependence for InGaP and InGaAs

- h=film thickness; d = thermal penetration depth

$$d = \sqrt{\Lambda / \pi C f}$$

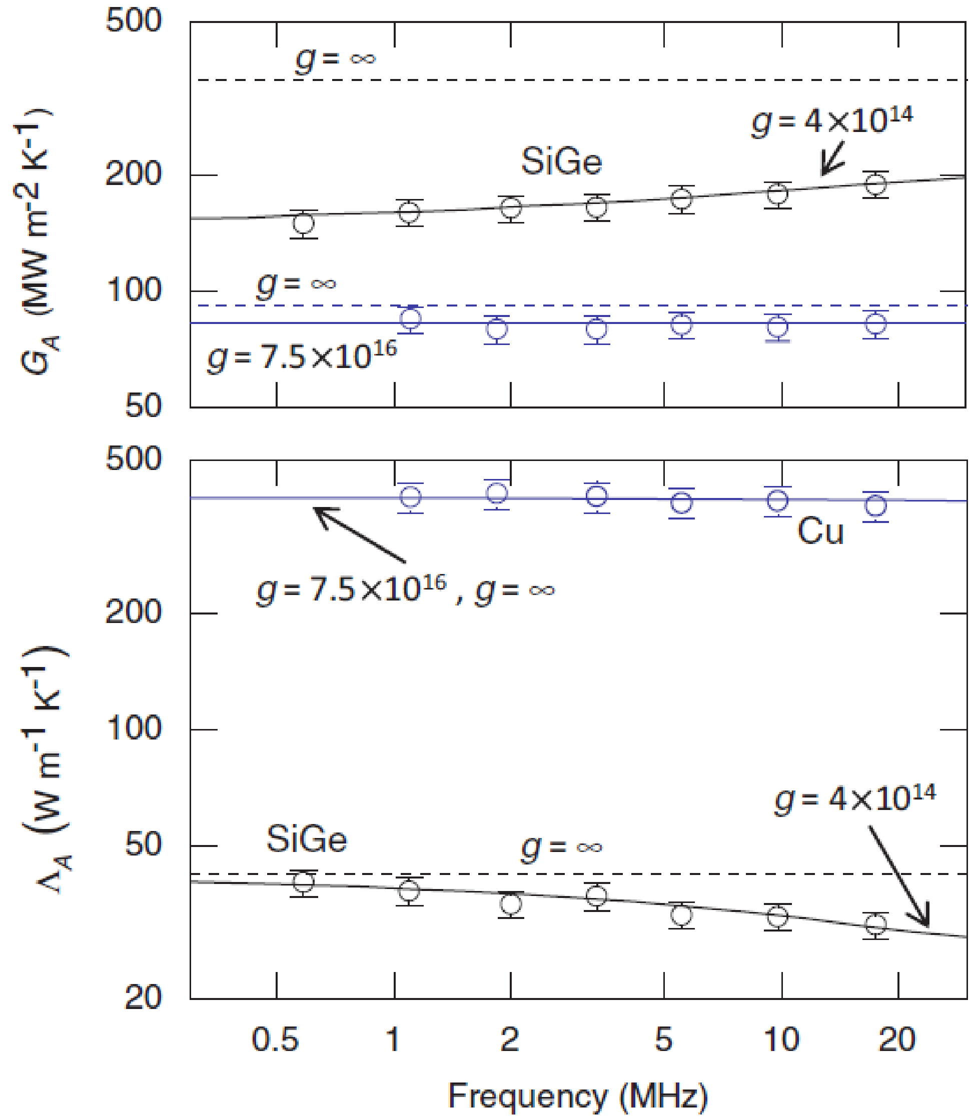


“Mean-free-path larger than thermal penetration depth” argument is probably not general; reliable only for the case a concentrated alloy (?)

- The suppression of magnon thermal conductivity as a function of frequency cannot be described in that manner even though the magnon mean-free-path is always smaller than the thermal penetration depth.
- Recent work by Rich Wilson has shown that both the apparent thermal conductivity and apparent interface conductance depend on frequency. The essence of this can be captured by a two-channel (or N-channel) model of low frequency phonons that have high thermal conductivity and low heat capacity and a thermal bath of high frequency phonons that have low thermal conductivity and high heat capacity.

Two-channel model for $Si_{99}Ge_{01}$ explains frequency dependence in both G and Λ

- Experiment and two-channel model for $Al/CuO_x/Cu$ and $Al/Si_{99}Ge_{01}$
- G_A and Λ_A are what would be derived from a one-channel model applied to the data.
- Solid and dashed lines are the predictions based on a two-channel model



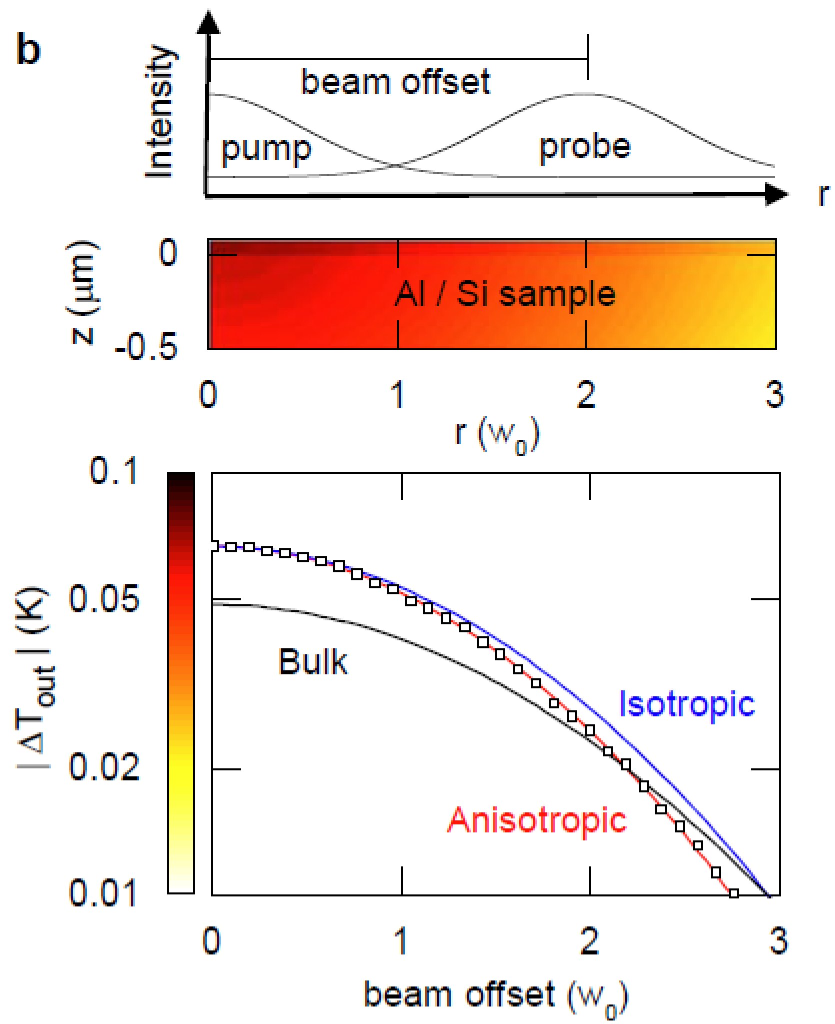
Wilson and Cahill, PRB (2013)

Beam-offset measurements on Si reveal anisotropy in apparent thermal conductivity

- Spot size w_0=1.05 μm.
- Measure V_{out} at negative delay time as a function of beam offset.
- Apparent thermal conductivity is anisotropic, radial component is reduced by nearly a factor of 2,

$$\Lambda_r \approx 80\ \mathrm{W\ m^{-1}\ K^{-1}}$$

$$\Lambda_z \approx 140\ \mathrm{W\ m^{-1}\ K^{-1}}$$

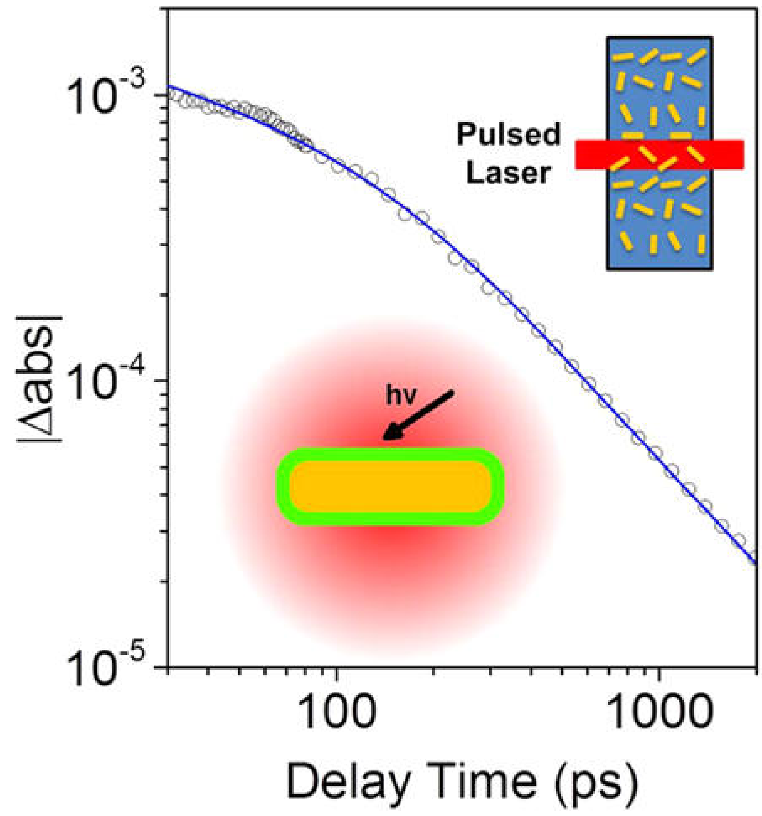


Wilson and Cahill, submitted

Thermoreflectance is not the only ultrafst optical thermometry we can use to study nanoscale thermal science

- Transient adsorption using plasmon resonances of Au nanostructures

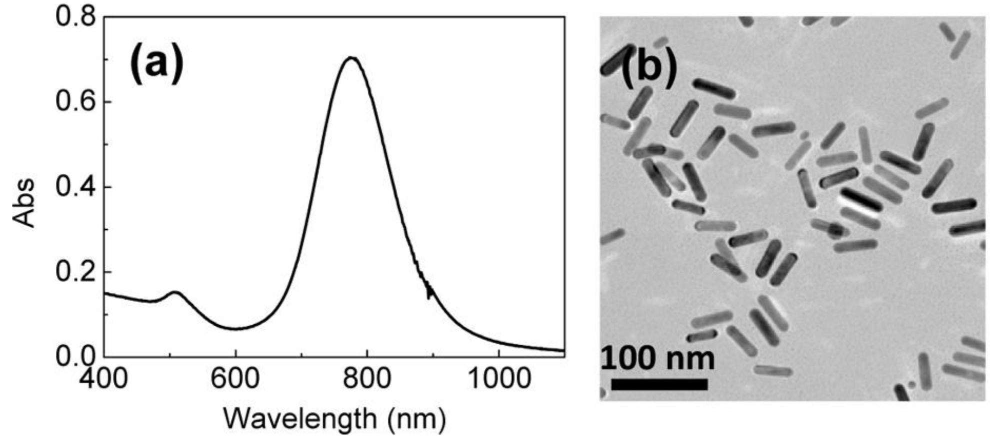
- Sensitive to both the temperature of the Au and the surrounding dielectric. Learning how to separate the effects.
  - At a wavelength near the peak absorption, only the Au temperature is important.
  - Signal from surrounding material can be isolated by realizing that the surrounding material cannot heat instantaneously.



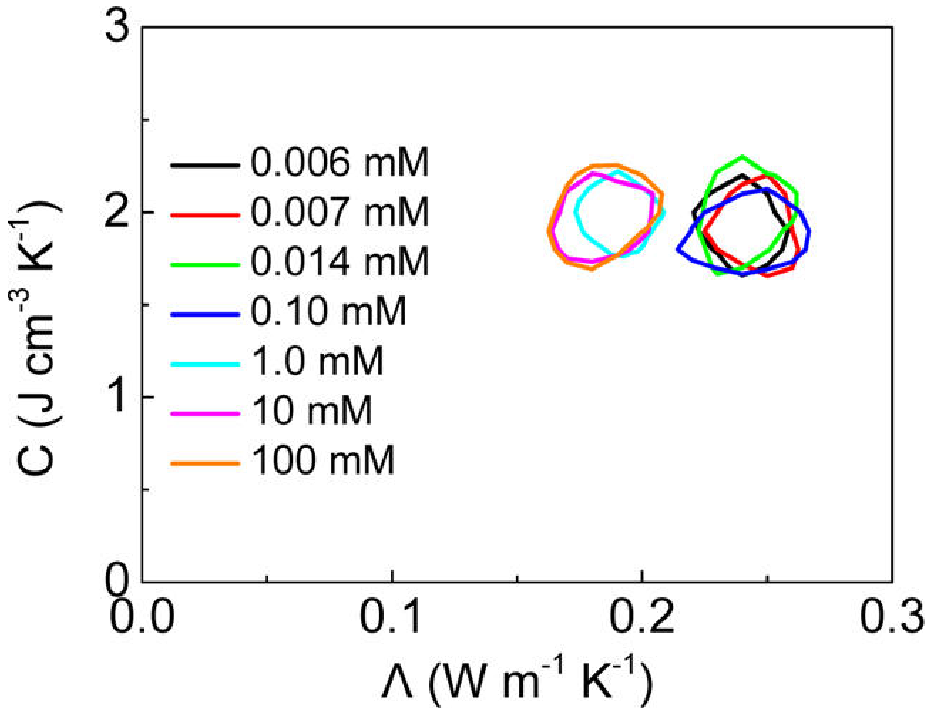
Huang et al, ACS Nano (2012)

Ultrafast thermal analysis of surfactant layers surrounding Au nanorods

- Aspect ratio tuned so that the absorption peak can be aligned with the Ti:sapphire laser wavelength.



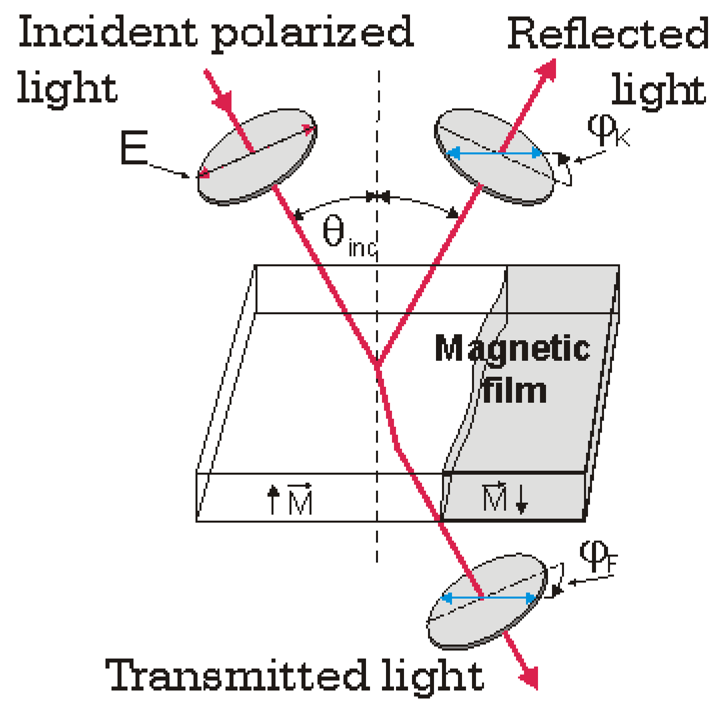
- Heat capacity and thermal conductivity of CTAB surfactant layers as a function of CTAB concentration in solution.



Huang et al, ACS Nano (2012)

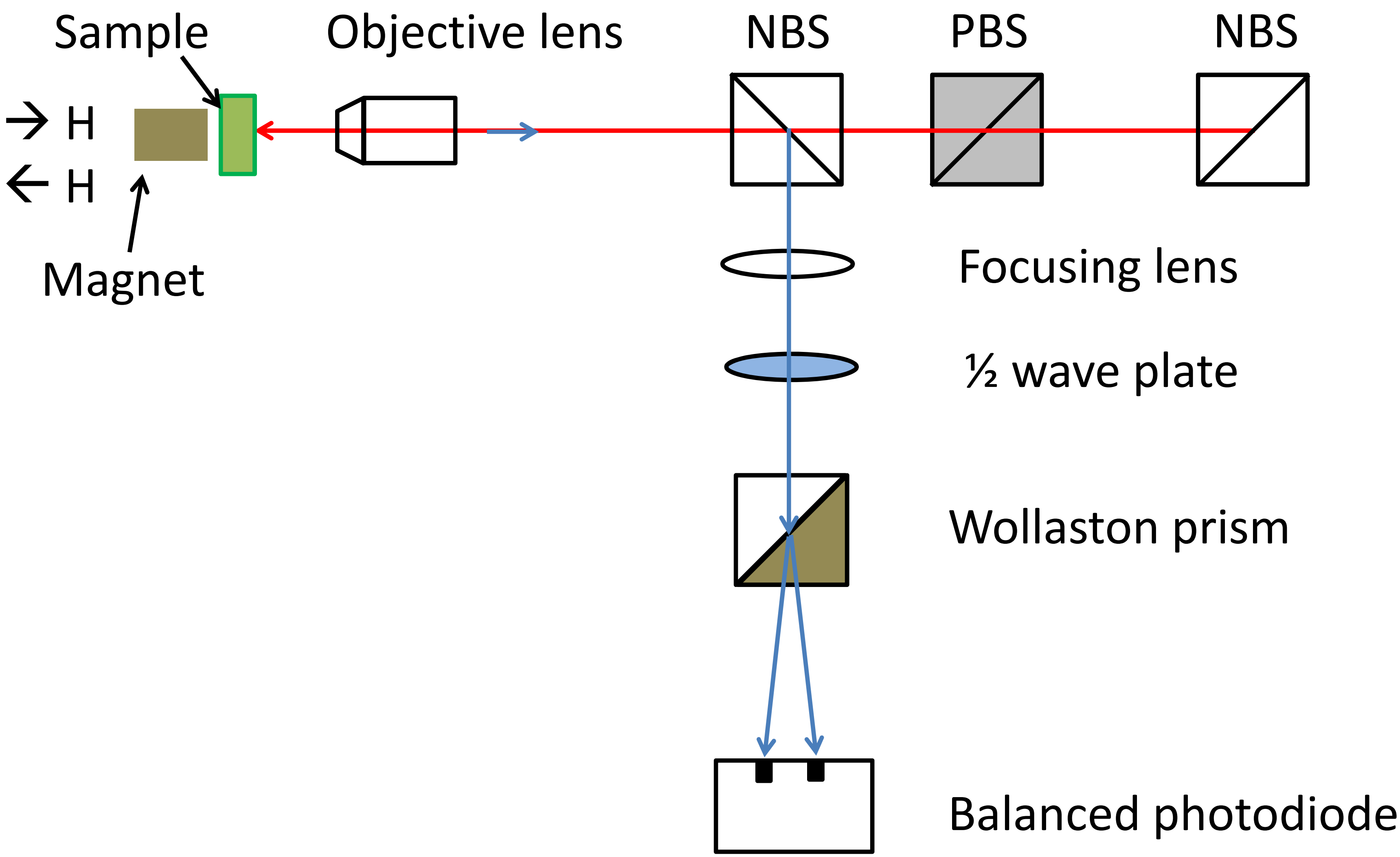
Thermoreflectance is not the only ultrafst optical thermometry we can use to study nanoscale thermal science

- Magnetic-optic Kerr effect
  - Polarization rotates upon reflection from a ferromagnetic material. Perpendicular magnetization simplifies the optical design



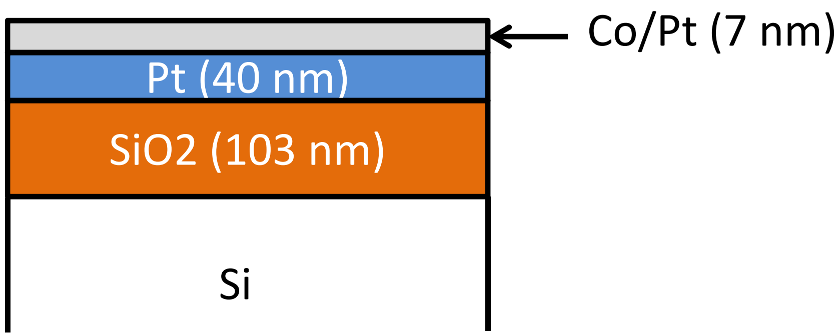
http://labfiz.uwb.edu.pl/exp/domeny/nowe/magnetooptic.php

Schematic of TR-MOKE Setup (Reflectance Configuration)

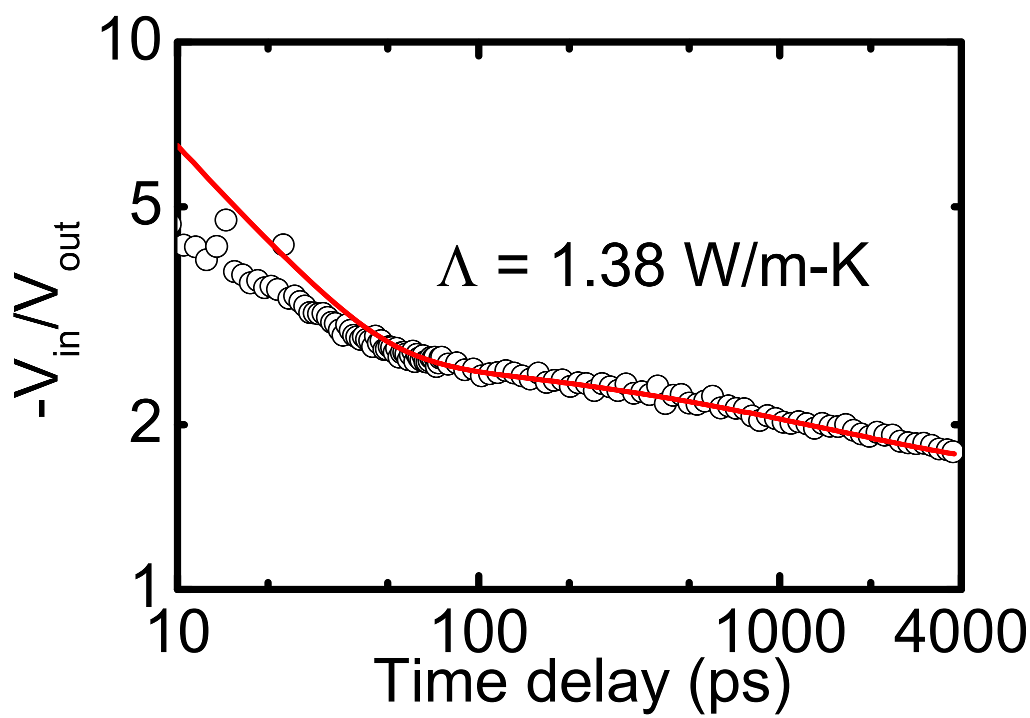


Validation Measurement

Co/Pt+Pt on SiO2/Si reference sample



Layer	Λ	C	h
	[W/m-K]	[J/cm^3-K]	[nm]
Co/Pt	20	3.15	7
Pt	40	2.84	40
G	0.2	0.1	1
SiO2	1.38 (fit)	1.62	103
G	0.1	0.1	1
Si	142	1.64	1e6



Summary

- Improvements to sensitivity to in-plane thermal conductivity will require smaller spot-sizes and lower thermal conductance transducer. Both of these goals might be best achieved by time-resolved magneto-optic Kerr effect. (Work in progress).
- Two-channel model is a significant advance that enables quantitative modeling of coupled electron-phonon transport in metals and magnon-phonon transport in quantum anti-ferromagnetic cuprates.
- Phonon-phonon non-equilibrium effects are complicated. Simple interpretation in terms of phonon-mean free paths and thermal penetration depths might be limited to concentrated alloy non-metallic crystals.