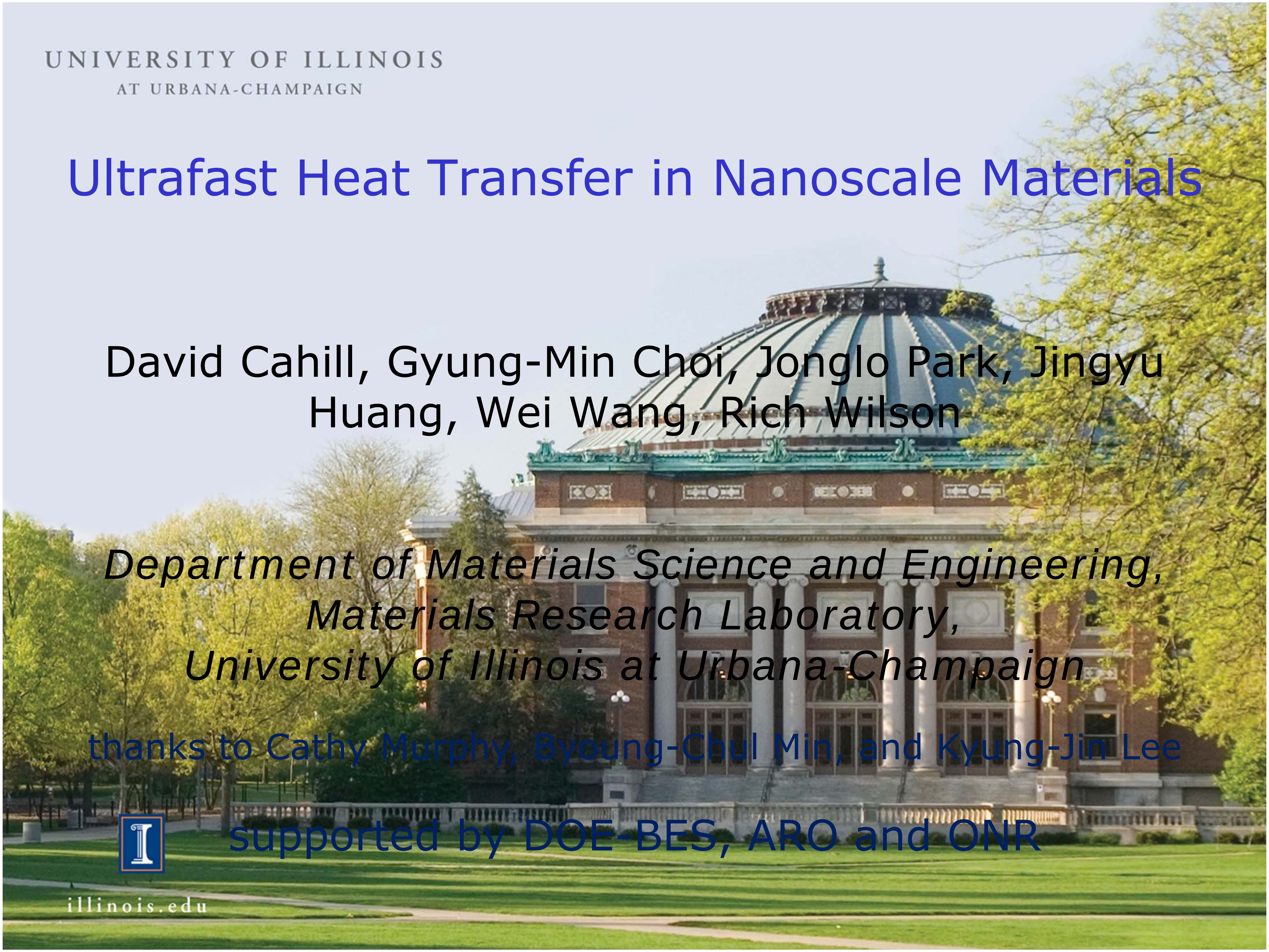

UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

Ultrafast Heat Transfer in Nanoscale Materials

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illinois.edu

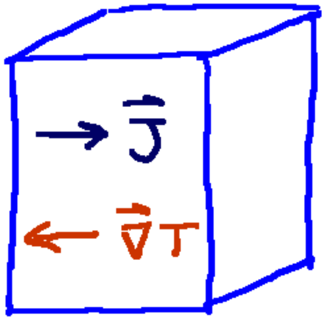
Outline

- Introduction: Heat transfer on length scales of nanometers and time-scales of picoseconds
- How fast can a nanoparticle cool?
  - Transfer of vibrational thermal energy across an interface
- How fast can heat be exchanged between two metals?
  - Transfer of electronic thermal energy across an interface and between electrons and phonons
- What is the largest heat current we can pass through a nanoscale ferromagnetic layer?
  - Thermal generation of spin currents by demagnetization and the spin-dependent Seebeck effect.

Thermal transport coefficients

- Thermal conductivity Λ is a property of the continuum

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

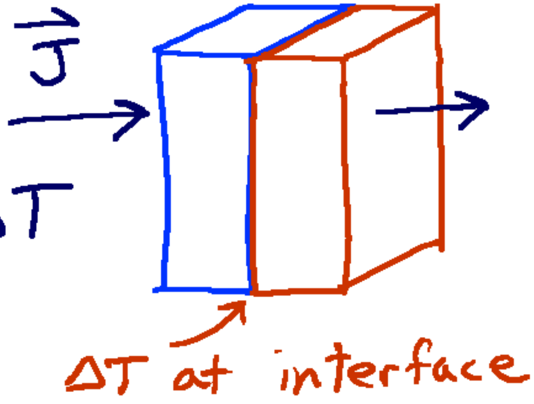


$$\Lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \vec{j}(t)\cdot\vec{j}(0)\rangle\, dt$$

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

$$\vec{J}$$

$$J = G \Delta T$$



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

Thermal transport coefficients

- Thermal conductivity Λ appears in the diffusion equation

$$C\frac{dT}{dt} = \Lambda\nabla^2 T$$

C = heat capacity per unit volume

Diffusivity $D = \frac{\Lambda}{C}$

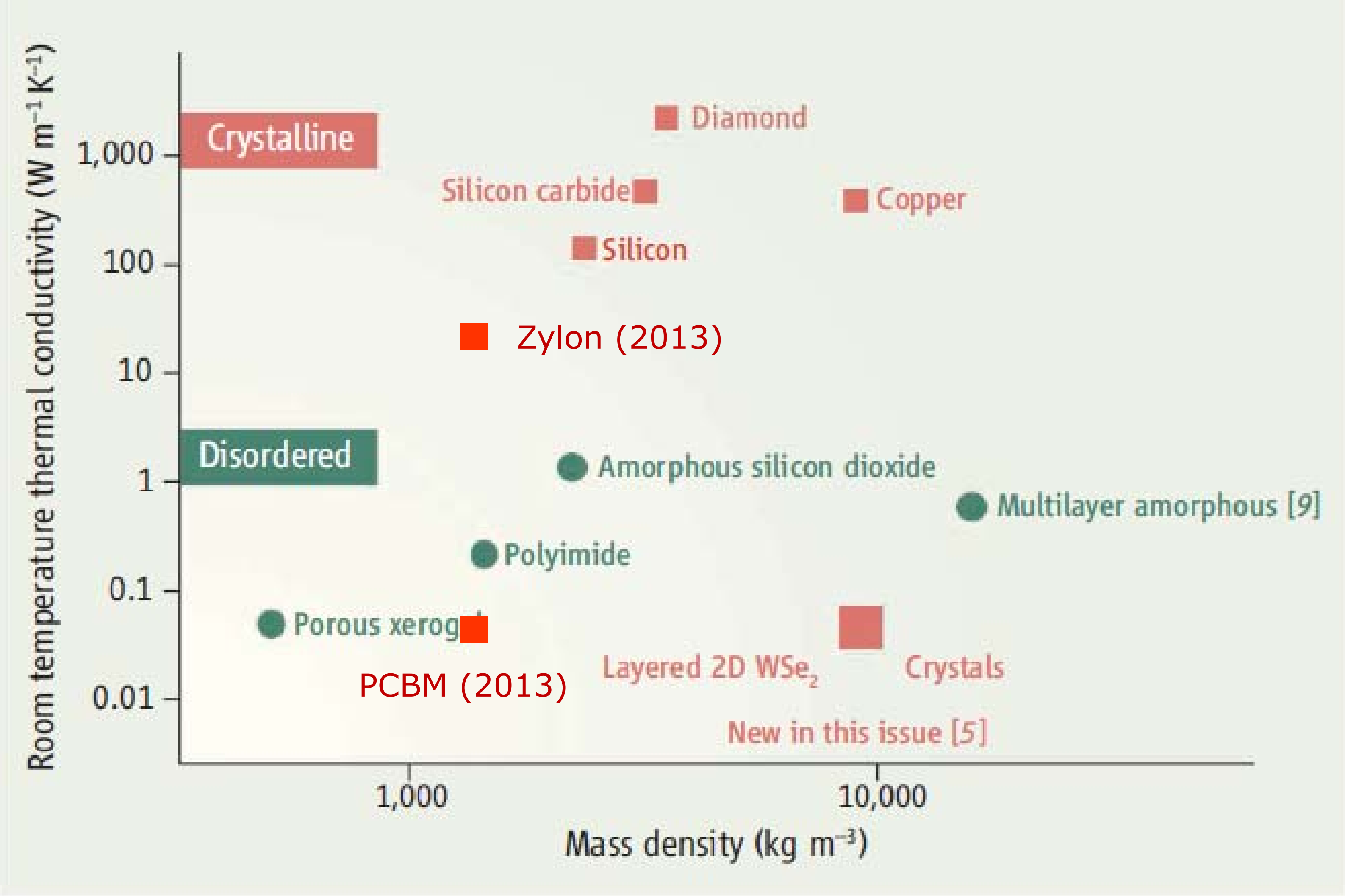
Effusivity $\varepsilon = \sqrt{\Lambda C}$

- Interface thermal conductance G is a radiative boundary condition

$$G\left(T_+ - T_-\right) = \Lambda \left.\frac{dT}{dz}\right|_{z=0}$$

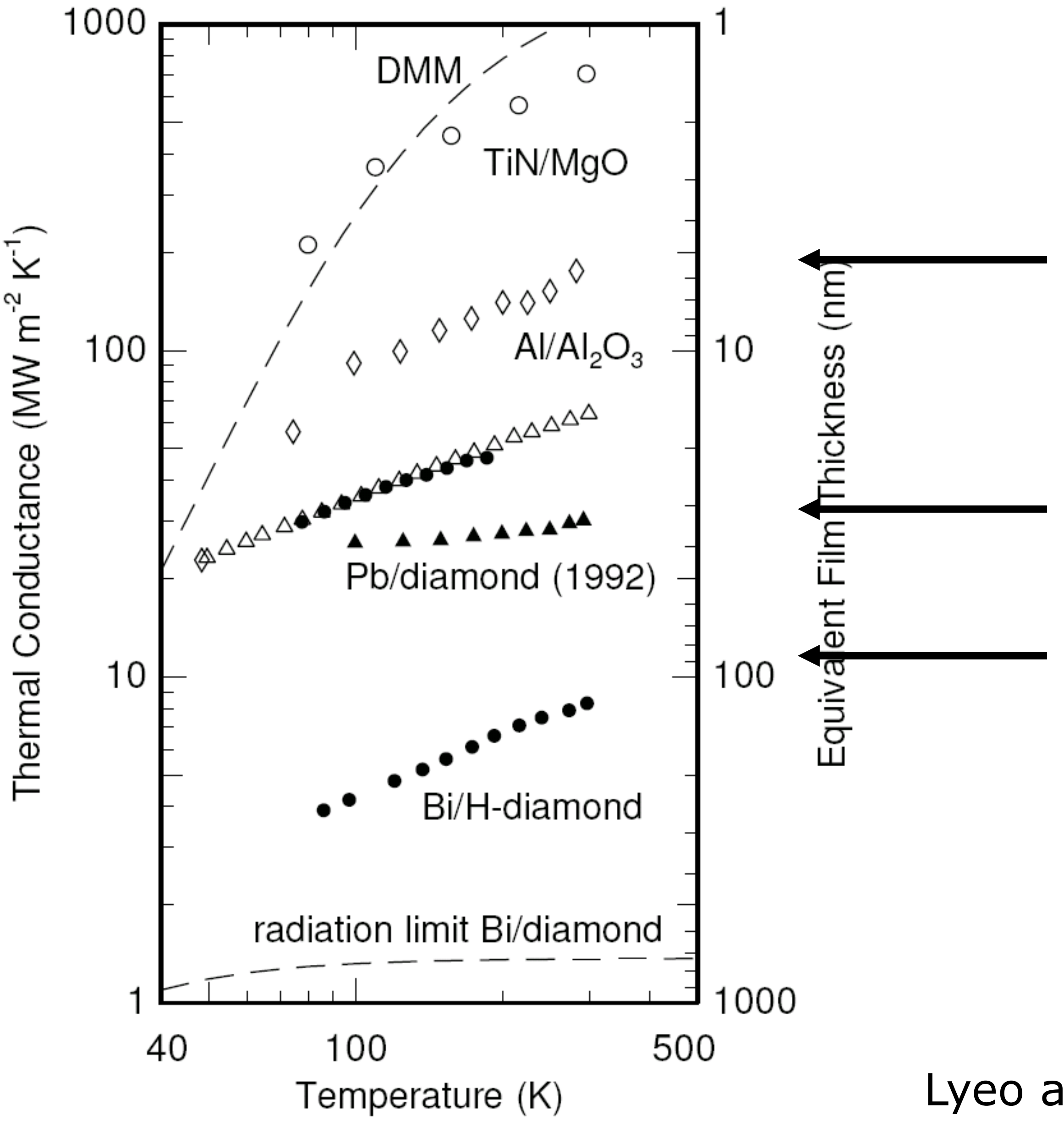
Kapitza length $L_K = \frac{\Lambda}{G}$

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



Adapted from Goodson, *Science* (2007)

Interface conductance spans a factor of 60 range at room temperature



W/Al_2O_3

Au/water

$PMMA/Al_2O_3$

nanotube/alkane

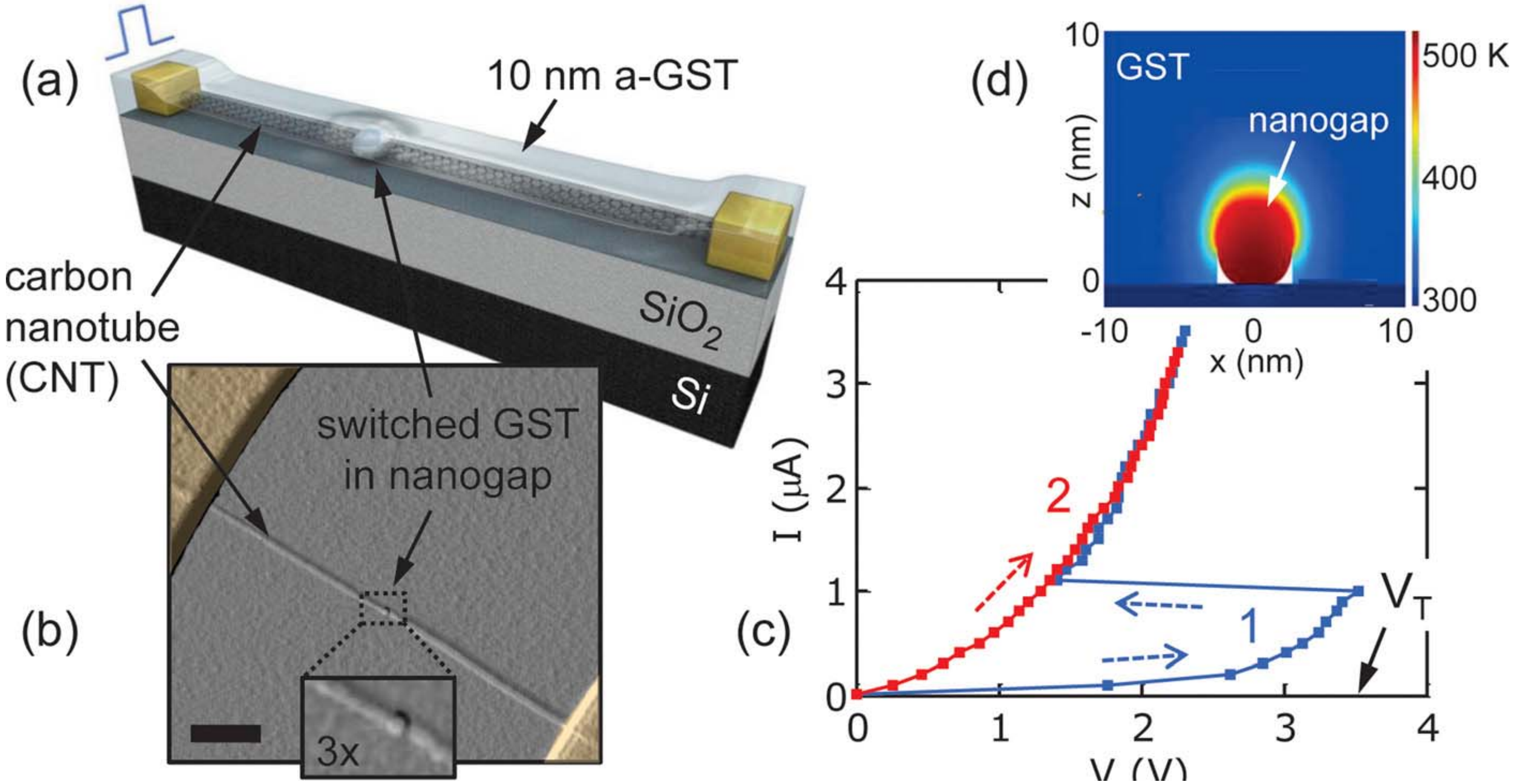
Lyeo and Cahill, PRB (2006)

Heat capacity per unit volume of solids spans only a factor of 4 at room temperature

Material	**C (MJ m^{-3} K^{-1})**
water	4.18
Ni	3.95
Al	2.42
Diamond	1.78
Polymer (PMMA)	1.8
PbTe	1.2

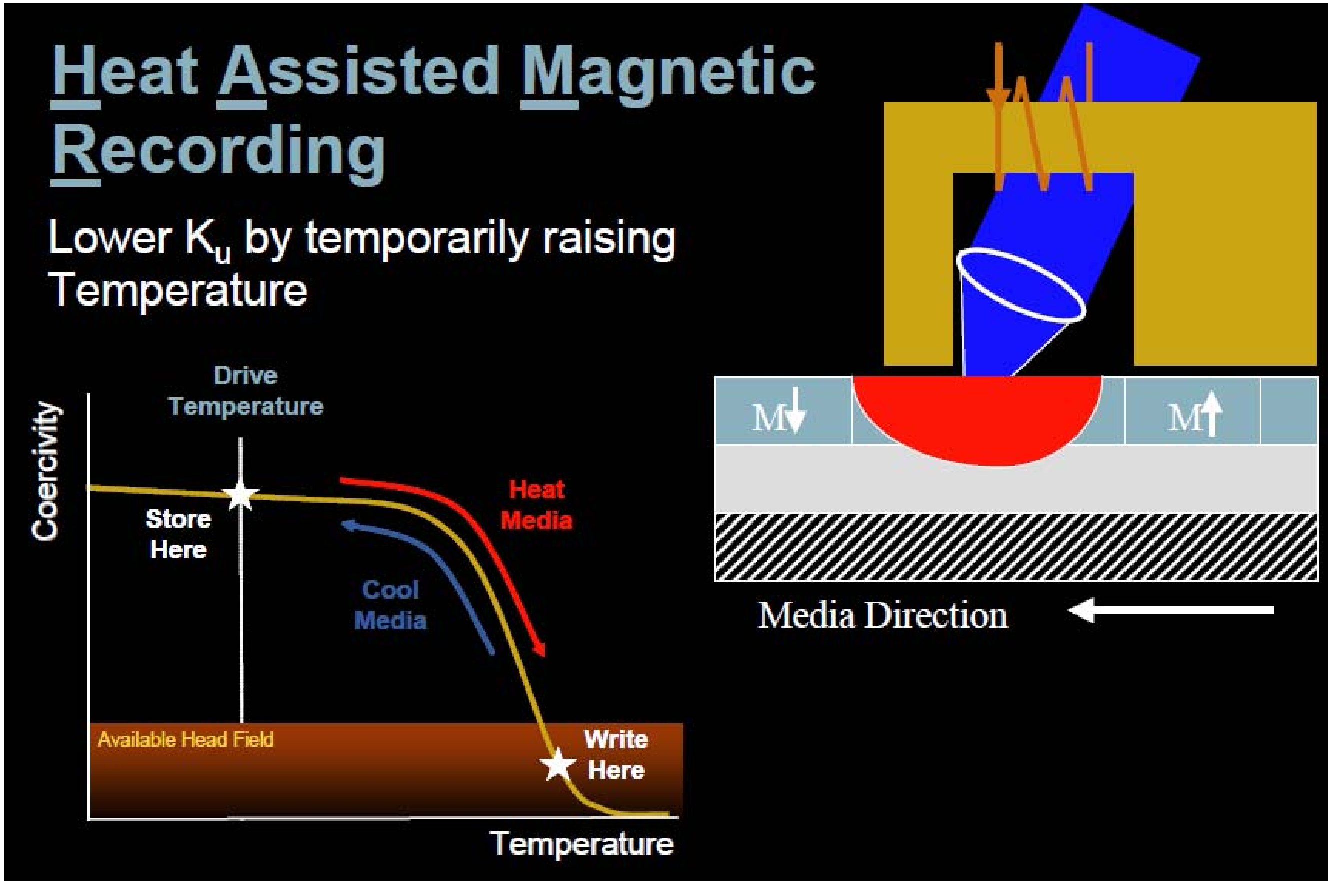
Technology drivers for fundamental studies of ultrafast heat transfer at the nanoscale

Proposed next generation phase change memory device



E. Pop and co-workers in *Science*, reviewed by Cahill *et al*., Appl. Phys. Rev. **1**, 011305 (2014)

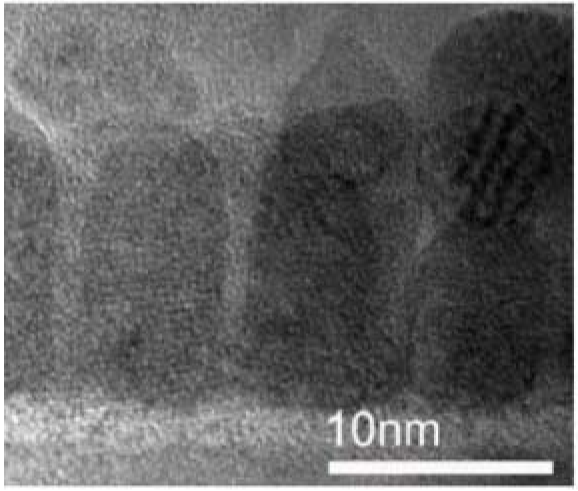
Technology drivers for fundamental studies of ultrafast heat transfer at the nanoscale



Heat Assisted Magnetic Recording

Lower K_u by temporarily raising Temperature

HAMR media FePt:C



Velocity of media 10 m s^{-1}. Size of bit 10 nm. Time-scale 1 ns.

Kryder *et al*., Proc. IEEE **96,** 1810 (2008)

I. How fast can a rapidly-heated nanoparticle cool?

- Limited by interface conductance.
  - Equivalent to discharging of a capacitor through a resistor

$$\tau_G = (VC)\left(\frac{1}{AG}\right) = \frac{1}{3}\frac{rC}{G}$$

  - Order of magnitude estimate

$r = 3$ nm; $C = 3$ MJ m^{-3} K^{-1}; $G = 100$ MW m^{-2} K^{-1}

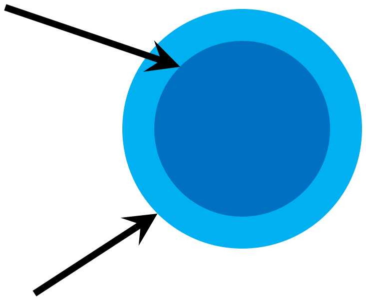
$\tau_G = 30$ ps

I. How fast can a rapidly-heated nanoparticle cool?

- Limited by effusivity of the surrounding fluid
  - Solvable but let’s instead approximate by asking “when does the heat capacity of a layer of the thermal diffusion distance in the fluid equal the heat capacity of the particle?”

$$\left(4\pi r^2\right)\left(\sqrt{D\tau_E}\right)C_f = \frac{4\pi}{3} r^3 C_p$$

$$C_f \approx C_p = C; \qquad \tau_E = \frac{r^2}{9D}$$

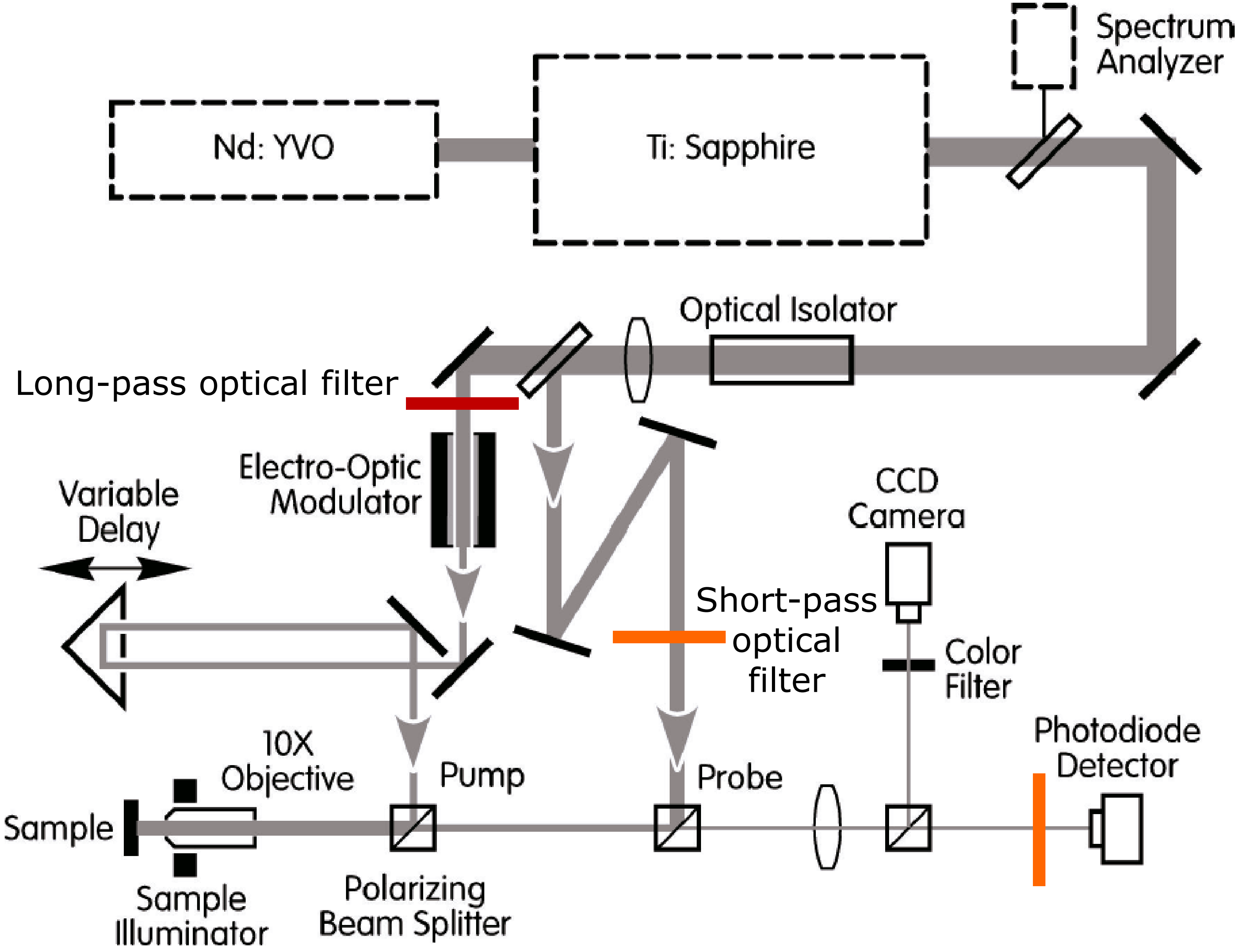


r = 3 nm; D = 10^{-7} m^2 s^{-1}

τ_E = 100 ps

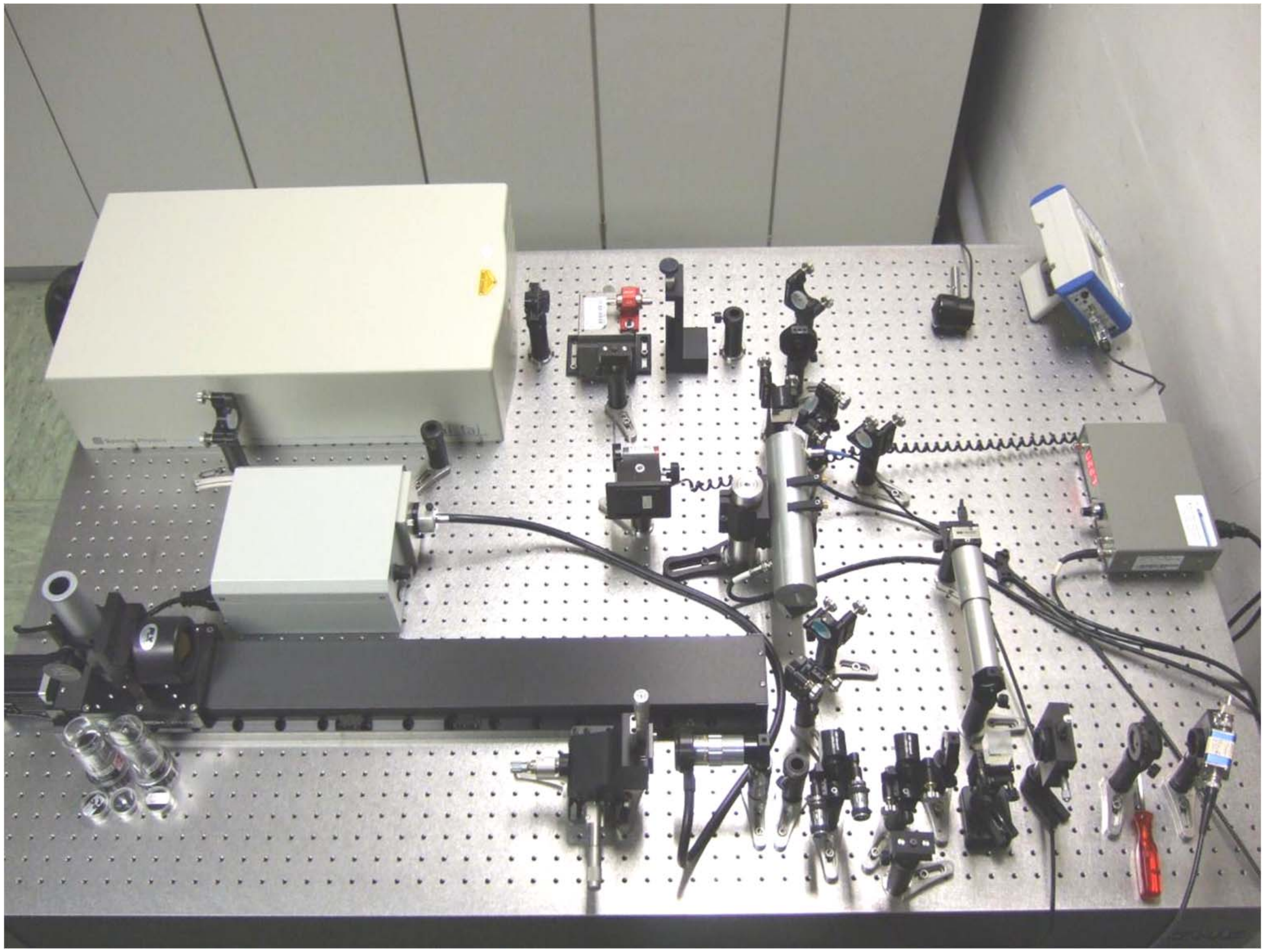
Wilson *et al*., PRB (2002)

Time-domain thermoreflectance



Kang *et al*., RSI (2008)

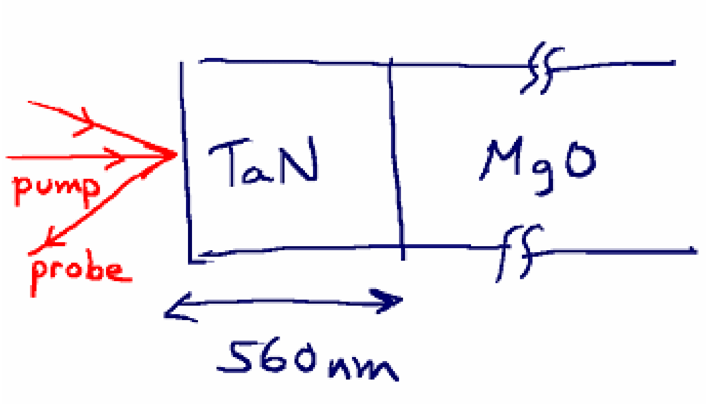
Time-domain thermoreflectance

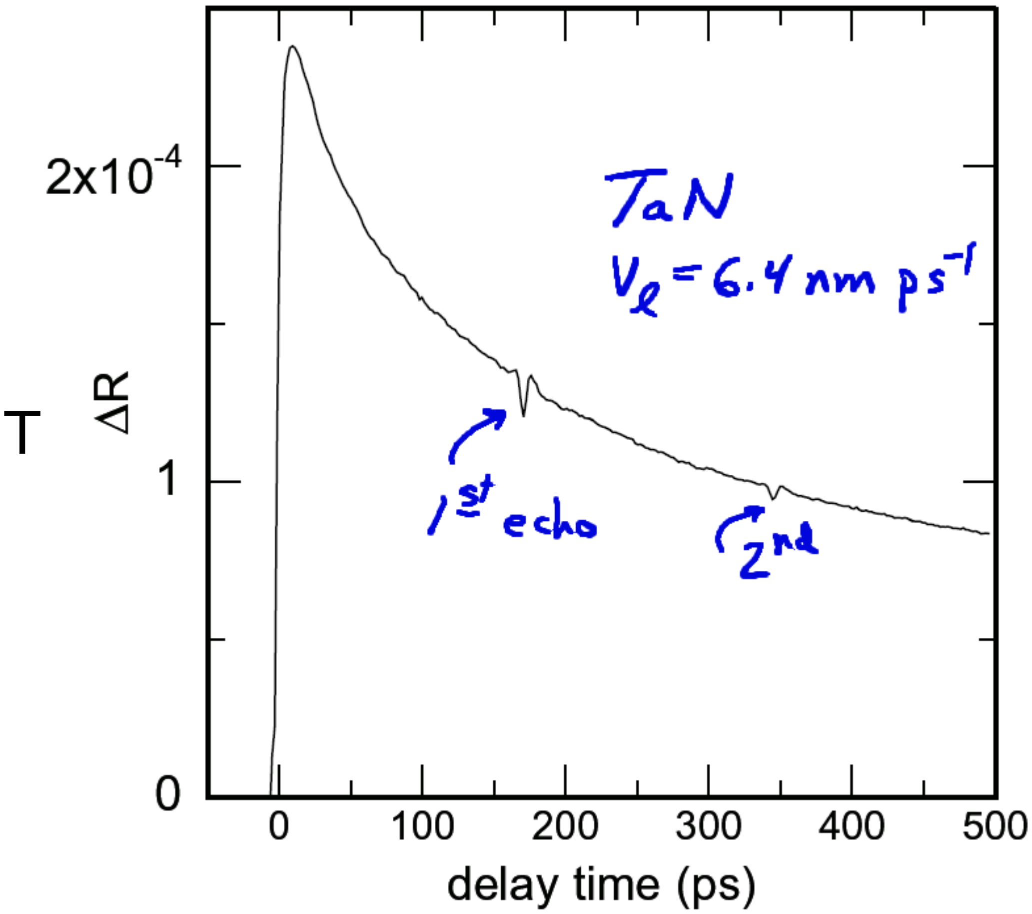


Clone built at Fraunhofer Institute for
Physical Measurement, Jan. 7-8 2008

psec acoustics and time-domain thermoreflectance

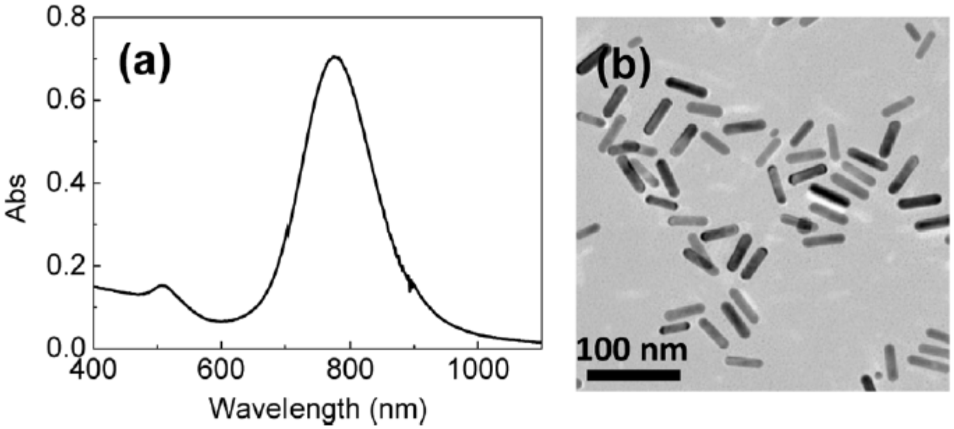
- Optical constants and reflectivity depend on strain and temperature
- Strain echoes give acoustic properties or film thickness
- Thermoreflectance dR/dT gives thermal properties

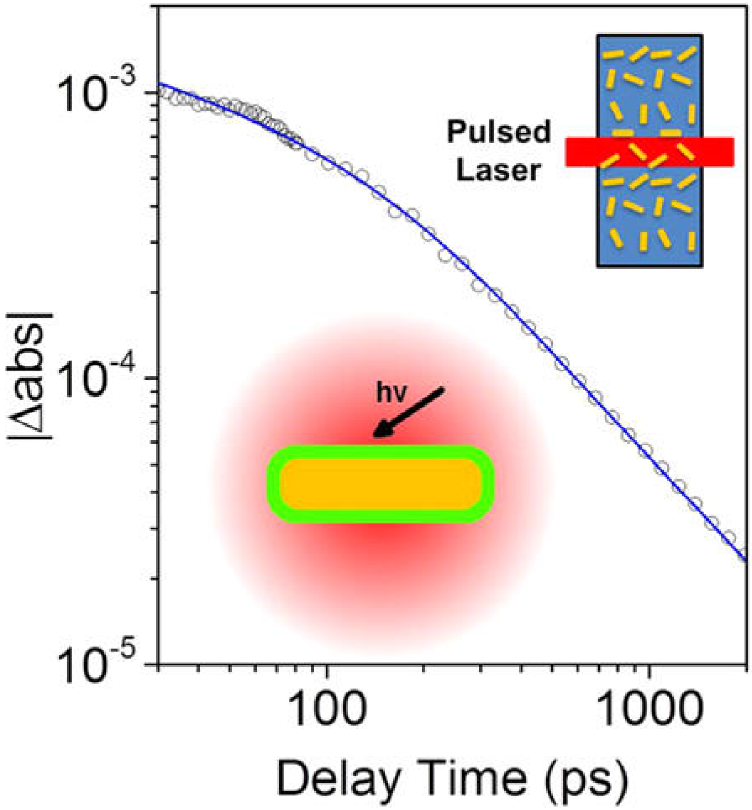




Thermoreflectance is only one of many methods for ultrafast optical thermometry

- Transient adsorption using plasmon resonances of Au nanostructures is sensitive to both the temperature of the Au and the surrounding dielectric.
  - At a wavelength near the peak absorption, only the Au temperature is important.

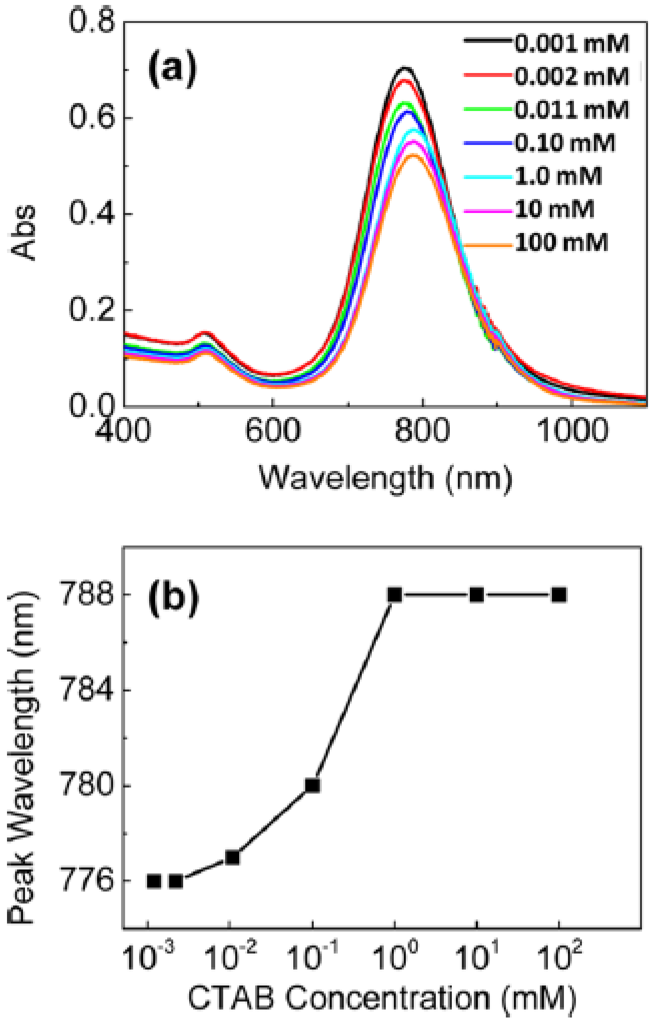




Huang et al, ACS Nano (2012)

Ultrafast thermal analysis of surfactant layers surrounding Au nanorods

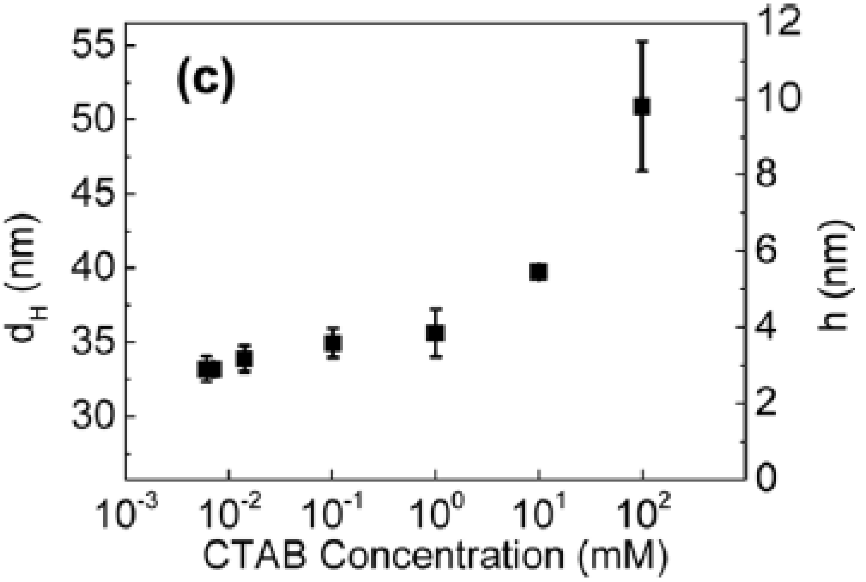
- Vary surfactant thickness by changing concentration of CTAB in aqueous solution.
- Index of refraction of CTAB surfactant is larger than water and creates a red-shift of the plasmon resonance.
- CTAB forms micelles in water at a concentration of ≈1 mM (critical concentration)



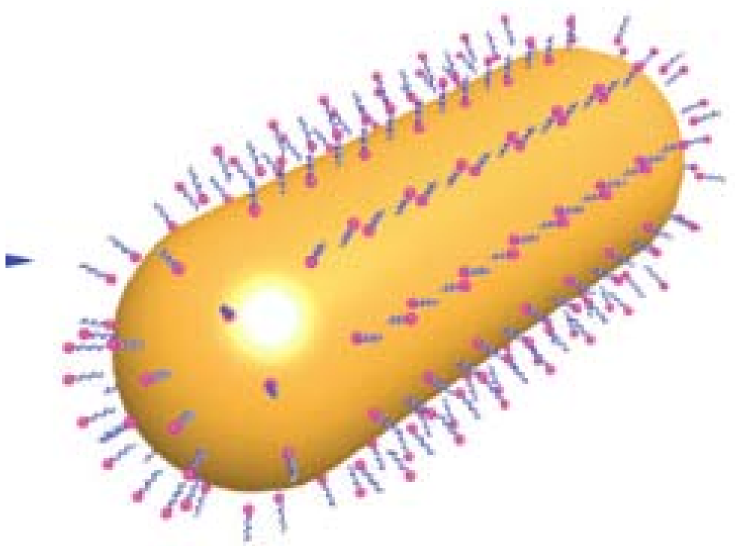
Huang et al, ACS Nano (2012)

Ultrafast thermal analysis of surfactant layers surrounding Au nanorods

- Measure surfactant thickness by dynamic light scattering to determine the hydrodynamic diameter d_H



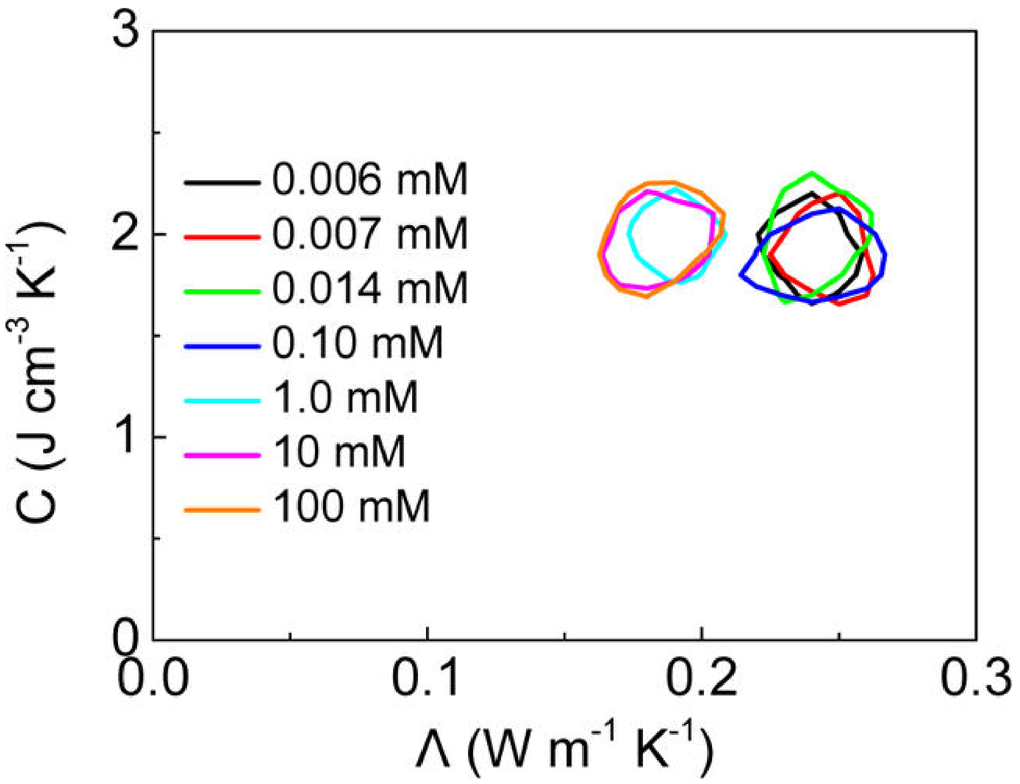
Huang et al, ACS Nano (2012)



Chen *e tal.*, Chem. Soc. Rev. (2013)

Ultrafast thermal analysis of surfactant layers surrounding Au nanorods

- Heat capacity and thermal conductivity of CTAB surfactant layers as a function of CTAB concentration in solution.
- Heat capacity is constant
- Thermal conductivity decreases above critical concentration.



Huang et al, ACS Nano (2012)

II. How fast can a laser pulse heat a metal layer?

- Electrons are heated directly by the laser pulse, i.e., electric fields in the optical pulse create electronic excitations.
  - Heat capacity of electrons is relatively small,

$$C_{el} \approx N_{el} k_B \left(\frac{T}{T_F} \right); \; T \ll T_F$$

- Takes time to heat the atomic vibrations. Most of the heat capacity of the solid is in the lattice vibrations, i.e., the phonons. Classical limit: $C_{ph} \approx 3Nk_B$

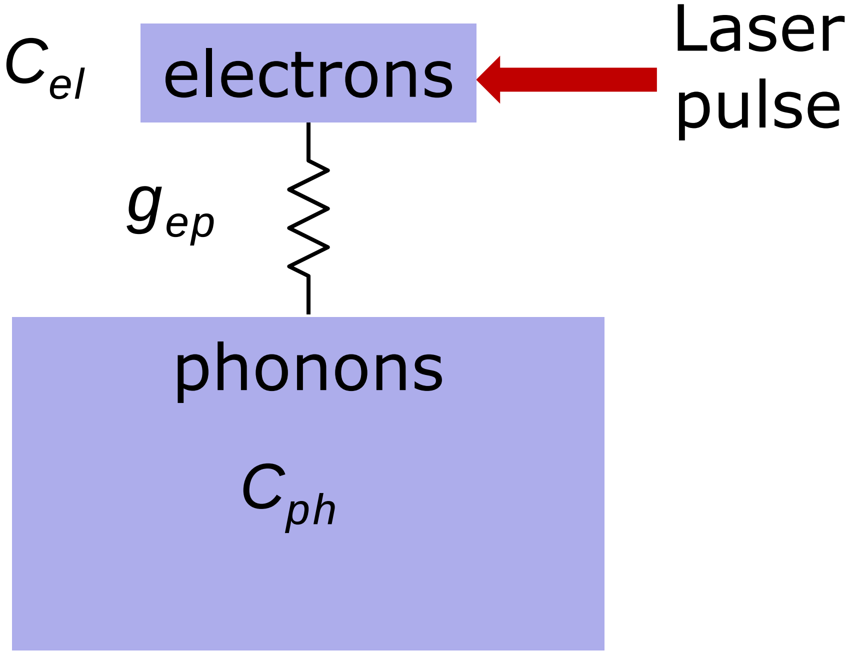
- Phenomenological two-temperature model treats each system as a thermal reservoir coupled by a thermal conductance (per unit volume) g_{ep}

II. How fast can a laser pulse heat a metal layer?

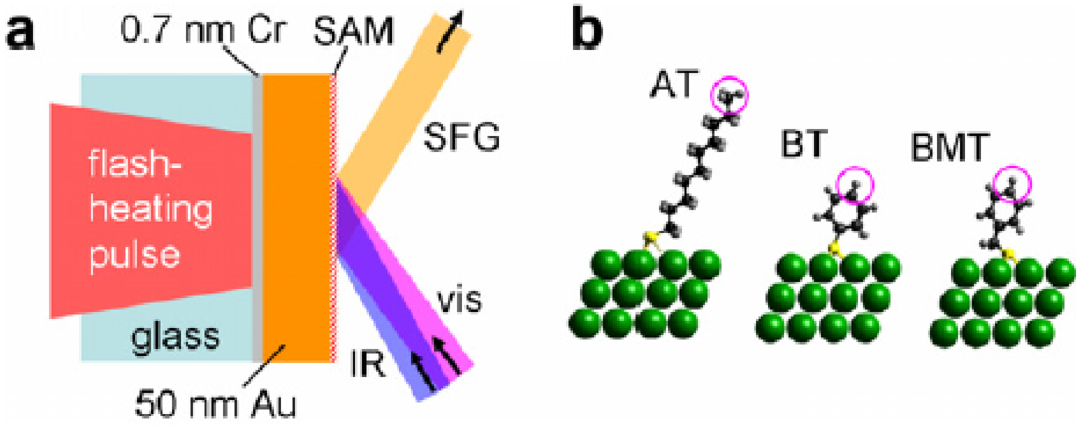
Electron thermalization time is on the order of 300 fs but varies over a wide range

$$\tau \approx \frac{C_{el}}{g_{ep}} \sim \frac{3\times10^{4}\ \mathrm{J\ m^{-3}\ K^{-1}}}{10^{17}\ \mathrm{W\ m^{-3}\ K^{-1}}} \sim 300\ \mathrm{fs}$$

$$0.1 \le \tau \le 1\ \mathrm{ps}$$



II. How fast can a laser pulse heat a metal layer?

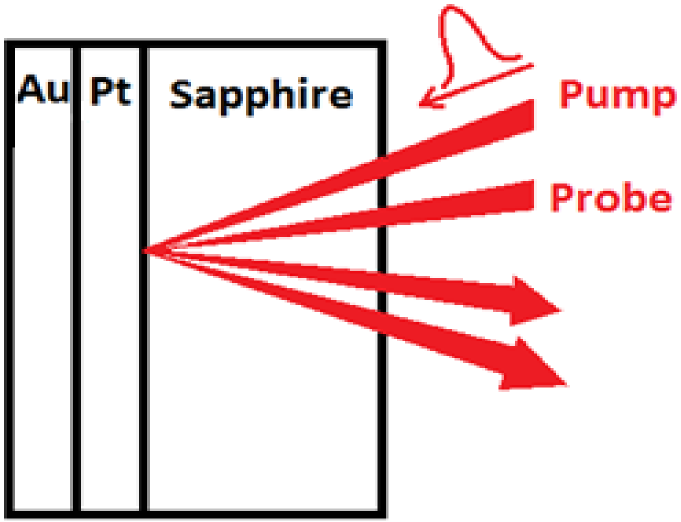


- Au provides well-defined chemistry for studies of molecular layers, however
  - hot-electron effects are a problem if we want to produce a large change in the Au lattice temperature

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

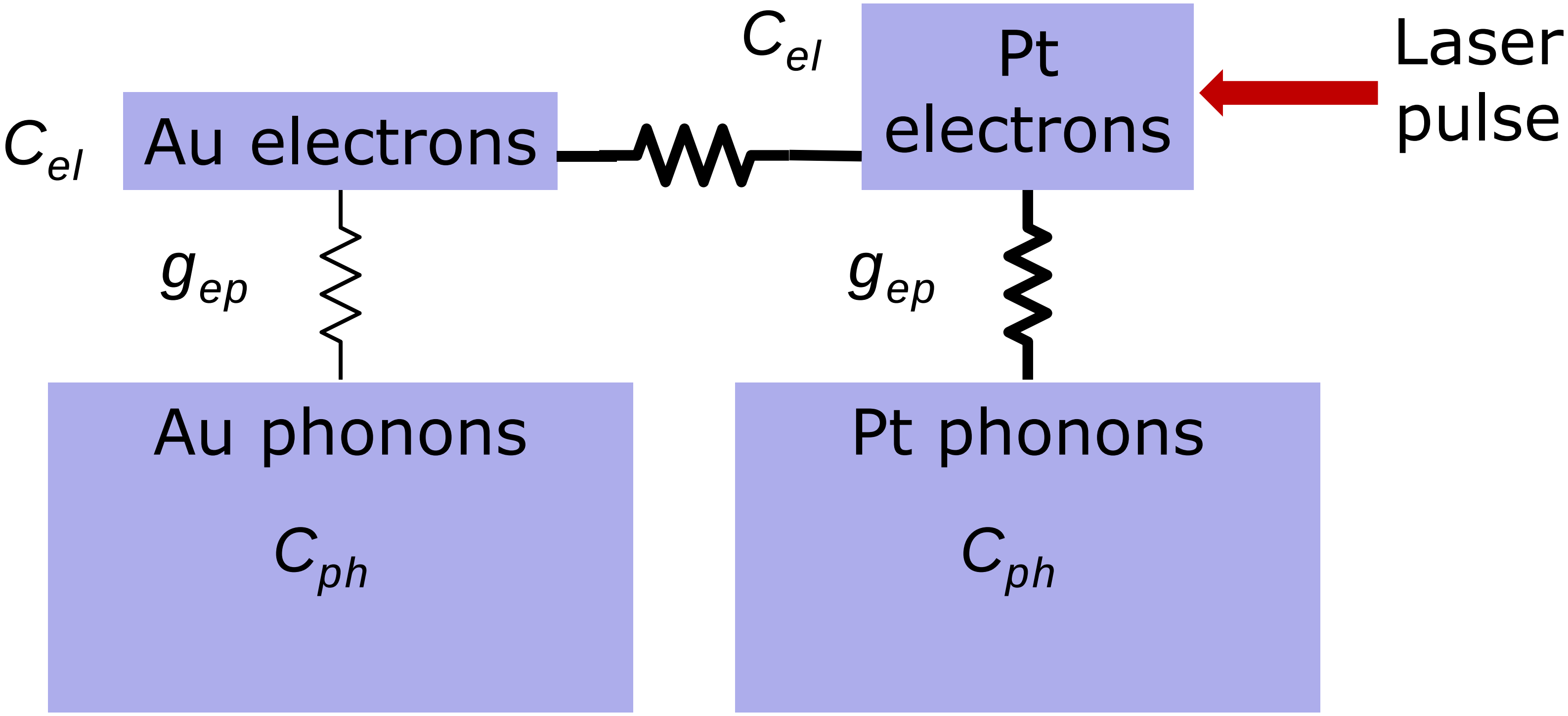
II. How fast can a laser pulse heat a metal bilayer?

- Let’s see what happens if we try to avoid the hot electron effects (keep the system closer to equilibrium) by adding a Pt layer with strong electron-phonon coupling and large electronic heat capacity



Wang and Cahill, PRL (2012)

II. How fast can a laser pulse heat a metal bilayer?



C_{el} Au electrons

C_{el} Pt electrons

Laser pulse

g_{ep}

g_{ep}

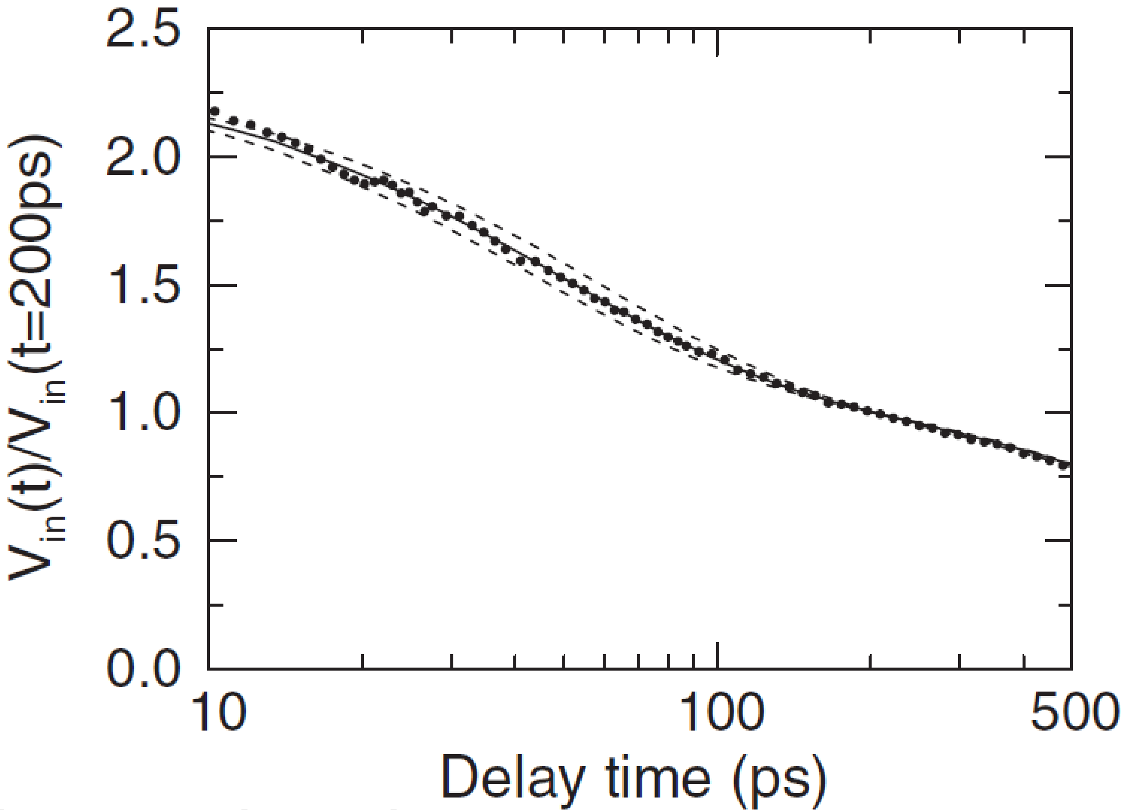
Au phonons C_{ph}

Pt phonons C_{ph}

Heating of the Au layer is slow because electron-phonon coupling in Au is the smallest conductance in the problem

- Characteristic time scale for the heating of the Au phonons

$$\tau = \frac{C_{Au,ph}}{g_{Au,ep}} \approx 80 \text{ ps}$$

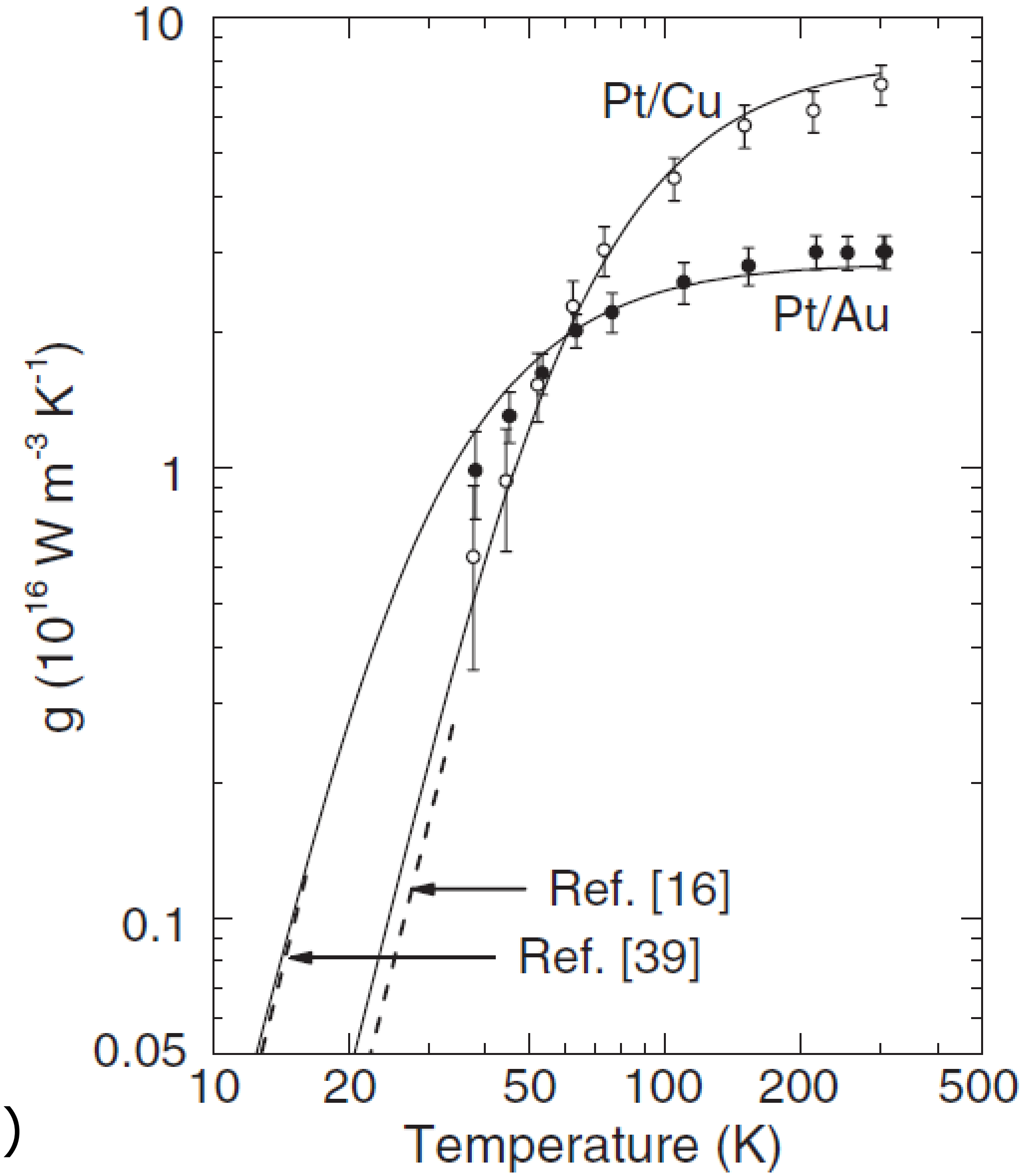


Pt temperature

Wang and Cahill, PRL (2012)

Lousy way to heat Au but excellent way to measure g_{ep}

- 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.

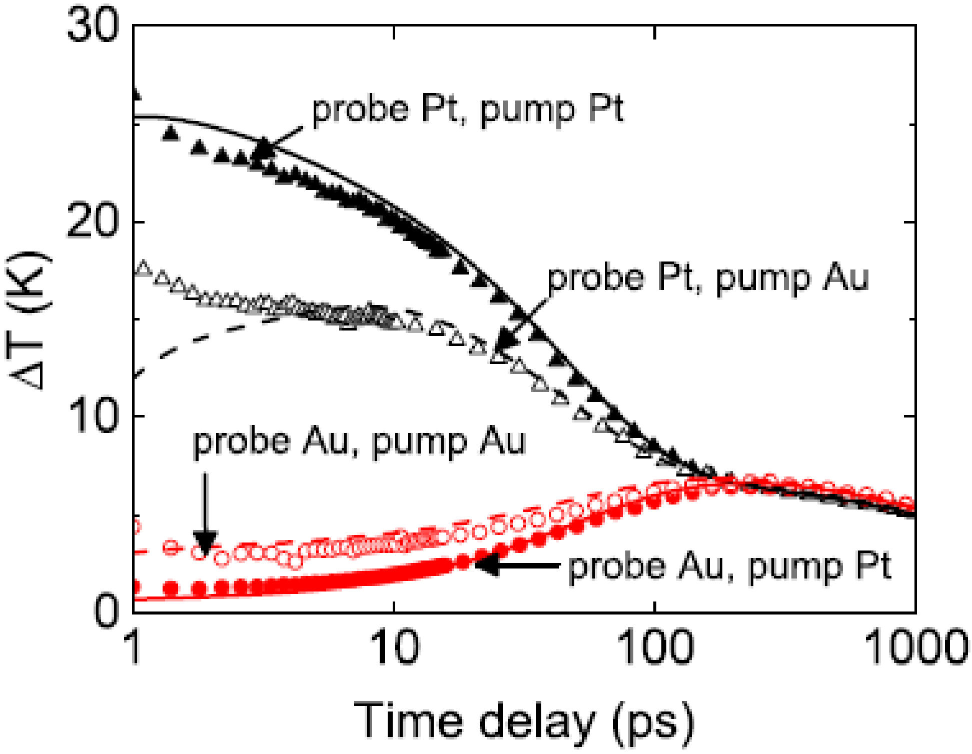


Wang and Cahill, PRL (2012)

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}



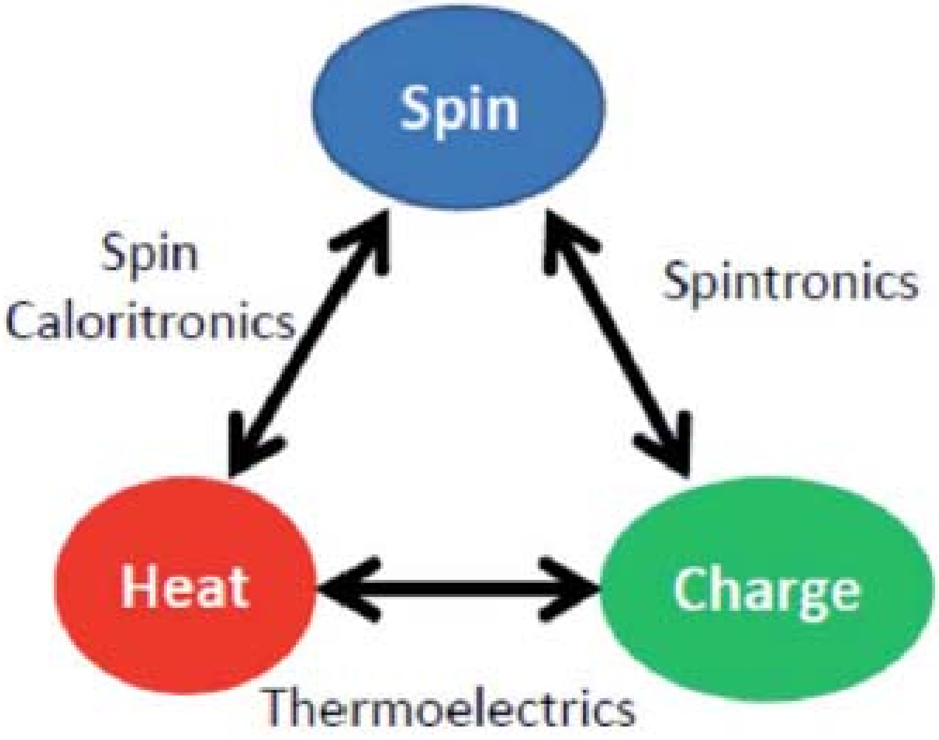
Choi *et al.*, PRB (2014)

III. How large of a heat current can we generate and can we do anything useful with an extremely large heat current?

- The big picture question: “How can we write magnetic information without resorting to magnetic fields, e.g., with spin currents?”
  - Rapid changes in magnetization and strong temperature gradients in magnetic materials should produce spin currents.
  - Magnitudes of the effects are only beginning to be understood.
  - Create huge heat currents 100 GW m^{-2} and detect spin current in real time with 1 ps time resolution.

Subset of an emerging topic of “spin caloritronics”

- Electronic states enumerated by energy, wave-vector, spin

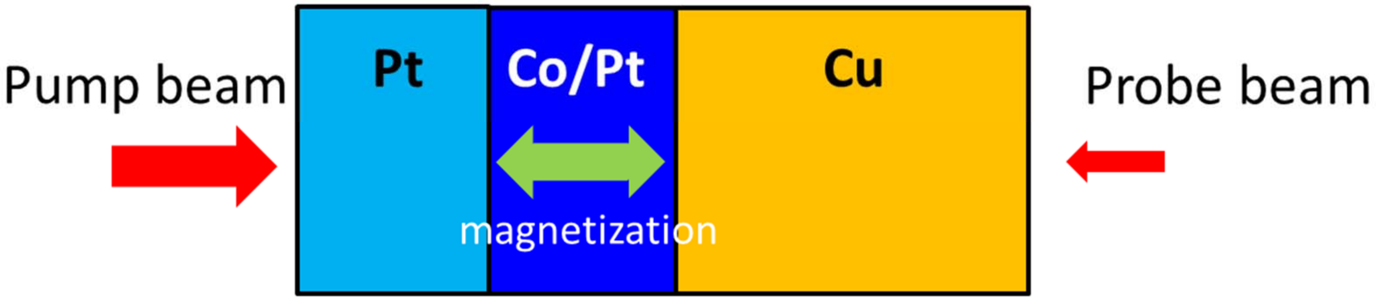


Boona, Myers, Heremans,
Energy and Env. Sci. (2014)

Tri-layer structure to study effects of rapid heating and high heat fluxes on ferromagnets

- Deposit laser pulse energy in Pt film (30 nm) with strong electron phonon coupling
- Heat flows through ferromagnetic (6 nm) layer and into the Cu heat sink (80 nm)

Sapphire/Pt(30)/[Co/Pt]$_{xn}$(6)/Cu(80)/MgO(10)/AlOx(5) (in nm)

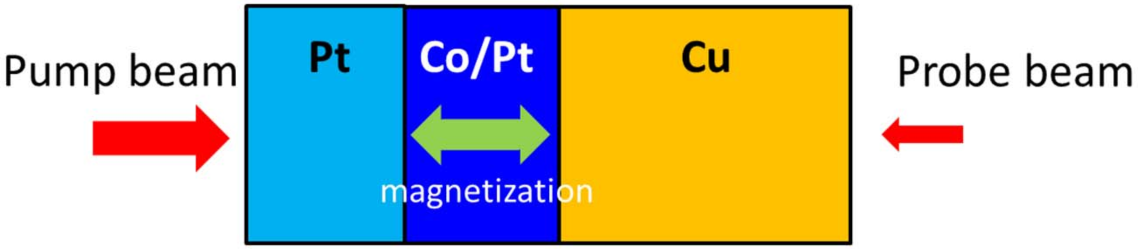


Choi et al., *Nat. Commun*. (2014)

Tri-layer structure to study effects of rapid heating and high heat currents on ferromagnets

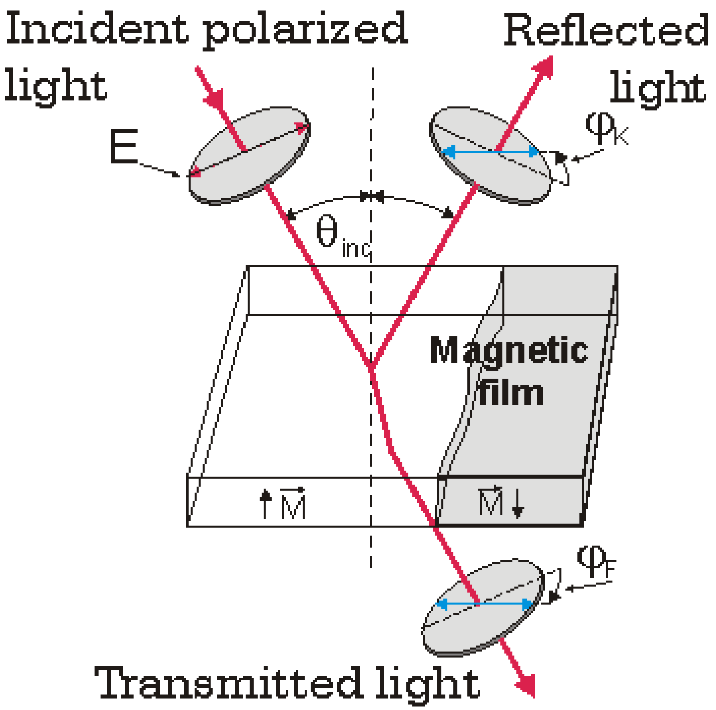
- Back-of-the-envelope analysis for size of heat flux
  - Restrict temperature rise to $\Delta T = 100\ \mathrm{K}$
  - Conductances acting in series
    - Metal-metal interface G_I
    - Thermal conductivity of Co/Pt $G_{FM} = \Lambda_{FM} / h$
    - Electron-phonon coupling $G_{ep} = \sqrt{g_{Cu} \Lambda_{Cu}}$
  - Heat current

$$J_Q = G_{series} \Delta T \sim 200\ \mathrm{GW\ m^{-2}}$$



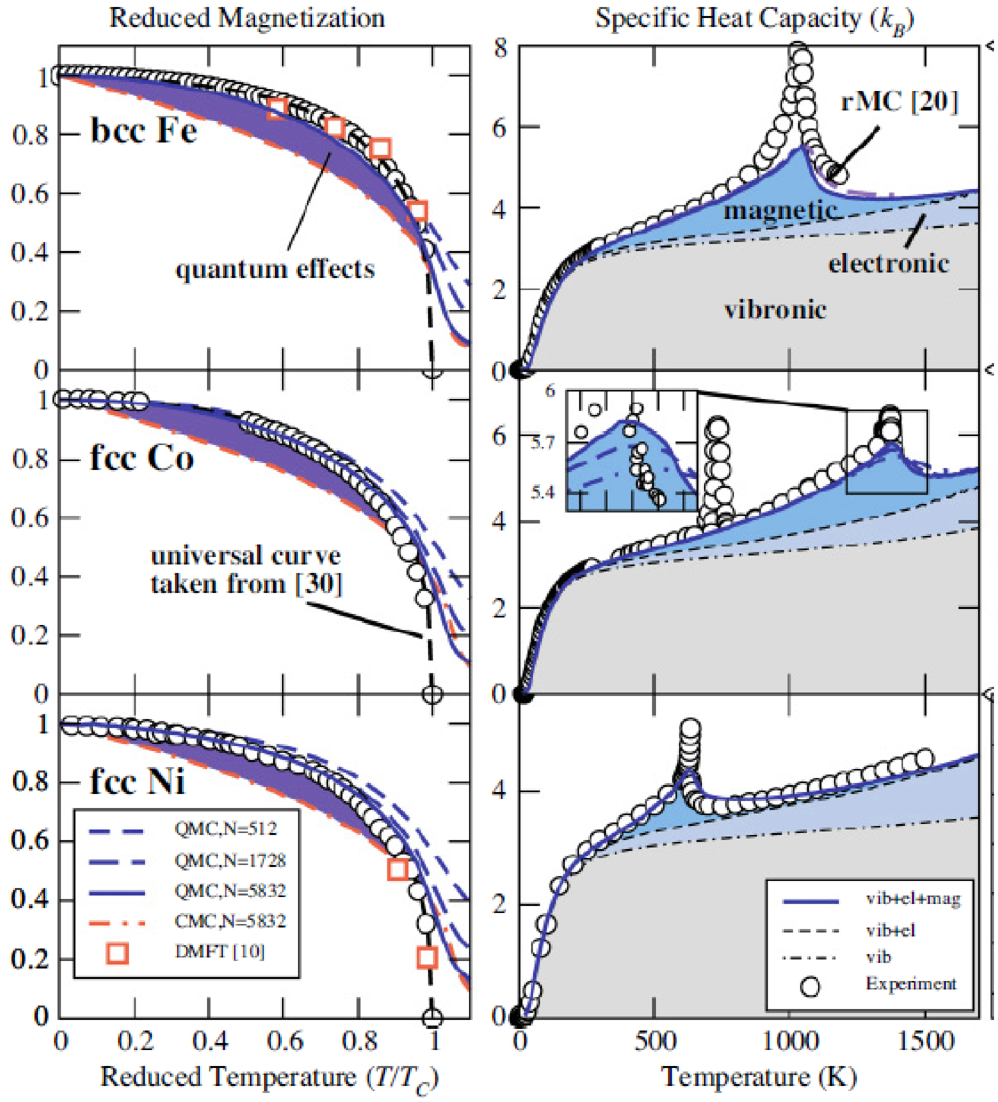
Time-resolved magneto-optic Kerr effect (TR-MOKE) to measure spin density or temperature through *M(T)*

Kerr rotation



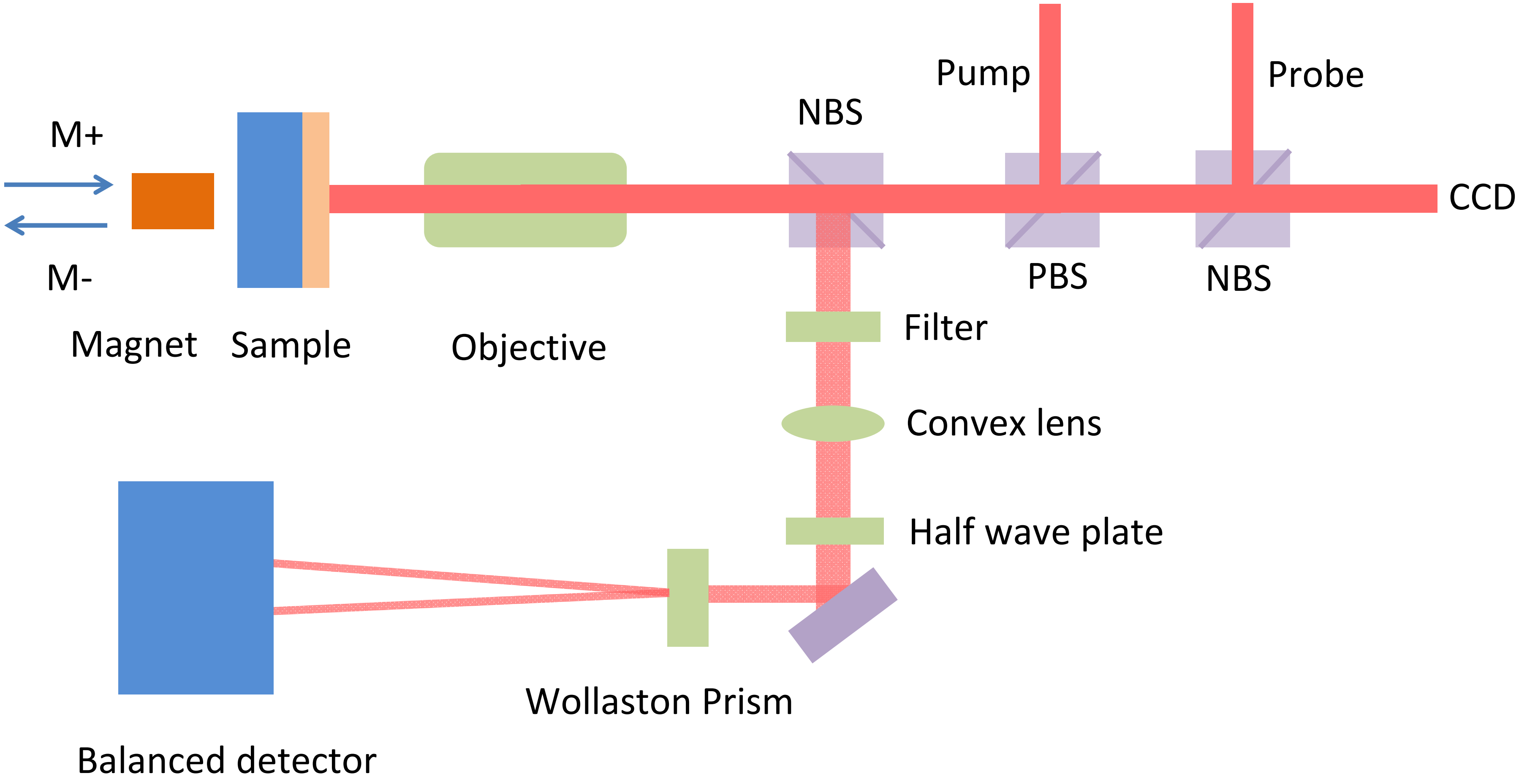
Faraday rotation

http://labfiz.uwb.edu.pl

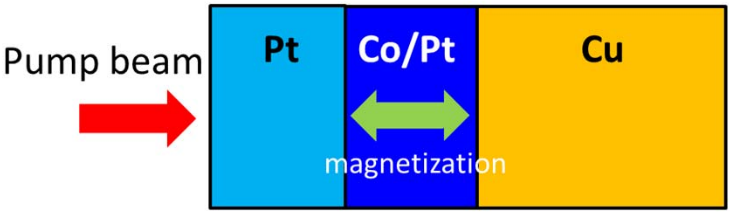


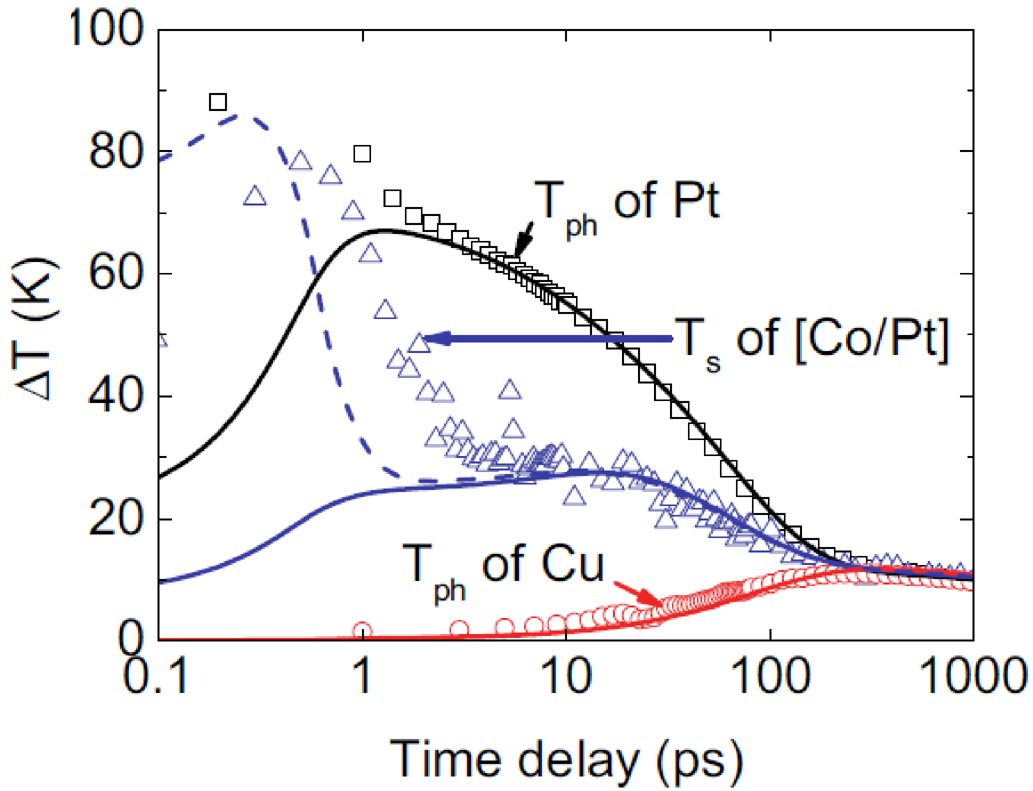
Körmann *et al*., PRB (2011)

Schematic of TR-MOKE Setup (Reflectance Configuration)



Pump Pt-side, probe either Pt-side or Cu side by either TDTR or TR-MOKE



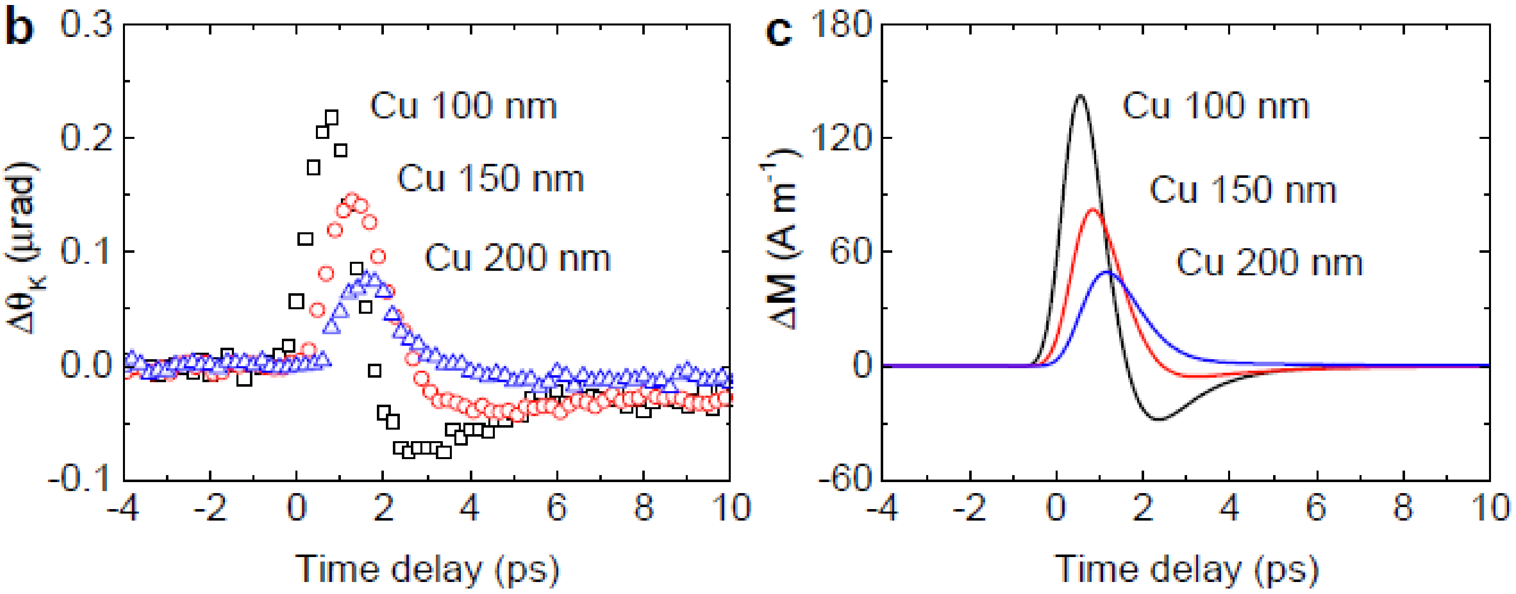


Choi et al., *Nat. Commun*. (2014)

Comparison between experiment and spin diffusion model using spin generation = *dM/dt*

Measured Kerr signal on Cu side

Spin diffusion model



Spin diffusion model

$$\frac{\partial \mu_S}{\partial t} = D\frac{\partial^2 \mu_S}{\partial^2 z} - \frac{\mu_S}{\tau_S}$$

spin generation rate per unit volume

$$G_S = -\frac{dM}{dt}$$

$\mu_S = \mu_\uparrow - \mu_\downarrow$ is the spin chemical potential

D is the spin diffusion constant

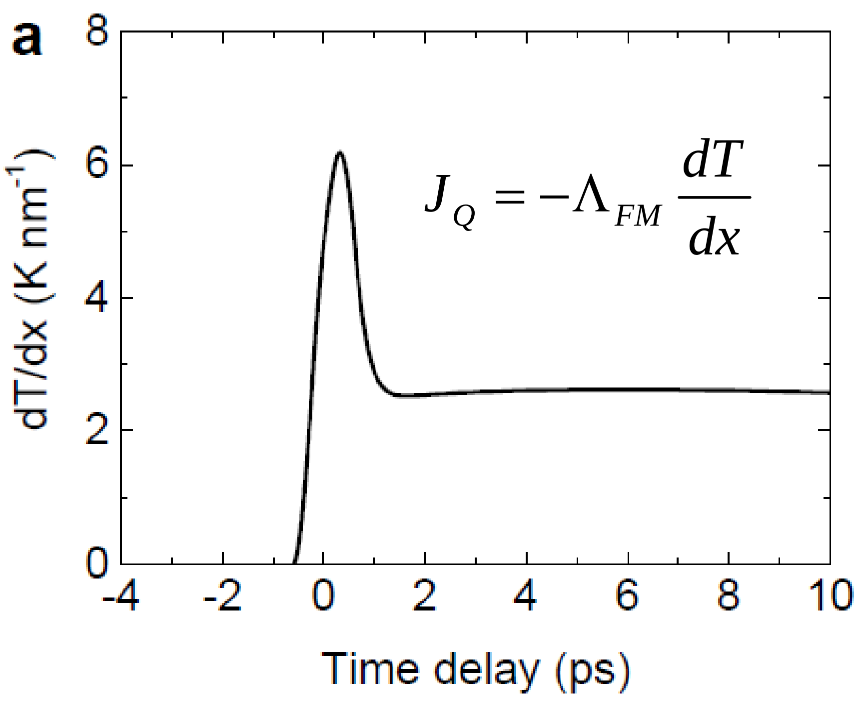
τ_S is the spin relaxation time.

	Pt	[Co/Pt]	Cu
D (nm^2/ps)	200	100	6500
τ_s (ps)	0.5	0.05	25
$(D\tau_s)^{1/2}$ (nm)	10	2.2	400

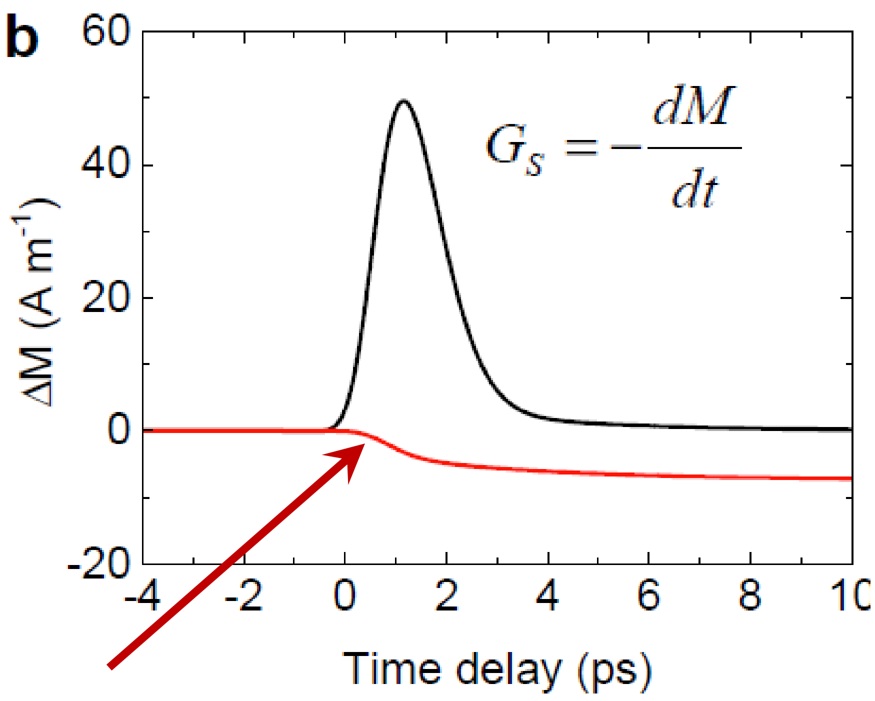
Temperature gradient also contributes to spin accumulation

$$J_S = -\frac{\mu_B}{e}\left(\sigma_\uparrow S_\uparrow - \sigma_\downarrow S_\downarrow\right)\nabla T = -\frac{\mu_B}{e}\frac{\sigma_\uparrow S_\uparrow - \sigma_\downarrow S_\downarrow}{\sigma_\uparrow + \sigma_\downarrow}\sigma\nabla T$$

Temperature gradient in the Pt/Co layer from thermal modeling



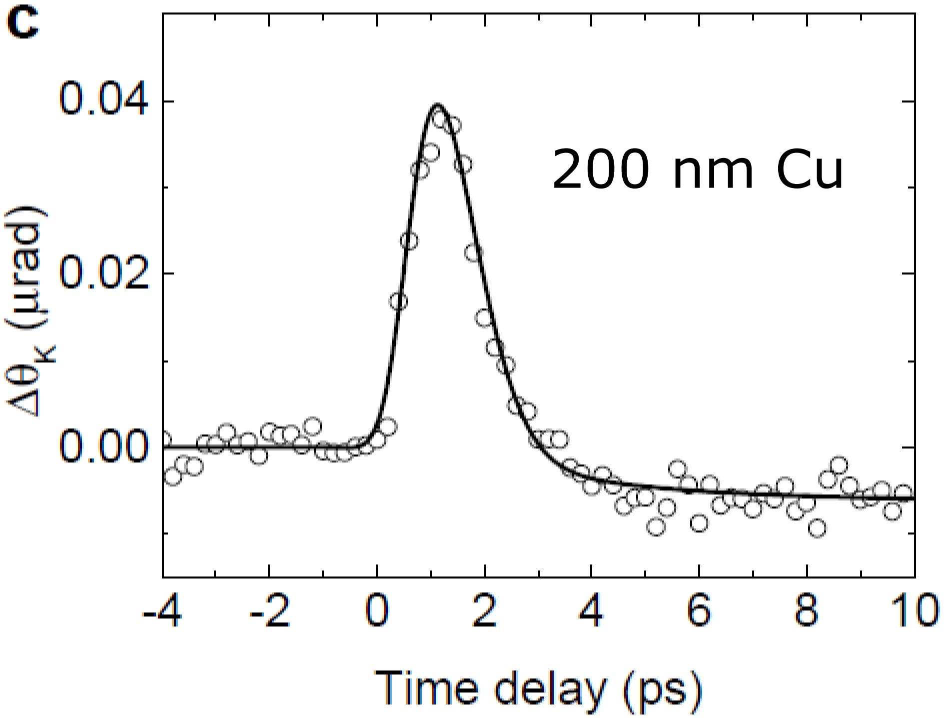
Calculated spin accumulations



$$\frac{\sigma_\uparrow S_\uparrow - \sigma_\downarrow S_\downarrow}{\sigma_\uparrow + \sigma_\downarrow} \approx 5\,\mu\mathrm{V\,K}^{-1}$$

Temperature gradient also contributes to spin accumulation

- More refined data with comparison to spin diffusion model including the spin-dependent Seebeck effect



Choi et al., *Nat. Commun*. (2014)

Summary

- How fast does a nanoparticle cool?
  - Scales with *r* for small *r*, r^2 for larger radius.
  - Order of 100 ps for $r=3$ nm.
  - Can independently analyze heat capacity and thermal conductivity of surfactant layers using plasmonic nanoparticles as the temperature sensor.
- How fast can we heat a metal layer?
  - Single layer, 0.1 to 1 ps due to electron-phonon coupling
  - Bilayers are surprisingly complicated and can be surprisingly slow, on the order of 100 ps.
- How large of heat flux can we generate and can you do anything with it?
  - 100 GW m^{-2}
  - Exploring thermal generation of spin currents and thermally-enabled manipulation of magnetic information