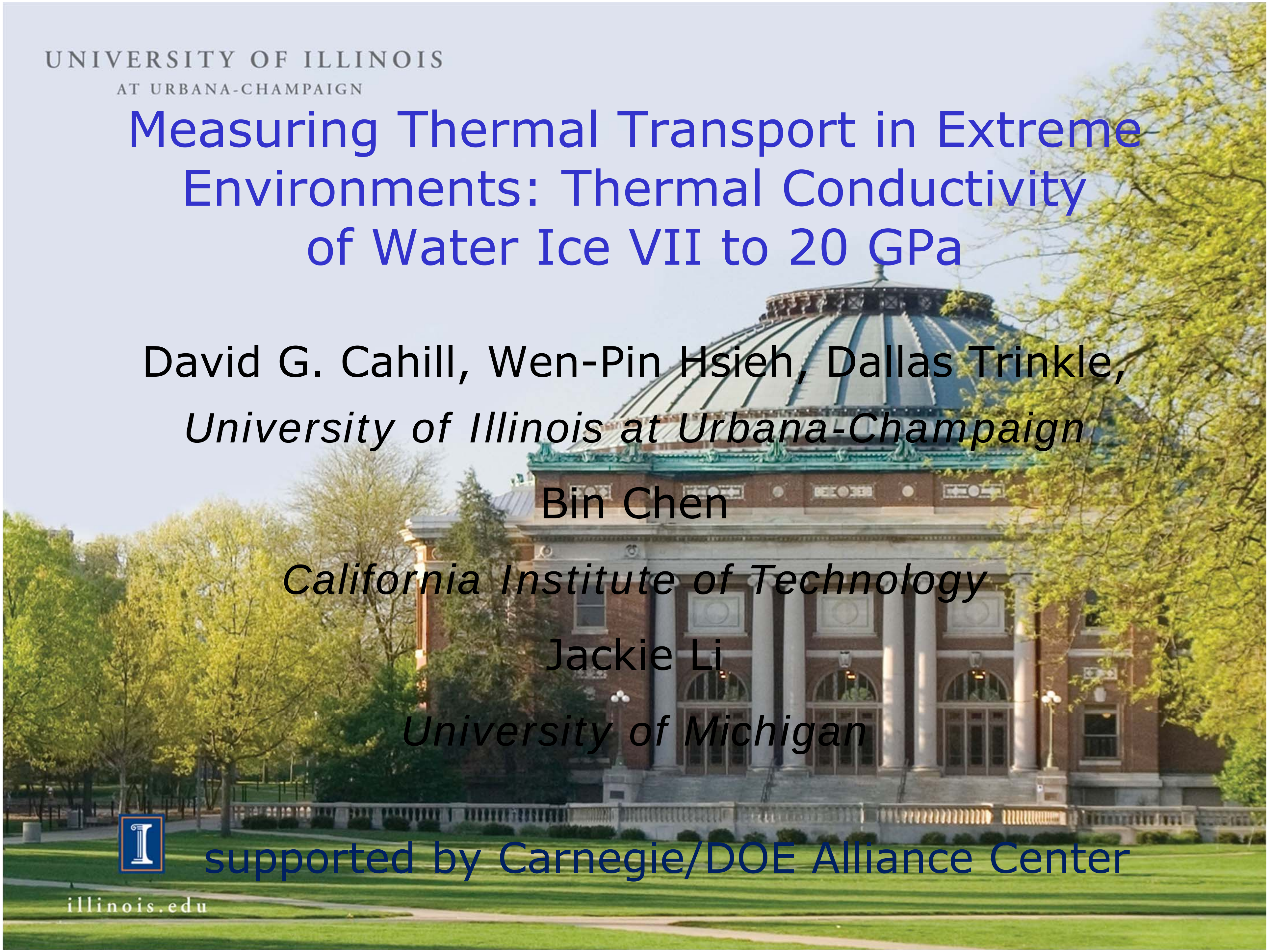
UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

Measuring Thermal Transport in Extreme Environments: Thermal Conductivity of Water Ice VII to 20 GPa



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supported by Carnegie/DOE Alliance Center

illinois.edu

Why do we measure thermophysical properties?

- Need the numbers for engineering design
  - How big of a compressor do I need?
- Test theory and validate computational models
  - I don’t want to have to measure everything
- Use transport coefficients and susceptibilities (e.g., calorimetry) to probe the state of a system.
  - hydrogen at a solid-solid boundary lowers the thermal conductance (?)

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

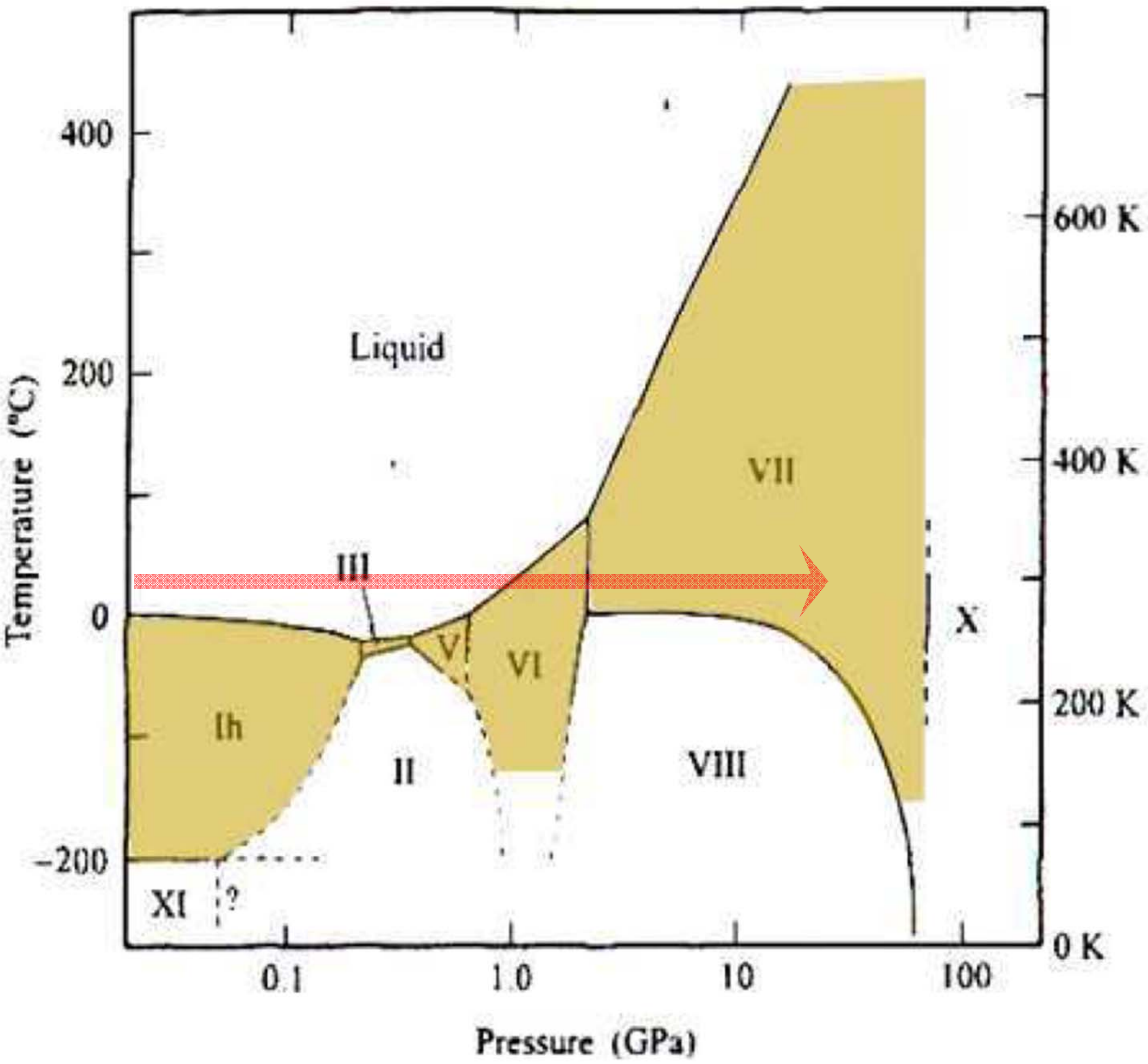
- Use high pressure (gem anvil cells) to modify phonon densities of states and lifetimes
- Measure the change in thermal conductivity by time-domain thermoreflectance (TDTR)
- Test classic models for heat conduction by phonons at high compression
  - Leibfried-Schlömann (LS) equation for perfect crystals
  - **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

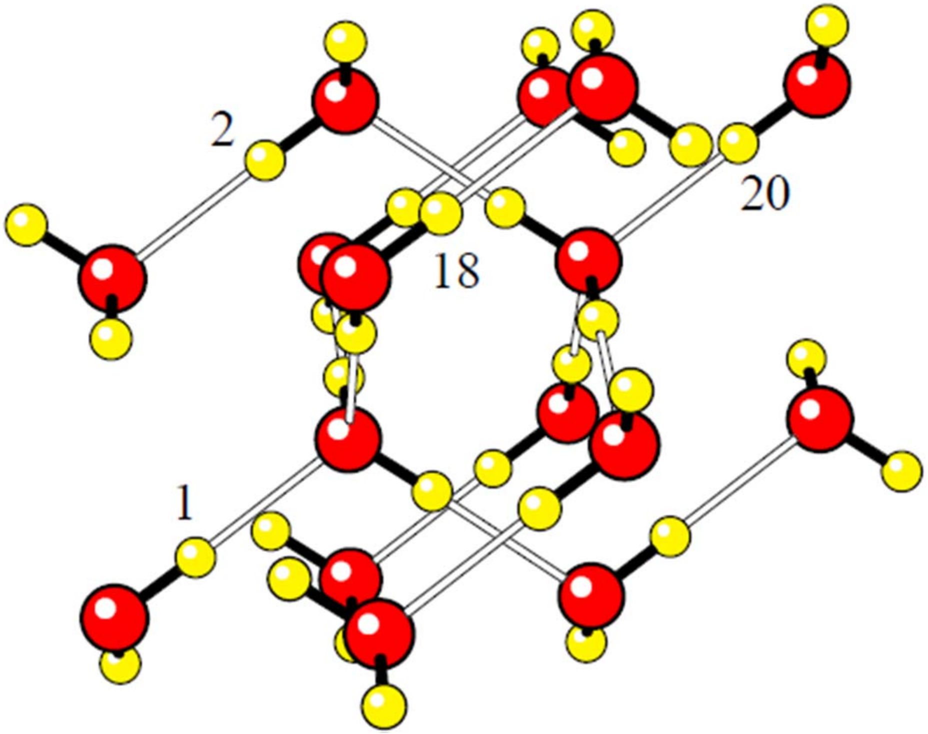
1 Mbar=100 GPa



Petrenko and Whitworth (1999)

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

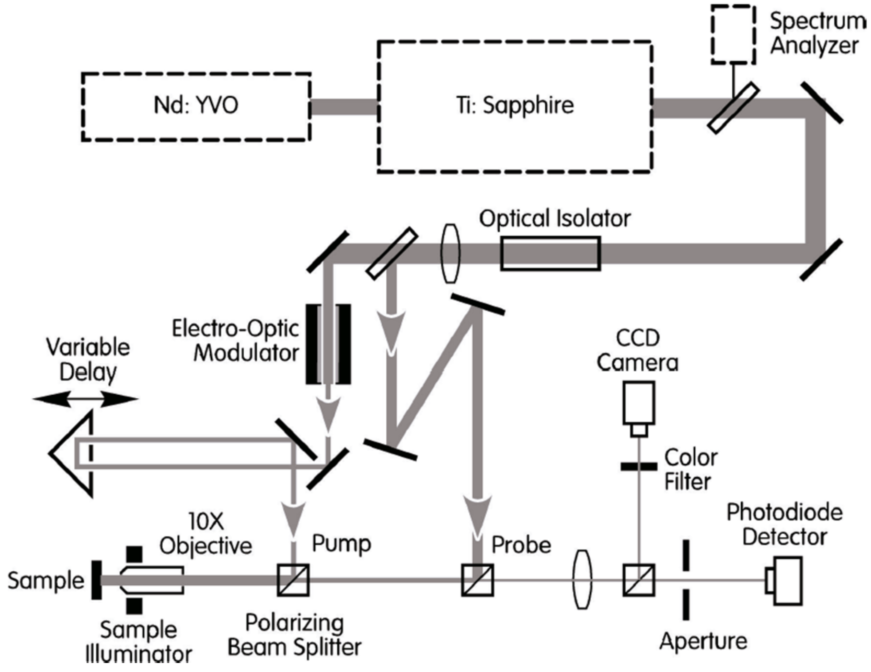
- Hydrogen-bonding in ice VII is disordered
- Ice VIII is the proton ordered form
- Ice X is thought to be “polymeric”: H-bond is symmetric



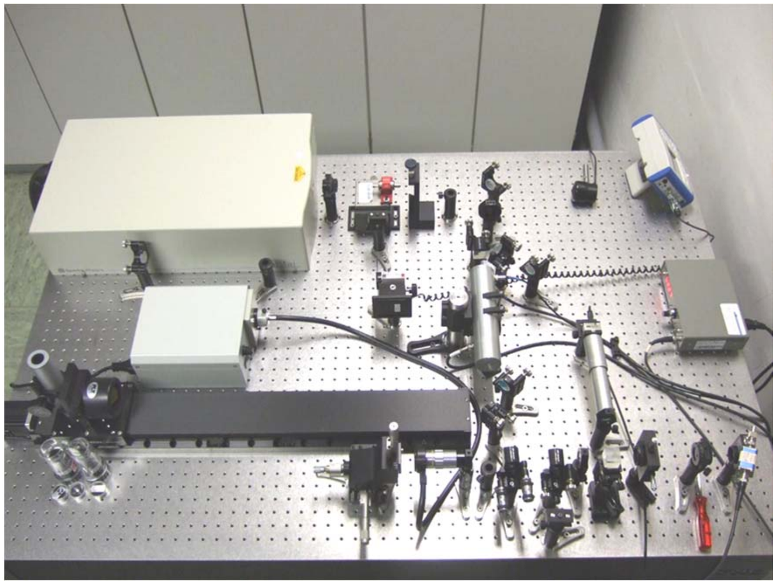
C.J. Knight, *Ph.D. thesis* (2009)

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

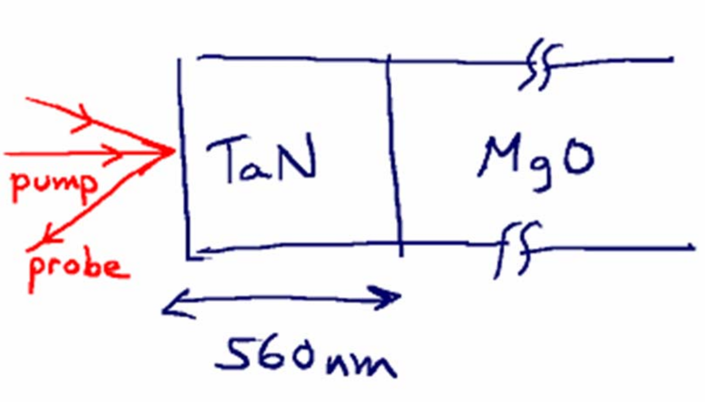


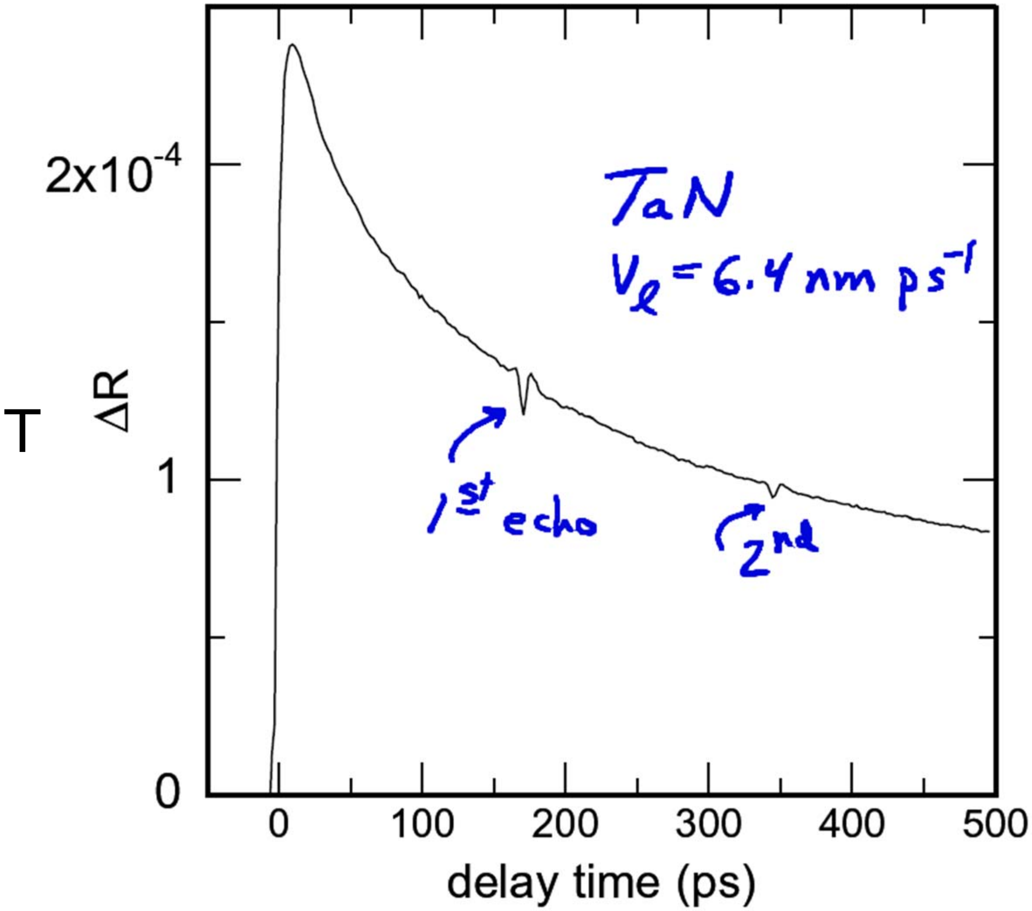
Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008



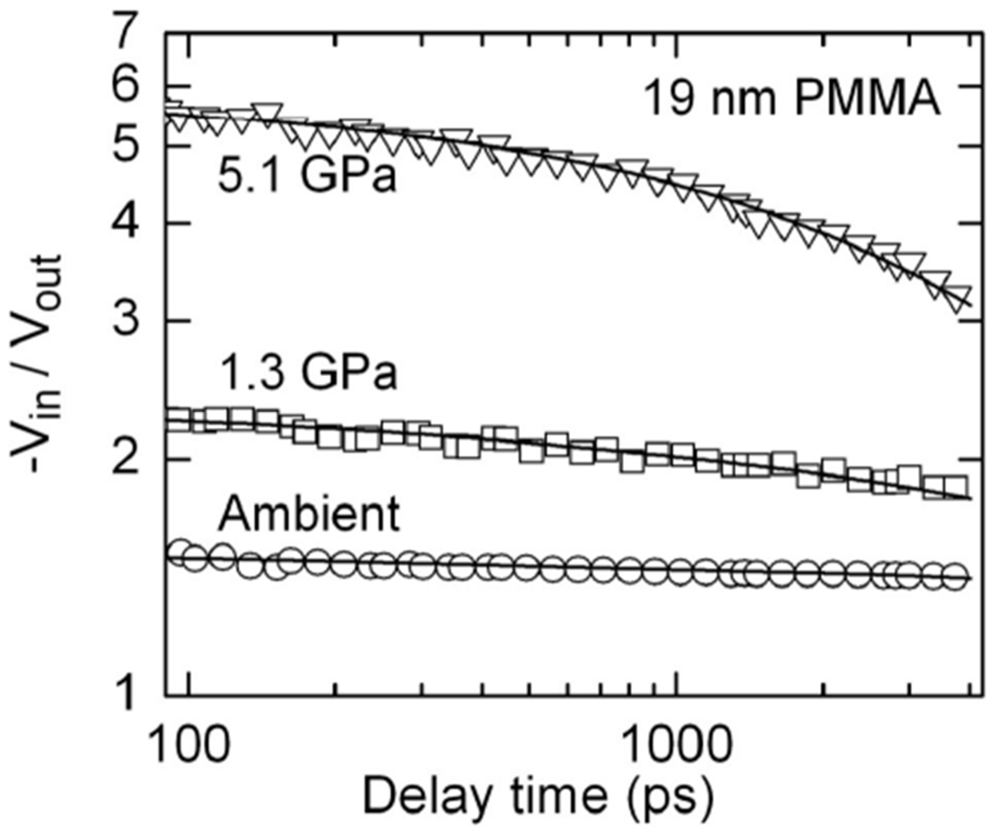
psec acoustics and time-domain thermoreflectance

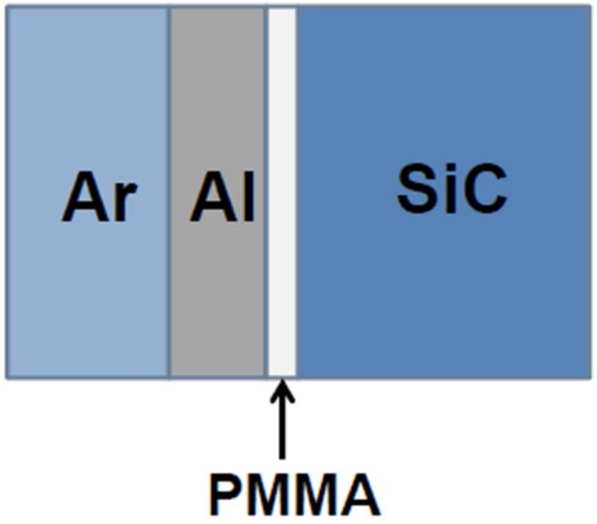
- Optical constants and reflectivity depend on strain and temperature
- Strain echoes give acoustic properties or film thickness
- Thermoreflectance dR/dT gives thermal properties





Analyze ratio V_{in}/V_{out} using an exact solution of the heat diffusion equation





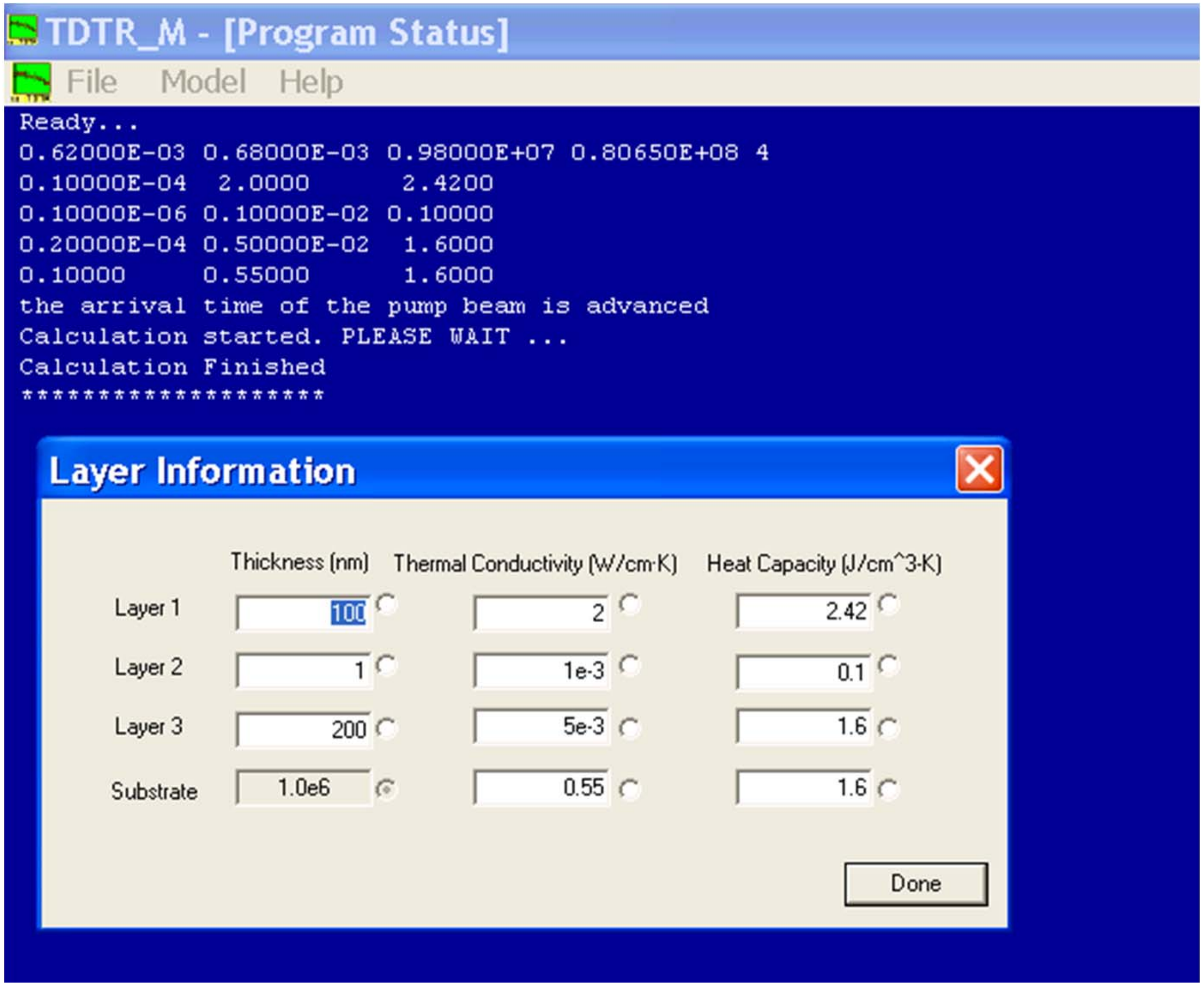
Thermal Model:

A. Laser spot size
B. Thickness and C(P) of Al
C. Interface conductance
D. $\Lambda(P)$ of PMMA?

Windows software

author: Catalin Chiritescu,

users.mrl.uiuc.edu/cahill/tcdata/tdtr_m.zip



```
Ready...
0.62000E-03 0.68000E-03 0.98000E+07 0.80650E+08 4
0.10000E-04  2.0000       2.4200
0.10000E-06 0.10000E-02 0.10000
0.20000E-04 0.50000E-02  1.6000
0.10000      0.55000      1.6000
the arrival time of the pump beam is advanced
Calculation started. PLEASE WAIT ...
Calculation Finished
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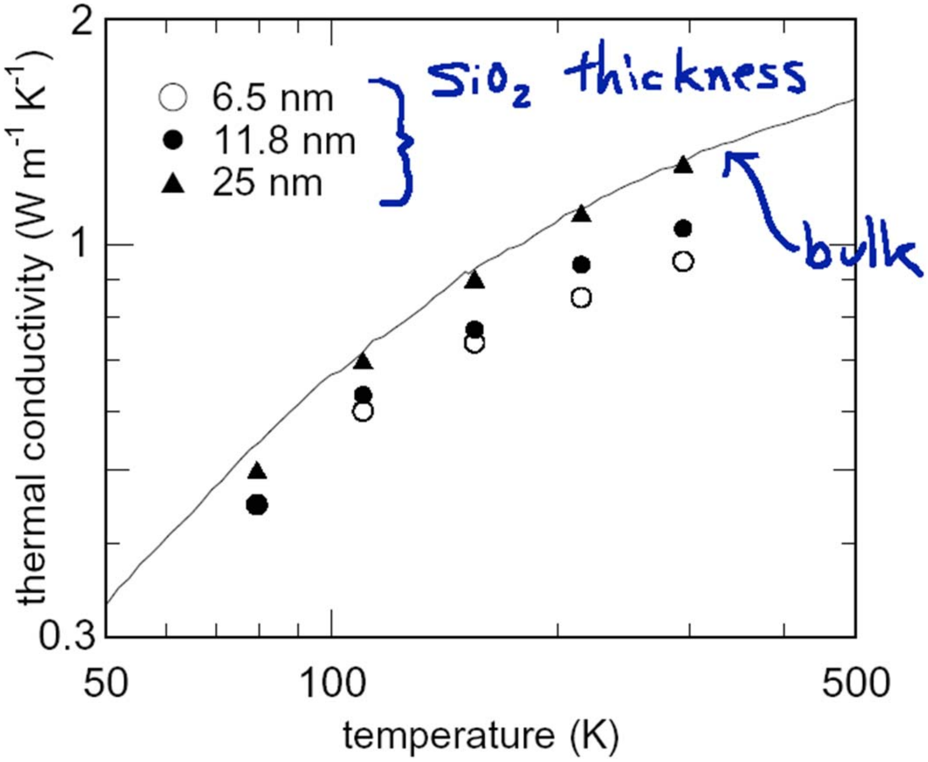
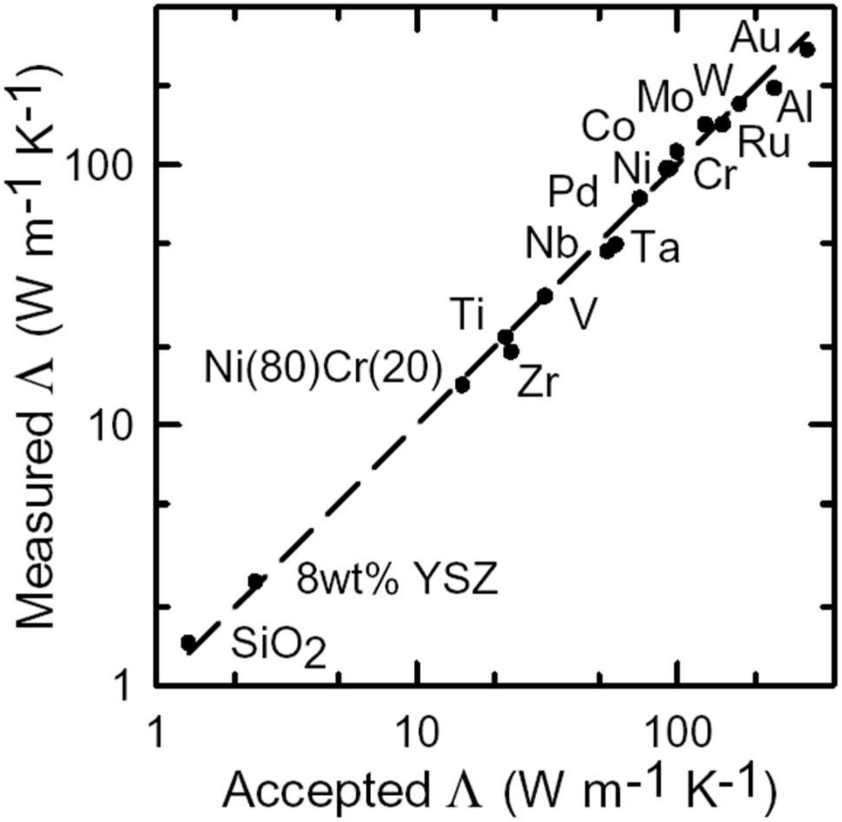
	Thickness (nm)		Thermal Conductivity (W/cm-K)		Heat Capacity (J/cm^3-K)	
Layer 1	100	○	2	○	2.42	○
Layer 2	1	○	1e-3	○	0.1	○
Layer 3	200	○	5e-3	○	1.6	○
Substrate	1.0e6	●	0.55	○	1.6	○

TDTR: Flexible, convenient, and accurate



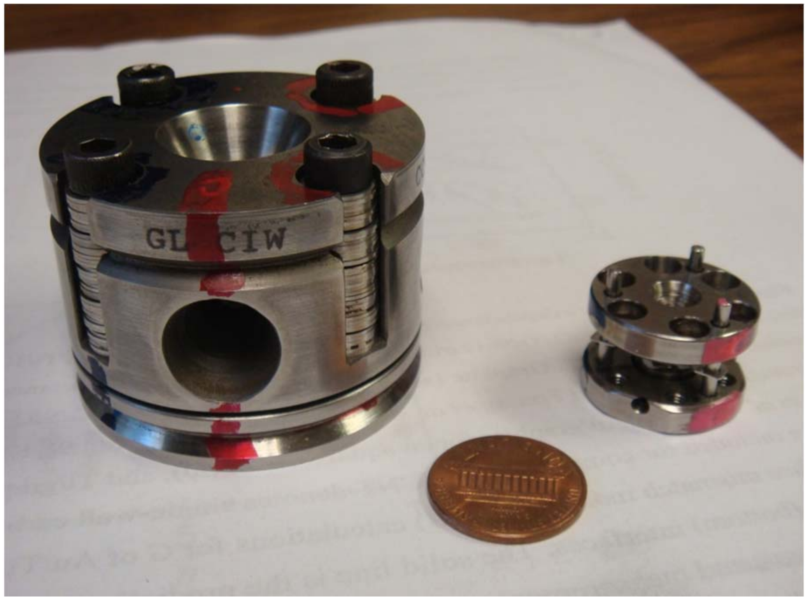
Costescu *et al.*, PRB (2003)

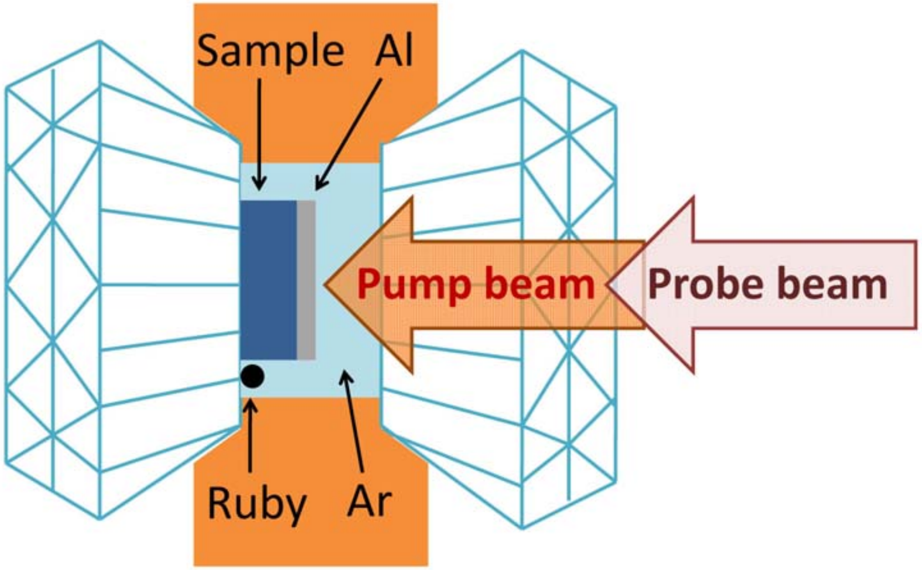


Zhao *et al.*, Materials Today (2005)

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

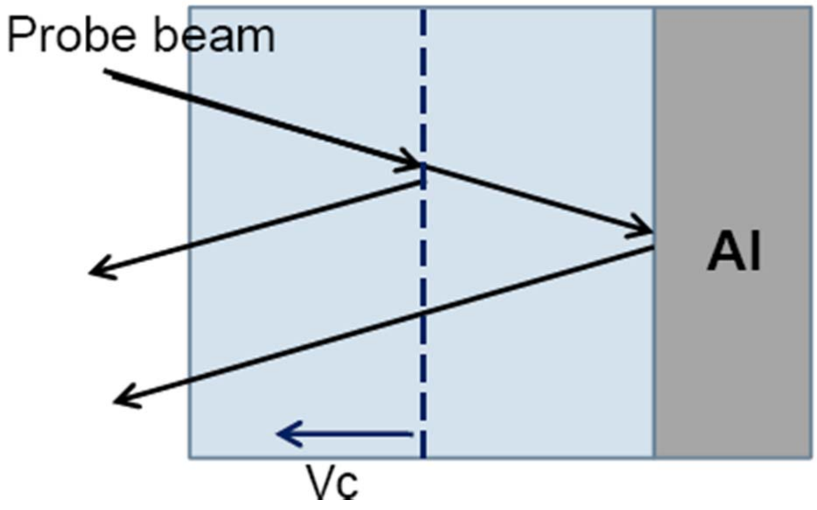
Diamond anvil cell



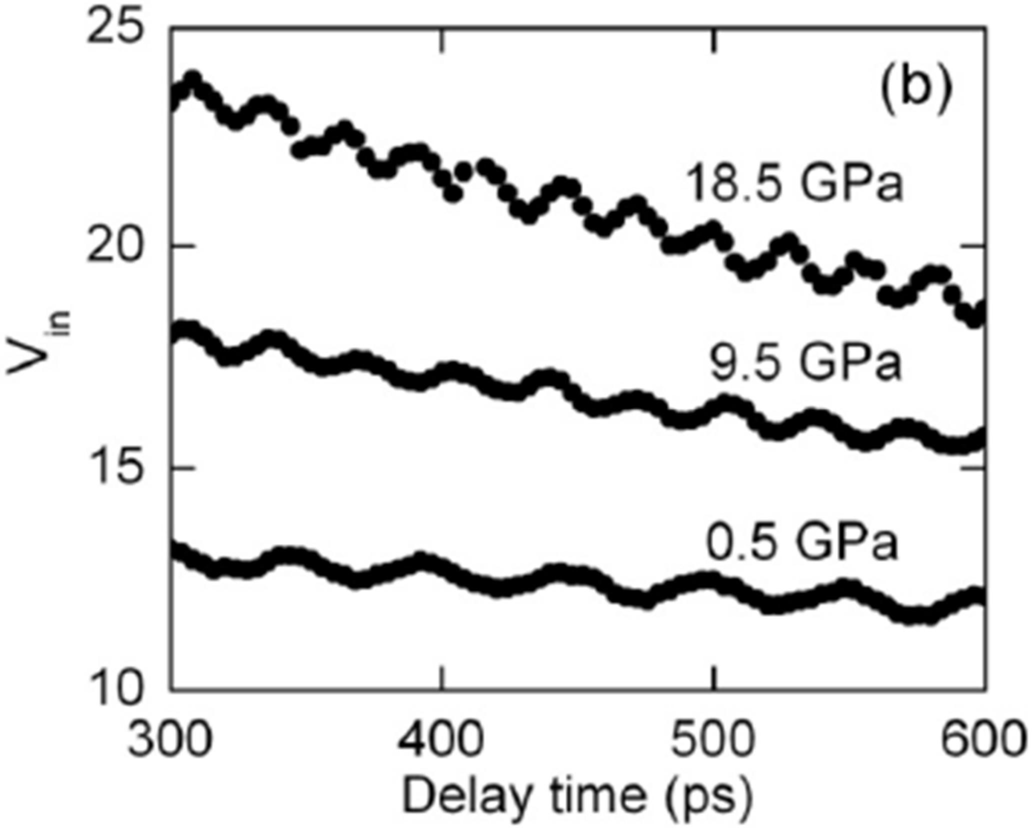


Time-domain stimulated Brillouin scattering (picosecond interferometry)

muscovite mica



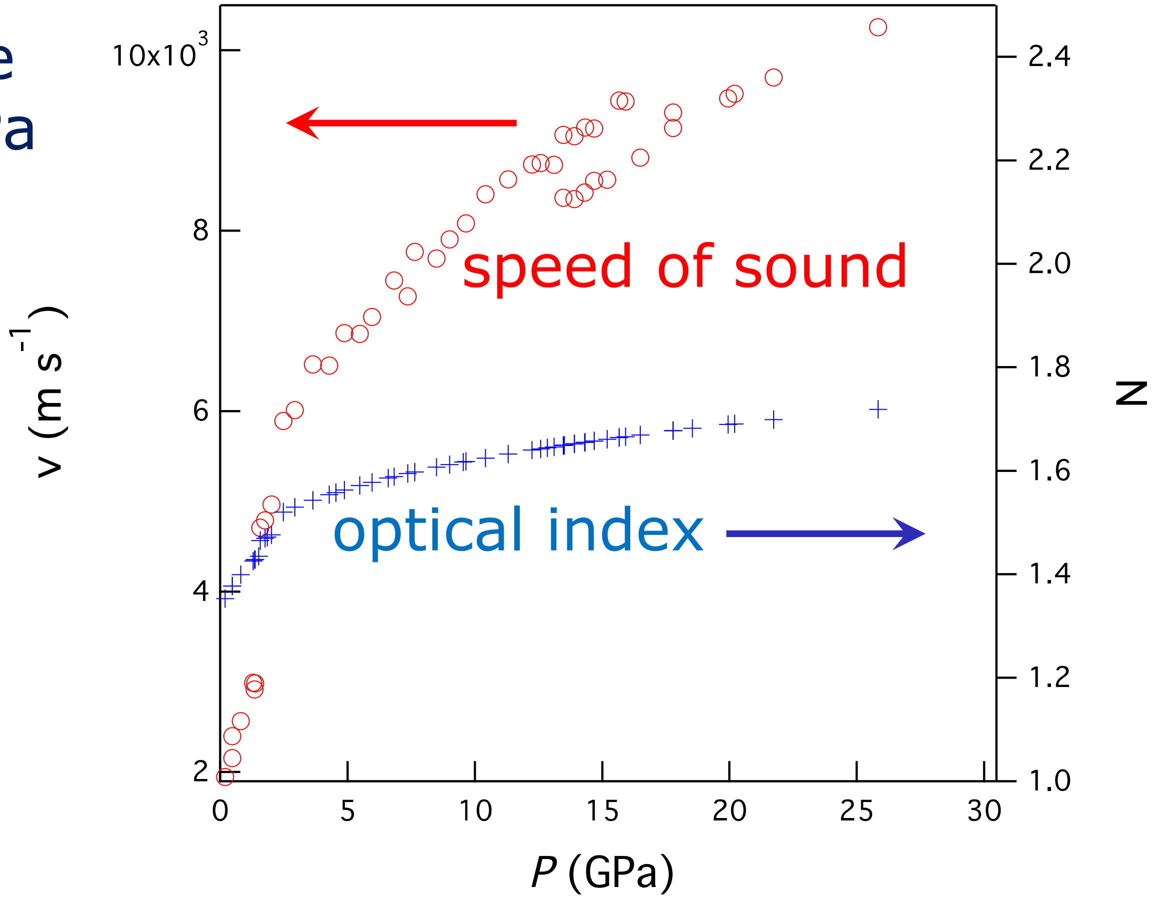
muscovite mica



Hsieh *et al*., PRB (2009)

Digression: sound velocity in ice VII from picosecond interferometry

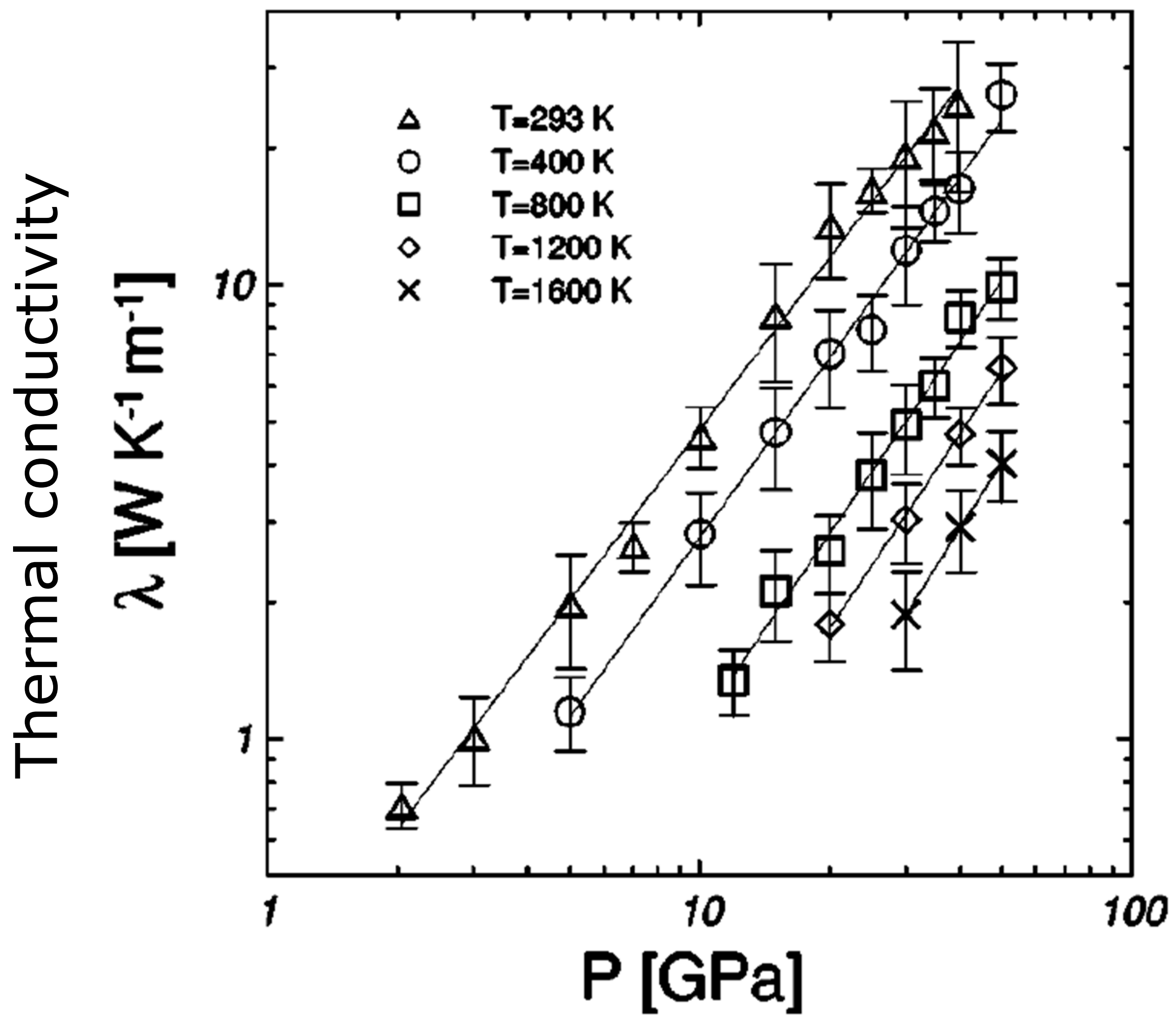
- Nothing in the phase diagram at P=15 GPa but other studies have also reported anomalies
- Cause unknown



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...

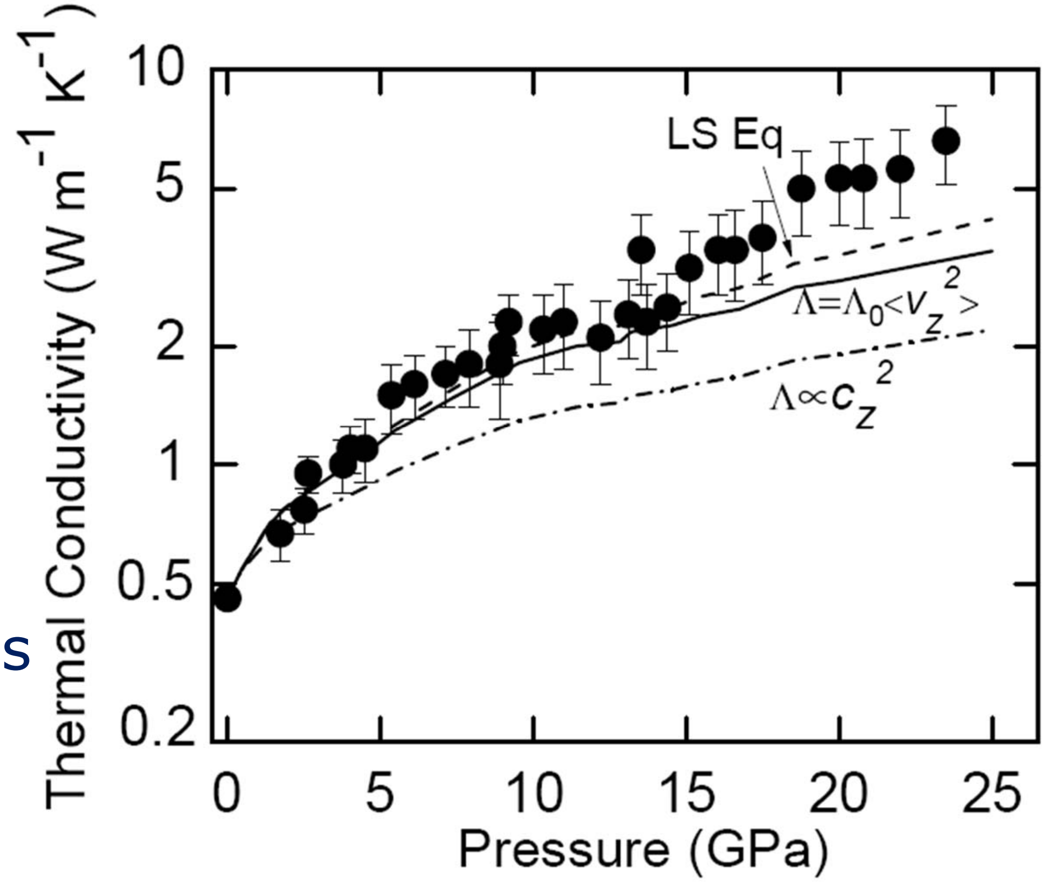
MD simulation for thermal conductivity of Ar



Tretiakov and Scandolo, J. Chem. Phys. (2004)

Analyze data for the muscovite mica substrate

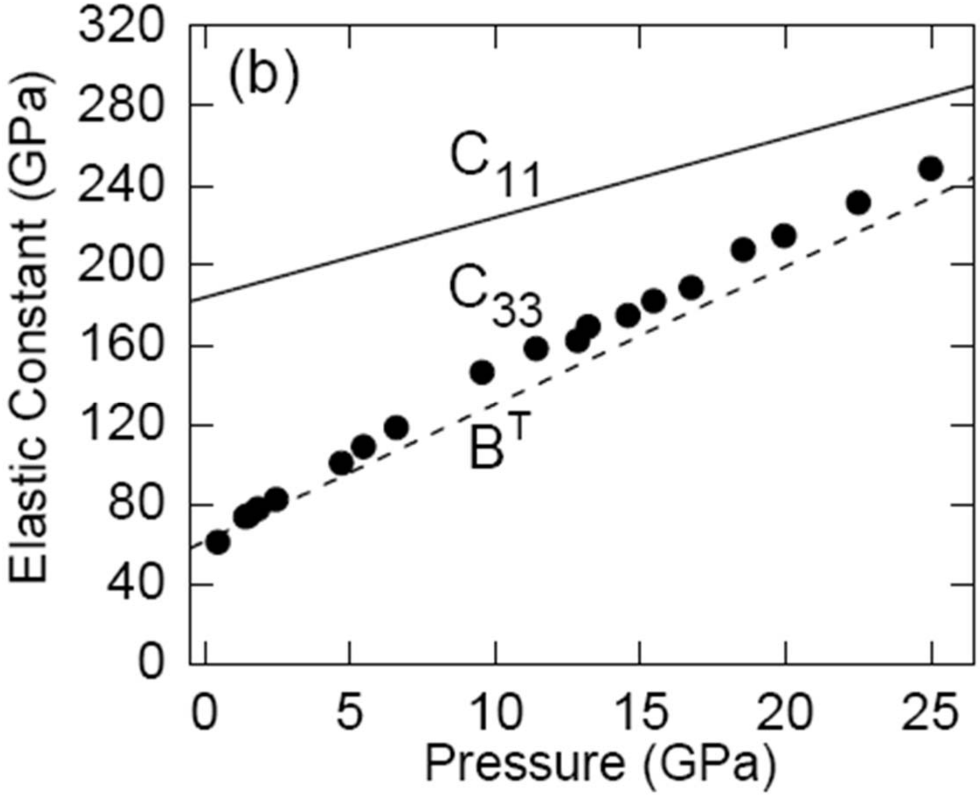
- Mica has its own interesting physics
- Anomalously low thermal conductivity at ambient pressure attributed to strong anisotropy
- High pressure strongly increases the cross-plane elastic constant and makes the crystal more isotropic



Hsieh, Chen, Li, Cahill, Keblinski, PRB (2009)

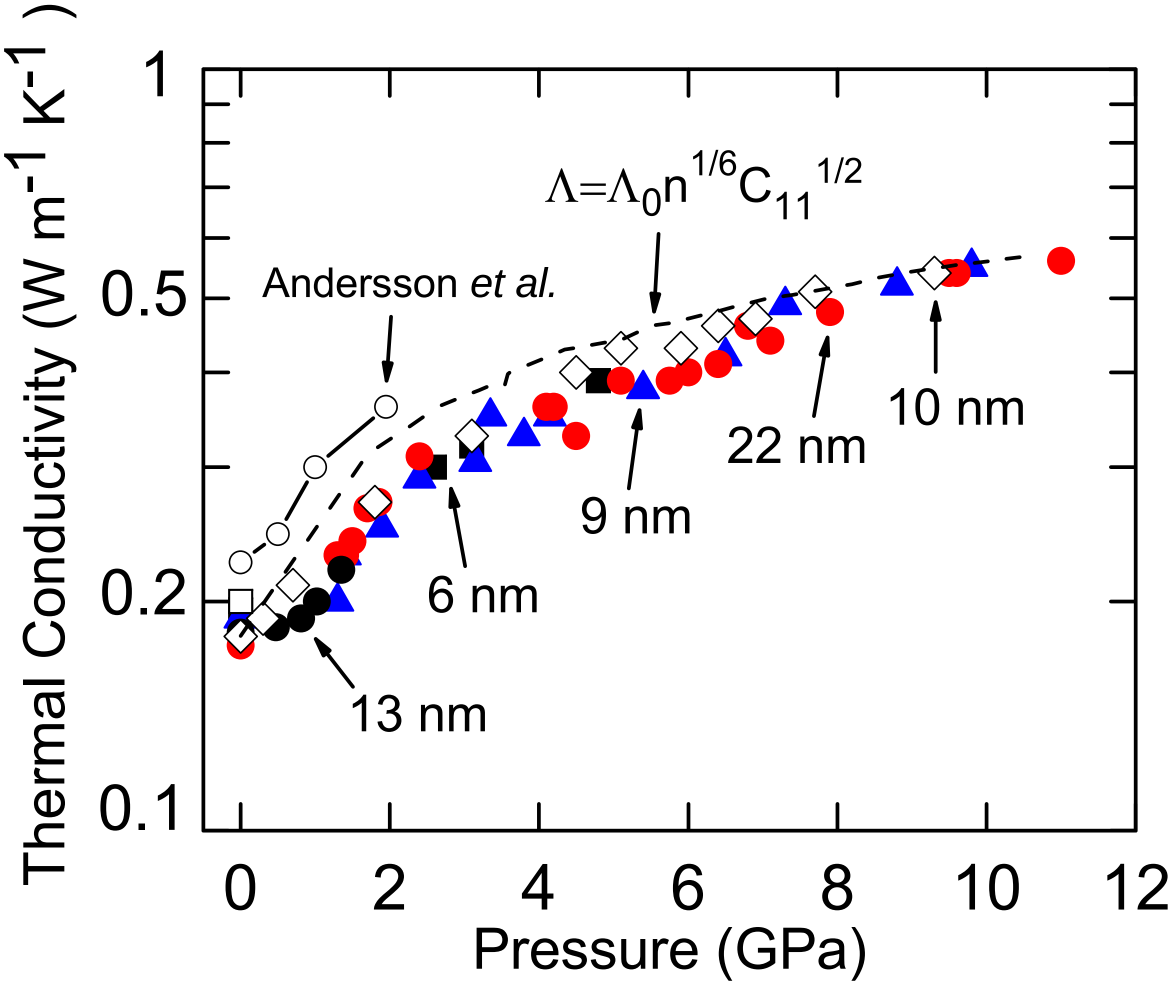
Pressure tuning of elastic anisotropy of muscovite mica

- Cross-plane elastic constants are more anharmonic and stiffen more rapidly with pressure
- C_{33} (cross-plane) measured by picosecond interferometry (time domain Brillouin scattering); Gruenisen constant is $\gamma \approx 4$.



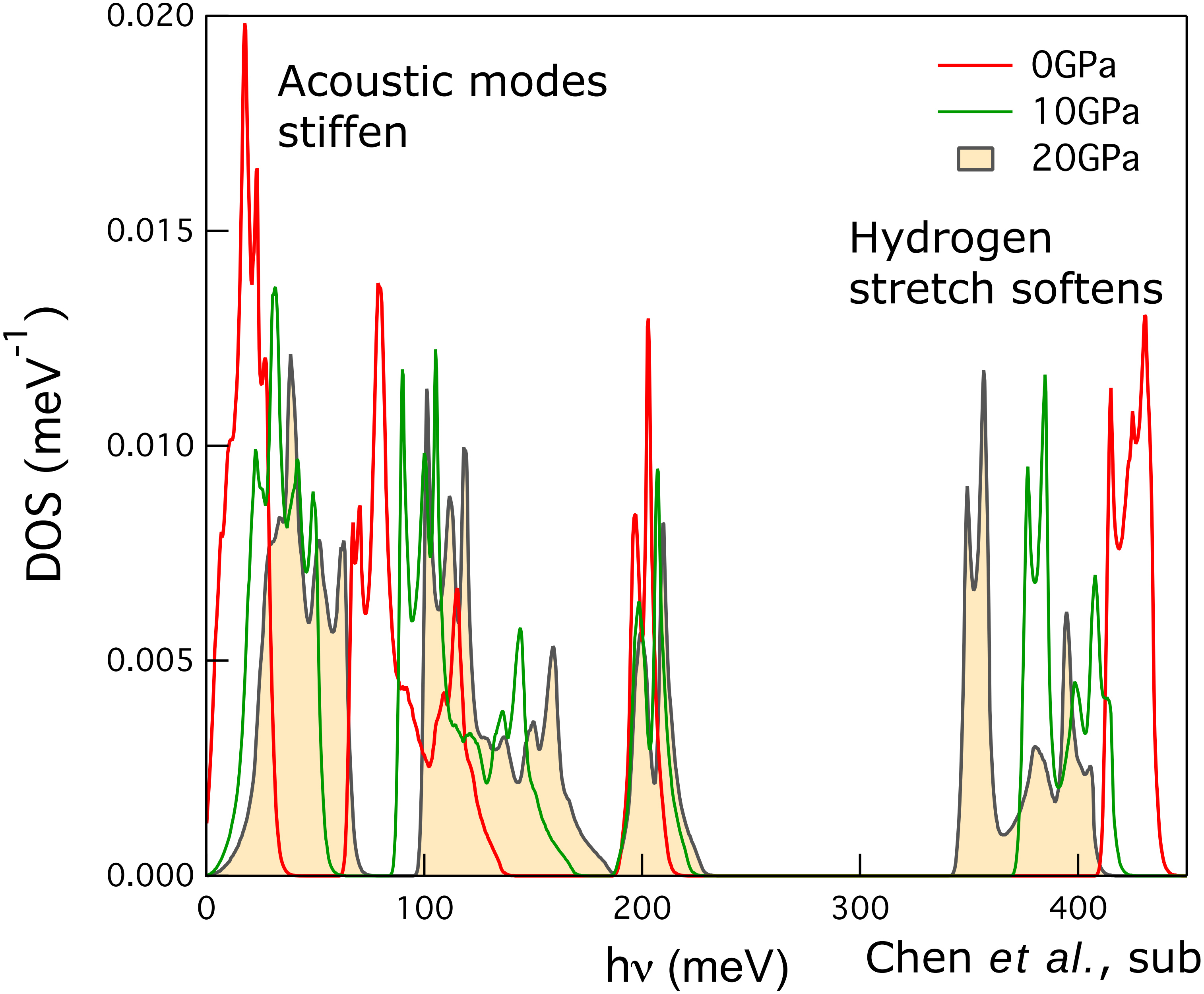
Hsieh, Chen, Li, Cahill, Keblinski, PRB (2009)

Digression: Coating of the anvil might be a better approach. Thermal conductivity of PMMA agrees well with predicted scaling with $(C_{11})^{1/2}$



Hsieh *et al.*, submitted

Density functional theory calculation of ice VIII lattice dynamics



Chen *et al.*, submitted

Heat capacity per unit volume of ice VIII is independent of pressure but this is a coincidence

- Ice VIII (proton ordered) used as a surrogate for ice VII (proton disordered)
- Pressure increases the number of molecules per unit volume,
- Pressure decreases the heat capacity per molecule because of quantum mechanics.
- The sizes of the opposing effects are about the same, 33% at P=22 GPa.

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

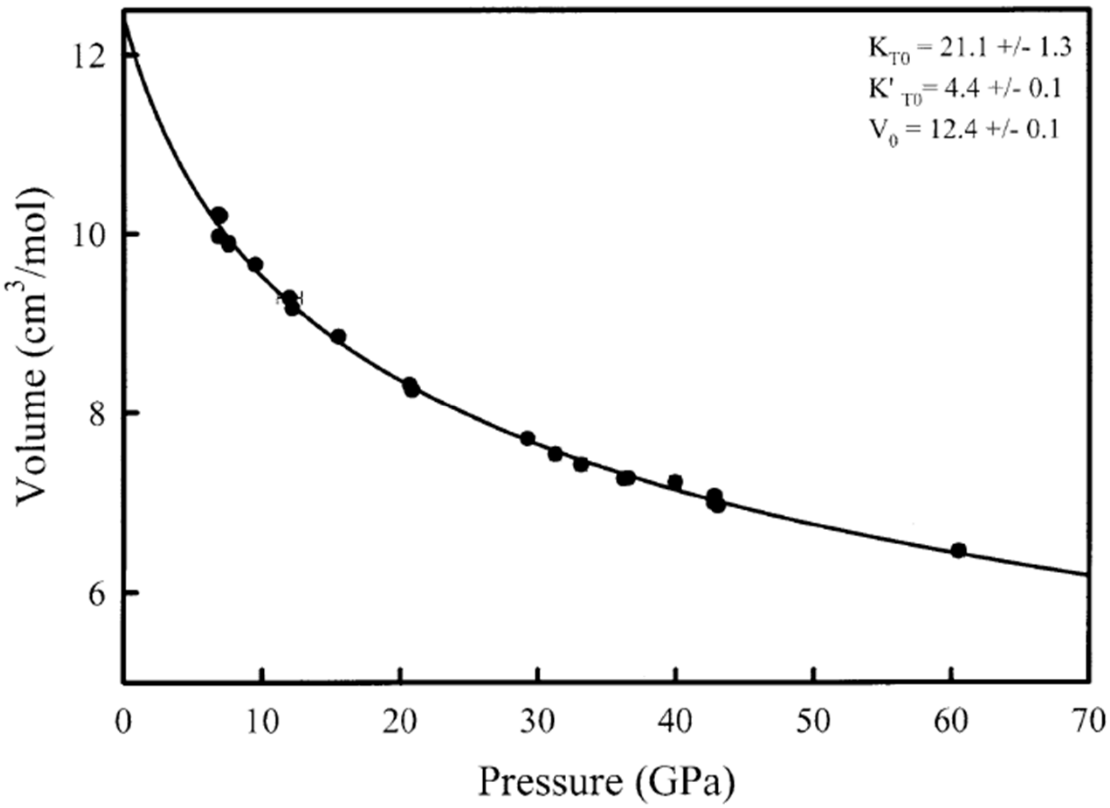
$\omega =$ Debye frequency

$\gamma =$ Grüneisen parameter

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

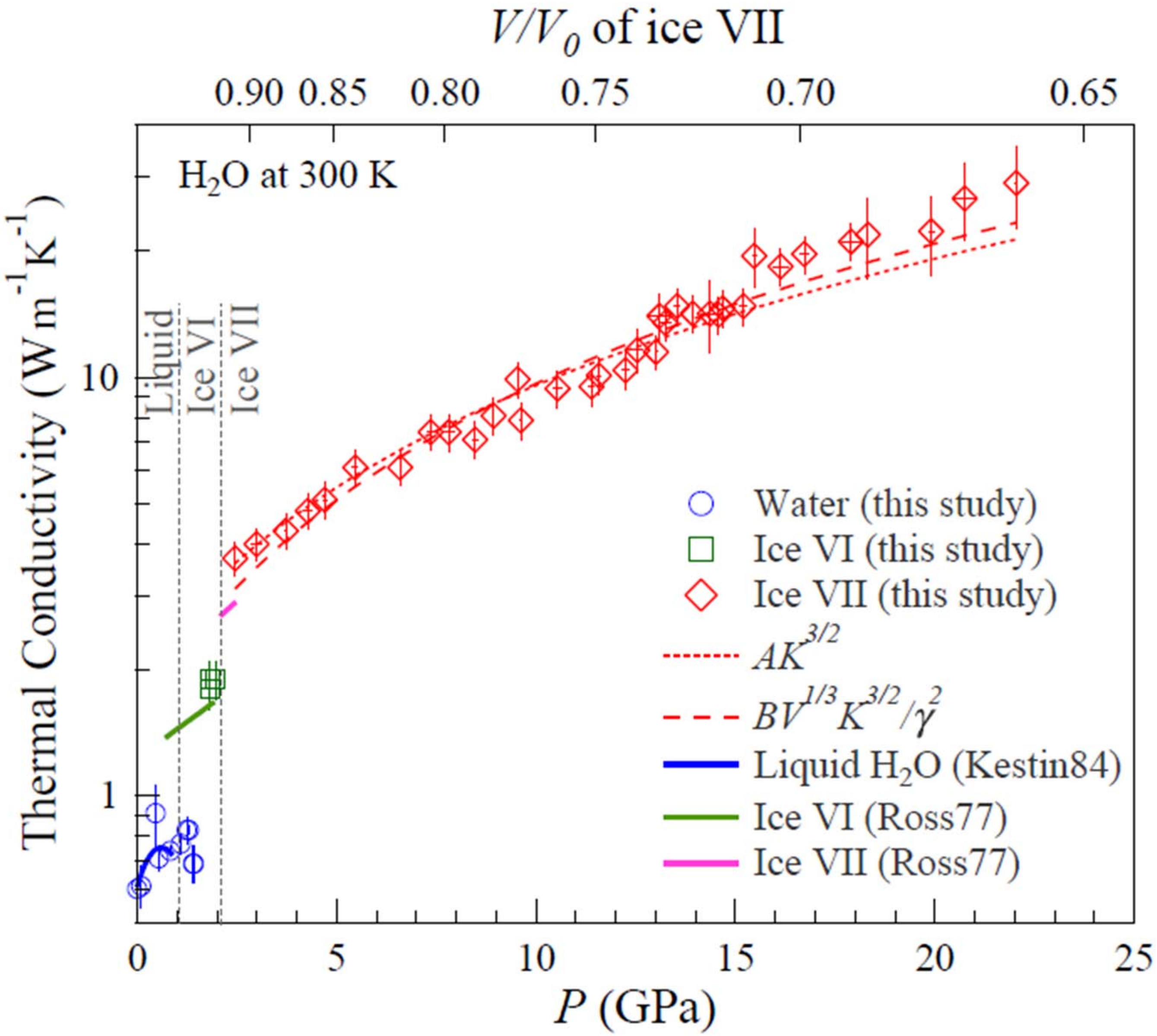
- Data for V(P) are fit to a model (e.g., Birch-Murnaghan)
- Assume ω_D scales with $K^{1/2}$
- γ is derived from a second derivative of the *V*(*P*) curve.

Many studies of *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



Summary

- Time domain thermoreflectance (TDTR) is a powerful method for measuring thermal conductivity under extreme conditions.
    - Calorimetry is also possible if the system under study is reversible at MHz frequencies.
- Pressure dependence of ice VII in good agreement with Leibfried-Schlömann equation
    - Optical phonons are not an important factor for thermal conductivity of water ice either as carriers or scattering mechanisms. Will this be true in other molecular solids?
    - Hydrogen bond disorder does not seem to be important either. Test with ice VIII.

Possible collaborations with Illinois

- Implement pump-probe system at Hydrogenius
- Create high pressure gas optical cell for measurements at Illinois
- Thermal conductivity and acoustic damping of H_2 to higher pressures and temperatures
- Calorimetry of hydrogen/material interactions
- Two phase CO_2/H_2O/porous-material systems probed by thermal conductivity, heat capacity, and acoustics
- Thermal management of fuel-cell, solid-state hydrogen storage