Resonant Ultrasound Spectroscopy at Elevated Temperatures

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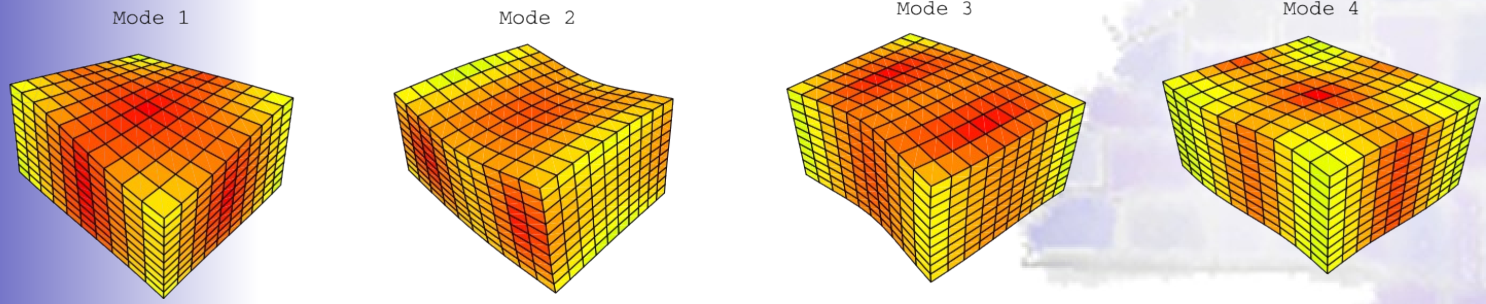


ICU 2009
Santiago, Chile

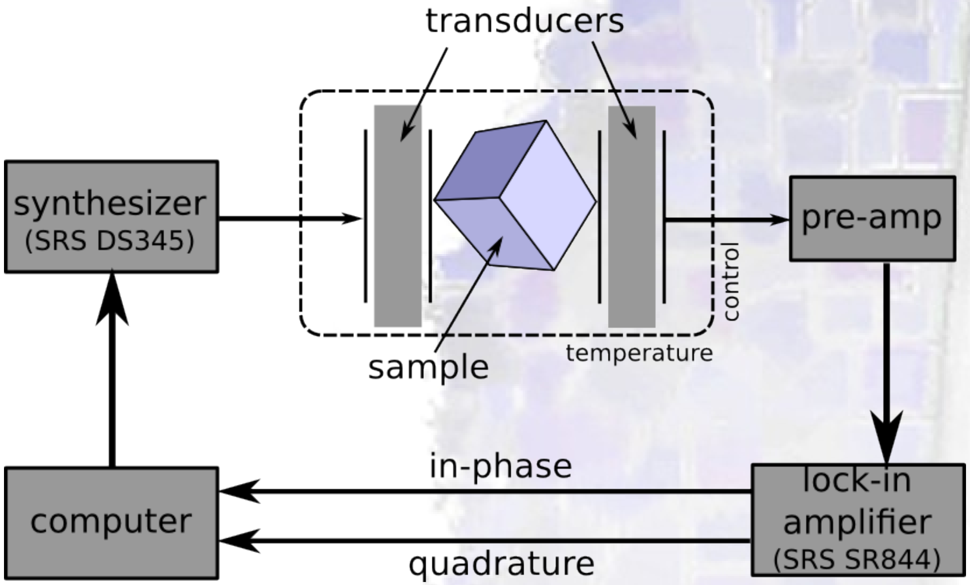
Outline

- **Brief Introduction and RUS at NCPA**
  - Fundamental concepts
  - RUS capabilities at the Univ. of Mississippi & NCPA
- **Hardware and Data Acquisition**
  - Furnace and temperature control
  - Direct contact & buffer rod transducers
  - Experimental procedures
- **Data Analysis and Fitting**
  - Peak fitting: Lorentzian fits vs rapid “peak picking”
  - Buffer rod peaks
  - Batch moduli fitting on a computer pool
- **Current Projects**
  - Novel thermoelectric materials
  - Charge order transition
  - Glass transition in bulk metallic glasses

Goals and Procedures

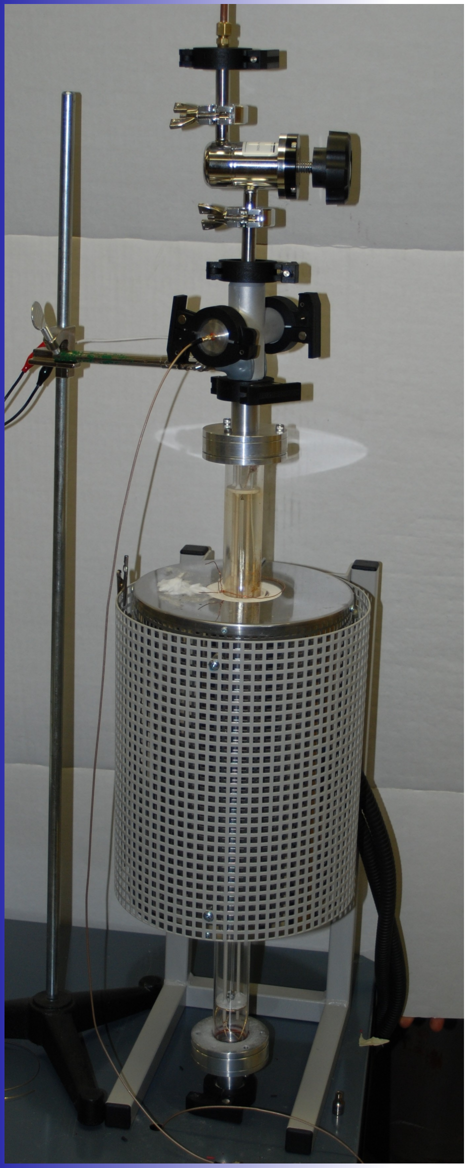
Goals of RUS

Measure elastic tensor and acoustic attenuation in a single crystal sample



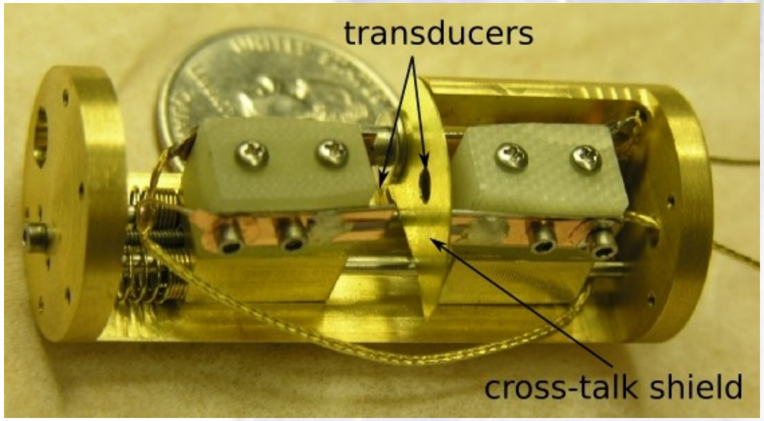
- **Procedure**
  - Measure resonance spectrum of a polished parallelepiped sample
  - Obtain a list of the center frequencies for lowest ~ 25 peaks
  - Use spectrum, geometry, density to compute elastic constants (nonlinear fitting scheme)

RUS at the NCPA

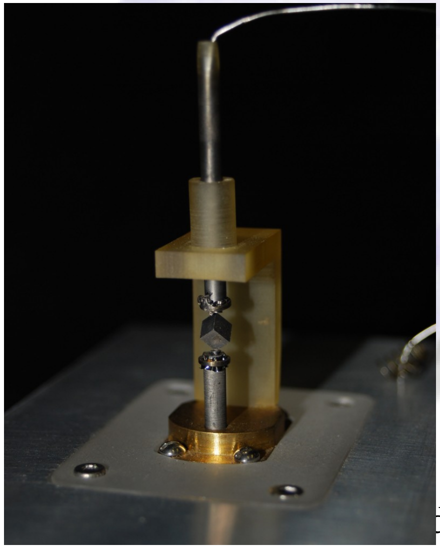


High Temperature
(up to 1000 °C)

Thin films and small samples



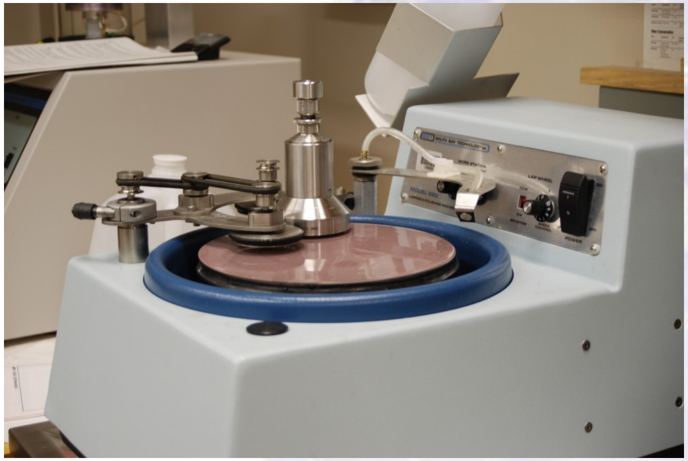
Rapid Room Temperature



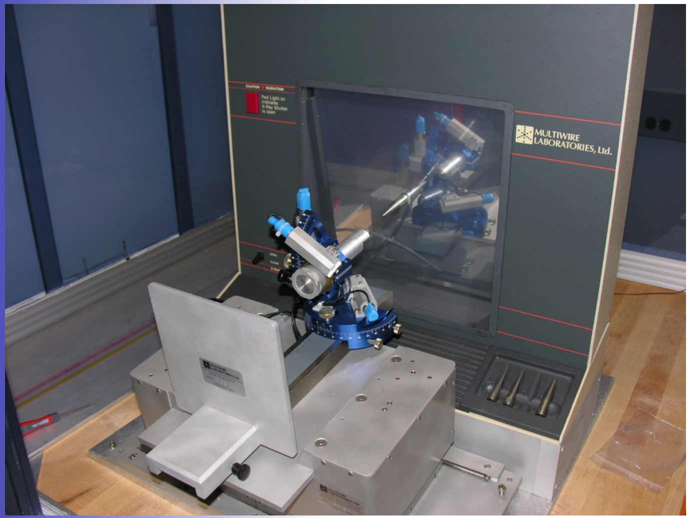
Supporting Facilities

Powder XRD

Lapping Machine



Backreflection XRD



Furnaces & Vacuum Oven

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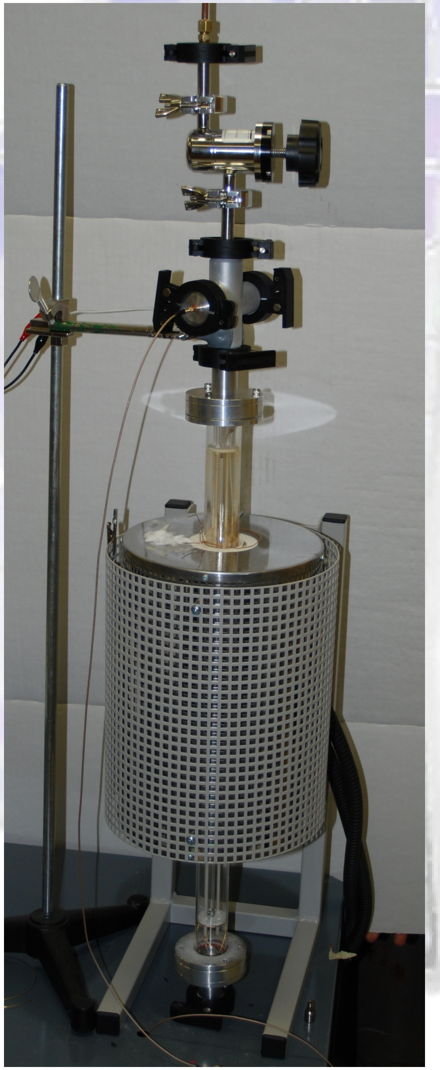
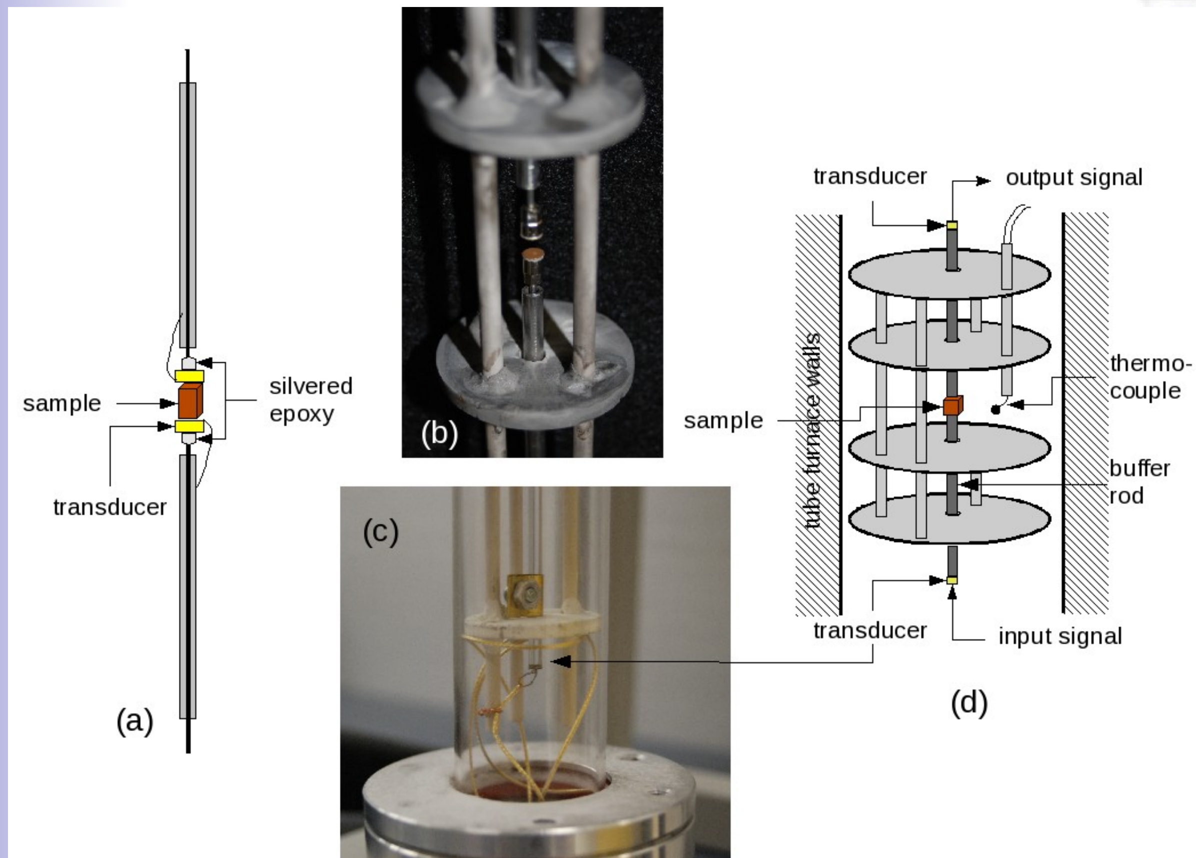
Temperature Control

- Carbolite furnace (<1050 °C)
- Low flow 95/5% Ar/H (~1LPM)
- Temperature stability: ~0.5 °C
- Temperature monitored during scans
- Oxygen scrubber
- O_2 meter: < 5 ppm
- Ceramic alumina infrastructure



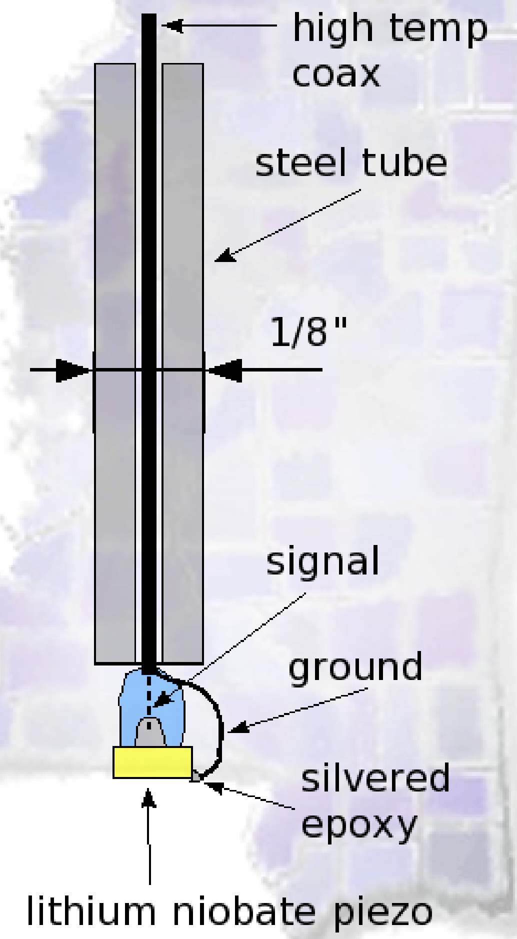
Direct Contact and Buffer Rods



- Below 650 °C → custom designed direct contact transducer system
- Above 650 °C → 25 cm fused quartz buffer rods are required.

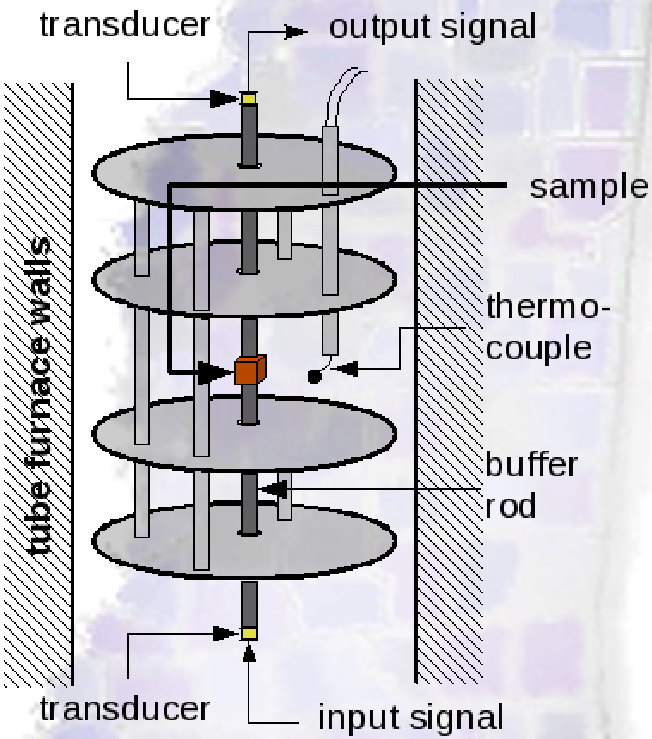
Direct Contact Transducers

- Lithium niobate piezoelectric (Au electrodes)
- Silvered epoxy (Epo-Tek)
- High temperature coax (Thermocoax)
- Upper temperature: ~650 °C
- Next generation
  - $GaPO_4$ or Langatate piezo w/ Pt electrodes
  - Conductive adhesive (1 part): Aremco Products Pyro-Duct
  - Expected upper range 950 °C



Buffer Rod System

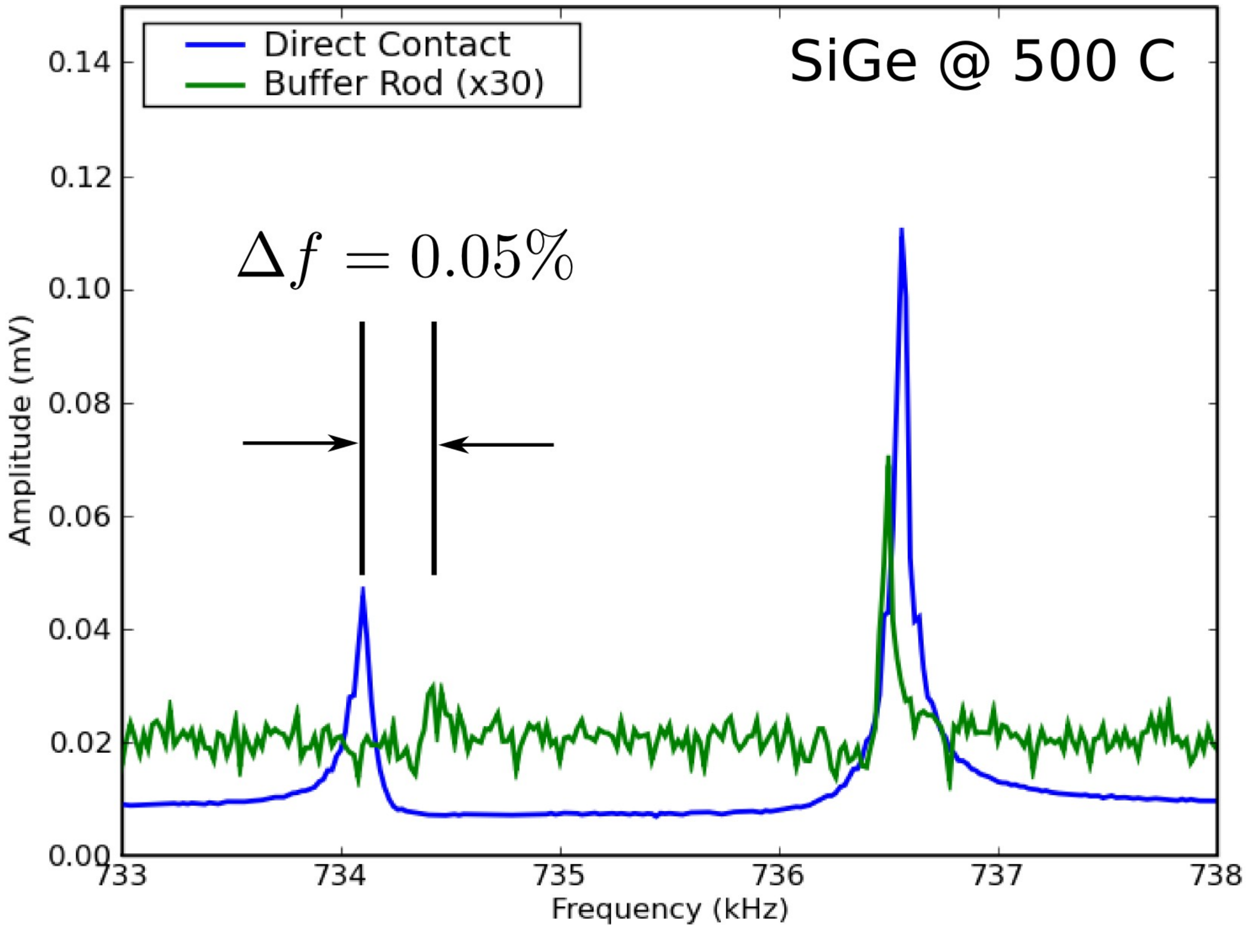
- Low attenuation and thermally stable materials: alumina or fused quartz
- Button type lithium niobate transducers bonded to end with conductive epoxy.



Problems

- Sample loading = 10 grams
  ⇉ mode dependent frequency upshifts ~0.1%
- High rod mode density in scan range → difficult to differentiate sample peaks from rod peaks
- SNR ratio down by ~ 100

Sample Data



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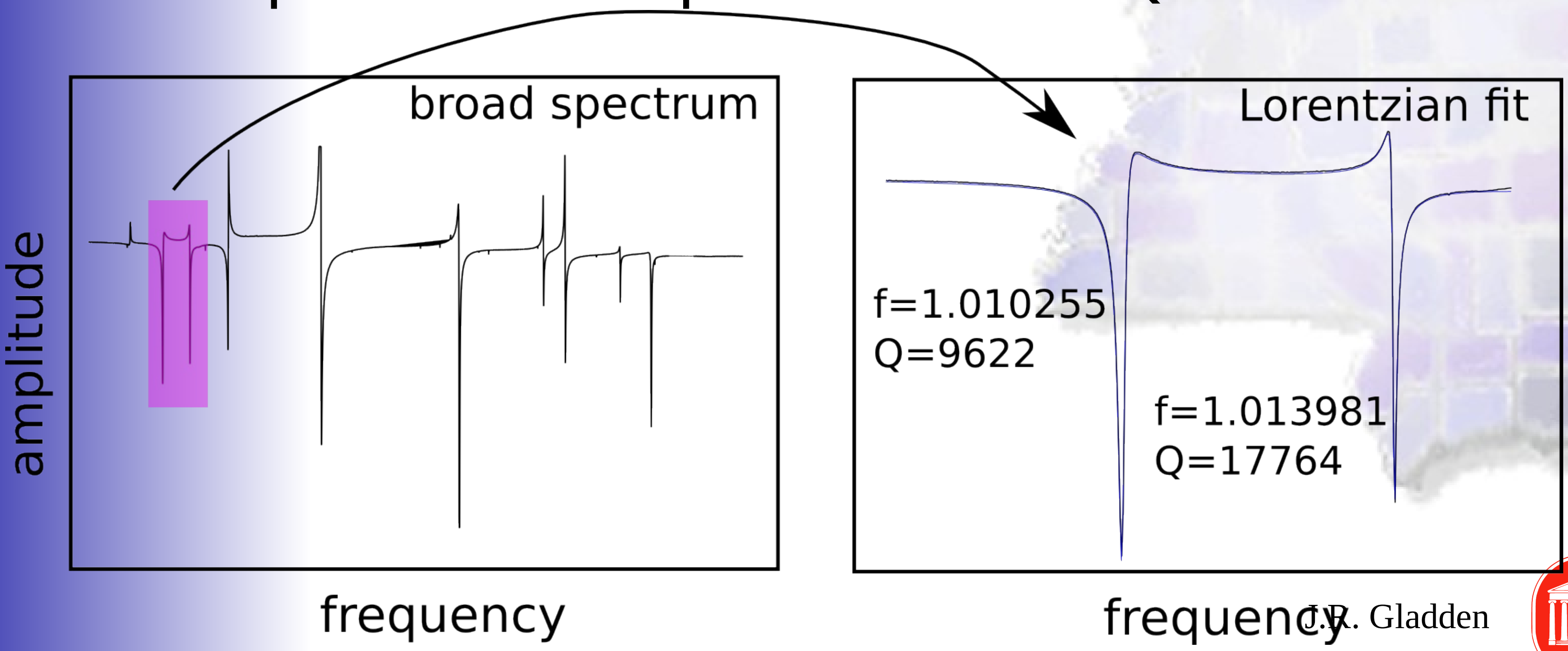
Procedures

T = room to 1000 C

- Direct contact measurement: 22 - 600 ^{o}C.
- Acquire data periodically as it cools, including room temperature.
  - Check for thermal cycling effects
- Transfer sample to buffer rod system.
- Acquire data periodically below 600 ^{o}C.
  - Check for loading effects
  - Aides in sample / buffer rod peak differentiation
- BR system requires continuous frequency scans
  - Time per temperature: ~ 25 min.

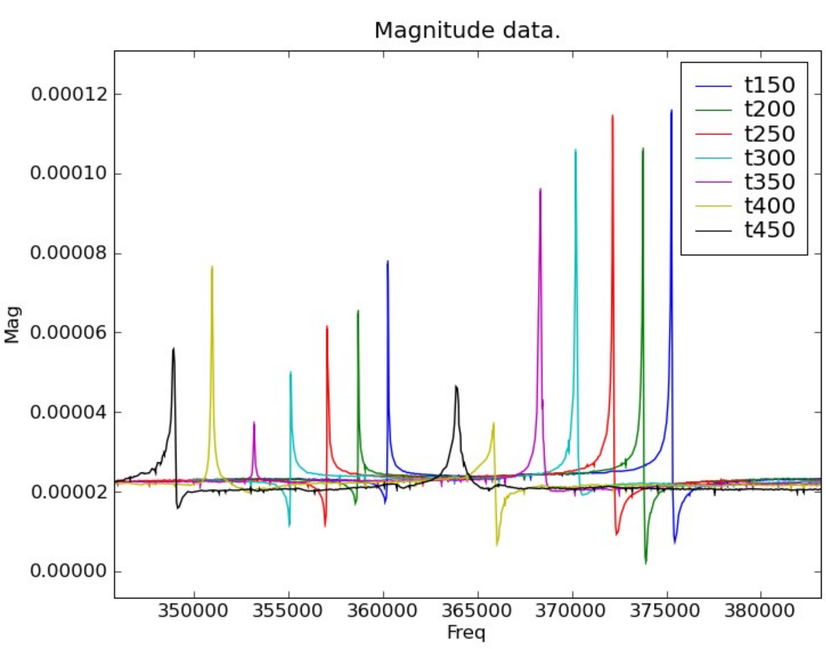
Peak fitting schemes

- Scilab script for slicing a section of a data file and fitting up to four peaks with a Lorentzian function.
- Pick starting frequencies from plots.
- Dump center frequencies and Q's to file.

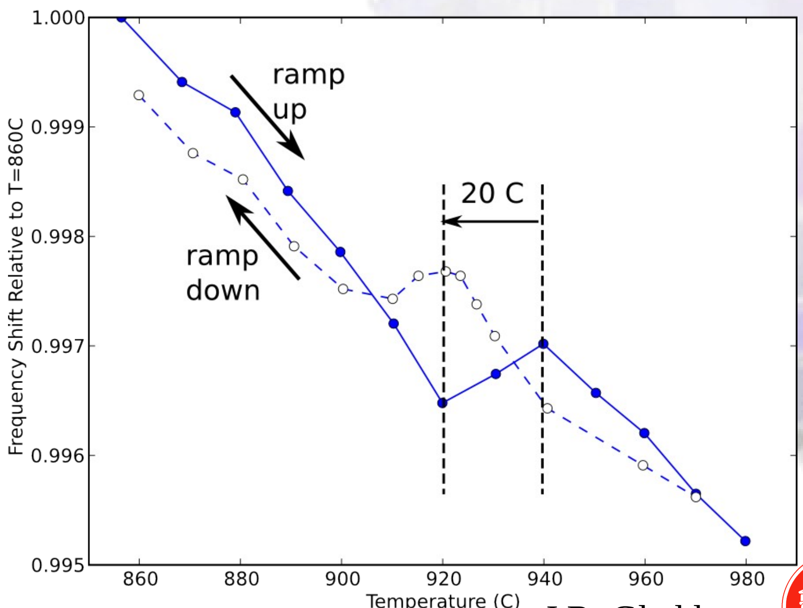


Quick Temperature Trends

- Python program for plotting magnitude for multiple scans
  - Matplotlib module provides convenient pan and zoom features
- Center frequencies recorded by clicking



Zintl phase thermoelectric



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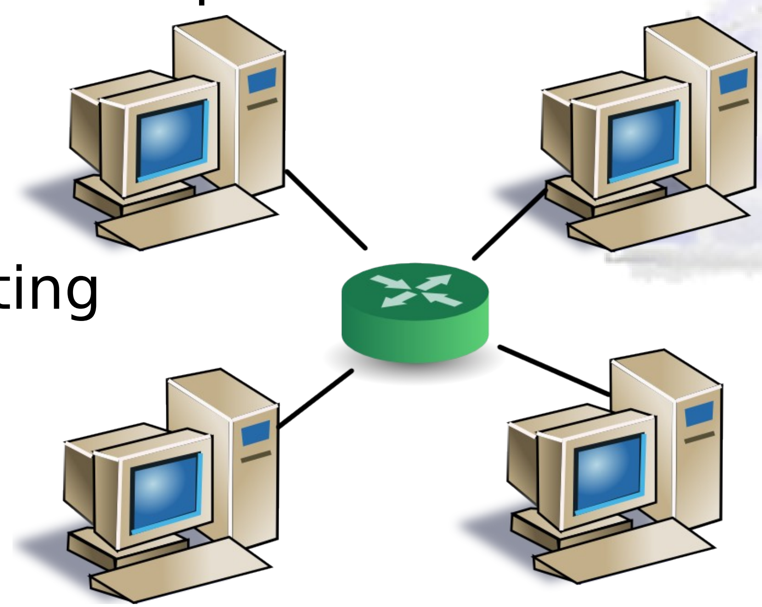
Parallel moduli fitting

- Low symmetry (i.e. trigonal) moduli fits require ~30 min per temperature X 30 temperatures.
- Python control script for running fitting program on multiple computers through SSH connections.
- Detects number of cores on each CPU
- Scalable – 1 desktop to a cluster
- Dimension adjustments
- Consistent mode weighting
- Results compiled on host



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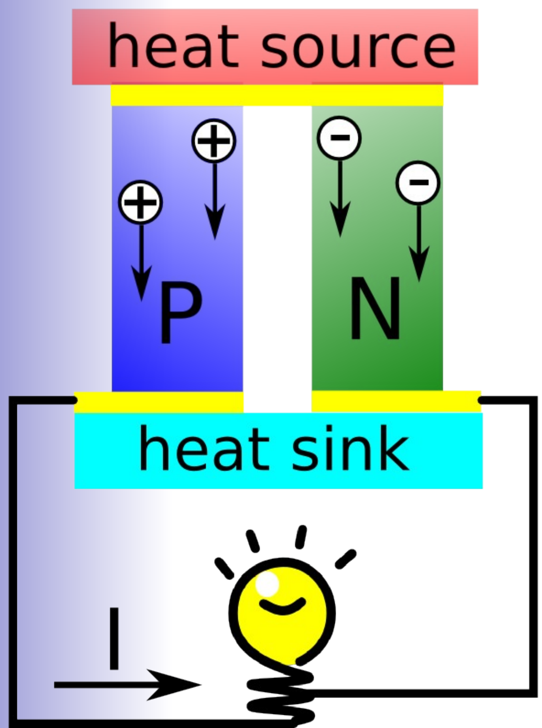
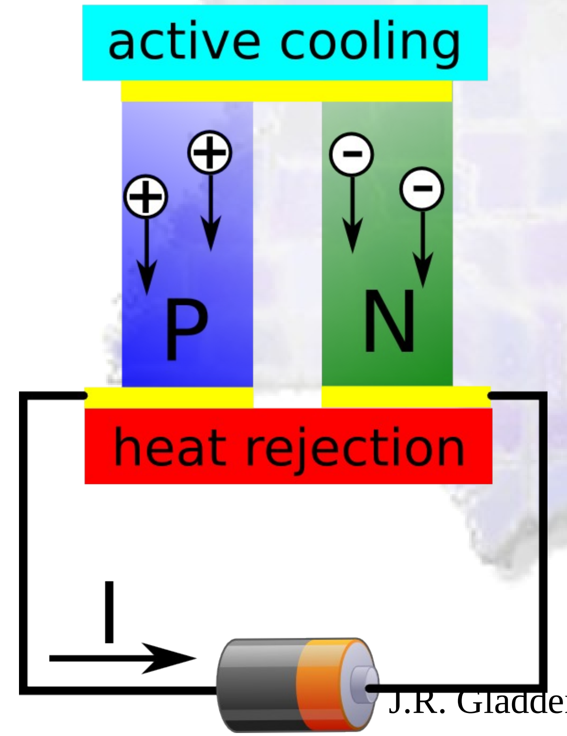
Thermoelectrics

- **Seebeck Effect**
  Thermal gradients ⇉ electric potential
- **Peltier Effect**
  Electric potential ⇉ thermal gradients

power generation

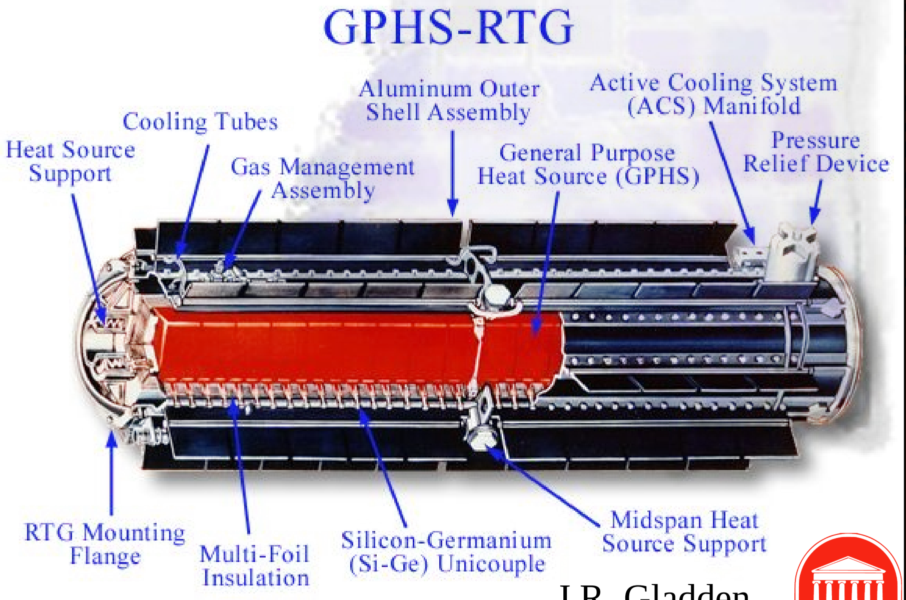


cooling mode



Thermoelectric Applications

- **Power Generation**
  - Waste heat recovery, power scavenging
  - Radioisotope Thermal Generators (RTGs) deep space probes (~14 year lifetime)
  - No carbon emissions
  - Scalable – car engines to manufacturing plants
- **Heating / Cooling**
  - Localized cooling
  - CPU chillers and car seat heaters
  - No moving parts or refrigerants



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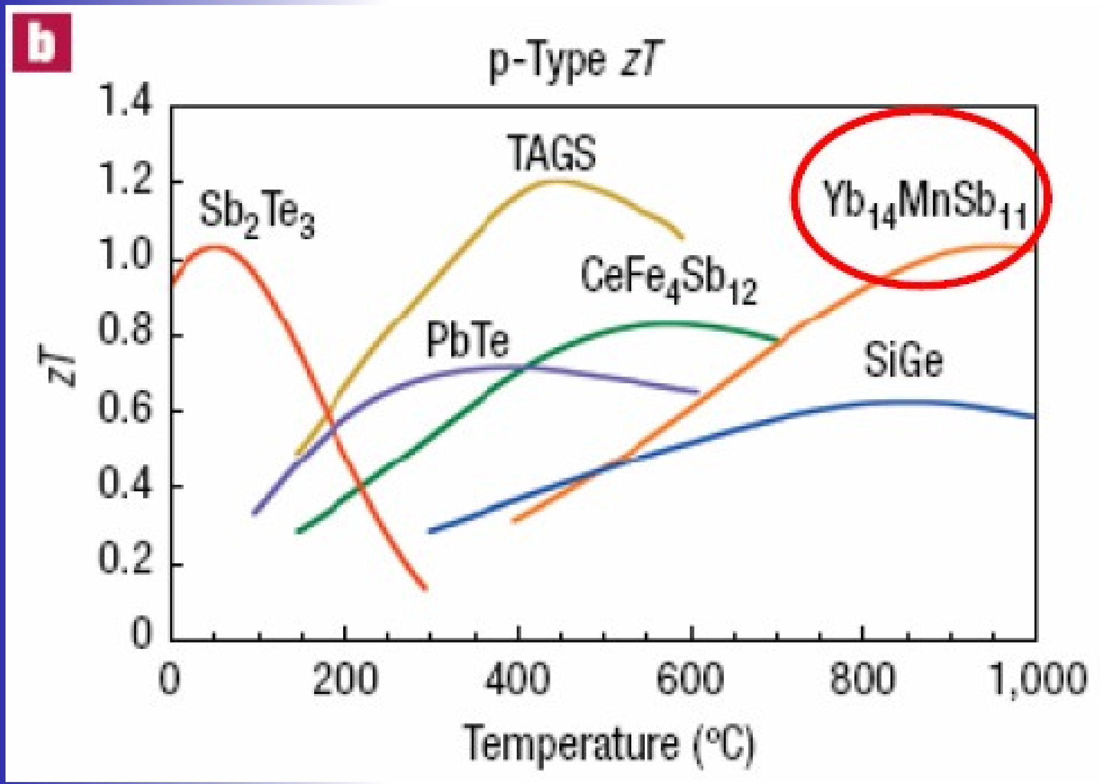
Thermoelectric Materials

Figure of merit (ZT)

σ : electrical conductivity , S : thermopower (μ V/K)
T : average temperature , κ : thermal conductivity

$$ZT = \frac{\sigma S^2 T}{\kappa_T}$$



Courtesy of Toberer & Snyder, Cal. Tech.

- Measure of efficiency
- ZT ~ 1-2 is good
- ZT > 3-4 is required for TE to be competitive
- Maximize S and minimize

$$\kappa_T = \kappa_{elec} + \kappa_{lattice}$$

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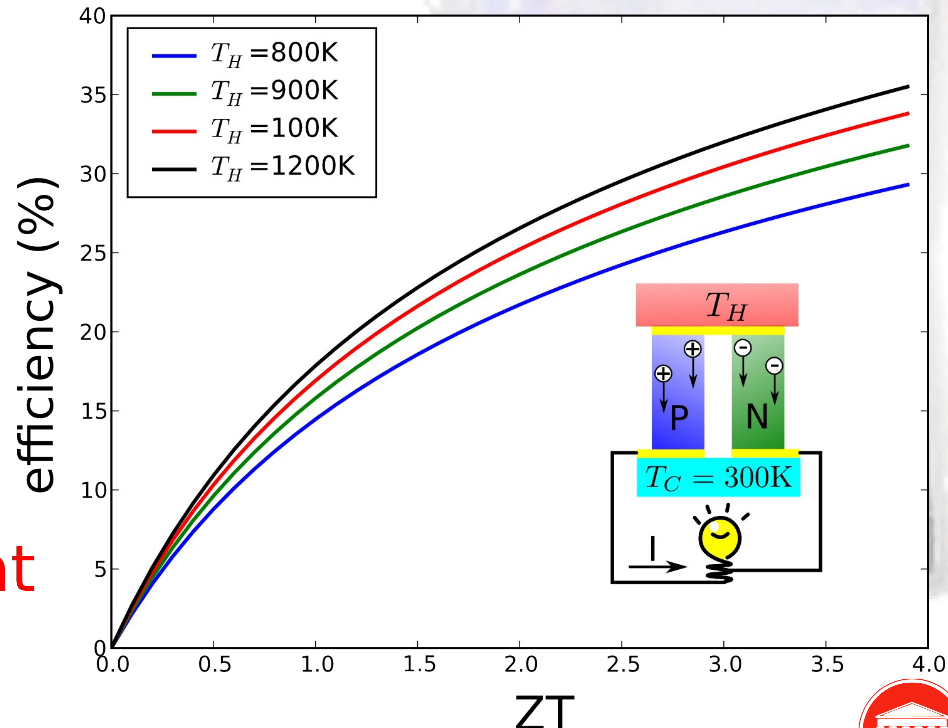
TE Device Efficiency

- Large thermal gradients
  $\rightrightarrows$ better efficiency
- Assumes ZT is same for
  P and N leg in TE.
- Typical waste heat application:
  T_C = 300K, T_H = 800K, with ZT = 1
  $\rightrightarrows$ 14.5% efficiency
- Need to understand mechanical and structural properties at high temperatures

$$\eta = \frac{(T_H - T_C)(\gamma - 1)}{T_c + \gamma T_H}$$

where $\gamma = \sqrt{1 + ZT_{avg}}$



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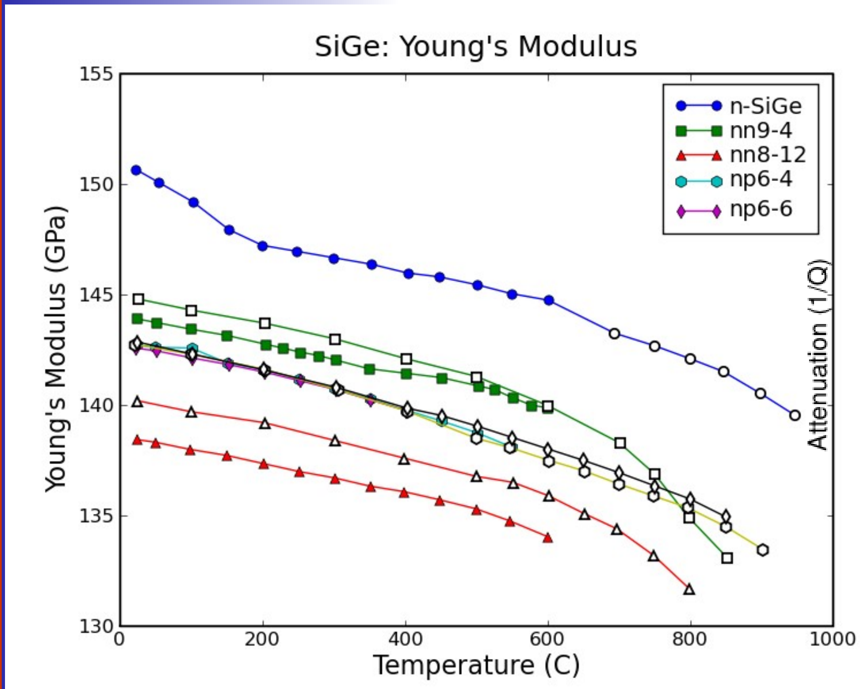
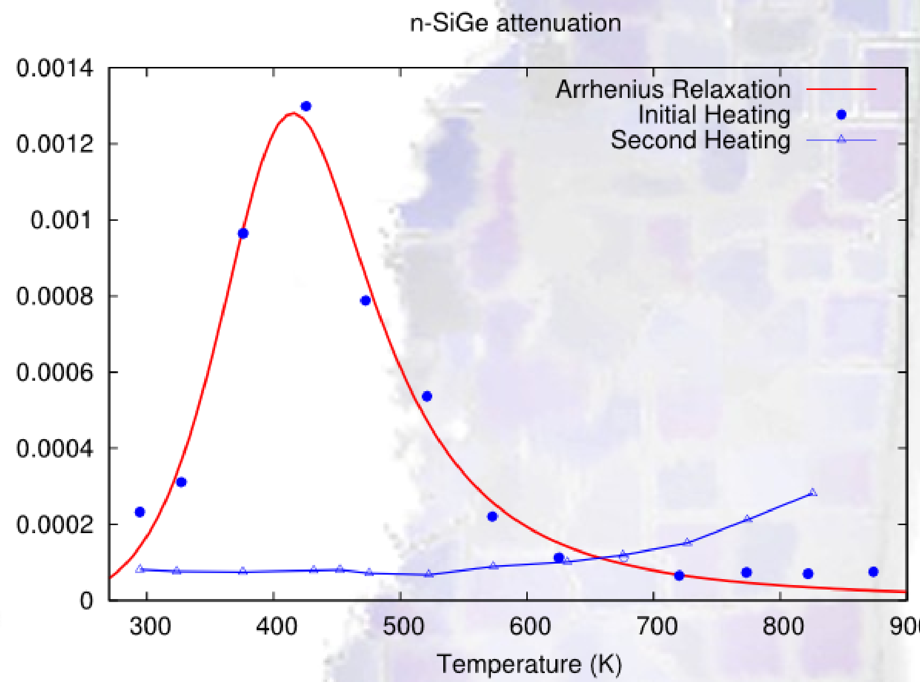
Silicon Germanium





Effect of doping levels and types on silicon germanium

Irreversible transition near 180 C (453 K)
Arrhenius relaxation model with activation energy of 0.27 eV

Zintl phase TEs

$$ZT = \frac{\sigma S^2 T}{\kappa_T}$$

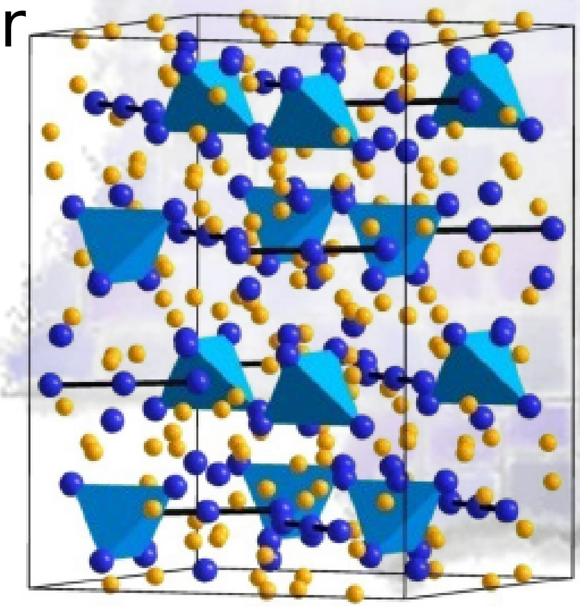
Zintl compounds

- Both ionic and covalent bonds
- Complex crystal structure
  $Yb_{14}MnSb_{11}$: tetragonal with 208 atom unit cell
- Narrow band gap semiconductor
- Good TE candidates

  - Low κ_{latt}
  - Highly tunable carrier concentration (n)

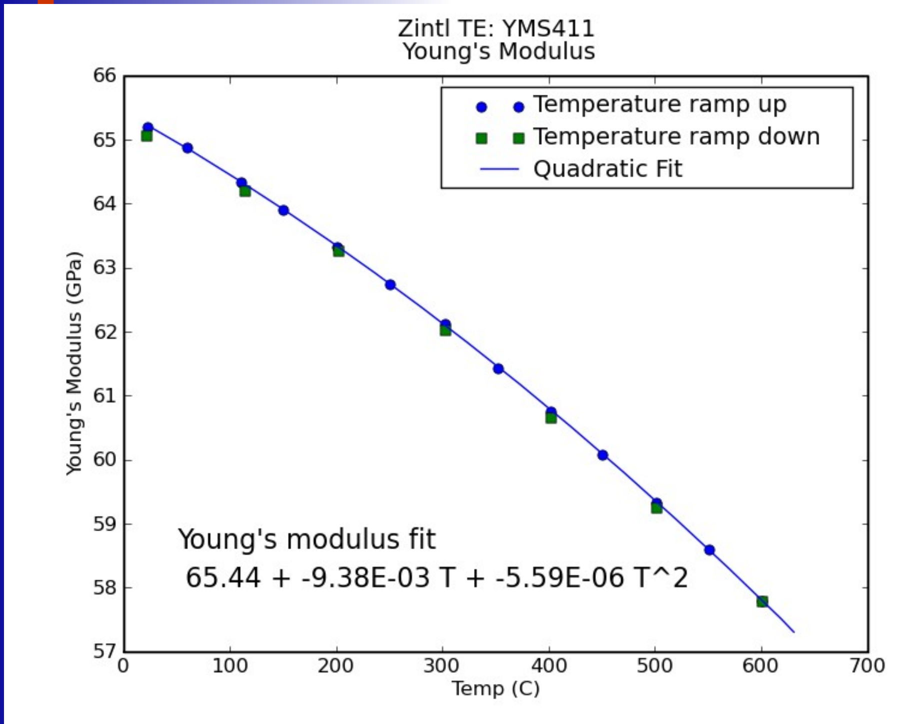
$$\kappa_T = \kappa_{elec} + \kappa_{latt}$$

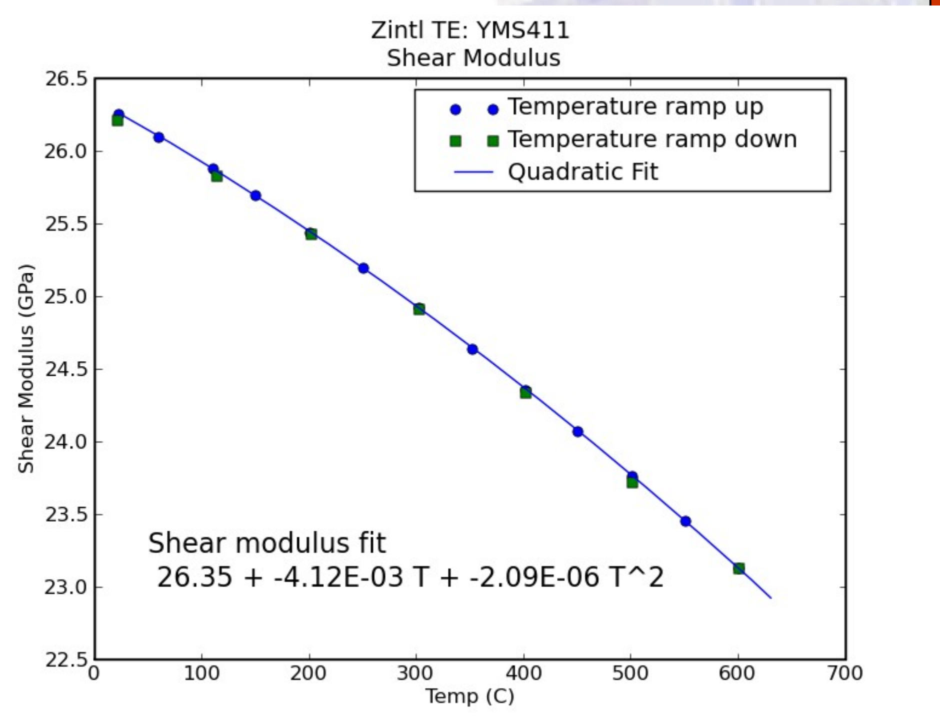
$$\kappa_{elec} = L T \sigma = L T n e \mu$$



Courtesy of Toberer & Snyder, Cal Tech

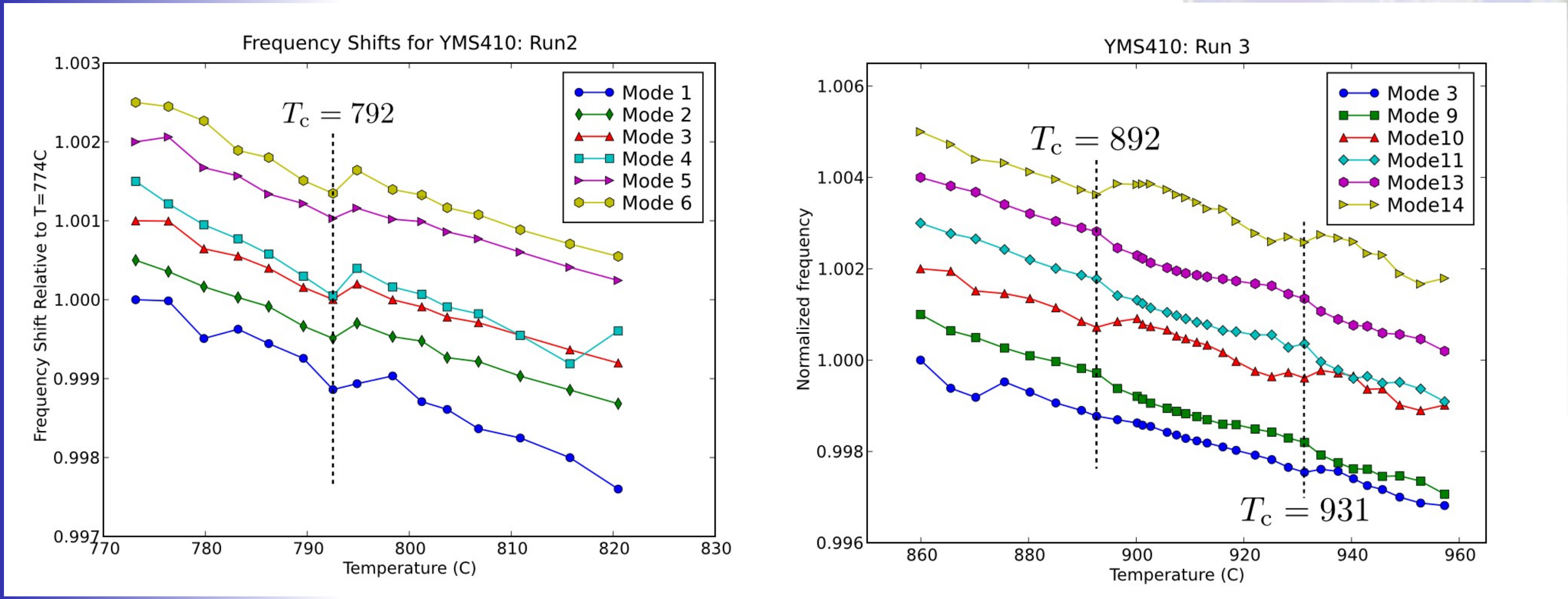
Polycrystalline Zintl TEs





- Frequency fit errors ~0.15% over 25 modes
- Elastically isotropic
- Quadratic temperature trends
- No hysteresis

Phase transitions in Zintl TEs



- Three high temperature transitions
- Correlation with other material properties
- Weak signals with buffer rods – need DC system to compute moduli

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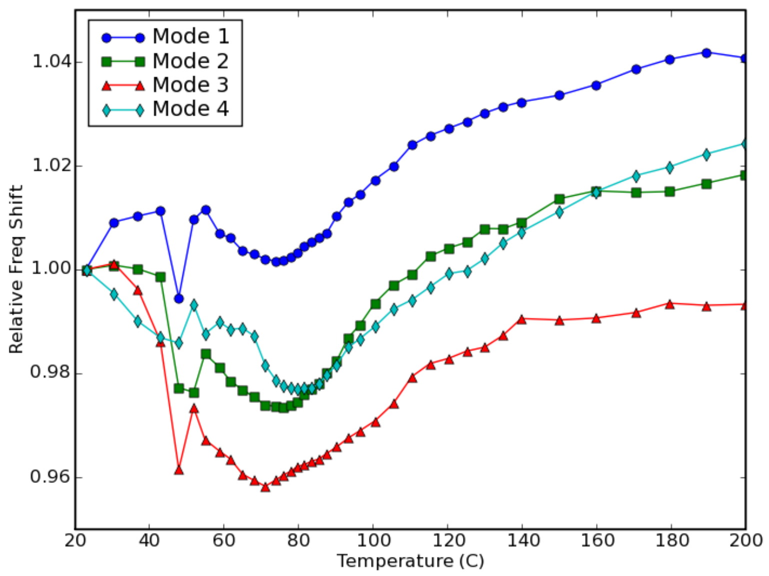
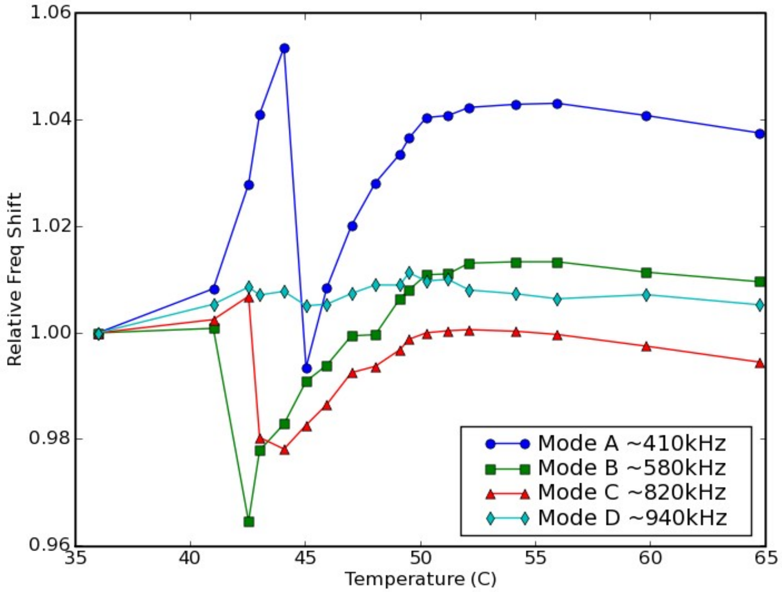
Charge order transition in transition metal oxides
(with Oak Ridge National Lab)



Discovery of a new (precursor?) transition at 44 °C



$LuFe_2O_4$

CO transition at 75 °C

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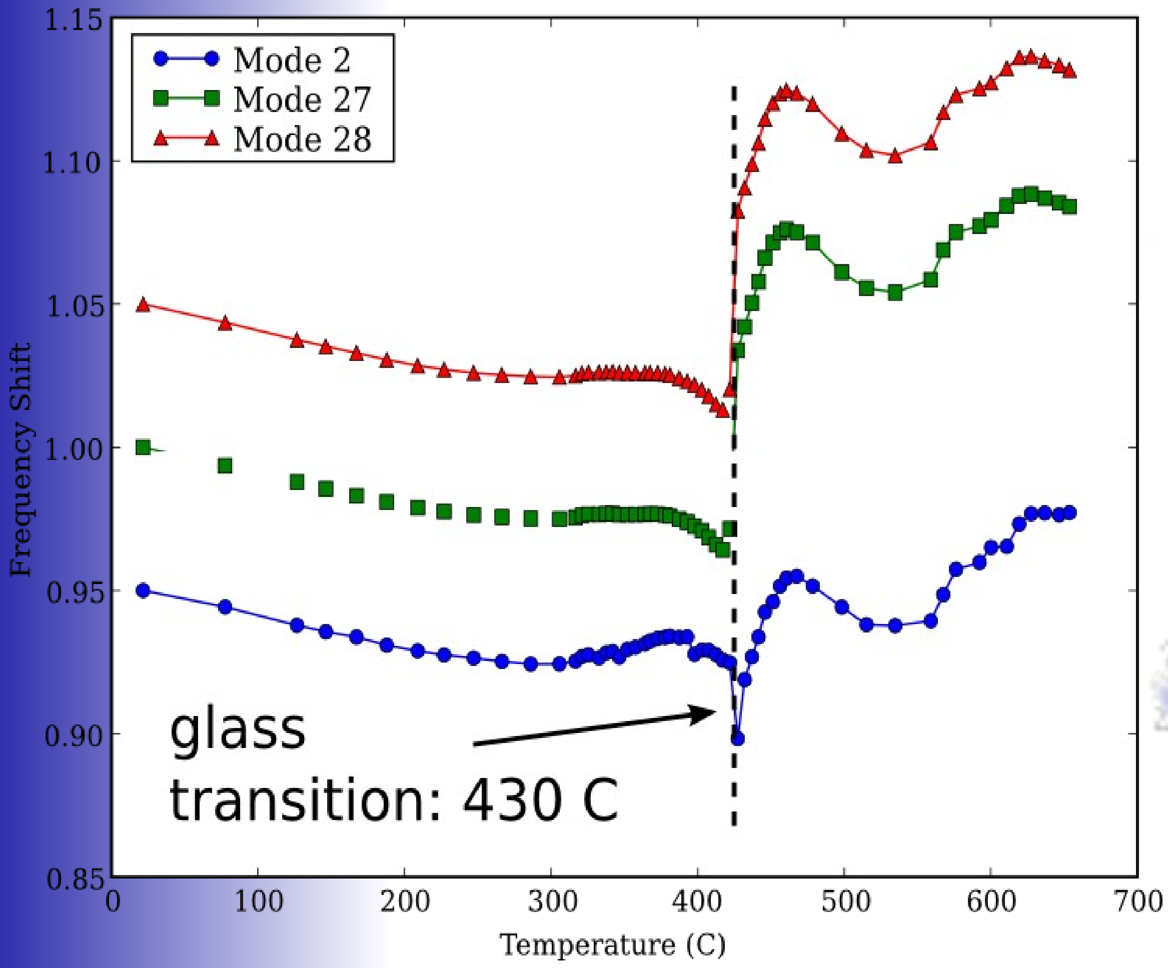
Bulk metallic glasses
(with UT - Knoxville)



- Irreversible transition from glassy to ordered state
- Very tough, wear resistant, sustainable materials
- Interesting fundamental physics and practical applications

Future Directions

- Complete new direct contact transducer assembly for full oven temperature range (1000 °C)
- Complete Zintl phase TE measurements
- Begin characterization of lanthanum telluride TE
- Develop non-contact, laser Doppler vibrometer based transduction system
- Add helium cryogenic capabilities to 4 K
- Expand work on bulk metallic glasses and other order/disorder transitions

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