# Properties of Materials: Physical Property Measurement System (PPMS)


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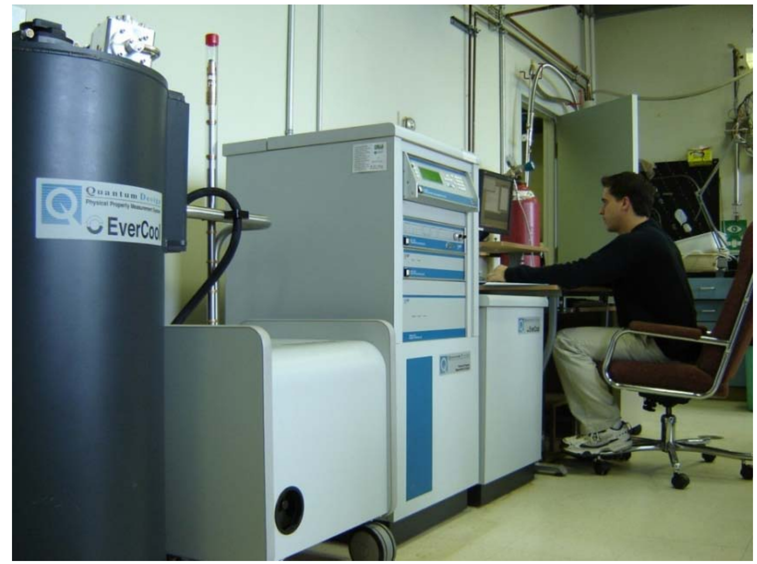
# Physical Property Measurement System (PPMS)

- Fully-automated variable temperature and magnetic field system with multiple measurement applications:
  - Thermal transport and heat capacity
  - DC magnetometry and AC susceptibility
  - Electro-transport
- Multi-function probe with integrated sample platforms ("pucks") using plug-in technology
  - Temperature control from 0.4 K - 400 K
    - Temperature range varies for each option
  - 9 Tesla longitudinal magnet
  - < $10^{-4}$ Torr high vacuum available

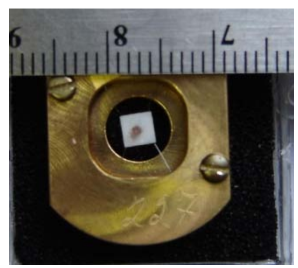


Research Associate Mike Johnson prepares for a routine performance test on the PPMS.

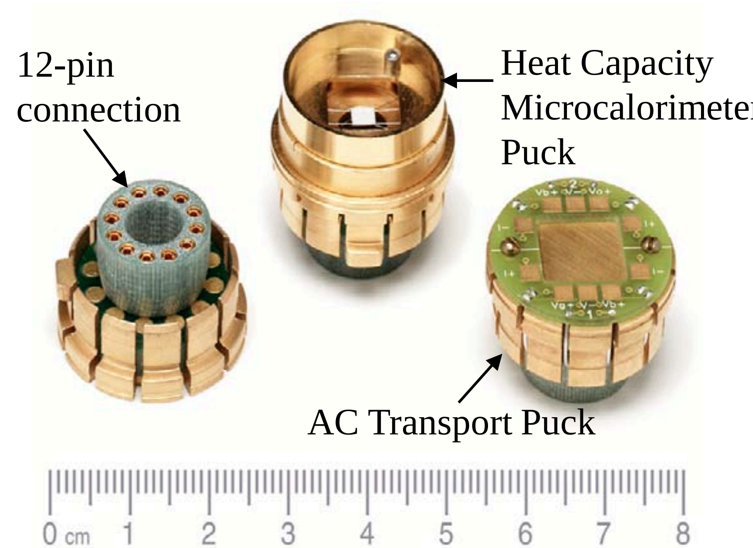
# Sample Puck Examples

$^{3}$He probe platform

$^{3}$He electro-transport puck



$^{3}$He $C_P$ puck with 3 mg sample used for measurements




Multiple sample platforms (pucks) available and easily installed into the chamber for experimentation.

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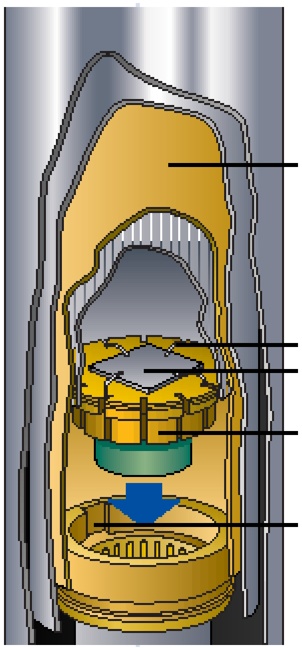
# Advantages of our PPMS

- Very low minimum temperature (350 mK) with the Helium-3 option
- Fast measurement times: up to 12 K/min slew rates
- Custom designed experiments
- Measure several physical properties at once, e.g.:
  - Electrical conductivity, thermal conductivity
  - Magnetic susceptibility, magnetization
  - Magnetic dependence of heat capacity
- Small sample sizes (typically 5 to 100 mg)
- EverCool Dewar with very low He loss
- 30 kbar pressure cell for electro-transport



PPMS Sample Chamber.

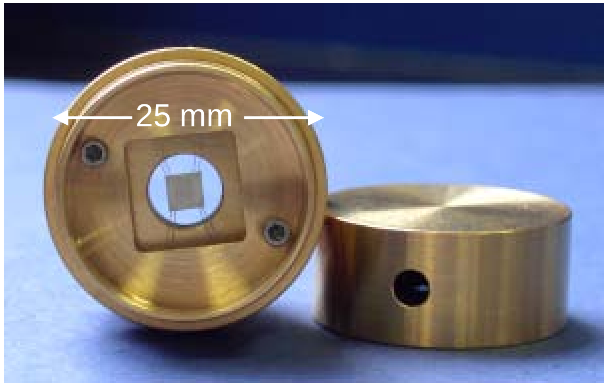
- **Only PPMS in Canada with all of these features!**

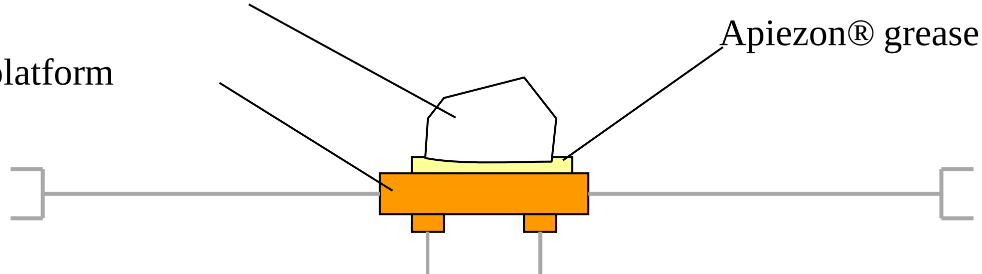
# PPMS Applications

- Heat Capacity
  - Microcalorimeter
  - Relaxation technique
  - ± 9 Tesla field
- Thermal Transport
  - Thermal conductivity
  - Seebeck coefficient
  - Thermoelectric figure of merit
  - ± 9 Tesla field
- Magnetometry
  - DC magnetometry
  - AC susceptibility
- Helium-3 System
  - Absolute temperature of 350 mK
  - Heat capacity and electro-transport options only
  - ± 9 Tesla field
- Electro-Transport
  - AC & DC resistivity
  - Magneto-resistance ± 9 Tesla
  - Hall effect
  - Critical current (to 2A)
  - I-V curves

# Heat Capacity

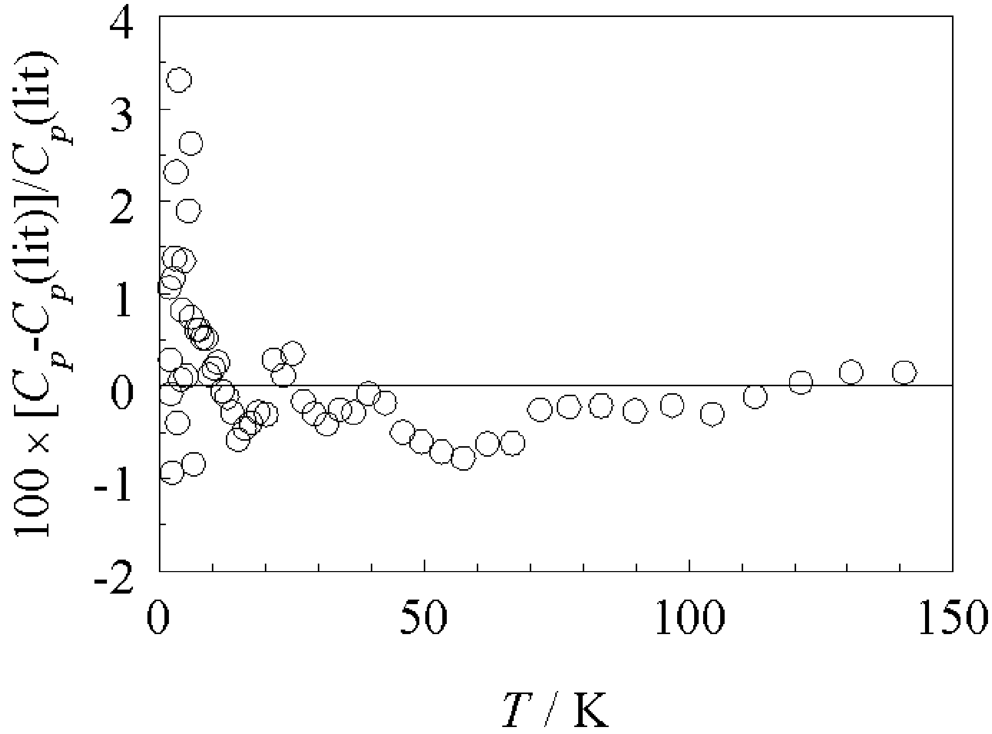
- Automated relaxation micro-calorimetry: $C_p=(dQ/dT)_p$
- High vacuum: $P < 10^{-4}$ Torr
- Sample masses ranging from 1-200 mg
- Temperature range: 0.4 K - 400 K ($^3$He option)
- Magnetic field range: ± 9 Tesla
- Measurement range: 1μJ/K to 100 mJ/K
- Resolution: 10 nJ/K at 2 K
- 5% @ 2-300 K; 2% typical



# Accuracy of PPMS

High-purity Cu (NIST RM5) with $^4$He system:




C. A. Kennedy, M. Stancescu, R. A. Marriott, M. A. White, *Cryogenics* 47, 107 (2007).

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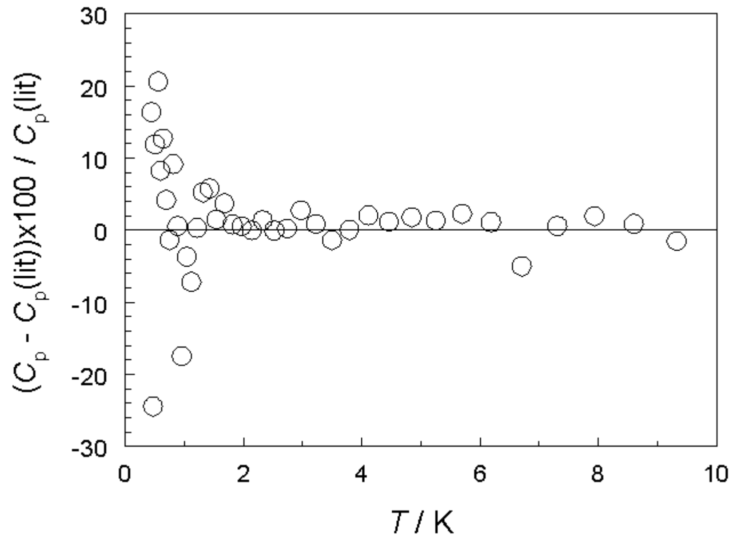
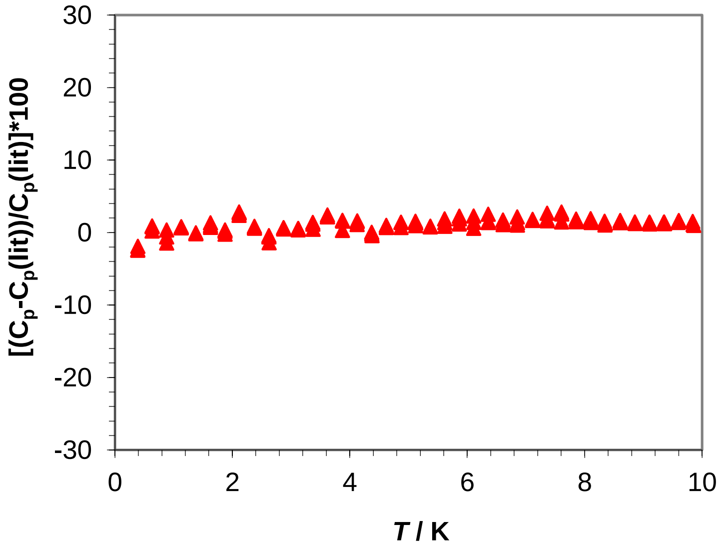
# Accuracy of PPMS

High-purity Cu (NIST RM5) at low *T* ($^3$He system):*




High-purity Cu (NIST RM5) at low *T* with improved baseline platform ($^3$He system, unpublished):




*C. A. Kennedy, M. Stancescu, R. A. Marriott, M. A. White, *Cryogenics* 47, 107 (2007).

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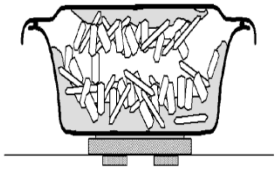
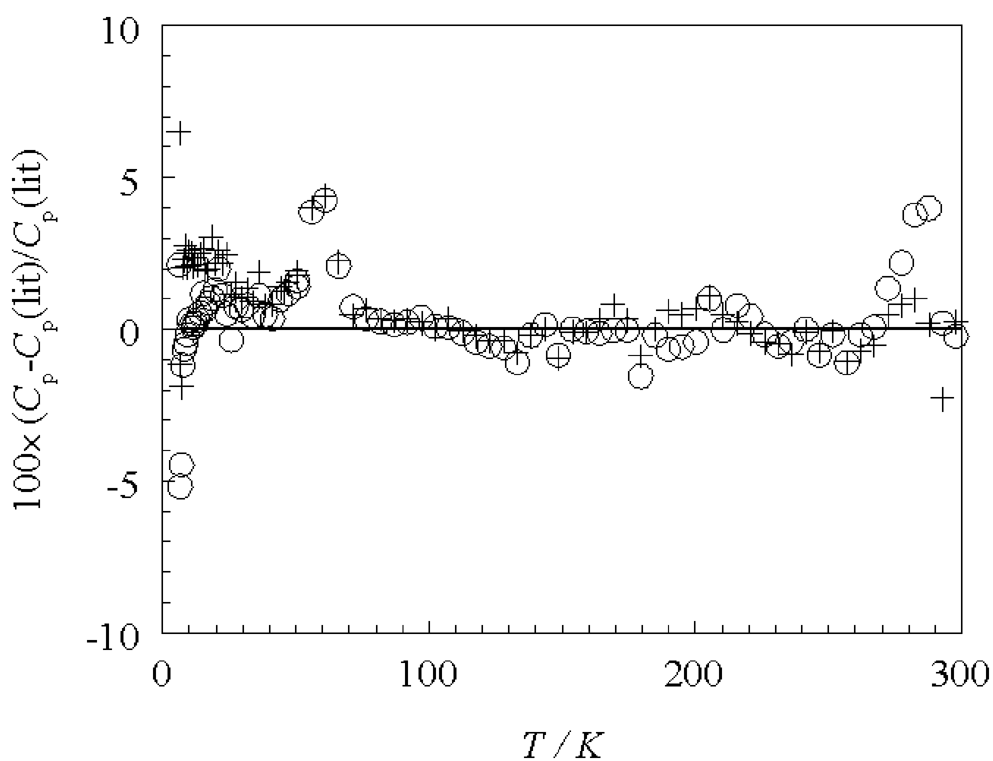
# Accuracy of PPMS

Standard benzoic acid (Calorimetry Conference) sealed in DSC pan:



- Powdered or air sensitive samples
  - Use Apiezon® grease to assist in thermal relaxation




R. A. Marriott, M. Stancescu, C. A. Kennedy, M. A. White, *Rev. Sci. Instrum*. **77**, 096108 (2006)

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# Heat Capacity: Practical Matters

- Single crystal: need flat face
- Powders: need to be able to consolidate into a pellet (best option) or place in an aluminum container (if not reactive with Apiezon ® grease)
- Sample size considerations, $C_{\mathrm{sample}}/C_{\mathrm{addenda}} > 0.5$; measure more than one sample mass
- Need to calibrate puck and Apiezon® grease
- Sample must tolerate high vacuum (or else seal in DSC pan with grease)

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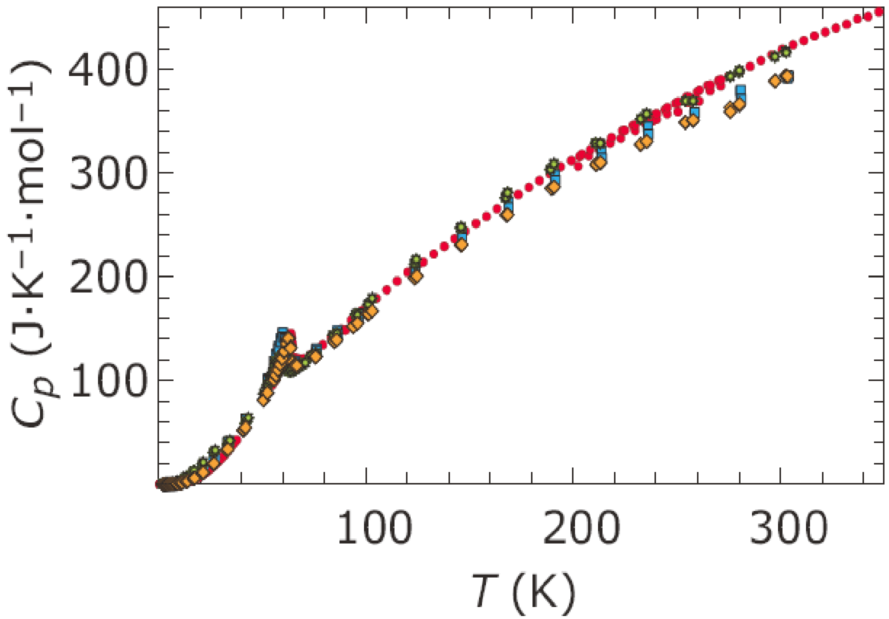
# Heat Capacity Example

Experimental heat capacities of synthesized K-, Na-, Rb-, and $NH_4$- jarosite showing a phase transition near 50 kelvin. These λ-shaped anomolies are from the iron transitioning from antiferromagnetic to paramagnetic state (on heating).




J. Majzlan, P. Glasnak, B. Fisher, M.A White, M.B. Johnson, B. Woodfield, J. Boerio-Goates. *Phys. Chem. Miner.* **37**, 635 (2010).

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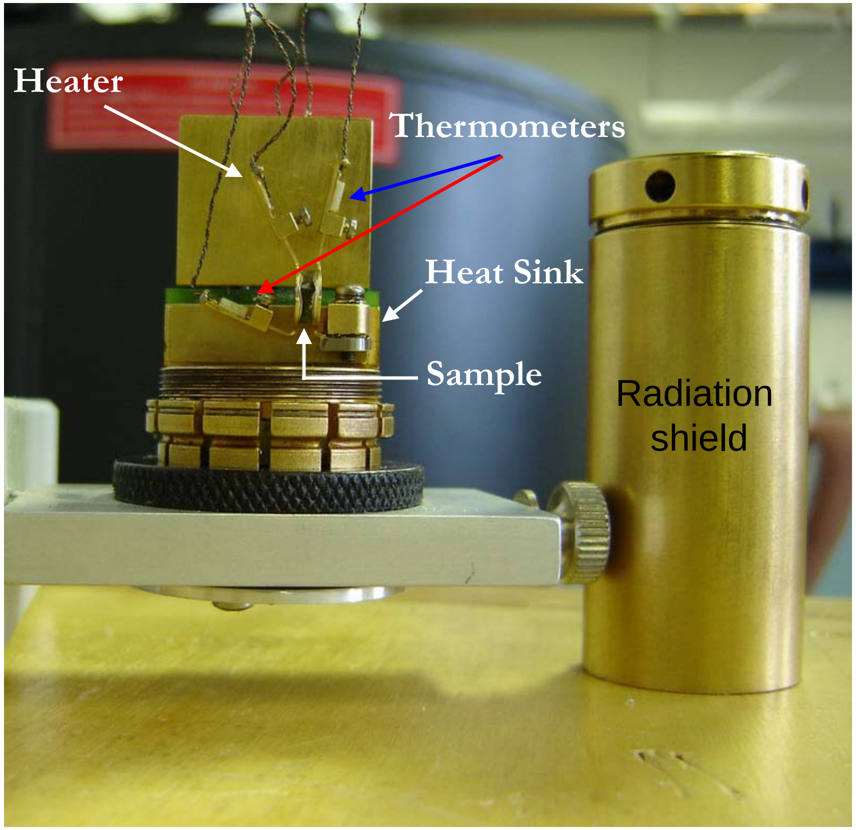
# Thermal Transport (TT)

- Thermal transport option can measure simultaneously:
  - Thermal conductivity: k = *K*(*L*/*A*)
  - Resistivity: ρ = *R*(*A*/*L*)
  - Seebeck coefficient: *S* = D*V*/D*T*
  - Thermoelectric figure of merit: $ZT = S^2T/(\rho k)$
- High vacuum: <$10^{-4}$ Torr
- Temperature range: 1.8 – 400 K
- Magnetic fields of ± 9T (> 20 K)

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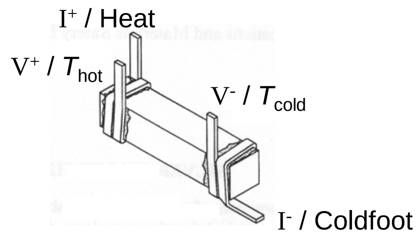
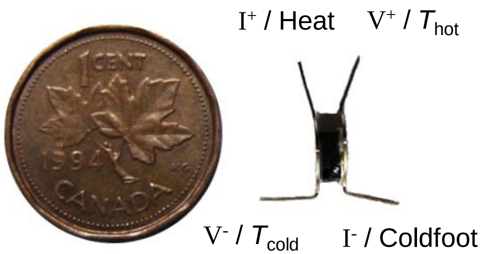
# Thermal Transport Specifications

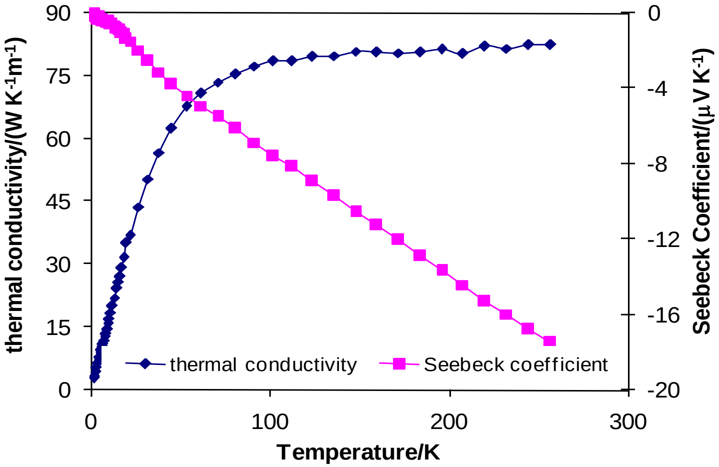
- Thermal Conductivity: $\kappa = K(L/A)$
  - Estimated dynamic range, for given sample geometry:
    - Sample: 3 x (4 x 4) $mm^3$: for $\kappa$: 0.1 - 2.5 $W*m^{-1}*K^{-1}$
    - Sample: 8 x (2 x 2) $mm^3$: for $\kappa$: 2 - 50 $W*m^{-1}*K^{-1}$
    - Sample: 10 x (1 x 1) $mm^3$: for $\kappa$: 10 - 250 $W*m^{-1}*K^{-1}$
- Thermal conductance error:
  - ± 5 % at $T < 200$ K
  - ± 5 % or ± 0.5 $mW*K^{-1}$, whichever is greater, for $200 < T < 300$ K
  - ± 5 % or ± 1 $mW*K^{-1}$, whichever is greater, for $T > 300$ K
- Estimated dynamic range:
  - 1 - 25 $mW*K^{-1}$ high for $T > 200$ K
  - μW/K – 100 $mW*K^{-1}$ for low $T < 50$ K
- Seebeck coefficient: $S = \Delta V/\Delta T$
  - Range: $\mu V*K^{-1}$ – $V*K^{-1}$
  - Error: ± 5 % or ± 2 mV, whichever is greater
- Thermoelectric figure of merit: $ZT = S^2T/(\rho\kappa)$
  - Errors compounded: ± 15 % -- determined largely by errors in $S$

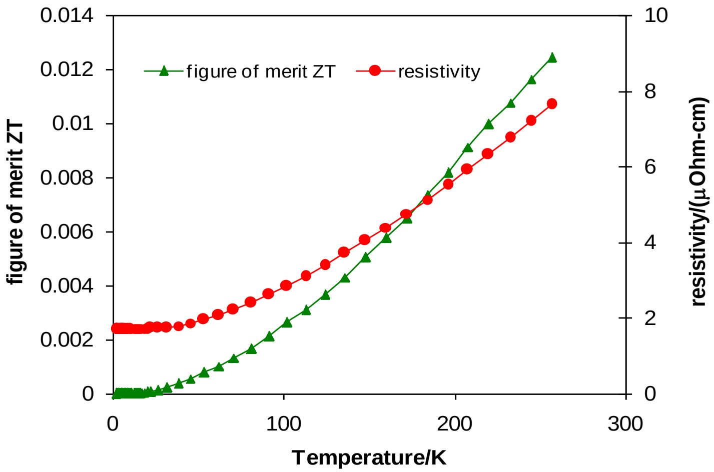
Typical sample morphologies:



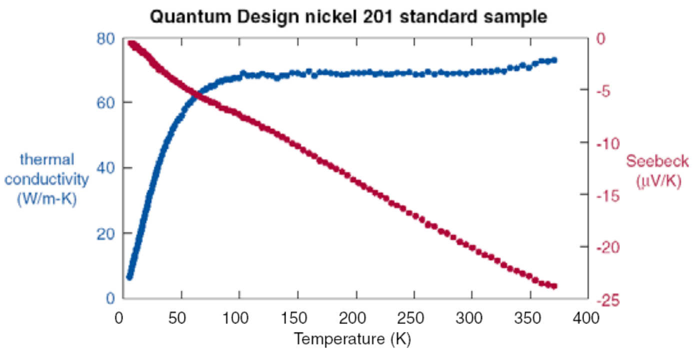



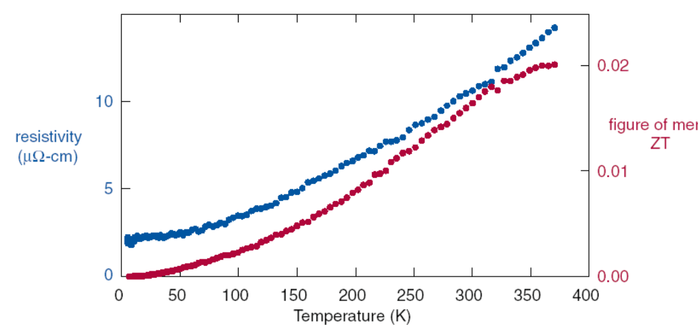
# Thermal Transport of Nickel




Thermal conductivity, resistivity, Seebeck coefficient and figure of merit measured and calculated with the IRM's PPMS for Nickel. Similar to that acquired by Quantum Design

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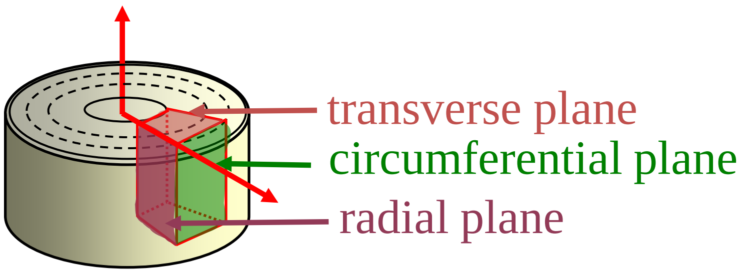
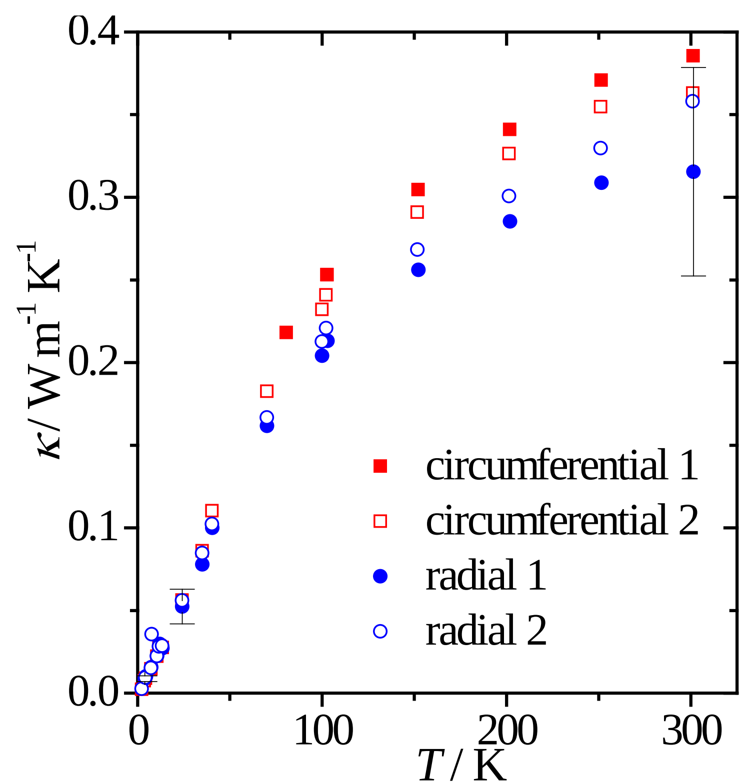
# Thermal Conductivity Example

Temperature dependence of thermal conductivity of elephant ivory as measured in the IRM's PPMS.



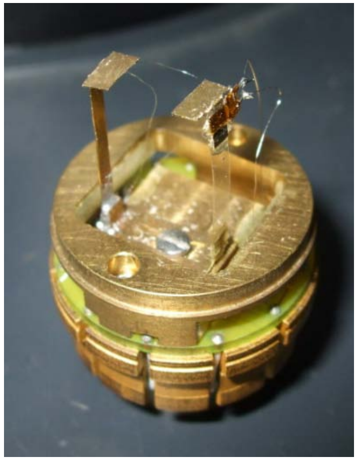

Elephant Ivory: a Low Thermal Conductivity, High Strength Nanocomposite. M.B. Jakubinek, C. Samarasekera and M.A. White, *J. Mat. Res.* 21, 287 (2006).

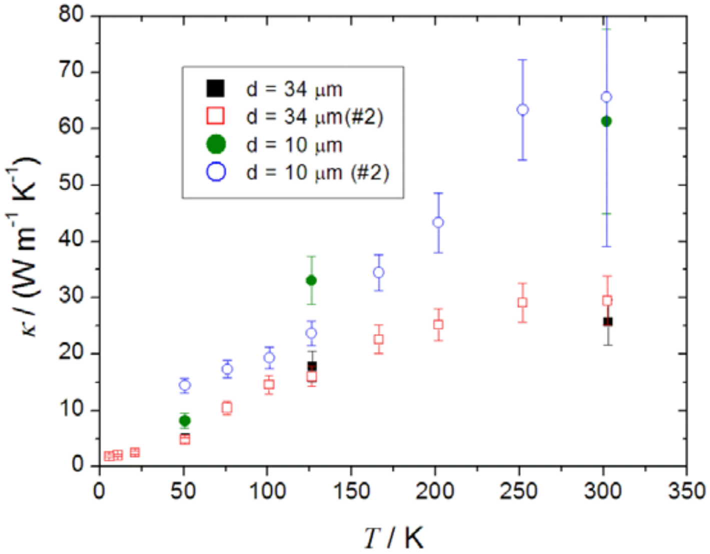


Physical Property Measurement System

# Thermal Conductivity Example

- Thermal conductivity of non-rigid samples can be measured in our lab with a lab-built Parallel Thermal Conductance stage (details in ‡).
- Investigated κ of 10 and 34 μm CNT yarns as a function of temperature
  - ∅ = 34 μm: κ = ~25 ± 5 W $m^{-1}K^{-1}$
  - ∅ = 10 μm : κ = ~62 ± 20 W $m^{-1}K^{-1}$
- Among the highest measured κ of bulk, pure CNT structure






‡M.B. Jakubinek, M.B. Johnson, M.A. White, C. Jayasinghe, G. Li, W. Cho, M.J. Schulz, and V. Shanov. *Carbon*. **50**, 244 (2012)

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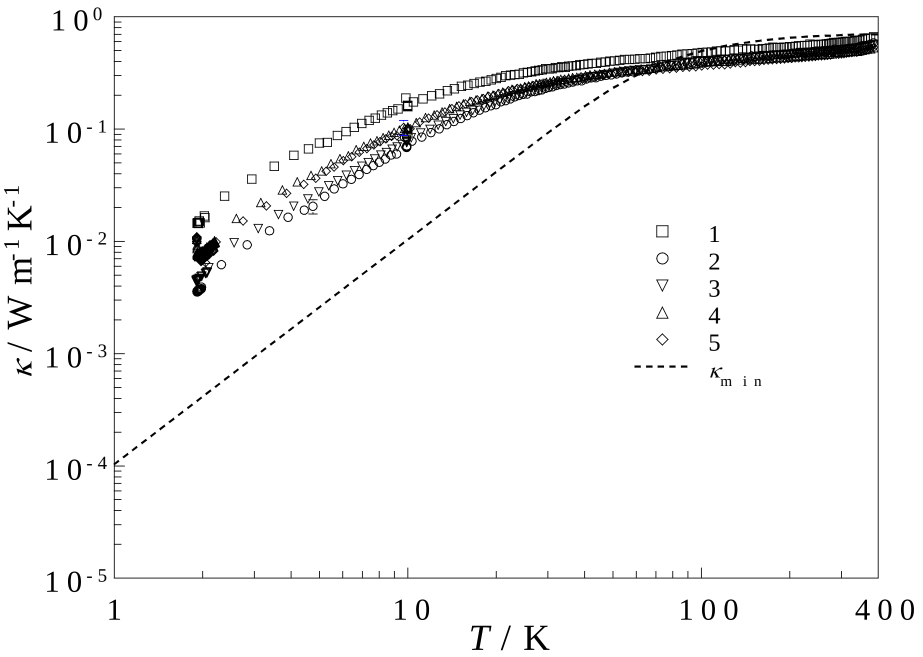
# Success Stories

- Thermal Conductivity of $ZrW_2O_8$ is glass-like
  - Due to very efficient low frequency modes
    - Leads to short phonon mean free paths due to high phonon coupling




- **New mechanism to reduce thermal conductivity in materials**

C.A. Kennedy and M.A. White, *Solid State Commun*. 134, 271-276 (2005).

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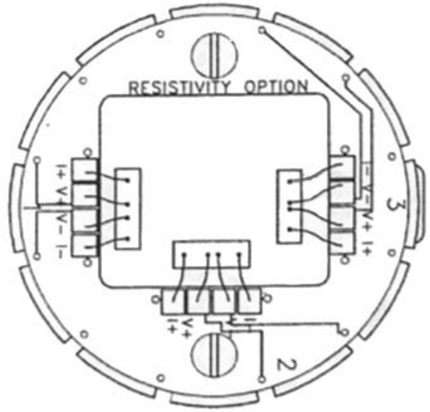
# Electro-Transport

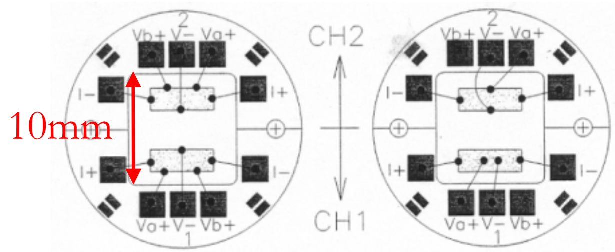
- Measure AC and DC resistivity, four and five-wire Hall effect, *I-V* curve and critical current
  - Temperature range: 0.4 K-400 K ($^3$He option)
  - Magnetic field range: ± 9 Tesla
- DC Resistivity: $\rho = R(A/L)$; use the 4-corner van der Pauw method for square samples
  - Current range: 5 nA – 5 mA
  - Sensitivity: 20 nV to 95 mV
  - Detection precision: 0.01% (typ.)
  - Up to 3 simultaneous measurements: automatic control
  - DC resistivity option eliminates the thermal electric effect by continuously flipping the polarity (~8 Hz)

Designated DC-resistivity puck with three samples for concurrent measurements



# Electro-Transport

Dedicated AC transport pucks




Left: 5-wire Hall coefficient.

Right: 4-wire Hall coefficient (top). Resistivity, *I-V* trace, and critical current (bottom).

- Up to 2 simultaneous AC measurements possible for AC resistivity, Hall effect, I-V curve and critical current
  - Current Range: 10 μA – 2 A (500 mA continuous)
  - Sensitivity: 1 nV @ 1 kHz
  - Frequency Range: 1 Hz – 1 kHz
  - Absolute Accuracy: 0.03% (typ), 1 Hz to 1 kHz
  - Relative Accuracy: ±5 nW (typ) @ $I = 1$ A
- Leads are attached to the sample with solder or silver epoxy paste cured at ~120 °C for ~30 minutes
- Thin films can be measured if isolated by a non-conducting substrate.

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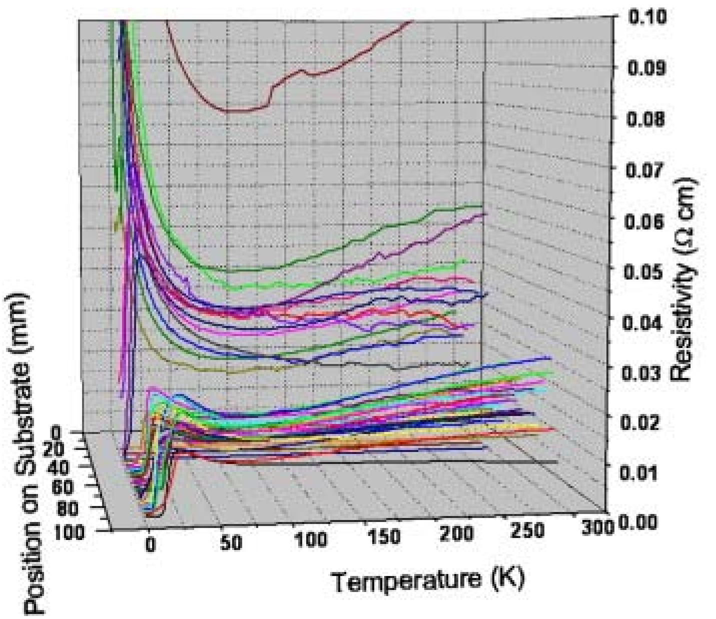
# Electro-Transport Example

- 4-wire resistivity measurements on a series of $La_{2-x}Sr_xCuO_4$ thin film samples† were collected as a function of temperature (samples prepared by combinatorial sputtering available through IRM).
- *ca.* 90 samples required DC measurement
  - Since puck can accommodate 3 samples, experimental time was cut to $^1/_3$, greatly expediting measurements.
- Resulting data mapped the chemical composition where the thin film underwent superconducting transition at low-$T$




†M. Saadat, A.E. George, and K.C. Hewitt. *Physica C*. **470**, S59 (2010)

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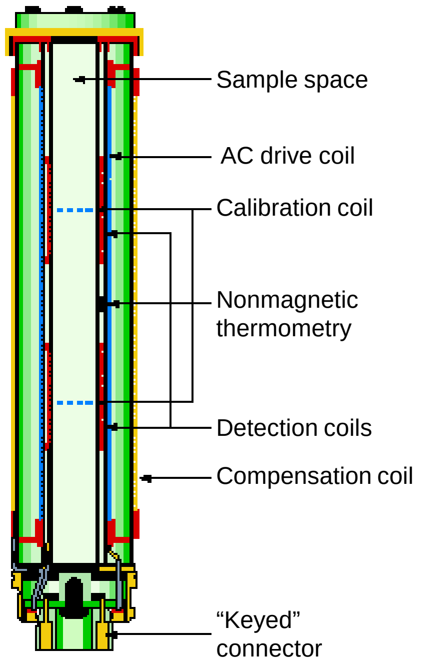
# Magnetometry

- Measures AC susceptibility: $\chi = dM/dH$, and DC magnetization: $M = M(H,T)$
- AC susceptibility sensitivity: $5 \times 10^{-8}$ emu @ 10 kHz
- DC magnetization measured with the extraction method: extraction speed: 100 cm/s; sensitivity of $2 \times 10^{-5}$ emu
- 1 -10 *f* harmonics calculated (software selectable)
  - AC Frequency Range: 10 Hz to 10 kHz
  - AC Field Amplitude Range: 2 mOe to 15 Oe
    - At low temperatures the range depends on the frequency and duration of the measurement
  - Temperature Range: 1.9 K - 350 K
  - Magnetic field range: ± 9 Tesla

Schematic of PPMS magnetometry coil set

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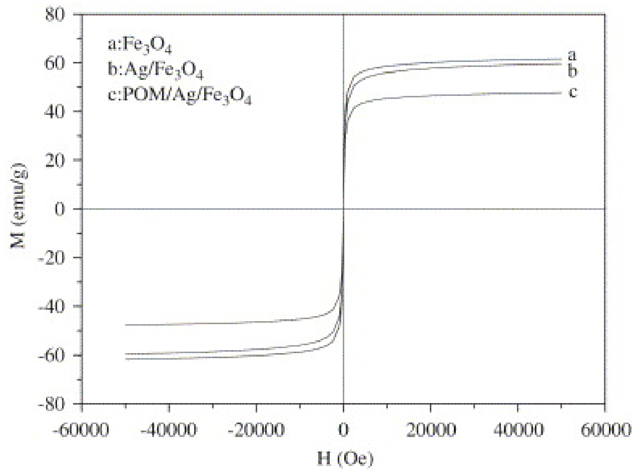
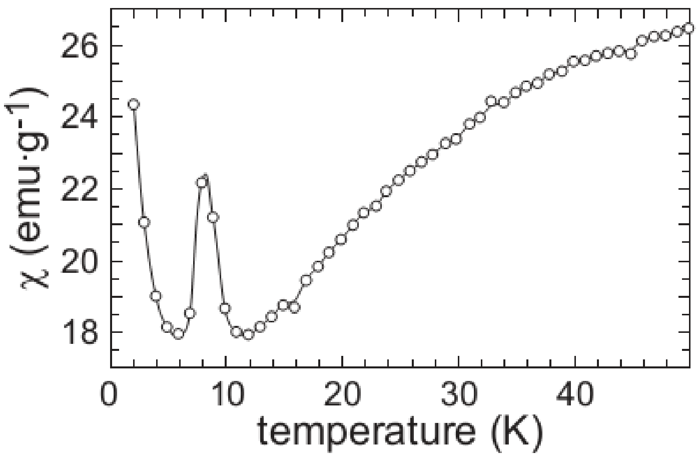
# Magnetometry Examples




- Magnetization curve of pristine and coated $Fe_3O_4$ nanoparticles*
  - Magnetization saturation of the nanoparticles decreases as particles have more layers added to $Fe_3O_4$ core

- Magnetic susceptibility the mineral Bukovskýite** as a function of temperature
  - A weak magnetic transition is observed at $T = 8$ K, attributed to long-range $Fe^{3+}$ ordering

* Y. Shi, W. Qiu, and Y. Zheng. *J. Phys. Chem. Solids*. **67** (11), 2409 (2006)
** J. Majzlan, B. Lazic, T. Armbruster, M.B. Johnson, M.A. White, R.A. Fisher, J. Plášil, J. Loun, R. Škoda, M. Novák. *J. Miner. Petrol. Sci*. **107**, 133 (2012)

# Helium-3 System

- Continuously circulating $^3$He refrigerator extends the PPMS lowest temperature to ~0.35 K
- Compatible only with Heat Capacity and Electro-Transport options
- Temperature range: ~ 0.35 K to 350 K with high-vacuum
- Cool-down time: 300 K to 0.5 K in under 3 hours
- ± 9 Tesla magnetic field
- Cooling power: 6 μW @ 0.5 K; 100 μW @ 1 K; 1.5 mW @ 3 K

# Selected Publications

M.B. Jakubinek, M.B. Johnson, M.A. White, C. Jayasinghe, G. Li, W. Cho, M.J. Schulz, and V. Shanov. Thermal and Electrical Conductivity of Array-spun Multi-walled Carbon Nanotube Yarns. *Carbon*. 50, 244 (2012).

J. Majzlan, B. Lazic, T. Armbruster, M.B. Johnson, M.A. White, R.A. Fisher, J. Plášil, J. Loun, R. Škoda, M. Novák. Crystal structure, thermodynamic properties, and paragenesis of bukovskýite, $Fe_2(AsO_4)(SO_4)(OH)\bullet 9H_2O$. *J. Miner. Petrol. Sci.* 107, 133 (2012).

N.D. Harper, K.D. Nizio, A.D. Hendsbee, J.D. Masuda, K.N. Robertson, L.J. Murphy, M.B. Johnson, C.C. Pye, and J.A.C. Clyburne. A Survey of Carbon Dioxide Capture in Phosphonium-based Ionic Liquids and End-capped Polyethylene Glycol Using DETA (DETA = diethylenetriamine) as a Model Absorbent. *Ind. Eng. Chem. Res.* 50(5), 2822 (2011).

M. Saadat, A.E. George, and K.C. Hewitt. Densely Mapping the Phase Diagram of Cuprate Superconductors Using a Spatial Composition Spread Approach. *Physica C*, 470, S59 (2010).

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