Measuring thermal and thermoelectric properties- principles, measuring techniques and analysis

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Thermoelectric materials

Thermoelectricity
- Thermoelectric conversion of energy – characteristics
- Electrical resistivity
- Thermoelectric power
- Thermal conductivity, thermal diffusivity (Wiedemann-Franz law in “non metals”)

Measuring techniques – compendium of measuring techniques and analysis

-Low temperature systems – commercial (Quantum Design), Thermal transport option & home made inset (5-350 K), magnetic field
- Home made sample holders ➔ objective to measure all thermoelectric characteristics simultaneously on one specimen (each specimen unique character)
- Close cycle refrigerators: Leybold (300>T>12 K) Janis (300> T>3.5 K) – snags, (temperature fluctuations, parasite heat flow,..), calibration, reliability
- Home made High temperature cells, principle, difficulties, calibration, reliability
Low temperature thermal and electrical measurements ($\lambda, \alpha, \rho, \kappa$) using close-cycle cryocooling systems
simultaneous measurement of $\lambda, \alpha, \rho, \kappa$ - steady state & dynamic

<table>
<thead>
<tr>
<th>Column Name</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
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</thead>
<tbody>
<tr>
<td>Signification</td>
<td>Temperature</td>
<td>$\Delta T$ between $\Delta T_{up}$ and $\Delta T_{down}$</td>
<td>$\Delta T$ between sample center and sink</td>
<td>Heater Power</td>
<td>Raw thermal Conductivity</td>
<td>Corrected Thermal Conductivity</td>
<td>Corrected Seebeck coefficient</td>
<td>Resistivity</td>
<td>Diffusivity</td>
<td>Heat capacity</td>
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<tr>
<td>Symbol</td>
<td>T</td>
<td>$\Delta T$</td>
<td>$\Delta T$</td>
<td>P</td>
<td>$\lambda_{raw}$</td>
<td>$\lambda$</td>
<td>TEP, S or $\alpha$</td>
<td>$\rho$</td>
<td>$\kappa$</td>
<td>$C_V$</td>
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<tr>
<td>Unit</td>
<td>K</td>
<td>K</td>
<td>K</td>
<td>W</td>
<td>$Wm^{-1}K^{-1}$</td>
<td>$Wm^{-1}K^{-1}$</td>
<td>$\mu VK^{-1}$</td>
<td>$m\Omega cm$</td>
<td>$mm^2/s$</td>
<td>$J/K/cm^3$</td>
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</table>

$F = \frac{Distance}{Area}$

$E = \frac{V}{Distance}; J = \frac{I}{Area}$

$\lambda_{raw} = \frac{R_{heater} I^2}{\Delta T * F}$

$\lambda = \lambda_{raw} - \lambda_{rad} - \lambda_{wires}$

$\rho = \frac{E}{J}$

$\alpha = \frac{\Delta V}{\Delta T} + \alpha_{leads}$
Low temperature thermal and electrical measurements \((\lambda, \alpha, \rho, \kappa)\) using close-cycle cryocooling systems
Simultaneous measurement of \(\lambda, \alpha, \rho, \kappa\)

4-point \(\lambda, S\) and \(\rho\) method for “normal” samples

- **Si calibrated diod**
  - Thermal anchor of E-differential thermocouples

- **E-thermocouple**
  - \(\Delta T\) **Heater**

- **E-thermocouple**
  - \(\Delta T\) **Up**
  - Chromel wire as voltage lead

- **E-thermocouple**
  - \(\Delta T\) **Down**
  - Chromel wire as voltage lead

- **Current lead** Cr-Ni wire **Up**

- **Current lead** Cr-Ni wire **Down**

- **Anchoring Cu hoop** (0.2 mm Wire) **Up**

- **Anchoring Cu hoop** (0.2 mm Wire) **Down**

- **Connector**

- **Protective frame**

- **Mini heater**

- **Pasted with Ge varnish-separated cigarette paper**

- **Sample**

- **Pasted with Ag-filled Cyanacrylate**
Thermal and electrical measurements I ($\lambda, \alpha, \rho$)

Sample mounting, topology

Steady state 4-point measurement
Acquisition performed after temperature (~50 mK) and thermal voltage (~1-5%+0.5$\mu$V) stability is achieved
Thermal and electrical measurements II ($\lambda, \alpha, \rho, \kappa, c_v$)

Low temperature 4-point cell
Close cycle He-cryostat (3.5-300K)
**Thermal and electrical measurements II** - \((\lambda, \alpha, \rho, \kappa, c_v)\)

**Software-**
- fully WXP 32 bit compatible, PCI HPIB card, external measuring system controlled via PC, program in DELPHI

**Hardware-**
- same cell, better temperature control needed, cold finger itself !! High temperature fluctuations!! + lower temperature, \(\Leftrightarrow\) stronger requirements for temperature measurement and control!

**Ultra-low temperature**
- 4-point cell
- Close cycle He-cryostat
- \((3.5-300K)\) operating since 2006
Thermal and electrical measurements II (\(\lambda, \alpha, \rho, \kappa, c_v\))

PROBLEMS-temperature fluctuations

![Graph showing temperature (K) over time (min)]
Thermal and electrical measurements II ($\lambda, \alpha, \rho, \kappa, c_v$)

PROBLEMS solved temperature fluctuations eliminated

$T_{(\text{set})} = 3.2 \text{ K}$

$T_{(\text{set})} = 6 \text{ K}$

$T_{(\text{set})} = 12 \text{ K}$

Temperature on measuring cell (after filtering) controlled by LakeShore

Natural temperature fluctuations on cold finger

Temperature on the sample at 6 K after temperature stabilization

Temperature on measuring cell (after filtering) controlled by LakeShore

Natural temperature fluctuations on cold finger during cooling

Temperature on the sample at 12 K after temperature stabilization
High temperature stability inspires to measure thermal diffusivity and then heat capacity $C_v \sim \lambda / \kappa$ before thermal equilibrium is achieved.
Reliability of thermal diffusivity \((C_v)\) data: “good” samples - relaxation time \(\tau 10^{0–10^2} s\)

- Diffusivity \((\Delta T_{up})\) measurement at various temperatures
- first readings 5 rds/s
- since \(~4s\) 1 rds/s
- Sample

\(\text{LaCo}_{0.95}\text{Ni}_{0.05}\text{O}\_3\)
Recent results, for temperature acquisition Keithley 2001/MEM2 High-Performance, 7-1/2-Digit DMM

Bad thermal conductors - correct Cv data

**Good measurement - Heat capacity measurements II**
Reliability of thermal diffusivity ($C_v$) data:
“good” sample - i.e. with bad thermal conductivity
-relaxation time $\tau \, 10^{0-2}$s

\[ C_p (\text{Jmol}^{-1} \cdot \text{K}^{-1}) \]

\[ T^2 (\text{K}) \]

$sintered$ $PPMS$

$sintered$ $CloseCycle$

$SrMoO_{1.73}N_{1.27}$

$SrMoO_{1.95}N_{1.05}$
Reliability of thermal diffusivity (Cv) data: “bad” sample - i.e with high thermal conductivity - thermal resistance between the sample and heat sink -

\[ \Delta T_{up} \]

- \((\Delta T_{up})\) does not decrease with decreasing temperature
- \(\tau\) decreases with decreasing temperature, but the measured thermal diffusivity is limited by glue joint with Cu-heat sink
- \(\text{Al}_2\text{O}_3\)
Bad measurement

Good thermal conductor - wrong Cv data

Cv data WRONG!! diffusivity limited by wrong thermal sample anchoring

error 4%

Cv data measured using diffusivity and thermal conductivity

- □ B PPMS Santava Praha
- ■ Cp NIST

Good thermal conductor - wrong Cv data

Cp (Al2O3)

T (K)

T (K)

T (K)

T (K)
Reliability of measured data:
Role of vacuum in thermal measurement

- Diffusivity ($\Delta T_{up}$) measurement - 300 K
- Sample LaCo$_{0.8}$Ti$_{0.2}$O$_3$
- At 400 Turbo-pump started ($10^{-2} \rightarrow 10^{-4}$ mbar)
Reliability of thermal and electrical measurements II
Thermal conductivity for “normal” thermal conductors (λ)-

Importance of knowledge $\Delta T_{\text{heater}}$

Correction formula:

$$\lambda_{\text{radation corrected}} = \text{factor} \times \frac{(\text{power} - \text{Heater Radiation} - \text{Sample radiation})/\Delta(T)}{\Delta(T)}$$

$$\lambda_{\text{radation corrected}} = \frac{\text{length/CrossSection} \times (R I^2 - T_{abs}^3 \alpha \Delta T(\text{heater}) \times 5.67 \times 15^{-6} \Delta T(\text{heater})/\Delta T(\text{up}) - T_{abs}^3 \Delta T(\text{sample center}) \times 5.67 \times 15^{-6} \text{SampleArea})/\Delta(T)}{\Delta(T)}$$

Mo$_3$Sb$_7$ small sample- perfect heater anchoring
Mo$_3$Sb$_7$ bad heater anchoring

Temperature difference (K)

Temperature (K)
Reliability of thermal and electrical measurements II
Thermal conductivity for "poor" thermal conductors ($\lambda$)

Correction on Heater radiation, sample radiation and parasitic heat flow via thermocouples and current leads

Correction formula: NEW CORRECTION

$$\lambda_{\text{radiation corrected}} = \text{factor} \times \left(\text{power - Heater Radiation - Sample radiation - Thermocouple heat flow}\right)/\Delta T$$

$$\lambda_{\text{radiation corrected}} = \frac{\text{length/CrossSection}\times(R)^2\times T_{\text{abs}}^3 \times \Delta T(\text{heater})\times 5.67\times10^{-8}\times40e^{-6} - T_{\text{abs}}^3 \times \Delta T(\text{up})\times 5.67\times10^{-8}\times3\times\text{Sample Area}}{(22-22\times0.992\times e^{-6}\times\Delta T(\text{heater}))}$$
Thermal and electrical measurements - low conducting materials

2-point geometry, flat sample - heat flow through the sample simplified

- bad geometry - 4-point! radiation error!! (factor=716)
- radiation corrected
- new geometry - 2-point!
  - no radiation, factor=88
  - new geometry - porosity corrected!
  - no radiation supposed, factor=88, corrected on porosity using $\lambda_{\text{cor}} = \frac{2\lambda_{\text{measured}}}{3(1-p)}$

conductance of thermocouples and leads
Reliability of thermal and electrical measurements II
Thermoelectric power for "good" metals - small $\alpha$
Tantalum metal between 3.5-300K

Compare with PPMS

PPMS Thermal transport:
SEEBECK COEFFICIENT ($S$)
Typical Accuracy:
- Error in $S = \pm 5$ % or
- Error in $S = \pm 0.5 \mu V/K$ or
- Error in $V = \pm 2 \mu V$, whichever is greater
Approximate Range: $1 \mu V/K - 1 V/K
Reliability of thermal measurements II
Thermal conductivity and thermoelectric power for “high” thermal conductors ($\lambda, \alpha$)

necessity of good thermal sink for correct definition of $\Delta T$

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**Yellow Brass**

$\lambda$ (Wm$^{-1}$K$^{-1}$) vs $T$ (K)

- + Hejtmanek, May 2006
- Reference Book1
- LakeShore figure

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**Mn-metal, May 2006**

Thermoelectric power (µVK$^{-1}$) vs $T$ (K)

- magnon drag peak

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$\lambda, \alpha$
Low temperature thermopower measurements: reliability, corrections

![Graph showing thermoelectric power vs. temperature for different Ag powder additions.]

Depends on used DMM (DnVM), shielding, wiring...
Thermal and electrical measurements II - software \((\lambda, \alpha, \rho, k, c_v)\)
Thermal and electrical measurements (l,a,r,k)

PPMS cell -home made+external measuring and control system

**Hardware-**
- sample holder, E-type thermocouples,
- calibration, thermal stability, sensitivity to magnetic field

**PPMS inset**
(Caen-Crismat)
(5-350 K)
Operating since 1999

**Software-**
- PPMS, external measuring system controlled via PC
- old-fashioned TurboPascal-DOS
E-type thermocouples
Isothermal magnetotransport
Impedance based on DMM, nanoVM
Proper criteria for thermal stability

Calibration, 2006
Bi-based superconducting cuprates

CMR manganites, 2000
Thermal and electrical measurements \((\lambda, \alpha, \rho, \kappa)\)

**Hardware-**
- Quantum Design introduced Thermal transport option

**Software-**
- PPMS delivered, dynamic regime

**THERMAL CONDUCTANCE \((\kappa)\)**

Typical Accuracy:

- \(\pm 5\%\) or \(\pm 2\ \mu W/K\), whichever is greater, for \(T < 15\ K\)
- \(\pm 5\%\) or \(\pm 20\ \mu W/K\), whichever is greater, for \(15\ K < T < 200\ K\)
- \(\pm 5\%\) or \(\pm 0.5\ mW/K\), whichever is greater, for \(200\ K < T < 300\ K\)
- \(\pm 5\%\) or \(\pm 1\ mW/K\), whichever is greater, for \(T > 300\ K\)

**SEEBECK COEFFICIENT \((S)\)**

Typical Accuracy:

- Error in \(S = \pm 5\%\) or,
- Error in \(S = \pm 0.5\ \mu V/K\) or,
- Error in \(V = \pm 2\ \mu V\), whichever is greater

**SPEED OF ACQUISITION:**

Typically temperature slew rate:

- \(\pm 0.5\ K/min, \ T > 20\ K\)
- \(\pm 0.2\ K/min, \ T < 20\ K\)
- 14 hour run from 390 to 1.9 K
Thermal and electrical measurements

**COMPARE** PPMS-Cryocooled ($\lambda, \alpha, \rho, \kappa$)

## PPMS sample topology

- Heater shoe
- Copper lead area
- Epoxy bond
- Two thermometers
- Coldfoot

$$\Delta T = \frac{\Delta V}{\Delta T}$$

Not steady state method

**ΔT calculated on a base** $\tau_1, \tau_2$

## Cryo-cooled sample topology

- ΔT heater
- Heater chip resistance
- Direction of electric current $J$
- Distance $\Delta T$ and $\Delta V$
- ΔT up
- ΔT down
- E
- Thermocouples
- Underlay

$$\lambda = F \times \frac{\text{Power}}{\Delta T}$$

$$F = \frac{l}{\text{area}} \quad \Delta T = T_1 - T_2$$

Steady state method $\Delta T$ measured

Arrangement of home-made thermal and transport measurement
**Arrangement of home-made 4-point thermal and transport measurement $\lambda$, S and $\rho$.**

**PPMS sample topology**
- 2 Cernox chip thermometers
- Heater chip resistance
- Protection for radiation

**Cryo cooled sample topology**
- 4-point $\lambda$, S and $\rho$ method for “normal” samples
- Mini heater
- Protective frame
- Connector

- Anchoring Cu hoop (0.2 mm Wire) **Up**
- Anchoring Cu hoop (0.2 mm Wire) **Down**

- Current lead Cr-Ni wire **Up**
- Current lead Cr-Ni wire **Down**

- Pasted with Ge varnish-separated cigarette paper
- Pasted with Ag-filled Cyanacrylate

- Si calibrated diod Thermal anchor of E-differential thermocouples
- E-thermocouple AT **Heater**
- E-thermocouple AT **Up** Chromel wire as voltage lead
- E-thermocouple AT **Down** Chromel wire as voltage lead

- Sample

- 2 for $I_{heater}$ and 1 for $I_{sample}$
- 4 for $T_{up}$ and 1 for $U_{up}$
- 4 for $T_{down}$ and 1 for $U_{down}$

**COMPARE PPMS-Cryocooled ($\lambda, \alpha, \rho, \kappa$)**

**Thermal and electrical measurements**
Thermal and electrical measurements **COMPARE** PPMS-Cryocooled ($\lambda, \alpha, \rho, \kappa$)

**PPMS-Principle of the measurement**

Time evolution of the:

(a) heater power

(b) hot and cold thermometer and drift of baseline

(c) hot thermometer with analysis of respective time constants
RESULTS: Electrical resistivity

La$_{0.2}$Ca$_{0.8}$CoO$_3$ - PT041

No problem

\[ \rho (\text{m}\Omega \cdot \text{cm}) \]

\[ T (K) \]

homemade

PPMS
RESULTS: Thermal conductivity

La$_{0.2}$Ca$_{0.8}$CoO$_3$ - PT041

Surprising agreement
RESULTS: Thermoelectric power

La_{0.2}Ca_{0.8}CoO_3 - PT041

Surprising agreement
HIGH TEMPERATURE measurements

High temperature 4-point cell (300 – 1200 K), Thermoelectric power and electrical resistivity

TEP4points : \( \Delta V(T_4-T_3) / (T_4-T_3) = U3/(T_4-T_3) \)

TEP3points : \( \Delta V(T_4-T_2) / (T_4-T_2) = (U3+U4)/(T_4-T_2) \)

TEP2points : \( \Delta V(T_1-T_2) / (T_1-T_2) = U1/(T_1-T_2) \)

RES = U3/I
High temperature cell

Stability:

\[ \Sigma U = U_1 + U_4 + U_3 + U_2 = 0 \]

\[ T_1 > T_4 > T_3 > T_2 \]
HIGH TEMPERATURE measurements

High temperature cell

Heater
Inserted in the holder

Pressing shank

Mica

K-thermocouple
Down
Chromel wire as **voltage** lead
Alumel wire as **current** lead

Lava based sample holder

Ag thin plate pasted with Ag-paste

K-thermocouple **Up**
Chromel wire as **voltage** lead
Alumel wire as **current** lead

K-thermocouple **High**
Chromel wire as **voltage** lead

K-thermocouple **Low**
Chromel wire as **voltage** lead

Piston attached to cold end

Sample hidden under mica

Ag thin plate pasted with Ag-paste
HIGH TEMPERATURE measurements-reliability of measured data

LaCo$_{0.95}$Mg$_{0.05}$O$_3$

$S = \frac{\Delta V}{\Delta T}$

- pressing sheet mica
- pressing sheet alumina
- alumina good conductor
- mica bad conductor
- heater
- cold finger
- relative error 30%
- relative error 8%
- relative error 65%
- relative error 53%
- 4 points method
- 3 points method
- 2 points method
- basic low temperature data
High temperature thermopower measurements: reliability, corrections

Ni metal

Fe₃O₄-xtal

Sample - pure nickel, measured in air
Thermoelectric power measurements II ($\alpha$)
Calibration using superconducting ceramics - matching between small $\alpha$
Close cycle He-cryostat (3.5-300K), High temperature cell
Thermoelectric power measurements II ($\alpha$)
Calibration using cobalt perovskites with M-I transition
- matching between high positive $\alpha$
Close cycle He-cryostat (3.5-300K), High temperature cell
Thermoelectric power measurements II (α)
Calibration using Mn perovskites
- matching between high negative α
Close cycle He-cryostat (3.5-300K), High temperature cell
Electrical resistivity measurements II ($\rho$)
Calibration using cobalt perovskites with M-I transition - matching of resistivity and data quality
Close cycle He-cryostat (3.5-300K), High temperature cell
**Program**

Segment: 1 of 2  Type: Seb&Res
Active: From: 300 To: 840 Step: 20.00
Already Measured Data: 3 of 56
Seebeck - Gr. Heat: 0 (5.5K: 0 of 1)
SetPoint[K]: 360.0  Ramp[K/m]: 0.0
P: 22.0  I: 382  D: 64  OP: 19.3
GradHeat: 0

**Sample**

Header: la0.2y0.3ca0.5coo3 sample fuj
FileName: ly3cach2
Dimensions[mm]: 2.72x1.95/4.77
Factor[cm]: 0.1112

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<th>10.000mA</th>
<th>0.915mV</th>
<th>-0.913mV</th>
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**Eurotherm**

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<th>M</th>
<th>Actual</th>
<th>Average (std.)</th>
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<tr>
<td>T[K]</td>
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<tr>
<td>WSP[K]</td>
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**VoltMeter**

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**END**