Thermal Transport of Nickel Alloy, Semiconductor and Lanthanide Samples (Thermal Transport Option)

Prof. Milton S. Torikachvili, San Diego State University

Description: The goal of this educational module (EM) is to guide the student through the steps for measuring the thermal and electrical properties of solids using the thermal transport option (TTO) of the VersaLab. The TTO permits the simultaneous measurement of the thermoelectric potential (usually represented by TEP or S), thermal conductivity (κ), and electrical resistivity (ρ) as a function of temperature and magnetic field. Initially the students will be guided to measure a sample of nickel, in order to get acquainted with the technique, hardware and software. This will be followed by measurements in semiconductors (undoped, n-type, and p-type), and a magnetically ordered sample (e.g. one of the heavier lanthanides). The study in semiconductors aims at exposing the students to issues in thermoelectric materials and devices. The measurements in the heavy rare-earths is intended to demonstrate how sensitive the thermal properties can be to the onset of magnetic ordering.

Background:

In this section we'll provide a brief introduction to the thermal properties that we can measure using the TTO, and the methodology used in the TTO operation.

Thermoelectric potential

The TEP is the potential difference developed across a sample when it is subjected to a temperature gradient, also known as the Seebeck effect. To a first approximation, the "free" electrons and holes of the sample can be thought of as the molecules of a gas. Particles of this gas will diffuse from the hot to the cold end due to the pressure difference. However, this diffusion builds an opposing concentration gradient, and a concentration-driven diffusion towards the hot end ensues as well. Equilibrium is reached when the two opposing currents match.

Therefore materials with preponderance of negative (or positive) charge carriers should yield a negative (or positive) TEP.

The two main contributors to the TEP are the charge-carrier diffusion and phonon drag. The TEP is very important both as a fundamental property as well as for applications. The high sensitivity to the carrier concentration and phonon spectrum makes the TEP very sensitive to phase transitions driven by external parameters, like temperature, magnetic field, pressure, etc. Devices based on the Seebeck effect are extensively used in thermometry (thermocouples), and their use in refrigeration, and power conversion has increased steadily over the years. Albeit not remarkable for the efficiency, TEP–based devices don't have moving parts, which makes them exceedingly reliable.

The TEP at ambient temperature spans from very small values in simple metals (e.g., ≈ 1.5 μV/K in Cu, Ag and Au; ≈ -22 μV/K in Ni) to much higher values in semiconducting Ge, and Si (≈ 330 and 440 μV/K, respectively) to even higher values in the chalcogens Te and Se (≈ 500 and 900 μV/K, respectively).

The Seebeck coefficient (or TEP) is obtained from

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

<u>Thermal conductivity</u>

The thermal conductivity (κ) measures the ability of a material to carry thermal energy through a sample subjected to a temperature gradient. It is also a very important property for technology and instrumentation design, particularly at the extremes. Thermal insulation and heat sink applications require materials with low and high κ, respectively. In general, the thermal energy between the hot and cold regions of the sample is carried mostly by phonons and electrons, underscoring the importance of their mean free path. In very pure metals, most of the thermal energy is carried by electrons. In less pure or disordered metals and alloys, phonons also play an important role.

The thermal conductivity κ is defined from

$$j_{TE} = -\kappa \frac{dT}{dx}$$

where j_{TE} is the thermal energy flux (in J/m^{2}s) and dT/dx (in K/m) is the temperature gradient across the sample. The thermal conductivity at ambient temperature spans from very high in pure metals (e.g. ≈ 400 W/m K in Cu) to very low in electrical insulators (e.g. ≈ 0.35 W/m K in epoxy). A noteworthy exception is diamond, an electrical insulator with a thermal conductivity 2.5 times higher than Cu. Graphene's thermal conductivity has been reported to be in the 1500-2500 W/m K range.

Electrical resistivity

In solids with free charge carriers to move about, a current density (*J*) can be established under an applied electric field (*E*). The relationship between *J* and *E* is

$$J = s E = \frac{E}{r}$$

where σ is the electrical conductivity and ρ is the electrical resistivity. Since the mean free path of the charge carriers is the dominant factor in their flow, it is not surprising that the electrical and thermal conductivities scale with one another in most metals. ρ is quite sensitive to changes in the density of charge carriers, collision with phonons, and phase transformations.

Figure of merit

In light of the ability of converting thermal to electrical energy in devices with a large thermoelectric effect, a "figure of merit" (Z) gauging the material's "efficiency" can also be determined from the measurements of S, κ, and ρ. The figure of merit ZT is a dimensionless quantity defined as follows:

$$ZT = \frac{S^2 T}{kr}$$

The figure of merit can be thought of as a benchmark for comparing and optimizing thermoelectric devices.

Sample data

The data acquisition, programing, and graphing with the VersaLab is carried out in the MultiVu environment, in a Windows-based platform. The temperature dependence of κ, *S*, and ρ for the standard Ni sample is shown in Fig. 1. A sample sequence to collect these data is shown below in section F3. Sample data files for Ni are included in this package. The ".raw" and ".dat" data files are text files that can be easily manipulated using data analysis software, e.g. Origin, Kaleidagraph, Igor, Excel, etc. The ".raw" data files contain all the detailed information that MultiVu uses to calculate κ, S, and ρ. The ".dat" files provide a more distilled version of the data, and only final values are reported. It is recommended to always collect both .dat and .raw files, as the latter permits further reprocessing using MultiVu.

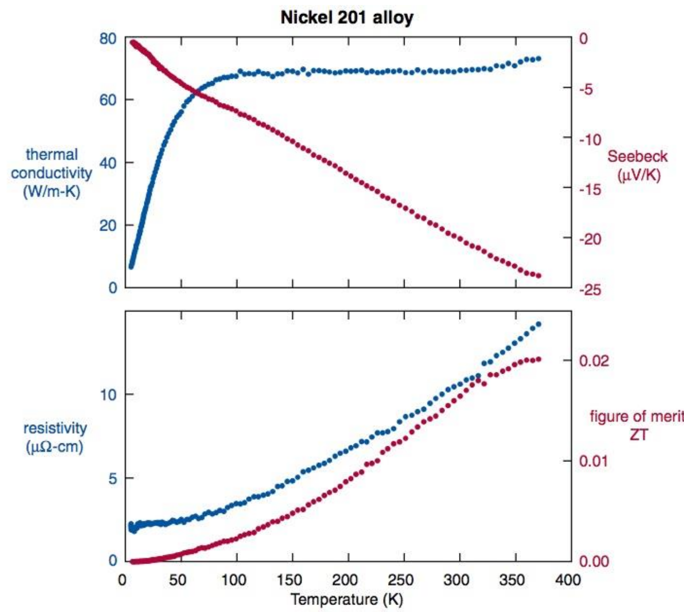

Figure 1: temperature dependence of the thermal conductivity and Seebeck coefficients in nickel (top), and electrical resistivity and figure of merit (bottom).

The behavior of S vs T in bulk samples of p- and n-type Si from in the 300-800 K range is shown in Fig. 2. (Note: Si-based nanowires is currently an active area of research in thermoelectrics).

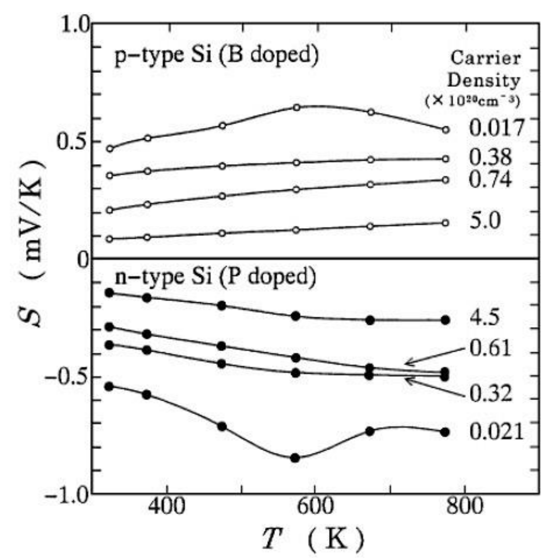

Figure 2: Temperature dependence of the Seebeck potential for n- and p-type Si. (After Ref. 1)

An indication of how sensitive the TEP and thermal conductivity can be to the magnetic ordering in the pure rare earth or their compounds is shown in Fig. 3 for terbium, and Figs. 4 and 5 for gadolinium.

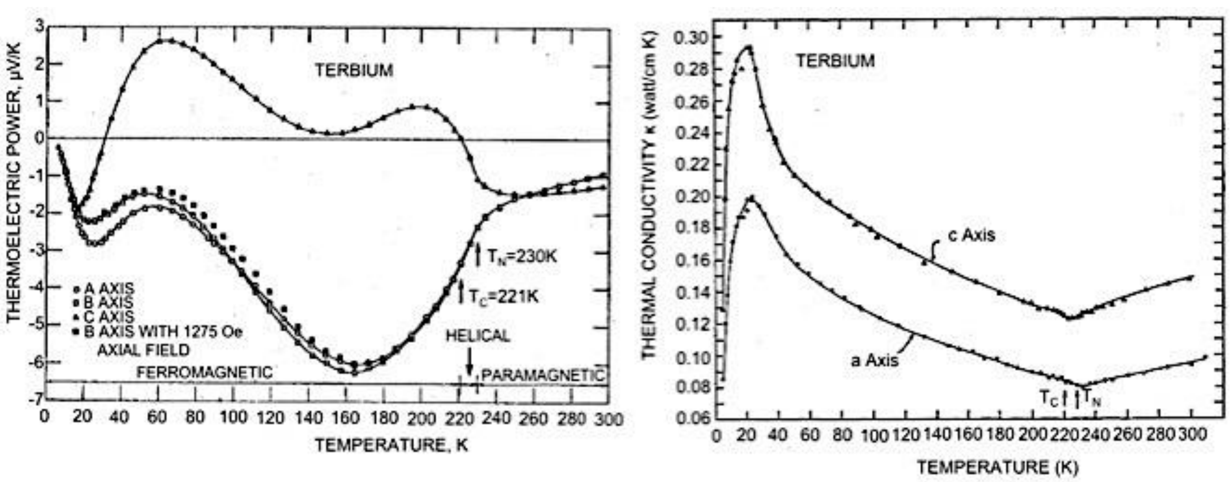

Figure 3: temperature dependence of the Seebeck potential and thermal conductivity in single crystalline terbium. (Adapted from Refs. 2 and 3)

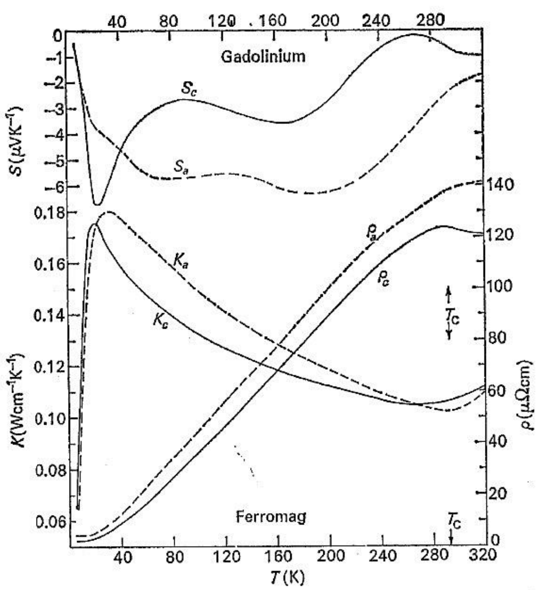

Figure 4: temperature dependence of the Seebeck potential, thermal conductivity, and electrical resistivity in single crystalline gadolinium. (After Ref. 4)

Gadolinium data collected near the Curie temperature $T_C \approx 293$ K, in magnetic fields up to 10 kOe are shown in Fig. 5.

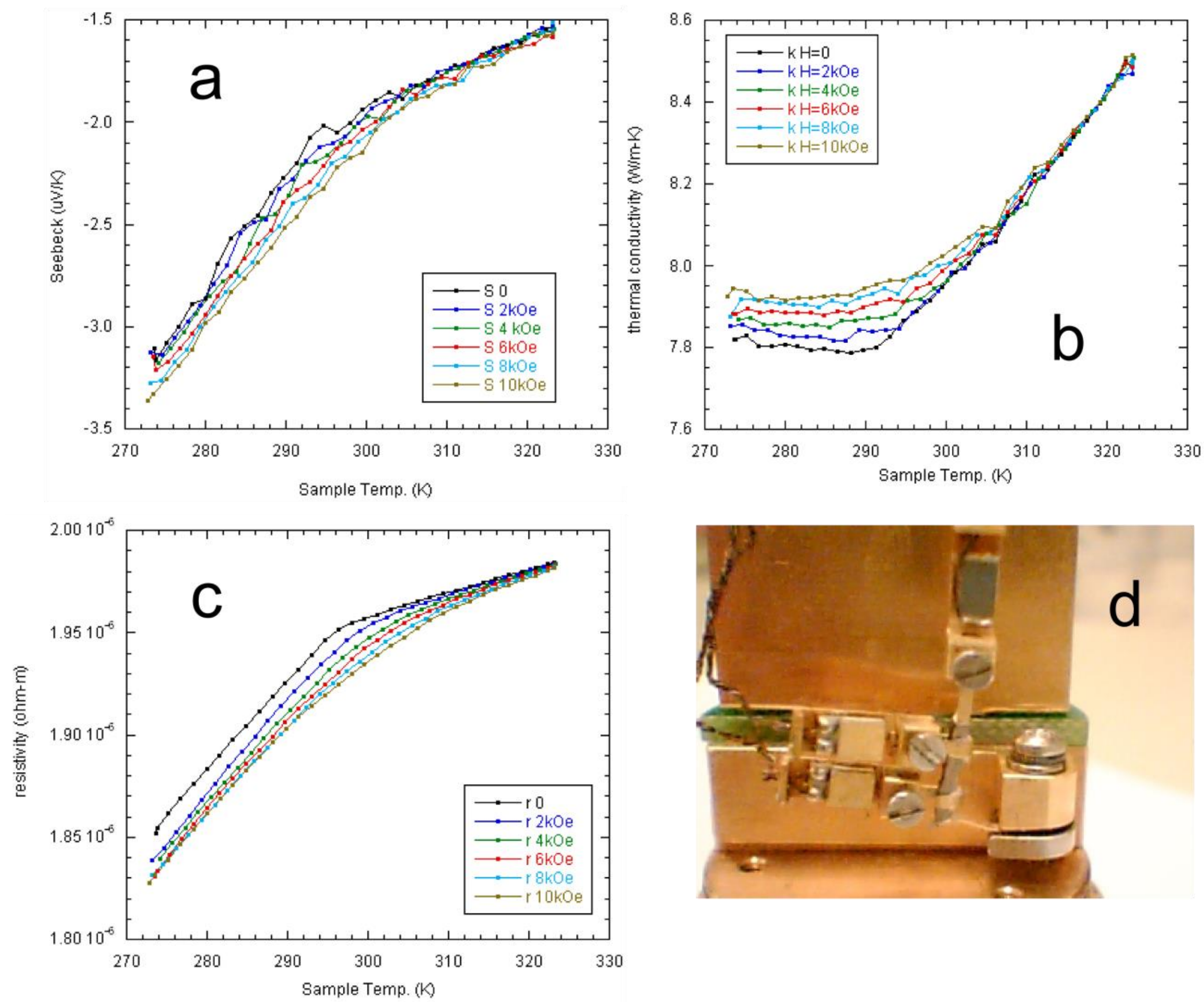

Figure 5: a-c) Measurements of S, κ, *and* ρ *in polycrystalline Gd in the 270-320 K temperature range, in magnetic fields up to 10 kOe, using Quantum Design's TTO; d) 4-probe configuration showing the heater shoe on top, and the 2 cernox temperature sensors on the side.*

<u>TTO methodology</u>

The value of κ is determined by applying a heat pulse at one end of the sample, and monitoring the temperature of the 2 sensors downstream, T_{hot} and T_{cold}, as a function of time, as the heat is dissipated in the coldfoot. The value of S is extracted from the ratio of the potential difference between the 2 sensors shoes and the distance between the leads. The electrical resistance is extracted from the ratio of the voltage difference between the 2 voltage leads and the current between the heater shoe and the coldfoot. Details of these measurements can be seen in the TTO manual.

Student Learning Outcomes:

- Students will develop proficiency in sample mounting techniques for thermal transport measurements.
- Students will operate the Thermal Transport option of the VersaLab cryostat and gain experience in low temperature experiments.
- Students will apply relevant and fundamental solid state physics knowledge to the thermal conductivity, Seebeck and resistivity measurements vs. temperature for the characterization of Nickel alloys and Lanthanide samples.

Safety Information:

Before attempting to perform any parts of this student experiment, please read the entire contents of: this Educational Module, the VersaLab User's Manual (1300-001), and Thermal Transport Option II Manual (1684-110), and observe all instructions, warnings and cautions. These are provided to help you understand how to safely and properly use the equipment, perform the experiments and reach the best student learning outcomes.

Quantum Design Inc. disclaims any liability for damage to the system or injury resulting from misuse, improper operation of the system and the information contained in this Educational Module.

The following Safety warnings apply to this Educational Module. We recommend that you study them carefully and discuss the details with your instructor before starting the work:

W A R N I N G !

Always use **P**ersonal **P**rotective **E**quipment (PPE) during every step of sample preparation. Failure to do so might cause bodily harm.

T O X I C   H A Z A R D !

Vanadium Oxide (VO_2) is hazardous in case of skin contact (irritant), or eye contact (irritant). For more information consult the Material Safety Data Sheet available on this website: http://www.guidechem.com/msds/12036-21-4.html

H O T S U R F A C E !

Never touch the tip of the soldering iron as it is typically at 400 °C and can cause serious burns. Please read the entire contents of the User's Manual specific to the soldering iron and solder and flux cleaners you are using, and observe all instructions, warnings and cautions. Failure to properly handle hot surfaces might cause bodily harm.

General guidelines for soldering safety can be found at: http://safety.eng.cam.ac.uk/procedures/Soldering/soldering-safety

H O T S U R F A C E !

Before using the desktop oven to cure the Ag-epoxy, please read the entire contents of the User's Manual specific to that equipment, and observe all instructions, warnings and cautions. Failure to properly handle hot surfaces might cause bodily harm.

F I R E H A Z A R D !

Before using the desktop oven to cure the Ag-epoxy, please read the entire contents of the User's Manual specific to that equipment, and observe all instructions, warnings and cautions. Failure to do so might cause a fire hazard, bodily harm.

Instructions:

The items needed to set up this experiments are:

- *nickel alloy reference sample provided with the VersaLab.*
- *undoped, n-type and p-type semiconductor samples with approximate dimensions: length = 15-20 mm, width = 1.0-1.5 mm, and thickness = 0.2-0.4 mm*
- *sample of a material that orders magnetically in the 50-400 K range, e.g. a bar piece of one of the heavier lanthanides (Gd...Er): see QD's periodic table to*

consult the magnetic ordering temperatures: http://www.qdusa.com/sitedocs/Quantum_Design_Periodic_Table.pdf

- *thin blade diamond wheel, wire saw, or spark cutter.*
- *soldering station.*
- *cotton swabs, kimwipes, ethanol (or acetone), nitrile (or latex) gloves.*
- *tweezers, glass slides, glue ribbon, and caliper gauge.*
- *copper leads, Ag-epoxy (e.g. H20E from Epotek), Ag-paint.*
- *stereoscopic microscope.*
- *desktop oven (temperatures ≈ 125 °C are needed to cure the Ag-epoxy).*
- *The TTO puck, puck testing box, and a multimeter.*

Sample and puck preparation

The hardware has many delicate components (TTO puck, cernox temperature sensors, thick film heater, etc.) and it should be handled accordingly. The electronics is able to resolve signals down to 0.1 μV range, which requires appropriate measures as well. In order to get reliable data it is important to develop the necessary skills for handling the hardware, programing the sequences for data acquisition, and carrying out the data analysis.

The schematics of the thermal and electrical connections in an idealized sample with 4-probe configuration is shown in Fig. 6.

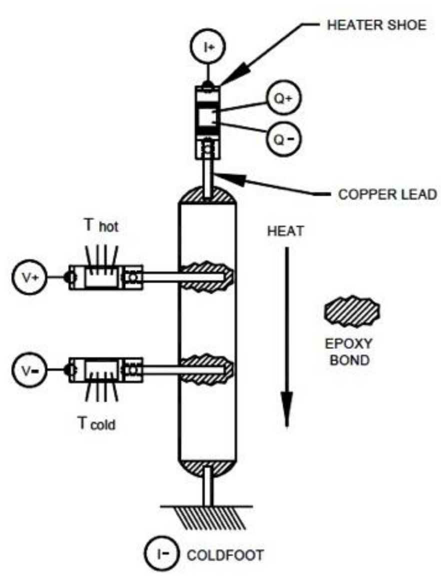

Figure 6: diagram of the thermal and electrical connections in an idealized sample.

The nickel sample

The nickel sample standard provided with the VersaLab is cut in a fashion that greatly facilitates mounting it on the TTO puck in a 4-probe configuration, as shown in 7. The heater and cernox temperature sensors are mounted on Au-plated copper “shoes”. The “ears” of the Ni sample can be bent and adjusted to fit in the narrow gap of the shoes, and secured with the M1 screws. Care must be taken not to overtighten the M1 screws, which can damage the shoe threads.

Students can use the mounting station, shoe tool, and provided jeweler screw drivers to attach the leads to the shoes. After developing a “soft touch” one may prefer to manipulate the sample, puck and shoes with his/her hands. Fig. 7b shows what the Ni sample looks like when mounted on the TTO puck. After the sample is secured in place, the student should inspect and correct any mechanical contact between the wires, and with the radiation shield, as they can be a source of thermal leakage.

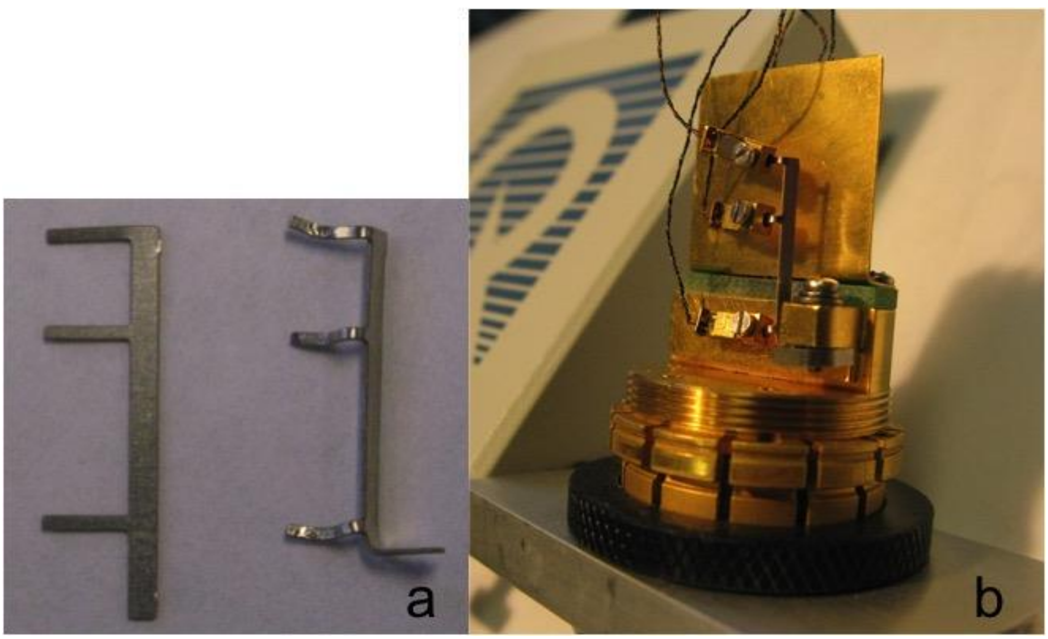

Figure 7: a) standard Ni sample; b) Ni sample mounted on the TTO puck.

<u>Real world samples</u>

Obtaining a sample in the format of the Ni standard is not usually possible, and not always desirable. Ni foil is malleable, and friendly to good electrical contacts. Adapting to the shape, size, fragility, and other characteristics of your sample requires some planning and creativity. Sometimes the sample size limits our ability mount the sample in a 4-probe configuration and we have to resort to 2-probe.

Four-probe is much preferred over 2-probe because contact resistance can bring in inaccuracies that are not trivial to account for.

A few simple and fast methods to attach leads for 2- and 4-probe measurements using the leads provided with VersaLab are shown in Fig. 8. The leads can be wrapped around (a and c) or sandwich (b) the sample, while the electrical contacts between the leads and sample are established with a dab of Ag-epoxy. (Epotek H20E's typical curing time is 15-30 min at 120 °C). A possible shortcoming of this method is the Ag-epoxy breaking off when the leads are secured to the shoes, due to the torque on the shoe screws.

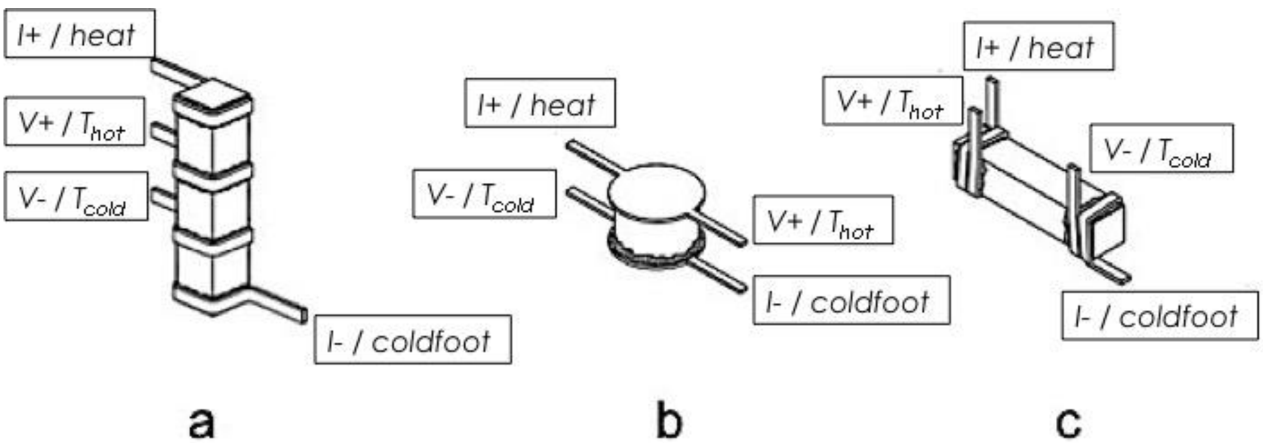

Figure 8: a) 4-probe configuration; b) and c) 2-probe configuration.

A method that prevents stress and breakage on the fragile Ag-epoxy sample-lead contacts upon attaching the shoes is shown in Fig. 9. Albeit more time-consuming this method isolates the contacts from the torque upon securing the shoes. In this case either Ag-epoxy or Ag-paint can be used as the electrical contact agent. There's a trade off when choosing between Ag-paint and Ag-epoxy. Ag-paint has lower resistivity (desirable) but is more fragile (undesirable) than Ag-apoxy. The pcb holders can be made by attaching copper leads to a pcb with epoxy, or ordered from a pcb making company. See ordering information on section G1.

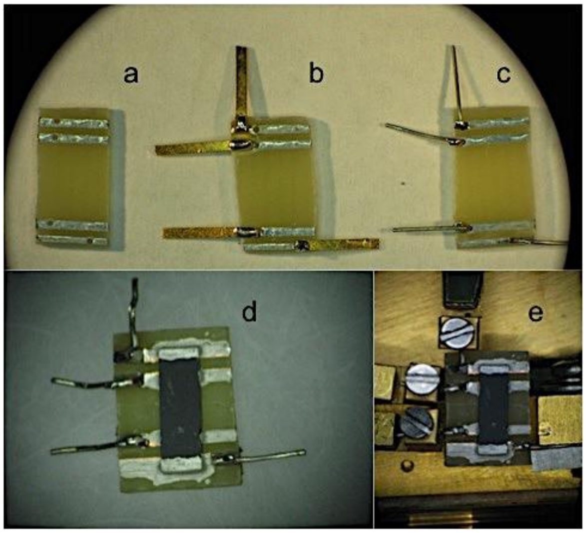

Figure 9: a) section of pcb with 4 tinned copper lines; b) pcb with Au-plated copper flat leads soldered to the lines; c) pcb with 0.25 mm dia. Cu wires soldered to the lines; d) sample attached with Ag paint; e) sample on pcb attached to the TTO puck.

Preparing to place the TTO puck in the VersaLab

After attaching leads to your sample, and connecting the leads to the shoes and cold foot, inspect the wires and ascertain that they are not touching. Attach the temperature shield, unscrew the top lid, and make sure the wires are not touching the shield. You are now ready to place the puck on the testing box, and verify that the heater, sensors, and sample are connected and giving the expected readings. If all is well, the TTO puck may be inserted in the VersaLab.

Figure 10: TTO puck on testing box.

Carrying out the measurements

1 – Verify that the cabling is correct for the TTO, and activate the TTO option. The **install** tab will open and guide you through installing the sample and carrying out the chamber operations. The **data** tab lets you create a new data file for your experiment. Make sure you check the "Capture Raw Data" box. It will give you the ability of reprocess scrutinize and reprocess the data if the need arrives. The **sample** tab permits entering the geometric details of your sample. Length is the distance between the 2 voltage leads. Cross section refers to the width x thickness, i.e. the area traversed by the thermal and electric currents; and surface area is the total external area of the sample. Typical values for the emissivity are ≈ 0.1 for highly reflective metallic surfaces, ≈ 0.3 for unpolished metallic surfaces, and ≈ 1 for dark unpolished surfaces. The loss of heat by thermal radiation is accounted for in the model for calculating κ. (Details of the model and theory of operation are given in the TTO manual)

2 – After loading the TTO puck in the VersaLab, insert the baffle assembly (with the contact baffle at the bottom) in the sample chamber, purge and seal. Take the VersaLab to the initial temperature of your measurement, and start the **HiVac**. TTO measurements require high vacuum, as "low vacuum" would have enough residual gas to help remove heat from the sample and affect the accuracy of the thermal conductivity measurements.

3 – You can now write a sequence to collect the data. The TTO software permits choosing between two **modes** of measurements, continuous, or steady-state. In continuous mode, the TTO collects data while the temperature of the samples drifts slowly. An algorithm to account for the change in temperature during the measurements is described in detail in the manual. In steady-state mode, the sample is first stabilized at the measurement's temperature, before the measurement starts. The continuous mode is faster, and unless sharp transitions are expected, the parameters can be chosen not to compromise the accuracy. A good start is to use the default parameters of the TTO measurement transport tab, and plan on ramping the temperature slowly ($dT/dtime \leq 2$ K/min) while measuring S, κ, and ρ simultaneously in the Ni sample. An example sequence is shown in Fig. 11. A few more "unusual" steps will become clearer as you become familiar with the methodology. Please refer to the TTO manual for more details. Note that: 1- we waited to reach the starting temperature before turning the Hivac on. The presence of exchange gas allows the TTO puck to reach the initial temperature of the measurement faster; 2- once we started the continuous measure with the TTO, we let the TTO soak at the initial temperature for 30 minutes. This gives the TTO enough time to tune in the appropriate parameters for the measurement (period, power, excitation current, etc.

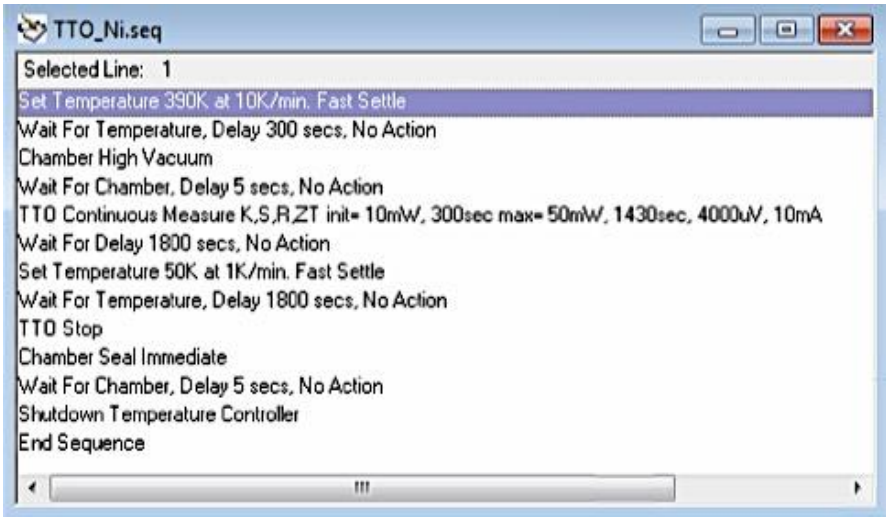

Figure 11: Example of a MultiVu sequence to measure the temperature dependence of S, κ, and ρ of the standard Ni sample.

Resources

Below is a brief list of resources that can help you set up, carry out your experiments, and understand the physics guiding the observations. This list is by no means comprehensive, and there are a very large number of excellent alternatives.

Supplies

Ag-loaded epoxy – 2-component H20E from Epotek can be purchased directly from Epotek (www.epotek.com), their local distributors, and a number of science supplies companies (e.g. Fisher, VWR, etc.). Typical curing time is 15-30 minutes at 120 °C. A small amount from each container can be removed with the tip of a toothpick, and mixed on a glass slide.

Ag-paint – There are a number of excellent Ag paints in the market. One that is quite useful for attaching leads is the Dupont 4929N. Mixing it with the butyl cellusolve acetate solvent permits adjusting the viscosity to find a good compromise between mechanical strength and low resistance. Heating up to 80-100 °C speeds up the drying process.

samples – Thin wafers of pure and doped silicon, germanium, and gallium arsenide can be purchased easily online, e.g. waferworld.com and universitywafer.com. An excellent site for acronyms used in the semiconductor industry can be found in wafernet.com/acronym.htm. Examples of 2 in. dia. Si wafers from universitywafer that you can cut for the TTO experiments are undoped (ID=2332), n-type (phosphorous doping, ID=736)), and p-type (boron doping, ID=763).

Lanthanides (rare-earths) can be purchased on alfa.com, materion.com, espimetals.com, etc. It's better to focus on the heavier rare-earths as they are much less reactive with air. Examples from the Alfa catalog are Gd foil (25 x 25 mm, 0.62 mm thickness, Item No. 00595), Tb foil (25 x 25 mm, 0.62 mm thickness, Item No. 39695), Dy foil (25 x 25 mm, 0.62 mm thickness, Item No. 00592), Ho foil (25 x 25 mm, 0.62 mm thickness, Item No. 00596), Er foil (25 x 25 mm, 0.62 mm thickness, Item No. 00593).

pcb boards – one can assemble a pcb sample holder similar to the ones in Fig. 9 by using a blank section of pcb (e.g. 5 x 12 mm^2), Cu ribbon, and epoxy. Custom made pcb boards can be ordered from a number of companies online. Some companies have online software for the design, e.g. pad2pad.com and expresspcb.com. An example of a pcb board ordered from pad2pad is shown in Fig. 12. The board is 2.5 x 4.0 in. The spacing between the voltage lines varies from 1.5 to 5.5 mm, in order to accommodate samples different sizes. The hole configuration is more clearly seen in Fig. 9. In this case the holes (0.014 in. dia.) are spaced by 0.18" in. across each horizontal line. Individual sample holders can be cut out with a jeweler's saw. 0.010-0.013 in. dia. bare copper wires can then be soldered to the lines.

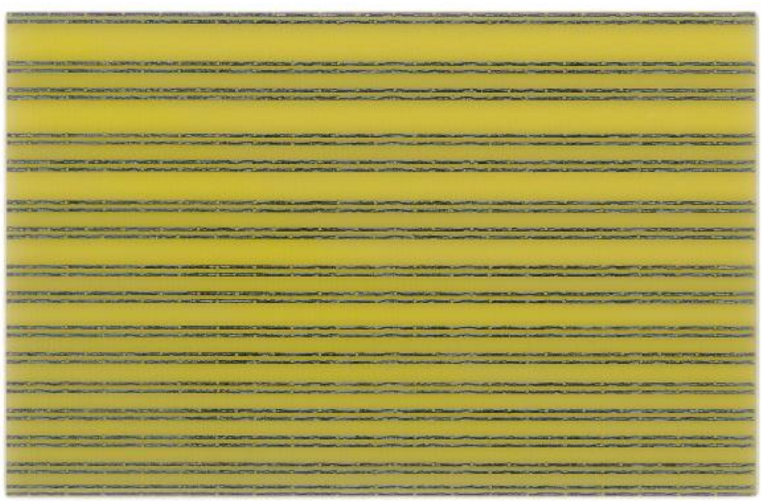

Figure 12: Custom made pcb for TTO application. The pcb dimensions are 2.5 x 4.0 in. The spacing between the voltage lines varies from 1.5 to 5.5 mm. The holes are 0.35 mm in diameter.

References

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[3] W. Nellis and S. Legvold, Phys. Rev. **180**, 581 (1969).
[4] S. Legvold, in *Magnetic Properties of Rare Earth Metals*, edited by R.J. Elliott (Springer US, 1972), pp. 335–381.

Books and articles

A. Bulusu and D.G. Walker, Superlattices Microstruct. **44**, (2008).
C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, 1996).
C. Kittel and H. Kroemer, *Thermal Physics* (Freeman, 1980).
G. S. Nolas, J. Sharp, and H. J. Goldsmith, Thermoelectrics (Springer, 2001).

Resources – online

http://thermoelectrics.matsci.northwestern.edu/thermoelectrics/index.html
http://en.wikipedia.org/wiki/Seebeck_coefficient

Questions

1- Thermal conductivity and sound in electrical insulators are carried mostly by phonons. Yet, it seems that sound waves travel across the sample much faster than heat. Where does the thermal resistivity come from?

2- The Wiedemann-Franz (WF) law seems to work fairly well for simple metals near ambient temperature. Use your data on the Ni sample to test it at 273 and 373 K.

3- What is the Lorentz number for Ni?

4- Why the WF law fails for semiconductors?

5- It is known that pure Si is not a great choice for a thermoelectric applications. Even though S can be large, the high thermal conductivity can hurt the figure of merit. Can you envision ways to mitigate this problem?