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# Probe Design for Thermopower Measurements Using a Differential Thermocouple

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## Abstract

Thermopower is a quantitative measurement of the Seebeck effect, and an intrinsic property of materials. The Seebeck effect is defined as the voltage developed across a conducting or semiconducting material when a temperature difference is established at the ends of the material, and it is understood as a net migration of charge carries, or diffusion from the hot side to the cold side. By this effect, thermal energy can be converted into electricity, or vice versa. Therefore, the Seebeck effect has been applied in power generation, temperature sensors, and refrigeration systems. In the Strongly Correlated Electron Laboratory at CSU, Fresno, there is an interest in characterizing the thermopower of intermetallic compounds. Thus, a thermopower prototype probe was designed to perform measurements in a cryocooler. The probe makes use of a type-T differential thermocouple, which also works under the Seebeck effect. The resolution of the probe was tested using nickel 201 alloy and platinum samples, and thus the probe provided an error within 3% between 100K and 300K. Measurements below 100K must be improved, and errors are attributed to the limitations of the thermocouple used. Hence, further work will be focused on adding a Cernox thermometer on the hot side to account for a more accurate temperature difference.

**Keywords: Thermopower, Seebeck, intermetallic compounds**

## 1. Introduction

When a temperature gradient is applied at the ends of a conducting or semiconducting material, an electromotive force will develop across this material. In other words, thermal energy can be converted into electricity, or vice versa. This is known as the Seebeck effect, named after Thomas Johann Seebeck who in 1821 discovered this phenomenon. The Seebeck coefficient, or thermopower, is thus a quantitative measurement of the Seebeck effect and an intrinsic property of materials.

As a considerable part of the energy produced by an engine is wasted as heat, using this thermal energy to generate electricity makes up the key to maximize the useful work done by a machine. The Seebeck effect precisely describes this type of processes. Understanding how the Seebeck effect works has helped develop applications such as thermoelectric generators[1], thermocouple thermometers[2], and thermoelectric coolers[3].

Illustrated in Fig. 1 is the concept of the Seebeck effect taking place in a semiconducting sample: a drive of charge carriers by thermal energy from the hot end (left side in Fig. 1) to the cold end of the material eventually balanced out by the electric potential energy. In the graph it is observable how the direction of the electric field goes from a positive voltage to a negative voltage. A diffusion of charge carriers occurs because the negative side has a higher density of electrons and lower density of holes, and the positive side has a lower density of electrons but a higher density of holes.

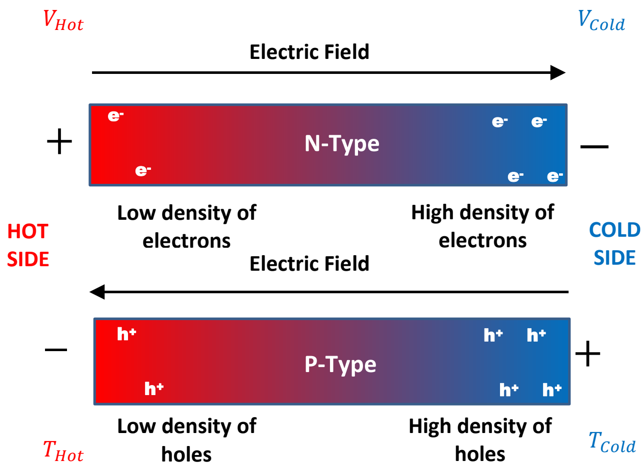


Figure 1 Diffusion of charge carriers. Two types of semiconductors are denoted according to the predominant charge carriers. N-Type (negative) has electrons as prevalent charge carriers; P-Type (Positive) has holes as predominant charge carriers.

The prevalent charge carrier determines the type of semiconductor, and precisely, the sign of the thermopower value reveals information on the prevalent type of charge carrier[4]. In this way we can distinguish N-Type and P-Type semiconductors, as shown in Fig. 1. In N-Type semiconductors, the predominant charge carriers are electrons, and in P-Type semiconductors most of the charge carriers are holes.

Thermopower (i.e., Seebeck coefficient), *S*, is then defined as the negative ratio of the voltage difference (△V) in voltage from the hot side to the cold side, to the temperature difference (△T) applied, △T, or difference between the temperature of the hot side to the cold side, displayed in Eq. (1).

$$S = -\frac{\Delta V}{\Delta T} = -\frac{V_{Hot}-V_{Cold}}{T_{Hot}-T_{Cold}}, \qquad (1)$$

In the scientific community there is an interest to study filled skutterudite compounds. These are materials with the formula $RT_4X_{12}$, where R is a rare-earth metal, T is a transition metal, and X is a pnictogen. Some of these compounds have exhibited exotic properties at extremely low temperatures, such as unconventional superconductivity, as in the compound $PrOs_4Sb_{12}$[5], ferromagnetism as in $NdOs_4Sb_{12}$[6], and large thermoelectric values at high temperatures, as it occurs in $R_{1-y}Fe_{4-x}Co_xSb_{12}$[7]. Thermoelectric properties are essential in applications for the conversion between thermal energy into electricity. In order to measure the Seebeck properties, an instrument is needed. However, with the limited budget available, it is difficult to purchase a commercial-grade apparatus. Therefore, a laboratory-built instrument is necessary.

The improvement of devices that measure thermopower has constantly advanced in the field of thermoelectrics. Developers in this field have investigated different setups in attempts to increase the accuracy of the method and functionality of the probe. S. Tripathi and others[8], for instance, reported on a setup for a dual measurement from 77K to 500K by setting up two resistors to create a temperature difference and a type E thermocouple to measure it. Ajay Soni and G. S. Okram[9] reported on their development of a resistivity and thermopower measurement device in the range from 5K to 325K, capable of holding eight metallic samples simultaneously. E. Mun and others[10], developed a system to function in a PPMS cryostat and measured the Seebeck coefficient from 2K to 350K within 16 hours in zero and applied magnetic fields. E. S. Choi[11] developed an apparatus to perform a parallel measurement of thermopower at <1 K with an applied magnetic field for milli-sized samples. Also, A. L. Pope and others[12] described the construction of an apparatus to measure resistivity and the Seebeck coefficient in a cryocooler. Their measurements range from 10K to 300K, and the samples in their setup are positioned in IC chips. The developed probe used in this paper shared some similarities with the ones described by E. Mun, E. S. Choi, and A. L. Pope but was also limited by the equipment and software that exist in the lab. Based on A. L Pope's apparatus' capability of incorporating samples of different sizes and E. S. Choi's parallel measurement, a future thermopower probe design has been envisioned.

In this paper we discuss the design of a thermopower probe that operates inside a cryocooler to take measurements in the temperature range from 11K to 300K with zero field. The prototype probe was tested with intermetallic compounds, nickel 201 alloy obtained from Quantum Design[13], and for corrections applied, platinum 99.95% samples.

## 2. Experimental Setup

Figure 2 portrays the present probe designed for thermopower measurements. The bottom of the probe was constructed to screw into a cryocooler's cold finger to maintain thermal equilibrium with the cooler for measurements in the range from 11K to 300K. All the elements of the probe are made of an oxygen-free high conductivity copper (OFHC) material. The base or "puck" is 1.102'' (27.99 mm) in diameter, as observed in Fig. 2b. The puck is covered by a copper cylindrical threaded cap, for heat shielding. The nickel 201 alloy sample is located between the hot (left) and cold (right) platform, both electrically insulated from the environment. Because the measurements are performed by the 2-wire method, background contribution must be subtracted by performing a second measurement of a reference material. Thus, another run using platinum wire 99.95% was executed.

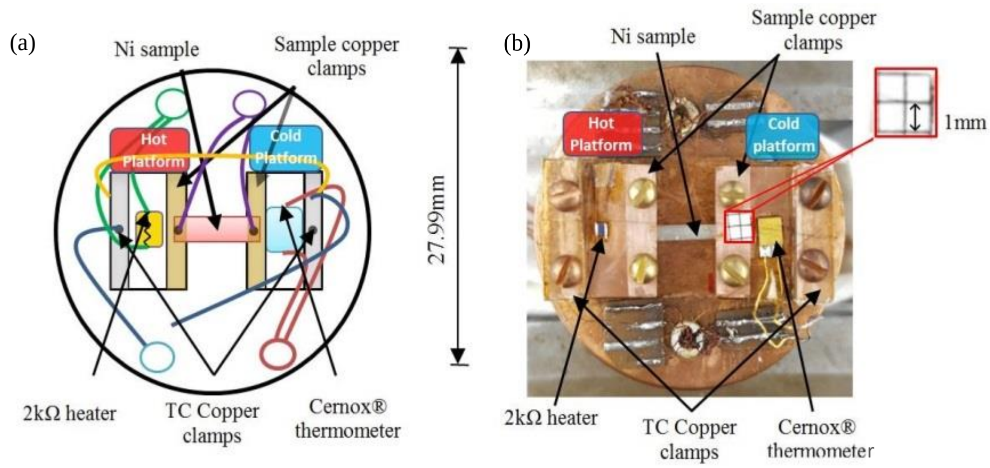


Figure 2 Top view. (a) Schematic of current design of measurement probe. Corresponding leads connect to measurement bridges accordingly. (b) Photo of prototype measurement probe. 1mm division grid paper was placed on cold platform for size comparison.

To create the temperature difference, a 2kΩ resistor was placed on the hot platform. To measure the voltage generated, two copper leads are spot welded onto the copper clamps securing the sample in place. The cold platform holds a Cernox® thermometer, which measures the cold platform temperature. To determine the temperature difference between platforms, the design makes use of a type-T differential thermocouple. Four solder pads are placed two above and two below the hot and cold platform. They serve as connection points that will later feed to external measurement bridges. With regards to the thermocouple, the constantan wire is shown in orange in Figure 2(a), for it is not distinguishable in Fig. 2 b). The thermocouple joints are in thermal contact with the platforms. To notice size comparison, a graphing paper with 1mm/division was placed on the cold platform. Data collection was achieved through a LabView program written in the lab.

Thermopower measurements rely on the steady state method to establish equilibrium in temperature and voltage. Reaching equilibrium means there is no net migration of charge carriers in the material. This is depicted in the temperature vs. time, and voltage vs. time graphs as a flat top in Fig. 3 a) and b), respectively. In Fig. 3a) the red line (or upper curve) represents the temperature of the hot platform as calculated from thermocouple data, while the blue line represents the temperature of the cold platform.

Experimentally, once inside the cryocooler, the system will undergo cooling down to 11K. Temperature was monitored and regulated by the silicone diode thermometer on the cold finger of the cryocooler. When temperature stability has been established, data collection begins. After 100 seconds, the heater will be supplied with a current for a period of time necessary for the temperature and voltage to reach equilibrium. The temperature is then swept for more data points to be taken and the process is repeated for a new target temperature.

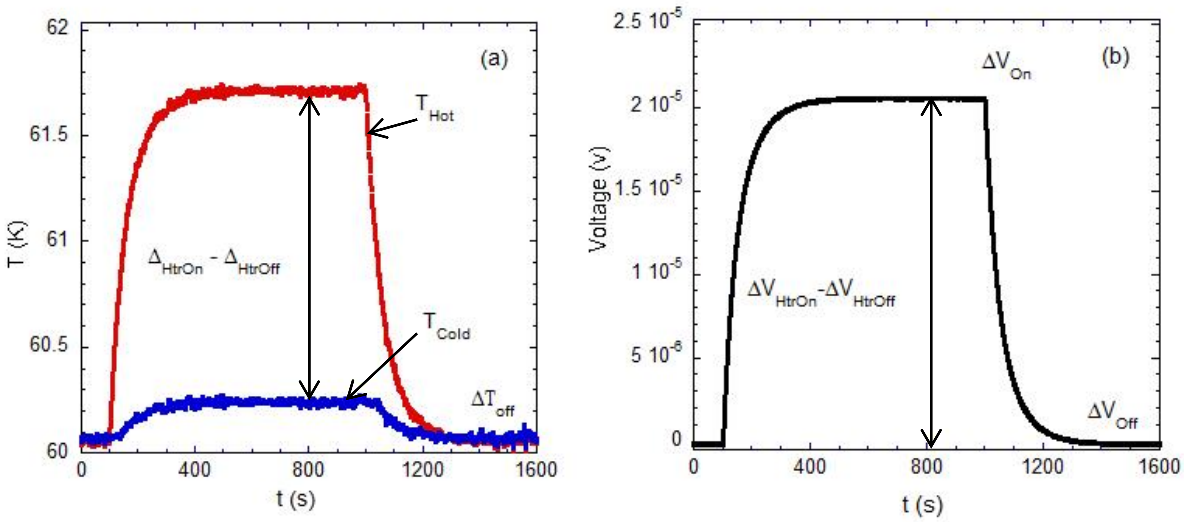


Figure 3 Steady state method by which it is establish equilibrium in temperature (a), and voltage (b). $T_{Hot}$ represents the temperature of the hot platform, and $T_{Cold}$ that of the cold platform.

In general, it was assured that the heating period was set up to be of at least five times the relaxation time, τ. Such heating period would assure the systematic error no more than 0.67%.
Figure 4 shows the relaxation time for the nickel run in blue squares, and for platinum in open black circles.

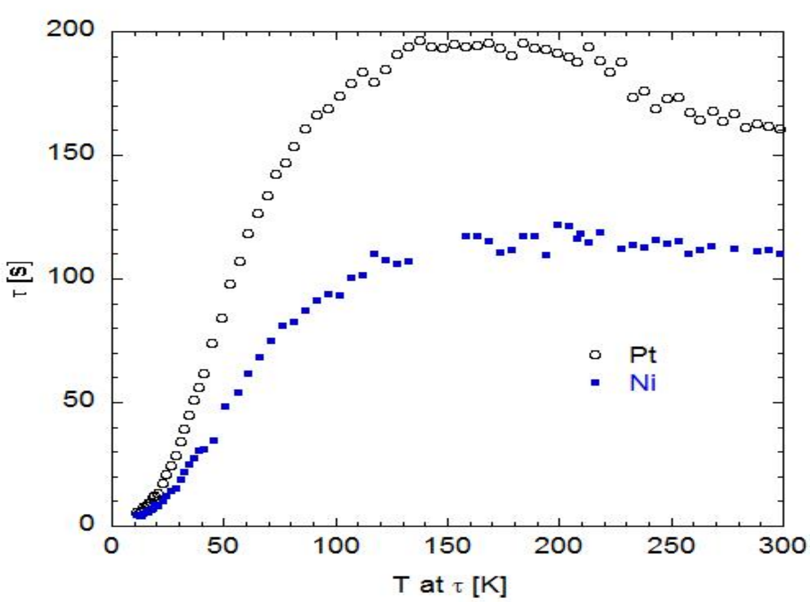


Figure 4 Thermal relaxation time τ as a function of temperature for platinum and nickel runs

Afterwards, the Seebeck coefficient is determined by:

$$S_{Meas} = -\frac{\Delta V_{\text{HtrOn}} - \Delta V_{\text{HtrOff}}}{\Delta T_{\text{HtrOn}} - \Delta T_{\text{HtrOff}}} \quad (2)$$

Where $S_{Meas}$ are the raw thermopower values obtained for each sample with background contributions. $\Delta V_{\text{HtrOn}}$ is the voltage difference measured when the heater in on, while $\Delta V_{\text{HtrOff}}$ refers to the voltage difference when the heater is off. $\Delta T_{\text{HtrOn}}$ corresponds to the temperature difference when the pulse width is applied, and so $\Delta T_{\text{HtrOff}}$ is the temperature difference when the pulse width is not applied to the sample.

Since $S_{\text{Meas}}$ contains background contributions, the measured thermopower values of nickel and platinum are described as in Eq. 3 and 4. Where $S_{\text{Ni\_Meas}}$ refers to the calculated Seebeck coefficient from the nickel run including background contributions. $S_{\text{Pt\_Meas}}$ is the thermopower data from the platinum run with background contributions, $S_{\text{Pt}}$ is the thermopower values for platinum only, and in our case, we use platinum literature data from the Handbook of Temperature Measurement, Vol. 3: Theory and Practice of Thermoelectric Thermometry[14]. $S_{\text{Ni}}$ is then the Seebeck coefficient of nickel alone.

$$S_{Ni\ Meas} = S_{Ni} + S_{Bkg} \quad (3)$$

$$S_{Pt\ Meas} = S_{Pt} + S_{Bkg} \quad (4)$$

If we substract equation 4 from 3, then background contributions can be disregarded, and thus we obtain:

$$S_{Ni} = S_{Ni\_Meas} - S_{Pt\_Meas} + S_{Pt} \quad (5)$$

This $S_{\text{Ni}}$ is the thermopower values of Nickel alone, or “corrected” thermopower values, $S_{\text{Ni\_Corrected}}$.

## 3. Results, Analysis, and Discussion

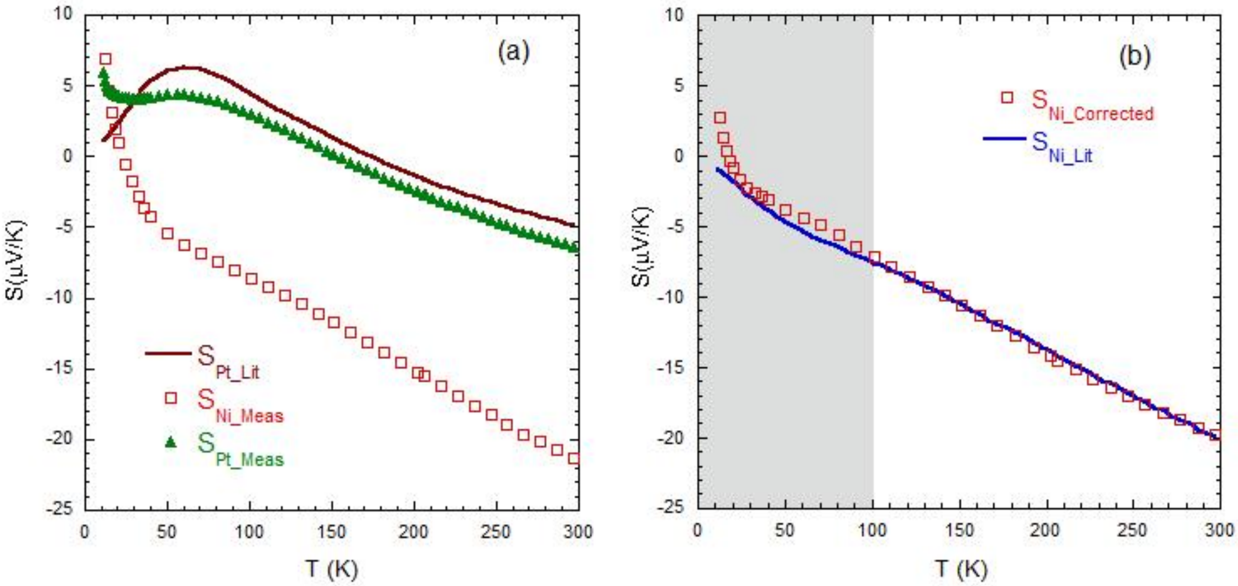


Figure 5 (a) Raw data for nickel and platinum with platinum literature data. (b) Data for nickel after applied corrections, alongside nickel literature data. For the clarity of display, only every other data points are shown here.

The Seebeck coefficient values of Nickel 201 alloy[13] and platinum 99.95%[14] were measured between 11K and 300K. Figure 5. (a) indicates measured thermopower values for nickel 201 alloy as open red squares –showing every other marker for distinguishability-, and platinum 99.95% measured values as green triangles. The platinum literature data is the upper most solid line in brown. In Fig. 5 (b), nickel data after applied correction is depicted as red squares. The nickel literature data is the solid line in blue, which was used to determine the resolution of the device. The literature data for nickel was obtained from quantum design [13].

Overall, the determined thermopower value for nickel agrees with the literature above 100K. Quantitatively speaking, between 100K and 300K the measurements are within 3% absolute error. Although, below this range we observed deviations especially in temperatures lower than 30K, or the gray area in the figure 5.b), where the graph grows exponentially, which seems to occur in the same fashion for our platinum data.

The deviation on the low temperature thermopower values is attributed to the type-T differential thermocouple used, for its working range is between 73K and 473K. Thus, in order to determine a more accurate temperature gradient, a Cernox® thermometer can be implemented on the hot side as well, and the temperature values obtained from the thermometers can then be compared to those using the thermocouple.

Moreover, regardless of how consistent the measurements are, performing the platinum correction asynchronous from the nickel run will inevitably result in discrepancies of the conditions and thus results obtained. Therefore, for future improvement of the probe, the puck should be able to perform both runs simultaneously.

The data analysis in this paperalso motivated the group to modify the current software configuration to regulate the lower temperature. As for now, the low temperature data was acquired from a bath thermometer inside the cryocooler, for it was assumed there will be a consistent thermal equilibrium between the puck and the interior of the cryocooler.

## 4. Conclusion

Seebeck coefficient measurements nickel and platinum were performed inside a cryocooler system. The current design of the thermopower probe used in this research was able to provide data in the range of 11 to 300K. Measurements above 100K are within 3% absolute error. Measurements below 100K need improvement. Limitations in the lower range are attributed to the type-T differential thermocouple used to calculate the temperature difference between platforms. Future work should be focused on implementing a thermometer on the hot platform as well and modifying the probe to take simultaneous runs of nickel and platinum. Currently, planned modifications to the probe include also modifications to our software to regulate the temperature of the cold platform. An objective is that by modifying the probe we can eventually take accurate measurements of the thermopower of filled-skutterudite compounds to characterize their normal state behavior and understand their properties.

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