Development of an Improved Probe Design and Analysis Method for Reliable Thermopower Measurements

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Abstract. Thermopower is a fundamental thermodynamic property that provides insight into the behavior of strongly correlated electron materials, such as their scattering time and density of state. Quantified by the Seebeck coefficient, this value represents the ratio of voltage generated over the temperature gradient applied across a sample. In our lab, previous thermopower measurements were hindered by lengthy experiments and complicated analysis. To improve efficiency, we implemented a faster analysis technique and began directly regulating temperature on the cold-side thermometer. Testing with 99.95% platinum showed consistent results between the slope and steady-state methods under a temperature gradient ~3% above the regulated cold-side temperature, as well as agreement with literature above 40 K. Deviations below 40 K were attributed to the differential type-T thermocouple, which has limited resolution for low-temperature measurements. These results confirm the slope method's validity, the use of the thermocouple as a reference sample, and our probe's overall effectiveness above 40 K. To enhance sub-40-K accuracy, we are developing a new probe incorporating a hot-side thermometer and simultaneous measurement of target and reference samples, enabling more precise removal of background contributions.

INTRODUCTION

Accurately measuring the properties of advanced materials is necessary to characterize and understand their behaviors. One key measurement is the Seebeck coefficient, a quantity that describes the thermoelectric ability of a material. Determining this is not only essential for evaluating a material's potential in thermoelectric applications, such as waste heat recovery and thermocouples, but also for gaining insight into its fundamental properties, including scattering time and density of states, due to its relationship with electrical conductivity.[1]

The Seebeck coefficient S is typically obtained by establishing a temperature gradient across a sample and measuring both the resulting temperature difference and the voltage between its two ends. It is defined as the negative ratio of the generated voltage ΔV over the applied temperature difference ΔT, shown in Eq. (1):

$$S = -\frac{\Delta V}{\Delta T}. \tag{1}$$

When experimentally determining the Seebeck coefficient of a sample, it is important to acknowledge challenges such as the contributions of background wiring to the measured voltage.[2] Figure 1 demonstrates a thermopower experiment with wires connecting to the hot and cold ends of a sample leading to a voltmeter. Here, the $+z$ direction is defined from cold to hot along the sample. Analyzing the electric potential ΔV across the sample and the wire, we integrate two definitions of the electric field E and set them equal, as shown in Eq. (2). The first definition of E is the negative change in voltage dV over dz such that $E = -\frac{dV}{dz}$. The second is the foundation of thermopower, relating E to the temperature gradient $\frac{dT}{dz}$ via the Seebeck coefficient S, defined as $E = S\frac{dT}{dz}$. Solving Eq. (2) for the measured Seebeck coefficient $S_{meas,sample}$ shows how wiring affects results, as seen in Eq. (3). Because of this, it is important to remove background contributions in the analysis to determine the true Seebeck coefficient values of a sample.

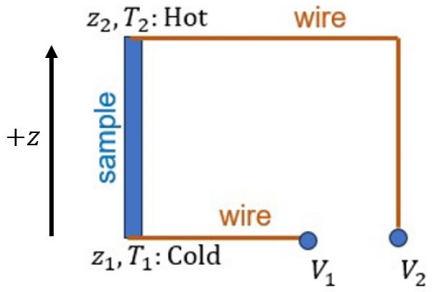

FIGURE 1. Schematic of the basic wiring to read the voltage generated across a sample when doing thermopower experiments. The $+z$ direction is defined from cold to hot along the sample.

$$\int_{z_1}^{z_2} E_{sample,z}\, dz + \int_{z_2}^{z_1} E_{wire,z}\, dz = \int_{z_1}^{z_2} S_{sample} \frac{dT}{dz}\, dz + \int_{z_2}^{z_1} S_{wire} \frac{dT}{dz}\, dz \tag{2}$$

$$S_{meas,\,sample} = -\frac{\Delta V}{\Delta T} = (S_{sample} - S_{wire}) \tag{3}$$

In the lab, we are developing a probe that can reliably measure the Seebeck coefficient of various samples. With our current design, we measured and analyzed the Seebeck coefficient of a 99.95% platinum (Pt) wire sample and compared it to known literature values.[3,4] The analysis was done using a trick that treats our differential type-T thermocouple as a reference sample, taking advantage of the probe's design and analyzing it as a constantan sample to remove the background contributions in the following method, shown in Eq. (4):[5]

$$S_{Pt} = S_{Pt,\,measured} - S_{Constantan,measured} + S_{Constantan}. \tag{4}$$

EXPERIMENTAL METHOD

Physical Instrumentation

The thermopower probe uses a heater mounted on a hot platform to establish controlled temperature gradients across a Pt wire sample suspended between two platforms, as seen in Fig 2. A Cernox thermometer measures temperature on the cold platform and a differential type-T thermocouple (a constantan wire) spans the platforms to read the temperature difference across them. Because the constantan wire experiences the same temperature gradient as the Pt sample, it can serve dual purposes as a reference to subtract background contributions.

FIGURE 2. (a) Top view of a thermopower probe with the hot platform on the left and the cold platform on the right. (b) Close-up view of a thermopower probe focused on the 99.95% Pt wire sample suspended across the platforms.

At a set regulated cold temperature, a temperature gradient within 1%–3% is established across the platforms using the heater, which is eventually turned off to allow cooling back to equilibrium. This is repeated to scan the range of our cryocooler from 300 to 8 K. We analyze data using the slope method, which requires a much shorter experimentation time than the traditional steady-state method because we do not need to reach thermal equilibrium during the heating period. Previous studies in the lab have shown that the two methods yield nearly identical values.[6]

Analysis Method

To determine the Seebeck coefficient using the slope method, the rise and decay of temperature and voltage are directly compared. As shown in Fig. 3(a), the cold-platform temperature is kept constant whilst the hot-platform temperature increases, creating a temperature gradient across the sample. This generates a voltage, shown in Fig. 3(b), which we measure for the Pt sample and then subtract that of the constantan wire. The voltage's clear response to temperature indicates very good thermal contact between the sample and the thermometer.

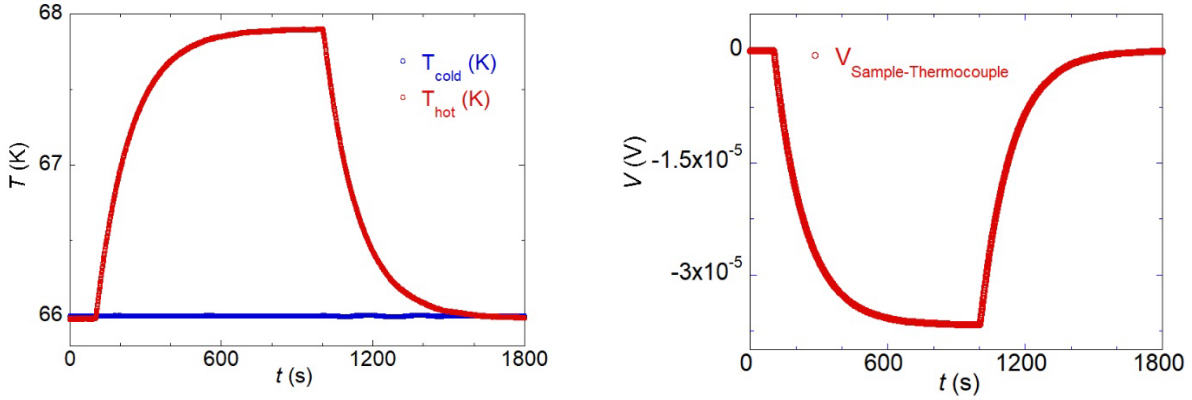

FIGURE 3. (a) Temperature versus time and (b) voltage versus time for a mean temperature $T = 66.9$ K.

To determine the exact relationship between the changing voltage and temperature gradient, we graph voltage against temperature and perform a linear fit, demonstrated in Figs. 4(a) and 4(b). The resulting slope represents the Seebeck coefficient. By averaging the values from both the heating and cooling periods, we determine the relative Seebeck coefficient of the sample with respect to the constantan wire. This is determined for the mean temperature, defined as $T_{cold} + \frac{\Delta T}{2}$, where ΔT is the largest measured temperature difference between the platforms. We then add Seebeck coefficient values of constantan from literature to get the final values of the Pt sample, as in Eq. (4). It is important to note that because this analysis method is highly dependent on a constant cold-side temperature, as shown in Fig 3(a), temperature fluctuations on the cold side can lead to significant errors in determining Seebeck values.

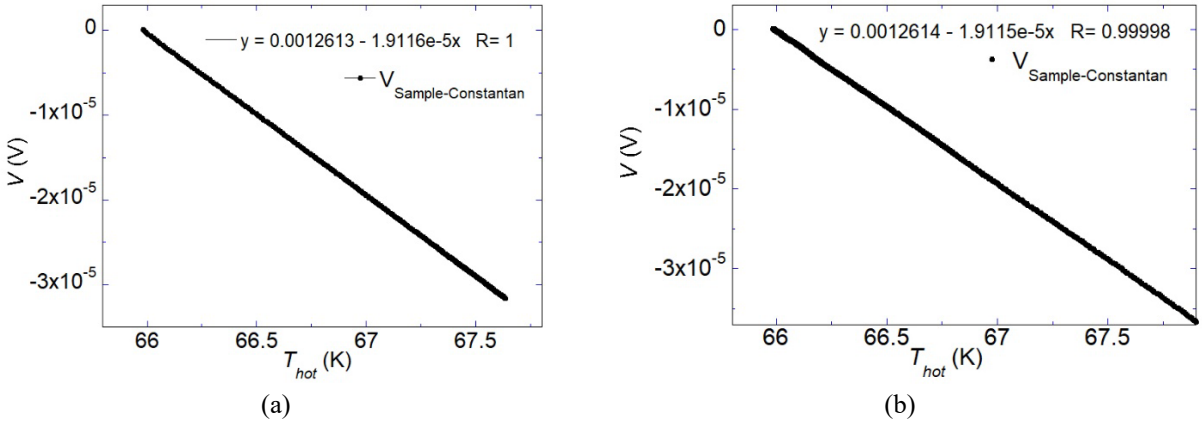

FIGURE 4. (a) Voltage versus hot-side temperature of the heating period and (b) voltage versus hot-side temperature of the cooling period for a mean temperature $T = 66.9$ K.

RESULTS AND FUTURE WORK

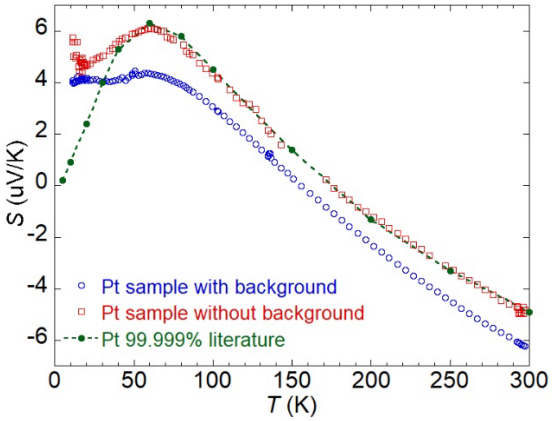

FIGURE 5. Seebeck coefficient versus temperature for a 99.999% platinum sample in the literature (green) and analyses of our 99.95% platinum sample without background removal (red) and with background removal (blue).

As shown in Fig. 5, our corrected measurements are in good agreement with literature values above 40 K, with an average absolute error of about 5%. This validates our use of both the slope method and the differential type-T thermocouple as a reference for removing background contributions in the 40–300-K range. Below 40 K, however, deviations arise from the limited resolution of the thermocouple. At very low temperatures, the Seebeck coefficient of constantan approaches zero. This creates an increasingly smaller voltage across the thermocouple we use to determine the temperature difference across the sample. As such, our resolution drops dramatically, prompting the need for a new probe design to improve low-temperature measurements.

Multiple attributes aimed at improving overall accuracy are still to be incorporated into the new design. There will be Cernox thermometers on both the hot and cold platforms, alongside the type-T thermocouple, to eliminate the reliance on the thermocouple at low temperatures. In addition, the new design will feature two sample positions to allow simultaneous measurement of a target and reference sample for more accurate background removal. It will also have a movable Delrin hot platform to accommodate various sized samples, topped with a sapphire window to ensure high thermal conductivity at low temperatures. Delrin is specifically chosen for the hot platform, as opposed to the copper cold platform, to create thermal insulation between the sample's hot side and copper puck.[7]

ACKNOWLEDGMENTS

This undergraduate research at California State University, Fresno, was supported by NSF DMR-1905636, Fresno State Smittcamp Family Honors College, and the Frank Sutton Research Fund.

REFERENCES

1. G. Prunet, F. Pawula, G. Fleury, E. Cloutet, A. J. Robinson, G. Hadziioannou, and A. Pakdel, Mater. Today Phys. **18**, 100402 (2021).
2. J. Martin, T. Tritt, and C. Uher, Jour. Appl. Phys. **108**, 121101 (2010).
3. R. E. Bentley, *Theory and Practice of Thermoelectric Thermometry* (Springer, Singapore, 1998), pp. 72, 214.
4. R. L. Powell, W. J. Hall, C. H. Hyink Jr., and L. L. Sparks, *Thermopower Reference Tables Based on the IPTS-68* (NBS Monogr. 125, Natl. Bur. Stand., USA, 1974), pp. 38–42.
5. A. L. Pope, R. T. Littleton IV, and T. Tritt, Rev. Sci. Instrum. **72**, 3129–3131 (2001).
6. A. Capa Salinas, J. Velasquez, and P.-C. Ho, Proceedings of the National Conference of Undergraduate Research (NCUR) 2019, pp. 171–177.
7. N. Sampathi, "Advancing Thermopower Measurement: Probe Design and Seebeck Coefficient Analysis," Master's thesis, California State University, Fresno, 2024.