Room Temperature Seebeck Coefficient Measurement of Metals and Semiconductors

BY

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Abstract

When two dissimilar metals are connected with different temperature in each end of the joints, an electrical potential is induced by the flow of excited electrons from the hot joint to the cold joint. The ratio of the induced potential to the difference in temperature of between both joints is called Seebeck coefficient. Semiconductors are known to have high Seebeck coefficient values($\sim$ 200-300 $^{\mu V}/_{K}$). Unlike semiconductors, metals have low Seebeck coefficient ($\sim$ 0-3 $^{\mu V}/_{K}$). Seebeck coefficient of metals, such as aluminum and niobium, and semiconductor, such as tin sulfide is measured at room temperature. These measurements show that our system is capable to measure Seebeck coefficient in range of ($\sim$ 0-300 $^{\mu V}/_{K}$). The error in the system is measured to be ± 0.14 $^{\mu V}/_{K}$.

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Chapter 1

Introduction

According to MacDonald(1962), there are three ways to investigate properties of electrical materials. The first way is applying an electric field to a material with no temperature gradient. This defines the electrical conductivity (σ) of the materials by taking the ratio between the current density and then applied electric field. The second way is applying a temperature gradient and measurement the heat flow. This defines the thermal conductivity(κ) of the material by taking the ratio of heat flow to unit area. The third way is applying a temperature gradient across two dissimilar homogeneous conductive materials. This defines the Seebeck coefficient(thermopower, thermoelectric power)(S) by taking the ratio between the voltage produced (Seebeck voltage) and the temperature difference.

1.1 Brief History to Thermoelectricity

The Seebeck effect, aside from Peltier and Thompson effect, is one of three thermolectric phenomenon. Seebeck effect is firstly discovered in 1821 by Thomas Seebeck while investigating thesrmal effect on galvanic arrangement. Seebeck accidentally connected parts of bismuth and copper which induced a thermoelectric emf that disturbed a compass nearby. Seebeck described this phenomenon as thermo-magnetism. Later on, the Seebeck effect was proven as one of the fundamental electrical properties of a conductor (Williams 1988). Not until 1854 by W. Thompson (Lord Kelvin)that a theoretical approach to thermoelectric properties was proposed (Heikes 1961).

The purpose of this research is to measure Seebeck coefficient of various metals and semiconductors in a room temperature. This thesis explains the theory behind the Seebeck effect, describes the apparatus used to measure Seebeck coefficient at room temperature, presents experimental values of SC for common alloys, metals, semiconductors and discusses the results of the experiment.

1.2 Theory

Understanding the physical behavior of a thermocouple and electron diffusion are crucial to study the Seebeck effect. Seebeck coefficient (SC) is one of the transport properties of a given material. SC is a measurement of the amount of potential induced per difference in temperature. Simply said, Seebeck effect is a conversion of a thermal energy to electrical energy.

1.2.1 Thermocouple

The first step to study Seebeck effect is to understand the physics of thermocouple. Thermocouple is a thermoelectric device made of two dissimilar metals connected at two points. Suppose one side of two connected copper wires is hotter than the other(Fig. 1.1). Since copper is a metal, its electrons are free to move. The electrons diffuse from the hot side to the cold side. When a voltmeter placed between two side, it detects no voltage difference because the electrons diffuse uniformly.

When one side of copper wire is exchanged by chromel[1] (Fig. 1.2) with the same temperature difference, the voltmeter will detect a voltage difference between both junctions. This difference in potential is caused by the difference in transport properties between copper and chromel. Put differently, the free electrons at the warmer side of copper has different speed than the free electrons at the warmer side of the chromel. The electrons then flow from the warmer side to the colder side which creates potential difference between both junctions.

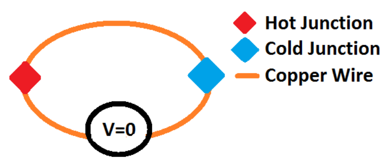

Figure 1.1: Copper-copper thermocouple.

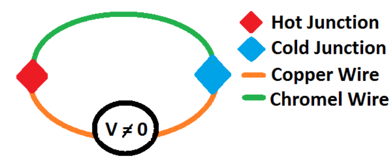

Figure 1.2: Chromel-copper thermocouple.

Note that figure 1.2 and 1.1 are electrically open circuits. The voltage difference between both junctions are caused by the difference in temperature of the junctions. Thermocouples are commonly used to measure temperature because the change in temperature is directly proportional to the difference in induced voltage. Commonly known thermocouples are K-type thermocouple which made of chromel and alumel, J-type thermocouple which made of iron and constantan, E-type thermocouple which made of chromel and constantan, etc.

1.2.2 Seebeck Effect and Diffusion of Electrons

When an end of a thermocouple is heated up, electrons in the warmer side of the thermocouple have more energy. Since they are free to move, the excited electrons diffuse toward

[1] Chromel is an alloy consists of approximately 90% nickel and 10% chromium.

the colder side of the thermocouple leaving *holes*[2] behind (Fig.1.3).

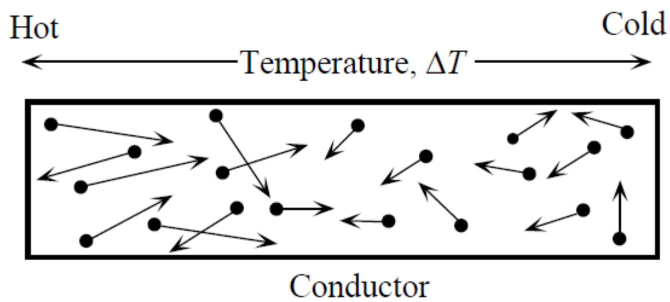

Figure 1.3: Representation of moving electrons on the conductor. Picture taken from Kasap

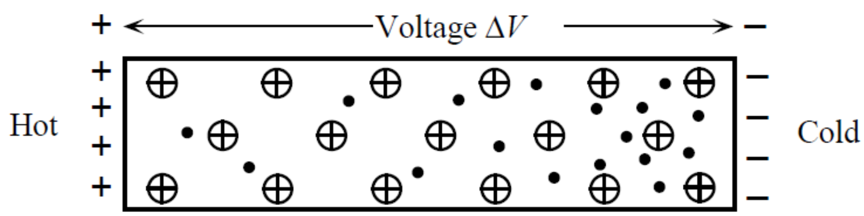

Figure 1.4: Representation of moving carriers on the conductor. Picture taken from Kasap

The electric field develops by the movement of these electrons point towards the colder side of the thermocouple which makes the cold side of the thermocouple negative relative to the warm side. The electrons will keep moving toward the colder side of the thermocouple until the potential established by the charge separation counteracts the flow of electrons which creates equilibrium. By convention, a material is defined to be an n-type when the electrons are diffused from the hot side to the cold side. On the other hand, a material is called p-type when the holes moved from the cold side to the hot side. The ratio between the voltage difference induced and the temperature difference is called the Seebeck coefficient.

[2]When electrons move from one place to another, they left positive vacancies behind, these vacancies are called *holes*

By this convention, mathematically, Seebeck coefficient is defined as

$$S = \frac{\Delta V}{\Delta T} \tag{1.1}$$
$$\therefore S = \frac{V_{cold} - V_{hot}}{T_{hot} - T_{cold}}$$

As explained in section 1.2.1, a thermocouple is consist of two different metals. This implies the measured Seebeck coefficient contains information for both metals. Hence the equation (1.1) expresses *relative Seebeck coefficient*. Equation (1.1) is better written as:

$$\Delta S = \frac{\Delta V}{\Delta T} \tag{1.2}$$

To find the *absolute Seebeck coefficient* of a material, one of the thermocouple's metal should have a Seebeck coefficient of zero. The only known material that has zero SC is superconductor. Many research have successfully been done to find the SC of common metals and alloys. Typically, metals have low SC ($\sim \pm$ 0-3 $^{\mu V}/_{K}$ [3], [2])

In this research, SC of common alloys, metals, and semiconductors are measured with respect to copper. Copper is a p-type material, therefore it has a positive SC value (the sign SC will be discuss in detail on the next section). The SC of copper is known to be +2.7 $^{\mu V}/_{K}$ Equation (1.2) can be re-write to find the ASC of a sample, therefore:

$$S_{sample} - S_{copper} = \frac{\Delta V}{\Delta T}$$
$$\therefore S_{sample} = \frac{\Delta V}{\Delta T} + S_{copper} \tag{1.3}$$

Where ΔV is the potential of the cold side of the junction with respect to the hot junction. Equation (1.3) will be used to determine the ASC of the samples.

1.2.3 Differential Thermocouple

Thermocouples are resourceful to measure a temperature of a single point. At room temperature with known SC of a thermocouple, the temperature of a point can be found using equation (1.2).A way to measure temperature between two points is to place two different known thermocouples on the desired points, convert the measured voltage to temperature and then subtract the value of temperatures from both points.

In this research, DTC (differential thermocouple) are used to measure the temperature difference between the hot and the cold junction instead of using two different thermocouples. DTC measure the temperature of the hot block in reference to the cold block. Hence eliminates the need to used two different TC.

Chapter 2

Experimental Apparatus

2.1 Overview

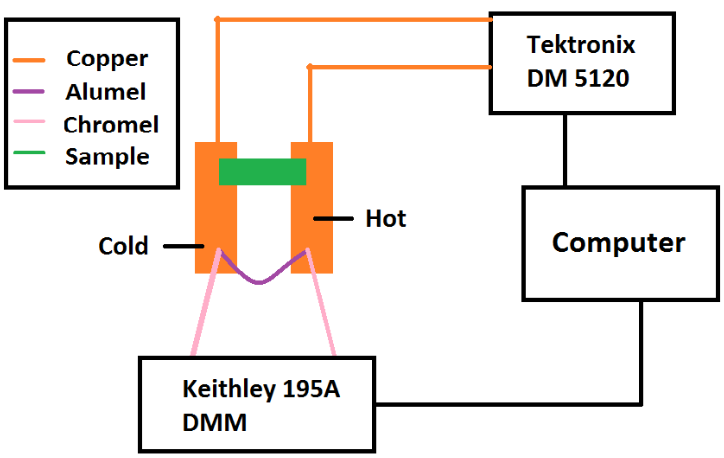

Figure 2.1: Schematic of the Seebeck system.

This chapter describes measurement made using a room temperature Seebeck system. Sample is mounted between two polished copper block with one block 1-5 K hotter than the other (figure 2.1). The voltage measured by Textronix DM 5120 (the Seebeck voltage) is the potential difference measured by the sample-copper differential thermocouple (DTC). The voltage measured by Keithley 195A DMM (the temperature voltage) is the potential difference across the chromel-alumel DTC. These measurements are gathered by computer using Seebeck 9.1 software. A plot of ΔV vs ΔT is generated using Mathematica to get the sample's Seebeck coefficient. This chapter also describes sample preparation and configuration procedure which help to minimize noise in the system.

2.2 Details of the Apparatus

There are two DTC playing roles in this experiment. Theoretically, measured Seebeck coefficient of an alloy is the coefficient of one material relative to its couple. To have a precise measurement, an unknown material should be coupled with a material with zero Seebeck coefficient. The only materials that has zero Seebeck coefficient are superconductors. Fortunately, Seebeck coefficient of common materials are known, i.e. copper, chromel, alumel, constantan. In this experiment, copper is used as the known material of the alloy. Therefore, sample-copper would be one of the differential thermocouples in this setup.

Another thermocouple that plays a role in this experiment is a chromel-alumel DTC. It is used to measure temperature difference between the hot and the cold block shown in figure 2.1. Ideally, the sample-copper k-type DTC are placed in the same points to ensure that both thermocouples will measure the same temperature difference. However, k-type DTC need not to be electrically connected to the sample-copper DTC to avoid coupling between the 4 different materials. K-type DTC can also introduce unwanted thermal voltage to the system. Hence k-type DTC need to be electrically insulated.

Copper blocks is used to connect these two DTC. A heater would be connected to one of the block as shown in figure 2.2. The copper blocks are adjustable according to the size of the sample.

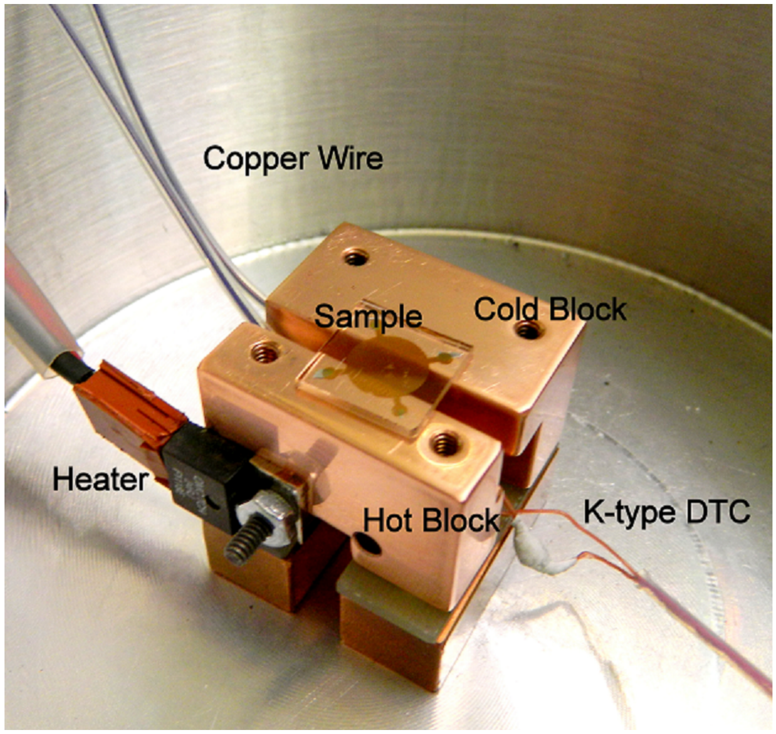

Figure 2.2: Experimental setup with sample.

2.3 Sample and System Preparation

There are few things that needed to be kept in mind as doing this experiment. Voltages measured are of order to 10 nanovolts which makes the system prone to noise, such as air current, movement of the apparatus, etc. Hence the need to prepare the system properly.

2.3.1 Seebeck System

The first step in preparing the system is to remove any oxidized materials from the copper blocks using a piece of sand paper. After polishing the blocks, ethanol is usually used to clean the copper blocks' surface to make sure no residue left.

The second step is to prepare the sample-copper DTC(figure 2.2). A clean contact needs to be established between the copper wires and the copper blocks. If the contact is not clean, the copper blocks and the copper oxide would coupled and introduce an extra thermal voltage to the system. The chromel-alumel DTC must be insulated. Teflon tape proved to be a better insulation for this system.

From section (refer to the sign of SC section), the sign of the Seebeck coefficient is crucial to this experiment. According to Kasap, by convention, the sign of the Seebeck coefficient represents the potential of the cold block with respect to the hot block. Hence the need to ground the hot side of the sample-copper DTC. The k-type DTC measures the difference in temperature between the hot block and the cold block so the cold side need to be grounded.

The last step is to thermally insulate the apparatus. This insulation is not only to make sure that the system is at a room temperature, but also to ensure that no air flow presents in the system. This measurement is temperature sensitive. The slightest change in temperature, or even air flow, would causes thermal noise. Also, the Seebeck coefficient of the k-type DTC varies with the temperature. So it is important to report the temperature of the room when taking data.

2.3.2 Sample Preparation

There are three different form of samples (wires, foils, and thins films) can be tested in this setup. To prepare a wire sample, it is important to make sure that there are no oxidized parts on the sample. A sharp blade is used to carefully remove any oxidized parts from the samples. Washers are used to make contact with the copper blocks. A foil sample on the other hand, must be polished and cleaned (similar to how the copper blocks prepared).

A semiconductor ,in form of thin film, is trickier to deal with. Usually the sample is placed on a glass or a silicon base so it is harder to make contact with the copper blocks. Taking the advantage of the soft texture of indium, indium foils are used to help making contact between a sample and the blocks.

A 1x1 cm sample usually is placed on indium foils. The blocks needed to be in appropriate distance. Experiments showed that the appropriate gap between the blocks depends on the length of the thin film sample. For 1x1 cm sample, the appropriate gap between the blocks is around 5 cm. More area of the thin film in contact with the blocks means stronger signals. But, the blocks shall not be too close to avoid thermal contact between two blocks.

Chapter 3

Results

3.1 Common Thermocouple Materials

There will be a sample mounted onto the blocks. The copper wires from Figure 3.2 will measure the voltage difference between the two blocks. The voltage measured is the voltage caused by the difference in temperature between the two blocks. These measurement are accumulated using the Seebeck 9.0 software. The data then were processed using Mathematica. The linear model fit function is used to construct a linear model that fits the accumulated data.

The first few samples measured are common thermocouple materials i.e. Chromel, Alumel, and Constantan. The Seebeck coefficient of these alloys were measured and represented by figure 3.1 and 3.2.

Figure 3.1 and 3.2 represent the induced voltage with respect to the difference in temperature between the two blocks. The slope of the graph represents the Seebeck coefficient of the chromel and alumel with respect to copper. As long as the difference in temperature is less than 5 degrees, the relationship between the voltage and the difference in temperature should approximately be linear. If the slope is positive, it means the material is p-type. Oth-

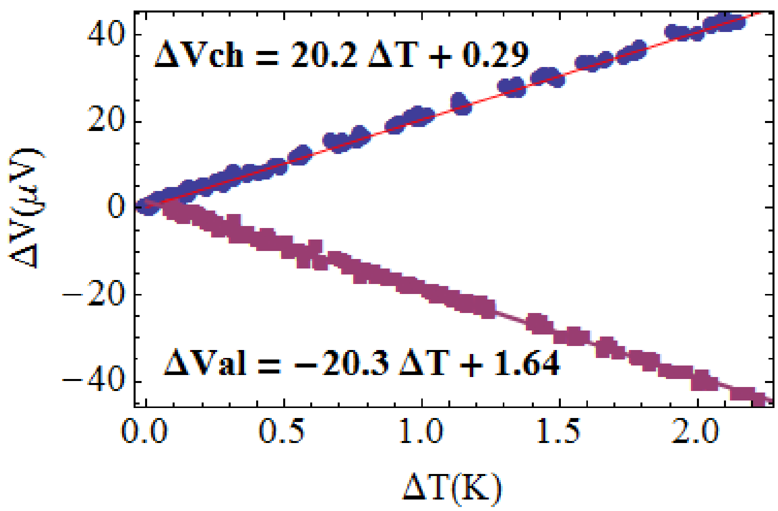

Figure 3.1: Results for Copper-Chromel-Copper (blue) and Copper-Alumel-Copper(purple) differential thermocouple. The relative Seebeck coefficients of these DTC are represented by the slope of each graph.

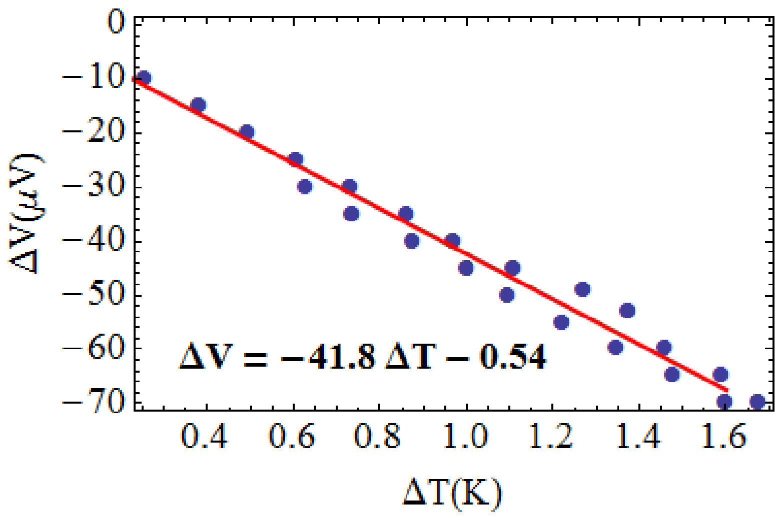

Figure 3.2: Result for Copper-Constantan-Copper differential thermocouple.

erwise it is n-type. For p-type semiconductors, the carriers are holes; for n-type, electrons.

The slope of the graph represents the SC of the samples with respect to copper. The absolute SC of the sample is found using equation (1.3). The ASC of chromel is

$$\begin{aligned} S_{\text{chromel}} &= \frac{\Delta V}{\Delta T} + S_{\text{copper}} \\ &= +20.2 + 1.94 \\ &= +22.2\,{}^{\mu\text{V}}/_{\text{K}} \end{aligned}$$

The ASC of alumel and constantan also found in the same manner. Results for these common alloys are listed in table 3.1.

Table 3.1: Comparison of experimental's values and literature's values of SC of commercial TCs

Alloys	Measured S (μV/K)	Lit. S values (μV/K) [1, p. 72]
Alumel	-18.3	-18
Chromel	+22.2	+22
Constantan	-39.9	-39

3.2 Metals

Even though metals have large amount of carriers, they have been known to have smaller Seebeck coefficient values due to their large electronic contribution to the thermal conductivity. In this research, measuring the SC of metals is used to test the precision of the system.

Measurements done in this system are relative to copper, therefore measuring copper is crucial to this experiment. The result of this measurement should be approximately zero. Section 1.2.1 explains that Seebeck effect only appeared when two dissimilar metals are connected. Hence measuring copper is equivalent to measure the noise in this system. The result from measuring copper is presented in figure 3.3.

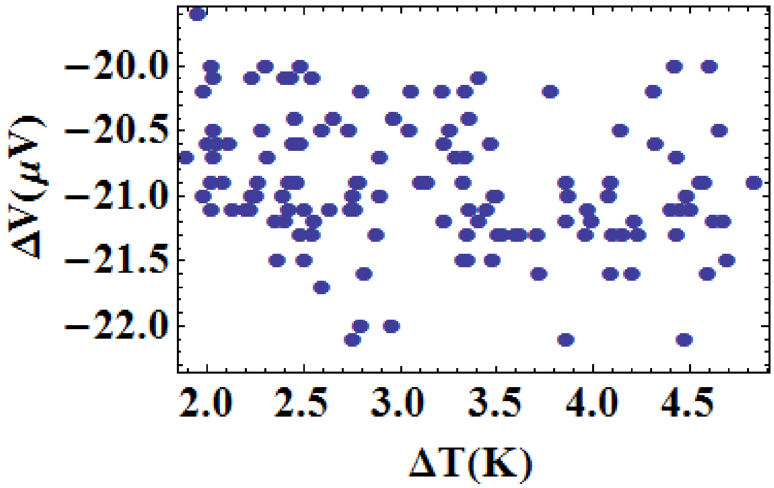

Figure 3.3: Result for copper-copper-copper differential thermocouple.

From Mathematica, the linear regression for this graph is -0.14ΔT. This implies that our system has error of $\pm 0.14\,{}^{\mu V}/_{K}$

Niobium and alimunium are measured using this system. The results are represented in figure 3.4 and 3.5.

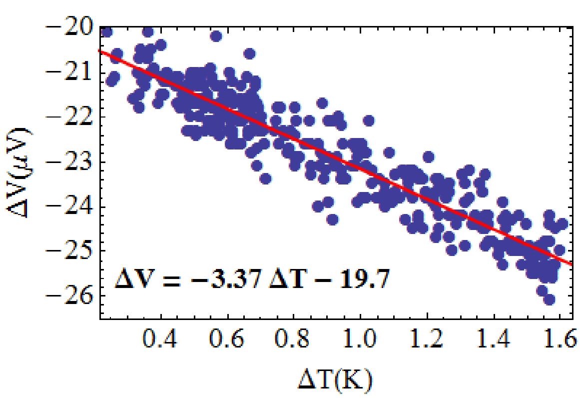

Figure 3.4: Result for aluminum-copper differential thermocouple. Red line represents the linear trend line of the data.

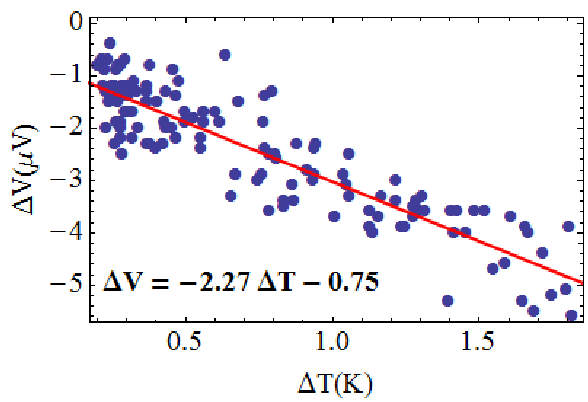

Figure 3.5: Result for niobium-copper differential thermocouple. Red line represents the linear trend line of the data.

The ASC value of the metals were found using the same method to find the SC of chromel, the ASC of these metals are tabulated in table **??**

Table 3.2: Comparison of experimental's values and literature's values of ASC of metals

Metals	Measured S at 20° ($\mu V/K$)	Known S value($\mu V/K$)
Aluminum	-1.43	-1.8[3]
Niobum	+0.33	$\sim$ 0[2, p.149]

3.3 Semiconductors

Semiconductors are known to have larger SC values because they have large amount of carrier like metals but have low thermal conductivity. The ideal semiconductors have large Seebeck coefficient, low thermal conductivity, and high electrical conductivity.

In this research, tin sulfide is annealed in different environment to study how the carrier moves on the this thin film. Figure 3.6 is the SC measurement of non-annealed tin sulfide. Figure 3.7 is the SC measurement of tin sulfide annealed in air. Figure 3.8 represents the SC measurement of tin sulfide annealed in vacuum.

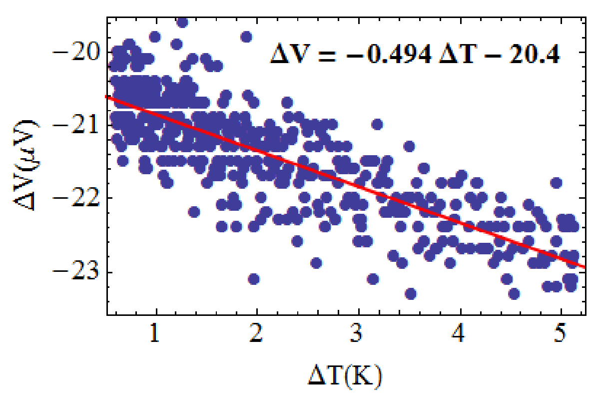

Figure 3.6: Result for copper-tin sulfide-copper differential thermocouple. This tin sulfide has not been annealed.

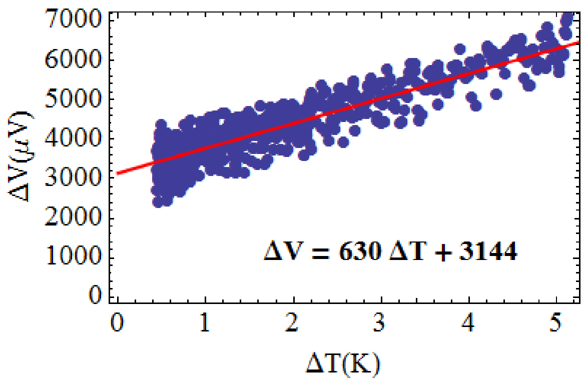

Figure 3.7: Result for copper-tin sulfide-copper differential thermocouple.This tin sulfide is annealed in air.

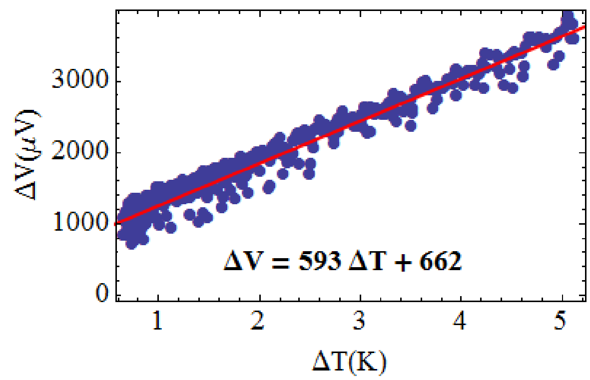

Figure 3.8: Result for copper-tin sulfide-copper differential thermocouple. This tin sulfide is annealed in vacuum.

The ASC values of these thin films are found using equation (1.3). The values are listed in table 3.3

Table 3.3: Results for tin sulfide.

Anneal environment	S at 20° C (μV/K)
No anneal	+1.45
Air	+632
Vacuum	+595

An interesting sample that comes up is tin sulfide that has been annealed in air. As shown by table 3.3, tin sulfide is a p-type material. This particular sample (Fig. 3.9)has negative ASC, which means that it is an n-type material. The conclusion for this sample is inconclusive at this point.

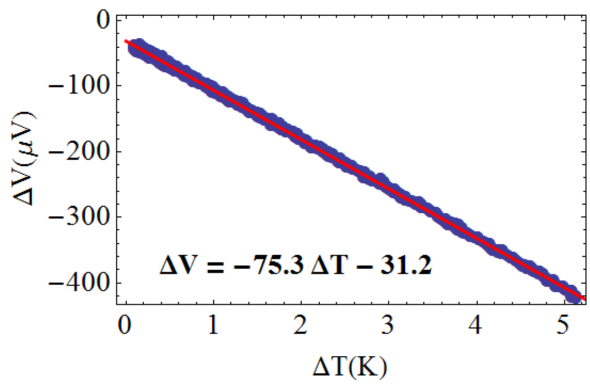

Figure 3.9: Result for tin sulfide-copper differential thermocouple. Tin sulfide annealed in air

Summary

Our system is capable of measuring Seebeck coefficient from $0.33\,{}^{\mu V}/_{K}$ to $\sim 600\,{}^{\mu V}/_{K}$. Our system has an error of $\pm 0.14\,{}^{\mu V}/_{K}$. Our system is a low-noise reliable system to measure the Seebeck coefficient of commercial TC, metals and semiconductors as reflected by our experimental results.

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