Cryogenic Cooling with a Single Crystal Bismuth Ettingshausen Cooler

Undergraduate Research Thesis

Presented in Partial Fulfillment of the Requirements for Graduation with Distinction
in the Department of Mechanical and Aerospace Engineering of The Ohio State University

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ABSTRACT

Conventional active cooling systems such as air conditioning and water heat pumps are cumbersome and involve moving parts, which can lead to wear over time. Alternatively, active cooling can be performed using thermomagnetic materials, providing a small form factor without any moving parts. Some semimetals, such as bismuth, can become a heat pump by using the Hall Effect; this is called a Nernst-Ettingshausen cooler. Under the influence of an electric current and a transverse magnetic field, electrons are forced to one side of the sample. The travel of electrons acts as a heat pump and creates a temperature gradient across the sample. The colder side could be used to draw heat from a desired surface to be cooled, without any moving parts. A drawback to Nernst-Ettingshausen coolers is that they are relatively inefficient as a heat pump, thus requiring more input energy to transfer a set amount of heat. Research is required to find semimetal alloys that can achieve a greater efficiency. This research seeks to create a bismuth single crystal to test its cooling characteristics. These results could provide insight into the feasibility of bismuth as a material for Nernst-Ettingshausen cooling and other solid-state cooling applications. The sample is placed in a chamber with a controlled ambient temperature. Electric current is passed through the sample in a transverse magnetic field. The resulting temperature gradient in the sample is then measured. This experiment is repeated by procedurally varying current and ambient temperature, while magnetic field is maintained constant. We found that the sample achieves a higher temperature gradient and exhibits greater cooling potential with higher applied current. The sample performs better at lower ambient temperatures. With improved mounting methods and strategically applied current, bismuth single crystal presents itself as a viable solution for Ettingshausen cooling.

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1 INTRODUCTION

1.1 Cryogenic cooling

Cooling to extremely low temperatures is commonly utilized in several applications, such as cold hardening metals, IR detectors, night vision systems super-conducting wires, and quantum computing. Cryogenic cooling is defined by the National Institute of Standards and Technology as cooling at or below 93K [1]. These low temperatures are most commonly achieved with the application of liquid nitrogen or liquid helium, which boil at 77K and 4K, respectively. To reach an exact cryogenic temperature, there must be a controller to balance the application of cooling agent, and a heater to adjust for excessive cooling. An Ettingshausen cooler could provide more control over temperature instead of balancing the application of heat with liquid nitrogen.

1.2 Nernst-Ettingshausen coolers

Nernst Ettingshausen coolers operate on the application of the Hall Effect. The Hall Effect is characterized by a transverse electromotive force along the y-axis induced on a charged particle traveling in the x-axis, normal to a magnetic field, as shown in Figure 1 below.

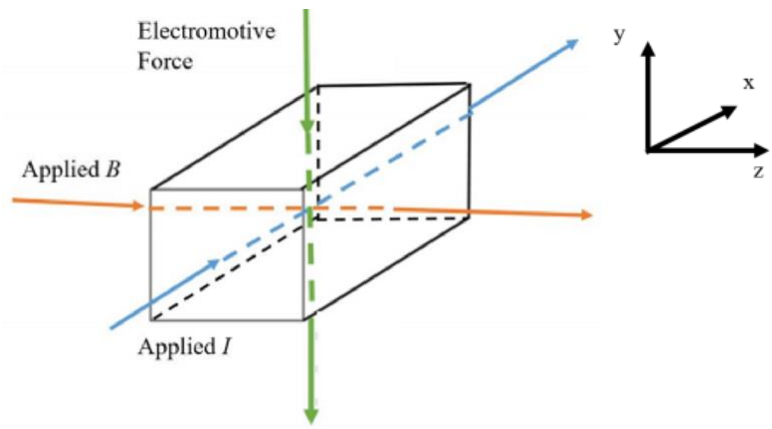

Figure 1: The Hall Effect and electromotive force on a charged particle

When a sample has an applied current, the electromotive force pushes a portion of the electrons towards the bottom. When electrons migrate to the bottom of the sample, they release their potential and kinetic energy as an exothermic reaction and heat the surrounding material, known as crystal heating [2]. On the other hand, resulting electron-hole pairs at the top will restructure and absorb energy from the lattice, which can decrease the temperature at the top below the ambient temperature. Figure 2, on the next page, graphically demonstrates the heat flow caused by Ettingshausen cooling that creates a temperature gradient across the sample.

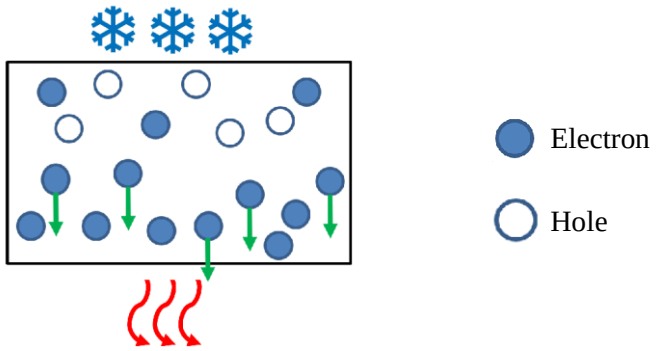

Figure 2: Ettingshausen effect takes the form of a temperature gradient across a sample from crystal heating/cooling of displaced electrons

The cold side of the sample can be used to remove heat from a desired surface. The warm side disperses heat through a heat sink to create a continuous heat pump.

1.3 Review of previous research

Alfred von Ettingshausen and Walter Nernst discovered the cooling potential of semimetals and the correlation to the Hall Effect in 1886. Research into thermoelectric and thermomagnetic materials came into form rapidly in the 1960's and 1970's. After that period, interest decreased due to the relatively low efficacy of these materials compared to established heating, cooling, and power generation methods [3]. Research has had a resurgence in the 21st century due to improved technology and unique benefits in niche applications.

Goldsmid et al. [4] outlined the advantages of Ettingshausen cooling over other active cooling methods. Ettingshausen cooling is simple in construction, in that it only requires one semimetal material, such as bismuth. The process operates with no moving parts, which eliminates the common problems of noise, vibration, and fatigue. They can operate in extreme environments, such as in cryogenic temperatures and in a vacuum. Ettingshausen coolers can be shaped into a small form factor, allowing the cooler to have custom sizes that can fit in small spaces. Additionally, the cooling takes effect immediately once the magnetic field and current are applied. This can allow for much more responsive and steady cooling [5].

Single crystal bismuth has been a target for study because of its unique properties as described by Matsuo et. al [6]. Bismuth has relatively low carrier densities and small effective masses, in combination with its *3m* trigonal crystal structure, it has become a prospective material for improved Ettingshausen coolers. The crystal structure creates anisotropic properties in bismuth single crystal, which can be used to maximize cooling performance [5].

The Ettingshausen figure of merit is a constant that characterizes the performance of a cooler, similar to the coefficient of performance for conventional heat pumps. The figure of merit has been studied extensively in the past [7][4][8][9]. Because of this, the figure of merit will not be analyzed in this project and other properties will be examined.

1.4 Research goal

A majority of research found in preparation for this thesis focuses on the figure of merit and the maximum temperature gradient achieved by the Ettingshausen cooler, without studying the time-dependent response. The goal of this research is to numerically characterize the temperature changes of a bismuth Ettingshausen cooler and how it is dependent on time.

In order to achieve this goal, a sample is developed and placed under conditions to measure the temperature behavior as an Ettingshausen cooler. From these measurements, results will indicate the temperature behavior of a bismuth Ettingshausen cooler and how it changes with time.

1.5 Overview of thesis

This thesis is organized as follows. Chapter 2 follows the creation of the single crystal bismuth sample. Chapter 3 describes the data acquisition apparatus and methods used to interpret data. Chapter 4 presents the experimental results, compares to theoretical calculations, and discusses the implications of results. Chapter 5 summarizes key results and proposes future strategies in the development of Ettingshausen coolers.

2 ETTINGSHAUSEN COOLER DESIGN AND PRODUCTION

2.1 Design

As described in Section 1.3, bismuth is considered to be a promising semimetal to produce a cooler. Single crystal formation is also known to be ideal for Ettingshausen cooling because of the uniform lattice structure that improves electrical conductivity and the Nernst coefficient [8]. Single crystal bismuth develops a 3*m* trigonal crystal structure as depicted in Figure 3 below. Therefore, the thermoelectric properties are anisotropic.

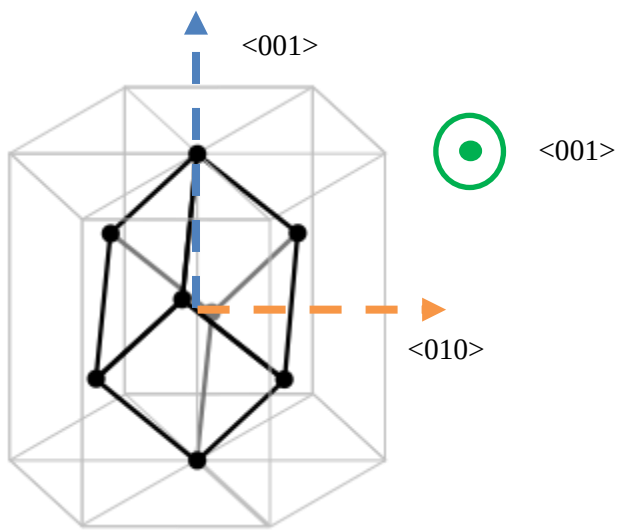

Figure 3: Single crystal structure of bismuth where <001> is the trigonal axis, <010> is bisectrix, and <100> is binary [9]

Goldsmid et. al. [10] characterized the figure of merit in different orientations of single crystal bismuth as shown in Table 1, below.

Table 1: Calculated thermomagnetic figure of merit for single crystal bismuth in different orientations

Direction of temperature gradient	Direction of electric current	Z_{NE} at 80 K $(\mu B)^2 \gg 1)$	Z_{NE} at 300 K $(\mu B)^2 \gg 1)$
Bisectrix	Binary	0.63×10^{-3} K^{-1}	0.82×10^{-3} K^{-1}
Binary	Bisectrix	0.63×10^{-3} K^{-1}	0.82×10^{-3} K^{-1}
Binary	Trigonal	2.1×10^{-3} K^{-1}	2.9×10^{-3} K^{-1}
Bisectrix	Trigonal	0.84×10^{-3} K^{-1}	1.1×10^{-3} K^{-1}
Trigonal	Binary	1.2×10^{-3} K^{-1}	1.8×10^{-3} K^{-1}
Trigonal	Bisectrix	1.2×10^{-3} K^{-1}	1.8×10^{-3} K^{-1}

The results indicate that the best figure of merit occurs when the temperature gradient is along the binary axis and the electric current is along the trigonal axis. For this research, the bismuth was oriented as such in order to achieve optimal results.

2.2 Production

The bismuth single crystal is produced using the horizontal melting technique [11]. Bismuth material is placed in a quartz tube with a piece of activated carbon to prevent oxidization of bismuth as it melts. The tube is placed in a box furnace at a slight angle, heated to 500°C to melt thoroughly, then cooled from 350°C to 24°C at a rate of 1°C per hour. This long cooling time allows the lattice structure to gradually orient in the single crystal formation. Figure 3, below, shows the bismuth single crystal after being removed from the furnace.

Figure 4: Bismuth single crystal after undergoing the horizontal melting technique.

The performance of a cooler can be dependent on its geometry as well as lattice structure. The cooler must distribute heat from the top to the bottom of the sample. Heat will travel more efficiently while moving from a smaller plane to a larger one [2]. This effect can be implemented by increasing the cross-sectional area in the direction of heat flow. For this reason, the sample is cut with an exponential curve with dimensions described in Figure 4(a), and the cut sample is shown in Figure 4(b). The curve is defined by Equation 1, as suggested by Goldsmid et. al. [12].

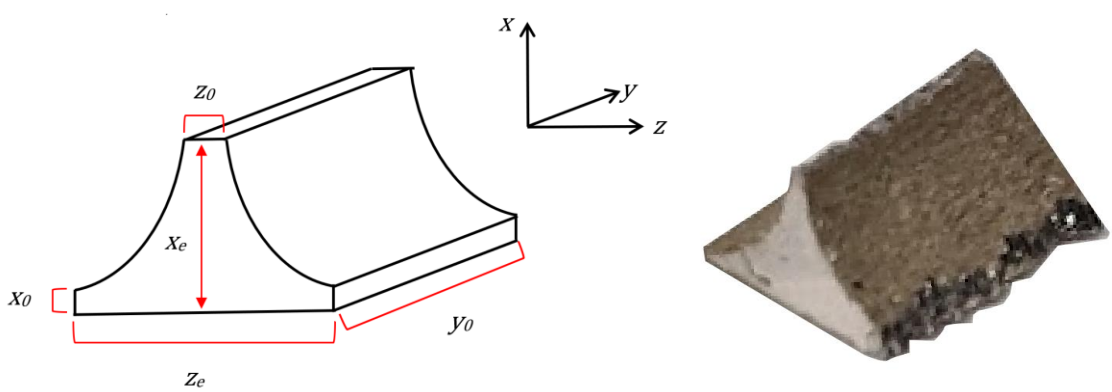

Figure 5: (a) Cascade formation of Ettingshausen cooler, where $z_e = 5mm, z_o = x_0 = 0.3mm, x_e = 5mm, y_0 = 8mm$ and (b) The bismuth single crystal sample after cut with electrical discharge machining.

$$z(x) = z_0 \left(\frac{z_e}{z_0}\right)^{\frac{x}{L_x}} \tag{1}$$

The dimensions are all on the scale of millimeters, so very precise machining was required to maintain accuracy and prevent destroying the sample. Electrical discharge machining (spark erosion) was chosen in order to cut a precise spline without damaging the sample.

3 EXPERIMENTAL METHODS

3.1 Cryostat preparation

A cryostat is used to conduct the experiment because it provides a contained environment for study. The cryostat consists of a chamber where the sample can be mounted. The air is evacuated, and the ambient temperature is controlled using liquid nitrogen. The cryostat provides electrical nodes which can connect the sample to equipment outside of the cryostat. Figure 6 below shows the direction of applied current, magnetic field, and the measured temperatures with respect to the sample.

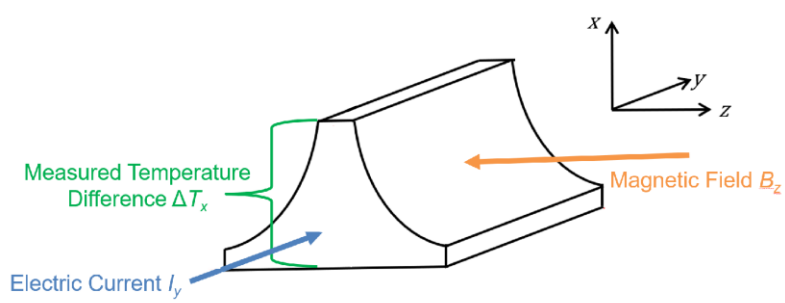

Figure 6: Orientation of sample, current, and magnetic field required to induce Ettingshausen cooling

To create this environment, the sample must be properly wired in the cryostat. Type T thermocouples are placed at the top and bottom of the sample and secured with silver epoxy. Brass plates are secured at both ends of the sample along the y-axis using Wood's metal solder and hold the current carrying wires. The sample was secured to an alumina heat sink to disperse heat from the bottom of the sample. Figure 7, on the next page, shows how the sample was wired to nodes within the cryostat that could be controlled from the outside.

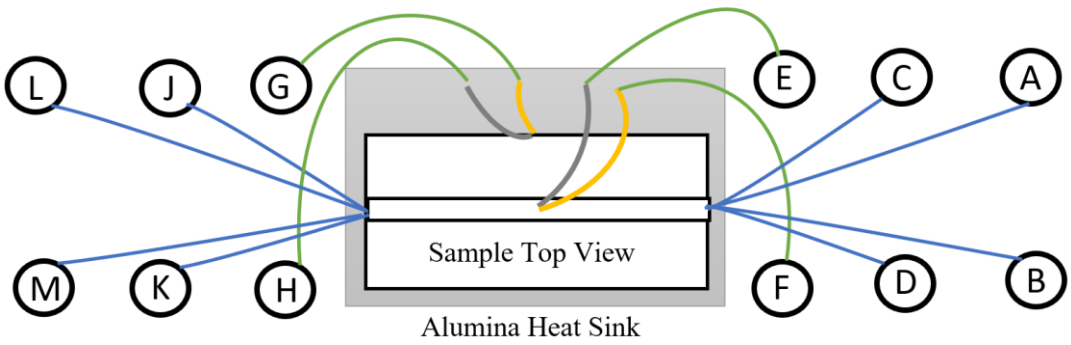

Figure 7: Cryostat wiring diagram to mount bismuth sample for Ettingshausen cooling

The blue wires connect the sample to nodes that carry current, thus creating a continuous current that goes in one side of the sample and out the other. The green wires connect nodes to two Type T thermocouples, where one measures the temperature at the top of the sample, and the other measures the bottom. Figure 8 shows the sample when it is mounted in the cryostat.

Figure 8: Bismuth single crystal sample (center) connected to nodes in order to communicate with exterior instruments

Next, the cryostat is placed in between a magnetic field generator. Once in place, the cryostat is supplied with liquid nitrogen and connected to a temperature controller, vacuum pump, current supply, and nanovoltmeter. A picture of the cryostat within the magnetic field generator is shown in Figure 9 on the next page.

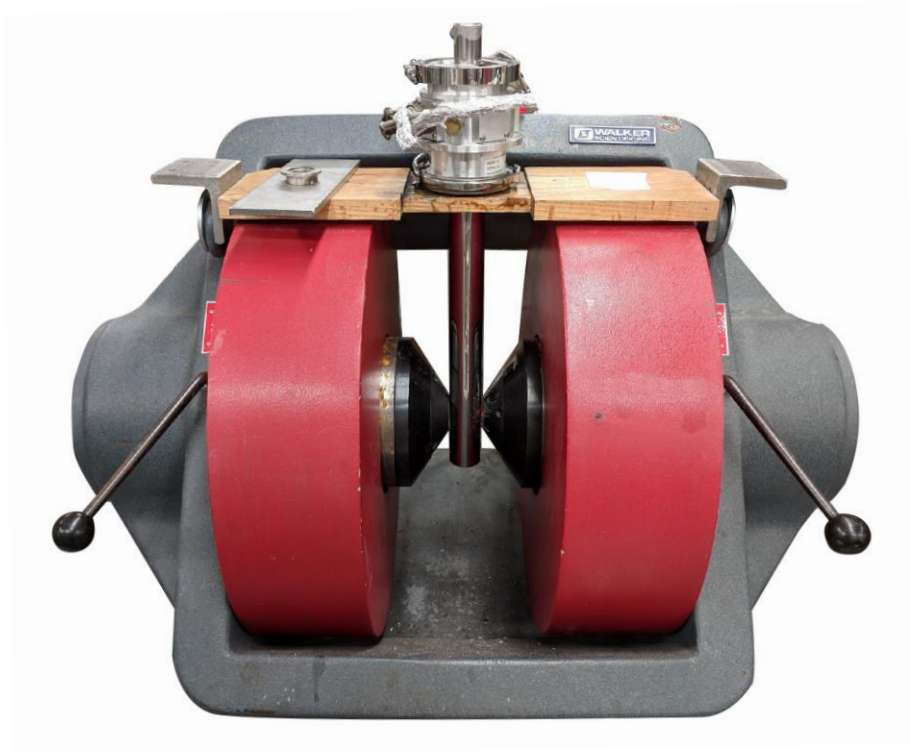

Figure 9: Cryostat vessel contains the bismuth sample and is placed within the magnetic field generator. Field is directed from right to left

3.2 Data Acquisition

The experiment begins by setting the ambient temperature to the appropriate value. Liquid nitrogen is used to cool to cryogenic temperatures and a temperature controller (LakeShore 331) is used to hold at the exact temperature. A magnetic field of 1.4 Tesla is applied with an electromagnet power supply (LakeShore 642) in each trial throughout the entire duration of the experiment. A LabVIEW data acquisition program was created to operate the experiment, shown in Appendix 1.

The procedure for each trial is as follows. The LabVIEW program is initiated and begins collecting temperature data using a nanovoltmeter (Keithley 2182A) and thermocouples at the top and bottom of the sample. An electric current is applied as a step input to the sample using a power supply. Under the influence of an electric current and transverse magnetic field, the sample produces a temperature gradient. The procedure is repeated by changing the input current, from 0.25A to 4A, incrementing by 0.25A. This is done at three ambient temperatures: 80K, 100K, and 120K.

At the ambient temperature of 80K the procedure is repeated once again by running the current in the opposite direction along the trigonal axis, therefore pumping heat towards the top of the sample. This test was only operated up to 2.50A due to avoid overheating the sample, for reasons explained in Chapter 4.3.

4 RESULTS AND DISCUSSION

4.1 Time-dependent temperature response

The first round of tests is run at an ambient temperature of 80K. The change in temperatures at the top and bottom of the bismuth single crystal were recorded over time and are presented in Figure 9, below. At the beginning of each plot, the current was turned on directly to the set value as a step input. The green dashed vertical line indicates the time at which the current was turned off and varies for each trial.

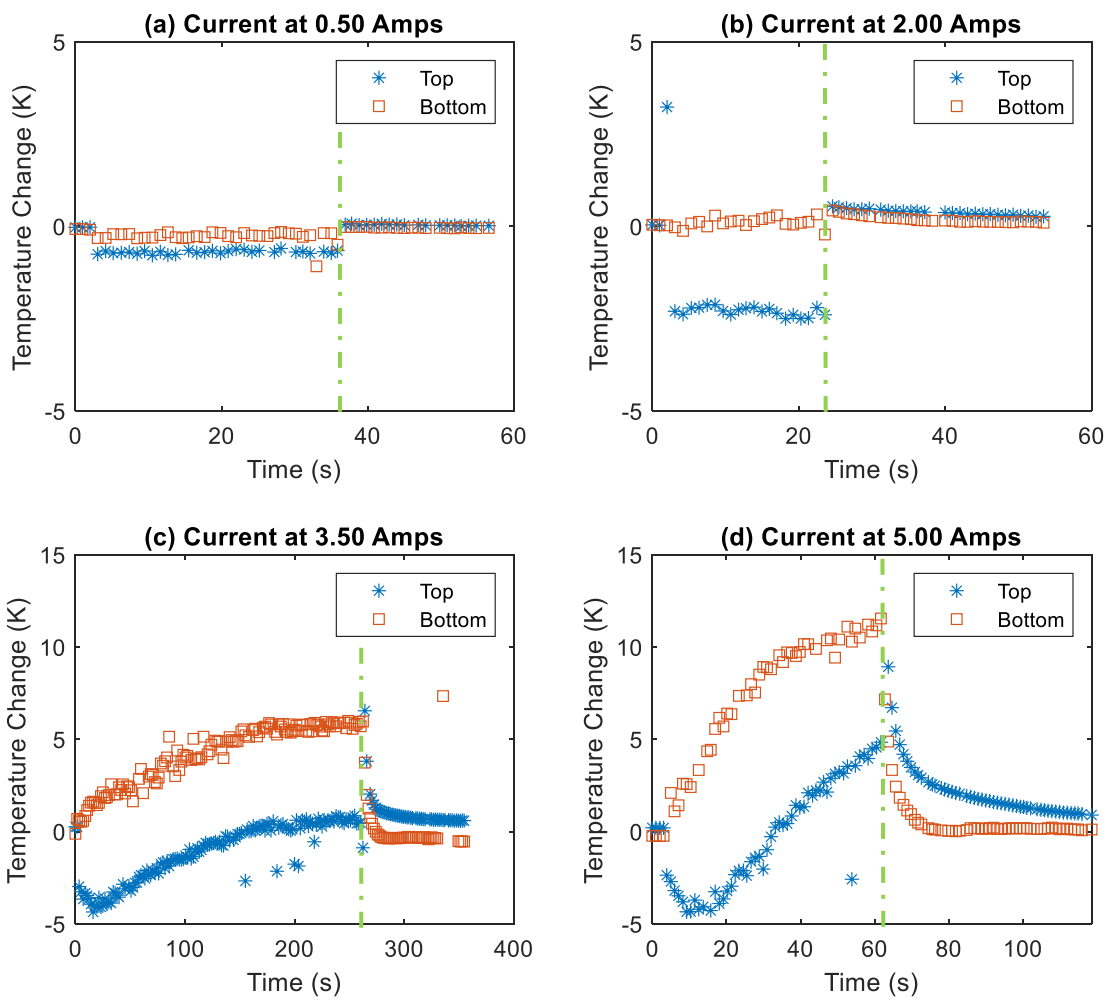

Figure 10: Time-dependent temperature responses of the top and bottom sample with the application of (a) 0.50 A, (b) 2.00A, (c) 3.50 A, and (d) 5.00 A

As mentioned above, the current was stopped irregularly for one of two reasons. First case was if the temperatures had reached a steady state, such as in Figures 9a and 9b. This was because the temperature was no longer varying and did not warrant more data. The current was also stopped if the temperature change at the top of the sample became a positive value. This is caused by Joule heating and will increase

the temperature of the sample over time. When the top of the sample is warmer than ambient temperature it negates the purpose of an Ettingshausen cooler.

Joule heating is a source of heat input due to a current running through a conductor with electrical resistance, and is defined by Equation 2, below [10].

$$Q = \frac{I_x^2 \rho L_x}{2 L_z L_y} \tag{2}$$

Where Q is the heat input, I_x^2 is the current squared, ρ is electrical resistivity, and L_x, L_z, L_y are sample dimensions.

Figures 9 (a) and (b) rapidly meet a steady state temperature and remain constant because the Ettingshausen heat flow into the heat sink can disperse the effects of Joule heating. Joule heating is proportional to the current squared, so at higher currents it is apparent that over time the heating overcomes the effect of Ettingshausen cooling and the entire sample becomes warmer than the ambient temperature. At 80K, a current of 3.50A was the lowest current at which Joule heating overpowered Ettingshausen cooling. This trend was nearly identical at 100K and 120K ambient temperatures, Joule heating increased the sample temperature above ambient temperature for the first time at around 3A.

To study the behavior of Joule heating at each ambient temperature, Figure 10 provides the temperature at the top of the sample with an applied current of 3.50A, starting from the lowest temperature and ending when the temperature exceeds ambient temperature. The data was fit with a second order polynomial function in order to eliminate noise and study this trend qualitatively.

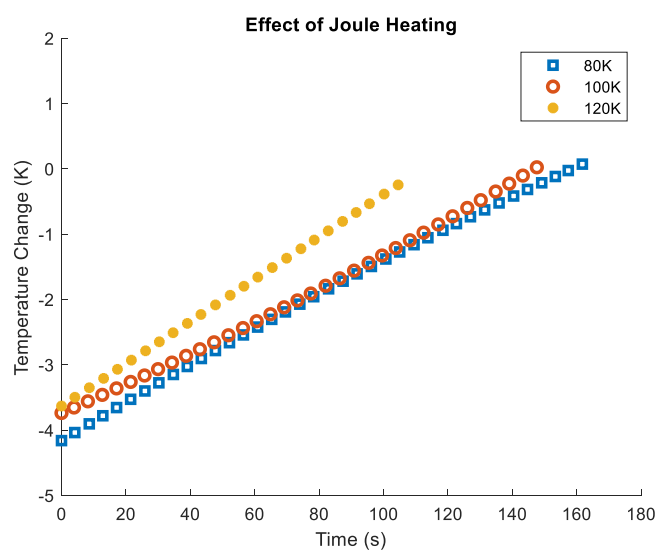

Figure 11: Effect of Joule heating compared at each ambient temperature

Figure 11 shows that at higher ambient temperatures, the sample will heat up quicker due to Joule heating. This could be caused by the sample having a higher electrical resistivity at warmer temperatures.

Results in Figure 9 show that the top of the sample will cool below ambient temperature, and the bottom will heat up because Ettingshausen heat flow moves to the bottom. The greatest temperature reduction achieved at the top for each applied current was recorded and is shown in Figure 12. The figure also compares the temperature decrease at each ambient temperature.

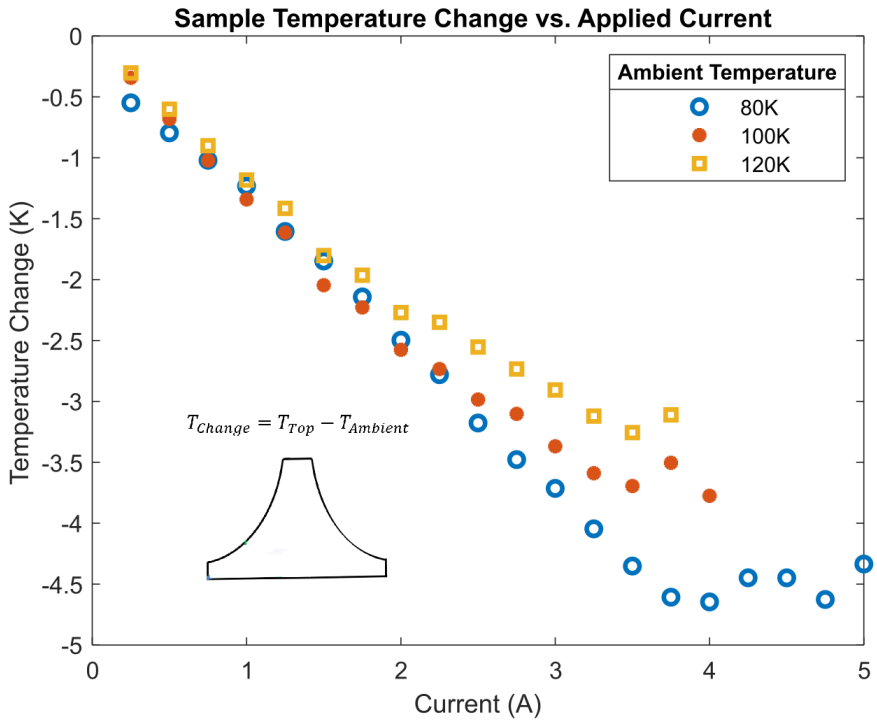

Figure 12: Temperature decrease at the top of the bismuth single crystal with increasing current, at each ambient temperature

Figure 12 shows several trends. With increasing current, the top of the sample will cool to a lower temperature, performing better as a heat pump. As current increases, samples at a lower ambient temperature can reach a lower temperature relative to their environment. At 80K, the top of the sample would decrease temperature by about 4.5K, meaning it was at an absolute temperature of about 75.5K. After current exceeds 3.50A, the performance seems to plateau, possibly due to Joule heating taking effect faster than it does at lower currents.

4.2 Temperature gradient

The performance of an Ettingshausen cooler is not only determined by the ability to cool lower than ambient temperature, but also the magnitude of the temperature gradient across the sample. The peak temperature difference across the sample was recorded for each trial and is shown in Figure 13, on the next page.

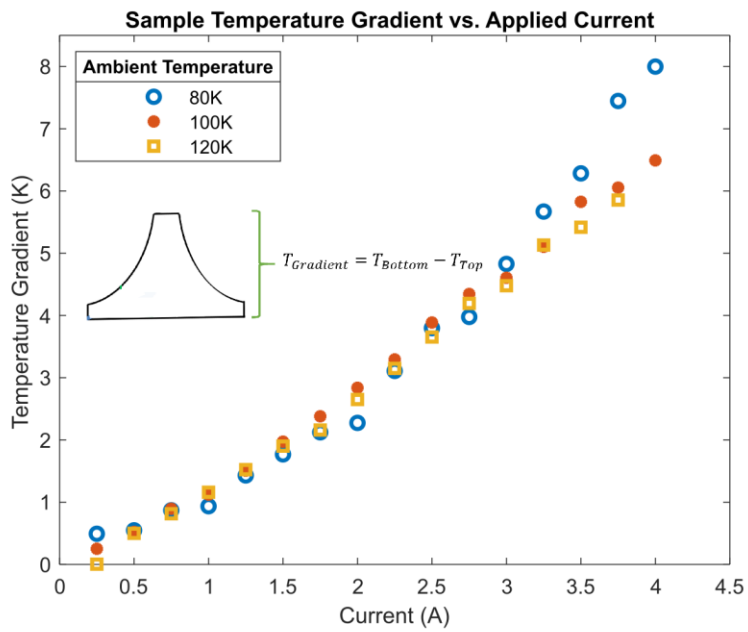

Figure 13: Maximum temperature difference across a bismuth single crystal Ettingshausen cooler.

The sample creates a larger temperature gradient with increased current. A difference of up to 8K was measured across a sample 5mm tall. Similar to the cooling ability mentioned above, the lower ambient temperatures begin to diverge and create a larger temperature difference than the sample did at higher ambient temperatures. This trend can be explained using Equation 3, which is derived from the Nernst and Ettingshausen coefficients [10].

$$\frac{dT}{dy} = \frac{I_x * B_z * N * T}{\lambda * A_c} \tag{3}$$

Where $\frac{dT}{dy}$ is the temperature gradient, B_z is the magnetic field, N is the Nernst coefficient, T is the ambient temperature, λ is the thermal conductivity, and A_c is the cross-sectional area. Given Equation 3, the curve is expected to be linear as current is increased, but as Joule heating increases the sample temperature, the material properties will become non-linear.

4.3 Reverse current

In addition to traditional Ettingshausen cooling techniques, trials were run with the current directed in the opposite direction along the trigonal axis, therefore directing heat from the bottom, to the top of the sample. Figure 14, on the next page, shows the time-dependent temperature response of the reverse current in an 80K ambient temperature.

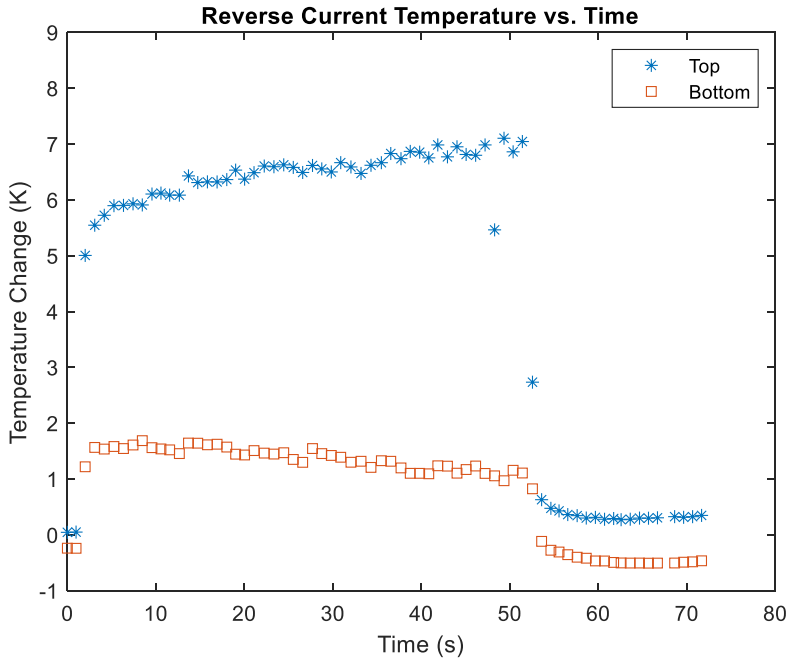

Figure 14: Temperature change when current is reversed, therefore pumping heat to the top of the sample

When the current runs in the opposite direction both the top and bottom of the sample will heat up. This is because heat is pumped to the top of the sample from the Ettingshausen effect, but the top is not connected to a heat sink so the only way it could disperse heat would be radiation to the surrounding cryostat. The bottom does not cool down below ambient temperature for a couple possible reasons. Joule heating will add heat to the system and the heat flow is working against the advantages of the cascade effect described in Chapter 2.

5 CONCLUSION

Ettingshausen coolers can provide an active and responsive cooling method at cryogenic temperatures. Bismuth single crystal has been known to perform as an Ettingshausen cooler and results show interesting behavior in the time domain.

At three different ambient temperatures, the application of an electric current less than 3.00A rapidly creates a steady state temperature gradient across the sample, where the top is cooler than ambient temperature. Higher currents create a larger temperature gradient, but over time Joule heating raises the temperature of the sample to the point where the top is above ambient temperature.

At lower ambient temperatures, the top is able to decrease temperature by a larger magnitude and create a larger temperature gradient across the sample. This agrees with previous research and shows that Ettingshausen coolers are more effective at cryogenic temperatures

5.1 Future Investigations

Joule heating is the greatest limitation in trials at higher electrical currents. In order to increase the performance of a cooler, methods to mitigate this effect should be studied. Future investigations could look at reducing contact resistance between the cooler and heat sink. By doing this, the cooler would more easily distribute heat, therefore delaying Joule heating and allowing the top of the sample to reach a lower temperature.

As described in Chapter 4, it is apparent that the sample will reach a peak cooling potential then gradually heat up as current is applied. The sample may be able to maintain cooling by pulsing the current. The current could be turned on to utilize Ettingshausen cooling, then turned off before Joule heating begins to negate the cooling. This could be done repeatedly to try to maintain cooling without heating up the sample.

Similarly, Woodbridge et. al. [13] study the effects of applying current in different methods than a step input. They found that if the current was ramped then the sample reached a lower temperature. A future study could combine ramp inputs in a pulsing fashion to try to improve performance.

Producing the sample and setting up the experiment was time consuming and limited to a controlled environment. A finite analysis model would provide a relatively quick simulation in a complex application. This could allow for estimates of the effectiveness of an Ettingshausen cooler without having to manufacture it.

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6 APPENDIX

6.1 LabVIEW Virtual Instrument