ABSTRACT

INSTRUMENT TO MEASURE THE HEAT CAPACITY OF SMALL SAMPLES

A calorimeter is used to make measurements of the internal energy of a material in order to probe its thermodynamic properties, such as crystalline lattice stiffness, electronic effective mass, phase transitions, and entropy. Rare-earth metallic compounds are of interest in our lab because they are known to exhibit strongly correlated electron behavior, which gives rise to interesting phenomenon such as conventional and unconventional superconductivity, metal-insulator transitions, magnetism, and the magnetocaloric effect. The temperature dependence of specific heat is an important quantity to investigate of these materials. With limited space of our cryogenic system, we are unable to construct a calorimeter that is perfectly thermally isolated; therefore, the use of a thermal relaxation method for our heat capacity measurements will be used. A discussion on the construction of a calorimeter and implementation of the relaxation calorimetry method will be presented.

Ulises Ivan Urbina
August 2010
INSTRUMENT TO MEASURE THE HEAT CAPACITY OF SMALL SAMPLES

by

Ulises Ivan Urbina

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Master of Science in Physics
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APPROVED

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INTRODUCTION

French scientists Antoine Lavoisier and Pierre-Simon Laplace first put the theory of a calorimeter to work during the winter of 1782-83. Their first calorimeter constructed was a phase transition calorimeter, in which the outer wall insulated an inner wall from the outside environment. The inner wall contained ice, which acted as the measuring device. In the center of the apparatus was a sample chamber. The heat expelled from the sample would go to the inner wall containing ice. The ice would melt and the resulting water would be measured. Knowing the amount of water that melted gave a rough measure of the heat given off by the sample. The heat given off by the sample should be equivalent to the latent heat needed to melt the ice.

In 1845 James Prescott Joule was the first to use a differential method to measure the heat capacity of a substance. Differential method means that the sample is heated in a controlled manner above a reference temperature and the change in temperature is measured. In 1910 Nernst and Euken were able to accurately measure the heat capacity of solids by heating up a sample by a few Kelvin then letting it cool to its initial temperature and repeating this process for a range of temperatures. Using this stepwise temperature method Nernst and Euken were able to find the heat capacity of a solid material over a wide range of temperatures down to 23 K.

Adiabatic calorimeters were the most popular devices for finding the heat capacity of a sample for the most part of the 19th century. In the adiabatic method the sample is isolated from any external heat exchange. The isolation of
the sample is accomplished through various methods such as keeping the calorimeter and the heat shield at the same temperature.\textsuperscript{5}

Automation of specific heat measurements has also been an important contribution in calorimetry. A specific heat measurement is automated by having a computer controller regulate temperature, take measurements, and processes data. Automating a calorimetric experiment began with using servo-mechanisms which regulated temperature through a feedback mechanism.\textsuperscript{3} Computers were later introduced to control all aspects of a heat capacity measurement.\textsuperscript{5,6} Improvements in processing speed have allowed greater resolution of heat capacity measurements by decreasing data taking intervals and thus allowing shorter relaxation times to be measured, which also means that smaller samples can be used such as for example small platinum particles.\textsuperscript{7}

Not only were accuracy and resolution of calorimeters being improved as well as the amount of sample needed was reduced, but also new techniques of measuring heat capacity were being developed. In 1971 a technique of heating up a sample and then letting the temperature relax was developed.\textsuperscript{8} An AC heat pulse method was developed where the input heat pulse with frequency $\omega$ was related to the output ac signal and from this relationship the heat capacity would be found.\textsuperscript{9-10} Numerous other methods were developed and each with their advantages and disadvantages.\textsuperscript{11}

Advances in etching, photolithography and other methods of designing small circuits have been employed in creating calorimeters with the high resolution to measure the heat capacity of materials with masses on the order of $\mu$g and ng.\textsuperscript{12-14} These calorimeters require rather expensive equipment to deposit the components. These calorimeters can have a resolution of $10^{-6}$ to $10^{-10}$ J/K for the heat capacity.
Currently there are several commercially available calorimeters from companies such as Quantum Design, Cryogenic Limited and Anter Corporation. The first problem with these devices is their prices range from a few thousand to several hundred-thousand dollars to purchase. This is problematic for a small research group with a limited budget. Another problem with these devices is the accuracy of the measurement is mostly dependent on data processing software included with the device. For example, after critical examination of a Quantum Design Physical Properties Measurement System heat capacity measurement it was found that the error increased to above 1% below 100 K.

The purpose of this work is to construct a device, which will be used to measure the heat capacity of a material. Due to the constraints of our budget we construct the calorimeter from scratch using typical materials found in cryogenic applications. The cooling system also imposes constraints on the amount of material and size of the apparatus used due to space limitations.
BACKGROUND

The specific heat is a measure of how a material’s temperature changes to a heat input or outflow.\textsuperscript{19-22} There are several methods of measuring heat capacity for different phases of materials such as gases, liquids or solids.\textsuperscript{1, 11} For this work we are mainly interested in the heat capacity of solid materials. Our laboratory is interested in rare earth metallic compounds, which are usually in a crystalline solid state when grown. The technique we will use to measure the heat capacity of rare earth compounds is a constant DC heat pulse relaxation method.

Heat Capacity

The heat capacity is a measure of the amount of heat needed to raise the temperature of an object by one Kelvin, where the object can be composed of more than one element or compound.\textsuperscript{19-22} Heat capacity is an extensive property of a material meaning that it is dependent on its size or amount and is dependent on the composition of the material as well. The units of heat capacity are energy over temperature and are denoted by a capital c. The heat capacity is related to the internal energy of the material. Throughout this thesis, the units that will be used are joules (J) for energy, Kelvin (K) for temperature and grams (g) for mass.

The heat capacity is the actual quantity measured in the experiment. In a measurement, the heat capacity of the sample, as well as the sample holder, heating element, temperature measuring device and additional materials will be lumped together. The heat capacity of the sample is usually of interest so it must be extracted by subtracting the heat capacity of the components and materials. Once the heat capacity of the sample is found, the variable of theoretical interest can be calculated, which is the specific heat.
Specific Heat

The specific heat is a measure of how much heat is needed to raise the temperature of a unit of mass of an element or compound by one Kelvin.\(^{19}\) Specific heat is an intensive property meaning that it only depends on the composition of the material. The units of specific heat are joules over temperature normalized by mass in grams or moles and are denoted by a lowercase \(c\). Once the specific heat of the material is calculated, other variables of interest can be further studied. The specific heat can be used to study the entropy, stiffness of a material, and effective electronic mass for example.

The Einstein-Debye model of specific heat details the contributions from the lattice.\(^{20-22}\) The lattice contribution of the specific heat can tell us the rigidity of the material by extracting the Debye temperature, which is proportional to the cube of the temperature. The Einstein model correctly predicts the specific heat of a crystal at high temperatures, which approaches the DeLong and Petit law.

The specific heat of a material over a temperature range can indicate where a phenomenon known as a phase transition has occurred. A phase transition occurs when some kind of ordering within the material takes place due to a change in temperature or pressure. An example of a phase transition occurs when the magnetic moments align in the rare earth metal gadolinium below its Currie temperature of 292 K making it ferromagnetic.\(^{23}\) Other phase transitions of interest include superconducting, metal-insulator, and other magnetic transitions to just name a few.

Adiabatic System

The ideal calorimeter does not have energy leaks into or out of the system due to perfect thermal isolation from the external environment.\(^{1, 2, 3}\) The thermal conductance between the calorimeter and the heat reservoir is zero. The heat
reservoir is where heat from the calorimeter is transferred and its temperature does not change no matter how much heat it absorbs. A calorimeter consists of a thermometer, a heating element and a sample stage. A constant DC heat pulse is applied through the installed heating element with a constant power of $P_0$ which has units of watts. The temperature of the calorimeter increases to a temperature $(T_0 + \Delta T)$, where, $T_0$ is the initial temperature and $\Delta T$ is the increase in temperature. The temperature remains constant after the heat pulse has been turned off since there is no heat transfer. The sample and the calorimeter have a good thermal contact so they are both at the same temperature. Figure 1 shows a diagram of this method.

![Diagram of a calorimeter method](image)

FIG 1. a) A heat pulse of width $t_f - t_i$ is applied. b) The temperature $T$ response before, during and after the heat pulse as applied in a).

The heat capacity in an adiabatic system can be found by the equation,

$$ C = \frac{Q}{\Delta T} $$

(1)
where $Q$ is the total amount of heat input into the calorimeter for a period $t_w$, and $\Delta T$ is the measured temperature change after equilibrium of the calorimeter has been reached. The heating power being input can be determined by the relation

$$P(t) = I(t) V(t) = \begin{cases} P_0 & t_i < t < t_f \\ 0 & t < t_i, \ t_f < t \end{cases}$$

(2)

where $I(t)$ is the current as a function of time through the heating element and $V(t)$ is the resulting voltage drop as a function of time. The units of power are in watts (W). The total amount of heat input into the calorimeter during a period of time $t_w$ is

$$Q = \int P(t) dt = \begin{cases} P_0 t_w & t_i < t < t_f \\ 0 & t < t_i, \ t_f < t \end{cases}$$

(3)

where the power $P(t)$ is a function of time and $t_w$ is defined as

$$t_w = t_f - t_i$$

(4)

The total heat input is the sum of the power taken for the time interval $t_w$.

**Semi-Adiabatic System**

A typical calorimeter will have some form of thermal link to the outside of the system. This thermal link to the outside allows heat to escape. The thermometers and heating elements typically used in calorimeters are solid-state devices, which introduce electrical wires that provide the thermal link to the outside environment. A semi-adiabatic calorimeter is one, in which there is a heat link but the behavior of the temperature deviates very slightly from the adiabatic behavior. If the heat leak is small enough, then the situation will be close enough to the adiabatic system that the heat capacity can be found using Eq. (1). Figure 2 is a sketch of semi-adiabatic behavior due to a small heat leak.
FIG 2. a). The dashed and solid line represents the heat applied for the adiabatic and semi-adiabatic methods. b) The temperature change $\Delta T$ decreases slowly after the heat pulse is removed. The heat pulse duration $\delta t$ is much shorter than the thermal equilibrium time constant of the system, so as to not allow an appreciable amount of heat to be leaked as compared to the input.

1-$\tau$ Relaxation Calorimetry Method

A calorimeter in the real world contains heat leaks because the components need to be wired to outside measuring devices. The thermal conductance between the calorimeter and the heat reservoir is non-zero and finite. The dynamic interplay between the heat input and heat leaks allow us to use a thermal relaxation method. The 1-$\tau$ relaxation model is a method used when the calorimeter and sample are in good thermal contact. The thermal time constant $\tau$ is related to how fast the material reaches a thermal equilibrium.

The calorimeter and the sample are in good thermal contact so they reach a uniform temperature at the same time. If the sample and calorimeter do not have
good thermal contact, then a 2-\(\tau\) effect appears. Since we are assuming good thermal contact between the calorimeter and sample, the 2-\(\tau\) effect is out of the scope of this work and will not be discussed in detail. The heat pulse is turned on long enough so the calorimeter reaches an equilibrium temperature, which is on the order of 8\(\tau\) in duration. During and after the heat pulse is removed, the temperature of the calorimeter and sample follows in accordance with the solution of the dynamic heat equation

\[
C \frac{dT_\theta(t)}{dt} = P(t) - K_b [T_\theta(t) - T_0], \quad P(t) = \begin{cases} P_0 & t_i < t < t_f \\ 0 & t < t_i \text{ and } t > t_f \end{cases}
\]

(5)

where \(C\) is the constant heat capacity, \(T_0(t)\) is the temperature measured at the calorimeter as a function of time, \(P(t)\) is the thermal energy input into the calorimeter as a function of time, \(K_b\) is the thermal conductance between the calorimeter and heat reservoir and, \(T_0\) is the temperature of the heat reservoir. The dynamic heat equation is derived from energy conservation under the assumption that the specific heat is constant. A constant specific heat can be assumed if

\[
\frac{\Delta T}{T_0} = \begin{cases} > 1\% \text{ and } < 3\% & t_i < t < t_f \\ 0 & t < t_i \text{ and } t > t_f \end{cases}
\]

(6)

is kept small enough. We also find from the dynamic heat equation that the thermal conductance is

\[
K_b = \frac{P}{\Delta T}.
\]

(7)

The thermal conductance for the link from the calorimeter to the reservoir is assumed to be much less than that for the sample and the calorimeter. The solution of the dynamic heat equation for the temperature trace as a function of time is

\[
T_\theta(t) - T_0 = \begin{cases} \Delta T \left[1 - \exp\left(-\frac{t-t_i}{\tau}\right)\right] & t_i < t < t_f \\ \Delta T \exp\left(-\frac{t-t_f}{\tau}\right) & t_f < t < \infty \end{cases}
\]

(8)
where $\Delta T$ is the maximum temperature gradient between the calorimeter and the heat reservoir $T_0$. Figure 3 shows a diagram of the traditional relaxation method.

![Diagram of the traditional relaxation method](image)

**FIG. 3.** a) A heat pulse is applied for a period of $t_f - t_i$. b) The temperature response of the applied heat pulse. The heat pulse is applied long enough to allow the system to reach an equilibrium temperature at $(T_0 + \Delta T)$ which is on the order of $8\tau$.

In solving the dynamic heat equation with the situation that there is a large enough thermal conductance between the calorimeter and heat reservoir and a heat input long enough for the temperature to reach equilibrium, we find the heat capacity to be,

$$C = \frac{P \tau}{\Delta T}. \quad (9)$$

We also find in solving the dynamic heat equation that the relationship between the thermal time constant, heat capacity, and thermal conductance is

$$\tau = \frac{C}{K_b}. \quad (10)$$
Modified 1-τ Relaxation Calorimetry Method

The disadvantage of using the traditional 1-τ thermal relaxation method is that the heat pulse must be long enough so the calorimeter and sample reach an equilibrium temperature plus an additional time for the temperature to relax back to $T_0$. The thermal relaxation time for our calorimeter is on the order of $10^2$ to $10^3$ seconds. The solution is to use a modified 1-τ relaxation method, which uses a shorter finite width heat pulse. The modified 1-τ method does not need the calorimeter to reach an equilibrium temperature. Figure 4 shows an example of a short heat pulse temperature trace.

FIG 4. a) A short heat pulse applied for a finite width $t_w$ with comparison to the long heat pulse as represented by the dashed line. b) The temperature response for the applied heat pulse as compared to the traditional long heat pulse method shown by the dashed line.
To calculate the specific heat using the dynamic heat equation for the modified 1-τ model we need to solve for $T_\theta(t)$ in Eq. (5) during and after the heat pulse. We find that the temperature follows an exponential increase during the heat pulse and decrease after the heat pulse as was the case with the traditional relaxation method. The heat pulse width is necessary to know in order to calculate the specific heat whereas in the traditional method it was not needed. The solution for the temperature trace during the heat pulse is

$$
\Delta T_\theta(t) - T_0 = \Delta T'\{1 - \exp[-(t - t_i)/\tau]\}, \quad t_i < t < t_f, \tag{11}
$$

where $t_i$ is the time the heat pulse was turned on and $\Delta T'$ is the measured temperature difference. $\Delta T'$ is related to $\Delta T$ in the traditional relaxation method by the relation

$$
\Delta T' = \Delta T\left[1 - \exp\left(-\frac{t_w}{\tau}\right)\right], \tag{12}
$$

where $t_w$ is the width of the short heat pulse and $\Delta T$ is the equilibrium temperature change for the traditional method. The solution for the traditional 1-τ solution is shown in detail in the Appendix. If $t_w$ is taken to be large in Eq. (12) we reach the equilibrium same temperature change $\Delta T$ as in the traditional long heat pulse method. The solution for the temperature trace after the heat pulse is turned off is

$$
\Delta T_\theta(t) - T_0 = \Delta T' \exp\left[-\frac{(t - t_f)}{\tau}\right], \quad t_f < t < \infty, \tag{13}
$$

where $t_f$ is the time when the heat is turned off and $\Delta T'$ is the measured temperature difference. We thus find the heat capacity for the short heat pulse method to be

$$
C = \frac{P_0\tau}{\Delta T\left[1 - \exp\left(-\frac{t_w}{\tau}\right)\right]} \tag{14}
$$
EXPERIMENT

Materials

The materials need to be chosen so that the calorimeter can be thermally isolated from the ambient environment. The heat capacity of the sample holder, components and materials in proximity to the sample must be kept to a minimum. The calorimeter consists of a sapphire disk as the platform, a solid-state thermometer and a heating chip. The sample is assumed to have good thermal contact with the sample platform.

Calorimeter Materials

A sapphire disk is chosen for the calorimeter sample stage because its crystalline properties allow it to reach a uniform temperature rather quickly. At lower temperatures the thermal energy in a crystal is propagated throughout the lattice by vibrations, which are known as phonons.\textsuperscript{24} The thermal conductance for a good crystal is proportional to $T^3$ due to the scattering of phonons. Sapphire was also chosen because it is an electric insulator, so its electronic contribution to the specific heat is zero compared to that of a metallic crystal such as copper.

The calorimeter needs to be thermally isolated from the thermal reservoir, which is accomplished with the use of certain materials and construction methods. The calorimeter is suspended by cotton threads because they are poor thermal conductors, do not burn easily during repairs with heat and, are relatively strong. The cryogenic wires connecting the thermometer and heater chip are lengthened to 406 mm in order to decrease their thermal conductance, which is described by the Fourier heat flow law as shown in Eq. (15),
\[ \frac{\Delta Q}{\Delta t} = -\kappa \frac{\Delta T}{\Delta x} \]  

where \( \Delta Q/\Delta t \) is the heat flow rate, \( A \) is the cross sectional area of the wire, \( \Delta T \) is the temperature difference between both ends of the wire, \( \Delta x \) is the distance between both ends, and \( \kappa \) is the thermal conductivity, which is a characteristic of a material. The heat flow rate decreases as the wire is lengthened. To further decrease the thermal conductance through wires, between the calorimeter and heat reservoir, their diameter meter is chosen to be 0.038 mm.

The heater chip is a resistor made of a SiO\(_2\) thin film on a silicon wafer with gold contact pads.\(^{25}\) The small size of the heater chip, 1.02mm x 1.02mm x 3mm (W x L x H), introduces a small amount of heat capacity into the background measurement. The resistance of the heater chip stays fairly constant within the temperature range of our interest. The resistance of the heater is measured using a four-wire measurement during the experiment in order to know accurately how much power is being input.

The thermometer used for the calorimeter is a Cernox model CX-1030-BG resistive temperature device.\(^{26}\) The resistance of the thermometer decreases with increasing temperature, and is important to know accurately. The change in resistance response to the change in temperature of the thermometer is on the order of \(-1\times10^{-1}\) Ohms/K. A four-wire method is used to measure the resistance of the thermometer in order to know the temperature accurately. A four-wire resistance measurement is more accurate than a two-wire measurement because the resistances of the leads are eliminated in the four-wire measurement whereas the lead resistance is included in a two-wire measurement. The leads of the thermometer are thermally anchored to the sapphire disk using varnish to reduce unwanted heat leaks.\(^{22}\)
The resistance of the thermometer and the heater chip is measured using 0.038 mm diameter constantan wire. Constantan wire is used because it has a very small temperature coefficient on the order of $10^{-6}$ meaning that its physical properties such as resistance and coefficient of thermal expansion will stay fairly constant over a wide range of temperatures. Constantan is a 55% copper and 45% nickel alloy and is a typical material in cryogenic applications.

Heat shrink tube is used to hold in place and isolate any cryogenic wire inside of the space that is in close proximity to the calorimeter from leaking heat. The cryogenic constantan wires are soldered to 0.127 mm copper wires, which are wound on the outside of the copper cylinder. Any surface where electrical wires are making contact with the copper is covered using a very thin piece of cigarette paper in order to avoid electrical shorts, which could produce accidental grounding from exposed wires. A thin monofilament nylon fishing line is used to tie down any wire that could vibrate.

**Calorimeter Construction**

A copper piece of oxygen-free high-conductivity (OFHC) copper was machined to the specifications given in Fig. 5. An OFHC copper was chosen for its good thermal conductance because it will make direct contact with the cryocooler and it will act as part of the thermal reservoir. The temperature will be regulated at the cryocooler and so the calorimeter supporting structure needs to conduct heat very well. The size of the calorimeter was chosen due to the size of the cryocooler space in, which it will be used.

In order to reduce heat leaks from the cryogenic wires they are both insulated by threading them through heat shrink tube. The cryogenic wires’ length is increased to reduce heat leaks into the calorimeter. Heat shrink tube is secured
FIG 5. Shown is a mechanical drawing of a cross-section view of the copper structure that encloses the calorimeter. The first and third platforms are 6.35 mm thick circular disks with 38.1 mm diameter. The second platform is a cylindrical piece of OFHC copper. (Sketch done by Johnathon J. Thompson).

along the inside of the central copper piece using monofilament fishing line. The cryogenic wires are wound twice around the inside perimeter of the copper structure and threaded through the heat shrink tubes. The cryogenic wires are held in place by tying them to the cotton wires supporting the calorimeter.

The first platform will be screwed on top of the cryocooler. The third platform will cap the top of the second platform. The 25.4 mm diameter cavity will contain the calorimeter itself. Four Phillips head screws will firmly hold all three platforms together. A diagram of the fully constructed calorimeter can be seen in Fig. 6.
Copper wires with a diameter of 0.127 mm are soldered directly to the cryogenic wires. The copper wires are used because they are stronger and will break less easily than the cryogenic wires when the calorimeter is being handled. The other end of these copper wires contains a four-pin header male connector, which will connect to wires from the cryocooler containing female four pin header connectors. The copper wires are wound around the outside well of the central copper piece. The heat radiated from these copper wires will go directly into the copper structure.

The copper wires are held firmly in place within the well by gluing them with a varnish. The varnish prevents the wires from vibrating and thus producing any electromagnetic noise since they carry current. After the varnish has completely cured, a layer of Teflon tape is wrapped directly over the copper wires to hold them in place. The Teflon tape is also used to protect the copper wires.
from the final layer of yellow Mylar tape because the Mylar tape can strip the copper wires of their insulation.

The calorimeter is floated inside the copper structure to keep it thermally isolated from the outside environment. The calorimeter is suspended in the center of the copper structure using cotton threads. The cotton threads are made taught to keep the calorimeter from vibrating and introducing electromagnetic noise. Cotton thread is chosen over fishing wire because it is more resistant to heat and does not break. A soldering gun will be used to repair or replace any soldering joints inside the instrument so the use of cotton prevents accidental breaks.

The calorimeter contains the thermometer and heater chip on opposite sides of the sapphire disk. The thermometer is placed directly in the center of the opposite side where the sample material will be placed. The heater chip is placed on the edge of the disk to give the sample material a maximum amount of space. The thermometer and heater chip are glued on the disk using a varnish. The quantity of varnish used to glue these components is just enough to glue them to the disk but not enough to cover the entire component. The leads going to the thermometer are thermally anchored to the sapphire disk using the same varnish. Figure 7 shows the bottom and top of the actual calorimeter.

The cryogenic wires are a shielded twisted pair constantan wire positive and negative current or voltage leads. The pair of twisted wires is then twisted with another pair of twisted wires, which are the positive and negative voltage leads. Figure 8 shows a schematic of the twisted pair wires. Current and voltage leads of the same polarity are soldered together, which will then be soldered on to one leg of either the heater or thermometer.
FIG 7. Image of the bottom (a.) and top (b.) of the calorimeter. There is no sample installed on the calorimeter. The outer orange object is the copper structure.

FIG 8. Two sets of twisted pair wires are twisted in order to reduce electromagnetic noise.
Experimental Methods

The copper structure containing the calorimeter is screwed on top of the closed cycle cryocooler. The copper sample mount found on top of the cryocooler comes into direct contact with the calorimeter enclosure. Since the cryocooler mount contains the temperature controlling heater and thermometer the cryocooler sample mount and the cryocooler holder then act as the heat reservoir.

The temperature of the heat reservoir is determined by monitoring the resulting voltage of the Silicon Diode thermometer found near the base of where the copper structure will be screwed. A Lakeshore 330 temperature controller (LS 330) is used to monitor the Silicon Diode model SD5598 thermometers resulting voltage from being excited with a constant 10µA current. The SD thermometer is a negative temperature coefficient meaning that as temperature increases that voltage drop decreases.27

The calorimeter’s temperature is monitored using a Cernox thermometer model number CX-1030-BG. A Lakeshore 340 (LS340) temperature controller sends an excitation current through the thermometer to energize it in order to get a signal response.27 The thermometer is provided with a recommended excitation current which, we use a lower value to avoid self heating (see Table 1). If a temperature sensor is not provided with sufficient excitation current the signal-to-noise ratio will be low and thus the resistance measurements cannot be trusted. If too much current flows through the sensor then excess heating will occur.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Recommended Excitation I (A)</th>
<th>Used Excitation I (A)</th>
<th>Resistance of RTD (Ohms)</th>
<th>Power (Watts)</th>
</tr>
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<tr>
<td>&gt;10K</td>
<td>140 µA or less</td>
<td>10 µA</td>
<td>&gt; 70</td>
<td>&gt; 7 nW</td>
</tr>
<tr>
<td>&lt; 130 K</td>
<td>140 µA or less</td>
<td>30 µA</td>
<td>&lt; 70</td>
<td>&lt; 63 nW</td>
</tr>
<tr>
<td>&gt;130 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To reduce unwanted heat leaks from thermal conduction of gases, the chamber in which the calorimeter is located is evacuated down to roughly $10^{-5}$ to $10^{-6}$ Torr. A radiation shield is screwed inside the aluminum can, which is inside the vacuum space. The radiation shield reduces the electromagnetic radiation from external sources. The radiation shield also maintains a uniform environment within the space where the copper structure is located. Figure 9 shows a schematic of the cryocooler with the calorimeter installed.

Once the vacuum reaches about $10^{-5}$ Torr, the cryogenic compressor can be turned on. The cryogenic compressor is turned on until after a sufficient vacuum has been reached to avoid getting any condensation inside the calorimeter, which will create ice. The calorimeter is then cooled down to the lowest temperature for the experiment.

Using a customized Labview program, the temperature is controlled and regulated at the desired reservoir temperature. Once the temperature is stable enough at the reservoir temperature, a current is sent through the heater chip to increase the temperature of the calorimeter. The heat pulse is applied for a finite period $t_w$, usually for about one minute. The amount of current used to heat the calorimeter is dependent on the criteria set for $\Delta T / T_0$. The criteria set for the heat input is $1% < \Delta T / T_0 < 3\%$. This criterion is needed to satisfy the assumption that the heat capacity is constant for each data set. This criterion also reduces the amount of heat being leaked in from the current-carrying cryogenic wires. The lower bound of the criteria is set such that the noise in the measurement is smaller than the sensitivity of the electronic equipment and RTD.

The modified Labview program only does a $1 - \tau$ fit at run time. Since the thermal equilibrium time is not constant for the calorimeter or sample we can see behavior other than a $1 - \tau$ profile. Using customized temperature trace fitting
program, a best fit is chosen by eye after the data has been taken. Once a best-fit curve is chosen, the resulting fit is used to calculate the heat capacity more accurately.

FIG 9. A front view of the cryocooler with the calorimeter installed. The entire space within the outer shield is vacuumed to about $10^{-5}$ Torr. As can be seen there is limited space to further isolate the calorimeter in order to achieve a good adiabatic environment.
RESULTS AND DISCUSSION

Background Heat Capacity

To get an accurate specific-heat measurement, the heat capacity from the addenda needs to be known in order for it to be subtracted from future measurements. The addendum includes the sapphire disk, the thermometer, the heater chip, bonding grease and any materials that are in proximity to the calorimeter. The first measurement to be completed is the heat capacity of the background. Figure 10 shows the background heat capacity measurement of the calorimeter.

![Graph showing background heat capacity](image)

FIG 10. Background heat capacity for temperature range between 15 K to 310 K.

The heat capacity of the calorimeter is not constant. The heat capacity value of each data point is that of the median value for the temperature rise $\Delta T$ and is assumed to be a constant value for that interval due to the $\Delta T/T_0$ criteria set. At 20
K the background heat capacity is about $3 \times 10^{-4}$ J/K and increases to approximately 0.1 J/K at room temperature.

The largest contributor to the heat capacity of the addenda is the sapphire disk. The sapphire disk is an artificially grown sapphire disk with a diameter of 9.525 mm and thickness of about 0.508 mm provided by the Swiss Jewel Company. Using the density of the sapphire 3.97 g/cm$^3$ and its dimensions we find the mass of the disk to be 0.1441 g. Using the calculated mass of the disk and the specific heat data from literature we can calculate the heat capacity of the disk and compare it with our background heat capacity. Figure 11 shows the comparison between our background heat capacity and the heat capacity of sapphire with a mass of 0.1441 g.

![FIG 11. The measured background heat capacity is in good agreement to the calculated heat capacity of the sapphire disk using literature values.](image-url)
Background Thermal Conductance

Another important specification of interest is the thermal conductance between the calorimeter and the heat reservoir. Most of the heat leaks are from the electrical wires connecting the thermometer and heater chip. The thermal conductance value is unique to each calorimeter since no two are constructed exactly the same. The thermal conductance can be obtained from the background heat capacity measurement by using Eq. (6). Figure 12 shows the thermal conductance schematic diagram.

![Figure 12](Image)

FIG. 12. Schematic of the thermal conductance $K_b$ between the calorimeter and thermal reservoir or heat reservoir.

The thermal conductance of the background increases with temperature as can be seen in Fig. 13. The higher the thermal conductance, the more easily heat flows from the calorimeter to the reservoir. The thermal conductance is related to the thermal equilibrium time as seen in Eq. (10).
FIG 13. Thermal conductance of the calorimeter without a sample. The thermal conductance goes from $1.0 \times 10^{-5}$ at 20 K to $7.0 \times 10^{-4}$ at 300 K.

**Thermal Equilibrium Time Constant**

The thermal equilibrium time of the calorimeter is a characteristic of the calorimeter useful in troubleshooting as well as knowing the resolution. The shorter the equilibrium time, the fewer data points are going to be recorded for that particular temperature region. If the thermal equilibrium time is too long, then the temperature measurement for that particular region will take an excessive amount of time. The LS340 takes 10 readings per second when the thermal compensation option is on. At low temperatures, the data-taking rate becomes important because the thermal time constant gets shorter (see Fig. 14). At 20 K the thermal time constant has a value of 45 s. Using the short heat pulse method and setting $t_w$ to 60 s we would take 600 data points.
FIG 14. Plot of the thermal time constant $\tau_b$ for the empty calorimeter. The thermal time constant is related to the thermal connection between the bath and calorimeter. The calorimeter reaches a uniform temperature below 100 K and above 250 K relatively quickly where as the time constant in the central temperature range because the ratio of heat capacity to thermal conductance is largest in that region.

The thermal time constant is not constant for the background. When a sample of different composition than that of the calorimeter is mounted its thermal equilibrium time will be different as well. Due to the difference in the internal thermal equilibrium times of calorimeter and sample we will see a 2-$\tau$ profile in the temperature response.

**Specific Heat of Standard Copper Sample**

In order to know if the calorimeter works, a measurement of the specific heat of a well-known sample must be taken. The sample chosen for the specific heat is an OFHC copper disk of 228.3 mg. The sample copper piece had dimensions of 5.130 mm diameter and 1.245 mm thickness. The copper disk was glued on to the sapphire disk with 1 to 2 mg of Apiezon N grease. The heat
capacity of the Apiezon N grease can be taken into account if absolute accuracy is needed.\textsuperscript{30}

To find the specific heat of a material the heat capacity of the calorimeter with the mounted sample must be measured. The heat capacity of the background is subtracted from the total heat capacity found when the sample was mounted in the calorimeter. Once the heat capacity of the sample is found it is normalized by its mass to calculate its specific heat.

By doing the specific heat measurements on the copper disk we find fairly good agreement with the specific heat found in literature (see Fig. 15). At temperatures below 100 K and above 200 K we get specific heat values in good agreement with values found in literature.\textsuperscript{31} For temperatures between 100 K and 200 K there is a slight deviation in the specific heat when compared with the literature data. The reason for the deviation is due to the cryogenic wires connecting the heating element having a resistance comparable to the heater chip. The cryogenic wires connecting the calorimeters components are lengthened in order to decrease their thermal conductance. By increasing the length of the wires the resistance was also increased thus increasing the amount of heat they leak into the calorimeter.

The extra heating coming from the wires was confirmed by using a lower heating power or reducing the current sent through the heater as was initially set. Lowering the heater current also lowered the criterion set for $\Delta T/T_0$ from

$$3\% < \frac{\Delta T}{T_0} < 7\%$$

to its current. This change in criterion resulted in the measured specific heat to be closer to the literature data.
FIG 15. The specific heat of 223.8 mg copper disk compared with specific heat values found in literature is found to be in good agreement.

Previously, we had an error of about 10% for temperatures around 100 K. Currently, we have a maximum error of 6.5% for temperatures around 100 K for the measured copper specific heat. Below 100 K, the percent error in the specific heat drops below 1%. The error for the specific heat between 200 K and 300 K and 285 K is about 1%. The noise in the region above 285 K increases the error from 2% to 4%.
CONCLUSION

The objective of this research was to produce an instrument that would give our lab the capability to measure the heat capacity and thus to determine the specific heat of a material. The design of the calorimeter built was chosen for its robust use in that several methods can be used such as adiabatic, semi-adiabatic and relaxation calorimetry. The design of the cryocooler also dictated to a degree the construction of the calorimeter.

The materials of the calorimeter were chosen to reduce the addenda heat capacity to allow a better resolution of the heat capacity and allow the use of a smaller sample. For example, the sapphire disk is a good a thermal conductor, but not as good as copper yet the addenda heat capacity is zero. The use of small components brings in a smaller amount of addenda as well as decreasing the thermal equilibrium time of the calorimeter. The construction of the calorimeter in conjunction with the chosen materials allowed a sufficient thermal isolation to use a thermal relaxation method taking into consideration the constraints set by the design of the cryocooler.

The calorimeter was not designed to use a particular method of calorimetry. Due to the change in the thermal time constant and thermal conductance throughout the experiment either, adiabatic, semi-adiabatic or 2-\(\tau\) behavior can arise. The different situations are handled partly by customized software in conjunction with the experimenter. After raw data has been recorded it is then further analyzed with separate software, which includes analysis for semi-adiabatic, 1-\(\tau\), and 2-\(\tau\) relaxation methods that can be chosen by the user.
Using a modified short heat pulse relaxation method the copper standard specific heat measurement is in good agreement with values found in literature. The main advantage of the short heat pulse method is that it greatly reduces the experiment time by an amount of approximately 4 to 7 times the thermal time constant. The temperature stabilization time only depends on the thermal equilibrium time and thermal conductance so does not change with using the modified method.

There was a deviation of the heat capacity measured for the copper sample due to an excess of heat being leaked through the cryogenic wires connecting the heater chip. To alleviate this problem the heater chip will be replaced with one of higher resistance. The resistance of the heater chip is 250 $\Omega$ and will be replaced with one of 2 k$\Omega$. The new heater chip will have eight times the resistance thus will need $\sqrt{8}$ of the current to output the same amount of heat since power is proportional to the square of the current.

The noise above 285 K is due to not having a sufficient vacuum. To reduce the noise in the measured heat capacity a better vacuum needs to be achieved. For the heat capacity measurements within this work the best vacuum achieved was approximately $2 \times 10^{-5}$ Torr. Future heat capacity measurements we will use a vacuum of approximately $1 \times 10^{-6}$ Torr.
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APPENDIX
The dynamic heat equation can be solved exactly if heat capacity $C$ is assumed to be a constant if $\Delta T/T_0$ is small and there is good thermal contact between the sample and calorimeter. $\Delta T$ is the temperature difference when equilibrium is reached and $T_0$ is the initial temperature.

$$C \frac{dT_\theta(t)}{dt} = P(t) - K_b [T_\theta(t) - T_0]. \tag{A.1}$$

During the heat pulse $P(t)$ is a constant value $P_0$, and elsewhere it is zero. The derivative of a function $T_\theta(t)$ shifted by a constant value $T_0$ is equal to the derivative of the function

$$\frac{dT_\theta(t)}{dt} = \frac{d[T_\theta(t) - T_0]}{dt}, \tag{A.2}$$

because the temperature difference does not depend on the initial temperature. A substitution can be made where

$$x(t) = T_\theta(t) - T_0, \tag{A.3}$$

which now gives us

$$C \frac{dx(t)}{dt} = P(t) - K_b [x(t)]. \tag{A.4}$$

$P(t)$ takes the following values in the following regions

$$P(t) = \begin{cases} P_0 & t_i < t < t_f \\ 0 & 0 < t < t_i \text{ and } t > t_f. \end{cases} \tag{A.5}$$

We then solve Eq. (A.4) for each region. For the regions of $0 < t < t_i$ and $t_f < t < \infty$ we get

$$C \frac{dx(t)}{dt} = -K_b x(t). \tag{A.6}$$

We let

$$\tau = \frac{C}{K_b}, \tag{A.7}$$
which is the thermal equilibrium time constant. For the region of $t_f < t < \infty$ we integrate Eq. (A.6) to find

$$T_o(t) - T_o = \Delta T \exp\left[-\frac{(t-t_f)}{\tau}\right] \quad (A.8)$$

For the region before the heat pulse or $0 < t < t_i$ we get

$$T_o(t) - T_0 = 0. \quad (A.9)$$

Next we solve for the region $t_i < t < t_f$. For this region we have $P(t) = P_0$ and substitute into Eq. (A.4) to get

$$C \frac{dT_o(t)}{dt} = P_0 - K_b[T_o(t) - T_o]. \quad (A.10)$$

We again use the substitution $A.3$ to get

$$C \frac{dx(t)}{dt} = P_0 - K_b[x(t)]. \quad (A.11)$$

We again do the substitution

$$y = K_b x(t) - P_0, \quad (A.12)$$

and its derivative into Eq. (A.11) to get

$$\tau \frac{dy}{dt} = -y, \quad (A.13)$$

where $\tau$ is defined in Eq. (A.7). Solving for the situation during the heat pulse and putting back the substitutions with the initial condition

$$T_o(t = t_i) - T_0 = 0, \quad (A.13)$$

we find that

$$T_o(t) - T_0 = \Delta T \{1 - \exp\left[-\frac{(t-t_i)}{\tau}\right]\}, \quad (A.14)$$

To find the heat capacity we substitute Eq. (A.14) into Eq. (A.11). To simplify we set time $t = t_i$. This is a valid substitution since we are assuming the heat capacity is constant throughout the interval $t_f$ to $t_i$. We find that the heat capacity is
We can also find the thermal conductance by substituting Eq. (A.7) into Eq. (A.15). The thermal conductance is constant and is found to be

\[ K_b = \frac{P_0}{\Delta T} \]  

\[ C = \frac{P_0 \tau}{\Delta T}. \] (A.15)
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Type full name as it appears on submission

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