

Constructing a Relaxation Calorimeter

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Abstract

Relaxation calorimetry is a technique used to determine the specific heat of various materials. Many strongly correlated electron materials exhibit interesting phenomenon such as superconductivity, magnetism, metal to insulator transition, and structural transformations. With the specific heat data we can determine the temperature at which many of these phase transitions occur. The specific heat can also provide insight into the internal energy of a material, which includes properties such as entropy, electronic behavior, and lattice stiffness. By developing a better understanding of these properties; the strongly correlated electron materials, can then be applied to new technology such as energy transfer and storage. The objective of our research is to develop calorimeters used to study the specific heat of rare earth compounds. Our calorimeter is connected to a cryocooler, which is isolated from the environment by a heat shield and vacuum shroud. When in operation this creates a cold reservoir referred to as the bath. The bath can be regulated between 11 K and 300 K. Inside the calorimeter the sample is mounted onto a substrate suspended by cotton threads, which thermally isolates the calorimeter from the bath. However, electrical wires attached to the calorimeter's heater and thermometer cause a finite thermal link to the bath. In addition, depending on the thermal contact between the sample and calorimeter substrate, relaxation calorimetry will show either a $1-\tau$ or $2-\tau$ effect. If the internal thermal conductance between the sample and calorimeter is large relative to the external thermal conductance from the calorimeter to the bath, a $1-\tau$ effect can be seen. This is characterized by a smooth exponential decay of the time dependent temperature curve. When the internal thermal conductance is small or comparable to the external thermal conductance, a more complicated decay curve is observed, known as the $2-\tau$ effect. In our experiment we use a Labview program that analyzes data by using $1-\tau$ and $2-\tau$ models to determine the heat capacity of the sample. By continuing to improve upon the design of our relaxation calorimeters we can obtain more accurately measured data.

Keywords: Relaxation, Calorimetry, τ

1. Introduction

Relaxation calorimetry is a technique used by our lab to study the thermodynamic properties of strongly correlated electron materials. The properties investigated include unconventional superconductivity, metal to insulator transitions, ferromagnetism, antiferromagnetism, as well as other heavy fermion behaviors. These interesting phenomena are produced by the strong interactions between electrons, which causes their behavior to deviate from the Fermi-liquid model.² This model describes the properties of most simple metals very well at low temperature. By measuring the specific heat for a material we can gain information about its internal energy, entropy, effective mass of conducting electrons, as well as its Debye temperature, which determines the stiffness of its crystal lattice structure. Due to the large amount of information that can be obtained with calorimetry this measurement technique has become the keystone to most Condensed Matter Physics research. In this report, we will describe the detailed construction process of a calorimeter as well as explain the experimental setup and methods used to analyze the collected data.

2. Building a Relaxation Calorimeter

In order to obtain an accurate measurement of a material's specific heat it is important to construct the calorimeter in a way that thermally isolates the sample and its substrate mount from the environment as best as possible. In our calorimeter the sample-substrate is suspended by cotton threads, which thermally isolates it from the calorimeter's outer casing, but wires attached to the heater and thermometer chips allows heat to escape to the cold reservoir. When building the calorimeter it is important that the materials be specifically chosen for their thermal and electrical properties. Figure 1 shows a schematic of the setup of a calorimeter. The external electrical wires and outer casing of the calorimeter are made of copper. Copper's low electrical resistivity is important for the wires, while its high thermal conductance allows the outer casing to act as a heat shield keeping the sample substrate thermally isolated from the heat radiation of the environment. The internal wires are made of manganin, instead of copper, because manganin has a temperature coefficient of resistivity nearly 2000 times less than that of copper⁶. This keeps the wires thermodynamic properties, such as resistance and conductivity, from changing as drastically with the change in temperature. It also keeps a reasonable level of thermal impedance to prevent a huge heat leak.

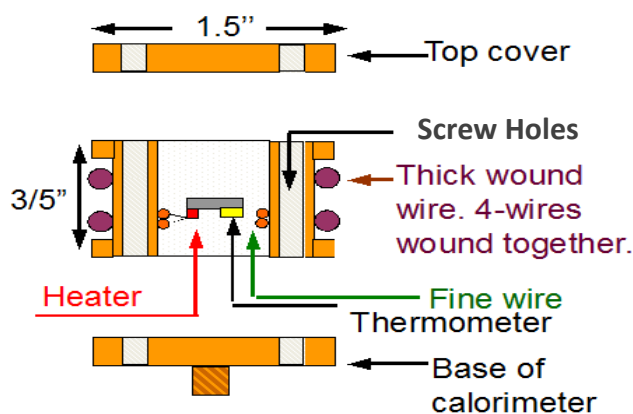


Figure 1: A schematic of the calorimeter.

The interior and exterior faces of the calorimeter are lined with cigarette paper to reduce the chance of electrical shortage to the casing. Varnish is used to glue the paper and wires into place. Two 16-inch-long copper cables are wrapped 3 times around the exterior of the calorimeter. An extra 6 inches are left in order to connect the wires to the electrical connections. The exterior ends of the copper cables are soldered to two electrical connectors, which can easily be plugged into the wiring system of the cryocooler to provide the room temperature connection to measurement equipment. The two manganin cables, which are connected to the copper wires by small solder pads, are 1.5 inches long and connect to the heater and thermometer on the calorimeter, respectively. Both cable types consist of four small wires twisted together in pairs with opposite polarities in order to reduce magnetic interference. These wires also provide the standard four wire measurement to accurately determine the resistance of the thermometer and the power of the heater. Once the wires are mounted into place they are tied down with cotton thread and fishing line. Plastic tubing is also used to insulate the internal manganin wires. Teflon tape and a 3M Mylar tape are then wrapped over the exterior wires to protect them from environmental hazards.

The substrate, which contains the heater and thermometer, is the mounting platform for the sample. This is made of a sapphire disk because its high thermal conductivity, 42 W/(m K) at room temperature, allowing it to distribute heat evenly to the sample^{5,6}. Four holes, used to suspend the substrate with cotton threads, are drilled and polished at an even spacing. Cotton thread is used due to its low thermal conductivity. On the bottom surface of the disk the heater and thermometer are glued into place with varnish. The heater is approximately 2000 ohms and has dimensions of 1 mm x 1 mm x 0.2 mm. The thermometer is a Cernox resistor with a 40 Ω resistance at room temperature and was calibrated by being placed in the cryocooler with a pre-calibrated thermometer⁴. Resistance of the Cernox thermometer was monitored by using a Lakeshore resistance bridge. The top and bottom copper covers are then screwed into place completing the calorimeter.

3. Experimental Setup

For our tests the calorimeter was held at a reasonably constant pressure below 10^{-5} torr and data was intermittently collected over the temperature range of 11 K to 300 K. The finished calorimeter is first mounted onto the cold head of the cryocooler without a sample, in order to measure its background heat capacity. This background data must be collected and then subtracted from the overall sample data, collected later, in order to accurately determine the heat capacity of the sample. The cold reservoir is the environment created around the calorimeter by attaching it to the cold head of a cryocooler and vacuum pump. This allows us to create a closed system where the temperature and pressure can be monitored. The heat shield of a cryocooler blocks the heat radiation from the external environment, the same way that the calorimeter casing does. While the vacuum shroud allows us to drop the system to an extremely low pressure, approximately 10^{-5} torr, by using a turbo pumping station. Once the pressure is sufficiently low a test data point is taken at room temperature in order to ensure that the device is working properly. Then a helium based cooling unit is used to bring the systems temperature down to approximately 11 K. In our experimental setup Keithley multimeters and Lakeshore resistivity bridges are used to monitor the experiment. A Labview program, developed within our lab was also used to record the data and monitor the aforementioned devices automatically.

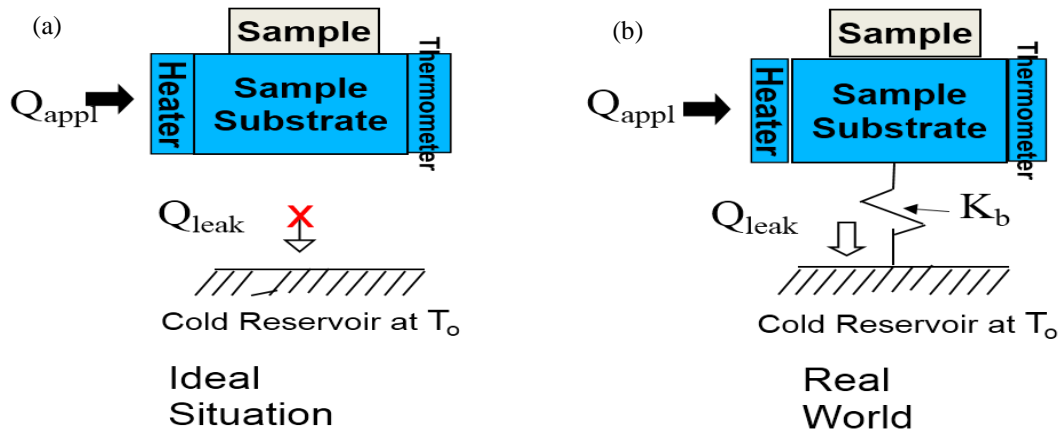


Figure 2: (a) Model for an ideal adiabatic calorimetry. (b) Model for a semi-adiabatic calorimetry

4. Calorimetry

In ideal adiabatic calorimetry a system is considered to have a perfect thermal isolation from its environment. This means that there is no heat leaked from the sample-substrate into the bath, shown in Fig. 2(a). This type of system is impossible to construct because of unavoidable heat exchanges caused by electrical wires and out-gassing of materials. However, as shown in Fig. 2(b), if the heat leak (Q_{Leak}) is small enough (i.e. the thermal conductance, K_b , is also small) then a “semi”-adiabatic form of calorimetry can still be used to measure the heat capacity. With the conservation of energy (Eq. (1)) we can see that the heat capacity, measured by adiabatic calorimetry, is calculated by dividing the amount of heat applied to the system by the change in temperature.

$$Q_{appl} = C\Delta T \rightarrow C = \frac{Q_{appl}}{\Delta T} \quad (1)$$

where Q_{appl} is the heat applied to the system, C is the heat capacity of the material and ΔT is the change in temperature. As previously mentioned, electrical wires can cause a significant amount of heat leak. This makes relaxation calorimetry a more appropriate technique for measuring the heat capacity of a sample. When the sample and the calorimeter have a good thermal contact between them there will only be one thermal relaxation time involved. This is known as the 1- τ method. Figure 3 (a) displays the time dependence of an applied heating power ($P(t)$) and the calorimeter temperature ($T_\sigma - T_0$) in a conventional 1- τ relaxation calorimetry. A DC power input is applied for a

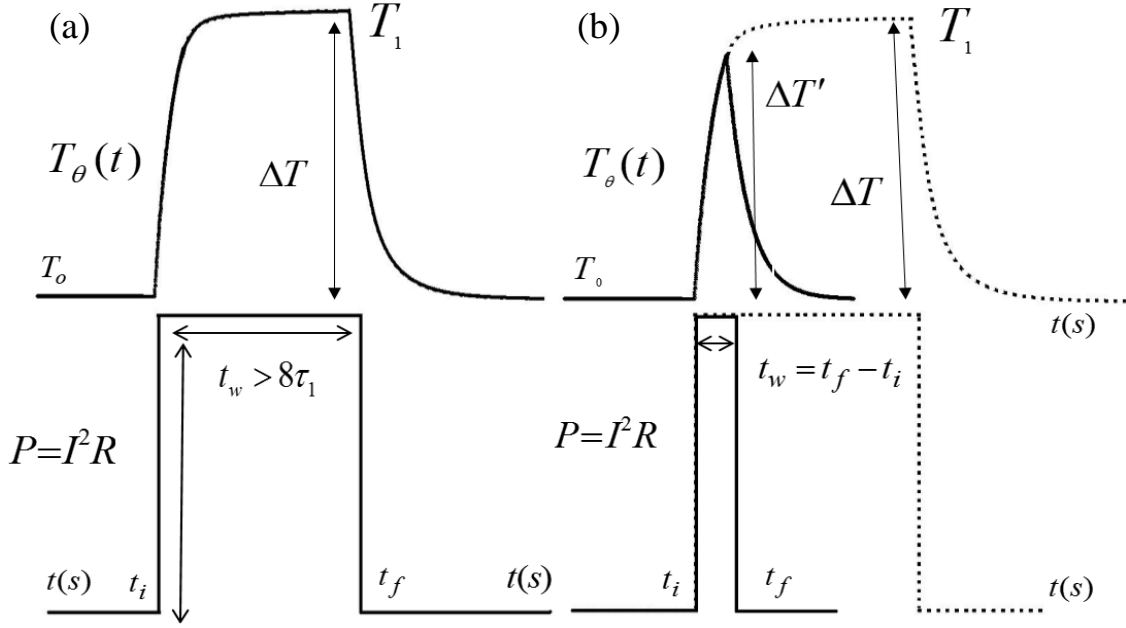


Figure 3: (a - top) the width of a heat pulse using the 1- τ method. (a - bottom) Graph of the time dependent temperature during a heat pulse cycle. (b) Same two graphs for the modified 1- τ method.

duration much greater than 8 times the thermal relaxation time, τ_1 , allowing the sample and substrate to reach thermal equilibrium at a new temperature, T_1 , from an initial temperature, T_0 . The power input can be calculated using the relationship $P = I^2 R$ where P is the power input, I is the current, and R is the resistance of the calorimeter heater. When the power is applied then removed an exponential rise to a new thermal equilibrium (T_1) then decay in calorimeters temperature is observed as time progresses. In the modified 1- τ method, seen in Fig. 3 (b), a much shorter heat pulse is applied.

This is the technique used in our experiment. This allows us to collect data at a much quicker rate by not allowing the sample-substrate to reach thermal equilibrium before removing the heat pulse. Although a smaller change in temperature ($\Delta T'$) is measured when using this method, the same thermal relaxation time constant is observed. The relaxation method is represented by the dynamic heat equation shown in Eq. (2). This is exactly like the equation for the 1- τ method except that it must first be solved using the measured $\Delta T'$ temperature change in order to determine what the equilibrium temperature change, ΔT would have been if the sample was given the chance to reach its thermal equilibrium.

$$C \frac{dT_\theta}{dt} = P(t) - K_b(T_\theta - T_0) \quad ; \quad P(t) = \begin{cases} 0 & t_i > t \\ P & t_i < t < t_f \\ 0 & t_f < t \end{cases} \quad (2)$$

In the dynamic heat equation (Eq. (2)) we see that the rate of change in internal energy of the system, represented by $C \frac{dT_\theta}{dt}$, is equal to the power applied, $P(t)$, minus the heat leak, $K_b(T_\theta - T_0)$, lost by the thermal connection between the calorimeter and the bath. The $P(t)$ term is referred to as the square DC heat pulse, which is a constant supply of power during the time $t_i < t < t_f$, where t_i is the time when we begin applying the DC heating power to the calorimeter and t_f is the time when the power is turned off. During the heat pulse the heat gained from power input is much greater than the effect of thermal conductance from the heat leak so the sample and mount begin to increase in temperature. In order for us to solve for the heat capacity using the modified 1- τ method we must first consider the case of the long pulse relaxation method. It is reasoned that over a very small change in temperatures, where T_0 is not far from T_1 , C and K_b can be considered approximately constants. By changing of a variable from T_θ to $T_\theta - T_0$ in a differential equation, we can rewrite Eq. (2) as

$$\frac{d(T_{\theta}-T_0)}{dt} = \frac{P(t)}{c} - \frac{K_b(T_{\theta}-T_0)}{c}. \quad (3)$$

In order for us to create the time dependent temperature equations that describe this system during the heat pulse ($t_i < t < t_f$) we want to apply another change of variable during this period from $T_{\theta}-T_0$ to $T_{\theta}-T_0 - \frac{P}{K_b}$.

$$\frac{d(T_{\theta}-T_0)}{dt} = \frac{d(T_{\theta}-T_0 - \frac{P}{K_b})}{dt} \quad (4)$$

Eq. (3) can then be represented as

$$\frac{d(T_{\theta}-T_0 - \frac{P}{K_b})}{dt} = -\frac{K_b}{c} \left(T_{\theta}-T_0 - \frac{P}{K_b} \right) \quad (5)$$

In a very long heat pulse width $t_w (\equiv t_f - t_i) \rightarrow \infty$, the system finally reaches a new thermal equilibrium T_1 , the rate of temperature changes will become 0 for t near t_f . Therefore, $T_{\theta}(t \rightarrow t_f) = T_1 = T_0 + \frac{P}{K_b}$, $\Delta T = \frac{P}{K_b}$, and the thermal relaxation time $\tau = \frac{c}{K_b}$. Once the heat pulse is removed, at $t_f < t$, the equation shows an exponential decay back to the initial bath temperature. The time dependent temperature equations for the relaxation method are

$$\Delta T_{\theta}(t) = \begin{cases} \Delta T [1 - \exp(-\frac{t-t_i}{\tau_1})] & t_i < t < t_f \\ \Delta T \exp(-\frac{t-t_f}{\tau_1}) & t_f < t \end{cases}, t_w \rightarrow \infty. \quad (6)$$

When using the modified 1- τ method the same equations are used except that the decay equation must be modified to include the actual temperature reached by the sample considering it had not reached equilibrium. The equations of (6) can then be expressed in a form representing the modified 1- τ method. Where $\Delta T'$ is the non-equilibrium temperature change.

$$\Delta T_{\theta}(t) = \begin{cases} \Delta T [1 - \exp(-\frac{t-t_i}{\tau_1})] & t_i < t < t_f \\ \Delta T' \exp(-\frac{t-t_f}{\tau_1}) & t_f < t \end{cases} \quad (7).$$

If the temperatures are accurately measured these equations can be used to solve for the thermal relaxation time using the relationship below.

$$\Delta T' = \Delta T \left[1 - \exp\left(-\frac{t_w}{\tau_1}\right) \right] \quad (8)$$

With the thermal relaxation time and equilibrium temperature we can then solve for the heat capacity and thermal conductance of the system using the following

$$C = \frac{P\tau_1}{\Delta T} \quad ; \quad K_b = \frac{P}{\Delta T} \quad (9)$$

A 2- τ effect can be seen when the thermal conductance of the sample and substrate (K_s) is finite and becomes comparable to the thermal conductance between the calorimeter and bath, as seen in Fig. 4¹.

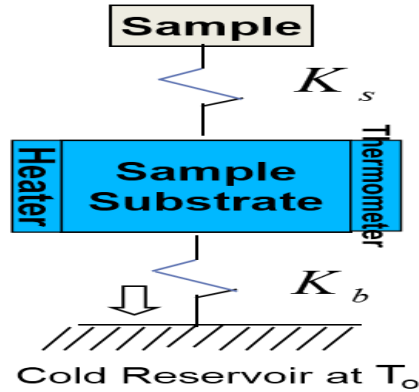


Figure 4. 2-- τ effect

This can happen if the sample has poor thermal contact with the mounting platform or if a sample is so large that it takes a very long time to reach an internal thermal equilibrium. In the time dependent temperature graph the 2- τ effect is observed as a steep initial curve which eventually levels off to more of an exponential decay. This is a much more difficult differential equation to solve requiring the use of two thermal relaxation time constants. In a 2- τ calorimetry, the dynamic heat equations include an additional heat transfer between the sample and the calorimeter substrate, which are displayed in Eq. (10).

$$C_s \frac{dT_\theta}{dt} = -K_s(T_s - T_\theta) \quad ; \quad C_b \frac{dT_\theta}{dt} = P(t) - K_b(T_\theta - T_0) - K_s(T_\theta - T_s) \quad (10)$$

Here C_s is the heat capacity of the sample, C_b is the heat capacity of the calorimeter, and T_s is the temperature of the sample. A Laplace transform was used in order to solve Eq. (11) and the solutions provided here were derived by John Shepard.¹ With the modified 2- τ model the exact results of the time dependence of the change in temperature (ΔT_θ) monitored by the calorimeter thermometer using a finite heat pulse can be expressed as

$$\Delta T_\theta(t) = \begin{cases} \Delta T_1[1 - \exp(-\frac{t-t_i}{\tau_1})] + \Delta T_2[1 - \exp(-\frac{t-t_i}{\tau_2})] & t_i < t < t_f \\ \Delta T_1[1 - \exp(-\frac{t-t_w}{\tau_1})] \exp(-\frac{t-t_f}{\tau_1}) + \Delta T_2[1 - \exp(-\frac{t-t_w}{\tau_2})] \exp(-\frac{t-t_f}{\tau_2}) & t_f < t \end{cases} \quad (11).$$

where $\Delta T_1 = \frac{P}{K_b} \left(\frac{\tau_1 - \tau_2}{\tau_1 - \tau_2} \right)$ and $\Delta T_2 = \frac{P}{K_s} \left(\frac{\tau_1 - \tau_2}{\tau_1 - \tau_2} \right)$. The experimentally determined τ_1 and τ_2 are associated to the external relaxation time $\tau_b \left(\equiv \frac{C_b}{K_b} \right)$ and the internal relaxation time $\tau_s \left(\equiv \frac{C_s}{K_s} \right)$ by the following relations:

$$\tau_b \tau_s = \tau_1 \tau_2 \quad \text{and} \quad \tau + \tau_s = \tau_1 + \tau_2 \quad (12)$$

τ_s and τ_b are the relaxation times required for the heat energy to be thermally conducted from the sample to the substrate and then from the substrate to the cold reservoir respectively, and τ is the overall thermal relaxation time, $\tau = \frac{C_s + C_b}{K_b}$. The total heat capacity is determined to be

$$C_{total} = C_s + C_b = \frac{P}{\Delta T} \left(\frac{\Delta T_1 \tau_1 + \Delta T_2 \tau_2}{\Delta T} \right) \quad (13)$$

where $\Delta T = \Delta T_1 + \Delta T_2$ is the temperature difference at equilibrium, and the thermal conductance between the calorimeter and the bath is

$$K_b = \frac{P}{\Delta T} \quad (14)$$

With the Labview based least square fitting program developed by our lab we can analyze the raw temperature trace, $T_\theta(t)$, for the 1- τ and 2- τ effects and determine the systems heat capacity very accurately. Figure 5 shows example raw temperature traces for both the 1- τ and 2- τ effects.

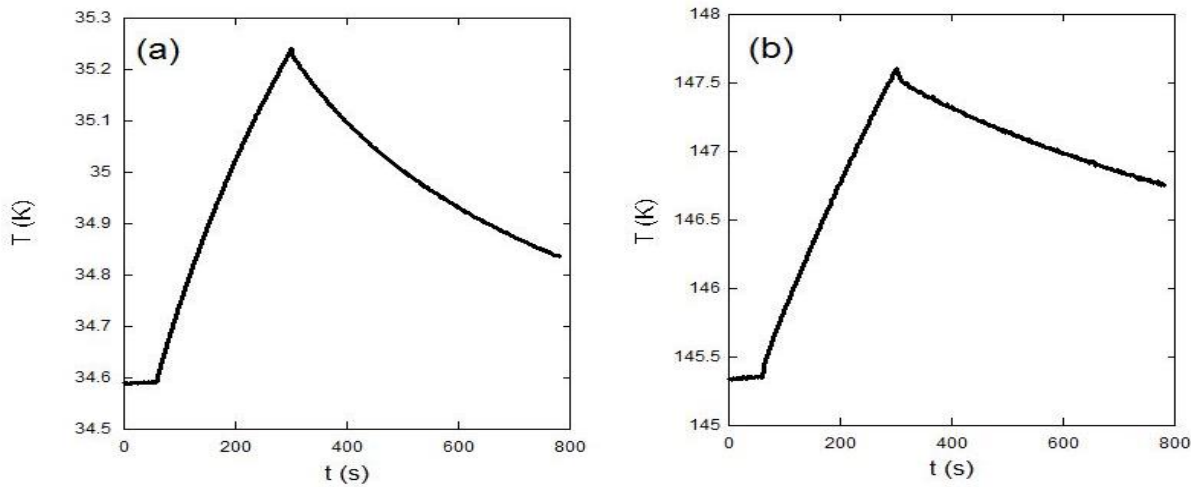


Figure 5: (a) Raw trace for the time dependent temperature exhibiting a 1- τ effect. This is seen as a smooth exponential decay. (b) The 2- τ effects is characterized by a steep initial curve followed by a more exponential decay.

5. Results and Discussion of Heat Capacity Measurements

The calorimeter is first placed in the cryocooler in order to measure its background heat capacity over the temperature range of 11 K to 300 K. This background heat capacity measurement is composed of the sapphire disk, heater element and Cernox thermometer. Next a copper standard is measured over the same temperature range in order to test the accuracy of the calorimeter. A 223.76 mg sample of copper is used as our standard and it is mounted onto the substrate and bounded by using Apiezon N-grease. These measurements include the heat capacities of the copper sample, the N-grease, and the background. Figure 6 shows the temperature dependence of heat capacities for both the empty

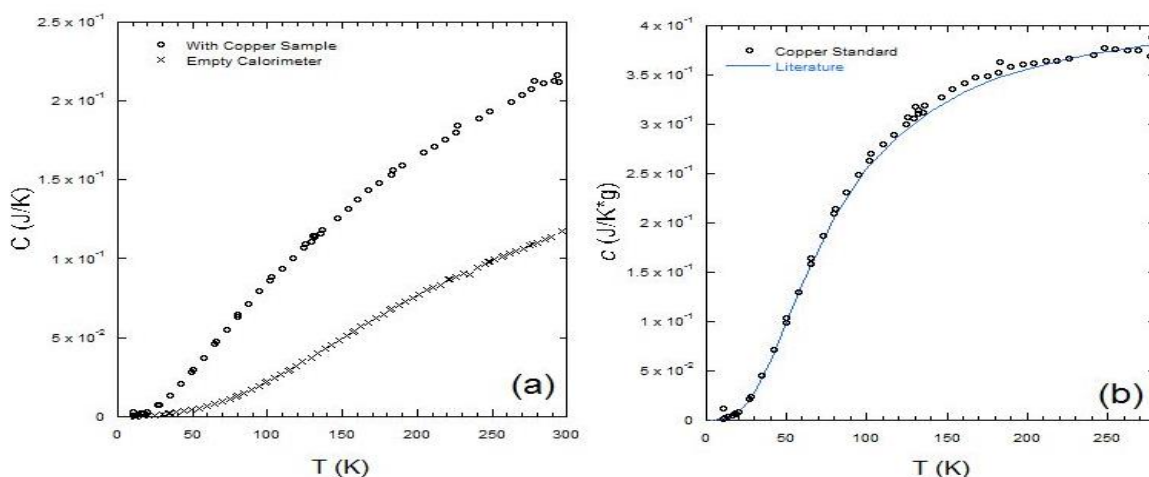


Figure 6: (a) Comparison of heat capacities of calorimeter with sample (O's) and empty (X's). (b) Comparison of experimental specific heat (O's) of copper and its literature value (solid line).

calorimeter and the calorimeter with the copper standard. The characteristics of our relaxation calorimeter: temperature dependence of the thermal conductance K_b between the calorimeter and cold bath and the associated relaxation time τ_1 are plotted in Fig. 7.

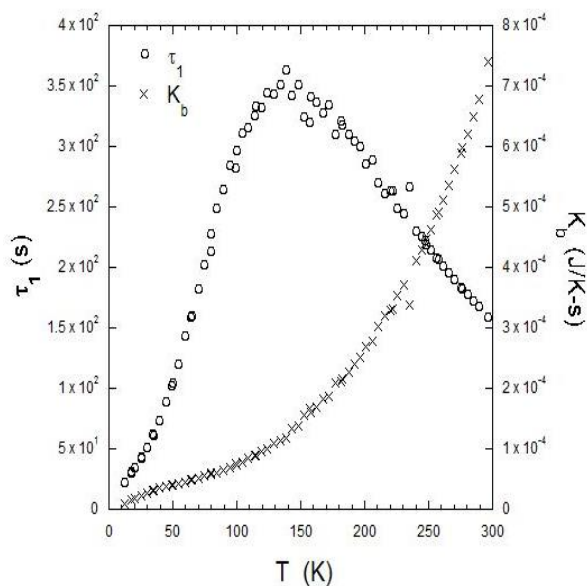


Figure 7: Graph of thermal relaxation time τ_1 and thermal conductance K_b of the empty calorimeter vs temperature.

The specific heat of N-grease has been previously measured by our lab and its heat capacity is easily scaled by weight. By subtracting the background and grease heat capacity measurements we can extract the copper standards heat capacity at each temperature. After dividing the heat capacities calculated at each temperature by the weight of the copper we can determine its specific heat and compare it to its literature value, shown in Fig 6 (b). Now that the calorimeter is tested and determined to work properly it will be used to take measurements of the rare earth metal compounds which are the focus of our lab. By measuring the specific heat of these samples we can determine if and when interesting phenomenon such as phase transitions will occur. We can also uncover if there are any deviations to the Fermi-liquid model which describes how electrons interact with each other and their lattice structures at extremely low temperatures².

6. Conclusion

A calorimeter was built and tested by using a copper standard. The specific heat of our copper standard agrees within 1-2 percent of the literature specific heat for copper. The modified 1- τ method was used to gather the data and it was analyzed using a refitting program using Labview. The refitting model used to determine the heat capacities depended on whether the sample displayed a 1- τ or 2- τ effect. A 2- τ effect occurred more frequently between 130 and 170 K. By analyzing the specific heats of various superconducting metals we can determine if and when these transitions will occur.

7. Acknowledgements

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8. References

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