Thermodynamic measurements of submilligram bulk samples using a membrane-based “calorimeter on a chip”

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Calorimetry offers a direct measurement of thermodynamic properties of materials, including information on the energetics of phase transitions. Many materials can only be prepared in thin film or small crystal (submilligram) form, negating the use of traditional bulk techniques. The use of micromachined, membrane-based calorimeters for submilligram bulk samples is detailed here. Numerical simulations of the heat flow for this use have been performed. These simulations describe the limits to which this calorimetric technique can be applied to the realm of small crystals (1–1000 μg). Experimental results confirm the feasibility of this application over a temperature range from 2 to 300 K. Limits on sample thermal conductivity as it relates to the application of the lumped and distributed models are explored. For a typical sample size, the simulations yield 2.5% absolute accuracy for the heat capacity of a sample with thermal conductivity as low as 2 × 10⁻⁵ W/cm K at 20 K, assuming a strong thermal link to the device. Silver paint is used to attach (both thermally and physically) the small samples; its heat capacity and reproducibility are discussed. Measurements taken of a submilligram single crystal of cobalt oxide (CoO) compare favorably to the results of a bulk calorimetric technique on a larger sample. © 2008 American Institute of Physics. [DOI: 10.1063/1.2912950]

I. INTRODUCTION

Thermodynamic measurements are an important tool in understanding the fundamental properties of novel systems, providing direct and quantifiable insight into densities of states and phase transitions. In many cases, these new materials may only be synthesized in thin film or small bulk form, scales at which traditional bulk calorimetric techniques are not applicable.1–3 Of primary focus in this article is the measurement of the specific heat of small samples (submilligram). These novel systems are numerous, including but not limited to metastable minerals of geological interest,4 nanocrystalline semiconductors,5 and granular6 and molecular ferromagnets. Despite the increasing interest in these materials, the last major review of small-sample calorimetry was tackled by Stewart almost 25 years ago.2 Traditional bulk sample calorimeters are limited either to rather large samples (≥1 mg) or to low temperatures (≤50 K).8 Modern differential-scanning and ac calorimetry work has yielded results on 0.1–100 μg sized samples.9–13 Because these are relative measurements, phase transitions can be resolved quite well using these methods; however, the absolute accuracy of the resultant specific heat diminishes significantly (≈15% at best) for these techniques due to limitations of the noise floor and the size of the addenda. In the present work, we take advantage of the low background heat capacity of membrane-based calorimeters and investigate the feasibility and accuracy limits of using the relaxation method to measure the heat capacity of small bulk samples from ≈2 to 300 K. This article describes the capabilities of this technique, starting first with a brief explanation of the method, a look at some heat flow simulation work, and finally a presentation of experimental results. From this analysis, we will quantify the region of validity of this calorimetric technique and identify potential systematic errors in the measurement.

Thermal relaxation calorimetry is a widely used technique for measuring heat capacity of small samples. In Bachmann’s pioneering design, the sample is thermally and physically bound to a silicon bolometer consisting of heater, thermometer, and sample platform. Thin gold wires form a weak thermal link between this bolometer and a frame which is strongly coupled to a sample block held at temperature $T_0$.14 This is considered a semiadiabatic calorimeter because it is impossible to completely thermally isolate the sample due to the need for electrical leads and bolometer support structure (the gold wires). This causes the thermal conductance between the bolometer and the environment to be less but not infinitely less than that between the sample and the bolometer.

This basic design has been modified and used by groups all over the world. A similar design is currently available in commercial form for Quantum Design’s physical properties measurement system PPMS system. However, there are limitations to this design given the macroscopic size of the bolometer and leads. The background contribution (commonly called the addenda) of the leads, heater, and sample platform, or stage, is quite large; Quantum Design’s PPMS system quotes a lower limit on sample size of 10 mg due to this large background signal. Additionally, a common material used to mount samples to these stages is thermal grease such as Apiezon® N. However, the glass transition in Apiezon®
N grease leads to a large and irreproducible temperature dependency in the background, or addenda, heat capacity.\textsuperscript{15–18} The limited thermal conductance through the grease also causes the time constant of the sample to the stage to become important, resulting in an internal time constant problem; this variant of the $\tau_2$ problem is known as a “lumped $\tau_2$” model. A different variation on the $\tau_2$ problem occurs with highly insulating samples. As the time constant internal to the sample itself becomes comparable to that between the sample and the frame, this results in what is known as the “distributed $\tau_2$” effect.\textsuperscript{14} Both of these lower boundaries are set by the thermal conductance between the sample stage and the frame, so decreasing this results in the ability to measure more thermally insulating samples.

Silicon-based microfabrication techniques have allowed the production of a much smaller calorimeter centered around a low-stress silicon nitride (Si–N) membrane.\textsuperscript{19} To create these microcalorimeters, we start from a (100)-oriented double-polished Si wafer. On this, we deposit via chemical vapor deposition (CVD) a high temperature “wet” oxide (steam\textsuperscript{+}O\textsubscript{2}), yielding a smooth buffer layer of 3000 Å; this oxide layer reduces capacitive links between thermometers and heaters. A low-stress (off-stoichiometry) silicon nitride layer of appropriate thickness is then deposited via low-pressure CVD to provide the sample platform and act as our weakly thermally conductive link. For larger samples (\(\geq 100 \mu g\)), we deposit a 1.5 μm thick Si–N layer which increases the addenda but yields stronger structural integrity for the large samples,\textsuperscript{6} while for thin films and small bulk samples, we use an 1800 Å thick Si–N layer. We then thermally evaporate and pattern Pt for electrical leads as well as thermometers and the stage heater. Furthermore, on calorimeters to be used for large bulk sample measurements, we deposit conductive Pt “wings” to reduce the otherwise long time constants due to the high heat capacity of these large samples. The Si is then etched away in the central area, leaving a Si frame around the outside and a thin Si–N membrane with heaters and thermometers in the center. The membrane provides a low thermal conductivity but relatively strong structural support for samples. The next step in processing of our devices is the sputtering of amorphous NbSi alloy thermometers (\(a\)-Nb\textsubscript{1−x}Si\textsubscript{x}, \(x=0.1\)) for use as sensitive low temperature thermometers. We then thermally evaporate a Cu conduction layer on the back side of the membrane in the central sample area. A more detailed description of most of this processing technique may be found in earlier work.\textsuperscript{19}

The resulting calorimeter is pictured below (Fig. 1) and consists of a silicon frame supporting the Si–N membrane where, in the center, reside a heater, thermometers, a thermal conduction layer, and the sample itself. Pictured as well are platinum wings, whose function will be described in further detail later in the paper (Sec. II A). The thermal conduction layer provides a uniform, isothermal region to ensure precise measurement of the sample’s temperature and clearly set the boundaries of the sample space and external sink. The Si–N membrane provides a weak thermal link to the Si frame, which, in turn, is tightly coupled to a copper block at $T_0$. This thin film construction reduces the addenda contribution of the conduction layer, membrane, and thermometers to

\[\Delta J/\Delta T \sim 1 \text{nJ/K at 2 K and } \sim 8 \mu\text{J/K at RT for our standard “thin” membrane devices or roughly seven times that for our “thick” membrane devices, many orders of magnitude below that of other bulk heat capacity measurement techniques.} \]

This is crucial to measuring small (submilligram) quantities of material.

Because our sample space is weakly linked to the frame, we employ the semiadiabatic relaxation method of calorimetry. For this method to work, $\tau_{\text{int}} \ll \tau$, where $\tau_{\text{int}}$ refers to internal thermal time constants within the sample and between the sample and the thermometers/heaters, and $\tau$ refers to the thermal relaxation time between the sample and the frame, often called an “external” time constant. If $\tau_{\text{int}}$ is comparable to $\tau$, this results in what is commonly referred to as a $\tau_2$ problem, complicating and often invalidating the measurement technique.

The relaxation technique consists first of applying a constant power $P$ to the sample via a heater (Pt for our devices), allowing it to reach a steady state. The equilibrium temperature difference $\Delta T$, measured by one of three thermometers in the central sample area (depending on temperature range), yields the value of the thermal conductance, $\kappa=P/\Delta T$, of our device. Once obtaining $\kappa$, we turn off the power to the system and monitor the temperature decay. In the limit $\Delta T \ll T_0$, this decay is exponential with a single time constant, $\tau$, assuming a good thermal link between the sample and the thermometers. The total heat capacity is then defined as $C = \kappa \times \tau$. This heat capacity $C$ includes that of the sample and addenda (membrane, thermometers, and heater). The addenda is separately measured (without sample) and subtracted to obtain the heat capacity of the sample. Further description of our methodology is available elsewhere.\textsuperscript{19}

Previous work on heat flow simulations of these membrane-based devices has established accuracy limits related to thermal conductivity of thin film samples and the conduction layer, film thickness, overall heat capacity, etc.\textsuperscript{20} This previous work, however, focused solely on thin film samples with geometry matching that of the conduction layer. Bulk samples lack this matching symmetry and could

\[\text{FIG. 1. (Color online) Photograph of the microcalorimeter. The arrows point to the contact pads for the heater and each pair of thermometers (one each on the frame and sample area).} \]
thus lead to significantly different heat flow for four reasons—(1) their mass is concentrated at a small point on the sample area; (2) their large heat capacity (even for a submilligram sample) leads to an excessively long \( \tau \); (3) their macroscopic out-of-plane dimension relative to the membrane necessitates the consideration of out-of-plane heat flow; and (4) an attachment method becomes necessary, unlike the thin films deposited directly onto the membrane surface. This last issue leads to a very well-defined \( \tau_2 \) problem, but the first three issues and how they influence systematic errors in a membrane-based calorimeter are not known. The third issue is particularly important for samples with low thermal conductivity and leads to what is commonly called a \( \tau_N \) or distributed \( \tau_2 \) problem.

In this paper, we employ a numerical simulation to address the heat flow questions presented in measuring a small bulk sample with a membrane-based calorimeter. Because computing power has improved significantly since the original simulation study,\(^20\) we are able to solve this problem in the exact two-dimensional (2D) geometry of the microcalorimeters instead of a more idealized geometry used previously. These results clearly show defined constraints on our technique related to sample size and sample thermal conductivity. We examine, in particular, the expression of a \( \tau_{\text{int}} \) effect and the consequent intrinsic systematic error in the small bulk sample measurement. Furthermore, our desire to measure over a wide temperature range (at least 2–500 K) makes the commonly used grease not an option for sample attachment, and the metastable nature of some of our samples eliminates the previous use of indium.\(^6\) We therefore examine the use of silver paint as a thermally conductive mount instead. Finally, we present experimental results of the heat capacity of a known small bulk sample measured with our membrane-based calorimeters to sum up our results.

## II. HEAT FLOW SIMULATIONS

The time constant associated with vertical heat flow from one side of the membrane to the other is negligible compared to that in the lateral direction due to the three to four orders of magnitude difference in path length, so a two-dimensional model is generally sufficient. Using the Mathworks PDETOOL for MATLAB to solve the 2D heat diffusion equation,

\[
\frac{\partial T(x,y,t)}{\partial t} - \frac{\partial}{\partial x} \left[ k_{2D}(x,y) \frac{\partial T(x,y,t)}{\partial x} \right] - \frac{\partial}{\partial y} \left[ k_{2D}(x,y) \frac{\partial T(x,y,t)}{\partial y} \right] = P(x,y,t),
\]

we are able to define the realms of parameter space where our devices operate most effectively and determine systematic error limits. Here, \( c_{2D}(x,y) \) is the heat capacity in units of J/cm\(^2\) K at point \((x,y)\). For example, if we examine a point in the central area of our membrane where the copper conduction layer lies, \( c_{2D} = c_{Si-N} \times h_{Si-N} \times \rho_{Si-N} + c_{Cu} \times h_{Cu} \times \rho_{Si-N} \), where \( h \) is the height, or thickness, of the material layer and \( \rho \) is its density. Similarly, \( k_{2D} = k \times h \). We define \( T \) relative to the block temperature \( T_0 \).

Similar to the actual experimental application of our microcalorimeters, two solutions are generated during the simulation, a steady-state solution \( (\partial T/\partial t = 0) \) and a time-dependent solution \( (P = 0) \). The steady-state solution is used to determine \( \kappa \), the thermal conductance of the device, and corresponds to the situation where the heater is generating a constant power but there is no net heat flow at any point on the surface. In the time-dependent solution, the power to the heater is turned off at \( t = 0 \), and the solution is calculated at each node as a function of time in intervals of set time. The resulting \( T(t) \) is fit to a single exponential, and from this the time constant, \( \tau \), is determined. Both solutions assume the boundary condition that the temperature is fixed at the membrane edges. It is also assumed that no heat is lost to the surrounding environment (i.e., the device is in a vacuum with no radiative heat loss). These two solutions are used to calculate the simulated heat capacities and compared to the initial values for \( c_s \) and \( k_s \) input into the program.

Using the PDETOOL outlined above, we individually studied the effects of adding the metallic wings and the measurement of a small, bulk sample placed at various positions within the sample area. Of primary interest is what happens to the thermal conductance \( \kappa \) of our devices and/or the \( \Delta T \) measured by the thermometer(s) compared to the \( \Delta T \) of the sample in each of these cases, as any changes may impede our ability to accurately obtain \( C_P \) and/or take us out of the range of applicability of our semiadiabatic technique. As the thermal conductance changes and the samples measured become larger, understanding possible deviations such as a \( \tau_2 \) effect become crucial to recognizing the feasibility and limitations of our technique. Moreover, it is important to quantify these limits in the regimes proposed as well as any systematic error for this new application.

In the discussion below, as in our earlier simulation paper for thin films,\(^20\) we have used 20.3 K as a nominal block temperature \( T_0 \). While all results obtained are in some sense independent of this choice of \( T_0 \), the large number of parameters in the problem (thermal conductivity and heat capacity for all the materials in our devices: Si–N, Pt, Cu) make it impossible to completely generalize. However, we have simulated over a much wider range of block temperatures (corresponding to different ratios of the relevant physical properties) without any qualitative changes.

### A. Metallic wings

One of the major concerns of using the semiadiabatic relaxation technique for measuring these small bulk crystals is that though these samples are tiny by traditional "bulk" standards, they are 10–100 times larger in mass than our standard thin film samples. Because the thermal conductance is determined by the device geometry, this 10-100 times larger mass (and, therefore, heat capacity) results in a 10–100 times increase in \( \tau \), the relaxation time. That places us in the regime where an individual decay could take tens of seconds and, given the number of decays for a standard measurement, extends the time for an individual point to an hour or more. To counteract this effect, we need to increase \( \kappa \), the thermal conductance of the device. While increasing the thickness of the low-stress nitride membrane would accom-
plish this, that increases the addenda by the same factor. A preferable technique is increasing the thermal link between the central sample region and the silicon frame using metallic wings. The shape of the wings (Fig. 1) stems from the need to isolate the wings electrically from the thermometers/heaters while being limited to the top side of the device due to our processing technique. However, this added asymmetric link can affect our technique by potentially disturbing the temperature contour lines, obfuscating the connection between the measured temperature difference \(T\) at the center of the device and the conductance \(g\). The simulated data shown for the winged devices are for typical parameters of thick membrane devices, but because this is simply a geometric scalar, the trends will hold for thin membrane devices as well.

Figure 2 shows how the thermal link between membrane and frame changes with the added Pt wings. Here, kappa is again defined as \(P/\Delta T\), where \(\Delta T\) is measured at the center of the device. With a moderate thickness of platinum, we see a considerable increase in the high temperature thermal conductance (e.g., \(\sim50\%\) increase with 1000 Å of Pt). In the low \(k_{2D,\text{wings}}\) limit, the contribution of the wings to \(\kappa\) is linearly additive \((\kappa_{\text{tot}}=\kappa_{\text{wings}}+\kappa_{\text{mem}})\), and we can extract the effective geometric factor for the wings \((\kappa_{\text{wings}}=k_{\text{Pt}}\alpha_h\), where \(\alpha\) is the geometric factor representing the effective width :length ratio of the conduction path). In a very naive idea of what the geometric factor should be, we would estimate \(\alpha=5.2\). Indeed, in the low Pt thickness linear regime shown in Fig. 2, the slope \(\alpha=4.8\pm0.1\), very close to our simple approximation.

As the conductance through the wings becomes a larger fraction of the thermal link between sample area and frame, the heat flow contours become distorted (Fig. 3). This distortion is what causes the apparent nonlinear behavior at wing thicknesses above \(\sim1\mu m\) in Fig. 2. It is not due to a nonlinear relationship in the real thermal conductance but to the fact that as the heat flow contours change in this way, \(\Delta T\) is no longer well defined, thus yielding an errant result for \(\kappa=P/\Delta T\). Clearly, remaining in the linear regime is crucial to the accurate measurement of specific heat with our devices.

B. The sample

Because these bulk samples are so much larger than our traditionally measured thin film samples and hence have much larger \(c_{2D,s}\) and \(k_{2D,s}\), it is important to quantify the potential effects that this may have on our devices and the relaxation method of determining \(c_s\), both in the steady-state and time-dependent aspects of the technique. The sample’s size brings into question the potential hazard of a weakly
thermally conductive sample; understanding under what conditions this introduces a distributed $\tau_2$ effect and how to recognize it are extremely relevant to the experimental application of this technique. Also of concern is the thermal link between the sample and the device, as that can lead to a lumped $\tau_2$ problem. Finally, quantifying any systematic errors is crucial to understanding the absolute precision of this methodology.

Because the path length for heat flow in the lateral direction is three to four orders of magnitude larger than that in the vertical direction, we have treated our devices with a two-dimensional model to this point. However, the geometry of a small bulk sample is inherently three dimensional. To add such a sample to our model, we must make the continued assumption that there is no radiative heat loss to the environment. If $k_s \approx k_{Cu}$, the internal time constants remain fast compared to $\tau$ for an average sized sample (we refer from here on to a disk of 50 $\mu$m high and 140 $\mu$m in diameter, but we have simulated for various diameter samples with no qualitative changes), and we may continue to use our traditional 2D model (which yields results of $<2\%$ error in heat capacity for all $c_s$ (Ref. 20)). However, as $k_s$ decreases, the internal time constants become longer and our simple model starts to break down. This is also the case if our sample is weakly coupled through the thermal link (referred to here as silver paint since that is what is used experimentally, as discussed in Sec. III). In either situation, the heat equations in the in-plane, or horizontal, and out-of-plane, or vertical, directions are controlled by diffusion constants

$$D_v = \frac{k_{2D,Ag} + k_{2D,Si-N} + k_{2D,Ag}}{c_{2D,Ag}}$$

$$D_h = \frac{k_{2D,Ag} (h_v + h_{Ag})^2}{(k_{2D,Ag} + k_{2D,Ag} h_v^2) (c_{2D,Ag} + c_{2D,Ag})},$$

respectively.\(^{19,21}\) Combining this with the diffusion equations that set the respective time constants, $l^2/2D_h \tau_h$ and $(h_v + h_{Ag})^2/2D_h \tau_v$ (where $l$ refers to the radius of the sample and $h_v$ and $h_{Ag}$ refer to the heights of the sample and thermal link, respectively), leaves us with a limit on the crucial time dependence of our system. Here, $\tau_v$ is limited by the thermal diffusivity and geometry of the sample and thermal link, while $\tau_h$ is the combined result of all device and sample layers (though often dominated by conduction through the conduction layer).

In the case of $\tau_h \geq \tau_v$, we are left in the two-dimensional model already well characterized in previous work on thin films.\(^{20}\) However, in the limit that $\tau_h \ll \tau_v$, we treat the tiny sample region as though the only link to the copper layer is through the thermal link. In this case, the 2D mesh in the sample area represents the path for heat flow in the vertical direction, into (and through) the sample. Thus, in the sample area of our simulated device, $k_{2D}$ is simply equal to $k_{2D,v}$.

As the thermal conductivity of the sample drops, this limit of $\tau_h \ll \tau_v$ occurs when $[l^2 / h_v k_{Cu}] \ll k_{Cu} / k_{Ag} + k_{Ag} (h_v / h_{Ag})$, which is true for many relevant small samples mounted on our thick devices. For example, in the case of the CoO sample measured at low temperature (here, values are quoted at 10 K), $l=50$ $\mu$m, $h_v=20$ $\mu$m, $h_v$

![FIG. 4. Temperature contour plot at constant power for a sample (circle near center of the membrane; the thick border represents the thermal link, silver paint) of comparable total heat capacity to the copper conduction layer (62.5 nJ/K) and thermal conductivity $k_s=0.1 \times k_{Si-N}$. 2% contour lines are shown. For this set of conditions, the central region is isothermal to 2.5% and thermometers are within 0.6% of sample.]

\[\tau_h = \frac{\tau_v}{1000}\] at low temperature due to the orders of magnitude lower thermal conductivity, while a metal may result in $\tau_h = \tau_v$.

1. Steady state; $\partial T/\partial t = 0$

A crucial step of this simulation is confirming that the added bulk sample is at the same temperature as the thermometers and does not perturb the temperature contours. Figure 4 shows contour lines for a sample of moderate thermal conductivity $(k_{2D,v}=k_{2D,Si-N})$ placed near the heater. We see that the sample area remains isothermal to 2.5% for a wide range of total heat capacities (1 $\times$ 10$^3$ $< c_v / c_{Cu} < 1 \times 10^5$). Changing the location of the sample did not affect the temperature contours. We note that the change in temperature $\Delta T$ measured by the thermometers remains the same, thus our measured $\kappa$ is unchanged upon the addition of a sample, as expected.

2. Time dependence; $P = 0$

In order to quantify the error in this technique, we treat the simulation as we would an experimental measurement. We simulate an addenda measurement without the sample, first obtaining the steady-state $\Delta T$ to find $\kappa = P/\Delta T$ and then the time-dependent data, $T(t)$. We then take this time-dependent data and fit it to an exponential to obtain the time constant $\tau$. Multiplying $\kappa$ by $\tau$ yields a measure of the addenda heat capacity.

After obtaining the “addenda,” we “add” the sample and repeat these simulations to obtain a measurement of the total
heat capacity and take the difference to be the heat capacity of the sample itself. The difference between this simulated value and the value input for \( c_s \) is what we define as the absolute error in our technique.

Because there is now a macroscopic thermal link between our sample and the device, we must consider how this affects the time constant(s) of the system. If the thermal link is weak, we expect to see a lumped \( \tau_2 \) effect.\(^{23}\)

In the region where the single tau model breaks down, we analyze the data using the standard lumped \( \tau_2 \) model:\(^{23}\)

\[
T(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2},
\]

\[
c_s + c_{\text{addenda}} = \frac{\kappa (A_1 \tau_1 + A_2 \tau_2)}{A_1 + A_2}.
\]

Our simulation reproduces the lumped \( \tau_2 \) behavior in the traditionally appropriate region (high \( k_s \), decreasing \( k_{Ag} \) as shown in Fig. 5).

Figure 6 shows the \( \chi^2 \) error between \( c_{s,\text{sim}} \) and \( c_{s,\text{actual}} \) as a function of \( k_{2D,\text{Ag}} \) for fixed \( k_{2D,\text{Ag}} = k_{2D,\text{Cu}} \) (i.e., for a strong thermal link). For these simulations, we have chosen \( c_s = c_{Cu} \). We have also simulated for other sample heat capacities (which then affects \( \tau_{int} \) and thus the region of deviation from a single \( \tau_1 \) model), but it did not affect the absolute error of the technique. Fitting to the classic single exponential model discussed, there is an abrupt increase in error at \( k_{2D,\text{Ag}} = 2 \times 10^{-6} \) W/K. This corresponds precisely to the region where \( \tau_{int} \approx \tau_s \), as expected.

The effect associated with this breakdown is considered the distributed \( \tau_2 \) problem, though it is better characterized as a \( \tau_N \) problem.\(^{24}\) As higher order time constants exhibit themselves, the analysis becomes exceedingly complicated. However, in the condition that the thermal link between the sample and device is extremely strong, the heat flow is typically dominated by the \( \tau_1 \) term, and the lumped \( \tau_2 \) model provides an adequate approximation to the solution.

Figure 6 shows that \( \chi^2 \) drops by an order of magnitude using this two-tau technique when in the regime where \( \tau_{int} \approx \tau_s \). This drastic decrease in error (order of magnitude smaller chi-squared error in fit) allows us to determine from the raw data whether or not we are observing any \( \tau_2 \) effects—namely, a single exponential model is appropriate if \( \chi^2(1\tau)/\chi^2(2\tau) < 2 \). Similarly, we define the \( \tau_N \) (or “distributed”) regime when \( \chi^2(2\tau)/\chi^2(3\tau) > 2 \). Table I lists the \( \chi^2 \) results for the various exponential fits, delineating the regime

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**FIG. 5.** (Color online) The percentage error in \( c_{s,\text{sim}} \) as a function of \( k_{2D,\text{Ag}} \) and \( k_{2D,\text{Cu}} \); \( c_s \) was held constant at \( c_s = c_{Cu} \). \( c_{s,\text{sim}} \) was calculated from the \( \tau_1 \) model in the region labeled “\( \tau_1 \)” and from the lumped \( \tau_2 \) model everywhere else. The borders between the different tau regimes correspond to the horizontal lines in Table I. Note that the error in the \( \tau_1 \) and \( \tau_2 \) regimes remains within 2.5%, comparable to our earlier work on thin films (Ref. 20). The cross-hatched region labeled CoO represents the approximate parameter space of our CoO experimental results (Sec. III). The hatched region labeled SiO\(_2\) is representative of where an \( \approx 1 \) mg size disk of SiO\(_2\) would approximately lie on this graph.

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**FIG. 6.** (Color online) Chi-squared error of the single and double exponential fits to the temperature decay as a function of \( k_{2D,\text{sample}} \) (\( k_{2D,\text{Ag}} = k_{2D,\text{Cu}} \)); \( c_s \) was held constant at \( c_s = c_{Cu} \), but we have simulated over a variety of values for \( c_s \) with no qualitative change in behavior. Note the extremely large increase in \( \chi^2 \) as the thermal conductivity of the sample becomes small (region where \( \tau_{int} \approx \tau_s \)).
where each model is appropriate. This ability to monitor deviations from the single exponential model is crucial for our experimental analysis of the semiadiabatic relaxation method with real samples, as parameters such as sample thermal conductivity remain unknown in our technique.

In Fig. 5, we show the percent error in the obtained $c_g$ as measured relative to $c_{g\text{,inpat}}$. Included in Fig. 5 is information about the parameter space for an cobalt oxide sample measured on one of our thick devices (Sec. III) as well as a small ($\approx 1 \mu g$, a disk roughly 200 $\mu m$ in diameter and 10 $\mu m$ tall) representative low conductivity sample, SiO$_2$, if it were to be measured on one of our thin devices. As a reminder, one must take into account the heights of the sample and copper layer as well as the temperature-dependent thermal conductivities when determining where on this plot a particular sample of interest may lie.

When fit to the appropriate experimental model (determined by the $\chi^2$ ratio as in Table I), the error in this new
contact yields a single exponential decay, while poor thermal relaxation method used for measurement directly shows samples poor wetting characteristics of Ga on the desired oxide phases. Our first attempt to use gallium for metastable samples such as quenched high-pressure heat necessary for the In attachment procedure is not suitable temperature range desired makes conducting grease good thermal contact between sample and calorimeter. We constant, justifying our assumption of the paint providing relaxation method for a bulk sample are that of a single time known mass 

\[\tau_2\]

rately weighed upon the evaporation of the solvent. Acetate to a useful consistency to attach samples and accurately weigh the diluted silver paint which is commonly used to attach electrical leads to samples. This can be diluted with butyl acetate to a useful consistency to attach samples and accurately weigh the evaporation of the solvent.

After placing the sample (one or more small crystals of known mass) on the center of the thermal conduction layer, the diluted silver paint is dropped onto the sample and allowed to dry overnight in a vacuum desiccator. We have measured the mass of the resulting system over a period of days after this process, and find an initial rapid decrease as the solvent evaporates which is further reduced less than 1% per day after 24 h.

Once the butyl acetate solvent has evaporated, the resulting thin layer of paint holds the sample securely. Silver paint is designed and experimentally found to give good electrical contact, and its thermal conductivity is also quite high. The relaxation method used for measurement directly shows whether this thermal contact is good or not, as good thermal contact yields a single exponential decay, while poor thermal contact would show the classic double exponential \(\tau_2\) effect. We have verified that the resulting thermal decays of the relaxation method for a bulk sample are that of a single time constant, justifying our assumption of the paint providing good thermal contact between sample and calorimeter. We have been able to achieve robust physical and thermal contact with silver paint mass below 10 \(\mu\)g. This new approach to mounting samples thus provides an avenue for measuring bulk samples with smaller mass than can be measured by traditional techniques.

We find that silver paint has a moderate heat capacity over the entire temperature range (Fig. 7), more than that of bulk silver, presumably because the bonding agent gives a significant contribution, but significantly less than (and more reproducible than) that of grease. This addenda contribution is consistent per bottle of silver paint (shown here as measurement B-1 and B-2), but we did see deviations between bottles A and B. At low temperatures (<23 K), we see that our measurement of silver paint is larger than that in the literature (there is no high temperature data to compare to). This difference is likely due to a different solvent and/or bonding agent due to different manufacturers. Also of note, the magnitude of the specific heat of the silver paint is actually lower than that of indium at low temperature, making this method experimentally preferable even in cases where heating the device would not damage or alter the sample in

**III. EXPERIMENT**

After obtaining the limits in our technique from numerical simulation, we can apply this knowledge toward the experimental measurement of small bulk samples on our membrane-based calorimeters. We have previously measured powder samples suspended in a liquid and dropped onto devices and have also successfully measured small single crystals or other bulk samples (200–500 \(\mu\)g) thermally anchored to thick membrane devices by using indium to attach the samples. The indium, however, requires physical pressure, which is incompatible with the thinner membranes needed for small single crystal (<100 \(\mu\)g) samples, and the heat necessary for the In attachment procedure is not suitable for metastable samples such as quenched high-pressure phases. Our first attempt to use gallium (which has a lower melting point) to replace the indium was unsuccessful due to poor wetting characteristics of Ga on the desired oxide samples (in contrast to good wetting on metals). The wide temperature range desired makes conducting grease (commonly used in the literature for low temperature measurements) a poor option, since Apiezon® N grease has a glass transition at 210–237 K and a history-dependent crystallization transition at 270–289 K [Fig. 7(a)], leading to a widely varying and very large heat capacity unsuitable for our technique. We therefore turned to and have developed the use of silver paint which is commonly used to attach electrical leads to samples. This can be diluted with butyl acetate to a useful consistency to attach samples and accurately weigh the evaporation of the solvent.

![Fig. 7](http://rsi.aip.org/rsi/copyright.jsp)

**Fig. 7.** (Color online) Measured specific heats of various sample mounting materials. The silver paint measurements labeled A, B-1, and B-2 were taken in our lab from two different bottles, the latter which was measured again (different sample from the same bottle). Also shown are literature values of silver paint (Ref. 30), bulk silver (Ref. 25), bulk indium (Ref. 25), and Apiezon® N grease (Ref. 17). (b) is a logarithmic plot of the same data to emphasize the low temperature differences.
any way. Unlike Apiezon® N grease, which clearly shows the strong temperature dependence characteristic of a glass transition, there are no apparent transitions in the silver paint. The total contribution of the silver paint to the aggregate heat capacity of a measurement is determined from its measured mass. The uncertainty in this mass (measured to $\pm 1 \mu g$) is often the largest contributor to the error in this new technique (outside of the 2% systematic error already discussed in Sec. II B 2).

As an experimental test of absolute accuracy, we obtained a single crystal of cobalt oxide whose heat capacity had been measured recently by conventional cryogenic calorimetry by Woodfield and Boerio-Goates. A 638 $\mu g$ sample was attached to a thick nitride membrane device (used for measuring large heat capacities) with 183 $\mu g$ of silver paint from bottle B. We then measured the heat capacity of this device using the semiadiabatic relaxation technique.\textsuperscript{10} The antiferromagnetic transition is quite well defined (Fig. 8) and its temperature agrees with the adiabatic measurement. The heat capacities are also in good agreement.

For the data shown here, the error bars shown are calculated by adding in quadrature the following: 2% of the total $C_p$ (due to systematic error in technique), 1 $\mu g/\text{[sample mass]} \times C_p$ (error due to $\pm 1 \mu g$ uncertainty of sample mass), 1 $\mu g \times c_Ag$ (error due to uncertainty in Ag paint mass), $\kappa$ times the error in $\tau$ (error due to $\tau$ fit), and $\tau$ times the error in $\kappa$ (calculated via 98% confidence bands in various polynomial fits). The error in $\kappa$ is small (0.1%–0.3%). The error in $\tau$ is on the order of 0.2%–1%. There is also a 1% uncertainty in temperature due to thermometer calibration. Propagating all these errors suggests that an absolute accuracy on the order of 3% in heat capacity, dominated by the systematic errors discussed above, is attainable, as evidenced by the good agreement with the previously measured CoO.

IV. CONCLUSIONS

Heat flow analysis of our microcalorimeters with attached simulated bulk samples shows the feasibility of obtaining the heat capacity of small (1–1000 $\mu g$) samples. We have quantified the regime in which our devices are applicable and how to recognize when we are outside this regime. The heat capacity of silver paint has been measured, showing that it can reliably be used to affix samples to our calorimeters on a chip for samples with thermal conductivity as low as $2 \times 10^{-5}$ W/cm K at 20 K for a typically sized sample. Experimental results show that this method works to similar accuracy (2.5%) as our traditional thin film calorimetric technique, expanding the realm of applicability to include such novel systems as quenched high-pressure materials, molecular magnets, and more.

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Here, we have modeled the lateral direction as a multi-layer, or parallel, system, while the vertical direction can be thought of as a series conductive path. The additional heat capacities of the membrane and copper layers are negligible (=0.1%), given the small region of the device we are examining and so do not appear in the equations.

This holds true assuming the limiting factor is the sample thermal conductivity (i.e., good thermal link). We also use the fact that $h_s < I$, for a typical sample.


