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A newly developed method is presented for measuring heat capacities on small samples, particularly where thermal isolation is not sufficient for the use of the traditional semiadiabatic heat-pulse technique. This "hybrid technique" is a modification of this heat-pulse method in case the temperature drift of the sample after the heat pulse is not linear but exponential. Deliberate extrapolations of these exponential drift curves, dependent on the evaluated relaxation time, yield reliable results for the temperature steps. The method is faster than the traditional relaxation method, and by comparing with the values published by the National Bureau of Standards (NBS) on copper, the accuracy is shown to be of the order of 1%. © *2008 American Institute of Physics.*
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I. INTRODUCTION

Heat-capacity measurements on bulk samples are, in general, performed by monitoring the temperature response caused by the input of a well known amount of heat into a system consisting of a sample and a sample holder with heater and thermometer. This system is hanging in a frame, from which it is, as good as possible, thermally isolated. Traditionally, for the measurement one of two methods is chosen—the relaxation method or the semiadiabatic heat-pulse method—dependent on the thermal isolation of the system from the frame. The semiadiabatic heat-pulse method[1] was already used for a long time by the authors on magnetic samples of the order of 1 g in a low-temperature calorimeter in magnetic fields up to 17.5 T.[2,3] However, it is shown that it can also be used on small samples using an automatic temperature adjustment of the environment.[4] In both cases it is necessary that the drift curves before and after the heat pulse are linear in time. For small samples, this is, in general, problematic because of the low mass of sample and holder and the need for electrical connections with the environment.

The relaxation method[5] is suitable in situations where the thermal isolation between the frame and the sample is poor. This means that the relaxation to the frame temperature shows an exponential behavior with characteristic time, τ, smaller than about 30 s. Care has to be taken that this relaxation time exceeds the internal relaxation times within the system sample plus holder.[6]

For the semiadiabatic heat-pulse method, the τ for the relaxation to the frame temperature has to be longer than 10 min in order to have the temperature drift just after the heat pulse sufficiently linear to admit linear extrapolations of

the drift curves before and after the heat pulse to the same time point, which is necessary to determine correct values for the temperature step.

The advantage of the semiadiabatic heat-pulse method is the low time demand of the method. It takes not more than 2 min to measure one heat-capacity value at a certain temperature. By measuring all points in a successive way, with the starting temperature of a measurement being equal to the final temperature of the predecessor, it is possible to measure 100 values from, for instance, 4 up to 78 K in not much more than about 3 h. The disadvantage of the method is the need for a heat switch, without use of which the sample in the well-isolated state will not, within a reasonable time interval, cool to a sufficiently low starting temperature. In particular in the case of small samples with low heat capacity, the use of a heat switch is problematic.

In the relaxation method, a constant power P leads to a constant temperature difference between the sample plus holder system and the frame, from which the strength of the thermal link is determined. Switching off the power and measuring the characteristic time, τ, results in the wanted heat-capacity value. This means that for each point, thermal equilibrium has to be attained twice, taking at least five relaxation times each. Apart from higher demands for electronic equipments (in particular a high-performance frame-temperature controller), the time demands may be much higher here, with a minimum of ten relaxation times. The advantage of the relaxation method is that there is no need for a heat switch.

Besides the situation with small samples, where the temperature will, because of the low heat capacity, decrease too fast to the frame temperature for accurate linear extrapolations, which are necessary in the traditional heat-pulse technique, the semiadiabatic heat-pulse method also yields problems at high temperatures, where radiation losses cause significant deviations from linearity of the drift, particularly if the temperature difference between the sample plus holder

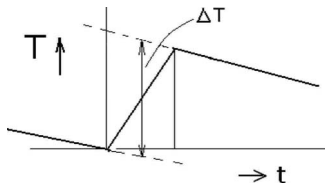a)Author to whom correspondence should be addressed. Electronic mail: j.c.p.klaasse@uva.nl.

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FIG. 1. Schematic diagram of the $T(t)$ curve during a standard semiadiabatic heat-pulse measurement.

FIG. 2. Schematic diagram of the $T(t)$ curve during a hybrid-method measurement.

system and the frame is large. In that case the frame—at high temperatures thermally connected to a radiation shield around it—has to be heated to a temperature close to the system temperature in order to keep radiation effects negligible.

However, for relaxation times between, say, 30 and 500 s, the relaxation method becomes very time consuming, and at the same time the drift curves are not sufficiently linear yet to allow for linear extrapolations. For this region, we developed a hybrid method, being a modification of the heat-pulse method. This new method has been operational in our equipment and has shown to yield reliable results. A test run on a pure copper sample showed the measured values to be at least as close to literature values as in the two traditional methods.

II. DESCRIPTION OF THE METHOD

The newly developed hybrid method can be applied in a situation where we have a frame with high heat capacity to which a sample holder is attached with a thermal link to the frame with characteristic time τ of the order of, say, 1 min. In our equipment, this thermal link only consisted of the eight thin tungsten wires providing the electrical connections to the heater and the thermometer on the holder. The basic idea is that the drift after the pulse is not linear but, as in the relaxation method, purely exponential: the system of sample plus holder drifts exponentially back to the frame temperature, which is taken as the starting temperature. The characteristic time, however, is not used for evaluating the heat capacity, as in the relaxation method, but only for determining the correct extrapolation of the exponential drift curve, analogous to the extrapolation in the semiadiabatic heat-pulse method. Knowledge of the strength of the link is not necessary.

In Fig. 1 we have schematically depicted the $T(t)$ curve for a semiadiabatic heat-pulse measurement. In case the two drift curves are not exactly parallel, which is, in fact, the normal situation, it can be shown that extrapolation to halfway the heat pulse yields the most accurate value for the temperature step ΔT. Both drift curves are, in fact, exponentials, but the characteristic time is sufficiently long to take them as linear curves.

In Fig. 2, an analogous diagram of $T(t)$ is given for the hybrid technique. In this scheme, the frame temperature is taken to be constant, and we suppose the sample temperature before the heat pulse to be equal to the frame temperature. However, this is not strictly necessary. Results show that a small linear drift in the frame and sample temperatures can be allowed for, provided that, in the evaluation, the differ-
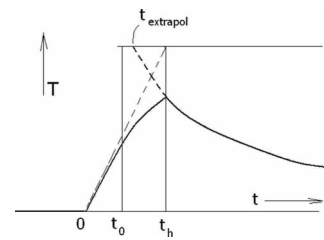
ence is taken between the observed temperature after the pulse and the extrapolated temperature derived from the linear drift curve before the pulse. For reasons of simplicity, here we restrict the discussion to the situation where $T(t)$ before the pulse is constant. It is clear that the crucial point in this method is the extrapolation. In the semiadiabatic heat-pulse technique the exact extrapolation point is of secondary importance, particularly if the two drift curves are nearly parallel; in the case of an exponential drift curve, choosing the wrong point leads to large errors in the evaluated ΔT. Therefore, this point has to be calculated accurately. In the figure we have also depicted the temperature behavior during the heat pulse in case the thermal link should be absent (thin dotted line). It is clear that the temperature step has to be determined at the point where the extrapolation of the drift curve after the heat pulse meets the temperature that should have been attained in the case of zero heat loss.

III. CALCULATING THE EXTRAPOLATION POINT

In order to calculate the extrapolation point (here in the text further given as t_e), we have to write correct formulas for the real $T(t)$ curve during and after the heat pulse. For simplicity, we start the pulse at $t=0$ and stop at t_h, and we keep the power P during the pulse constant. Because of the temperature dependence of the heater resistance, this is not strictly the case, but the deviations are completely negligible. Point t_0 is taken halfway the heat pulse. Because of the heat loss during the pulse, the temperature increase is not linear. Without heat loss, the slope should be P/C, with C as the total heat capacity of sample plus holder. With heat loss, leading to relaxation to the frame with characteristic time τ, this becomes

$$\Delta T(t) = (P\tau/C)[1 - \exp(-t/\tau)]. \tag{1}$$

It is easily verified that for small values of t/τ, this reduces to Pt/C, as expected.

After the pulse, the temperature decreases according to

$$\Delta T(t) = \Delta T(t_h)\exp[-(t - t_h)/\tau]. \tag{2}$$

This latter curve has to be extrapolated back to point t_e where $\Delta T = Pt_h/C$.

This leads to the equation

$$Pt_h/C = (P\tau/C)[1 - \exp(-t_h/\tau)]\exp[-(t_e - t_h)/\tau]. \tag{3}$$

From this we have to solve t_e, which leads to

$$t_e/t_h = -(\tau/t_h)\log\left[\frac{(t_h/\tau)\exp(-t_h/\tau)}{1-\exp(-t_h/\tau)}\right]. \tag{4}$$

For small values of t_h/τ, relation (4) shows that t_e is close to t_0, halfway the heat pulse, and moreover, the deviation is a nearly linear function of $1/\tau$,

$$t_e - t_0 \equiv t_e - (t_h/2) \approx Dt_h^2/\tau. \tag{5}$$

The value for the factor D can be calculated exactly for $t_h/\tau \ll 1$ and amounts to $1/24$ ($\approx 0.041\,67$). This value is shown to decrease only slowly to 0.0415 by increasing t_h/τ to 0.7. In our software the value of 0.0416 has been implemented, a value derived from a simulation program of the heat-pulse technique with non-negligible heat loss. The results from the simulation were shown to be in perfect agreement with the results calculated above. During the measurements, we keep the length of the heat pulse restricted to $t_h/\tau < 0.5$. This means that for a relaxation time of 30 s, the heat pulse has to be shorter than 15 s, which is no serious constriction.

IV. INTERNAL RELAXATIONS

In the above paragraph we have assumed that the influence of internal relaxations is negligible. This means that the system of sample plus holder is in thermal equilibrium throughout the whole process. In this paragraph we will discuss the consequences in case the thermal conduction within this system is finite.

In order to make things manageable, we consider a simplified system of a sample and a sample holder, both with negligible internal thermal resistance, interconnected by a finite thermal link. A temperature difference between the two, ΔT_i, will therefore exponentially decrease to zero with a characteristic time τ_i. In our system, we estimate this internal relaxation time to be of the order of 1 s or less.

In the case of a changing sample-holder temperature (caused by heating or heat loss through the link to the frame), the sample will follow at some distance. In a steady-state situation, this distance is constant, leading to the condition that the slopes of the two temperature curves, that of the sample and that of the sample holder, are equal.

Consequently, in steady state this constant internal temperature difference ΔT_i follows, at any arbitrary moment t_a, from the relation

$$\frac{d}{dt}\{\Delta T_i \exp[-(t-t_a)/\tau_i]\} = (-\Delta T_i/\tau_i)\exp[-(t-t_a)/\tau_i]$$

$$= \frac{d}{dt}[T_{\text{sh}}(t)], \tag{6}$$

with $T_{\text{sh}}(t)$ as the sample-holder temperature.

Because we look at t_a, the exponential function equals 1, and we have

$$\Delta T_i = -\tau_i \frac{d}{dt}[T_{\text{sh}}(t)]. \tag{7}$$

During the heat pulse, the slope of $T_{\text{sh}}(t)$ can be reasonably approximated by the temperature step caused by the heat pulse, ΔT, divided by the pulse length t_h, leading to

$$t_h \approx \tau_i(\Delta T/\Delta T_i). \tag{8}$$

In order to make the analysis in the previous paragraph meaningful, we want ΔT_i during the heat pulse to be at least an order of magnitude smaller than the step. This means that the pulse length has to be at least an order of magnitude larger than the internal relaxation time. For our system the pulse length was therefore chosen to be of the order of 10 s.

During the drift process after the heat pulse, the requirements for internal equilibrium are even more severe because these data are crucial to determine the step. However, the drift is not linear, so ΔT_i is not a constant. But in a small time interval, say, $\Delta t/\tau < 0.1$, with τ as the relaxation time for cooling to the frame, we may suppose the drift curve to be approximately linear and, in consequence, ΔT_i to be approximately constant. If we approximate the behavior of the sample holder during the drift interval by

$$T_{\text{sh}}(t) \approx T_{\text{frame}} + \Delta T \exp[-(t-t_e)/\tau], \tag{9}$$

with ΔT as the temperature step and t_e as the extrapolation time, and if we apply Eq. (7), we will arrive for an arbitrary time t_a at

$$\Delta T_i \approx \tau_i(\Delta T/\tau)\exp[-(t_a-t_e)/\tau]. \tag{10}$$

During the first part of the drift interval, when the slope is highest, the exponential function is not much smaller than 1, and we see that if we want $\Delta T_i/\Delta T$ to be smaller than 0.01, the relaxation time to the frame has to be at least two orders of magnitude larger than the internal relaxation time. For our system, this gives $\tau \geq 100$ s. However, we found reasonable values for the heat capacity already at $\tau \approx 30$ s, but we have to admit that at values around 100 s and higher, the accuracy was significantly better. The performance was determined from an analysis of the drift data, implemented in our data analysis software, mainly consisting of extrapolations from fits of different parts of the drift curve. These extrapolations have to yield consistent values. If the performance was not sufficient, we skipped the value and changed the parameters concerned (step size, pulse length, waiting time, and length drift interval) in order to do the measurement once more under more appropriate conditions.

The lower limit, given in Sec. I, is not a sharp boundary but gives the value of τ around which the performance rapidly changes and the choice between the relaxation method and the hybrid method, described above, may be reconsidered.

The given higher limit is determined as the value of τ below which the semiadiabatic heat-pulse technique is not applicable. The hybrid method has, in fact, no high-end limit for τ, aside from the need for a heat switch at low intrinsic cooling rates.

For the semiadiabatic heat-pulse technique, the drift during the drift interval has to be linear within, say, 1%. Furthermore, the interval has to be long enough to allow for an accurate extrapolation to halfway the heat pulse. From previous results[2,3] we know that for sufficiently accurate extrapolations, the drift interval has to be at least two times longer than the extrapolation interval to be bridged. Since we have to wait after the pulse some time Δt_w (in our case about 10 s) for attaining a quasi-steady-state situation in the drift-

ing
system, the extrapolation interval, $[t_e, t_h - t_e + \Delta t_w]$, is at least 15 s. This means that the drift curve has to be linear within a time interval of the order of somewhat less than 1 min. For an exponential function $\exp(x)$, we know from the Taylor expansion that the deviation from linearity for $x < 0.1$ is only about 0.5%. For $x = 0.2$, the deviation is already about 2%, which is not acceptable for the extrapolation. That means that τ has to be at least ten times higher than the sum of the drift and extrapolation intervals to allow for sufficiently accurate linear extrapolations. In our case we arrive at $\tau \approx 10$ min, the high-end limit mentioned in Sec. I. Below this limit, the hybrid method has to be seriously considered above the semiadiabatic method.

Another problem with the semiadiabatic method is the higher ΔT_i because the temperature difference between sample and frame is much larger. This difference is, in a low-temperature equipment, of the same order of magnitude as the temperature itself. In formula (10), the step ΔT has to be replaced by the temperature difference between sample and frame. In case the step is chosen to be a few percent of the temperature, as is common use in the semiadiabatic method, this difference can attain values up to two orders of magnitude higher than the step. From internal stability arguments, this means that also τ has to be two orders of magnitude higher than in the hybrid method. In our case this means that τ should be about 1 h or larger. However, the situation is not that bad.

Also the drift curve before the pulse has to be extrapolated to the same extrapolation time halfway the heat pulse. In the semiadiabatic method, the slope of this curve is about the same as the slope of the drift curve after the pulse and will show, by consequence, about the same systematic error. Therefore, the errors in the two extrapolations, with both errors consisting of a nearly equal vertical shift, cancel each other out. It is clear that this problem does not come up in case the frame temperature is kept close to the temperature of the system of sample and holder. For all these reasons we have put the upper limit for τ at 10 min, determined by the requirement of linearity of the drift curve.

We conclude that starting with the assumption of an internal relaxation to be present with a characteristic time of about 1 s, the hybrid method works for $\tau > 100$ s (and with some lower performance also between 30 and 100 s), where for $\tau < 10$ min the semiadiabatic method is not accurate and the hybrid method is recommended. Because the hybrid method has no intrinsic high limit for τ to be applicable, this method gives anyhow the best prospects for all systems with sufficiently large τ in which the frame temperature can be set close to the temperature of the system to be measured.

For other equipments with different system characteristics, the numbers mentioned here may be different, but following the above given reasoning it will be easy to come to the, for that system, correct values. Since $\tau = C/k$, with k as the heat link, a large heat capacity, C, is favorable for a long relaxation time to the frame. However, the inner relaxation effects can only be reduced by optimizing the heat conduction within the system of sample and holder (for instance, a

flat sample with a large contact area). The heat capacity of the sample holder has, anyhow, to be kept as small as possible.

V. RESULTS AND DISCUSSION

In order to test the performance of the method, we measured the heat capacity of a piece of 60 mg spec-pure copper. The relaxation times we found were in the range between 30 and 300 s and were therefore in the appropriate order of magnitude for this technique to be applicable. The procedure during the measurement is as follows.

First we bring the frame to the wanted temperature. As stated above, for the method to be working well, it is not necessary that the frame temperature during the pulse is constant. A slow linear drift of the order of a few mK/s can be allowed for. With a high frame heat capacity (big mass), this is easily realized. It is necessary that the total drift during the measurement, which latter takes about 1 min, is small compared to the temperature step of the sample plus holder system, caused by the heat pulse of the measurement.

Second, we follow the temperature of the system of sample plus holder until the drift is sufficiently small. Our criterion was smaller than 1.2 mK/s. The last 20 s are recorded (we take temperature values at a rate of 1/s). These last 20 points will, at these low drift values, show a linear behavior.

After these 20 points we start a heat pulse. The length has to be shorter than $\tau/2$. The value of τ can be guessed from the previous measurement: in most cases the previous point was at a neighboring temperature and τ will, in general, behave smoothly as a function of temperature. Next, we follow and store the temperature after the pulse for about 1 min. The difference of the recorded values with the extrapolated values from the array before the pulse will show a nearly exponential behavior. Even at negligible internal relaxation, this curve, because of the drift in the frame temperature, may not be an exact exponential, but deviations are well within experimental error.

Then we determine the τ of the drift process and, from this value and the heat-pulse length, the correct extrapolation time t_e. At this point we determine ΔT as the difference between the extrapolated values of the two drift curves, the linear one from before and the exponential one from after the heat pulse.

Finally, we can determine ΔQ from current and voltage values, as in the standard semiadiabatic heat-pulse technique. The heat capacity, C, follows from the standard formula

$$C = \Delta Q / \Delta T.$$

Thereupon we can bring the frame to the next temperature with a well guessed heat pulse to the frame heater, accompanied by some warming up of the system of sample plus holder, if necessary. In our experience, within about 10 min the thermal situation will be sufficiently stable for measuring the next value.

The test measurements were done in an equipment consisting of a sapphire plate sample holder with a thin film heater (750 Ω) and a Cernox sensor (from Lake Shore) delivered by Oxford Instruments Ltd. The heat capacity of the
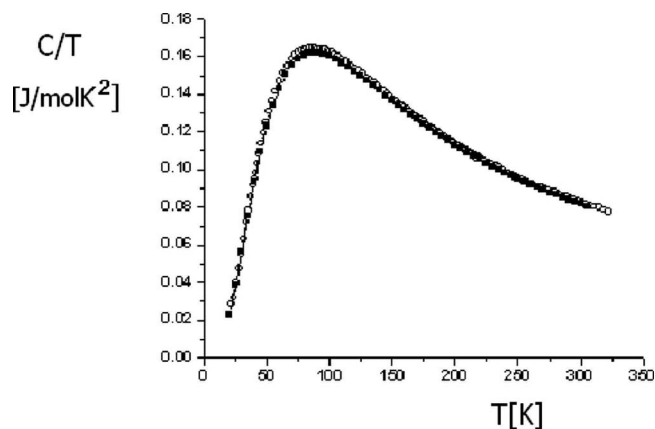
FIG. 3. Results on a 60 mg Cu sample measured with the hybrid method (open symbols) and the NBS values on Cu (Ref. 7) (closed symbols).

empty holder was comparable to that of about 30 mg copper. In the beginning, this holder was connected with the frame by the above-mentioned eight tungsten wires only, yielding the thermal link. This showed to be too vulnerable. Four extra composite wires, attached in a later stage of the project, resulted in upgraded mechanical robustness without considerably changing the relaxation characteristics. The frame was positioned in a vacuum can, thermally connected to the frame and thus working as a radiation shield at frame temperature. This system was placed in the variable temperature insert (VTI) of an Oxford Instruments MagLab Exa system, equipped with a 9 T superconducting coil. The temperature of the VTI was adjusted to a value not too far away from the frame temperature in order to keep the frame-temperature drift at low values. Small changes in VTI temperature had no short-term effects on the frame temperature.

The results for the copper measurement are given in Fig. 3 where the observed values are given together with the NBS values.[7] Our results are 1%–2% larger than the values published by the National Bureau of Standards (NBS) values, which is satisfying. We have to state that the copper sample was glued to the holder with some grease, which was not corrected for. The contribution of the grease was guessed to be responsible for at least half of the extra contribution, bringing the agreement with the NBS values to within 1%. This copper sample is of the same order of magnitude as the samples (about $1 \times 2 \times 3$ mm^3) we intend to measure with this setup.

VI. CONCLUDING REMARKS

We have shown that it is possible to measure specific heat with a modified heat-pulse technique in case the heat loss is too large for the standard semiadiabatic method to be applicable. The advantage of the new method over the well known relaxation method is that the time demand is lower and not dependent on the relaxation time and that a high-performance frame-temperature controller is not needed. Furthermore, the relaxation is sufficiently fast for cooling the sample to low temperatures without use of a heat switch. We believe that this method can bridge the gap between the two traditional methods, particularly if the relaxation time is in the range between 30 and 500 s.

For the frame having a high heat capacity, a well determined heat pulse shows to be sufficient for attaining a next somewhat higher temperature. The use of an active controller is even not recommended because of possible fast changes in the frame temperature during the measurement. If it shows to be necessary to heat the frame during the measurement, we recommend the use of a constant power. As we have stated above, a slow drift in the frame temperature can be allowed for, and with a high heat capacity for the frame it is easy to keep the drift sufficiently low during the heat pulse and subsequent relaxation of sample plus holder. Controller-induced oscillating behavior has, anyhow, to be avoided strongly.

With appropriate frame-heating and sample (holder)–heating procedures, it may be possible to measure one heat-capacity value every 10 min, not dependent on increasing relaxation times. This is considerably faster than in the relaxation method and is only a factor of 4–5 slower than in the semiadiabatic heat-pulse method. The accuracy is of the same level as in the two other methods.

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