



A new heat capacity measurement scheme based on the scanning relaxation method for the Si–N membrane microcalorimeter at high temperatures up to 700 K

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ABSTRACT

We present a sensitive heat capacity measurement method for use at temperatures between 300 and 700 K using a home-made calorimeter incorporating a Si–N membrane microcalorimeter and a commercial tube furnace. We employ a scanning relaxation method with the two relaxation times, in which temperature is scanned with a maximum speed up to ~ 30 K/min to measure the heat capacity of sub-mg single crystals. The heat capacity of the addenda composed of the Si–N membrane and thermal grease is measured to be as small as ~ 30 μ J/K. For the high temperature thermal grease, several materials such as In, Wood's metal, and silicone oil have been tested. We demonstrate the successful performance of this method with different scanning speeds by measuring the specific heat of Cu up to 620 K. A brief summary of advantages/disadvantages of this method vis-à-vis commercially available differential scanning calorimeters (DSCs) is given.

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1. Introduction

Accurate measurements of the specific heat (C_p) have been essential in understanding physical properties of numerous materials. The C_p , for example, provides a direct evidence of a thermodynamic phase transition as well as entropy change involved in the phase transition. In particular, measurements of C_p above room temperature become increasingly important as numerous materials of interest have phase transitions in the high temperature region. To list a few examples, BaTiO₃ shows a ferroelectric to paraelectric phase transition around 408 K [1] while Y₃Fe₅O₁₂ exhibits a ferrimagnetic to paramagnetic transition around 553 K [2]. Identifying those phase transitions and extracting related entropy changes through C_p measurements have been common practice to understand the nature of the phase transition.

Even with such continual demands in various scientific sub-fields, high temperature C_p measurements usually become more challenging than at low temperatures due to several experimental restrictions encountered. For example, in the high temperature region, the contribution of the addenda heat capacity to the total

can become quite large so that extracting the heat capacity of the sample using a conventional calorimeter is difficult. In addition, controlling the base temperature (T) within ± 0.5 K of the target T in the high temperature region is challenging so that the application of a conventional relaxation method, which requires a stable T over a long period of time, becomes difficult. To overcome those technical hurdles, differential scanning calorimetry (DSC) has been frequently used. In the DSC scheme, a signal from a reference calorimeter is subtracted from that of the sample calorimeter to give a sensitive measure of the temperature variation due to the sample heat capacity. Furthermore, rather than relying on the isothermal condition, the DSC employs a scanning temperature mode with variable scanning speeds and as well can be utilized up to a pressure of at least 150 bar. One drawback of the conventional DSC technique, however, is in its sensitivity limit that is not still enough to measure a tiny heat capacity involved in micro- or nanometer scale materials. Progress toward improving these drawbacks has been recently made, for example, through the high-speed scanning microcalorimeter [3,4] and differential ac-chip calorimeter techniques [5]. These works have demonstrated high measurement speeds up to $\sim 200,000$ K/s [4] as well as very high sensitivity down to ~ 1 pJ/K [5].

On the other hand, applications of such high-speed techniques may be yet challenging when one wants to measure accurately C_p of a ~ 100 μ g single crystal and to exchange samples repeatedly

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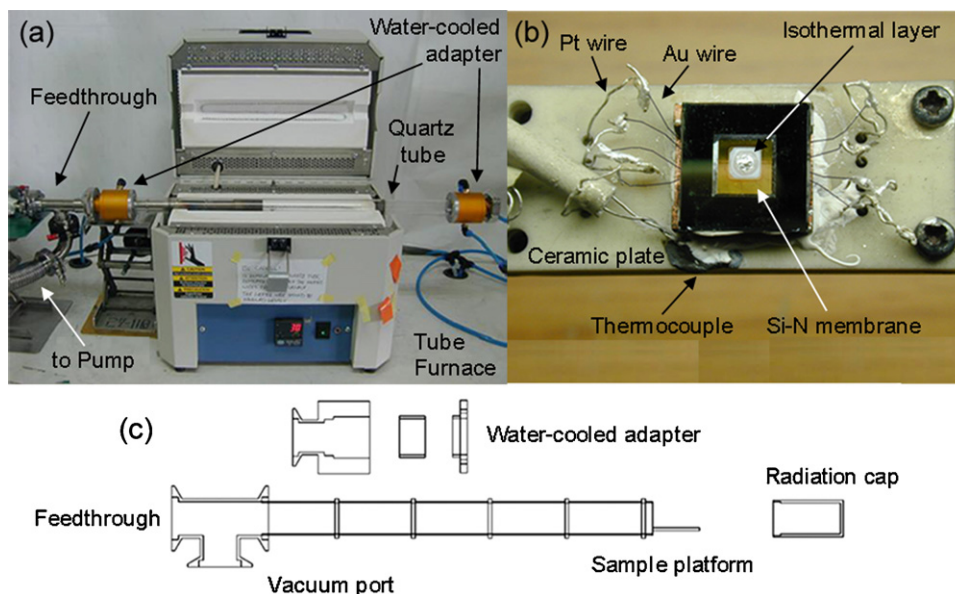


Fig. 1. (a) A picture of the high temperature heat capacity measurement setup. Water-cooled vacuum seal adapters are placed at both ends of the quartz tube. The left vacuum port of the adapter is attached to a stainless steel tee that has two vacuum ports to connect a turbo-molecular pump and an electrical feedthrough. (b) An enlarged view of the ceramic holder with the microcalorimeter attached. The microcalorimeter is placed on top of a Cu holder, which is glued to the ceramic holder. (c) Drawings for the tee, the radiation cap, and the water-cooled adapter, which are all made of stainless steel (SUS304). Three layers of ceramic plates are placed on top of the stainless steel holder to hold the microcalorimeter and to electrically insulate the Pt wires and the thermocouple.

by reusing the same calorimeter without further sensor calibration efforts. For this specific purpose, utilizing the conventional relaxation method can be also advantageous as it allows one to measure C_p of many samples repeatedly with a single calibration. Moreover, it can provide absolute C_p values in a broad temperature window once the addenda composed of the membrane platform and thermal grease is premeasured. Even with these advantages, however, the relaxation method has been rarely used in the temperature region above 300 K, mainly because of the several hurdles described above such as temperature stability and sensitivity limit that must be overcome.

Recently, we have demonstrated in the use of the Si–N membrane microcalorimeter that employing a numerical least square fitting scheme based on the relaxation method with the two-relaxation times, called as the curve fitting method (CFM) [6], can produce absolute C_p data at low temperatures from 20 to 300 K with a sensitivity of $\sim 0.01\text{--}0.1 \mu\text{J/K}$ with a resolution of $\Delta C_p/C_p < 0.01$ [7–9]. The relaxation method considers the so-called τ_2 effect and it has been also termed as the lumped τ_2 model in the original literature [10]. The same microcalorimeter could be repeatedly used for many samples as well. In this report, by extending our previous work, we present a new C_p measurement scheme that works at high temperatures from 300 to 700 K based on the CFM. In particular, we have developed a custom-made probe with the Si–N membrane microcalorimeter loaded, which is then adapted into a commercial tube furnace. The new measurement scheme can produce absolute C_p data in a broad temperature window from 300 to 700 K with a sensitivity of $\sim 1 \mu\text{J/K}$ while the base T is linearly scanned up and down with a maximum speed up to $\sim 30 \text{ K/min}$. Commercially available DSCs have a sensitivity more in the range of 0.5 mJ/K in the same temperature range, along with a much larger ‘background’ or addenda contribution to the specific heat. AC calorimetry (see [11] for the discovery work) can resolve changes in the specific heat of 1 part in 10^4 but is less often used for absolute measurements. The microcalorimeter described in the present work can be repeatedly used as well without further sensor calibration to get absolute C_p data. We demonstrate the successful performance of the method

by presenting the C_p data of several materials such as In, Wood’s metal and Cu using different scanning speeds. The present work owes much to the pioneering works [12] by the Hellman group, see also [13] for their recent design. In those previous works, the authors have used similar type of the microcalorimeter as ours that can be extendable up to $\sim 700 \text{ K}$ in principle. However, in practice, real published data using the relaxation method are only available in the temperature window below 300 K so far [12,13].

2. Experimental

2.1. Measurement probe and experimental conditions

Since the C_p measurement scheme based on the CFM uses a lock-in amplifier operating at $f = 1\text{--}2 \text{ kHz}$ for measuring the temperature sensor resistance, the electrical shielding of the apparatus is essential in the calorimeter probe design. Thus, we have fabricated a tube-shaped C_p measurement probe made of stainless steel (SUS304) for electrical shielding. The C_p measurement probe consists of an electrical feedthrough, a vacuum port, and a sample holder on which the Si–N membrane microcalorimeter is mounted (Fig. 1). The enlarged picture of the sample holder is shown in Fig. 1(b). There are 8 Pt wires (0.01 in. diameter) for electrical connection to the microcalorimeter and a type-B thermocouple (Pt–30%Rh versus Pt–6%Rh) for measuring the block T . All the Pt wires are covered with ceramic tubes for insulation. The gold wires (0.005 in. diameter) were first fixed into the sensor/heater pads by use of a silver epoxy cured at 420 K for 10 min. Then, the gold wires were electrically connected to the Pt wires in the sample holder using a conductive silver paste. We have used the ‘‘type III’’ microcalorimeter that has been proved to have measurement errors less than $\pm 5\%$ in a temperature region from 20 to 300 K [8,9]. After the microcalorimeter is properly mounted, an Al foil was wrapped over the membrane area for radiation shielding. Then the sample holder is covered with a radiation shield made of the stainless steel (SUS304). The probe is then inserted into a long cylindrical quartz tube with water-cooled vacuum seal adapters and evacuated by

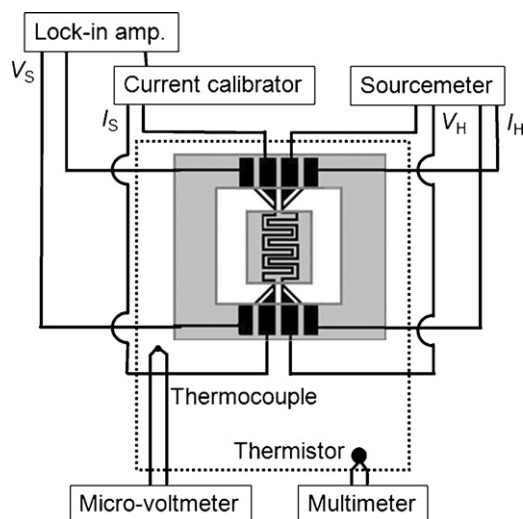


Fig. 2. A schematic diagram of the instrumentation and the electrical connections for the high temperature heat capacity measurement using the resistive sensor-based microcalorimeter. The cold junction is formed at the electrical feedthrough and a thermistor is used to read the temperature of the cold junction.

a turbo molecular pump. The assembled apparatus with the probe and the quartz tube is placed into a commercial tube furnace (Lindberg Blue/M), in which T can be ramped up to ~ 1400 K (Fig. 1(a)). On the other hand, we find that if the furnace temperature is increased up to ~ 900 K, the heater/sensor resistance in the membrane platform changes significantly. Measurements above 700 K can be thus performed only limited times with one microcalorimeter. In this work, we have limited the maximum operation temperature up to 700 K, below which the heat capacity can be measured repeatedly in a single microcalorimeter with minimal variation of the sensor resistance as will be explained below.

The base T of the microcalorimeter is read by a type-B thermocouple. The thermocouple is firmly attached to the ceramic holder using a cement adhesive. The cold junction for the thermocouple is formed at the electric feedthrough. Even though the cooling water in the quartz-adaptor keeps the electric feedthrough cold, the cold junction T slowly increases as the base T increases due to the thermal radiation and the heat conduction through the wires. Therefore, we have used a thermistor to measure the cold junction T simultaneously, and used it as a compensation T of the thermocouple. A custom-made program then automatically calculates the proper base T from the readings of the hot junction voltage and the compensation T .

The detailed fabrication procedure and the structure of the type III microcalorimeter used in this work are described in Refs. [7,9]. Before the C_p measurement, the sensor strip made of the Au/Cr layers has been calibrated by measuring four-probe ac resistance with temperature variation. A schematic diagram for electronic equipment connections is shown in Fig. 2. An ac voltage output of $f = 1$ kHz from a lock-in amplifier (SR830, Stanford research), is sent to the input of a current calibrator (2500EP, Valhalla) to produce ac current, I_s , across the thin film sensor (Au/Cr layer) in the Si-N membrane. The amplitude of the voltage output is set to generate the current value of ~ 100 μ A. The same lock-in amplifier measures the sensor voltage, V_s , generated across the sensor strip. For the sensor calibration, the temperature of the tube furnace is slowly ramped up and down repeatedly with a typical ramp rate 3.3 K/min while the pressure is maintained at ~ 1 mbar using a diaphragm pump. The measured resistance is almost linear in T as expected for metallic films and reproducible in repeated cycling up to 500 K. However, repeated cycling up to 700 K, results in a resistance varia-

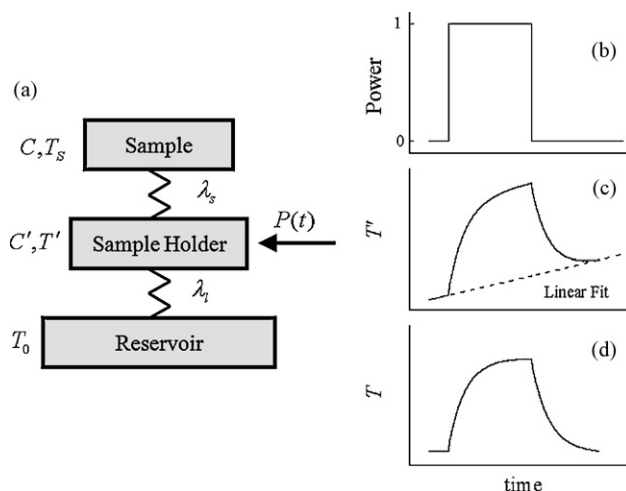


Fig. 3. (a) A schematic diagram showing the scanning relaxation scheme based on the curve fitting method (CFM). Note that, in the CFM, we consider a finite thermal conductance (λ_s) between the sample and the sample holder. (b) The time evolution of the normalized power, (c) the membrane platform temperature $T(t)$ and (d) $T(t) \equiv T(t) - T_{BC}(t)$ is shown. T_{BC} (dashed line in (c)) is taken prior to the heater-on process and linearly extrapolated until the end of the measurement. The thus obtained $T(t)$ is used to fit a theoretical curve by the least square fitting method to calculate the total heat capacity.

tion of about 0.5–1% in each run. As the change is quite predictable and small between 500 and 700 K, we can correct the slight change of calibration after each run by adding up a small constant resistance without performing further calibration of the sensor. During the C_p measurement, another thin film strip made of the Au/Cr layers is used as a heater (Fig. 2). A source meter (Keithley 236) is used to apply dc current, I_H , while measuring dc voltage, V_H , generated across the film heater. The total power level, i.e., $I_H V_H$, is adjusted to induce a temperature increase of about 2–3% of the base T . A custom-made program using LabVIEW™ is used to control the above sequence automatically. In our measurement scheme, we note that the base T is not stabilized at each measurement step but ramped linearly in time. Therefore, the sensor T variation with heater-on/off procedure has two components, i.e., the exponentially varying term and the linearly varying baseline term. The CFM scheme is capable of extracting the linear term before the heater-on procedure as discussed in the following section.

We have used a micro-balance (SE2, Satorius) to accurately measure the mass of the sample. The sample is placed on the Au-isothermal region of the microcalorimeter by using a very thin 60 μ m diameter Cu wire. To find the optimal thermal grease at high temperatures for small single crystal samples we have tested several materials such as In, Wood's metal, high vacuum grease (Dow Corning), and silicone-oil (KF-96-1000CS, Shin-etsu). Details of their performance are discussed in Section 3.1.

2.2. High temperature C_p measurement scheme using the scanning relaxation method

As depicted in Fig. 3(a), the relaxation method used here is based on the so-called lumped τ_2 model that considers a finite thermal conductance (λ_s) between the sample and the membrane platform as well as the thermal conductance (λ_l) between the membrane and the Si substrate, i.e., the thermal reservoir [6]. In the case of the microcalorimeter, the (non-optimal) finite value of λ_s often comes from the inability to press the sample firmly enough to the membrane platform due to the membrane's fragility. The additional consideration of λ_s results in better fits to the exponential thermal variation because the least square fitting scheme, called as the

CFM here, is then able to determine the secondary relaxation time, τ_2 [6,7]. In addition, the total measurement time of the CFM in a single measurement cycle is shorter than that of a conventional relaxation method; typically the CFM can fit the T profile in a time duration about $1\text{--}2\tau$ (τ is the main exponential decay time) to get all the required information while the conventional relaxation method often needs pulse duration about $\sim 10\tau$.

Another advantage of the CFM, which is especially useful for the present work, is that the linear variation of the membrane temperature as well as the heat reservoir temperature can be taken into account when one fits the membrane temperature profile during a single heater-on and -off cycle. The heat balance equations considering the λ_s as in Fig. 3(a) are given as [6]

$$P(t) = c' \frac{dT'}{dt} + \lambda_s(T' - T_s) + \lambda_l(T' - T_0) \quad (1)$$

$$0 = c \frac{dT_s}{dt} + \lambda_s(T_s - T') \quad (2)$$

where c , c' , T_s and T' are the heat capacity of the sample, heat capacity of the addenda, temperature of the sample, and temperature of the membrane platform, respectively. T_0 is the temperature of the thermal reservoir and $P(t)$ is the power applied to the membrane platform. As we practically measure the temperature of the membrane platform (T') through the resistance measurements of the Au/Cr thin film, one can remove T_s in Eq. (1) and (2) to get the following:

$$\frac{cc'}{\lambda_s} \frac{d^2T'}{dt^2} + \left(c' + c + c \frac{\lambda_l}{\lambda_s} \right) \frac{dT'}{dt} + \lambda_l T' = \frac{c}{\lambda_s} \frac{dP(t)}{dt} + P(t) + \lambda_l T_0 + \frac{c\lambda_l}{\lambda_s} \frac{dT_0}{dt} \quad (3)$$

Note that the time-derivative of T_0 is allowed to be non-zero in Eq. (3) as our measurements are performed in a varying T_0 condition while T_0 is assumed to be constant in the original CFM method [6,7]. When $P(t)$ is zero, the response of the membrane platform temperature under the slowly varying T_0 is governed by

$$\frac{cc'}{\lambda_s} \frac{d^2T'}{dt^2} + \left(c' + c + c \frac{\lambda_l}{\lambda_s} \right) \frac{dT'}{dt} + \lambda_l T' = \lambda_l T_0 + \frac{c\lambda_l}{\lambda_s} \frac{dT_0}{dt} \quad (4)$$

If T_0 is controlled to be linearly varying in time, a steady-state solution for T' in Eq. (4), T'_{BG} , is also a linear function of time. If we subtract Eq. (4) with the steady state solution T'_{BG} from Eq. (3), and define $T(t) \equiv T'(t) - T'_{BG}(t)$, the remaining equation is the same as the original CFM equation with a variable $T(t)$ (Eq. (4) of [6]). In other words, the solution for Eq. (3) with linearly varying temperature T_0 is the sum of T'_{BG} , and the solution of the original CFM. Thus, the CFM is capable of measuring the heat capacity even in the presence of linear temperature drift of T_0 . In practice, in each heat-pulse-cycle, we measure T'_{BG} as a linear extrapolation of the measured T' before the heater is turned-on for few seconds, and calculate $T(t) \equiv T'(t) - T'_{BG}(t)$ before fitting to a theoretical curve. These procedures are illustrated in Fig. 3(b). In the original CFM [6] as well as in our recent works in the low temperature region below 300 K [7–9], the CFM has been applied always when the $T'_{BG}(t)$ is constant, i.e., $T'_{BG}(t) = T'_{BG}(0)$. What is newly shown in this work is the fact that the profile $T(t) \equiv T'(t) - T'_{BG}(t)$ is same up to the linearly varying time-dependence of $T'_{BG}(t)$. Thus, the resultant $T(t)$ profile was quite similar in its shape after subtracting the predetermined $T'_{BG}(t)$ that is linearly varying or constant in time. Once the experimental $T(t)$ is determined in this way, the fitting procedure is the same as previous procedures [6,7,9]. In other words, the determined experimental $T(t)$ profile digitized with n -time segments is used to compare with the prediction of T by Eq. (4) (with T' replaced with T). In this process, the least square fitting for the n -equations

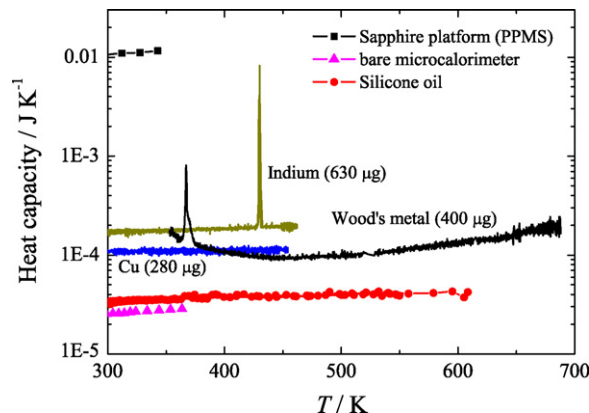


Fig. 4. Heat capacity data for several materials at high temperatures. The heat capacity of the membrane platform without any thermal grease shows the lowest heat capacity value (magenta triangles). Addition of a small amount of silicone-oil to the membrane isothermal layer produces a slightly higher value (red circles). The heat capacity data of indium (630 μg , dark yellow line), Cu (280 μg , blue line), and Wood's metal (410 μg , black line) are also drawn. For comparison, the heat capacity of a commercial sapphire platform used in PPMS (Quantum Design) is also shown. While the sapphire platform was measured in a stabilized temperature inside the PPMS, all other data were measured in slow ramping rates between 1.0 and 3.3 K/min. Note the logarithmic vertical axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

from each time segment is used to minimize errors with the theoretical curve by optimizing the unknown coefficients such as C , λ_s and λ_l . (See, for further details [6,7,9].)

3. Results and discussion

3.1. C_p measurements of several materials based on the scanning relaxation method

Finding an appropriate thermal grease above 300 K has been crucial to realize the high temperature C_p measurement scheme presented here. For example, the well-known thermal grease at low temperatures, Apiezon N-grease, evaporates at temperatures above 470 K. Another kind of thermal grease, i.e., white thermal grease (Dow Corning, 340 heat sink compound), did not show any significant evaporation up to 500 K but it turned out to become dry after repeated measurements above 500 K. Thus, it is less useful for repeated measurements of solid samples with a single microcalorimeter as the removal of the white grease as well as the sample becomes difficult. Another trial with silicone-vacuum grease (Dow Corning) did not show any significant evaporation up to 600 K nor the drying-out effect. However, thermal conductivity of the silicone-vacuum grease appears to be too low at high temperatures as the so-called τ_2 effect has significantly increased above 400 K.

As an alternative to circumvent the above difficulties, we have tried to use a small piece of metal with low melting temperature such as In or Wood's metal (an alloy made of Bi, Pb, Sn, and Cd). Above their melting temperatures, they are expected to become liquids but smaller vapor pressure than the N-grease. As shown in Fig. 4, a piece of In (630 μg) shows a sharp delta-like peak at 430 K in a warming run due to its first-order solid–liquid transition. The transition temperature in a cooling run was found to be about 0.1 K lower, due to the hysteresis coming from the first-order transition. These transition temperatures are quite consistent with the reported values [14], confirming the accuracy of our setup. The use of a small piece of In as a thermal ‘grease’ has been successful in a temperature window above 430 K because In in the liquid state gives a good thermal contact without serious evaporation. Once

the microcalorimeter is heated up above 430 K and cooled down again, most solid samples are well-embedded in the solid matrix of In so that it acts as a good thermal grease even below 430 K. Another metallic thermal 'grease', Wood's metal (410 μg) has been also useful because it shows its solid–liquid transition around 367 K (Fig. 4) and thus requires a lower T for heat treatment. However, both the metallic greases hinder repeated solid sample loadings as the sample is well-attached to the solid metal matrix at room temperature. Furthermore, after the measurements around ~ 700 K, we find that both In and Wood's metal reacts with the Au isothermal layer due to the eutectic point of Au–In alloy or Wood's metal–Au alloy [15]. As a result, the addenda platform often forms a solid alloy with the metallic grease, again hindering repeated usage of the same microcalorimeter. Another drawback of the metallic thermal grease that the addenda heat capacity with a small piece of In or Wood's metal of about few hundred μg increases significantly (by an order of magnitude) from that of the bare membrane, as shown in Fig. 4.

We find that using silicone oil (KF-96-1000CS, Shin-etsu) as the thermal grease shows significant improvements over the several drawbacks of the 'grease' materials discussed above. First of all, the silicone-oil shows relatively small evaporation at high temperature. Second, because it is easy to control the amount in the liquid form at room temperature, smaller addenda value can be achieved, as evident in Fig. 4. Third, repeated usage of the same microcalorimeter for measurements of different solid samples becomes possible as the silicone-oil is easier to remove or reapply to the membrane platform. Fourth, the thermal conductivity of the silicone-oil seems to be good enough not to show any significant τ_2 effect up to 700 K so that the CFM fitting scheme has worked well. We postulate that the low viscosity and different molecular makeup for the silicon oil has caused the enhancement over the silicone-vacuum grease (Dow Corning) although the basic ingredients are similarly silicone for both cases. In fact, the lower viscosity of the silicone-oil over the silicone-vacuum grease often allows a tiny solid sample to sink into the silicone-oil. Thus, thermal contact between the sample and membrane surface should be also enhanced.

3.2. C_p measurements of Cu with different scanning speeds

To test the accuracy of the microcalorimeter at high temperatures, we have measured the heat capacity of a piece of oxygen-free-highly-conducting Cu (280 μg). Before loading, we have polished the sample surface for good thermal adhesion. Then, we have applied a small drop of silicone-oil (KF-96-1000CS, Shin-etsu) to the isothermal platform and measured the addenda heat capacity first. After carefully loading the Cu sample onto the thermal grease area by use of a thin Cu wire, the sample heat capacity has been measured. The resultant heat capacity data (blue line) of the Cu specimen is plotted in Fig. 4. In this measurement, the base temperature was linearly varying with the scanning speed of 3.3 K/min.

To see the effect of the scanning speed on the measurement accuracy, the temperature of the tube furnace was ramped with different ramping rates. The results are shown in Fig. 5. We find that with systematic increase of the scanning speed, the calculated C_p curve shows slight deviations from the reported values at high temperature [16]. The maximum deviations become 4.4, 8.7, and 11.9% in scanning speeds of 3.3, 12, and 26 K/min, respectively. The origin of the positive error of 4.4% from the relatively slow ramping rate 3.3 K/min is not yet clear. It might be due to rather an imperfect isothermal condition of the membrane platform caused by the imperfect isothermal condition of the membrane layer or internal thermal resistance of the sample that still exists at such a high temperature [7]. The former can be linked to the radiation

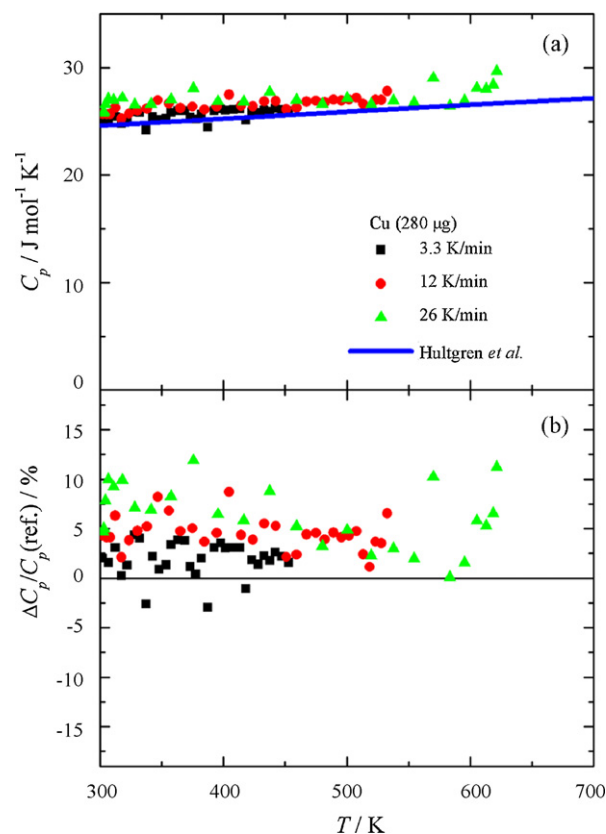


Fig. 5. Heating rate dependence of (a) the measured C_p of Cu (280 μg) and (b) relative errors as compared with the standard data of Hultgren et al. [16].

loss in the high temperature furnace and/or the low thermal conductance of the membrane platform. For the latter, the present fitting scheme based on the lumped τ_2 model cannot consider this additional relaxation time effect perfectly, which can cause the increased errors in the fitting process [10]. The systematic increase of the error with the increased ramping speed suggests the more significant contributions from the error sources above as the fast ramping is expected to create more non-adiabatic conditions in the membrane platform as well as inside the sample. Further efforts are currently being made to pin down those error sources.

In summary, within about 10% errors from the absolute value, we can apply our measurement scheme successfully up to 620 K. Although we have measured the Cu data only up to 620 K in Fig. 5 to mainly test the scanning speed dependence, we believe the same microcalorimeter with the silicone-oil grease and the Cu specimen will be able to operate up to 700 K without any difficulty. Therefore, the capability of operating the microcalorimeter in a scanning speed up to ~ 30 K/min in the current measurement scheme can be useful in future for exploration of non-equilibrium process of phase transitions or for fast measurements of C_p up to as high as 700 K.

We note that even if we have tried to increase the scanning speed via controlling the ramping rate of the tube furnace, the base T of the microcalorimeter did not increase further, possibly due to the thermal mass of the probe head. Thus, the scanning speed of ~ 30 K/min is currently the maximum in our scanning relaxation method. On the other hand, by employing the so-called large ΔT method (or sweeping method) [10], the scanning speed of our Si–N membrane microcalorimeter can be further enhanced. In this case, we apply a constant large amount of power at a base temperature to reach a final temperature. In a test run with a 55 μg YCrO_3 crystal [8], we could reach a maximum temperature step $\Delta T \sim 100$ K

in 10 s, or 600 K/min. With the larger temperature step, the sensor resistance has increased permanently or the membrane has broken down. However, if we reduce the sample mass used, we expect that the scanning speed can be further enhanced.

4. Conclusion

We have fabricated a sensitive microcalorimeter to measure heat capacity of solids at temperatures from 300 to 700 K by use of a Si–N membrane microcalorimeter and a commercial tube furnace. We have employed a new measurement scheme, termed scanning relaxation method that uses a continuous scanning of the base temperature during the C_p measurements with the curve fitting method to greatly overcome several experimental difficulties encountered at high temperatures. The measurement of a standard Cu sample up to 550 K matches the reported value within 5% at a slow scanning speed of 3.3 K/min and within 12% with a maximum scanning speed of ~ 30 K/min. The scanning relaxation method can measure the heat capacity with a sensitivity of $\sim 1 \mu\text{J}/\text{K}$ in a broad temperature range from 300 to 700 K.

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