

EXPLORATION OF A NEW METHOD OF SMALL SAMPLE AC-CALORIMETRY AT LOW TEMPERATURES

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Abstract: A new method for measuring heat capacities of small samples (\sim mg) at low temperatures (2–10 K) using an AC heating has been described. The incoming pulse has a special time dependence and under some circumstances gives a linear response. It is possible (on the basis of this linear response) to calculate the sample heat capacity from two independent results of the solution of the analogous differential equation.

1. Introduction

One of the main disadvantages of conventional low temperature calorimetry is the transient nature of the measurements a characteristic that makes difficult the use of any of the now highly developed signal averaging techniques to extract the wanted signal from noise. This limitation is of little importance in the measurement of the absolute value of the heat capacity where other considerations (mainly thermometer calibration) already limit the accuracy of the measurements. When measuring small changes in the heat capacity of small samples, however, the signal — to — noise ratio can become the limiting factor.

Additional disadvantages of conventional techniques system from the necessity of thermal isolation of the sample from its surroundings. The sample must be quite large to minimize the effects of stray heat leaks. Helium exchange gas or complicated heat switches are required in order to obtain sufficient isolation

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during the measurement and yet the sample must be cooled down in a reasonable length of time. Desorption of the helium gas causes appreciable calorimetric inaccuracies, whereas the heat generated when heat switches open impede measurements near the low extreme of the cryostat range. Finally, each experimental run yields only one point for each temperature. Thus if several points are required in a given temperature range, several complete runs must be made. This last point is especially bothersome in studies of heat capacities near second order phase transitions, where the density of points along the temperature axis must be high in order to follow the rapidly changing heat capacity and in studies where the heat capacity varies as a function of some external parameter such as magnetic field.

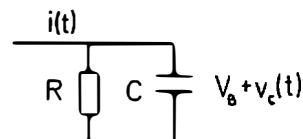


Fig. 1.
Analogous electrical circuit.

To alleviate the problems outlined above, a steady state calorimetry technique employing AC heating was developed¹⁾. In this technique heat is applied sinusoidally in time at a low frequency to a sample coupled to a thermal reservoir through a thermal leak (with a time constant of the order of seconds). This method makes possible a much more precise measurement of heat capacity changes as a

function of an external parameter, although the absolute accuracy of the heat capacity data is no better than that obtainable with traditional methods.

In the following Sections we describe a new method for measuring heat capacities at low temperatures. The incoming pulse, which is used for heating the sample, has a special time dependence which under some circumstances gives a linear response. The sample can be quite small.

2. The theory of linear response

We consider a system (consisting of a heater, thermometer and sample of heat capacity C_s) which is connected by a finite thermal conductivity K_s to a heat sink of large thermal capacity. System — to — sink relaxation time $\tau_s = C_s/K_s$ must be of the order of pulse interval $\Delta t = 1/2 f$ (where f is the heating frequency) so as to obtain good measurement conditions.

An analogous electrical circuit can be considered (Fig. 1) to find the conditions under which the response of the system to the heating pulse will be linear.

Let the thermal current $i(t)$ be of the form (Fig. 1a)

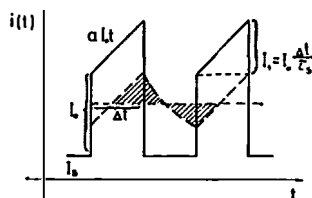


Fig. 1a. Form of the heating current (—), and response of the system (---).

$$i(t) = I_B + I_0 + a I_0 t, \quad (1)$$

where I_B is the base current, I_0 is the amplitude of the square wave on which a linear rise is added.

On the other hand it is equal to the sum of the currents through the resistance R and the capacitance C

$$i(t) = \frac{v_c(t) + V_B}{R} + C \frac{dv_c}{dt} \quad (2)$$

from which it follows

$$V_B + V_0 + a V_0 t = v_c(t) + V_B + \tau_s \frac{dv_c(t)}{dt},$$

where $\tau_s = RC$ is the time constant analogous to the relaxation time from the system to the heat sink.

If we assume a solution of the form

$$v_c(t) = C(t) \exp(-t/\tau_s) \quad (3)$$

than using the initial condition $v_c = 0$ for $t = 0$ we obtain

$$v_c(t) = a V_0 t + (V_0 - a V_0 \tau_s) [1 - \exp(-t/\tau_s)]. \quad (4)$$

In order to achieve a linear response, the term in the first bracket must be zero

$$V_0 - a V_0 \tau_s = 0, \text{ and then we have,}$$

$$v_c(t) = V_0 t/\tau_s = \left(\frac{I_0}{C}\right) \cdot t \quad (5)$$

or

$$v_c(t_0) = V_c = I_0 \Delta t/C = I_0/2fC \quad (6)$$

and

$$\frac{dv_c(t)}{dt} = \frac{I_0}{C}. \quad (7)$$

We note that analogously to the voltage variations (Fig. 1 a) the slope of the linear part of the temperature — time response as well as the amplitude of the temperature oscillations are inversely proportional to C , the total heat capacity. When linear response is obtained, we can calculate from Eqs. (6) or (7) the heat capacity of our system.

3. Experimental realization

Our problem was to find materials for the heater and the thermometer which would have small heat capacities and would be easily mounted on to the sample.

We used a colloidal graphite suspension in methyl isobutyl ketone (Acheson dag 305) for the heater. This material has an almost constant resistivity down to 4K. The heater is electrically isolated from the sample with a thin ($6\ \mu\text{m}$) mica sheet (Fig. 2). Mica was chosen because of its relatively high thermal conductivity,

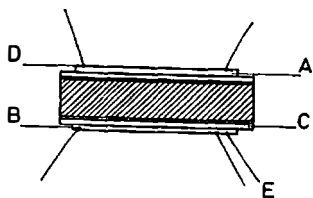


Fig. 2. Sample arrangement
A-heater, B-thermometer, C-mica
sheet, D-Ag contacts, E-copper
wires.

and the possibility to obtain thin sheets. The slab is mounted to the sample with G. E. 7031 varnish. The two copper current leads $50\ \mu\text{m}$ in diam. are fixed with silver conducting paint on to the mica sheet. When contacts are dry a layer of colloidal graphite is painted between them. The layer thickness of about $10\ \mu\text{m}$ and the distance between the silver paint contacts, about 10 mm, was chosen so as to obtain a room temperature resistance of about 2K.

The mass of the heater thus obtained is about 1 mg, which is important because our samples are very small ($\sim\text{mg}$).

It has been rather difficult to fabricate the right material for the thermometer. The requirements to be met are high sensitivity, low noise and low heat capacity. At high temperatures thermocouples serve quite well²⁾ but at low temperatures their sensitivity falls off drastically. Carbon resistors play an important role in low temperature thermometry. Their main advantage is a high sensitivity (dR/RdT), which may reach values of 500% per deg near 1K. This makes them very useful when small temperature differences have to be measured with high accuracy.

We have developed a technique of painting carbon resistors directly on a thin ($10\ \mu\text{m}$) mica slab. The technique is based on the method of de Vroomen³⁾, but we used another binding agent (Acryloid 75) in place of Araldite, because our samples are mostly metastable and cannot be thermally treated.

We chose a colloidal graphite suspension as a basic low resistance material for our thermometers. A component was sought that could increase the sensitivity. It was found that the addition of lampblack causes a moderate increase in resistivity but an important increase in sensitivity. We used two different kinds of lampblacks: Medium Thermax and the sample which was furnished to us by a local rubber manufacturer^{*)}. We also tested two kinds of graphite: Colloidal graphite in methyl isobutyl ketone (Acheson dag 305), and a fine graphite dust with a grain size of about $15\ \mu\text{m}$ in diam.^{**)}

^{*)} Marijan Čavić Co, Zagreb.

^{**)} Lonza Co. Ltd.

The thermometer mixture is prepared in several steps. The colloidal graphite, the lampblack and Acryloid are mixed thoroughly and then homogenised by passing through a glass mill. Toluene is added to the mixture, so that a layer can be painted on to the mica. Toluene is allowed to evaporate and then three copper current leads ($25 \mu\text{m}$ in diam.) are mounted on the thermometer with silver paint.

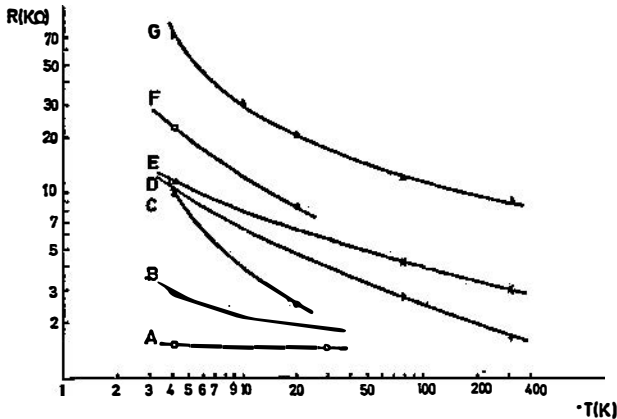


Fig. 3. Resistance — temperature curves of some carbon thermometers: A-aquadag, B-dag 305, C-Allen Bradley, D-Čavić — dag 305 — acryloid, E-Thermax — dag 305-acryloid, F-de Vroomen, G-Čavić — Lonza — acryloid.

In Fig. 3, the resistivity of various mixtures is plotted against the temperature. It can be seen that the mixture »Čavić-Lonza« is the best of all we have tested. It is better than that of de Vroomen, and almost as good as the Allen-Bradley thermometer. The advantage of this method lies in the possibility of preparing thermometers with different sensitivities by varying the composition.

Our measurements have shown that the binding agent has little influence on the thermometer characteristics.

4. *Electronic equipment*

We have seen in Sect 2. that special requirement is put on the shape of the heating pulse in order to obtain linear response. The additional heating power has to be linear in time, which means that the additional heating current must vary as the square root of time.

The block diagram of the electronic apparatus used for the specific heat measurement is shown on Fig. 4.

5. Measurements on aluminium and copper

In order to verify the effectiveness of our method we performed measurements on aluminium and copper.

The measurements were carried out in the calorimeter shown in Fig. 5. The heat sink is made of thick (4 mm) copper sheet. The sample is connected to the heat sink by copper wires about 1 cm long. The temperature of the sink is determined

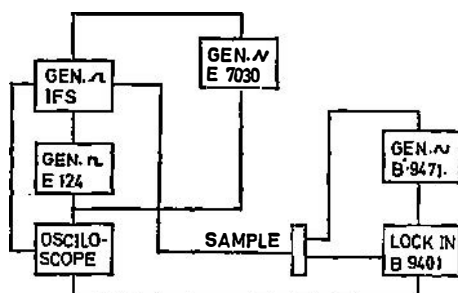


Fig. 4. Block diagram of the electronic apparatus used for specific heat measurement.

with a Ge-thermometer. The inner chamber is evacuated through a stainless steel tube (to about $10 \mu\text{-Torr}$). Carbon thermometers which measure temperature oscillations have to be calibrated during every measurement. After thermal cycling to room temperature the calibration generally shifts a few mdeg K at liquid helium temperature. Long term stability is only achieved when thermometers are kept below 20 K. The calibration is made against the Ge-thermometer.

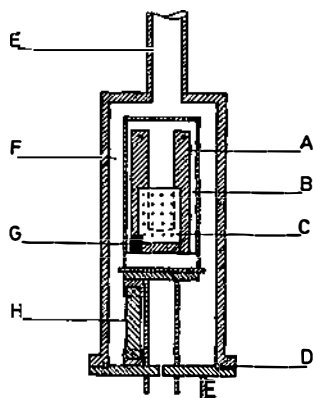


Fig. 5. Calorimeter

A-heat sink, B-inner chamber, C-sheet with contacts, D-In O-ring, E-stainless steel tube, F-outer chamber, G-Ge thermometer, H-thermal connection.

Our samples were 10 mm long, 5 mm wide and $15 \mu\text{m}$ thick. The heat dissipated in the heater was about 10^{-7}W , which corresponded to the incoming pulse of some 10 mV in magnitude.

Then the temperature oscillations are about $5 \cdot 10^{-3}\text{K}$ at a frequency of 4–5 Hz. We measured the thermal capacity of pure aluminium and copper at liquid helium temperature. A comparison was made with the value given in Ref.⁴⁾. Our values were a little higher (up to 5%) which can be explained by the fact that the heat sink may have been heated up a little by a stray DC component of the heat pulse.

Also, the vacuum inside the calorimeter may not have been quite high enough. Our aim at this stage however was to demonstrate the feasibility of the method rather than to achieve very high accuracies.

6. Conclusion

We have described a new AC method for measuring heat capacities, at low temperatures (2–10 K). Samples can be quite small, a very important feature because we cannot always obtain metastable samples large enough for measurements with a standard calorimetric method. Neither exchange gas nor a heat switch is required. It is possible to perform measurements simultaneously on several (3–5) samples. The method can be adapted to continuous data recording.

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ISPITIVANJE NOVE METODE NISKOTEMPERATURNE AC-KALORIMetriJE ZA MALE UZORKE

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Sadržaj

Opisan je razvoj i navedeni su rezultati nove metode niskotemperaturne kalorimetrije (2–10 K) vrlo malih uzoraka (\sim mg). Metoda se zasniva na principu mjerenja pomoću izmjeničnog signala, no ulazni termalni puls ima naročitu funkcionalnu zavisnost o vremenu, tako da pod određenim uvjetima daje linearni odziv. Na osnovu takvog linearnog odziva moguće je odrediti toplinski kapacitet pomoću dva nezavisna rezultata rješenja analogne diferencijalne jednadžbe.