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High-resolution adiabatic scanning calorimeter for small samples[☆]

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Abstract

An improved version of a low-temperature double calorimeter for the temperature range 20–320 K is presented. The temperature of the adiabatic shield is increased at a programmable rate, while the temperature differences to the samples are regulated to zero. Temperature control and data acquisition are achieved by software algorithms integrated in a single computer program. The apparatus yields a typical precision $\Delta C_p/C_p$ of 10^{-3} with ≈ 50 data K^{-1} .

Keywords: Adiabatic scanning calorimetry; Double calorimetry; High resolution calorimeter; Small samples

1. Introduction

For temperatures below that of liquid nitrogen (77 K) there has long been a lack of commercially available calorimeters. Usually calorimeters for this temperature range are home-made constructions and measurements with these machines are tedious, and often complicated, so that they have to be performed by specially trained personnel. Generally the classical Nernst heat pulse method is utilized.

Low temperature scanning calorimetry offers some advantages over the Nernst method. The resolution $\Delta C_p(T)/C_p(T)$ is usually better and can be as good as ca. 10^{-4} (see, e.g., Refs. [1–6]), which favours the detection of small or broad phase transitions. The number of independent data points per Kelvin can be much larger and measuring time is shorter than for a discontinuous method. However, the accuracy of $C_p(T)$

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depends strongly on the adiabatic shielding and on the temperature control of the shield.

Here we present an improved version of an adiabatic double calorimeter [7] that is suitable for small sample masses (≤ 100 mg copper). During the design of the apparatus aspects of full automation and easy sample and coolant handling were carefully considered. Because of the very flexible configuration of the hardware the calorimeter is operated in several scanning and discontinuous measuring modes. In the following we will discuss only one of these three possible measuring modes in more detail:

a Adiabatic scanning I

A calorimeter with one sample holder is used and the sample is heated with constant power P (or constant current I). The time derivative of the temperature \dot{T}_1 is measured and the heat capacity $C_p(T_1) = P/\dot{T}_1$ is deduced. The temperature of the adiabatic shield T_0 is kept at the sample temperature T_1 by a temperature controller.

b Adiabatic scanning II

The temperature T_0 of the adiabatic shield is increased by a programmed rate \dot{T}_0 and the temperature differences δT_i between the shield and the samples are kept at zero by temperature controllers. With this concept it is possible to use more than a single sample holder. It enables direct comparison between an unknown sample and a reference sample or the simultaneous measurement of two samples. The double calorimeter and data acquisition for this method will be discussed below in detail.

c Heat pulse method (Nernst method)

The temperature of the adiabatic shield is stabilized at T_0 . A heat pulse is then given to the sample holder and the temperature difference δT_1 is measured and interpolated in the usual way (see, e.g., Ref. [8]). This method is used preferentially with a calorimeter with one sample holder.

Each method has its specific advantages and drawbacks. Method a yields experimental data with very high resolution and good accuracy. Detection and detailed analysis of the very small (less than 1% of the total specific heat capacity) and broad (≈ 10 K) anomalies in $c_p(T)$ at the superconducting transitions of the bismuth and thallium high- T_c superconductors were recently achieved successfully with this method (see, e.g., Refs. [4] and [5]). However, at high temperatures, heat radiation limits the accuracy of this method.

Method b has some advantages over method a. More than a single sample can be measured at the same time under identical external conditions. Using a reference sample (calorimetric standard material, or non-superconducting/magnetic reference sample), it enables us to correct for errors of the absolute values at higher temperature or to detect small differences in the $c_p(T)$ curves of the samples. If lower accuracy (or only lower temperatures) is acceptable two samples can be measured at the same time. One important disadvantage is that extremely accurate control of sample temperature

is an essential part of the experiment. A related technique has been used for the separation of the electronic part of the specific heat capacity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ from the overwhelming phononic contributions [2].

The “classical” Nernst method (method c) yields good resolution and very good absolute accuracy, but has the disadvantage of being very time-consuming, when a large density of data points on the temperature axis is demanded.

Often very specialized electronic equipment is utilized for research calorimeters, allowing for only one specific method. Because of the extensive use of computer control, here we realize a highly flexible configuration of our measurement with one single calorimeter (and even with other calorimeters). The calorimeters are screwed on the cold plate of a ^4He continuous flow cryostat and are easily interchangeable (see also Ref. [7]). The samples can be changed quickly, because neither an indium seal nor a long pumping time is required. The electronic equipment can be “scaled down” to less expensive devices if the highest resolution and accuracy are not needed.

In the following we describe the double calorimeter which is used preferentially with the adiabatic scanning method b.

2. The double calorimeter

The calorimeter (for two sample holders) is schematically shown in Fig. 1. It consists of a gold-plated copper baseplate (73 mm diameter) and a similar radiation shield, which fits tightly onto the baseplate. The sample holders are $5 \times 6 \times 0.1$ mm sapphire plates, which are suspended with cotton threads. On the lower side a metallic thin film meander is used as a heater. A Pt100 platinum resistance thermometer is glued (GE-7031 varnish) on the same side. The samples are mounted on top of the sapphire plates with a minimum amount of high-vacuum grease (Apiezon N).

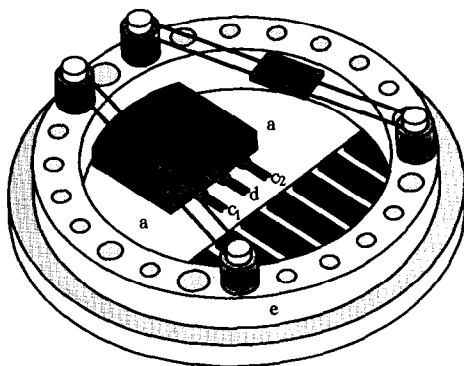


Fig. 1. The sample holder disc (simplified, without wiring): a, copper baseplate; b_1 , b_2 , sample holder sapphire plates with thin film heaters and Pt100 resistance thermometers, suspended with cotton threads; c_1 , c_2 , Pt100 resistance thermometers on the baseplate; d, Pt100 resistor for T_0 ; e, flange for the radiation shield; f, isolated copper strips (heat sinks for the wiring).

The Pt100 resistors on each sample holder form one arm of two independent Wheatstone-type bridges. The other arms are Pt100 (with selected, very similar $T(R)$ characteristics) situated in holes in the baseplate and (four) highly stable $10\text{ k}\Omega$ resistors outside the cryostat. With this arrangement the temperature differences δT_1 and δT_2 between each sample holder and the baseplate are measured. A fifth calibrated Pt100 resistor monitors the absolute temperature T_0 of the baseplate.

All electrical wiring (manganin or copper) is soldered to a heat sink on the baseplate. The wires of the calorimeter end in IC-pins, which are plugged into receptacles below the top-plate of the continuous flow ^4He cryostat.

3. Temperature control and data acquisition

Data acquisition and temperature control for all parts of the calorimeter are performed by a single computer program running on a multitasking Unix workstation (HP 300, 68040 processor). The advantage of performing the temperature control by the computer itself becomes clear when one remembers that measuring $C_p(T)$ means essentially measuring temperatures with resistance thermometers, i.e. measuring electrical voltages and currents that have to be converted to temperatures by the use of calibration curves $T(R)$.

The temperature control system for our double calorimeter consists of three independent control loops. A schematic diagram of operation is given in Fig. 2. The first loop (displayed in the lower part of Fig. 2) controls the programmed temperature increase \dot{T}_0 of the baseplate (typically $2\text{--}5\text{ mK s}^{-1}$, precision better than $\pm 10\text{ }\mu\text{K s}^{-1}$). It is formed by a calibrated Pt100 resistor monitored by a high resolution digital voltmeter (DVM, HP 3458A). The computer calculates the temperature T_0 , reads the time t and compares it with the setpoint temperature $T_{0,s}(t)$. The difference $T_0 - T_{0,s}$ is fed to an algorithm, which simulates an improved three-term controller with proportional (P), integral (I), derivative (D) and offset (O) terms and a reset time interval (R) for the I-part (PIDOR). An output signal is calculated, converted to an analogue voltage, by a D/A converter, and fed to a current source I_{h1} and I_{h2} which supply the sample holders.

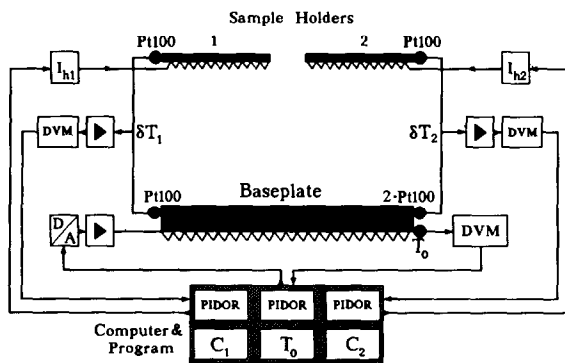


Fig. 2. Schematic diagram of temperature control and data acquisition for the double calorimeter (see text).

amplified by a constant current supply and then given to a heater below the calorimeter baseplate.

Similar control circuits keep the sample holder temperatures T_1 and T_2 at the baseplate temperature, i.e. $\delta T_i = T_i - T_0 = 0$ ($i = 1, 2$). Here the sensors for the temperature differences δT_i are Wheatstone-type Pt100 bridges. The zero-deflections are amplified by two analogue nanovoltmeters (EM, N1a) and digitized by two $5\frac{1}{2}$ digit DVMs (Keithley 197). The sensitivity of this arrangement is $\approx 10 \mu\text{K}$. The computer calculates the temperature differences δT_i and again feeds them to two PIDOR algorithms. The output signals are given to two programmable current sources (Burster 6707) and the dc currents I_{h1} and I_{h2} heat the samples. The temperature control can be as good as $\pm 30 \mu\text{K}$. The voltage drops U_{h1} and U_{h2} at the heaters are measured by a $6\frac{1}{2}$ digit DVM (Datron 1071). The heating powers $P_h = I_h \times U_h$ on the sample heaters are proportional to the heat capacities $C_p(T)$ of the samples plus their addenda contributions, i.e. $C_p(T) = U_h I_h / \dot{T}_0$.

4. First results

Fig. 3 shows the results of two measurements: In the first run (curve a) a relatively large mass of well characterized copper [9] was attached to the sample holder 1. In the second run (curve c) the empty sample holder 1 was measured. Both measurements were taken with heating rates of 2.5 mK s^{-1} , i.e. each run from 18 to 320 K took 33.5 h. The difference between the measurements is plotted in curve b of Fig. 3. The deviations of the specific heat capacity $c_p(T)$ of copper are $\pm 1\%$ in the temperature range 25–200 K as compared with the recommended copper data given in Ref. [10]. Above 200 K the specific heat capacities of Apiezon N grease and of GE-7031 varnish are not

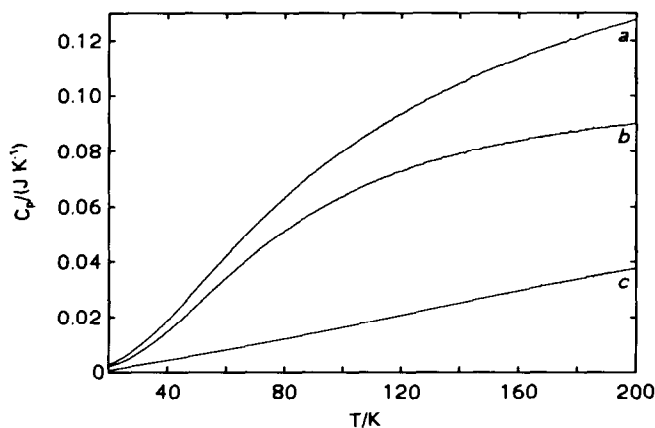


Fig. 3. a: Heat capacity measurement $C_p(T)$ of sample holder 1 and a 0.2528 g sample of 1965 Calorimetry Conference standard copper (sample T6.5); b: heat capacity $C_p(T)$ of the sample after subtraction of the heat capacity of sample holder 1; c: heat capacity measurement of sample holder 1.

well defined and hamper the evaluation of the $C_p(T)$ of the sample. The corresponding curves $C_p(T)$ for sample holder 2 and sample holder 2 plus sample were recorded simultaneously.

The rms deviation of curve a in Fig. 3 from a smooth fit is 1×10^{-3} of the absolute value for temperatures from 40 to 200 K. This precision depends strongly on the parameters P, I and D of the computerized temperature controller. If these parameters are not chosen suitably for the temperature range, oscillations with an amplitude of some 10^{-3} of the absolute value of $C_p(T)$ are found. They can limit the resolution of the method severely. Fine tuning of these parameters should make it possible to obtain resolution as good as the digital resolution of our heater current sources, i.e. 10^{-4} .

5. Conclusions

We have presented a double calorimeter for small sample masses for the temperature range 20–320 K. It is part of the computer-controlled measuring system which can be used with this or other calorimeter inserts in several measuring modes (two scanning methods, Nernst heat pulse method). The precision of a scanning measurement of 252.8 mg of standard copper is $\Delta C_p/C_p \approx 1 \times 10^{-3}$, the accuracy is 1%.

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