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LOW TEMPERATURE MICRO-CALORIMETRY BY DIFFERENTIAL SCANNING

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We describe the construction, operation and performance of a fully automated low temperature differential micro-calorimeter for heat capacity measurements on small samples ($m < 100$ mg) in the temperature range from 15 K to 300 K. The instrument is operated using different calorimetric methods, in particular adiabatic differential scanning. Its reliability is demonstrated by measuring the heat capacity of 23 mg of copper and 37 mg of cyclopentane with an error of less than 2%.

Keywords: differential microcalorimeter, heat capacity

Introduction

Low temperature calorimetry is a standard method for thermodynamic investigations. In recent years it found more and more applications in the study of phase transitions and critical phenomena. The temperature range above $T \sim 120$ K is covered by commercial DSC and DTA instruments. Calorimetry below $T = 120$ K, however, remained a domain of cryogenic laboratories working with individually designed equipment. Traditionally, the specific heat c_p of large samples (5–100 g) is determined using adiabatic calorimeters. On the other hand, modern material science requires investigation of much smaller sample quantities. The size of the samples available often excludes the application of standard calorimetric methods. Miniaturization therefore has become a permanent subject of innovation for scientist working in this field.

Since it is often difficult to maintain adiabatic conditions for small samples (below 1 g) at low temperatures, in the last decade, numerous non-adiabatic techniques were developed: AC-calorimetry [1], relaxation-time method [2], differential methods [3–6], dual-slope method [7, 8] and other

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methods [9, 10]. At the same time, the classical step-heating (NERNST) method was improved. Efforts were made to construct quasi-adiabatic low temperature calorimeters [11, 12] that work with small sample masses. Now it has become possible to measure routinely samples in the 0.1 g to 1 g range.

In order to minimize measuring time dynamical methods are favourable. Thus the continuous heating (or cooling) principle [13] – under adiabatic [14, 15] or non-adiabatic [16, 17] conditions – found broad application. This method has two advantages; first, the rather tedious and time-consuming classical adiabatic method – although still the most precise one – is overcome and, second, the use of small samples considerably reduces the internal relaxation times so that with sufficiently slow heating speed continuous data acquisition becomes available.

It is evident that miniaturization of calorimeters and reduction of sample size increase the difficulties to measure and to control heat transfer (losses by radiation or conduction) between sample and its surrounding.

The new calorimeter described in this paper is based on earlier instruments constructed in our laboratory [5, 18]. It was found that the use of high precision, small-sized Pt-100 thermometers instead of Au-0.03% Fe thermocouples as employed in the former set-up considerably improves the precision and reproducibility of temperature measurement. In addition, asymmetries in the thermometer circuit due to parasitic thermoelectric voltages disappeared. In order to establish low temperature calorimetry on small samples as a routine technique for solid state physics and chemical thermodynamics our calorimeter was designed to fulfil the following specifications:

- measurement of small masses, 10 to 100 mg,
- wide temperature range, 15 K to 320 K,
- precision of 1–2%,
- differential sample holder arrangement avoids systematic errors,
- highly reproducible and rigidly installed sample holder,
- high precision and reproducible (calibration-independent) thermometry,
- high flexibility: possibility to measure solids or liquids of any morphology,
- fully automatic operation, data collection and computation,
- reliable, simple and easy-to-handle cryo-technique.

We report on the details of construction of our new micro-calorimeter. The operation and performance are demonstrated by measuring standard copper and three phase transitions of cyclopentane.

Measuring method

A software was developed that allows to determine c_p by various methods: adiabatic step-heating, quasi-adiabatic and relaxation-time method, differential isoperibol scanning and adiabatic or non-adiabatic differential scanning. In the following we focus on quasi-adiabatic step-heating and adiabatic scanning techniques.

General description of the set-up

Calorimetric measuring cell and electronics

The calorimetric cell is cooled by an upside-down positioned continuous flow (cf) cryostat [19] which is mounted directly on top of a liquid helium vessel. The measuring cell is shown in Fig. 1. Two sample holders are arranged in a symmetrical twin cell, to perform difference measurements which reduce systematic errors and significantly increase the accuracy of the measured absolute c_p - values. One sample holder is used for a sample of unknown heat capacity and the other one for the reference sample. The support of the sample-holders, a ring shaped copper plate (diameter 70 mm, 2–5 mm thick), is screwed to the evaporator of the cf-cryostat by interlaying

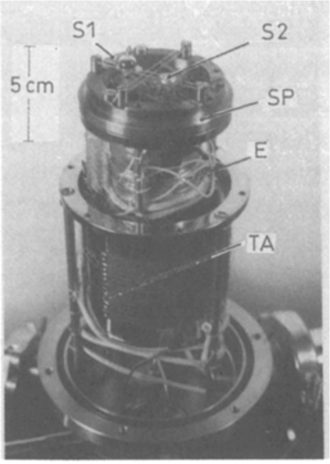

Fig. 1 Calorimeter cell and continuous flow helium cryostat without thermal shield.
E – evaporator of helium cryostat, SP – sample holder support, S1, S2 – sample holders with samples, TA – thermal anchoring of electrical wiring

three 1 mm thick brass rings as thermal resistance R_{Th}. The measuring cell is located in high-vacuum and covered with a gold-plated radiation shield. Thus both, thermal shield and support (measuring cell), are at the same base temperature. The electrical lines are thermally anchored to the evaporator by Kapton foil on which metallic stripes are evaporated. The foil is glued to the evaporator by GE-7031 varnish. The two sample holders of the plateform-type [20] consist of polished sapphire (12 mm diameter, 0.1 mm thickness) discs and are suspended by a grid of very thin cotton wires which provide excellent thermal insulation. On to the lower side of each sapphire a 1.2 kOhm NiCr resistance is sputtered as heater and a calibrated 100 Ohm platinum resistance (ROSEMOUNT type 118MF 100°C, $3.5 \cdot 3.3 \cdot 1$ mm^3 in size) is attached (by GE 7031 varnish) as thermometer. Two further identical Pt-thermometers are placed on the sample-holder support. Electrical wiring between the sample holders and the support is made by 3 manganin wires of 0.05 mm diameter for the potential probes and 4 times 0.07 mm for the current leads, respectively (for each sample holder).

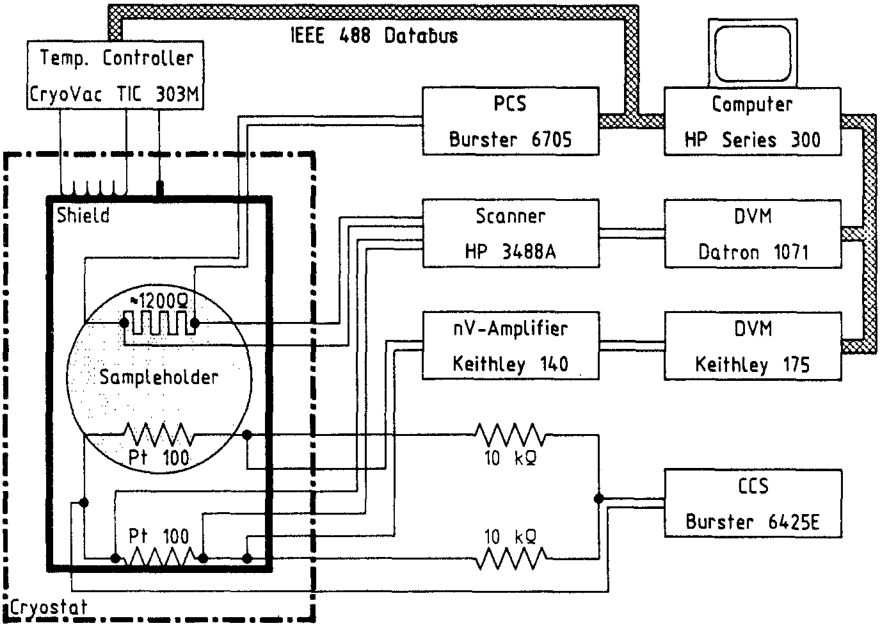

Fig. 2 Block diagram of the electronics; PCS, CCS – Programable and constant current sources, respectively. For reason of clarity, only one sample holder of the differential set-up is shown

The micro-calorimeter is controlled by a computer (HEWLETT-PACKARD, HP 9000/300). The electronic components are interconnected by

IEEE-488 data bus. Figure 2 displays the block diagram. – The temperature of the evaporator is roughly set by a computer controlled valve installed in the helium gas outlet line (not shown in Fig. 2) and regulated by a temperature controller (CRYOVAC, TIC-303) using a 30 Ohm heater and a Si diode as temperature sensor, both connected to the evaporator of the cf-cryostat. In combination with the thermal resistance R_{Th}, the base temperature of the sample-support is stabilized to 5 mK. – Heater power and absolute temperature are determined by use of 4 wire dc-technique. Variable heater power (on both sample holders) is provided by programmable current source (BURSTER, Digistant 6705) and determined by a digital voltmeter (DATRON 1071) via a scanner (HP 3844A). The absolute base temperature is measured in an analogous circuit (Fig. 2). Thermoelectric voltages are eliminated by reversing the direction of the current. Voltages are measured better than 0.005%; effective currents are determined by the voltage drop on standard resistors. – Temperature variations of the sample holders are detected as temperature differences between holders and support by a highly sensitive bridge arrangement (see lower left of Fig. 2). The bridges, one for each sample holder unit, are built up of two identical 10 kOhm resistors at room temperature and two calibrated Pt-100 sensors, one located on the sample-holder and the second as a reference at the base temperature (support). The bridge is supplied with 1 mA current (BURSTER 6425E). The out-of-equilibrium voltage, that is proportional to the temperature difference between sample and support, indicates the time dependence of the sample temperature. This voltage is fed into a Nanovolt amplifier (KEITHLEY 140) and recorded by a DVM (KEITHLEY 175). The temperature resolution is better than 0.001% (1 mK at 100 K).

Operation of the calorimeter and data computation procedure

For the measurement, the reference sample and the sample to be investigated are top-loaded on the sapphire plates. Thermal contact is ensured by a precisely weighed amount of Apiezon-N grease (<0.2 mg) with well known heat capacity [21] which is subtracted from the measured heat capacity during the measurement. An advantage of the calorimetric cell is that it must not be displaced when changing samples. Its heat capacity remains unmodified and therefore is highly reproducible (better than 0.5%). Replacement of a sample is done in less than 15 min. The heat capacities of the two sample holders are determined in a separate run and stored as a polynomial fit for direct computation during the experiment. Similarly, the thermometric function of the Pt-100 sensors (resistance *vs.* temperature relation) and the temperature dependent heat capacities $C(T)$ of aluminium and copper are fitted and stored on file [11].

Within about 30 min the calorimeter cell is cooled down to its lowest temperature of about 15 K, further 5-6 h are needed to equilibrate the samples and to reach the same low temperature. A run from 15 K to 300 K, performed with the quasi-adiabatic method is lasting about 3 to 4 days and consumes nearly 16 l of liquid helium; about 200–300 c_p – data are taken for such a run. For the adiabatic scanning, 10 l are needed during about 15 h.

Data computation procedure

Measurements with the quasi-adiabatic method are carried out similar to the procedure described in our earlier papers [11, 18]. However, the evaluation of the temperature driftcurves is slightly modified since, dealing with small samples, they are no more linear in temperature. The standard method for extracting c_p from the driftlines by linear extrapolation of the pre-heating and post-heating periods is particular sensitive to temperature variation of the thermal shield and to any overshooting of the heating curve. Such effects become increasingly important with decreasing sample mass (heat capacity). To correct for the resulting non-linear T-driftcurves, we expand the correct mathematical exponential solution for the heating and post-heating period to second order [22] and obtain:

$$C = (P \cdot t_H / \Delta T) \cdot (1 + (1/24) \cdot (\beta \cdot t_H)^2),$$

where P denotes the heater power, t_H the heating time and $\beta = c/k$ is the inverse thermal relaxation time of the system with c, heat capacity, and k, thermal conductance to the surrounding. The application of this correction has decreased the scatter of the measured c_p – data by a factor of 3.

In adiabatic scanning the base temperature (support and thermal screen) is rised either at an uniform rate (dT/dt) adjusted by the temperature controller or nearly uniformly by disconnecting the liquid helium vessel. In practice, heating rates vary from 1 to 10 mK/s (typically 3 mK/s). Temperature differences (up to 50 mK) which develop between each sample holder and surrounding are detected by the thermometer bridges and balanced to zero by corresponding setting of the two programmable current sources for the sample heaters. Such adjustments occur at constant time intervals, typically every 10 to 100 s. The new heater currents for the next time interval are calculated by expanding a chosen number (typically 3) of the preceedingly measured temperatures of the samples and of their calculated heat capacities in a (Taylor) series. The heat capacity is finally calculated as the derivative of the heating curve taking into account deviations from shield temperature and averaging over a preselected number of measuring points (1 to 10):

$$C(T) = \frac{P}{(\mathrm{d}T/\mathrm{d}t)_s - \delta(\mathrm{d}T/\mathrm{d}t)} \quad \text{with } \delta(\mathrm{d}T/T) = (\mathrm{d}T/T)_s - (\mathrm{d}T/T)_{ts}$$

In this relation *P* is the heating power and d*T*/d*t* denotes the time dependent temperature variations of sample (*s*) and thermal screen (*ts*).

The essential parts of the programs for the different measuring methods are very similar to that described in Refs [11, 18].

Results of calibration measurements

Copper sample

The absolute accuracy of the micro-calorimeter was checked by measuring the heat capacity *c* of standard copper samples of 23 mg, 70 mg and 280 mg [23]. Figure 3 presents one result, the measurement for the 23 mg sample using the quasi-adiabatic method. The insert displays the deviations of *c* for two samples. Over the investigated temperature range, the absolute error is less than 3%. The sample holder (addenda) heat capacity amounts to about 50% of the total one near 30 K, and to nearly 80% for $T > 100$ K;

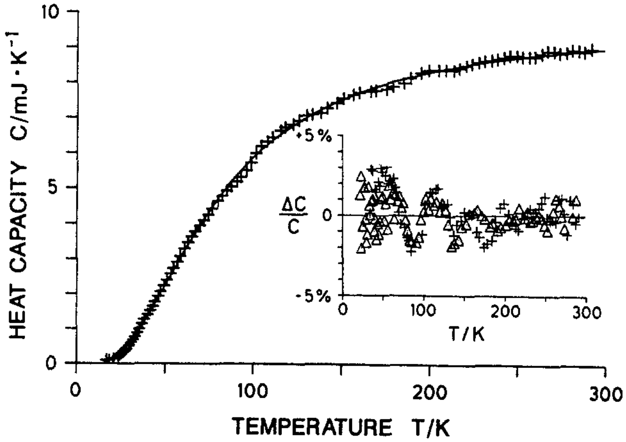

Fig. 3 Heat capacity of the 23 mg copper standard sample [23] as a function of temperature, measured with the quasi-adiabatic method. The continuous line indicates values recommended by D. L. Martin [23]. Insert: Percentage deviation between measured heat capacities and values from literature (zero line) [23]: 23 mg sample (+ + + +), 70 mg sample (ΔΔΔΔ)

its heat capacity is 17 mJ/K near 70 K. The energy resolution achieved 2.5 μJ at 20 K and 34 μJ near 100 K; the temperature resolution is always much better than 1 mK.

Cyclopentane

Further calibration and tests of the capabilities of the calorimeter were performed with two samples (37 mg for C-measurement and 8.9 mg for determination of transitions T_c) of cyclopentane [24], encapsulated in aluminium pans taken from Perkin-Elmer DSC-2. The specific heat of the 37 mg sample, measured by adiabatic scanning, is given in semilogarithmic plot in Fig. 4. The absolute error of the specific heat is generally less than 2%. In the insert of Fig. 4 the three phase transitions are depicted. The transition temperatures T_c are detected at:

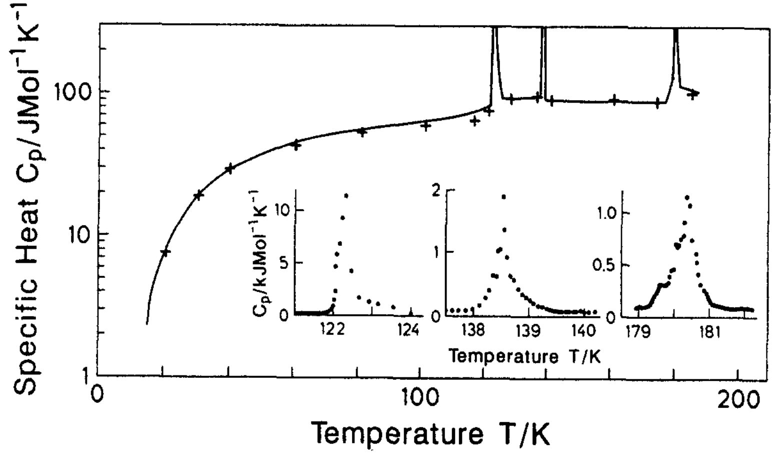

Fig. 4 Specific heat of a 37 mg sample of cyclopentane measured with the adiabatic scanning method (—) and selected data from Aston *et al.* [25] (+ + + +) Insert: Phase transitions at about 122, 138 and 179 K

T_{c1} = 121.95 (0.15) K, T_{c2} = 138.22 (0.12) K and T_{c3} = 179.21 (0.1) K. The corresponding enthalpies are found to be ΔH = 5195 (250) J/mol, 361 (19) J/mol and 615 (24) J/mol. Our data for T_c and ΔH are, within the given errors, in agreement with the values obtained by adiabatic precision calorimetry [25].

The use of aluminium pans has several advantages:

(i) it provides reproducible conditions for the heat exchange by thermal radiation between samples and surrounding,

(ii) the thermal coupling to the sample holder remains constant,

(iii) it makes the systems less susceptible for thermal perturbations

(iv) using vapour-pressure tight pans any solid or liquid sample can be investigated.

Due to computer-controlled and selectable measuring procedures, simple sample-loading and handling of the cryogenic equipment, the described new microcalorimeter is a precise, very reliable, highly flexible and easy-to-handle instrument. It enables to investigate samples of any morphology; even very air sensitive ones sealed in DURAN glass bottles (120 mg) were also investigated.

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Zusammenfassung — Es wird der Aufbau, die Funktions- und Arbeitsweise eines vollautomatisierten Differential-Mikrokalorimeters für Wärmekapazitätsmessungen kleiner Proben ($m < 100$ mg) im Temperaturbereich 15-300 K beschrieben. Die Funktionsweise des

Gerätes beruht auf verschiedenen kalorimetrischen Methoden, insbesondere auf *adiabatischem Differential-Scanning*. Seine Zuverlässigkeit wird durch die Messung der Wärmekapazität einer 23 mg-Kupferprobe und einer 37 mg-Cyclopentanprobe mit einem Meßfehler von kleiner als 2% demonstriert.