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DISC – A DIFFERENTIAL ISOPERIBOL SCANNING CALORIMETER

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The construction and operation of a new fully automated microcalorimeter is described. This instrument allows specific heat measurements to be performed on small samples in the 10 mg-range at low temperatures (10 K $< T <$ 350 K). The new method consists of combining the non-adiabatic relaxation-time 'calorimetry with a twin arrangement and simultaneous temperature scanning. Some experimental details of the calorimeter and sample holders are presented. The accuracy of the calorimeter was verified by calibration measurements on 56 mg of copper. An energy resolution of 0.1 μJ/K has been reached near 12 K. To demonstrate the reliability of the microcalorimeter the heat capacity of the new high T_c superconductor $YBa_2Cu_3O_{7-y}$ was determined.

Calorimetry is a powerful tool for the entire field of natural science. The measurement of the heat capacity C_p provides the fundamental thermal parameters concerning the energy states of solids and liquids, thermodynamic functions and phase transitions. In spite of the rapid development in instrumentation and automatization in the last 15 years [1–4], the overwhelming number of calorimetric investigations still remains restricted to temperatures above 120 K. Nevertheless, design and handling of adiabatic low temperature calorimeters for *routine* measurements were simplified and the necessary sample masses were reduced substantially to 0.2–0.5 g[5–7]. In order to determine still smaller heat capacities, in particular of very small samples, (m $<$ 50 mg) new experimental techniques were developed. Among these techniques the non-adiabatic AC-method [8] and the relaxation-time method [9] turned out to be the most profitable ones. Both have found a wide spread application and have been further developed and modified [10, 11]. A focal point for todays materials science research is to make calorimetric measurements in the extreme small mass regime (1–50 mg) more routine and more accurate.

In this contribution we describe some essential features as the principle, construction and operation of a new automated microcalorimeter [12]. In our opinion this instrument meets all requirements to determine heat capacities of small samples in the 10 mg range between 10 K room temperature.

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Principle and experimental set-up

The new microcalorimeter is based on the relaxation method, that means it works under isoperibol conditions. This is the only warranted technique suitable to detect heat capacities of small samples at low temperatures. A twin arrangement was chosen in order to take into account the strongly temperature-dependent thermal heat transfer between sample and surrounding at any temperature (4 K $< T <$ 300 K) and therefore to rule out systematic errors. The scanning technique was applied to make almost continuous and to accelerate the measuring procedure.

Two sample holders of the platform-type are symmetrically arranged in the middle of a ring-shaped copper plate (diameter 80 mm) which is placed on top of an up-side-down positioned continuous flow cryostat. Two sapphire discs (thickness $\cong$ 0.10 mm) suspended by cotton threads are each equipped with a 1.3kΩ heater (NiCr evaporated on the lower side) and with a difference thermocouple (Au0.07%Fe *vs.* chromel; diameter 75 μm) to the surrounding, as shown in Fig. 1. Each of the sample holders behaves like that in the commonly used relaxation-time method. The heat leak is provided essentially by the 4 electrical connections of the heater (5 μm thick gold wires) bonded to the sample holder on one side and glued with silver epoxy to the copper support on the other side. The copper support serves as a surrounding T_o bath and acts as a thermal shield. At higher temperatures it is crucial to prevent any radiation to the sample holders; therefore it is covered by a copper radiation shield. The sample to be investigated and the reference specimen are placed directly onto the sapphire plates. Thermal contact is ensured by a precisely weighted amount of Apiezon-N grease, the heat capacity of which is well known.

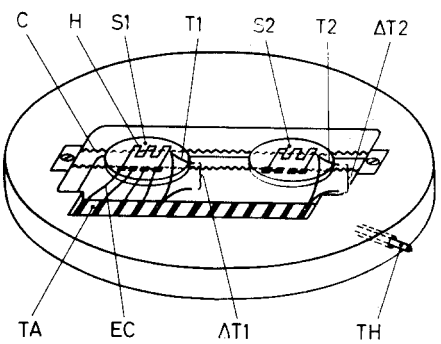

Fig. 1 Support plate with two symmetric sample holders: *H* heater; *S*1, *S*2 sample holders; *T*1, *T*2 thermocouples; $\Delta T1$, $\Delta T2$ temperature differences of the thermocouples; *TH* thermometer; *TA* thermal anchoring; *EC* electrical connections; *C* cotton wires

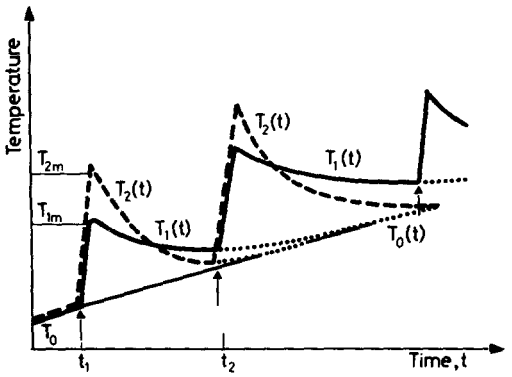

Fig. 2 Temperature-time behaviour of the differential, non-adiabatic heating curves

The temperature-time behaviour of the twin arrangement is displayed in Fig. 2. A heat pulse is supplied simultaneously to both sample holders. The subsequent decay of both, right- and left hand side sample temperature increments ΔT_j ($j = 1,2$) occurs, with two different relaxation times τ_j according to the different total heat capacities C_j (sample and addenda) and slightly different thermal links K_j. Instead of waiting for a new temperature equilibrium in the present method the shield temperature is continuously swept with a speed S[K/s] during successive heat pulses given to both sample assemblies. The resulting non-adiabatic, continuously step-wise increase of the samples temperature can mathematically be described.

$$\Delta T_{jk}(t) = (\Delta T_{jk}^{max} + S\tau_{jk})[\exp(-t/\tau_{jk})] + S(t-\tau_{jk}) \qquad (1)$$

where $k = 1$ to n denotes the number of the non-adiabatic heating cycle. During an automatic measurement approximated C_p-data are calculated from the temperature increments in order to control the experiment. After having performed a complete experiment the specific heats are recalculated precisely by iterating equation 1 with respect to τ_j (T) and use of smoothly fitted K_j (T)-values for the thermal link S: $C_j = \tau_j K_j$. The K_j-values are determined in a preceding run. The heat capacities can be computed by different methods: i) logarithmic fitting of the temperature decays $\Delta T_j(T)$, ii) computation of the maximal temperature increment ΔT_j^{max} of the short heating times (less than 5 sec), iii) calculation of the surface area of the relaxation curve by the integral $\int_o^\infty \Delta T_j(t)\mathrm{d}t$, or iv) exact solution of Eq. 1.

The microcalorimeter is working fully automatic. The hardware, being similar to that described in [2] is interconnected via an IEEE-488 data bus. The temperature of the surrounding is measured by a calibrated germanium or platinum resistor. The temperature differences between each sample and T_o are detected by Nanovoltmeters (Keithley Type 140) which amplify the very small thermovoltages ($\simeq$ 10 μV at 12 K). Special efforts have been made to simplify the cryogenic equipment and its handling and to integrate this equipment into the automatization; details will be reported elsewhere.

Results

The DISC set-up has proven to give reliable data. Calibration measurements between 10 K and 100 K of 56 mg standard copper were in agreement with literature data within 3%. The capability of the microcalorimeter has been also demonstrated by measuring 20 mg of the new high T_c-superconductor $YBa_2Cu_3O_{7-y}$ in the temperature range from 30 K to 120 K. An anomaly in the heat capacity amounting to 4 mJ/(Mol K) was resolved at the superconducting transition temperature at 91 K [13]. The pure heat capacity of the transition (the lattice contribution being subtracted) is plotted in Fig. 3 as $\Delta C_T/T$ *vs.* T.
These two examples demonstrate that our calorimeter is well suited for the investigation of mg-samples below 100 K. The heat capacities of both

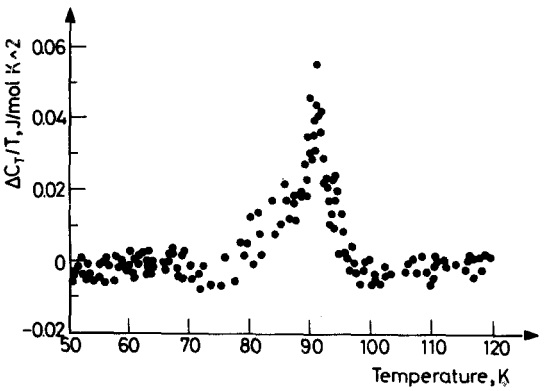

Fig. 3 Specific heat $\Delta C_T = C_{total} - C_{lattice}$ of the superconducting transition of $YBa_2Cu_3O_{7-y}$ plotted as $\Delta C_T/T$ *vs.* T

samples have been measured with the relaxation-time method and scanning technique. Typical heating times were 4 sec. The resulting thermal relaxation times τ_j varied rapidly with temperature due to the strong variation of $C_p(T)$. Thus, τ_j changed from 20 sec near 30 K to 190 sec at 80 K and 265 sec near 120 K for a 20 mg copper sample including the addenda. Because of the short relaxation times at low temperatures, at present the scanning technique is restricted to temperatures above 30 K. At lower temperatures ($T < 30$ K) we use the conventional relaxation-time method with constant surrounding temperature [9]. At sufficiently high temperatures, in general above 100 K, we can work with the microcalorimeter under quasi-adiabatic conditions. Obviously adiabatic or "quasi-adiabatic" measurements are more favourable if the sample mass is large enough. The DISC is used under high vacuum conditions. However our experiments showed that above 80 K reliable results can be achieved even in the presence of exchange gas (ca. 0.1 Torr). According to our experience the determination of the heat capacities of small samples requires careful inspection of the heating curves. For optimized results, relaxation-time type experiments, isoperibol scanning or quasi-adiabatic measurements had to be choosen appropriately as function of the temperature-range and the sample mass. Our ultimately achieved resolution with this instrument was 0.1 μJ/K at low temperatures (12 K).

In conclusion, the new twin type scanning calorimeter enables calorimetric studies of samples weighting 10 mg to 50 mg at low temperatures ($10 \text{ K} < T < 300$ K). We emphasize that the set-up is not limited to certain type of samples rather than it was designed as a routine technique applyable to any type of specimen.

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Zusammenfassung – Konstruktion und Betrieb eines neuen vollautomatischen Mikrokalorimeters werden beschrieben. Mit dem Instrument können Messungen von spezifischen Wärmen an kleinen Proben im 10-mg-Bereich bei tiefen Temperaturen ($10\ K < T < 350\ K$) durchgeführt werden. Mit der neuen Methode werden die nichtadiabatische Relaxationskalorimetrie mit der Zwillingsanordnung und gleichzeitigem Temperaturscanning kombiniert. Das Meßsystem des Kalorimeters mit der Probenhalterung wird genauer vorgestellt. Die Genauigkeit des Kalorimeters wird durch Eichmessungen mit einer Kupferprobe (56 mg) geprüft. Nahe 12 K wurde eine Auflösung von 0.1 $\mu J\ K^{-1}$ erzielt. Die Zuverlässigkeit des Mikrokalorimeters wird an einer Bestimmung der spezifischen Wärme des neuen Supraleiters $YBa_2Cu_3O_{7-y}$ demonstriert.

РЕЗЮМЕ — Описана конструкция и принцип действия нового полностью автоматизированного микрокалориметра. Прибор позволяет проводить измерения удельной теплоемкости с малым количеством образца (около 10 мг) при низких температурах в интервале $10\ K < T < 350\ K$. Метод состоит в комбинировании неадиабатического время-релаксационного калориметра с двойным расположением и с одновременным измерением температуры. Представлены некоторые экспериментальные детали калориметра и держателей образцов. Точность калориметра была проверена калибровочными измерениями 56 мг меди. Разрешение по энергии составляло 0,1 мкдж/К и было достигнуто при температуре около 12 К. С целью показа надежности микрокалориметра была определена теплоемкость нового T_C сверхпроводника $YBa_2Cu_3O_{7-y}$.