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AN A.C. CALORIMETER FOR HIGH-RESOLUTION HEAT CAPACITY MEASUREMENTS IN A MAGNETIC FIELD *

V. CALZONA, M. PUTTI and A.S. SIRI
CNR, INFM, Dipartimento di Fisica, Via Dodecaneso 33, 16146 Genova (Italy)
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ABSTRACT

We are developing a calorimeter operating from 4.2 to 200 K in a magnetic field of up to 8 T for measurements on high-temperature superconductors. To measure the heat capacity we have modified the a.c. method in use for low-temperature measurements (1–10 K) and adjusted it for measurements at intermediate temperatures (50–200 K). This method is very sensitive and allows a high resolution.

Preliminary measurements on YBCO samples are shown. Good temperature resolution (40 mK) and quite good precision (0.6%) were obtained. Reference is also made to the great length of time needed for each measurement.

INTRODUCTION

High-resolution heat capacity measurements on YBCO samples have shown anomalous behaviour at the superconducting transition. Butera [1] observed a λ-transition at 86.65 K and measured a latent heat at 90.30 K. Inderhees et al. and Salamon et al. studied the effect of fluctuations on the specific heat close to the critical temperature, T_c, with and without a magnetic field [2,3].

Indeed, the critical region, δT_c near the critical temperature where the Ginzburg mean-field theory breaks down, increases when the coherence length decreases [4]. Although δT_c was negligible (10^{-7} to 10^{-14} K) on conventional superconductors, it can become important for the high T_c superconductors (10 mK–1 K) [5].

These effect can only be detected with high-resolution measurements. We have therefore developed a calorimeter which measures from 4.2 to 200 K in a magnetic field of up to 8 T using an a.c. method [6].

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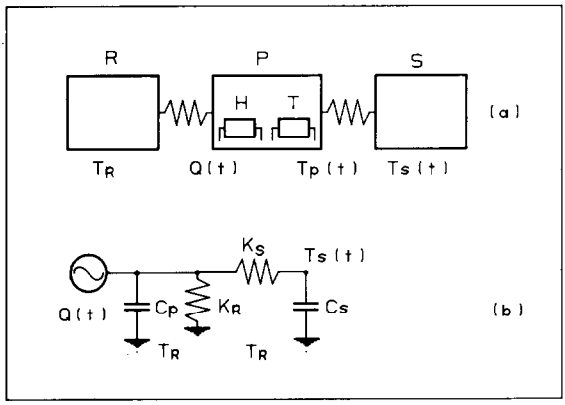

Fig. 1. Calorimeter diagrams: a, the system consisting of the heat reservoir, R, the platform, P, with attached heater, H, and thermometer, T, and the sample S; b, the system in the case of infinite thermal conductivity of S and P.

THE A.C. TECHNIQUE

A stationary a.c. heating is supplied to the sample, and the heat capacity is obtained through the periodic component of the temperature $T(\omega)$.

Figure 1a shows a diagram of the system. The calorimeter consists of a platform (P) with a heater (H) and a thermometer (T) attached. The platform is thermally coupled to the reservoir (R) and the sample (S). Assuming that the various parts of the calorimeter have infinite thermal conductivity, the system may be pictured as in Fig. 1b, where C_P and C_S are the platform's and the sample's heat capacities, and K_R and K_S are the thermal conductivities to the reservoir and the sample respectively.

In this case, we have the following equations

$$Q(t) = C_P\dot{T}_P(t) + K_R[T_P(t) - T_R] + K_S[T_P(t) - T_S(t)] \tag{1}$$

$$K_S[T_P(t) - T_S(t)] = C_S\dot{T}_S \tag{2}$$

If the heater supplies a heat wave $Q = Q_0 + Q_0 \sin \omega t$, we have

$$|T_P(\omega)| = \frac{Q_0}{\omega C}\{1 + \omega^2\tau_{int}^2\}x$$

$$\times\left\{1 + \frac{1}{\omega^2\tau_{ext}^2} + 2\frac{\tau_{int}}{\tau_{ext}}\frac{C_S}{C} + \left(1 + \frac{C_P^2}{C^2}\right)\omega^2\tau_{int}^2\right\}^{-\frac{1}{2}} \tag{3}$$

$$|T_S(\omega)| = \frac{Q_0}{\omega C}\left\{1 + \frac{1}{\omega^2\tau_{ext}^2} + 2\frac{\tau_{int}}{\tau_{ext}}\frac{C_S}{S} + \omega^2\tau_{int}^2\frac{C_P^2}{C^2}\right\}^{-\frac{1}{2}} \tag{4}$$

$$T_P(\omega) = (1 + i\omega\tau_{int})T_S(\omega) \tag{5}$$

where $C = C_P + C_S$, $\tau_{int} = C_S/K_S$ is the heat response time of the sample and $\tau_{ext} = C/K_R$ is the sample–reservoir relaxation time.

If we meet the condition $\tau_{int} \ll 1/\omega \ll \tau_{ext}$ it follows from eqns. (3)–(5) that

$$T_P(\omega) \simeq T_S(\omega) = T(\omega)$$

and

$$C = \frac{Q_0}{\omega T(\omega)} \tag{6}$$

If not, we obtain τ_{int}, τ_{ext} and C.

APPARATUS

The calorimeter consists of a silicon single-crystal platform ($14 \times 14 \times 0.3$ mm^3) with a heater (100 Ω RuO_2, thick-film resistor), and two thermometers (100 K Ω RuO_2, thick-film resistor for $T < 40$ K and platinum resistor for $T > 40$ K). Two thermocouples (Au 0.07 at.% Fe–chromel) measure the temperature differences between platform and reservoir and between sample and reservoir. The heat capacity of the whole platform (+heater and +thermometers) is 70 mJ K^{-1} at 77 K. The calorimeter is placed inside a Nb–Ti superconducting solenoid which reaches 8 T.

Careful consideration has been given to the choice of thermometers with low magnetoresistance. RuO_2 is practically unaffected by the magnetic field and is used to calibrate the thermocouples in a magnetic field at low temperatures.

Figure 2 is a block diagram of the measurement system. A computer generates the power $Q(t)$ at frequencies ω and 2ω, Fourier-transforms these signals and acquires $T_P(t)$ and $T_S(t)$ from two 140 Keithley nanovoltmeters. It then calculates C using the double-data series $(T_P(\omega), T_S(\omega))$ and $(T_P(2\omega), T_S(2\omega))$, and asynchronously provides for the thermoregulation as well as the choice of the best Q_0 and ω values.

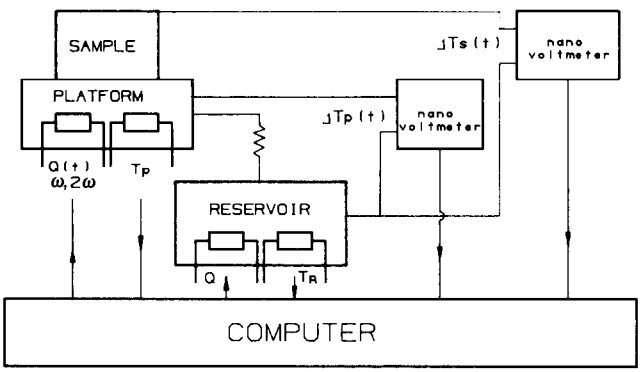

Fig. 2. Block diagram of the measurement system.

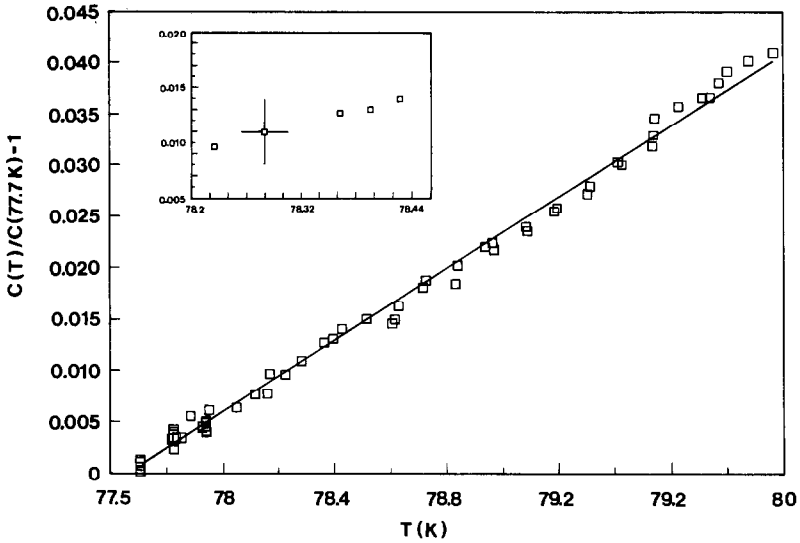

Fig. 3. Relative variation of the platform heat capacity vs. temperature. The straight line represents the best-fit curve. The temperature resolution (40 mK) and the stochastic error are shown in the inset.

With this system, it was possible to detect an oscillating temperature, $T(\omega)$, of less than 20 mK with a signal/noise ratio of 100. The temperature drift, ΔT_d, during the steady-state measurements was typically 0.02% of the mean temperature. We obtained, therefore, a temperature resolution given by $\Delta T = [(2T(\omega))^2 + (\Delta T_d)^2]^{1/2} \simeq 50$ mK at 100 K. This is satisfactory for the analysis of the fluctuation effects.

The heat capacity of the platform was measured to check the precision of the method. Figure 3 shows a data series taken in the temperature range 77.7–80 K with 50 mK increments. The temperature resolution (40 mK) and the stochastic error are shown in the inset. The standard deviation of this data series from the best-fit curve was 0.1%.

Preliminary measurements were performed on a sintered $YBa_2Cu_3O_{7-x}$ sample prepared by a technique described elsewhere [7,8]. This sample was a cylinder 12.7 mm in diameter and 0.4 mm high weighing 0.25 g. At 77 K, $\tau_{int} \cong 6$ s and $\tau_{ext} \simeq 1000$ s were the measured values with $\omega \simeq 3\text{–}4 \times 10^{-2}$ s^{-1}. Providing that τ_{int} calculated by eqn. (5) at ω is equal to τ_{int} calculated at 2ω, we are sure that the sample reaches thermal equilibrium at this frequency. Each heat capacity value was obtained on 4–8 periods; therefore each measurement takes about 20 min.

Figure 4 shows the heat capacity of the sample from 78 to 100 K. At $T = 90.5$ K, the anomaly appears to be quite broad because of the phonon contribution to the specific heat. From these measurements, a 0.6% precision can be estimated.

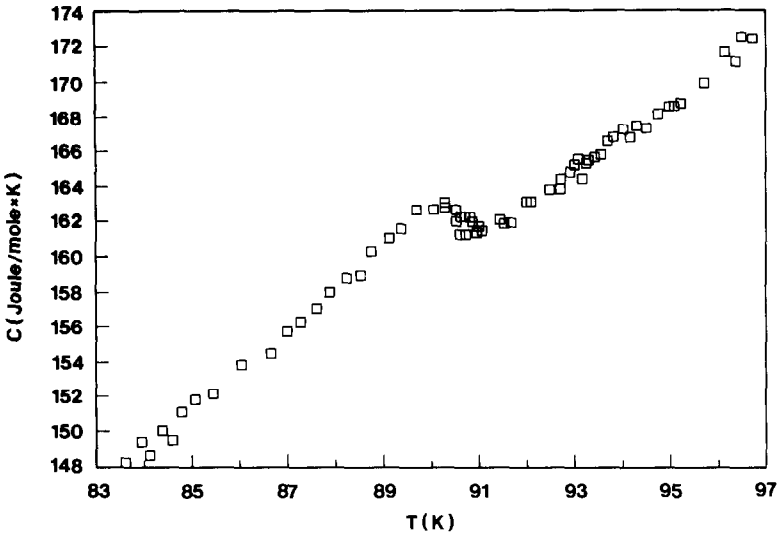

Fig. 4. Specific heat of sintered $YBa_2Cu_3O_{7-x}$ sample vs. temperature. The superconducting transition appears at 90.5 K.

The poorer quality of these data compared to the platform data in Fig. 3 may be due to the excessive time taken for the $YBa_2Cu_3O_{7-x}$ heat capacity measurements. Each measurement takes about 1 h (20 min plus the time needed to reach the next equilibrium condition), and the experimental conditions may change during this time.

CONCLUSION

We have developed a calorimeter for measurements from 4.2 to 200 K in a magnetic field of up to 8 T. We have adapted the conventional low-temperature a.c. technique for measurements at intermediate temperatures.

Preliminary measurements on the platform indicate a temperature resolution of 40 mK at 100 K and a precision of 0.1%. This precision was not observed when a superconducting sample was measured. We are now attempting to reduce the response time of the sample, τ_{int}. If the frequency can be increased and the measurement times decreased, we hope to improve the quality of the measurement.

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