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SPECIFIC HEAT MEASUREMENTS OF PURE COPPER BELOW ONE KELVIN

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ABSTRACT

The specific heat of pure copper has been measured in the temperature range of 130 to 1000 mK. The transient technique with a permanent heat link to the heat sink used for the measurement of the heat capacities is described.

RESUMEN

El calor específico del cobre puro ha sido medido en el intervalo de temperaturas de 130 a 1000 mK. Se describe la técnica transitoria con una unión térmica permanente al sumidero del calor usada para las mediciones de las capacidades caloríficas.

INTRODUCTION

The calorimetric measurements are important especially at very low temperatures where the heat capacity of many substances varies greatly with temperature and impurity content, and anomalies are frequent. Temperatures below one kelvin have been obtained with a dilution refrigerator of ^{3}He in ^{4}He which was constructed at the IIM, UNAM$^{(1)}$.

Temperatures as low as 50 mK in a continuous mode can be obtained in the mixing chamber of the refrigerator. Transient techniques for the measurement of heat capacities have been reported by Saint Paul$^{(2)}$ for temperatures above 0.3 K and more recently by Lasjaunias *et al.*$^{(3)}$ for temperatures down to 25 mK. Here a simplified description of the method used is presented.

PRINCIPLE OF THE METHOD

A sample with heat capacity C is connected to a heat sink through a thermal resistance R_{th} (Fig. 1.a). The temperature of the heat sink is kept constant and the temperature of the sample is stabilized at a certain initial value. The sample is heated by a sharp pulse of heat Q at some instant t_i (ideally heated case) and its initial temperature increment is ΔT_i (Fig. 2.a). By the definition of heat capacity the temperature increment is

$$\Delta T_i = Q/C \quad . \tag{1}$$

The temperature increment ΔT decreases continuously because heat flows to the sink through the thermal resistance (Fig. 2.a). The evolution of the temperature for $t > t_i$ is

$$\Delta T = \Delta T_i \exp\left(-\frac{t - t_i}{R_{th}\ C}\right) \quad . \qquad (2)$$

For clearness, the cooling process of the former thermal system can be compared to one of an electrical R C_e circuit (Fig. 1.b) as follows.

A capacitor C_e is charged (closing interruptor 1) and its initial potential difference at this ends is ΔE_i. When current is allowed to flow through the resistance R by closing the interruptor 2 and opening interruptor 1 (Fig. 1.b) at the instant t_i, the potential difference ΔE as a function of time is given by

$$\Delta E = \Delta E_i \exp\left(-\frac{t - t_i}{R\ C_e}\right) \quad . \qquad (3)$$

The analogy with thermal system, Eq. (2) is obtained when

ΔE (Volt) is replaced by ΔT (Kelvin)
C_e (Farad) is replaced by C (Joule/Kelvin)
R (Ohm) is replaced by R_{th} (Kelvin/Watt) .

In the thermal system, in practice (real case), the heat pulse Q to the sample is applied during a time interval t_1 (one to ten seconds). The sample temperature increment $\Delta T'$ increases in time as is shown in Fig. 2.b. However for the same quantity of heat Q as was used in the ideally heated case, the maximum increase in temperature ΔT_1 which is obtained at t_1 is lower than ΔT_i. This is so because some of the heat flows to the heat sink during the time interval t_1. The cooling speed of the sample depends on the heat capacity of the sample, the thermal resistance and the temperature difference between the sample and the heat sink. Then for times $t > t_1$, the decrease of temperature increment $\Delta T'$ during cooling process is exactly the same as in the ideally heated case. Also all the heat Q supplied to the sample will eventually go to the heat sink and it is the same for the real heating case and the ideal case. This can be written as:

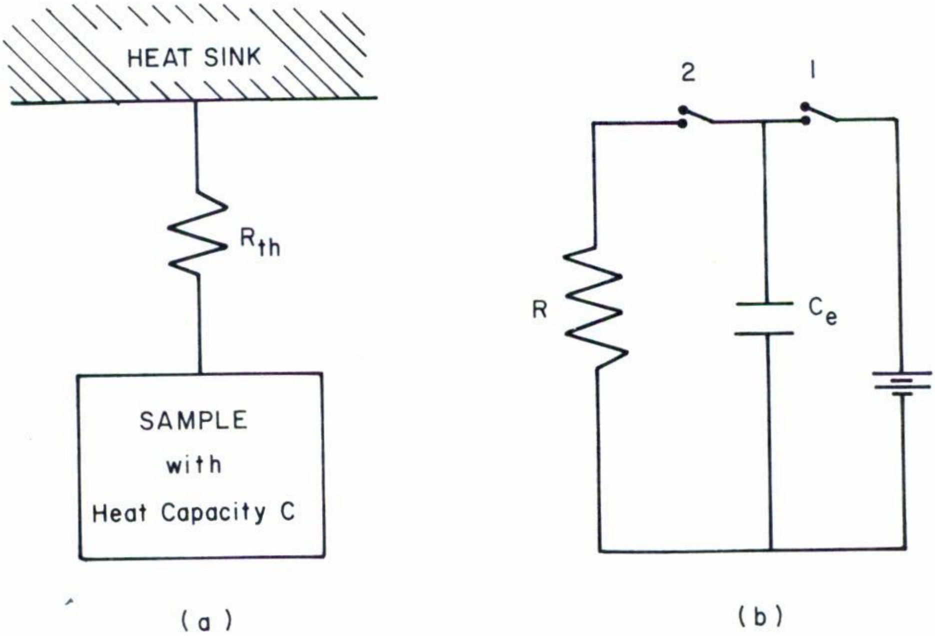

Fig. 1. a) Sample cooled by the heat sink through a thermal resistance R_{th}
b) Electrical R C_e circuit (in parallel).

$$Q = \int_0^\infty \frac{1}{R_{th}} \;\Delta T(t)\; dt = \int_0^\infty \frac{1}{R_{th}} \;\Delta T'(t)\; dt \quad . \tag{4}$$

If we assume that R_{th} is constant in the small temperature range $\Delta T(t)$ then the equality of Eq. (4) is equivalent to requiring that the areas under the curves of ΔT and $\Delta T'$ (ideal and real cases) as a function of time are equal. The time t_i of the idealised pulse can clearly be chosen such that for $t > t_1$, the two decay curves are coincident (see Fig. 3). From Eq. (4) we see that the two shaded areas A and B must be equal.

The value of ΔT_i and hence C can therefore be obtained by extrapolating the exponentially decaying part of the curve to t = 0 and choosing the value of t_i such that this equality of the shaded areas A and

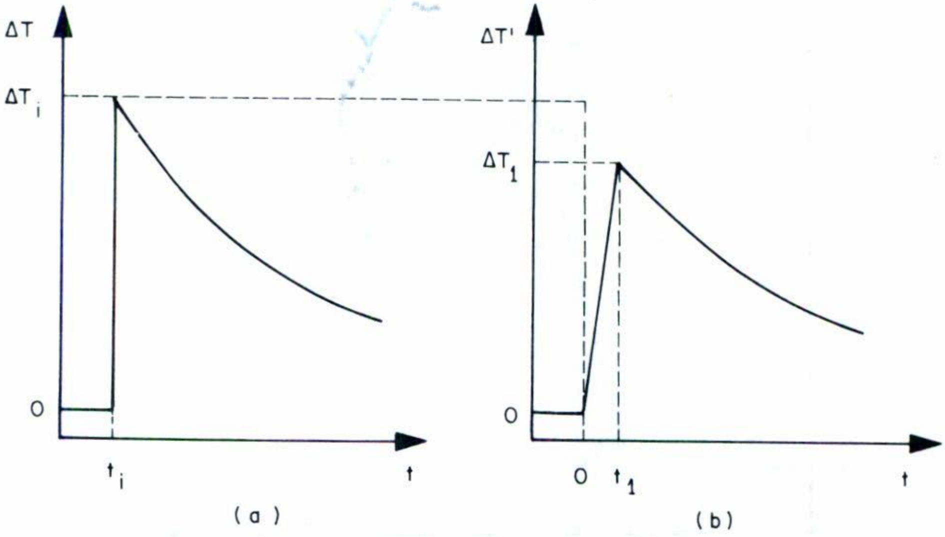

Fig. 2. Temperature variation of the sample before, during and after a heat pulse.
a) Ideally heated case. b) Real case.

B is obtained.

SAMPLE, ADDENDA AND HEAT SINK

The sample and sample holder under vaccum are located inside a box, the temperature of which is regulated. This box acts as the heat sink for the sample and it is cooled down by the mixing chamber of the refrigerator through a thermal link (Fig. 4.a). The box is made of copper with a carbon resistor thermometer and a commercial constantan strain gauge as a heater for the temperature regulation. The temperature is measured and kept constant at the desired value with the aid of a Conductance Bridge and a Temperature Controller (made by SHE Company)(4). The temperature variations of the heat sink are always negligible in

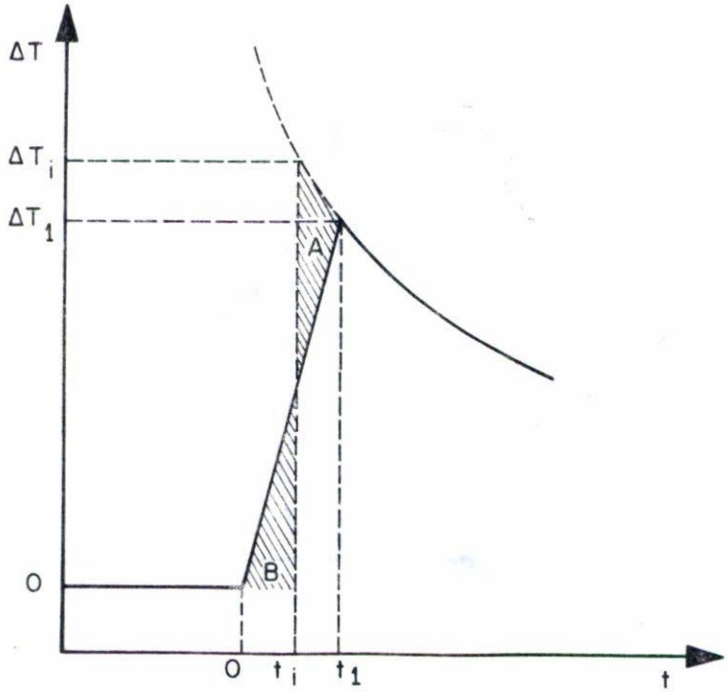

Fig. 3. Extrapolation of cooling curve (real case) to zero time and the selection of t_i by equalizing areas A and B.

comparison with the temperature increase of the sample ΔT generated for the specific heat measurement in the temperature range of 100 to 1000 mK.

The sample is a cylindrical copper bar, 5N from Johnson Matthey Chemicals Limited (diameter = 7 mm, length = 2.5 cm, mass = 9.3557 gr.). The sample holder consists of two pieces of copper (Fig. 4.b). One has a heater of a 8% W - 92% Pt, 12 µm diameter wire and the other has a Silicon (ionically dopped with Phosphorous) resistance thermometer. Leads to the heater and thermometer are NbTi superconducting wires coated with CuNi (diameter = 50 µm) which are thermally anchored on the mixing chamber and on the heat sink to minimize any heat input by thermal conduction. The thermometer was calibrated against a primary CMN. Thermometer during special calibration run at CRTBT, Grenoble. The experimentaly controlled reproducibility of the thermometer ($\Delta T/T$) from run to run is better than a few x 10^{-3}.

The calibration curve resistance as a function of Temperature R(T) is well fitted by laws like $\log R = A(\log T)^2 + B \log T + C$ on small ranges of temperatures (for example seven calibration points). The accuracy of the fit reaches the experimental dispersion (0.5%) below 200 mK and less than 0.17% at highest temperature. The sample and the sample holder are pressed together with nylon thread, using Apiezon N grease as a thermal bonding agent.

The shape of the sample holder ensures a uniform distribution of the heat in the sample during specific heat measurements. The sample holder is rigidly suspended with nylon threads and is connected thermally to the heat sink through a thermal resistance R_{th}. It consist of 40 um diameter, 2.5 to 3.5 cm long copper wire.

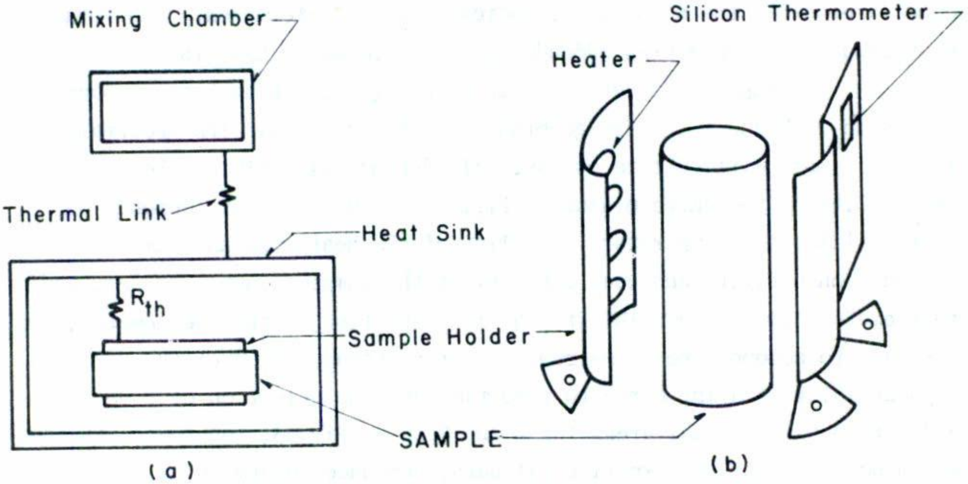

Fig. 4. a) Sample, sample holder, heat sink and mixing chamber distribution.
b) Details of the sample holder.

EXPERIMENTAL STEPS

Once the temperature of the sample is stable, a small heat pulse Q is sent to the sample which immediately changes temperature as was shown in Fig. 2. A current source, constructed by one of us (JPF), sends a chosen current I (10^{-5} to 10^{-6} A) during a selected time interval t_s(10 s). The potential difference V across the heater resistance is measured with a digital voltmeter. The total heat to the sample Q is given by

$$Q = I\ V\ t_s \quad . \tag{5}$$

The resistance of the sample thermometer is measured with a double synchronous detector bridge$^{(5)}$ and a resistance box. With a given value in the resistance box, the difference in resistance from that of the thermometer can be obtained from the output of the bridge. During heat capacity measurements the resistance differences are plotted in a chart recorder as a function of time (equivalent to Fig. 2.b). After the extrapolation of the exponential decay to the initial time, using the equal areas law, the temperature increase ΔT_i is determined. The total heat capacity (sample plus addenda) is obtained using Eqs. (5) and (1).

The expected uncertainty in Q (Eq. (5)), taking into account the errors in I, V and t_i, is in generan smaller than 0.1%. The uncertainty in ΔT_i is more difficult to assess. ΔT_i depends directly on the reliability of the curve measured (Fig. 2.b), which in turn depends on factors like: the temperature stability of the heat sink and sample; the thermal conductivity and heat capacity of the sample, sample holder, and thermometer; the reproducibility and response time of the thermometer, etc. Taking into account the errors caused by the extrapolation of the exponentially decaying curve to zero time and the selection of time t_i in order to obtained equal areas for A and B as in Fig. 3, together with the reproducibility of the experimental data, the uncertainty in ΔT_i is probably around 3 - 5%, which is the same uncertainty for the heat capacity data.

RESULTS

Measured total heat capacity (sample plus addenda) data are shown in logaritmic scale in Fig. 5. The heat capacity of the addenda C_{ad} was measured formerly and it can be represented by

$$C_{ad} = 2.85 \times 10^{-5} T \ (J/K) \quad . \qquad (6)$$

Equation 6 is shown in Fig. 5 as a continues line and it represents approximately 20% of the total heat Capacity. The data of specific heat of Copper c_{Cu} is shown in Fig. 6. The electronic specific heat for Copper calculated with the value given by Osborne *et al.*(6) is represented with a continuos line in Fig. 6. The experimental specific heat data and the percent difference between the experimental and calculated data are given in Table I. In general the agreement is within 5%.

With a stable temperature of the heat sink at 50 mK, the lowest temperature attained in the sample was around 100 mK and with a bad temperature stability. Two possible sources of stray heat input of the sample were considered: 1) Conduction by residual helium gas in the vacuum jacket, and 2) vibrations. To test the first possibility, the sample was cooled using hydrogen as a heat exchange gas instead of helium gas.

The hydrogen solidifies around 14 K and below 1 K the conduction of heat due to the presence of hydrogen molecules is insignificant. However the sample did not get below 100 mK. Several attempts were made to see if the vibration of the vacuum pumps were the cause of the 100 mK barrier.

The pump of the one Kelvin pot and the ^{3}He - ^{4}He mixture circulation pump were turned off under different conditions but no clear indication of improvement was observed. To be sure the pure copper(7) sample was not related to the cooling problem, a piece of commercial copper rod with a mass of 4% greater than the pure copper rod was cooled. Again it was not possible to cool the sample below 100 mK. On the other hand the data of heat capacity measurements of commercial copper indicated a good agreement with the values of pure copper as it is shown with squares

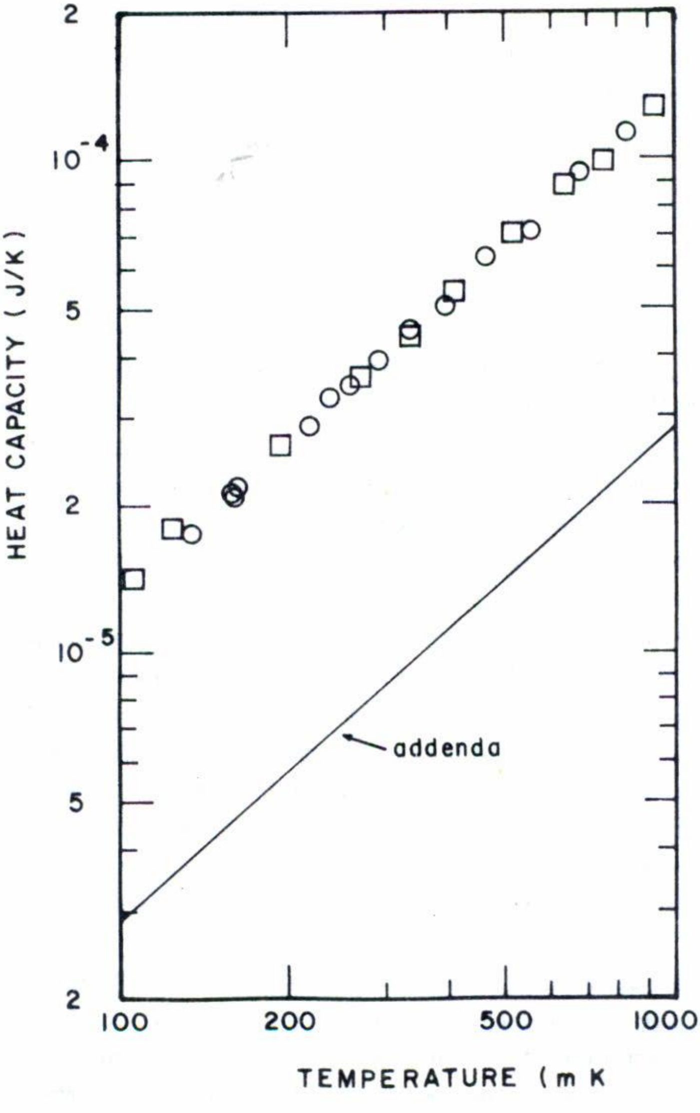

Fig. 5. Total Heat Capacity of addenda with pure O and commercial □ copper. Heat capacity of addenda — .

in Fig. 5. Also the specific heat data are given in Table I and shown in

TABLE I

Temperature (mK)	Specific Heat (μJ/gK)	%
107	1.15*	-2
125	1.48*	8
134	1.47	1
158	1.76	2
161	1.74	-1
163	1.86	4
195	2.17*	2
219	2.40	0
239	2.77	6
261	2.94	2
272	2.99*	0
293	3.31	3
335	3.79	3
336	3.57*	-4
388	4.22	-2
399	4.46*	1
460	5.30	4
510	5.87*	3
548	6.01	-2
630	7.41*	5
670	8.09	7
742	8.13*	-3
818	9.59	3
912	10.61*	1

Table I. Specific Heat of pure and commercial * copper below one kelvin. % represents the percentage difference $100\times(c_{exp} - c_{cal})/c_{cal}$ where c_{exp} and c_{cal} are the experimental and calculated (ref. 6) specific heats.

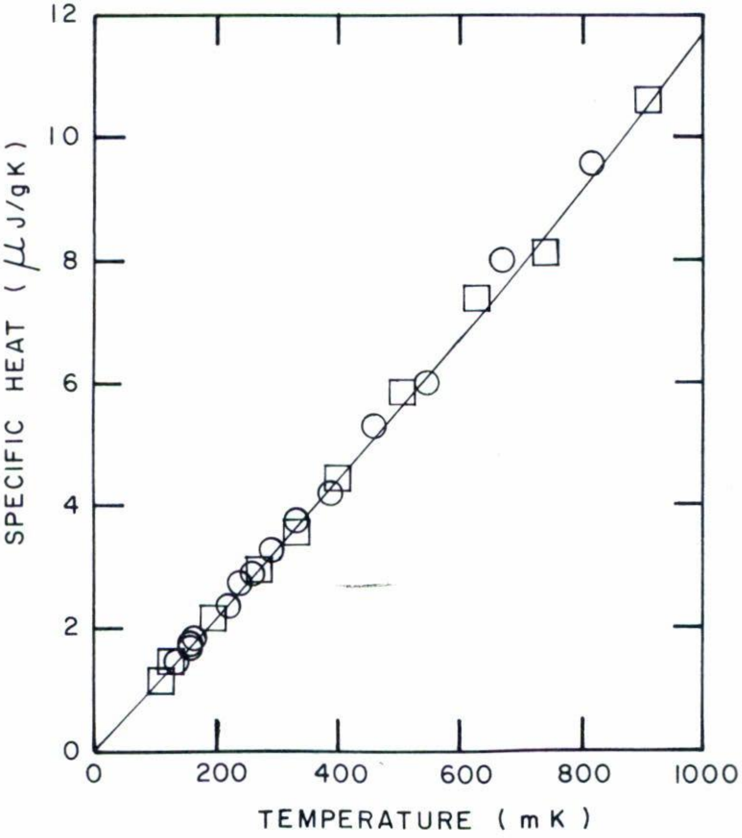

Fig. 6. Specific Heat of pure ○ and commercial □ cooper below one kelvin.

figure 6 with squares.

CONCLUSION

The difference in temperature at the lowest temperatures between the heat sink (50 mK) and the sample (100 mK) is caused by a high stray heat input. The design of the refrigerator and calorimeter must be reviewed and corrected in order to be able to measure at lower temperatures. Nevertheless the described system and procedure has proved suitable for heat capacity measurements and also to be advantageous in many aspects.

Because of its simplicity, the calorimeter can be a very compact device (in this case 3 cm in heigh and 7 cm in diameter) and allows repetition of heat capacity points at the same temperature as many time as it is needed.

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5. The resistance Bridge was built at CRTBT and now it is commercially available through Barras Provence, 35 Quai du Drac - 38600 Fontaine, France.
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7. It has been observed (M. Schwark, F. Pobell, W.P. Halperin, Ch. Buchal, J. Hanssen, M. Kubota and R.M. Muller, *J. Low Temp. Phys.*, 53 (1983) 685 and Ph. Gandit, private communication) that a few p.p.m. of molecular hydrogen in copper can produce a heat release due to the ortho-para conversion sufficient to limit the lowest temperature attainable in an experiment using a heat leak. The presence of hydrogen can be due to thermal treatments under reducting atmosphere used in the preparation of ultra pure copper.