

Specific heat measurements in small samples at low temperature

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Abstract. We describe a calorimeter which has been used to measure the heat capacity of small samples weighing 50 to 200 mg in the temperature range of 1.5 K to 20 K. We have used the thermal relaxation method as well the heat pulse method for our measurements with the same experimental set-up. An accuracy of better than 5% is obtained with this system.

Keywords. Specific heat; low temperature.

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1. Introduction

In the study of low temperature properties it is often necessary to work with small samples because of the costs involved. In this paper we discuss a calorimeter which has been used to measure the heat capacity of small samples weighing 50 to 200 mg in the temperature range 1.5 K to 20 K. The introduction of small samples for specific heat measurements was done by the pioneering work of Sullivan and Seidel (1968), who developed an a.c. method for their measurements. Since then another method known as the relaxation method has been developed by Bachmann *et al* (1972). These two are non-adiabatic methods and were used and modified by many researchers (Griffing and Shivashankar 1980; Stokka and Fossheim 1982). The low temperature calorimetry has been well reviewed by Gmelin (1979) and Stewart (1983). We have designed a system to use the thermal relaxation technique for the measurements but the semiadiabatic heat pulse method is also used to obtain results. In this paper we describe in detail the measurement methods and the instrumentation involved. A few measurements are also presented.

2. Measurement methods

The thermal relaxation method is illustrated in figure 1a. In this method the sample is connected to a heat reservoir at temperature T_0 through a weak link. In equilibrium, the sample temperature T_s is the same as T_0 . When a constant power is supplied to the sample, its temperature rises to a steady state value $T_0 + \Delta T_0$. The temperature rise ΔT_0

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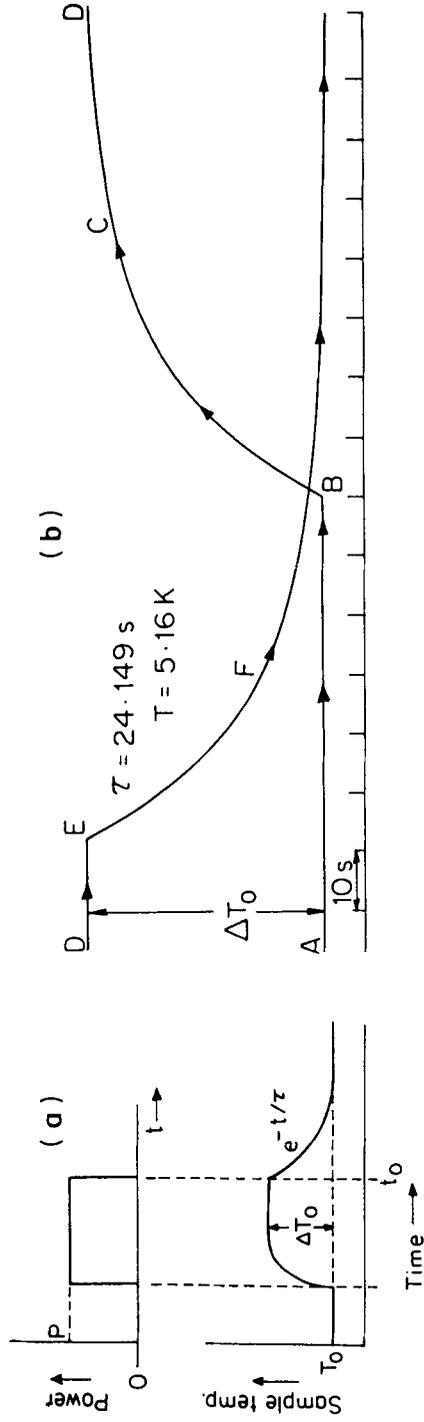


Figure 1. a. Principle of the thermal relaxation method. b. Typical curve during thermal relaxation method plotted on the recorder. ABCD shows the heating cycle and DEF shows the cooling cycle.

is given by P/K , where P is the power applied and K is the thermal conductance of the weak link. After this steady state is reached the heat input is suddenly stopped and the sample temperature relaxes to T_0 through the link. If the heat balance equation is solved for the cooling cycle it is found that the relaxation is exponential for small ΔT_0 , and is given by

$$\Delta T = T_s - T_0 = \Delta T_0 \exp(-t/\tau). \quad (1)$$

The relaxation time is given by $\tau = C/K$, where C is the specific heat of the sample. Explained above is a simple model of relaxation calorimeter and it is necessary that the time constant with which the sample, the thermometer and the heater come to equilibrium (τ_{internal}) is much less than the relaxation time constant τ . In case this internal time constant is comparable to τ , which can be due to poor thermal conductivity of the sample or poor bonding of any of the sample holder components and the sample, the relaxation is non-exponential and has the form

$$T = A \exp(-t/\tau) + B \exp(-t/\tau_{\text{internal}}). \quad (2)$$

This is known as the τ_2 ($\tau_2 = \tau_{\text{internal}}$) effect and proper corrections must be done to get results. This τ_2 effect is very well discussed by Bachmann *et al* (1972) and Schwall *et al* (1975). In practice, with careful selection of the sample holder components it is generally possible to avoid τ_2 effects. In our case the thermal link is so chosen that the time constant τ is greater than 1 second at the lowest temperature. Figure 1b shows a typical data curve obtained during the run with the blank sample holder at 5.16 K. The relaxation is exponential within 1% which is the measuring limit of our system.

In the relaxation arrangements specific heat can also be measured by heat pulse method provided the relaxation time is large compared to the duration of the heat pulse. We have used pulse method when time constants are more than 50 seconds. In this method (figure 2) a heat pulse ΔQ is applied to the sample and the resultant temperature rise ΔT is noted. $\Delta Q/\Delta T$ gives the heat capacity of the sample. ΔT is determined by extrapolating the cooling curve to the start of the pulse. In the figure an initial spike is shown and this is because the applied heat reaches the thermometer first

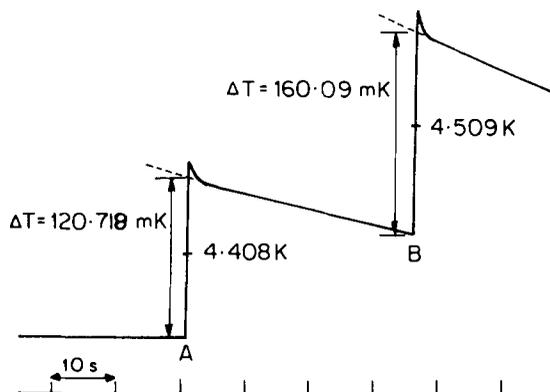


Figure 2. Typical curve during the heat pulse method.

before equilibrating. The width of this overshoot is larger than that of the heat pulse, but as the applied heat does not escape out of the system, the spikes have little effect on the ΔT measurements. The pulse widths of the heat input range from 100 ms to 600 ms. Figure 2 is a typical curve obtained during the run with PdPb₂ samples.

3. Sample holder

The sample holder (figure 3) consists of a sapphire disk of the size $8 \times 8 \text{ mm}^2$, $25 \mu\text{m}$ thick. A thin film of nichrome resistance deposited on one side of the sapphire disk acts as a heater. A bare element of germanium resistance supported away from the substrate with thin gold wires serves as the thermometer. The substrate is linked to a copper ring, which sits on a temperature controlled heat reservoir by four constantan wires, $50 \mu\text{m}$ thin. These wires act as electrical leads for the heater and the thermometer, and also as the thermal link as required in the thermal relaxation method.

The addenda heat capacity, i.e. the heat capacity of the blank sample holder was always less than 10% of the total. The heater, the thermometer and the sample holder contribute to this addenda. Bachmann *et al* (1972) in a detailed analysis have shown that 1/3rd of the heat capacity of the linking wires also contributes to this addenda. The sample under measurement is polished on one side and attached to the bare side of sapphire substrate with a very thin layer (few micrograms) of Apiezon-N grease. All the

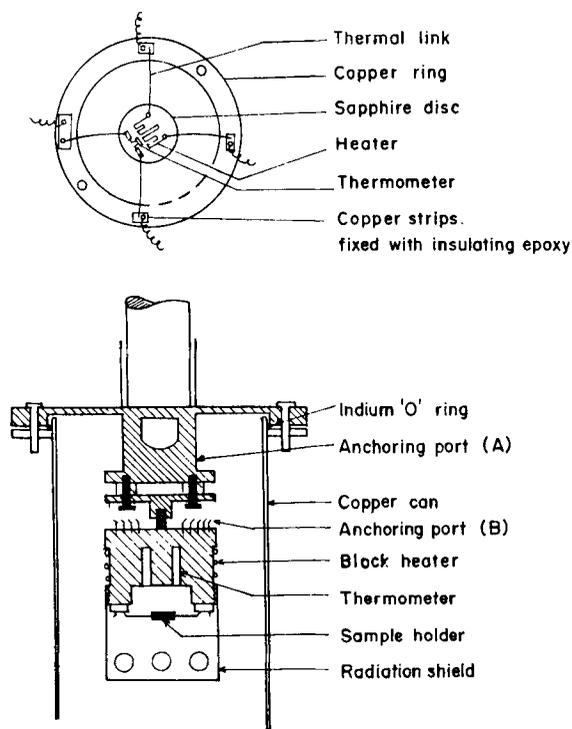


Figure 3. Sample holder.

electrical leads going to the sample holder are first anchored at a port in contact with liquid helium, and then on copper block which acts as a heat reservoir.

4. Instrumentation

The block diagram for the experimental set-up is shown in figure 4. A pulse width controller controls the output of a constant current source to which the sample heater is connected. The values of the current and the pulse widths are estimated and adjusted so that the temperature throws (ΔT_0) will be about 1% to 2% of the measurement temperature. The typical throws in our measurement range from 20 mK to 200 mK. To achieve a good temperature stability and noise-free environment special attention was paid to the grounding and shielding of all the instruments, signal cables and the cryostat.

4.1 Thermometry

The bare germanium resistance was calibrated in the operating temperature range against a calibrated germanium thermometer. The resistance values $R(T)$ were fitted to a 7th degree polynomial of the type

$$T^{-0.25} = \sum_0^n A_n (\ln R)^n. \quad (3)$$

The fitting was achieved by using the method of least squares and finding the polynomial coefficients by Gaussian elimination method. The deviations obtained are less than 0.5% and the temperature can be read accurately within 50 mK.

The thermometer resistance was measured by an a.c. bridge with a lock-in amplifier (PAR-186A) as a null detector operating at 183 Hz. The thermometer is connected to

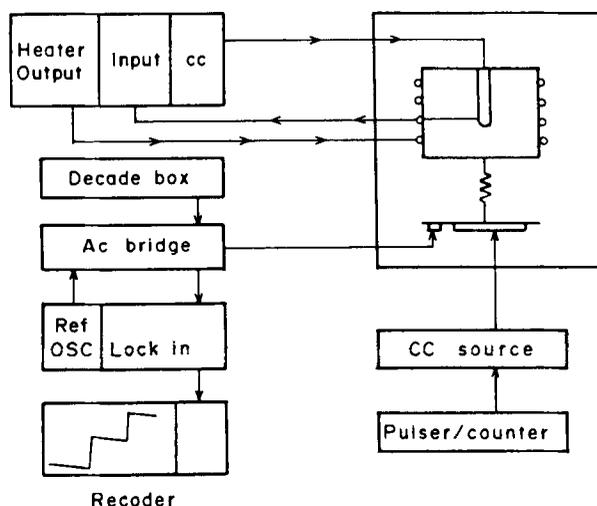


Figure 4. Instrumentation—block diagram.

the measuring arm of the bridge in a standard 3 wire mode. The bridge excitation is always adjusted so as to keep the dissipation in the thermometer to less than 10^{-8} watts. A change of 10 ppm in the thermometer resistance could be detected with this bridge. The output of the null detector is connected to a recorder where the heating and cooling cycles in the measurements are recorded.

4.2 Constant current source

The heart of the constant current source is the OPAMP LM324 (figure 5) used in the comparator mode. To avoid any interference from the mains the circuit was designed to operate with batteries. The reference voltage required was also generated using diodes D1 and D2 biased by R1. These diodes draw much less than $100\ \mu\text{A}$, while a conventional zener diode would draw about 10 mA.

The load current through the load R1 can be set to a required value by selecting the reference voltage, proper series resistance R_s , and by measuring the voltage drop across the standard resistance ($100\ \Omega$ or $1000\ \Omega$) in series with the load. The output of the OPAMP controls the resistance of E-C section of the transistors TR2 and TR3 in such a way that a constant current flows through R1 depending upon the feedback voltage measured across R_s . To increase the load current capacity to 100 mA we have used two transistors. The transistor at the OPAMP output acts as a buffer and can source about 10 mA to the base drives of TR2 and TR3 during the high current operations. The circuit can give currents from $1\ \mu\text{A}$ to 100 mA.

The switch SW6 enables one to measure the voltage drop across the load resistance R1 and the standard resistance R_d by an external voltmeter. Whenever the voltmeter is not required it is shorted by the switch SW7, so as to avoid even any minute stray current flow through the load due to pick-up in the voltmeter leads.

The load current can be switched externally by a 5 V TTL level, coupled to the circuit through an IC MCT6 which has two optocouplers. With the input high, the photo-transistors (PT1 and PT2) conduct, PT1 shorting the reference supply and PT2 shorting the B-E section of the control transistors putting off the load current. With this arrangement the current pulses of pulse widths in the range 7 ms to 7 s can be obtained. The rise time of these pulses is $80\ \mu\text{s}$ for low currents and less than $10\ \mu\text{s}$ for higher currents.

4.3 Pulse width controller

Precise pulse widths are generated by one of the monostables in the IC 74LS221 (figure 6). This IC has two monostables. The first is set for a fixed pulse width and is triggered on the release of a manual push button switch. The second monostable is triggered on the falling edge of the first one. The first monostable is used to avoid the mistrigging of the second due to switch bounce and debounce at the switch release. The pulse widths of the second monostable can be preselected by a proper RC combination via switch SW1b, the thumbwheel switch, and a $10\ \text{K}\Omega$ 10 turn potentiometer. The pulse width is measured by gating a fixed frequency pulse train during the on period of the second monostable. The number of pulses gated is then counted and displayed by the combination of IC 74C926N and 7416. A 1 MHz pulse train generated by a crystal clock is then passed through a three-stage decade divider consisting of 74LS390 and 74LS90, so that the frequency of the pulse train at the gate

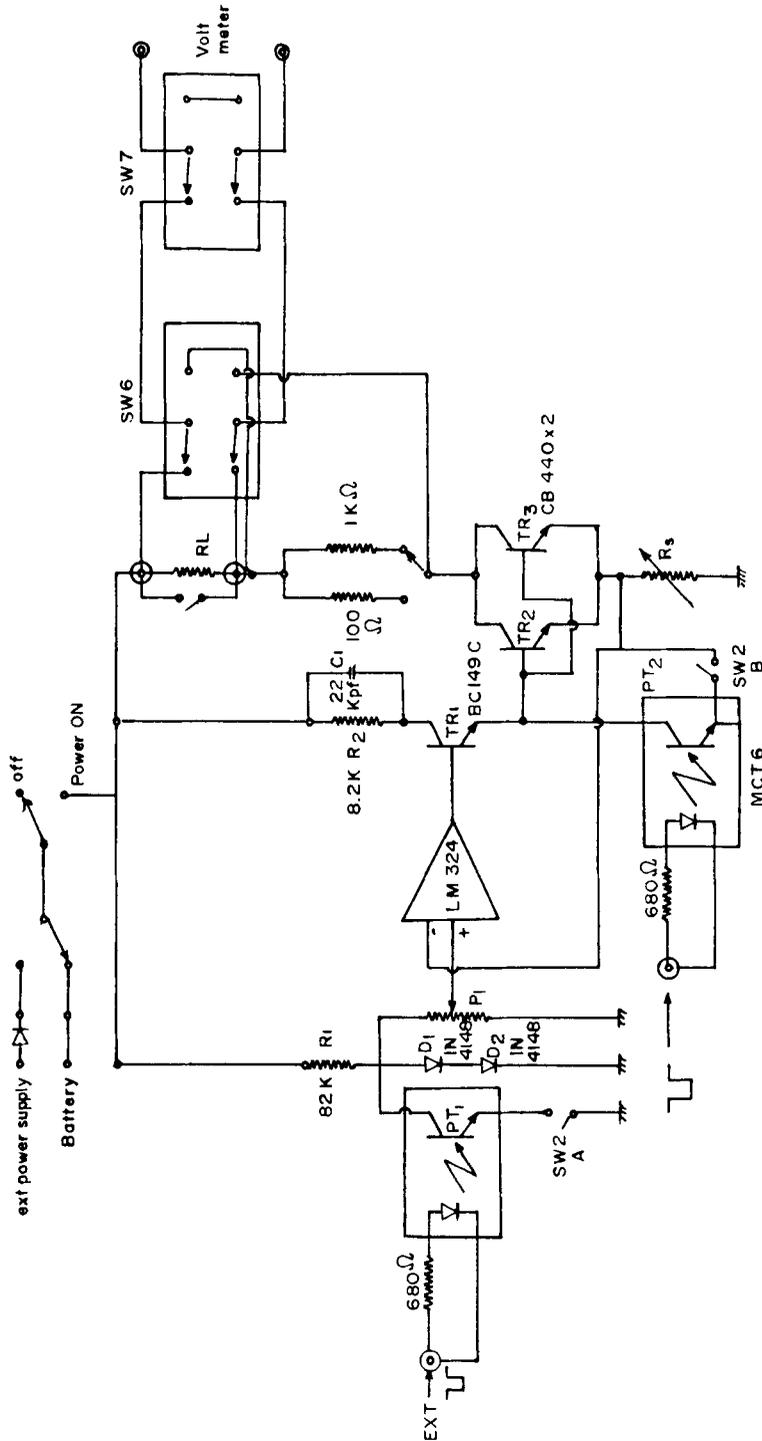


Figure 5. Constant current source.

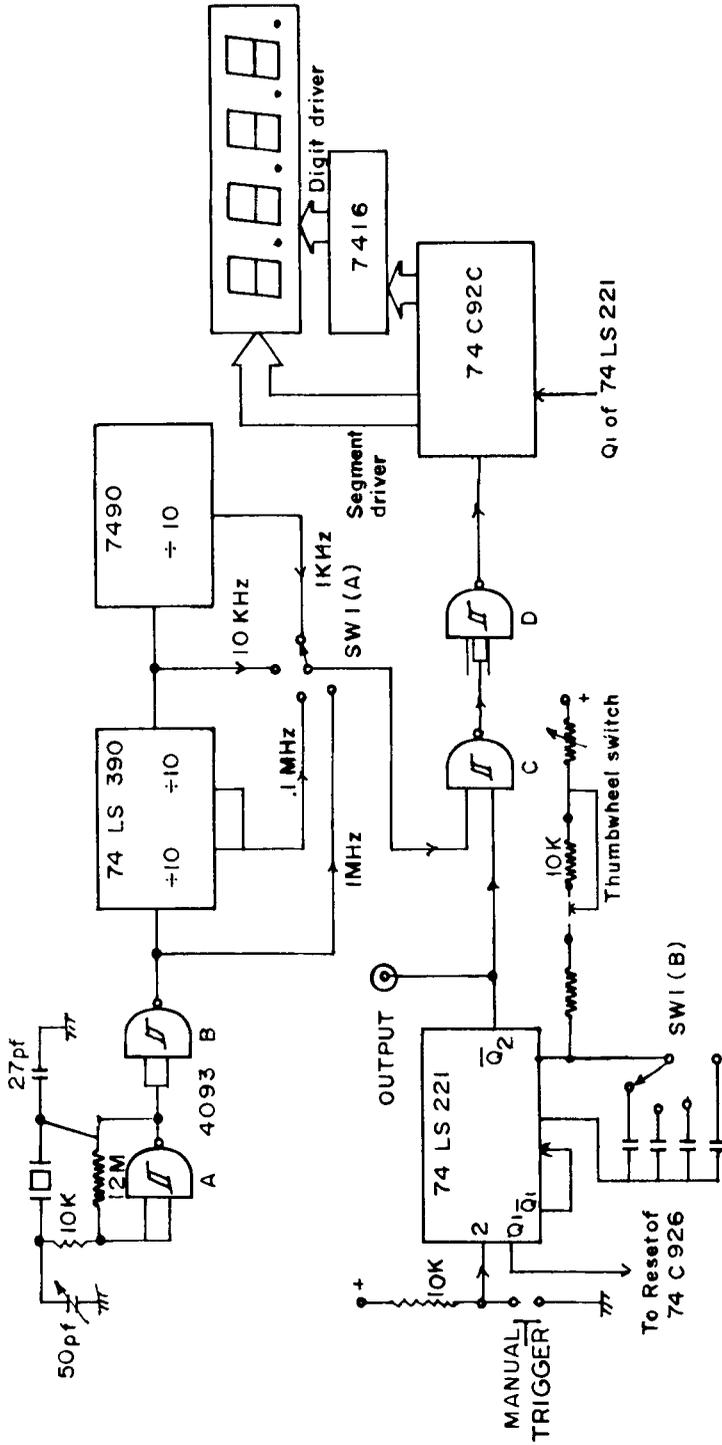


Figure 6. Pulse width controller.

input can be selected from 1 MHz to 1 kHz depending on the range of the output pulse width. With this we get a $1\ \mu\text{s}$ resolution in 7 ms range, $10\ \mu\text{s}$ in 70 ms range and so on. The pulse widths of 7 ms to 7 s can be selected within 1% but each pulse can be measured with 0.1% resolution.

5. Results

In order to check our apparatus we have measured the specific heat of many metallic samples and obtained good results. Figure 7 gives a plot of C/T against T^2 for a single crystal of silver of 99.99% purity. In a metallic sample the specific heat at low temperatures is given by $C = \gamma T + \beta T^3$, where the first term gives the electronic contribution and the second term gives the lattice contribution. γ and β are the constants. Despite repeated measurements the curve in figure 7 gives two slopes, one above 12 K and the other below it. Although the reasons for the two slopes are not clear we have no reason to doubt our measurements. From the plot of the curve below 12 K we find $\gamma = 0.68\ \text{mJ/g.-atom K}^2$ and $\beta = 0.187\ \text{mJ/g.-atom K}^4$. The γ value agrees closely with the value given in the literature: $0.695\ \text{mJ/g.-atom K}^2$. From the value of β we obtained the Debye temperature θ_D as 218 K. This can be compared with the value of 225 K given in the literature (Gopal 1966).

Measurements were also done on a single crystal of PdPb_2 which is superconducting below 3 K. Figure 8 shows a plot of C against T in the normal and superconducting states, in the temperature range 1.6 K to 4.0 K. The normal state data below $T_c = 3\ \text{K}$

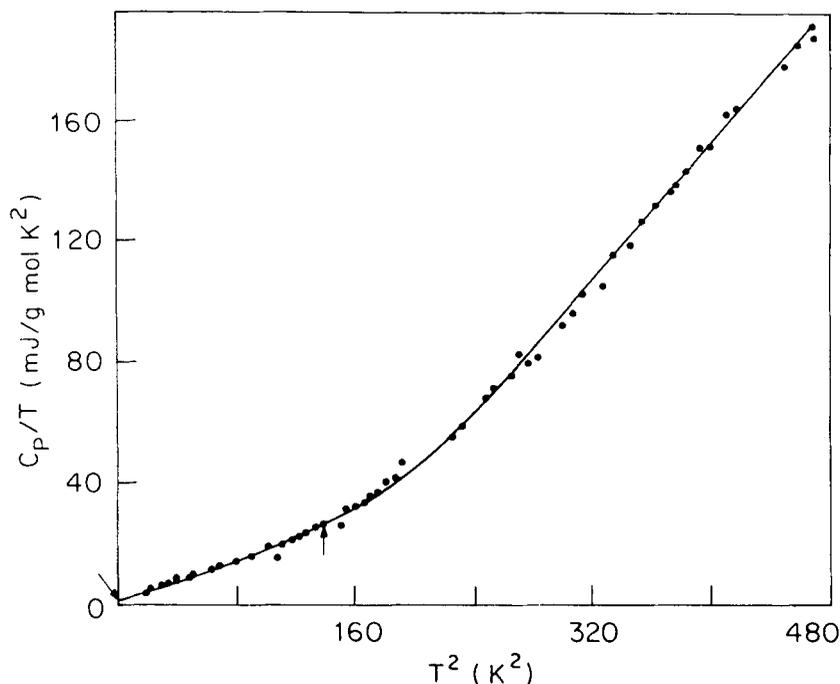


Figure 7. C/T vs T^2 for silver.

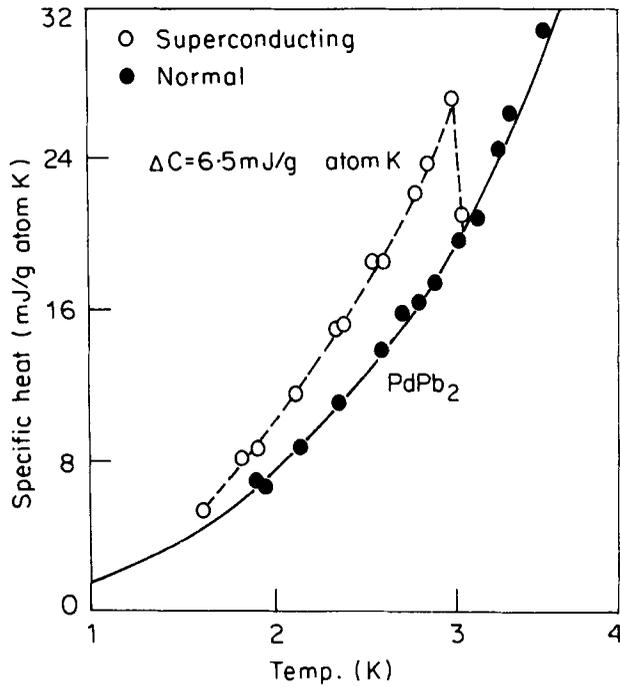


Figure 8. Specific heat of PdPb₂ in the normal and superconducting states.

was obtained in the magnetic field of 200 G which was found to be sufficient to turn the sample to the normal state. Detailed results on PdPb₂ are being published separately (Pattalwar *et al* 1988).

References

- Bachmann R, Di Salvo Jr F J, Geballe T H, Howard R E, King C N, Kirsh H C, Lee K N, Schwall R E, Thomas H U and Zubeck R B 1972 *Rev. Sci. Instrum.* **43** 205
 Gmelin E 1979 *Thermochem. Acta* **29** 1
 Gopal E S R 1966 *Specific heats at low temperatures* p. 63
 Griffing B F and Shivashankar S A 1980 *Rev. Sci. Instrum.* **51** 1030
 Pattalwar S M, Dixit R N, Shete S Y and Basu B K 1988 *Phys. Rev. B* (to be published).
 Schwall R E, Howard R E and Stewart G R 1975 *Rev. Sci. Instrum.* **46** 1054
 Stewart G R 1983 *Rev. Sci. Instrum.* **54** 1
 Stokka S and Fossheim K 1982 *J. Phys.* **E15**
 Sullivan P F and Seidel G 1968 *Phys. Rev.* **173** 679