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A calorimeter for operation in the temperature range 2–150 K

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Abstract. The description of a calorimeter for measurement of heat-capacity in the temperature range, 2–150 K, by semi-adiabatic heat-pulse method is presented. The data collection is computerized and various parameters monitored through the software ensure high quality of the data. The performance of the calorimeter was verified with the well-known standard materials. Results on the alloys, $PrCu_2Si_2$ and $GdCu_2Si_2$, are also presented.

Keywords. Heat-capacity; calorimeter.

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1. Introduction

It is well-known that the measurement of heat-capacity (C) as a function of temperature is valuable in obtaining information about the Debye temperature, the density of states at Fermi level (E_F) and phase transitions in materials [1–3]. There are different ways of measuring C, for instance, semi-adiabatic, thermal relaxation, continuous heating and AC calorimetric methods. The complexities of the calorimeter design, designed by solid state physicists in different laboratories around the world vary, even for the same method of measurement (see the references cited in [1, 3–8]), suiting to the specific need of the user, for instance, the temperature range of interest. One has to take special care to design a calorimeter, which can be employed over a wide temperature range; particularly, at temperatures above 20 K, the heat transfer by radiation varying as T^4, becomes significant and maintaining the adiabatic conditions becomes very crucial. As brought out by Gmelin [3], the temperature range 2–120 K offers most calorimetric problems and hence the total number of successfully operating calorimeters in this temperature range around the world is rather limited in spite of tremendous importance for thermoanalysis data.

In this article, we describe a simple calorimeter designed by us to measure C by semi-adiabatic heat-pulse method with the following salient features: (i) It is a top-loading type; therefore, the method of isolation of the sample chamber by indium wire or woods alloy for the vacuum purpose as is the case with most of the designs is avoided and hence this design reduces the vacuum problems due to cold leaks; the interchange of samples is very quick and easy; (ii) there is no mechanical switch for cooling the sample; (iii) it can be operated in the temperature range 5–150 K with a very good accuracy (less than 2%); by letting in traces of helium gas in the sample chamber when the helium bath is pumped to 1·5 K, the sample could be cooled to 2 K and the data collected in the temperature interval 2–6 K are fairly reliable at least to look for qualitative features. The measurement is automated by using a PC/XT and the software ensures minimum scatter in the data; the temperature-time curve can be seen on the monitor and the program facilitates the change of parameters intermittently to improve the quality of the data. Reliable data could be obtained even for smaller amount, for instance, 400 mg of the sample and the amount required is still smaller for materials with a large low temperature heat-capacity.

2. Experimental details

2.1 *Calorimeter*

Schematic illustration of our heat-capacity measuring set-up is shown in figure 1. The cryostat employed is a superinsulated fibre-glass dewar, D, of about 3 litres capacity supplied by Precision Cryogenics (USA) and, in this way, liquid nitrogen

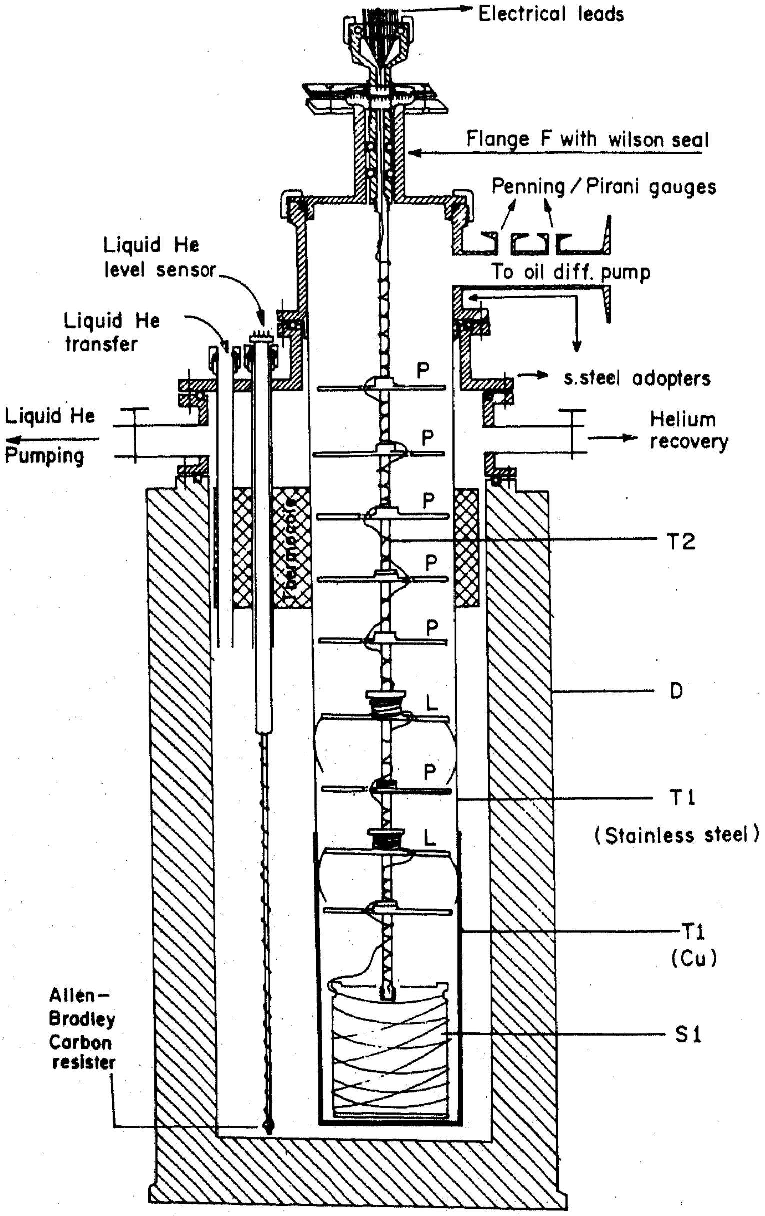

Figure 1. Schematic of the complete set-up of the calorimeter.

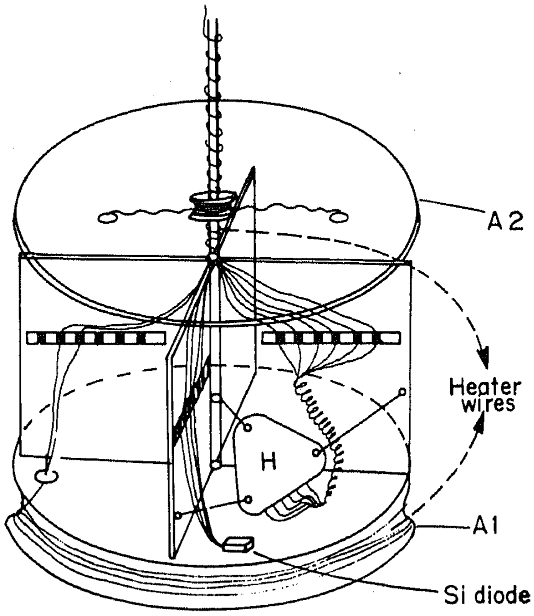

Figure 2. The assembly A surrounding the sample holder is shown separately. The specifications marked in the figure are described in the text.

jacket is made redundant. T1 is a 1 m long tube; the bottom portion (about 1 foot long) is made up of Cu tube (wall thickness 1 mm) and the top portion is made up of a thin walled (0·25 mm thick; 50 cm dia) stainless steel tube; the Cu tube facilitates thermal homogeneity in the region of interest. The calorimeter-insert essentially consists of a (gold-plated) Cu shield (S1), a Cu assembly, A, (figure 2) made up of gold plated Cu, the sample holder (H) and a 1 metre long stainless steel tube (T2) of 6 mm diameter.

The assembly A (figure 2) consists of two circular Cu plates, A1 (5 mm thick) and A2 (1 mm thick), joined together by about 6 cm long Cu rod (4 mm dia). The dimensions of S1 are chosen such that it can rest on A1 thereby making very good thermal contact and S1 needs to be lifted up whenever a sample is to be mounted. The bottom portion of the region between A1 and A2 is divided vertically into four segments by 1 mm thick Cu plates (this division is not necessary for measuring C of only one sample; this provision is made to try out the measurement of C for 4 samples simultaneously at a later stage). Heater wires are wound around the groove provided on A1, the top portion of the 4 mm diameter Cu rod (between A1 and A2) and also at the outer surface of the Cu cylinder S1. The terminals provided on one of the four quarters are used to connect these heaters in series; the corresponding heater wire resistances are 25 Ω, 6 Ω, and 12 Ω respectively. A silicon diode temperature sensor fixed on the Cu plate A1 is used to control the temperature of the shield and the Cu assembly. The sample holder (H) is made up of a high purity oxygen free copper sheet (0·25 mm thick and about 10 mm dia); one side of this Cu plate contains a Ge thermometer (Lakeshore, Model GR-200B–1500) and two thin film strain gauges (Tokyo Sokkai Kenkyujo Co., CFLA–1–1350 Ω) as a sample heater glued with GE7031 varnish. The sample holder is suspended by three nylon strings at one of the four segments. Electric lead wires from the thermometer and the heater (fixed on H) are connected to the terminal provided on the Cu plates via some springs made out of Cu wire (ϕ 0·03 mm × 60 cm), as shown in the figure; the utility of these thin long Cu wires to maintain semi-adiabatic conditions during the course of the measurements was also verified (*vide infra*).

The assembly described above is connected to an approximately 1 m long stainless steel tube of 6 mm diameter, T2, and the other end of this tube is coupled to a stainless steel flange F (which in turn is provided with a O-ring seal so as to be able to mount on the stainless adopters at the top of T1). The movement of this stainless steel tube by a few cm, if necessary, is made possible via the use of a wilson sealing arrangement provided on the flange. Two lotus-shaped Cu assemblies, L, are provided on T2 and the dimensions are chosen in such a way that they are in good thermal contact with T1; this arrangement serves as a sink for the heat-flow from the top. Additional radiation shields made out of Cu plates, P (about 2 mm thickness) are also fixed at various places on T2.

The electronic instruments employed in the set-up are commonly available general purpose type, like Keithley Programmable Constant Current source (Model 220), Keithley nanovoltmeter (Model 181) and Lakeshore temperature controller (Model DRC93C). These instruments are interfaced to a PC/XT via GPIB and the program for controlling the parameter and automatic data collection was developed using quickbasic language.

2.2 *Thermometer calibration and data acquisition*

We have first calibrated the Ge thermometer mounted on the sample holder. The calibration is performed in the presence of small traces of helium exchange gas (about 1 torr) against a calibrated Ge thermometer up to 100 K and a calibrated silicon-diode sensor in the temperature range 100–160 K using a four-wire DC technique. The calibrated sensors were mounted on the other side of the Cu plate H. We have employed Keithley constant current source and Keithley nanovoltmeter (resolution 10 nV) in the above calibration. In Ge sensors, the current values were chosen in such a way that the voltage (as measured by the nanovoltmeter) falls in the range 1 to 2 mV to avoid self-heating error. After stabilizing the temperature of the assembly A at a desired value with the help of the Lakeshore temperature controller and silicon diode sensor (mounted on Al), the resistance/voltage values of the thermometers on the sample holder are collected; in the case of resistance thermometers, the voltage values for both positive and negative current directions were recorded to correct for thermal EMF's. This calibration process above 1·6 K is computer controlled and the calibration data were collected automatically for every 0·1 K below 4 K, 0·2 K interval in the temperature range 4 to 10 K and 0·5 K interval above 10 K. The data points do not always correspond to integer temperatures and a polynomial equation (Chebychev polynomials as prescribed by Lakeshore Cryotronics) was employed to fit the curves of temperature versus resistance/voltage.

The preparation for the data collection is performed by the usual procedure. The weighed amount of the sample, which can be of any shape and polished on one side is fixed to the Cu sample holder with a thin layer of Apiezon N grease (about 5 mg) for good thermal contact. We normally keep track of the amount of the grease used, so that the contribution to C from this grease can be taken into account while obtaining the C of the sample. After mounting the sample, the insert is sealed with a viton O-ring to the tube T1 at the top. The calorimeter chamber is pumped down to 2×10^{-6} torr. Now, helium exchange gas of about 1 torr is let inside the calorimeter and liquid nitrogen is transferred in the fibreglass dewar. After waiting for a minimum period of about 2 h, the exchange gas is pumped out. Liquid nitrogen is then removed and liquid helium (about 3 litres including precooling) is transferred in the dewar. We wait for a few hours for the sample holder to reach around 8 K and the wilson seal provided at the top enables us to move the insert down so as to make the contact with the Cu plate at the bottom of the tube T1 which is at the temperature of the helium bath. The liquid helium bath is pumped down to about 1·5 K. After a waiting period of about 1 h at this stage, the sample holder reaches a temperature of about 5 K. We start data collection at this stage. If the measurements are required down to 2 K, we let 1 torr of helium gas inside the sample chamber as a result of which the entire region surrounding sample reaches the temperature of the bath immediately. Due to cryopumping, the measured vacuum in the sample space is better than 1×10^{-5} torr. In order to maintain adiabatic conditions during the course of measurement, this adsorbed gas should be completely removed. This requires an efficient pumping system [2] and, to achieve this, the inner diameter of the pumping line leading to the oil diffusion pump (not shown in the figure) from the top of the tube T_1 should be sufficiently large (in our case 2″). This continuous pumping with this arrangement results in a vacuum of about 4×10^{-6} in half an hour. If necessary, one can wait for a sufficiently long time to make sure that there is no further degassing in the sample chamber. We subsequently start the collection of the data. Since the exchange gas absorbed on the walls of T1 and A is not released till 6 K, the data collected in this way are found to be reliable.

The sequence of operations in a pulse calorimeter is well-known and is illustrated in terms of a temperature-time graph in figure 3. During the period AB, the temperature is recorded every 2 s by measuring the resistance of the germanium resistance thermometer by a four-probe method. Then a known quantity of heat, ΔQ (decided by the current applied through the strain gauge heaters for a fixed duration t) so as to cause an increment (ΔT) in the temperature of the sample, is fed, simultaneously measuring the temperature. The increase in the temperature at low temperatures after the heat-pulse is typically 1 to 4%, which is about two to three orders of magnitude larger than the temperature resolution at a given temperature.

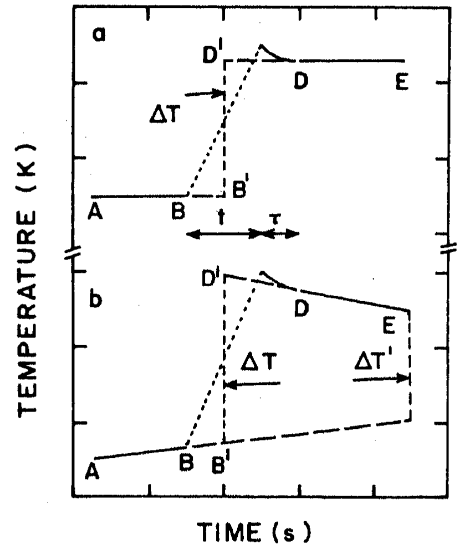

Figure 3. (**a**) Temperature-time curve (heat-pulse curve) when there is no heat-leak; (**b**) Heat-pulse curve when there is a heat-leak. Other details are described in the text.

After the heat pulse is terminated, the temperature is recorded in the drift period. Before the heat-pulse is applied, the temperature of the surrounding is made equal (within desired accuracy) to that of the sample with the help of the heater coils provided on the Cu assembly, A, and this temperature is made to follow the heating curve shown in figure 3; that is achieved with the help of Si diode sensor mounted on A1 and the Lakeshore temperature controller. This ensures that there is no heat-leak to and from the sample holder and that AB and DE are not only parallel to each other, but also to the X-axis (figure 3a). Therefore, the increment in the temperature (ΔT) due to the heat-pulse (ΔQ) is straightaway given by B′D′; the heat-capacity, C, of the sample (+ the sample holder) is given by $\Delta Q/\Delta T$. At this juncture, we like to mention that even if the temperature of the surrounding is intentionally kept different (say, much more than 10% of that of the sample), the time taken (external relaxation time) for the sample holder to reach the initial temperature (that is, at B on the line AB) is found to be extremely large compared to the duration of a heating-cycle, thereby confirming the fulfillment of semi-adiabatic conditions by the use of Cu springs. In the event of such a slow heat leak, AB cannot be perfectly parallel to DE (figure 3b) and the C values obtained as above will not be accurate. To have an estimate of such an error, we calculate C values from two different values of ΔT(i) ΔT given by B′D′, that is, by the usual extrapolation procedure and (ii) N temperature values (N is typically 10 along the line DE) taken as a function of time in 2 s interval after the delay period (internal relaxation time), τ, which is typically a few seconds below about 30 K and a few tenths for higher temperatures, are least square fit to a straight line and the temperature corresponding to the time of the Nth point on this fitted line is assumed to be the final temperatures; the temperature corresponding to the time of the Nth point on the line AB, obtained by extrapolation of the line AB, is assumed to be the initial temperature. From this procedure, the change in the temperature due to the heat pulse is obtained as $\Delta T'$ and the corresponding heat-capacity as C1. Since the heating-curve is displayed on the computer monitor, we can control various parameters, like τ, pulse duration, temperature of the surrounding, (approximately required) percentage increase in temperature etc, so as to keep the difference, C–C1, within 1%. The care taken to ensure that the lines AB and DE are parallel to X-axis results in good quality data with minimum scatter. The entire measurement in the temperature range 2–150 K can be performed within 10 h. One has to be careful while taking data in the temperature range 2–5 K, particularly for materials with very low heat-capacity values, to make sure that the liberation of the exchange gas above 5 K does not falsify the data, in case the measurement is started from 2 K. The procedure we normally follow is to take the data in the temperature interval 6–50 K after removing the exchange gas (at 77 K) and then let very little exchange gas in when liquid helium bath is at 1·5 K so as to enable us to take the data below 5 K. Then the sample chamber is pumped by an oil diffusion pump. (A liquid nitrogen trap is provided between the calorimeter and the diffusion pump). We continue to pump the sample chamber throughout the course of measurement. We constantly monitor the pressure in the sample chamber and if the pressure is worse than 1×10^{-5} torr, the data collection is disrupted for some time till the vacuum improves.

Needless to point out that the heat-capacity of the addenda without the sample was obtained in order to take into account the contributions from Cu sample holder, the thermometer, the strain gauge heaters, varnishes etc. We have also measured the heat-capacity of the Apiezon-N grease employed for mounting the sample. These heat-capacity values were fit to some functional forms and incorporated in the software for data collection.

3. Illustrations

We have measured the temperature dependent heat-capacity behavior in Cu and single crystalline Pb (purity 99·99%) above 5 K and also looked for various phase transitions in some standard materials. The measured heat capacity values of Cu are plotted in figure 4 and selected temperatures are also shown in table 1. In order to compare our values with those reported in the literature, we reproduce alongwith, the data reported by two different groups [9, 10]. It is to be noted that the heat-capacity of Cu below 10 K is extremely small and the low temperature values reported by different groups often differ at least by 1% (see, for instance, Gmelin and Rodhammer [11]). The data on Cu are found to be reproducible within 1% below

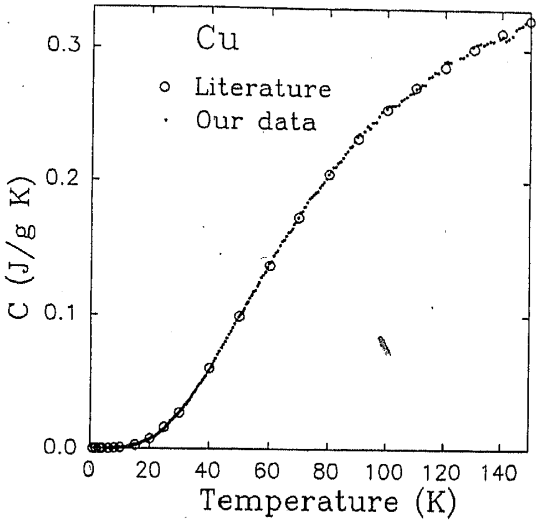

Figure 4. The heat-capacity of Cu in a wide temperature range. The literature data points are taken from a table in Weast [9].

Table 1. The heat-capacity (J/gK) of Cu at selected temperatures. Our data are given in the second column and two representative literature data are shown in the next two columns.

T(K)	Our data	Weast [9]	Martin [10]
6	0·00023	0·00023	—
10	0·00090	0·00086	—
20	0·00757	0·0077	0·00724
40	0·0591	0·060	0·0586
60	0·138	0·137	0·136
80	0·205	0·205	0·203
100	0·256	0·254	0·252
120	0·291	—	0·287
140	0·311	—	0·312
150	0·318	—	0·321

80 K and within 2% at higher temperatures from one measurement to the other. Considering all these factors, it can be stated that our values agree with those reported in the literature within a few per cent in the temperature range 5–150 K and that the present design can be successfully used for heat-capacity measurements in this temperature range. In fact, we have extended the measurements to 2 K for some of the rare-earth intermetallic compounds [12–14], the C data for some of which were obtained in other laboratories abroad and such experiments prove that our set-up could be employed even below 5 K without losing much accuracy, particularly to look for qualitative features in the materials with heat-capacity values much larger than those of Cu. The features due to various phase transitions (figure 5) are found

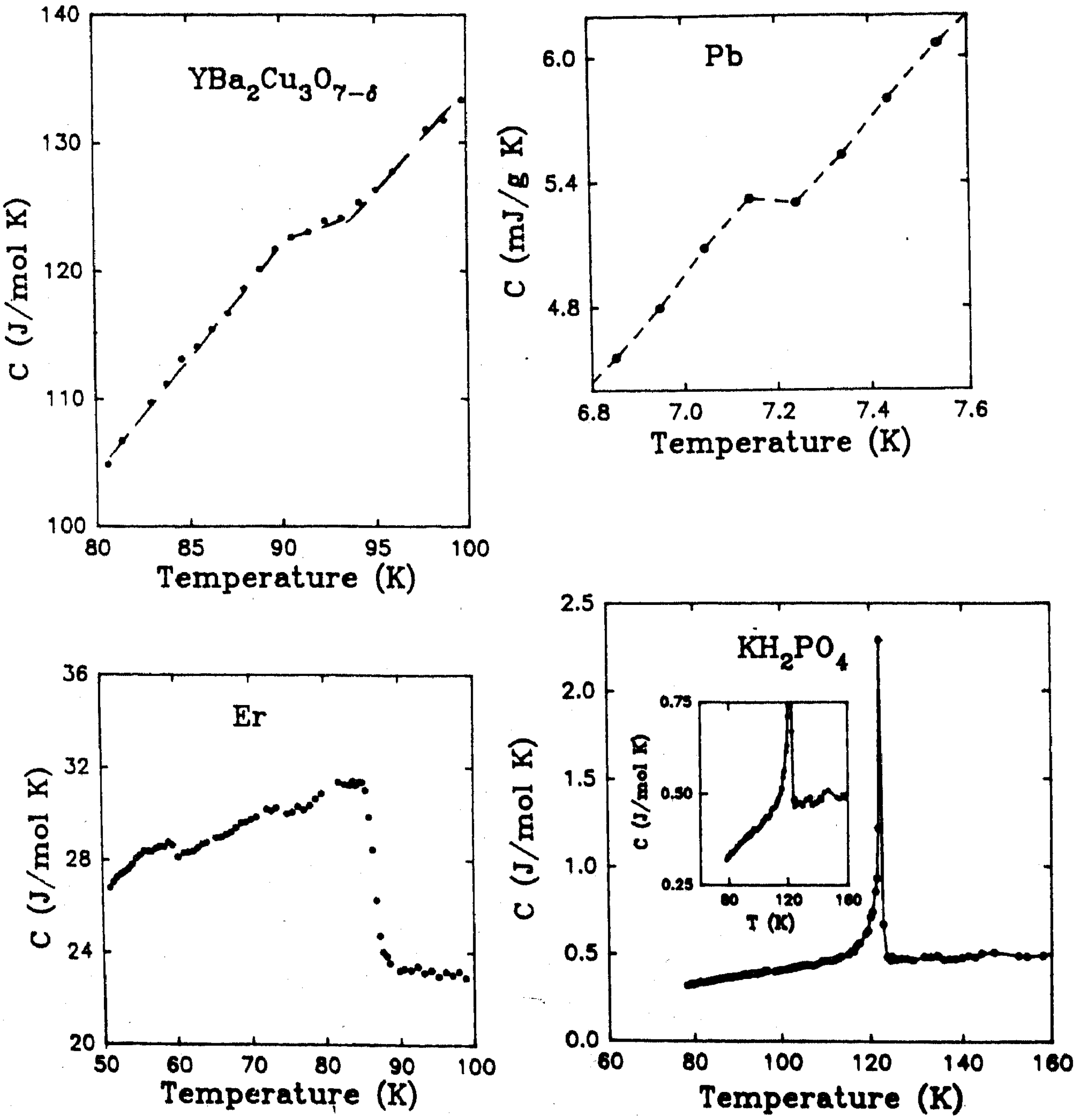

Figure 5. The temperature dependence of heat-capacity across superconducting transitions in Pb and $YBa_2Cu_3O_{7-\delta}$, magnetic transition in Er and ferroelectric transition in KH_2PO_4. In order to highlight the fact that the variation of C with T in the near vicinity of ferroelectric transition in KH_2PO_4 is in agreement with that known in literature [1], the plot is shown in an expanded form in the inset. A feature for Er at 60 K [1] is also reproducible in our data. The lines drawn through the data points are the guides to the eyes.

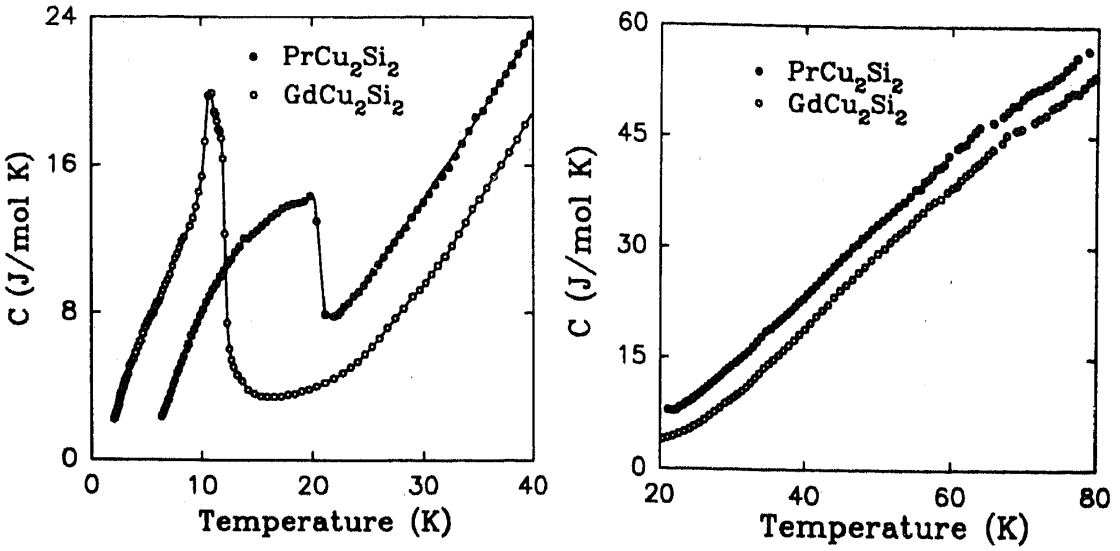

Figure 6. The heat-capacity as a function of temperature in $PrCu_2Si_2$ and $GdCu_2Si_2$. The lines drawn through the data points are the guides to the eyes. The C values in the temperature interval 20–80 K are plotted separately in order to show that these plots are parallel in the temperature interval 30–80 K.

to be in excellent agreement with the literature data, for instance, superconducting transition in Pb ($T_c = 7{\cdot}2$ K) and $YBa_2Cu_3O_{7-\delta}$ ($T_c = 90$ K) magnetic ordering in Er at 84·5 K and ferroelectric transition in KH_2PO_4 ($T_c = 122$ K) (see [1]).

We also measured the heat-capacity of the two alloys of interest to us, viz., $PrCu_2Si_2$ and $GdCu_2Si_2$ in the temperature range 2–120 K. The results are shown in figure 6. These alloys are known to undergo antiferromagnetic phase transitions at 21 K and 13 K respectively [15]. The data shown in figure 6 are in agreement with this. It may be remarked that the heat-capacity data reported earlier [16] were restricted to 40 K. The C values of the Pr alloy was found to be higher than that of Gd alloy by about 3·5 to 4 J/mol K in the temperature range 25–40 K; the origin of this excess heat-capacity was speculated to arise from the heavy-fermion-like character of Pr ions, a phenomenon unexplored in Pr-based intermetallics. In order to place this speculation on firm grounds, there is a need to exclude possible interference from the Schottky peaks (due to crystal-field effects) in the temperature range of interest (viz., above 20 K in $PrCu_2Si_2$). If the Schottky anomalies interfere, then the C versus T plots for Pr and Gd are not expected to be parallel. The data shown in figure 6 clearly suggest that the plots are practically parallel in a wide temperature range, thereby suggesting that the contribution due to Schottky peaks in the temperature interval 30–80 K for the Pr sample is presumably insignificant. Above 80 K, there is a marginal deviation from this behavior (not shown in the figure), which can also arise from different Debye temperature values. It may be remarked that Boulier *et al* [17] have shown that short range order effects persist up to 30 K in $GdCu_2Si_2$, and hence the two curves in figure 6 below 30 K are not expected to be parallel. We would like to avoid further discussion of these results, as it is not the main aim of this article.

4. Conclusion

We have described a simple and unconventional design of a calorimeter to measure heat-capacity in a wide temperature range employing semi-adiabatic heat-pulse method.

The results shown in figures 4–6 convince that the statistics and the quality of the data are satisfactory. We believe that the same calorimeter can be used to measure heat-capacity at much higher temperatures by making the following provisions: (i) replacement of the Ge sensor by Pt sensor and (ii) another stainless steel tube can be provided surrounding the tube T1 and the temperature of the Cu tube in T1 can be controlled (to that of sample) after evacuation of the annular space. We hope that the design described here can be employed to make thermopower and thermal conductivity measuring instruments of top-loading type with necessary modifications of the sample holder.

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