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An automatic adiabatic calorimeter for heat capacity measurements of solids in the range 4.2–30 K ☆

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Abstract

An adiabatic calorimeter equipped with a mechanical heat switch, for use in the temperature range 4.2–30 K, was constructed and tested by making heat capacity measurements on the calorimetry conference sample of high purity copper (99.9999 wt%). The results obtained are compared with those published by the National Bureau of Standards.

Keywords: Adiabatic; Calorimeter; Heat capacity; High-purity copper; Low temperature

1. Introduction

The low-temperature heat capacity of substances is of significant importance in both theoretical research and practical applications concerned with energy sources and materials science. Due to the rapid developments in cryogenic science and technology in China, both in terms of basic research and research into practical applications, there is a growing need of low-temperature heat capacity data for a wide variety of new materials. To satisfy these increasing demands, using our previous resutls [1, 2] and extending the measurement region down to a temperature

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of 4.2 K, we constructed an adiabatic calorimeter equipped with a mechanical heat switch which can be used to make measurements in the 4.2-30 K. In order to verify the reliability of the calorimetric apparatus, we measured the heat capacity of high-purity copper (the standard reference material for low-temperature calorimetry).

2. Experimental

2.1. Calorimeter and cryostat

The adiabatic calorimeter and the liquid helium cryostat assembly are shown schematically in Fig. 1. The sample vessel is a thin-walled cylinder with a screw lid, constructed of gold-plated oxygen-free copper. The main body of the vessel is 40 mm in diameter and 60 mm high. Manganin wire (0.05 mm diameter) with a resistance of 1700 Ω is wound around the outer wall of the vessel to serve as a heater.

The temperature of the vessel is measured by a germaniun resistance thermometer (Type GR 1000, Lake Shore Co.) mounted in the bottom of the cylinder. The thermometer was calibrated at the National Laboratory of Australia in terms of the EPT-76 within the temperature range 1.5-30 K with an uncertainty of about ± 2 mK.

All the electrical leads of the calorimeter are precooled in a liquid helium bath before entering the vacuum can through a hermetic seal (subzero-epoxide resin). The leads are then wound several times around a temperature-control ring (thermal shield) and, finally introduced into the sample vessel. Heating wires are wound on the ring and a set of two junction chromel/Au + 0.03 mol% Fe differential thermocouples between the ring and the vessel maintain the temperature of the ring at that of the vessel. In this way, leakage of heat from the calorimeter vessel along the wires to the surroundings is reduced to a minimum.

The mechanical heat switch is of a gear-driven mechanism, comprising a fine stainless-steel rod with upper and lower bellows. By turning the handle on the mechanical heat switch the sample vessel can be brought to touch or released from the bottom of the vacuum can immersed in liquid helium. The sample can therefore be cooled to the temperature of the liquid helium bath without using helium exchange gas in the vacuum can, thus preventing the unstable adsorption and desorption of helium gas at the sample-vessel surface during heat capacity measurements at very low temperatures, and hence avoiding errors in the data obtained that arise from the adsorption/desorption of helium exchange gas.

The cryostat is a stainless-steel Dewar vessel with a capacity of about 24 l. To make a heat-capacity measurement, the Dewar vessel is first filled with liquid nitrogen and the sample vessel cooled to about 77 K. The liquid nitrogen is then replaced with liquid helium and the sample cooled further to about 4.2 K. The level of liquid helium in the Dewar vessel is monitored by means of a superconductor level device.

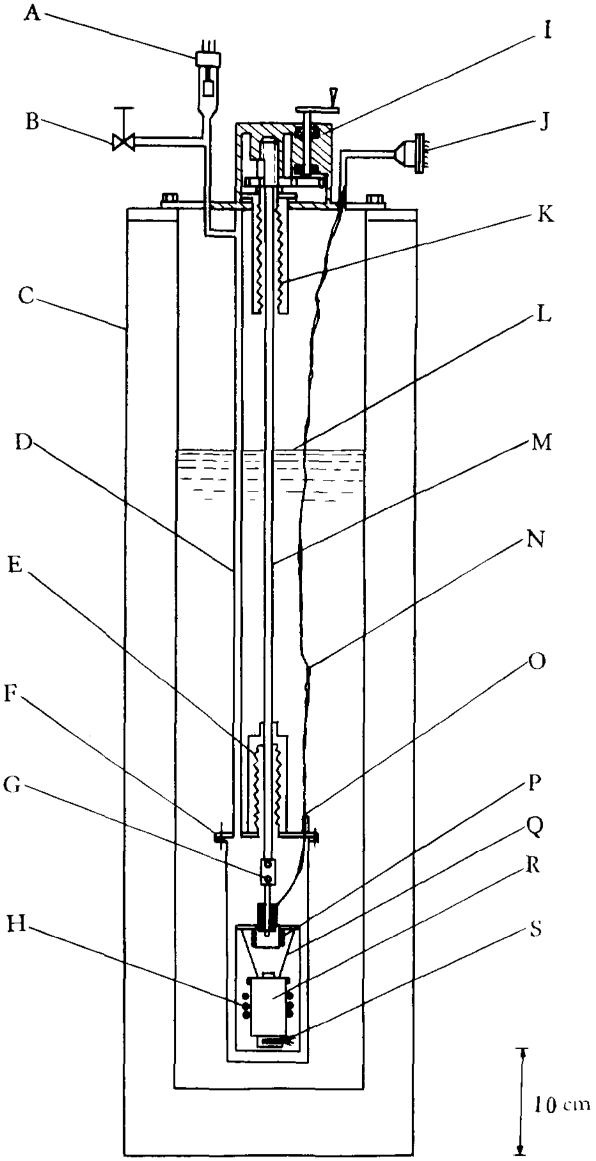

Fig. 1. The 4.2-30 K adiabatic calorimeter and liquid helium cryostat assembly. A, ionization gauge; B, high vacuum valve; C, stainless-steel Dewar vessel; D, vacuum line; E, lower bellows; F, vacuum can; G, thermal-insulation link; H, calorimeter heater; I, gear-driven mechanism for the heat switch; J, high vacuum seal joints; K, upper bellows; L, liquid helium; M, fine stainless-steel rod; N, lead wires; O, hermetic seal for lead outlet (subzero expoxide resin); P, temperature control ring for lead wires; Q, nylon thread; R, sample vessel; S, germanium resistance thermometer.

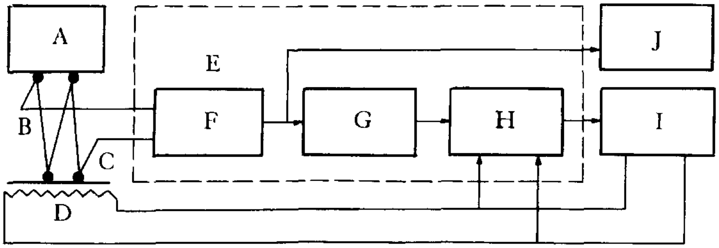

Fig. 2. Automatic adiabatic shield control circuit. A, Sample vessel; B, differential thermocouples; C, adiabatic shield ring; D, shield-ring heater; E, ACD-79 adiabatic controller; F, microvolt amplifier; G, PID controller; H, silicon controlled trigger; I, silicon controlled performer; J, temperature-difference recorder.

2.2. Temperature-control system

Adiabatic conditions are obtained in the calorimetric vessel by controlling the temperature of the adiabatic shield ring by means of an automatic adiabatic controller (Model ACD-79, made in our thermochemistry laboratory) in conjunction with a set of differential thermocouples installed between the adiabatic shield ring and the sample vessel. The principle of the control circuit is illustrated in Fig. 2. Briefly, the signal from the differential thermocouples is amplified by a microvolt amplifier. The amplified signal is monitored by means of a recorder and adjusted by a regulator which provides a PID control mode. The output of the PID controller is transferred to a silicon controlled trigger which actuates the silicon controlled performer. An appropriate current is delivered to the ring heater to raise the temperature of the ring to that required.

When the adiabatic control circuit is operating, the temperature difference between the adiabatic shield ring and the sample vessel can be kept within ±5 mK during the heating period and ± 1 mK during the drift period; the observed temperature drift rate of the sample vessel can be maintained within ±0.1 mK min^{-1} or better during the equilibration period.

2.3. Temperature and energy measurements

The temperature of the calorimeter vessel is determined by measuring the resistance of the germanium thermometer. The resistance of the thermometer is determined by comparing the potential drop across the thermometer with that across a 1000 Ω standard resistor connected in series with the thermometer. The drop in potential is measured by means of a D.C. comparator potentiometer with a resolution of 0.01 μV (Model UJ-42, Shanghai Electric Meter Manufacturing Co.). The measured resistance is converted into temperature in terms of EPT-76 according to calibration data. The resolution of the measurements obtained is about 0.1 mK over the temperature range 4.2–30 K.

Electrical energy is supplied to the calorimeter vessel by a d.c. constant-voltage power supply with a stability of 1 ppm. The energy supplied is determined

Table 1
Experimental molar heat capacity of copper (M(Cu) = 63.546)

T/K	C_p/(mJ K^{-1} mol^{-1})	T/K	C_p/(mJ K^{-1} mol^{-1})	T/K	C_p/(mJ K^{-1} mol^{-1})
3.760	5.096	7.678	26.98	13.212	125.7
4.162	6.275	7.906	29.43	13.283	126.9
4.289	6.773	7.970	30.07	13.795	143.3
4.496	7.432	8.344	34.03	14.280	159.3
4.837	8.719	8.388	34.51	14.408	162.3
5.190	10.25	8.653	37.51	15.233	194.5
5.249	10.52	8.793	39.24	15.634	208.4
5.424	11.33	9.018	42.06	15.944	223.9
5.760	13.12	9.104	43.17	16.566	252.4
5.843	13.62	9.237	44.89	16.809	263.4
5.988	14.43	9.566	49.55	17.768	314.0
6.182	15.62	9.733	51.59	17.814	317.3
6.303	16.38	9.876	53.44	19.040	393.4
6.627	18.59	10.215	59.61	19.628	432.9
6.722	19.06	10.323	61.21	20.377	491.3
6.751	19.49	10.381	62.19	21.128	550.3
6.807	19.90	11.030	73.68	21.808	614.4
7.196	22.97	11.179	77.17	22.812	713.9
7.288	23.74	11.282	79.25	23.217	754.8
7.331	24.11	11.679	87.31	24.751	933.5
7.411	24.64	12.313	102.3	24.952	960.1
7.468	25.26	12.469	106.1		

by measuring the potential drop across the sample heater and a 1000 Ω standard resistor connected in series with the heater and by the duration of the energy input. The potential drop is observed using a digital voltmeter with a resolution of 1 μV (Model DO-17, Beijing Radio Instrument Co.). The heating range is controlled and measured by a digital-display electronic timer–controller with a measuring error of 1 ms (Model JK-1, made in our thermochemistry laboratory).

The temperature and energy data obtained were processed using an IBM PC.

2.4. Sample and treatment

The high-purity copper specimen was prepared by the First Manufactory of Instruments in Sichuan, China, and had a claimed purity of 99.9999 wt%. Spectrochemical analysis showed that the copper specimen contained the following inpurities (in parts per million by weight): Sn 0.1, Pb 0.1, Bi 0.1, Sb 0.1, Fe 0.1, As 0.1, Ag 0.1, Mg 0.05, Co 0.05, and Mn 0.02.

The specimen was a rod 35 mm in diameter and 60 mm in length. Prior to making the heat-capacity measurements, the specimen was etched using a 1:1 solution of nitric acid, followed by a 1:1 solution of hydrochloric acid. The speciman was rinsed with distilled water and dried in air on a piece of filter paper. Finally, it was annealed at 800°C under high vacuum (10^{-4} Pa) for 2 h.

The mass of the sample used was 406.393 g after a buoyancy correction. This is equal to 6.39525 mol based on a molar mass of 63.546 g mol^{-1} [3].

3. Results and discussion

In order to determine the reliability of our low-temperature calorimeter, we measured the heat capacity of the high-purity copper sample in the temperature range 4–25 K. Experimentally determined values of the molar heat capacity of copper (Table 1) were fitted, by using a weighted least-squares method, to a sixth-degree polynomial: $C_p/(\mathrm{mJ\ mol^{-1}\ K^{-1}}) = \Sigma_{i=1}^{6} A_i T^{2i-1}$ in which $A_1 = 6.704 \times 10^{-1}$, $A_2 = 4.821153 \times 10^{-2}$, $A_3 = 5.426395 \times 10^{-6}$, $A_4 = 8.336319 \times 10^{-8}$, $A_5 = -1.792599 \times 10^{-10}$, and $A_6 = 1.397155 \times 10^{-13}$.

High purity copper is used as a standard substance in low-temperature heat capacity calorimetry. Furukawa et al. [4] have made a critical analysis of the heat capacity data for copper reported in the literature. We assessed the accuracy of our calorimeter by comparing our results with the commonly accepted data published by the National Bureau of Standards. The standard percentage deviation (percentage root-mean-square deviation) of the molar heat-capacity values for copper obtained in the present research from those reported by Osborne et al. [5] is $\pm 0.8\%$ over the temperature range 4–25 K.

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