Construction of a ^{3}He Calorimeter and Heat Capacity Measurement of the 1965 Calorimetry Conference Copper Standard between 0.4 and 20 K

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Construction of an isoperibol-type calorimeter with a ^{3}He cryostat is described. A system of charcoal-adsorption-pump is adopted. A Ge-thermometer used in the heat capacity measurements is calibrated in the temperature range from 0.4 to 1.5 K against the magnetic susceptibility of chromium potassium alum. The precision and the accuracy of the calorimeter is ascertained by the heat capacity measurement of the 1965 Calorimetry Conference Copper Standard (T-8.6) in the temperature range from 0.420 to 19.46 K. The deviation of the experimental points from the "copper reference equation" is within the experimental error of $\pm 2.5\%$ between 0.4 and 0.9 K, $\pm 1.5\%$ between 0.9 and 1.5 K, $\pm 1.2\%$ between 1.5 and 4 K, and $\pm 0.6\%$ between 4 and 20 K. The highest deviation of absolute value of the present heat capacity data of copper is 1.86% smaller than the "selected values (Furukawa *et al.*)" around 6 K. This difference may be primarily attributable to the NBS-65 temperature scale adopted in the present experiment.

In the field of magnetism, weak interactions among the magnetic moments are unambiguously interpreted based on the heat capacity measurements at extremely low temperatures where the lattice contribution is negligibly small. In the temperature region below 1 K, there are known considerable number of inorganic and metallic substances on which magnetic heat capacity measurements are performed. However, precise heat capacity measurements of organometallic and complex compounds are very scanty because these compounds are usually obtained as a polycrystalline form. In this work we constructed a calorimeter capable of measuring precisely the heat capacity of polycrystalline sample in the temperature range from 0.4 to 20 K. Two kinds of calorimeter cell suitable for this purpose were also designed.

The calorimeter constructed here is an isoperibol ^{3}He evaporation-type. To attain temperature significantly below 1 K there are two possible ways for evaporation; one is to pump out ^{3}He vapor by use of a diffusion pump or a rotary pump[1,2] and the other is to use a charcoal adsorption pump.[3,4] The latter is superior to the former due to the following three reasons. (i) The evaporation rate by an adsorption pump is much larger than that by an oil diffusion pump because it is possible to connect an adsorption pump to a ^{3}He pot *via* the extremely short pumping line which is everywhere near 1 K. (ii) In case of an adsorption pump one can avoid the heat generation arising from mechanical vibration of a rotary pump. Mechanical vibration causes very large temperature drift of a calorimeter cell at very low temperatures. (iii) A gas handling system using an adsorption pump is much simpler and securer than that consisting of a rotary pump. Based on our design Oxford Instrument Co., Ltd. constructed a part of the evaporation system of the present ^{3}He cryostat. In the present investigation a charcoal adsorption pump is adopted to avoid mechanical vibrations. A germanium resistance thermometer used here was calibrated against the magnetic temperature scale derived from the magnetic susceptibility of chromium potassium alum. For this end, an a.c. Hartshorn mutual inductance bridge and a coil assembly were constructed. The working principle of the ^{3}He cryostat and the calibration of Ge-thermometer will be described rather in detail.

Any physical quantity can exhibit its exact meaning only when the precision and the accuracy are critically evaluated. A convenient method of their estimation is to compare particular physical quantity with a well-established "standard" value. As to the low temperature calorimetry, heat capacity of high purity copper has been recommended as the calorimetry standard since last decade or so. At the 19th Annual Calorimetry Conference (U. S. A.), it was recommended to use a specially prepared and characterized copper sample for this purpose. In response to this recommendation, standard samples were prepared by Osborne *et al.*, and these samples are now available from Argonne National Laboratory.[5]

To estimate the precision and the accuracy for the present low temperature calorimetry, we measured the heat capacity of the 1965 Calorimetry Conference Copper Standard (Argonne Designation "T-8.6") in the temperature range from 0.4 to 20 K. The results and comparison with those by other investigators will be described below.

Experimental

1. Construction of Apparatus. The calorimeter consists of four major parts, namely a ^{3}He cryostat of isoperibol type, calorimeter cell, temperature measuring circuit, and energy measuring circuit.

1.1 ^{3}He Cryostat: The cryostat consists of three precooling steps and the innermost ^{3}He refrigerant system. The three precoolants are liquid N_2 and liquid ^{4}He at 4.2 and 1.2 K, respectively. The liquid containers for these coolants are designated hereafter as the N_2 reservoir, the ^{4}He main bath and 1.2 K pot, respectively. In order to minimize a heat evolution caused by mechanical vibration due to both a rotary pump used for a vacuum system and the laboratory building, the metal frame supporting the cryostat has been installed on rubber-dampers "Rubloc" and suitable bellows are inserted into the pipings, which cut off the vibration conducted from the building.

Figure 1 illustrates a schematic drawing of the main part of the ^{3}He evaporation cryostat. In this figure the drawing of a part of the dewar vessel and the N_2 reservoir is omitted. A gold-plated copper vacuum jacket (G) immersed in the ^{4}He main bath (C) houses the 1.2 K pot (K), a charcoal adsorption pump (N), a ^{3}He evaporator or the ^{3}He pot (P)

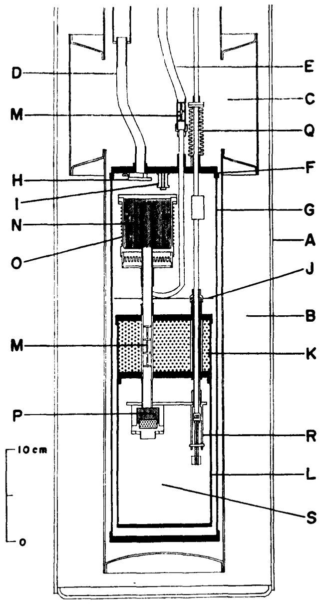

Fig. 1. Schematic drawing of the main part of ^{3}He evaporation-type cryostat (0.4—20 K): (A) aluminium jacket (liquid N_2 temperature), (B) vacuum space, (C) ^{4}He main bath, (D) vacuum pumping tube, (E) ^{3}He filling tube, (F) Wood's alloy joint, (G) gold-plated copper vacuum jacket, (H) radiation shield, (I) thermal anchor for leads, (J) radiation shield, (K) 1.2 K pot, (L) 1.2 K shield, (M) flow-impedance, (N) charcoal adsorption pump, (O) heater, (P) ^{3}He evaporator, (Q) bellows, (R) mechanical thermal switch, (S) experimental space.

and a mechanical thermal switch (R). The 1.2 K pot (inner volume of 400 cm^{3}) is filled with the liquid ^{4}He in the main bath *via* a needle valve. The 1.2 K pot is pumped down slowly to 1.2 K. The charcoal adsorption pump is heated to about 30 K by use of a heater (O) wound around it. The ^{3}He gas admitted through a flow-impedance (M) from an external storage tank is liquefied by passing it through a tube which is in thermal contact with the 1.2 K pot. The liquid ^{3}He drops into the ^{3}He pot. Then the heater is switched off and at the same time a compartment attached to the bottom of the adsorption pump is filled with liquid ^{4}He *via* a needle valve. The adsorption pump is cooled down to 4.2 K and the ^{3}He evaporator reaches rapidly its lowest temperature (0.26 K). The lowest temperature is sustained for more than ten hours in the heat capacity measurements.

The mechanical thermal switch has the gold-plated copper jaws, which are anchored to the ^{3}He evaporator by the copper braids. A stainless steel frame for sample mounting, which is not drawn in Fig. 1, is set in an experimental space (S) and supports a calorimeter cell with fine nylon threads. All the leads between the hermetic seals at the top of the cryostat at room temperature and the tag located under the 1.2 K pot are 46 S.W.G. enamelled copper and are thermally anchored at the 4.2 K spot (I) and at the 1.2 K pot, respectively.

Figure 2 is a sketch of the experimental space inside the 1.2 K shield. Here, a calorimeter cell is already mounted.

1.2 Calorimeter Cells: Tow kinds of calorimeter cells were constructed for the heat capacity measurements of polycrystalline specimen in the low temperature region. One is to use a small amount of ^{3}He gas as a heat exchanger, while the other is to use an organic material (Apiezon-N grease) forming a glassy state for good thermal contact. For convenience, these two cells are designated hereafter the calorimeter cell-type 1 and -type 2, respectively.

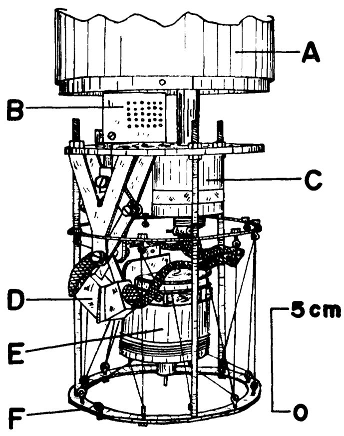

Fig. 2. Sketch of experimental space. The 1.2 K shield is dismantled and a calorimeter cell of type-1 is mounted: (A) 1.2 K pot, (B) tag for leads, (C) ^{3}He evaporator, (D) mechanical thermal switch, (E) calorimeter cell, (F) sample mounting frame.

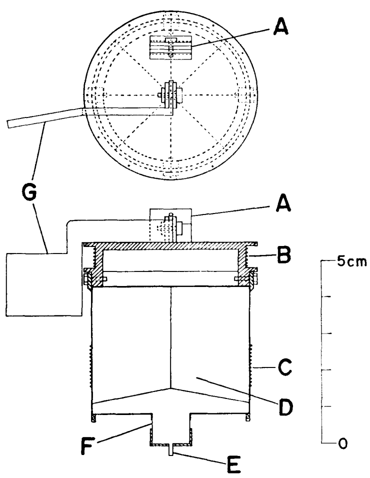

Fig. 3. Schematic diagram of calorimeter cell-type 1: (A) germanium thermometer holder, (B) leads for germanium thermometer, (C) heater, (D) eight vertical radial vanes, (E) ^{3}He gas filling tube, (F) sample filling tube, (G) clamping post.

1.2.1 Calorimeter Cell-Type 1: The calorimeter cell-type 1 (Fig. 3) consists of two parts: the upper part made of gold-plated copper is equipped with a clamping post (G) and a germanium thermometer holder (A), while the lower part is a sample container made of 20 carat gold which has a cylindrical form with the dimension of 4.2 cm in diameter, 3.5 cm in height and *ca.* 42 cm^{3} of capacity. Both parts are connected mechanically. This device is necessary to protect the Ge-thermometer from contamination and mechanical vibration when the sample is loaded. Eight vertical radial vanes (D) in the cell makes the thermal equilibration within the cell easier and to the same end a small amount of ^{3}He gas (*ca.* 2 kPa at room temperature) is also sealed. The heater (C) is formed of a strain-free manganin wire of about 1.5 kΩ (49 S.W.G.) wound non-inductively. The heater is wound directly on to the periphery of the cell for assurance of good thermal contact at very low temperatures. For improvement of electric insulation and thermal contact between

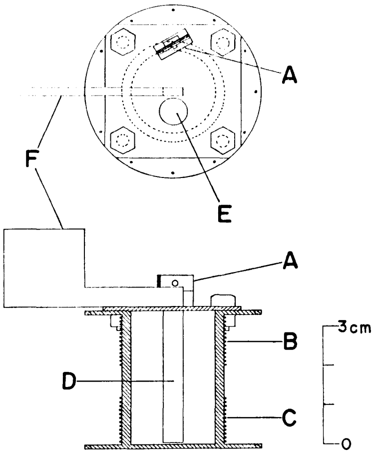

Fig. 4. Schematic diagram of calorimeter cell-type 2: (A) germanium thermometer holder, (B) thermometer leads, (C) heater, (D) copper stirring rod, (E) evacuating hole, (F) clamping post.

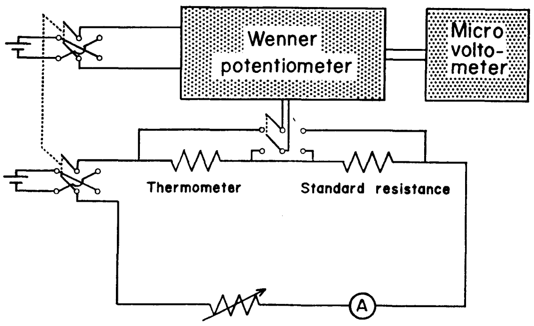

Fig. 5. Block-diagram of temperature measuring circuit.

the cell and the heater, the manganin wire is coated with GE7031 varnish. Thermal contact between the Ge-thermometer and the holder is increased by use of a small quantity of Apiezon-N grease between them. A part of the leads is thermally anchored to the upper part of the cell by means of GE7031 varnish. The cell is fixed to the sample mounting frame by fine nylon threads. The clamping post is adjusted to locate symmetrically between the jaws of the mechanical thermal switch (see Fig. 2).

1.2.2 Calorimeter Cell-Type 2: Figure 4 shows the calorimeter cell-type 2. In this case a polycrystalline sample is mixed with Apiezon-N grease. Heat transfer within the cell is promoted by a copper stirring rod (D) attached to one end of the clamping post. The cell is a copper cylinder of 2.5 cm in diameter, 3.5 cm in length and *ca.* 12 cm^3 of capacity. The clamping post (F), the thermometer holder (A) and so on are similar to those of the type 1.

1.3 Temperature Measuring Circuit: The measurement of temperature is achieved by the potential drops across both a germanium resistance thermometer (CryoCal, Inc., type CR100) and a standard resistor (1 kΩ, Shimadzu Electrical Measuring Instruments Co., Ltd.) arranged in series with it (see Fig. 5). These measurements are made by use of a Wenner-type potentiometer (Leeds & Northrup Co.). The degree of imbalance of the potentiometer is monitored by a d.c. micro voltmeter (Ohkura Electric Co., model AM-1001). The electric current used for the resistance measurements of the Ge-thermometer is selected to be 3.6—46 μA in the temperature range from 0.9 to 20 K, while below 0.9 K 1 μA or less is used so that the self-heating effect can be minimized. The thermal electromotive force generated in the circuit is compensated by the reversion of the electric current. The apparent temperature difference caused by the current reversion were, *e.g.*, 0.6 mK at 0.61 K and 1.0 mK at 1.3 K. The standard resistor and an unsaturated-type standard cell (Epply Laboratory, Inc.) necessary for the potentiometer are kept at constant temperature.

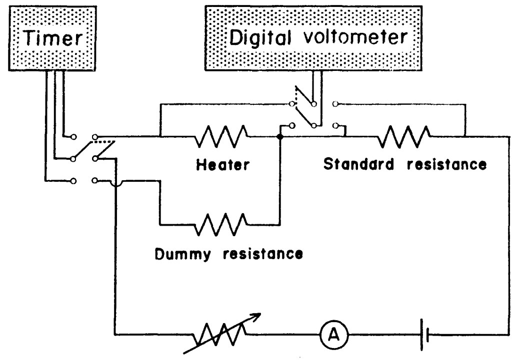

Fig. 6. Block-diagram of heating circuit.

1.4 Heating Circuit: Figure 6 shows the heating circuit. The heater current is supplied from a bank of low discharge lead storage batteries. The circuit is arranged to give a continuously variable current from 20 μA to 3.7 mA. The electric current flowing through the heater is determined by the potential drop across a standard resistor (1 kΩ). The heating element consists of a 49 S.W.G. manganin wire whose resistance is *ca.* 1.5 kΩ at room temperature. The d.c. voltages across the heater and the standard resistor are displayed on an integrating digital voltmeter (Takeda Riken Industry Co., Ltd., model TR-6515D, 5 digits). A dummy resistor having a similar resistance to the heater is placed in parallel to the heater. This dummy circuit enables the batteries to supply a stable current for a long period. The duration of the heating period is determined by an electronic counter (Takeda Riken Industry Co., Ltd., model TR-5104/04F, 6 digits).

2. Calibration of Ge-thermometer between 0.4 and 1.5 K. The germanium resistance thermometer (CryoCal, Inc., type CR100) used for the present heat capacity measurements has been already calibrated in the temperature range from 1.5 to 20 K at CryoCal, Inc. The temperature scale between 1.5 and 2.0 K is based on the helium-4 vapor pressure scale of 1958 (T_{58}). The 2.25 to 13 K readings are traceable to the National Bureau of Standards Provisional Scale 2—20 (1965) through a secondary standard. The temperature scale between 14 and 20 K is based on the International Practical Temperature Scale of 1968 (T_{68}) through a secondary standard.

Then the calibration below 1.5 K is made against the magnetic temperature scale derived from our measurement of magnetic susceptibility for chromium potassium alum. For this end, an a.c. Hartshorn mutual inductance bridge and a coil assembly for it were constructed. The oscillator is a commercially available audio-frequency signal generator (General Radio Co., type 1301-A). The frequency used here is 100 Hz. The inductive unbalance of the measuring secondary coil can be resolved into two components; the first component corresponds to the real part of the magnetic susceptibility of the paramagnetic salt and can be compensated by a variable mutual inductor (H. Tinsley & Co., Ltd., type 4229). The second component corresponds to the imaginary part of the susceptibility and can be compensated by taking off a small voltage from a potentiometer. The null balance of the circuit is attained by visual observation on the oscil-

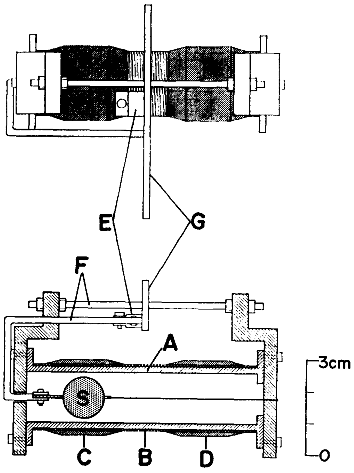

Fig. 7. Schematic diagram of the coil assembly: (S) paramagnetic salt, (A) nylon bobbin, (B) primary coil, (C) measuring secondary coil, (D) compensating secondary coil, (E) germanium thermometer holder, (F) copper rod, (G) clamping post.

lograph.

In the coil assembly (see Fig. 7), the Nb–Ti superconducting wire is wound on a nylon bobbin as a primary coil. The use of superconducting wire prevents the heat evolution due to Joule-effect in the primary coil at low temperatures. The measuring and the compensating secondary coils (copper wire) are wound directly onto the primary coil in opposite directions so that the mutual inductance due to the empty coil may be reduced to a conveniently small value. A single crystal of chromium potassium alum (*ca.* 2 g) is mounted in the bobbin.

The calibration procedure is as follows; in the first place, the magnetic susceptibility of the specimen was measured in the range from 1.5 to 7.0 K by use of the temperature scale of the Ge-thermometer. Based on these measurements we determined the Curie constant, the geometry factor of the salt, and the constant mutual inductance characteristic of the present apparatus. By assuming that these factors would not change below 1.5 K the Ge-thermometer was calibrated against the magnetic susceptibility in this temperature region. At each temperature the readings of the mutual inductor and the resistance of the thermometer were recorded over a period of 15—30 min. Twenty-seven sets of the experimental points were determined in the range between *ca.* 0.4 and 7 K. During the calibration the temperature of the coil assembly was controlled by both the mechanical thermal switch and the heater.

The calibration data, together with those above 1.5 K, were fitted to the following polynomial by using the method of least squares in the fractional deviations with equal weight:

$$\ln R = \sum_{i=0}^{13} A_i (\ln T)^i. \tag{1}$$

This polynomial with fourteen parameters can reproduce the calibration points within ±2 mK below 6 K, within ±5 mK between 6 and 15 K, and within ±8 mK between 15 and 20 K (see Fig. 8).

The main source of experimental errors lies in the inaccuracy of the measurement of the mutual inductance. Its readings have an uncertainty of ±0.1 μH owing to the small current in the primary coil. On the other hand, the lowest range of the mutual inductor showed different values of the reading taken in the clockwise and the counterclockwise directions. This may be caused by the external electromagnetic coupling around the mutual inductor.

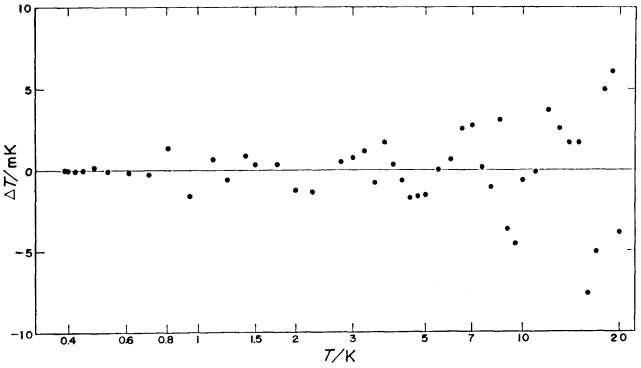

Fig. 8. Deviation plot for the germanium thermometer. $\Delta T = T_{\text{calcd}} - T_{\text{obsd}}$, where T_{obsd} is the calibrated temperature and T_{calcd} is the temperature calculated from the observed resistance R and the polynomial of the form given by Eq. 1.

The validity of temperature calibration will be discussed later in connection with the heat capacity data of the 1965 Calorimetry Conference Copper Standard.

3. *Heat Capacity Measurement of Standard Copper Sample.*

To evaluate the precision and the accuracy for the present low temperature calorimetry, we measured the heat capacity of the 1965 Calorimetry Conference Copper Standard (Argonne Designation "T-8.6")[5] in the temperature range from 0.4 to 20 K. The purity of the present copper sample is guaranteed to be better than 99.999%.

3.1 Preparation of Standard Copper Sample: The standard copper sample employed for the present purpose was the 1965 Calorimetry Conference Copper Standard (T-8.6), which was prepared in Argonne National Laboratory by vacuum casting 99.999+% High Purity Copper (American Smelting and Refining Co.) into rods. The sample has a cylindrical form of 5.3 cm in height and 3.1 cm in diameter. It was cleaned first with nitric acid and then with hydrochloric acid, rinsed with distilled water and dried *in vacuo*. After the surface treatments was over it was annealed in H_2 atmosphere for 2 h at 670 K, in ^{4}He atmosphere for 4.5 h at 720 K, and cooled *in vacuo* overnight in a Pyrex vessel. The final mass of the sample was 376.605 g ($\triangleq$5.92649 mol).

For the heat capacity measurement the sample was mounted in a sample holder (Fig. 9). The sample holder consists of two flat copper disks (B) and (C); the upper one (B) is equipped with a clamping post (D) and a germanium thermometer holder (A). The sample (E) was interposed mechanically between these two disks. The calibrated germanium thermometer was inserted into the thermometer holder. Small amount of Apiezon-N grease was used for the attainment of good thermal contact between each part. A heater consists of a manganin wire (49 S.W.G.) with about 1.5 kΩ, which was wound directly onto the periphery of the sample rod and glued with GE7031 varnish. The sample holder was tightly hung in the calorimeter mounting frame in the cryostat by fine nylon threads. The clamping post was adjusted to locate centrally between the pair of jaws of the mechanical thermal switch. The weight of the sample holder and other addenda was 84.333 g.

3.2 Heat Capacity Measurement of Standard Copper Sample: The heat capacity measurement was made by an impulse method. The principle of this method is to measure a tem-

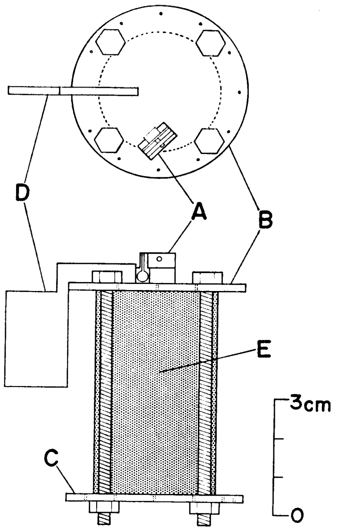

Fig. 9. Schematic diagram of the sample holder for standard copper: (A) germanium thermometer holder, (B) upper disk, (C) lower disk, (D) clamping post, (E) copper sample.

perature increment ΔT after a known quantity of heat ΔQ is introduced to a sample at a temperature T. The average heat capacity C_{av} in the temperature interval between T and $T+\Delta T$ may be given by $C_{av}=\Delta Q/\Delta T$. On the other hand, the true heat capacity (C) is defined as $C=\lim_{\Delta T\to 0}(\Delta Q/\Delta T)=dQ/dT$. When the ΔT is small enough, C_{av} approximates well to C and can be regarded as the true heat capacity at the average temperature T_{av} $(=T+\Delta T/2)$. However, in the temperature region where the heat capacity is largely varied with temperature, the curvature correction should be made.

The temperature drift was monitored over a period of *ca.* 8 min and the attainment of thermal equilibrium in the sample was confirmed. The heat leak into the sample was estimated to be 20 nW at 0.45 K and −21 nW at 0.68 K. On the other hand, a breaking-off operation of the thermal switch brought about a temperature rise of 50 mK from the realized lowest temperature (*ca.* 0.32 K). This heat evolution is caused by the friction between the clamping post and the jaws of the thermal switch.

The heat capacity of the copper plus addenda was first measured in the temperature range from 0.391 to 20.02 K. Then the auxiliary measurement of the heat capacity of addenda was made between 0.456 and 19.18 K. The same amount of Apiezon-N grease was used for both sets of measurements. The ratio of the heat capacity of the addenda to the total amounts to about 20% at 0.42 K and becomes smaller with increasing temperature.

Results and Discussion

Table 1. Heat capacity of the sample T-8.6 from the 1965 calorimetry conference copper standard (atomic weight=63.546)

T/K	C_p/mJ K^{-1} mol^{-1}	ΔT/K	T/K	C_p/mJ K^{-1} mol^{-1}	ΔT/K
0.420	0.2934	0.024	1.161	0.8840	0.056
0.448	0.3182	0.026	1.210	0.9247	0.064
0.481	0.3484	0.033	1.291	1.001	0.071
0.520	0.3645	0.037	1.348	1.058	0.067
0.554	0.4024	0.028	1.406	1.114	0.064
0.581	0.4264	0.026	1.465	1.171	0.076
0.607	0.4359	0.025	1.529	1.234	0.072
0.631	0.4542	0.024	1.600	1.308	0.121
0.656	0.4742	0.026	1.767	1.478	0.231
0.678	0.4974	0.022	1.971	1.711	0.200
0.702	0.5071	0.029	2.224	2.030	0.339
0.729	0.5188	0.030	2.506	2.457	0.332
0.748	0.5414	0.022	2.794	2.937	0.278
0.767	0.5575	0.022	3.113	3.577	0.392
0.786	0.5648	0.024	3.514	4.500	0.451
0.816	0.5819	0.024	3.981	5.694	0.589
0.834	0.6026	0.025	4.523	7.374	0.549
0.852	0.6274	0.023	4.961	9.083	0.440
0.859	0.6294	0.022	5.400	11.10	0.481
0.873	0.6366	0.022	5.941	13.86	0.647
0.889	0.6468	0.024	6.574	17.91	0.667
0.905	0.6525	0.022	7.151	22.23	0.534
0.920	0.6601	0.024	7.616	26.13	0.445
0.935	0.6816	0.023	8.068	30.27	0.510
0.950	0.7017	0.022	8.518	35.35	0.442
0.965	0.7184	0.025	8.913	39.89	0.393
0.978	0.7314	0.023	9.217	43.71	0.362
0.992	0.7316	0.023	9.600	48.84	0.436
1.007	0.7433	0.028	11.06	72.93	2.538
1.007	0.7474	0.029	12.93	116.1	1.239
1.024	0.7660	0.024	14.10	150.6	1.135
1.044	0.7751	0.036	15.13	187.6	1.003
1.058	0.7994	0.026	16.04	226.5	0.835
1.076	0.8126	0.033	16.97	269.4	1.052
1.101	0.8363	0.035	18.19	334.9	1.414
1.126	0.8537	0.033	19.46	423.0	1.119

The experimental heat capacities, average temperatures and temperature increments are given in Table 1. The curvature correction has been applied for the determination of the heat capacity over the whole temperature region investigated. The experimental values below 2.0 K are compared in Fig. 10 with the results of previous measurements on copper in this temperature region. The open triangle and square represent the individual experimental points of previous measurements,[5,9] while a solid line is a smoothed curve calculated as an average of the data obtained by other two groups.[6–8] The present data (solid circle) agree well with these previous results except for several points around 1.0 K, which are scattered within ±2%. It may be mainly caused by rather small temperature increments in the present heat capacity measurement in this temperature region. On the whole, however, the calibration accuracy of the present thermometer below 1.5 K seems to be satisfactory.

The heat capacities of copper were fitted to the following equation proposed by Barron and Morrison[10] for the heat capacity of metallic solids,

$$C_p=\sum_{i=1}^{n}A_iT^{2i-1}, \tag{2}$$

by using the method of least squares weighted with $1/C_p^2$, so that the sum of squares of the fractional deviations of the observed C_p values from the calculated ones may be minimized. Here, the first term propor-

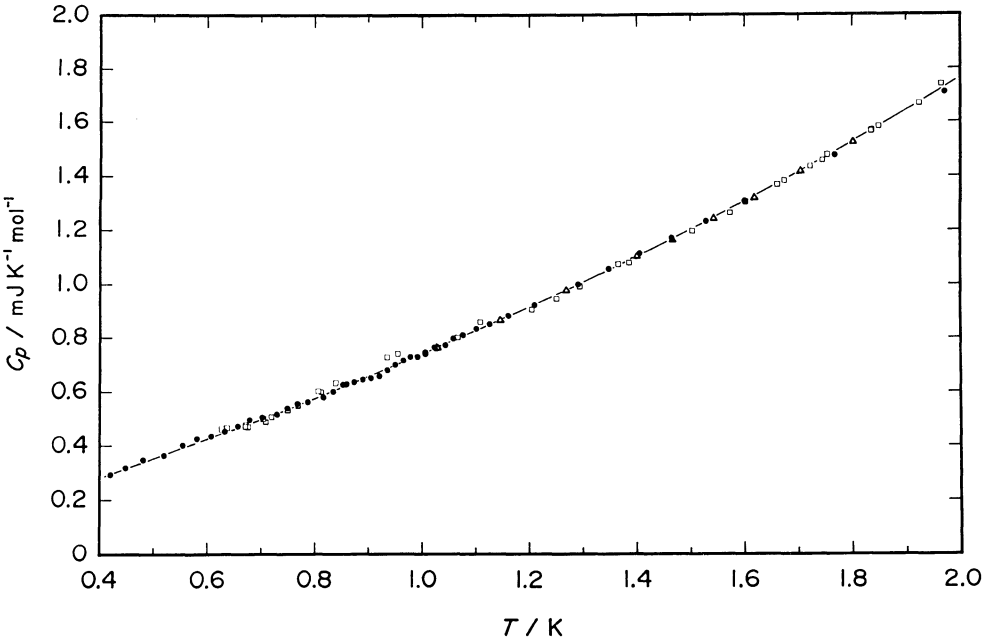

Fig. 10. Heat capacity of copper below 2.0 K: solid curve, Martin,[6,7] and Gmelin and Gobrecht;[8] □, Hurley and Gerstein;[9] △, Osborne *et al.*;[5] ●, present work.

tional to T is the "electronic heat capacity" due to conduction electrons and the remaining higher terms such as T^3, T^5 and so on correspond to the contributions from lattice heat capacity. Osborne *et al.*[5] designated the polynomial as "the copper reference equation" and used it for the purpose of interlaboratory comparison of heat capacity measurements. For the calculation the higher terms greater than $n=6$ were truncated. The "best fit" values of the coefficients were determined to be

$$A_1/\text{mJ K}^{-2}\,\text{mol}^{-1} = 0.69783,$$

$$A_2/\text{mJ K}^{-4}\,\text{mol}^{-1} = 0.45586 \times 10^{-1},$$

$$A_3/\text{mJ K}^{-6}\,\text{mol}^{-1} = 0.26336 \times 10^{-4},$$

$$A_4/\text{mJ K}^{-8}\,\text{mol}^{-1} = -0.39043 \times 10^{-7},$$

$$A_5/\text{mJ K}^{-10}\,\text{mol}^{-1} = 0.16039 \times 10^{-9},$$

and

$$A_6/\text{mJ K}^{-12}\,\text{mol}^{-1} = -0.15882 \times 10^{-12}.$$

The percentage deviations of the present results from the polynomial are shown in Fig. 11. The deviation of the experimental points is within the experimental error of ±0.6% above 4 K, ±1.2% between 4 and 1.5 K, ±1.5% in the range from 1.5 to 0.9 K, and ±2.5% below 0.9 K. As described above, the rather large scatter between 0.9 and 1.5 K may attributable to the small temperature increment in the heat capacity measurement, while the systematic deviation between 1.5 and 4 K may be caused by the discrepancy between the NBS-65 and the T_{58} scales. This problem will be discussed below together with the effect of both temperature scales upon the heat capacity values of copper.

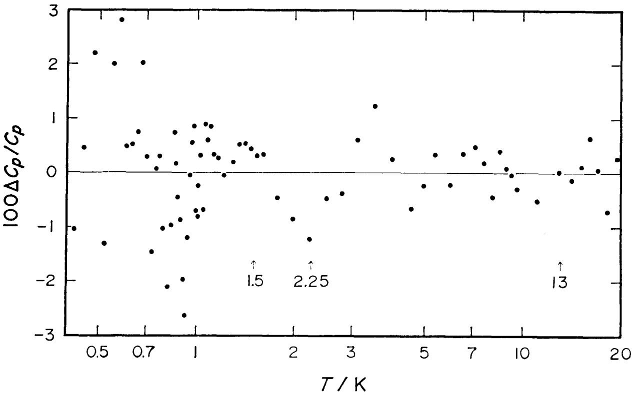

Fig. 11. Percentage deviations of the experimental C_p values from the calculated values, C_p(calcd), by the aid of the copper reference equation; $\Delta C_p = C_p - C_p$(calcd).

A_1 is the coefficient of electronic heat capacity. The coefficient A_2 corresponds to $12\pi^4R/5[\theta_D(0)]^3$ and thus yields the Debye characteristic temperature $\theta_D(0)$ at 0 K, where R is the gas constant. In Table 2, both values are compared with those reported in recent years by a number of workers.[5–9,11–15] Almost all the measurements have been made by using thermometers calibrated against the T_{58} scale, except for the case of Bloom *et al.*[14] They have used the thermometer based on a combination of the T_{58} and the NBS-65 acoustic scales, as is in our case. The present value of $\theta_D(0)$ is slightly larger than the previous results. The difference may be primarily attributed to the temperature scale above 1.5 K because the data below 1.5 K coincide well with the reported values (see Fig. 10). In the present case, the calibration of the germanium thermometer between 1.5 and 2.0 K is based on the helium-4 vapor pressure scale of 1958 and that between 2.25 and 13 K on the National Bureau of Standards Provisional Scale 2—20 (1965). The temperature scale between 14 and 20 K is based on the International Practical Temperature Scale of 1968. The NBS-65 scale was determined on the assumption that the speed of sound

Table 2. Comparison of the electronic coefficient and the Debye temperature of copper at 0 K with the reported values by several workers

	A_1 / μJ K^{-2} mol^{-1}	$\theta_D(0)$ / K	Temperature range / K	Sample	Ref.
Furukawa *et al.*	695±5	344.5±1.5	0—5	Selected value	(11)
Martin (1968)	691.5	345.8	0.3—3	ASARCO	(6)
Martin (1969)	689.0	347.7	0.4—3	Single crystal	(7)
	689.9	346.6	0.4—3	ASARCO	
Osborne *et al.*	694.3	344.5	1—25	T-1.1	(5)
Ahlers	696.0	343.8	1.3—20	T-1.2	(12)
Boerstoel *et al.*	696.8	344.4	1—30	T-3.4	(13)
Gmelin and Gobrecht	696.0	344.4	0.4—2.2	T-4.4	(8)
	696.9	344.6	2—30	T-4.4	
Bloom *et al.*	690.3	345.4	1.5—20	T-5.4	(14)
Holste *et al.*	694.5	343.7	1.5—30	ASARCO (degassed)	(15)
	696.5	343.3	1.5—30	ASARCO	
Hurley and Gerstein	691.4	343.9	0.6—28	T-6.2	(9)
Present work	697.8	349.4	0.4—20	T-8.6	
	698.1	348.5	1—5	T-8.6	
	697.3	346.5	1—5 (corrected)	T-8.6	

in helium gas is proportional to the square root of thermodynamic temperature. The NBS-65 scale is known to be higher than the T_{58} scale.[11,16] Therefore, in order to investigate more critically the dependence of the heat capacity of copper on both temperature scales, we should convert the present data based on the NBS-65 scale into those based on the T_{58} scale in the temperature range between 1 and 5 K.

To do this, we estimated the relationship between the T_{58} and the $T_{\text{NBS-65}}$ scales by use of the numerical values listed in reference (11) and obtained the following equation;

$$T_{58} = -0.1534\times10^{-2} + 0.9982\ (T_{\text{NBS-65}}) -0.5340\times10^{-4}\ (T_{\text{NBS-65}})^2. \tag{3}$$

For examination of the dependence of heat capacity on the two different temperature scales, two sets of values concerning A_1 and $\theta_D(0)$ were calculated by use of the heat capacity data in the range from 1 to 5 K. Firstly, the data due to the $T_{\text{NBS-65}}$ scale were fitted to the equation,

$$C_p = A_1T + A_2T^3, \tag{4}$$

by the method of least squares with a weight of $1/C_p^2$ and A_1 and $\theta_D(0)$ were determined. Secondly, the heat capacity data recalculated based on the T_{58} scale (Eq. 3) were also fitted to Eq. 4. Two sets of the parameters A_1 and $\theta_D(0)$ are given in Table 2. The corrected values show evidently a tendency to approach the reported values. The $T_{\text{NBS-65}}$ scale itself is smoother than the T_{58} scale as previously described, but it is, for the moment, realized by use of only the acoustic thermometer in U. S. National Bureau of Standards. The present germanium thermometer has been calibrated above 2.25 K not directly against the $T_{\text{NBS-65}}$ scale but through a secondary thermometer possessed by CryoCal Co. It is, therefore, plausible to consider that the extra errors have been included in the process of calibration. Another possible reason for the deviation of the heat capacity of copper may be caused by different qualities of copper from sample to sample, because the original data for the evaluation of the standard values[11] include heat capacity measurements on a variety of coppers other than the calorimetry standard copper. At any rate, the temperature scales at low temperatures are hoped to be unified internationally as soon as possible.

By use of this calorimeter, we have measured the heat capacity of a five-coordinated ferromagnet, Fe[$S_2CN(C_2H_5)_2]_2Cl$, in the temperature range from 0.4 to 20 K. The detailed results will be published in due course.[17]

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