

THE HEAT CAPACITY OF COPPER BELOW 4.2 °K

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Summary

The heat capacity of copper has been measured below 4.2 °K with a calorimeter using a mechanical heat switch. The effects of changes in the chemical and physical state of the copper have been investigated with a view to understanding discrepancies between the results of previous workers.

It is found that the γ and θ values for copper of spectroscopic purity are in good agreement with those of Corak *et al.* (1955). Experiments on other specimens, however, reveal a marked dependence of the electronic heat capacity on purity. Possible reasons for this behaviour are discussed, and an evaluation of previous work is given in the light of these results.

I. INTRODUCTION

At sufficiently low temperatures, the heat capacity of a normal metal can be expressed in the form

$$C = \gamma T + A \left(\frac{T}{\theta} \right)^3, \dots\dots\dots (1)$$

where $A = (12\pi^4/5)R$, R being the molar gas constant. In this expression the first term represents the electronic contribution, γ being given by the relation

$$\gamma = \frac{\pi^2}{3} k^2 \left(\frac{dN}{dE} \right)_{E=E(0)}, \dots\dots\dots (2)$$

where $(dN/dE)_{E=E(0)}$ is the density of states at the top of the Fermi surface. The second term represents the lattice contribution, it being supposed that $T \ll \theta$ so that only long-wavelength phonons make an appreciable contribution to the lattice entropy. For many metals this condition is fulfilled in the liquid helium region.

A number of workers (Keesom and Kok 1936; Estermann, Friedberg, and Goldman 1952; Corak *et al.* 1955) have measured the heat capacity of copper in the liquid helium region. When fitted to equation (1), however, these determinations give a range of values for γ and θ considerably in excess of the estimated errors. Possible reasons for the discrepancies are:

- (1) Differences between the vapour pressure-temperature tables used in calibrating the calorimeter thermometers,
- (2) experimental errors and in particular effects due to exchange gas adsorbed on the surface of the specimen,
- (3) effects due to differences in the chemical or physical states of the specimens.

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To date it has been impossible to evaluate the experiments on the basis of these possibilities, since the magnitude of the last-mentioned effect was not known. For this reason the present work was undertaken.

II. EXPERIMENTAL DETAILS

(a) Cryostat

The apparatus is shown schematically in Figure 1. Liquid helium at atmospheric pressure is contained in vessel *A* and is thermally shielded by liquid nitrogen in the outer Dewar *B* and in the radiation shield *C*. By means

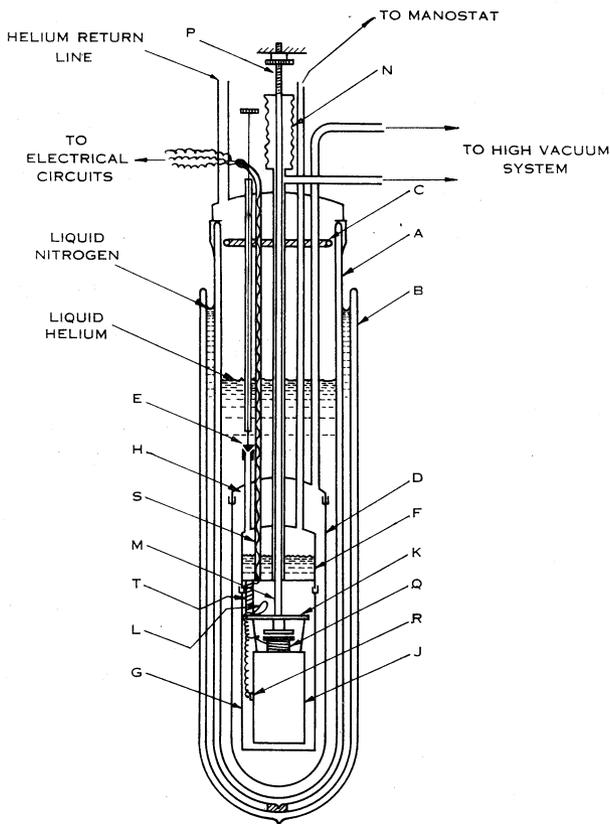


Fig. 1.—Schematic diagram of cryostat.

of the needle valve *E*, liquid can be admitted to the chamber *F* which forms part of the inner can *G*. The space *H* between this can and the outer container *D* is evacuated, and, by controlled pumping on the liquid in *F*, *G* can be kept at any temperature in the range $1.5\text{--}4.2^\circ\text{K}$. The control is effected by means of a glass Cartesian manostat (Gilmont 1951) in the pumping line, temperatures being determined from the vapour pressure of the liquid using either a mercury or butyl phthallate manometer.

The calorimeter is similar to that described by Ramanathan and Srinivasan (1955), except that the working space within the inner can is continuously evacuated. Provision is made, however, for admitting exchange gas to permit calibration of the resistance thermometer at the conclusion of an experiment.

Within the working space, the specimen J is suspended by nylon threads from the disk K , which is thermally anchored to the bath F by the flexible copper strap L . Movement of the disk is effected by means of a stainless steel tube M connected to a bellows N , which can be actuated by the screw mechanism P . Thermal contact between the specimen J and the can G is obtained by lowering the disk and pressing the specimen against the flat bottom of the can. When the disk is raised so that the specimen is hanging freely the only heat leak to the specimen arises from conduction down the thread and the electrical connections, stray radiation, and vibration. This heat leak is kept below 100 erg/min.

The heater for the specimen is a manganin resistance of approximately 5000 Ω , which is wound on a copper former Q screwed into the top of the specimen. A 10 Ω Allen-Bradley carbon resistance, which is mounted in a copper sleeve R screwed into the side of the specimen, is used as a thermometer. Electrical connections to both the heater and thermometer are made with fine manganin wires, which are sealed into and pass down the fine German silver tube S . These wires are wound several times around the copper rod T to effect thermal contact with the helium bath and hence to reduce the heat leak to the specimen.

(b) *Electrical Circuits*

A 1.5 V dry cell supplies energy to the heating circuit, the current being stabilized by a dummy load during the quiescent periods. Switching from the dummy load to the heater is effected by a Leach relay which is actuated by a timer capable of giving a predetermined time interval correct to 1 msec. The heater power is determined by measuring the potential differences across the heater and a 2000 Ω standard resistance on a Diesselhorst potentiometer.

This potentiometer is used to determine the thermometer resistance in the same way. The thermometer circuit is fed from a 6 V accumulator through an 0.6 M Ω resistance in order to minimize variations in the current arising from changes in the thermometer resistance. The current is maintained at approximately 10 μ A; the resulting power input never exceeded 25 erg/min.

(c) *Thermometer Calibration*

In the liquid helium region the thermometer characteristics can be approximated by the formula

$$\sqrt{(\log_{10} R/T)} = 0.770 \log_{10} R - 0.746. \quad \dots \dots (3)$$

This expression is of the form proposed by Clement, Logan, and Gaffney (1955).

Defining T_R as the value of T corresponding to a given value of R in the above expression, values of $\Delta = T - T_R$ were determined experimentally for a number of temperatures throughout the range 1.5–4.2 °K using the 1949 vapour pressure-temperature tables (Van Dijk and Schoenberg 1949) as corrected

by Erickson and Roberts (1954). From these results a correction curve relating Δ to T_R was constructed which, together with equation (3), was used to relate measured values of R to the temperature T .

(d) *Specimens*

Three specimens were used in these experiments, namely :

Specimen I—spectroscopically pure copper ;

Specimen II—commercially pure copper ;

Specimen III—copper-1 per cent. cadmium.

Specimen I, obtained from Johnson, Matthey & Co. Ltd., was prepared from material of 99.999 per cent. purity. Measurements on this were made in the "as received" condition. Specimen II was machined from commercial high conductivity, oxygen-free copper of quoted 99.9 per cent. purity. Spectroscopic analysis revealed traces of iron, nickel, and lead, but no estimate of the more volatile impurities is available. Measurements were made on this specimen in both the "as received" and annealed (400 °C, 6 hr) conditions. Specimen III was machined from an ingot of commercial alloy with a nominal cadmium content of 1 per cent. Chemical analysis gave the actual composition as 0.7 per cent. cadmium, 0.5 per cent. zinc. This specimen was measured in the "as received" condition.

(e) *Measurements*

Heat capacity measurements were made in the usual manner by following the natural warm-up rate of the specimen and by applying known heat inputs at appropriate intervals. By extrapolating the warm-up curve to the mid points of the heating intervals, the temperature rise ΔT corresponding to a given heat input ΔQ was found. From this the heat capacity at temperature $T + \frac{1}{2}\Delta T$ was calculated from the formula

$$C = \Delta Q / \Delta T. \quad \dots\dots\dots (4)$$

Corrections for the heat capacity of the heater and thermometer were determined by measuring the heat capacity of two specimens of commercially pure copper having different masses.

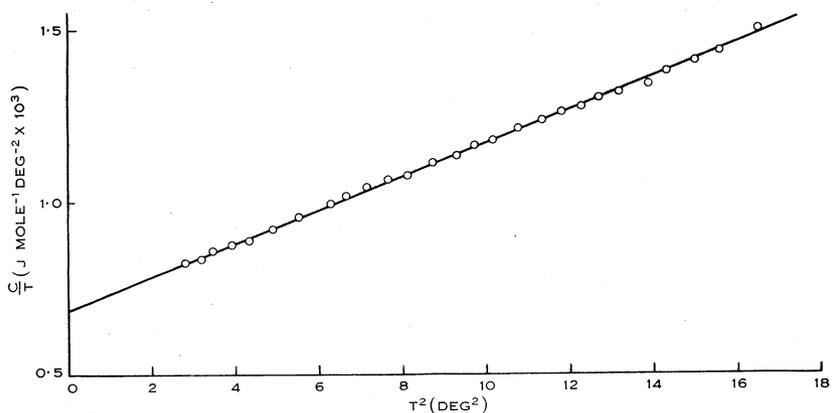
III. RESULTS

The experimental results are presented in Figures 2 (a) and 2 (b) as plots of C/T versus T^2 . From equation (1) it can be seen that such a plot should give a straight line whose ordinate at $T=0$ is the value of γ and whose slope is related to the Debye temperature of the material. In each case, it has been possible to fit a straight line to the results with a maximum deviation of any point from the line of less than 2 per cent.

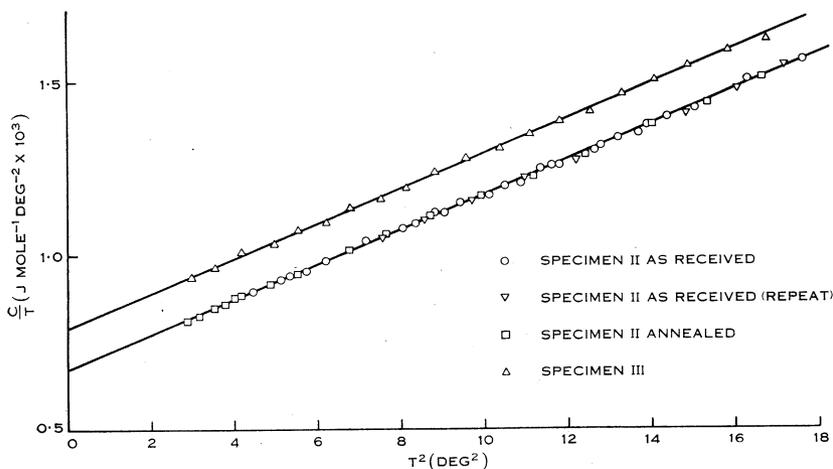
The resulting values of γ and θ , as determined by the method of least squares, are given in Table 1 together with the data obtained by previous workers.

The error estimates for the present work include both random errors, corresponding to the scatter of the experimental data around the lines of best fit, and systematic errors. The latter arise from a number of sources, namely :

- (i) Errors in the measurement of heating power arising from the potentiometer and its associated circuit, from the finite resistance of the heater connections, and from drift in the dry cell voltage. These do not exceed 0.1 per cent.



(a)



(b)

Fig. 2.—Atomic heat of copper. (a) Specimen I; (b) specimens II and III.

- (ii) Errors in the measurement of heating intervals caused by delays in the timer and actuating relay. These amount to about 4 msec and give an error less than 0.05 per cent.
- (iii) Errors in the calibration curve of the thermometer arising from the potentiometer, from the vapour pressure measurements, and from the vapour pressure-temperature relations themselves. The systematic

errors resulting from these causes affect the values of mean temperatures, the average uncertainty being 2 millidegrees which corresponds to an error of less than 0.1 per cent. Local errors in slope affect the values of ΔT and hence the heat capacity, but these tend to change sign a number of times and so are effectively included in the estimate of random error.

- (iv) Errors in calculating the heat capacity using finite temperature increments ΔT . It can be shown that this error is less than $\frac{1}{4}(\Delta T/T)^2$, which is kept below 0.1 per cent.
- (v) Errors in the corrections for the heat capacity of the thermometer and heater. The uncertainties are approximately 5 per cent., but since the correction is only 5 per cent. of the total heat capacity, the resulting error in the latter is only 0.25 per cent.

TABLE I
VALUES OF γ AND θ

Worker	Specimen and Purity (%)	γ (J mole ⁻¹ deg ⁻² × 10 ³)	θ (°K)
Present author	I, 99.999	0.686 ± 0.005	345.1 ± 0.9
” ”	II, 99.9	0.670 ± 0.005	338.9 ± 0.9
” ”	II, 99.9 annealed	0.670 ± 0.005	338.9 ± 0.9
” ”	III, 99	0.799 ± 0.005	344.7 ± 0.9
Keesom and Kok	99.9	0.74 ± 0.02*	335 ± 4*
Estermann, Friedberg, and Goldman	99.6	0.75 ± 0.01*	315 ± 2*
Corak <i>et al.</i>	99.999	0.688 ± 0.002	343.8 ± 0.5

* Error estimated by present author from plots of C/T versus T^2 .

In all it is estimated that the systematic errors in the value of γ are less than 0.5 per cent., the overall accuracy being approximately 0.8 per cent. The error estimates of Corak *et al.* (1955) given in Table 1 refer only to random errors. When corrected for the systematic error, their overall accuracy is substantially the same as that stated for the present work. No attempt has been made to include any estimate of systematic errors in the other results, since insufficient data are given to assess their magnitude.

IV. DISCUSSION

Reference to Table 1 shows that the present results for material of 99.999 per cent. purity agree with those of Corak *et al.* within the combined limits of systematic and random error, thereby confirming the accuracy of their work

and the present work. Since the specimens came from different sources, it is unlikely that they would be identical as regards grain size, state of anneal, etc. From this, together with the fact that specimen II gave identical results in both the strained and annealed states, one can conclude that the values of γ and θ for copper are unaffected by its physical state at least to the accuracy of the present experiments. It would also appear that the value of the Debye temperature is relatively insensitive to impurities.

The results for specimens II and III reveal a marked dependence of electronic heat capacity on impurity content. Such a dependence cannot be understood on the basis of currently accepted theory. According to this, the band structure of copper consists of a narrow, fully occupied d -band overlapped by a wide, half filled s -band, the density of states being roughly that of a free electron gas with one electron per atom. Impurity atoms, if present, are presumed to contribute their outermost electrons to the collective band system without materially altering its shape, so that a divalent impurity would shift the Fermi level in the direction of increasing energy. Owing to the small slope of the density-of-states curve, however, the resulting change in $(dN/dE)_{E=E(0)}$ and hence γ would be quite small for a small impurity concentration. In fact, for the free electron approximation, the relative change in γ is proportional to the relative impurity concentration, the constant of proportionality being of the order unity.

These conclusions are obviously at variance with the present results. One possible explanation for the discrepancy is that the changes in γ are due to changes in the band structure arising from distortions of the lattice caused by impurity atoms. Clearly the magnitude of the effect would depend on the nature of the solute atoms. Elements like cadmium, having a low limit of solid solubility in copper, are known to produce relatively large distortions in the parent lattice and hence one would expect a large effect in this case even though the actual number of impurity atoms was small.

Another possible explanation is to suppose that the actual band structure for copper, in the vicinity of the Fermi level, is a rapidly varying function of energy. Under these conditions relatively small changes in the concentration of valence electrons would produce considerable changes in the density of states and hence γ . Such a situation is not improbable, since in the calculation of the band shape of copper (Krutter 1935) only linear combinations of $3d$ and $4s$ ion core functions were used to compute the metallic wave functions. Actually $4p$ states should also be considered and it is possible that the corresponding $4p$ band overlaps the $4s$ band near the Fermi level. Such a situation would produce an energy band of the required shape to explain the present results. It is of interest to note that Klemens (1954), in explaining the low-temperature conduction properties of the noble metals, has postulated that their Fermi surfaces touch the zone boundaries. Such a situation would also produce a strong energy dependence of the density of states. Further experiments are planned to distinguish between these possibilities.

From the present work, it is possible to draw some conclusions regarding the experiments of Keesom and Kok (1936) and Estermann, Friedberg, and Goldman (1952). In both cases the scatter of points in the plots of C/T versus T^2 is considerable and no substantial improvement results from applying corrections for the errors in the vapour pressure tables used in the corresponding thermometer calibrations. The values of γ and θ still are as good a representation of the data as can be obtained, but the disagreement with the values for pure copper is well outside the combined limits of error, and hence must be due to a combination of experimental error and effects arising from differences in the chemical states of the specimens. In the case of Keesom and Kok, the possible change in γ resulting from the use of a lower purity specimen has been shown here to be at most 3 per cent. Even allowing for this, the difference from the present value for pure copper is outside the limit of error. It would thus seem that at least part of the discrepancy must be attributed to experimental error, the most likely cause arising from the use of exchange gas. The situation regarding the work of Estermann, Friedberg, and Goldman is somewhat more complicated. From the results for the copper-1 per cent. cadmium specimen it would seem that impurity effects could indeed account for the observed discrepancy. It must be remembered, however, that the principal impurity in their sample was lead and that this is virtually insoluble in copper. Apart from the purely bulk effect of lead, the electronic properties of the aggregate would thus be influenced by an extremely small number of atoms and these could scarcely produce the effect observed. Thus the discrepancy must again be due to experimental error although its cause in this case is open to some doubt. There is reason to believe that in part it is due to the neglect of corrections for heat capacity of the heater and thermometer assembly. Such an omission would give too high a value of γ and too low a value of θ . The fact that their value of θ is about 30 °K too low lends considerable weight to this viewpoint, the results of the present work having shown that θ is relatively insensitive to impurity concentration. It appears, however, that the disagreement between the corrected value of γ and the figure for pure copper is still outside the possible limits of error. Thus effects due to exchange gas must also have been present, though their magnitude is difficult to assess.

V. CONCLUSIONS

The present work thus substantiates the work of Corak *et al.* (1955) on the low-temperature heat capacity of copper. It shows also the marked dependence of this property on impurity content and allows a critical evaluation of the work of previous observers.

VI. ACKNOWLEDGMENTS

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VII. REFERENCES

- CLEMENT, J. R., LOGAN, J. K., and GAFFNEY, J. (1955).—Rep. U.S. Nav. Res. Lab. No. 4542.
- CORAK, W. S., GARFUNKEL, M. P., SATTERTHWAITE, C. B., and WEXLER, A. (1955).—*Phys. Rev.* **98** : 1699.
- ERICKSON, R. A., and ROBERTS, L. D. (1954).—*Phys. Rev.* **93** : 957.
- ESTERMANN, I., FRIEDBERG, S. A., and GOLDMAN, J. E. (1952).—*Phys. Rev.* **87** : 582.
- GILMONT, R. (1951).—*Analyt. Chem.* **23** : 157.
- KESOM, W. H., and KOK, J. A. (1936).—*Physica, 's Grav.* **3** : 1035.
- KLEMENS, P. G. (1954).—*Aust. J. Phys.* **7** : 70.
- KRUTTER, H. M. (1935).—*Phys. Rev.* **48** : 664.
- RAMANATHAN, K. G., and SRINIVASAN, T. M. (1955).—*Phil. Mag.* **46** : 338.
- VAN DIJK, H., and SCHOENBERG, D. (1949).—*Nature* **164** : 151.