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Specific Heat of Copper, Silver, and Gold below 30 °K

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The specific heats of pure copper, silver, and gold have been measured in an automatic calorimeter in the range 2.5–30 °K. Above 20 °K the results on copper and gold differ by up to 1% from the author's previous results on these metals—most probably owing to an unstable germanium thermometer used in the earlier work. The new results are analyzed together with data in the 0.4–3.0 °K range and give the following values for electronic-specific-heat coefficient (γ), electron effective mass (m^*/m), and low-temperature limiting Debye temperature (Θ_0^c). The error limits are 95% confidence limits from the statistical analysis and do not include possible systematic errors. Copper: $\gamma = 165.0 \pm 0.2$ μcal/°K^2 g atom (0.691 ± 0.001 mJ/°K^2 g atom); $m^*/m = 1.38$, $\Theta_0^c = (344.3 \pm 0.2)$ °K. Silver: $\gamma = 152.8 \pm 0.2$ μcal/°K^2 g atom (0.640 ± 0.001 mJ/°K^2 g atom); $m^*/m = 1.00$; $\Theta_0^c = (226.6 \pm 0.2)$°K. Gold: $\gamma = 164.7 \pm 0.3$ μcal/°K^2 g atom (0.689 ± 0.001 mJ/°K^2 g atom); $m^*/m = 1.08$; $\Theta_0^c = (161.8 \pm 0.2)$ °K. The results are briefly compared with other recent work on these metals.

INTRODUCTION

At the 1964 Calorimetry Conference it was proposed that pure copper be used as the standard calorimetric sample below 20 °K. Osborne, Flotow, and Schreiner[1] used their own and many other measurements to obtain the so-called copper reference equation (CRE) valid in the range 1–25 °K. This has proved very useful as a basis for comparison of specific-heat measurements from different laboratories. More recent results on copper have been within 1% of the CRE values, the deviations probably being the result of differences in temperature scales, although systematic deviations would point to other problems. Above 23 °K, the CRE was based solely on the present author's earlier results on copper.[2] Later work[3–5] showed both positive and negative deviations from Ref. 2 above 20 °K. Most worrying was the deviation of up to 1% observed with the data of Cetas, Tilford, and Swenson[5] because the temperature scales of both Refs. 2 and 5 were nominally based on the NBS-1955 provisional platinum temperature scale. Very recently, copper has been remeasured in this laboratory using an automated calorimeter[6] and the new results[6] are in good agreement with those of Cetas *et al.*[5] It was initially thought that our earlier data on copper[2] might have been in error owing to a long calorimeter time constant at higher temperatures in that apparatus. However, the present results on silver and gold and other results on gold-silver alloys[7] point to an unstable germanium thermometer (used only for the earlier[2] copper and gold measurements) as being the cause of the error.

EXPERIMENTAL

Measurements were made in a "quasiadiabatic" discrete-heating apparatus using a copper-tray calorimeter with germanium thermometer calibrated on the temperature scale established previously.[2] The calorimeter was controlled by a computer-supervised automatic-data-aquisition system[6] with on-line computation of results. The copper sample used is described in Ref. 6, the silver and gold samples being those used previously.[2] The thermometer calibration (and measuring circuit) were checked during every run by making ^{4}He vapor-pressure measurements (using a small pot on the calorimeter). The stability was considerably better than 1 m°K at 4 °K.

RESULTS

All samples were measured twice, warming the apparatus to room temperature between runs, as a check on the reproducibility of results. The copper raw data have been published elsewhere.[6] Data obtained with the automatic apparatus in the 2.5–30 °K range were combined with data obtained previously[8] at lower temperatures (0.4 to 3 or 4 °K) and fitted to a power series in temperature by the least-squares method, minimizing percentage rather than absolute deviations. An attempt was made to eliminate erroneous points by rejecting points deviating by more than three standard deviations and repeating the curve fit until no further points were rejected. The copper data were fitted to the series $C_p = \sum_{n=0}^{n=6} A_n T^{2n+1}$ because of the excellent fit to copper data obtained in this way by Holste, Cetas, and Swenson (HCS)[9] when the data of Ref. 5 were recalculated on their new paramagnetic-salt temperature scale. The curve fitting program available allowed terms up to $n = 10$ (T^{21}) and for silver the best fit was found for $n = 9$. For gold the fit with $n = 10$ still left significant "wiggles" in the 20–30 °K region. To eliminate this, the gold data below 20 °K were fitted to the equation with $n = 10$, and another fit was made of the data in the 15–30 °K range to $C_p = \sum_{n=0}^{6} A_n T^n$. The former equation was used to represent results below 17.5 °K and the latter for higher temperatures. The two equations give specific heats differing by <0.01% at 17.5 °K and slopes dC_p/dT differing by <1.0% here. For copper with a total of 274 points, 6 were rejected during the curve fit, the final standard deviation being 0.37%. For silver 7 out of 290 points were rejected, the final standard deviation being 0.30%. For gold below 20 °K, 4 out of 249 points were rejected with a final standard deviation of 0.34%, while the second fit in the 15–30 °K range was of 51 points, with 1 rejection leading to a final standard deviation of 0.14%. The copper curve fit given here differs slightly from that of Ref. 6 because (i) data were run on a different computer with different input formats and (ii) in Ref. 6 the lowest-temperature data were referred to a slightly different atomic weight than the other data. This error has been corrected in the present curve fit. The coefficients obtained in the curve fits are given in Table I and the deviations of the experimental data from the fitted curves are given in Fig. 1.

TABLE I. Polynomial coefficients representing specific heat $C_p = \sum A_N T^N$. Units cal/°K g atom. $J = 4.186$. Error limits are 95% confidence limits for each coefficient from the statistical analysis. Each polynomial reproduces the smoothed specific heat to within 0.01% up to 30°K (except for gold where two polynomials are used).

Copper:	Atomic weight = 63.54
	$A_1 = (0.164\,99 \pm 0.00016) \times 10^{-3}$
	$A_3 = (0.113\,81 \pm 0.00036) \times 10^{-4}$
	$A_5 = (0.007\,333 \pm 0.10) \times 10^{-8}$
	$A_7 = (0.257\,35 \pm 0.085) \times 10^{-10}$
	$A_9 = -(0.432\,85 \pm 0.28) \times 10^{-13}$
	$A_{11} = (0.249\,99 \pm 0.40) \times 10^{-16}$
	$A_{13} = -(0.040\,511 \pm 0.20) \times 10^{-19}$
Silver:	Atomic weight = 107.87
	$A_1 = (0.152\,796 \pm 0.00016) \times 10^{-3}$
	$A_3 = (0.399\,012 \pm 0.00091) \times 10^{-4}$
	$A_5 = -(0.106\,099 \pm 0.059) \times 10^{-7}$
	$A_7 = (0.467\,857 \pm 0.12) \times 10^{-9}$
	$A_9 = -(0.172\,020 \pm 0.11) \times 10^{-11}$
	$A_{11} = (0.176\,165 \pm 0.49) \times 10^{-14}$
	$A_{13} = (0.024\,7367 \pm 0.12) \times 10^{-16}$
	$A_{15} = -(0.078\,9427 \pm 0.17) \times 10^{-19}$
	$A_{17} = (0.073\,1169 \pm 0.13) \times 10^{-22}$
	$A_{19} = -(0.239\,793 \pm 0.38) \times 10^{-26}$
Gold:	Atomic weight = 196.967
	Temperatures below 17.5 °K
	$A_1 = (0.164\,661 \pm 0.00027) \times 10^{-3}$
	$A_3 = (0.109\,5772 \pm 0.00033) \times 10^{-3}$
	$A_5 = -(0.438\,6925 \pm 0.053) \times 10^{-6}$
	$A_7 = (0.699\,3098 \pm 0.28) \times 10^{-8}$
	$A_9 = -(0.392\,1645 \pm 0.65) \times 10^{-10}$
	$A_{11} = -(0.056\,04519 \pm 0.83) \times 10^{-12}$
	$A_{13} = (0.195\,7801 \pm 0.60) \times 10^{-14}$
	$A_{15} = -(0.115\,0758 \pm 0.26) \times 10^{-16}$
	$A_{17} = (0.333\,0329 \pm 0.66) \times 10^{-19}$
	$A_{19} = -(0.492\,0411 \pm 0.91) \times 10^{-22}$
	$A_{21} = (0.295\,8440 \pm 0.52) \times 10^{-25}$
	Temperatures above 17.5 °K
	$A_0 = 0.116\,4968 \times 10^{2}$
	$A_1 = -0.328\,2359 \times 10^{1}$
	$A_2 = 0.377\,5046$
	$A_3 = -0.226\,1976 \times 10^{-1}$
	$A_4 = 0.759\,1352 \times 10^{-3}$
	$A_5 = -0.134\,3689 \times 10^{-4}$
	$A_6 = 0.976\,0899 \times 10^{-7}$

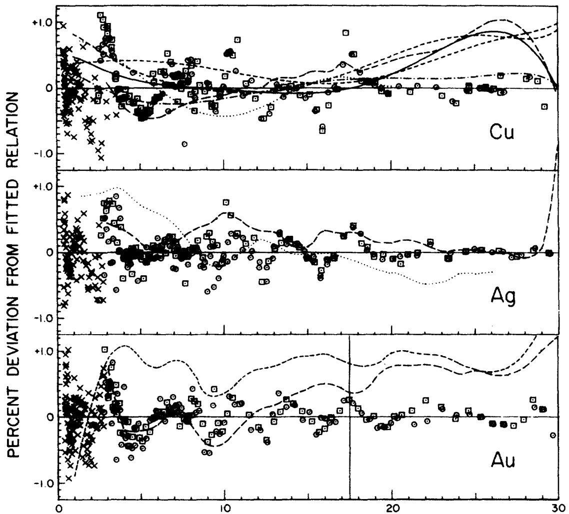

FIG. 1. Percentage deviation of raw specific-heat data from the fitted relation. □ and ○ are points obtained with the apparatus of Ref. 6; × represents raw data from Ref. 8. The solid line is the copper reference equation (Ref. 1), the dot-dash line is the smoothed results of Holste, Cetas, and Swenson (Ref. 9), the dotted lines are smoothed results of Ahlers (Refs. 16 and 17), the short-dash lines are smoothed results of Boerstoel *et al.* (Refs. 3 and 18) and the long-dash lines are earlier results of the present author (Ref. 2).

DISCUSSION

Referring to Fig. 1, it is seen that for all three metals the raw data deviate in a similar way from the fitted curve, suggesting that the major cause is temperature-scale imperfections. Minor differences between the metals probably reflect incorrect selection of the function to represent the data. In the earlier work from this laboratory[2] the germanium thermometer used for the measurements on copper and gold was found to be much less stable than that used for the silver measurements (and was therefore discarded). The smoothed earlier results[2] are shown as a long-dash line in Fig. 1, and above 20 °K are seen to be systematically high for both copper and gold, but in good agreement with the latest data for silver. Comparison of unpublished data on silver-gold alloys with recent measurements[7] also shows good reproducibility. Hence the strong probability that the shift observed in the copper and gold data is owing to an unstable germanium thermometer having been used in the earlier work. Below 20 °K agreement for all three metals is generally within the 0.5% accuracy claimed for the earlier work.[2]

As explained elsewhere[6] the present data above 2.5 °K have been combined with lower-temperature data in an effort to minimize the errors in both apparatuses that are becoming large in the region of overlap. From the curve-fit result (Table I) the electronic-specific-heat coefficient is directly obtained (A_1) and the low-temperature limiting Debye temperature (Θ_0^c) is obtained from A_3. The results are

Copper:

$$\gamma = 165.0 \pm 0.2\ \mu\text{cal}/{}^\circ\text{K}^2\,\text{g atom}$$

$$(0.691 \pm 0.001\ \text{mJ}/{}^\circ\text{K}^2\,\text{g atom})\ ,$$

$$\Theta_0^c = (344.3 \pm 0.2)^\circ\text{K};$$

Silver:

$$\gamma = 152.8 \pm 0.2\ \mu\text{cal}/{}^\circ\text{K}^2\,\text{g atom}$$

$$(0.640 \pm 0.001\ \text{mJ}/{}^\circ\text{K}^2\,\text{g atom})\ ,$$

$$\Theta_0^c = (226.6 \pm 0.2)^\circ\text{K};$$

Gold:

$$\gamma = 164.7 \pm 0.3\ \mu\text{cal}/{}^\circ\text{g atom}$$

$$(0.689 \pm 0.001\ \text{mJ}/{}^\circ\text{K}^2\,\text{g atom})\ ,$$

$$\Theta_0^c = (161.8 \pm 0.2)^\circ\text{K}\ .$$

The error limits are 95% confidence limits from the statistical analysis. Possible systematic errors would increase these limits but are hard to estimate. It was previously estimated that the data[8] below 3 °K might have a systematic error of ±0.4%, but the present method of analysis over a wider temperature range should minimize temperature-scale errors. The present result for copper should be compared with the selected values of Furukawa, Saba, and Reilly[10] [$\gamma = 0.695 \pm 0.005$ mJ/°K^2 g atom, $\Theta = (344.5 \pm 1.5)^\circ$K]. Agreement is seen to be excellent.

The effective masses of the conduction electrons in copper, silver, and gold obtained from the present γ values are 1.38_3, 1.00_4, and 1.08_4, respectively, based on lattice constants of 3.6029, 4.0689, and 4.0651 Å at 0 °K.

The Debye temperatures found for all three metals are in good agreement with the Debye temperatures calculated from elastic constants.[11] The coefficient for the T^5 term in the specific heat is seen from Table I to be essentially zero for copper, very weakly negative for silver, and strongly negative for gold. It is possible that these results are influenced by errors in the temperature scale or fitted function, so it is not certain that silver shows (to a very slight degree) the anomalous variation of Debye temperature with temperature shown by gold. This anomalous variation has recently[12] been identified with positive dispersion in the T_1 branch of the phonon spectrum of gold (as obtained experimentally by coherent inelastic scattering of neutrons). Examination of neutron scattering results on silver[13] and copper[14] show similar positive dispersions in the T_1 branch. For copper[14] the published computed Debye temperature decreased initially with temperature in the usual way. For silver, the phonon spectrum[12] obtained from the results of Ref. 13 leads to an initial increase of about 1 °K in Θ^c, the maximum occurring at about 3.5 °K.[15] If this small "bump" is real it would confirm the negative T^5-term coefficient obtained in analyzing the specific-heat data.

Referring again to Fig. 1, the present data on copper are seen to be close to the CRE[1] (solid line) below 20 °K and close to HCS[9] (dot-dash line) over the whole range. Ahlers measured copper[16] and silver,[17] and his results are shown as a dotted line with agreement within a few tenths of a percent over most of the temperature range, although the deviations differ for copper and silver. Boerstoel *et al.* have made measurements on copper[3] and gold[18] that are shown as a short-dash line (two separate measurements on copper). It will be seen that, except for gold at the lowest temperatures, where the sample thermal capacity is becoming rather small, these measurements tend to be systematically higher than the present results. However, the deviations differ in the case of copper and gold. A systematic deviation could indicate some error in evaluating the heat supplied to the calorimeter in one or both pieces of work. It might be supposed that the Leiden work[3,18] is less reliable than the other work discussed here because the temperature scale is carried on carbon thermometers with long interpolations between calibration points, whereas most other recent work has been with germanium thermometers calibrated at numerous points.

For clarity, two recent sets of results on copper have not been shown in Fig. 1. Leadbetter and Wycherley[19] published results in the range 1.4–20 °K. Their thermometry was based on ^{3}He, ^{4}He, and H_2 vapor-pressure scales interpolated with their own gas-thermometer scale. The smoothed specific-heat results deviate by up to about ±0.7% from the CRE values. Hurley and Gerstein[20] measured in the range 0.6–28 °K with thermometry based on the paramagnetic-salt temperature scale of Ref. 9. Their smoothed results agree with the CRE at about 3 and 20 °K, deviating smoothly up to +0.6% at about 12 °K. Above 20 °K, the results agree closely with those of HCS.[9]

It will be seen that the CRE[1] still appears to be an excellent representation of copper data below

20 °K. Above this temperature the data of Refs. 9, 20, and this work[6] agree well and lie below the CRE values, whereas other data[3,4] (based on carbon thermometry) tend to lie above. Obviously, new results in this range would be valuable. Below 20 °K the CRE was based on gas-thermometry temperature scales joining well with the 1958 ^{4}He vapor pressure scale[21] on which the lower-temperature data were based. It is now thought that the 1958 ^{4}He vapor pressure scale is some 10 mK low at 4 °K, but that most gas thermometry spanning 4–20 °K can be satisfactorily joined to the revised scale by appropriate choice of virial coefficients.[22] It has also been shown[9] that calorimetric data evaluated on gas-thermometer and the NBS-acoustic temperature scales show structure similar to that observed in the present work, whereas smooth results are obtained with a paramagnetic-salt temperature scale. It would therefore appear premature to modify the CRE until (i) more data on copper are published in the 4–25 °K range and (ii) international agreement is reached on the temperature scale down to 1 °K.

CONCLUSION

Previously published data on copper and gold from this laboratory[2] were significantly in error above 20 °K, owing to the use of an unstable germanium thermometer. There are discrepancies of up to 1% in more recent data on copper, silver, and gold reported from various laboratories.

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