A generalization of this result is that the local field arising from two groups of electrons, each with a different effective mass labeled, respectively, as m_α and m_β, will be

$$H_\alpha=4\pi(8/3)k_F^2[M_\alpha R_{(\alpha\alpha)}^2+M_\beta R_{(\alpha\beta)}^2], \quad (13)$$

$$H_\beta=4\pi(8/3)k_F^2[M_\alpha R_{(\beta\alpha)}^2+M_\beta R_{(\beta\beta)}^2], \quad (14)$$

where the total magnetization is $M_\alpha+M_\beta$ and the R's represent the screening constants between the various types of electrons. If all the R's are the same, the local fields will be equal and proportional to the magnetization. This would be the case for the usual dielectric screening approximation. At present, experimental results are not clear as to whether electrons on different parts of the Fermi surface see the same or different effective fields.

Obvious extentions of this work will be to include the spin magnetization[5] and to go to a Hartree-Fock approximation. Although the former appears to pose no special difficulties, the reduction of the nonlocal exchange operator to a local effective field will involve further approximations; a possible approach has been indicated by Luttinger.[6]

We wish to thank P. Wolff for his comments on screening in the multimass case and G. Seidel for comments concerning the present experimental situation as regards the local field.

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[6] J. M. Luttinger, Phys. Rev. 121, 1251 (1961); see Appendix therein.

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Specific Heats below 3°K of Pure Copper, Silver, and Gold, and of Extremely Dilute Gold–Transition-Metal Alloys

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The electronic specific-heat coefficient γ and the limiting low-temperature Debye temperature (Θ_0^c) are estimated as 165.2±0.8 μcal/°K^2 (g atom) and 345.8±1.2°K for copper, 153.1±0.9 μcal/°K^2 (g atom) and 227.3±0.6°K for silver, and 165.1±1.0 μcal/°K^2 (g atom) and 162.3±0.5°K for gold. The coefficient of the T^5 term in the expansion representing the lattice specific heat is -0.23 ± 0.11 μcal/°K^6 (g atom) for gold, and negligible for copper and silver. The γ value for gold is significantly lower than previously reported values. Effective masses of the electrons are: copper, 1.38; silver, 1.01; and gold, 1.09. Two alloys of gold with very small amounts of transition-metal impurity were also measured. For one of these, containing 2.5 ppm by weight Fe and 0.45-ppm Mn, the specific heat is about 5% higher than that of pure gold at 0.4°K and about 1% higher at 1°K.

INTRODUCTION

SPECIFIC-HEAT measurements below 3°K reported previously from this laboratory have been made in an apparatus described some time ago.[1] The apparatus has recently been altered, improving the precision, and the measurements on vacuum-cast pure copper were made to check the performance and also to refine the temperature scale below 0.7°K. It was recently discovered[2] that the specific heat of high-purity copper in the as-received condition might be significantly higher than material which had been vacuum melted or vacuum annealed, perhaps because of slight oxide contamination. Previous measurements on pure silver from this laboratory[3] were on a sample which had been annealed when sealed under vacuum in a quartz envelope. Since a vacuum-cast sample was now available it seemed worthwhile to measure this to check that the previous result for silver was correct. The new measurements agree quite well with the earlier results. Recent work on silver-gold alloys[4] suggested that the earlier result[5] for the electronic specific heat of gold was too high and the same sample of pure gold was therefore remeasured, the new result differing significantly from the earlier result. In the work on Ag-Au alloys[4] it was impossible to avoid very slight contamination with transition-metal impurities and two extremely dilute gold–transition-metal alloys were therefore measured to investigate the effect of such contamination.

EXPERIMENTAL

The calorimeter as described previously[1] was in a ^{3}He cryostat and was cooled via a superconducting heat switch. The superconducting heat switch limited the upper operating temperature to about 1.5°K. Three changes were made to this apparatus:

(i) The carbon thermometer was replaced by a germanium thermometer. Initially two Honeywell low-resistance thermometers were used but these proved unreliable. (Some work on zinc and zinc-managnese alloys

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[1] D. L. Martin, Proc. Roy. Soc. (London) A263, 378 (1961).

[2] D. L. Martin, Rev. Sci. Instr. 38, 1738 (1967).

[3] J. D. Filby and D. L. Martin, Can. J. Phys. 40, 791 (1962).

[4] D. L. Martin (to be published).

[5] D. L. Martin, Phys. Rev. 141, 576 (1966).

TABLE I. Weight and purity of samples.

			Impurities, ppm by weight									
			Quantitative spectrographic analysis[a]		Qualitative spectrographic analysis							
Sample	Weight	Atomic weight	Fe	Mn	Si	Mg	Ag	Cu	Pd	Al	B	Ti
Copper	140.663	63.57	0.2	[b]	0.5–5.0	0.05–0.5	...	...	...	...	...	...
			0.2		0.5–5.0	0.05–0.5	...	...	...	...	...	...
Silver	134.271	107.88	0.43	0.02	0.1–1.0	0.01–0.1	...	...	...	...	...	...
			0.50	0.02	0.1–1.0	0.01–0.1	...	...	...	...	...	...
Gold	198.887	196.967	0.16	0.016	0.2	0.3	0.5	<0.2	...	...	...	...
			0.17	0.018	0.2	0.3	0.5	<0.2	...	...	...	...
Mint Gold	193.615	196.967	1.9	0.14	0.3–3.0	0.03–0.3	1.0–10.0	0.3–3.0	0.3–3.0	0.1–1.0	0.03–0.3	0.03–0.3
			2.2	0.16	0.3–3.0	0.03–0.3	1.0–10.0	0.3–3.0	0.3–3.0	0.1–1.0	0.03–0.3	0.03–0.3
Mint Gold+1 ppm (atomic) Mn	247.218	196.967	2.4	0.45	0.3–3.0	0.03–3.0	1.0–10.0	0.3–3.0	0.3–3.0	0.1–1.0	0.01–0.1	0.03–0.3
			2.5	0.45	0.3–3.0	0.03–3.0	1.0–10.0	0.3–3.0	0.3–3.0	0.1–1.0	...	0.03–0.3

[a] By carrier distillation method [P. Tymchuk, J. A. H. Desaulniers, D. S. Russell, and S. S. Berman, Appl. Spectr. **21**, 151 (1967)].
[b] No quantitative analysis run. Semiquantitative result: Mn <0.05 for both samples.

was done with one of these thermometers and is reported elsewhere.[6]) The present work was done with a Cryocal thermometer which has proved to be very stable over a long period of time. (However, not all Cryocal thermometers are sufficiently stable for accurate calorimetry.) This thermometer was nitrogen-filled to prevent thermal effects associated with helium-exchange gas and had a resistance of about 45 Ω at 4°K, 90 Ω at 1.5°K, and 300 Ω at 0.4°K. The sensitivity is therefore much lower than many workers use but is quite adequate with currents in the 3- to 5-μA range. The advantage of a low-resistance thermometer is that electrical-leakage problems are minimized and conventional electronic detection equipment often performs better with relatively low resistances. The thermometer resistance is still measured with the current-reversing isolating potential comparator circuit[7] but the 4-terminal variable resistor is now a Guildline type 9801.

(ii) Some strange results with the earlier apparatus were attributed[8] to slight radio-frequency pickup causing heating of the thermometer and consequent calibration shift. In an effort to reduce this problem more attention was given to lead shielding and every lead wire into the inner cryostat was connected to ground via a 1000 pF mica condenser at the lower ^{4}He stage.

(iii) A digital voltmeter was used to measure the electrical energy supplied to the heater. Measurements were made of the voltage across the heater and the voltage across a known resistance in series with the heater. Time was measured, as before, on an electric stopclock driven from a 50-cps standard frequency source. The digital voltmeter used was a Hewlett-Packard H04-3460A. On the lowest range (1.2 V used for the present work) the stability was monitored with a standard cell and, with no adjustments whatsoever, the stability has been within 1 in 10^5 over a period of more than one year. Linearity is still well within 50 ppm (which is claimed for only 90 days by the manufacturers). The zero is sensitive to room temperature and cycles by several μV as the airconditioning cycles (by ~1°C). This is not important because the voltages measured are greater than 20 mV.

The net effect of the first two changes is a great improvement in precision. The third change has made possible much shorter heating periods thus improving the heating-rate/drift-rate ratio, and has extended the useful upper operating temperature to 3°K.

In the original apparatus[1] the temperature scale was based on ^{3}He vapor-pressure thermometry in the range[9] 0.7 to 1.5°K. Temperatures below 0.7°K were obtained by extrapolating the calibration of the Speer carbon thermometers then used. It was verified that this procedure was satisfactory by examining the results of specific-heat measurements on pure copper. A similar procedure was used with the germanium thermometers. They were calibrated in another apparatus[5] at temperatures above 1.5°K, against the ^{3}He vapor-pressure thermometer between 1.5 and 0.7°K and against a Speer carbon thermometer below 0.7°K. The temperature scale below 0.7°K was then refined by making specific-heat measurements on pure copper and adjusting the calibration to reduce bumps. The adjustments required were less than 1 m°K at any temperature, an indication of the reliability of extrapolating the Speer carbon-

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[6] D. L. Martin, Phys. Rev. **167**, 640 (1968).

[7] T. M. Dauphinee and E. Mooser, Rev. Sci. Instr. **26**, 660 (1955).

[8] J. D. Filby and D. L. Martin. Proc. Roy. Soc. (London) **A284**, 83 (1965).

[9] The lower limit is set by the sensitivity of the oil manometer used for pressure measurement. It has recently been pointed out [R. A. Watkins, W. L. Taylor, and W. J. Haubach, J. Chem. Phys. **46**, 1007 (1967); erratum: J. Chem. Phys. **47**, 3692 (1967)] that the Weber-Schmidt equation used for thermomolecular pressure corrections is probably incorrect below 0.7°K for ^{3}He. The present calibration method has fortuitously avoided any error from this cause.

TABLE II. Analysis of results. $J=4.186$. Error limits are 95% confidence limits from the statistical analysis.

	$C=(HT^{-2})+\gamma T+[464.34/(\Theta_0{}^c)^3]T^3$				$C=(HT^{-2})+\gamma T+[464.34/(\Theta_0{}^c)^3]T^3+BT^5$				
Sample	Range (°K)	H (μcal°K/ g atom)	γ [μcal/°K^2 (g atom)]	$\Theta_0{}^c$ (°K)	Range (°K)	H (μcal°K/ g atom)	γ [μcal/°K^2 g atom)]	$\Theta_0{}^c$ (°K)	B [μcal/°K^6 (g atom)]
Pure Cu	0–4.0	···	165.2±0.2	345.8±0.8	0–4.0	···	165.3±0.2	347.7±2.0	0.02±0.02
Pure Ag	0–3.0	···	153.1±0.3	227.3±0.3	0–3.0	···	153.0±0.3	226.7±0.8	−0.06±0.07
Pure Au	0–1.5	···	165.0±0.4	162.3±0.3	0–3.0	···	165.1±0.4	162.3±0.3	−0.23±0.11
Mint Au	0–2.0	0.32±0.10	168.8±1.0	163.2±0.5	0–2.0	0.23±0.15	170.4±2.2	164.9±2.2	1.30±1.59
Mint Au+1 ppm (atomic) Mn	0–2.0	0.43±0.09	169.2±1.0	163.1±0.4	0–2.0	0.36±0.13	170.4±2.0	164.4±1.9	1.00±1.39

thermometer calibration. The resulting temperature scale is not completely smooth, as inspection of the specific-heat results will show. The remaining structure suggests that the lowest vapor-pressure calibration temperature (0.7°K) might have been in error by 1 m°K. For the Cryocal thermometer used in the present work the calibration was accurately represented by the polynomial[5]

$$\ln R=\sum_{n=1}^{8} a_n(\ln T)^{n-1}.$$

The stability of the germanium-thermometer calibration was checked by making some ^{3}He vapor-pressure measurements every time the apparatus was used.

The pure copper, silver, and gold samples were those used in some previous work[5] and were all vacuum cast. The weights of these samples and recent analysis results are given in Table I. The two very dilute gold–transition-metal alloy samples were induction melted under high vacuum in alumina crucibles. One was made from "fine" gold (99.99% pure) from the Royal Canadian Mint, the other was made from the same gold by making a dilute alloy with "highest purity electrolytic" flakes of manganese and then diluting this alloy still further so that the calculated manganese impurity added was 1 ppm (atomic). These samples are also described in Table I.

All the samples were measured on a copper "tray" calorimeter.[1] Previously,[3] attempts to measure silver on a copper tray had been unsuccessful because the silicone grease bond broke on cooling. Since then the measured amount of silicone grease used has been reduced[10] from 0.1 to 0.01 cc, and this might be the reason for success in the present experiment.

Possible errors in the results may be summarized under three headings: (a) temperature scale errors, (b) errors in measuring the energy supplied to the calorimeter, and (c) errors in measuring the temperature rise during a heating period. The temperature increment 0.7 to 1.5°K is estimated to be measured with an accuracy of 2 m°K and the slope error is therefore within ±0.3%. Heater power measurements should be accurate to better than ±0.1%. The third error is a random error which is estimated during the statistical analysis of results. The over-all error is therefore taken as the 95% confidence limit from the statistical analysis plus 0.4%.

RESULTS

Two sets of measurements were made on each of the pure metal samples, the apparatus being warmed to room temperature between sets. In the case of copper, eight specific-heat runs on other materials were made between the two copper runs. The results were fitted by the least-squares method to equations of the form

$$C=\gamma T+[464.34/(\Theta_0{}^c)^3]T^3 \quad \text{(2 term)}$$

and

$$C=\gamma T+[464.34/(\Theta_0{}^c)^3]T^3+BT^5 \quad \text{(3 term)},$$

where C is in calorie units. [Each point (T_i,C_i) was assigned a weight $(1/C_i{}^2)$ in the least-squares analysis so that fractional, rather than absolute, deviations from the fitted curve are minimized.] One silver point, deviating 3% at 2.76°K, was rejected before final analysis. The coefficients are given in Table II where the error limits are 95% confidence limits. For copper and silver there is good reason[5] to suppose that the two-term equation should be adequate in the present temperature range and the coefficients obtained with this equation have been adopted. For gold a significant negative B term was expected and the results from the three-term analysis are preferred. As explained above, the error limits obtained from the statistical analysis must be increased by ±0.4% to get the estimated absolute error of the results, which are, therefore,

copper:

$$\gamma=165.2\pm0.8\ \mu\text{cal}/{}^\circ\text{K}^2\ \text{(g atom)}\quad [691.5\pm3.4\ \mu J/{}^\circ\text{K}^2\ \text{(g atom)}],$$

$$\Theta_0{}^c=345.8\pm1.2{}^\circ\text{K},$$

silver:

$$\gamma=153.1\pm0.9\ \mu\text{cal}/{}^\circ\text{K}^2\ \text{(g atom)}\quad [640.9\pm3.7\ \mu J/{}^\circ\text{K}^2\ \text{(g atom)}],$$

$$\Theta_0{}^c=227.3\pm0.5{}^\circ\text{K},$$

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[10] The amount of grease was originally reduced in an effort to cure thermal equilibrium problems which might have been associated with small lumps of grease; see J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) A276, 187 (1963).

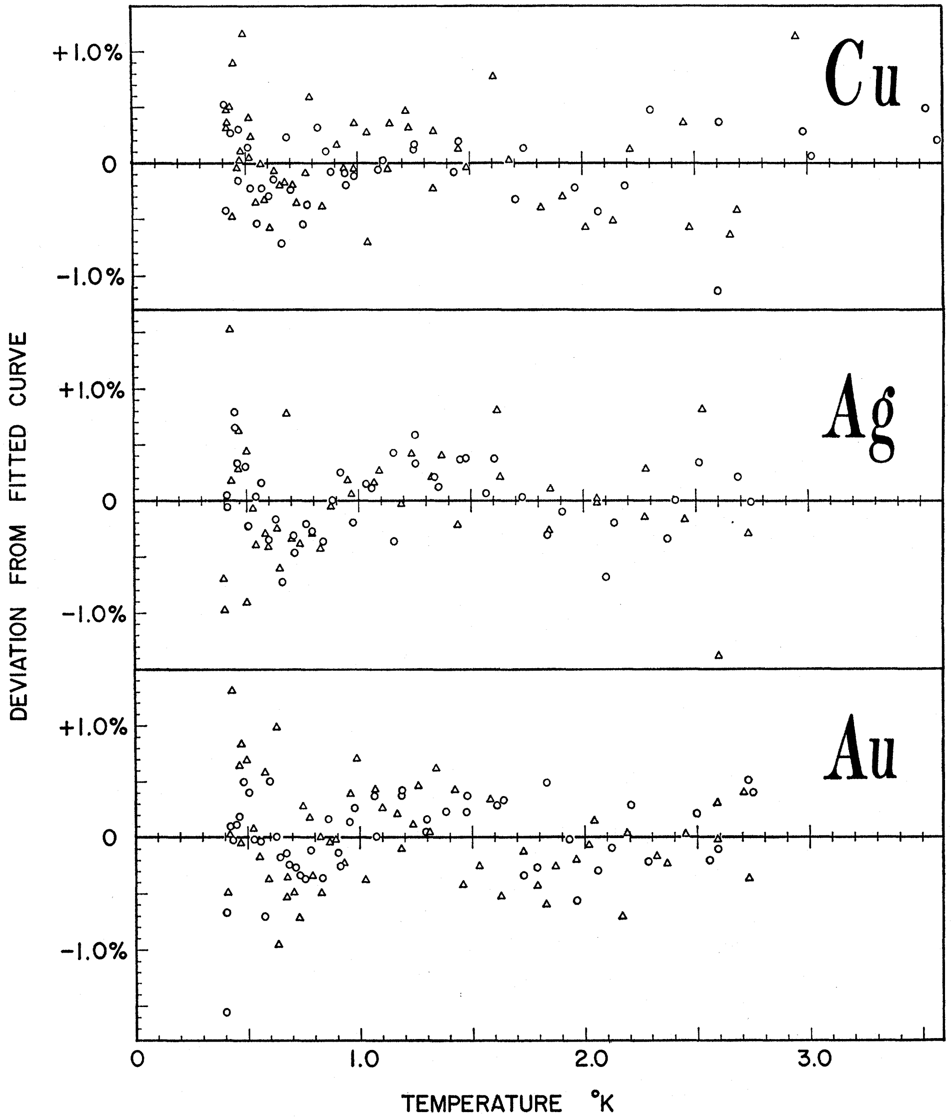

FIG. 1. Deviation of individual results from the fitted relations (see text).

gold:

$$\gamma = 165.1 \pm 1.0\ \mu\text{cal}/^\circ\text{K}^2\ (\text{g atom})\quad [691.1 \pm 4.2\ \mu J/^\circ\text{K}^2\ (\text{g atom})],$$

$$\Theta_0{}^c = 162.3 \pm 0.6^\circ\text{K},$$

$$B = -0.23 \pm 0.11\ \mu\text{cal}/^\circ\text{K}^6\ (\text{g atom}).$$

Deviations of the individual specific-heat results from the fitted equations are shown in Fig. 1.

A single set of measurements was made on the Mint gold sample and two sets of measurements were made on the Mint gold+1 ppm (atomic) Mn sample. The results were fitted to the equations given above with the addition of a "nuclear" type specific-heat term HT^{-2} (the apparent "nuclear" specific-heat term in these alloys is probably associated with the localized magnetic moments on the transition-metal impurities and is *not* a nuclear specific heat). The coefficients are given in Table II, and Fig. 2 is a plot of the difference of specific heat between these alloys and pure gold.

DISCUSSION

The $\Theta_0{}^c$ values obtained from the specific-heat results should be the same as the $\Theta_0{}^{el}$ values computed from elastic constants results extrapolated to the absolute zero. The best values[11] for $\Theta_0{}^{el}$ are: copper, 345.2±0.9°K; silver, 226.4±0.6°K; and gold, 161.6 ±0.4°K. In all cases agreement between calorimetric and elastic data is within the combined error limits.

Recent specific-heat measurements on pure copper, silver, and gold have been summarized by Massalski, Sargent, and Isaacs.[12] A more extensive review of

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[11] G. A. Alers (private communication).

[12] T. B. Massalski, G. A. Sargent, and L. L. Isaacs, in *Phase Stability in Metals and Alloys*, edited by P. S. Rudman *et al.* (McGraw-Hill Book Co., New York, 1967), p. 291.

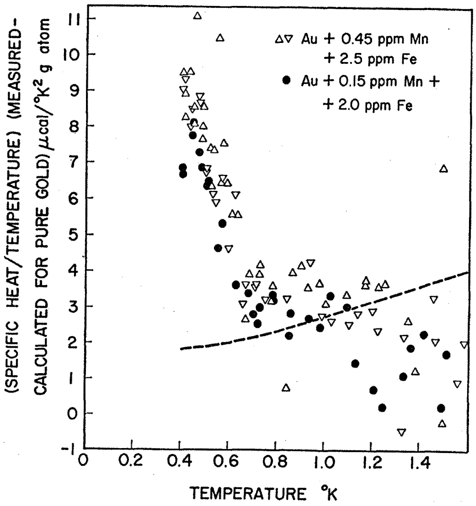

FIG. 2. Results on the "impure" gold samples as a difference from pure gold. The dashed line represents 1% of the specific heat of pure gold.

results on pure copper has been given by Osborne, Flotow, and Schreiner,[13] who obtained a mean γ value of 694.3 $\mu J/°K^2$ (g atom) from the results of 15 different papers. The present value is in agreement with this result. For silver the present γ value agrees with other results[12] within the estimated error limit. For gold the γ value is several percent lower than the previous lowest values,[12] which include a measurement from this laboratory[5] on the same sample. The old and new measurements from this laboratory are plotted in Fig. 3 and it will be clear that the higher γ value obtained previously was mainly because the points below about 0.7°K were too high. This had happened more obviously with some other results[8] from the original apparatus and was presumed to occur because slight radio-frequency heating of the thermometer had invalidated the extrapolation below 0.7°K of the calibration of the carbon thermometer then used. The most recent work from other laboratories on gold is that of Isaacs[14] (1.5 to 4.2°K) and of Will and Green[15] (2 to 4°K). Isaacs's claimed accuracy is 2% and his work agrees with the present work within this accuracy. Will and Green estimate their accuracy at about 0.5% and, as discussed above, the accuracy of the present work is similar. Agreement between Will and Green's data and the present work is well within the combined error limits with the single exception of their lowest temperature point (~1.9°K), where the difference is about 1.2%. As a check on the new value for the γ of gold, the specific heat of a small sample of vacuum-cast ASARCO copper was measured.[2] This sample had almost the same thermal capacity as the gold sample at the lowest temperatures and the result was $\gamma = 164.4 \pm 0.6\ \mu\text{cal}/°K^2$ (g atom) and $\Theta_0{}^c = 338.8 \pm 6.6°K$, where the error limits are 95% confidence limits from the statistical analysis. Within the rather large limits (due to the small thermal capacity of the sample) this result is in satisfactory agreement with the result obtained from the larger sample. (Because of the low Debye temperature the specific heat of gold increases much more rapidly with temperature than does the specific heat of copper and the thermal capacity of the gold sample was only relatively small at the lowest temperatures.) To summarize, the new value for the γ of gold is believed to be correct because (i) the measurements extend to much lower temperatures than does work reported from other laboratories, and (ii) the apparatus has been checked by measuring a pure copper sample of the same thermal capacity as the gold sample at the lowest temperatures. It should be noted that the new value for the electronic specific heat of gold does not significantly affect the previously reported[5] anomalous variation of lattice specific heat at higher temperatures because the electronic specific heat is a very small part of the total specific heat here.

The effective mass of the electrons has been calculated from the above values of γ and the free-electron values of γ. (The lattice parameters at 4°K were obtained from room-temperature x-ray values[16] and the tabulated thermal expansions[17] and are: copper, 3.6029 Å; silver, 4.0689 Å; gold, 4.0651 Å.) The effective masses are: copper, 1.38; silver, 1.01; gold 1.09. These effective masses are very similar to the "belly" cyclotron effective masses observed for copper,[18] silver,[19] and gold,[20] respectively. Fermi surfaces[21] for these metals obtained from de Haas–van Alphen-effect[22] results show that gold is the most anisotropic and that silver, apart from the neck regions, is closest to a free-electron sphere. The volume enclosed by the Fermi surfaces confirms that there is exactly one conduction electron per atom.

Recent work[4] on silver-gold and copper-gold alloys has shown a small nuclear specific-heat term, the maximum value so far observed being about 0.7 μcal °K/(g atom). It is possible that a very small apparent nuclear term might be observed in the pure metals as a result of transition-metal impurities (cf. the measurements on impure gold reported in this paper). To check for this on the present samples the results were fitted to an equation $C = HT^{-2} + AT + BT^3 + CT^5$. For copper, $H = 0.04 \pm 0.05$ μcal °K/(g atom), for silver,

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[13] D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. **38**, 159 (1967).

[14] L. L. Isaacs, J. Chem. Phys. **43**, 307 (1965).

[15] T. A. Will and B. A. Green, Phys. Rev. **150**, 519 (1966).

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[18] J. F. Koch, R. A. Stradling, and A. F. Kip, Phys. Rev. **133**, A240 (1964).

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[21] D. J. Roaf, Phil. Trans. Roy. Soc. London **A255**, 135 (1962).

[22] D. Shoenberg, Phil. Trans. Roy. Soc. London **A255**, 85 (1962).

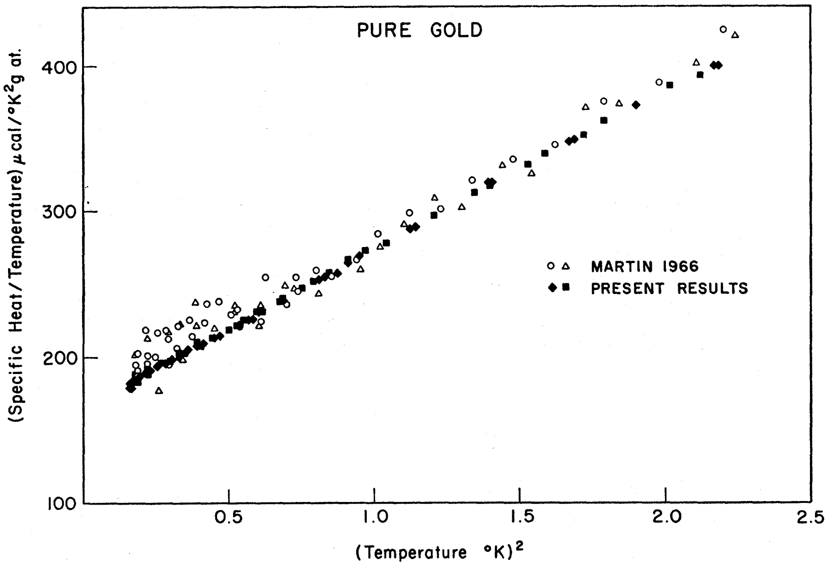

Fig. 3. Earlier and current results on the same sample of pure gold.

$H = 0.05 \pm 0.06$ μcal °K/(g atom) and for gold, $H = -0.01 \pm 0.07$ μcal °K/(g atom); the error limits being 95% confidence limits from the statistical analysis. In no case is the "nuclear" specific-heat term significant. (For copper, of course, the temperature scale had been adjusted to ensure this result.)

Turning now to the results for impure gold, it will be clear from Fig. 2 that very small amounts of transition-metal impurity can affect the specific heat drastically at these low temperatures. It has been shown many times in the past that to get the correct values of γ and Θ_0^c it is advisable to make measurements to very low temperatures. However, if the sample is a material in which transition-metal impurities form localized moments it is clear that measurements to extremely low temperatures may lead to incorrect results. Examining the results for the impure gold samples in Table II suggests that 0.3 ppm (by weight) Mn in gold will result in an apparent nuclear specific-heat term with coefficient 0.12 μcal °K/(g atom) while about 2.3 ppm (by weight) Fe in gold leads to an apparent nuclear term with coefficient 0.20 μcal °K²/(g atom), an apparent increase in γ of 4.5 μcal/°K² (g atom) and an increase in Θ_0^c of about 1°K. As mentioned above, the apparent nuclear specific-heat terms represent mainly the low-temperature ordering associated with the localized moments, as does the increase observed in γ.

CONCLUSION

The results obtained for copper and silver are in agreement with previous results from this laboratory and elsewhere. The electronic specific-heat coefficient found for gold is significantly lower than previous values. Transition-metal impurities at the 1-ppm level are shown to have a drastic effect on the specific heat of gold.

ACKNOWLEDGMENTS

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