VI. CONCLUSION

Our results on the temperature dependence of photoluminescence and photoionization yield of F centers in NaF support the following model: When an F center undergoes an absorption transition to the first excited state (Fig. 6a), the electron can either return to the ground state or be excited to the conduction band, according to the three processes sketched in Fig. 6 (b), (c), (d). The ionization energy obtained from the temperature dependence of the ratio η_I/η_L is $\Delta E_I = 0.12$ eV. The activation energy for a radiationless transition [Fig. 6(c)] is given by the thermal activation energy evaluated from the photoluminescence decay. In fact, in the temperature range where an exponential behavior of η_L has been observed (Fig. 2), i.e., between 130 and 200°K the factor $\exp(-\Delta E_L/KT)$ with $\Delta E_L = 0.06$ eV assumes the following values:

$$\text{at } 130°\text{K}, \approx 4.7\times10^{-3}; \quad \text{at } 200°\text{K}, \approx 3.1\times10^{-2}.$$

On the other hand, for $\exp(-\Delta E_I/KT)$, with $\Delta E_I = 0.12$ eV, we found:

$$\text{at } 130°\text{K}, \approx 0.022\times10^{-3}; \quad \text{at } 200°\text{K}, \approx 0.81\times10^{-3}.$$

Since in this temperature range $\exp(-\Delta E_L/KT) \gg \exp(-\Delta E_I/KT)$, the ionization has little influence on the process and we conclude that 0.06 eV is effectively the activation energy of the F luminescence.

Our experimental results do not show what is the mechanism of the process of probability P_d. We can only suggest that its activation energy is 0.06 eV and that the electrons which undergo it finally return to the ground state of the F center.

ACKNOWLEDGMENTS

The author would like to acknowledge helpful discussions with Professor R. Fieschi and Dr. G. Spinolo. Thanks are due also to Miss L. Paschini, who has carried out many measurements.

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Specific Heats 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 the range 3 to 30°K. Gold has also been measured in the range 0.4 to 1.5°K. The $\Theta_0{}^c$ and γ values are estimated as 345.6±1.0°K and 166.3±1.3 μcal °K^{-2}(g atom)$^{-1}$ for copper, 226.6±1.0°K and 154.4±1.0 μcal °K^{-2} (g atom)$^{-1}$ for silver, and 162.4±2.0°K and 174.1±4.3 μcal °K (g atom)$^{-1}$ for gold. The $\Theta_0{}^c$ values are in good agreement with the most recent estimates for $\Theta_0{}^{el}$, the Debye temperature computed from the zero-temperature elastic constants. However, the lattice specific heat of gold is anomalous in that, on increasing the temperature from zero temperature, a maximum is first observed in the value of Θ^c. The maximum is followed by the usual minimum on further increase of temperature. The results are discussed in terms of models due to Blackman and to Bhatia and Horton. The paper includes some remarks on thermometry below 30°K.

INTRODUCTION

MEASUREMENTS on pure copper in the temperature range 3–30°K have been reported previously from this laboratory.[1] Since these measurements were made, the apparatus has been improved in a number of ways, resulting in increased precision at the lower temperatures. Very recently the original carbon secondary thermometers have been replaced by germanium thermometers. It was chiefly in order to check the performance of the altered apparatus that the present measurements on copper were made. However, they should also be of interest in relation to the proposal made at the 1964 Calorimetry Conference to consider the use of pure copper as a calorimetric standard substance in the temperature range below 20°K.

Measurements on gold were initially undertaken because of the significant discrepancy between the Debye temperature obtained from zero-temperature elastic constants ($\Theta_0{}^{el}$) and the low-temperature limiting value obtained from specific-heat results ($\Theta_0{}^c$). These measurements have been briefly reported[2] and it was shown that by making measurements at sufficiently low temperatures the discrepancy between the Debye temperatures was removed. However, the lattice specific heat of gold at higher temperatures was anomalous. As an independent check on these results, the measurements above 3°K have been repeated with the altered apparatus. The present results are in excellent agreement with the earlier results.[2]

The normal behavior of copper and the anomalous behavior of gold indicated that accurate measurements on silver, the intermediate metal in the periodic

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[1] J. P. Franck, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).

[2] D. L. Martin, Phys. Rev. Letters **12**, 723 (1964).

classification, would be of interest. As was to be expected from a study of the elastic constants, as discussed later, the low-temperature specific heat of silver was found to behave normally.

Reliable determinations of the electronic specific-heat coefficient (γ) were available for copper and silver and hence no measurements were made below 3°K for these metals.

EXPERIMENTAL

The measurements from 3–30°K were made in an adiabatic calorimeter[1,3] with semi-automatic shield control. There is provision for calibrating the secondary thermometer on the calorimeter against the vapor pressures[3a] of liquid hydrogen and ^{4}He and against a gas thermometer.[3,4] Since it was to be hoped that the calibrations would be semipermanent, the two germanium thermometers used for the present work were calibrated at the same time. A capsule-type platinum thermometer, calibrated by the Division of Applied Physics, N.R.C., on the 1955 N.B.S. Provisional Temperature Scale[5] was also installed in the calibration block. The germanium thermometers were Radiation Research Laboratory Type CG1. A small hole was drilled in the case of each thermometer to allow the original helium filling to diffuse out and, after some weeks, the holes were plugged with soft solder. This procedure was considered advisable to prevent any thermal effects at low temperatures due to the desorption of helium gas. As previously,[1] the thermometer resistance was measured using the thermal-free square-wave isolating potential comparator circuit of Dauphinee and Mooser.[6] The thermometer resistance was compared with a four-terminal variable resistor (Guildline Type 9801) which was designed for use with germanium thermometers and, on the basic range, reads up to 100 000 Ω in steps of 0.001 Ω with an accuracy of 0.01%.

The germanium thermometers were calibrated against the vapor-pressure thermometers below 4 and at 20°K, against the gas thermometer below 20°K, and against the platinum thermometer above 20°K.

The best representation of the variation of resistance of the thermometers as a function of temperature was found to be a polynomial of the form[7]

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

For the present thermometers it was found that the standard deviation of the calibration points decreased as the number of terms was increased up to nine. From 9 to 13 terms there was no significant change in the standard deviation. Using the polynomial with nine terms the calibration data showed an approximately sinusoidal deviation as a function of temperature. (The maximum deviation was about 50 m °K.) The thermometer calibration was therefore represented by a nine-term polynomial (solved by the "*regula falsi*" method) together with a Lagrange cubic interpolation in a difference table tabulated at 1°K intervals. The resulting specific heats show small irregularities as a function of temperature. These are not significant but result from the approximate representation of the thermometer characteristics.

Later experience with other thermometers of this type showed that for some thermometers the fit of the polynomial could be improved by taking the maximum number of terms available (13) on the present computer program. Osborne, Flotow, and Schreiner (private communication) have found that their calibration data on Radiation Research CG1 germanium thermometers can be accurately represented, in the temperature range 0.8 to 25°K, by a polynomial of the above form with 15 terms.

During each of the specific-heat experiments, the germanium thermometer stability was checked by comparing with temperatures derived from the vapor pressure of liquid helium condensed into the bulb on the calorimeter. The germanium thermometer used for the measurements on copper and gold (see later) appeared less stable than that used for the silver measurements. The former showed deviations as high as 5 m°K on some runs, whereas deviations on the latter were less than 1 m°K except on one run where the deviation was 2 m°K. At the conclusion of the experiments the germanium thermometers were again compared with one another and with the vapor-pressure and platinum thermometers. Three such comparison experiments were made. In each case the "silver" germanium thermometer calibration was found to be accurate within 1 m°K. However, the "copper" germanium thermometer showed a deviation of about 5 m°K above 20°K and a deviation, varying from run to run, of up to 5 m°K at 4°K and below. Furthermore, the deviation between temperatures obtained on the two germanium-thermometer calibrations reached a maximum of 20 m°K around 12°K, a region of minimum sensitivity (dR/dT) for these thermometers. A rough comparison with the platinum thermometer in this region showed that most, if not all, of this deviation was

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[3a] *Footnote added in proof.* The hydrogen vapor pressure measurements were made using normal hydrogen and temperatures were obtained by subtracting 0.012°K from temperatures given by the equation of H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Natl. Bur. Std. (U. S.) **41**, 379 (1948). (See Refs. 4 and 14.) For ^{4}He, the 1958 vapor pressure scale was used. [F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. (U. S.) **64A**, 1 (1960)].

[3] J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **A276**, 187 (1963).

[4] J. P. Franck and D. L. Martin, Can. J. Phys. **39**, 1320 (1961).

[5] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Res. Natl. Bur. Std. (U. S.) **57**, 67 (1958).

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

[7] H. Plumb (private communication).

due to a calibration shift of the 'copper' germanium thermometer. The random calibration shifts at 4°K, compared with the systematic shift at higher temperatures made the possibility of error due to electrical leakage between leads seem remote but, as a check, a further run was made, using different leads, and the calibration shifts observed were similar to those seen previously. The conclusion from this investigation of the germanium thermometers is as follows: (i) It should not be assumed that all commercial germanium thermometers have stable calibrations. Careful testing over a period of time is necessary and continual "spot" checks are advisable. (ii) If the calibration does shift, the resulting errors in some parts of the temperature range may be much higher than those observed at 4°K.

The measurements from 0.4–1.5°K were made in an apparatus which has been described previously,[8] the only difference being the use of the 1962 ^{3}He vapor-pressure scale.[9]

The measurements on gold and copper were made in a copper-clamp-type[1] calorimeter. The over-all thermal contractions of copper and gold are the same[10] on cooling from room temperature to liquid-helium temperatures. However the thermal contraction of silver is rather different[10] and hence a silver-clamp-type calorimeter was used for the silver measurements. Two different germanium thermometers were used, one in each of the two calorimeters.

The samples measured were cylinders of 1-in. diam. Great care was taken to ensure sample purity. (The effects of traces of transition-metal impurity can be particularly serious.[1]) Pieces were taken from each end of each sample and analyzed by the Analytical Chemistry Section of N.R.C. The results are shown in Table I, together with the weights of the samples as used for the specific-heat measurements. The normal semiquantitative spectrographic analysis was suspected of giving too high values for the iron impurities and a recently developed method,[11] using a carrier-distillation technique, was used to determine quantitatively the amount of iron in the copper and silver samples.

Table I. Purity and weight of samples.

	Impurities in parts per million (by weight)		
Sample	Semiquantitative spectrographic analysis	Quantitative spectrographic analysis	Weight (g)
Cu	Mg<0.5, Mn<0.05, Si 5–0.5, Fe 5–0.5	Fe 0.2	140.669
Ag	Mg<0.5, Si 1–0.1, Cu<0.2, Ca<0.5, Fe 5–0.5	Fe 0.25	135.963
Au	Mg 0.3, Si 0.2, Fe<1.0, Cu<0.2, Ag 0.5	···	201.435

The copper sample was the same as that used by Franck *et al.*[1] and had been cast in 1957 from American Smelting and Refining 99.999% pure copper. The silver and gold samples were cast by the Consolidated Mining and Smelting Company Ltd., Trail, B.C., Canada, from 99.9999% pure material. Reference to Table I shows that all three samples were of very high purity. The copper sample had been very carefully machined to size. Etching showed large crystals averaging about 1 cm across. The silver and gold samples were cast to the exact diameter required and were not machined. All three samples were therefore in an "annealed" condition.

The accuracy of the measurements will depend upon the accuracy of the temperature scale, the accuracy of the heater power measurements, and the accuracy of the adiabatic shield control. No significant errors are likely to arise from the heater power measurements, and while adiabatic shield control becomes increasingly difficult below 5°K the resulting errors are likely to be random. The temperature range between 4 and 20°K is covered by the gas thermometer with an over-all error[11a] of 3 m°K in this span of 16°K. The excellent agreement between gas-thermometer and vapor-pressure-thermometer temperatures at 4°K, following gas-thermometer calibration at 20°K, may of course be fortuitous and there is a possibility of errors at intermediate temperatures. However, gas-thermometer runs with two different filling pressures (differing by a factor of 2) showed no significant deviations below 20°K. Thus, provided the germanium thermometers retained their calibration, no large systematic temperature-scale errors are expected. (Errors of not greater than ±0.2% are expected and correspond to errors of ±1 m°K in calibration points at 1°K intervals.) However, as detailed above, the germanium thermometers used for the measurements on copper and gold did change its calibration. By comparing the calibrations of this thermometer before and after the specific-heat measurements, a maximum error due to this cause can be determined and is as follows. The specific heat is expected to be correct at 4°K, then increasingly too low

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

[9] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. (U. S.) **68A**, 579 (1964).

[10] R. J. Corruccini and J. J. Gniewek, Natl. Bur. Std. (U.S.), Monograph 29 (1961).

[11] P. Tymchuk, D. S. Russell, and S. Berman (to be published in Acta Spectrochemica). This method was calibrated by wet analysis of samples with iron impurities in the 1-ppm range.

[11a] *Footnote added in proof.* Recent work with an acoustic thermometer at the National Bureau of Standards has suggested that the boiling point of ^{4}He on the 1958 scale may be 0.01°K too low [H. H. Plumb and G. Cataland, Science **150**, 155 (1965)]. In this connection it should be pointed out that, as previously,[4] the present gas thermometer results were obtained using the Keesom virial coefficients and that the temperature obtained at 4°K with the gas thermometer is 3 m°K higher than that given by the ^{4}He vapor pressure thermometer (average of three independent runs). In previous work reported from this laboratory[4] (using a different manometer system) the mean temperature obtained from the gas thermometer at 4°K was 2 m°K lower than that given by the ^{4}He vapor pressure thermometer. These results are within the estimated accuracy[4] of ±0.005°K. If the Kilpatrick, Keller, and Hammel virial coefficients are used instead of the Keesom virial coefficients,[4] then the average temperatures obtained at 4°K from the gas thermometer are increased by about 5 m°K and would then be in better accord with the recent acoustic thermometer results.

(as the temperature is increased) reaching a maximum error of 0.4% at 10°K and decreasing to zero error at 12°K. The specific heat may then be too high by 0.2% between 14 and 19°K and too low by 0.2% at 21°K. Above this temperature no significant errors would be expected. To summarize, the silver results are expected to be more accurate than the gold or copper results. Errors in the latter results are not likely to exceed ±0.5%.

COMPARISON OF PLATINUM-THERMOMETER TEMPERATURE SCALE WITH GAS AND VAPOR-PRESSURE THERMOMETERS

From the germanium-thermometer calibration data it was possible to make a direct comparison of the 1955 N.B.S. Provisional Platinum Temperature Scale,[5] as reproduced by the present thermometer (Meyers No. 320), with both gas and hydrogen-vapor-pressure thermometers. It was found that from 12 to 20°K the readings of platinum and gas thermometers agreed within 0.01°K (which is within the estimated accuracy of the N.B.S. Temperature Scale), the platinum-thermometer temperatures being systematically lower. Below 12°K the deviations of the platinum- and gas-thermometer temperatures did not exceed the accuracy of the measurements, which becomes poor due to the rapidly decreasing sensitivity of the platinum thermometer. Above 20°K the readings of gas and platinum thermometers diverged, the difference being 0.009°K at 25°K and 0.023°K at 30°K, the platinum thermometer reading the higher temperature. The difference becomes significant about 25°K and is due either to errors in gas thermometry or an error in the platinum-thermometer calibration or scale or a combination of all three. A recent summary[12] of work on the temperature scale below 90°K suggests that an error of this magnitude in the 1955 N.B.S. Provisional Temperature Scale is unlikely. After the specific-heat measurements were completed the platinum thermometer was compared with the stable germanium thermometer. A galvanometer amplifier detector was used in the platinum-thermometer circuit and the precision of temperature measurements was greatly improved.[13] The root-mean-square difference between temperatures as measured on the two thermometers was 7 m°K in the range 11 to 20°K. The greatest difference (10 m°K) was at 16°K. At all temperatures in this range the temperature obtained from the platinum thermometer was lower than the temperature obtained from the germanium thermometer (which is assumed to be the same as that given by the gas thermometer).

Comparison of the temperature derived from the platinum thermometer with temperatures obtained from the hydrogen-vapor-pressure thermometer near 20°K showed the former to be 3 m°K higher (average of six comparisons). The boiling point of normal hydrogen on the 1955 N.B.S. platinum scale[5,13a] is 20.380°K, whereas the vapor-pressure results are based on a normal hydrogen boiling point of 20.368°K.[14] The agreement between the platinum and vapor-pressure thermometers is therefore within 1 m°K which is better than the accuracy with which the platinum thermometer was read.

These comparisons of the platinum thermometer with gas and vapor-pressure thermometers show that, with the possible exception of the region 25 to 30°K, the temperature scale has been well preserved even though the present platinum thermometer has been calibrated against a thermometer which is itself several stages removed from those on which the scale was originally carried.

It has been mentioned that there is a small discrepancy between the platinum- and gas-thermometer scales above 25°K. This would lead, in the range 25 to 30°K, to an average difference of about 0.3% in specific heats measured on the two temperature scales. To ensure continuity with previous work from this laboratory the germanium thermometers were calibrated on the platinum-thermometer scale above 20°K. Below 20°K only the gas-thermometer readings were used.

RESULTS

Two sets of measurements were made on each sample-plus-calorimeter and each empty calorimeter, the apparatus being warmed to room temperature between these sets.

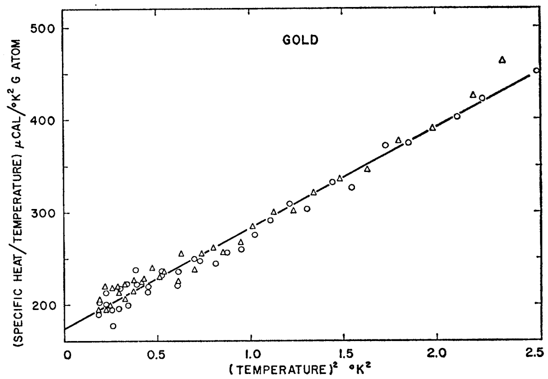

FIG. 1. Plot of (specific heat/temperature) versus (temperature²) for gold.

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[12] D. N. Astrov, M. P. Orlova, and D. I. Charovskaya, Comité Consultatif de Thermometrie, 1964 session, Paris (to be published).

[13] This equipment was kindly loaned by R. J. Berry, who also took the measurements.

[13a] *Footnote added in proof.* This figure follows from the paper by H. J. Hoge and F. G. Brickwedde, J. Res. Natl. Bur. Std. (U. S.) **22**, 351 (1939) which describes the establishment of the 1939 N.B.S. provisional platinum thermometer temperature scale below 90°K. Later work at the N.B.S. [H. J. Hoge and R. D. Arnold, J. Res. Natl. Bur. Std. (U. S.) **47**, 63 (1951) and H. H. Plumb and G. Cataland *ibid.* **69A**, 375 (1965)] has cast some doubt on this figure and at present the exact value of the normal hydrogen boiling point on the 1955 N.B.S. scale is a matter of some doubt. The results of the present work suggest that Hoge and Brickwedde's value is not seriously in error.

[14] H. van Dijk and M. Durieux, Physica **24**, 1 (1958).

TABLE II. Smoothed specific-heat values. $J=4.186$. Units C_p, cal °K^{-1} (g atom)$^{-1}$; Θ^c, °K. Atomic weights: copper, 63.57; silver, 107.88; gold, 196.967.

Temperature (°K)	Copper C_p	Copper Θ^c	Silver C_p	Silver Θ^c	Gold C_p	Gold Θ^c
3	0.000803	345.6	0.001541	226.6	0.003385	163.6
4	0.001385	345.6	0.003172	226.6	0.007312	165.0
5	0.002240	345.4	0.005760	226.6	0.01359	165.9
6	0.003440	345.0	0.009569	226.4	0.02278	166.5
7	0.005063	344.4	0.01492	225.8	0.03559	166.8
8	0.007181	343.8	0.02214	224.9	0.05265	166.8
9	0.009878	343.1	0.03160	223.8	0.07474	166.7
10	0.01324	342.3	0.04378	222.4	0.1030	166.2
11	0.01738	341.3	0.05899	221.0	0.1382	165.5
12	0.02238	340.2	0.07776	219.5	0.1806	165.0
13	0.02841	338.8	0.1007	217.9	0.2303	164.6
14	0.03555	337.3	0.1279	216.4	0.2877	164.3
15	0.04398	335.6	0.1601	214.9	0.3523	164.1
16	0.05382	333.8	0.1978	213.4	0.4236	164.1
17	0.06531	331.8	0.2400	212.3	0.5008	164.3
18	0.07839	330.0	0.2872	211.4	0.5834	164.5
19	0.09346	328.0	0.3387	210.8	0.6712	164.8
20	0.1106	326.0	0.3950	210.3	0.7626	165.2
21	0.1299	324.0	0.4559	209.9	0.8560	165.8
22	0.1514	322.2	0.5203	209.7	0.9524	166.3
23	0.1752	320.5	0.5883	209.6	1.051	166.9
24	0.2015	318.9	0.6603	209.5	1.151	167.4
25	0.2302	317.4	0.7351	209.5	1.254	167.9
26	0.2612	316.1	0.8120	209.6	1.356	168.5
27	0.2942	315.1	0.8915	209.7	1.458	169.0
28	0.3289	314.4	0.9728	209.9	1.560	169.6
29	0.3651	314.0	1.056	210.0	1.662	170.1
30	0.4028	313.8	1.140	210.2	1.761	170.6

The results obtained for gold in the 0.4 to 1.5°K temperature range are shown in Fig. 1. The line is a least-squares fit made on the assumption, which may not be quite correct, that the results may be fitted by the sum of terms linear and cubic in temperature. From the least-squares analysis it is found that γ is 174.1 ± 4.3 μcal/°K^2 g atom and Θ_0^c is 162.4±2.0°K, where the error limits are 95% confidence limits.

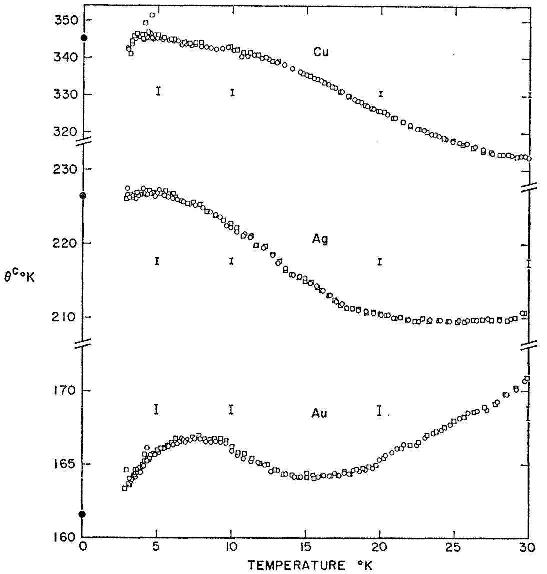

FIG. 2. Plot of Debye temperature against temperature for copper, silver, and gold. The points on the 0°K axis represent Θ_0^{el} values (see text) and the vertical bars the effect on Θ^c of a change of 1% in the specific heat, the electronic specific heat assumed to remain constant.

Results in the 3–30°K temperature range are shown in Fig. 2 as a plot of Debye temperatures obtained from the specific-heat results. (The γ value for copper[15] was taken as 166.3 μcal/°K^2 g atom and for silver[16] as 154.4 μcal/°K^{2}g atom. The γ value for gold is given above.) Smoothed values, obtained by drawing smooth curves on the Θ^c plot, are given in Table II. The C_p to C_v correction is negligibly small for all these metals in the temperature range of the present measurements.

DISCUSSION

Recent specific-heat results below 4.2°K on copper and silver have been summarized by Phillips[17] and Green and Culbert,[18] respectively. In evaluating the present results, the electronic specific-heat coefficients determined by Manchester[15] for copper (on the present sample) and by Filby and Martin[16] for silver have been used. These values are in good agreement with other recent results. The resulting values for Θ_0^c are also in good arreement with other recent results, tending to be slightly higher.

At higher temperatures the present results for copper are in quite good agreement with the previous measurements of Franck *et al.*[1] on the same sample and they join smoothly onto the results of Martin[19] at 20°K and above. Other recent results in the 4 to 20°K range are those of du Chatenier[20] and Ahlers.[21] Du Chatenier's results are several percent higher than the present results over the whole temperature range. His Θ_0^c and γ values are not in agreement with the majority of other workers[17] and it appears that some systematic error must have occurred in his work on copper. Ahlers made significant measurements only in the 2 to 4°K and 10 to 20°K ranges. (Between 4 and 10°K his temperature scale was not established with sufficient accuracy for calorimetry, as he points out.) His results agree quite well with the present work except in the region of 20°K where his specific-heat results are about 2% lower than the present values. Giauque and Meads' results[22] (from 15°K up) are higher than the present values by 2 or 3%.

The only recent results for silver in the 4 to 20°K temperature range are those of du Chatenier.[20] Below 12°K his results are systematically higher than the

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[15] F. D. Manchester, Can. J. Phys. **37**, 989 (1959). Note, the error limits given in this paper are too high, see Ref. 1.

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

[17] N. E. Phillips, Phys. Rev. **134**, A385 (1964).

[18] B. A. Green and H. V. Culbert, Phys. Rev. **137**, A1168 (1965).

[19] D. L. Martin, Can. J. Phys. **40**, 1166 (1962).

[20] F. J. du Chatenier and J. de Nobel, Physica **28**, 181 (1962); F. J. du Chatenier, thesis, University of Leiden, 1964 (unpublished).

[21] G. Ahlers, J. Chem. Phys. **41**, 86 (1964).

[22] W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941).

present results, above 12°K they are systematically lower, the deviations do not exceed 3%. This suggests a temperature-scale error. His temperature scale was based on an interpolation relation for carbon thermometers. This procedure is much less reliable than direct calibration against a gas thermometer. Meads, Forsythe, and Giauque[23] measured silver from 15°K up. Their results are, on average, a percent higher than the present results.

Several measurements[20,24,25] have been made on gold in the region 1 to 4.2°K. They all gave Θ_0^c values in the 164 and 165°K region, showing a significant difference from the Θ_0^{el} value. The present measurements in the 1 to 4°K temperature range give a similar result if fitted to terms cubic and linear in temperature. However, the present measurements extend to both higher and lower temperatures and the discrepancy is clearly seen to result from the usual variation of Θ^c with temperature. Measurement to sufficiently low temperatures removes the discrepancy between Θ_0^c and Θ_0^{el} values. Isaacs[26] analyzed his recent results in the 1 to 4°K range by fitting to terms proportional to the first, third, and fifth powers of temperature. He obtained Θ_0^c and γ values in good agreement with the present results and also showed that Θ^c initially increases with increasing temperature. This agreement may be fortuitous since Isaacs' results for silver[26] show some differences from the present and other recent results.

Du Chatenier[20] measured gold from 1 to 30°K. His values are higher than the present results from 4 to 12°K, lower from 12 to 26°K and again higher above 26°K. The deviations, which do not exceed 3%, are therefore similar to those found between the present results and those of du Chatenier for silver. Geballe and Giauque[27] have measured gold from 15°K up and agreement is within 1%, their smoothed values scattering about the present results.

The low-temperature limiting Debye temperature obtained from the specific-heat results (Θ_0^c) is expected to be the same as the corresponding temperature obtained from elastic constant values (Θ_0^{el}). This equality holds even if the lattice vibrations are anharmonic.[28] The most recent compilation of Θ_0^{el} data is due to Alers[29] and the best values[30] of Θ_0^{el} for copper, silver, and gold are 345.2, 226.4, and 161.6°K, respectively. The present specific-heat results give Θ_0^c values of 345.6 ± 1.0, 226.6 ± 1.0, and 162.4 ± 2.0°K, respectively, and agreement between Θ_0^c and Θ_0^{el} is seen to be excellent. It is probable that if measurements on gold were extended to still lower temperatures a slightly lower value for Θ_0^c would be obtained, further improving the agreement with the elastic-constant result.

Reference to Fig. 2 shows that the Θ^c values of copper and silver appear to remain at the Θ_0^c value up to a temperature of about 5°K. (Phillips[15] finds this to be the case for copper up to 4.2°K and Ahlers'[31] results on silver confirm the present observations.) At higher temperatures the Θ^c value decreases and goes through the usual minimum. The Θ^c for gold is seen to go through a maximum before decreasing to the usual minimum. It is, of course, possible that the copper and silver Θ^c curves have small "bumps" centered about 5°K. These "bumps" would be of much smaller magnitude and at lower reduced temperatures than the "bump" observed in gold. At very low temperatures the specific heat of a metal is usually represented by an equation of the form[32]

$$C_v=\gamma T+AT^3+BT^5+CT^7+\cdots,$$

where the first term is the electronic specific heat and the other terms are a series expansion derived from lattice theory. Bhatia and Horton,[33] using a simple model, have investigated how the coefficient of the second term in the lattice-theory expansion depends upon the elastic constants. They showed that both regions of constant Θ^c and of initially increasing Θ^c were possible. However, the elastic constants of gold do not fall within the range required for initially increasing Θ^c, although they are near the critical value. A better model might give closer agreement with observation. The possibility of an initial upward rise of Θ^c with increasing temperature has also been considered by Marcus and Kennedy[34] and Horton and Schiff.[35]

Blackman[36] showed that when the elastic constants satisfied certain equalities the velocities of some elastic waves become zero (but the crystal would not be stable). At low frequencies, the frequency spectrum then becomes similar to that of a one-or two-dimensional lattice. It seems possible, therefore, that if the elastic constants of a crystal approach these equalities there may be a region at low frequencies where the rise of the vibration spectrum $[f(\nu)]$ varies less rapidly than with the square of the frequency, resulting in the type of Θ^c curve observed for gold. From the diagram given in Blackman's paper (which is not significantly altered

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if more recent elastic data is used) it is clear that gold is considerably closer to satisfying these equalities than either copper or silver. Hence on Blackman's theory it is to be expected that copper and silver have "normal" vibration spectra whereas an abnormality in gold would not be unexpected.

Barron and Morrison[32] rewrote the expression for the specific heat of a metal, given above, as

$$(C_v-\gamma T)/T^3=A+BT^2+CT^4+\cdots$$

and pointed out that $\Theta_0{}^c$ (obtained from A) may be determined from a plot of $(C_v-\gamma T)/T^3$ against T^2. The lattice specific heat can usually be approximated by the first two terms in the expansion for temperatures below $(\Theta^c/50)$. Applying this method to the present results it seems that the value of B may be negative for silver and is certainly negative for gold. For copper the method yields a positive value for B, but the value obtained for $\Theta_0{}^c$ is about one percent higher than the $\Theta_0{}^{el}$ result. Better agreement between the $\Theta_0{}^c$ and $\Theta_0{}^{el}$ values for copper can be obtained if higher order terms in the expansion are taken into account below $(\Theta^c/50)$ °K. The possibility of a negative value for B then arises. The interpretation of the copper and silver results is rather tentative since the probable variation of Θ^c in the 3 to 5°K region is not much greater than the estimated accuracy of the experiments; furthermore, the precision of the experiments is least here due to the increasing difficulty of adiabatic shield control (see above). However, it does seem that the copper results, in particular, do not fit too well into the Barron-Morrison analysis method. The possibility then arises that the expression used above to represent the specific heat of a metal is not correct. This equation assumes that the electronic and lattice specific heats may be treated separately but the electron-phonon interaction in a metal might alter the picture. De Launay[37] showed that the free electrons probably participate completely in the motion of the ions for low-frequency vibrations but at higher frequencies the participation is negligible. For the case of copper the $\Theta_0{}^{el}$ values obtained on the assumption that the free electrons do and do not participate in the ionic motion differ by about 5°K, the latter case having the lower $\Theta_0{}^{el}$ value. If de Launay's model[37] is correct, then at some intermediate temperature region (probably below 20°K for copper[37]), the Θ^c value would be expected to change more rapidly than is predicted by the simple lattice-theory expansion. This suggests that some caution might be necessary in applying the Barron-Morrison analysis method to metals. However, the method has been conspicuously successful for nonmetals (where the γT term is, of course, zero).

Further information on the lattice-vibration spectrum of gold would be of considerable interest. This might be obtained from neutron-scattering experiments. Accurate measurements on the thermal expansion of gold in the region below 10°K might reflect the anomalous specific heat. Also, it might be expected that the variation of the velocity of sound with direction within a gold crystal would be unusual. Alers[38] has calculated (from elastic-constant results) the function which appears in the Debye formula, that is,

$$1/V_1{}^3+1/V_2{}^3+1/V_3{}^3=P(\Theta,\phi),$$

where Θ and ϕ are the spherical coordinates of a direction in the lattice and V_1, V_2, and V_3 are the three sound velocities associated with that direction. P is found to vary considerably with direction but the differences between the three noble metals are very small. Thus it appears unlikely that the differences in the Θ^c-versus-T curves for these metals can be explained on the basis of differences in elastic anisotropy.

Other anomalous variations of Θ^c with temperature have been reported recently. Van der Hoeven and Keesom[39] found that thallium shows a variation of Θ^c with temperature of the type observed for gold. Filby and Martin[3] and Veal and Rayne[40] have reported Θ^c curves for lithium (two-phase, predominantly hcp) and palladium, respectively, which rise steadily from the $\Theta_0{}^c$ value and show no minimum.

CONCLUSIONS

The $\Theta_0{}^c$ and $\Theta_0{}^{el}$ values for copper, silver, and gold, respectively, are shown to be in excellent agreement. The specific heats of copper and silver are found to vary with temperature in the usual way but the specific heat of gold varies in an anomalous manner.

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