across the zone boundary, and it is quite likely that the mechanism discussed by Elcock[21] is also operative as well as others. Nevertheless, on the above model one might predict observable temperature-dependent de Haas-van Alphen parameters in other crystals having very anisotropic thermal expansion coefficients, low Debye characteristic temperatures, and small overlap energies, but the scarcity of data on low-temperature thermal expansion coefficients precludes any concrete conclusions along this line.

We are indebted to the members of the Cryogenics Branch for many stimulating discussions.

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Specific Heats of Metals Below One Degree Absolute*

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The heat capacities of a number of metals have been measured in the region below 1°K, using the technique of adiabatic demagnetization. Copper, silver, platinum, palladium, tungsten, molybdenum, and sodium have been investigated. Apart from sodium, all exhibit a linear dependence of electronic specific heat on temperature. The values of γ are in agreement with those obtained in the liquid helium region, except in the case of tungsten, which gives $\gamma=3.5\pm0.2\times10^{-4}$ cal/mole deg^2 in contrast to the previous value $\gamma=1.8\pm0.7\times10^{-4}$ cal/mole deg^2 reported in the literature. Sodium exhibits an anomalous peak in its specific heat curve. A low-temperature, martensitic-type transformation is advanced as a likely cause of this behavior.

In the course of the experiments, an independent measurement of the heat capacity of copper potassium sulfate has been made. The relation $C=A/T^2$ appears to be obeyed, the value of the specific heat constant A being $5.8\pm0.2\times10^{-4}R$ deg^2/mole.

INTRODUCTION

According to the simple one-electron approximation,[1] the electronic specific heat of a normal metal is given by an expression

$$C=\frac{\pi^2}{3}k^2T\left(\frac{dN}{dE}\right)_{E=E_0}=\gamma T, \qquad (1)$$

where $(dN/dE)_{E=E_0}$ is the density of states at the top of the Fermi distribution. Experimental data in the liquid helium region seem to be in agreement with this prediction. The resulting values of γ are explained in terms of the variation of the density of states at the Fermi surface. Thus, in the case of the noble metals, where the d shell is completely full, the density of states corresponds roughly to that of a free electron gas with one electron per atom. Again, in the transition metals like platinum, with incomplete d shells and narrow d bands, the density of states is much higher, corresponding to the large values observed experimentally.

Equation (1) is based on the explicit assumption that the energy levels of a solid can be described correctly by a self-consistent field approximation. In particular, it is assumed that the total wave function can be represented by a simple product of one-electron wave functions, which are solutions of a Schrödinger equation for a periodic, self-consistent potential. Such a wave function cannot be correct since it does not give any recognition to the fact that the electrons in a metal, which interact strongly, tend to keep as far apart as possible. Thus the resulting energies must be too high. Admittedly, it is still possible that their differences may still give correctly the energy level spacings, but this would have to be established. It is thus a matter of conjecture as to whether Eq. (1) really does describe the behavior of an actual metal.

Now it is known that in the case of atomic systems, the Hartree-Fock approximation, which uses antisymmetrized wave functions, is more satisfactory than the Hartree approximation. Thus it gives lower energies and, furthermore, it produces a correct qualitative description of the spectroscopic terms actually observed in atoms. It might therefore be expected (although this expectation proves to be incorrect) that a similar situation exists in metals.

Here, the application of the Hartree-Fock approximation leads to an additional energy known as the exchange energy. For free electrons this exchange term is given by an equation

$$E_{\mathrm{ex}}=-\frac{e^2k_0}{\pi}\left(1+\frac{k_0^2-k^2}{2kk_0}\ln\frac{k+k_0}{|k-k_0|}\right), \qquad (2)$$

where k_0 is the value of the wave number corresponding to the surface of the Fermi distribution. It will be seen

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[1] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 15–159.

that the resulting curve of E *versus* k has an infinite slope at $k=k_0$. As a consequence, the assumptions made in deriving Eq. (1) break down, and a more careful analysis must be made to obtain the electronic specific heat.

A number of workers[2–5] have investigated the effect of the exchange energy on the electronic heat capacity. In the case of sodium, it is found that the heat capacity is now given by an equation

$$C=\frac{C_s}{8.9-1.7\log_{10}T}, \tag{3}$$

where C_s is the usual free-electron value. Thus the linear relationship with temperature is no longer obeyed, and the magnitude of the heat capacity is much lower than that predicted by the simple theory.

These results appear to be in contradiction with experiment and so it seems that the Hartree-Fock approximation does not correctly describe the behavior of a metal. As Wigner[6] points out, this conclusion is supported by considerations regarding the magnetic properties of an electron gas of low density. Here the Hartree-Fock theory predicts that the system should be ferromagnetic, whereas it is known from an exact solution that such is not the case.

Wohlfarth[4] has shown that the peculiar specific heat behavior given by Eq. (3) disappears if the exchange term is evaluated using a screened Coulomb potential. A similar potential was employed by Landsberg[7] to explain the soft x-ray emission spectrum of sodium. In both cases, the procedure was purely an *ad hoc* one. Recently, however, Macke,[8] and Bohm and Pines[9] have made considerable progress in justifying the use of a screened Coulomb field from a fundamental point of view. Although their work cannot be regarded as complete, the results seem promising.

In view of such progress, it appears likely that a theory really capable of being compared with experiment will be produced in the near future. Since sodium is the closest approximation to an ideal metal, experimental data on its electronic heat capacity would provide the best means of comparison with such a theory. It is thus of some importance to measure the temperature dependence of its electronic specific heat over as wide a temperature range as possible.

The present series of experiments extends specific heat measurements down to 0.2°K for a representative group of metals including sodium. Over the region of interest, the lattice heat capacity is negligible, so that it has been unnecessary to make any assumption regarding its temperature dependence.

Except in the case of sodium, the results indicate that the linear variation of electronic heat capacity with temperature holds down to the lowest temperatures obtainable in these experiments. The corresponding γ values are in substantial agreement with those obtained in the liquid helium region.

Previous work[10] on sodium revealed an anomaly in its specific heat at 7°K. As a consequence, no data concerning its electronic heat capacity had been obtained. It was hoped that measurements below 1°K would provide such data. Unfortunately, however, experiments here also fail owing to the presence of an anomaly at 0.87°K. It is thought that the anomaly arises from a martensitic-type transformation similar to that reported in lithium.[11] Some evidence for such a transformation is given by x-ray studies on cold-worked sodium.[12]

APPARATUS

Essentially the method consisted in measuring the combined heat capacity of the metal specimen and a paramagnetic salt. The heat capacity of the salt being known, that of the metal could be obtained by subtraction. The low temperatures were obtained by adiabatic demagnetization of the salt pill, starting from a temperature of 1.30°K and an initial field of about 6000 gauss. The latter was produced by a Weiss-type electromagnet having a 4-inch pole gap and mounted on rails so as to permit easy removal after demagnetization. Thermal contact between the salt pill and the helium bath was obtained using exchange gas at a pressure of approximately 10^{-4} mm of mercury. A mercury diffusion pump was used to produce an insulating vacuum when required.

The only item requiring detailed description is the vacuum can. Details of this are shown in Fig. 1. The outer case is in two sections, the upper half A being made of brass. Glass construction is used in the lower half B to eliminate disturbances arising from eddy currents in the circuit for measuring the susceptibility of the paramagnetic salt. Junction between the two parts is effected by a copper-glass seal C. The glass section of the can is necked down over its lower portion so as to accommodate the coil system used in measuring the susceptibility of the salt.

The exterior of the vacuum can is completed by the cap D which slides snugly into the top of the can, a seal between the two being obtained by a Rose's metal joint. Passing through the cap is the super-nickel pumping tube E, which communicates with the interior of the vacuum can by means of the aperture F. Radiation is prevented from entering the can by means of the trap G, by positioning the pumping hole on the side

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[2] J. Bardeen, Phys. Rev. **50**, 1098 (1935).

[3] H. Koppe, Z. Naturforsch. **2a**, 185 (1947).

[4] E. P. Wohlfarth, Phil. Mag. **41**, 534 (1950).

[5] A. B. Lidiard, Phil. Mag. **42**, 1325 (1951).

[6] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[7] P. T. Landsberg, Proc. Phys. Soc. (London) **62**, 806 (1949).

[8] W. Macke, Z. Naturforsch. **A5**, 192 (1950).

[9] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[10] G. L. Pickard and F. E. Simon, Proc. Phys. Soc. (London) **61**, 1 (1948).

[11] C. S. Barrett and O. R. Trautz, Trans. Am. Inst. Mining Met. Engrs. **175**, 579 (1948).

[12] C. S. Barrett, Am. Mineralogist **33**, 749 (1948).

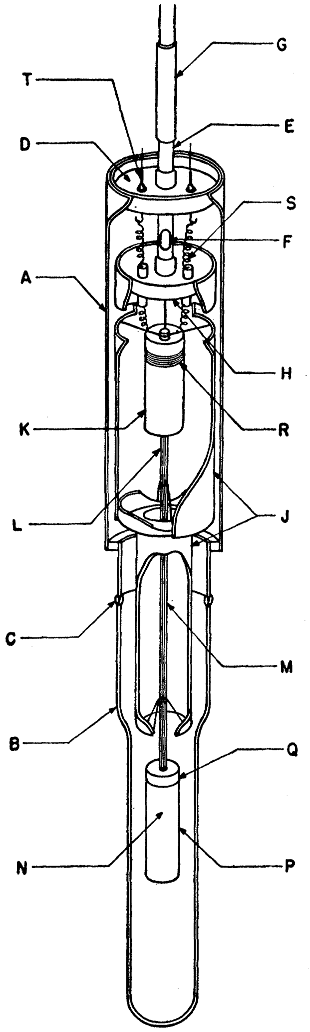

FIG. 1. Details of calorimeter.

of the tube and by covering the glass parts of the can with opaque cloth. The end of the pumping tube is blocked off by the brass plate H, which supports the fiber cage J. This is made in two parts so as to permit easy assembly of the system.

Within the cage, and supported from it by nylon threads, is the actual specimen. The metal under test is in the form of a cylinder K, to which is soldered a thick copper wire L. At its lower end the wire, which is stiffened by a glass rod M, is connected to the salt pill N. The resulting geometry prevents eddy currents from being induced in the metal and thereby affecting the measurements of the susceptibility of the salt.

The salt pill consists of about 20 grams of copper potassium sulfate molded (under a pressure of about 8 tons) into a cylinder $\frac{5}{8}$ inch in diameter and 2 inches in length. Embedded in the salt is a copper vane system[13] which, being joined to the copper wire, insures adequate thermal contact between the salt and the metal. A Lucite case P, sealed at the end Q by cold-setting Araldite, covers the salt pill and serves to minimize adsorption of helium.

Heat is supplied to the system by means of the heater R. This is made of No. 45 gauge enameled manganin wire and is cemented with clear Glyptal directly onto the specimen K. Electrical connections to the heater are made through spirals S of tinned No. 40 gauge manganin wire. At helium temperatures these become super-conducting and so provide a path of high electrical conductivity and low thermal conductivity. Kovar seals T are used to bring out the heater connections to the exterior of the vacuum can. The remainder of the heating circuit is quite conventional and will not be described here.

TEMPERATURE MEASUREMENT

The temperature of the combined specimen was obtained by ballistic measurements[14] of the susceptibility of the paramagnetic salt. A short period (5 seconds) galvanometer was used in order to obtain temperature readings as quickly as possible. In the case of copper potassium sulfate, measurements by Garrett[15] have shown that it obeys a Curie-Weiss law down to 0.1°K. Thus the absolute temperature is readily obtained from the galvanometer deflection θ, using the relation

$$\theta=\frac{\alpha}{T-(\delta_1+\delta_2)}+\beta, \tag{4}$$

where α, β are constants depending on the coil geometry and δ_1 is the Curie-Weiss constant for the salt. The values of δ_1 for copper potassium sulfate, as quoted in the literature, vary considerably (see Table I). Here Garrett's value of 0.034°K has been used. The constant δ_2 is given by the formula

$$\delta_2=fC(4\pi/3-N), \tag{5}$$

where C is the Curie constant for the material, f is the filling factor, and N is the demagnetization factor for the shape of pill used. The latter cannot be calculated exactly in the case of a cylinder but a good estimate can be obtained on the assumption that the cylinder

TABLE I. Various determinations of the Curie-Weiss constant δ_1 and the quantity A in the relation $C=AT^{-2}+\gamma T$.

Worker	δ_1 (°K)	A ($10^{-4}R$ deg²/mole)
de Klerk[a]	0.052	6.8
Garrett[b]	0.034	6.1
Benzie and Cooke[c]	0.035	6.0

[a] D. de Klerk, Physica **12**, 513 (1946).
[b] See reference 15.
[c] R. J. Benzie and A. H. Cooke, Proc. Phys. Soc. (London) **63**, 213 (1950).

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[13] E. Mendoza, *Ceromonies Langevin-Perrin* (Paris, 1948), p. 53.

[14] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **149**, 152 (1935).

[15] C. G. B. Garrett, Proc. Roy. Soc. (London) **203**, 375 (1950).

can be replaced by an ellipsoid of equivalent dimensions. Using a value of 0.96 for the filling factor and Garrett's value for the constant C, δ_2 was calculated to be 0.006°K. This figure is so small that the above-mentioned assumptions have comparatively little effect on the accuracy of the temperature measurements.

Calibration of the system was effected against the vapor pressure of helium, using the 1949 temperature scale.[16]

SPECIMENS

The general form of the specimen has already been described. For most of the experiments, the mass of the salt pill was kept around 20 grams. This value was influenced principally by sensitivity requirements in the ballastic circuit. Thus, with a measuring field of about 30 gauss, it was possible to obtain a deflection of roughly 40 cm at 1°K. This was sufficient to give an accurate calibration in the liquid helium region. The mass of the metal was chosen so as to give a value of heat capacity at 0.5°K equal to that of the salt. All specimens were analyzed spectroscopically for impurities and, except for one platinum sample, proved to be 99.9 percent pure or better. Further details of the samples are given below.

Copper

This sample was in the form of a cylinder, 1.9 cm in diameter and 5.0 cm in length, turned from commercial stock. The total mass, including the copper vane system and connecting rod, was 141.2 grams.

Silver

Here the specimen consisted of a cylinder 3 cm in diameter and 5.0 cm in length, turned from an ingot of extra high purity stock. The total mass of silver was 485.0 grams, while that of the associated copper vane system was 5.7 grams.

Platinum

Two specimens of this metal were used. The first was melted down from scrap foil. Spectroscopic analysis showed it to have an unusually high (approximately 2 percent) impurity content, undoubtedly acquired during fabrication. The lattice constant as measured by x-rays was (3.9141±0.0004) A as compared with the accepted value 3.9237 A at 20° given by Barrett.[17] A second sample in the form of a cylinder 0.75 cm in diameter and 1.5 cm in length was obtained from Goldsmith Brothers Smelting and Refining Company. This analyzed 99.99 percent pure and gave a lattice constant 3.9236 A, in good agreement with the accepted value. The mass of the second sample was 36.8 grams, that of the copper vane system being 7.4 grams.

Palladium

Here the specimen was a cylinder approximately 0.75 cm in diameter and 1.5 cm in length, also obtained from Goldsmith Brothers. Its mass was 21.6 grams and that of the copper vane system 7.2 grams.

Tungsten

This was obtained in the form of a sintered rod from Fansteel Metallurgical Company. It was machined into a cylinder 1.75 cm in diameter and 5.0 cm in length. To insure better thermal contact between the salt and the specimen itself, copper disks were soldered to either end. The mass of tungsten was 255.5 grams and that of the vane system 17.3 grams.

Molybdenum

The same company also supplied a sintered rod of this metal. It was turned down into a cylinder of about the same dimensions as the tungsten sample, copper disks being soldered to either end as before. The mass of molybdenum was 100.6 grams, that of the copper being 14.3 grams.

Sodium

Two forms of specimen were used in this case. In the first, metal was melted under vacuum into a glass envelope, thermal contact between the specimen and salt being obtained by a copper-glass seal at the bottom of the container. This was used only once, owing to the tendency of the glass envelope to crack. In the second specimen a thin copper container was used, the metal being melted in under vacuum as before. Before sealing, the dead space in the can was filled with nitrogen at one atmosphere pressure. A copper wire extended some distance into the container, so that on cooling the sodium would contract onto it, thereby insuring adequate thermal contact throughout the specimen. The mass of sodium was 21.8 grams and that of the copper 40.8 grams. Spectroscopic analysis showed that the principal impurity in the metal was about 0.02 percent potassium.

PROCEDURE

In making a run, the specimen was first cooled down to about 0.15°K. Details of the demagnetization procedure are well known and will not be described here. Temperature readings were then taken every 15 seconds to establish a warmup curve. At appropriate intervals, known heat inputs were applied, resulting in distinct breaks in the curve. No appreciable after periods were observed except at the lowest temperatures and then only in the poorer conductors like tungsten. This showed that thermal contact between the salt and metal was always quite good and also that the temperature difference between them was small. Thus, by extrapolating the sections of the curve to the midpoints

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[16] H. van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

[17] C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1952), p. 647.

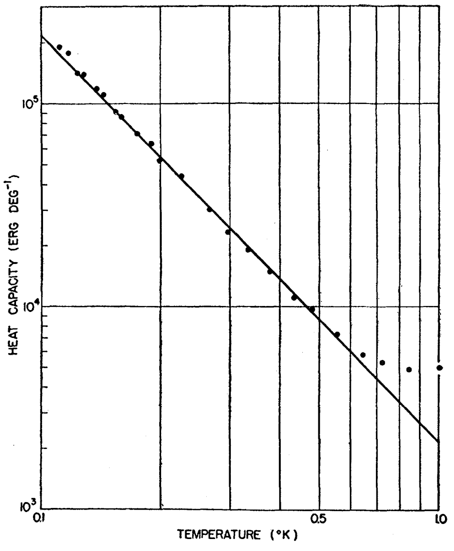

FIG. 2. Heat capacity of copper potassium sulfate.

of the heating periods, it was possible to calculate the resulting temperature rises of the combined system. From these it was a simple matter to calculate the combined heat capacity.

In analyzing the data, use was made of the fact that in the region of interest the total heat capacity can be represented by an equation

$$C=AT^{-2}+\gamma T, \qquad (6)$$

provided that the lattice specific heats of both the salt and metal are negligible. In this expression the first term represents the heat capacity of the salt, the last representing the electronic heat capacity of the metal, assuming a linear temperature relation to hold. Rearranging the above equation, we have

$$CT^2=A+\gamma T^3. \qquad (7)$$

Thus, if the above assumptions are true, a plot of CT^2 *versus* T^3 should give a straight line whose slope is γ and whose intercept on the vertical axis is the specific heat constant of the salt. The latter, of course, constitutes a check on the accuracy of the experiment, since the mass of the salt is known.

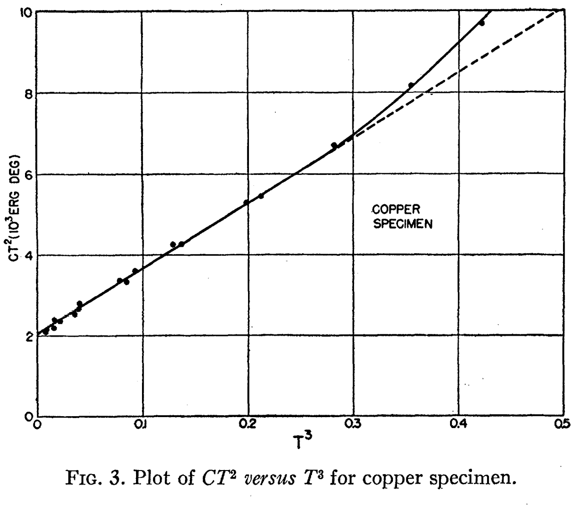

FIG. 3. Plot of CT^2 *versus* T^3 for copper specimen.

RESULTS

Considerable variation in the value of A for copper potassium sulfate exists in the literature. The various determinations are given in Table I.

In order to check on these determinations, an independent measurement was made using the above apparatus. The results for a salt pill of mass 19.8 grams are shown in Fig. 2. It will be seen that from 0.1°K to 0.65°K the experimental points lie quite well on a line of slope -2 corresponding to the postulated inverse square law. The resulting value of the constant A is $(5.8\pm0.2)\times10^{-4}R$ deg^2/mole, in good agreement with the figures of Benzie and Cooke and of Barrett, so that it would appear that de Klerk's value is in error.

Beyond 0.65°K there is considerable deviation of the experimental points from the straight line. The deviation is too large to be attributed solely to the lattice specific heat. It is believed that the real cause is the adsorbed helium film on the surface of the salt. This adsorption has been minimized by covering the salt with a plastic container, but, even so, measurements above 0.65°K can hardly be expected to be reliable.

Similar adsorption effects are observed in the results for the metal specimens. For example, Fig. 3 shows a plot of CT^2 *versus* T^3 for the composite copper-salt sample. The initial part of the graph is a straight line, showing that the electronic specific heat of the metal is indeed a linear function of temperature. Beyond about $T^3=0.25$, however, the curvature is quite pronounced and cannot be explained by the effects of lattice heat capacity alone. Accordingly, in fitting a straight line to the experimental data, the points above 0.65°K have been given no weight. The intercept on the vertical axis corresponds within 2 percent to the value of A calculated from the mass of the salt. Figure 4 shows the results for copper plotted in a more usual form. The dotted curves give the specific heats of the salt and metal as obtained from the CT^2 *vs* T^3 plot and the full curve gives their resultant.

In all cases except sodium, it was found that the data below 0.65°K could be fitted quite well to a straight line on a CT^2 *vs* T^3 plot. As in the case of copper, the intercept on the vertical axis corresponded quite closely to that calculated from the mass of salt. The resulting values of γ are given in Table II.[18–25] In

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[18] J. A. Kok and W. H. Keesom, Physica 3, 1035 (1936).

[19] Estermann, Friedberg, and Goldman, Phys. Rev. **87**, 582 (1952).

[20] A. Wexler and W. S. Corak, Third International Conference on Low Temperature Physics and Chemistry, Houston, 1953 (unpublished).

[21] J. A. Kok and W. H. Keesom, Physica 1, 770 (1933).

[22] P. H. Keesom and N. Pearlman, Phys. Rev. 88, 140 (1952).

computing these, due allowance was made for the mass of the copper vane system.

In the case of sodium, extremely peculiar behavior was observed. Using copper potassium sulphate as a cooling agent, it was not possible to obtain appreciable demagnetization. Thus, final temperatures of the order of 0.85°K were reached instead of the expected value of 0.2°K. Allowing the specimen to remain overnight at liquid helium temperatures appeared to increase the cooling slightly on subsequent demagnetization.

In order to check these results, another experiment was carried out using iron ammonium alum as a refrigerant. This salt, having a much higher entropy of magnetization, produces a greater cooling effect. As expected, the final temperature of the system was considerably lower, being of the order of 0.3°K. The results for the combined heat capacity of the system, using this salt, are shown in Fig. 5. The curve for the salt pill alone is also shown. From these it can be seen that there is a pronounced maximum in the specific heat of sodium at about 0.87°K. Owing to the sharpness of the peak and the effects of exchange gas, the shape of the anomaly is not known with any great certainty. The entropy associated with the anomaly, as calculated from the curve, is less than 5×10^4 erg/deg. Another estimate of this entropy may be obtained from the final temperature reached after demagnetization. The resulting figure is 5×10^5 erg/deg, in marked disagreement with the value given above.

TABLE II. Values of γ in the relation $C=AT^{-2}+\gamma T$.

Metal	γ 10^{-4} cal/mole deg^2 Present work	Previous work	Reference
Copper	1.73±0.08	1.78 1.80 1.60	a b c
Platinum	16.5 ±0.8	16.1	a
Silver	1.60±0.15	1.60 ··· 1.48	d e c
Palladium	25.6 ±1.3	31.0	f
Tungsten	3.53±0.18	50.0 5.0 1.8	g h i
Molybdenum	5.25±0.26	5.1	i

[a] See reference 18.
[b] See reference 19.
[c] See reference 20.
[d] See reference 21.
[e] See reference 22.
[f] See reference 10.
[g] See reference 23.
[h] See reference 24.
[i] See reference 25.

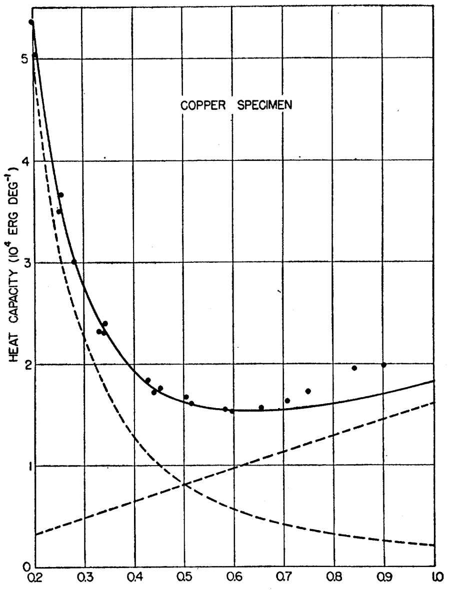

FIG. 4. Heat capacity of copper specimen.

DISCUSSION

Referring to Table II, it will be seen that the agreement between the two sets of values is quite good except for the case of tungsten. There is considerable variation in the values of γ for this metal as reported in the literature. Since the experimental error in the latest liquid helium determination[25] appears to be quite large, it is believed that the value obtained in the present work is more reliable.

Our figure for palladium is somewhat lower than that given by Simon.[10] To eliminate the possibility that could be due to the presence of hydrogen dissolved in

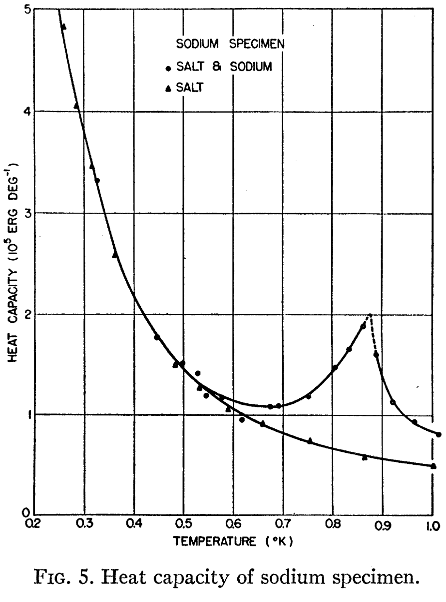

FIG. 5. Heat capacity of sodium specimen.

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[23] A. A. Silvidi and J. G. Daunt, Phys. Rev. **77**, 125 (1950).
[24] M. Horowitz, Master of Science thesis, Ohio State University, 1950 (unpublished).
[25] M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953).

the metal, the specimen was vacuum annealed at 500°C for 8 hours, and the heat capacity was remeasured. No noticeable change in the value of γ was observed. It would appear, then, that the difference is real. One possible explanation is that Simon's data extends over a wider temperature range (1.5 to 20°K) and hence might be affected by variation in the Debye temperature. This is somewhat unlikely, since the lattice contribution to the specific heat only becomes equal to the electronic contribution at about 11°K.

A more likely explanation is that the two specimens had somewhat different purities. Experiments on the contaminated platinum sample gave the abnormally high γ value of 41.6×10^{-4} cal/mole deg^2. This specimen also had an anomalous lattice spacing. It would thus seem likely that the two effects are correlated and that the band structure is very sensitive to impurities. Such a situation could conceivably exist in all of the transition metals. The discrepancy between the two γ values for palladium would then be easily explicable.

In the case of silver, the present results are in fair agreement with those of Keesom and Kok,[18] and of Wexler and Corak.[20] The assumption of negligible lattice specific heat fails in this case. As a result, there is an increased curvature in the CT^2 *vs* T^3 plot, and hence it is difficult to obtain an accurate value of γ. It is fairly certain, however, that the present data are in disagreement with the results of Keesom and Pearlman.[22] As Clement[26] has pointed out, it is likely that the anomalous behavior reported by these workers is due to errors in thermometer calibration.

In general, therefore, the present work shows that the linear variation of electronic heat capacity with temperature holds down to 0.2°K. The present state of the theory does not permit any quantitative conclusions to be justifiably drawn from the data for the transition and noble metals. It is certain, however, that no such behavior as indicated by Eq. (3) is observed. The data for sodium cannot be analyzed owing to the presence of the specific heat anomaly at 0.87°K.

Concerning the anomaly in sodium, the differences in entropy on cooling and warming suggest that it is due to a martensitic-type of transformation occurring at low temperatures. Barrett[11] has observed x-ray evidence for the existence of such a transformation. Thus sodium, cold-worked at liquid hydrogen temperatures, showed a small diffraction peak in addition to that of the body-centered cubic pattern. This was taken as indicating the formation of a strain-induced face-centered cubic modification, similar to that found in lithium cold-worked at liquid nitrogen temperatures. Now in lithium a related structural change occurs spontaneously at liquid hydrogen temperatures. It is not unlikely, then, that a similar change occurs at low temperatures in the case of sodium.

Such a transformation as that described above could explain the behavior of sodium which is observed in these experiments. Thus the hysteresis associated with a martensitic transformation would account for the difference in entropy on cooling and warming. Again, the cusp-shaped nature of the anomaly could be explained by assuming that the steepest slope of the reverse transformation curve occurred in the vicinity of 0.87°K. This hypothesis would not prevent the possibility that the major part of the transition occupied an extended region above 1°K, thereby accounting for the large difference in the two entropy values.

A significant feature of the experimental curve of Fig. 5 is that the points were not all obtained on the same demagnetization. The shape of the anomaly would thus appear to be reproducible. To account for this fact, it is necessary to suppose that the thermal treatment prior to each demagnetization is able to restore the sample condition to its original position on the transformation curve.

It is clear, however, that the above explanation needs further confirmation from experiment. Such experimental data could be obtained by the x-ray analysis of sodium at liquid helium temperatures.

ACKNOWLEDGMENT

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This research was supported by a Charles A. Coffin Fellowship and by a grant from the Commonwealth Scientific and Industrial Research Organisation, Australia.

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[26] J. R. Clement, Phys. Rev. **93**, 1420 (1954).