PHYSICAL REVIEW VOLUME 107, NUMBER 3 AUGUST 1, 1957

Heat Capacity of Palladium below 4.2°K

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(Received April 30, 1957)

Heat capacity measurements below 4.2°K have been made on extremely pure palladium. The resulting values of electronic heat capacity and Debye temperature differ from previous work, it being found that $\gamma=(9.87\pm0.11)\times10^{-3}$ joule mole^{-1} deg^{-2} and $\theta=299\pm12$°K. The effects of changes in the physical and chemical state of the specimen have been investigated with a view to understanding the discrepancies between the various determinations of the low-temperature atomic heat of palladium.

I. INTRODUCTION

THERE have been a number of determinations of the electronic heat capacity of palladium. The data of Simon and Pickard[1] in the region 2–22°K can be represented by the usual expression

$$C=\gamma T+A(T/\theta)^3, \tag{1}$$

with a large value of γ, which is attributed to an unfilled d band in the metal. Clusius and Schachinger,[2] who measured the heat capacity of palladium in the range 14–270°K, concluded that their low-temperature data were consistent with the above-mentioned values of γ and θ.

More recent experiments by Rayne[3] below 1°K and by Yates and Hoare[4] in the liquid-helium range give values for the electronic heat capacity of palladium considerably lower than those of Simon and Pickard. The disagreement between these latter two determinations, however, is considerably larger than the estimated errors. The present work was undertaken to try to resolve these various discrepancies, firstly by making accurate measurements on spectrographically standardized material and secondly by measuring the effects of variation on the physical state and purity of the specimen employed.

II. EXPERIMENTAL

Measurements were made in a modified form of the calorimeter used by Corak *et al.*[5] in their work on the noble metals. Measuring techniques were substantially unaltered except that the carbon resistance thermometer was calibrated against the 1955 vapor pressure-temperature scale of Clement, Logan, and Gaffney.[6]

Two specimens were used in this work. The first was a sample of Johnson-Matthey spectrographically standardized material (Lab No. 10369) in the form of a wire 1.5 mm in diameter and weighing 9.960 gram. Its purity was greater than 99.999%, the impurities being copper, silver, iron, calcium, magnesium, and silicon, each present in a quantity less than 1 ppm. In the annealed state, the residual resistance ratio was 0.7×10^{-3}.

The wire was coiled into a loose spiral about $\frac{3}{4}$ inch in diameter and was attached by means of a small copper-beryllium screw to a thin-walled copper holder of mass 23.90 gram. By measuring the heat capacity of this composite specimen, that of the palladium could be obtained by subtracting the known value for the copper holder and thermometer assembly. Data were obtained for this palladium sample both in a strained state and after annealing *in vacuo* for four hours at 600°C.

The second sample was a cylinder of palladium, mass 18.79 gram, used by the author in previous measurements below 1°K.[3] Its purity was 99.98%, the principal impurity being iron. Measurements were made on this specimen in the annealed state, the copper holder being connected to the specimen by the copper-beryllium screw as before.

III. RESULTS AND DISCUSSION

The experimental atomic-heat data for the spectroscopically pure sample of palladium in both the strained

TABLE I. Atomic heat of spectrocopically pure palladium in strained and annealed states.

T(°K)	C(millijoule mole^{-1} deg^{-1}) Strained	T(°K)	C(millijoule mole^{-1} deg^{-1}) Annealed
1.522	15.30	1.539	15.36
1.622	16.61	1.665	16.81
1.866	18.93	1.861	18.64
1.981	20.51	2.008	20.60
2.051	21.24	2.236	23.08
2.151	22.16	2.319	23.91
2.238	23.21	2.440	24.93
2.539	26.15	2.574	26.27
2.659	27.49	2.783	28.59
2.757	28.64	2.963	30.84
2.890	30.19	3.086	32.21
2.986	31.57	3.169	33.29
3.116	32.68	3.311	34.90
3.231	34.27	3.473	36.74
3.297	34.97	3.592	38.86
3.369	36.26	3.719	40.46
3.446	36.83	3.847	42.20
3.536	38.15	3.962	43.90
3.631	39.34	4.094	45.66
3.736	40.73		
3.853	42.59		
3.977	44.09		
4.068	45.54		

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[2] K. Clusius and L. Schachinger, Z. Naturforsch. **2a**, 90 (1947).

[3] J. Rayne, Phys. Rev. **95**, 1428 (1954).

[4] B. Yates and F. E. Hoare, Proc. Roy. Soc. (London) **240**, 42 (1957).

[5] Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. **98**, 1699 (1955).

[6] Clement, Logan, and Gaffney, Phys. Rev. **100**, 743 (1955).

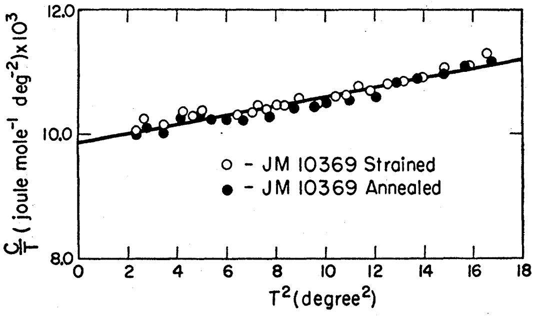

FIG. 1. Heat capacity of spectroscopically pure palladium.

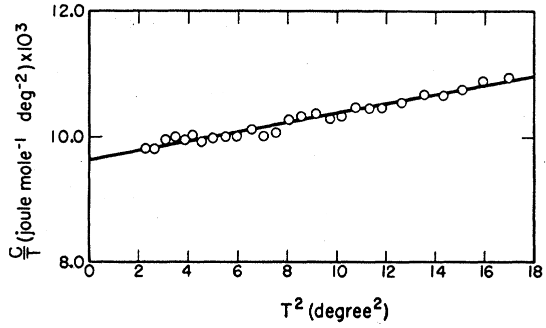

FIG. 2. Heat capacity of commercial palladium.

and annealed states are given in Table I. Figure 1 shows these results in the form of a graph of C/T *versus* T^2. It can be seen that the two sets of data agree to within the experimental error, the straight line of best fit determined by a least-squares analysis being as shown. Figure 2 shows the C/T *versus* T^2 plot for the second specimen. The resulting values of γ and θ for the two samples, together with those obtained by previous observers, are given in Table II. In this table, the uncertainties for the present results include both random errors estimated at a 99% confidence level from the least squares data and systematic errors. The estimate of the latter has been increased in the case of the spectroscopically pure material to take into account the small specimen mass employed (see Fig. 1).

Reference to Table II shows that there is a significant difference between the values of electronic heat capacity obtained for the two specimens. It would thus appear that specimen purity can appreciably affect the γ value of a metal, a conclusion reached by the author[3,7] in connection with previous experiments.

The values of γ and θ for pure palladium obtained in the present work differ considerably from those of previous observers. In the case of the data of Simon and Pickard the discrepancy between their γ value and ours is extremely large, being well outside the estimated combined error. Since their specimen purity is not known, it is conceivable that impurities in their sample were the cause of the disagreement. It is possible, however, that undetected systematic errors were also present in their work.

TABLE II. Comparison of atomic heat constants for palladium from this work with previous data.

Observer	Specimen purity (%)	γ (millijoule mole^{-1} deg^{-2})	θ (°K)
Simon and Pickard[a]	Unstated	13.0 ± 0.5[b]	275
Clusius and Schachinger[c]	Unstated	13.0	275
Yates and Hoare[d]	~99.99[e]	9.31 ± 0.05[f]	274 ± 3
Rayne[g]	99.98	10.7 ± 0.5[h]	...
Present work	99.98[i]	9.64 ± 0.08[j]	297 ± 9
Present work	99.999	9.87 ± 0.11[j]	299 ± 12

[a] See reference 1.
[b] Random error estimated from plot of C/T *versus* T^2.
[c] See reference 2.
[d] See reference 4.
[e] Qualitative spectroscopic analysis giving silver as major impurity.
[f] Random probable error estimated from plot of C/T *versus* T^2.
[g] See reference 3.
[h] Random error estimated from plot of CT^2 *versus* T^3.
[i] Same sample as used in reference 3.
[j] Random and systematic error estimated at 99% confidence level.

In view of the rather low accuracy of their data, it is not possible to obtain a value of θ independently of results in the hydrogen region. Now, as is well known, the value of θ can change considerably in going from helium to hydrogen temperatures. It is thus not surprising that their value of Debye temperature is lower than that obtained here. In this connection, it is of interest to note that the θ value decreases as the temperature increases, as would be expected. Similar conclusions hold for the low-temperature data of Clusius and Schachinger, which were also obtained in the hydrogen region.

Reference to Table II shows that the γ value obtained above 1°K on the less pure specimen differs significantly from that previously found for the same sample below 1°K. It is unlikely that the present measurements are responsible for the discrepancy, since such measurements in our laboratory have proved to be both reproducible and of high accuracy. It would appear, therefore, that there were undetected systematic uncertainties in the earlier determinations which were not included in the error estimate. Possible sources of this error are effects due to desorption of helium from the specimen and also uncertainties in the magnetic temperature scale below 1°K.

Owing to the large electronic heat capacity of palladium, there is considerable uncertainty in the θ value as determined from helium data alone. The agreement between our value and that of Hoare and Yates must, therefore, be considered to be satisfactory. The discrepancy between the γ values is, however, definitely outside the combined limit of error. It is possible that this disagreement is due to the lower purity of their sample. In view of the high purity of the last specimen in Table II, it is believed that the γ and θ values listed for it are the best available constants for the low-temperature heat capacity of palladium.

ACKNOWLEDGMENTS

Thanks are due to Mr. G. T. Cunningham for his help on setting up the calorimeter and to Dr. C. B. Satterthwaite for much valuable advice concerning its operation.

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