Electronic Specific Heats in Tungsten and Zinc

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Calorimetric measurements have been made in the liquid helium temperature region on tungsten and zinc. For tungsten, the specific heat could be resolved into a lattice T^3 function with Debye $\theta = 169°$K and an electronic term γT with $\gamma = 51.1 \times 10^{-4}$ cal./mole/degree². The anomalously low θ-value may indicate the existence of a hidden transition at low temperatures. A discussion is given of the high value of γ and it is suggested that a recalculation of the energy spectrum at both high and low temperatures may be required and that correlation forces may be partly responsible for the observed result. For zinc, measurements were also carried out on a powder with average particle size $= 1.3 \times 10^{-4}$ cm in order to assess the significance of size effects. The results showed that the powder had a specific heat identical with that for zinc in bulk, given by a Debye $\theta = 291°$K and an electronic term γT with $\gamma = 1.50 \times 10^{-4}$ cal./mole/degree².

1. INTRODUCTION

LOW temperature calorimetric measurements in the liquid helium temperature region have been carried out on tungsten and zinc and are reported herewith. By making the generally accepted assumption that at sufficiently low temperatures the measured specific heat is the sum of two terms, one proportional to T^3 caused by the lattice vibrations and the other proportional to T caused by the electronic contribution, it is possible to assess the specific heats of the lattice and of the electrons separately.

In the case of tungsten a measurement of the specific heat appeared to be of twofold interest. In the first place, no measurements had been previously made below 25°K[1] although detailed computations had been carried out on the electronic energy spectrum by Manning and Chodorow[2] and on the lattice vibrational energy by Fine[3] which could only be checked by very low temperature measurement. In the second place, the electronic energy of the transition elements has been the subject of many investigations in view of the high values of the density of states these elements exhibit[4] and it seemed worth while to extend measurements to include for the first time a metal in group 6 of the periodic table.

The measurements on zinc were carried out partly as a check on other measurements of the electronic specific heat in zinc simultaneously being carried out in the same laboratory by an entirely different method[5] and partly in order to investigate the possible existence of size effects in a powder having small average linear dimensions and at the same time a high purity.

2. EXPERIMENTAL ARRANGEMENTS

(a) The Tungsten Specimen

The tungsten was obtained from the Fansteel Corporation and had a stated purity of 99.9+ percent. The specimen was cylindrical, 7.31 cm long, 1.585-cm diameter and mass of 271.17 g.

The thermometer wire was of leaded phosphor-bronze (diameter 0.002 in.) kindly given to us by Dr. M. C. Desirant and it showed a satisfactory variation of resistance with temperature in the liquid helium range. It was wound on the outside of the specimen together with the electrical heater coil which was of manganin wire (0.0031-in. diameter). The mass of the thermometer and heater coils was 0.030 g, and the coils were insulated from and secured to the specimen by thin layers of varnish. Finally a radiation shield of tin foil of mass 0.153 g covered the entire specimen. The electrical leads to the heater and thermometer coils were of tantalum wire, 0.007-in. diameter, which were maintained at the temperature of the liquid helium bath ($<4.2°$K) at their upper ends. These leads, therefore, were superconducting during the experiments and so electrical and thermal losses were minimized.

(b) The Zinc Specimen

The zinc was obtained from Mallinckradt Chemical Works in the form of powder, of average grain diameter 1.3×10^{-4} cm. A spectrographic analysis revealed a purity of 99.9 percent with a largest single impurity of Pb of about 0.1 percent. For the first measurements on the zinc, 53.347 g of the powder were placed in a small copper vessel, of mass 16.48 g, together with 3×10^{-7} mole of pure helium gas to serve as heat exchanger. This helium gas was admitted through a small tube attached to the copper vessel, after the powder has been thoroughly degassed and subsequently this tube was sealed off.

Thermometer and heater coils, similar to those used for the tungsten, were wound on the copper vessel with suitable varnish insulation and a tin foil radiation shield, of mass 0.153 g. Subsequent measurements on zinc were made on a specimen formed by fusing the powder in vacuum into the form of a solid cylinder of length 8.0 cm, diameter 1.28 cm, and of mass 65.026 g. Thermometer and heater wires, again similar to those used for the tungsten, were wound directly on the zinc cylinder with suitable varnish insulation and again a

[1] Lange, Zeits. f. physik. Chemie **110**, 343 (1924).
[2] M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, 787 (1939). (See also H. Jones and N. F. Mott, Proc. Roy. Soc. **A162**, 49 (1937).
[3] P. C. Fine, Phys. Rev. **56**, 355 (1939).
[4] See N. F. Mott and H. Jones, Properties of Metals and Alloys (Oxford University Press, New York, 1936).
[5] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 1324 (1949).

TABLE I. Data on specific heat of the tungsten specimen.

Points	Heater Voltage volts ×10⁻³	Time sec.	Current amp. ×10⁻³	ΔQ×10⁻³ cal./mole	ΔT°K	T°K	C_v ×10⁻² cal./ mole- deg.
May 4th, 1949. Thermometer measuring current=0.2 ma
1	53.9	65.0	1.222	0.699	0.063	2.063	11.01
2	53.9	119.8	1.222	1.294	0.110	2.140	11.75
3	53.9	119.8	1.222	1.294	0.098	2.229	13.20
4	53.9	119.8	1.222	1.294	0.103	2.273	12.55
5	53.9	119.8	1.222	1.294	0.101	2.320	12.81
6	53.9	179.5	1.222	1.935	0.145	2.377	13.32
7	53.9	181.0	1.222	1.951	0.140	2.430	13.95
8	53.9	150.4	1.222	1.620	0.105	2.675	15.40
9	53.9	149.9	1.222	1.615	0.097	2.738	16.65
10	53.9	179.3	1.222	1.930	0.110	2.895	17.55
11	53.9	119.2	1.222	1.280	0.070	2.955	18.30
May 9th, 1949. Thermometer measuring current=0.4 ma
1	84.7	119.9	1.776	2.955	0.339	1.686	8.70
2	84.7	120.0	1.796	2.990	0.307	1.793	9.74
3	84.7	99.9	1.786	2.471	0.252	1.849	9.81
4	84.7	120.0	1.786	2.970	0.281	1.953	10.56
5	84.7	120.0	1.776	2.962	0.265	2.027	11.17
6	84.7	120.5	1.776	2.970	0.257	2.128	11.55
7	84.7	59.5	1.776	1.465	0.120	2.135	12.21
May 16th, 1949. Thermometer measuring current=0.4 ma
1	84.7	60.2	1.766	1.481	0.185	1.533	8.00
2	84.7	90.2	1.766	2.210	0.265	1.593	8.34
3	84.7	90.5	1.766	2.210	0.253	1.614	8.73
4	84.7	90.0	1.766	2.189	0.250	1.655	8.77
5	84.7	60.2	1.766	1.472	0.165	1.633	8.87
6	84.7	82.4	1.766	2.020	0.205	1.823	9.84
7	84.7	111.0	1.766	2.721	0.235	2.088	11.55
8	84.7	127.0	1.766	3.112	0.237	2.362	13.10
9	84.7	91.0	1.766	2.311	0.163	2.464	13.70
10	84.7	94.0	1.766	2.305	0.145	2.806	15.89
11	84.7	240.0	1.766	5.880	0.305	3.093	19.25
12	84.7	203.1	1.766	4.972	0.220	3.505	22.60
13	84.7	60.8	1.766	1.489	0.157	1.792	9.49
14	84.7	82.0	1.766	2.011	0.205	1.848	9.81
15	84.7	95.0	1.766	2.330	0.211	1.974	10.61
16	84.7	147.0	1.766	3.612	0.360	1.825	10.01

radiation shield attached. Both heater and thermometer coils were connected by tantalum leads in the same way as for the tungsten.

(c) The Apparatus

Each specimen was hung by three Nylon threads, 0.2-mm diameter, inside a copper vacuum jacket which could either have pure helium exchange gas admitted into it or be highly evacuated. This apparatus was placed in a Dewar vessel filled with liquid helium, the temperature of which could be held at any desired value between 1.3°K and 4.2°K by means of pumping the liquid helium. The temperature of the bath was ascertained by measuring the vapour pressure of the helium over the liquid surface. The liquid helium was provided by a small Simon type liquifier[6] modified to enable the liquid to be withdrawn into exterior Dewar vessels, as reported elsewhere.[7,8]

[6] F. E. Simon, Physik. Zeits. 34, 232 (1933).
[7] R. B. Scott and J. W. Cook, Rev. Sci. Inst. 19, 889 (1948).
[8] Daunt, Heer, and Silvidi, Phys. Rev. 75, 113 (1949).

(d) The Electrical Measuring System

The resistances of the heater coils at 4.2°K were about 40 ohms. To measure the power input, current and potential measurements were made for each heating with an accuracy of ±0.25 percent.

The current in the heater coil was switched on and off by a special switch which simultaneously automatically started and stopped a previously calibrated stop watch, capable of reading to 0.1 sec.

No signs of overheating of the specimens were observed, indicating good thermal contact between the heaters and the specimens.

The resistances of the thermometer coils were about 3.5 ohms. The calibration of the thermometer was made against the vapour pressure of liquid helium, above 1.6°K the measurements of Schmidt and Keesom[9] being taken, whereas below 1.6°K the scale of Bleaney and Simon[10] was used. It was found that below 3°K the variation of the resistance of each thermometer with temperature was essentially linear, having a temperature coefficient of resistance in this region of about 18 percent per degree. Since the resistance of the thermometer wire was current sensitive, care was taken to maintain the measuring current through it constant during any one experiment. Calibrations were made immediately before and after the measurements were taken.

To calculate the resistance of the thermometer coils, current and potential measurements were made, and during experiments the temperature differences ob-

TABLE II. Data on specific heat of the powdered zinc specimen.

Points	Heater Voltage volts ×10⁻³	time sec.	Current amp. ×10⁻³	Total ΔQ cal. ×(10⁻³)	ΔT°K	T°K	ΔQ/ΔT ×10⁻³ cal./ deg.	Heat cap. 0.259 mole Cu ×10⁻³ cal./ deg.	Heat cap. of 0.817 mole of Zn ×10⁻³ cal./ deg.	C_v ×10⁻³ cal./ mole- deg.
July 5th, 1949. Thermometer measuring current—0.1 ma
1	30.8	5.0	0.944	0.0342	0.0975	1.544	0.351	0.0826	0.2684	0.328
2	30.8	5.6	0.944	0.0383	0.109	1.567	0.351	0.0846	0.2664	0.325
3	30.8	9.6	0.944	0.0657	0.179	1.596	0.367	0.0863	0.2807	0.343
4	30.8	9.2	0.944	0.0630	0.161	1.599	0.391	0.0877	0.3033	0.370
5	30.8	10.0	0.944	0.0684	0.177	1.619	0.387	0.0881	0.2989	0.368
6	30.8	5.0	0.944	0.0342	0.091	1.592	0.376	0.0863	0.2897	0.354
7	30.8	5.0	0.944	0.0342	0.089	1.766	0.385	0.0983	0.2867	0.351
8	30.8	5.4	0.944	0.0370	0.091	1.772	0.408	0.0991	0.3089	0.377
9	30.8	5.8	0.944	0.0397	0.095	1.780	0.417	0.1001	0.3169	0.387
10	30.8	9.0	0.944	0.0616	0.140	1.820	0.440	0.1030	0.3370	0.412
11	30.8	7.2	0.944	0.0493	0.096	2.097	0.513	0.1252	0.3878	0.471
12	30.8	6.4	0.944	0.0438	0.089	2.098	0.493	0.1262	0.3668	0.449
13	30.8	14.0	0.944	0.0959	0.178	2.174	0.538	0.1325	0.4045	0.495
14	30.8	9.8	0.944	0.0671	0.120	2.178	0.559	0.1335	0.4225	0.520
15	30.8	10.1	0.944	0.0692	0.094	2.479	0.736	0.1635	0.5725	0.698
16	30.8	9.1	0.944	0.0623	0.087	2.509	0.717	0.1651	0.5519	0.675
17	30.8	5.9	0.944	0.0404	0.058	2.529	0.696	0.1681	0.5279	0.645
18	30.8	9.2	0.944	0.0630	0.087	2.566	0.724	0.1716	0.5524	0.674
19	30.8	12.0	0.944	0.0823	0.096	2.799	0.886	0.1940	0.6920	0.846
20	30.8	11.0	0.944	0.0754	0.078	2.881	0.966	0.2087	0.7573	0.923
21	30.8	15.0	0.944	0.1029	0.099	2.967	1.036	0.2210	0.8150	0.996
22	30.8	10.0	0.944	0.0684	0.068	2.992	1.005	0.2231	0.7819	0.955
23	30.8	25.5	0.944	0.1745	0.124	3.422	1.345	0.286	1.049	1.280
24	30.8	20.0	0.944	0.1370	0.100	3.483	1.370	0.296	1.074	1.310
25	39.6	15.2	1.128	0.1620	0.109	3.570	1.485	0.312	1.173	1.425
26	49.5	15.0	1.460	0.259	0.165	3.667	1.570	0.328	1.242	1.520
27	30.8	30.0	0.944	0.205	0.111	4.012	1.850	0.392	1.458	1.780

[9] G. Schmidt and W. H. Keesom, Leid. Comm., 250 c.
[10] B. Bleaney and F. E. Simon, Trans. Faraday Soc. 35, 1205 (1939).

TABLE III. Data on specific heat of the fused zinc specimen.

June 23rd, 1949. Thermometer measuring current =0.1 ma

Points	Heater Voltage volts $\times 10^{-3}$	Time sec.	Current amp. $\times 10^{-3}$	$\Delta Q \times 10^{-3}$ cal./mole	$\Delta T°K$	$T°K$	$C_v \times 10^{-3}$ cal./mole-deg.
1	69.3	2.5	1.374	0.0574	0.210	1.515	0.283
2	69.3	3.2	1.374	0.0735	0.226	1.520	0.325
3	69.3	3.5	1.374	0.0805	0.243	1.528	0.331
4	69.3	2.0	1.374	0.046	0.141	1.692	0.328
5	69.3	5.0	1.374	0.115	0.276	1.777	0.417
6	69.3	4.5	1.374	0.1032	0.260	1.793	0.398
7	46.2	4.8	0.916	0.0485	0.140	1.585	0.347
8	46.2	4.0	0.916	0.0408	0.135	1.543	0.303
9	46.2	5.1	0.916	0.0521	0.170	1.590	0.307
10	46.2	5.1	0.916	0.0521	0.129	1.909	0.404
11	46.2	5.7	0.916	0.0581	0.140	1.910	0.416
12	46.2	4.8	0.916	0.0489	0.120	1.901	0.407
13	46.2	6.0	0.916	0.0612	0.1475	1.921	0.416
14	46.2	4.9	0.916	0.0499	0.110	2.005	0.454
15	46.2	5.2	0.916	0.0530	0.124	2.008	0.428
16	46.2	9.8	0.916	0.100	0.201	2.052	0.499
17	46.2	5.8	0.916	0.0591	0.107	2.221	0.552
18	46.2	6.0	0.916	0.0611	0.122	2.230	0.501
19	46.2	3.5	0.916	0.0357	0.060	2.363	0.595
20	46.2	7.1	0.916	0.0724	0.086	2.831	0.841
21	46.2	7.0	0.916	0.0715	0.0865	2.823	0.827
22	46.2	7.1	0.916	0.0724	0.075	3.034	0.965
23	46.2	7.0	0.916	0.0715	0.075	3.022	0.954
24	69.3	6.2	1.374	0.1425	0.1075	3.498	1.325
25	69.3	6.0	1.374	0.138	0.105	3.491	1.310

tained could be estimated with an accuracy of less than 1 percent.

3. EXPERIMENTAL RESULTS

The experimental results are given in Tables I, II, and III and curves of the measured specific heats as functions of temperature are shown in Figs. 1 and 2, the full curves being drawn through the smoothed values.

The total mass of the radiation shield, thermometer coil and heater coil was 0.26 percent of the mass of the zinc powder and only 0.08 percent of the mass of the tungsten. This factor, therefore, made a negligible correction. In the experiments on the zinc powder, corrections were made for the heat capacity of the copper vessel using the specific heat values of copper given by Keesom and Kok.[11] To correct for the heat capacity of the helium gas filling and to check possible effects of adsorption in the experiments on the zinc powder, measurements were made with different fillings of gas. The results given in Table II and Fig. 2 are for the smallest gas filling used, for which it was found that the corrections were negligible.

The accuracy of the results both for W and Zn as represented by the smoothed specific heat curves of Figs. 1 and 2 is estimated to be within ±0.5 percent.

4. DISCUSSION

(a) Tungsten

Assuming that the full specific heat in this temperature range to be the sum of a Debye term (AT^3) due

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

to the lattice and of a Sommerfeld term (γT) due to the electronic contribution, a plot of the ratio of C_v/T against T^2 should give a straight line. Such plots have been drawn up from our measurements on tungsten and zinc and have been found to be satisfactorily linear, giving support to the assumption made. From such plots the numerical values of A and γ have been obtained. For tungsten:

$$C_v = 464.5(T/169)^3 + 51.1 \times 10^{-4}T \text{ cal./mole/degree.}$$

At the highest temperature of measurement, $T=3.5°K$, the lattice contribution to the total specific heat was only 19 percent, a result which made the evaluation of θ (Debye) difficult. It is estimated, however, that $\theta = 169°K \pm 20$, a value which is considerably lower than that estimated by Lange,[1] $(\theta_D = 310°K)$, from measurements of the specific heat between 26°K and 90°K. Moreover, the value of θ_D obtained from the high temperature elastic constants is still higher, being given by Honnefelder[12] as 384°K. Calculations of the specific heat of tungsten based on the normal modes of vibration of the lattice have been made by Fine[3] which have indicated the possibility that some of the apparent discrepancies between high and low temperature meas-
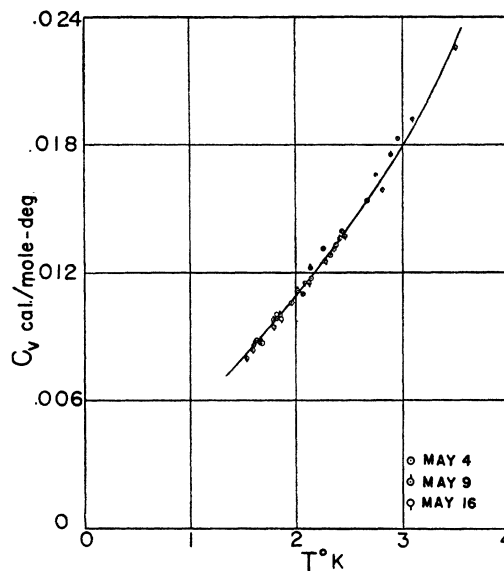

FIG. 1. The specific heat of tungsten as function of temperature.

urement of the lattice specific heat might be resolved. Fine, however, suggests that at the lowest temperatures his atomic model would give a T^3 specific heat corresponding to a Debye function with $\theta_D = 367°K$. It is considered, therefore, that the low observed value of θ may not be characteristic of the lattice but may be due to an additional term dependent on some hidden transition. The proximity of W to superconducting Ta in the periodic table and in atomic volume and its similarity in crystal structure suggests that such a

[12] Honnefelder, Zeits. f. physik. Chemie 21, 53 (1933).

transition might be calorimetrically analogous to the phenomenon of superconductivity. Such calorimetric anomalies have been previously observed by Simon and co-workers in beryllium[13] and sodium.[14]

The value of $\gamma = 51.1 \times 10^{-4}$ obtained from our measurements is very high, a feature which has been established generally for the transition elements. For comparison with other transition elements, the values of γ obtained by low temperature measurement are tabulated in Table IV (column 4).

TABLE IV.*

Ele-ment	Crystal structure	γ-value (cal./mole/degree²) Calc. $\times 10^{-4}$	Obs. $\times 10^{-4}$	Expt. method	Expt. authors
W	b.c.C.	4.8	51.1	C	This paper
Cb	b.c.C.	...	60.0	S-C	Daunt and Mendelssohn[15]
Ta	b.c.C.	6.2	19.4	S-C	Daunt and Mendelssohn[15]
			14.1	C	Keesom and Desirant[16]
Mn	b.c.C.	...	42.1	C	Elson, Grayson Smith and Wilhelm[17]
Fe	b.c.C.	4.6	12.0	C	Duyckaerts[18]
			12.0	C	Keesom and Kurrelmeyer[19]
Co	f.c.C.	...	12.0	C	Duyckaerts[20]
Ni	f.c.C.	11.0	17.4	C	Keesom and Clark[21]
Pd	f.c.C.	...	31.0	C	Pickard[22]
Pt	f.c.C.	...	16.0	C	Keesom and Kok[11]

* In this table the fifth column indicates "C" calorimetric measurements and "S-C" magnetic measurements on superconductors, both methods being carried out at low temperatures. For references to calculated values (column 3), see text.

In Table IV, the third column gives the values of obtained from detailed calculations of the band structure which have been made for W and Ta by Manning and Chodorow,[2] for Fe by Manning,[23] and for Ni by Slater.[24]

The high values of γ for the transition elements cannot be due to s electrons, for which $\gamma \approx 1 \times 10^{-4}$, and the general trend has been explained by Mott[25] as being due to the unoccupied d states for which the density of states per unit energy range is high.

The only transition metals for which a detailed calculation of the density of states has been made are listed in Table IV, column 3. Whereas in the case of

Ni, the calculated and observed values are in moderate agreement, for Fe, W, and Ta there are large differences, the observed values being much the higher.

One might suppose these high observed values of γ to be associated with low degeneracy temperatures, and as a result the contribution to the specific heat at high temperatures (circa 1200°K for example) to be approximately $3/2k$ per "positive hole" due to the approximate non-degeneracy of the gas at such temperatures. The observed specific heats at high temperatures for W and Ta measured by Mangus and Holtzmann[26] are 6.44 and 6.77 cal./mole-deg. respectively at 1173°K, values which do not appear sufficiently larger than the lattice specific heat (5.959 cal./mole-deg.) at this temperature to allow for a non-degenerate "positive hole" gas. Such a difficulty in correlating the observed low temperature and high temperature electronic specific heats has already been pointed out by Mott and Jones[4] for the case of Pt and Pd, and again more recently by Mott.[27]

An additional difficulty in the case of W and Ta lies in the fact that the excess specific heat over the Debye term at high temperatures as observed by Mangus and Holtzmann[26] is essentially linearly proportional to temperature, given by $c = \alpha T$, where $\alpha = 5.1 \times 10^{-4}$ per mole of W and $\alpha = 7.2 \times 10^{-4}$ per mole of Ta. If one associates this excess specific heat with the electronic contribution[25] rather than being due to anharmonicity terms,[28] then the correlation between these values and those calculated for γ by Manning and Chodorow might appear too close to be entirely fortuitous. It cannot, however, be excluded that the high apparent γ-value of W at low temperatures may be partly due to a hidden transition, as has been suggested to account also for the anomalous lattice specific heat. Such an argument, on the other hand, cannot be applied to Ta for which one
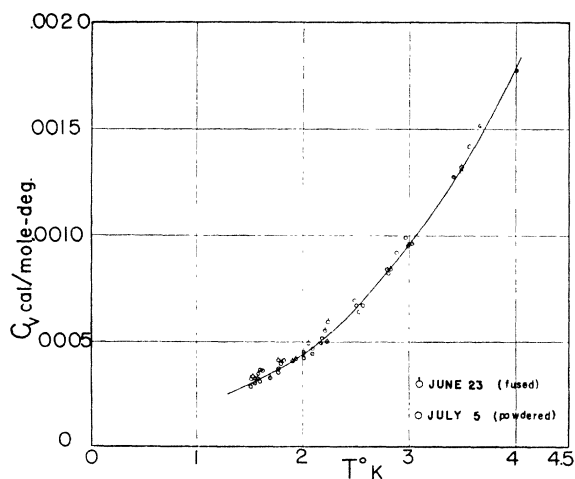

FIG. 2. The specific heat of zinc (powdered and fused) as function of temperature.

[13] Cristescu and F. Simon, Zeits. f. physik. Chemie 25, 273 (1934).
[14] G. L. Pickard, and F. E. Simon, Proc. Phys. Soc. 61, 1 (1948).
[15] J. G. Daunt, and K. Mendelssohn, Proc. Roy. Soc. A160, 127 (1937).
[16] W. H. Keesom, and M. C. Desirant, Physica 8, 273 (1941).
[17] Elson, Grayson Smith, and Wilhelm, Can. J. Research 18, 82 (1940).
[18] G. Duyckaerts, Physica 6, 401 (1939).
[19] W. H. Keesom, and B. Kurrelmeyer, Physica 6,364,633 (1939).
[20] G. Duyckaerts, Physica 6, 817 (1939).
[21] W. H. Keesom and C. W. Clark, Physica 2, 513 (1935).
[22] G. L. Pickard, Nature 138, 123 (1936). (See also reference 14.)
[23] M. F. Manning, Phys. Rev. 63, 190 (1943).
[24] J. C. Slater, Phys. Rev. 49, 537 (1936).
[25] N. F. Mott, Proc. Phys. Soc. 47, 571 (1935). (See references 2 and 4 also.)

[26] A. Mangus and H. Holtzmann, Ann. d. Physik 3, 602 (1929).
[27] N. F. Mott, Proc. Phys. Soc. 62, 416 (1949).
[28] M. Born, and E. Brody, Zeits. f. Physik 6, 132 (1921); 8, 205 (1922).

must suppose the γ-value is due to the normal electronic contribution.

It has been suggested by Mott[27] that the apparent discrepancies between the low temperature and high temperature specific heats of the positive holes could be due to a particular form and filling of the d-band which at high temperatures might result in a lower specific heat than corresponds to the high density of states at low temperatures. No detailed calculation of these effects has been made. It would appear, however, that the low temperature density of states on such a picture would correspond to the values already calculated (see column 3, Table IV) by Manning[2] for which the discrepancy between theory and observation remains.

On the other hand, it has been pointed out by Wigner[29] that the inclusion of the effects of correlation forces would result in an increase in the density of states and hence the high values of γ at low temperatures might be the result of such correlation effects. The necessity for the inclusion of correlation forces to account for the high paramagnetic susceptibilities of Pd and Pt has already been stressed by Mott and Jones.[4] Other transition metals undoubtedly require the inclusion of similar interaction forces to account for their paramagnetism and hence the high value of γ for tungsten and tantalum may be partly due to the existence of such an extra term, a feature which in the case of W may also be reflected in the observed low θ-value. Further specific heat measurements on W with a more extensive temperature range would be, therefore, of value and are being carried out, and additional experimental investigations of the low temperature paramagnetic susceptibility would appear to be of interest in view of these considerations.

(b) Zinc

By considering the observed specific heat (see Fig. 2) to be the sum of a Debye term (AT^3) and an electronic term (γT), we obtain the following evaluation:

$$C_v = 464.5(T/291)^3 + 1.50 \times 10^{-4}T \text{ cal./mole/deg.}$$

Since the maximum temperature employed in the measurements on zinc was less than $(1/50)$ θ (Debye), the T^3 approximation for the lattice specific heat should be valid.[30]

The Debye θ-value of 291°K obtained is in fair agreement with that previously obtained by Keesom and Van den Ende,[31] (320°K), and with that calculated by Gruneisen and Goens,[32] (305°K), from elastic data. The value of γ giving the electronic specific heat is slightly higher than that which can be interpreted from Keesom and Van den Ende's measurements.* It is in

good agreement with the value recently obtained by magnetic measurements on superconducting zinc by Heer and one of us.[5] The value of γ calculated according to the Sommerfeld formula for a perfect electron gas[33] assuming one free electron per atom is 1.43×10^{-4}, whereas, assuming two free electrons per atom the value is 1.80×10^{-4}. The measured value lies between these two values, as might be expected.[34]

The measurements carried out on the zinc in the form of a finely divided powder (average linear dimensions of the particles = 1.3 microns) were made in order to give some indication, or limit to the order of magnitude, of the size at which size effects in the specific heat might appear. From the work of Frohlich[35] variations from the bulk value of γ are not to be expected in metal pieces of 1 micron linear dimension until temperatures of about 10^{-3}°K are reached. For the lattice contribution to the specific heat, however, effects due to the increase of the ratio of surface to volume in small sizes might be expected in the helium temperature region. It is estimated** that for zinc particles of the size used by us differences in the Debye term of about 5 percent might be expected between the specific heats of the fused and powdered samples at 1.5°K. At this temperature, however, it was found that the Debye term only contributed approximately 20 percent to the total specific heat and consequently any variations due to size effects should have been only about 1 percent, which was within the experimental scatter of individual points. As is shown in Fig. 2, the measured specific heat curve for the zinc in powder form is within experimental error identical with that for the zinc in fused form. It is considered, therefore, that size effects in specific heat measurements should be carried out with insulating materials, having Debye θ-values as high or higher than for zinc.

[29] E. Wigner, Tran. Faraday Soc. 34, 678 (1938).
[30] M. Blackman, Proc. Roy. Soc. A149, 117 (1935).
[31] W. H. Keesom and J. N. Van den Ende, Leid. Comm. 219 b; Proc. Roy. Acad. Amsterdam 35, 143 (1932).
[32] E. Gruneisen, and E. Goens, Zeits. f. Physik 26, 250 (1924).
* By plotting C/T against T^2 from Keesom and Van den Ende's measurements, we arrive at a γ-value of 1.25×10^{-4} cal./mole-deg., as against 1.55×10^{-4} cal./mole-deg. as calculated by Burton,

Grayson Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 348, from the same measurements. The discussion given by W. H. Keesom and J. A. Kok, Physica 1, 770 (1934), of Keesom and Van den Ende's measurements also leads to the lower value of γ.
[33] Sommerfeld, Houston, and Eckart, Zeits. f. Physik 47, 1 (1928).
[34] A. Sommerfeld, and H. Bethe, *Handbuch der Physik* 24/2, 33 (1933).
[35] H. Frohlich, Physica 4, 406 (1937).
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