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The Electronic and Lattice Specific Heats in W, Mo, and Re*

M. HOROWITZ AND J. G. DAUNT
Department of Physics and Astronomy, Ohio State University, Columbus, Ohio

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Calorimetric measurements have been made in the temperature range 1°K to 77°K on W, Mo, and Re. At the lowest temperatures for W and Mo the specific heat could be resolved into a lattice T^3 function together with an electric term, γT. It was found that at the lowest temperatures (a), for W, $\theta=250$°K to 380°K and $\gamma=(1.8\pm0.7)\times10^{-4}$ cal/mole-deg^2 (b), for Mo, $\theta=445$°K and $\gamma=(5.1\pm0.4)\times10^{-4}$ cal/mole-deg^2. These new measurements on tungsten indicate the need for revising previously quoted data.

The measured lattice specific heat of tungsten agreed approximately with the theoretical computations made by Fine. The measured lattice specific heat of molybdenum varied with temperature in the manner predicted by Fine for the body-centered cubic lattice of tungsten. The measured electronic specific heat of tungsten was in moderate agreement with the theoretical computation of Manning and Chodorow, and the measured electronic specific heats of W and Mo were considerably less than those of most other transition elements except Cr, a result which may be approximately explained by assuming a *d* band similar to that calculated by Slater. The question of the *d*-band shape is discussed in detail in the light of recent experimental results.

Pure rhenium powder has been measured in the temperature range 68°K to 77°K. At these temperatures the Debye temperature θ was found equal to 262°K.

I. INTRODUCTION

HAVING developed a satisfactory semi-automatic recording calorimeter for low temperature specific heat measurements,[1] it was considered of interest to extend its use to measurements of the specific heats of W and Mo and Re. These metals were of interest in view of the fact that previous measurements had indicated that both the lattice and electronic specific heats in W might be anomalous[2] and in view of the fact that no very low temperature measurements had been previously made on Mo or Re.

The interest in obtaining satisfactory experimental information on the lattice specific heats in metals stems from the fact that in recent years a number of detailed computations have been made of the normal modes of vibration in crystals of various structures. Our previous observations[1] on an f.c.c. structure, namely Pb, showed remarkable agreement between the experimental results and the theoretical predictions. It was therefore considered of interest to extend, as we have done, our measurements to some b.c.c. structures, as represented by W and Mo.

The determination of the electronic energy spectrum in metals is of primary importance in understanding many of their properties, and it is possible to make at least a partial approach to this determination by assessing the electronic density of states through measurements of the electronic specific heats. By making calorimetric measurements of the over-all specific heat of a metal at sufficiently low temperature, it is possible to assess the separate contributions due to the lattice and due to the electron system. It is possible therefore to obtain a great deal of information regarding diverse properties of metals from an extended and intercorrelated study of their specific heats, and the results which we report below on W, Mo, and Re are discussed in their relationship to previous data which has been gathered for other transition elements.

II. THE SPECIMENS

a. The Tungsten Specimens

Two different specimens of tungsten were employed in order to provide a check on the possible effects on their specific heats of the metallurgical processes involved in their fabrication. The first was in the form of a cylindrical rod 1.585 cm in diameter, 7.31 cm long, and of mass 271.17 grams, formed by sintering. The rod was obtained from the Fansteel Corporation, with a stated purity of 99.9 percent. It was actually the same specimen which had been previously measured by Silvidi and Daunt[2] in the liquid helium temperature region and by Horowitz[3] in the liquid hydrogen temperature region. The second specimen was formed from tungsten wire of diameter 0.0501 cm, also obtained from the Fansteel Corporation and having a stated purity of 99.9 percent. The tungsten wire was cut in pieces 5.72 cm long and packed in a cylindrical copper container of height 5.96 cm and diameter 4.44 cm, the total mass of tungsten being 790.7 grams, that of the copper container being 219.0 grams, and that of the soft solder used to seal the container being 7.3 grams. 4.84×10^{-6} moles of helium gas were introduced at room temperature into the container for exchange purposes, and the container then was sealed off. In computing the specific heats, appropriate corrections were always made for the heat capacities of the various

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* Assisted by a contract between the U. S. Atomic Energy Commission and The Ohio State University Research Foundation.

[1] Horowitz, Silvidi, Malaker, and Daunt, Phys. Rev. 88, 1182 (1952).

[2] A. A. Silvidi and J. G. Daunt, Phys. Rev. 77, 125 (1950).

[3] M. Horowitz, Master-of-Science thesis, Ohio State University, 1950 (unpublished).

TABLE I. Data on specific heat of tungsten.

T°K	ΔT°K	C_p cal/mole-deg
Wire at liquid hydrogen temperatures		
20.13	0.313	0.0813
19.84	0.310	0.0866
19.51	0.322	0.0803
19.17	0.338	0.0637
18.86	0.284	0.0626
18.57	0.306	0.0604
18.26	0.306	0.0592
18.02	0.188	0.0454
17.83	0.160	0.0431
17.67	0.169	0.0494
17.50	0.144	0.0518
16.83	0.154	0.0466
16.68	0.145	0.0373
16.53	0.142	0.0345
16.40	0.137	0.0400
16.30	0.0798	0.0418
16.24	0.112	0.0423
16.14	0.0913	0.0425
16.04	0.0983	0.0399
15.94	0.1020	0.0385
15.84	0.1200	0.0395
15.73	0.0932	0.0348
15.64	0.0862	0.0414
15.54	0.0836	0.0402
15.47	0.0813	0.0332
15.37	0.1090	0.0325
15.27	0.0810	0.0321
15.19	0.0982	0.0350
Wire at liquid helium temperatures		
4.180	0.185	0.00257
4.021	0.158	0.00243
3.750	0.130	0.00185
3.607	0.108	0.00170
3.474	0.0885	0.00143
3.341	0.103	0.00162
3.262	0.0858	0.00134
3.185	0.0809	0.00134
3.102	0.0660	0.00122
2.483	0.0506	0.000933
2.387	0.0360	0.000781
2.340	0.0344	0.000848
2.290	0.0268	0.000763
2.125	0.0253	0.000622
2.059	0.0254	0.000656
Rod at liquid helium temperatures		
4.043	0.465	0.00197
2.922	0.240	0.000913
2.733	0.182	0.000896
2.717	0.145	0.000983
2.503	0.169	0.000758
2.270	0.100	0.000599

foreign materials in the specimen and of the heater and thermometer elements.

b. The Molybdenum Specimen

The molybdenum specimen, obtained from the Fansteel Corporation, of purity 99.9 percent, was in the form of a cylinder of height 6.37 cm and diameter 4.11 cm, the total mass being 825.7 grams.

c. The Rhenium Specimen

High purity rhenium powder was obtained on loan from the Department of Chemistry of the University of Tennessee through the kindness of Dr. A. D. Melaven. 107.9 grams of this rhenium powder, of stated purity 99.8 percent, were placed in a copper container of mass 84.9 grams together with 1.02×10^{-5} moles of helium gas for exchange purposes, and the container was sealed off at room temperature. 4.8 grams of solder were used in sealing up the container.

III. EXPERIMENTAL PROCEDURES

The specific heats of all the specimens were measured using the same adiabatic calorimeter as described previously by us.[1] The electrical heaters on the specimens were wound from manganin wire of diameter 0.0079 cm. All the measurements of temperature, except those on the tungsten rod, were made using 10-ohm carbon radio resistors, as we have successfully employed previously[1] and as have been described by Clement and Quinnell[4] and by Brown, Zemansky, and Boorse.[5] The resistance thermometer used with the tungsten rod specimen was a leaded phosphor-bronze wire of diameter 0.00508 cm and resistance 17.0 ohms at 0°C.

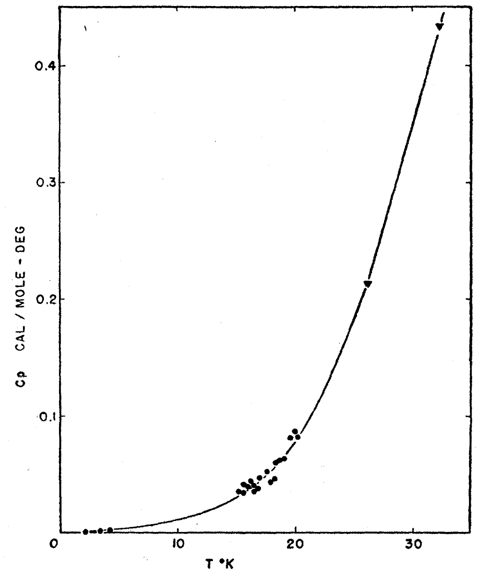

FIG. 1. The specific heat of tungsten below 32°K. ● Our observations. ▼ Lange (reference 6).

The same semi-automatic temperature recording system was employed as that used previously by us in specific heat measurements on Pb,[1] a system which we have found provides high accuracy of measurement. In the measurements the temperature differences between the specimen and its surroundings were always kept less than 0.3°K, a feature which minimized unwanted heat flows to and from the specimen.

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[4] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[5] Brown, Zemansky, and Boorse, Phys. Rev. **84**, 1050 (1951).

IV. RESULTS

Our results for C_p for tungsten, molybdenum, and rhenium are given in Tables I, II, and III respectively. The temperature given in the first columns is the average temperature of each measurement and ΔT is the observed temperature rise.

A graph showing the specific heat of tungsten in the range 1°K to 32°K is given in Fig. 1. The points shown in the figure for temperatures below 21°K are taken from our present results and those above 21°K are from Lange's measurements made in 1924.[6] It will be seen that a smooth curve, showing no indications of any anomalies, can be drawn through all the points. Moreover, the measurements reported here in the liquid hydrogen temperature range are in general agreement with unpublished data obtained earlier by one of us.[7]

Our results below 5°K are graphically displayed in Fig. 2 which plots C_v/T *versus* T^2 and it will be seen that, although there is some scatter, these results do not refute the possibility which one expects theoretically that C_v/T should be a linear function of T^2. These results, together with the previous measurements[3] in the liquid hydrogen temperature range, indicate that there is no systematic difference in the specific heats of the two different forms of tungsten used.

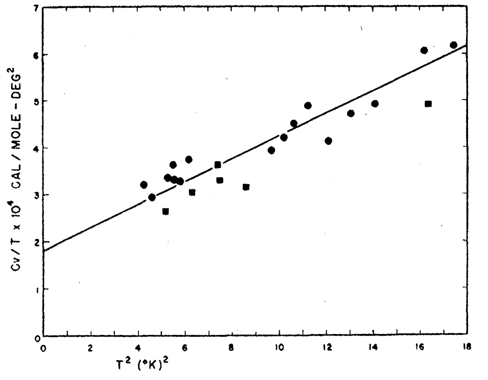

FIG. 2. C_v/T *versus* T^2 for tungsten below 5°K. ● Our observations on wire specimen. ■ Our observations on rod specimen.

Our results for molybdenum are shown in Fig. 3, which plots C_v/T *versus* T^2. If these results, together with the earlier measurements of Simon and Zeidler,[8] are plotted on a more extensive temperature scale than that given in Fig. 3, it will be found that a smooth curve with no indications of anomalies can describe all the data.

The results for rhenium in the temperature range 68°K to 77°K are shown in Fig. 4. We were unable to obtain satisfactory specific heat measurements in the liquid helium and liquid hydrogen temperature range on the rhenium specimen owing, it is thought, to the rather long relaxation times necessary for the establishment of temperature equilibrium in the powder.

V. INTERPRETATION OF RESULTS

a. Tungsten

If it is supposed that at sufficiently low temperatures the specific heat can be written as[9]

$$C_p = C_v = 464.4(T/\theta)^3 + \gamma T \text{ cal/mole-deg}, \tag{1}$$

where the first term represents the lattice specific heat and the second term that of the electrons, then a plot of C_v/T *versus* T^2 should yield a straight line, the intercept of which with the ordinate axis should yield the numerical value of γ.

TABLE II. Data on specific heat of molybdenum.

T°K	ΔT°K	C_p cal/mole-deg
10.445	0.488	0.0125
9.910	0.574	0.0107
9.429	0.263	0.00915
9.179	0.344	0.00880
4.873	0.0915	0.00293
4.769	0.0824	0.00295
4.603	0.0831	0.00259
4.495	0.0618	0.00279
3.478	0.0689	0.00200
2.980	0.0688	0.00162
2.878	0.0618	0.00148
2.741	0.0543	0.00153
2.523	0.0503	0.00145
2.412	0.0467	0.00141
1.420	0.0229	0.000742
1.392	0.0233	0.000724
1.365	0.0149	0.000742
1.339	0.0141	0.000692

TABLE III. Data on specific heat of rhenium.

T°K	ΔT°K	C_p cal/mole-deg
	At liquid nitrogen temperatures	
77.1	0.363	3.29
76.9	0.285	3.49
71.9	0.885	3.27
70.9	0.785	3.35
70.2	0.369	3.37
70.0	0.317	3.10
69.7	0.388	3.19
69.4	0.373	3.23
69.0	0.303	3.23
68.6	0.335	3.26
68.0	0.267	3.15

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[6] F. Lange, Z. Physik. Chem. **110**, 343 (1924).

[7] This earlier work by M. Horowitz (see reference 3) was undertaken partly to investigate the possible influence of an externally applied magnetic field on the specific heat of W between 10°K and 20°K. No evidence of any influence of fields up to 5200 gauss was observed.

[8] F. Simon and W. Zeidler, Z. Physik. Chem. **123**, 383 (1926).

[9] For the range of temperature discussed in this paper ($T<80$°K), C_p is equal to C_v in metals with high accuracy. The largest difference between C_p and C_v occurring in the present work is for Re at 75°K where the difference amounts only to 0.1 percent of C_p. In the discussion that follows, therefore, C_p and C_v are used indiscriminately.

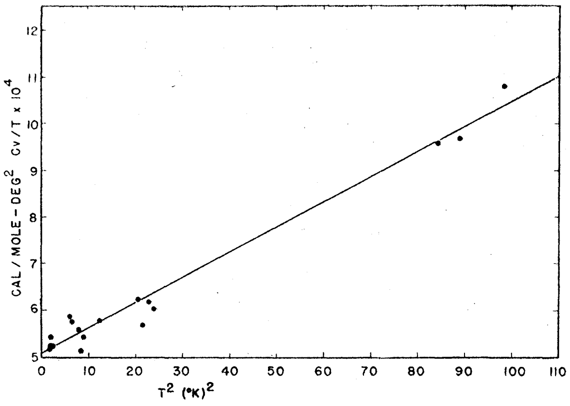

FIG. 3. C_v/T *versus* T^2 for molybdenum below 10°K.

Such a plot of C_v/T *versus* T^2 from our results on tungsten is shown in Fig. 2. Here it will be seen that, if a straight line drawn through the observed points, then a numerical value of γ of 1.8×10^{-4} cal/mole-deg^2 can be obtained. Owing, unfortunately, to the scatter of the points, the value of γ cannot be stated with an accuracy greater than $\pm0.7\times10^{-4}$ cal/mole-deg^2. Our results indicate, however, that the value of γ could not be much greater than 2.5×10^{-4} cal/mole-deg^2, a value which is very much smaller than that reported previously by Silvidi and Daunt.[2] Owing to the more accurate semiautomatic temperature recording instrumentation used for our present observations, we feel that the present results are the more trustworthy.

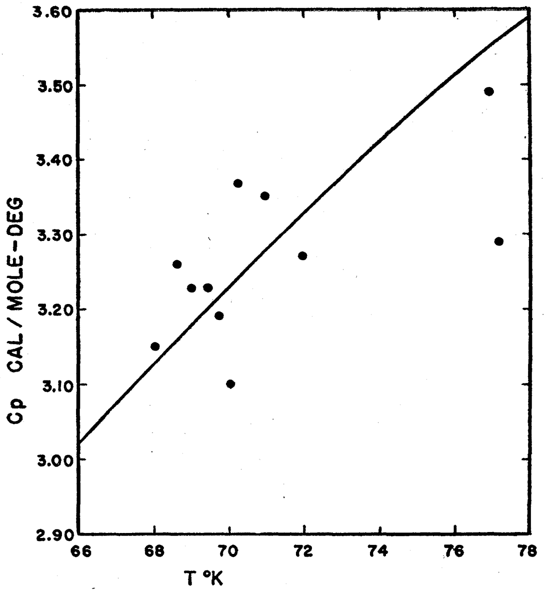

FIG. 4. The specific heat of rhenium at liquid nitrogen temperatures. ● Our observations. ——— Fitted Debye curve ($\theta=262$°K).

In order to describe the variation of the lattice specific heat with temperature, we have computed the characteristic Debye θ temperatures corresponding to each measured point. In doing this the electronic specific heat was first subtracted off the observed total specific heat, and then the Debye θ value obtained by comparing the remainder with the tabulated Debye function.[10] The results of these computations for tungsten are shown in Fig. 5, in which the values due

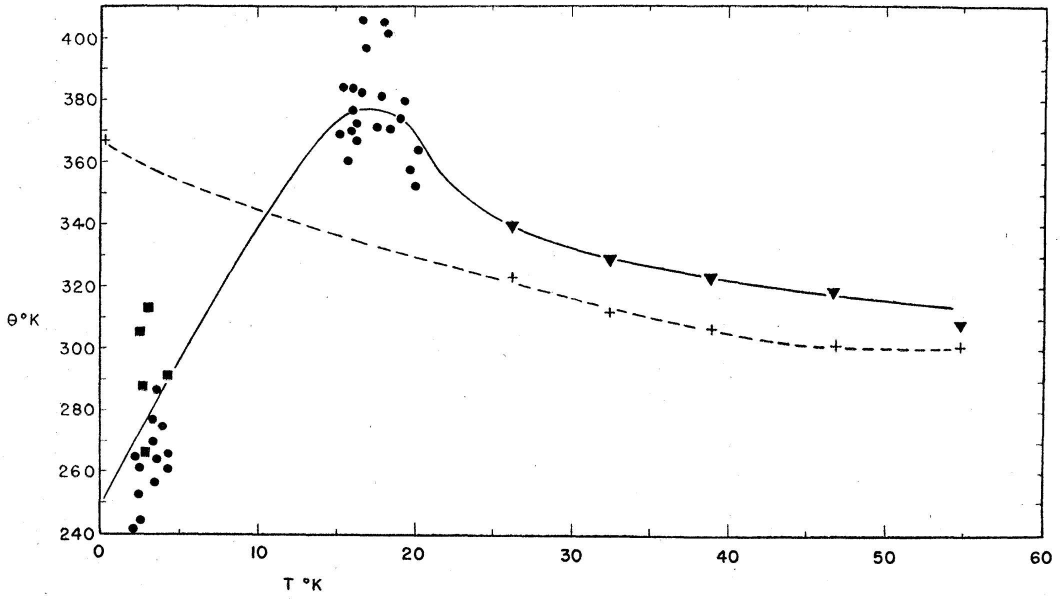

FIG. 5. Debye temperature for tungsten below 55°K. ● Our observations on wire specimen. ■ Our observations on rod specimen. ▼ Lange (reference 6). - - - + - - - Theory (fine, atomic model, reference 20). —Best fit measured points.

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[10] P. Debye, Ann. Physik 39, 789 (1912).

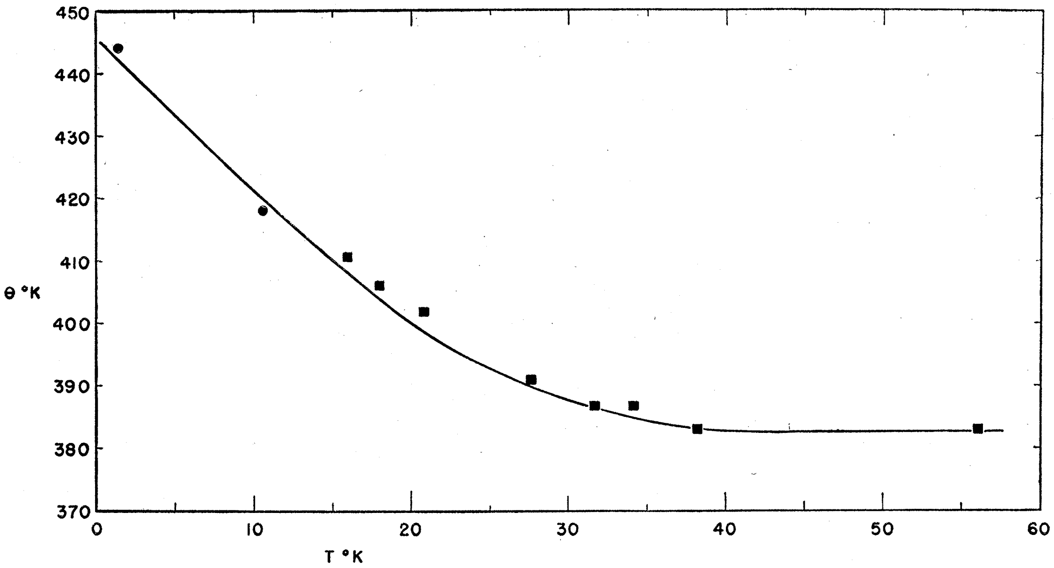

FIG. 6. Debye temperatures for molybdenum below 60°K. ● Our observations. ■ Simon and Zeidler (reference 8).

to Lange[6] in the temperature range 25°K to 55°K are also included. Our results for the tungsten rod and for the tungsten wire specimen, indicated by the squares and circles respectively, show some scatter. In the helium temperature range, where the scatter is most apparent, it must be remembered that relatively small variations in the chosen γ value will yield large variations in the Debye θ value.[11] The scatter, therefore, is a reflection of the uncertainty in the γ value for the electronic specific heat. In Fig. 5 the full curve indicates the best fit through the measured points and shows that the Debye θ value rises from a value of about 250°K at absolute zero to a maximum at about 18°K of approximately 375°K and then falls slowly and continuously to an approximately temperature independent value of 320°K at 55°K. This variation of the Debye θ values with temperature follows the general predictions given by Blackman[12] and is discussed in more detail in Sec. VI.

b. Molybdenum

The curve for C_v/T *versus* T^2 for molybdenum shown in Fig. 3 appears adequately linear to enable an estimate to be made of the electronic γ value by linear extrapolation to the absolute zero. By so doing we assess the γ value to be 5.1×10^{-4} cal/mole-deg$^2\pm0.4\times10^{-4}$ cal/mole-deg^2.

The Debye θ values for the lattice specific heat of molybdenum have been computed from the observed results in the manner described above for tungsten and the smoothed results are shown in Fig. 6. In obtaining the data for Fig. 6 we used both our own results described in this paper and the specific heat data above 15°K previously reported by Simon and Zeidler.[8] The curve in Fig. 6 indicates that the Debye θ value has its highest value at about 445°K at the absolute zero and that as the temperature increases the θ value decreases monotonically and appears to reach a steady temperature independent value of about 383°K at 55°K.

c. Rhenium

The points of Fig. 4 show the observed values of C_p for rhenium as a function of temperature, and the full curve represents what would be expected from Debye's theory for a θ value of 262°K. This value of $\theta=262$°K is somewhat lower than the value obtained by Meissner[13] of 310°K from resistance measurements. It is in agreement, however, with the value of 275°K which can be

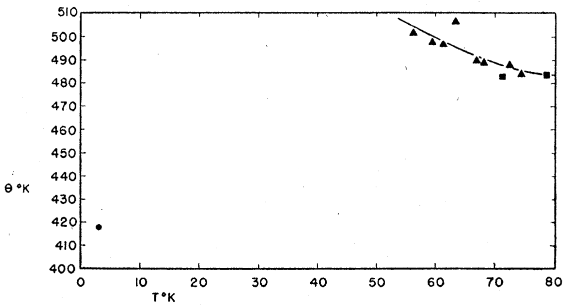

FIG. 7 Debye temperatures for chromium below 80°K. ● Estermann, Friedberg, and Goldman (reference 17). ▲ Anderson (reference 16). ■ Simon and Ruhemann (reference 15).

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[11] If, for example, a value of $\gamma=2.5\times10^{-4}$ cal/mole-deg^2 were chosen instead of 1.8×10^{-4} cal/mole-deg^2, then the θ values would increase and center about 380°K.

[12] M. Blackman, Repts. Progr. Phys. 8, 11 (1941).

[13] W. Meissner, *Handbuch der experimentalphysik* (Akademische Verlagsgisellschaft, Leipzig, 1935), Vol. 11/2, p. 50.

TABLE IV. Calorimetric data for the transition elements.

No. of valence electrons	4	5	6	7	8	9	10
Element	Ti	V	Cr	Mn	Fe	Co	Ni
Crystal structure	h.c.p.	b.c.c.	b.c.c.	complex	b.c.c.	f.c.c.	f.c.c.
γ cal/mole-deg$^2\times 10^4$	8.0(1.1)[a]	15(22.2)	3.80	42	12.0	12.0	17.4
θ°K	280	326	418	410[b]	464	443	413
Melting point °K	2073	1988	2070	1533	1812	1768	1728
Element	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Crystal structure	h.c.p.	b.c.c.	b.c.c.	h.c.p.	h.c.p.	f.c.c.	f.c.c
γ cal/mole-deg$^2\times 10^4$	6.92(3.92)[c]	21	5.1	–	3.04	–	31.0
θ°K	265	254	445	–	426	370	275
Melting point °K	1973	2223	2893	–	2723	2239	1828
Element	Hf	Ta	W	Re	Os	Ir	Pt
Crystal structure	h.c.p.	b.c.c.	b.c.c.	h.c.p.	h.c.p.	f.c.c.	f.c.c.
γ cal/mole-deg$^2\times 10^4$	–	14.1	1.8–2.5	4.6	2.7	–	16.0
θ°K	213	264	250–380	262	256	285	233
Melting point °K	2480	3123	3673	3713	2973	2727	2046

[a] Value of 1.1 obtained from magnetic measurements on superconducting Ti.[28]
[b] 410°K given by Elson *et al.* (reference 31). Shomate (reference 32) and Kelly (J. Am. Chem. Soc. **61**, 203 (1939)), from measurements above 54°K, give θ = 344°K.
[c] Value of 3.92 obtained from magnetic measurements on superconducting Zr.[29]

deduced from the recent calorimetric observations of Cobble, Smith, and Oliver.[14]

Owing to the relatively small range of temperature over which we took our measurements, no significant estimate can be made of the possible variation of θ with temperature.

VI. DISCUSSION

a. The Lattice Specific Heats of W, Mo, and Cr

It is of interest to consider together the lattice specific heats of W, Mo, and Cr since they all fall in the same group VI of the Periodic Table and since they are all b.c.c. structures.

Whereas the experimental data on W and Mo is reported above (see Figs. 5 and 6), that on Cr has previously been given by Simon and Ruhemann[15] and by Anderson[16] for temperatures above 55°K and by Estermann, Friedberg, and Goldman[17] for the liquid helium temperature range only. Unfortunately, no data are available for the temperature range between 4°K and 55°K. Figure 7 shows the Debye θ values as a function of temperature for Cr taken from these references.

In a previous paper, reporting measurements of the specific heat of Pb, we showed that there was excellent agreement between the measured lattice specific heat over a broad range of temperature from 1°K to 80°K and the computed values of the same quantity, the computations being made by Leighton[18] from estimates of the normal modes of vibration of the lattice. Leighton himself showed that for another f.c.c. structure, namely Ag, the agreement between theory and experiment was satisfactory.[19] It is considered of interest therefore to compare such theoretical computations for b.c.c. structures as there are of the variation of θ with temperature, with our experimental results.

The only detailed computations of the normal modes of vibration for a b.c.c. structure are those of Fine[20] for W. These computations are based on the known elastic constants of single crystals of W, as measured by Bridgman.[21] The results of these calculations are shown by the broken curve of Fig. 5. It will be seen that the curve starts from a value of 367°K at 0°K and falls monotonically with increasing temperature to a constant value of approximately 300 at 55°K.

Although the elastic constants for Mo are known,[22] it is not immediately possible to make the necessary computations in view of the fact that the crystal is elastically markedly nonisotropic.[23] The elastic constants for single crystals of Cr are not known.

A computation of the θ value for Mo, using Debye's theory, however, can be made using the known elastic constants[22] and the measured compressibility, and this yields a value of 495°K. This is somewhat larger than our measured values, even at the lowest temperatures.

The comparison between the theory and experiment for the lattice specific heat in W shown in Fig. 5 indicates considerable disagreement at temperatures below

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[14] Private communication from Dr. J. W. Cobble [J. Am. Chem. Soc. (to be published)].

[15] F. Simon and M. Ruhemann, Z. Physik. Chem. **129**, 321 and 338 (1927).

[16] C. T. Anderson, J. Am. Chem. Soc. **59**, 488 (1937).

[17] Estermann, Friedberg, and Goldman, Phys. Rev. **87**, 582 (1952) and Phys. Rev. **85**, 375 (1952).

[18] R. B. Leighton, Revs. Modern Phys. **20**, 165 (1948).

[19] The apparent deviations at about 6°K reported by Leighton have subsequently been essentially removed by the more recent experimental observations of the specific heat of Ag by Keesom and Perlman in this temperature region. [See P. H. Keesom and N. Pearlman, Phys. Rev. **88**, 141 (1952).]

[20] P. C. Fine, Phys. Rev. **56**, 355 (1939).

[21] P. W. Bridgman, Proc. Nat. Acad. Sci. U. S. **10**, 411 (1924).

[22] M. J. Druyvesteyn, Physica **8**, 439 (1941).

[23] For a recent discussion of anisotropy in metals see W. Boas and J. K. Mackenzie. Progr. Metal Phys. **2**, 90 (1950).

about 20°K. This disagreement however may not be as serious as it appears. As pointed out in Sec. V above, there is a considerable latitude in the choice of the γ value and in consequence there is also considerable latitude in the chioce of the appropriate θ value in the liquid helium temperature range. If, for example, the correct γ value were 2.5×10^{-4} cal/mole-deg,^{2} instead of the value of 1.8×10^{-4} chosen earlier, then the θ values would all be considerably increased, and would center about 380°K. This would be in agreement with the theoretical value of Fine.

On the other hand the measurements on Cr, shown in Fig. 7, indicate that the θ values at the lowest temperature fall considerably below what one might expect by extrapolation of the higher temperature values. The apparent maximum in the θ *versus* T curves in Cr and W may therefore be real and may indicate the necessity for further refinement of the theory. The measured θ values for Mo, as shown in Fig. 6, increase monotonically with decreasing temperature to the lowest possible temperatures of observation. It seems therefore that it may not be possible to represent the variation of the lattice specific heat with temperature in these three very similar b.c.c. structures by any general function.

b. The Electronic Specific Heats

Measurement of the electronic specific heats is of interest in that it provides information on the values of the density of states, $N(E)$. The relation between the electronic specific heat, C_{el}, and $N(E)$ is

$$C_{el}=\gamma T=\tfrac{2}{3}\pi^2k^2N(E)T \text{ cal/deg-cm}^3, \qquad (2)$$

where $N(E)$ is the number of electronic energy states per unit energy range per cm^3 at the Fermi level.

In the transition metals, a large contribution to C_{el} is provided by the positive holes in the d band, as was first pointed out by Mott.[24] It is of interest therefore to discuss the evaluations of γ and hence of $N(E)$ for the transition series of metals in order to obtain some picture of the shape of the d bands. The γ values which we have observed in W and Mo are set out, together with those of other transition metals in Table IV. This table, which represents a section of the Periodic Table also displays other measured parameters of interest for each element. The data used in this table have been taken mostly from previous partial compilations by author (J.G.D.),[25–27] which give the references to the original sources. New data have been included as follows: Ti,[28] Zr,[29] Cr,[17] Ru,[30] Os.[30] The γ values quoted in the table for Re, Ru, and Os are somewhat doubtful since it is not certain how reversible were the magnetic superconductive transition curves from which the γ values were computed. It would be of value to have calorimetric measurements carried out on the elements of doubtful γ value listed above, as well as on Tc, Rh, Hf, and Ir.

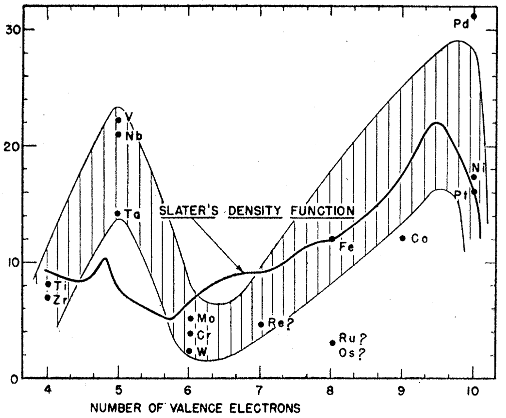

FIG. 8. Electronic specific heats of the transition elements.

All the known experimental results (with the exception of the γ value for Mn) are plotted in Fig. 8 as a function of the total number, n, of "valence" electrons. As is indicated by the shaded areas, the γ values, and hence the $N(E)$ curve, show two distinct maxima as the d band is steadily filled up. Moreover, this general picture is probably valid for all three series of transition elements.

The first maximum occurs for $n=5$, i.e., for V, Nb, and Ta, and the second maximum is at the end of the series for Ni, Pd, and Pt. The value of $\gamma=42\times10^{-4}$ cal/mole-deg^2 obtained by Elson, Grayson-Smith, and Wilhelm[31] from measurements in the relatively high temperature range of from 15°K to 22°K seems to lie well outside these considerations, and remains unexplained.[32]

It is of interest to note the low minimum exhibited at $n=6$ for Cr, Mo, and W and to compare the measured γ value for W with the value of 4.8×10^{-4} cal/mole-deg^2 computed by Manning and Chodorow[33] from a d-band structure computation.

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[24] N. F. Mott, Proc. Phys. Soc. (London) **47**, 571 (1935). See also N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936).

[25] A. A. Silvidi and J. G. Daunt, Phys. Rev. **77**, 125 (1950).

[26] J. G. Daunt, Phys. Rev. **80**, 911 (1950).

[27] J. G. Daunt and T. S. Smith, Phys. Rev. **88**, 309 (1952).

[28] Smith, Gager, and Daunt, Phys. Rev. **89**, 654 (1953).

[29] T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952).

[30] B. B. Goodman, Nature **167**, 111 (1951).

[31] Elson, Grayson-Smith, and Wilhelm, Can. J. Research **18**, 82 (1940).

[32] These measurements were made on so-called "powdered manganese" of unstated purity and of unstated phase. It is possible to have both the α and γ phases stable at low temperatures; [see, e.g., C. H. Shomate, J. Chem. Phys. **13**, 326 (1945)]. The stability of the latter being assisted on an admixture of impurities. The specific heat of the α phase is known to be anomalous (see Shomate above), due probably to the transition to antiferromagnetism at about 100°K as observed by Shull [C. G. Shull and M. K. Wilkinson, Phys. Rev. **86**, 599 (1952)], and this may be a contributory factor in the apparent high γ value. It would be of value to have calorimetric measurements made in the liquid helium temperature region both on α and γ Mn.

[33] M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, 787 (1939).

The probable shape of the $N(E)$ curve illustrated by the shaded areas of Fig. 8 confirms in broad outline the theoretical computation by Krutter[34] and by Slater[35] of the 3d band in Cu. Slater's curve is shown also in Fig. 8, normalized arbitrarily to fit the measured Fe point at $n=8$. Computations subsequently made of the energy band structure by Manning and Chodorow[33] for W, by Manning[36] for Fe (b.c.c.), and by Fletcher and Wohlfarth[37] for Ni also indicate the existence of a second maximum at the smaller n values. In the $N(E)$ curve given by the latter authors this is most marked.

In making such general $N(E)$ curves, as we have given in Fig. 8 by the shaded area, its very approximate nature must be borne in mind, since some modifications must be necessary in going from one crystal structure to another. It is very likely, however, that these modifications would not alter greatly the general picture of the maxima in the curves, but rather as a first approximation affect only the band width, as has been pointed out by Smoluchowski.[38]

The observed low values of γ for all three transition metals of Group 6, namely Cr, Mo, and W, may simply reflect the minimum existing here in the $N(E)$ curve. This view has also been adopted recently by Kriessman,[39] who supports it from his observation of the positive temperature coefficient of the magnetic susceptibility in these metals. An alternative explanation of the low γ values has been suggested by Estermann *et al.*[17] They noted Zener's observation[40] that Cr may be antiferromagnetic and hence have its *d* band split, as was shown to be a general requirement for antiferromagnetism in such metals by Slater,[41] into a filled half and an unfilled half. The filled half would not be able to contribute to the specific heat and hence a low γ value would result. Antiferromagnetism, with a Néel temperature of about 150°C, has indeed been observed by Shull and Wilkinson[42] from neutron diffraction studies. However, they observed no antiferromagnetism in either Mo or W even down to temperatures as low as 20°K, and hence one must conclude that the explanation put forward by Estermann *et al.*[17] for the low γ value of Cr is not generally operative for all the transition metals of Group 6.

One final point should be mentioned, namely the possibility of there being a third maximum in the $N(E)$ curve at $n=7$, i.e., for the Group 7 transition metals Mn, Tc, and Re. In the rough drawing of the $N(E)$ curve of Fig. 8 this possibility has not been included. It should be noted that, besides the unexplained high γ value for Mn,[32] the temperature coefficients of the magnetic susceptibility of Mn and Tc are negative.[43] This could mean, as pointed out by Kriessman,[39] that the γ values are passing through a maximum. Against this, however, the magnetic susceptibility of Re is known to be temperature independent,[44] thereby disposing of the requirement of a maximum in the $N(E)$ curve for this metal. Exact calorimetric measurements on these metals to liquid helium temperatures are therefore highly desirable.

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