infinite layers or perpendicular to ξ-axis, each shell being one cell thick. The contribution to the potential at the origin from one such shell when n is large, will be given by

$$s_n=(-1)^n(\tfrac{1}{2}\tau_n-\tau_{n+1}+\tfrac{1}{2}\tau_{n+2}), \quad (2)$$

in which n will be consistently even for all the shells, or consistently odd, depending on how the unit cell has been chosen, whether with a negative ion at the center or with a positive ion there. n will take both positive and negative values, s_n obviously tends to zero as n becomes large, and the sum of the series $\sum s_n$, n increasing in steps of 2, is finite, as it is the sum of an absolutely convergent series. In other words, depending on the particular choice of the cubic unit cell, the resulting absolutely convergent series $\sum s_n$ will have different sums S_{I} and S_{II} the difference between them being $\tau_{n+1}-\tau_n=-\pi/2$. The same result can also be obtained by grouping the unit cells into cubic shells about the origin as center, each shell being again one cell thick. Thus the rearrangement of the terms of the series (1) involved in grouping them into cubic cells alters the sum.

As we mentioned earlier the positive and the negative ions in CsCl separate out in layers parallel to faces of the type {100}. Any unit cell whose faces are parallel to these faces will not therefore be suitable for our present purpose. The condition stated above requiring the electrical neutrality of the faces of the unit cell is to preclude such a choice.

On the other hand when the parallelopiped described above is chosen as the unit cell, there can be no such separation of charges. The resulting absolutely convergent series, besides giving the same sum S as the original series, is also found to be rapidly convergent, and can therefore be used conveniently for the numerical computation of S.

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The Specific Heats of Several Metals between 1.8° and 4.2°K*

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The specific heats of magnesium, titanium, zirconium, and chromium have been measured between 1.8° and 4.2°K by the vacuum calorimeter method. In each case it has been possible to represent the results by an expression containing an electronic term linear in the temperature and a lattice term cubic in the temperature. The electronic contribution to the specific heats of these metals is in reasonable agreement with expectations based on the Sommerfeld theory and, in particular, with the results of more recent detailed calculations of energy bands in transition metals.

This work has been facilitated by the development of a sensitive semiconducting resistance thermometer of germanium-indium alloy for use at liquid helium temperatures.

INTRODUCTION

THROUGH measurements at liquid helium temperatures it is possible to separate with reasonable certainty the contributions to the specific heat of a metal originating in its lattice vibrations from those originating in the motion of its conduction electrons. Analysis of these quantities results in the determination of a value of the characteristic temperature of the lattice approximating the low temperature limit of that parameter and the density of electronic energy states at the top of the filled portion of the conduction band of the metal.

In the work to be described measurements have been carried out between 1.8° and 4.2°K. The substances whose specific heats have been determined are representative of Groups Ib, IIa, IVa, and VIa of the periodic table. Included are copper, magnesium, and the transition metals zirconium, titanium, and chromium. With the exception of copper they are substances on which no specific heat measurements have previously been made at these temperatures. Facts which have directed attention to these particular metals will be discussed in connection with descriptions of the individual samples.

THEORETICAL

The specific heat of a metal at sufficiently low temperatures varies with the temperature according to a relation of the form $C_v=\gamma T+\beta T^3$. The term γT has been shown[1] to represent the contribution of the conduction electrons of the metal, while the term βT^3 corresponds to the contribution of its atoms vibrating harmonically about their lattice positions.

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[1] A. Sommerfeld, Z. Physik 47, 1 (1928).

Debye's theory of the lattice specific heat[2] is based on the assumption that the vibrational spectrum of a lattice of discrete particles may be approximated by that of an elastic continuum. A formula for the variation of C_v with T is obtained which contains a single parameter θ, the Debye characteristic temperature, related directly to the elastic constants of the continuum model representing a crystal. The value of θ is presumably independent of the temperature. In magnitude it is of the order of several hundred degrees for most solids. For temperatures below about $\theta/12$ Debye's formula reduces to βT^3 where $\beta = 464.5/\theta^3$, C_v being in units of cal/deg, mole.

Blackman[3] and others have shown that deviations from the simple Debye theory observed at low temperatures result from the fact that the vibrational spectra of real crystal lattices are much more complex than that of the continuum model. The consequences of this complexity may be included within the formalism of Debye's theory by allowing θ to vary with the temperature. Theoretical calculation and experiment indicate that, generally, θ will approach a constant value at high temperatures, decrease or increase continuously with decreasing temperature, pass through a minimum or maximum, and assume a constant value again only within a few degrees of absolute zero. This low temperature limiting value of θ generally differs from the high temperature quantity. Blackman[4] estimates that it is reached only at temperatures below the order of $\theta/50$ (where θ is the high temperature value).

At liquid helium temperatures the electronic term γT will be comparable with βT^3. Fortunately, it is here that we can assume θ to take on a constant value for most substances. Thus it becomes a simple matter to determine γ and β in the expression for C_v if we limit our measurements to the helium range. A plot of C_v/T *vs* T^2 will then determine a straight line whose slope is β and whose intercept on the C_v/T axis is γ.

The results of the present measurements have been analyzed in this manner. The assumption that θ remains constant throughout the helium range has been found to be justified in each case. In the discussion of these results the θ-values obtained will be compared with θ-values at higher temperatures where possible.

The coefficient γ of the electronic term is directly related to the density of electronic energy states at the level in the conduction band of a solid to which that band would be filled with electrons at 0°K, i.e., the Fermi level, E_0. It may be shown[5] that for a band of arbitrary form partially filled with electrons,

$$C_v(\text{elect.}) = \gamma T = \tfrac{2}{3}\pi^2 k^2 N(E_0) T \text{ cal/deg, cm}^3, \quad (1)$$

where k is Boltzmann's constant and $N(E_0)$ is the number of energy states per unit energy per cm^3 at the Fermi level.

To permit direct comparison with the observed quantities C_v(elect.) should be expressed in units of cal/deg, mole. Multiplying Eq. (1) by Avogadro's number L and dividing by the number of atoms per cm^3, n_a, we get

$$\begin{aligned} C_v(\text{elect.}) &= \tfrac{2}{3}\pi^2 k[N(E_0)/n_a]RT \\ &= 17.9\times 10^{-16}[N(E_0)/n_a]T \text{ cal/deg, mole.} \quad (2) \end{aligned}$$

A convenient measure of the density of states at the Fermi level is the number of energy levels/atom-ev, which is simply

$$N(E_0)/(n_a \times 1.59\times 10^{-12}) = 8.9\times 10^2 \times \gamma. \quad (3)$$

EXPERIMENTAL

The vacuum calorimeter method of Nernst and Eucken as adapted by Keesom and his collaborators[6] has been used almost exclusively for the determination of the specific heats of solids at liquid helium temperatures. Descriptions of such apparatus and discussions of the problems associated with its use are given in numerous references.[7] The experimental arrangement used in the present work involves no basic departure from previous designs. Some details, particularly those concerning temperature measurement, are thought to be of interest, however, and are therefore included here.

a. The Calorimeter

Samples of the metals studied were prepared in the form of solid polycrystalline cylinders about 3.5 cm high and 2.0 cm in diameter. A heater coil (No. 39 Manganin wire, resistance at 300°K: 100Ω) was wound on each sample and cemented to it with thin layers of Glyptal lacquer to insure good thermal contact. A germanium resistance thermometer, which will be described, was applied to the polished bottom of the sample. The cylinder was covered with a thin radiation shield of aluminum foil and suspended by three fine threads inside a copper can immersed in a liquid helium bath. The usual provisions were made to permit the can either to be very highly evacuated or filled with helium gas to transfer heat from the sample to the bath. The temperature of the helium bath could be reduced by pumping, permitting the sample to be cooled to the temperature at which measurements were begun. Evacuation of the transfer gas isolated the sample thermally except for a small heat flow through the electrical leads.

Known heat increments were applied to the samples for periods timed to 0.01 sec by a special synchronous

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

[3] See the review article, M. Blackman, Reports on Progress in Physics VIII, 11, (1941), in which complete references on the theory of lattice specific heats are given.

[4] M. Blackman, Proc. Roy. Soc. (London) **A149**, 117 (1935).

[5] See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1936), p. 185.

[6] W. H. Keesom and V. N. Van den Ende, Proc. Acad. Sci. Amsterdam **33**, 243 (1930); **35**, 143 (1932); W. H. Keesom and K. Clusius, Proc. Acad. Sci. Amsterdam **35**, 309 (1932).

[7] See, for example, Burton, Grayson-Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 126.

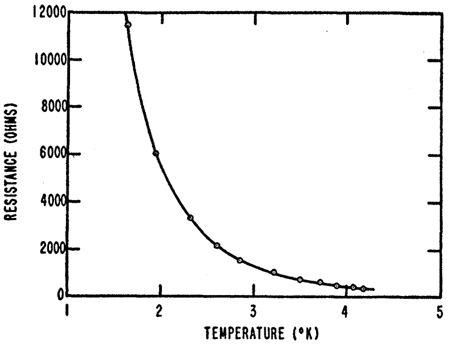

FIG. 1. Calibration curve for the germanium thermometer.

electric stopclock. By measuring the temperature at 15-second intervals before, during, and after a heating, sufficient information was obtained to permit correction of the observed temperature rise for unavoidable heat exchange between sample and bath. The specific heat was thus determined at the mean temperature of each heating period. The process was repeated throughout the helium range, the bath temperature being chosen for a given set of points so as to produce a minimum of heat exchange.

The liquid helium Dewar used in this work was totally immersed in a liquid nitrogen bath. To permit this the top of the Dewar was sealed to a Kovar ring carrying a copper flange. A copper cap through which passed the pumping lines and electrical leads was soldered to the flange with Wood's metal. Liquid helium was transferred directly into the precooled cryostat from a Collins liquefier by inserting the latter's transfer tube through the cap by way of the pumping tube.

b. The Semiconducting Resistance Thermometer[8]

The dynamical nature of calorimetry at helium temperatures with the vacuum calorimeter makes it practically mandatory that an electrical secondary thermometer of some sort be used. At present resistance thermometers of phosphor bronze, constantan, and carbon in various forms of sufficient sensitivity and reliability are available. None of these, however, could be said to combine in a completely satisfactory manner the characteristics: high temperature sensitivity, reproducibility, and insensitivity to measuring current and external fields.

Recent studies of the properties of the semiconductors germanium and silicon have resulted in the preparation of specimens of these materials having a wide range of resistivity characteristics. Estermann[9] has surveyed the resistivities of a large number of samples (both n and p type between 1.8° and 20°K) of these materials containing various amounts of added impurities. It was found that samples with moderate impurity concentration ($\sim 2\times 10^{17}$ impurity centers/cm^3 for Ge) and room temperature resistivities of about 0.05 ohm-cm often have large temperature coefficients of resistivity in the helium range. As thermometers these samples were found to be reproducible to within 0.01°K after warming to room temperature.

Guided by these results, a further survey was made of the resistivities of samples cut from an ingot of germanium containing 0.001 atomic percent indium. The ingot had been cooled slowly, and consequently the concentration of impurities was found to vary continuously along its vertical axis. By slicing the ingot perpendicular to the vertical axis it was possible to obtain layers of the material 1 mm thick of rather high homogeneity, each of which contained a slightly different amount of indium.

Samples 10 mm$\times$3 mm$\times$1 mm were cut from each layer. Current leads were soldered to their end surfaces and potential leads soldered to form two parallel line contacts 6 mm apart on one surface. The resistivity of a sample at 300°K increased with its original distance from the bottom of the ingot. Those of the topmost samples were about 0.09 ohm cm, while those of lower samples were all less than 0.05 ohm cm.

Between 1.6° and 4.2°K only the specimens from the top layer of the ingot showed large temperature coefficients of resistivity. Typical values of $(1/R)(dR/dT)$ for these samples are -1 per °K at 4°K and -370 per °K at 2°K. In spite of repeated warmings from liquid helium to room temperature, several of them exhibited reproducibility as resistance thermometers of 0.001°K throughout the helium range. In addition their resistances were found to be relatively insensitive to the size of the measuring current used. No measurable difference was found between resistance curves obtained with measuring currents of 0.01 and 0.1 ma.

Hall effect measurements at room temperature on samples from the top layer of the ingot show a hole concentration of about 1.5×10^{17}/cm^3 in agreement with the indications of the original survey. The improvement in reproducibility observed in these specimens is apparently associated with their higher room-temperature resistivity as compared with the preliminary criterion of 0.05 ohm cm.

A resistance thermometer for use with the calorimeter was chosen from among the germanium strips described above. Satisfactory thermal contact between the thermometer and the calorimetric samples was achieved by pressing the smooth side of the germanium strip against the flat bottom surface of the metallic cylinder with a simple clamp. This consisted of a small rectangular Plexiglas bar passing over the thermometer (perpendicular to its long axis) and fastened to the sample by means of small screws through either end. A thin mica sheet between the thermometer and metal provided electrical insulation while permitting heat flow. The same thermometer and clamp assembly was used with each sample.

The thermometer was calibrated against the vapor

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[8] A preliminary account of the work of this section was reported in abstract form by S. A. Friedberg in Phys. Rev. **82**, 764 (1951).

[9] I. Estermann, Phys. Rev. **78**, 83 (1950).

pressure of the helium bath between 1.6° and 4.2°K by means of the tabulated results of vapor pressure determinations of Schmidt and Keesom.[10] The calibration (measuring current 0.01 ma) is shown in Fig. 1. Checks of the calibration were made at several temperatures in the course of each experimental run. No deviations from the original calibration were observed.

MATERIALS

a. Copper

In order to test the equipment and the operating procedure the specific heat of copper which had been very accurately determined at helium temperatures by Keesom and Kok[11] was measured again. The specimen used in these measurements was not of high enough purity to be strictly comparable with that of the cited investigators. However, measurement of its specific heat does permit an approximate check, at the same time providing information about copper of a particular impurity content which was used subsequently in the fabrication of a capsule to contain granular samples being studied in this laboratory.

Analysis showed the specimen to be about 99.6 percent copper, the principal impurity being lead. Traces of iron, nickel, and silver were also found. The amount of material used was 151.59 g (2.38 mole).

b. Magnesium

The electrical resistivity and magnetic susceptibility of magnesium have been investigated recently at very low temperatures. In both instances the observed effects are striking although not unique. The resistivity[12,13] is found to increase with decreasing temperature after passing through a minimum (near 15°K). The susceptibility[14] varies periodically with magnetic field intensity (de Haas-van Alphen effect). While this effect is qualitatively understood[15] in the metals exhibiting it, the electrical resistivity phenomenon in magnesium still awaits satisfactory theoretical discussion.

Measurements of the specific heat of magnesium below 4°K permit the investigation of the possibility that the resistivity minimum (in magnesium, at least) might be associated with a significant deviation from the electronic band structure as predicted theoretically for the metal and confirmed at room temperatures by soft x-ray studies. It seems probable that peculiarities of the band scheme (such as failure of the $3s$ and $3p$ bands to overlap) which could be correlated with the resistivity minimum would be reflected in an abnormal electronic specific heat, particularly at temperatures below that of the minimum, and so be detectable in the helium region.

A specimen of Dow magnesium having a mass of 29.697 g (1.22 mole) was used. Its purity was stated to be at least 99.96 percent.

c. Titanium and Zirconium

The electronic specific heats of several transition metals have already been measured and are found to be quite high ($\gamma > 10\times 10^{-4}$). These results have received at least qualitative interpretation in the light of the theory of Mott[16] and Slater.[17] A narrow, incompletely filled d band is pictured as overlapping the broad s band of the transition metal. The density of states at the Fermi level, which lies with in the region of overlap of the two bands, is high as a result of the high density of states in the d band. The electronic specific heat is thus much larger than that found for ordinary metals.

The transition metals whose electronic specific heats have previously been measured belong to Groups V through VIII of the periodic table. It is considered of interest to extend these measurements to the transition metals of Group IVa in which the overlapping ds band may be expected to be filled to a relatively low level. This has been made possible through the cooperation of the Oak Ridge National Laboratory of the United States Atomic Energy Commission, which has supplied titanium and zirconium samples of high purity in a form appropriate for study.

The mass of the titanium specimen was 33.622 g (0.702 mole). Its purity exceeded 99 percent.

The zirconium specimen was machined from a crystal bar of the metal having a purity of 99.5 percent. The principal impurity was sodium. The mass of the specimen was 47.538 g (0.521 mole).

d. Chromium

The abnormally high specific heat of chromium at high temperatures,[18] as well as the unusual character of its magnetic[19] and elastic properties, have suggested the desirability of measuring its thermal properties at low temperatures. Of particular interest is the density of electronic states at the Fermi level, a knowledge of which would permit a more critical examination of the magnetic susceptibility curve and of the suggestion that the unusual properties observed might be due to antiferromagnetism as first suggested by Néel[20] and more recently amplified by Zener[21] in contrast with

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[10] G. Schmidt and W. H. Keesom, Leiden Communications 250C (1937).

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

[12] D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A202**, 523 (1950).

[13] Garfunkel, Dunnington, and Serin, Phys. Rev. **79**, 211 (1950).

[14] D. Schoenberg, Proc. of the International Conference on Low Temperature Physics, Oxford, August 1951, p. 134.

[15] M. Blackman, Proc. Roy. Soc. (London) **A166**, 1 (1938); L. Landau, unpublished work quoted by D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

[16] N. F. Mott, Proc. Roy. Soc. (London) **47**, 571 (1935).

[17] J. C. Slater, Phys. Rev. **49**, 537 (1936).

[18] L. D. Armstrong and H. Grayson-Smith, Can. J. Research **A28**, 51 (1950).

[19] T. R. McGuire and C. J. Kriessman, Phys. Rev. **82**, 774 (1951).

[20] L. Néel, Ann. phys. **18**, 5 (1932).

[21] C. Zener, Phys. Rev. **81**, 440 (1951).

the energy band approximation and the Pauli theory of spin paramagnetism in metals.

The specimen studied was prepared by melting down flakes of electrolytic chromium[22] in an argon atmosphere. Machining removed most of the material which had become slightly contaminated with aluminum from the alumina crucible in which the melting was carried out. Analysis indicated a purity of about 99.9 percent with traces of Al, Cu, and Si comprising the major impurities. The specimen had a mass of 75.372 g (1.41 mole).

DISCUSSION OF RESULTS

As shown in Fig. 2, where the experimental data are plotted as C_v/T *vs* T^2, the results for all the metals may be represented by an equation of the form

$$C_v=\gamma T+\beta T^3=\gamma T+464.5(T/\theta)^3 \text{ cal/deg, mole.}$$

From the slopes and the intercepts of the straight lines shown in Fig. 2 the constants γ and θ were calculated. These are given in Table I together with the density of states at the Fermi level $N(E_0)/n_a$, as calculated from Eq. (3). The last column contains values for the m^*/m, wherein m^* is the "effective mass" of the conduction electrons. The calculation of this quantity depends on the form on the band, i.e., the way in which $N(E)$ varies with E. This relation is not generally known for real metals. By assuming a rather restricted model of a metal[23] one obtains the relation

$$N(E)=2\pi(2m^*)^{\frac{3}{2}}/h^3\sqrt{E}, \tag{4}$$

and in particular at the Fermi level

$$N(E_0)=(2\pi m^*)(3n_aq/\pi)^{\frac{1}{3}}, \tag{5}$$

where q is the number of free electrons per atom. This relation is often used with appropriate choice of q for a calculation of m^* from the experimentally determined value of γ. For the values of m^* given in Table I, q was approximated from the chemical valency of the metallic ion in question. Even so, it should be remembered that these calculations are based on the assumption that the conduction band has a quadratic form at the Fermi level, a condition which is generally satisfied only if E_0 lies near the bottom or the top of the band. (In the latter case m^* will be the effective mass of the unfilled holes just above E_0 which may be regarded as conducting particles.) Moreover, the quantity m^* as used here is defined uniquely only within a single band and would lose its meaning if E_0 should lie in a region of overlap between two bands. Thus, though it may be interesting to compare m^* with the free electron mass m in considering the results of the measurements, attention should be directed principally to the quantity $N(E_0)$, whose physical significance is more general.

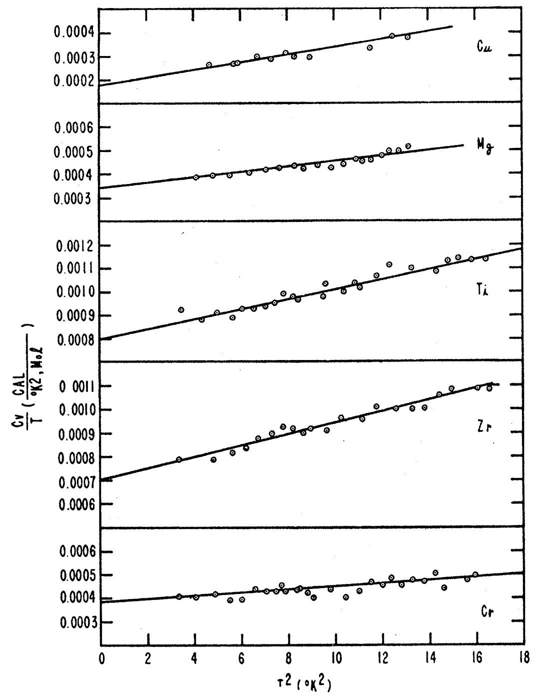

FIG. 2. Specific heat of various metals, plotted as C_v/T *vs* T^2.

a. Copper

The values obtained in this work can be represented by the formula

$$C_v=1.80\times 10^{-4}T+464.5(T/315)^3 \text{ cal/deg, mole.}$$

Keesom and Kok[11] have given

$$C_v=1.777\times 10^{-4}T+464.5(T/335)^3 \text{ cal/deg, mole.}$$

The agreement between these results is rather good, particularly in the electronic terms. Some of the 6 percent discrepancy between the θ-values probably arises from the lead impurity in our sample, which because of its insolubility is deposited in crystalline form on the copper grain boundaries. Owing to its low characteristic temperature ($\theta\approx 90$°K) even a small amount of lead can produce an apparent lowering of the θ-value of the copper, leaving its γ-value unchanged. Correction for 0.4 percent lead would increase the θ-value of our specimen to about 325°K.

b. Magnesium

There appears to be nothing anomalous in the behavior of the C_v *vs* T curve or in the magnitudes of γ and θ which could be interpreted as a link between the peculiarities in the electrical conductivity of the metal and its band structure. On the contrary, both the electronic and lattice contributions appear to agree with expectations based on the observation of the

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[22] We are indebted to Dr. L. C. Hicks of the Allegheny Ludlum Steel Company for supplying this material.

[23] A. H. Wilson, *Semiconductors and Metals* (Cambridge University Press, Cambridge, England, 1939), p. 26.

properties of the metal at higher temperatures and on general theoretical considerations.

The soft x-ray emission data for magnesium at room temperature obtained by O'Bryan and Skinner[24] provide direct confirmation of the picture of overlapping $3s$ and $3p$ bands postulated by the theory of metals to account for the metallic properties of the solid.[25] The Fermi level of magnesium should thus lie in the region of overlap at a point where the density of states may well exceed the value expected for two completely free ($m^*=m$) valence electrons per atom. For the latter case calculation by Eq. (5) would lead to $\gamma=2.43\times10^{-4}$. The observed value of γ is 3.25×10^{-4} corresponding to $N(E_0)/n_a=0.286$ level/atom/ev.

It should be noted that for zinc, another metal having the hexagonal close-packed structure and two valence electrons per atom, the observed[26] value ($\gamma=1.50\times10^{-4}$) is less than the free electron value, $\gamma=1.84\times10^{-4}$. This difference in behavior between magnesium and zinc may be related to the fact that $c/a>1.63$ for zinc and $c/a<1.63$ for magnesium (where c and a are lattice constants and $c/a=1.63$ corresponds to closest packing). Differences in overlap of s and p bands when the axial ratio is changed have been explained by Mott and Jones.[25]

The characteristic temperature, θ, for the magnesium lattice below 4.0°K has been found to be constant at 342°K. We may compare this value with the values obtained by Clusius and Vaughan,[27] whose specific heat measurements for magnesium extended from 11°K to 230°K. Down to 40°K θ was found to be practically constant at 320°K. Between 40°K and 11°K θ increased continuously, apparently approaching a maximum value of about 370°K. The value $\theta=342$°K found below 4°K indicates, therefore, that θ passes through a maximum before reaching a low temperature limiting value. Such behavior has been observed previously for silver.

c. Titanium and Zirconium

The electronic structures of titanium and zirconium are expected to be quite similar, since zirconium lies directly beneath titanium in Group IVa of the periodic table. These elements are characterized in the atomic state by outer s shells filled with two electrons and next lower d shells containing only two of a possible ten electrons. In the metallic state, according to the picture developed by Mott and by Slater for other transition metals, one would expect the d and s states of these atoms to form overlapping bands. The bands produced by N atoms would consist of a wide s band containing $2N$ states and a narrow d band having $10N$ states, thus leading to a high density of states at the Fermi level. Since for both titanium and zirconium there are available only $4N$ electrons to go into the combined d-s bands, their Fermi levels probably lie somewhere in the region of overlap. Because of the high density of states in the d band, $N(E_0)$ should be higher than for the equivalent situation with free electrons. Slater and Krutter[28] and more recently Fletcher and Wohlfarth[29] have calculated the band shape for the overlapping s and p bands of copper and nickel, respectively. It is reasonable to extrapolate their results back to the other elements of the first transition series. On this basis one would expect to obtain a reasonably large density of states for titanium but perhaps not as large as for the later elements of the series, e.g., manganese and iron. As shown in Table I, the values of $N(E_0)/n_a$ for titanium and zirconium obtained in the present measurements are 0.711 and 0.615 level/atom-ev, respectively. These quantities are several times larger than 0.159, the value for copper, while considerably less than 4.00, the value of $N(E_0)n_a$ for manganese.[30] These results are consistent with the simple model for a transition metal given by Mott and Slater.

TABLE I. Summary of results.

Sample	θ(°K)	$\gamma\times10^4$ (cal/°K², mole	$N(E_0)/n_a$ (levels/ atom-ev)	m^*/m
Copper	315	1.80	0.159	1.47
Magnesium	342	3.25	0.286	1.33
Titanium	280	8.00	0.711	3.15
Zirconium	265	6.92	0.615	2.24
Chromium	418	3.80	0.338	2.93

The values of θ found below 4.2°K for titanium and zirconium are 280°K and 265°K, respectively. Until recently the only other values of θ available for these metals were those obtained from electrical resistivity data by Meissner[31] using the semiempirical formula of Grüneisen.[32] Meissner found $\theta=342$°K for titanium and $\theta=288$°K for zirconium. These are essentially average high temperature values which may not be readily compared with the results given above.

Recently, the specific heat of zirconium of high purity has been measured between 14°K and 300°K by Skinner and Johnston.[33] They find a constant value of $\theta=242$°K at least up to the temperatures where C_p and C_v begin to differ appreciably. If, however, C_v includes a term $6.9\times10^{-4}T$ as indicated in the present measurements, a correction must be applied to the

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[24] H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).

[25] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936), p. 161.

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

[27] K. Clusius and J. V. Vaughan, J. Am. Chem. Soc. **52**, 4686 (1930).

[28] H. M. Krutter, Phys. Rev. **48**, 664 (1935); J. C. Slater, Phys. Rev. **49**, 537 (1936).

[29] G. C. Fletcher and E. P. Wohlfarth, Phil. Mag. **42**, 106 (1951).

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

[31] W. Meissner, *Handbuch der Physik* (Springer, Berlin, Germany, 1935), Vol. 11, Chap. 2, p. 50.

[32] G. Grüneisen, Ann. Physik **16**, 530 (1933).

[33] G. B. Skinner and H. L. Johnston, J. Am. Chem. Soc. **73**, 4549 (1951).

observed values of Johnston and Skinner near 14°K. When this is done, θ is found to increase slightly with decreasing temperatures, being equal to 253°K at 14.4°K. The value 265°K observed below 4.2°K is in good agreement with this trend.

Similar higher temperature data are not yet available for titanium. It is to be expected, however, that θ will behave for titanium in roughly the same way as it does for zirconium.

d. Chromium

Chromium is a transition metal which in the atomic state has five electrons in the 3*d* shell and one electron in the 4*s* shell. In the metallic state one would expect the band structure to fit qualitatively into the simple scheme of Mott and Jones, as was the case for titanium and zirconium. Consequently, the γ-value for chromium could be expected to lie near the values for vanadium[34] ($\gamma=15\times10^{-4}$) and manganese[30] ($\gamma=42\times10^{-4}$) which lie on either side of chromium in the periodic table. The observed γ-value for chromium, however, is only 3.80×10^{-4}. The density of states at the Fermi level in chromium is, therefore, much smaller than expected if it is assumed that these three metals have *d-s* bands of the same form containing no abrupt minimum. Our results, however, can be explained on the basis of the band calculations of Slater and Krutter and of Fletcher and Wohlfarth, both of which show a minimum in the $N(E)$ *vs* E curve near the center of the band where the Fermi level in chromium should be located. The experimental data for chromium which at first sight seem to be very low for a transition metal are, in fact, in striking agreement with the calculated band shapes. An alternative explanation of the low γ-value has been suggested by Zener[21] and is based on the possible antiferromagnetism of this metal. It has been suggested by Slater[35] that the energy bands of an antiferromagnetic crystal may be split into two halves separated by a gap, as the result of a periodic perturbation of potential with a period twice the lattice spacing due to the exchange interaction. Such a perturbation is presumed to result from the different potentials experienced by electrons of + or − spin in atoms of like and opposite spin constituting the two sublattices of the typical antiferromagnetic crystal.

According to this view, a band which in the absence of antiferromagnetism would be considered half-full may in the antiferromagnetic case be divided into two halves of which the lowest in energy is completely filled. Electrons in such a filled half-band would thus be unable to contribute to the electrical conductivity of the solid or to its electronic specific heat. The *d* band in chromium may be split in just this way. The five *d* electrons per atom could then just fill the lower half and thus be prevented from contributing to the electronic specific heat. The observed electronic specific heat could, therefore, be attributed to the one *s* electron per atom. The observed γ-value (3.80×10^{-4}) is higher than that found in other metals known to have one *s* electron per atom. It is possible, however, that overlap of the 4*s* and 4*p* bands would produce a density of states at the Fermi level high enough to account for it.

Below 4.2°K the characteristic temperature of the chromium lattice has been found to assume a constant value, $\theta=418$°K. Anderson[36] has measured the specific heat of chromium between 56°K and 291°K and finds that near 56°K, $\theta=485$°K. The discrepancy between these values, although high, is not unreasonable in view of the possible variation of θ with temperature. There seems to be little reason to regard θ as anomalously low for chromium below 4.2°K in the manner discussed for tungsten by Silvidi and Daunt.[26]

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[34] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952). (We are indebted to Dr. A. Wexler of the Westinghouse Research Laboratories for communicating this result to us prior to publication.)

[35] J. C. Slater, Phys. Rev. **82**, 538 (1951).

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