vacuum is considered more reliable than any value previously reported.

In measuring coefficient of linear expansion the total length observable with the comparator was only about 4 mm. Temperature measurements could be made only at room temperature and in the pyrometer range. Transition points, if they exist, lie between these limits. Repeated readings were not satisfactorily consistent. Doubtless the peculiar properties of uranium described at the beginning of this section partially account for the fact. The average value obtained for the coefficient of linear expansion over the range of 25°C to 1000°C is 4×10^{-5}, which is exceptionally large. No other value has appeared in the literature.

ACKNOWLEDGMENTS

Gladly is our indebtedness acknowledged to Dr. H. C. Rentschler, for providing one of the specimens; to the Wisconsin Alumni Research Foundation, for a grant in partial support of the project; and to Dr. H. B. Wahlin, for essential cooperation and assistance continued throughout the course of the experiments.

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Electronic Energy Bands in Metallic Tungsten[1]

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Calculations of the electronic energy bands in metallic tungsten are carried out by the Wigner-Seitz-Slater method. All numerical integrations were carried out on the M. I. T. differential analyzer. It is found that the d band is broken up into five sub-bands. Some of these d bands are found to be about fifteen electron volts in width. One is about two electron volts in width. The occupied energy range extends about five electron volts. The s band starts at a higher energy than the d bands and is occupied by much less than one electron per atom at the equilibrium interatomic distance. From the results of a previous paper, curves of E *vs.* k are plotted for the principal directions of propagation. From these, curves of the number of energy levels per unit energy range were determined by numerical and graphical methods which are described in an appendix. It is assumed that the $n(E)$ curve for tantalum is not greatly different from that for tungsten except that there is one less electron per atom. From the $n(E)$ curves the electronic contribution to the specific heat is calculated for the two metals and the results found to be in good agreement with the excess specific heat at high temperatures for both metals. The computed value does not agree with low temperature data on tantalum. There are no low temperature data for tungsten. Qualitative discussions of the differences in electrical resistance, temperature coefficient of resistance, and thermoelectric power of the two metals are given. The contribution of exchange effects to the paramagnetic susceptibility is treated by a rough model and it is shown that the assumption of the same value of the exchange integral for both metals gives satisfactory agreement with observed data.

CALCULATIONS of the electronic energy bands in solids have been carried out by either the Wigner-Seitz cellular method or by Slater's modification of that method for monovalent metals, for calcium, and for a number of insulators.[2, 3] No calculations by either of these methods have been reported for any transition metals, although some general characteristics have been discussed by Mott[4, 5, 6] in a series of

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[1] A preliminary report of this work was presented at the Washington Meeting of the American Physical Society in April, 1938. Phys. Rev. **53**, 673 (1938).

* This work was started at M. I. T. and some of the senior author's part was done while he was at the University of Toledo, Toledo, Ohio.

[2] Na: E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934). Cu: H. M. Kritter, Phys. Rev. **48**, 664 (1935). Li: F. Seitz, Phys. Rev. **47**, 400 (1935); J. Millman, Phys. Rev. **47**, 286 (1935). Ca: M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937). C: G. E. Kimball, J. Chem. Phys. **3**, 560 (1935); F. Hund, Physik. Zeits. **36**, 888 (1935). C *et al.*: F. Hund and B. Mrowka, Ber. d. Sachs. Akad. d. Wiss. **87**, 185, 325 (1935). LiF: D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936). NaCl: W. Shockley, Phys. Rev. **50**, 754 (1936).

[3] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[4] N. F. Mott, Proc. Phys. Soc. **47**, 571 (1935).

[5] N. F. Mott, Proc. Roy. Soc. **A153**, 699 (1936).

[6] N. F. Mott, Proc. Roy. Soc. **A156**, 368 (1936).

papers and by Jones and Mott[7] in a recent paper which used a different approximation from that used here. In view of the great interest in the transition metals, it was believed that the detailed information obtained by the cellular method would justify the considerable amount of labor required to compute electronic energy bands for a transition element by Slater's method. Tungsten was chosen for this detailed study because of its practical importance and because for this metal there is a large amount of experimental material available. Necessary preliminaries to metallic calculations were self-consistent field calculations. These have been completed and reported in this journal.[8] Another necessary preliminary was the extension of Slater's discussion[3] of the electronic energy bands for the body-centered lattice. In his original paper, Slater used only eight atomic functions and satisfied boundary conditions at the centers of only eight faces of the atomic polyhedron. The difficulty in applying his results to a transition metal is that, in the eight functions, he included only three of the five d functions. Since the transition metals have a partly-filled d shell in the free atom, all of the d bands may be partly occupied in the metal, and hence if only three d functions are included, the band picture may be quite inaccurate. Slater's method has been extended to include boundary conditions at all fourteen faces of the atomic polyhedron. In setting up the wave function for a valence electron, the eight functions used by Slater and in addition the other two d functions, three more f functions, and a g function were included.[9] The details of this work are given in a previous paper to be referred to as *I*. In that paper relations were obtained between the energy of a valence electron and its momentum for important directions of propagation. The relations are transcendental equations in which the momentum k appears in certain tangent factors and the energy appears implicitly in the values of the radial wave functions and their derivatives at the radii corresponding to half the distance between nearest neighbors and at half the distance between next-nearest neighbors. The values of s_1, s_2, s_1', s_2',[10] etc. were found by numerical integration as in the Hartree method of calculating self-consistent fields. The potential used in this calculation was a modified form of that found by self-consistent field calculations for the tungsten atom. For all electrons inside of the $5p$ electron, the charge density used was the same as for the free atom. The results of the self-consistent field calculation for tungsten indicate that in the metal there will be a slight overlapping of the $5p$ wave functions. An attempt was made to allow for this, but it seems probable that it would have been as satisfactory to neglect this effect or allow for it by simply renormalizing the atomic charge density. The self-consistent field results show that nearly three-fourths of the charge density of the two $6s$ electrons in a tungsten atom lies *outside* the atomic sphere for metallic tungsten. This was taken as indicating that in the metal the s band would contain only a small fraction of an electron per atom. The self-consistent field results for the atom also show that about a third of the charge density of the four $5d$ electrons lies outside of the atomic sphere for the metal. Since in going from the atom to the metal a charge of over three electrons must be redistributed, the potential for a valence electron in metallic tungsten will be quite different from the potential of a valence electron in the atom and some correction must be made. As a first approximation to the potential for a valence electron in metallic tungsten, the potential due to the nucleus, inner electrons, and five $5d$ electrons was used. In finding the potential due to the $5d$ electrons, the atomic charge density normalized to the atomic sphere was used.

With this potential, integrations for the d and s functions were carried out. The results of the integration indicated the total width of the d bands to be about one and a half Bohr units,

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[7] H. Jones and N. F. Mott, Proc. Roy. Soc. **A162**, 49 (1937).

[8] M. F. Manning and J. Millman, Phys. Rev. **49**, 848 (1936). M. F. Manning and L. Goldberg, Phys. Rev. **53**, 662 (1938).

[9] M. I. Chodorow and M. F. Manning, Phys. Rev. **52**, 731 (1934). Some errors appear in Table I of this paper. A corrected reprint may be obtained from one of the authors (M. F. M.) at the University of Pittsburgh.

[10] The notation is the same as in the previous paper—s_1 stands for the value of the s function of a given energy at the half-distance between nearest neighbors; s_2 is the value of the s function of a given energy at the half-distance between next nearest neighbors; and s_1' and s_2' are the derivatives with respect to r at the corresponding radii.

and that the bottom of the *s* band is at a considerably higher energy than the bottom of the *d* bands. Since the *s* band is very broad at this inter-atomic distance, the number of electrons per atom in the *s* band is small. Since there are spaces in the *d* bands for ten electrons per atom, these bands will be somewhat more than half-filled in tungsten.

For the next approximation, the same core potential was used as in the first approximation and the charge densities for the other five valence electrons were taken from the results of the first approximation. Since the first approximation shows that the two bottom *d* bands which can accommodate four electrons per atom are quite narrow, the charge distribution for two of the electrons was assumed to be the same as for a *d* function at the bottom of the *d* bands and the charge densities for the other three electrons were assumed to be those found for *d* functions with energies evenly spaced in the lower half of the *d* bands. With this new potential, integrations[11] were again carried out.

As a check on the consistency of the assumptions about the potential, the width of the *d* bands and curves of d' *vs.* E for the different approximations were compared. The discrepancies were so small as to indicate that little change would be produced by further stages of approximation. For the energy range considered, the *d* functions are the most sensitive to changes in the assumed field and hence the field is probably as near to being self-consistent as could be obtained without more elaborate methods of calculation. Furthermore, in the method used here, all exchange and correlation effects are neglected, and they would presumably have more effect than any departures from an exactly self-consistent field.

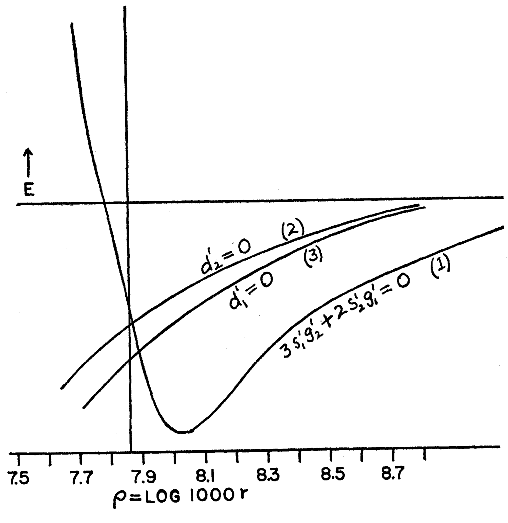

FIG. 1. E *vs.* log r. (E in Bohr units.)

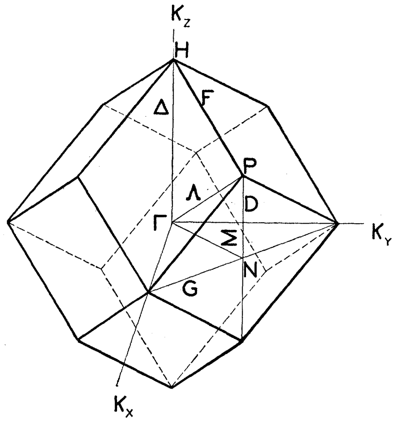

FIG. 2. Brillouin zone for body-centered lattice.

Rough calculations were also made of the way the positions of the bottoms of the various bands change with interatomic distance. Since the potential used in calculating these curves was either that of the free atom or that proper for the normal spacing, the curves of Fig. 1 are to be regarded as schematic. As shown in *I*, there will be three bands beginning at the energy for which $d_1'=0$, two bands beginning at the energy for which $d_2'=0$, and one band beginning at the energy for which $3s_1'g_2'+2s_2'g_1'=0$. There are other bands at higher energies, but they are not occupied under ordinary conditions and probably could not be accurately calculated by the method used here.

For a more detailed discussion of the electronic structure, it is necessary to determine the energy as a function of the momentum. As was discussed in *I*, for a general direction of propagation this would require the solution of a fourteenth-order secular determinant. This is too complicated for practical computation. However, for certain par-

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[11] All of the integrations were carried out on the M. I. T. differential analyzer which was placed at the authors' disposal by Professor S. H. Caldwell of the Department of Electrical Engineering. The authors wish to thank Professor Caldwell and Mr. D. D. Terwilliger for their cooperation during the use of the differential analyzer.

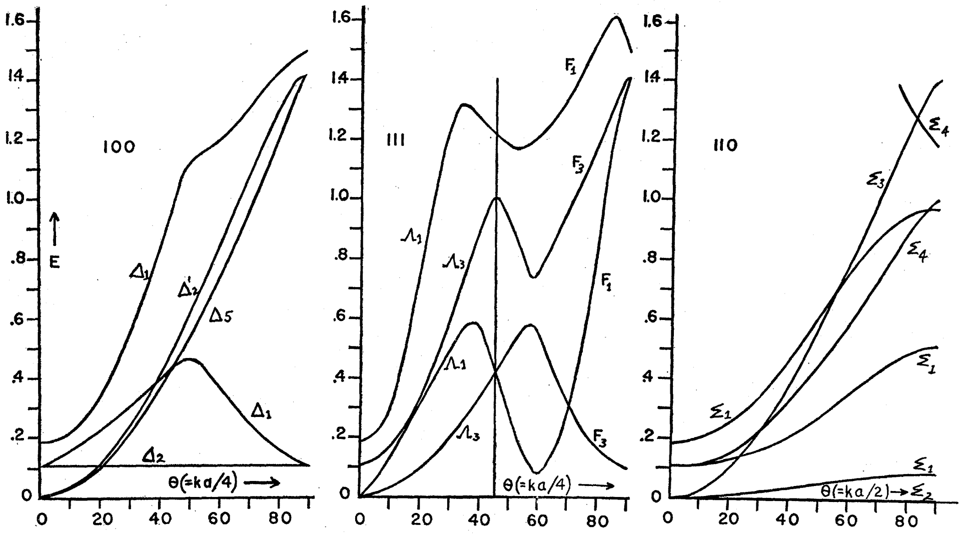

FIG. 3. *E vs. k* for the different directions of propagation.*

ticular directions of propagation, the fourteenth-order determinant can be factored into determinants of order not higher than the sixth. Expansion of such a determinant gives a transcendental equation, which usually has to be solved by numerical methods. The process is rather slow but once tables of the appropriate tangent factors have been made, it proceeds quite readily.

Figure 2 is the Brillouin zone for a body-centered lattice and on it the directions that have been investigated are indicated. Because of the symmetry of the body-centered cubic lattice, the polyhedron can be considered as consisting of forty-eight pyramids, each bounded by the 111, 110, and 100 lines and a quarter of one of the faces of the polyhedron. It is to be noted that for all the bounding edges of these pyramids, the energy as a function of k can be found by the solution of equations in *I*.

In Fig. 3 are the E *vs.* k curves for the directions of propagation, 111, 110, and 100. A certain amount of information can be obtained directly from these graphs, but for many properties it is more useful to have the density of states as a function of energy, $n(E)$. This requires a knowledge of E as a function of k throughout the Brillouin zone, i.e., the contours of constant energy in k space. Approximate contours can be obtained from our calculations by interpolation between the known directions. All the information obtained from the solutions for known directions can be represented on the developed surface of one of the pyramids, previously mentioned, which has one forty-eighth of the volume of the Brillouin zone. This developed surface is shown in Fig. 4. As can be seen, the known lines form a network on this surface. From the known lines and a knowledge of the manner in which the energy contours must intersect certain symmetry planes, plausible contours can be drawn. The details of determining these contours and also the method of calculating from them the density of energy states, $n(E)$, are discussed in the appendix. As an example, the contours of the band of lowest energy are shown in Fig. 5.

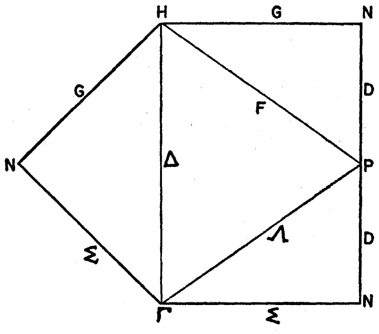

FIG. 4. Developed section of Brillouin zone.

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* k in the scales for the abscissae refers to one of the components of the wave vector e.g. the wave vector along 111 is (k, k, k), along 110 it is $(k, k, 0)$ etc.

It is to be noticed that, when viewed in connection with the other contours in the same plane, the zero width *E vs. k* curves along various special directions, e.g. 100, 110, etc., are not as surprising as when only a particular direction is considered. The peculiar shape of the contours and in particular, the sharp corners, are a consequence of the intersection of two sets of contours, one set with wave functions odd with respect to reflection in the plane, and the other with wave functions even. This matter is discussed further in the appendix.

Graphs similar to Fig. 5 were also drawn for the other five bands, but they are not reproduced here. A comparison of the contours for the various bands show marked differences. The lowest band is narrow and, as can be seen, the contours are not at all like those for free electrons. The next two higher bands are wider, but do not have the characteristics of free electrons. The highest three bands are still wider and the contours resemble somewhat those for free electrons. The density of energy states, $n(E)$, was determined for each of the bands, the calculation being carried to energy levels several volts higher than those occupied in tungsten under normal conditions. The results for the separate bands are shown in the lower curves of Fig. 6 and the combined result for all the bands is shown in the upper curve.

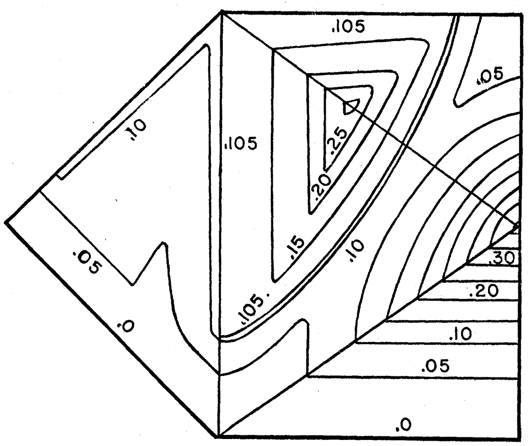

FIG. 5. Contours for band I.

Tungsten has six valence electrons per atom and the highest energy level which is occupied at the absolute zero of temperature is indicated by the right-hand vertical line in Fig. 6. Tantalum immediately precedes tungsten in the periodic table and has the same crystal structure. The calculations of $n(E)$ for tungsten should be roughly applicable to tantalum also. The left-hand vertical line in Fig. 6 corresponds to five valence electrons per atom.

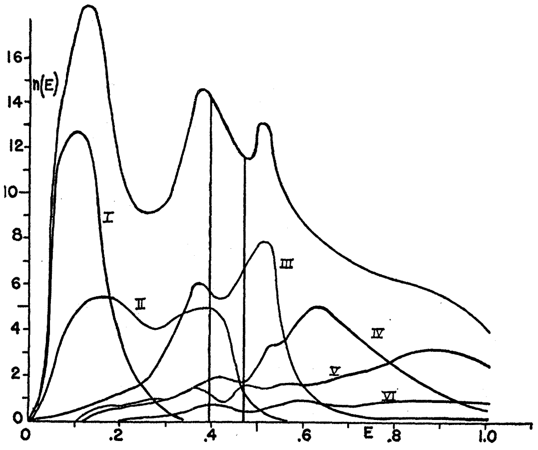

FIG. 6. $n(E)$ *vs.* E curves for the six lowest bands. The upper curve is the sum of the six lower curves. $n(E)$ = No. of states per unit energy range.

From the results expressed in Figs. 1 and 6, some general conclusions about the electronic structure of metallic tungsten and tantalum can be drawn. First, it is interesting to note the position and character of band VI which may be called the *s* band. It is seen that the number of electrons in this band is much less than one per atom and hence the neglect of *s* electrons in computing the potential is justified. More refined calculations might show an increase in the number in the *s* band, but the effect could hardly be appreciable. The position and nature of this band are of course in agreement with the very great "overlap" of the 6*s* atomic wave functions.

The lowest three bands and particularly band I probably contribute most of the binding energy which is known to be very large for these elements. Calculations of the binding energy[12] by the method used here are not practical, but rough calculations indicate that the zero of energy is about 0.5 or 0.6 of a Bohr unit below

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[12] N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford Press, 1934), p. 146. This book will be referred to hereafter as M. & J. F. D. Rossini and F. R. Bichowsky, *Thermochemistry of Chemical Substances* (Reinhold, New York, 1936), p. 98.

the 5d and 6s eigenvalues. This is not inconsistent with the observed binding energies (about 225 kilocalories per mole or 9 ev per atom for tungsten).

The process of formation of the solid from the separate atoms may be visualized as follows: At large distances between atoms the configuration is d^4s^2 and the eigenvalues are about the same for the two types of electron. As the atoms are brought closer together, the s functions begin to overlap and the single level is broadened into a band of levels, while the d levels still maintain their atomic character. As the atoms are brought still closer together, the d levels become broadened into bands, and the s band becomes broadened so much that the upper levels in this band will have higher energies than the narrower d band, and hence there will be transitions from the s to the d band. This process will continue until the minimum of the s curve in Fig. 1 is reached. If the atoms are brought still further together the energy changes become more complicated. The binding energy of the electrons in the s band will now decrease. Since the d band is only about half filled, the binding energy of the electrons in this band will continue to increase.[13] For the first row of transition elements, evidence of various kinds indicates that these two effects balance each other at about the minimum of the s curve. For tungsten and tantalum the gain in binding energy due to the d band more than balances the decrease in binding in the s band and the interatomic distance will therefore be smaller than that corresponding to the minimum of the s curve. At smaller distances between atoms, the d band begins to broaden upward more than downward, corresponding to a repulsive force between atoms. At the actual interatomic distance there has been a considerable redistribution of charge—for tungsten, the self-consistent field calculations for the atom indicate nearly three electrons have been displaced from a position outside of the atomic sphere to a position inside of the atomic sphere. This large redistribution of charge and the change in shape of the d band are responsible for the repulsive force between the atoms and also for the comparatively low compressibility of tungsten and tantalum.

ELECTRONIC SPECIFIC HEAT

As was first shown by Sommerfeld,[14] the electrons in a metal contribute to the specific heat a term which is proportional to the absolute temperature, and which at ordinary temperatures is negligible compared with the contribution of the lattice vibrations. At low temperatures the lattice contributions are proportional to T^3, and hence at very low temperatures the electronic contribution will be appreciable and may even predominate. At temperatures above the Debye characteristic temperature the contribution from the lattice vibrations approaches the constant value of 3R. However, Born and Brody have shown that if lattice vibrations have any anharmonicity, there will be, at high temperatures, a contribution to the specific heat which is proportional to the absolute temperature and may be positive or negative, depending upon the nature of the anharmonic terms in the potential energy of the lattice. It is difficult to estimate the sign of the anharmonic terms, as they will be positive for some directions of motion and negative for others.[15] It seems, however, to be reasonable to assume that at temperatures well below the melting point the anharmonic terms in the potential will make a negligible contribution to the specific heat.

The electronic contribution to the specific heat can be determined from a formula given by Stoner.[16] When higher powers of the temperature

TABLE I. *Electronic specific heat for tungsten and tantalum as determined by different methods.*

	THEORETICAL	EXPERIMENTAL (LOW TEMP.)	EXPERIMENTAL (HIGH TEMP.)
Tungsten	$4.8\times10^{-4}T$		$5.1\times10^{-4}T$
Tantalum	$6.2\times10^{-4}T$	$27\times10^{-4}T$	$7\times10^{-4}T$

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[13] For the noble metals and the elements immediately preceding them in the periodic table, the d band is full or nearly full, and this statement will no longer be true. For these elements the equilibrium distance will thus be determined to a considerable extent by the behavior of the s band.

[14] Sommerfeld, Houston and Eckart, Zeits. f. Physik **47**, 1 (1928).

[15] One of the authors (M. F. M.) has discussed the material of this section with Professor N. F. Mott, Dr. Frederick Seitz and Dr. Lloyd A. Young. He wishes to thank them for their suggestions.

[16] E. C. Stoner, Proc. Roy. Soc. **154**, 656 (1936).

are neglected, this formula is:

$$(C_v)_e = (5.670/27.08)\times 10^{-4} n(E_0)RT, \qquad (1)$$

where $(C_v)_e$ is the electronic contribution to the specific heat of a gram-atom, R is the universal gas constant, T is the absolute temperature, and $n(E_0)$ is the number of states of both spins per Rydberg unit of energy at the edge of the Fermi distribution. The value of $n(E_0)$ for tungsten found from Fig. 6 is 11.6 energy states per Rydberg unit of energy. For tantalum, the value is 14.7 energy states per Rydberg unit of energy.

Table I gives all of the pertinent data. The high temperature data are from measurements by Magnus and Holzmann.[17] The data for tantalum can be fitted quite well by an expression of the form $3R+AT$, where A has the value given. For tungsten the value given for A is that valid for temperatures above about 1000°K. The low temperature data for tantalum are from measurements by Daunt and Mendelssohn[18] upon the effect of a magnetic field upon the transition temperature of a super-conductor. As can be seen from Table I, the theoretical calculations for tungsten are in good agreement with the values for the excess specific heat at high temperatures. For tantalum, the theoretical calculations check the high temperature value which, however, is not at all in agreement with the low temperature value.

When the possibility of error in the measurements or in the reduction of the data is neglected, there are two possibilities of accounting for the discrepancy between the high and low temperature data for tantalum. One possibility is that the formula derived by Stoner is not applicable at low temperatures because it does not take exchange or correlation effects into account. A discussion of this point by Bardeen[19] and by Wigner[20] indicates that the effect of exchange is to spread out the levels near the top of the Fermi distribution and thus make the specific heat lower than is given by the Stoner formula, and thus increase the discrepancy. The correlation between electrons of the same spin tends to increase the specific heat, but no calculations have been made. The calculations of Wigner and Bardeen are based on a free electron model which is probably not applicable to a transition metal where the electrons retain much of their atomic character. Since tungsten has not been observed to be superconducting and since it has a high characteristic temperature, it should be possible to determine the electronic specific heat by direct measurements at liquid helium temperatures. The result of such a determination would help to clarify the points discussed here.

Another possibility for reconciling the high and low temperature data for tantalum is to assume that the difference is due to negative contributions to the specific heat from the anharmonic terms in the potential. The acceptance of this explanation would imply that the method used in this paper to calculate the energy levels in a metal is very inaccurate and that the numerical agreement with the high temperature data for *both* metals is highly fortuitous. It also implies a larger anharmonicity than seems reasonable.

It is difficult to obtain information about the anharmonic contributions to the specific heat because direct measurements of specific heats at liquid helium temperatures have been carried out for only a few metals. For nickel there are data available for both high and low temperature specific heats and a detailed analysis of these data by Stoner[21] seems to indicate that the anharmonic contribution to the specific heat is very small. Another line of evidence indicating that for nickel there is a large electronic contribution is the fact that for Ni-Cu alloys the excess specific heat decreases very rapidly with the addition of Cu.

Electrical and Related Properties

The detailed discussion of the resistance of a transition metal offers unsurmounted difficulties. Some general features of the problem have been discussed by Mott.[6] His discussion was based upon a model of two overlapping bands—an s band with approximately free electron characteristics and a d band with a high density of

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[17] A. Magnus and H. Holzmann, Ann. d. Physik **3**, 602 (1929).

[18] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **A160**, 127 (1937).

[19] J. A. Bardeen, Phys. Rev. **50**, 1098 (1936).

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

[21] E. C. Stoner, Phil. Mag. **22**, 81 (1936).

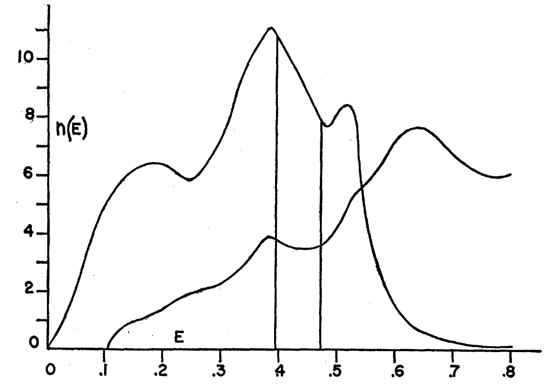

FIG. 7. $n(E)$ curves for bands II+III, and for bands IV+V+VI.

states and a high effective mass. His discussion can be carried over to our case, except that where he speaks of a *d* band we shall consider bands II and III which have a high density of vacant states and a low value for the effective number[22] of free electrons per atom. Where Mott refers to an *s* band we shall consider the highest three bands which have roughly free-electron characteristics and account for most of the conductivity. On the other hand, the vacant states in the lower bands contribute greatly to the scattering probability and hence make the mean free path much shorter. This is the essence of Mott's explanation of the low conductivity of the transition metals. In Fig. 7 are plotted the total number of states per unit energy range for bands II and III and the total number of states per unit energy range in the three higher bands. Since the lowest band is filled, it contributes to neither the conductivity nor the scattering and therefore is omitted from the graph. If Mott's explanation of the effect of the density of scattering states upon the resistance is correct, the different resistivities of tungsten and tantalum should be due in part to the greater density of scattering states for tantalum.

If the relation of the electrical conductivities of two different elements to their electronic structure is to be studied, it is necessary to make corrections for the different amplitudes of thermal vibration at a given temperature, for the different atomic volumes, and for the different scattering powers of the ions. Mott and Jones[23] have shown that the dependence upon the amplitude can be eliminated by comparing values of $\sigma/M\Theta^2$ where σ is the conductivity for a unit cube, M is the mass of the vibrating ion, and Θ is the Debye characteristic temperature. As Bridgman[24] and Hume-Rothery[25] have pointed out, the differing atomic volumes can be taken into account by considering not the conductivity of a unit volume, but the conductivity of a cube containing a constant number of atoms. This is equivalent to considering the quotient of σ/r where r is the atomic radius. For tantalum the value of $\sigma/Mr\Theta^2$ is 0.47 and for tungsten the value is 0.64. The ratio of these two values is 1.36. Neglecting the differing scattering powers of the two ions, this ratio should be very nearly equal to the ratio of the number of vacant states for tantalum to the number of vacant states for tungsten. The actual value as obtained from Fig. 7 is 1.27. The agreement between these values is an indication of the reasonableness of the explanation.

Variation of resistance of high temperatures

For temperatures above the characteristic temperature the change in resistance is caused chiefly by the increase in the amplitude of vibration of the scattering ions. There is also a change caused by the thermal expansion of the lattice. In addition, there may be an effect due to the change with temperature of the effective number of scattering states. A theory for the latter effect has been given by Mott.[26] The resistance at a high temperature can be written as

$$R/T=\text{const.}\ (1+BT)(1+AT^2), \qquad (2)$$

where R is the resistance, T the absolute temperature, B a constant determined from the thermal and mechanical properties, and A related to the shape of the $n(E)$ curve near the top of the filled states. If one assumes with Mott that the time of relaxation τ is proportional to

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[22] The effective number of free electrons per unit volume is given by the formula:

$$N_{\text{eff}}=\frac{m}{4\pi^3\hbar^2}\int\left(\frac{\partial E}{\partial k_x}\right)^2\frac{dS_k}{|\text{grad.}_kE|}\,.$$

See M. & J., p. 97.

[23] M. & J., p. 245.

[24] P. W. Bridgman, Proc. Am. Acad. **60**, 305 (1924).

[25] W. Hume-Rothery, *The Metallic State* (Oxford Press, 1931), p. 5.

[26] M. & J., p. 270; N. F. Mott, Proc. Roy. Soc. **153**, 699 (1936).

$1/n(E)$, A is proportional to $-[3(n')^2/n-n'']$, where the derivatives are taken at the top of the filled states. If the $n(E)$ curve for the scattering bands is concave toward the energy axis in the neighborhood of the highest occupied levels, then n'' is negative and hence A is negative. For this case it is to be expected that R/T would tend to decrease with increasing temperature. If the $n(E)$ curve is convex, the sign of A will depend on the comparative magnitude of the two terms comprising it. Reference to Fig. 7 indicates immediately that A should be negative for tantalum. Using analytic approximations to the $n(E)$ curve near the top of the filled states for both tantalum and tungsten, it was found that A was positive for tungsten and appreciably smaller in magnitude than for tantalum. Actually, the observed resistance[27] *vs.* temperature curve for tantalum is definitely concave toward the temperature axis and the curve for tungsten is slightly convex in agreement with the above considerations.

Thermoelectric power

Interpretations of the thermoelectric power have been given by Mott,[6] and by Jones and Mott.[7, 28] They point out that when the resistance is due to a high density of levels in a scattering band, the thermoelectric power will be negative if the density of scattering states decreases rapidly with E and positive if the density of scattering states increases rapidly with E. From this argument and Fig. 6, we conclude that tantalum should have a negative thermoelectric power. The observed values[29] are -5.0 microvolts/°C and -6.7 microvolts/°C at 100°C. As Mott[6] points out, the argument involving the density of states in the scattering bands is incomplete as it leaves out any discussion of the mechanism which produces the entire effect in a metal like copper or silver. Since these metals show a positive thermoelectric power of about 2 microvolts/°C, we might expect that when the density of scattering states changes only slightly with energy, the thermoelectric power would have about this value. Reference to Fig. 6 shows that for tungsten the slope of the $n(E)$ curve in the neighborhood of the highest occupied levels is small, so that we should expect a small, positive thermoelectric power. The observed values are $+0.4$ microvolt/°C at 0°C and $+3.6$ microvolts/°C at 100°C.

PARAMAGNETIC SUSCEPTIBILITY*

When exchange effects are neglected, the formula for the molar paramagnetic susceptibility is[30]

$$\chi_A=\mu^2 n(E_0)N, \qquad (3)$$

where μ is the Bohr magneton, $n(E_0)$ is the number of energy states per atom per unit energy range, and N is Avogadro's number. When one takes the values of $n(E)$ as 11.6 for tungsten, and 14.7 for tantalum, the computed susceptibilities are 28 for tungsten and 35 for tantalum. The observed values are 45 for tungsten and 145 for tantalum.[31] The actual paramagnetic contribution from the electrons is greater than these amounts due to the diamagnetic contribution of the cores and of the valence electrons. The diamagnetic susceptibilities of the cores have been estimated by Stoner[31] and values of about 35 units found. We can thus say that the paramagnetic susceptibilities of the valence electrons must be at least 80 for tungsten and 180 for tantalum. These values are very much greater than those obtained from the simple formula. The difference has usually been believed due to exchange effects. There does not seem to have been any detailed analysis of the effect of exchange.

An approximate discussion can be carried out by the method suggested by Slater[32] for ferromagnetic substances. For each atom there are $n/2$ electrons per unit energy range for each direction of spin. Suppose that $\nu/2$ of them reverse their direction of spin, yielding a magnetic moment of $\nu\mu$ per atom. If this takes place in the presence of a magnetic field H, the changes in energy accompanying the process are: $H\nu\mu/2$,

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[27] E. Gruneisen, *Handbuch der Physik* **10**, 16 (1928).

[28] M. & J., p. 310.

[29] G. Borelius, *Handbuch der Metall-Physik*, Vol. I, page 399.

* The authors wish to thank Dr. William Shockley for discussion about this section.

[30] M. & J., p. 185. The n used in this article is twice as large as that used in this reference.

[31] E. C. Stoner, *Magnetism and Matter* (Methuen, 1934), pp. 508, 271.

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

due to reorientation, and $\nu^2/4J$, due to the fact that there are more exchange integrals between electrons of parallel spin than there were in the unmagnetized state. When the electrons reverse their spins, they must be lifted to higher energy levels and this requires an energy $\nu^2/2n$. Hence we have

$$\nu^2 J/4+H\mu\nu/2=\nu^2/2n \tag{4}$$

or

$$\nu\mu=\frac{\mu^2 n}{1-Jn/2}H \tag{5}$$

and the expression for the molar susceptibility becomes

$$\chi_A=\frac{\mu^2 n(E_0)N}{1-Jn(E_0)/2}. \tag{6}$$

It is noted that the correction factor is in the proper direction and has the correct dependence upon n to explain the fact that the discrepancy between the observed value and that calculated from the simple equation is greater for tantalum than for tungsten. If there were some satisfactory method of determining J, it would be possible to compute χ_A. Since there does not seem to be any method of computing J, we shall proceed differently and use the measured values of χ_A to solve for J. For tungsten this gives

$$1-5.8J=28/80;\quad J=.11 \text{ Rydberg units.} \tag{7}$$

For tantalum

$$1-7.3J=35/180;\quad J=.11 \text{ Rydberg units.} \tag{8}$$

The fact that the values of J for the two elements come out so nearly equal is evidence for the part that exchange forces play in determining the paramagnetic susceptibility. The value of J is rather large, but there does not seem to be any independent method of checking it.

VALIDITY OF THE METHOD

There are a number of approximations involved in the method of calculation used and it is difficult to estimate the accuracy of the results. However, the authors believe that the agreement with experimental results, although usually only qualitative, indicates that the computations give a representative picture of the electronic structure of metallic tungsten and tantalum.

Perhaps the most serious approximation is the complete neglect of exchange and correlation effects. These effects are important in determining the binding energy and for this reason no attempt to calculate it has been made. Exchange effects might be expected to cause a contraction of the wave functions and hence a narrowing of the bands. For instance, Hartree[33] has found that exchange effects produce an appreciable change in the outer portions of the $3d$ wave functions for copper. There are, however, reasons for believing that this effect will be less pronounced in tungsten. For all of the electrons inside of the $4f$ electrons in tungsten the electrostatic contribution to the potential is so large that exchange effects will produce only a small effect. For the $4f$, $5s$, $5p$ electrons the solutions of Fock's equations will undoubtedly give an appreciable contraction. As far as the $5d$ electrons are concerned, this contraction acts to decrease the effective electrostatic potential. This decrease in the electrostatic potential has the opposite effect upon the $5d$ wave functions from the exchange effects, which furthermore are not as important in a partly-filled shell as in a filled shell. Another reason for discounting the effect of exchange on the $5d$ electrons in tungsten is the fact that throughout the self-consistent field calculations for the atom and the metal, these wave functions were not unduly sensitive to changes in the assumed field. For copper, Hartree found that the $3d$ wave functions were very sensitive to the assumed field.

Another point where errors may have entered was in the use of the differential analyzer. A problem as complicated as this could be handled even on the differential analyzer only by a compromise between the accuracy desired and the time required. None of the calculations for either the atom or the metal was checked by numerical integration, but certain cross-checks indicated that the errors introduced in the computation are not serious.

In general, it might be remarked that the entire computational process showed a considerable tendency toward cancellation of errors. For instance, the principal effect of a change in the assumed potential is to shift the entire band

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[33] D. R. and W. Hartree, Proc. Roy. Soc. **157**, 490 (1936).

structure in energy without changing its shape. Slight changes in the curves of s, s', d, d', as a function of energy produced no appreciable changes in the E *vs.* k curves. In addition, it turned out that the final $n(E)$ curves were quite insensitive to changes in the contours in k space. (See Appendix A.)

The Slater method of computing metallic wave functions is, of course, only approximate. In an attempt to estimate the accuracy of the approximation, Shockley[34] has tested the cellular method by applying it to the case of a constant potential where the exact answer is available for comparison. He finds that when there is a single occupied band and a number of excited bands at higher energies, the lowest band will be determined with satisfactory accuracy, but the excited bands will be much less accurately determined. The argument is not as definite when there are a number of occupied bands, all having about the same energy, but it seems likely that for this case all of the bands will be determined with some intermediate accuracy. There is also the point that for metallic tungsten, the wave functions retain much of their atomic character, and therefore it might be expected that the results are better than Shockley's argument would indicate.

Jones and Mott[7] have carried out a discussion of the transition metals, using the approximation of tight binding. This approximation is more accurate than the cellular method when the overlap of the d functions is small and less accurate when the overlap is large. Using this criterion and the results of self-consistent field calculations, it seems that their method might be more accurate for the first row of transition elements, and the cellular method for the second and third rows.

The calculations of which this paper is a report were carried out under the general direction of Professor J. C. Slater. The authors wish to thank him for his helpful comments and suggestions.

APPENDIX A

We shall outline briefly here the method of obtaining approximate energy contours and $n(E)$ curves. To obtain the contours, we have available the E *vs.* k curves for the various special directions (Δ, Λ, Σ, D, G, F) and also the exact contours in the 100 and 110 planes for those states whose wave functions are odd with respect to reflection in those planes. From this information, all of which is obtained from the solution of equations in I, we must determine the contours throughout the Brillouin zone for each of the six bands. Mention must be made here that in classifying the energy levels in bands, all of one E *vs.* k curve, (obtained from one equation) does not necessarily belong to one band. The same applies to the exact contours in the special planes which we have mentioned above. In each band the energy is a continuous function of the reduced wave vector k and for two bands the energy level of one (for each k) is always higher than, or equal to, the corresponding level of the other. Thus, although the bands may touch at some values of k (degeneracy), they can never cross. For two E *vs.* k curves, on the other hand, this is not true. An E *vs.* k curve for a particular direction is determined by the property that all the energy states have wave functions of the same symmetry.[35] Thus there is nothing to prevent two E *vs.* k curves from crossing and if two curves for a given direction do cross, the two lower halves are taken as belonging to one band and the two upper halves to the other band. This procedure often gives the energy contours in a band queer shapes, including corners, where we have shifted from the lower (upper) half of one E *vs.* k curve to the lower (upper) half of another curve which intersects the first. In such a shift, the wave function in the band changes discontinuously with k, but the energy is continuous.

Our general procedure in finding the contours of a band was first to find the contours for the developed surface shown in Fig. 5. These contours were obtained by interpolation between the various lines on the surface, for which the energy as a function of k is known. The contours inside the pyramid bounded by the surface of Fig. 5 were obtained by interpolation from the contours on the surface. We have previously mentioned the possibility of the wave function in a band changing discontinuously at a point of degeneracy, with a corresponding peculiarity in the shape of the contour. This would seem to militate against results obtained by interpolation, if many of these points of contact occur distributed throughout the Brillouin zone. Actually, however, Herring[36] in a study of the types of contacts possible, has shown that two bands can touch only along symmetry axes and planes.[35] In terms of our basic pyramid, this means that corners, or any other irregularities due to band contacts, will be confined to the surface of the pyramid only, the surface being composed entirely of symmetry planes. If by some method we can get the contours on the surface, including any "contact" irregularities, fairly accurately, we can interpolate the interior contours with confidence since none of these "contact" irregularities can occur in the interior. In obtaining these surface contours, another property of the "contacts" found by Herring has been useful. He showed that in any symmetry axis or plane only E *vs.* k curves of

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[34] W. Shockley, Phys. Rev. **52**, 866 (1937).

[35] In the language of group theory, all the states of one E *vs.* k curve for a particular direction belong to the same irreducible representation of the group which leaves a k vector in that direction invariant.

[36] C. Herring, Phys. Rev. **52**, 365 (1937).

different symmetries, belonging to different irreducible representations, can cross. For the symmetry planes constituting the surface of the pyramid, there are two symmetry types—contours with wave functions odd under reflection and contours with wave functions even. Applied to these contours, Herring's[37] result means that the only band contacts which can occur on the surface are due to the intersection of odd and even contours. (By even or odd contours we mean, of course, contours with wave functions having these symmetries.) Intersections between two sets of even contours or two sets of odd contours are forbidden. These statements about the nature of band contacts in symmetry planes, apply only to such portions of the symmetry planes as are not symmetry axes. For the latter, there are more than two symmetry types and we can no longer speak of odd and even contours. Two sets of contours which are odd (even) in a plane, may belong to different irreducible representations of an axis and may intersect *along the axis*. This actually does occur in our case, both Δ_1 and Δ_2' are even in the 110 plane, but these intersections offer no difficulty, as we know the energy exactly for all the axes. The fact that for all other portions of the symmetry planes, only odd and even contours can intersect, gives us a method of determining the contours in these regions quite accurately, even to the corners occurring at the intersections.

We can obtain all of the odd contours in the various planes from the solutions of equations given in I. For the even contours, similar equations could be found, but these would be so unwieldy that no attempt was made to use them. Instead, the even contours were interpolated from the known portions of these contours, that is, the E *vs.* k curves along the various axes. Since two sets of even contours cannot intersect, there is no problem of "contact" irregularities to vitiate interpolation methods. The lowest energy states along each axis belong to one set of contours, the next higher states to another set, etc. Having thus obtained both even and odd contours, we can determine the intersections of the two and apportion the various sections among the six bands according to their energy. With the contours on the surface of the basic pyramid known, the interior contours for each band can be found by interpolation.

From these contours, we determine the number of states per unit of energy, $n(E)$. In practice, it is easier to find first the number of states with energy less than a particular energy E. $n(E)$ is then determined by numerical differentiation. For any band the number of states with energy less than E is proportional to the volume of that portion of the Brillouin zone contained within the surface of energy E. This surface may consist of two or more sheets if the energy does not vary monotonically within the band. To obtain approximately the volume contained within an energy surface, we proceed as follows: The basic pyramid of the Brillouin zone is cut by ten evenly-spaced planes parallel to the 100 plane. In each of these planes the area enclosed by the cross section of the energy surface was measured by a planimeter. From these areas, plotted as a function of the height above the 100 plane, another integration gives the volume inside the energy surface.

In obtaining the contours, we have gone through the somewhat elaborate process of obtaining the odd and even contours in the symmetry planes separately, and then putting together pieces of each to obtain the contours of the individual bands. One could use the simpler, although theoretically less justifiable method of interpolating the contours of each band directly from the known energy states along the axis, that is, connect the lowest states along each axis by one set of contours for the lowest band, the next higher states by another set of contours for the next higher band, etc. As previously pointed out, such procedure tends to smooth out any irregularities in the bands. One cannot say *a priori* how important these irregularities will be and how seriously smoothing them out will affect the final results. Therefore, the more elaborate method which locates these contacts would seem to be preferable. We have also used the simpler method of interpolating each band directly. The resultant contours, of course, had no corners, but did resemble quite closely the contours found by the more accurate method. The change in the $n(E)$ curves would be even smaller than in the contours. In general, the entire process of determining the $n(E)$ curves turned out to be surprisingly insensitive to the assumed interpolations between known directions.

Note added in proof:—The value of $27\times10^{-4}T$ for the low temperature electronic specific heat of Ta was taken from a paper by Mott and Jones (reference 7). A closer examination of the data given by Daunt and Mendelssohn makes us believe that this value is higher than the data warrant and that for Ta the experimental uncertainties are considerably larger than for other elements measured by Daunt and Mendelssohn.

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[37] One of the authors (M. I. C.) wishes to thank Dr. Herring for enlightening discussions about the results in his paper.