

Electronic Energy Bands in Body-Centered Iron

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Calculations of the electronic energy bands in body-centered iron by the Wigner-Seitz-Slater method are reported. There are found to be two filled and four partially-filled bands. The lowest two filled bands are responsible for the cohesion; the next three partially-filled bands for the ferromagnetism; and the highest band is responsible for the electrical conduction. The width of the occupied levels is about 0.6 Rydberg but the density of states is high for only about 0.4 Rydberg in good agreement with the data obtained from x-ray emission bands. The density of states is calculated as a function of the energy and compared with

similar results obtained by Greene for face-centered iron. The density of states at the highest occupied energy level is 17 electrons/atom-Rydberg compared with 11 electrons/atom-Rydberg for face-centered iron. This higher density of states accounts for the fact that body-centered iron is ferromagnetic, but face-centered iron is not. It also indicates a greater electronic specific heat for body-centered iron than for face-centered iron. This higher electronic specific heat is responsible for the high temperature change from a face-centered to a body-centered structure.

INTRODUCTION

THERE is considerable scientific interest in metallic iron because it is one of the few elements which show ferromagnetism and because of the phase changes from body-centered to face-centered and back to body-centered as the temperature is raised.

The method of calculating the electronic energy levels reported in this paper is that developed by Wigner and Seitz¹ and extended by Slater² and others.³ The essential feature of this method is that the wave function within the polyhedron surrounding any one atom is expressed as a sum of terms (fourteen for the body-centered lattice) each of which consists of a spherical harmonic multiplied by the appropriate radial function. The radial functions are found by a modified Hartree procedure and the arbitrary coefficients in the linear combination are chosen so that the wave functions satisfy the Bloch⁴ periodicity condition and join smoothly in passing from one atom to its eight nearest and six next-nearest neighbors. It turns out that these conditions impose a determinantal relationship between the energy of an electron and the components of the momentum or wave number

vector $\mathbf{k}$. For a general direction of $\mathbf{k}$ the determinantal relations become very complicated, but for a number of symmetrical directions, simpler relations are obtained. For the body-centered lattice the results of the expansion of the determinant for the special directions are given in reference 3. The directions of $\mathbf{k}$ for which solutions have been obtained are indicated in Fig. 1, which is a drawing of the first Brillouin zone corresponding to a body-centered structure.⁵

RESULTS

In the calculations the first step was the determination of an effective field for the calculation of the radial factors of the different wave

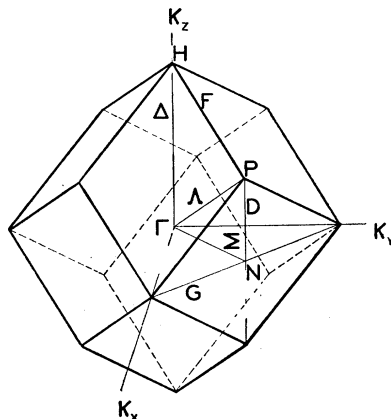


FIG. 1. The first Brillouin zone for the body-centered lattice.

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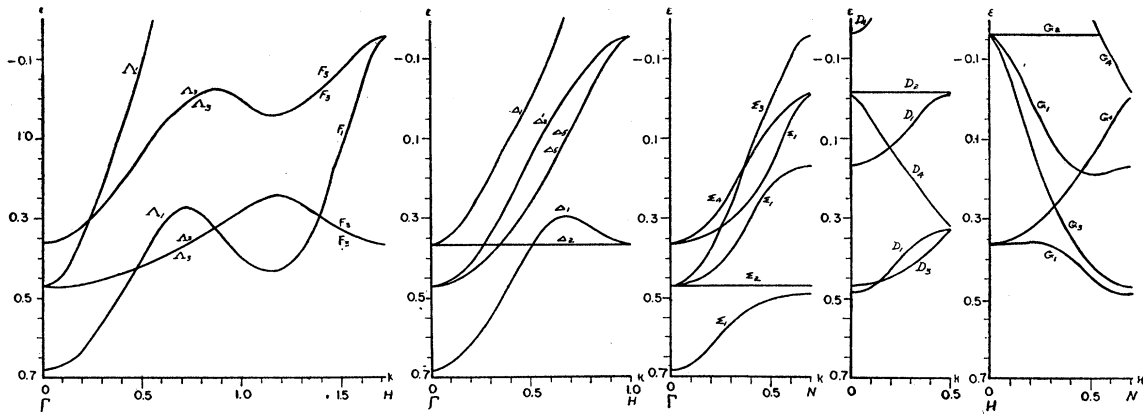
¹ E. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933); *Phys. Rev.* **46**, 509 (1934).

² J. C. Slater, *Phys. Rev.* **45**, 794 (1934).

³ M. I. Chodorow and M. F. Manning, *Phys. Rev.* **52**, 731 (1937). For a list of other applications of this method, see M. F. Manning and M. I. Chodorow, *Phys. Rev.* **56**, 787 (1939).

⁴ F. Bloch, *Zeits. f. Physik* **52**, 555 (1928).

⁵ The notation is that of L. Bouckaert, R. Smoluchowski, and E. Wigner, *Phys. Rev.* **50**, 58 (1936).

FIG. 2. Energy ϵ vs. momentum K for the different directions of propagation.

functions. In determining the effective field for the metal, the charge-densities for $1s$ to $3p$ electrons were assumed the same as found for the iron atom by Manning and Goldberg.⁶ The charge-densities for the $4s$ and $3d$ were renormalized to the volume of the atomic sphere in metallic iron and other readjustments made. Further details are given in Appendix I.

By use of the field so obtained, the radial wave functions were found by numerical integration as

TABLE I. Values of ϵ for which certain important functions vanish. The notation is that of Chodorow and Manning (reference 3).

Function	ϵ
$3s_1'g_2'+2s_2'g_1'$	0.684
$2D_1D_2S_4+2D_2S_2+D_1S_3+S_1$	0.490
d_1'	0.470
d_2'	0.365
$D_1B_3+B_1$	0.325
$2D_1D_2S_4+2D_2S_2+D_1S_3+S_1$	0.165
B_1	-0.008
d_2	-0.015
d_1	-0.160

TABLE II. Maximum and minimum values of ϵ for each band and values of ϵ at the symmetry points (reference 3).

	I	II	III	IV	V	VI
Min. E	0.684	0.470	0.470	0.470	0.365	0.365
Max. E	0.292	0.240	-0.160	-0.160	-0.160	
r	0.684	0.470	0.470	0.470	0.365	0.365
P	0.325	0.325	0.325	-0.015	-0.015	
N	0.490	0.470	0.165	-0.008	-0.015	-0.160
H	0.365	0.365	-0.160	-0.160	-0.160	

⁶ M. F. Manning and L. Goldberg, Phys. Rev. **53**, 662 (1938).

in the Hartree self-consistent field method for atoms. The values of the functions and their radial derivatives at the half-distances between nearest neighbors and between next-nearest neighbors were then determined by standard methods of interpolation and numerical differentiation. (For iron the lattice parameter at room temperature is 2.86Å. The corresponding distance between nearest neighbors is 2.345 Bohr units and the distance between next-nearest neighbors is 2.71 Bohr units. The corresponding values of $\rho(\equiv \log_e 1000r)$ are 7.760 and 7.904.)

The values of the functions and derivatives are then used to calculate the coefficients in the transcendental equations relating E and k given in reference 3. The procedure in solving these equations was very similar to that used in the calculations for metallic tungsten.⁷ A few comments about slight modifications in the procedure are given in Appendix II. The results of the calculation of the energy as a function of the momentum are given in Fig. 2. It does not seem necessary to tabulate the numerical values from which the figures were plotted, but Table I gives the energies at which certain key combinations of functions and derivatives vanish, and Table II gives the maximum and minimum energies for each band and the energies at a number of special points in the Brillouin zone. In these tables and elsewhere in this paper ϵ is the negative of the energy expressed in Rydbergs.

Although energy-momentum relations are ob-

⁷ M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, 787 (1939).

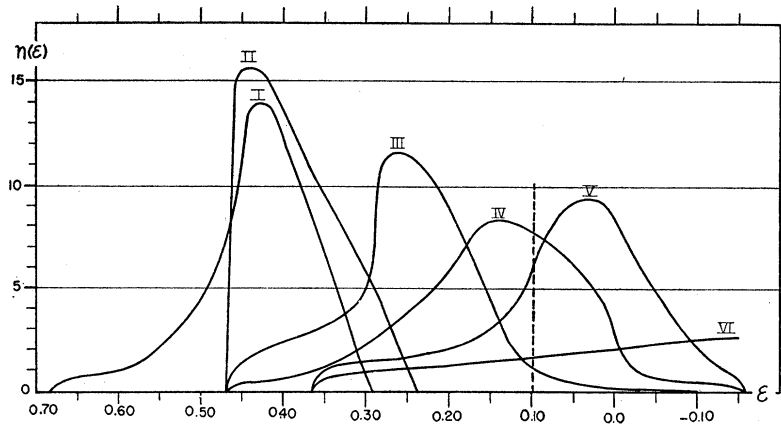


FIG. 3. $n(\epsilon)$ vs. ϵ for the separate bands. $n(\epsilon)$ = number of states per unit energy range.

tained directly for only a limited number of lines in $\mathbf{k}$ space, very plausible constant energy contours based on these known lines can be drawn for the principal planes in $\mathbf{k}$ space. By considering the contours in these planes as known, energy contours for a number of planes $K_z = 0, 0.1, 0.2$, etc., can be interpolated. Each of the planes $K_z = \text{constant}$ can be divided into a region in which the energy is greater than a particular value and a region in which the energy is less than this particular value. For each plane the area of the region with energy less than a particular energy was obtained by using a planimeter. This procedure was repeated for all of the planes and by numerical integration the volume in $\mathbf{k}$ space with energy less than a particular energy was determined. Since this volume is proportional to the number of electrons with energy less than the energy considered, the corresponding number of electrons can be found by using the normalizing relation that there are two electrons per atom in each energy band. In the present paper this quantity is designated by $N(\epsilon)$. The values of $N(\epsilon)$ for each of the energy bands and for the sum of the six bands are given in Table III. Since there are eight valence electrons per atom in iron, the highest occupied level at absolute zero in non-magnetic iron occurs at $\epsilon = 0.105$.

From the values of $N(\epsilon)$, the values of $n(\epsilon) (\equiv -dN/d\epsilon)$ can be found by numerical differentiation. $(n(\epsilon)d\epsilon)$ is the number of energy levels per atom with energy between ϵ and $\epsilon + d\epsilon$. Since numerical differentiation is a process

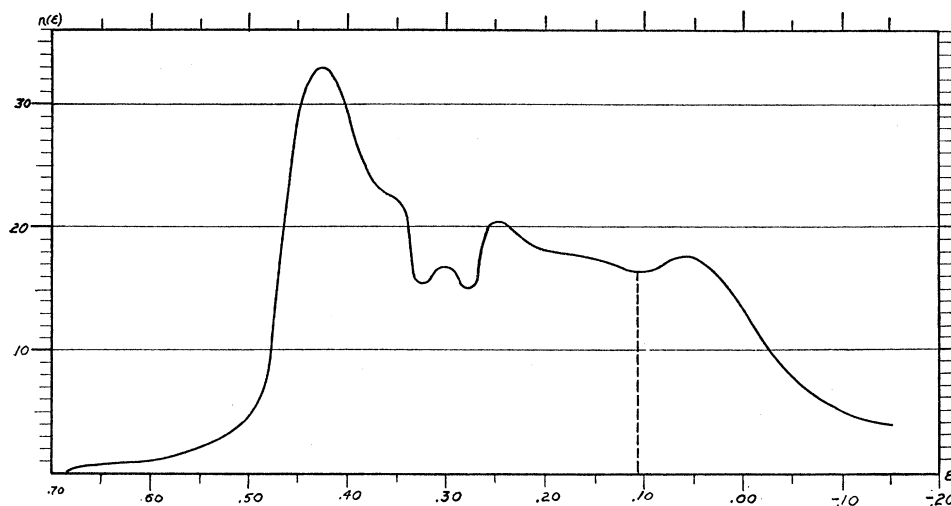
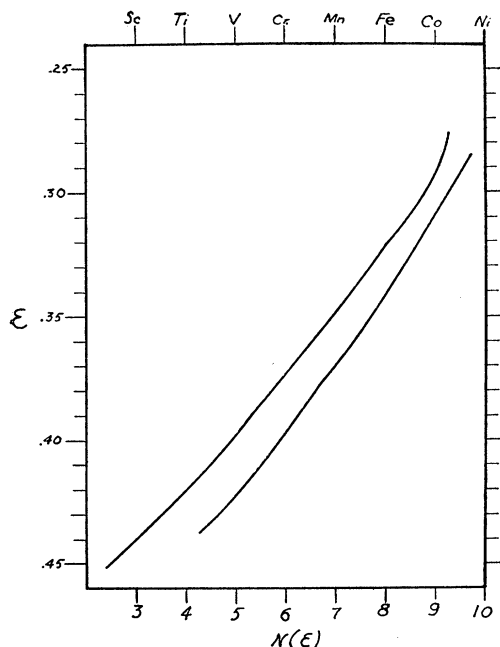
in which considerable accuracy is lost, the values of $n(\epsilon)$ found by differentiation were adjusted so that

$$\int_{\epsilon_1}^{\epsilon_2} n(\epsilon) d\epsilon$$

as found by a planimeter checked the corresponding increment in $N(\epsilon)$. The resulting values of $n(\epsilon)$ for the separate bands and for the total are given in Figs. 3 and 4.

TABLE III. Values of $N(\epsilon)$ as a function of ϵ .

ϵ	I	II	III	IV	V	VI	Total
0.70	0.003						
0.65	0.017						0.017
0.60	0.032						
	0.058						0.058
0.55	0.090						
	0.122						0.122
0.50	0.199						
	0.275						0.275
0.45	0.456						
	0.623	0.306	0.025	0.003			0.957
0.40	1.003	0.599					
	1.328	0.902	0.118	0.025			2.373
0.35	1.614	1.138					
	1.970	1.494	0.288	0.063	0.033		3.848
0.30	2.000	1.651					
	2.000	1.802	0.460	0.156	0.103	0.034	4.555
0.25		1.969					
	2.000	1.998	0.968	0.336	0.170	0.078	5.550
0.20		2.000	1.477	0.541	0.245	0.121	6.384
0.15		2.000	1.895	0.904	0.372	0.188	7.359
0.10			1.939	1.302	0.552	0.255	8.048
0.05			1.967	1.677	0.945	0.406	8.995
0.00			1.982	1.937	1.405	0.468	9.792
-0.05			1.992	1.971	1.747	0.589	10.299
-0.10			1.997	1.993	1.904	0.816	10.710
-0.15			2.000	1.998	1.979	0.882	10.859

FIG. 4. $n(\epsilon)$ vs. ϵ for the sum of the six bands.FIG. 5. The average Fermi energy $\bar{\epsilon}$ as a function of the number of electrons per atom. The upper curve is for body-centered iron, the lower one for face-centered.

From the results depicted in these figures, some general remarks about the electronic structure of metallic iron can be made. Bands I and II are completely filled in the metal and hence do not contribute to either the electrical conductivity or the ferromagnetic properties. Band VI is a wide band with a considerable admixture of s functions and probably accounts for most of

the conductivity. Bands III, IV, and V are narrow bands with a high density of states and are the important bands in connection with ferromagnetism.

This model for the electronic structure of metallic iron combines many of the features of the “ d ” band model suggested by Mott⁸ and the homopolar group of levels suggested by Pauling.⁹

The general features of the energy bands for body-centered iron are very similar to those found for tungsten.⁷ The only important difference is that for tungsten the energy for which $3s_1'g_2' + 2s_2'g_1' = 0$ lies above the energies for which d_1' and d_2' are zero, while for iron this condition is fulfilled for an energy lower than the energies for which d_1' and d_2' vanish. (See Fig. 6.) The general results are also quite similar to those obtained by Greene¹⁰ for face-centered iron. However, the lowest band in face-centered iron begins at the energy for which $s' = 0$ and all five of the d bands start at the energy for which $d' = 0$. (Actually this is due to an approximation in the theory as Bethe¹¹ and Chodorow¹² have pointed out that even at the center of the momentum cell the d level should split into a group of two levels and a group of three levels.)

⁸ N. F. Mott, Proc. Phys. Soc. **47**, 571 (1935).

⁹ L. Pauling, Phys. Rev. **54**, 899 (1938).

¹⁰ J. B. Greene and M. F. Manning, Phys. Rev. **63**, 203 (1943).

¹¹ H. Bethe, Ann. d. Physik **87**, 55 (1928).

¹² M. I. Chodorow, Phys. Rev. **55**, 675 (1939) and M.I.T. thesis (1936).

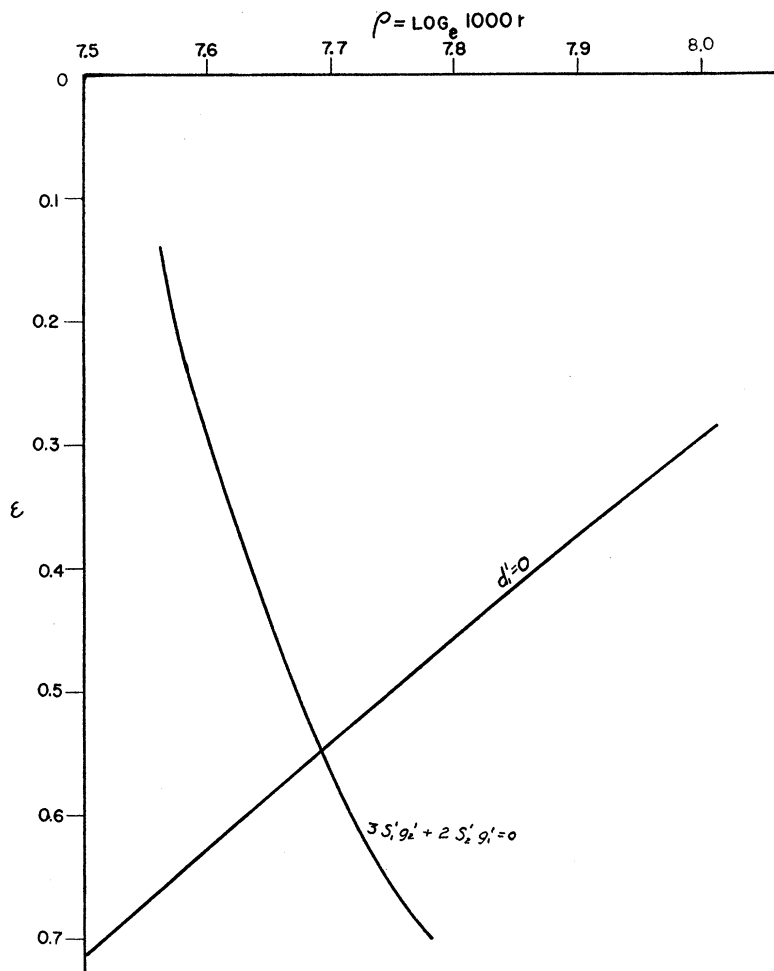


FIG. 6. The energy for which certain functions vanish *vs.* $\log_e r$.
 r is the interatomic distance in Bohr units.

APPLICATIONS

Energy Relations

A quantitative calculation of the binding energy of body-centered iron and its stability relative to the face-centered structure would require a consideration of the exchange and correlation energies which is not possible by the method used here. It is, however, interesting to compute the average Fermi energy as a function of the total number of electrons per atom and compare with the same results obtained for the face-centered structure.

The average Fermi energy is defined by the equation:

$$N(\epsilon_m)(\bar{\epsilon} - \epsilon_0) = - \int_{\epsilon_0}^{\epsilon_m} n(\epsilon)(\epsilon - \epsilon_0) d\epsilon, \quad (1)$$

where ϵ_0 refers to the lowest level and ϵ_m to the highest level occupied at absolute zero. This integral could be evaluated from the information in Fig. 4, but since $n(\epsilon)$ is obtained only as the derivative of another function, it is preferable to integrate Eq. (1) by parts to obtain:

$$\bar{\epsilon} = \epsilon_m + \frac{1}{N(\epsilon_m)} \int_{\epsilon_0}^{\epsilon_m} N(\epsilon) d\epsilon. \quad (2)$$

Although the results calculated are based on iron, they should be approximately valid for neighboring elements in the same row of the periodic table if the appropriate number of electrons per atom is used. Similar calculations have been made by Greene¹⁰ for the face-centered structure and the results are plotted in Fig. 5. In

the neighborhood of iron the difference in mean Fermi energy is about 0.02 Rydberg/atom. Since the extra magnetic energy of the body-centered lattice is of this same order of magnitude and there are a number of other corrections which may be different for the two structures, it is easy to see why iron might show phase changes. In the neighborhood of ten electrons per atom the average Fermi energy for the body-centered structure rises much more rapidly than for the face-centered structure, thus indicating that for nickel the face-centered structure should be more stable. This gives no information about cobalt, although here the face-centered structure is favored over the body-centered structure by the magnetic energy.

The considerable concentration of states near the bottom of the d band has been found for all of the transition elements which have been studied^{13,14,7} and may be considered responsible for their relatively high binding energies. This possibility has been emphasized by Manning and Chodorow⁷ and by Seitz.^{15,16}

The behavior of the lowest energy in each type of band is qualitatively similar to that found by Greene¹⁰ for face-centered iron. However, the method used by Greene does not show the splitting of the d band at $\mathbf{k}=0$, and the lowest band for the face-centered lattice begins at the energy for which $s'=0$ while for the body-centered lattice the lowest band begins at the energy for $3s_1'g_2'+2s_2'g_1'=0$. It turns out that for the portion of the $s'=0$ curve inside of the minimum (it seems probable that this is always the important part for transition metals) the second condition corresponds to a curve shifted slightly toward smaller values of interatomic distance but otherwise similar. The behavior of the energies for which $d_1'=0$ and $3s_1'g_2'+2s_2'g_1'=0$ as a function of interatomic distance is shown in Fig. 6. It is interesting to note that for tungsten with its smaller number of d electrons and a recently-filled f shell, the normal interatomic distance corresponds to the $3s_1'g_2'+2s_2'g_1'$ curve, being higher than the d' curves.

Ferromagnetism

The relation of the ferromagnetic behavior of iron, cobalt, and nickel to the structure of their electronic energy bands has been discussed by Slater in a series of papers.^{14,17,18} There are unsurmounted difficulties in the formulation of a complete theory of ferromagnetism, but certain general features can be discussed in terms of the present model.

In the non-magnetic state there are equal numbers of electrons with each spin, whereas in the magnetic state there are more electrons with positive than with negative spin. In the magnetized state the Fermi energy is of course greater, because in order to reverse the spins it is necessary to transfer electrons to higher vacant levels of the opposite spin. For substances which are ferromagnetic this increase in energy is more than compensated by the increase in the number of exchange integrals between electrons with parallel spin. Slater¹⁴ showed that this change in exchange energy is proportional to the square of the number of uncompensated spins. The change in Fermi energy is also proportional to the square of the number of uncompensated spins if $n(\epsilon)$ can be regarded as constant. The actual relation is

$$\Delta\epsilon_f = \mu^2/2n(\epsilon_m), \quad (3)$$

where μ is the number of uncompensated spins expressed in Bohr magnetons per atom, $n(\epsilon_m)$ is the number of energy levels (both spins) per Rydberg unit of energy at the highest occupied level for the non-magnetic state, and $\Delta\epsilon_f$ is the change in Fermi energy upon reversing $\mu/2$ spins. For ferromagnetism $\Delta\epsilon_e$, the change in exchange energy accompanying the change to the magnetic state, must be larger numerically than $\Delta\epsilon_f$. Hence, it follows that only those substances are ferromagnetic for which $n(\epsilon)$ is large. In this connection it is interesting to note that Greene's results for face-centered iron indicate a much smaller density of states near ϵ_m than reported here for body-centered iron; therefore, it is quite understandable that face-centered iron should not be ferromagnetic.¹⁹

¹³ H. M. Krutter, Phys. Rev. **48**, 664 (1935).

¹⁴ J. C. Slater, Phys. Rev. **49**, 537 (1936).

¹⁵ F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 430 ff.

¹⁶ F. Seitz and R. P. Johnson, J. App. Phys. **8**, 186 (1937).

¹⁷ J. C. Slater, Phys. Rev. **49**, 931 (1936).

¹⁸ J. C. Slater, Phys. Rev. **52**, 198 (1937).

¹⁹ Since face-centered iron is stable only at temperatures above the Curie point and cannot be retained at lower temperatures, no direct evidence about its ferromagnetism

If the number of states per unit energy range is not constant, the change in Fermi energy accompanying the change to the magnetic state is no longer given by Eq. (3) but can be found by using Eq. (1) for each direction of spin. In computing the change in Fermi energy, Bands I and II can be neglected because they are completely filled. Also, it is usually considered that Band VI can be neglected because of the low density of states and because the s and p functions which predominate in this band are concentrated further from the nucleus than the d functions which predominate in the other bands and hence contribute less to the exchange energy. The actual result of the computation of Fermi energy as a function of μ showed that the Fermi energy increased slightly more rapidly than proportional to the square of μ , but the difference from strict proportionality was not enough greater than the computational error to be significant.

For iron there are eight valence electrons per atom; four in the two lowest filled bands, and 0.25 electron in Band VI. There are thus 3.75 electrons per atom in the three bands which are assumed to contribute to the ferromagnetism. With only the three bands contributing to the ferromagnetism, the saturation magnetic moment is determined by one of three conditions:²⁰

1. The number of negative spins per atom cannot be negative.
2. The number of positive spins per atom cannot be greater than three.
3. If $\Delta\epsilon_e$ increases less rapidly with μ^2 than $\Delta\epsilon_f$, the difference may vanish at some value of μ less than that determined by either of the above conditions.

There does not seem to be any element or alloy in the iron group for which the first condition is the determining one. The second would give a saturation moment of $3.00 - 0.75 = 2.25$ Bohr magnetons per atom. The experimental value is about 2.20 or 2.22 magnetons per atom. This small difference cannot be regarded as conclusive

can be obtained. However, any reasonable extrapolation of the high-temperature paramagnetic susceptibility of face-centered iron and the Curie points in the face-centered portion of the Fe-Ni alloy system indicate that face-centered iron would not be ferromagnetic.

²⁰ F. Seitz, reference 15, page 430.

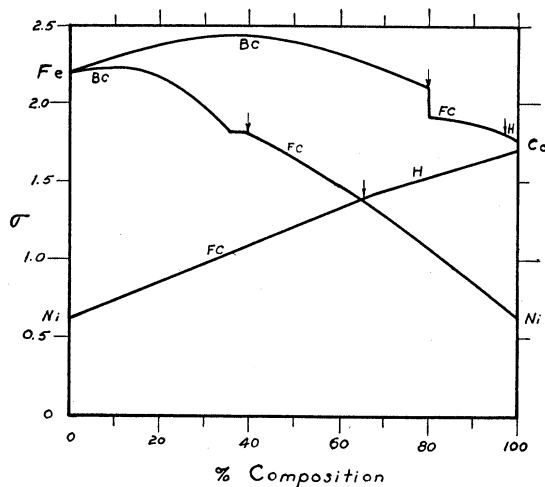


FIG. 7. Magnetic moments of Fe-Ni-Co alloys as a function of composition. (After Borelius.)

evidence against the assumption that the second condition is the important one. In order to say definitely about the third, it would be necessary to have more definite information about the variation of the Fermi and exchange energies with μ .

For the alloys of iron with manganese, chromium, and vanadium the saturation moments decrease with addition of alloying element²¹ and the Curie point also decreases except for a slight initial rise in one or two cases. Since, according to Fig. 4, the $n(\epsilon_m)$ values increase with a decrease in the number of electrons per atom, the most likely explanation of the decreasing saturation moments and Curie temperatures is that they are due to a decrease in the exchange energy gained upon reversal of spin. This decrease in exchange energy is due to the fact that for atoms with smaller nuclear charge, the d functions are concentrated further from the nucleus and hence contribute a smaller exchange integral.²²

For the Fe-Ni (Fig. 7) system the saturation moment increases slightly with the addition of Ni, and then decreases to the phase boundary²³ where the saturation moment is about 2.2 magnetons. Since the corresponding number of electrons per atom is 8.4, it is necessary to assign

²¹ Data quoted by J. C. Slater, reference 17, page 935.

²² J. C. Slater, reference 17, page 934.

²³ G. Borelius, *Handbuch der Metallphysik* (Leipzig, 1935), Vol. I, p. 291.

0.6 electron per atom in order to account for the observed moment.

For cobalt-iron alloys the saturation moment reaches a maximum of 2.4 magnetons at 8.4 electrons per atom and then decreases to 2.0 magnetons at the phase boundary which occurs at 8.8 electrons per atom. For both cases the corresponding number of electrons per atom in Band VI is equal to 0.80.

The number of electrons per atom in Band VI for nickel and cobalt alloys is much greater than the values extrapolated from the present calculations. Two possibilities of accounting for this difference can be suggested. It may be that for these elements the energy at the top of Band VI is much lower than for iron and the density of states is so much higher, that the number of electrons in Band VI can be as large as 0.80. (It is also possible that there is such an effect in iron and that the saturation moment is determined by a balance of exchange and Fermi terms.) It is also conceivable that Band VI contributes to the ferromagnetism. It would not be ferromagnetic by itself, but a net spin for this band might be produced by a coupling with the net spins in other bands.

Electronic Specific Heat²⁴

The electronic contribution to the specific heat is given by the formula^{25,26}

$$(C_v)_e = 0.209 \times 10^{-4} n(\epsilon_m) RT, \quad (4)$$

where $(C_v)_e$ is in cal./g-atom $^{\circ}\text{C}$, $n(\epsilon_m)$ is the number of energy levels per atom per Rydberg unit of energy at the top of the Fermi distribution, R is the universal gas constant, and T is the

absolute temperature. For body-centered iron $n(\epsilon_m)$ is 17 for the non-magnetic state. Hence the corresponding electronic contribution to the specific heat is $6.9 \times 10^{-4} T$. This result is valid only at temperatures well above the Curie temperature. Any possibility of checking this against an excess of C_v above the Dulong and Petit value at high temperatures is made impossible by the phase change. At higher temperatures where the body-centered phase is again stable, there are no satisfactory data for determining the dilatation correction.

In one respect there is satisfactory agreement with experiment. As shown in detail in a later section the body-centered structure can become more stable than the face-centered structure at high temperatures only if the specific heat at constant pressure for this structure is higher in this region than the specific heat²⁷ for the face-centered structure. It is very probable (see reference 40) that the difference is due chiefly to electronic contributions and hence it is a qualitative check on the theory that the value found for body-centered iron is about one and a half times the value found by Greene for face-centered iron.

At low temperatures the distribution of electrons is different and the specific heat for each direction of spin must be computed separately. If the observed value of the saturation moment and the computed $n(\epsilon)$ curves are used to determine the correct values of $n(\epsilon_m)$ to use in Eq. (4), the computed electronic specific heat is found to be $4.6 \times 10^{-4} T$. Measurements by Duyckaerts²⁸ and Keesom and Kurrelmeyer²⁹ at liquid helium temperatures yielded a term $12 \times 10^{-4} T$ in the specific heat.

X-Ray Emission Bands³⁰

The $K\beta_s$ -emission band of iron has been studied

²⁴ In a previous paper (reference 7) Manning and Chodorow reported calculations of the electronic specific heat of metallic tungsten and tantalum. For both of these metals the computed electronic specific heat checked the excess of C_v above 6.0 cal./g-atom $^{\circ}\text{C}$, at high temperatures within the accuracy of the $C_p - C_v$ correction. There were not then and are not yet available any low temperature data for tungsten. For tantalum the electronic specific heat had been computed from data on the effect of a magnetic field on the superconducting transition temperature and a result of approximately $27 \times 10^{-4} T$ had been obtained. More recent data by Keesom and Desirant [Proc. Roy. Soc. Ams. **42**, 536 (1939)] and by Mendelssohn [Nature **148**, 316 (1941)] yield a value $14 \times 10^{-4} T$ compared with the calculated value of $6 \times 10^{-4} T$.

²⁵ E. C. Stoner, Proc. Roy. Soc. **A154**, 656 (1936).

²⁶ H. Bethe, *Handbuch der Physik* (Julius Springer, Berlin), Vol. 24, Part 2, p. 430.

²⁷ J. B. Austin, Ind. and Eng. Chem. **24**, 1225 (1932).

²⁸ G. Duyckaerts, Physica **6**, 401 (1939).

²⁹ W. H. Keesom and B. Kurrelmeyer, Physica **6**, 633 (1939).

³⁰ Bearden and Snyder [Phys. Rev. **59**, 162 (1941)] have reported studies of x-ray emission and absorption of metallic tungsten and compared their results with the $n(\epsilon)$ curves calculated by Manning and Chodorow. Bearden and Snyder compute from their data that the range of occupied levels in the metal is about 6.5 or 7.0 ev. In comparing with the calculated values they use 10.0 ev. as the calculated width. The present author's estimate of this width is 6.0 ev. This is in considerably better agree-

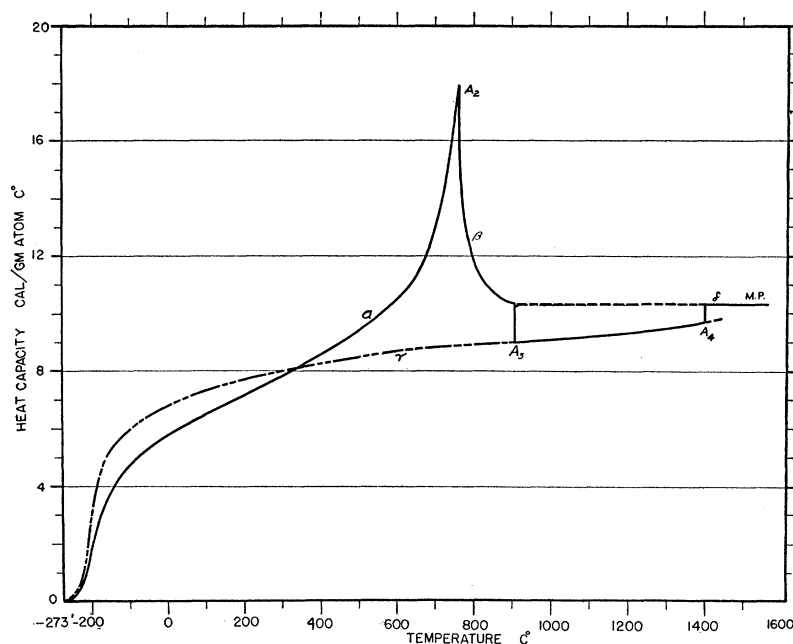


FIG. 8. Specific heat of Fe vs. temperature. (After Austin.)

by Beeman and Friedman³¹ and the $L\alpha$ and $L\beta$ bands by Farineau.³² Beeman and Friedman obtained a width of about 7 ev and Farineau obtained a width of about 5.5 ev. The width of the calculated $n(\epsilon)$ curve is about 5 or 5.5 ev depending upon how much weight is given to the low energy portion of the $n(\epsilon)$ curve. The agreement is probably better than should be expected, as the experimental lines are broadened by the finite width of the lower levels and the Auger effect.

Electrical Conductivity

At room temperatures the conductivity of iron is only about one-eighth of the conductivity of

copper and only a small part of this difference can be accounted for by differences in Debye temperature and atomic volume. The lowest two bands can make no contribution to the conductivity and it is probably correct to assume that Bands III, IV, and V make little contribution to the conductivity because of the high effective mass of the electrons in these narrow bands. Most of the conductivity is therefore due to the electrons in Band VI. Since there is only 0.25 electron per atom in this band, a lower conductivity than for copper should be expected. Since the conductivity varies as the one-third power³³ of the number of conduction electrons per unit volume, the smaller number of conduction electrons in iron than in copper is responsible for an appreciable, but not a major part, of the difference in conductivity. Mott^{8,34} has proposed that the low conductivity of the transition metals is due to the fact that the vacant states in the poorly-conducting bands increase the probability of scattering for the conduction electrons. This theory is able to account qualitatively for a number of features such as the thermoelectric power and high tem-

ment with the experimental results, but the question of addition of line widths probably needs special consideration when the $n(\epsilon)$ curves have such irregular shapes and when the relative proportions of the different types of wave function change with the energy.

The reason for the discrepancy between the 6 ev and the 10 ev has been explained to the author by Dr. Snyder in personal conversation. It arose because the meaning of the term "atomic unit of energy" was not stated carefully enough. In both that paper and this one the unit of energy is the Rydberg unit of energy—13.54 ev—and not twice this quantity which is frequently referred to as an atomic unit. The author regrets any misunderstanding which this may have caused.

³¹ W. W. Beeman and H. Friedman, *Phys. Rev.* **56**, 392 (1939).

³² J. Farineau, *Comptes rendus* **206**, 1011 (1938).

³³ F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 537.

³⁴ N. F. Mott, *Proc. Roy. Soc.* **A153**, 699 (1936); **A156**, 368 (1936).

perature variation of resistance of transition metals.^{34,35} However, Wilson³⁶ has carried out a more detailed investigation in which he shows that transitions from one band to another can take place only if states represented by the same coordinates in the reduced zone scheme have energy differences of the order of magnitude of thermal energies. This is equivalent to assuming that the constant energy surfaces for the different bands intersect or are close together at a number of points in the reduced zone in order for Mott's model to be applicable.³⁷ The energy contours obtained in the present calculations have been examined to see if this condition is satisfied for any appreciable number of points in $\mathbf{k}$ space and it was found that the energy differences between corresponding points in different bands³⁸ were much larger than thermal energies at all points of the momentum cell. Hence either Mott's model is not applicable or the condition discussed by Wilson is not valid. Seitz³⁷ suggests that where d bands are involved the Δk selection rule used by Wilson may not be applicable.

Phase Changes in Metallic Iron

The phase changes which take place in iron as the temperature is raised are rather unusual. At low temperatures the stable structure is body-centered cubic, between 1179° and 1773°K the stable structure is face-centered cubic, and between 1773°K and the melting point the stable structure is again body-centered cubic.

The thermodynamic condition which determines the relative stability of two phases at constant pressure is that the Gibbs³⁹ free energy $U-TS+PV$ shall be a minimum. For phase changes in the solid state the PV term can usually be neglected. In the following discussion the body-centered phase will be denoted by the subscript 1 and the face-centered phase by the subscript 2. We then have at any

temperature:

$$G_1(T) - G_2(T) = [U_1(0) - U_2(0)] + \int_0^T (C_1 - C_2) dT - T \int_0^T (1/T)(C_1 - C_2) dT, \quad (5)$$

where C_1 and C_2 stand for the specific heats at constant pressure.

If the right-hand side of this equation is negative at a given temperature the body-centered structure is stable, and if it is positive the face-centered structure is stable. The empirical specific heats⁴⁰ as chosen by Austin²⁷ are shown in Fig. 8. Since the face-centered structure cannot be retained at low temperatures by quenching, the specific heats for this structure are not obtained directly but by a process of extrapolation from a series of alloys for which the face-centered structure can be retained. At low temperatures it seems definite that the face-centered phase has the lower Debye temperature and hence the higher specific heat. At higher temperatures the specific heat associated with the disappearance of ferromagnetism gives the body-centered phase the higher specific heat. At the transition temperature the free energy of the two phases must be equal. To see how this happens Eq. (5) can be written

$$G_1(B) - G_2(B) = [U_1(0) - U_2(0)] + \int_0^{T_A} (C_1 - C_2) dT - T_A \int_0^{T_A} (1/T)(C_1 - C_2) dT + \int_{T_A}^{T_B} (C_1 - C_2)[1 - (T_B/T)] dT + (T_B - T_A) \int_0^{T_A} (1/T)(C_2 - C_1) dT. \quad (6)$$

In this equation T_A is the temperature at which the specific heats of the two phases become equal,

³⁵ N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford, 1936), p. 267.

³⁶ A. H. Wilson, Proc. Roy. Soc. **167**, 580 (1938).

³⁷ F. Seitz, *Modern Theory of Solids*, page 540.

³⁸ This result can also be obtained by reference to Fig. 2. The condition could be satisfied only for energies near the energies.

³⁹ J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, New York, 1939), p. 23.

⁴⁰ For more recent data and for a review of the literature subsequent to Austin's paper see J. W. Awberry and Ezer Griffiths, Proc. Roy. Soc. **A174**, 1 (1940). Although it seems probable that these data supersede those quoted by Austin, the data quoted by him are sufficiently accurate for the present arguments.

and T_B is the temperature of the transition from the body-centered to the face-centered structure. The sum of the first three terms on the right-hand side is just the difference in free energies at the temperature T_A . Since the body-centered structure is stable at T_A the sum of these three terms must be negative. The fourth term on the right is also negative, so that it is the fifth term which is responsible for making the free energy become positive above T_B . It is interesting to note that this term is merely the entropy at T_A multiplied by the temperature interval between T_A and T_B .

If T_C denotes the transition point at which the body-centered structure again becomes stable, we have:

$$G_1(C) - G_2(C) = (T_C - T_B) \times \left[\int_0^{T_B} (1/T) C_2 dT - \int_0^{T_B} (1/T) C_1 dT \right] - \int_{T_B}^{T_C} (C_1 - C_2) [(T_C/T) - 1] dT. \quad (7)$$

In the bracket the first term represents the entropy of the face-centered structure and the second integral represents the entropy of the body-centered structure at T_B . Since the body-centered structure is stable at 0°K , and the entropy term increases more rapidly with temperature than the energy, the only possibility of making the face-centered structure stable at T_B is for it to have a greater entropy. Hence the first term on the right-hand side of Eq. (7) must be positive. For the body-centered structure to be stable above T_C the second term must be negative and this can be true only if the specific heat at constant pressure is higher for the body-centered phase. Part of this difference in the specific heat might come from a difference in the dilatation correction, but it is probable that most of it comes from the higher electronic specific heat⁴¹ in agreement with the calculations of this paper and the following one.¹⁰

A few remarks on the effect of alloying elements on the transition temperatures can be made. For some substances such as nickel and cobalt the

face-centered structure is more stable than the body-centered structure at absolute zero. Hence if we assume that the energy difference between the phases varies monotonically with composition it follows that adding these elements to iron should widen the temperature range in which the face-centered or γ -phase is stable. In general the energy difference term will favor the face-centered structure whenever the added element has more electrons per atom because the spreading of the energy bands favors the face-centered structure. The Debye temperature will also be affected by alloying elements but general remarks are difficult to make. The variation of the Curie point with composition will also have a marked effect on the lower transition temperature because without the excess specific heat of demagnetization the face-centered structure would become stable at a much lower temperature. It is also true that because of the greater density of states at the top of the Fermi distribution for body-centered iron it becomes ferromagnetic and at absolute zero there is a magnetic term in the free energy which favors the body-centered structure. It thus follows that an element such as manganese which produces a marked lowering of the Curie point will, because of this effect, increase the range of stability of the γ -phase.

When there is such a close balance between opposing factors as has been indicated, the electronic contribution to the specific heat can have an appreciable effect on the transition temperature. This point has been discussed by Smoluchowski⁴² who pointed out that if the addition of an alloying element shifted ϵ_m to a portion of the $n(\epsilon)$ curve where the density of states was decreased for the body-centered structure and increased for the face-centered structure, this would increase the stability range of the face-centered or gamma-structure. The $n(\epsilon)$ curves obtained in this paper and the following paper do not yield conclusive evidence in either agreement or disagreement with this theory. This may indicate either that the method used does not give sufficient detail to answer questions involving the

⁴¹ The importance of the electronic specific heat in making the body-centered structure stable at high temperatures has been pointed out by Seitz in *Modern Theory of Solids*, page 488.

⁴² R. Smoluchowski, Princeton Meeting of the American Physical Society, December, 1941. Abstract: Phys. Rev. **61**, 390 (1942). The author wishes to thank Dr. Smoluchowski for sending him a brief abstract of his talk and for other interesting correspondence on the subject.

TABLE IV. Values of $2rZ_p$ for metallic iron.

ρ	$2rZ_p$	ρ	$2rZ_p$	ρ	$2rZ_p$
0.0	0.0518	4.0	2.2936	6.0	7.524
0.2	0.0632	4.1	2.4875	6.1	7.711
0.4	0.0771	4.2	2.6937	6.2	7.835
0.6	0.0940	4.3	2.9122	6.3	7.886
0.8	0.1146	4.4	3.1423	6.4	7.858
1.0	0.1396	4.5	3.3835	6.5	7.753
1.2	0.1702	4.6	3.6349	6.6	7.581
1.4	0.2072	4.7	3.8953	6.7	7.351
1.6	0.2520	4.8	4.1629	6.8	7.105
1.8	0.3063	4.9	4.4367	6.9	6.845
2.0	0.3720	5.0	4.7145	7.0	6.571
2.2	0.4511	5.1	4.9975	7.1	6.312
2.4	0.5462	5.2	5.2809	7.2	6.063
2.6	0.6601	5.3	5.5699	7.3	5.821
2.8	0.7962	5.4	5.8909	7.4	5.587
3.0	0.9578	5.5	6.1544	7.5	5.363
3.2	1.1490	5.6	6.4492	7.6	5.169
3.4	1.3738	5.7	6.7419	7.7	5.053
3.6	1.6367	5.8	7.0255	7.8	5.089
3.8	1.9422	5.9	7.2906	7.9	5.111
4.0	2.2936	6.0	7.5244	8.0	5.130

change of $n(\epsilon)$ with ϵ or it may be that some of the other effects mentioned above may be important.

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APPENDIX I

Determination of Effective Field in the Metal

Since the method of finding the effective field to use in computing metallic wave functions is slightly different from that for the free atom, it will be described briefly. Atomic calculations are normally carried out in terms of quantities which Hartree denotes by Z and Z_p (Z/r^2 determines the effective force on an electron and Z_p/r determines the potential energy of an electron at a distance r from the nucleus). Z is determined by numerical evaluation of a definite integral and Z_p by solution of the differential equation:

$$dZ_p/d\rho = Z_p - Z \quad (8)$$

which is integrated inwards subject to the boundary condition that Z_p approaches zero at large values of r . The effective field of a valence electron in the metal was assumed to be due to the nucleus, the $1s$ to $3p$ core, and to one s type and six d type functions. The field due to the inner electrons and the nucleus was taken to be the same as found by Manning and Goldberg⁶ for the iron atom. As a first approximation to the charge distribution of the other valence electrons the atomic charge distributions were used

except that they were normalized to the atomic volume characteristic of the metal. In computing the field due to such a charge distribution the ordinary method of inward integration of Eq. (8) is not satisfactory because of the difficulty in determining initial values of $2Z_p$. If the electronic charge due to the valence electrons within a sphere of radius r is designated by ζ , then $2\zeta/r^2$ is the force on one valence electron due to the remaining valence electrons, and the inward integration of this quantity with respect to r yields the potential energy due to the other valence electrons. This method is not applicable to inner shell electrons because of the rapid variation of $2\zeta/r^2$.

By use of the potential field thus found, integrations for d functions for a range of energies were carried out by the same methods as used in self-consistent field calculations.⁴³⁻⁴⁵ The energy for which the radial factor of the d function became zero and also the energy at which the radial derivative became zero at the half distance between nearest neighbors were thus determined. Since the method by which the first approximation was found concentrated the charge too close to the nucleus, the charge densities for these new wave functions would be concentrated too far from the nucleus. An attempt was made to allow for this in a manner similar to that used in atomic calculation by choosing for the next approximation a field obtained by averaging the initial field with one found by using wave functions based upon that field. A weighting of six-tenths initial to four-tenths final has been used. For the final field six different charge distributions corresponding to energies between that for which $d_1' = 0$ and that for which $d_1 = 0$ were used. Since previous experience with transition metals indicated a considerable concentration of levels near $d' = 0$, additional weight was given to levels in this region. Two more approximations were made and at the end of the last approximation the total width of the d band checked the width at the end of the previous approximation within a tenth of a unit. It was therefore decided that approximations made in using this field would be less than other errors inherent in the general method.

Since the effective potential for metallic iron may be useful for other calculations, the values are given in Table IV.

APPENDIX II

Computational Procedure

After the wave functions and their radial derivatives at the half-distances between neighbors and next-nearest neighbors have been obtained, the next step is the solution of the transcendental equations which relate the energy and the components of the wave number vector $\mathbf{k}$. The procedure was similar to that used in the calculations for

⁴³ D. R. Hartree, Proc. Roy. Soc. **A141**, 282 (1933); D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A149**, 210 (1935).

⁴⁴ A. A. Bennett, W. E. Milne, and H. Bateman, *Numerical Integration of Differential Equations*, Bulletin of the National Research Council, No. 92 (1933).

⁴⁵ M. F. Manning and J. Millman, Phys. Rev. **53**, 673 (1938).

tungsten, but one change was made which seems worth recording. A typical example of the transcendental equations to be solved has the form:

$$A_1 T_1^2 T_2^2 + A_2 T_1 T_2 + A_3 T_2^2 + A_4 T_1^2 + A_5 = 0, \quad (9)$$

where $T_1 = \tan(ka/4)$, $T_2 = \tan(ka/2)$ and the A 's are tabulated functions of the wave functions and their derivatives and hence of the energy. One method of solution is to evaluate the expression for two values of $ka/4$, interpolate or extrapolate for a value of $ka/4$ which makes the expression vanish; try another value of $ka/4$ and so forth until the desired accuracy is obtained. Another method is to express T_2 in terms of T_1 and thus obtain a polynomial in T_1^2 which can be evaluated very rapidly by the method of synthetic division.⁴⁶ This procedure was used for all of the transcendental equations except that for F_1 which has twelve different tangent factors. However, a table of these tangent factors as a function of the argument made by Dr. Chodorow in connection with the calculations for tungsten shortened the computations for this direction considerably. Details of the computational method for obtaining $n(\epsilon)$ and $N(\epsilon)$ are given in the appendix of the paper on tungsten.³

APPENDIX III

In reporting calculations such as these, some estimate of the approximations made is in order. The most obvious and probably the most important approximation is the neglect of all exchange effects. This precludes any detailed discussion of ferromagnetism. Correlation effects are also neglected. The neglect of exchange and correlation effects means that calculation of the binding energy cannot be made and remarks about the relative stability of different structures can be only qualitative. The net effect of exchange and correlation would be to make the energy bands narrower and hence $n(\epsilon_m)$ larger. It is to be expected that the effects of exchange and correlation will be greater for iron than for tungsten because of the smaller number of d electrons in tungsten and also because the incomplete shielding of the f electrons in tungsten makes the electrostatic contribution to the potential energy greater.

Another approximation is involved in the Slater method of fitting boundary conditions. Only fourteen functions are used and the continuity condition on functions and derivatives is satisfied only at fourteen points rather than over the entire surface of the Wigner-Seitz polyhedron. An attempt to estimate the magnitude of this error has been made by Shockley,⁴⁷ but it is not certain to what extent his results are applicable to the present problem. More elaborate methods of calculating energy levels in metals have been developed by Slater,¹⁷ Chodorow,¹² and by Herring.^{48,49} The present calculations yield a good general picture of the energy levels, and can serve as a starting point for more elaborate calculations.

Even within the method itself certain approximations are made. Without much more elaborate calculations it is not possible to determine a completely satisfactory charge distribution because the criterion for self-consistency is more difficult to apply in the case of a solid. Another approximation is made in using only known lines and interpolating contours. Similarly, when using sections 0.1 unit apart in finding $N(\epsilon)$ by a volume integration in $\mathbf{k}$ space, some detail in determining the $N(\epsilon)$ curves is lost. The method of determining $n(\epsilon)$ always leads to a further smoothing effect so that the net effect of the last three approximations mentioned is to make the $n(\epsilon)$ less irregular than might be the case if a more elaborate method of calculation were used.

In summary, it seems probable that the general features of the electronic structure of metallic iron as obtained by this method are essentially correct and that detailed numerical agreement is not possible without much more elaborate methods of calculation. It seems probable that the classification of the energy bands into two responsible for the binding, three responsible for the magnetic behavior, and one for conduction is fundamental to the problem. It is interesting to note that the markedly greater value (17 vs. 11) of $n(\epsilon_m)$ for the body-centered structure than for the face-centered structure is necessary in order to account for the observed differences in magnetic behavior and in electronic specific heat, and also to account for the high temperature phase change.

⁴⁶ I. S. and E. S. Sokolnikoff, *Higher Mathematics for Engineers and Physicists* (McGraw-Hill, New York, 1934), Chapter II.

⁴⁷ W. Shockley, Phys. Rev. **52**, 866 (1937).

⁴⁸ C. Herring, Phys. Rev. **57**, 1169 (1940).

⁴⁹ C. Herring and A. G. Hill, Phys. Rev. **58**, 132 (1940).