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Electronic Energy Bands in Face-Centered Iron

Jack B. Greene* and Millard F. Manning**
University of Pittsburgh, Pittsburgh, Pennsylvania

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Calculations of the electronic energy bands for face-centered iron by the Wigner-Seitz-Slater method are reported. There are found to be two filled and four partially-filled bands. The density of states is calculated as a function of the energy; the curves of the density of states *vs.* energy appear quite similar to those calculated by Slater for copper but resemble more closely those for body-centered iron. The density of states at the highest occupied energy level at absolute zero is 11.4 states per Rydberg unit of energy per atom. These results have been used to calculate the average Fermi energy as a function of the total number of valence electrons; to investigate the ferromagnetism of Ni and Co by calculating the change in Fermi energy as a function of the number of uncompensated spins; and to calculate the electronic specific heat at an elevated temperature. The calculated electronic specific heat is found to agree fairly well with the difference from $3R$ of the experimentally-measured specific heat. There are no experimental data for the specific heat of face-centered iron at low temperatures.

INTRODUCTION AND PROCEDURE

At ordinary temperatures metallic iron has a body-centered structure (α-iron), but from 870°C to 1390°C the face-centered structure (γ-iron) is the stable one. Above 1390°C the body-centered structure is again stable. γ-iron is of scientific interest principally because many of its properties are quite different from those of α-iron. The most important of these differences is that γ-iron is not ferromagnetic. Although γ-iron is stable only above the Curie temperature, all extrapolations to room temperature indicate that it would not be ferromagnetic. γ-iron does exist at ordinary temperatures in the form of austenitic steel, since the steel has been quenched from a temperature where γ-iron is the stable form.

The Wigner-Seitz-Slater cellular method of calculating energy bands in metals[1,2] has been applied to sodium,[2] to lithium,[3] to copper,[4] to calcium,[5] and to one transition metal, tungsten.[6] With modifications it has also been applied to some insulators.[7] In this paper it has been applied to face-centered iron. In applying this method one starts with the radial part of the wave function and the radial derivative of the wave function at a distance half-way between nearest atoms in the face-centered lattice. For face-centered iron the lattice parameter at 900°C is 3.63A and the corresponding distance r between nearest neighbors is 4.85 Bohr units. The corresponding value of ($\rho \equiv \log_e 1000r$) is 7.79, where r is in Bohr units. These radial wave functions were found by a modified Hartree procedure in which the Schroedinger equation was integrated numerically, with the same effective field as that used by Manning[8] in the work on body-centered iron and explained fully by him in Appendix I of his report. These integrations were carried out for s, p, d, and f functions over a range of energy values wide enough to give six complete energy bands.

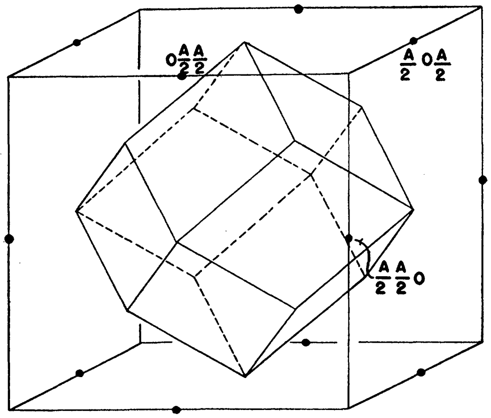

Fig. 1. The polyhedral cell for the face-centered lattice.

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* Now at the University of Illinois, Urbana, Illinois.

** Deceased June 1, 1942.

[1] E. P. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

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

[3] F. Seitz, Phys. Rev. **47**, 400 (1935).

[4] H. M. Krutter, Phys. Rev. **48**, 664 (1935).

[5] M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937).

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

[7] M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, footnote 2, p. 787 (1939).

[8] M. F. Manning, Phys. Rev. **63**, 190 (1943).

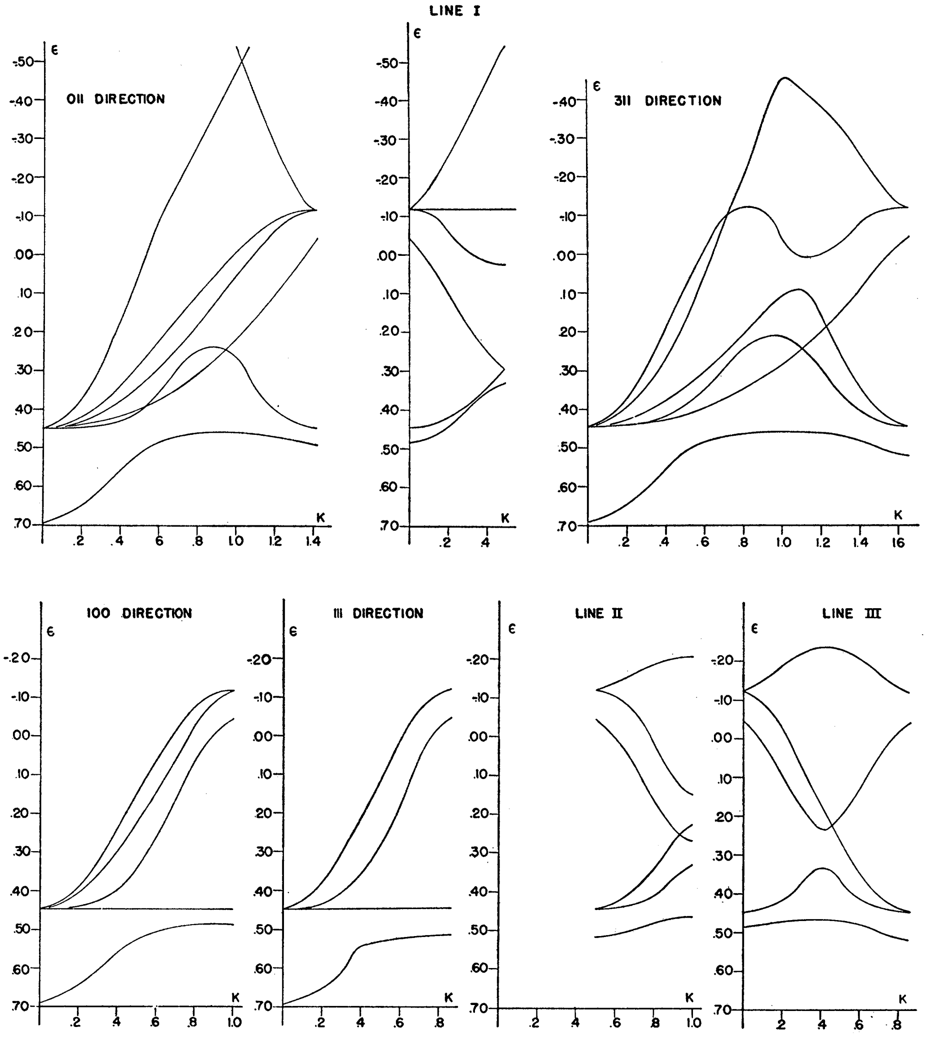

FIG. 2. Energy *vs.* momentum for the different directions of propagation.

The next step was to express the wave function within the polyhedron surrounding an atom in the face-centered lattice (see Fig. 1) as the sum of twelve terms (since there are twelve sides to this cell), each term being the product of a radial wave function times a spherical harmonic. The arbitrary coefficients of these terms must be chosen so that the wave functions satisfy the Bloch[9] periodicity condition and join smoothly in passing from one atom to its twelve nearest neighbors. The application of these conditions leads to a determinant, the solution of which gives the momentum of the electron in certain directions in terms of the radial wave functions and radial derivatives; this momentum of the electron is expressed by the wave number vector K. Since the radial wave functions are in turn functions of the energy, a relationship is established between the energy and the wave number vector or momentum in that particular direction. The solution of the determinant in the general direction is too laborious to attempt, but for a

TABLE I. Maximum and minimum energies for each band.

Band	I	II	III	IV	V	VI
Max. ϵ	0.688	0.443	0.443	0.443	0.443	0.443
Min. ϵ	0.327	0.240	-0.0475	-0.124	-0.124	-0.525

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[9] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

number of symmetrical directions the solution simplifies a great deal. For the face-centered lattice the results of the expansion of the determinant for a number of special directions have been given by Shockley.[10]

RESULTS

The results of the calculation of the energy as a function of the momentum are given in Fig. 2. In Table I the maximum and minimum energies for each band are given, and in Table II the energies at a number of special points in the first Brillouin zone (the momentum cell) are tabulated. Figure 3 shows the first Brillouin zone for the face-centered lattice with the location of these special points indicated. (The point O is the center of the cell but is not shown in this figure.) In these tables and elsewhere in this paper ϵ is the negative of the energy expressed in Rydbergs. The curves for the 011 direction, for the 100 direction, and for the 111 direction are quite similar to those for copper.[4] These were the only directions for copper available for comparison.

Using the energy-momentum relationships for the known lines in K space, one can draw fairly good energy contours for the principal planes in K space. One can then interpolate from these to get energy contours in the planes $K_z=0.1$, 0.2, $\cdots 1.0$. In each of these planes the area enclosed by each constant-energy contour, within which the energy was less than (i.e., ϵ greater than) the value of the energy for this contour, was found by means of a planimeter. This was done for each of the ten planes and then the results integrated to get the volume enclosed by the surface of constant energy. This volume is then proportional to the number of electrons per atom or states per atom with energy less than the energy considered. The number of electrons with energy less than a given energy can be found by the normalizing condition that the total volume of the momentum cell represents two electrons per atom in each energy band. This quantity is called $N(\epsilon)$. The values of $N(\epsilon)$ for each of the energy bands and for the sum of the six bands are given in Tables IIIa and IIIb. It will be noticed that in the first three bands, values of $N(\epsilon)$ are tabulated every 0.025 unit of ϵ. For Bands IV and V they are tabulated every 0.05 unit of ϵ, and for Band VI every 0.10 unit of ϵ. This was done because the last three bands extended through a wider energy range and would have required more contours than it was felt the accuracy of the method justified.

TABLE II. Values of ϵ for some points in the Brillouin zone.

Point	Band I	II	III	IV	V	VI
O	0.69	0.44	0.44	0.44	0.44	0.44
A	0.517	0.44	0.44	−0.0475	−0.125	−0.125
B	0.48	0.44	−0.0475	−0.125	−0.125	−0.125
C	0.46	0.31	0.18	0.01	−0.05	−0.45
D	0.325	0.29	0.29	0.02	−0.125	−0.55
E	0.46	0.31	0.18	0.01	−0.05	−0.45

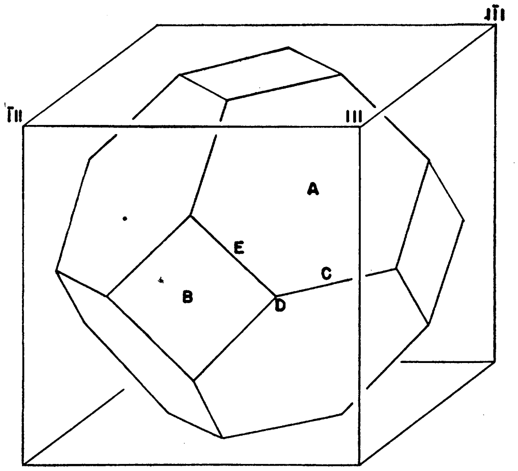

FIG. 3. The first Brillouin zone for the face-centered lattice, showing the points referred to in Table II.

From the values of $N(\epsilon)$ the values of $n(\epsilon)[=-(dN/d\epsilon)]$ can be found by numerical differentiation. $[n(\epsilon)d\epsilon$ is the number of energy levels per atom with energy between ϵ and $(\epsilon+d\epsilon)$.$]$ The resulting values of $n(\epsilon)$ for the separate bands and the total value of $n(\epsilon)$ for all six bands as functions of ϵ are given in Fig. 4.

Bands I and II, being completely filled, would not be expected to contribute either to the electrical conductivity or to ferromagnetism. Bands III, IV, and V are the ones to be investigated to see why face-centered iron is not ferromagnetic. Band VI looks more like a band predicted from the "free electron" picture than any of the others. It probably accounts for the

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[10] W. Shockley, Phys. Rev. **51**, 129 (1937).

TABLE IIIa. Number of states having energies less than a given energy.

Band I		Band II		Band III		Band IV		Band V		Band VI	
ϵ	$N(\epsilon)$	ϵ	$N(\epsilon)$	ϵ	$N(\epsilon)$	ϵ	$N(\epsilon)$	ϵ	$N(\epsilon)$	ϵ	$N(\epsilon)$
0.675	0.001	0.425	0.496	0.425	0.165	0.40	0.045	0.40	0.016	0.40	0.006
0.65	0.009	0.40	0.905	0.40	0.349	0.35	0.146	0.35	0.056	0.35	0.024
0.625	0.029	0.375	1.24	0.375	0.502	0.30	0.274	0.30	0.104	0.30	0.049
0.60	0.057	0.35	1.52	0.35	0.615	0.25	0.430	0.25	0.182	0.25	0.082
0.575	0.084	0.325	1.72	0.325	0.731	0.20	0.625	0.20	0.284	0.20	0.126
0.55	0.126	0.30	1.86	0.30	0.850	0.15	1.03	0.15	0.387	0.15	0.174
0.525	0.206	0.275	1.99	0.275	0.982	0.10	1.40	0.10	0.520	0.10	0.238
0.50	0.399	0.25	2.00	0.25	1.21	0.05	1.62	0.05	0.684	0.05	0.304
0.475	0.850			0.225	1.64	0.00	1.88	0.00	0.859	0.00	0.394
0.45	1.57			0.20	1.74	−0.05	1.96	−0.05	1.13	−0.10	0.642
0.425	1.77			0.175	1.82	−0.10	1.99	−0.10	1.60	−0.20	1.05
0.40	1.89			0.15	1.87					−0.30	1.47
0.375	1.95			0.125	1.91					−0.40	1.82
0.35	1.99			0.10	1.94					−0.50	1.99
				0.075	1.96						
				0.05	1.98						
				0.025	1.99						
				0.00	2.00						

TABLE IIIb. Summation of $N(\epsilon)$ values for all bands.

ϵ	$\Sigma N(\epsilon)$	ϵ	$\Sigma N(\epsilon)$
0.675	0.001	0.30	5.14
0.65	0.009	0.25	5.90
0.625	0.029	0.20	6.78
0.60	0.057	0.15	7.46
0.575	0.084	0.10	8.10
0.55	0.126	0.05	8 59
0.525	0.206	0.00	9.13
0.50	0.399	−0.10	10.2
0.475	0.850	−0.20	11.0
0.45	1.57	−0.30	11.5
0.425	2.43	−0.40	11.8
0.40	3.21	−0.50	12.0
0.35	4.35		

electrical conductivity. Band VI also is the widest band of those investigated. In general features the energy bands for face-centered iron resemble those of body-centered iron[8] more than any other metal that has been investigated. In general features the total $n(\epsilon)$ curve resembles that for copper,[11] but since the energy units are different for the two cases, closer comparison is difficult. Band VI in copper is very much like Band VI for face-centered iron; that is the only single energy band shown for copper.[11]

Since there are eight valence electrons per atom in face-centered iron, reference to Table IIIb shows that the highest occupied level at absolute zero in face-centered iron occurs at $\epsilon=0.117$. The corresponding value of $n(\epsilon)$ is 11.4. Thus the density of states at the edge of the Fermi distribution is 11.4 states per atom per Rydberg unit of energy.

APPLICATIONS

Energy Relations

The average Fermi energy has been computed as a function of the total number of valence electrons per atom. The average Fermi energy $\bar{\epsilon}$ is defined by the equation

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

where ϵ_0 refers to the lowest level occupied at absolute zero and ϵ_m to the highest. Equation (1) can be integrated by parts, giving

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

This avoids the inaccuracies that arose when $N(\epsilon)$ was differentiated numerically to give $n(\epsilon)$. The results of these computations for the face-centered lattice are shown in Fig. 5; the average Fermi energy is plotted against the total number of valence electrons per atom. In the preceding paper,[8] Manning has discussed the average Fermi energy for the two kinds of iron and the possible extrapolations to predict the structure of the other neighboring elements in the periodic table.

For the face-centered lattice the lowest band begins at the energy for which $s'=0$ and the other five bands begin at the energy for which $d'=0$. The behavior of the energies for which

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

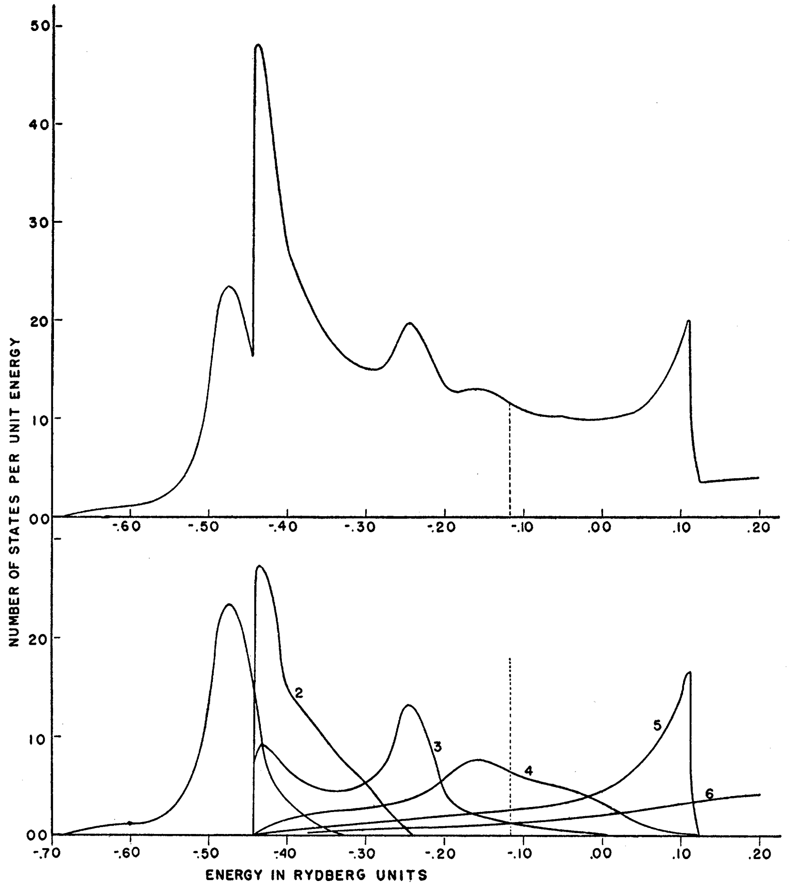

FIG. 4. Number of states per unit energy range *vs.* energy. The upper curve is the sum of the six lower curves.

$s'=0$ and for which $d'=0$ as a function of interatomic distance is shown in Fig. 6. It should be noted that the abscissa is r, the actual interatomic distance, and not ρ, the $\log_e$ of the interatomic distance.

Magnetism

It is interesting to see whether these calculations can offer at least a qualitative explanation of why body-centered iron is ferromagnetic and face-centered iron is not. According to the discussion of ferromagnetism in the paper on body-centered iron,[8] when a substance changes from a non-magnetic state to a magnetic state there is an increase in the Fermi energy, and an increase in the binding energy due to the increase in the number of exchange integrals between electrons of parallel spin. A ferromagnetic substance is one in which the change in Fermi energy is more than compensated for by the increase in the number of exchange integrals. Slater[11] 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 expression for the change in Fermi energy being

$$\Delta\epsilon_F=\mu^2/2n(\epsilon_m), \tag{2}$$

where μ is the number of uncompensated spins in Bohr magnetons, and $n(\epsilon_m)$ is the number of energy levels of 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. The smaller $\Delta\epsilon_F$ is, the more likely it is to be compensated for by the increase in exchange integrals;

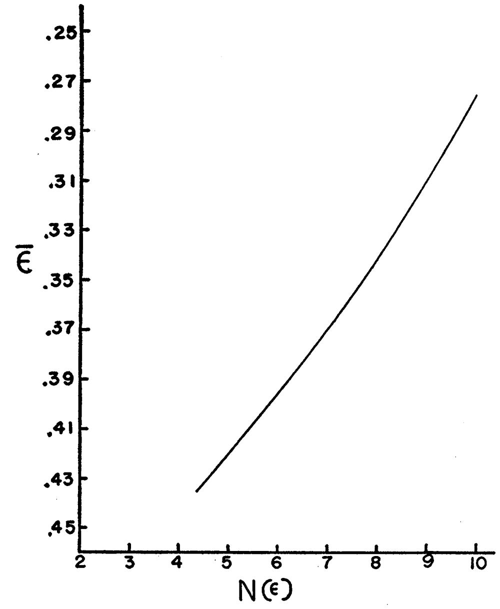

FIG. 5. Average Fermi energy *vs.* total number of valence electrons per atom.

hence, the larger $n(\epsilon_m)$ is, the more likely the metal is to be ferromagnetic. For body-centered iron $n(\epsilon_m)$ is 17 and for face-centered iron $n(\epsilon_m)$ is 11.4. Hence the body-centered metal would be more likely to be ferromagnetic.

If the number of states per unit energy range is not constant, the change in Fermi energy is no longer given by Eq. (2), but must be found by using Eq. (1) for each direction of spin. In computing this change Bands I and II, being closed bands, are neglected, and Band VI, being concentrated relatively far from the nucleus, is also neglected. In the hope of applying these calculations to the neighboring ferromagnetic metals, cobalt and nickel, the change in Fermi energy as μ increases was computed for the total number of valence electrons equal to 8.0, 8.5, 9.0, 9.5, and 10.0, respectively. Equation (1) was used for each direction of spin, and it was applied only to Bands III, IV, and V. In general, the Fermi energy increased less rapidly than did μ^2 but there were some fluctuations which indicated the computational error was rather large.

The saturation magnetic moment of a ferromagnetic metal is determined by one of the following conditions:[8]

(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 the exchange contribution to the energy increases less rapidly with μ^2 than does the increase in the Fermi energy, the difference between the two may vanish at some value of μ less than that determined by either of the other two conditions.

The first condition never seems to occur in any atom or alloy involving iron group elements. Since, for face-centered iron, the Fermi energy did not increase as rapidly as μ^2 for the total number of valence electrons equal to 8.0, 8.5, 9.0, 9.5, and 10.0, it would indicate that condition (3) did not determine the maximum value of μ. Then the number of positive spins per atom must be equal to three; i.e., all the levels with plus spins are filled. Table IV shows a comparison of the value of the saturation magnetic moment calculated on this assumption and the experimentally-observed value[12] for Ni and Co.

The calculated magnetic moment for Ni is arrived at in the following way: There are 10 outside electrons, of which 4 are in Bands I and II; from the results for face-centered iron there are 0.64 electron in Band VI. Thus there are 5.36 electrons in the bands that contribute to magnetism. If there are 3 electrons with plus spin there are 2.36 electrons with minus spin and the magnetic moment is 0.64 spin per atom. This agrees fairly well with the observed value

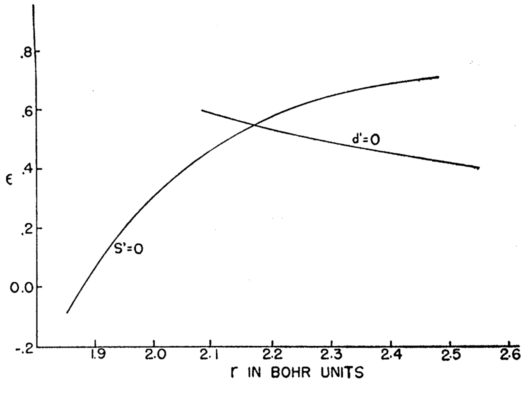

FIG. 6. The energy for which $d'=0$ and the energy for which $s'=0$ as a function of interatomic distance.

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[12] E. C. Stoner, *Magnetism and Matter* (Methuen and Company, Ltd., London, 1934), p. 366.

of the saturation magnetic moment, but the value calculated in the same way for cobalt is somewhat different from the observed value. This might be due to the fact that the results for face-centered iron cannot be applied to hexagonal cobalt; it might be due to errors in these calculations; or possibly, the levels with plus spin are not filled. If one uses the observed saturation magnetic moment and assumes the levels of plus spin are all filled, then one finds that the corresponding number of electrons in Band VI has to be 0.71. This value is much larger than the value indicated by the calculations for face-centered iron. Manning[8] found this same difficulty with cobalt-iron alloys. He suggested the possibility that the electrons in Band VI, by coupling with electrons in other bands, contribute to the magnetic moment.

Electronic Specific Heat

The electronic contribution to the specific heat may be computed from the formula[13]

$$(C_v)_e=(5.670/27.08)\times 10^{-4}n(\epsilon_m)RT, \qquad (3)$$

where $(C_v)_e$ is the electronic contribution to the specific heat per gram atom, R is the universal gas constant, T is the absolute temperature, and $n(\epsilon_m)$ is the number of states of both spins per Rydberg unit of energy at the edge of the Fermi distribution.

It is only at very high and very low temperatures that the electronic contribution to the specific heat is appreciable. The contribution at very low temperatures was not computed because there are no experimental data available for comparison. For high temperatures it was decided to compare the theoretical contribution to the specific heat with that computed from experimental data at a particular temperature. The temperature of 960°C is well above the transition temperature from α- to γ-iron and there are very good data for the specific heat of iron at this point.

Specific heat measurements are made at constant pressure, but for comparison purposes one needs to have the specific heat at constant volume, C_v. This is generally computed from the equation

$$C_p-C_v=9\alpha^2VT/\beta, \qquad (4)$$

where 3α is the thermal coefficient of volume expansion per degree centigrade, V is the specific volume, T is the absolute temperature, and β is the compressibility. All the quantities except β are available at the required temperature. β is ordinarily measured at room temperature and extrapolated to higher temperatures, but face-centered iron is unstable at room temperature. However, if we make use of Grüneisen's law,

TABLE IV. Saturation magnetic moments for nickel and cobalt.

Element	Calculated magnetic moment	Observed magnetic moment
Co	1.39	1.71
Ni	0.64	0.61

$$\gamma=3\alpha V/C_v\beta, \qquad (5)$$

where γ has an approximately constant value for all temperatures,[14] then, writing Eq. (4) in terms of γ, we get

$$C_p/C_v=1+3\gamma\alpha T. \qquad (6)$$

The value of γ used[15] is an extrapolated value, since there is no experimental one available for face-centered iron. The value of γ does not vary much from metal to metal; for α-iron it is 1.68; for copper, 1.96; for nickel, 2.2; and for cobalt, 2.1. Since copper and nickel both have face-centered structures, the value for face-centered iron should be about 2.0.

Substituting the following values[16] of C_p, α, γ, and T in Eq. (6):

$$(C_p)_{960^\circ\mathrm{C}}=7.94\ \text{cal./g atom °C},$$

$$(\alpha)_{960^\circ\mathrm{C}}=25\times 10^{-6}\ \text{per °C},$$

$$\gamma=2.0,$$

$$T=1233^\circ\mathrm{A},$$

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[13] E. C. Stoner, Proc. Roy. Soc. **154**, 656 (1936); also H. Bethe, *Handbuch der Physik* (J. Springer, Berlin, 1933), Vol. 24, Part 2, p. 430.

[14] See F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 138.

[15] Values of γ are from J. C. Slater, Phys. Rev. **57**, 744 (1940).

[16] Value of $(C_p)_{960^\circ\mathrm{C}}$ is an experimentally-determined value, reported by E. Lapp, Ann. de physique **6**, 826–855 (1936); Value of $(\alpha)_{960^\circ\mathrm{C}}$ is from *Metals Handbook* (American Society for Metals, Cleveland. 1939), p. 434.

one gets[17]

$$C_v = 6.70 \text{ cal./g atom °C.}$$

If one assumes that the specific heat due to the lattice vibrations at this temperature is the Dulong and Petit value of $3R$, then the quantity

$$C_v - 3R = 0.73 \text{ cal./g atom °C}$$

represents the electronic specific heat at this temperature. The theoretical value of the electronic specific heat computed by Eq. (3) is 0.59 cal./g atom °C, and the agreement between these two values is very good.

It is to be expected that the theoretical value of the electronic specific heat would be smaller than the other value. If the lattice vibrations were not entirely harmonic the value of $(C_v - 3R)$ would contain contributions due to the anharmonicity as well as the contribution of the electronic specific heat. Furthermore, the method of calculating the electronic energy bands reported here did not consider such corrections as exchange and correlation, which would tend to make the total spread in energy smaller and hence $n(\epsilon)$ larger. This would make the electronic contribution greater than that found here.

Qualitatively one can see that the electronic specific heat of body-centered iron would be greater than that of face-centered iron because $n(\epsilon_m)$ is greater for the body-centered iron. Manning[8] has already pointed out that it is because of this high electronic specific heat for the body-centered phase that this phase again becomes stable as the temperature increases.

In conclusion it should be pointed out that the same approximations have been made in the calculations for face-centered iron as were made for body-centered iron. A detailed discussion of these approximations and their accuracy has been given by Manning[8] in Appendix III of the paper on body-centered iron.

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[17] By a method involving an extrapolation of β, Mme. Lapp has calculated a value of C_v to be 7.66 cal./g atom °C; see reference 16.

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The Nature of the Primary Particles Responsible for Cosmic-Ray Phenomena

W. F. G. SWANN
Bartol Research Foundation of The Franklin Institute, Swarthmore, Pennsylvania

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LATITUDE EFFECT CONSIDERATIONS

As a preliminary, we notice that if $\beta = v/c$, the minimum value for vertical entry through the earth's magnetic field H of a particle of mass m and charge ne is given by

$$(m/n)[\beta_m/(1-\beta_m{}^2)^{\frac{1}{2}}] = ef(H), \tag{1}$$

where $f(H)$ involves only the field and terrestrial dimensions, and e is the electronic charge.

We note, therefore, that if subscripts (1) and (2) refer to magnetic latitudes φ_1 and φ_2

$$\frac{\beta_{m1}}{(1-\beta^2_{m1})^{\frac{1}{2}}}\,\frac{(1-\beta^2_{m2})^{\frac{1}{2}}}{\beta_{m2}} = \frac{f(H_1)}{f(H_2)}. \tag{2}$$

We note further that if the primary particle splits into mesotrons which are born at rest in the frame of reference of the primary particles, then the value of β for the primary particle is equal to that for the corresponding mesotrons, and (2) applies for the minimum velocities of the mesotrons at the two latitudes.

Now the writer has shown[1] that if $F(E)dE$ represents the energy distribution of the vertically directed mesotrons at the point of production, then the number of mesotrons at a distance x below this point, and resulting from the group representing the integrated value of $F(E)dE$, is N_x where

$$N_x = \int_{Em}^{\infty} \{[1 + A/(\gamma+1)]e^{-\lambda x} - A/(\gamma+1)\}^{[\lambda c\tau_0(\gamma+1+A)]^{-1}} F(E)dE, \tag{3}$$

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[1] W. F. G. Swann, Phys. Rev. **60**, 470 (1941).