Electronic Energy Bands in Iron*†

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The method of orthogonalized plane waves has been used to calculate the energy band structure of valence electrons in iron. Application of the results is made to the energy band theory of ferromagnetism. The exchange splitting of the energy bands and the tendency to ferromagnetism at absolute zero have been calculated.

INTRODUCTION

A CALCULATION of electronic energy bands in iron is of interest for the information it may reveal about the theory of ferromagnetism. The form of iron considered here is α iron, which has the body-centered cubic lattice.[1] The band structure of this form of iron was first calculated by Manning,[2] who used the cellular method. The results reported here bear little quantitative resemblance to those of Manning.

The calculation was performed principally by the orthogonalized plane wave (OPW) method.[3,4] In this method, the wave function for the states of interest is expanded in orthogonalized plane waves, which are plane waves made orthogonal to the assumed known eigenfunctions of the core electrons. The states of interest here are those formed from the $3d$ and $4s$ atomic levels. The OPW method requires solution of a determinantal equation of high order and would be impractical if high-speed electronic computing facilities were not available. Success of this method depends on the core functions to which the plane waves are made orthogonal being reasonably close approximations to eigenfunctions of the crystal potential. Because of the inclusion of exchange in the crystal potential where the core functions are formed from a Hartree free atom field, this condition is not satisfied. Consequently the OPW method failed for states of S-like symmetry and these had to be treated by the cellular method.[4] Also, a modification of the OPW method had to be made to obtain reasonable convergence of the expansion for states of D-like symmetry since these are orthogonal by reason of symmetry to all the core eigenfunctions. This is accomplished by adding to the expansion a function having the character of an atomic d function close to any nucleus.[4]

The principal physical problem in a band structure calculation is the determination of a crystal potential. If it were possible to calculate a self-consistent field for a crystal, errors in the assumed potential would be eliminated when the final result was obtained. Calculation of a self-consistent field for iron is impractical with present computing techniques, and it is unfortunately true that some of the results are sensitive to the choice of potential. Some features: the relative positions of the d-band levels at symmetry points in the Brillouin zone, and the exchange splitting of corresponding states of electrons of $+$ and $-$ spin are reasonably insensitive to details of the potential. Other results, such as the width of the d band and the relative position of the $3d$ and $4s$ levels at the center of the Brillouin zone, are much more sensitive to the potential and must be viewed with some reserve.

The calculation can now be outlined briefly. A starting charge density was formed from superposed Hartree charge densities for the d^6s^2 configuration of the free iron atom arranged in the proper crystal lattice. The starting potential was computed from this; exchange effects for a nonmagnetic state were included by means of Slater's free electron approximation to the exchange potential.[5] Convergent OPW expansions were obtained for nine states in the Brillouin zone: Γ_{12}, $\Gamma_{25'}$, Γ_{15}, H_{12}, $H_{25'}$, H_{15}, N_2, N_3, and N_4. An interpolation scheme recently proposed by Slater and Koster[6] was used to extend these results to other states.

The width of the $3d$ band was calculated to be about two electron volts. The separation of the $3d$ levels at the center of the Brillouin zone is considerably smaller than it is at the corners and faces of the zone. The charge density of the $3d$ electrons is more compact than that of the Hartree free atom field. This is due to the inclusion of exchange, and is in agreement with the interpretation of neutron polarization experiments.[7]

The relative position of the $4s$ and $3d$ bands is sensitive to the potential used and is apparently incorrectly given by the potential mentioned. The $4s$ band was predicted to be above the $3d$ band at all points. An improved potential was obtained by assuming seven $3d$ electrons instead of six and by recalculating the exchange potential on the basis of the Hartree-Fock equa-

* Preliminary results were presented at the New York Meeting of the American Physical Society, January 27, 1955 [Phys. Rev. **98**, 1150 (1955)].
† Part of material contained in a thesis submitted to the faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctotor of Philosophy.
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[1] The lattice parameter is taken to be 2.86645×10^{-8} cm. The radius of the atomic sphere is then 2.667 Bohr units. D. E. Thomas, J. Sci. Instr. **25**, 440 (1948).
[2] M. F. Manning, Phys. Rev. **63**, 190 (1943).
[3] C. Herring, Phys. Rev. **57**, 1169 (1940).
[4] A discussion of some features of the OPW method especially pertinent to this calculation is given by J. Callaway, Phys. Rev. **97**, 933 (1955).

[5] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[6] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).
[7] J. Steinberger and G. C. Wick, Phys. Rev. **76**, 994 (1949).

tions. It was revealed that the Slater free electron approximation overestimates the exchange energy by about 15 percent for $3d$ electrons and by 20 percent for $4s$ electrons. The improvement in potential taken in first order perturbation theory placed the $4s$ level Γ_1 about 1.4 ev below the bottom of the $3d$ band.

Application was made to the theory of ferromagnetism by calculating from the Hartree-Fock equations the change in potential energy of a $3d$ electron when one $3d$ electron per atom reverses its spin. This energy was found to be between 1.23 and 1.58 ev. A density of states curve was calculated for the unmagnetized state, and the change in kinetic energy upon magnetization was computed to be 0.69 ev. This gives a tendency to ferromagnetism between 0.54 and 0.89 ev at absolute zero. This is considerably too large. Most of the error probably results from underestimation of the change in kinetic energy caused in turn by underestimation of the d-band width.

The exchange splitting of the band structure was considered. Corresponding states of D symmetry are separated by a gap or the order of 3 ev; the S-like levels Γ_1 are separated by about 1 ev. A total band width of 4.1 ev from the bottom of the $4s$ band to the Fermi level in the $3d$ band (magnetized state) was obtained.

Finally, on the basis of this calculation, one would expect a rigorous self-consistent field calculation of the energy levels of electrons in iron would give overlapping d and s bands with a d-band width of the order of that which has been estimated empirically, and would give an energy change on magnetization which might be of the same order as the observed change, or which might be considerably larger (due to neglect of correlation).

CRYSTAL POTENTIAL

The energy band theory of solids is conceptually based on the Hartree-Fock equations. However, it has not been possible to solve the Hartree-Fock equations exactly for a solid. There are two principal difficulties: (1) The effective potential for an electron state $\psi_k{}^i$ (ith irreducible representation of wave vector $\mathbf{k}$) depends on $\psi_k{}^i$ and is different for each state $\psi_k{}^i$. This leads to great complication and is almost never handled exactly. One approximation often used is that each electron moves in the field of an ion. It has also been proposed to simplify the Hartree-Fock equations so that there is a common potential for all states.[5] One convenient method is by means of a free-electron approximation: it is assumed that the exchange potential at any point is determined by the local charge density of electrons of the same spin and is the same as for a free-electron gas of the same density.[5] A somewhat better approximation is to assume that the exchange potential is the same for all states of a given angular momentum and spin,[8] or in the case of a solid, is determined by the

predominant angular momentum in the decomposition of $\psi_k{}^i$ into spherical harmonics.

(2) Since it is not practical to calculate a self-consistent field for a solid, a charge distribution or a potential must be chosen. In some cases, particularly the alkali metals, it is possible to use spectroscopic data to determine the potential (or an equivalent). For more complicated cases, recourse is made to a Hartree (or Hartree-Fock) field for the free atom and from this a starting charge density and a potential are computed. Since the charge density around an atom in the crystal may differ from what it is for a free atom, it is sometimes attempted to superpose free atom charge densities arranged on atomic sites in the crystal lattice. The numerical reliability of such procedures is questionable, but it is doubtful whether better methods are available.

In this calculation, free atom charge densities obtained from the Hartree field for the d^6s^2 configuration of atomic iron calculated by Manning and Goldberg[9] placed on lattice sites were superposed. The result was spherically averaged and normalized to 26 electrons in the unit cell. For convenience in calculating exchange potentials, the d electrons were also treated separately. A Coulomb potential was computed from this charge density in the usual way, and an exchange potential was obtained by Slater's free electron approximation for an unmagnetized state with three $3d$ electrons of each spin. In this approximation,

$$V_+ = -6(3\rho_+/4\pi)^{\frac{1}{3}}; \qquad (1)$$

V_+ is the exchange potential in atomic units for an electron of positive spin and ρ_+ is the local charge density of electrons of positive spin.

The observed saturation magnetic moment of iron has been interpreted as indicating there are considerably less than two $4s$ electrons per atom in metallic iron.[10] Also, the reliability of the free electron approximation to the exchange potential can be questioned. When it was found that the results obtained with the potential just described were unsatisfactory in certain respects, it was decided to investigate the effect of assuming that there are seven $3d$ electrons instead of six and of computing the exchange potential from the Hartree-Fock equations. An examination of various methods of averaging exchange potentials has been reported by Herman, Callaway, and Acton.[8] It can be deduced from the data in this paper that the free electron approximation overestimates the exchange energy for a $3d$ electron by about 20 percent compared to the Hartree-Fock equations for the case of a free germanium atom. The situation turns out to be similar for iron.

The Hartree-Fock exchange potential appearing in the wave equation for a state $\psi_{nlm}(r_1)$ may be written

[8] Herman, Callaway, and Acton, Phys. Rev. **95**, 371 (1954).

[9] M. F. Manning and L. Goldberg, Phys. Rev. **53**, 662 (1938).
[10] N. F. Mott, Proc. Phys. Soc. (London) **47**, 571 (1935).

as follows:

$$V_{nlm}(r_1) = \frac{\sum_{n'l'm'}\left[\int \psi_{n'l'm'}{}^*(r_2)\frac{2}{r_{12}}\psi_{nlm}(r_1)dr_2\right]\psi_{n'l'm'}(r_1)}{\psi_{nlm}(r_1)}. \quad (2)$$

The summation over $n'l'm'$ is restricted to all occupied states having the same spin as nlm. If for a given $n'l'$, all the m' states are occupied, the contribution to the exchange potential from those states is independent of m and m'. If a shell is incompletely filled, as is the case for the d electrons (assuming the unmagnetized condition), some assumption has to be made about the occupancy of the m levels. For the purpose of calculating an exchange potential, it is convenient to assume, in the absence of other information, that they are occupied with equal probability. In this case, the exchange potential will be spherically symmetric. In calculating that part of the exchange potential for the state Γ_1 that is due to the interaction of the $3d$ and the $4s$ electrons it is sufficient to use just $n/5$ of the $4s$-$3d$ exchange for a closed $3d$ shell. (Here n is the number of $3d$ electrons of spin parallel to that of the $4s$ electron.)

The situation is more complicated when one considers the $3d$-$3d$ interaction in calculating the exchange potential for a $3d$ state. It can be shown that the exchange potential for a $3d$ electron in a closed shell can be written as[11]

$$V_{3d}(r) = \frac{2}{r}\left[Y_0(3d,3d,r)+\frac{2}{7}\left\{Y_2(3d,3d,r)+Y_4(3d,3d,r)\right\}\right]$$

$$+\frac{2}{5r}\sum_{n=1}^{4}Y_2(ns,3d,r)\frac{P_{ns}(r)}{P_{3d}(r)}+\frac{1}{r}\sum_{n=2}\left[\left\{\frac{4}{5}Y_2(np,3d,r)\right.\right.$$

$$\left.\left.+\frac{18}{35}Y_3(np,3d,r)\right\}\frac{P_{np}(r)}{P_{3d}(r)}\right], \quad (3)$$

where

$$Y_k(nl,n'l',r) = \int_0^r P_{nl}(r_1)P_{n'l'}(r_1)\left(\frac{r_1}{r}\right)^k dr_1$$

$$+\int_r^\infty P_{nl}(r_1)P_{n'l'}(r_1)\left(\frac{r}{r_1}\right)^{k+1} dr_1, \quad (4)$$

and

$$\psi_{nlm}(r) = \frac{P_{nl}(r)}{r}Y_{lm}(\theta,\phi), \quad (5)$$

and the P_{nl} are normalized to one. Similarly, for the $4s$ state Γ_1 we write (assuming closed shells):

$$V_{4s} = \frac{2}{r}\frac{1}{P_{4s}}\left[\sum_{n=1}^{4}P_{ns}(r)Y_0(4s,ns,r)\right.$$

$$\left.+\sum_{n=2}^{3}P_{np}(r)Y_1(4s,np,r)+P_{3d}(r)Y_2(4s,3d,r)\right]. \quad (6)$$

[11] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A157, 490 (1936).

Now suppose there are n $3d$ electrons of $+$ spin. A simple argument shows that in order to preserve the spherical symmetry of the potential, one should modify Eq. (3) by multiplying the braces containing Y_2 and Y_4 by $(n-1)/4$, i.e., we have

$$V_{3d} = \frac{2}{r}\left[Y_0(3d,3d,r)+\frac{2}{7}\frac{(n-1)}{4}\right.$$

$$\left.\times\left\{Y_2(3d,3d,r)+Y_4(3d,3d,r)\right\}\right]+\cdots, \quad (7)$$

the remainder being unchanged. This prescription will be seen at once to yield the correct result when the $3d$ shell is full, or contains but one electron. To obtain this result for a different case, consider the situation of two $3d$ electrons of $+$ spin. Let one of the electrons be in the state $m=0$; the other is distributed with probability $\frac{1}{4}$ over all other states. The exchange terms in the Hartree-Fock equation, i.e., the coefficient of $Y_2(3d,3d,r)$ and $Y_4(3d,3d,r)$ will be $\frac{1}{4}$ of the closed-shell values plus certain terms which are not spherically symmetric. If we now say that the first electron is distributed with probability $\frac{1}{5}$ over all the m levels, and average the exchange terms in this way, the nonsymmetric terms disappear, and we are left with just $\frac{1}{4}$ of the closed-shell result.

Under the assumption that for the purpose of computing a starting potential, all the m levels can be treated as degenerate, we have the following important result: the change in the exchange potential for a $3d$ electron of $+$ spin when we increase the number of $3d$ electrons per atom with positive spin by one is

$$\Delta V_{+,3d} = \frac{1}{7r}\{Y_2(3d,3d,r)+Y_4(3d,3d,r)\}, \quad (8)$$

where this is to be taken with the proper algebraic sign to decrease the energies of these electrons. This result is useful when we wish to consider the ferromagnetism of iron.

On the basis of these results, an improved exchange potential was calculated from the starting charge density for the unmagnetized state. It was found that the Slater free electron approximation to the exchange potential overestimates exchange badly for small r and is reasonably close for large r to the Hartree-Fock potential. If the expectation value of the difference between the Hartree-Fock and free-electron exchange potentials is found with the $3d$ radial function determined for the state $\Gamma_{25'}$, the result is that the Slater approximation overestimates the exchange energy by 0.49 Rydberg or 15 percent.

The exchange potential for a $4s$ electron was then calculated from (6), using for the $4s$ wave function, the wave function for Γ_1 calculated by the cellular method. Since this function has nodes, the exchange potential has infinities, but these do not contribute to

the exchange energy, being removed when we calculate the expectation value. Except very close to one of the peaks in the exchange potential, it was found that the free-electron approximation overestimates the exchange potential. The error in the exchange energy for the Γ_1 state is 0.23 Rydberg or 20 percent. Most of this error seems to be due to overestimation of the interaction between the $4s$ and the $3d$ electrons.

The usefulness of the free-electron approximation depends on the state considered and the accuracy required. It seems to compare favorably with other methods of averaging exchange potentials.[8] Unfortunately, the dependence of the exchange potential on the wave function for the particular state may be too great to justify use of an exchange potential averaged over all states. Accuracy in the potential is important because of the sensitivity of some features of the band structure to details of the potential.

The effect of using a Coulomb potential computed from a d^7s^1 configuration of the free iron atom was also examined. The principal change comes from the fact that the charge density is now more compact and the potential is less attractive for moderate values of r. The expectation value of this change in potential found with the $\Gamma_{25'}$ function (see next section) is 0.697 Rydberg, while the change in exchange energy occasioned by increasing the number of $3d$ electrons by one is 0.035 Rydberg in the opposite direction. The state Γ_1 is not affected so strongly; the change in the Coulomb energy is 0.122 Rydberg while the change in the exchange energy is -0.020 Rydberg.

It was not feasible to examine the effect of the changes in potential on the bandwidth, since a repetition of the entire band structure calculation would have been required in order to obtain an accurate answer.

BAND STRUCTURE OF THE NONMAGNETIC STATE

OPW expansions were constructed for the levels Γ_1, Γ_{12}, $\Gamma_{25'}$, and Γ_{15} at the center of the Brillouin zone; H_1, H_{15}, $H_{25'}$, and H_{12} at the corner point H, $2\pi/a$ $(1,0,0)$; P_3 and P_4 at the corner P, $2\pi/a(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; and N_1, N_2, N_3, and N_4 at the point N, $2\pi/a(\frac{1}{2},\frac{1}{2},0)$ which is the center of a face. The Brillouin zone for the body-centered lattice is shown in Fig. 1. As indicated in the introduction, the expansions for Γ_1, H_1, and N_1 gave unreasonably low energies. Γ_1 and H_1 were treated by the cellular method. The expansions for P_3 and P_4 apparently did not contain enough plane waves to yield reliable results, but further calculations for P_4 in particular would have required a prohibitively large secular determinant to obtain accuracy commensurate with that obtained at Γ and H. It is believed that reliable solutions from the point of view of convergence of the OPW expansions were obtained for the following nine states: Γ_{12}, $\Gamma_{25'}$, Γ_{15}, H_{12}, $H_{25'}$, H_{15}, N_2, N_3, and N_4. The appropriate determinantal equations were solved on the high-speed electronic computing machine at the
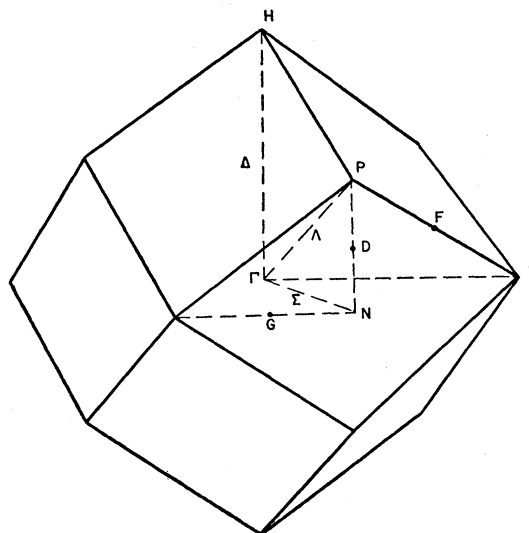

FIG. 1. Brillouin zone for the body-centered cubic lattice. Symmetry points and axes are indicated.

Institute for Advanced Study, Princeton, New Jersey. All the eigenvalues and eigenvectors of the matrices (usually of seventh order) were determined in the process.

The results of the calculation up to this point were unsatisfactory in one respect: the $4s$ level Γ_1 was placed some seven volts above the d band. This is contrary to reasonable expectations based on existing knowledge of the transition metals. This result prompted the previously mentioned study of the crystal potential. A potential was constructed, based on a d^7s^1 configuration of the free iron atom (but with the same wave functions as the d^6s^2) and on the Hartree-Fock exchange integrals. The difference between this potential and the one previously used was treated by first order perturbation theory, but only as regards the position of the levels. The Γ_1 level was now found to lie satisfactorily below the $3d$ band.

Slater and Koster have proposed an interpolation scheme for energy bands in crystals based on the tight binding approximation.[6] These authors regard the integrals occurring in the matrix components of the energy between different Bloch sums as disposable parameters to be determined from energy values obtained by other methods at symmetry points in the Brillouin zone. They have applied this scheme to d bands in the transition metals for both the body-centered[6] and face-centered cubic lattices,[12] using parameters determined from a previous calculation for nickel.[13] Some of their results, particularly the symmetry about $E=0$ of the density of states for the body-centered lattice, are rather critically dependent on their

[12] G. F. Koster, Quarterly Progress Report of the Solid State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1954, (unpublished), p. 4.

[13] G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952).

approximation and are removed if more parameters are used. They have also applied their method to the diamond lattice,[6] using the results of Herman[14] obtained by the OPW method to determine the parameters. The band structure they draw is in rather serious disagreement with the calculations by Herman of effective masses near the center of the Brillouin zone in that the free-electron-like behavior of the Δ_1 band from Γ_1 is not reproduced, nor the downward curvature of the Δ_1 band from the state Γ_{15}, nor the downward curvature of $\Delta_{2'}$ from the state $\Gamma_{25'}$.

We might expect that better fitting with a tight binding scheme could be obtained for the transition metals since the d bands are relatively narrow. Difficulty could be expected for the band formed from the $4s$ electron levels since it would be likely to show free electron like behavior except near points of crossover. If it can be reasonably asserted that the distortion produced by crossover of the $4s$ and $3d$ bands is not so great as to effect strongly the density of states, then it might be reasonable to try to use the interpolation scheme to compute the density of states.
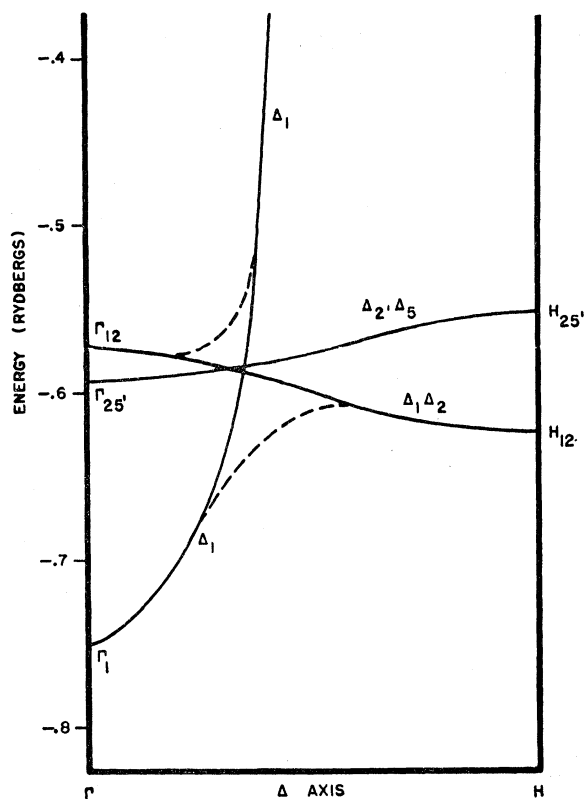

FIG. 2. Energy bands in iron parallel to 100 axis (unmagnetized state). Intermediate points are determined by the interpolation scheme. Use of more parameters would remove the degeneracy of Δ_1 and Δ_2; of $\Delta_{2'}$ and Δ_5. Dotted lines show possible alteration of predicted band structure in order to avoid crossover of Δ_1 bands.

[14] F. Herman, Phys. Rev. 88, 1210 (1952).

It was decided to apply Slater's scheme in the two-center approximation using nearest neighbor interactions only. If we allow for the possibility of different central interactions for the states at $\mathbf{k}=0$, there are five parameters to fit. These parameters were determined from the energies of the levels Γ_{12}, $\Gamma_{25'}$, $H_{25'}$, H_{12}, N_2, N_3, and N_4. Since there are seven levels there are two relations which the matrix elements have to satisfy if the fitting is exact. These relations are not exactly satisfied, but are obeyed sufficiently well to suggest there is some truth in the approximation. This form of the interpolation scheme leaves one unwanted degeneracy: the bands along the 100 axis in the Brillouin zone are split into a doubly degenerate band and a triply degenerate band instead of three nondegenerate bands and one doubly degenerate band. However, the symmetry of the density of states about its midpoint is removed.

By using Slater's interpolation scheme, energy levels were calculated at several points in the Brillouin zone in order to determine the form of the bands and the density of states. The density of states is found in the following way: For various values of k_x and k_y, the band structure parallel to the k_z axis in the Brillouin zone was determined by the interpolation scheme. For each of these curves, the energy was divided into small intervals (0.01 Rydberg) and the relative extent of the k_z axis for which each curve lay within the given energy range was computed. This gives a rough density of states for each band. These curves are step curves and they all have to be added with the proper weighting. The result is a step curve for $\eta(E)$.

Table I gives the lowest eigenvalues for all the representations for which convergent solutions were found. Diagrams of the band structure are shown in Figs. 2 and 3 (intermediate states and also the two N_1 levels have been located by the interpolation scheme). The Δ_1 and Σ_1 bands from Γ_1 are drawn as free-electron bands. Since cross over of equivalent bands is rendered extremely unlikely by group theory, the band structure will be distorted somewhat from the solid lines of these diagrams. A possible modification of the band structure to prevent such cross over is shown by dotted lines in Fig. 2.

The splitting of the $3d$ levels at the center of the Brillouin zone is only 0.3 ev; much less than it is at the corners and faces of the zone. The bottom of the $3d$ band at the point N_1 lies 1.35 ev above the lowest point of the $4s$ band at Γ_1. The location of the top of the d band is ambiguous because of the mixing of s and d states: The state N_4 (which is determined by the OPW method) lies 1.57 ev above the lowest N_1 (which is found by the interpolation scheme). There is another state of type N_1 about 1.8 ev (estimated from a single OPW) above N_4; this may be predominately S-like although N_1 contains a mixture of s and d states. The top of the d band is not determined with precision, but

it would be reasonable to say that this calculation gives a d band width of about two electron volts. Unfortunately, these numerical values are sensitive to the potential.

A much smaller splitting of the d-band states at $k=0$ than at other points of the zone is also a feature of the band structures calculated for nickel by Fletcher[13] and for copper by Howarth.[15] These elements have the face-centered cubic structure. It does not agree with the predictions of Slater and Koster[6] for the body-centered lattice, based on their interpolation scheme.

Some confidence in the relative order of the $3d$ levels among themselves (at least for the ones found from OPW expansions) was furnished by an exploratory calculation for the points Γ and H with a potential which did not include any exchange. Although the magnitudes of the separations were changed the order and relative separation of the levels was the same. The result that the separation of the $3d$ bands at Γ is roughly one third that at H may be viewed with some confidence.

TABLE I. Lowest eigenvalues.

Representation	Energy (Rydbergs)
Γ_1	-0.750
H_{12}	-0.625
N_2	-0.595
$\Gamma_{25'}$	-0.595
N_3	-0.574
Γ_{12}	-0.573
$H_{25'}$	-0.555
N_4	-0.548
H_{15}	$+0.154$[a]
H_1	$+0.64$[a]
Γ_{15}	$+2.00$[a]

[a] Correction to potential not included.

The separation between the levels Γ_1 and H_{15} is 1.238 Rydbergs (16.8 electron volts) before correction of the potential. These levels are presumably the limits of the s-p bands. The width of this band according to the free electron approximation is 1.345 Rydbergs, which is in error by 8.6 percent. It then seems reasonable to draw the $4s$ bands as free-electron bands. Since the states Γ_{15} and H_{15} formed from $4p$ electron levels lie far above the d band, one might conclude that the mixing of p and d states in the d band is small. P_4 is a state where mixing of this kind is permitted by group theory. The form of the OPW expansion, although poorly convergent, suggests that this mixing is small.

There is no experimental information as yet which bears directly on the form of the band structure suggested here. However, experiments on the polarization of slow neutrons by magnetized iron give information as to the charge distribution of a magnetically active electron. These experiments have been analyzed by Steinberger and Wick.[7] Although their cellular method calculation of the wave functions of d electrons was

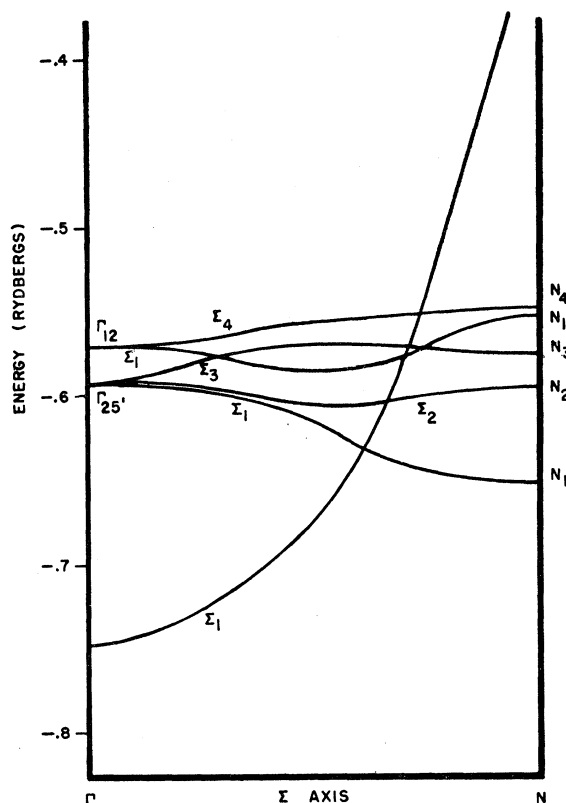[15] D. J. Howarth, Proc. Roy. Soc. (London) A220, 513 (1953).

FIG. 3. Energy bands in iron parallel to 110 axis (unmagnetized state). N_1 levels and intermediate points are determined from the interpolation scheme. Effects of prohibiting crossover of Σ_1 bands are not shown.

performed with boundary conditions which are not appropriate for $3d$ electron states, their principal conclusion is probably sound. They find that the charge distribution of a magnetically active electron must be somewhat more compact than are the Hartree functions for a free iron atom.[9] The additional binding is provided by exchange.

The wave function for a $3d$ electron depends, of course, on the particular state in the band. But inspection of the OPW eigenfunctions suggests that the wave function does not change much over the $3d$ band. This result is consistent with the small width of the band. It would seem that a reasonable idea of the radial charge distribution of a $3d$ electron could be obtained by summing the $l=2$ part of the expansion for one of the states. This was done for the state $\Gamma_{25'}$; the result is shown in Fig. 4 where it is compared with the $3d$ radial function of Manning and Goldberg.[9] The $\Gamma_{25'}$ function has been altered in the right direction from the Hartree field.

The density of states for the unmagnetized state obtained from the calculation based on the interpolation scheme is shown in Fig. 5. It has the two-hump structure suggested by information on the electron specific
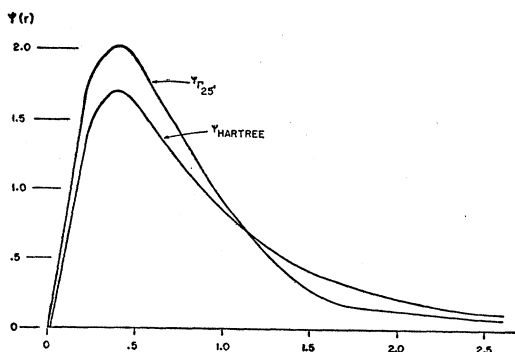
FIG. 4. Comparison of $3d$ radial wave functions obtained from Γ_{25}' and the Hartree wave function of Manning and Goldberg.

heat[16] and temperature variation of the magnetic susceptibility of the transition elements.[17] However, these results are based on an extrapolation of the density of states curve from element to element, regardless of changes in the crystal structure and the potential. The validity of such procedure remains to be established. Before definite comparison of the density of states curve with experiment can be given, allowance must be made for the splitting of the band structure of the magnetized state introduced by exchange.

The calculated energy bands are probably too narrow. The improvement in the potential previously discussed would tend to widen the bands, but it was not possible to calculate this. An accurate calculation of the d-band width must wait for a self-consistent field.

An estimate of the self-consistency of this calculation can be made by comparing the Coulomb potential calculated from the $\Gamma_{25'}$ function previously discussed with the Coulomb potential of the assumed initial distribution. The potentials are found to disagree considerably since the charge density obtained in this calculation is more compact than the initial one. Consequently, results of this calculation which are dependent on the details of the potential are open to some question.

APPLICATIONS TO FERROMAGNETISM

Equation (8) gives the change in the potential energy of a $3d$ electron in the Hartree-Fock scheme when one $3d$ electron per atom reverses its spin. We shall assume (1) that this potential is the same for all electrons in the d band, (2) that we can calculate its effect by first order perturbation theory, and (3) that the expectation values of this potential are the same to a sufficient approximation for all the states in the d band. This potential was computed by using the radial function for the state $\Gamma_{25'}$, and also by using the starting charge density for a $3d$ electron. The expectation value of these potentials were found by using the $\Gamma_{25'}$ function. For the potential constructed from the starting charge density, the expectation value is -1.23 ev. For the

potential constructed from the $\Gamma_{25'}$ function, the value is -1.58 ev. Since the latter potential is derived from a charge distribution that may be too compact and the former from one that is too loose, the correct figure should lie between these limits. The energy computed here represents the lowering of the levels of majority spin electrons from the unmagnetized state, and we must remember that the levels of minority spin electrons are raised by a like amount. Corresponding levels of opposite spin are separated by an energy between 2.46 and 3.16 ev. The figures obtained here from the Hartree-Fock exchange potential agree reasonably well with the corresponding results of Slater's free-electron approximation to the exchange potential.

The change in cohesive energy due to exchange when one $3d$ electron per atom reverses its spin is just one-half the separation between corresponding levels in the magnetized state. The factor of one-half arises from the fact that when we add the one-electron eigenvalues of the Hartree-Fock equations, we have counted the exchange interactions twice. Thus the change in cohesive energy due to spin reversal will be between 1.23 and 1.58 ev. These numbers are slightly larger than those obtained by Slater for the case of nickel by examination of spectroscopic data.[18] Slater obtains a value of 0.99 ev for this quantity. The discrepancy arises from two causes: (1) a different method of averaging the exchange interactions over the $3d$ states, and (2) slightly larger values for the appropriate integrals in this case. The difference in the method of averaging amounts to one fifth of the change in spin energy.

We must now compute the change in the kinetic energy on going to the magnetized state. This can be determined from the density of states curve. We have to calculate the integrals $\int E\eta(E)dE$ for the magnetized
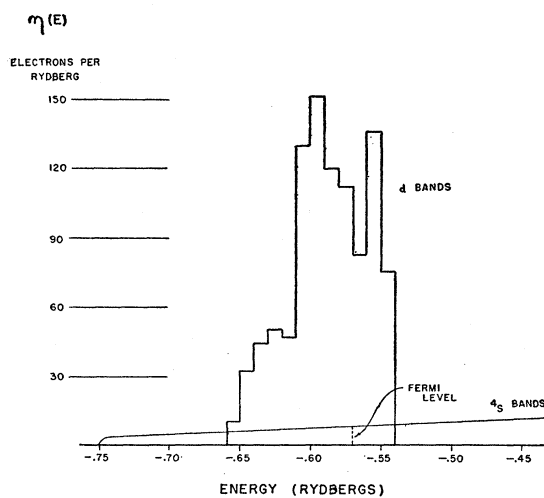

FIG. 5. Density of states for iron (unmagnetized state). The $4s$ band is drawn as a free electron band. $\eta(E)$ for the $4s$ band is enlarged by a factor of ten.

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[16] M. Horowitz and J. G. Daunt, Phys. Rev. 91, 1099 (1953).
[17] C. J. Kreissman and H. B. Callen, Phys. Rev. 94, 837 (1954).

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

and unmagnetized electron distributions. These integrals have been computed and yield the result that the change in Fermi energy upon magnetization is 0.69 ev. This figure is not very accurate since it is the difference between two large numbers. The net energy of magnetization at absolute zero is then between 0.89 and 0.54 ev per atom; a result that is considerably larger than would be suggested by the Curie temperature. Most of this discrepancy may be due to having too narrow a calculated $3d$ band. One might expect that for a band width of 3.0 ev a change in Fermi energy approximately $\frac{3}{2}$ the above value or 1 ev might be obtained.

Although these calculations were made for a situation in which there would be a net magnetic moment of 2.0 Bohr magnetons per atom (neglecting a small contribution from the $4s$ electrons and from the orbital moment), the situation should not be appreciably different for the observed saturation magnetic moment of 2.2 Bohr magnetons per atom.[19]

The principal change in the band structure on passing to the magnetized state is that the levels of electrons of $+$ and $-$ spin will be split. This splitting was calculated to be between 2.46 and 3.16 ev. Since these figures are somewhat greater than the predicted width of the unmagnetized $3d$ band, one might expect that the $3d$ band will be split into halves, the lower being full and containing electrons of the majority spin. There will, of course, be some change in the band form due to the difference in the exchange energies of these states; in particular, the upper band should be somewhat wider than the lower. When this change is estimated using Slater's free electron exchange potential, one finds that the upper band should be about 0.1 ev wider than the lower if the individual halves are about 2.0 ev wide.

The $4s$-electron levels will serve to connect the halves of the d band. The alignment of the spins of the $3d$ electrons will necessarily cause a splitting of the $4s$-electron levels. This splitting is smaller than that of the $3d$ levels. It can be determined from the alteration of the potential of a $4s$ electron:

$$\frac{n}{5} \cdot \frac{2}{r} \frac{P_{3d}(r)}{P_{4s}(r)} Y_2(4s,3d,r), \qquad (9)$$

when n $3d$ electrons per atom change their spin. The functions P are proportional to r times the radial part of the wave functions, and Y_2 is defined in (4). Here it is assumed that all the $3d$ and all the $4s$ electrons have the same wave function. This potential has been computed using wave functions for the Γ_1 and $\Gamma_{25'}$ states. The expectation value of the potential is -0.040 Rydberg, taken with the Γ_1 function. Thus the Γ_1

[19] The observed magneton number, 2.2 Bohr magnetons per atom, can be approximately accounted for in terms of two excess spins per atom and a contribution from the orbital angular momentum. C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953).
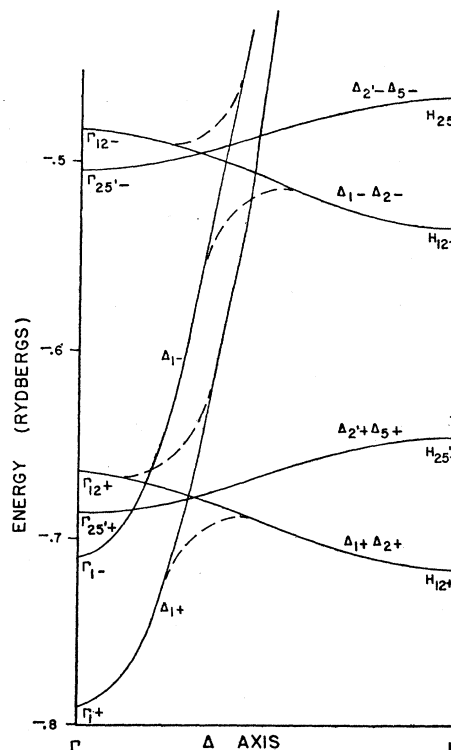

FIG. 6. Energy bands in iron parallel to 100 axis for magnetized state. The $4s$ bands are drawn as free electron bands. Levels of electrons of $+$ and $-$ spin are indicated by $+$ or $-$ sign after the standard symbol. Dotted lines indicate possible elimination of crossover of Δ_1 bands of the same spin.

levels of $+$ and $-$ spin will be separated by 0.080 Rydberg or 1.1 ev if one $3d$ electron per atom reverses its spin. Consequently there will be an alteration in the relation of the s and d states from that obtaining in the nonmagnetic state and one may expect a small number of $4s$ electrons to participate in the magnetization.

The band structure along the 100 axis in the Brillouin zone for the magnetized state is shown in Fig. 6 for two excess $3d$ electrons of $+$ spin, under the assumption that the position but not the form of the bands has been altered. The curvature of the $4s$ bands is that of free-electron bands. We have the following picture: the d band is split into halves connected by bands which should show a mixing of s and d states, perhaps predominantely s-like. The Fermi level comes approximately in the middle of the upper d band. The minimum separation of the split d bands is at the point N where they are separated by a gap of the order of one electron volt. However, if the separated d bands are somewhat wider than calculated here, there may be some overlap of predominately d states. Because some of the $3d$ electrons will drop into lower $4s$ states in the magnetic state, the Fermi level will be slightly lower than predicted on the basis of d bands alone. The width of the filled portion of the bands, from the lowest state Γ_1 to the Fermi level will be about 0.30 Rydberg or 4.1

electron volts. This is in reasonable agreement with the experiment of Gyorgy and Harvey on soft x-ray emission[20] where a band width of 3.7 ev is observed. The density of states curve is a combination of two like the one shown in Fig. 4, separated by a gap, and laced together by the 4s free-electron bands. There is a decided dip in the middle corresponding to the region in which s like states predominate. Such a dip has not been observed experimentally. This dip is different from that predicted by previous studies of the transition metals, since it is a result of the ferromagnetism.

The electron specific heat of magnetic iron at absolute zero according to this predicted density of states is

$$C_v = 18 \times 10^{-4} T \text{ cal/mole-deg,}$$

compared to the experimental value $12 \times 10^{-4} T$.[16] The disagreement is presumably due to the calculated d bands being too narrow.

It is rather difficult to determine a quantity to be called the number of s electrons in the crystal. This is ambiguous because of the mixing of states. If the $4s$ band were entirely free-electron-like and no mixing of angular momentum states occurred, one would obtain 0.11 $4s$ electron per atom in the nonmagnetic state and 0.19 in the magnetic state, with an excess in the latter case of 0.07 $4s$ electron of majority spin.

The energy balance in magnetization must be recomputed if the role of the $4s$ electrons is taken into account. The result is nearly the same as before. There are three effects which, when added, very nearly cancel: (1) the decrease in energy due to exchange which comes from the $3d$-$4s$ exchange, (2) the increase in kinetic energy upon magnetization, and (3) a decrease in energy due to electrons dropping from higher $3d$ states into $4s$ states. To the accuracy possible here, these effects cancel. Readjustment of the $4s$ levels represents an improvement in the wave function of the system and must lead to a state of lower energy,[21] but this decrease is probably small.

ACKNOWLEDGMENTS

[20] E. M. Gyorgy and G. C. Harvey, Phys. Rev. 93, 365 (1954).
[21] C. Herring (private communication).

APPENDIX

Use of Group Theory to Simplify the Eigenvale Problem

Only those orthogonalized plane waves appear in the expansion for the wave function at a point k in the Brillouin zone which are formed by adding to k all reciprocal lattice vectors. In order to obtain a convergent expansion, it is necessary to employ a large number of orthogonalized plane waves (for instance 86 are used in the expansion of the level Γ_{15} at $k = 0$). This would seem to lead to impossibly large secular equations which, for a general k, we should have to solve; but at certain points in the Brillouin zone, a simplification is possible.

Consider the operations belonging to the point group of the reciprocal lattice which carry a point k of the Brillouin zone into itself or an equivalent point (a point k' is said to be equivalent to k if $k = k + g$, where g is a reciprocal lattice vector). These operations are said to form the group of the point k.[22] For a general k, the group of k will consist only of the identity. There exist, however, symmetry points in whose group there are several operations. Then the wave function of a state of that k can be classified according as it belongs to a particular irreducible representation of the group of k. Because the Hamiltonian will have no nonvanishing matrix elements between functions belonging to different irreducible representations, the OPW secular equation can be factored. In particular, we can choose a linear combination of orthogonalized plane waves of a given type which belongs to a (particular row of a) particular irreducible representation. Only combinations belonging to this symmetry type need be considered in setting up the secular equation.

For example, consider the point Γ. The group of Γ consists of the 48 operations of the cubic point group. There are ten irreducible representations of this group: four one-dimensional, two two-dimensional, and four three-dimensional representations. The orthogonalized plane waves which can participate in the expansion of the wave function of one of these representations are: the wave 000, the 12 waves 110, the six waves of type 200, the twenty-four waves of type 211, the twelve waves 220, the twenty-four waves 210, the eight waves 222, the forty-eight waves 321, etc.[23] Suppose we wish to find the lowest energy of a state belonging to the representation $\Gamma_{25'}$. Such a state will be triply degenerate, and if expanded in spherical harmonics will have as harmonic of lowest order a function of type xy/r^2 (or xz, or yz, or a linear combination of these).[24] Since the functions xy, yz, and zx are linearly independent, they form a basis for the expansion of any function

[22] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 50, 58 (1936).
[23] $2\pi/a$ is omitted.
[24] F. C. Von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

belonging to $\Gamma_{25'}$. Let us choose to construct the expansion of the wave function in $\Gamma_{25'}$ which transforms like xy. To do this, we choose a plane wave of a particular type, say 110, and apply the formula[25]

$$\sum_T D_{xy,\,xy}(T)T\chi_k = \sum D_{xy,\,xy}(T)\chi_{(Tk)}. \qquad (10)$$

Here, T runs over all 48 operations of the group of Γ. $D_{xy,\,xy}(T)$ is the xy, xy element of the matrix representing the operation of T on the basis xy, yz, zx. The result is a linear combination of plane waves which transforms according to the xy row of the representation $\Gamma_{25'}$. We then proceed in a similar manner for all of the plane waves we intend to use in the expansion. In this manner, we express the wave function for a state of $\Gamma_{25'}$ as a series in orthogonalized plane waves, taking advantage of symmetry. The Hamiltonian will have no matrix elements between this function and functions belonging to different irreducible representations, or between orthogonal members of this representation.

In the general case, to construct an expansion which will transform according to the ith row of the jth irreducible representation of the wave vector k, we first determine the types of waves which belong in the expansion and construct

$$\sum_T D_{ij,\,ij}(T)T\chi_k, \qquad (11)$$

for all the plane wave types. Only these functions now need be employed in constructing the secular equation. There is one unknown coefficient for each such linear combination.

In the case the representation is nondegenerate, it is sufficient to use[25]

$$\sum_T C_j(T)T\chi_k, \qquad (12)$$

where C_j is the character of the operation T in the jth irreducible representation and χ_k is an orthogonalized plane wave. The result is a function transforming according to the jth irreducible representation of wave vector k.

[25] E. P. Wigner, *Group Theory and Quantum Mechanics* (Edwards Brothers, Inc., Ann Arbor, 1944).

TABLE II. Wave functions for Γ ($k=000$).

Wave	Representation									
	Γ_1	$\Gamma_{1'}$	Γ_2	$\Gamma_{2'}$	Γ_{12}	$\Gamma_{12'}$	$\Gamma_{15'}$	Γ_{25}	Γ_{15}	$\Gamma_{25'}$
110	+	0	0	0	0	0	0	0	+	+
101	+	0	0	0	+	0	0	+	+	0
011	+	0	0	0	−	0	0	−	0	0
$\bar{1}$10	+	0	0	0	0	0	0	0	−	−
$\bar{1}$01	+	0	0	0	+	0	0	+	−	0
0$\bar{1}$1	+	0	0	0	−	0	0	−	0	0
1$\bar{1}$0	+	0	0	0	0	0	0	0	+	−
10$\bar{1}$	+	0	0	0	+	0	0	−	+	0
01$\bar{1}$	+	0	0	0	−	0	0	+	0	0
$\bar{1}\bar{1}$0	+	0	0	0	0	0	0	0	−	+
$\bar{1}$0$\bar{1}$	+	0	0	0	+	0	0	−	−	0
0$\bar{1}\bar{1}$	+	0	0	0	−	0	0	+	0	0
200	+	0	0	0	+	0	0	0	+	0
020	+	0	0	0	−	0	0	0	0	0
002	+	0	0	0	0	0	0	0	0	0
$\bar{2}$00	+	0	0	0	+	0	0	0	−	0
0$\bar{2}$0	+	0	0	0	−	0	0	0	0	0
00$\bar{2}$	+	0	0	0	0	0	0	0	0	0
(000)	(+)				x^2-y^2			$z(x^2-y^2)$	x	xy

In certain cases, a given irreducible representation may occur more than once in a given plane wave type. For instance, the representation $\Gamma_{25'}$ occurs twice among the plane waves 211. This means that it will be possible to construct two linearly independent wave functions of xy symmetry from the waves 211. Both will have to be included in the expansion. The rule for determining the number of times a particular representation is contained in a particular plane wave type is as follows[21]: (1) Determine the number of plane waves carried into themselves (i.e., aab into aab) by an operation of the group. (2) Multiply this by the character of the operation. (3) Form the sum of (2) for all operations. (4) Divide the number obtained in (3) by the number of operations contained in the group.

Table II gives the appropriate linear combinations for the first nineteen waves belonging to Γ. The linear combinations for other points may be obtained from the author.