

tion of the validity of our suggestion on uniform magnetization in relaxation. This means that our results are valid up to temperatures of $T \gg T_c (\mu M / k T_c)^{4/7}$. When $T_c \sim 10^3$ °K, $M \sim 10^3$; this would mean that $T \gg T_c / 100$. The results on correlation times in a ferromagnetic spin system, as obtained in experiments on inelastic magnetic scattering of neutrons,¹² also are in favor of uniform distribution, Eq. (6), at $T < T_c$.

Uniform precession of the M vector in ferromagnets is known to be related also to the alternating-field value. H. Suhl has shown that instabilities tending to disturb uniform precession⁷ will arise in a spin system at high values of the alternating field. This effect, treated by

Suhl on the basis of the phenomenological spin-wave theory, is due to transfer of energy from uniform to some other type of precession, resulting in an increase in the latter's amplitude and disturbance of the magnetization uniformity. The effect appears to be unimportant when the alternating-field amplitude is lower than a certain critical value. According to Suhl the critical value of this field is about 10% of the linewidth, i.e., considerably higher than the alternating-field values used in experiments other than those investigating the above-mentioned instabilities. This means that our results will be valid until the alternating-field amplitude is below the critical value.

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Tight-Binding Calculation of 3d Bands of Fe with and without Spin-Orbit Coupling

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The electronic structure of the 3d band in Fe is calculated in the tight-binding approximation; the energy values in the Brillouin zone and the density-of-states curve are evaluated. A comparison with other theoretical results suggests that the approximations and hypotheses used do not influence the results markedly; a comparison with the results previously obtained with the same method for Cr does not support the rigid-band hypothesis. The spin-orbit interaction matrix is reported for a general direction of magnetization, and the effect of spin-orbit coupling on the structure of bcc transition metals is investigated.

1. INTRODUCTION

IN previous research^{1,2} the electron energy was calculated for Cr as a function of the wave vector \mathbf{k} ; the density-of-states curve $g(E)$ and the Fermi surface were consequently determined. As part of a systematic investigation on the electronic structure of bcc transition metals, the present paper is concerned with Fe.

The previous calculations were made with the tight-binding method for two different orders of approximation: (AI), in which only the nearest-neighbor interaction was taken into account; and (AII), in which the second-neighbor interaction was added and proved to be not negligible, and was such as to remove some accidental degeneracies present in the first case.

Calculations of this kind are quite sensitive to the chosen assumptions and approximations; it is therefore useful to compare both results obtained with the same

method for different materials and results obtained for the same metal but with different assumptions and approximations.

Concerning the first kind of comparison, results were reported by Mattheiss³: It can be seen that the energy curves along Δ line in the \mathbf{k} space have a quite similar behavior for metals with the same lattice, which supports the rigid-band model, but the results are not complete enough to draw precise conclusions.

In the present work we have calculated, with the same method (AII) previously applied to Cr, the behavior of $E(\mathbf{k})$ and $g(E)$ for Fe, for which a comparison with other calculations⁴⁻⁷ is also possible.

Subsequently, some results have been obtained by introducing into the Hamiltonian a spin-orbit interaction term which is responsible for the anisotropic behavior of the magnetic energy of Fe. Such a term is

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¹ M. Asdente and J. Friedel, Phys. Rev. **124**, 384 (1961); *ibid.* **126**, 2262(E) (1961).

² M. Asdente, Phys. Rev. **127**, 1949 (1962).

³ L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

⁴ J. H. Wood, Phys. Rev. **117**, 714 (1960).

⁵ E. F. Belding, Phil. Mag. **4**, 1145 (1959).

⁶ J. Callaway, Phys. Rev. **99**, 500 (1955).

⁷ F. Stern, Phys. Rev. **116**, 1399 (1959).

probably more important for the elements of the II and III series if the less conspicuous magnetic characteristics of these elements as well as other differences are to be ascribed to spin-orbit interaction, for instance, differences in the de Haas-van Alphen effect.

2. METHOD OF CALCULATION

Let us briefly summarize the most important assumptions and approximations:

(1) The s and d electrons are treated separately. The s electrons are considered free, while for the d electrons the energy matrix is written in the tight-binding approximation. As already pointed out by Mott,⁸ this approach is particularly useful for treating the ferromagnetic state, because it allows one to ascribe a different exchange energy to the s and d electrons. Afterwards, the hybridization can be carried out separately for the two bands with opposite spin.

(2) A $3d^7 4s$ configuration is assumed, as suggested by Stern's calculations on the cohesion energy⁷ and by the behavior of some physical properties of iron metal and its alloys.^{8,9}

(3) The effect of the exchange interaction is treated in the usual approximation as an additional energy $\pm\delta$, the sign depending on the spin orientation of the single electron. In other words the eigenfunctions were supposed to remain unchanged and the off-diagonal elements of the exchange-interaction operator to be negligible.

(4) A set of Bloch functions ϕ_n has been constructed from the 10 normalized functions f_n belonging to the tenfold-degenerate d level of the single atom:

$$\begin{aligned} f_{1,\alpha} &= (1/N_1)xyf(r)\alpha, & f_{2,\alpha} &= (1/N_1)yzf(r)\alpha, \\ f_{3,\alpha} &= (1/N_1)zx f(r)\alpha, & f_{4,\alpha} &= (1/N_2)(x^2-y^2)f(r)\alpha, \\ f_{5,\alpha} &= (1/N_3)(3z^2-r^2)f(r)\alpha, & \alpha &= +, -; \\ \Phi_{n,\alpha}(\mathbf{r},\mathbf{k}) &= N^{-1/2} \sum_1 \exp(i\mathbf{k}\cdot\mathbf{R}_1) f_{n,\alpha}(\mathbf{r}-\mathbf{R}_1), \\ & & n &= 1, 2, 3, 4, 5, \end{aligned}$$

where α is the spin eigenfunction, \mathbf{k} is the wave vector and \mathbf{R}_1 the distance between the origin and the atom position characterized by the index \mathbf{l} . A suitable linear combination of the above Bloch functions has been taken for the wave function of the d electrons in the crystal:

$$\Psi_n(\mathbf{r},\mathbf{k}) = \sum_{m,\alpha} A_{m\alpha}(\mathbf{k})\Phi_{m,\alpha}(\mathbf{k}). \quad (1)$$

Assuming that the overlapping of functions centered on different atoms is negligible, and choosing N equal to the total number of atoms, we find the functions (1) are orthogonal and normalized.

(5) The lattice potential $V(\mathbf{r})$ has been constructed from a set of atomic potentials. Around each lattice position \mathbf{R}_1 it was taken that

$$\begin{aligned} V(\mathbf{r}) &= 5.3[(1/|\mathbf{r}-\mathbf{R}_1|) - (1/(d/2))], & \text{for } |\mathbf{r}-\mathbf{R}_1| \leq d/2; \\ V(\mathbf{r}) &= 0, & \text{for } |\mathbf{r}-\mathbf{R}_1| > d/2. \end{aligned}$$

It was further assumed that

$$\begin{aligned} V(\mathbf{r}) - V_0 &= 0, & \text{for } |\mathbf{r}| \leq \frac{1}{2}d; \\ V(\mathbf{r}) - V_0 &= V(\mathbf{r}), & \text{for } |\mathbf{r}| > \frac{1}{2}d, \end{aligned}$$

d being the nearest-neighbor distance, V_0 the potential of the atom at the origin, and the coefficient 5.3 the effective nuclear charge obtained from Slater's rule.¹⁰

3. ENERGY MATRIX

A. Spin-Independent Terms

The Hamiltonian for the single electron takes the form

$$H = (\mathbf{p}^2/2m) + \sum_l V(\mathbf{r}-\mathbf{R}_l).$$

Using Ritz's variational principle and the tight-binding approximation, we obtain the following secular equation:

$$|H_{nm}(\mathbf{k}) - E(\mathbf{k})\delta_{nm}| = 0,$$

where the indices n and m range from 1 to 5, as there is no dependence on the index α of the spin eigenfunction.

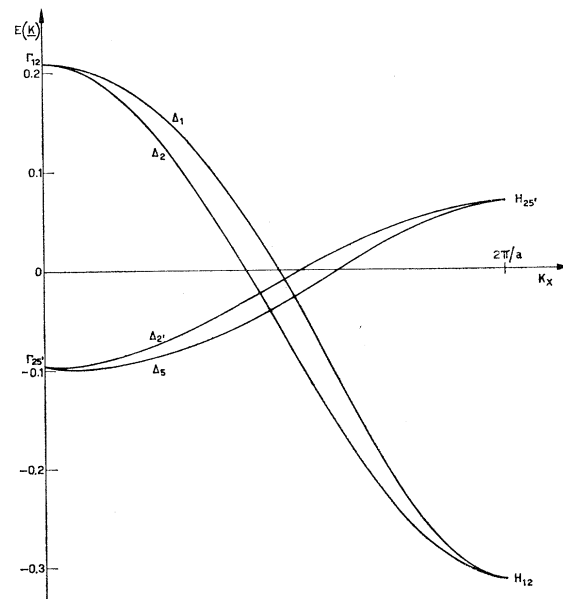


FIG. 1. Energy bands $E(\mathbf{k})$ along the ΓH line. {Energy in atomic units (a.u.).

⁸ N. F. Mott, *Advan. Phys.* **13**, 325 (1964).

⁹ L. R. Walker, K. G. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 236 (1961).

¹⁰ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

TABLE I. Terms of the energy matrix and overlap integrals for Fe. $R_2(a,0,0)$, $R_2^*(0,0,a)$, where a is the lattice spacing.

$H_{11} = A_1 + 8B_1 \cos\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$	$+ 2D_1(\cos k_x a + \cos k_y a) + 2D_2 \cos k_z a$
$H_{22} = A_1 + 8B_1 \cos\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$	$+ 2D_1(\cos k_y a + \cos k_z a) + 2D_2 \cos k_x a$
$H_{33} = A_1 + 8B_1 \cos\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$	$+ 2D_1(\cos k_x a + \cos k_z a) + 2D_2 \cos k_y a$
$H_{44} = A_2 + 8B_2 \cos\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$	$+ 2C_1(\cos k_x a + \cos k_y a) + 2C_2 \cos k_z a$
$H_{55} = A_2 + 8B_2 \cos\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$	$+ 2C_4(\cos k_y a + \cos k_x a) + 2C_5 \cos k_z a$
$H_{12} = -8B_4 \sin\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \sin\frac{1}{2}k_z a$	
$H_{23} = -8B_4 \sin\frac{1}{2}k_x a \sin\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$	
$H_{31} = -8B_4 \cos\frac{1}{2}k_x a \sin\frac{1}{2}k_y a \sin\frac{1}{2}k_z a$	
$H_{14} = 0$	
$H_{24} = -8B_5 \cos\frac{1}{2}k_x a \sin\frac{1}{2}k_y a \sin\frac{1}{2}k_z a$	
$H_{34} = 8B_5 \sin\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \sin\frac{1}{2}k_z a$	
$H_{45} = 2C_8(\cos k_x a - \cos k_y a)$	
$H_{15} = -8B_8 \sin\frac{1}{2}k_x a \sin\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$	
$H_{25} = -8B_9 \cos\frac{1}{2}k_x a \sin\frac{1}{2}k_y a \sin\frac{1}{2}k_z a$	
$H_{35} = -8B_9 \sin\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \sin\frac{1}{2}k_z a$	
$H_{ij} = H_{ji}$	
$A_1 = \int f_1(\mathbf{r})[V(\mathbf{r}) - V_0]f_1(\mathbf{r})d\mathbf{r} = -0.035628$ atomic units (a.u.)	
$A_2 = \int f_4(\mathbf{r})[V(\mathbf{r}) - V_0]f_4(\mathbf{r})d\mathbf{r} = -0.006210$ a.u.	
$B_1 = \int f_1(\mathbf{r} - \mathbf{R}_1)[V(\mathbf{r}) - V_0]f_1(\mathbf{r})d\mathbf{r} = -0.010309$ a.u.	
$B_2 = \int f_4(\mathbf{r} - \mathbf{R}_1)[V(\mathbf{r}) - V_0]f_4(\mathbf{r})d\mathbf{r} = 0.032705$ a.u.	
$B_4 = \int f_1(\mathbf{r} - \mathbf{R}_1)[V(\mathbf{r}) - V_0]f_2(\mathbf{r})d\mathbf{r} = -0.014751$ a.u.	
$B_5 = \int f_2(\mathbf{r} - \mathbf{R}_1)[V(\mathbf{r}) - V_0]f_4(\mathbf{r})d\mathbf{r} = -0.006576$ a.u.	
$B_8 = \int f_1(\mathbf{r} - \mathbf{R}_1)[V(\mathbf{r}) - V_0]f_5(\mathbf{r})d\mathbf{r} = (2/\sqrt{3})B_5$	
$B_9 = \int f_2(\mathbf{r} - \mathbf{R}_1)[V(\mathbf{r}) - V_0]f_5(\mathbf{r})d\mathbf{r} = -(1/\sqrt{3})B_5$	
$C_1 = \int f_1(\mathbf{r} - \mathbf{R}_2)[V(\mathbf{r}) - V_0]f_1(\mathbf{r})d\mathbf{r} = -0.011387$ a.u.	
$C_2 = \int f_4(\mathbf{r} - \mathbf{R}_2^*)[V(\mathbf{r}) - V_0]f_4(\mathbf{r})d\mathbf{r} = -0.000582$ a.u.	
$C_3 = \int f_5(\mathbf{r} - \mathbf{R}_2^*)[V(\mathbf{r}) - V_0]f_5(\mathbf{r})d\mathbf{r} = -0.014989$ a.u.	
$C_4 = \int f_5(\mathbf{r} - \mathbf{R}_2)[V(\mathbf{r}) - V_0]f_5(\mathbf{r})d\mathbf{r} = -0.004184$ a.u.	
$C_8 = \int f_4(\mathbf{r} - \mathbf{R}_2)[V(\mathbf{r}) - V_0]f_5(\mathbf{r})d\mathbf{r} = 0.006238$ a.u.	
$D_1 = \int f_1(\mathbf{r} - \mathbf{R}_2)[V(\mathbf{r}) - V_0]f_1(\mathbf{r})d\mathbf{r} = 0.005381$ a.u.	
$D_2 = \int f_1(\mathbf{r} - \mathbf{R}_2^*)[V(\mathbf{r}) - V_0]f_1(\mathbf{r})d\mathbf{r} = C_2$	

The elements H_{nm} take the following form:

$$H_{nm} = E_0 \delta_{nm} + \delta_{nm} \int f_n(\mathbf{r})[V(\mathbf{r}) - V_0]f_m(\mathbf{r})d\mathbf{r} \\ + \sum_l \exp(i\mathbf{k} \cdot \mathbf{R}_l) \int f_n(\mathbf{r} - \mathbf{R}_l)[V(\mathbf{r}) - V_0]f_m(\mathbf{r})d\mathbf{r},$$

where E_0 is the energy of the degenerate d level in the free atom; henceforth this energy is assumed as reference energy.

Only the two-center overlap integrals concerning the first and second neighbors have been taken into account. Table I reports the terms of the energy matrix obtained for the bcc lattice, and also the overlap integrals calculated for Fe with the lattice potential and the Bloch functions introduced above.

B. Spin-Dependent Terms

As stated above, the exchange energy is formally represented by an additional contribution $\pm\delta$ depending

on the direction of the electron spin, the δ value having been selected in such a way to fit the experimental data on spontaneous magnetization.

The spin-orbit interaction term for the crystal is represented by the operator

$$O_{L,S} = \sum_l \xi(|\mathbf{r} - \mathbf{R}_l|) \mathbf{S} \cdot \mathbf{L}(\mathbf{r} - \mathbf{R}_l),$$

where

$$\xi(\mathbf{r}) = (1/2m^2c^2\mathbf{r})[dV(\mathbf{r})/d\mathbf{r}].$$

The matrix elements between the Bloch functions $\Phi_n(\mathbf{k})$ involve one-center and many-center integrals, of which only the one concerning the central atom is taken into account. Owing to the behavior of the $\xi(\mathbf{r})$ function, this fact should not involve an error larger than that made by neglecting the overlap integrals.

With this simplification the matrix elements between the Bloch functions are reduced to the similar ones between the corresponding atomic functions f_n :

$$\bar{\xi} \langle f_{n,\alpha} | \mathbf{S} \cdot \mathbf{L} | f_{m,\alpha} \rangle,$$

where $\bar{\xi}$ corresponds to the a_i parameter in the Goudsmit notation¹¹ and α is more generally the spin eigenfunction relative to the direction of quantization characterized by the Euler angles θ , φ .

In Fe the crystal field is strong enough to quench the orbital moments; the spin-orbit interaction also connects weakly the electronic spins with the crystal field and gives rise to the anisotropy of the magnetic crystal energy. The corresponding interaction matrix $H_{L,S}$ is reported in Table II.

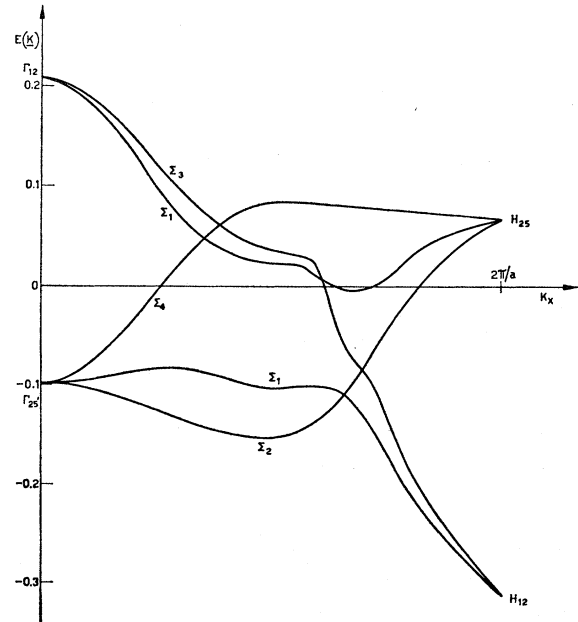


FIG. 2. Energy bands $E(\mathbf{k})$ along ΓN and NH lines. Energy in a.u. The point N corresponds to $k_x = \pi/a$, $k_y = \pi/a$, $k_z = 0$.

¹¹ S. Goudsmit, Phys. Rev. 31, 946 (1928).

TABLE II. Terms of the spin-orbit

0	$\frac{1}{2}i \sin\theta \sin\varphi$	$-\frac{1}{2}i \sin\theta \cos\varphi$	$i \cos\theta$	0
$-\frac{1}{2}i \sin\theta \sin\varphi$	0	$\frac{1}{2}i \cos\theta$	$-\frac{1}{2}i \sin\theta \cos\varphi$	$-\frac{1}{2}\sqrt{3}i \sin\theta \cos\varphi$
$\frac{1}{2}i \sin\theta \cos\varphi$	$-\frac{1}{2}i \cos\theta$	0	$-\frac{1}{2}i \sin\theta \sin\varphi$	$\frac{1}{2}\sqrt{3}i \sin\theta \sin\varphi$
$-i \cos\theta$	$\frac{1}{2}i \sin\theta \cos\varphi$	$\frac{1}{2}i \sin\theta \sin\varphi$	0	0
0	$\frac{1}{2}\sqrt{3}i \sin\theta \cos\varphi$	$-\frac{1}{2}\sqrt{3}i \sin\theta \sin\varphi$	0	0
0	$\frac{1}{2}(-\cos\varphi + i \cos\theta \sin\varphi)$	$-\frac{1}{2}(\sin\varphi + i \cos\theta \cos\varphi)$	$-i \sin\theta$	0
$\frac{1}{2}(\cos\varphi - i \cos\theta \sin\varphi)$	0	$-\frac{1}{2}i \sin\theta$	$-\frac{1}{2}(\sin\varphi + i \cos\theta \cos\varphi)$	$-\frac{1}{2}\sqrt{3}(\sin\varphi + i \cos\theta \cos\varphi)$
$\frac{1}{2}(\sin\varphi + i \cos\theta \cos\varphi)$	$\frac{1}{2}i \sin\theta$	0	$\frac{1}{2}(\cos\varphi - i \cos\theta \sin\varphi)$	$\frac{1}{2}\sqrt{3}(-\cos\varphi + i \cos\theta \sin\varphi)$
$i \sin\theta$	$\frac{1}{2}(\sin\varphi + i \cos\theta \cos\varphi)$	$\frac{1}{2}(-\cos\varphi + i \cos\theta \sin\varphi)$	0	0
0	$\frac{1}{2}\sqrt{3}(\sin\varphi + i \cos\theta \cos\varphi)$	$\frac{1}{2}\sqrt{3}(\cos\varphi - i \cos\theta \sin\varphi)$	0	0

Two general remarks can be made:

(1) The trace of the matrix is zero; therefore for each \mathbf{k} the mean value of the energy levels is not affected by the spin-orbit interaction.

(2) As the symmetry group of the crystal contains the spatial inversion J , the invariance of the Hamiltonian under time reversal K gives rise to at least a double degeneracy for each \mathbf{k} .¹² Consequently, the eigenfunctions belonging to each doubly degenerate level can be deduced from each other by the anti-unitary operator JK which reverses the spin and does not change the wave vector.

Also the peculiar form taken by the interaction matrix $H_{L,S}$

$$H_{L,S} = \begin{pmatrix} M & N \\ -N^* & M^* \end{pmatrix}$$

is due to the invariance of the Hamiltonian under time reversal and to the fact that each basic function is connected by the operator JK with another function of the same set.

4. RESULTS

A. Without Spin-Orbit Interaction

The $E(\mathbf{k})$ values were calculated for 385 nonequivalent \mathbf{k} points equally spaced in the Brillouin zone.

$E(\mathbf{k})$ curves obtained in the Δ , Σ and Λ directions are shown in Figs. 1, 2 and 3¹³; they are similar to the ones previously found for Cr in the same approximations and, at least from a qualitative point of view, they can be compared with the results given by Mattheiss,³ if s - d mixing is taken into account.

Also the general features of the density-of-states curve (Fig. 4) are reproduced: One observes the strong mini-

mum at the middle of the band, which was previously found for Cr with a similar calculation¹ and also for several bcc transition metals as results of other calculations carried out with different methods and approximations.^{5,14} This fact is related, as is well known, to various properties of metals and alloys with a Fermi level near the middle of the band; for instance, the relatively low values of electronic specific heat¹⁵ and magnetic susceptibility¹⁶ as well the much lower capacity to

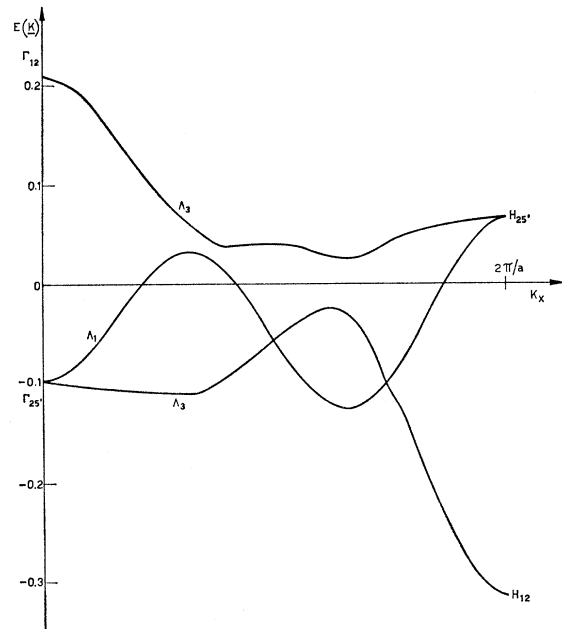


FIG. 3. Energy bands $E(\mathbf{k})$ along ΓP and PH lines. Energy in a.u. The point P corresponds to $k_x = \pi/a$, $k_y = \pi/a$, $k_z = \pi/a$.

¹⁴ J. F. Cornwell and E. P. Wohlfarth, J. Phys. Soc. Japan **17**, Suppl. B1, 32 (1961); E. P. Wohlfarth and I. F. Cornwell, Phys. Rev. Letters **7**, 342 (1961).

¹⁵ D. H. Parkinson, Rept. Progr. Phys. **21**, 226 (1958); C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

¹⁶ See, for instance, W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (Institute of Metals, London, 1955), p. 322; S. Taniguchi, R. S. Tebble, and D. E. Williams, Proc. Roy. Soc. (London) **A265**, 502 (1962).

¹² R. J. Elliott, Phys. Rev. **96**, 280 (1954).

¹³ In the figures the symbols are the same as those used by G. F. Koster in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, pp. 173, 256. Conversion of the notation of L. P. Bouckaert, R. Smoluchowsky, and E. Wigner, Phys. Rev. **50**, 58 (1936), can be made by interchanging the labels Σ_3 and Σ_4 .

interaction matrix. $H_L, s = \frac{1}{2}$.

0	$\frac{1}{2}(\cos\varphi + i \cos\theta \sin\varphi)$	$\frac{1}{2}(\sin\varphi - i \cos\theta \cos\varphi)$	$-i \sin\theta$	0
$-\frac{1}{2}(\cos\varphi + i \cos\theta \sin\varphi)$	0	$-\frac{1}{2}i \sin\theta$	$\frac{1}{2}(\sin\varphi - i \cos\theta \cos\varphi)$	$\frac{1}{2}\sqrt{3}i(\sin\varphi - i \cos\theta \cos\varphi)$
$\frac{1}{2}(-\sin\varphi + i \cos\theta \cos\varphi)$	$\frac{1}{2}i \sin\theta$	0	$-\frac{1}{2}(\cos\varphi + i \cos\theta \sin\varphi)$	$+\frac{1}{2}\sqrt{3}(\cos\varphi + i \cos\theta \sin\varphi)$
$i \sin\theta$	$\frac{1}{2}(-\sin\varphi + i \cos\theta \cos\varphi)$	$\frac{1}{2}(\cos\varphi + i \cos\theta \sin\varphi)$	0	0
0	$\frac{1}{2}\sqrt{3}(-\sin\varphi + i \cos\theta \cos\varphi)$	$-\frac{1}{2}\sqrt{3}(\cos\varphi + i \cos\theta \sin\varphi)$	0	0
0	$-\frac{1}{2}i \sin\theta \sin\varphi$	$\frac{1}{2}i \sin\theta \cos\varphi$	$-i \cos\theta$	0
$\frac{1}{2}i \sin\theta \sin\varphi$	0	$-\frac{1}{2}i \cos\theta$	$\frac{1}{2}i \sin\theta \cos\varphi$	$\frac{1}{2}\sqrt{3}i \sin\theta \cos\varphi$
$-\frac{1}{2}i \sin\theta \cos\varphi$	$\frac{1}{2}i \cos\theta$	0	$\frac{1}{2}i \sin\theta \sin\varphi$	$-\frac{1}{2}\sqrt{3}i \sin\theta \sin\varphi$
$i \cos\theta$	$-\frac{1}{2}i \sin\theta \sin\varphi$	$-\frac{1}{2}i \sin\theta \cos\varphi$	0	0
0	$-\frac{1}{2}\sqrt{3}i \sin\theta \cos\varphi$	$\frac{1}{2}i \sqrt{3} \sin\theta \sin\varphi$	0	0

absorb hydrogen in comparison with other transition metals.¹⁷

On the other hand, we do not find the sharp peak immediately at the right of the minimum, which has been suggested¹⁸ by the interpretation of specific-heat and magnetization data concerning Cr-Fe, Cr-Mn, and Fe-Co alloys. It is not possible to draw definite conclusions on this point: on the one hand, it may happen that the numerical integration in \mathbf{k} space, from which $g(E)$ curves are deduced, is not sufficiently detailed to reveal sharp and narrow peaks connected with critical points of $E(\mathbf{k})$ in the Brillouin zone¹⁹; on the other hand, this point is also ambiguous as to the interpretation of experimental data. In fact a sharp peak for alloys at an electron concentration close to that where ferromagnetism starts is not necessarily caused by any singularity in the trend of the density-of-states curve²⁰ and moreover it is possible that at least a part of this peak is due to localized moments.⁸

All the calculated curves exhibit another general

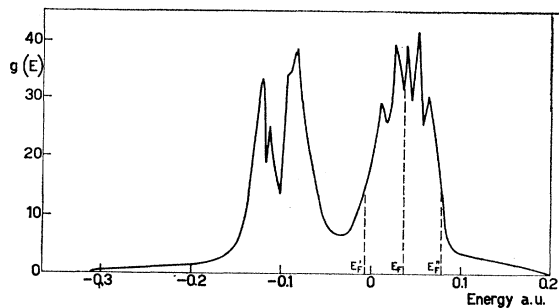


FIG. 4. Density-of-states curve $g(E)$ (number of states/atom and atomic energy units). E_F is the Fermi level in the paramagnetic state and E_F', E_F'' the Fermi level for the two directions of spin in the ferromagnetic state.

¹⁷ D. W. Johes, N. Pessall, and A. D. McQuillan, *Phil. Mag.* **6**, 455 (1961).

¹⁸ K. P. Gupta, C. H. Cheng, and P. A. Beck, *J. Phys. Radium* **23**, 721 (1962).

¹⁹ L. Van Hove, *Phys. Rev.* **89**, 1189 (1953).

²⁰ L. Berger, *Phys. Rev.* **137**, A220 (1965).

feature: A minimum, which is not as conspicuous as the central one, can be noticed in the high density-of-states region at the side corresponding to low energies; also this minimum may be related to the electronic-specific-heat data.²¹

In spite of these analogies it is difficult to find in these results a support for the rigid-band hypothesis; the various calculated curves are not similar in details and the two for Cr and Fe (see Fig. 7 of Ref. 1 and Fig. 4 of the present work) do not particularly agree though they have been deduced with the same method and approximations.

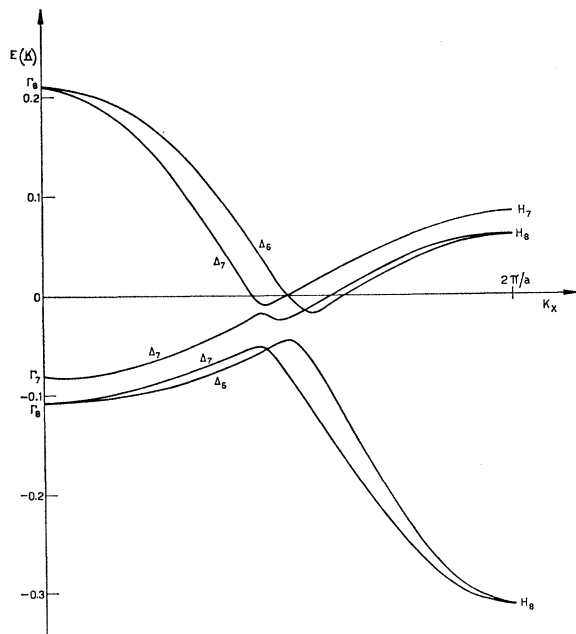


FIG. 5. Energy bands along ΓH line, spin-orbit interaction being taken into account. Energy in a.u.

²¹ M. Shimizu, T. Takahashi, and A. Katsuki, *J. Phys. Soc. Japan* **17**, 1740 (1962); M. Shimizu, *J. Phys. Soc. Japan* **18**, 1192 (1963).

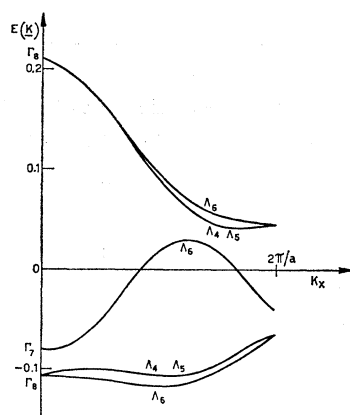


FIG. 6. Energy bands along ΓP line, spin-orbit interaction being taken into account. Energy in a.u.

In the present results two long side tails make the band rather broad; nevertheless the region where the density of states is large covers a much narrower energy interval. Table III reports the widths of high density-of-states intervals found for Fe by various authors.

TABLE III. High density-of-states energy interval for the d band of Fe.

Source	Interval (eV)
Belding (Ref. 5)	4
Wohlfarth (Ref. 14)	6.8
Present work	6.0
Mattheiss ^a (Ref. 3)	~4
Stern ^a (Ref. 7)	~9

^a In these cases the value is not deduced from a density-of-states curve, but from the behavior of $E(k)$ along some directions.

B. With Spin-Orbit Interaction

The introduction of a spin-orbit coupling leads to a 10×10 interaction matrix with imaginary terms, which cannot be easily diagonalized for any \mathbf{k} . The group theory tells one the degeneracy of the various levels at particular points of the Brillouin zone, where symmetry considerations enable one to simplify and diagonalize the interaction matrix.²²

Figures 5 and 6 report the results obtained for directions Δ and Λ , the z axis being taken as the quantization direction for the spin.

Degeneracies of levels $\Gamma_{25'}$, $H_{25'}$, Δ_5 , and Λ_3 are removed as well as other accidental ones along line Δ .

²² J. Friedel, P. Lenglard, and G. Leman, J. Phys. Chem. Solids 25, 781 (1964).

These curves are reported for $\xi=0.016$ atomic units (a.u.), a value which is probably more suitable for the elements of the III series, for instance for W. For $\xi=0.0016$ a.u., i.e., equal to the value obtained for the $3d^7$ configuration of the free Fe ion in the ground state,²³ the behavior is qualitatively the same but obviously the differences with regard to Figs. 1 and 3 are less remarkable.

5. CONCLUSIONS

The electronic structure of the $3d$ band in Fe has been studied with the tight-binding method. A comparison with the data concerning calculations carried out with various methods and approximations, suggests that some features are rather general for bcc transition metals. Such features are the general trend of the eigenvalues in \mathbf{k} space, the minimum at the middle of the $g(E)$ curve between two high density-of-states regions, the bonding and antibonding characters, respectively, for eigenfunctions concerning the bottom and top of the band. Particular agreement in the details was not found with the results previously obtained for Cr with the identical method, which would perhaps be expected on the basis of the rigid-band hypothesis.

The introduction into the Hamiltonian of the spin-orbit-coupling term made it possible to study subsequently the influence of this interaction on the d -band structure for bcc transition metals. From a quantitative point of view the effect depends obviously on the value of the parameter; the most conspicuous influence is noticed at the middle of Brillouin zone along lines Δ and Λ , where various degeneracies, either accidental or not, are eliminated, particularly around the middle of the band. Probably this interaction does not markedly modify the density-of-states curve, but it may be more important in determining some details of Fermi surface, and in fact it might be responsible for the differences in the de Haas-van Alphen effect found for corresponding metals in the III series.

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²³ E. Moore, Natl. Bur. Std. (U. S.), Circ. No. 467 (1952).