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The magnetic state of the ϵ phase of iron

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Abstract. A band calculation has been made for hexagonal close packed (ϵ phase) iron in order to investigate whether a ferro- or antiferromagnetic state might be expected theoretically. For this purpose the Stoner criterion and a similar one for the occurrence of antiferromagnetism were applied and it was found that neither magnetic state would be predicted by these because of a low value for the density of states at the Fermi energy. Because of the width of the relevant dip in the density of states curve rigid band theory failed to explain the occurrence of antiferromagnetism in alloys of ϵ-Fe with Mn, Os and Ru as observed.

1. Introduction

The occurrence of a hexagonal close packed (hcp) ϵ phase of iron has been known for some time although it only appears to exist under pressures exceeding 100 kbar. Investigations by Mössbauer technique at room temperature (Nicol *et al* 1963, Pipkorn *et al* 1964) indicated that it is paramagnetic but, by comparison with γ-Fe (face centred cubic (fcc)) Pipkorn *et al* (1964) and Ohno (1971) suggested that it should become antiferromagnetic at a low enough temperature ($T_N \sim 8$ K for γ-Fe). Thus hcp alloys of iron with 20–30% Mn, Os or Ru all prove to be antiferromagnetic with Néel temperatures between 25 and 240 K and extrapolation to pure hcp Fe suggests that it should have a Néel temperature of about 100 K, a view supported by the antiferromagnetism of fcc FeMn alloys and of pure fcc Fe (in a Cu matrix). However, Williamson *et al* (1972) investigated pure hcp Fe at 20 K and a pressure of 148 kbar as well as at 48 K and 176 kbar very thoroughly and failed to find indications of an antiferromagnetic state nor was it ferromagnetic which would appear to be another possibility. In the present work a band calculation was carried out by the Hubbard method for hcp Fe with a view to seeing whether the simplest itinerant electron magnetism criteria could explain this behaviour and perhaps the antiferromagnetism of its alloys.

2. Band calculation for hcp iron

The hcp lattice of identical atoms consists of two simple hexagonal sublattices and contains two atoms per unit cell which was chosen most conveniently for the present purposes in the form of two Wigner–Seitz cells centred on neighbouring atoms, one from each sublattice (Schiff 1955, figure 1(*b*)). The two cells have a common face and it is easily

verified that together they form a valid unit cell. For iron the lattice parameters were taken as $a = 4{\cdot}660$ au, $c = 7{\cdot}656$ au, (Clendenen and Drickamer 1964) the c/a ratio being slightly greater than the ideal value $\sqrt{\frac{8}{3}}$; these values were measured at a pressure of 150 kbar. A muffin tin potential was calculated in the usual way (Loucks 1967) from atomic wavefunctions for iron in the $3d^6 4s^2$ configurations due to Clementi (1965) but assuming the configuration $3d^7 4s$ for the atoms in the crystal. It is certainly true that transition metals contain less than two nearly free electrons per atom and this procedure has proved to yield consistent results in terms of occupied states in the nearly free electron band in previous band calculations and those performed here. Equal muffin tin radii $R_s = 2{\cdot}340$ au were chosen round all atoms and full Slater exchange was incorporated. The constant potential between the spheres proved to be $V_0 = -1{\cdot}442$ Ryd, a value 0·018 Ryd higher than the potential round each atom at the sphere surfaces. The band calculation was carried out by the method of Hubbard (1969) as generalized by Wakoh (1970). For the monatomic case it is possible by choosing the origin halfway between the two sublattices to make the problem entirely real, as Wakoh comments, the determinantal equation to determine the eigenvalues having the form

$$\begin{vmatrix} \boldsymbol{A}_{11} - \bar{\epsilon}\boldsymbol{I} & \boldsymbol{A}_{12} & \boldsymbol{h}'_1 \\ \boldsymbol{A}_{12} & \boldsymbol{A}_{22} - \bar{\epsilon}\boldsymbol{I} & \boldsymbol{h}'_2 \\ \boldsymbol{h}_1 & \boldsymbol{h}_2 & \boldsymbol{K} + \boldsymbol{V} - \bar{\epsilon}\boldsymbol{I} \end{vmatrix} = 0 \tag{1}$$

where

$$(\boldsymbol{A}_{11})_{mm'} = \bar{\epsilon}_0 \delta_{mm'} - \frac{32\pi^2}{\Omega} \Gamma R_s^2 \sum_{\boldsymbol{p}}^{(R)} \frac{j_2^2(k_p R_s)}{k_p^2 - \bar{\epsilon}} Y_{2m}(\check{\boldsymbol{k}}_p)\, Y_{2m'}(\check{\boldsymbol{k}}_p) \cos^2(\boldsymbol{K}_p \cdot \boldsymbol{\rho}). \tag{2}$$

$\boldsymbol{A}_{22}$ is similar but with $\sin^2(\boldsymbol{K}_p \cdot \boldsymbol{\rho})$ in the second term while $\boldsymbol{A}_{12}$ has no first term and $\sin(\boldsymbol{K}_p \cdot \boldsymbol{\rho}) \cos(\boldsymbol{K}_p \cdot \boldsymbol{\rho})$ in the second term.

$$(\boldsymbol{h}_1)_{pm} = 4\pi R_s \left(\frac{2\Gamma}{\Omega}\right)^{1/2} j_2(k_p R_s)\, Y_{2m}(\check{\boldsymbol{k}}_p) \cos(\boldsymbol{K}_p \cdot \boldsymbol{\rho}) \tag{3}$$

and $\boldsymbol{h}_2$ is similar but with a factor $\sin(\boldsymbol{K}_p \cdot \boldsymbol{\rho})$ and finally

$$(\boldsymbol{V})_{pq} = \frac{8\pi}{\Omega} \sum_l (2l+1) R_l^2 \gamma_l(\bar{\epsilon})\, j_l(k_p R_s)\, j_l(k_q R_s)\, P_l(\cos\theta_{pq}) \cos(\boldsymbol{K}_p - \boldsymbol{K}_q) \cdot \boldsymbol{\rho}. \tag{4}$$

As usual Ω is the volume of unit cell, $\boldsymbol{K}_p$ is a reciprocal lattice vector and $\boldsymbol{k}_p = \boldsymbol{k} + \boldsymbol{K}_p$, θ_{pq} is the angle between vectors $\boldsymbol{k}_p$ and $\boldsymbol{k}_q$, R_l is the smaller of R_s and the distance to the first zero of $n_l(\bar{\epsilon}^{1/2} r)$ (Pendry and Capart 1969), Γ is the strength 1·013 Ryd and $\bar{\epsilon}_0$ the energy of the $l = 2$ resonance and $\gamma_l(\bar{\epsilon})$ are related to the phase shifts at the muffin tin spheres (after subtracting the resonance for $l = 2$). The spherical harmonics Y_{2m} are real, bars over energies indicate that V_0 has been deducted from the potential everywhere so that absolute energies $\epsilon = \bar{\epsilon} + V_0$ and $2\boldsymbol{\rho}$ is the vector separating the two sublattices. The summation in (2) is over the remainder set (R) of reciprocal lattice vectors and as usual the parts for large vectors were approximated by integrals. Even with the further approximation of $\sin x/x$ for $j_2(x)$ exact evaluation of the integrals produces complicated formulae because of the occurrence of the cos and sin factors. However, since we are only concerned with large $\boldsymbol{K}_p$, we can use a parity argument on the factor $\sin(\boldsymbol{K}_p \cdot \boldsymbol{\rho}) \cos(\boldsymbol{K}_p \cdot \boldsymbol{\rho})$ to treat the integral for $\boldsymbol{A}_{12}$ as negligible and take the integrals for $\boldsymbol{A}_{11}$, $\boldsymbol{A}_{22}$ as both equal to

$$\frac{2}{\pi}\Gamma R_s\left(\frac{1-\cos x}{x}+\tfrac{1}{2}\pi-\mathrm{Si}(x)\right)_{x=2k_0R_s} \tag{5}$$

where $\Omega k_0^3/6\pi^2 = n$ and n is the number of reciprocal lattice vectors in the preferred set (P) and the set left for explicit summation in (2). The energy dependence of the matrices A and V was simplified in the usual way by putting

$$\begin{aligned} A(\bar{\epsilon}) &\simeq A(\bar{\epsilon}_1) + (\bar{\epsilon}-\bar{\epsilon}_1)\,A'(\bar{\epsilon}) \\ V(\bar{\epsilon}) &\simeq [(\bar{\epsilon}-\bar{\epsilon}_1)\,V(\bar{\epsilon}_c) + (\bar{\epsilon}_c-\bar{\epsilon})\,V(\bar{\epsilon}_1)]/(\bar{\epsilon}_c-\bar{\epsilon}_1) \end{aligned} \tag{6}$$

where the so called conduction band energy

$$\bar{\epsilon}_c = k^2 + (V)_{00}(k^2) \tag{7}$$

and the d band energy $\bar{\epsilon}_1$ was the energy for zero $l = 2$ phase shift, having the value 0·753 Ryd.

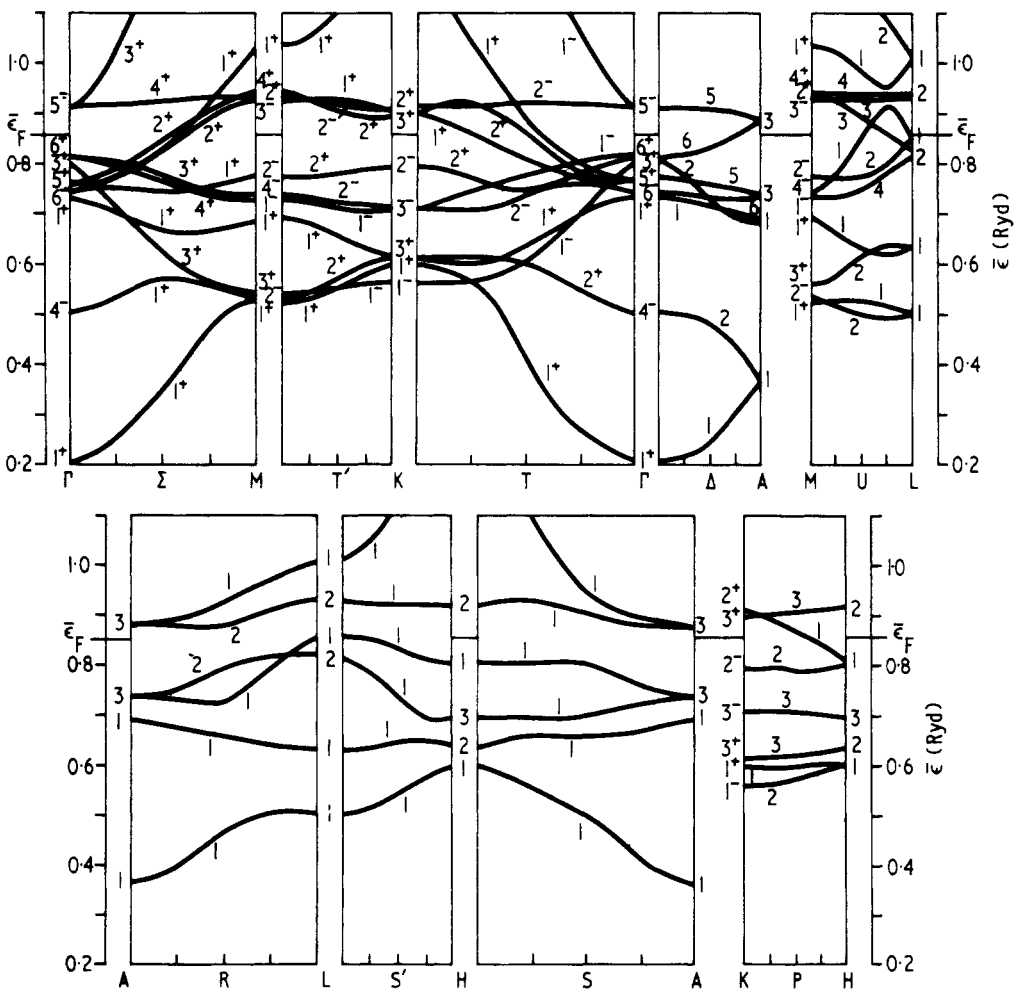

Figure 1. $\epsilon(\boldsymbol{k})$ curves for ϵ-Fe for various symmetry lines in the Brillouin zone. Letters below the diagrams indicate symmetry points and lines and numbers above the letters indicate the irreducible representation of the relevant symmetry groups (see appendix for explanation). The Fermi level at 0·856 Ryd is also indicated. Absolute energies $\epsilon = \bar{\epsilon} - 1{\cdot}442$ Ryd.

In the actual calculation 99 reciprocal lattice vectors were used, of which the first 12, namely (000), (00 ±1), (−200), (−1 −10), (−20 ±1), (−1 −1 ±1), (00 −2), (−20 −2), (−1 −1 −2) in units of $2\pi(1/\sqrt{3}a,\ 1/a,\ 1/c)$, were preferred vectors so that the matrices involved were of dimensions 22 × 22, and the maximum value of l involved in the matrix V was taken as 4. As a check of the computer programme some calculations were carried out for hcp cobalt and compared with Wakoh's results although exact agreement could not be expected in ignorance of the potential used by him. For Fe calculations were performed for 125 wavevectors $\boldsymbol{k}$ in $\frac{1}{24}$ of the Brillouin zone on a mesh which was equilateral triangular in the (k_x, k_y) plane and equally spaced in the k_z direction. Dispersion curves along various symmetry directions are shown in figure 1 and are typical of those obtained by other workers for hcp transition metals. Linear interpolation of the calculated eigenvalues to a mesh in $\boldsymbol{k}$ space five times as fine in each direction was then carried out and the numbers of eigenvalues in intervals of energy $\Delta\epsilon = 0{\cdot}01$ Ryd evaluated to give a density of state histogram from which the smoothed curve shown in figure 2 was

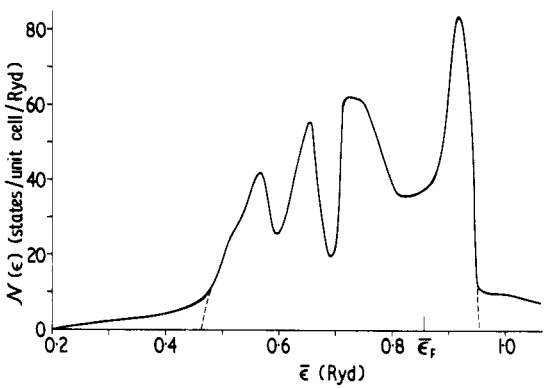

Figure 2. Density of states curve for ϵ-Fe. The dashed lines indicate the portion defined as the d band. Absolute energies $\epsilon = \bar{\epsilon} - 1{\cdot}442$ Ryd.

derived. This is similar in general shape to that obtained in other calculations for hcp transition metals, the important feature for our purposes being the relatively low dip immediately below the final high energy peak of the d band. The d bandwidth is about 0·49 Ryd, greater than the 0·34 Ryd obtained by Wakoh and Yamashita (1970) for Co as might be expected since the Co atoms are more widely spaced than in this high pressure phase of Fe. Filling the band with the 16 3d and 4s electrons per unit cell, the Fermi energy proved to have a value $\bar{\epsilon}_F = 0{\cdot}856$ Ryd, ie within the dip in the density of states already mentioned, the density of states there having a value of

$$\mathcal{N}(\epsilon_F) = 35{\cdot}6 \text{ states/unit cell/Ryd.} \tag{8}$$

To complete the results obtained in the band calculation the Fermi surface is shown in figure 3; apart from some very small hole pockets in the 7th band whose existence would not be guaranteed the 9th and 10th bands each contain separated, roughly cylindrical electron pockets and for the 8th band we have a connected structure on the periodically extended zone scheme.

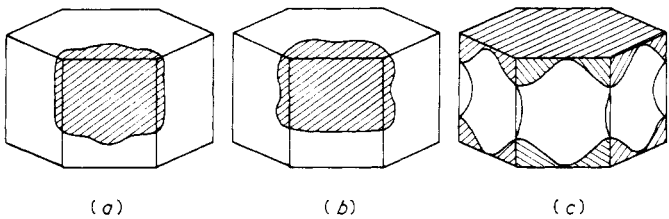

Figure 3. Fermi surfaces for ϵ-Fe in the (*a*) 10th, (*b*) 9th, (*c*) 8th bands. Shading indicates the occupied regions of the Brillouin zone.

3. Criteria for ferromagnetism and antiferromagnetism

The simplest criterion for the occurrence of a ferromagnetic ground state for an itinerant electron metal is that due to Stoner (1938) as generalized by Edwards and Wohlfarth (1968), namely that the exchange field parameter θ' shall satisfy the inequality

$$k_B\theta' > n/\mathcal{N}(\epsilon_F) \tag{9}$$

where n is the number of electrons or holes per atom in the possibly magnetic band and $\mathcal{N}(\epsilon)$ the corresponding density of states (of both spins). To use this criterion an estimate of $k_B\theta'$ is necessary; the theory on which the Stoner criterion is based assumes that in the ferromagnetic state identical up- and down-spin densities of states become shifted relative to one another by an energy $\Delta\epsilon$ and then contain respectively n_+ and n_- electrons (or holes). Then it can be shown that

$$k_B\theta' = n\Delta\epsilon/2(n_+ - n_-). \tag{10}$$

Wohlfarth (1964, 1968) has discussed various possibilities of estimating the quantities on the right hand side of this, in particular band calculations for nonmagnetic and ferromagnetic states of the same metal may be used to obtain all of them although obviously $(n_+ - n_-)$ and n should agree with experimental values of the magnetic moment and total number of magnetic carriers per atom respectively if these are known. In the case of iron Wohlfarth's best estimate for $\Delta\epsilon$ is $1{\cdot}40 \pm 0{\cdot}02$ eV, the band calculation for ferromagnetic (bcc) iron by Wakoh and Yamashita (1966) gives $n = 2{\cdot}9$ holes in the d band, $n_+ - n_- = 2{\cdot}2$ (which agrees with experiment) and these values give $k_B\theta' = 0{\cdot}069$ Ryd. A band calculation carried out for nonmagnetic bcc Fe (Fletcher and Nudel 1973) gave a value $\mathcal{N}(\epsilon_F) = 52{\cdot}0$ states/atom/Ryd and $n = 2{\cdot}60$ holes/atom. This value for n is smaller than the generally accepted value for bcc Fe for reasons discussed later. However, since use of the Stoner criterion amounts to comparison of $1/\mathcal{N}(\epsilon_F)$ with $n^{-1}k_B\theta' = \Delta\epsilon/2(n_+ - n_-)$, this discrepancy does not matter. Thus, we have $n^{-1}k_B\theta' = 0{\cdot}023$ Ryd and $\mathcal{N}^{-1}(\epsilon_F) = 0{\cdot}019$ Ryd and the Stoner criterion is in agreement with the fact that the ground state of bcc Fe is ferromagnetic. From the present calculation for nonmagnetic hcp Fe the values $n = 2{\cdot}72$ holes per atom and $\mathcal{N}(\epsilon_F) = 17{\cdot}8$ states/atom/Ryd were obtained so that

$$\mathcal{N}^{-1}(\epsilon_F) = 0{\cdot}056\,\text{Ryd} \tag{11}$$

is much greater than the value of $n^{-1}k_B\theta'$ given above. Of course it is not obvious that the latter should be the same in both forms of iron. $k_B\theta'$ is an effective field parameter and in

particular an atom in hcp Fe has 12 nearest neighbours at a distance of 4·66 au whereas in bcc Fe there are only 8 at 4·69 au. However, it has been argued, eg by Hubbard (1963, 1964), that interatomic contributions will be relatively small, so that it seems reasonable to use the same value for $k_B\theta'$. On the other hand the different values for n suggest reducing $n^{-1}k_B\theta'$ in the ratio 2·60/2·72 to a value of 0·022 Ryd and the Stoner criterion supports the contention that hcp Fe should not be ferromagnetic. Obviously no sensible variation in $n^{-1}k_B\theta'$ between bcc and hcp Fe would upset this conclusion. Finally from a band calculation for nonmagnetic fcc Fe (Fletcher and Nudel 1973) values of $n = 2{\cdot}56$ holes per atom and $\mathcal{N}(\epsilon_F) = 30{\cdot}47$ states/atom/Ryd were obtained, giving by the same argument $n^{-1}k_B\theta' = 0{\cdot}023$ Ryd and $\mathcal{N}^{-1}(\epsilon_F) = 0{\cdot}033$ Ryd so that again the Stoner criterion supports the fact that fcc Fe is not ferromagnetic.

In the case of antiferromagnetism it is possible to obtain a very similar criterion to that of Stoner by a similar argument, based on introduction of a slight antiferromagnetic ordering and investigation of its energetic stability, as follows. In a previous band calculation for antiferromagnetic γ-Mn (Fletcher 1971a) it was commented that the one electron wavefunctions could be regarded as mixtures of right-spin functions (up-spin on up-spin atoms, down-spin on down-spin ones) and wrong-spin functions (down-spin on up-spins atoms and vice versa). Herring (1966, p 119) had already introduced the same description and obviously we can regard the nonmagnetic state as the superposition of two identical bands, one of right-spin and the other of wrong-spin states, equally as well as the superposition of up-spin and down-spin bands. We shall only consider simple antiferromagnetic ordering with two similar sublattices of identical but opposite spin as in γ-Mn and in this case we can consider the effect of slight ordering as producing a relative shift of the right-spin and wrong-spin bands by an energy $\Delta\epsilon$ and filled to a common level ϵ_{FA} with different numbers n_R, n_W of electrons per atom where $n_R + n_W = n$ is the total number of magnetic electrons. We can introduce a relative magnetization $\zeta \propto (n_R - n_W)$ where $\zeta = 1$ corresponds to the maximum antiferromagnetic ordering and $\zeta = 0$ to the nonmagnetic situation. We assume there is a corresponding exchange field proportional to ζ acting on the electrons on any atom and consider the change in energy when an electron described by a right-spin function is changed to a wrong-spin state. If there are N atoms in the crystal, such functions correspond to $1/N$ of an electron on each atom. If we write the change in energy of a single electron on an atom as $2k_B\theta'_A\zeta$ (as in the ferromagnetic case) then the energy change due to the flipping of a right-spin Bloch state to a wrong-spin one is $N(2k_B\theta'_A\zeta/N) = 2k_B\theta'_A\zeta$. Now we can write the total change of energy when the nonmagnetic crystal acquires a small antiferromagnetic ordering ζ as

$$E(\zeta) = \int_{\epsilon_F}^{\epsilon_R} \epsilon g(\epsilon)\,d\epsilon - \int_{\epsilon_W}^{\epsilon_F} \epsilon g(\epsilon)\,d\epsilon - \tfrac{1}{2}nk_B\theta'_A\zeta^2 \tag{12}$$

where $g(\epsilon) = \frac{1}{2}\,\mathcal{N}(\epsilon)$ is the density of states per atom for either spin in the nonmagnetic case, ϵ_F the nonmagnetic Fermi energy and ϵ_R, ϵ_W the levels on the same energy scale to which the right-spin and wrong-spin bands are filled in the antiferromagnetic state. Considering the stability of this expression with respect to variation of ζ in the limit as $\zeta \to 0$ we obtain just as in the ferromagnetic case as a first approximation

$$k_B\theta'_A > \frac{n}{2g(\epsilon_F)} = \frac{n}{\mathcal{N}(\epsilon_F)} \tag{13}$$

as the criterion for an antiferromagnetic ground state.

In applying this criterion to the case of hcp Fe the problem remains of obtaining an

estimate of $k_B\theta'_A$ since the experimental and theoretical data used for estimating the ferromagnetic $k_B\theta'$ is not available. However, it is known that an antiferromagnetic state of fcc Fe exists (Kondorskii and Sedov 1959, see also Johanson *et al* 1970 for further references) and, if this is described by identical right- and wrong-spin bands shifted relative to one another by an energy $\Delta\epsilon$, this may be equated to $2k_B\theta'_A\zeta$ as in the ferromagnetic case. Experimental estimates of the magnetization per atom (and hence $n_R - n_W$) differ greatly and there are none of n nor $\Delta\epsilon$ so that the following procedure was adopted.

Firstly, a band calculation was carried out for nonmagnetic fcc Fe with the lattice constant $a = 6{\cdot}834$ au reported for the antiferromagnetic state (Taylor and Kagle 1963). The same Clementi atomic wavefunctions and configuration $3d^7 4s$ were used as described for the hcp calculation and full Slater exchange was incorporated. From the resulting density of states filled from the bottom with 8 electrons per atom the number of holes in the d band was estimated to be $n = 2{\cdot}593$ holes/atom and a density of states at the Fermi energy $\mathcal{N}(\epsilon_F) = 33{\cdot}5$ states/atom/Ryd. At least to estimate $\Delta\epsilon$ it was next necessary to carry out a band calculation for antiferromagnetic fcc Fe; this was assumed to have the same ordering as γ-Mn (without any tetragonal distortion and with $a = 6{\cdot}834$ au) but to calculate a crystal potential it was necessary to assume some value for the magnetization per atom. As mentioned above experimental estimates vary greatly but opinion amongst the author's colleagues was that it was small and a configuration $3d_\uparrow^{3\cdot75}3d_\downarrow^{3\cdot25}4s_\uparrow^{0\cdot5}4s_\downarrow^{0\cdot5}$ was assumed for the atoms in the solid. The same Clementi atomic functions and full Slater exchange were again assumed. The resultant d band width proved to be 0·46 Ryd as compared with 0·437 Ryd for the nonmagnetic calculation, so that a splitting $\Delta\epsilon = 0{\cdot}023$ Ryd was applied to the nonmagnetic bands, producing a value for $n_R - n_W$ of 0·325/atom. The latter is not selfconsistent with the value of 0·5 assumed in constructing the antiferromagnetic crystal potential but can be said to be consistent with the value for $\Delta\epsilon$ and, since only the ratio of these is used in determining $n^{-1}k_B\theta'_A$, it was decided to use them. The value then obtained for the effective field parameter was

$$n^{-1}k_B\theta'_A = \frac{\Delta\epsilon}{2(n_R - n_W)} = 0{\cdot}035\,\text{Ryd}. \tag{14}$$

As a test of this value the value of $\mathcal{N}(\epsilon_F)$ obtained from the calculation for nonmagnetic fcc Fe gives $\mathcal{N}^{-1}(\epsilon_F) = 0{\cdot}030$ Ryd which is slightly less than $k_B\theta'_A$ so that the criterion (13) would just support the occurrence of antiferromagnetism. By similar arguments to those used in the ferromagnetic case we can estimate $n^{-1}k_B\theta'_A$ for hcp Fe as $2{\cdot}59 \times 0{\cdot}035/2{\cdot}72 = 0{\cdot}034$ Ryd which is much less than the value obtained for $\mathcal{N}^{-1}(\epsilon_F)$ as that the criterion supports the experimental observation that hcp Fe does not seem to be antiferromagnetic. In the case of bcc Fe we estimate $n^{-1}k_B\theta'_A = 0{\cdot}035$ Ryd $> \mathcal{N}^{-1}(\epsilon_F)$ so that the ground state has the possibility of being either ferro- or antiferromagnetic with apparently a preference for the latter, for which the inequality is more extreme, obviously in disagreement with observation. However, the simple theory behind the criteria used cannot be expected to distinguish between the possibility of a strongly ferromagnetic state and a possible antiferromagnetic one.

It would be very satisfying if we could explain the experimentally observed occurrence of antiferromagnetism in hcp alloys of iron with Mn, Os and Ru (Ohno 1971) and at first sight this seems possible. Assuming $k_B\theta'_A$ is unaltered by alloying a value of $n/\mathcal{N}(\epsilon_F)$ considerably smaller than that obtained for pure hcp Fe is necessary for antiferromagnetism, ie a larger $\mathcal{N}(\epsilon_F)$ and/or a smaller value for n. Mn has one less d electron per atom than

Fe so that on a rigid band picture the d band of Fe should be emptied as we add Mn while similarly Os and Ru have one more d electron than Fe and should fill the band more as they are added. In either case, if ϵ_F moves onto the peaks of the density of states curve either side of the dip where it lies for pure iron, then $\mathcal{N}(\epsilon_F)$ could become large enough for the criterion to predict antiferromagnetism. However, by the Stoner criterion ferromagnetism would occur first and in any case the dip in the density of states curve is too broad for ϵ_F to move onto the peaks for the alloys which prove to be antiferromagnetic. With regard to the second point the corresponding dip obtained for Co by Wakoh and Yamashita (1970) is much narrower and could produce the desired behaviour. With regard to the first point a value of $k_B\theta'_A < k_B\theta'$ would support the occurrence of antiferromagnetism rather than ferromagnetism in the hcp Fe alloys and also the ferromagnetism rather than antiferromagnetism of bcc Fe. However, the antiferromagnetism of fcc Fe would then not be predicted.

4. Conclusions and comments

The conclusions reached as a result of a band calculation for hcp Fe is that by the Stoner criterion it would not be expected to be ferromagnetic (as Wohlfarth (see Williamson *et al* 1972) forecast from a consideration of Wakoh and Yamashita's calculation for Co) nor by a similar criterion would it be expected to be antiferromagnetic. The reason is the occurrence of the Fermi energy at the bottom of a large dip in the density of states curve giving a small value for $\mathcal{N}(\epsilon_F)$. For fcc Fe ϵ_F is near the bottom of a similar but shallower dip and under circumstances where it is found to be antiferromagnetic the criterion supports this. For bcc Fe ϵ_F is on a peak of the density of states curve and could by the criteria be either ferro- or antiferromagnetic. The dip in the hcp Fe density of states curve is too broad to explain the occurrence of antiferromagnetism in alloys with Mn, Os and Ru on rigid band theory which is not surprising as the alloys investigated have all been fairly concentrated.

One point concerning the band calculations here is that all give values for the total number of holes in the d band which are lower than that generally accepted for iron. This is probably the result of using full Slater exchange in calculating the crystal potentials since experience shows that reducing this exchange lowers the nearly free electron band relative to the d band and this would move the Fermi energy towards the bottom of the latter. Estimates indicate that the effect of using two-thirds of the Slater exchange, as is commonly done, would be more than sufficient to give $n \sim 2{\cdot}9$ holes/atom. Such relocation of the nearly free electron band relative to the d band would hardly affect the positions and magnitudes of troughs and peaks in the latter nor would the small change in d band width expected from reducing the exchange so that the conclusions based on the Stoner criteria should not be affected. The other point is whether, since the theory behind the criteria is essentially based on a single, doubly degenerate band of magnetic carriers, ie a d band, the overlapping nearly free electron band in these calculations should be deducted before measuring values of $\mathcal{N}(\epsilon_F)$. If this is done, however, the d band, as defined somewhat arbitrarily here as indicated in figure 2, is found to contain far less than 10 states per atom simply because the states taken away contain a lot of d character. None of the electrons (or holes) can be said to be pure d or pure conduction electrons and it was therefore decided to treat the d band as defined here (and which in all cases proved to contain almost exactly 10 states/atom) as the single band considered in the theory.

Acknowledgments

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Appendix

The lettering of the symmetry points and lines of the Brillouin zone in figure 1 is that used by Fletcher (1971b). The numbering of the irreducible representations follows that of Jones (1960) where possible but to make this clear and to amplify it tables are given below of the parts of the eigenfunctions which involve d type tight binding functions. Such a function based on one sublattice ϕ_m is denoted by m and one based on the other sublattice by $\bar{m}$ with $m = 1 \equiv xy, 2 \equiv yz, 3 \equiv (3z^2 - r^2)/2\sqrt{3}, 4 \equiv zx$ and $5 \equiv \frac{1}{2}(x^2 - y^2)$. Commas separate functions of the same symmetry while several functions in brackets form a basis for a multidimensional representation. Only relevant representations are given and, in particular, no d functions are involved in the representation Γ_3^+. In tables $\omega = \exp(\frac{1}{6}i\pi)$, $\alpha = \exp(\frac{1}{2}iak)$, $\beta = \exp(\frac{1}{2}iak_y)$, $\gamma = \exp(\frac{1}{2}ick)$, $\delta = \exp(ick_z)$, $f = \frac{1}{2}$ and $g = \frac{1}{2}\sqrt{3}$.

Table 1.

Γ	Γ_1^+	Γ_5^+	Γ_6^+	Γ_4^-	Γ_5^-	Γ_6^-		
	$3+\bar{3}$	$\{1+\bar{1}, 5+\bar{5}\}$	$\{2+\bar{2}, 4+\bar{4}\}$	$3-\bar{3}$	$\{2-\bar{2}, 4-\bar{4}\}$	$\{1-\bar{1}, 5-\bar{5}\}$		
M	M_1^+	M_2^+	M_3^+	M_4^+	M_1^-	M_2^-	M_3^-	M_4^-
	$3-\bar{3}, 5-\bar{5}$	$2-\bar{2}$	$4-\bar{4}$	$1-\bar{1}$	$2+\bar{2}$	$3+\bar{3}, 5+\bar{5}$	$1+\bar{1}$	$4+\bar{4}$
K	K_1^+		K_2^+		K_3^+			
	$\omega^3 1+\omega^5\bar{1}+5-\omega^2\bar{5}$		$\omega^4 2+\bar{2}-\omega 4-\omega^3\bar{4}$		$\{3, \bar{3}\}$			
	K_1^-		K_2^-		K_3^-			
	$\omega+\omega^3 2+\omega^4 4+\bar{4}$		$\omega^4 1+\bar{1}+\omega 5+\omega^3\bar{5}$		$\{2-i4, \bar{2}+i\bar{4}\}$			
Σ	Σ_1^+	Σ_2^+	Σ_3^+	Σ_4^+				
	$3, \bar{3}, 5, \bar{5}$	$1, \bar{1}$	$4, \bar{4}$	$2, \bar{2}$				
A	A_1	A_3						
	$\{3, \bar{3}\}$	$\{1, 5, \bar{1}, \bar{5}\}, \{2, 4, \bar{2}, \bar{4}\}$						
T	T_1^+			T_2^+				
	$1+\alpha(f\bar{1}+g\bar{5}), \alpha\bar{1}+f1+g5, 3+\alpha\bar{3}$			$1-\alpha(f\bar{1}+g\bar{5}), \alpha\bar{1}-f1-g5, 3-\alpha\bar{3}$				
	T_1^-			T_2^-				
	$2+\alpha(f\bar{2}-g\bar{4}), \alpha\bar{2}+f2-g4$			$2-\alpha(f\bar{2}-g\bar{4}), \alpha\bar{2}-f2+g4$				
T′	$T_1'^+$		$T_2'^+$		$T_1'^-$		$T_2'^-$	
	$1+\beta\bar{1}, 3-\beta\bar{3}, 5-\beta\bar{5}$		$1-\beta\bar{1}, 3+\beta\bar{3}, 5+\beta\bar{5}$		$2+\beta\bar{2}, 4-\beta\bar{4}$		$2-\beta\bar{2}, 4+\beta\bar{4}$	
L	L_1			L_2				
	$\{3, \bar{3}\}, \{4+\bar{5}, 5+\bar{4}\}, \{4-\bar{5}, 5-\bar{4}\}$			$\{1+\bar{2}, 2+\bar{1}\}, \{1-\bar{2}, 2-\bar{1}\}$				
H	H_1			H_2		H_3		
	$\{1-i5, \bar{1}+i\bar{5}\}, \{2+i4, \bar{2}+i\bar{4}\}$			$\{2-i4, \bar{2}+i\bar{4}\}$		$\{1+i5, \bar{1}-i\bar{5}\}, \{3, \bar{3}\}$		

Table 1—*continued*

R	R_1^-	R_2^-	R_3^-	R_4^-
	$3, 5, \bar{4}$	$1, \bar{2}$	$4, \bar{3}, \bar{5}$	$2, \bar{1}$
S′	S_1'			
	$\{1, \bar{1}\}, \{2, \bar{2}\}, \{3, \bar{3}\}, \{4, \bar{4}\}, \{5, \bar{5}\}$			
S	S_1			
	$\{3, \bar{3}\}, \{1, f\bar{1}+g\bar{5}\}, \{2, f\bar{2}-g\bar{4}\}, \{4, g\bar{2}+f\bar{4}\}, \{5, g\bar{1}-f\bar{5}\}$			
Δ	Δ_1	Δ_2	Δ_5	Δ_6
	$3+\bar{3}$	$3-\bar{3}$	$\{1+\gamma\bar{1}, 5+\gamma\bar{5}\}, \{2-\gamma\bar{2}, 4-\gamma\bar{4}\}$	$\{1-\gamma\bar{1}, 5-\gamma\bar{5}\}, \{2+\gamma\bar{2}, 4+\gamma\bar{4}\}$
P	P_1			
	$1-i5+\delta(f+ig), \bar{1}-\delta(g-if)\bar{5}, 2+i4-\delta(f+ig)\bar{2}-\delta(g-if)\bar{4}$			
	P_2			
	$1+i5-\delta(f+ig)\bar{1}-\delta(g-if)\bar{5}, 2-i4+\delta(f+ig)\bar{2}-\delta(g-if)\bar{4}$			
	P_3			
	$\{1+\delta(g+if)\bar{5}, 5+\delta(g+if)\bar{1}\}, \{2+\delta(g+if)\bar{4}, 4+\delta(g+if)\bar{2}\}, \{3, \bar{3}\}$			
U	U_1	U_2	U_3	U_4
	$3-\delta\bar{3}, 4+\delta\bar{4}, 5-\delta\bar{5}$	$3+\delta\bar{3}, 4-\delta\bar{4}, 5+\delta\bar{5}$	$1+\delta\bar{1}, 2-\delta\bar{2}$	$1-\delta\bar{1}, 2+\delta\bar{2}$

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