Magnetism in iron around the Curie temperature: recursion calculations on regular spin configuration, with a full SPD Hamiltonian

1989 J. Phys.: Condens. Matter 1 8961

(http://iopscience.iop.org/0953-8984/1/45/019)

J. Phys.: Condens. Matter 1 (1989) 8961–8977. Printed in the UK

Magnetism in iron around the Curie temperature: recursion calculations on regular spin configurations with a full spd Hamiltonian

M U Luchini† and Volker Heine
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Received 20 March 1989, in final form 2 August 1989

Abstract. Previous numerical investigations of the degree and nature of short-range order around the Curie temperature, T_C, in Fe using spin spirals and other regular configurations have been limited almost exclusively to d-band-only models. We report on calculations that fully include spd hybridisation which is known to be important in itinerant systems. The local moments and total energies which we obtain are rather different from the previous results and substantiate a recent hypothesis of Heine and Joynt who suggested coarse-grained disordering on the scale of the Stoner wavevector. We found that to a first approximation Fe behaves like a Heisenberg ferromagnet but the corrections obtained from different configurations have contradictory implications. This suggests the existence of multi-atom forces. We obtained a value for the spin wave stiffness in excellent agreement with experiment and comment on the implications of our results for models of the disordering of Fe around T_C.

1. Introduction

The present work is an attempt to contribute to an understanding of the magnetic interactions in metallic magnets and will deal in particular with Fe above the Curie temperature, T_C. The subject is controversial both theoretically and experimentally. Though the existence of substantial magnetic behaviour in the paramagnetic state is now established, the origin of the short-range magnetic order is still unclear. We have performed some electronic structure calculations on particular spin configurations, typical of the true high-temperature state, which characterise a recently proposed model (Heine and Joynt 1988).

Macroscopic magnetism in metals can disappear through the action of two main microscopic mechanisms. It can be destroyed by one-electron excitations across the Fermi surface as in the original Stoner model of itinerant electron magnetism. This picture implies the destruction of local moments and the absence of substantial magnetic behaviour in the paramagnetic state. Alternatively, the atomic moments can rotate as in the formation of domain walls, and the macroscopic magnetism disappears through the disordering of the local moments.

In Fe a large body of evidence has shown that the second mechanism is dominant. For example the Stoner value of T_C is far too high and local moments are known

† Present address: Theoretische Physik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland.

0953-8984/89/458961+17$02.50

to survive in this material at all temperatures. The spin wave modes dominate the low-temperature properties and represent the first corrections to mean field theory. Fluctuating mean field theories (see Korenman (1985) for a recent review) incorporate the spin wave corrections and assume a local mean field whose direction varies in space and time. Above T_C only the total vector magnetisation need vanish, thus allowing substantial magnetic behaviour in the paramagnetic state.

This raises the question of which local moment configurations are important and it is mostly the choice of these that distinguishes the several varieties of fluctuating mean field theories. Some theoretical calculations have shown that the interaction is not far removed from a nearest-neighbour Heisenberg form. However, this by itself leads to very little short-range magnetic order above T_C, contrary to the results of neutron scattering experiments (Mook *et al* 1973, Lynn 1975, Mook and Lynn 1985). Therefore this simple model cannot represent the whole picture.

The main importance of our calculations is perhaps that they support the picture of the magnetic phase transition proposed recently by Heine and Joynt (1988). Following the approach of Korenman *et al* (1977) and Prange and Korenman (1979), they suggested a new model which is characterised by coarse-grained magnetic disorder. They pictured the local moments in the disordered state above T_C as twisting fairly smoothly in direction. Such configurations can be typified and idealised by spin spirals. Taking a clue from Cyrot (1984) they assumed that the system at high temperature can be described as being filled with Bloch walls. By developing a formula for the entropy of such configurations coupled with calculations of their energy, they showed that the magnetisation in Fe could disappear around T_C leading to a state of coarse-grained magnetic disorder. Thus the amount of short-range order (SRO) is derived by the theory instead of being assumed *a priori* in the set of allowed spin configurations. Only quite modest deviations from the nearest-neighbour Heisenberg form for the interaction energy are required for this picture to be applicable. They showed, from general considerations, that the plot of the spirals' energy as a function of wavevector q is determined by the spin wave stiffness at low q, but crosses over to a much steeper curve at higher q. This upward bend occurs at $q = q_S$ and leads to SRO on a lengthscale $2\pi/q_S$, where q_S is the wavevector where the spin waves enter the Stoner continuum. This implies SRO around T_C with nearest-neighbour angle $\theta_C \simeq 60°$. The main purpose of the present paper is to look again at the high-temperature state of Fe as typified by the energies of ideal configurations like spin spirals using a realistic spd parametrisation of the band structure.

In order to throw some light on the origin of the magnetic interactions and the controversy on SRO above T_C we have performed some electronic structure calculations, using the recursion method (Haydock 1980), on a few simple configurations of well defined ordering. These are the spin spirals mentioned above and the alternating tilts, both previously examined in the context of a d-band-only model by You and Heine (1982) and Holden and You (1982). Spin spirals (SS) are 'smooth' variations of the magnetisation in a particular direction such that the local moments on atoms in successive planes are rotated by an angle θ. Alternating tilts (AT) represent 'rough' variations such that moments on successive planes are rotated by $\pm\theta/2$. Figure 2 of You and Heine (1982) shows both configurations.

It is important to include fully the effect of the s and p electrons in the calculations if one wants to obtain quantitative comparison with experiment. The magnetic properties, in particular the spin wave stiffness, are notoriously sensitive to the details of the electronic structure. In Fe, hybridisation between the d and sp electrons seems to be of

paramount importance in determining the low-q behaviour and spin wave stiffnesses obtained from d-band-only models are usually too small (Muniz *et al* 1985).

The inclusion of sp electrons leads to a very large overall bandwidth though the essential magnetic interactions are still confined to the relatively narrow d bands with substantial weight, and forces us to use a large number ($\simeq 90$) of levels in the continued fraction. This results in considerable numerical problems of accuracy and stability. In §3 we thoroughly examine and compare the various techniques available for carrying out the recursion calculation and for the final evaluation of the continued fraction.

While there are several interesting details concerning the behaviour of the sp and d parts of the moments, the main results concern the SS and AT energy densities (figure 1). These are plotted, as usual, against $(1-\cos\theta)$ since in such a plot for a nearest-neighbour Heisenberg model both energies would lie on the same straight line. It is quite clear that *all* the results in figure 1 are fitted quite well by the Heisenberg form. These include the spin spirals in two directions, [100] and [110], alternating tilts [100] and some configurations with randomly oriented spins. A single exact straight line would result from a Heisenberg model and conversely would seem to be implied by it. Thus to a reasonable approximation we confirm a nearest-neighbour interactions among atomic moments.

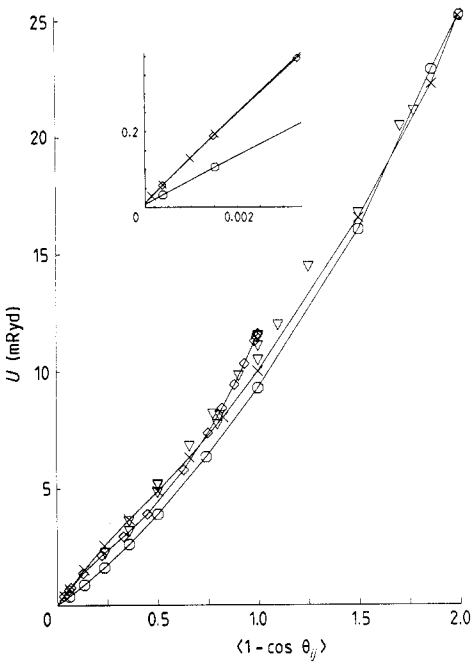

Figure 1. Total energies of various spin configurations relative to the ferromagnetic ground state against the average of the nearest-neighbour angle, $\langle 1-\cos\theta_{ij}\rangle$. The inset shows the very-low-θ part of the plot from which the spin wave stiffness is deduced. ×: spin spiral in [100]; ○: alternating tilts in [100]; ◇: spin spiral in [110]; ▽: randomly oriented spins.

However, looking in more detail, we note that *all* the curves in figure 1 are concave upwards. This implies that configurations with small nearest-neighbour angle θ_{ij}, i.e. with more smoothly varying magnetisation, have a lower energy than those with

large θ_{ij} relative to the Heisenberg model. The effect is quite substantial when the full range of θ_{ij} and the different types of configuration examined are taken into account. Indeed the two SS results are slightly S shaped with maximum dip (relative to the Heisenberg line) around $\theta_C \simeq 60°$. This is precisely the effect which in the proposal of Heine and Joynt gives coarse-grained magnetic disorder on a lengthscale of the order of $2\pi/q_S$ and occurs at the correct value of θ.

From the low-θ part of the curve we derive an excellent value for the spin wave stiffness ($D = 313$ meV Å^2). It is in this region of the curves that the effect of the sp electrons is most noticeable. The curves do not differ very significantly from the d-band-only results at higher θ.

Surprisingly, $U_{AT}(\theta)$ is lower than $U_{SS}(\theta)$ over most of the range of θ, contrary to previous results. We believe this could be due to the fact that they are more ferromagnetic than spirals. This could be an indication of multi-atom forces, i.e. the energy is lowest when there is a substantial net moment over a region of several atoms, but this remains to be investigated. We have also performed a limited series of calculations on randomly oriented moment configurations and to a good first approximation the interactions are again seen to be Heisenberg like. It can be seen that all random clusters have an energy higher than that of the equivalent spiral, providing evidence for the hypothesis of Heine and Joynt that, for a given nearest-neighbour angle, smooth variations of magnetisation like spirals have a lower energy than more ragged arrangements and therefore have a larger weight in the thermodynamics.

If we ignore the possibility of multi-atom interactions we can Fourier transform $U_{SS}(\theta)$ and $U_{AT}(\theta)$ in the manner of Holden and You (1982) to obtain pairwise Heisenberg interaction parameters J_{ij}. We have found long-range interactions of oscillating sign extending at least as far as the fifth shell of neighbours, though the corrections seem to decay faster than in d-band-only calculations. These parameters yield a good value for the mean field Curie temperature, $T_C = 1260$ K. However, we also have evidence of greater non-Heisenberg contributions to the interactions making the whole question of the fit more dubious than ever and the possibility of multi-atom effects more probable.

The self-consistent moments for all our configurations are shown in figure 2. The most important feature of the plot is the stability of the magnetisation up to at least $\theta = 90°$ for the regular configurations and over the whole range of θ for the random ones. This stability of the moment to perturbations in the local environment validates the local moment picture and is consistent with the experimental observation of substantial local moments in Fe over the whole range of temperature. Consideration of all the results suggests that the moments are more sensitive probes of the environment than the total energies and from a detailed examination of all the evidence from parallel and perpendicular d and sp moments we infer that the sp cloud polarises freely with the local d moments but does not carry a substantial magnetic interaction. This is directly a d–d effect whose range is lengthened by hybridisation.

In §2 we specify our model in more physical and mathematical detail. The numerical implementation is discussed in §3 while §4 and §5 contain our complete results and their interpretation.

2. Physical specification of the model

The physical picture of itinerant magnetism on which our model is constructed is basically the same as that of You and Heine (1982). The main motivation behind our

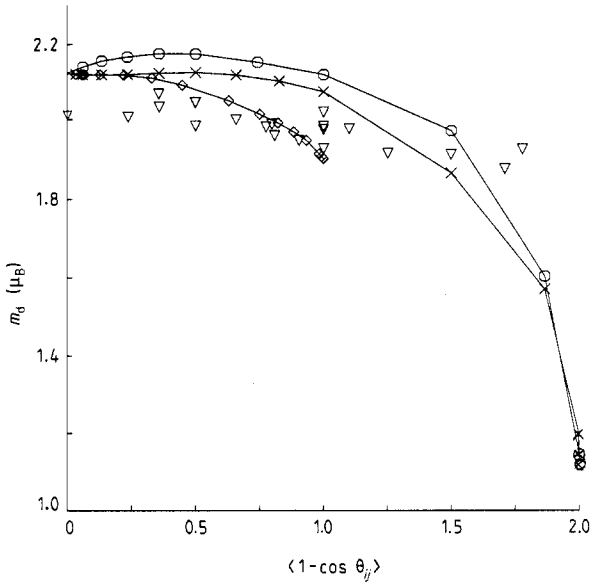

Figure 2. Self-consistent total moments of various spin configurations relative to the ferromagnetic ground state against the average of the nearest-neighbour angle, $\langle 1-\cos\theta_{ij}\rangle$. The plots for the d moments are indistinguishable on this scale except for a small shift upwards. ×: spin spiral in [100]; ○: alternating tilts in [100]; ◇: spin spiral in [110]; ▽: randomly oriented spins.

new set of calculations is the examination of the effects of the inclusion of s and p bands in the context of a realistic band structure. We summarise below the physical justification and numerical implementation of the model while referring the reader to the exhaustive discussion in You and Heine for greater detail.

In this work we start with a non-magnetic band structure and then impose splittings $\pm\Delta_{jl}$ in the one-electron equations for each atomic orbital l and for all atoms j in the cluster. The spin splittings refer to local axes of quantisation for up and down electrons in predetermined directions. Thus electrons in the solid will polarise in the direction of the Δ_j, giving rise to local moments $\mathbf{m}_j$ more or less in the same direction. We make the calculation self-consistent on each site using a simple Stoner *ansatz*:

$$\Delta_{jl} = \sum_{l'} I_{ll'} m_{jl'} \tag{2.1}$$

where m_{jl} is the component of the atomic moment parallel to the direction of Δ_{jl}. The small components of $\mathbf{m}_j$ orthogonal to Δ_j are caused by the polarisation of the electron cloud with the environment and are related to the magnetic couple acting on the atom (Small and Heine 1984). By choosing the directions and magnitudes of the set of $\{\Delta_j\}$ we can represent *any* configuration of local moments. In this way we can investigate the whole range of configurations from those envisaged by theories which postulate giant SRO to those which are representative of the disordered local moment picture.

We employ an spd tight-binding parametrisation of Wood's APW non-magnetic band structure (Wood 1962) in terms of the usual Slater–Koster (Slater and Koster 1954) formulation. This has previously been used by Muniz *et al* (1985) who obtained

from it a theoretical estimate for the spin wave stiffness in good agreement with experiment.

Our main improvement over You and Heine consists in the inclusion of the s and p electrons which is reflected in the form of the matrix $I_{ll'}$. First-principles spin-polarised calculations indicate that the spin splitting of s- and p-like states is very small compared to that of the d-like states (Fritsche *et al* 1987). So we can safely set to zero all elements of Δ_{jl} for which l corresponds to s or p. The calculations of Cooke *et al* (1980) indicated that there is very little difference between the splittings for d electrons of t_{2g} and e_g symmetry. Hence we can take Δ_{jl} to be the same for all d electrons. The self-consistency procedure is embodied in the form of $I_{ll'}$ which we specify as

$$I\begin{pmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \tag{2.2}$$

between d electrons and zero otherwise. Since the d electron density at the edge of the Wigner–Seitz cell is rather small we also assume that I is purely intra-atomic. We have checked the features of our ferromagnetic state against more recent calculations in various respects (see §3) and we believe that our calculations are carried out with a proper representation of the full band structure.

We now specify our model in more mathematical detail. Since the exchange is mostly intra-atomic the conventional description of our calculation starts by examining the Hubbard Hamiltonian

$$H = H_{\text{band}} + H_{\text{ex}} \tag{2.3}$$

$$H_{\text{band}} = \sum_{jj'll'} h(j,l,j',l')c_{jl}^{\dagger}c_{j'l'} + \text{HC} \tag{2.4}$$

$$H_{\text{ex}} = \sum_{jll'} I_{ll'}n_{jl\uparrow}n_{jl'\downarrow}. \tag{2.5}$$

We solve equation (2.3) in the usual Hartree–Fock approximation by inserting an exchange splitting on each site j

$$-\tfrac{1}{2}\Delta_j \cdot \sigma_j \tag{2.6}$$

in the one-electron equations. Here σ_j is the vector of Pauli spin matrices on site j. The magnitudes of all Δ_j are then made self-consistent as discussed earlier (equation (2.1)) and the solution is found to have total energy

$$U = \sum_j \left(\int_{-\infty}^{E_F} En_j(E)\,\mathrm{d}E + \frac{1}{4}Im_j^2 \right) \tag{2.7}$$

expressed in terms of $n_j(E)$, the local density of states on site j.

Although the conventional description of the calculation given above is correct it is not the most useful. Suppose we carried out a density functional calculation which used a tight-binding basis set for expanding the one-electron auxiliary wavefunctions. We would obtain the conventional model without any Hartree–Fock approximation, all approximations being included in the form of the exchange and correlation energy functional. If the spin-dependent part of the latter is taken as purely intra-atomic and the same for all electrons than the conventional model with constant I will result (Stollhoff *et al* 1989).

3. Computational details and the ferromagnetic ground state

The local densities of states are the central quantities of our calculation and are obtained using the recursion method (Haydock 1980). The density of states of Fe consists of a set of narrow d-band peaks with considerable weight on top of a very broad, roughly featureless sp band with little weight. The total bandwidth ($\simeq$ 2 Ryd) is much larger than that of a pure d band ($\simeq$ 0.45 Ryd). However, the main interactions, and therefore the most important changes in the density of states, still take place in the relatively narrow region of the d band. Therefore in order to obtain the same energy resolution in this crucial region as one had in d-band-only calculations it is necessary to sample the band structure at many more points. In our calculations using the recursion method this implies a correspondingly larger number of levels of the continued fraction.

The processing of the recursion coefficients to obtain the density of states is usually carried out in one of two ways. One can append an analytic terminator to a small number of exact levels obtained from a large cluster. This procedure is well known for emphasising the peaks in the density of states and though we have used the most recent method which enables considerably better smoothing (Luchini and Nex 1987), we found that the moment as a function of the number of levels and the cluster size did not converge. The peaks in the density of states have too much weight and the moment is unstable as the parameters are changed.

The alternative approach of Gaussian quadrature (Nex 1978, 1984) uses a large number of inexact levels obtained from a relatively small cluster and copes considerably better. It is clearly the correct approach for our problem in the light of the above considerations on the energy resolution required. With quadrature the calculations show stability and convergence with respect to cluster size and number of levels. However, before the details in the centre of the band, where the d peaks lie, are resolved one must carry out the recursion until $\simeq$ 90 levels. When one uses such a large number of levels there is a considerable danger of surface effects and eigenvalue ghosting becoming dominant. One has to use a fairly large clusters of 1000–2000 atoms to prevent this. Though conventional wisdom prefers the use of periodic boundary conditions we found that for large numbers of levels ($>$ 30) the convergence of moments computed with no periodic (or 'cluster') boundary conditions was considerably better than that obtained from periodic boundary conditions. Finally we note that for such large numbers of levels we do not run into the problems of rotational invariance of the continued fraction with respect to the cluster axes, highlighted by Inoue and Ohta (1987). Block recursion (Paxton *et al* 1987, Nex 1989) is the correct solution to these difficulties but for our purposes conventional scalar recursion is sufficient.

Figure 3 shows our best total density of states for the ferromagnetic ground state obtained at 120 levels on a 2000 atom cluster. This can be compared with figure 2(*b*) of Muniz *et al* (1985) which resulted from $\boldsymbol{k}$-space integrations using linear analytic tetrahedra and the same tight-binding parameters[†]. The small spikes at the band edge are due to near-resolution of eigenvalues and have negligible weight in the integrated density of states. The agreement can be seen to be excellent, justifying our choice of recursion parameters and method of analysis. All the data in the other figures were

[†] We take this occasion to point out that a sign error in the spσ matrix element crept into the parametrisation used in figure 4 of Luchini and Nex (1987) so that their density of states does not correspond to figure 2(*b*) of Muniz *et al* (1985) as they stated. Hence one cannot compare their terminator results with our quadrature ones. This does not affect the points made in that paper about termination methods.

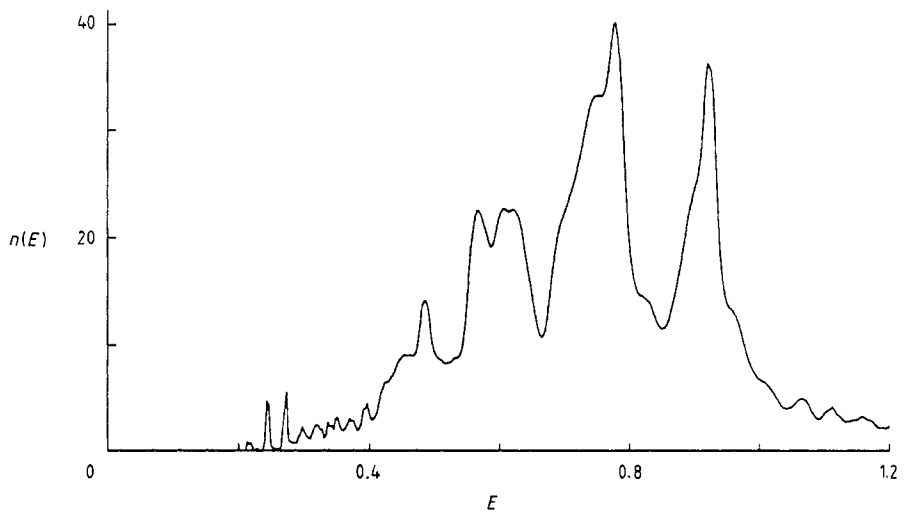

Figure 3. Total density of states for ferromagnetic Fe at 120 levels and a 2000 atom cubic cluster with 'cluster' boundary conditions. The continued fraction was analysed with the quadrature approach.

obtained with 91 levels and 1024 atoms.

The numerical value of I is determined by imposing a splitting Δ on the ferromagnetic ground state and requiring the total magnetisation to be in agreement with experiment. We used the same values as Muniz *et al* (1985): $\Delta_d = 0.1427$ Ryd and $m_{tot} = 2.125\,\mu_B$, where $m_{tot} = m_s + m_p + m_d$ is the total moment of the ferromagnetic ground state. We obtained $I_{dd} = \Delta_d/m_d = 0.067\,1529$ Ryd. The values of Δ and I lie in the accepted ranges. Our Fermi energy is determined by filling up the bands with 8.0 electrons.

Lastly we check the characteristics of the ferromagnetic ground state of the model against the most recent density functional calculation to ensure that the parametrisation is indeed realistic. For example, our values for the angular momentum decompositions of the effective occupation numbers agree rather well with those obtained from the relativistic self-consistent spin density functional calculation of Fritsche *et al* (1987): $N_s = 0.652$, $N_p = 0.767$ and $N_d = 6.581$ compared with $N_s = 0.614$, $N_p = 0.747$ and $N_d = 6.639$, where $N_l = N_{l\uparrow} + N_{l\downarrow}$ and we have added the very small occupation numbers with $l > 2$ into the d-orbital contribution. From $N_{d\uparrow} = 4.395$ and $N_{d\downarrow} = 2.186$ one can see that the majority d band is not quite full, again a well known characteristic of Fe. The sp moment has the value $-0.085\,\mu_B$ which agrees well with observations of the magnetic form factor of Shull and Yamada (1962).

Since we will also be concerned with spin spirals in the [110] direction and clusters of randomly oriented spins, it is important to be able to compare the results for all these different configurations in a unified way. We do this by considering the Heisenberg model where the total energy of any configuration is written as

$$\Delta U = \frac{1}{2}\sum_{ij} J_{ij}(1 - \cos\theta_{ij}) \tag{3.1}$$

relative to the ferromagnetic ground state, where θ_{ij} is the angle between atom i and

atom j. Our results indicate that nearest-neighbour interactions are dominant (§1) so that the natural quantity against which to plot all energies is

$$\langle 1-\cos\theta_{ij}\rangle = \frac{1}{8}\sum_{j=1}^{8}(1-\cos\theta_{ij}). \tag{3.2}$$

For a Heisenberg model $U_{SS}(\theta)$, $U_{AT}(\theta)$ and $U_{SS[110]}(\theta)$ all fall on the same straight line when plotted against $\langle 1-\cos\theta_{ij}\rangle$. Note though that the maximum value of $\langle 1-\cos\theta_{ij}\rangle$ for an SS[110] is 1 not 2 as for an SS[100]. This represents the configuration with four neighbours aligned ferromagnetically and four antiferromagnetically. Rigorously, and for a general model, all three energies should be proportional to θ^2 for small θ though only those of the two spirals need be equal.

4. Results

Our main results are contained in the plots of the energies of the various configurations. Figure 1 shows $U_{SS}(\theta)$, $U_{AT}(\theta)$ and $U_{SS[110]}(\theta)$ together with the energies of some random clusters which we will discuss later.

Our first consideration is that there is remarkably little difference between the energies of all configurations. The Heisenberg model is a very good zeroth-order approximation to all the data. You and Heine (1982) (hereafter referred to as YH) had obtained rather larger deviations with a d-band-only model. Small and Heine (1984), in their examination of magnetic couples, had also obtained some deviations from Heisenberg behaviour. In the framework of coarse-grained magnetic disorder of Heine and Joynt (1988) which we described in §1, we notice that $U_{SS}(\theta)$ *does* have an upward bend at $\theta \simeq 60°$ as prescribed by them. Moreover $U_{SS[110]}(\theta)$ has the same shape, confirming that the universal form for spiral energies supposed by Heine and Joynt is correct.

Surprisingly, we observe that $U_{AT}(\theta) < U_{SS}(\theta)$ over almost the whole range of θ. This is contrary to the previous calculations which had suggested the view 'smooth' excitations (spirals) were energetically favoured over 'rough' disordering (tilts). It is in the low-θ region that the greatest difference between the present and previous calculations is found and is consistent with the sensitivity of the spin wave stiffness to the inclusion of sp electrons. $U_{SS}(90°)$ is very close to its previous value if scaled appropriately by the overall energy range, $U(180°)-U(0°)$.

Concentrating now on this region where the energies of all configurations have a linear dependence on $\langle 1-\cos\theta_{ij}\rangle$, we note that the gradient of $U_{AT}(\theta)$ at the origin is almost exactly half of that of $U_{SS}(\theta)$. This factor of two seems too precise to be accidental and must contain valuable information which examination of our limited set of configurations does not enable us to extract. We note that when a model s band had been added to the pure d-band model in the calculations of Holden and You (1982), the two curves had moved closer. The present results continue the trend. With the benefit of hindsight, one can understand why the AT curve has a lower energy. For a given nearest-neighbour angle ($< 90°$), when a region of several atoms is considered the AT has a substantially larger net magnetisation compared to an SS. The arrangement is closer to ferromagnetic alignment and has a lower energy. This observation provides evidence for the existence of multi-atom forces but cannot distinguish between multi-atom and long-range pairwise interactions or a combination of the two. A direct

calculation of the couples between sites in environments with a varying degree of disorder is in progress and should distinguish between these alternatives. Since all these effects are strongly dependent on the environment they will be more notable in a model in which the itineracy of the d electrons is strongly enhanced by hybridisation. This is consistent with the trend in the different calculations of the relative energies of the SS and AT.

From the gradient of $U_{SS}(\theta)$ we can easily derive the spin wave stiffness D, since there is no difference between spin waves and spirals in the limit $\theta \to 0$ (Herring 1966),

$$D = (a^2/m) \lim_{\theta \to 0} (U_{SS}(\theta)/\theta^2). \tag{4.1}$$

With $a = 2.86\,\text{Å}$ and $m = 2.125\,\mu_B$ we obtain $D = 313\,\text{meV Å}^2$ which compares rather well with the representative value extrapolated at $T = 0$ of $D = 314\,\text{meV Å}^2$ given by Stringfellow (1968). D is a notoriously difficult quantity to calculate and theoretical estimates have ranged from one quarter of the observed value (Wakoh *et al* 1971) to $562\,\text{meV Å}^2$ (Wang *et al* 1982). Muniz *et al* (1985) using essentially the same band structure considered in our calculation but a different method obtained $D = 280\,\text{meV Å}^2$, already a very good result. They concluded that the spin wave stiffness is a very sensitive function of the band structure but that the sp hybridisation is essential to ensure the stability of the ferromagnetic ground state. Our results seem to confirm this point of view and increase our confidence in the model.

We note, in passing, the very small ($\simeq 0.000\,01$ Ryd) point discontinuity in the energy curves at $\theta = 0$. This is due to preservation of symmetries in the recursion since the computer treats zero more accurately than any other number. Since the Hamiltonian was stored in single precision this gives a very small but noticeable discontinuity. In more recent calculations, with a double precision Hamiltonian the discontinuity is absent.

There is an alternative way to plot $U_{SS[110]}(\theta)$. We could consider, as YH did, the equivalent angle per unit length as being the natural unit with which to compare different configurations of infinite long-range order. For spirals in the [110] direction the equivalent angle α is given by $\alpha = \theta/\sqrt{2}$ where θ is now the angle between spins in adjacent planes in the [110] direction. The two ways of plotting the data are strictly identical in the small-θ limit. Figure 4 shows the equivalent angle plot with $U_{SS}(\theta)$ shown for comparison ($\alpha = \theta$ for an SS). $U_{SS[110]}(\theta)$ deviates significantly from $U_{SS}(\theta)$ at quite low values of θ, in contrast with the results of YH where the two curves were substantially the same until $\theta = 90°$.

In figure 2 we plot the self-consistent d momen. for the SS, AT, SS[110] and for clusters with randomly oriented spins. Our first consideration concerns the remarkable stability of the magnetisation for both the SS and AT until $\theta \simeq 90°$. For $\theta > 90°$ the local moments rapidly decrease to the antiferromagnetic value: $m(\theta = 180°) = 1.134\,\mu_B$. Considering the steepness of $U_{SS}(\theta)$ in this region the difference from Kübler's value of $m(\theta = 180°) = 0.8\,\mu_B$, obtained from a self-consistent spin density functional calculation for antiferromagnetic BCC Fe (Kübler 1980), makes very little difference to the overall shape of the curve in figure 2. The energy difference between the non-magnetic state and the antiferromagnetic one is minute (0.186 mRyd), reflecting the steepness of the fall of the moment. Kübler had obtained 1 mRyd.

It is notable that $m_{AT}(\theta)$ increases above the ferromagnetic value for $0 < \theta < 80°$ while $m_{SS}(\theta)$ is monotonically decreasing. This again is different from the previous

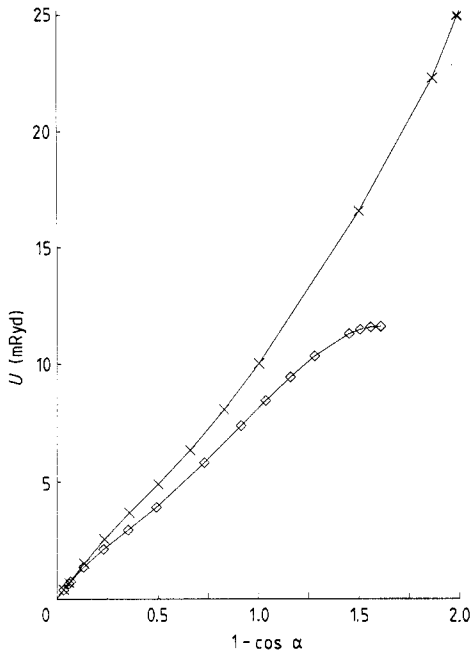

Figure 4. Total energies of spin spirals in the [100] (×) and in the [110] (◇) directions plotted against the equivalent angle per unit length, α.

results of YH who found both moments to be monotonically decreasing. This increase correlates with the lower energy of the AT with respect to the SS. Indeed consideration of all the data including that on random clusters below leads one to the conclusion that a relative increase in magnetisation correlates with a relative decrease in energy.

The physical picture behind the suggestion of Heine and Joynt (1988), was based on the assumption that SS have lower energy than other configurations and that therefore one can use them as normal modes in doing the thermodynamics. Our results seem to contradict this picture. However ATs represent spin waves at the zone boundary and are not true high-temperature configurations. It is more correct to consider clusters with randomly oriented spin directions. With these clusters the complications of self-consistency in both magnetic moments and charge transfer on all sites arise. Since we are only interested in doing an order of magnitude check on the energy we will neglect these. Thus we fix the Δ_j in a random configuration and self-consist on the central atom only making all the $|\Delta_j|$ the same. The rationale is that in a truly random cluster we would expect each atom to see approximately the same environment. We expect charge transfers between sites to be an even smaller effect because there is considerable on-site interband transfer which neutralises most of the effects of different exchange splittings.

The Heisenberg framework we have established allows us to define the proper statistics of random clusters quite easily. The average cluster has $\langle 1 - \cos\theta_{ij}\rangle = 1$. We can extend this to next-nearest neighbours with $\langle 1 - \cos\theta_{ik}\rangle$ and so on. The correct procedure would be to average over the distribution with a given $\langle 1 - \cos\theta_{ij}\rangle$. In practice we evaluate the spread of results for a few clusters of given $\langle 1 - \cos\theta_{ij}\rangle$

by choosing the extreme cluster cases, i.e. those with next-nearest neighbours close to ferromagnetic and antiferromagnetic alignment with the central atom. The spread in the energy differences turns out to be quite small and is shown in the plot for $\langle 1-\cos\theta_{ij}\rangle = 0.5$ and 1 corresponding to $\langle\theta_{ij}\rangle = 60°$ and 90°. For all the other points we have chosen $\langle 1-\cos\theta_{ik}\rangle \sim 1$ thus attempting to evaluate a typical cluster with a given $\langle 1-\cos\theta_{ij}\rangle$.

The energy of all clusters is reasonably well fitted by a nearest-neighbour Heisenberg form since they all lie pretty close to a straight line. Corrections to the energies from next-nearest neighbours seem rather small. The energies of all random clusters, except at very low θ, is higher than that of the equivalent spiral. The middle of the range of $\langle 1-\cos\theta_{ij}\rangle$ contains the data that we trust most since for it the approximation that all the atoms see the same environment is best satisfied. These truly disordered configurations, with $\langle 1-\cos\theta_{ij}\rangle \simeq 1$, have a considerably higher energy than the equivalent spirals. Thus this set of calculations lends support to the hypothesis of Heine and Joynt. We note that, again, for clusters with the same value of $\langle 1-\cos\theta_{ij}\rangle$ those with the higher magnetisation have the lower energy in accordance with what we observed earlier.

The results for the self-consistent moment are also interesting. To zeroth order they are constant over the whole range and 5% smaller than the ferromagnetic value. The survival of very substantial moments in the disordered state agrees with the results from photoemission above T_C as well as other calculations. Indeed the reduction in moment we observe is smaller than that obtained by previous calculations of the disordered local moment picture. Early d-band-only results showed 20–30% reductions (Hubbard 1979, Hasegawa 1980) while the more recent self-consistent KKR CPA calculations of Pindor *et al* (1983) and Staunton *et al* (1985) yielded 15% reductions.

We would also expect the moment to decrease with increasing $\langle 1-\cos\theta_{ij}\rangle$ and this is observed but the magnitude of the decrease is remarkably small. The spread of the data is almost as large as the overall decrease in the moment across the plot. In other words the value of the moment seems to be determined almost as much by the next-nearest neighbours as it is by the nearest. By contrast the energy seems to be affected almost exclusively by the nearest neighbours. For example in the case with $\langle 1-\cos\theta_{ij}\rangle = 0$, though the energy is extremely close to the ferromagnetic value the moment is considerably below (by $0.1\,\mu_B$). If we also align the next-nearest neighbours the moment almost rises to its ferromagnetic value but still not quite. We are left with the impression that the moments are much more sensitive probes of the environment and the interactions than the total energies.

With the above in mind we turn our attention to a more detailed consideration of the moments. In particular we examine the components of the moments in the directions orthogonal to $\boldsymbol{\Delta}_j$. These transferred moments are induced by the environment and are more sensitive to the details of the interactions than the total configuration energies. For the spirals, by symmetry, these moments are all zero but for the tilts they yield valuable information.

For the d electrons these components are always quite small reaching a maximum of $\simeq 0.3\,\mu_B$ which represents 15% of the parallel moments for ATs around 90°. However, $m_{sp}^{\perp}(\theta)$ reaches nearly 40% of $m_{sp}^{\parallel}(\theta)$ around $\theta = 90°$ for a maximum value of $0.02\,\mu_B$. We now concentrate on the behaviour as function of θ and in figure 5 plot $m_{sp}^{\perp}(\theta)/m_{d}^{\parallel}(\theta)$. Here $m_{sp}^{\perp}(\theta)$ is the moment perpendicular to the direction of $\boldsymbol{\Delta}_j$ which we choose to divide by $m_{d}^{\parallel}(\theta)$ since it is just a polarisation moment and its absolute magnitude is

proportional to the d moment. We would expect $m_{sp}^{\perp}(\theta)$ to be proportional to $\sin\theta$ and indeed this is the case to very high accuracy. However, the plot of $m_d^{\perp}(\theta)/m_d^{\parallel}(\theta)$ is considerably different, showing substantial nonlinearity in the transferred d moment. From these two results and from the relative magnitudes of the perpendicular moments one can propose that the sp cloud seems to polarise freely with the local d moments but does not carry a substantial magnetic interaction. This is instead directly a d–d effect and though its range is lengthened by hybridisation there is still considerable rigidity in the bands. The sp moment is *created* on the neighbouring sites by polarisation with the split d bands since there is no direct on-site exchange for the sp electrons in our calculation.

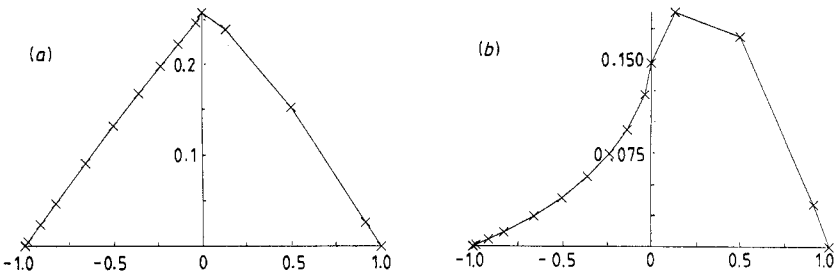

Figure 5. Scaled perpendicular moments for the tilts plotted against $\sin(\theta-\pi/2)$. The latter is chosen for plotting convenience since the perpendicular moments increase in the range $0<\theta<\pi/2$ and then decrease over the remaining range $\pi/2<\theta<\pi$. (*a*) $-m_{sp}^{\perp}(\theta)/m_d^{\parallel}(\theta)$; (*b*) $m_d^{\perp}(\theta)/m_d^{\parallel}(\theta)$.

To investigate this further we examine the transferred moments in configurations of randomly oriented moments. From the moments in the x and y directions (Δ_j is in the z direction) we can construct the polar angle ϕ of the resultant induced moment. In figure 6 we plot the difference between ϕ and the average ϕ of the direction of the moments on the atoms belonging to the shell of nearest neighbours, for both sp and d moments. We find that the average ϕ is quite a good first approximation but deviations are quite significant. We note that the standard deviation of the sp moments is twice that of the d moments (16.8° as against 33.6°). This clearly confirms that the sp electrons sample over a much larger region of space than the d electrons. The latter do not interact much further than with the nearest neighbours.

In the light of the above remarks the issue of the appropriateness or otherwise of a description of the interactions in terms of an effective Heisenberg model becomes crucial. In the context of the regular configurations above this has been examined by Holden and You (1982) (hereafter referred to as HY), and the analysis of our data will follow theirs. In order to quantify deviations from equation (3.1) we define a $\cos n\theta$ expansion of the functional form of the interaction and look at the AT results. We find that one only needs to include the $n=2$ contributions the results being quite adequately fitted by

$$U_{AT}(\theta) = \alpha(1-\cos\theta) + \beta(1-\cos 2\theta) \tag{4.2}$$

with $\alpha = 12.6$ mRyd and $\beta = -1.6$ mRyd. Here β represents some average nonlinearity in the interaction but also includes longer-range interactions and multi-atom effects. It

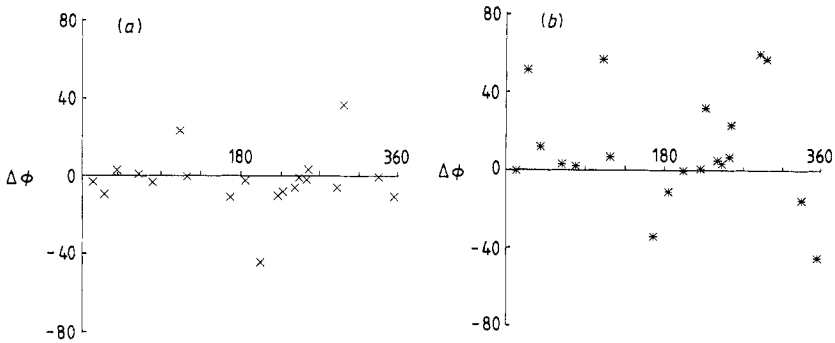

Figure 6. Polar angles in random clusters. $\Delta\phi$ is the difference between the polar angle of the perpendicular components of the moment and the average polar angle ϕ of the moments on the nearest neighbours. We choose to plot $\Delta\phi$ against ϕ for convenience: we are only interested in the scatter of the plot. (*a*) d electrons; (*b*) sp electrons.

is clearly not small representing a 13% correction to the normal Heisenberg term. HY had obtained a much smaller deviation of the opposite sign. We shall neglect it in the remainder of our analysis and use the straight $\cos\theta$ Heisenberg form. We note that the J_{ij} we will obtain are effective quantities which include some average of these effects.

Fitting separate $\cos n\theta$ expansions to $U_{SS}(\theta)$, $U_{AT}(\theta)$ and $U_{SS[110]}(\theta)$ as detailed in HY†, and then obtaining a least-squares fit to the resulting set of overdetermined equations, we find (in mRyd)

$$J_1 = 1.36 \qquad (2.68)$$
$$J' = J_2 + 2J_3 = 0.85 \qquad (0.02)$$
$$J'' = J_3 + 2J_5 = -1.24 \qquad (-0.72)$$
$$J_4 = 0.34 \qquad (0.1).$$

The individual values of J_2, J_3 and J_5 are undetermined by the equations as only the combinations J' and J'' appear. A few remarks about the fitting procedure are in order. HY had been forced to weight the low-θ data in order to obtain a fit which represented a stable ferromagnetic ground state. Our data is evenly weighted over the whole range of θ. The first set of values corresponds to a free fit of the J while the second corresponds to a fit constrained by $J_4 = 0.1$ mRyd, the value directly obtained from the data. The rather substantial difference between the two fits reflects the inadequacies of a pairwise decomposition of the interactions.

It is instructive to calculate T_C and the spin wave stiffness D using these effective J. In the mean field approximation to the Heisenberg model for a BCC structure, including interactions up to fifth neighbour, T_C is given by

$$T_C = \frac{1}{3k_B}\left[8J_1 + 6(J_2 + 2J_3) + 24J_4 + 8J_5\right]. \qquad (4.3)$$

Since we have no precise information about J_5, we set it to zero and obtain $T_C = 1261$ K from the first set of fitting parameters and $T_C = 1260$ K from the second. This is quite good compared to the experimental value of 1040 K especially considering that mean

† Note that equation (5.10) of HY should read $A_3 = J_2 + 4J_3 + 4J_5$.

field theory always overestimates T_C if short-range order is present. The experimental result implies a value of $J_5 \simeq -0.5$ mRyd which is considerably smaller than those obtained by HY, −2.3 mRyd, Lin-Chung and Holden (1981), −1.7 mRyd, and Small and Heine (1984), −1.1 mRyd but of the same sign. However, it is still appreciable and one must conclude that neglecting J_5 altogether is dangerous.

We are now in a position to estimate D from the effective J and again we use the expressions in HY. The first fit yields 346 meV Å^2 and the second 280 meV Å^2 which compare well with the value of 313 meV Å^2 we obtained previously from $U_{SS}(\theta)$ only. Clearly by appropriately weighting the low-θ points one would be able to narrow the gap between the two sets of fitting parameters but this seems a rather futile exercise. Due to the long-range and oscillatory nature of the effective couplings, reminiscent of Friedel oscillations, though the overall interactions are quite close to the Heisenberg form the individual couplings are much more undetermined. Hence T_C is remarkably insensitive to the fitting details and even the notoriously unstable spin wave stiffness is quite well behaved. This explains why the model has found so much success in iron. However, a microscopic decomposition of the interactions fails to be convincing.

5. The emerging physical picture

We set out to examine a range of questions relating to ferromagnetism in Fe especially around T_C. Our most immediate objective was the proper inclusion of sp electrons in the context of a reliable computation on a realistic band structure and the examination of its effects on the magnetic interactions. We have shown that our calculation is stable and accurate. The ferromagnetic ground state compares well with experimental data and with the features of other more sophisticated calculations.

Our results show that full considerations of the hybridisation between sp and d electrons is necessary to obtain quantitative agreement with experiment. The sp moment is small and just polarises locally with little effect on the properties of the system. However, the effects of the substantial broadening of the d bands are very important and lead to long-range, non-Heisenberg interactions. It is the hybridisation which makes the majority d band not quite full and reduces the moment from the d-band-only value of 2.6 μ_B to 2.2 μ_B. And it is still hybridisation which raises the value of the spin wave stiffness to good agreement with experiment.

We have examined a variety of spin configurations with a view to contributing to the continuing debate on short-range magnetic order in itinerant ferromagnets above T_C. The recent contradictory results for Ni of Mook and Lynn (1986) and Shirane *et al* (1987) have rekindled the controversy. We have found that $U_{SS}(\theta)$ has the shape required by the hypothesis of Heine and Joynt (1988). The indication of coarse-grained magnetic disorder modelled by spiralling arrangements of spins having nearest angle $\theta_{ij} \simeq 60°$ finds considerable validation. These spirals have lower energy than totally disordered environments and therefore imply a certain amount of short-range order. However, the surprising behaviour of the alternating tilts compels us to use some caution.

The behaviour of the moments offers a more consistent interpretation. For all configurations short of considerable antiferromagnetic ordering we have a substantial moment, even higher than that of the ferromagnetic ground state for the tilts. This agrees with what can be inferred from photoemission data above T_C and from magnetovolume measurements as well as other calculations. However, it is difficult to square

up our results with those of Brown *et al* (1983) for the integrated energy density from which a value of $1.3\mu_B$ above T_C was deduced. These experiments were also strongly challenged by Edwards (1983) on other grounds.

The above discussion naturally leads to an examination of the nature of the magnetic interactions and in particular of a pairwise Heisenberg decomposition of the energy densities. There are (at least) three separate issues to address: the existence of long-range interactions, the deviations from the Heisenberg ($\cos\theta$) form and possible multi-atom or collective effects.

There are certainly long-range interactions of oscillatory nature extending at least to the fifth shell of neighbours, as evidenced by our non-negligible estimate for J_5. However, the limited range of configurations we have examined makes it very hard to distinguish between deviations from the Heisenberg form and genuine multi-atom effects. The deviation of $U_{AT}(\theta)$ from the $\cos\theta$ form at low θ is quite definite though not very big. Either effect or both could be responsible. One should be able to distinguish between them from a careful study of randomly oriented clusters of spins. Calculations which focus on the couples between different sites in a random cluster are in progress and should supply the answer. These couples are expressed in terms of the transferred moments which, as we have seen, are a very sensitive probe of the interactions. The present set of data already shows non-Heisenberg behaviour in the transferred moments. Some indication of multi-atom effects comes from the remarkable stability of the moment for random configurations. This seems to imply that the interactions depend on a more averaged quantity than just the first shell of neighbours.

Notwithstanding all the above we have obtained generalised Heisenberg fits to all the data which give good estimates for the spin wave stiffness and T_C. This explains the past successes of the model in iron. At the same time though, the individual values of the effective interactions are rather badly determined reflecting the fact that a pairwise decomposition is inappropriate.

Acknowledgments

We acknowledge with pleasure many conversations with J H Samson and R Haydock and the help and computational expertise of C M M Nex. We thank R B Muniz for providing us with the set of tight-binding parameters for Fe that we have used. One of us (MUL) wishes to acknowledge the financial support of the Fondazione *Angelo Della Riccia*, Florence.

References

Brown P J, Capellmann H, Déportes J, Givard D and Ziebeck K R A 1983 *J. Magn. Magn. Mater.* **31** 295
Cooke J F, Lynn J W and Davis H L 1980 *Phys. Rev. B* **21** 4118
Cyrot M 1984 *J. Magn. Magn. Mater.* **45** 9
Edwards D M 1983 *J. Magn. Magn. Mater.* **36** 213
Fritsche L, Noffke J and Eckardt H 1987 *J. Phys. F: Metal Phys.* **17** 943
Hasegawa H 1980 *J. Phys. Soc. Japan* **49** 178
Haydock R 1980 *Solid State Phys.* **35** 215 (London: Academic)
Heine V and Joynt R 1988 *Europhys. Lett.* **5** 81
Herring C 1966 *Magnetism* ed. G T Rado and H Suhl (New York: Academic)
Holden A J and You M V 1982 *J. Phys. F: Metal Phys.* **12** 195

Hubbard J 1979 *Phys. Rev. B* **20** 4584
Inoue J and Ohta Y 1987 *J. Phys. C: Solid State Phys.* **20** 1947
Korenman V 1985 *J. Appl. Phys.* **57** 3000
Korenman V, Murray J L and Prange R E 1977 *Phys. Rev. B* **16** 4058
Kübler J 1980 *Phys. Lett.* **79A** 210
Lin-Chung P J and Holden A J 1981 *Phys. Rev. B* **23** 3414
Lynn J W 1975 *Phys. Rev.* **B11** 2624
Luchini M U and Nex C M M 1987 *J. Phys. C: Solid State Phys.* **20** 3125
Mook H A and Lynn J W 1985 *J. Appl. Phys.* **57** 3006
—— 1986 *Phys. Rev. Lett.* **57** 150
Mook H A, Lynn J W and Nicklow R M 1973 *Phys. Rev. Lett.* **30** 556
Muniz R B, Cooke J F and Edwards D M 1985 *J. Phys. F: Metal Phys.* **15** 2357
Nex C M M 1978 *J. Phys. A: Math. Gen.* **11** 653
—— 1984 *Comput. Phys. Comm.* **34** 101
—— 1989 *Comput. Phys. Comm.* **53** 141
Paxton A T, Sutton A P and Nex C M M 1987 *J. Phys. C: Solid State Phys.* **20** L266
Pindor A J, Staunton J, Stocks G M and Winter H 1983 *J. Phys. F: Metal Phys.* **13** 979
Prange R E and Korenman V 1979 *Phys. Rev. B* **19** 4691
Shirane G, Böni P and Martínez J L 1987 *Phys. Rev. B* **36** 881
Shull C G and Yamada Y 1962 *J. Phys. Soc. Japan* **17** 1
Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
Small L M and Heine V 1984 *J. Phys. F: Metal Phys.* **14** 3041
Staunton J, Gyorffy B L, Pindor A J, Stocks G M and Winter H 1985 *J. Phys. F: Metal Phys.* **15** 1387
Stollhoff G, Olés A M and Heine V 1989 *Phys. Rev. B* to appear
Stringfellow M W 1968 *J. Phys. C: Solid State Phys.* **1** 950
Wakoh S, Edwards D M and Wohlfarth E P 1971 *J. Physique Coll.* **32** C1 1073
Wang C S, Prange R E and Korenman V 1982 *Phys. Rev. B* **25** 5766
Wood J H 1962 *Phys. Rev.* **126** 517
You M V and Heine V 1982 *J. Phys. F: Metal Phys.* **12** 177