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Band structures of non-collinear magnets in γ -Mn and γ -Fe

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Abstract. Local spin density functional theory is applied within the linearized muffin-tin orbital atomic sphere approximation (LMTO ASA) method to calculate the electronic structures of non-collinear antiferromagnets in FCC manganese and iron. Direct application of the theory leads to a Hamiltonian which is doubly degenerate for every band at every k -point. An irreducible representation is found which overcomes this problem. The total energies of single, double and triple spin density wave structures are found to be essentially indistinguishable within the limits of the calculation.

1. Introduction

The magnetic properties of iron and manganese in the FCC structure (i.e. γ -Fe and γ -Mn) have received considerable attention since it was found that γ -Fe could be stabilized by precipitation in a copper matrix (Abrahams *et al* 1962) and γ -Mn by alloying with small amounts of other transition metals (Bacon *et al* 1957, Endoh and Ishikawa 1971, Honda *et al* 1976). Experimentally, they are found to be type I antiferromagnets but the detail of their magnetic structure has proved difficult to determine and has been a subject of some debate (Tsunoda *et al* 1987, Jo and Hirai 1986, Long *et al* 1987). The key feature of all these systems is that the FCC lattice is frustrated, i.e. it is impossible to arrange for every atomic spin to have nearest neighbours of the opposite spin only. As a consequence, it is believed that in some of these phases the magnetism may be *non-collinear*, so there is no unique quantization axis for the spins.

The Heisenberg model in its classical limit can be used to show how non-collinear structures may arise as ground states in frustrated topologies. Applied to the FCC lattice one obtains a family of degenerate solutions (Kouvel and Kasper 1962, Long 1989) which may include up to three independent spin density waves of equal amplitude. Adopting the notation of Long and Yeung (1986) we shall consider three particular cases of the multiple spin density wave or MSDW (figure 1), where the FCC structure is treated as a simple cubic lattice with a four point basis. It can be seen that the single spin density wave (SSDW) is just the collinear antiferromagnet and is characterized by a single wavevector Q in direction [001]. The double spin density wave (DSDW) has Q s in the [100] and [010] directions, while the triple spin density wave (TSDW) has Q s along all three crystal axes. In figure 1 it is assumed that the spin vector $S(Q)$ associated with each Q is parallel to Q , as observed in experiment (Long *et al* 1987).

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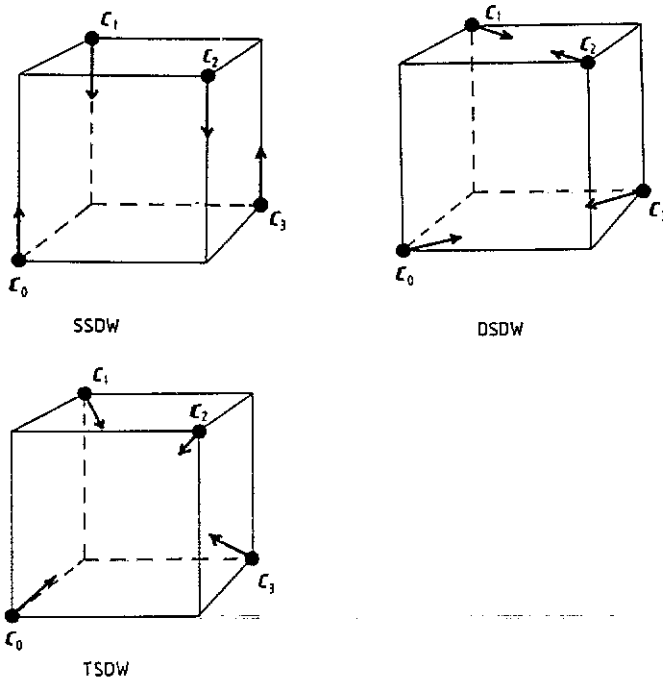


Figure 1. Spin arrangements in an octant of the FCC lattice for the (a) SSDW, (b) DSDW and (c) TSDW antiferromagnets.

However, in the absence of spin-orbit coupling there is no interaction which ties the spin direction to the lattice and so any relation between \mathbf{S} and \mathbf{Q} would be equivalent.

Much work has been done on the electronic structure of the collinear SSDW in γ -Fe and γ -Mn (Cade 1980 and 1981a, Wang *et al* 1985, Pinski *et al* 1986, Moruzzi *et al* 1989). Here we present LMTO ASA (Andersen 1975) band structure calculations on the MSDW structures of figure 1. The aim is to investigate the degree to which the classical degeneracy between different MSDW states is lifted in an itinerant electron calculation. This could have interesting implications for understanding the magnetism of γ -Fe and γ -Mn, in particular the alternating SSDW and DSDW domains which have been proposed by Tsunoda *et al* (1987) for the structure of γ -Fe.

The basic theory for the treatment of non-collinear systems in the local density approximation was developed by von Barth and Hedin (1972). This was first systematically applied by Kübler *et al* (1988) (see also Sticht *et al* 1989) who used the linearized augmented spherical wave atomic sphere approximation (LASW ASA) (Williams *et al* 1979) to perform self-consistent calculations on a number of non-collinear systems, including γ -Mn₂Fe₂. The theory may be similarly applied to linearized muffin-tin orbital atomic sphere approximation (LMTO ASA) calculations. For antiferromagnets it is also desirable to take into account the spin/sublattice symmetry associated with the magnetism. For the collinear SSDW this symmetry is clear: translate the up sublattice (say) onto the down sublattice, reverse all spin directions, and the system is invariant. The symmetry means that the Hamiltonian is reducible, and if not reduced all bands are doubly degenerate at every k -point. At the very least this can lead to a waste of computer time, as the time required to diagonalize a matrix varies as the cube of the dimension, so an unnecessary factor of two leads to an eight-fold increase in time. At

worse, the degeneracies may be artificially split due to computational rounding errors, leading to incorrect ground states. The way around this problem for a simple anti-ferromagnet is well known: include only up spin electrons (say) in the band structure part of the calculation and use the symmetry of the structure to put the down spin electron densities into the atomic part. For a non-collinear antiferromagnet, however, the solution is not so clear. The general form of the antiferromagnetic symmetry for a MSDW has already been given (Long and Yeung, 1986) and it is to the problem of the reduction of the MSDW Hamiltonian that we address ourselves in this article.

In the next section the theory of LMTO ASA for the non-collinear spin configurations of γ -Mn and γ -Fe will be developed and the degeneracy of the bands will be demonstrated. The representation obtained is initially in terms of 72×72 matrices, but it will be shown that this can be replaced by an equivalent representation involving 36×36 matrices only. In section 3 the implementation of the scheme in a standard LMTO ASA program will be described and in section 4 we present and discuss the results of self-consistent band structure calculations for the SSDW, DSDW and TSDW phases. The article is concluded in section 5. Our calculations assume that in each of the MSDW phases the crystal retains its cubic lattice parameters. We therefore ignore the small tetragonal distortion which accompanies the symmetry-breaking SSDW and DSDW structures. The theory of section 2 can be extended to the calculation of the axial pressure (Cade 1981b) in these phases, which enables us to discuss the origin of the tetragonal distortion. This will be the subject of a forthcoming article (Crockford *et al* 1991).

2. The Hamiltonian for MSDW systems

Implicit in the spin density functional formalism is the choice of a set of common axes to which all spins in the problem are referred. For a ferromagnet or a collinear antiferromagnet (SSDW) all spins are either parallel or antiparallel to a single axis. The operators used to build the Hamiltonian can be chosen to be diagonal in spin space and the theory yields a pair of single particle equations, one for each spin direction. For non-collinear systems the problem is more complicated as there is no unique choice for the spin axes. To solve the problem exactly it would be necessary to have local spin axes for each volume element considered. The adoption of the ASA allows the local spin axes to be defined at the scale of the atomic spheres and renders the problem tractable.

It is characteristic of LMTO ASA that there is a separation of the potential and crystal structure dependence of the band structure problem through the potential parameters and structure constants respectively (Andersen *et al* 1985). As the structure constants embody the spatial relationships in the crystal it is convenient to define them to be independent of spin: the spin dependence then resides solely in the potential parameters. We define the potential parameters in terms of direct products of the paramagnetic (l , m and atomic species dependent) potential parameters and Pauli matrices. To represent non-collinear structures we shall require the full set of Pauli matrices, in contrast to the collinear case, where only the diagonal matrices are needed. As a result, the Hamiltonian for non-collinear systems will be non-diagonal in spin space and cannot be simply separated to yield an independent equation for each spin.

We shall represent the FCC structure of undistorted γ -Mn or Fe as a simple cubic lattice with a four point basis labelled as in figure 1. This is a convenient choice for

the MSDW, which can be regarded as four simple cubic sublattices, each composed of atoms with parallel spin directions. The SSDW can be described as a crystal with two atoms per unit cell, but in order to make comparisons between the states easier we use the same cell for all three structures. In the elemental metals all atomic species are identical and occupy equivalent positions in the crystal, and hence the potential parameters P relative to any *local* spin axis must be the same, independent of sublattice. Defining P' with respect to a set of common axes, which we choose to be the crystal axes, the sublattice components of P' and P can differ only by a unitary transformation in spin space. For a given atom this will correspond to the rotation necessary to make the local axes coincide with the crystal axes, and this is a function of sublattice only. We can therefore determine P' by calculating P and making use of the symmetry of the spin directions in sublattice space. When this is done (appendix A) we obtain

$$P' = n\beta_0 + m\hat{d} \cdot \beta \quad (1)$$

where \hat{d} is the spin direction on sublattice 0, $\beta = (\beta_1, \beta_2, \beta_3)$ and the β_i are 8×8 matrices in spin/sublattice space, as defined by (A3). Note that we ignore the lm indices of the potential parameters here, as they are not relevant to the spin/sublattice representation. As indicated in appendix A the expectations of β_1 , β_2 and β_3 are the respective spin wave amplitudes in the global x , y and z directions. The form of P' is comparable to that of the 'potential matrix' w^{eff} of the LASW method (Kübler *et al* 1988).

The LMTO structure constants, which are independent of spin, can be represented in the 8×8 spin/sublattice space by the direct product of sublattice dependent matrices and σ_0 (the identity). Together with the potential parameters these quantities determine the LMTO Hamiltonian \hat{H} . The treatment so far is parallel to that of Kübler *et al* (1988) for the LASW method. What we now do is to demonstrate that this Hamiltonian gives degenerate bands, regardless of k , and that it can be replaced by an equivalent Hamiltonian involving only 4×4 matrices. To do this it is first necessary to define new structure constants S' with a sublattice dependence given by (appendix B)

$$(S')_{pp'}^k = \sum_j (\alpha_j)_{pp'} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{c}_j)} S_{0, \mathbf{R} + \mathbf{c}_j}. \quad (2)$$

Here α_j is one of the set of four 4×4 matrices defined in (B4), $j \in \{0, 1, 2, 3\}$, and p and p' are sublattice indices. The vectors \mathbf{c}_j are sublattice vectors for the FCC structure, as given in (B2). It is clear from (2) that the sublattice (pp') dependence of S' is embodied entirely in the set of α matrices. This definition differs from the standard definition for structure constants (Andersen *et al* 1985) only in the absence of a sublattice dependent phase factor, and can be shown to yield identical physical results (appendix B).

It can be shown that the LMTO ASA Hamiltonian \hat{H} can be expressed as a power series in quantities involving only the structure constants and potential parameters (Andersen *et al* 1985). It follows from (1) and (2) that the Hamiltonian for a MSDW structure can be written as a power series in the matrices β_i and $\alpha_j \sigma_0$. The algebra of these matrices is presented in appendix C but the significant features are that the sets $\{\beta_i\}$ and $\{\alpha_j \sigma_0\}$ are respectively closed under matrix multiplication, and

that there exist simple commutation relationships between members of the two sets. Hence the spin/sublattice dependence of the Hamiltonian can always be expressed as a linear combination of products of the form $\alpha_j \sigma_0 \cdot \beta_i$ (appendix C). It is then easy to show that the three matrices $\alpha_j \sigma_j$, $j \in \{1, 2, 3\}$ commute with the Hamiltonian but not with each other, and it follows by a standard theorem (Schiff 1968) that the eigenvalues must be degenerate. It is interesting to note that the matrices $\alpha_j \sigma_j$ are just the transformation matrices which describe the symmetries of the MSDW antiferromagnets (Long and Yeung 1986). It can be seen in figure 1 that the system is invariant if the lattice is translated by sublattice vector \mathbf{c}_j (equivalent to operating on the Hamiltonian with α_j) and the spins are rotated by π about the axis perpendicular to the plane of \mathbf{c}_j (equivalent to σ_j).

The fact that the Hamiltonian as it stands gives degenerate eigenvalues regardless of k -point indicates that the representation in terms of 8×8 matrices in spin/sublattice space is reducible. There are two approaches to finding an equivalent representation in terms of smaller matrices: either find a transformation that converts the Hamiltonian into a block diagonal form with equivalent blocks, or search for sets of smaller matrices with the same algebra as $\alpha_j \sigma_0$ and β_i . The former approach, along with the general problem of the reduction of a system with AF symmetry, will be the subject of a future article (Bird *et al* 1991). In appendix C we present two sets of 4×4 matrices which correspond to the $\alpha_j \sigma_0$ and β_i sets, and have the same algebra. The first of these sets consists simply of the matrices α_j , without the direct product with σ_0 , and the matrices of the second set we have labelled β'_i (see (C3)). The fact that the algebra of these matrices is the same as that of the 8×8 sets means that they form an equally valid representation for the MSDW Hamiltonian and can be substituted directly for their 8×8 counterparts in (1) and (2).

3. Implementation

A standard LMTO ASA program was adapted to use the spin/sublattice representation described previously. This involved the multiplication of the standard structure constants by the phase factor necessary to obtain (2), and the inclusion of code to calculate the P' defined by (1), with β'_i substituted for β_i , given the standard potential parameters as input. After the diagonalization of \hat{H} the 'angular momentum weights' (Skriver 1984) were calculated as

$$A_{ii}(\mathbf{k}) = \sum_m \mathbf{u}_{im}^\dagger(\mathbf{k}) \beta'_i \mathbf{u}_{im}(\mathbf{k}). \quad (3)$$

Here the index $i \in \{0, 1, 2, 3\}$ and the corresponding weights, when integrated over the Brillouin zone, give, respectively, the total charge and the (x , y , z) spin wave amplitudes for the unit cell. This follows from the properties of the original 8×8 matrices (appendix A) and the fact that the 4×4 matrices have the same algebra. From these the up and down spin densities in the spheres are easily calculated. It should be emphasized that $\mathbf{u}_{im}(\mathbf{k})$ is a vector in spin/sublattice space, so each term in (3) is a contraction of two vectors with matrix β'_i . It should also be noted that the spin wave amplitudes produced this way must be appropriate to the MSDW being considered. For example, in a DSDW the integral of (3) must yield equal values for $i = 1$ and $i = 2$, and zero for $i = 3$. This gives a good test of the correctness of an

implementation. In addition, the point group symmetries of the three MSDWs are not the same: the SSDW and DSDW are tetragonal whereas the TSDW is cubic. In practice all calculations were done using the irreducible wedge for a primitive orthorhombic lattice. This is the smallest zone which, for all three MSDWs, gives correct integrals of (3) without the need for careful consideration of the spin/space symmetries (Long and Yeung 1987).

The atomic charge part of the LMTO code was not changed from the original. In the atomic part of the self-consistency cycle the representation is the local (diagonal) one for the atomic sphere: the non-collinearity of the structure is dealt with entirely in the band structure part of the program.

4. Results and discussion

Self-consistent calculations were performed on γ -Mn with $S_{ws} = 2.73$ au and on γ -Fe with $S_{ws} = 2.555$ au. The Mn radius was chosen for consistency with the magnetic moment obtained by Cade (1980); the Fe radius was that which gave zero pressure in the paramagnetic material. The pressure of paramagnetic Mn at 2.73 au is strongly negative (-0.3 Mbar) and at a radius that yields zero pressure the system does not go magnetic, so the manganese calculations could not be done at equilibrium volume. The Brillouin zone integrations were performed using the tetrahedron method (Jepsen and Andersen 1971) in an irreducible wedge of the primitive orthorhombic zone, with 64 k -points in the wedge. The convergence of the MSDW states was particularly slow, the results presented being the product of at least three hundred band structure iterations for each case. Numerical results are converged to the last digit.

The values obtained for the magnetization and total energy of the three MSDW systems in Mn and Fe are given in tables 1 and 2. Experimentally the moment obtained for the SSDW structure in Mn has been determined to be in the region $2 \mu_B$ (Smith and Vance 1969) to $2.4 \mu_B$ (Bacon *et al* 1957). The moment of what was believed to be the the SSDW in Fe was given as $0.72 \mu_B$ (Abrahams *et al* 1962). Our results for the SSDWs are in reasonable agreement with those of Moruzzi *et al* (1989), who show that the calculated moment is a very sensitive function of the lattice parameter. The most significant feature of our results is that the total energy differences between the different phases are very small, and are essentially zero within the accuracy of the calculations. This is consistent with the results of the classical Heisenberg model, where the phases are all degenerate, and suggests that non-collinear magnetism will naturally arise in these systems.

Table 1. Magnetization and total energy for Mn systems.

	SSDW	DSDW	TSDW
Magnetization/atom/ μ_B	1.903	1.866	1.827
Total energy/Ryd	-126.126	-126.126	-126.125

The band structures for Mn in the paramagnetic and MSDW phases are given in figure 2, and those for Fe in figure 3. The Brillouin zone used is the small cubic one corresponding to a cubic lattice with a four point basis (figure 1). This zone is the most appropriate for the TSDW: the other structures have larger zones and the bands

Table 2. Magnetization and total energy for Fe systems.

	SSDW	DSDW	TSDW
Magnetization/atom/ μ_B	0.711	0.748	0.732
Total energy/Ryd	-178.236	-178.238	-178.237

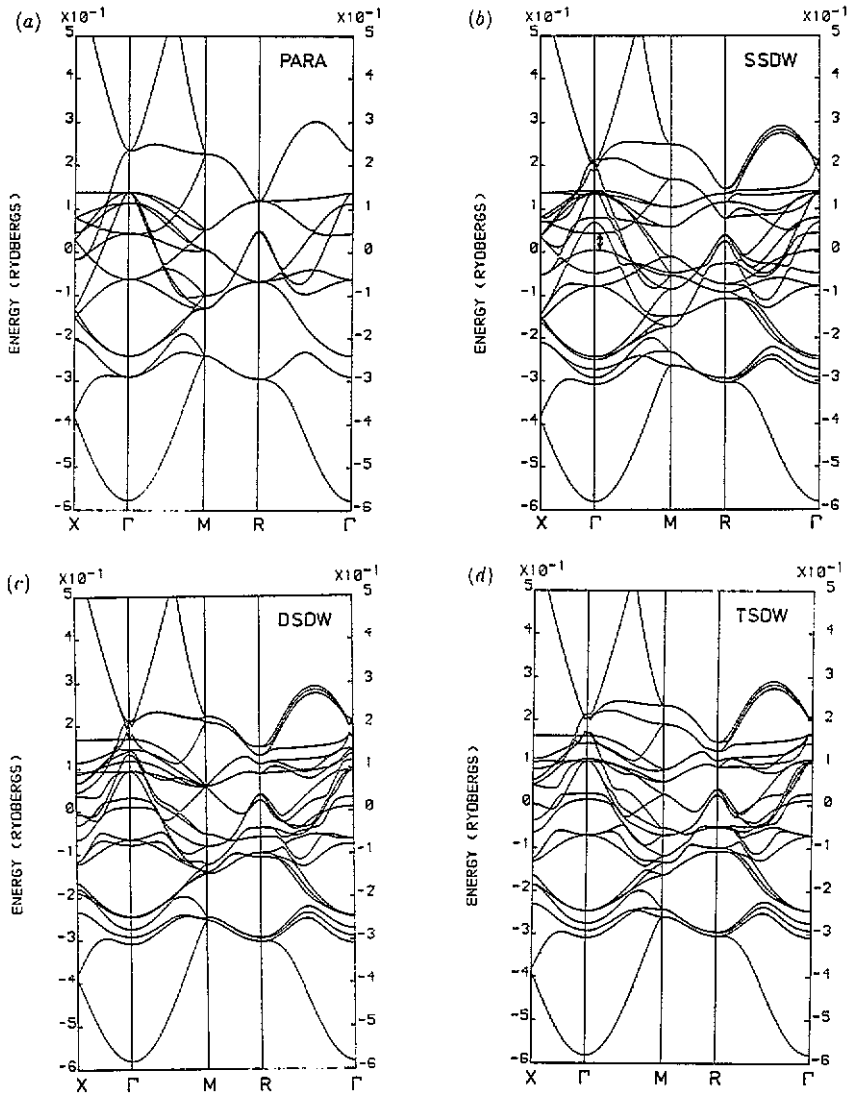


Figure 2. Band structures for FCC Mn: (a) paramagnetic; (b) SSDW; (c) DSDW; and (d) TSDW.

fold back onto this zone. The symmetry labels used are those of Bradley and Cracknell (1972) and the path is that used by Kübler *et al* (1988) in their work on γ - Mn_2Fe_2 . Plots were also made of the band structures of the SSDW and TSDW in Mn for the zones and paths used by Cade (1980, 1981a), and were found to be in good agreement. In all band structures the Fermi level is shifted to zero.

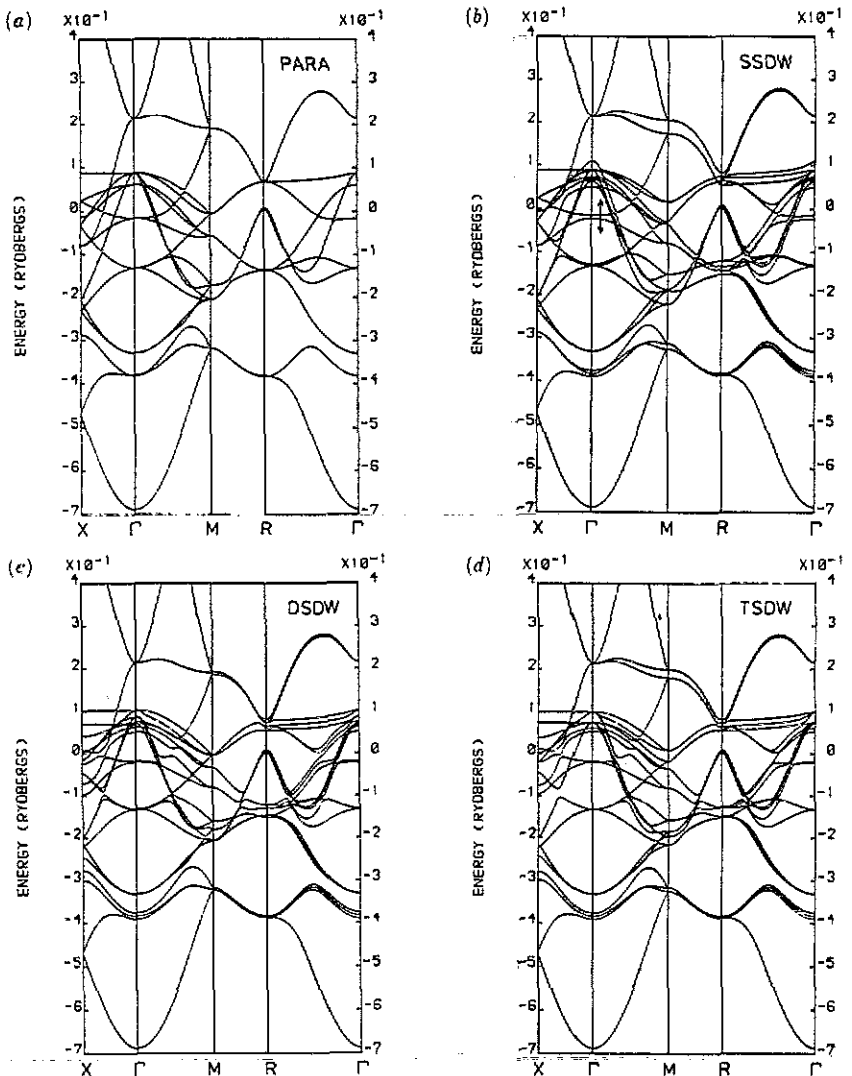


Figure 3. As in figure 2, but for FCC Fe.

It is apparent that the paramagnetic band structures of Mn and Fe are very similar, the Fermi level in Fe being about 0.1 Ryd higher than in Mn, taken relative to the common features. This is only to be expected, given that Fe has one more electron than Mn. The MSDW band structures for a given material are also very similar. Comparing the magnetic structures with the paramagnetic ones it can be seen that the chief effect of the magnetism is to split bands that were degenerate in the paramagnetic case. For example, at the Γ -point of the SSDW in Mn the parabolic bands between -0.2 and -0.3 Ryd have been split, a band has been forced up from the concave/convex pair that meet just above -0.1 Ryd, and the pair above that have been split apart altogether. In addition, looking around -0.3 and 0.2 Ryd, between R and Γ , it is clear that bands that were at least triply degenerate in the paramagnetic material are running almost parallel. It is the magnitude of the splitting that really distinguishes Mn from Fe. For the SSDW, for example, this can be estimated from the band marked \dagger in the figures,

which is split by 0.04 Ryd in Mn and 0.006 Ryd in Fe, and it seems that the splitting in Mn is generally an order of magnitude greater than in the corresponding Fe phase.

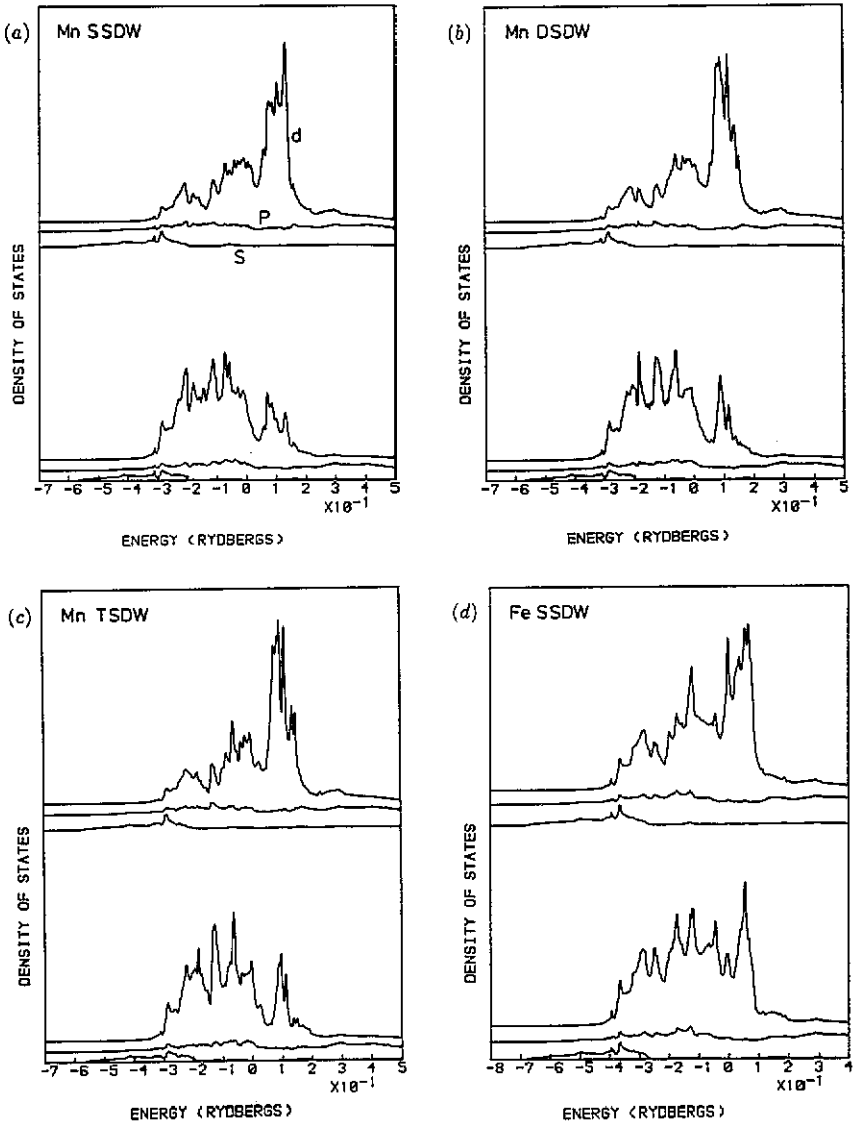


Figure 4. Majority (lower plots) and minority (upper plots) densities of states for s, p and d projections in FCC Mn: (a) SSDW; (b) DSDW; (c) TSDW and FCC Fe; (d) SSDW.

The densities of states for the MSDWs in Mn, projected onto angular momentum and spin, are given in figure 4. Again, the Fermi level is set to zero. It is evident that the s and p densities of states are very small and do not distinguish between MSDW structures. However, even in the d densities of states, where one might expect the magnetic effects to be strongest, the different MSDWs can be distinguished only by the relative magnitudes of the small spikes within an overall peak area. The plots for the MSDWs in Fe show similar features and that for the SSDW is given in figure 4(d).

Energy integrals of the d-magnetization density (majority density of states minus minority) show that the magnetism is built up evenly throughout the band. The position of the Fermi level is slightly more favourable to the moment in Mn than in Fe: in Fe it occurs just after the peak in magnetization.

More interesting than the behaviour of the total d density of states is that of its projections onto azimuthal angular momentum m . The magnetizations carried by the various orbitals, in cubic harmonic form, are given in tables 3 and 4, and the magnetization densities in figures 5 and 6. The yz and zx orbitals are equivalent in all the structures owing to the symmetry under reflection in $x = y$. It can be seen from the tables that the two projections that carry most of the moment are $3z^2 - r^2$ and $x^2 - y^2$. In addition, these projections exchange first and second position on going from the SSDW to the DSDW. A similar exchange occurs with the xy and the yz/zx projections. In the TSDWs the projections within the e_g ($3z^2 - r^2$ and $x^2 - y^2$) and t_{2g} (xy , yz , zx) groups respectively carry the same magnetic moment. Similar behaviour is shown in the graphs of the magnetization density: the $3z^2 - r^2$ and $x^2 - y^2$ graphs do to some extent swap over on going from the SSDW to the DSDW, and similarly the xy and yz/zx graphs. It should be noted that for the DSDW there is a general loss of distinction between graphs within a symmetry group (e_g or t_{2g}). This is an intermediate step on the way to the TSDW, where the graphs within a group are identical.

Table 3. m -projected magnetization for Mn systems (in μ_B).

Orbital	SSDW	DSDW	TSDW
$3z^2 - r^2$	0.419	0.456	0.433
$x^2 - y^2$	0.499	0.430	0.433
xy	0.217	0.348	0.300
$yz = zx$	0.354	0.286	0.300
Total d	1.842	1.804	1.768

Table 4. m -projected magnetization for Fe systems (in μ_B).

Orbital	SSDW	DSDW	TSDW
$3z^2 - r^2$	0.136	0.217	0.190
$x^2 - y^2$	0.229	0.168	0.190
xy	0.049	0.141	0.109
$yz = zx$	0.136	0.098	0.109
Total d	0.686	0.721	0.706

The behaviour of the e_g orbitals can be understood by consideration of their hopping in and out of the xy plane. The $x^2 - y^2$ orbitals have a large overlap in the xy plane, while the $3z^2 - r^2$ orbitals 'point' out of the plane. For the SSDW this implies that hopping between $x^2 - y^2$ orbitals is to some extent blocked by Pauli exclusion. The $x^2 - y^2$ orbital is therefore more localized than the others and it carries a larger moment. For the DSDW, however, $x^2 - y^2$ hopping in the xy plane is between opposite spins and the orbital can delocalize. In this case the out of plane hopping of the $3z^2 - r^2$ orbital is less favourable than for the SSDW, and so the roles of the $x^2 - y^2$

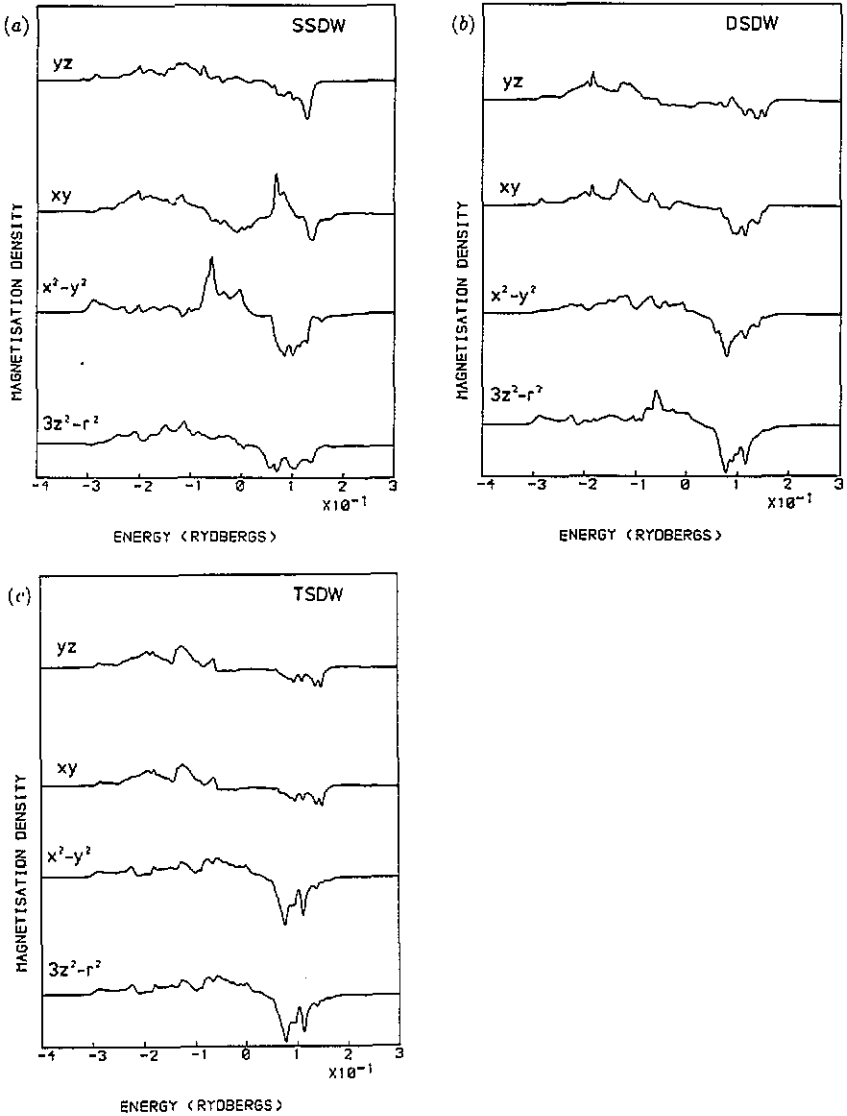


Figure 5. *d* magnetization densities projected onto $3z^2 - r^2$, $x^2 - y^2$, xy and $yz = zx$ orbitals for FCC Mn: (a) SSDW; (b) DSDW; and (c) TSDW.

and $3z^2 - r^2$ orbitals are swapped. We would not want to push this localized orbital picture too far, however, in the interpretation of the results of an itinerant electron calculation.

5. Conclusion

Two main points come out of this work. The first is a technical issue, concerned with the reducibility of the most direct representation of the Hamiltonian of the MSDW structures. We have shown how an irreducible representation can be constructed and in another article we discuss how this can be done for any antiferromagnetic structure

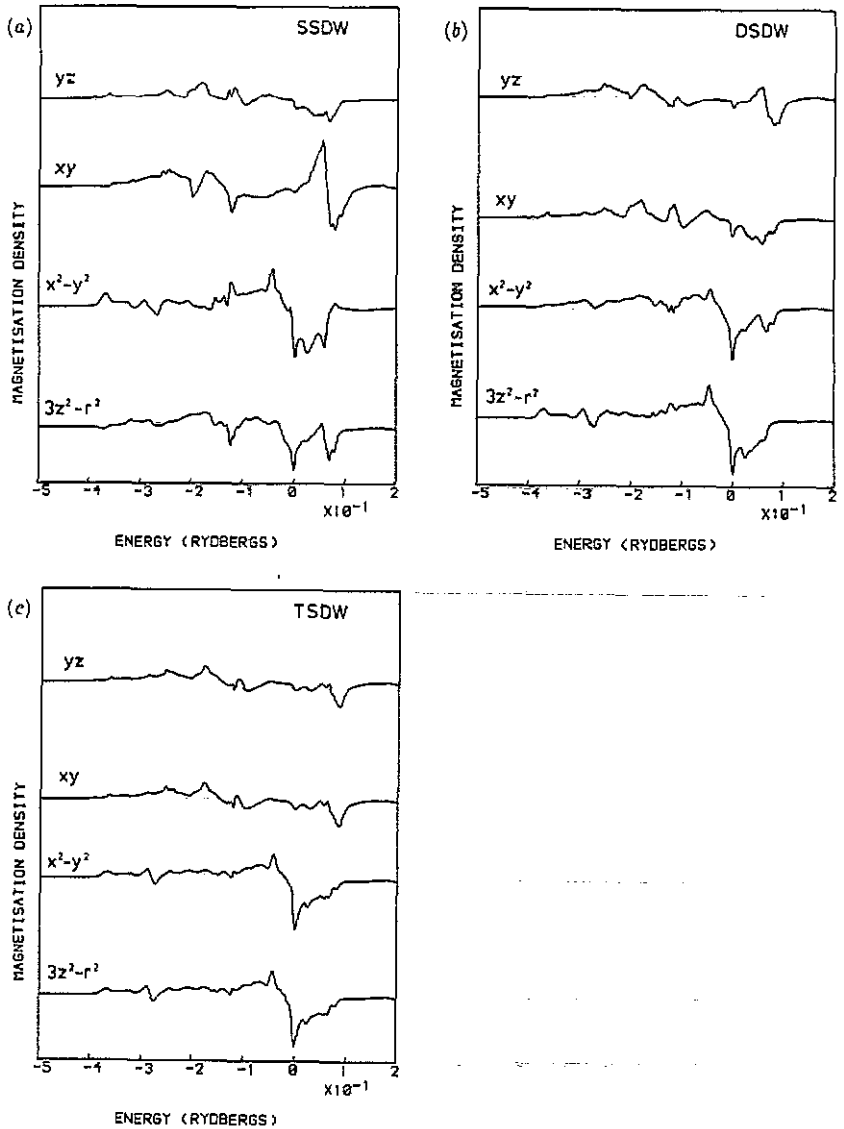


Figure 6. As in figure 5, but for PCC Fe.

(Bird *et al* 1991). The second is that our calculations show only small differences in the band structures, density of states, magnetizations and total energies between the different MSDW phases. This implies that itinerant electron effects do not significantly lift the degeneracy found between these phases in the classical Heisenberg model.

Acknowledgments

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Appendix A

To obtain the specific form of the potential parameters consider an atom on arbitrary sublattice 0 with total spin in the direction of the Cartesian unit vector \hat{d} . Defining the local spin axis to be in direction \hat{d} the potential parameter P takes the form,

$$P = \begin{pmatrix} P\uparrow & 0 \\ 0 & P\downarrow \end{pmatrix}. \quad (\text{A1})$$

Here $P\uparrow$ and $P\downarrow$ are the values yielded for P by the spin-up and spin-down charge densities respectively in the atomic sphere. Given that \hat{d} is expressed with respect to the set of crystal axes we need to know what P becomes when referred to these axes. We shall call this object P' . As P is a 2×2 matrix in spin space we know that P must transform as a second order tensor in the $j = \frac{1}{2}$ representation of \mathcal{R}^3 . Hence if the local axis is given in spherical polars by $(1, \theta, \phi)$ then \hat{d} is given by $(\cos \theta, \sin \theta \cos \phi, \sin \theta \sin \phi)$ and P' must be given by (Edmonds 1960),

$$P' = n\sigma_0 + m\hat{d} \cdot \sigma \quad (\text{A2})$$

where $n = \frac{1}{2}(P\uparrow + P\downarrow)$, $m = \frac{1}{2}(P\uparrow - P\downarrow)$, σ_0 is the 2×2 identity matrix, $\sigma = (\sigma_x, \sigma_y, \sigma_z)$, and the σ_i s are Pauli matrices. The coefficients n and m are clearly related to the charge and magnetic moment respectively. The form of (A2) is identical to that of the 'potential matrix' of Kübler *et al* (1988).

Equation (A2) gives P' for an atom on the arbitrary sublattice 0. To find P' for any other sublattice it is necessary to substitute the appropriate \hat{d} in (A2). In a MSDW state the vector \hat{d} is constrained by certain symmetries. Labelling the four basis points according to figure 1 it is not difficult to see that in the SSDW P' is the diagonal matrix

$$P' = \begin{pmatrix} n + m\sigma_3 & & & \\ & n - m\sigma_3 & & \\ & & n - m\sigma_3 & \\ & & & n + m\sigma_3 \end{pmatrix}.$$

Similarly, in the DSDW and TSDW respectively P' is given by the matrices

$$P' = \begin{pmatrix} n + \frac{m}{\sqrt{2}}(\sigma_1 + \sigma_2) & & & \\ & n + \frac{m}{\sqrt{2}}(\sigma_1 - \sigma_2) & & \\ & & n + \frac{m}{\sqrt{2}}(-\sigma_1 + \sigma_2) & \\ & & & n + \frac{m}{\sqrt{2}}(-\sigma_1 - \sigma_2) \end{pmatrix}$$

and

$$P' = \begin{pmatrix} n + \frac{m}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3) & & & \\ & n + \frac{m}{\sqrt{3}}(\sigma_1 - \sigma_2 - \sigma_3) & & \\ & & n + \frac{m}{\sqrt{3}}(-\sigma_1 + \sigma_2 - \sigma_3) & \\ & & & n + \frac{m}{\sqrt{3}}(-\sigma_1 - \sigma_2 + \sigma_3) \end{pmatrix}.$$

Hence P' can always be written in terms of the matrices:

$$\begin{aligned} \beta_0 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \sigma_0 & \beta_1 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \sigma_1 \\ \beta_2 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \sigma_2 & \beta_3 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \sigma_3. \end{aligned} \quad (\text{A3})$$

Defining γ_i , $i = 0, 1, 2, 3$ to be the previous 4×4 matrices this result can be written more concisely as

$$\beta_i = \gamma_i \sigma_i \quad i = 0, 1, 2, 3 \quad (\text{A4})$$

where the juxtaposition represents a direct product. The P' for a general MSDW can therefore be written as

$$P' = n\beta_0 + m\hat{d} \cdot \beta \quad (\text{A5})$$

where $\beta = (\beta_1, \beta_2, \beta_3)$ and \hat{d} is the spin direction for sublattice 0.

The β matrices given by (A3) represent the operators for the charge and spin wave amplitudes per unit cell, as can be seen by looking at their effects on the spinor wavefunction Ψ for the unit cell (expressed with respect to the global axes)

$$\Psi = (\psi_0 \uparrow \quad \psi_0 \downarrow \quad \psi_1 \uparrow \quad \psi_1 \downarrow \quad \psi_2 \uparrow \quad \psi_2 \downarrow \quad \psi_3 \uparrow \quad \psi_3 \downarrow).$$

For example

$$\langle \Psi | \beta_0 | \Psi \rangle = \sum_{i=0}^3 |\psi_i \uparrow|^2 + |\psi_i \downarrow|^2 \equiv Q$$

where Q is the charge in the cell and

$$\begin{aligned} \langle \Psi | \beta_3 | \Psi \rangle &= |\psi_0 \uparrow|^2 - |\psi_0 \downarrow|^2 - (|\psi_1 \uparrow|^2 - |\psi_1 \downarrow|^2 + |\psi_2 \uparrow|^2 - |\psi_2 \downarrow|^2) \\ &\quad + |\psi_3 \uparrow|^2 - |\psi_3 \downarrow|^2 \\ &\equiv M_z \end{aligned}$$

where M_z is the amplitude of the spin wave in the global z direction. It can be seen that the elements of the β matrices give the relative phase of the spin polarization as a function of sublattice. The expectations of β_1 , β_2 and β_3 respectively are the spin wave amplitudes in the x , y and z directions. To obtain the spin polarization in a sphere (i.e. the value of the spin with respect to \hat{d} , the local spin axis) we simply calculate the magnitude of the vector $\frac{1}{4}(\langle \beta_1 \rangle, \langle \beta_2 \rangle, \langle \beta_3 \rangle)$.

Appendix B

In order to perform self-consistent calculations on the MSDW systems described we need to reduce the 8×8 representation to an equivalent 4×4 . It is therefore necessary to know the algebra satisfied by the structure constants in spin/sublattice space. In this section we shall derive a set of structure constants which is equivalent physically to the conventional constants but for which the algebra takes a more simple form.

We take as our starting point the standard definition of the structure constants (Andersen *et al* 1985)

$$S_{r_0,r}^k = \sum_{R'} e^{ik \cdot R'} S_{r_0,r+R'} = e^{ik \cdot (r_0-r)} \sum_{R'} e^{ik \cdot (R'+r-r_0)} S_{0,R'+r-r_0}. \tag{B1}$$

In the second line we simply removed a phase factor and used the identity,

$$S_{r_0,r+R'} = S_{0,R'+r-r_0}$$

(Andersen 1975).

The FCC structure in manganese or iron can be regarded as a simple cubic lattice with a four point basis $\{c_p, p = 0, 1, 2, 3\}$. Defining the basis vectors according to figure 1 we have,

$$\begin{aligned} c_0 &= (0, 0, 0) \\ c_1 &= \frac{a}{2}(0, 1, 1) \\ c_2 &= \frac{a}{2}(1, 0, 1) \\ c_3 &= \frac{a}{2}(1, 1, 0) \end{aligned} \tag{B2}$$

where a is the lattice constant of the cubic lattice. It is these c vectors that replace the arbitrary r, r_0 of (B1). To determine the form of the structure constants we have to know $c_p - c_{p'}$, for all possible p, p' . As the set of FCC lattice vectors is closed under addition we have,

$$c_{p'} - c_p = R_{pp'} + \sum_{\zeta=0}^3 (\alpha_{\zeta})_{pp'} c_{\zeta}. \tag{B3}$$

where α_{ζ} has only a single non-zero element, unity, in any row or column. The simple cubic vector $R_{pp'}$ takes account of the fact that on taking the difference we may end up in a different (cubic) unit cell to the one we start in, but the form of $R_{pp'}$ is not relevant here. The α matrices are now easily determined owing to the small number of non-trivial combinations (six) of the cs .

$$\begin{aligned} \alpha_0 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \alpha_1 &= \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \\ \alpha_2 &= \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} & \alpha_3 &= \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \end{aligned} \tag{B4}$$

Equations (B1) and (B3) give

$$\begin{aligned}
 S_{pp'}^k &= e^{ik \cdot (c_p - c_{p'})} \sum_{R'} e^{ik \cdot (R' + c_{p'} - c_p)} S_{0, R' + c_{p'} - c_p} \\
 &= e^{ik \cdot (c_p - c_{p'})} \sum_R e^{ik \cdot [R + \sum_\eta (\alpha_\eta)_{pp'} c_\eta]} S_{[0, R + \sum_\zeta (\alpha_\zeta)_{pp'} c_\zeta]} \\
 &= e^{ik \cdot (c_p - c_{p'})} \left[\prod_{\eta=0}^3 e^{ik \cdot (\alpha_\eta)_{pp'} c_\eta} \right] \sum_R e^{ik \cdot R} S_{[0, R + \sum_\zeta (\alpha_\zeta)_{pp'} c_\zeta]} \quad (B5)
 \end{aligned}$$

where we have put $R = R' + R_{pp'}$, and η is a dummy index. It is clear from (B4) that for any p, p' there is only one value of ζ for which $(\alpha_\zeta)_{pp'}$ is non-zero, and thus only one value of $e^{ik \cdot (\alpha_\zeta)_{pp'} c_\zeta}$ which is not equal to one. Hence

$$S_{pp'}^k = e^{ik \cdot (c_p - c_{p'})} \sum_\zeta (\alpha_\zeta)_{pp'} \sum_R e^{ik \cdot (R + c_\zeta)} S_{0, R + c_\zeta} \quad (B6)$$

Equation (B6) shows that, up to a phase factor, the sublattice dependence of the structure constants can be written down entirely in terms of the α matrices. In fact, we can simply drop this phase factor altogether and define our structure constants by

$$(S')_{pp'}^k = \sum_j (\alpha_j)_{pp'} \sum_R e^{ik \cdot (R + c_j)} S_{0, R + c_j} \quad (B7)$$

which is the same as (2). To see why consider what has to be done to get from (B6) to (B7). It is not difficult to show that

$$S = DS' D^{-1} \quad (B8)$$

where D is given by,

$$D = \begin{pmatrix} e^{ik \cdot c_0} & 0 & 0 & 0 \\ 0 & e^{ik \cdot c_1} & 0 & 0 \\ 0 & 0 & e^{ik \cdot c_2} & 0 \\ 0 & 0 & 0 & e^{ik \cdot c_3} \end{pmatrix} \quad (B9)$$

In the standard LMTO ASA code the full LMTO problem is not solved but rather the second order problem (Andersen *et al* 1985), with third order effects included afterwards as a perturbation. The second order problem can be written

$$[C + \Delta^{1/2} S (1 - \alpha S)^{-1} \Delta^{1/2}] u = E u \quad (B10)$$

where the potential parameters C , Δ and α are *diagonal* in sublattice space (but not, for a non-collinear structure, in spin space). As D is diagonal in sublattice space and is the identity in spin space it must commute with the potential parameters. Hence (B10) may be rewritten

$$[C + D \Delta^{1/2} S' (1 - \alpha S')^{-1} \Delta^{1/2} D^{-1}] u = E u \Rightarrow [C + \Delta^{1/2} S' (1 - \alpha S')^{-1} \Delta^{1/2}] u' = E u' \quad (B11)$$

where $u' = D^{-1} u$. So by solving the eigenvalue problem with constants defined by (B7) rather than (B1) we obtain eigenvectors that differ by a phase factor. The presence of this phase factor cannot affect the expectation of a physical observable.

Appendix C

In this appendix we identify the algebra which is satisfied by the β and $\alpha\sigma_0$ matrices introduced in section 2 and we present a set of 4×4 matrices which satisfy the same algebra. Thinking first about the multiplication of the β matrices it is not difficult to show that:

$$\beta_l \beta_m = \delta_{lm} + i \varepsilon_{lmn} \beta_n \quad l, m, n \in \{1, 2, 3\}. \tag{C1}$$

The exact multiplication rules obeyed by the α matrices are not important here: all that matters is that the set is closed under multiplication. The remaining elements of the algebra are the commutation relations, which can be shown by direct multiplication to be,

$$\beta_\nu \alpha_\mu = (\gamma^\nu)_{\mu\mu} \alpha_\mu \beta_\nu \tag{C2}$$

where $(\gamma^\nu)_{\mu\mu}$ is the entry $\mu\mu$ in the matrix γ_ν of (A3). The importance of the commutation relations are that they enable us to express any linear combination of products of powers of the α s and β s as a linear combination of products $\alpha_i \beta_j$. All one has to do is to use (C2) to reorder the terms in any product of powers to get all the α s on the left, say, and all the β s on the right. The rules for the simplification of products involving α s or β s only can then be invoked. Hence a Hamiltonian expressed as a power series in these matrices can always be reduced to a linear combination of products.

Knowing that the algebra is defined by (C1) and (C2) we first search for a set of 4×4 matrices β' which can replace the β s. It can be verified that the following set is suitable

$$\begin{aligned} \beta'_0 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \beta'_1 &= \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \\ \beta'_2 &= \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix} & \beta'_3 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \end{aligned} \tag{C3}$$

These matrices are not uniquely determined by (C1) and (C2) and the set given here was obtained by requiring β'_3 to be diagonal. In the simpler case of the SSDW, with the spin axis in the z direction, the real space symmetry of the spins is then evident (the elements of β'_3 correspond to spin up moments on sublattices 0 and 3, and down on 1 and 2, see figure 1). The matrices $\alpha\sigma_0$ are already represented by the identity in spin space, and an algebraically equivalent 4×4 set may be obtained by simply omitting the direct product with σ_0 .

Once the reduced Hamiltonian has been diagonalized there is one further task to perform, which is to extract the spin information from the eigenfunctions. To do this it must be recognized that in the new representation the matrices β' are the operators for the charge and spin wave amplitudes per the unit cell (see appendix A). This is so because the β' s are algebraically equivalent to the old matrices β . So to get the charge or spin component on atom 0 we find the expectation of the appropriate

β' in the solution state Ψ for the cell, and divide by two rather than four (as the representation is 4×4 rather than 8×8). The spin polarization on any atom is given by the magnitude of $\frac{1}{2}(\langle \Psi | \beta'_1 | \Psi \rangle, \langle \Psi | \beta'_2 | \Psi \rangle, \langle \Psi | \beta'_3 | \Psi \rangle)$.

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