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Abstract. Antiferromagnetism on the face-centred cubic lattice is frustrated. The different competing spin arrangements are degenerate in the classical limit of the Heisenberg model. We consider quantum-mechanical spin fluctuations, using the Holstein–Primakoff transformation, as a perturbation to lift this degeneracy and find that the collinear spin arrangement is stabilised. When we consider the inclusion of paramagnetic impurities, however, we find that non-collinear arrangements are locally preferred. We suggest this scenario as a possible explanation for the fact that manganese, when quenched in a face-centred cubic lattice, can be driven from a collinear to non-collinear spin arrangement by doping with either nickel, iron or iridium.

1. Introduction

A lot of effort in the field of 'frustrated' antiferromagnetism has gone into finding the physical characteristics of different multiple spin-density wave (MSDW) states [1] and then designing and performing experiments to try to differentiate between the exotic MSDW and domains of collinear antiferromagnetism [2]. In this paper we will *not* be concerned with the physical properties of the different MSDW but we will ask questions about which physical effects tend to stabilise the different spin arrangements. In particular we will consider the effect of atomic impurities.

There are two main classes of systems that we will consider; first, localised systems typified by the actinides, USb [3] and UO_2 [4], and the lanthanides, CeAs [5] and CeSb [6]; and secondly, itinerant transition-metal systems, i.e. manganese alloys quenched into a face-centred cubic structure, $Mn_{1-x}Ni_x$ [7], $Mn_{1-x}Fe_x$ [8] and $Mn_{1-x}Ir_x$ [9].

For the localised systems the magnetic atoms are well separated and interact weakly through a mixture of superexchange and RKKY processes. The fact that the atoms are 'heavy' yields strong spin–orbit coupling effects and the induced charge component then interacts strongly with the crystal field. The particular arrangement of 'spins' for these systems seems likely to be decided by the crystal structure and in particular by the position and charge of the surrounding 'passive' atoms. The problem we wish to address here is the following: In the absence of these crystal-field effects, what are the likely consequences of substitutional atoms replacing magnetic atoms on the choice of MSDW for the system?

For the delocalised, transition-metal systems, the physical picture is very different. The spin–oirbit coupling effects are minor (yielding a 4 meV gap in a 100 meV spin-wave dispersion [10], for example) and so one has more confidence that charge does not play a dominant role. In this context our modelling will suit these systems more than the

localised systems. The transition metals can be modelled using a spin-polarised band structure, and the self-consistently chosen moments deduced from these calculations [11] agree fairly well with the $2.0\mu_B$ experimentally determined [12] for the manganese atom in a face-centred cubic lattice. With this degree of success, one can ask whether the band structure contributions break the degeneracy between different MSDW states that is found in a simple Heisenberg description. The degeneracy *is* broken by such effects and various authors have pointed this out [13].

The similar problem of ordering of nuclear spins on a face-centred cubic lattice has previously been studied [14]. The physical source of the interaction is very different since the nuclei are effectively distinguishable and cannot move on the relevant energy scales. This precludes exchange and superexchange, which are the dominant physical effects in our systems. It is worth noting that when the RKKY interaction dominates, these treatments predict collinear arrangements in agreement with our conclusions.

Manganese alloys exhibit various structural phase tranitions as a function of alloy concentration while they are in the antiferromagnetic phase [15]. The most natural explanation to this observation is that the type of MSDW changes as a function of alloy concentration [16]. Attempts to predict the lattice distortion induced by the large magnetoelasticity in these systems [17] agrees fairly well with the observed distortions, experimentally of order 5% [18]. Further, a neutron scattering analysis of the elastic magnetic scattering through such a transition [19] yields fairly conclusive proof that the magnetism takes an active role in these transitions. Can the band structure effects explain a change in MSDW behaviour? If one associates alloy concentration with band filling, then one can readily model a sequence of phase transitions in good agreement with those observed in $Mn_{1-x}Ni_x$ [20].

It is the assumption of a direct relationship between alloy concentration and band filling that we wish to analyse in this paper. The nickel atom has three more electrons than the manganese atom and so at a superficial level it would seem that the main effect of alloying nickel into manganese would be to raise the chemical potential. This is precisely the motivation behind the band filling explanation for the changes in MSDW behaviour. We would like to point out a couple of facts that might undermine confidence in this explanation.

First, a diffuse neutron scattering experiment has shown that the moment on the nickel sites is small [21]. The nickel atoms behave more like paramagnetic impurities than simple electron donors. Secondly, most of the alloys have become cubic by 25% doping. Careful studies of order in the alloys show a tendency for the atoms to order in a Cu_3Au structure. Indeed, some care must be taken because the ordered alloy is thermodynamically relatively stable. The cubic antiferromagnetic phase has four atoms per unit cell and the ordered alloy replaces one sublattice with paramagnetic impurities. The collinear phase has only two atoms per unit cell and so one sublattice would become diluted by 50% in the ordered alloy. For the cubic antiferromagnetic phase in the ordered lattice, it is easy to maintain antiferromagnetism by relaxing the spins into a coplanar arrangements (see figure 1), maintaining a unique manganese site. For the case of Mn_3Ir one finds an *increase* in the Néel temperature for the ordered state over the disordered state, suggesting that the ordered antiferromagnetism in the Cu_3Au structure is 'more' ordered than the corresponding disordered alloy antiferromagnetism and as such might be 'locally' a good picture for the preferred ordering of the disordered alloy. For the collinear arrangement, the ordered alloy would find two distinct manganese sites and the two sites would require quite contrasting spins in order to maintain antiferromagnetism. Can this 'ease of relaxation around impurities' be a driving force behind the formation
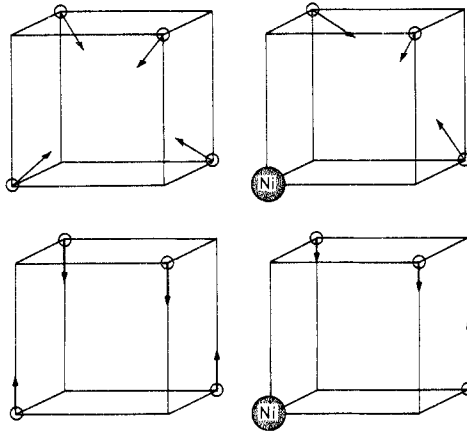
Figure 1. The top two diagrams are the MSDW spin arrangements with three *equal*-amplitude spin-density waves. The lower two diagrams are collinear arrangements. The antiferromagnetism can only be maintained in the final diagram by postulating two distinct manganese sites.

of a non-collinear spin arrangement?

The main purpose of this paper is to analyse paramagnetic impurities in face-centred cubic antiferromagnets and to find out which of the MSDW states they favour energetically. In § 2 we look at the classical limit of the Heisenberg model, a situation applicable to high-spin localised systems. In § 3 we look at the spin arrangements on the Cu_3Au lattice for this high-spin limit and in § 4 we look at the weak-coupling solution to the one-band Hubbard model, a very simple model for delocalised electrons. In § 5 we conclude.

2. The classical limit of the Heisenberg model

We consider the Heisenberg model with nearest-neighbour antiferromagnetic coupling:

$$H = J \sum_{\langle ii' \rangle} S_i \cdot S_{i'} \tag{2.1}$$

where $\langle ii' \rangle$ denotes two nearest-neighbour sites and S_i is a spin operator. The limit we take is the classical limit where the length of the spin is large. The manganese atom has a moment of $2.0\mu_B$, which is not very large, and being a rather delocalised system, the moment on an atom can also fluctuate in length. The results from the classical limit are more important from the point of view of physical ideas than they are quantitatively useful.

The classical limit simply chooses the minimum energy configuration for fixed spin lengths, optimising over their individual directions. We take the Fourier transform of the spins:

$$S_k = (1/\sqrt{N}) \sum_i \exp(-i k \cdot R_i) S_i \tag{2.2a}$$

$$S_i = (1/\sqrt{N}) \sum_k \exp(i k \cdot R_i) S_k \tag{2.2b}$$

where N is the number of atoms in the lattice. In this basis the Hamiltonian becomes

$$H = XJ \sum_k \gamma_k S_k \cdot S_k^* \tag{2.3}$$

where X is the number of nearest-neighbour atoms. We are assuming a centrosymmetric lattice (viz. $S_{-k} = S_k^*$) and

$$\gamma_k = (1/XN) \sum_{\langle ii' \rangle} \exp[i k \cdot (R_i - R_{i'})] \tag{2.4}$$

is the structure factor for the lattice in question. Finally we have the constraints on the length of the spins, which become

$$S^2 N \delta_{q=0} = \sum_{Gk} S_{k+q+G} \cdot S_k^* \tag{2.5a}$$

where G is a reciprocal lattice vector, and so the combinations of different Fourier components are orthogonal, while at $q = 0$ we find

$$S^2 N = \sum_k S_k \cdot S_k^* \tag{2.5b}$$

which yields a normalisation for the sum of moduli.

The minimum energy solution is that where the only non-vanishing Fourier components are those for which the structure factor is minimised. The solution therefore reduces to finding the set Ω of points where this minimum value of the structure factor, $\gamma_{\min} = \text{minimum}\{\gamma_q : q \in \text{Brillouin zone}\}$, is obtained, viz.

$$\Omega = \{k : \gamma_k = \gamma_{\min}\}. \tag{2.6}$$

We can build various degenerate ground-state solutions from the Fourier components corresponding to different points in Ω, subject to the above orthogonality constraints. The structure factor is obviously bounded below by -1 and achieves this value in systems that are not antiferromagnetically frustrated. The set Ω usually contains only one point in unfrustrated systems, and this becomes the Q for any antiferromagnetic order at low temperatures. This Q being essentially unique, we usually find a non-degenerate ground-state manifold up to the usual trivial choice of quantisation direction for the moment.

For frustrated system Ω contains more than one point and can be quite large. For the two-dimensional triangular lattice, we find that the minimum structure factor is $-\frac{1}{2}$ and this is achieved at two reciprocal space points. The classical ground state has a non-trivial degeneracy which is associated with the 'chirality' of any triangle of spins [22]. The case of interest here is the face-centred cubic lattice where we find that

$$\Omega = \left\{ \frac{2\pi}{a}(1, 0, x), \frac{2\pi}{a}(1, x, 0), \frac{2\pi}{a}(x, 1, 0), \frac{2\pi}{a}(0, 1, x), \frac{2\pi}{a}(0, x, 1), \frac{2\pi}{a}(x, 0, 1) : \right.$$

$$\left. x \in \left(\frac{-1}{2}, \frac{1}{2} \right) \right\} \tag{2.7}$$

where the minimum value for the structure factor is $-\frac{1}{3}$. The ground state is multiply degenerate and includes types I and III antiferromagnetic ordering as particular cases.

In manganese, type I ordering is observed, so we will restrict attention to states of this form:

$$S_i = \tilde{S}_1 \cos(Q_1 \cdot R_i) + \tilde{S}_2 \cos(Q_2 \cdot R_i) + \tilde{S}_3 \cos(Q_3 \cdot R_i) \tag{2.8a}$$

with the three vectors $\tilde{S}_\alpha$ being averages of two of the spins in the unit cell, S_0 and S_α,

viz $\tilde{S}_\alpha = \frac{1}{2}(S_0 + S_\alpha)$. These vectors are related directly to magnetic neutron scattering intensity at the reciprocal space points $Q_\alpha + G$ with $I \propto |\tilde{S}_\alpha|^2$ and satisfying the constraints

$$\tilde{S}_\alpha \cdot \tilde{S}_{\alpha'} = \delta_{\alpha\alpha'} \tilde{S}_\alpha^2 \tag{2.8b}$$

$$\sum_\alpha \tilde{S}_\alpha^2 = S^2 \tag{2.8c}$$

and associated with the three distinct points in Ω:

$$Q_1 = \frac{2\pi}{a}(1, 0, 0) \qquad Q_2 = \frac{2\pi}{a}(0, 1, 0) \qquad Q_3 = \frac{2\pi}{a}(0, 0, 1). \tag{2.8d}$$

Associated with these three values of Q_α, there is a large degeneracy for the anti-ferromagnetic ground state. Subject to the orthogonality constraints (2.8b, c), the three vectors $\tilde{S}_\alpha$ can take any values and to each choice corresponds a distinct spin arrangement. The terms MSDW corresponds to when more than one $\tilde{S}_\alpha$ is non-zero. The object of our calculation is to determine how this degeneracy is broken by quantum-mechanical fluctuations in two cases: first, in the pure lattice and, secondly, in the presence of a paramagnetic impurity.

In the classical limit, fluctuations are best described by the Holstein–Primakoff transformation about the classical spin directions. A spatial frame is chosen on each site with the classical spin in the z direction. The spin operators are then expanded as

$$\bar{S}_i^z = S - b_i^\dagger b_i \tag{2.9a}$$

$$\bar{S}_i^+ = \sqrt{(2S - b_i^\dagger b_i)}\, b_i \tag{2.9b}$$

$$\bar{S}_i^- = b_i^\dagger \sqrt{(2S - b_i^\dagger b_i)} \tag{2.9c}$$

in terms of bosonic operators $b_i^\dagger$ which create spin fluctuations. We proceed by performing perturbation theory, treating the spin fluctuations as a perturbation. The classical vacuum satisfies $b_i|0\rangle = 0$ and so

$$\bar{S}_i|0\rangle = (\sqrt{(S/2)}\, b_i^\dagger,\ \sqrt{(S/2)}\, i b_i^\dagger,\ S)|0\rangle \tag{2.10a}$$

$$\bar{S}_i|0\rangle = S|0\rangle \hat{e}_3 + \sqrt{S}\, b_i^\dagger|0\rangle \hat{e}_+ \tag{2.10b}$$

with $\hat{e}_+ = (1/\sqrt{2})(\hat{e}_1 + i\hat{e}_2)$.

So far we have considered an isolated spin in terms of its own natural quantisation frame. If we now consider a single global frame, then for each site we need a rotation matrix $R_i^{\alpha\alpha'}$ which transforms us into the correct local frame for the atom:

$$\bar{S}_i = R_i^{-1} S_i. \tag{2.11}$$

In this representation the Hamiltonian becomes

$$H = J \sum_{\langle ii'\rangle} \bar{S}_i^T (R_i^{-1} R_{i'}) \bar{S}_{i'} \tag{2.12}$$

and so

$$H|0\rangle = JS^2 \sum_{\langle ii'\rangle} \hat{e}_3^T R_i^{-1} R_{i'} \hat{e}_3|0\rangle + 2JS\sqrt{S} \sum_{\langle ii'\rangle} \hat{e}_3^T R_i^{-1} R_{i'} \hat{e}_+ b_{i'}^\dagger|0\rangle$$

$$+ JS \sum_{\langle ii'\rangle} \hat{e}_+^T R_i^{-1} R_{i'} \hat{e}_+ b_i^\dagger b_{i'}^\dagger|0\rangle. \tag{2.13}$$

The first term is the classical energy. The second and third terms are quantum

fluctuations about the classical ground state. If we break the lattice up into the four natural sublattices, then there is a quantisation direction for which four rotation matrices, which are the identity and then rotations through 180° about each of the three lattice directions, map the spin at the origin onto the spins on each of the other sublattices. Combining these rotations with a rotation independent of site, to put the classical spin along the z axis, we have a representation for which the symmetries of type I antiferromagnetism are manifest. Our first observation is that if we take one element from each of the four sublattices then

$$\sum_{\alpha=0}^{3} R_\alpha = 0 \tag{2.14}$$

and so

$$JS^2 \sum_{\langle ii'\rangle} \hat{e}_3^T R_i^{-1} R_{i'} \hat{e}_3 |0\rangle = -JS^2 \tfrac{1}{3} NX|0\rangle \tag{2.15a}$$

$$2JS\sqrt{S} \sum_{\langle ii'\rangle} \hat{e}_3^T R_i^{-1} R_{i'} \hat{e}_+ b_i^+ |0\rangle = 0 \tag{2.15b}$$

which yields the classical ground-state energy and a stability criterion for that ground state, respectively. Note that there is a hidden factor of 2 because each bond is included twice.

We are now in a position to determine the quantum fluctuation-induced degeneracy-breaking contribution, which arises from the third term in (2.13). To the order to which we are working, the energy of the single spin fluctuation is $\tfrac{1}{3}XJS$ and the two fluctuations are effectively 'independent', only being coupled at a higher order, so

$$\delta E_2 = -[3/(2XJS)] \sum_{\langle ii'\rangle} 2J^2 S^2 |\hat{e}_+^T R_i^{-1} R_{i'} \hat{e}_+|^2$$

$$= -JSN \sum_{\alpha=1}^{3} |X^T T_\alpha X|^2 \tag{2.16}$$

where $X = R\hat{e}_+$ is the uniformly rotated displacement and T_α are the three 180° rotations. We find

$$\delta E_2 = -JSN[4(|x_1|^4 + |x_2|^4 + |x_3|^4) - |x_1^2 + x_2^2 + x_3^2|^2] \tag{2.17}$$

and performing the complex analysis and using $X \cdot X = 0$ we obtain

$$\delta E_2 = -JSN(1 - 2\sin^2\theta\cos^2\theta - 2\sin^2\varphi\cos^2\varphi\sin^4\theta) \tag{2.18}$$

which is the largest energy gain for the collinear arrangement at $\delta E_2 = -JSN$ and the smallest energy gain for the cubic spin arrangement at $\delta E_2 = -\tfrac{1}{3}JSN$. We find that the quantum fluctuations favour the *collinear* arrangement.

Now let us turn to the main topic of this section, having gained a result for future use in comparison. What MSDW state does a paramagnetic impurity prefer? In order to try partially to answer this question, we may take out one of the spins and determine the perturbative local distortion in the spin arrangement using an identical spin fluctuation technique to that of the above argument.

The perturbation is now the decoupling of the impurity spin from its neighbours:

$$H_1 = -2J \sum_{[0i]} S_0 \cdot S_i \tag{2.19}$$

where the impurity site is assumed at the origin and the neighbours are now ordered. Applying this operator to the ground state yields

$$H_1|0\rangle = 8JS^2|0\rangle - 2JS\sqrt{S}\sum_{[0i]} \hat{e}_3^T R_i^{-1} R_0 \hat{e}_+ b_0^\dagger|0\rangle - 2JS\sqrt{S}\sum_{[0i]} \hat{e}_3^T R_0^{-1} R_i \hat{e}_+ b_i^\dagger|0\rangle$$

$$- 2JS\sum_{[0i]} \hat{e}_+^T R_0^{-1} R_i \hat{e}_+ b_i^\dagger b_0^\dagger|0\rangle. \tag{2.20}$$

The first term yields the loss of magnetic energy due to the impurity site. The second term vanishes as it did for the previous calculation because the field from the surrounding spins is parallel to the spin and so orthogonal to the fluctuations. The third term does not necessarily vanish and yields the leading-order correction. For spin fluctuations on the sites neighbouring the impurity, the field from its neighbours is now missing a contribution from the impurity. The local field is not necessarily parallel to the spin and so the spin can move in order to benefit from it.

The perturbative contribution is simply

$$\delta E_2 = (6/XJS)\sum_{[0i]} J^2 S^3 |\hat{e}_3^T R_0^{-1} R_i \hat{e}_+|^2$$

$$= 2JS^2 \sum_{\alpha=1}^{3} |Y^T T_\alpha X|^2 \tag{2.21}$$

where $Y = R\hat{e}_3$ is the uniformly rotated classical spin direction. Performing the complex analysis and using $X \cdot Y = 0$ we obtain

$$\delta E_2 = -2JS^2 \sin^2 \theta(\cos^2 \theta + \sin^2 \varphi \cos^2 \varphi \sin^2 \theta) \tag{2.22}$$

which has the same angular dependence as the previous result (2.18), as it must have from symmetry arguments. We find no energy saving for the collinear case and a maximum energy saving for the cubic case at $\delta E_2 = -\frac{2}{3}JS^2$. Before we go on to compare these two results, we should say a little about the limitations of this perturbative approach.

The energy scale for the perturbative impurity calculation is *not small*. Indeed, we find an energy on precisely the same scale as the unperturbed result. This is symptomatic of the fact that the spins move through finite angles in the vicinity of the impurity and no perturbative calculation can deal effectively with this fact. We know that the spin order will be changed at *large* distances by the impurity because it breaks the classical MSDW degeneracy. This is the reason we are restricted to performing simple perturbative arguments rather than solving the true classical problem.

We are, however, led to a rather instructive argument which has earlier been presented to compare 'thermal fluctuations' with 'impurity dilution' [23]. If all the spins are collinear, then all the local fields induced on a site are collinear. Since perturbative spin fluctuations are orthogonal to the spin direction, the only way one can get a linear change in energy from a perturbation is to introduce a perturbative field that is *not* parallel to the spin direction. For the case of a paramagnetic impurity, a spin extracted needs to be non-collinear to a spin that it couples to in order to give a first-order change in energy.

So far we have treated the quantum fluctuations associated with the impurity potential. The impurity breaks the degeneracy at the *classical level* and this is the more fundamental problem. Although we cannot solve this problem, further evidence for the ground state can be found from a 'cluster' calculation.

We replace the spin at the origin with a spin in the same direction but of reduced magnitude, κS. The surrounding nearest-neighbour spins to the origin are then allowed to relax in such a way as to minimise the classical Heisenberg energy. The spins outside this cluster take up one of the different MSDW spin arrangements where the sublattice spins satisfy $S_0 + S_1 + S_2 + S_3 = 0$. Although the spins in our cluster will be in equilibrium, the spins neighbouring the cluster may not be. We will make one further assumption, namely that all the spins that are on the same sublattice belonging to the cluster are parallel. We are left to find the three variable spins, T_1, T_2 and T_3, for the three sublattices found in the cluster.

The change in energy around the cluster is

$$\Delta H = 2J \sum_{[0j]} S_0 \cdot (\kappa T_j - S_j) + 2J \sum_{[ji]} S_i \cdot (T_j - S_j)$$
$$+ J \sum_{\langle jj' \rangle} T_j \cdot T_{j'} - J \sum_{\langle jj' \rangle} S_j \cdot S_{j'} \tag{2.23}$$

where j is an index running over the cluster and i is an index running over the neighbours of the cluster.

Minimising the energy subject to the constraints that the spins T_i are of fixed magnitude, we find

$$F_j = \frac{\partial \Delta H}{\partial T_j} = 2J \left(\kappa S_0 + \sum_{[ji]} S_i + \sum_{[jj']} T_{j'} \right) = (-1)(1 + \mu_j) 4 J T_j \tag{2.24}$$

where μ_j are Lagrange multipliers to ensure the constraints.

We can rewrite this problem as

$$\begin{bmatrix} 1+\mu_1 & 1 & 1 \\ 1 & 1+\mu_2 & 1 \\ 1 & 1 & 1+\mu_3 \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \end{bmatrix} = \begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} - \frac{(1+\kappa)}{2} S_0 \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{2.25}$$

and hence solve it to find

$$\begin{bmatrix} T_1 \\ T_2 \\ T_3 \end{bmatrix} = \frac{1}{\Delta} \begin{bmatrix} \mu_2\mu_3 + \mu_2 + \mu_3 & -\mu_3 & -\mu_2 \\ -\mu_3 & \mu_3\mu_1 + \mu_3 + \mu_1 & -\mu_1 \\ -\mu_2 & -\mu_1 & \mu_1\mu_2 + \mu_1 + \mu_2 \end{bmatrix}$$

$$\times \begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} - \frac{(1+\kappa)}{2\Delta} S_0 \begin{bmatrix} \mu_2\mu_3 \\ \mu_3\mu_1 \\ \mu_1\mu_2 \end{bmatrix} \tag{2.26a}$$

$$\Delta = \mu_1\mu_2\mu_3 + \mu_2\mu_3 + \mu_3\mu_1 + \mu_1\mu_2. \tag{2.26b}$$

We consider two cases: first, the collinear arrangement and, secondly, the cubic arrangement.

For the collinear arrangement we see that the T_i must be parallel to the quantisation direction and then from the normalisation we find that $T_i = S_i$ and

$$\Delta H = 8JS^2(1 - \kappa). \tag{2.27}$$

For the cubic spin arrangement we find that the cubic point-group symmetry is maintained about the impurity and so $\mu = \mu_i$ and
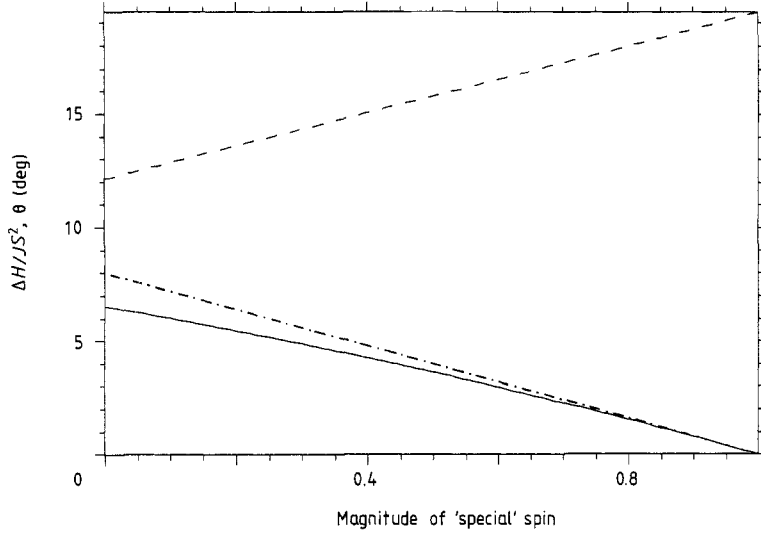
Figure 2. The normalised energies of a cluster surrounding an impurity spin, as the length but not direction of the impurity spin is varied. Collinear (–·–·–) and non-collinear (——) spin arrangements are shown. The non-collinear arrangement is seen to be relatively stable. We also show the angle between one of the cluster spin and the 'Cu$_3$' plane in the Cu$_3$Au structure (– – – –).

$$T_i = (1/\mu)S_i + [(2 - \mu - \mu\kappa)/2\mu(\mu + 3)]S_0 \tag{2.28}$$

where from the magnitude we find

$$\mu^4 + 6\mu^3 + (\tfrac{89}{12} - 5\kappa/6 - \kappa^2/4)\mu^2 - \tfrac{16}{3}\mu - 8 = 0 \tag{2.29}$$

and the non-collinear change in energy satisfies

$$\Delta H = 8JS^2[6(1 - \mu) + (8/\mu^2)(1 - \mu^2)]. \tag{2.30}$$

We plot the two energies as functions of the impurity spin magnitude in figure 2. We find that the non-collinear spin arrangement is relatively stable and yields a saving of $1.47JS^2$ over the collinear arrangement as the impurity spin vanishes. This is a variational estimate and as such yields a lower bound on this energy.

We can find out the degree of local distortion about the impurity by calculating the angle through which the cluster spins relax. If we consider the four atoms in a unit cell (see figure 1), then we have calculated the angle that a spin makes with the plane containing the three atoms not at the origin. For the Cu$_3$Au arrangement this angle would vanish, which acts as a benchmark. This quantity, θ, given by

$$\sin \theta = (5 + 3\kappa)/6(\mu + 3) \tag{2.31}$$

is also plotted in figure 2, and we find that the spins cant over to a significant degree.

Now let us compare the two results we have derived. The energy scale upon which quantum fluctuations stabilise the collinear arrangement is JSN. The energy scale upon which a classical paramagnetic impurity stabilises a non-collinear arrangement is JS^2. If the concentration of independent impurities were greater than or less than $1/S$, we would expect the non-collinear or collinear states to be stable respectively from this argument. For the case of manganese, where the spin is $2.0\mu_B$, we would require a sizable fraction of impurities. Although this simplistic argument breaks down

for high concentrations of impurities, not to mention the fact that the modelling assumptions are dubious for manganese, doping levels of 20% are experimentally required to drive the materials non-collinear.

3. The classical limit for antiferromagnetism in the Cu_3Au structure

In this section we look at the classical limit of the Heisenberg model where the lengths of the spins are identical on each of the four cubic sublattices but can disagree on different sublattices. A special case of this is where three sublattices have identical moments and we have the Cu_3Au structure.

We must make the sublattice label manifest and so we set $R_i = R_j + c_\alpha$, where the label j runs over a cubic sublattice and c_α are the sublattice vectors in the face-centred cubic zone. In real space we have

$$H = J \sum_{\langle ii' \rangle} S_i \cdot S_{i'} \tag{3.1a}$$

subject to the constraints

$$S_{j\alpha} \cdot S_{j\alpha} = S^2 \lambda_\alpha^2. \tag{3.1b}$$

Analogous to the treatment in § 2, we make a transformation into reciprocal space to find

$$H = JX \sum_k [S_{k0}^* \quad S_{k1}^* \quad S_{k2}^* \quad S_{k3}^*]
\begin{bmatrix}
0 & \gamma_{k1} & \gamma_{k2} & \gamma_{k3} \\
\gamma_{k1} & 0 & \gamma_{k3} & \gamma_{k2} \\
\gamma_{k2} & \gamma_{k3} & 0 & \gamma_{k1} \\
\gamma_{k3} & \gamma_{k2} & \gamma_{k1} & 0
\end{bmatrix}
\begin{bmatrix}
S_{k0} \\
S_{k1} \\
S_{k2} \\
S_{k3}
\end{bmatrix} \tag{3.2a}$$

subject to the constraints

$$\sum_k S_{k\alpha}^* S_{k-q\alpha} = (N/4)\delta_{q=0} S^2 \lambda_\alpha^2 \tag{3.2b}$$

where

$$\gamma_{k1} = \tfrac{1}{3}\cos(\tfrac{1}{2}ak_2) \cos(\tfrac{1}{2}ak_3)$$
$$\gamma_{k2} = \tfrac{1}{3}\cos(\tfrac{1}{2}ak_3) \cos(\tfrac{1}{2}ak_1) \tag{3.2c}$$
$$\gamma_{k3} = \tfrac{1}{3}\cos(\tfrac{1}{2}ak_1) \cos(\tfrac{1}{2}ak_2)$$

are the relevant structure factors, and the structure factor for the face-centred cubic lattice is

$$\gamma_k = \gamma_{k1} + \gamma_{k2} + \gamma_{k3}.$$

The solution to this problem depends strongly on the degeneracy of the λ_α. The minimum energy solution is usually found at a unique k in reciprocal space and satisfies

$$E = -\frac{JXS^2}{3} \frac{N}{4} \sum_\alpha \lambda_\alpha^2 S^2 \tag{3.3a}$$

$$S_{k0} + S_{k1} + S_{k2} + S_{k3} = 0 \tag{3.3b}$$

and usually $k = 0$ and then also

$$S_{0\alpha} \cdot S_{0\alpha} = (N/4)S^2 \lambda_\alpha^2. \tag{3.3c}$$

There is one situation where this k is not unique and this is when two pairs of sublattices have identical total moments. For the case $\lambda_0 = \lambda_1$ and $\lambda_2 = \lambda_3$, we find solutions along $(k, 0, 0)$. These solutions correspond to the degeneracies observed in the face-centred cubic lattice and are subject to the constraints $S_{k0} + S_{k1} + S_{k2} + S_{k3} = 0$, which explains the extra phases in the description involving the larger Brillouin zone of the previous section. The only case where the solution is not a simple antiferromagnet is where one spin (S_0 say) has a very large moment $\lambda_0 > \lambda_1 + \lambda_2 + \lambda_3$ and then it is not possible to achieve antiferromagnetism with this unit cell.

If we restrict attention to the origin in reciprocal space, then we restrict attention to states that tend continuously onto type I antiferromagnetism. Since this is the symmetry of our experimental systems, we will make this assumption.

For the case of Cu_3Au structure, we find that the lattice is *still* frustrated since the three 'Cu' sites in a unit cell are all nearest neighbours and as such form the equilateral triangle used in the standard frustration argument. The ground state has only the constraint that the total moment vanishes, and is hence antiferromagnetic. There are *still* three degenerate spin-density waves corresponding to the three for the face-centred cubic system. For the Cu_3Au structure, however, there is no longer a collinear solution and therefore independent superposition of the spin-density waves using the three spatial dimensions is no longer trivial. Any neutron scattering is still related directly to the $\tilde{S}_\alpha = \frac{1}{2}(S_0 + S_\alpha)$ by $I \propto |\tilde{S}_\alpha|^2$. We now find the result that *none* of the magnetic Bragg spots can vanish when $\lambda_0 \neq \lambda_1 = \lambda_2 = \lambda_3$. The antiferromagnetism in a Cu_3Au structure must be a MSDW state, although the relative amplitudes of the spin-density waves can be quite different. For the case when the 'Au' sites have paramagnetic 'impurities', viz. $\lambda_0 = 0$, we find that the three amplitudes are equal for the three spin-density waves and we have the state corresponding to the cubic spin arrangement.

For the solution continuous with the collinear spin arrangement, we find a loss of both translational and point-group symmetry. For the solution continuous with the cubic spin arrangement we find only a minor loss of point-group symmetry, essentially that which is broken by the change in structural group itself. It is to this fact that we attribute the stability of the solution which is continuous with the face-centred cubic spin arrangement of cubic symmetry.

When the 'special' spin of a different length vanishes, we are left with an essentially unique non-collinear but coplanar structure where the spins on the three sublattices form an equilateral triangle. This spin state has an obvious triangular symmetry which is lost in all but the fluctuations towards the cubic spin arrangement.

4. The 'weak-coupling' Hubbard model

In the preceding sections we analysed a localised description for MSDW anti-ferromagnetism, although we know that for manganese alloys there is experimental evidence that an itinerant starting platform might be more reasonable. In this section we analyse probably the simplest itinerant model that displays MSDW anti-ferromagnetism, the single-band Hubbard model in the Hartree–Fock approximation. This model has been much studied previously in this context [24], although the earlier motivation has been concerned with the physical properties of different MSDW and comparisons between them and *not* with the problem of impurities, our present concern.

The Hubbard model is a tight-binding Hamiltonian with two competing terms

$$H = -t \sum_{\langle ii' \rangle} c_{i\sigma}^{\dagger} c_{i'\sigma} + U \sum_{i} c_{i\sigma}^{\dagger} c_{i\bar{\sigma}}^{\dagger} c_{i\bar{\sigma}} c_{i\sigma}. \tag{4.1}$$

The first term is the hybridisation energy between electrons on neighbouring sites, known as the 'hopping', and the second term is a short-range repulsion between two electrons on the same site. The longer-range Coulomb interaction is assumed screened in this description and the Hubbard parameter U is usually assumed of a similar magnitude to the 'hopping' parameter t, in order that the behaviour is *not* strong coupling. For simple magnetic applications a mean-field Hartree–Fock approximation is applied to the on-site repulsion term, yielding self-consistently chosen, magnetic symmetry-breaking fields, $g_\mu = U m_\mu$, on each of the atomic sites, where m_μ are the magnetic moments corresponding directly to the $\tilde{S}_\alpha$ of § 2. The solution to this problem is documented in our earlier work [25]. We require the Green function for the present work and we relegate this to the Appendix.

The problem we wish to tackle is that of an impurity atom in the MSDW phases and which of the various states is relatively stabilised by its inclusion. We employ a simple on-site change in potential on the paramagnetic impurity site:

$$\Delta H = \delta_{j0} \delta_{\alpha0} V \delta_{0\alpha'} \delta_{0j'} \delta_{\sigma\sigma'} \tag{4.2}$$

where j is a unit-cell label, α is a sublattice label and σ is the spin label.

The technique we employ is that of Green functions. The Green function for the problem is simply

$$G_I^{-1}(z) = z - H - \Delta H \tag{4.3a}$$

for the Green function of the system in the presence of the impurity and

$$G^{-1}(z) = z - H \tag{4.3b}$$

for the Green function of the periodic system in the absence of the impurity. Because the impurity is short-range, the solution is best obtained using a short-range potential, $\Sigma(z)$, defined by

$$G_I(z) = G(z) + G(z)\Sigma(z)G(z) \tag{4.4a}$$

where

$$\Sigma(z) = \Delta H + \Delta H G(z)\Sigma(z) = [1 - \Delta H G(z)]^{-1} \Delta H \tag{4.4b}$$

which is also necessarily short-range if ΔH is.

The quantity we wish to study is the change in energy at fixed electron number:

$$\Delta E - \mu \Delta N_e = E_I - \mu N_I - (E - \mu N_e) = \oint_C \frac{dz}{2\pi i} (z - \mu) f(z - \mu) \, \mathrm{tr}[G_I(z) - G(z)]$$

$$= \oint_C \frac{dz}{2\pi i} (z - \mu) f(z - \mu) \, \mathrm{tr}[G(z)\Sigma(z)G(z)] \tag{4.5}$$

where the trace is over the cell, sublattice and spin degrees of freedom, μ is the chemical potential, $f(z)$ is a Fermi function and the contour, C, captures either the poles of the Fermi function or, by Cauchy's theorem, the real axis.

Employing the fact that

$$\mathrm{d}G(z)/\mathrm{d}z = (-1)G(z)^2 \tag{4.6}$$

we can show that

$$\Delta E - \mu \Delta N_e = \oint_C \frac{dz}{2\pi i} (z - \mu) f(z - \mu) \, \text{tr}\left((-1)\Delta H \frac{dG_0(z)}{dz} [1 - \Delta H G_0(z)]^{-1}\right) \qquad (4.7)$$

where the trace over lattice sites has been performed to leave $G_0(z)$ the periodic Green function at the impurity site and the residual trace is only over the spin degrees of freedom. The spin trace is also straightforward and if we set

$$G_0(z) = F_0 - \boldsymbol{F} \cdot \boldsymbol{\sigma} \qquad (4.8)$$

where $\boldsymbol{\sigma}$ are the Pauli matrices, then we immediately discover that

$$\Delta E - \mu \Delta N_e = \oint_C \frac{dz}{2\pi i} (z - \mu) f(z - \mu) \frac{d}{dz} \{\ln[(1 - VF_0)^2 - V^2 |\boldsymbol{F}|^2]\}. \qquad (4.9)$$

This is a very general formula true for any impurity of form (4.2) in a single-band, single-particle potential. For the case of our face-centred cubic MSDW solution we can go one stage further and show that

$$F_0(z) = \partial F(z)/\partial z \qquad (4.10a)$$

$$F_\mu(z) = \partial F(z)/\partial g_\mu \qquad (4.10b)$$

where

$$F(z) = \frac{1}{4N} \sum_k \ln \Delta_k(z) = \frac{1}{4N} \sum_{k\alpha} \ln(z - \varepsilon_{k\alpha}) \qquad (4.10c)$$

where $\Delta_k(z)$ is the simple determinant defined in the Appendix. In the remainder of this section we attempt to find the behaviour of this master formula:

$$\Delta E - \mu \Delta N_e = \oint_C \frac{dz}{2\pi i} (z - \mu) f(z - \mu) \frac{d}{dz} \left\{ \ln\left[\left(1 - V \frac{\partial F}{\partial z}\right)^2 \right. \right.$$

$$\left. \left. - V^2 \sum_\mu \left(\frac{\partial F}{\partial g_\mu}\right)^2 \right] \right\} \qquad (4.11)$$

for the change in energy induced by the impurity level.

The energy spectrum and in particular the position of the impurity level is found by studying the zeros of

$$S(z) = \left(1 - V \frac{\partial F}{\partial z}\right)^2 - V^2 \sum_\mu \left(\frac{\partial F}{\partial g_\mu}\right)^2 \qquad (4.12)$$

and by analysing the relative 'depths' of the impurities a first pass at the relative stabilities of the different MSDW states can be found.

In general even this subsidiary problem is very difficult, but there are a few simple limits which are amenable to analysis. First we consider the limit where the local field energy dominates the 'hopping' energy, $|\boldsymbol{g}| \mapsto \infty$, a limit for which the model is admittedly not well suited, but nonetheless some physical insight can be deduced from this study. In this limit the energy bands satisfy

$$\varepsilon_{k\sigma\tau} = \tau g + \sigma \lambda_k \qquad (4.13a)$$

where τ and σ are ± 1 and

$$g^2 \lambda_k^2 = g_1^2 s_{k1}^2 + g_2^2 s_{k2}^2 + g_3^2 s_{k3}^2 \tag{4.13b}$$

and $s_{k\mu}$ are the structure factors for the face-centred cubic lattice (see Appendix) and λ_k is the quantity that determines which of the MSDW is relatively stable. The two spin states are split on the energy scale g and so we consider each spin state separately. For the lower spin state on the impurity we set $z = -g + x$ and then

$$S(-g + x) = 1 - \frac{V}{N} \sum_k \frac{x}{x^2 - \lambda_k^2} \tag{4.14}$$

is satisfied by the impurity level. For our nearest-neighbour interactions we find that this becomes

$$1 = V \left(\frac{2}{\pi}\right)^3 \int_0^{\pi/2} d\varphi_1 \, d\varphi_2 \, d\varphi_3 \frac{x}{x^2 - (Xt/3g)^2 (g_1^2 c_2^2 c_3^2 + g_2^2 c_3^2 c_1^2 + g_3^2 c_1^2 c_2^2)} \tag{4.15}$$

where $c_i = \cos \varphi_i$.

First, we can readily solve this perturbatively at large (V/t) to determine

$$x = V \left[1 + \frac{1}{4} \left(\frac{Xt}{3V}\right)^2 + \frac{1}{64} \left(\frac{Xt}{3V}\right)^4 \left(\frac{3}{g^4} (g_1^4 + g_2^4 + g_3^4) - 2\right) \dots \right] \tag{4.16}$$

and we immediately deduce that when the chemical potential is in the lower band, this argument suggests that the collinear state is stabilised by the impurity.

Secondly, by analysing the case that the impurity level coincides with the bottom of the band, we find that a pure impurity state is found only if

$$|V| > \left| \frac{Xt}{3} \right| \left[\left(\frac{2}{\pi}\right)^3 \int_0^{\pi/2} d\varphi_1 \, d\varphi_2 \, d\varphi_3 \frac{g^2}{g_1^2(1 - c_2^2 c_3^2) + g_2^2(1 - c_3^2 c_1^2) + g_3^2(1 - c_1^2 c_2^2)} \right]^{-1} \tag{4.17}$$

and once again this is *always* satisfied by the collinear arrangement but is a bound on the existence of the impurity level for all other spin arrangements.

We can trace the stability in the collinear spin arrangement back to the dimensionality of the band structure in this limit. Only for the collinear case is the band structure two-dimensional, and it is well known that *any* attractive potential produces a bound state in two dimensions but that in three dimensions there is a minimum size to the potential below which it cannot form a bound state. In this limit, the strong anisotropy of the collinear phase pulls many states to the bottom of the band which can be used in forming the impurity state. If the magnetic potential were much weaker, then the impurity would lie in the heart of the band structure where the non-collinear arrangement does better energetically.

The second limit that we consider is that where the magnetic fields are small. The degeneracy breaking occurs at fourth order in $|g|$ and so we need to consider contributions to this order to break the degeneracy.

The calculations are straightforward but tedious and we find

$$\partial F / \partial z = F_0 + g^2 F_1 + g^4 F_2 + O(g^6) \tag{4.18a}$$

$$\partial F / \partial g_\mu = g_\mu [H_0 + g^2 H_1^\mu + O(g^4)] \tag{4.18b}$$

where the dependence on the MSDW character occurs first at the level of F_2 and H_1^μ. At this order the impurity level satisfies

$$(1/V) - F_0 - g^2 F_1 - g^4 F_2 = \pm g \left(H_0 + \sum_\mu H_1^\mu g_\mu^2 \right) + O(g^5) \tag{4.19}$$

where we have two solutions corresponding to the different behaviour of the spin in the magnetic phase.

If we analyse the simple limit $|V| \mapsto \infty$, in order to obtain a well defined impurity level, we find that the impurity level approximately satisfies

$$z = V\left[1 + g^2 F_1(V) + g^4 F_2(V) \pm g\left(H_0(V) + \sum_{\mu} g_{\mu}^2 H_1^{\mu}(V)\right)\right] \quad (4.20)$$

and we find two possible ways for the degeneracy to be broken. If only one of the two impurity states is filled, we have a magnetic impurity and the degeneracy is broken to order g^3 and the most stable MSDW state has the maximum value for

$$P(g) = (1/N) \sum_{k} \lambda_k^4. \quad (4.21)$$

We would expect both states to be filled in this limit and for this, the paramagnetic impurity case, we find that the degeneracy is broken to order g^4 but that again the most stable MSDW has the maximum value of $P(g)$. For our nearest-neighbour hopping, we can readily calculate $P(g)$ and we find

$$P(g) = \tfrac{1}{64}[1 + (3/g^4)(g_1^4 + g_2^4 + g_3^4)] \quad (4.22)$$

and so once again the collinear phase is favoured.

For all the limits so far considered, we can argue fairly readily that the collinear phase is favoured because more states move towards the band edge than for the non-collinear phases. The impurity state can make use of these states to form a more localised wavepacket around the impurity site at the same cost in kinetic energy. Would we expect this argument to survive for the case of manganese with a moment of $2.0\mu_B$ and five relevant bands? The simple answer is *no*. The band structures of the different MSDW states have very different symmetries and the impurity level is almost certainly somewhere in the middle of the band and not beyond the band edge. The nickel atom is unlikely to have either a full or empty d shell. In order to study the more reasonable physical case, one needs to look at the case where the impurity is a resonance in the band.

An even more disturbing fact is that the Hubbard model has only spin-half orbitals on the sites. There is no possibility of weak angular fluctuations in the spin directions and so the subtle ideas of § 2 can play no role at all.

Also when we perform perturbation theory in the impurity potential, we find that to leading order we obtain Vn_e where n_e is the electron density on the impurity site, a constant quantity in a one-band model. The spatial symmetry of the orbitals used to make up the different MSDW moments are quite different and will couple quite differently to the impurity in a many-band system. The effect that seems to be the physically most natural for degeneracy breaking is absent from our calculations.

We therefore feel that the results obtained in this section are probably not applicable to manganese, for which a many-band model is required and a more carefully defined impurity needs to be considered.

5. Conclusions

The basic question tackled in this paper is the following: Which of the different degenerate MSDW spin arrangements in frustrated face-centred cubic systems is stabilised by a paramagnetic impurity? We have in mind the transition-metal manganese,

which shows transitions between different such phases upon doping of nickel, which is thought to be paramagnetic in this environment. First let us consider the arguments about localised spins interacting via the Heisenberg Hamiltonian in the classical limit.

Quantum fluctuations favour collinear arrangements. The basic reason for this is that spin fluctuations are orthogonal to the spin direction in the classical limit. The stability of the state of the moving of a particular spin ensures that the field from the surrounding spins is parallel to the relevant spin. This in turn ensures that the fluctuations are orthogonal to the local field and can gain no energy from the Heisenberg interaction. The energy gain comes from the interaction between *two* neighbouring fluctuations and this is largest in the collinear arrangement because the fluctuations are coplanar and therefore have a larger overlap on average.

Quantum impurities favour the non-collinear arrangements. A perturbative argument is presented for this. Again, since fluctuations are orthogonal to the spin direction, there can only be a linear contribution from the Heisenberg Hamiltonian if the local field is not parallel to the relevant spin. In collinear arrangements the local fields are always parallel to the special direction and so a linear contribution can only be found in non-collinear arrangements.

There is experimental evidence for Cu_3Au ordering of the paramagnetic impurities in face-centred cubic manganese. We have therefore analysed the possible spin arrangements of this structure, seeking clues as to which phase a denser concentration of impurities might favour. We find that when the spin on the 'Au' site vanishes the spin structure is essentially unique and is a non-collinear arrangement with three *equal*-amplitude spin-density waves, suggesting that local Cu_3Au ordering will stabilise the cubic MSDW in agreement with the impurity argument.

If we now move on to itinerant analysis, we find that the itinerant single-band Hubbard model suggests that the inclusion of a substitutional paramagnetic impurity will stabilise the collinear spin arrangement in direct opposition to the localised case. Impurities prefer anisotropy in this analysis because this suggests an effective reduction in dimensionality, and the lower the dimension, the more stable an impurity state. This result is probably not relevant to manganese, where there are five relevant orbitals with different spatial symmetries that couple to a paramagnetic impurity in different ways.

A problem that we have not tackled but do consider interesting is that of the classical impurity problem. How do the spins in the classical limit of the Heisenberg Hamiltonian arrange themselves about an impurity in the frustrated face-centred cubic lattice? The act that spins infinitely far from the impurity are affected makes this a hard problem. We conjecture that the solution has the cubic arrangement at infinity.

Appendix. The MSDW Green function

The system has a cubic periodic symmetry together with four atoms per unit cell and two spin degrees of freedom. The Green function is therefore an 8×8 matrix which

is a function of a reciprocal lattice vector, k, defined in a cubic Brillouin zone.

We define two types of 4×4 matrices to represent the sublattice degrees of freedom:

$$
\gamma_1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}
\quad
\gamma_2 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}
\quad
\gamma_3 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}
$$

$$\text{(A1)}$$

$$
\alpha_1 = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}
\quad
\alpha_2 = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}
\quad
\alpha_3 = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}
\quad \text{(A2)}
$$

together with $\gamma_0 = \alpha_0 = 1$ the identity. The algebra that α_i, γ_i satisfy is interchangeable under $\alpha \leftrightarrow \gamma$ and so we may choose a basis where either the α_i or γ_i are diagonal.

We define the Green function in terms of

$$
A_0 = A_k = z - s_{k0}\alpha_0 - s_{k1}\alpha_1 - s_{k2}\alpha_2 - s_{k3}\alpha_3 \tag{A3}
$$

with the 'structure factors', s_{ki}, which in terms of the paramagnetic energy $\varepsilon(q)$ satisfy

$$
\begin{aligned}
s_{k0} &= \tfrac{1}{4}[\varepsilon(q) + \varepsilon(q + Q_1) + \varepsilon(q + Q_2) + \varepsilon(q + Q_3)] \\
s_{k1} &= \tfrac{1}{4}[\varepsilon(q) + \varepsilon(q + Q_1) - \varepsilon(q + Q_2) - \varepsilon(q + Q_3)] \\
s_{k2} &= \tfrac{1}{4}[\varepsilon(q) - \varepsilon(q + Q_1) + \varepsilon(q + Q_2) - \varepsilon(q + Q_3)] \\
s_{k3} &= \tfrac{1}{4}[\varepsilon(q) - \varepsilon(q + Q_1) - \varepsilon(q + Q_2) + \varepsilon(q + Q_3)].
\end{aligned}
\tag{A4}
$$

The Green function is

$$
\begin{aligned}
G_k(z) = [1/\Delta_k(z)]|A_1 A_2 A_3 &- g_1^2 A_1 - g_2^2 A_2 - g_3^2 A_3 \\
&+ [g_1^2 A_2 A_3 - g_1 g^2 + i g_2 g_3 (A_3 - A_2)]\gamma_1 \sigma_1 \\
&+ [g_2^2 A_3 A_1 - g_2 g^2 + i g_3 g_1 (A_1 - A_3)]\gamma_2 \sigma_2 \\
&+ [g_3^2 A_1 A_2 - g_3 g^2 + i g_1 g_2 (A_2 - A_1)]\gamma_3 \sigma_3|
\end{aligned}
\tag{A5}
$$

where $A_i = \gamma_i A_0 \gamma_i = A_{k+Q_i}$ and the determinant, $\Delta_k(z)$, satisfies

$$
\begin{aligned}
\Delta_k(z) = A_0 A_1 A_2 A_3 &- g_1^2 (A_0 A_1 + A_2 A_3) - g_2^2 (A_0 A_2 + A_3 A_1) \\
&- g_1^2 (A_0 A_3 + A_1 A_2)
\end{aligned}
\tag{A6}
$$

$$
\begin{aligned}
\Delta_k(z) = (z - s_{k0})^4 &- 2(c_1 + g^2)(z - s_{k0})^2 - 8 c_3 (z - s_{k0}) \\
&+ (c_1 + g^2)^2 - 4(c_2 + \lambda_k^2 g^2)
\end{aligned}
\tag{A7}
$$

$$
c_1 = s_{k1}^2 + s_{k2}^2 + s_{k3}^2 \tag{A8}
$$

$$
c_2 = s_{k2}^2 s_{k3}^2 + s_{k3}^2 s_{k1}^2 + s_{k1}^2 s_{k2}^2 \tag{A9}
$$

$$c_3 = s_{k1}s_{k2}s_{k3} \tag{A10}$$

and the contribution which breaks the MSDW symmetry

$$g^2\lambda_k^2 = g_1^2 s_{k1}^2 + g_2^2 s_{k2}^2 + g_3^2 s_{k3}^2. \tag{A11}$$

It is straightforward to see that the determinant, $\Delta_k(z)$, vanishes when z coincides with an eigenvalue and direct differentiation leads to the results (4.10), which underpin § 4.

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