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Spin impurities in non-collinear antiferromagnets with Mn_3Pt as an example

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Abstract. We develop a linearized theory for the classical Heisenberg model, which allows us to approximately solve for the local distortion of spins around an impurity in a non-collinear antiferromagnet. Provided that the ratio of disturbed to undisturbed bonds is small, the theory should be applicable. The theory is particularly useful when alloying lifts the degeneracy often found in non-collinear magnets. We look at the cases of γ-Mn alloys in general, and Mn_3Pt in particular. We can successfully predict the experimentally observed phase transitions caused by alloying in these materials, providing further evidence for the exotic 'hedgehog' phase.

1. Introduction

Geometrically frustrated lattices provide some of the most sophisticated and interesting types of antiferromagnet. The fundamental cause is that the frustration forces some of the bonds to gain less than their optimum energy. There is usually a variety of ways in which this loss can be spread amongst the different bonds, often leading to degenerate ground states at leading order. This degeneracy is usually lifted on a smaller energy scale than that promoting the magnetism, and this in turn leads to the possibility of *phase transitions* between different magnetic ground states caused by fairly small changes in the magnetic interactions. In particular, alloying a frustrated antiferromagnet can lead to such a phase transition at quite modest doping.

In this paper we will primarily be concerned with lattices related to the face-centred-cubic lattice. γ-manganese is the face-centred-cubic variety of Mn and Mn_3Pt orders into a Cu_3Au structure, which finds the atoms on a face-centred-cubic lattice with one of the four natural sublattices substitutionally replacing Mn with platinum. Both of these systems show a variety of antiferromagnetic phases; γ-Mn shows four experimentally [1], and Mn_3Pt has two [2]. Many different theoretical explanations have been presented for the cause of these phase transitions [3], and we have recently proposed the alloy disorder as being responsible [4]. The current paper develops our description for the effect of alloying on the antiferromagnetism, and yields a prediction for which type of antiferromagnetic order is promoted by the different possible alloy disorderings.

In these frustrated antiferromagnets the different phases observed can be explained in terms of the several ways in which the loss in bonding energy can be distributed. Since the bonding energy is usually related to the relative angle between the spins, a redistribution of bonding energy corresponds to a change in the local distribution of neighbouring spin orientations. There are several possibilities: firstly, a certain fraction of the bonds can be selected and made completely antiparallel. This leads to a collinear phase, which is

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theoretically preferred by both quantum mechanics [5] and magnetoelasticity theory [6]. Secondly, the loss in bonding energy can be shared equally between all bonds, and then we find a non-collinear phase with the spins all oriented at a fixed angle with respect to their neighbours. Thirdly, there can be a compromise solution with some bonds sharing the loss and others remaining unfrustrated. Whether or not these different possibilities exist is case dependent, and each particular geometry should be considered independently. The more exotic phases with non-collinear spins may be stabilized by both non-linear spin interactions [7] and Fermi surface effects in itinerant systems [8], although to our knowledge there is no convincing experimental system that typifies these explanations. As we shall see, paramagnetic impurities doped into the magnet prefer non-collinear states.

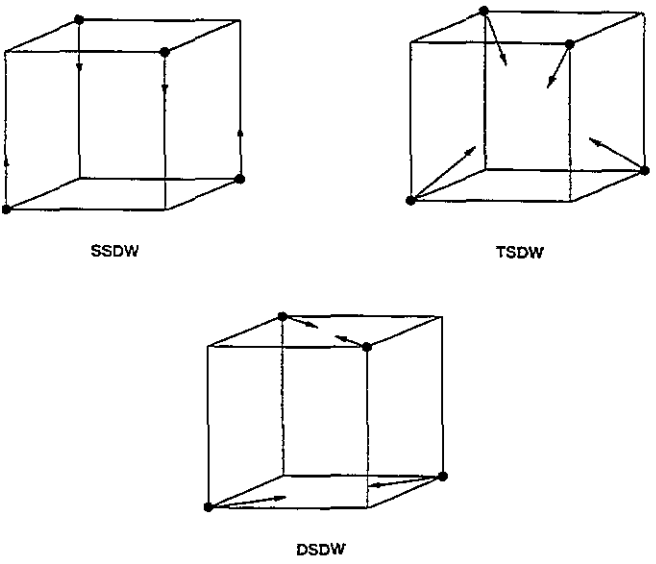

Figure 1. The spin structures of the three highly symmetric ground states of the Heisenberg model on the face-centred-cubic lattice. This type of antiferromagnetism, which is built up from orthogonal components that have parallel planes of atoms alternating in orientation as one travels in a direction perpendicular to the planes, is type I. The collinear phase is called SSDW, the coplanar phase DSDW and the three-dimensional cubic phase is called TSDW.

γ-Mn has type-I antiferromagnetism, which means that the magnetic Bragg spots appear half way between nuclear Bragg spots along each of the three Cartesian directions. This type of magnetism can best be described in terms of the collinear state for which we find alternating planes of up and down spins as we travel parallel to one of the three Cartesian directions (see figure 1). This state finds precisely one third of the nearest neighbours parallel and hence frustrated. However, there is a large degeneracy to leading order, which can be described in terms of a superposition of the three possible collinear states. Equal amounts of all three possibilities shares the frustration equally between all bonds, and there are also phases for which there is a compromise, for example when we superimpose two collinear states. On a practical level, the magnetic Bragg intensity does not vary much in magnitude, although at a phase transition the Bragg intensity would be shifted from one Bragg spot to another that is symmetrically related, as a second or third collinear component is introduced. In a multi-domain sample one sees very little effect from such a phase

transition, since different domains compensate each other with equal intensity transferred out as transferred in. For the current investigation, it is important to realise that as more paramagnetic impurities are doped into the Mn, the ground state becomes progressively more non-collinear. For almost pure Mn we have a collinear phase, which transforms eventually to the equal-bond phase via a sequence of compromise phases [1].

Mn_3Pt shows quite different behaviour, involving a transfer of magnetic scattering between symmetrically unrelated Bragg spots. In face-centred-cubic nomenclature, the Bragg spots shift from being type I to type III, although the particular phases involved are quite unrelated to their face-centred-cubic counterparts. This phase transition occurs for the stoichiometric alloy as a function of temperature, but a brief look at the phase diagram [2], shows that the transition is strongly affected by alloying. The initial problem of magnetic structure determination has proved to be non-trivial, with the original proposal [2] being recently challenged by one of the present authors [9]. In the new description the phase transition involves a reorientation of the spins between two phases that have identical angles between all the nearest-neighbour spins, and are only different at next-nearest neighbours (see figure 3). One phase has three possible orientations for the spins, much akin to the triangular lattice phase, while the new phase is predicted to have *twelve* different possible spin orientations, which has led to the name 'hedgehog' phase being proposed. In this article we will predict this change of phase observed with alloying, giving further evidence that the proposed 'hedgehog' phase is correct.

In section 2 we will introduce our approximation scheme for solving for magnetic impurities in non-collinear magnets. In section 3 we apply our theory to the two systems of experimental interest and in section 4 we conclude.

2. The linearized Heisenberg model

We are dealing with the most elementary description of magnetism, since the non-collinear nature of the states is significantly difficult to deal with: we work with the classical limit of the Heisenberg model. We use the representation:

$$H_0 = \frac{1}{2}\sum_{ij} J_{ij}\hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j + \frac{1}{2}\sum_i \lambda_i\left(\hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_i - 1\right) \tag{2.1a}$$

where the second term constitutes Lagrange multipliers which will be used to constrain the lengths of the spins to unity. This Hamiltonian can be minimized directly:

$$\frac{\partial H_0}{\partial \hat{\boldsymbol{S}}_i} = \sum_j J_{ij}\hat{\boldsymbol{S}}_j + \lambda_i \hat{\boldsymbol{S}}_i = \boldsymbol{0} \tag{2.1b}$$

from which we can deduce a ground-state solution, $\hat{\boldsymbol{S}}_i^0$ say, which has energy

$$E_0 = -\frac{1}{2}\sum_i \lambda_i^0 \tag{2.1c}$$

in terms of the Lagrange multipliers. In principle we would have liked to have solved this Hamiltonian for systems that involve periodic choices of coupling constants J_{ij} that have local disturbances, such as missing bonds corresponding to paramagnetic impurities. In practice this type of problem is prohibitively difficult in all but the most elementary cases

[10], and so in this article we will discuss a linearization scheme from which we can deduce the likely physics.

We include an infinitesimal interaction to some external field and solve the resulting problem perturbatively. This is *not* the problem that we truly want to solve, since finite changes would be more physically appropriate. We have introduced a parameter, δ, to describe this linearization procedure. The physical problem involves $\delta = 1$, and the linearized problem that we actually solve involves $\delta \mapsto 0$. We elect to couple our external field to several of the existing spins, with

$$H_1 = \delta \sum_i \kappa_i \hat{\boldsymbol{T}} \cdot \hat{\boldsymbol{S}}_i \tag{2.2a}$$

where δ is this infinitesimal coupling constant, κ_i measures the strengths with which the different spins feel the disturbance and $\hat{\boldsymbol{T}}$ is the orientation of the external field. In the presence of this 'source' term the ground state satisfies

$$\frac{\partial H}{\partial \hat{\boldsymbol{S}}_i} = \sum_j J_{ij} \hat{\boldsymbol{S}}_j + \lambda_i \hat{\boldsymbol{S}}_i + \delta \kappa_i \hat{\boldsymbol{T}} = \boldsymbol{0} \tag{2.2b}$$

with energy

$$E = \frac{\delta}{2} \sum_i \kappa_i \hat{\boldsymbol{T}} \cdot \hat{\boldsymbol{S}}_i - \frac{1}{2} \sum_i \lambda_i. \tag{2.2c}$$

This constitutes the problem that we will attempt to solve. It is useful to realize that we are dealing with a fairly general Hamiltonian, which includes, as special cases, both a substitutional missing spin and an additional interstitial spin. To omit a spin we can orient $\hat{\boldsymbol{T}}$ antiparallel to the offending spin, couple it in precisely the same way as the existing spin, and then choose $\delta = 1$ to 'cancel' out the existing spin. In order to add a new interstitial spin, we can couple $\hat{\boldsymbol{T}}$ to the relevant neighbouring spins and then optimize the resulting solution over the orientation of $\hat{\boldsymbol{T}}$, effectively allowing the additional spin to choose its orientation.

Since we have been unable to solve our problem exactly, we have resorted to a perturbative expansion. We are intending to work with small distortions around a known solution and so we reformulate the problem in terms of the change with respect to some reference solution: that of the original Hamiltonian H_0. We set:

$$\hat{\boldsymbol{S}}_i = \hat{\boldsymbol{S}}_i^0 + \delta \boldsymbol{S}_i \qquad \lambda_i = \lambda_i^0 + \delta \lambda_i \tag{2.3}$$

where the additional contributions will eventually become linear in the parameter δ. The notation we use will involve Δ to indicate other than linear dependence in δ. In terms of these small displacements the constraints become $2\hat{\boldsymbol{S}}_i^0 \cdot \delta \boldsymbol{S}_i + \delta \boldsymbol{S}_i \cdot \delta \boldsymbol{S}_i = 0$. Inserting this assumption into the governing equations and using the constraints and known solution we obtain

$$\lambda_i^0 \delta \boldsymbol{S}_i + \sum_j J_{ij} \left[\delta \boldsymbol{S}_j - (\delta \boldsymbol{S}_j \cdot \hat{\boldsymbol{S}}_i^0) \hat{\boldsymbol{S}}_i^0 \right] + \delta \kappa_i \left[\hat{\boldsymbol{T}} - (\hat{\boldsymbol{T}} \cdot \hat{\boldsymbol{S}}_i^0) \hat{\boldsymbol{S}}_i^0 \right]$$
$$= -\delta \lambda_i \delta \boldsymbol{S}_i - \tfrac{1}{2} (\lambda_i^0 + \delta \lambda_i) \delta \boldsymbol{S}_i \cdot \delta \boldsymbol{S}_i \hat{\boldsymbol{S}}_i^0 \tag{2.4a}$$

with energy

$$\Delta E = \delta \sum_i \kappa_i \hat{\boldsymbol{T}} \cdot \hat{\boldsymbol{S}}_i^0 + \frac{\delta}{2} \sum_i \kappa_i \hat{\boldsymbol{T}} \cdot \delta \boldsymbol{S}_i - \frac{1}{4} \sum_i \delta\lambda_i \delta \boldsymbol{S}_i \cdot \delta \boldsymbol{S}_i. \tag{2.4b}$$

This result is exact and enables us to deduce the leading order perturbative correction directly: the right-hand side of (2.4*a*) can be neglected as can the final term in the energy (2.4*b*). Although we will not be concerned with the result here, if we wanted to proceed with the perturbation theory, we would also need the change in Lagrange multipliers

$$\delta\lambda_i = -\sum_j J_{ij} \hat{\boldsymbol{S}}_i^0 \cdot \delta \boldsymbol{S}_j - \delta\kappa_i \hat{\boldsymbol{S}}_i^0 \cdot \hat{\boldsymbol{T}} + \tfrac{1}{2}(\lambda_i^0 + \delta\lambda_i)\delta \boldsymbol{S}_i \cdot \delta \boldsymbol{S}_i \tag{2.4c}$$

to complete the theory.

One of the more interesting issues is that of how several impurities interact with each other. Unfortunately, in the present analysis there is no point in including several impurities, because to the order in which we solve the problem different impurities do not interact. The analysis is effectively identical when there are several impurities; the only difference being an additional label on the vector, $\hat{\boldsymbol{T}}$, and coupling constant, κ, to label the impurity type. In this article we will be concerned only with the leading order effect of which type of ground state a particular type of impurity prefers, and we leave the effects of correlations between impurities to later. Subject to this fact, our choice of Hamiltonian then becomes effectively unique.

In order to proceed further we have been forced into linearizing the problem. In practice, this amounts to allowing each spin the freedom to rotate through a small angle picking up an additional small component perpendicular to its original direction. To describe this freedom, we need to choose a local two-dimensional basis perpendicular to the original spin direction; one for each site. If we elect to use

$$\hat{\boldsymbol{X}}_i = \left[\hat{\boldsymbol{T}} - \left(\hat{\boldsymbol{T}} \cdot \hat{\boldsymbol{S}}_i^0\right) \hat{\boldsymbol{S}}_i^0\right] / \mid \hat{\boldsymbol{S}}_i^0 \times \hat{\boldsymbol{T}} \mid \tag{2.5a}$$

$$\hat{\boldsymbol{Y}}_i = \left(\hat{\boldsymbol{S}}_i^0 \times \hat{\boldsymbol{T}}\right) / \mid \hat{\boldsymbol{S}}_i^0 \times \hat{\boldsymbol{T}} \mid \tag{2.5b}$$

for atoms which are not originally parallel to $\hat{\boldsymbol{T}}$, and choose $\hat{\boldsymbol{X}}$ and $\hat{\boldsymbol{Y}}$ arbitrarily if $\hat{\boldsymbol{S}}_i^0$ is parallel to $\hat{\boldsymbol{T}}$, then in terms of

$$\hat{\boldsymbol{T}} \cdot \hat{\boldsymbol{S}}_i^0 = \cos\phi_i \qquad \phi_i \in (0, \pi) \tag{2.5c}$$

and

$$\delta \boldsymbol{S}_i = -\delta \left(x_i \hat{\boldsymbol{X}}_i + y_i \hat{\boldsymbol{Y}}_i\right) \tag{2.5d}$$

to leading order

$$\lambda_i^0 x_i + \sum_j J_{ij} \left(\hat{\boldsymbol{X}}_i \cdot \hat{\boldsymbol{X}}_j x_j + \hat{\boldsymbol{X}}_i \cdot \hat{\boldsymbol{Y}}_j y_j\right) = \kappa_i \sin\phi_i \tag{2.6a}$$

$$\lambda_i^0 y_i + \sum_j J_{ij} \left(\hat{\boldsymbol{Y}}_i \cdot \hat{\boldsymbol{Y}}_j y_j + \hat{\boldsymbol{Y}}_i \cdot \hat{\boldsymbol{X}}_j x_j\right) = 0 \tag{2.6b}$$

$$\Delta E = \delta \sum_i \kappa_i \hat{\boldsymbol{T}} \cdot \hat{\boldsymbol{S}}_i^0 - \frac{\delta^2}{2} \sum_i \kappa_i \sin\phi_i x_i \tag{2.6c}$$

where we now recognize a linear problem for finding x_i and y_i. The coupling between the different components depends strongly on the allowed local rotational freedom, and for our particular chosen representation we find that

$$\hat{X}_i \cdot \hat{X}_j = (1 - \cos^2\phi_i - \cos^2\phi_j + \cos\phi_i \cos\phi_j \hat{S}_i^0 \cdot \hat{S}_j^0)/\sin\phi_i \sin\phi_j \tag{2.7a}$$

$$\hat{X}_j \cdot \hat{Y}_i = \left[\cos\phi_j \hat{T} \cdot \left(\hat{S}_i^0 \times \hat{S}_j^0\right)\right]/\sin\phi_i \sin\phi_j \tag{2.7b}$$

$$\hat{Y}_i \cdot \hat{Y}_j = \left(\hat{S}_i^0 \cdot \hat{S}_j^0 - \cos\phi_i \cos\phi_j\right)/\sin\phi_i \sin\phi_j. \tag{2.7c}$$

The first observation we make is that for coplanar distortions (namely $\hat{T}$ in the plane of a coplanar spin state), we have no need of the y_i because the fluctuations perpendicular to the plane do not couple to the fluctuations in the plane. Secondly, if the impurity spin $\hat{T}$ is orthogonal to a coplanar spin state, then all the $\cos\phi_i$ vanish and so again we have no need of the y_i. We should point out that on a practical level this real-space formulation is not greatly useful, and we have only used it on finite clusters as an independent check for our analysis.

The problems that we have tackled have involved a periodic undistorted ground state, and the extraction of this underlying periodicity makes the problem ultimately tractable. There are still many antiferromagnetic sublattices in our chosen materials, four for γ-Mn and either four or twenty-four for Mn_3Pt. The technical problem then reduces to that of matrices over sublattice degrees of freedom, α say, combined with the reciprocal space degrees of freedom originating from the *antiferromagnetic* periodicity, which are diagonal. In terms of the Bloch transforms

$$(x, y)_{k\alpha} = \sum_l \exp[i\boldsymbol{k} \cdot (\boldsymbol{R}_l + \boldsymbol{c}_\alpha)]\,(x, y)_{l\alpha} \tag{2.8a}$$

$$K_{k\alpha} = \sum_l \exp[i\boldsymbol{k} \cdot (\boldsymbol{R}_l + \boldsymbol{c}_\alpha)]\,\kappa_{l\alpha} \sin\phi_\alpha \tag{2.8b}$$

$$\epsilon_{k\alpha\alpha'} = \delta_{\alpha\alpha'}\lambda_\alpha^0 + \frac{1}{N}\sum_{ll'} \exp[i\boldsymbol{k} \cdot (\boldsymbol{R}_l + \boldsymbol{c}_\alpha - \boldsymbol{R}_{l'} + \boldsymbol{c}_{\alpha'})]\,J_{l\alpha l'\alpha'} \tag{2.8c}$$

where $\boldsymbol{c}_\alpha$ are the positions of the atoms in the unit cell, we eventually derive

$$\sum_{\alpha'} \hat{X}_\alpha \cdot \hat{X}_{\alpha'} \epsilon_{k\alpha\alpha'} x_{k\alpha'} + \sum_{\alpha'} \hat{X}_\alpha \cdot \hat{Y}_{\alpha'} \epsilon_{k\alpha\alpha'} y_{k\alpha'} = K_{k\alpha} \tag{2.9a}$$

$$\sum_{\alpha'} \hat{Y}_\alpha \cdot \hat{X}_{\alpha'} \epsilon_{k\alpha\alpha'} x_{k\alpha'} + \sum_{\alpha'} \hat{Y}_\alpha \cdot \hat{Y}_{\alpha'} \epsilon_{k\alpha\alpha'} y_{k\alpha'} = 0 \tag{2.9b}$$

$$\Delta E = \delta E + \delta^2 E = \delta \sum_i \kappa_i \hat{T} \cdot \hat{S}_i^0 - \frac{\delta^2}{2}\frac{1}{N}\sum_{k\alpha} K_{k\alpha}^* x_{k\alpha} \tag{2.9c}$$

for the induced spin distortion, $x_{k\alpha}$ $y_{k\alpha}$, and its energy, ΔE. The final theoretical task is to try to use the theory to make experimental predictions: this involves finding the local spin distortion. The natural experimental probe for spin distortions surrounding an impurity is magnetic diffuse scattering [11]. The diffuse scattering profiles from our impurities can be deduced from the local spin deformation δS_k, which is elementary to deduce:

$$\delta S_k = \delta\left(\hat{T} - \sum_\alpha \left(x_{k\alpha}\hat{X}_\alpha + y_{k\alpha}\hat{Y}_\alpha\right)\right). \tag{2.10}$$

Although the actual observable scattering is restricted to the component perpendicular to the momentum transfer direction, and the range of the scattering is limited by the local-moment form factor, we will ignore these complications and restrict our attention to the square modulus of the spin density, $|\delta S_k|^2$. The remainder of this article is devoted to gaining an insight into the predictions of this simple theory. In the rest of this section we will deal with some general aspects, and in the next section we will look at our particular experimental systems.

The linear term in the energy is dominant if it exists. For the case of a missing spin, the orientation of the perturbation $\hat{T}$ is necessarily anti-parallel to one of the spins, $\hat{S}_0^0$ say, and the coupling is via the original bonding, namely $K_i = J_{0i}$. We find that $\delta E = -\delta \sum_i J_{0i} \hat{S}_0^0 \cdot \hat{S}_i^0 = \delta\lambda_0^0$ and simply measures the loss in energy from the omitted spin. For the case of an additional spin, the vector $\hat{T}$ represents the orientation of this additional spin and is free to rotate towards its preferred direction. The linear term then chooses this orientation so as to be antiparallel to the local field

$$\boldsymbol{F} = \sum_i \kappa_i \hat{S}_i^0 \tag{2.11}$$

and yields a contribution to the energy from the additional spin originating from its interaction with this local field. The quadratic term in the energy originates from the *polarization* of the surrounding spins by the local impurity and constitutes the effect that we are predominantly interested in.

It is quite common for the systems in which we are interested that an additional spin is placed at a local 'dead spot', namely a point for which the local field $\boldsymbol{F}$ vanishes. The reason for this is that the substitutional site is usually one of high symmetry, and if there are an equal number of bonds to *all* of the possible sublattices (or at least a subset with a helpful symmetry group), then the local field will cancel in a pure antiferromagnet. For this situation it is the *polarizability* of the spin state that will select the preferred spin orientation for the moment impurity, and the impurity moment will be held in place much more weakly than usual.

We ought to explain the limitations of our linearisation procedure. In the search for a small parameter with which to justify the theory, the natural choice is J/λ^0, where λ^0 is the local field holding a spin in place for the undistorted spin state. The basic idea is that λ^0/J is the excess number of anti-parallel neighbours and corresponds to the number of bonds that a particular spin feels. If a spin is removed, then its neighbours will feel a change from only one of these neighbours, hence our suggestion for the small parameter. In fact this result is fundamentally correct, although the explanation is bogus. Thinking in terms of the linear response to the distortion, the dispersion does scale with λ^0 on average, but there are the low-energy Goldstone modes to contend with, which would allow the distortion to extend over arbitrarily large distances. The local symmetries of the distortions that we consider preclude coupling to three long-range modes, and so the distortions decay very fast and there are usually only one or two relevant neighbours controlling the spread of the distortion for any particular spin, thereby justifying the assertion.

There is one possible disaster that can overcome this theory, however: *spontaneous symmetry breaking in the distortion.* We have presumed that the dominant response to the impurity will come from the component parallel to the impurity: this is not necessarily the case. It is possible for the response to be dominated by a distortion *perpendicular* to the original spin state with magnitude $\sqrt{\delta}$. This type of behaviour can occur when the original ground state is heavily degenerate, and shows up as additional solutions to the original linear equations (2.9). This type of solution is the manner in which the theory indicates that

the 'wrong' ground state has been chosen for the reference state, and can be interpreted as the distortion changing the ground state. This type of behaviour is relevant to Kagome or perchlorate lattice systems, which have local degeneracy, but will not be directly relevant to us, *provided* that we select the correct ground-state to calculate with. We could preclude such problems with the inclusion of small terms to stabilize the chosen ground state, by arguing that although the *local* energy gain outweighs the degeneracy-breaking energy scale, the only changes in the ground-state for our systems involve *long-range* distortion which would not be energetically favourable. For the Kagome case, however, even this would be physically unreasonable, since there are *local* changes of ground state which involve a negligible change in the weak degeneracy breaking interactions, but locally optimize the polarization around the impurity. For our linearization scheme this range argument is bogus: any small degeneracy-breaking inclusion would *necessarily* dominate changes in ground state on *all* length scales, since even a small inclusion is larger than an *infinitesimal* distortion.

In fact, our limiting procedure has 'hidden' the physics. For *finite* changes of spin magnitudes, the possibility of spontaneous symmetry breaking reemerges, but one must then consider the balance between the local energy gain and the degeneracy-breaking field at longer distance. Our limiting procedure does not permit this comparison, because we would have had to include a limiting degeneracy-breaking interaction to maintain the balance. This particular problem has been considered before [10], and is not directly relevant to the rather coarse energetic arguments that we are dealing with here.

The fundamental physical point is that although in our simple models there is degeneracy, in real physical systems this degeneracy is lifted. We have omitted the physics that lifts the degeneracy. A single isolated impurity cannot really overcome this macroscopic interaction. If we consider a system with a phase transition, then two distinct phases are independently stable in different regimes, and we can consider impurities in both phases. If the actual doping itself *causes* the phase transition, then the energy difference between the two impurities in the two phases will pick this up. Problems emerge when we look at the *details* of the phase transition: if we get quite close to the phase transition, then locally around the impurity a small region of the incoming phase can become trapped. The system then benefits from the new phase locally and from the old phase at longer range. In practice, the phase transition becomes a 'mess', and occurs at a concentration which is quite difficult to predict, but the fundamental energetics are controlled by a comparison between the two impurities in the two phases. We will presume that the degeneracy-breaking interaction is strong enough to eliminate spontaneous orthogonal distortion and look to energetic predictions for first-order phase transitions only.

3. Predictions for Mn alloys

In order to set the scene, we should initially study the simplest variants of our model in order to check the internal consistency and validity of our results. Several features are peculiar to non-collinear ground states: if we have a collinear ground state, then the omission of a spin has absolutely no polarization effect on the spin configuration predicted by our perturbation theory. This result originates from the fact that the local perturbation is parallel to the affected spins and so is attempting to alter their length, which is not permitted by the spin constraints. For a *finite* perturbation it is possible for a perpendicular distortion to *self-trap* [12]. This behaviour is not permitted by our linearization, which prohibits such a non-linear response. For an impurity addition, on the other hand, there is no polarization if

there is a local field $\boldsymbol{F}$ for the same reason, but if the impurity spin is added at a 'dead spot' then there is a polarization effect. The impurity spin orients itself perpendicular to the collinear spin direction and induces a short-range perpendicular distortion. At first sight one might have expected a long-range response to the impurity, because of the low-energy 'Goldstone modes', but because we are at a 'dead spot' there is no coupling to the underlying antiferromagnetism and the distortion necessarily decays. If we arbitrarily include a local impurity that is not at a 'dead spot', but has an orientation other than the local field direction, then the quadratic response of the system is divergent indicating that there is another ground state with a stronger *linear* response. For non-collinear states there is almost always some form of polarization originating from a local impurity, because usually not all of the affected spins are parallel to the impurity and so some of the neighbours can reorient and make use of the impurity.

Perhaps the simplest system to study is the square lattice Neel state. Due to collinearity, the only non-trivial polarization effects originate from impurities added at 'dead spots'. A spin sitting centrally above a 'square', which couples uniformly to its four neighbours, yields a polarization energy of $\delta^2 E = -0.363\,38\delta^2\kappa^2/J$, where κ is the coupling constant. Since there are four bonds, for similar magnitude coupling constants the system only manages about $\frac{1}{11}$ of the available bonding. This form might be anticipated from the fact that the competition is between one additional bond versus four original bonds (namely $\lambda_\alpha^0 = 4J$) and second-order perturbation theory, although the magnitude is rather more difficult to guess. The scale of the effect is the same order as the antiferromagnetism, and so for the more interesting frustrated antiferromagnets the disorder can lift any underlying degeneracy and predict the ground state.

Probably the simplest non-collinear system to study is the triangular lattice with its 120° ground state. This particular system has only a discrete chiral degeneracy and local defects are unable to effect a transition between the degenerate ground states. The example is instructive, however, because it suggests what we might expect from a general non-collinear spin state. If a particular spin is infinitesimally reduced in length, the nearest neighbours are able to rotate to compensate, because the local field they feel is at 120° to their direction. Although the moments are highly coordinated, with $Z = 6$, the frustration in the lattice ensures that only half of the bonds can be achieved in the ground state and so the stabilizing field is smaller than that of the square lattice (namely $\lambda_\alpha^0 = 3J$). The natural site for an impurity lies above the plane, connecting to a triangle of moments below. Once again we are sitting at a 'dead spot', and so the additional moment is free to rotate. The impurity spin orients itself perpendicular to the coplanar spin configuration and induces a polarization energy of $\delta^2 E = -0.5\kappa^2/J$, more than that for the square lattice. Considering the fact that there are now fewer bonds, this is a large difference. This difference can be attributed to two effects: firstly, the local field holding the spins in place is smaller; and secondly, the larger intrinsic coordination plays a role in extending the polarization further from the impurity. In other words, since we only need *three* neighbours to balance the local field and we have *six* to choose from, there is more opportunity for the deformation to spread. This argument is fairly general and quite central to an interpretation of these phenomena. The distortion in a frustrated antiferromagnet is usually stronger and longer range than that in a non-frustrated magnet. When we consider the reduction of the magnitude of a spin, however, the characteristics are quite different. The infinitesimal reduction yields a linear loss of $\delta E = 3\delta J$ from the local field and a polarization contribution of $\delta^2 E = -0.576\,08\delta^2 J$. This polarization energy comes from a surprisingly small region with the distortion decaying very fast. Unlike the previous case, where the distortion was perpendicular to the plane of moments, the distortion is now in the plane of moments. The fact that all the spins

are at 120° to each other now means that there is a loss of a factor of two in transmitting the coupling between spins and we would now need all six of the spins to compensate the local stabilizing field of three. Even worse, some of the spins are actually parallel to the imposed distortion and these spins find it more difficult to reorient, further reducing the polarization spread. Impurities composed of omitted spins polarize subject to the frustration, but impurity moments added at 'dead spots' can sometimes polarize effectively in a less frustrated way.

3.1. γ-manganese

γ-Mn alloys are a much studied example of a frustrated antiferromagnet [1, 13]. Their behaviour is characteristic of the physical phenomenon which instigated our study: phase transitions between different antiferromagnetic ground states. The classical Heisenberg model exhibits a host of degenerate ground states for the face-centred-cubic lattice, of which the most relevant three for us are depicted in figure 1 and are called the SSDW, DSDW and TSDW states (standing for single, double and treble spin density waves). The most sensible explanation for the observed experimental phase diagram of γ-Mn_xNi_{1-x} [1] with nickel doping is that of a sequence of phase transitions between the SSDW state for undoped γ-Mn, through an intermediate DSDW state, eventually reaching a cubic TSDW state at about a quarter doping. The dominant antiferromagnetic interaction is probably representable as nearest-neighbour Heisenberg-like and therefore the interaction which lifts the degeneracy is expected to have a smaller energy scale. Although many possible mechanisms for lifting this degeneracy have been proposed [13], we believe that the role of the alloy disorder is central to an explanation for the phase diagram. The present model makes predictions for the amount of energy available to each of the different states from isolated impurities and thereby enables a comparison between the different states to be made.

Before we move on to a comparison with the experiments, which involve the consideration of substitutional impurities, firstly we will consider the role of interstitial impurities. This is not as absurd as might at first be considered, if one remembers that adding a small quantity of interstitial carbon into the alloys alters the phase diagram considerably [14]. There are two natural sites to add an interstitial impurity: firstly there is a tetrahedral site in the centre of a tetrahedron of Mn atoms and secondly there is an octahedral site with six nearest neighbours.

Tetrahedral interstitials lie at 'dead spots'. The additional spin tries to align itself orthogonal to as many existing spins as it can. For the case of the SSDW and DSDW there is a direction that is orthogonal to all the collinear or coplanar spins respectively, and impurities oriented in this direction yield a polarization energy of $\delta^2 E = -0.5\kappa^2/J$. For the TSDW state, however, all three spin dimensions are used in the ground state and there is no preferred direction for the impurity. Whatever the orientation of the impurity, the polarization energy is: $\delta^2 E = -0.33\,333\kappa^2/J$ for the TSDW state. This type of impurity prefers a spin state employing a low number of spin dimensions. This basic result appears to be true for *all* 'dead-spot' impurities, which like to orient anti-parallel to existing spins and therefore prefer an unused spin direction.

Octahedral interstitials do not lie at 'dead spots', since they only neighbour three out of the four natural antiferromagnetic sublattices. The local field $\boldsymbol{F} = -2\kappa\hat{\boldsymbol{S}}_\alpha^0$ for the spin to which the impurity is not a neighbour. The linear contribution does not break the degeneracy and yields a contribution of $-2\delta\kappa$ to each state, when the impurity is aligned parallel to the sublattice that it does not neighbour. The polarization contribution does lift the degeneracy, however, and yields 0, $-0.363\,38\kappa^2/J$ and $-0.401\,26\kappa^2/J$ for the SSDW, DSDW and TSDW states respectively. The SSDW cannot benefit because it is collinear, and the TSDW is the

best choice because it is the 'most' non-collinear state. It is possible (but unlikely) that octahedrally coordinated carbon impurities might explain the observed contraction of the Mn-Ni phase diagram under the action of a small amount of doped C. Once again, this result appears to be quite general and robust: when additional moments are included at sites that feel a local field, the states that are preferred are those with the highest degree of non-collinearity.

Now we turn to the experimentally relevant case of substitutional doping. In these alloys it is generally believed that the Ni impurities do not develop moments and behave as paramagnetic defects [13]. This leads us quite naturally to consider the predictions of our theory when a moment is infinitesimally reduced in magnitude. The linear contribution does not lift the degeneracy, yielding $\delta E = 4\delta J$ for each state. The polarization does lift the degeneracy quite strongly, however, yielding 0, $-0.726\,76J$ and $-0.909\,05J$ for the SSDW, DSDW and TSDW respectively. The collinear SSDW can gain nothing but the other two form a strong polarization cloud and recoup a sizeable fraction of the lost bonding energy, namely about a quarter. This calculation gives a satisfactory explanation for the phase transitions in γ-Mn alloys. In the collinear phase the paramagnetic impurities can recoup none of their lost bonding energy, whereas in the non-collinear phases a contribution proportional to the impurity concentration times the original antiferromagnetic energy is regained. Since the energy scale that lifts the degeneracy is likely to be a small fraction of the antiferromagnetic energy scale, a doping level of a quarter to cause the phase transition seems perfectly reasonable. Remember that the undoped alloy suffers a distortion of around 6% [15] and therefore the energy scale which lifts the degeneracy cannot be much smaller than J. Indeed, the magnetoelastic component must be of the order of J.

If we proceed to a more direct verification of the theory, then we arrive at some problems. The definitive experiment that analyses local spin configurations around alloy disorder is magnetic diffuse neutron scattering. The relevant experiments have been performed, and large peaks associated with non-collinear deformations around the alloy impurities have been observed [16]. The form of this scattering can be understood in terms of a minor reorientation of the surrounding shell of nearest neighbours. The present theory is for an isolated impurity, and the resulting distortion is much longer range. It is quite natural to ask whether there is still agreement with the diffuse scattering. It is elementary to deduce the reciprocal-space spin density from the local impurity and polarization cloud, and if we ignore the perpendicular nature of the scattering, which is sensible in the highly non-collinear states, then we can associate the diffuse scattering with the square of the magnitude of the spin density. We plot this quantity for the TSDW state in figure 2. Although there is obviously a large amount of scattering around the relevant Bragg spots, the form of this scattering is violently anisotropic and is dominantly found *away* from the line connecting the zone centre to the 'vanishing' magnetic Bragg spots. Although this result is rather disappointing, the fact that the experiments were performed when the doping fraction was about a quarter implies that each Mn atom has *several* neighbouring impurities on average, and so it is not that surprising that the longer-range aspects of the diffuse scattering are poorly described.

One quite general feature of the impurity spin density, appears to be the lack of scattering at points that correspond to the existing ground state. For our simple isolated impurity case the way in which this scattering is lost is via the point-group symmetry of the impurity deformation. Since the impurity has a lower point symmetry there are lines of zeroes induced in the scattering which are not expected to be found in a more highly doped alloy. The most we can hope to deduce from our calculations is the area of the Brillouin zone in which we might expect to find diffuse scattering and the plausible range of the scattering if

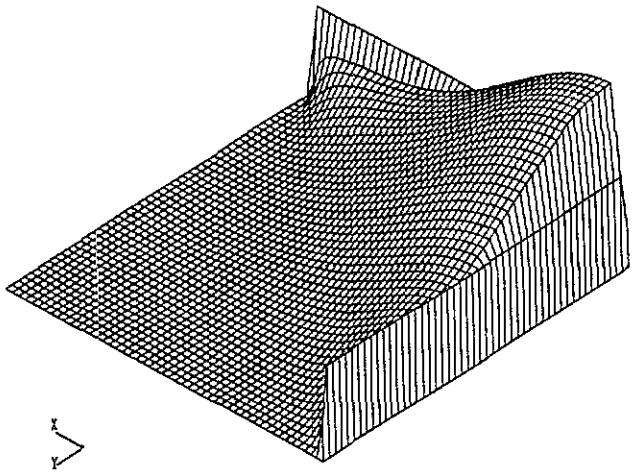

Figure 2. The magnetic diffuse scattering profile from the TSDW state with one of the atoms having an infinitesimally reduced moment. We have plotted the scattering from the xy plane using the point (0, 0, 1) as the origin. The observed scattering is peaked at the point (0, 0, 1), but bear in mind that there is also scattering around the (1, 0, 1) and (0, 1, 1) positions, which does not show up in this section because the symmetry of the scattering does not allow it to show up. The (1, 1, 1) point corresponds to a chemical Bragg spot and finds no observable scattering in its vicinity at all.

this is less than the impurity–impurity separation. For a very low concentration of impurities, we would hope for more.

3.2. Mn_3Pt

The compound Mn_3Pt is a rather less well studied but equally interesting antiferromagnetic material. The Cu_3Au chemical structure means that the basic unit of frustration is the triangle rather than the tetrahedron. The natural antiferromagnetism on a triangle is the at 120° phase, with all nearest-neighbour spins being 120° to each other, thereby achieving 50% of the available bonding shared equally between all the bonds.

Experimentally the system exhibits an antiferromagnetic phase transition between two distinct magnetic phases [2] as a function of both temperature and alloying. At the phase transition the Bragg spots move and the antiferromagnetic unit cell doubles in all directions, taking the original three magnetic atoms per unit cell up to twenty-four. Early theoretical descriptions were exotic [2], but recently one of the present authors has pointed out [9] that even if all nearest-neighbour spins are constrained to be at a relative angle of 120°, there is still residual ground-state degeneracy, including two phases with precisely the right symmetry to explain the low- and high-temperature Bragg spots. We depict these two phases in figure 3. The low-temperature or triangular phase is coplanar, while the high-temperature or hedgehog phase is truly three dimensional. There is as yet no convincing experimental evidence for the hedgehog phase, and one line of research is to try to provide predictions for possible experimental verification.

Unlike the γ-Mn system, where the disorder is huge, Mn_3Pt is a well-ordered stoichiometric alloy for which the experimentally induced compositional changes are small [2]. This material is therefore a much more suitable candidate for our theory. The experimental phase diagram indicates that there is a strong dependence of the phase boundary

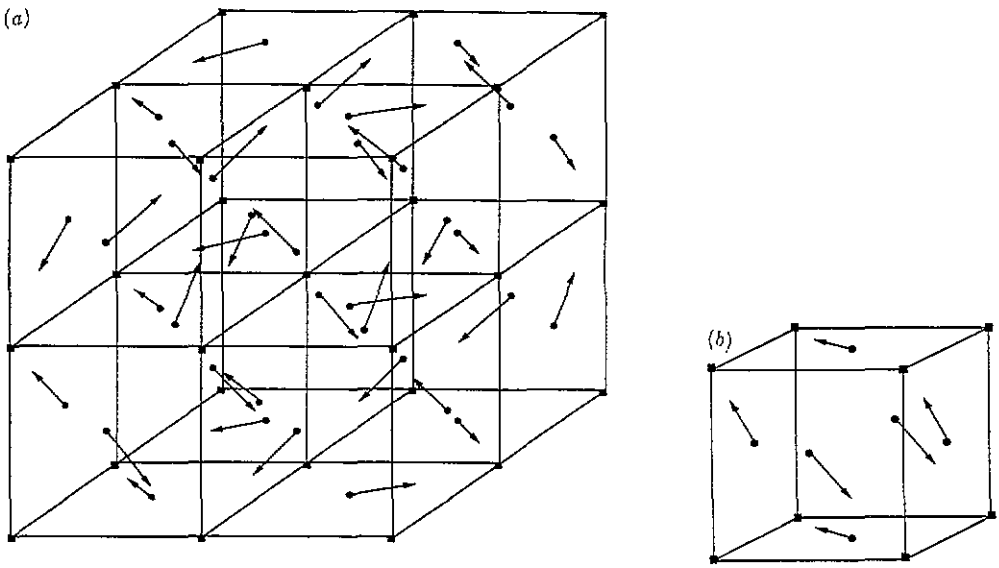

Figure 3. The spin structures of the two proposed ground states for Mn_3Pt. We have depicted a unit cell of each phase, with squares denoting Pt atoms and circles denoting Mn atoms. All spins are oriented to point from Mn atoms towards Pt atoms. Since the hedgehog phase (*a*) is rather tricky to picture, the reader might like to construct the spin orientations from the triangular phase unit cell (*b*). The hedgehog phase can be constructed using simultaneous translations of the triangular phase unit cell, combined with spin-space reflections in the plane perpendicular to the translation vector.

on the alloy concentration, with additional Mn stabilizing the triangular phase and with additional Pt stabilizing the hedgehog phase. The theory should predict this.

When we consider the substitution of a Pt atom by a Mn atom, there is a minor difference from previous examples: the bond lengths are equal and so the additional bonds will have a very similar strength to the underlying bonds. We will treat all bonds as being equal, namely $\kappa = J$. There are twelve nearest-neighbour Mn atoms at each Pt site. For both phases we are adding at a 'dead spot', with one each of the twelve hedgehog spin orientations and an equal mixture of the three sublattices for the triangular phase. The polarization contribution to the hedgehog phase is independent of the orientation of the impurity spin at $-0.708\,23\delta^2 J$. For the coplanar triangular phase the polarization depends strongly on the orientation of the impurity spin, ranging from $-0.616\,54\delta^2 J$ when the impurity is coplanar with the spin state to $-0.954\,93\delta^2 J$ when the spin is perpendicular to the spin state. The prediction is straightforward, additional Mn should favour the triangular phase, with an energy saving of about $\frac{1}{4}J$ per impurity. This is perfectly consistent with the experimental phase diagram. The physical explanation for the effect is identical to our previous examples, with the impurity at the 'dead spot' preferring the phase with a spin-space dimension that is unused.

When we consider the diffuse scattering profile for this triangular impurity, we find scattering very similar to that found for the γ-Mn system, as depicted in figure 4. The scattering is peaked around the existing Bragg spots and indicates a susceptibility towards

the TSDW state as doping is increased. This is as might be expected, since from the point of view of the local impurity, we may also consider this type of doping to be locally γ-Mn with more distant 'disorder' from the ordered Pt sites. In this picture the impurity reinstates the third dimension of the TSDW instead of eliminating it as was the case for the omission of a spin in the TSDW.

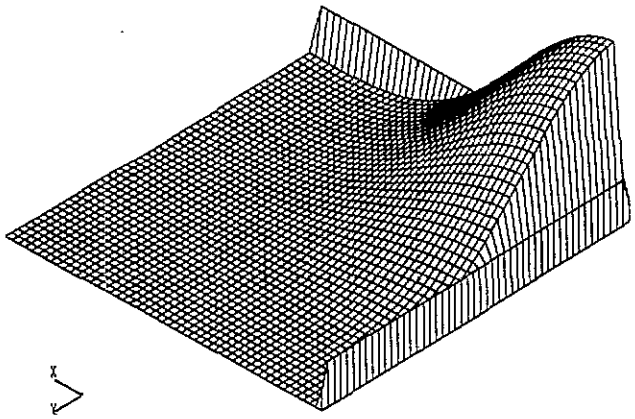

Figure 4. The magnetic diffuse scattering profile from the distortion surrounding a Mn atom substitutionally replacing a Pt atom in the triangular phase of Mn_3Pt. The form of the scattering and interpretation are identical to that for the TSDW case of figure 2.

The second type of impurity in this system is the substitution of a Mn atom by a Pt atom. There is very little similarity to the γ-Mn system for this case. Each Mn atom has eight nearest-neighbour Mn atoms and four nearest-neighbour Pt atoms. Since all the neighbouring spin orientations are 120°, the first shell of neighbours polarizes in an identical way when considered independently; it is only the manner in which the polarization cloud extends to more distant neighbours that lifts the degeneracy. Since there are eight nearest neighbours achieving 50% of the bonding, the linear term is $\delta E = \delta\lambda_\alpha^0 = 4\delta J$. The degeneracy is lifted by the polarization energy which is: $-0.666\,79\delta^2 J$ for the triangular phase and: $-0.758\,50\delta^2 J$ for the hedgehog phase. The experimental prediction is again clear; additional Pt atoms should stabilize the hedgehog phase. The energy saving per bond is much smaller than that for the Mn substitution, being around $\frac{1}{10}J$ per impurity. Since the polarization only behaves differently at second nearest-neighbours, this difference is to be expected. The physical explanation for the stability fits well with our existing interpretation, where omission of spins prefers more highly non-collinear phases because the polarization can spread further, there being fewer parallel spins that are difficult to polarize and more options in terms of neighbours to use. The theory agrees with experiment, in the sense that the observed phase boundary points in the right direction, although we would predict a change in slope for the phase boundary at the stoichiometric compound with the hedgehog phase dying out faster with Mn doping than the triangular phase does with Pt doping. There is no clear evidence for this prediction, since the experiments are rather unclear [2].

The diffuse-scattering calculation for the impurity in the hedgehog phase yields the profile depicted in figure 5. The scattering is again peaked at the type-I antiferromagnetic Bragg spots, and there is a clear dip where the existing hedgehog-phase Bragg spots sit.

Unlike the previous calculations, there is now a strong peak *centred* on the type-I Bragg spots. This result provides a profile for experimental verification, but also provides us with a picture for what we might anticipate in a more highly disordered material. When the spin orientations are in many directions we can anticipate a smoother scattering profile, with weaker dependence on the underlying long-range order.

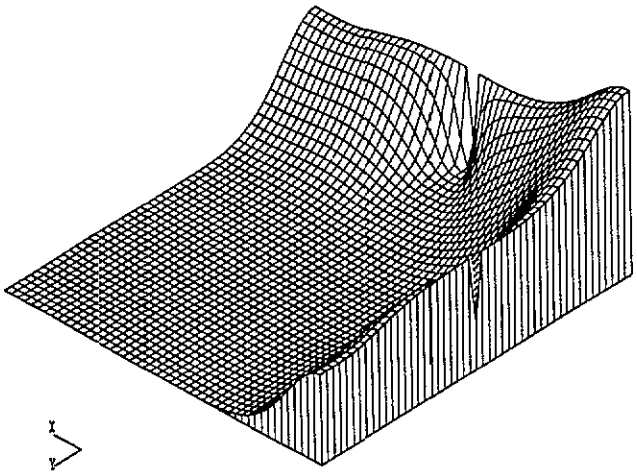

Figure 5. The magnetic diffuse scattering profile from the distortion surrounding a Pt atom substitutionally replacing a Mn atom in the hedgehog phase of Mn_3Pt. The chosen plane is the same as in figures 2 and 4, and the dominant scattering is seen to be much smoother and lies along the lines that correspond to the classical ground-state degeneracy. The 'holes' in the scattering correspond to the sites of the underlying antiferromagnetic Bragg spots.

In order to test this basic idea that the lack of symmetry found in the hedgehog phase should lead to smoother scattering profiles, we also calculated the diffuse scattering from an added impurity in the hedgehog phase, which we plot in figure 6. The smooth scattering is observed.

One rather less immediate prediction is that stoichiometric disorder should stabilize the triangular phase: a *pair* of distant impurities, one composed of a Pt on a Mn site and the other being a Mn on a Pt site, corresponds to such disorder. The energetics are such that the relative energy gain from the addition into the coplanar state outweighs the relative loss from the omission from the triangular phase, and the triangular phase should be stabilized by about $(-0.954\,93 + 0.708\,23 - 0.666\,79 + 0.758\,50)J = -0.154\,99J$ per pair of impurities. The phase diagram is consistent with this idea, with the hedgehog phase not extending into the disordered phase.

4. Conclusions

We have developed a linearized theory that approximately solves the Heisenberg model for the magnetic distortion around a local moment impurity in a non-collinear ground-state. We

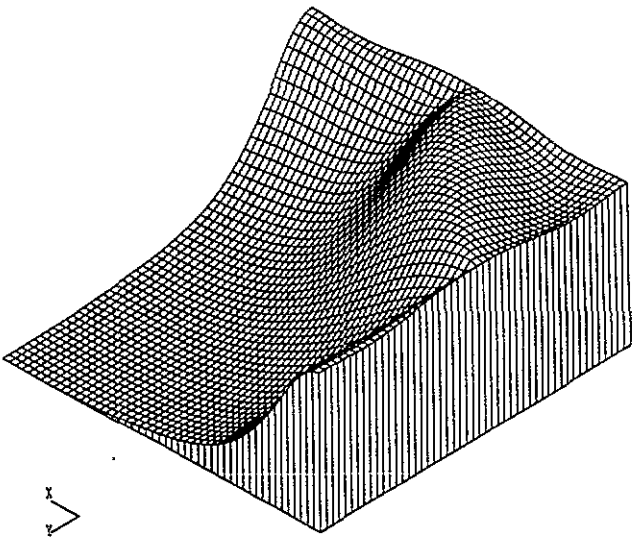

Figure 6. The magnetic diffuse scattering profile from the distortion surrounding a Mn atom substitutionally replacing a Pt atom in the hedgehog phase of Mn_3Pt. The chosen plane is the same as in figures 2 and 4, and the scattering is seen to be smooth, although there is now no 'hole' where the underlying Bragg scattering is found.

have looked at both total energies and induced spin densities. Although the theory can be applied to any non-collinear spin state, we have in mind the description of phase transitions between different antiferromagnetic states for applications. Non-collinear ground states are necessarily found in geometrically frustrated lattices, where not all the possible bonds can be simultaneously maximized and a compromise solution is required. Together with the non-collinearity is often found *degeneracy* and this is the root cause of the experimentally observed phase transitions. If the dominant magnetic interaction yields degenerate ground states, then this degeneracy will be lifted by weaker phenomena. Transitions between different states from a degenerate class can then be accomplished using alloying, which involves the dominant magnetic energy scale and might be expected to dominate the weaker effects that lift the degeneracy. All our calculations corroborate this basic hypothesis, with the energy scale from magnetic distortions being a sizable fraction of the original bond strengths.

We have recognized three basic impurity types: (1) the substitution of an existing magnetic atom by a paramagnetic impurity; (2) either substitution or interstitial doping of a magnetic impurity at a local 'dead spot'; and (3) either substitution or interstitial doping of a paramagnetic impurity at a site with a local field. For both (1) and (3), the doping prefers the member of the degeneracy class that has the highest degree of non-collinearity. The reason for this choice is that the polarization cloud surrounding the impurity spreads out further and more effectively in a high dimensional spin state. As well as the obvious idea that there are fewer collinear spins that are difficult to polarize, there is also the idea of using rotations of different directions for different purposes, with polarization along different paths ending up polarizing in different directions, rather than cancelling out as usually happens in coplanar states. For (2), however, we find an opposite result, with local 'dead-spot' impurities preferring low-dimensional spin states. When optimizing the distortion for this case, the impurity is free to take up any direction it might want. For a low-dimensional

spin state, it is best for the impurity to orient perpendicular to the spin state and then, since all the relative angles are at 90° to the impurity field, there is no competition with the spin-magnitude constraint and the polarizability is maximum. For a three-dimensional spin state there are always some spins with components parallel to the impurity spin, which are less easy to polarize.

We have applied our theory to both γ-Mn alloys and Mn_3Pt. The theory successfully predicts the expected phase diagrams as far as the energetics go, with the the relevant degree of non-collinearity being either increased or decreased in agreement with the type of impurity found. The energy scales for which impurities break the degeneracy are always a small but significant fraction of the dominant antiferromagnetic coupling constant, and so we should usually expect alloying to cause phase transitions in frustrated systems with degeneracy.

Alloying non-magnetic impurities into γ-Mn is expected to destabilize the collinear ground state in favour of the fully non-collinear TSDW state. Substitution of Mn for Pt in Mn_3Pt is expected to stabilize the triangular phase and substitution of Pt for Mn is expected to stabilize the hedgehog phase.

As far as magnetic diffuse scattering is concerned, all the Mn alloys considered showed a preponderance of scattering at type I Bragg spots. This is *not* immediately obvious, because all the fundamental geometries considered have ground-state degeneracies that range over all the edges of the antiferromagnetic Brillouin zone and do not connect to the chemical Bragg spots. It would appear that the additional symmetry inherent in type-I antiferromagnetism is favoured by paramagnetic impurities. The details of the scattering are controlled by the point-symmetry of the isolated defects that we have considered, and this symmetry will not be representative of a heavily doped system. The *range* of the diffuse scattering has always proved to be about half of the Brillouin zone, and there has been no opportunity for dramatic effects. This result ought to provide an experimental test for spontaneous local deformation, since long-range phenomena are *not* expected for our linear deformations.

The theory is restricted to isolated impurities, and it would be useful to extend the perturbation theory to cope with interactions between impurities, effects which will attempt to drive the phase transitions between different antiferromagnets.

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