Long-range magnetic impurities in gamma -MnCu alloys

1993 J. Phys.: Condens. Matter 5 L15

(http://iopscience.iop.org/0953-8984/5/2/001)

J. Phys.: Condens. Matter 5 (1993) L15–L22. Printed in the UK

LETTER TO THE EDITOR

Long-range magnetic impurities in γ-MnCu alloys

M W Long† and A Bayri‡

† School of Physics, Birmingham University, Edgbaston, Birmingham B15 2TT, UK
‡ School Of Physics, Bath University, Claverton Down, Bath BA2 7AY, UK

Received 21 October 1992

Abstract. γ-Mn alloys show a host of antiferromagnetic phase transitions. Recently it has been suggested that the alloy disorder causes these phase transitions by locally trapping 'islands' of non-collinear spin density. Practical experimental studies of this possibility have previously been reported in the literature, employing magnetic diffuse scattering. Although basic agreement was obtained for some alloys, γ-$Mn_{1-x}Cu_x$ exhibited spectacular effects which have so far proven rather difficult to explain: so-called 'giant staggered moments'. We present a model which successfully predicts the magnetic diffuse scattering and explains the special behaviour observed in γ-$Mn_{1-x}Cu_x$ as arising from the local clustering of copper impurities.

γ-Mn alloys [1] are face-centred cubic, and as such have additional antiferromagnetic ordering degeneracies due to the geometric frustration inherent in the face-centred cubic lattice [2]. The existence of this additional degeneracy has been used to successfully explain the host of antiferromagnetic phase transitions in these systems. Phases of different crystal symmetry are interpreted as multiple-Q states with varying numbers of magnetic spin-components simultaneously present [3]. Although the fact of phase transitions between different multiple-Q states seems established, the *cause* remains unresolved. Previous attempts at explanations have involved *average* properties of the system, such as the raising of the chemical potential leading to nesting instabilities [4] or the smooth changing of a parameter in the model as in the four-spin exchange model of Jo [5]. Recently a new idea has surfaced, that the effect might be driven by the inhomogeneity and is spatially very variable in magnitude.

A picture based upon local impurities which trap a small quantity of a new antiferromagnetic phase has been proposed [6], with long-range coherence being caused by interactions between impurities on some longer lengthscale. Although the short-range characteristics of this model successfully explained the magnetic diffuse scattering in *cubic* γ-$Mn_{1-x}Ni_x$ alloys [6], the doping for this case is too great for us to have faith in the independence of impurities. It seems more natural to ask questions in the much lower-doped alloys, where one might anticipate observing isolated impurities and testing the internal consistency and predictive power of the model. Due to the existence of the phase transitions, most studies of γ-$Mn_{1-x}Ni_x$ crystals have centred on the high doping regions, but for the case of γ-$Mn_{1-x}Cu_x$, large single crystals with modest, i.e. about 10%, concentrations of impurities have been studied with diffuse scattering [7]. The results are spectacular: clustering of

copper atoms occurs very strongly over a fairly long lengthscale and associated with this clustering is a much longer-range antiferromagnetic impurity associated with the original magnetic symmetry, but *perpendicular* to the original quantization direction.

At first sight this result might appear to support the idea of trapped local non-collinear impurities, but there are severe interpretational difficulties. Firstly, the basic idea is that locally some of a secondary phase is trapped. This second phase is associated with scattering at new reciprocal space points which are related to the original by point-group symmetries, whereas the observed scattering occurs at the *original* scattering centres. The scattering is 'miles' away from where it would naively be expected. A second related problem, is that the basic *symmetry* of our distortions must be different to that of the ground state. The reason for this is subtle, but for most simple cases the point-group symmetry of the impurity is different to the ground state. In practice, non-collinear scattering exactly on the original Bragg spot corresponds to rotating all the spins together. This process is irrelevant in our model, which remains isotropic in the presence of the impurities, and we require a spontaneous breaking of a different type of symmetry. We might have tried to search for a new type of impurity which could cant the quantization axis, but the present analysis of the longer-range aspects to our impurities successfully resolves these problems.

We elect to use the classical Heisenberg model for simplicity, but we include a parameter, x, whose existence can be attributed to the tetragonal distortion

$$H = \frac{J}{2} \sum_{(jj')_-} \boldsymbol{S}_j \cdot \boldsymbol{S}_{j'} + \frac{Jx}{2} \sum_{(jj')_+} \boldsymbol{S}_j \cdot \boldsymbol{S}_{j'} \tag{1}$$

where we assume that there is a unique collinear ground state, the first summation includes all anti-parallel bonds and the second summation includes all parallel bonds. The magnetic state which is stable finds alternating planes of 'up' and 'down' moments as we travel parallel to the z axis. This state is magnetoelastically 'self-trapped', in the sense that this state gains more magnetic energy from bonds between moments on neighbouring layers than between moments in the same layer, and so a small tetragonal distortion is induced by the magnetoelastic coupling in order to strengthen the antiparallel bonds at the expense of the parallel bonds, thereby unfrustrating the system. This modification to the bonds is controlled by our parameter x, which should be less than unity. Experimentally, additional copper reduces the size of the tetragonal distortion [8], and so we ought to consider the consequences of increasing x in our model (over and above some unknown starting value).

We are interested in non-collinear distortions, and we have found that coplanar distortions are almost invariably the most stable. We therefore restrict attention to planar rotations, allowing each spin to be described by an angle, Φ_j say. In this representation we find

$$H = \frac{JS^2}{2} \sum_{(jj')_-} \cos(\Phi_j - \Phi_{j'}) + \frac{JS^2x}{2} \sum_{(jj')_+} \cos(\Phi_j - \Phi_{j'}). \tag{2}$$

This problem is still rather tricky to treat exactly, but by restricting attention to the moment at which an impurity becomes stable and the distortion is infinitesimal, we can effectively linearize the problem. We can then let $\Phi \rightarrow \Phi_0 + \phi$ where ϕ is the

infinitesimal change, and then

$$H \to -\frac{JS^2}{2}N(Z_- - xZ_+) + \frac{JS^2}{4}\sum_{(jj')_-}(\phi_j - \phi_{j'})^2 - \frac{JS^2x}{4}\sum_{(jj')_+}(\phi_j - \phi_{j'})^2 \quad (3)$$

where Z_- and Z_+ are the coordination numbers of antiparallel and parallel neighbours respectively ($Z_- = 8$ and $Z_+ = 4$ for face-centred cubic). For the pure system we have translational symmetry and so we can transform to reciprocal space

$$H_{\text{inf}} = -\frac{JS^2}{2}N(Z_- - Z_+x) + \frac{JS^2}{2}\sum_{k} |\phi_k|^2 [Z_-(1-\gamma_{k-}) - xZ_+(1-\gamma_{k+})] \quad (4)$$

where $\gamma_{k\pm}$ are the relevant normalized structure factors (for face-centred cubic, $\gamma_{k-} = c_3(c_1 + c_2)/2$ and $\gamma_{k+} = c_1c_2$, in terms of $c_i = \cos(ak_i)$). We now clearly recognize a linear problem with an associated dispersion

$$\epsilon_k = (JS^2/2)[Z_-(1-\gamma_{k-}) - xZ_+(1-\gamma_{k+})] \quad (5)$$

from which we can define Green's functions, allowing us to solve problems with local impurities present.

One might presume that the dispersion we derive is simply the spin-wave dispersion, but this is simply not true, there being no obvious relationship between the two concepts. Indeed, our dispersion is quadratic as $k \to 0$, in contrast to the linear spin-wave dispersion law. This fact is quite crucial to our explanation of the diffuse magnetic scattering.

We now move on to impurity calculations. The way we introduce paramagnetic impurities into the model is simply to 'cut' all the bonds to the relevant impurities and to henceforth ignore the dangling moment. The impurity potential is just

$$H_{\text{imp}} = JS^2N_{\text{imp}}(Z_- - Z_+x) - \frac{JS^2}{2}\sum_{(j_{\text{imp}}j)_-}(\phi_{j_{\text{imp}}} - \phi_j)^2 + \frac{JS^2x}{2}\sum_{(j_{\text{imp}}j)_+}(\phi_{j_{\text{imp}}} - \phi_j)^2 \quad (6)$$

where N_{imp} is the number of impurities and j_{imp} denote their positions. It is straightforward to construct reciprocal space Green's functions from our dispersion, then to transform them into real space, combine them with the impurity potential and thence find the Green's functions for the system with the impurities included. Usually what one then does is to determine any bound states that the impurities might trap, but for us we must *simultaneously* demand that any distortion must be infinitesimal. In practice, we must isolate the bound states at *zero* energy, by choosing x to be the specific value at which a bound state first becomes stable, x_c say. There is one technical difficulty: The existence of a host of irrelevant impurity states at zero energy. The states associated with the free spins can be extracted analytically and the Goldstone modes can be avoided with care. We can quite easily deduce the value

of x_c for any small cluster of impurities and further deduce the wavefunction of the bound state u_j which satisfies

$$\sum_{j'} \left[H_{\text{imp}}^{-1}\right]_{jj'} u_{j'} = \sum_{j'} \left[G^0(\epsilon = 0)\right]_{jj'} u_{j'} \tag{7}$$

for a local basis on which H_{imp} is invertible. The final technical requirement from our calculation is to deduce the form of the diffuse scattering. This can be shown to be proportional to

$$| \delta S_{k+Q}^{\perp} |^2 \propto | u_k |^2 / (\epsilon_k)^2 \tag{8}$$

in reciprocal space, where Q is the position of the Bragg scattering from the original magnetism and u_k is the Fourier transform of the bound-state wavefunction. Admittedly, we have ignored the important fact that neutrons only scatter off moments perpendicular to the direction of momentum transfer, but we are dominantly interested in the region of a Bragg spot which is extinguished for this very reason, and so any transverse moments will automatically be orthogonal to the momentum transfer.

First of all we analyse the role of x_c in the model. Obviously, the smaller x_c the more stable the impurity. To set the scene we quote the results that

(i) for an isolated impurity the lowest values of x_c are $0.95546J$ and $0.97893J$;

(ii) for two impurities one above the other in next-nearest-neighbour z-planes the lowest values of x_c are $0.86115J$, $0.96944J$ and $0.97088J$;

(iii) for two impurities neighbouring each other in the same z-plane the lowest values of x_c are $0.87598J$ and $0.91204J$;

For most three-dimensional models, only the impurities with the strongest potentials would be bound, but for our nearest-neighbour Heisenberg Hamiltonian on the face-centred cubic lattice, there is additional degeneracy which reduces the effective dimensionality to two, thereby guaranteeing bound-states.

We can understand these results quite readily in terms of the two natural sublattices. All three choices put the impurities onto the *same* sublattice. The induced distortion is then almost wholly contained within the other sublattice. The reason is that neighbouring moments parallel to the original orientation of the impurity moment have an increased field maintaining their original direction, but neighbouring moments antiparallel to the original orientation of the impurity moment lose an antiparallel neighbour which alters the balance between the parallel and antiparallel forces weakening the field holding the moments in place. We can view planes of moments without impurities as being susceptible to trapping non-collinear moments. Looking at the single impurity, we can interpret the two values of x_c as being bonding and anti-bonding mixtures of transverse distortions trapped in the planes above and below the impurity. The x_c for a single plane is then around $0.97J$. Two impurities in the same plane yield a similar bonding and antibonding combination with x_c for a single plane being about $0.9J$. The two impurities on next-nearest-neighbour planes have *three* neighbouring planes, with the intermediate plane yielding the strongly bound x_c and the two external planes yielding a weaker bonding and anti-bonding combination around $0.97J$. This way of interpreting the values of x_c is surprisingly

powerful, classifying quite exotic clusters by the particular configuration of impurities which neighbour the closest pure planes.

Now let us consider the physical consequences of these results for γ-$Mn_{1-x}Cu_x$. For pure γ-Mn the c/a ratio is reduced by about 6% and increases to unity with increasing copper doping [8]. The expected value of x will therefore increase from its starting value towards unity with copper concentration. Due to the fact that atomic overlaps are exponential, we might naively expect that the variation in x would be faster than that in c/a, and so variations of larger than 6% might be anticipated. This would in turn suggest that the possibility of a single copper atom trapping a transverse distortion is small but that a pair of nearby impurities might be able to do it. It is consequently possible that a 'phase transition', where the majority of the isolated impurities pick up moments, can be conceived of, as a function of increasing copper concentration. It should be borne in mind that this assertion is pure conjecture.

The actual value that x_c takes up is dominantly controlled by the few spins actually neighbouring the impurity, whereas the magnetic diffuse scattering is dominated by the longer-range tails of the non-collinear impurities which make little contribution to the energetics. Before we move onto an interpretation of what one might expect from the magnetic diffuse scattering off our impurities, firstly we will simply present some of the results. In figure 1 we plot the magnetic diffuse profile for the three particular impurity clusters that we have so far considered. The most obvious feature is that the first two configurations, which are more likely to be relevant for anti-clustering impurities, yield scattering as expected at the positions where the new phase appears, whereas for the third configuration, more relevant to clustering systems, there is a huge peak centred on the existing position of the magnetic Bragg scattering. The point-group symmetries of all three clusters are different from the ground state, with the first two being antisymmetric under 90° rotations and the third being antisymmetric under 180° rotations. We have the scattering in the correct place, but not quite of the required form.

There are two things to grasp immediately: why sometimes we find a huge peak at the original magnetic Bragg spot and secondly why sometimes we do not. It is quite easy to understand the peak physically: there are zero-energy excitations at the Bragg spot and at no other place in the Brillouin zone. The long-range characteristics of the distortion are controlled by these low-energy modes, and therefore the long-range contribution is expected to be peaked at this position. The lack of this scattering depends on whether or not *symmetry* requirements eliminate it. In equation (8), the denominator looks like k^4 as $k \rightarrow \mathbf{0}$. The numerator has a form controlled by symmetry. The constant term always vanishes, and the leading-order contribution is either quadratic $\sim (k_x \pm k_y)^2$ for a single reflection symmetry (as in the third configuration), or quartic $\sim (k_x^2 - k_y^2)^2$ for 'square' symmetry (as in the first two cases). For reflection symmetry we have a quadratic (but integrable) divergence, while for 'square' symmetry we have smooth behaviour. It should be remembered here that this argument is totally different for spin waves, which are *linear* at low energies.

One feature that is worth stressing, is the fact that a comparison between the single impurity and the pair of impurities in next-nearest-neighbour planes, immediately establishes that the scattering is much sharper for the isolated impurity (see figure 1). The reason for this is the different values of x_c. The excitation gap to the new type of phase which is being locally trapped is just $\epsilon_{Q'}$, for us $= 4JS^2(1-x)$, and so values of x_c closer to unity have a smaller gap. A smaller gap means a longer-range distortion

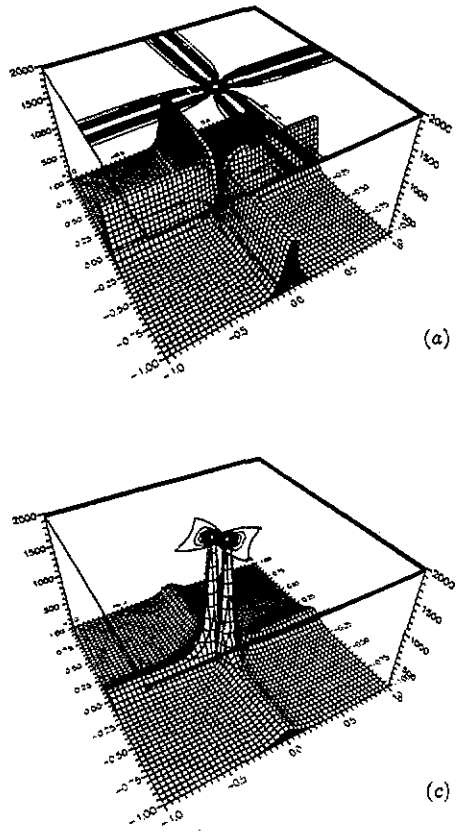

Figure 1. Magnetic diffuse scattering profiles of the x-y plane passing through the point $(0,0,1)$. The x, y and z axes in reciprocal space are in units of (π/a) and the z axis in the picture is the intensity of scattering in physically arbitrary units. (a) A single isolated impurity. (b) Two impurities in next-nearest-neighbour planes, one directly above the other. (c) Two nearest-neighbour impurities in the same plane.

and a sharper reciprocal-space peak. As the concentration of copper is increased, the increase in x ought to provide a sharpening of the magnetic diffuse scattering around the reciprocal-space points corresponding to the additional degenerate phases.

Experimentally [7], there is no evidence of our asymmetric peak, which might be viewed as a weakness in the theory, but if the theory is considered more carefully, this defect disappears. To verify this we analyse a compact cluster of four atoms, each nearest neighbours to the other three. The two nearest pure planes are above and below, and we would expect a pair of bonding and anti-bonding states close to $x = 0.9J$. In fact, the local symmetry of the impurities means that they do not couple and so we find a doubly degenerate solution at $x_c = 0.891857J$. Since we have two transverse spin directions, we can occupy both impurity states independently, and then we find the scattering depicted in figure 2. There is now no asymmetry, and we can see that the superposition of impurities with different symmetries will 'fill in the gaps'.

Obviously, the divergence that we find is not physical, and arises from our omission of the spin–lattice coupling. In transition metals the spin–orbit interaction is several orders of magnitude smaller than the direct antiferromagnetic interactions and although it cuts off the divergence, it would only be expected to dominate very close to the origin, and certainly closer to the origin than where we have artificially cut off our calculations.

In conclusion, we have been able to predict the observed relationship between

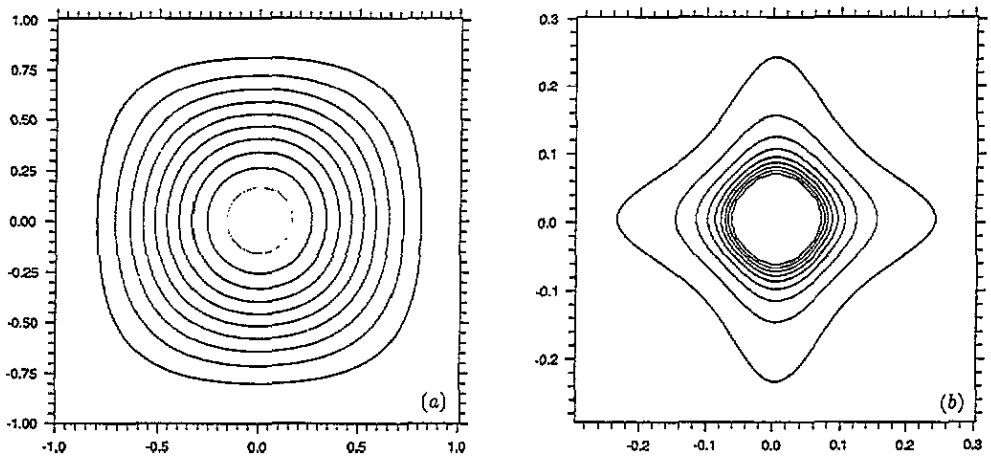

Figure 2. (*a*) Contour plot of the structure factor for a cluster of four nearest-neighbour atoms. We plot the x–y plane passing through the point (0,0,0), to be compared with the nuclear diffuse scattering profile. (*b*) Contour plot of the magnetic diffuse scattering profile of the x–y plane passing through the point (0,0,1), for the two magnetic impurities bound to the same four nuclear impurities. We have assumed that the two magnetic impurities are perpendicular both to the Bragg moments and to each other.

nuclear diffuse scattering and magnetic diffuse scattering found in γ-$Mn_{1-x}Cu_x$ [7]. The clustering found in γ-$Mn_{1-x}Cu_x$ ensures that there will be a preponderance of non-collinear impurities bound to planes with nearest-neighbour copper atoms, and therefore a large amount of scattering near the original magnetic Bragg spots. The situation in γ-$Mn_{1-x}Ni_x$ may be quite different however, since one would anticipate isolated impurities to dominate, and the local symmetry of isolated non-collinear impurities does *not* peak at the original Bragg spot.

We will provide a more detailed description of the generic behaviour expected from our model in a separate article. Simultaneously, we will deal with the fact that our model has *additional* symmetry, making it effectively two-dimensional, by allowing next-nearest-neighbour interactions. This complication also eliminates all ground states except type I, which is experimentally a requirement and ignored in the present article.

Much appreciation to O Moze and T J Hicks (whom I have never met), because of their tenacity and skill in continuing their experiments on these theoretically fascinating materials.

B D Rainford should also be acknowledged for introducing all of us to these problems and for coining the phrase 'giant staggered moments' which nicely describes the physical effect.

References

[1] Endoh Y and Ishikawa Y 1971 *J. Phys. Soc. Japan* **30** 1614
Yamaoka T, Mekata Y and Takaki H 1974 *J. Phys. Soc. Japan* **36** 438
Yamaoka T 1974 *J. Phys. Soc. Japan* **36** 445
Honda N, Tanji Y and Nakagawa Y 1976 *J. Phys. Soc. Japan* **41** 1931

Coles B R 1977 *Physica* B+C **91** 167
Makhurane P and Gaunt P 1969 *J. Phys. C: Solid State Phys.* 2 959
[2] For a review of geometric frustration in antiferromagnets see
Long M W 1992 *Int. J. Mod. Phys.* B at press
[3] Kouvel J S and Kasper J S 1963 *J. Phys. Chem. Solids* **24** 529
Cade N A and Young W 1977 *Adv. Phys.* **26** 393
Hirai K and Jo T 1985 *J. Phys. Soc. Japan* **54** 3567
Long M W and Yeung W 1987 *J. Phys. C: Solid State Phys.* **20** 5839
[4] Cade N A and Young W 1980 *J. Phys. F: Met. Phys.* **10** 2035
Kubler J, Hock K H, J Sticht and Williams A R 1988 *J. Appl. Phys.* **63** 3482
[5] Jo T 1983 *J. Phys. F: Met. Phys.* **13** L211
[6] Long M W and Moze O 1990 *J. Phys.: Condens. Matter* **2** 6013
Long M W 1990 *J. Phys.: Condens. Matter* **2** 5383
[7] Moze O and Hicks T J 1992 *Phys. Rev.* B **46** 915
Tsunoda Y and Cable J 1992 *Phys. Rev.* B **46** 930
[8] Cowlam N, Bacon G E and Gillott L 1977 *J. Phys. F: Met. Phys.* 7 L315