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DISORDER, RANDOM FIELDS, AND COMPETING INTERACTIONS IN ANTIFERROMAGNETS

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ABSTRACT

Neutron-scattering studies of disordered antiferromagnets have proved to be a very-profitable way of studying random systems. Several recent examples are selected and include a detailed study of the phase transition of a $d=3$ Ising system showing a well-defined transition with properties different from those of a pure $d=3$ Ising system. Much of the article is then concerned with the effect of a random field on the ordering and phase transitions. It is shown that random fields do have a large effect on the critical properties and in practice destroy the long-range order in the good Ising systems with $d=2$ and $d=3$, although not in a nearly Heisenberg-like system. These results are compared with current theories and the discrepancies discussed. Finally, measurements on a system with competing interactions are discussed and shown to be strongly influenced by the random fields produced in that system.

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INTRODUCTION

The fluorides and chlorides of the 3d transition metals are ideal materials on which to study the properties of disordered systems. Transition metal ions such as Mn^{++} , Co^{++} , Fe^{++} and Mg^{++} are chemically very similar but magnetically very different. Consequently it is possible to grow single crystals in which the magnetically very different ions are distributed at random over the transition metal sites, so that the systems are chemically quite uniform but magnetically very disordered. The magnetic properties can then be studied in detail by various experimental techniques, but particularly detailed information is provided by neutron scattering techniques. These results often provide very stringent tests of the theories of disordered systems because the magnetic interactions in these systems are well known, and often of short range, and so are very similar to the theoretical models for which calculations are most often performed. Secondly by choosing different magnetic ions and different crystal structures a variety of different models can be studied — Ising or Heisenberg-like magnetic interactions — magnetic systems in which the interactions are largely confined to, $d=1$, lines of ions, or $d=2$, planes of ions, or throughout the whole crystal when the dimensionality $d=3$.

At an earlier Geilo school in 1979, we¹ reviewed some of the measurements which had been made on these systems to study the properties of the excitations and phase transitions of disordered systems. In this article, we shall not repeat that review but concentrate on the progress which has been made since 1979. All of the work reviewed earlier was on antiferromagnetic materials containing either two different magnetic ions, or a magnetic ion and a non-magnetic ion. There is then no doubt about the nature of the long range order, if any, because there is no competition between the different interactions. Since 1979 a large part of the work has been the extension of these studies into systems, where there are competing interactions and the nature of the ground state is by no means so clear or even understood. A large part of this article describes the experiments which have been performed on these more complicated systems. Since the nature of the ground state in these systems is still not yet understood, there has been comparatively little progress made on the study of the excitations; consequently we concentrate on the properties of the phase diagram and the nature of the phase transitions.

Before describing the work performed on systems with competing interactions, we describe one experiment on the phase transition in a relatively simple disordered antiferromagnet. The reason for describing this is that it sheds light on one of the questions raised in our earlier review — namely whether the phase transition in a disordered system is sharp or rounded. This experiment is described in the next section.

The remainder of this article is then a discussion of the results found so far for systems with competing interactions. The third section describes the effect of applying a random field to the systems so that there is a competition between the random field and the antiferromagnetic exchange interactions. Because the strength of the random field can be altered continuously, this problem is in many ways the most amenable of the systems with competing interactions for detailed study and has attracted the most experimental effort recently. Another type of system with competing interactions are those with random anisotropies so that the anisotropy favours one spin direction on some of the ions and a different direction on the other ions. These systems are described in the fourth section. Finally we should mention measurements made on systems with mixtures of ferromagnetic and antiferromagnetic exchange constants which, in principle at least, should give insight into the behaviour of the metallic spin glasses. One system which has been studied in considerable detail is that of $\text{Eu}_x\text{Sr}_{1-x}\text{S}$, and the results for this system will be described by Coles in his lectures. Another very interesting system is $\text{Rb}_2\text{Mn}_x\text{Cr}_{1-x}\text{Cl}_4$, where the Mn ions are coupled antiferromagnetically and the Cr ions ferromagnetically, and the magnetic ions lie in sheets. Although there is evidence for a $d=2$ spin glass phase in this system, detailed studies have not yet been performed and so we do not discuss it further here.

Most of the measurements which will be described, have been performed with neutron scattering techniques. Except when explicitly stated these were performed at the High Flux Beam Reactor at the Brookhaven National Laboratory. They were mostly performed with a two-axis spectrometer and an incident neutron energy of 14 meV and with pyrolytic graphite used as both monochromator and as a filter to suppress the higher order contaminant neutrons in the incident beam. The critical scattering observed close to the phase transition was analysed by convoluting the appropriate functional form with the experimental resolution and fitting the parameters of that assumed form to give a good fit to the experimental results.

PHASE TRANSITIONS WITHOUT COMPETING INTERACTIONS

The nature of the phase transitions in disordered systems with exchange constants of the same sign has been the subject of a considerable amount of work. Harris² showed that if the specific heat exponent, α , of the pure system was negative then the critical phenomena would be very similar (have the same universal behaviour) as that of the corresponding pure systems. In contrast if α was positive the disorder would have a larger effect which might lead either to a first order transition or to a continuous transition but with different exponents from those of the analogous pure systems. These results have also been obtained using renormalisation group

theory³ and explicit predictions made for some of the exponents⁴ which differ from those of the pure system.

Experimental work on these systems has not until recently been able to confirm these results. Although these predictions agreed with the measurements⁵ on the mixed $d=2$ Ising system $\text{Rb}_2\text{Ni}_{0.5}\text{Mn}_{0.5}\text{F}_4$ for which $\alpha = 0$, measurements on three dimensional systems⁶ gave a smeared transition which made the determination of the exponents very difficult if not illegitimate. It was impossible to ascertain whether the smearing was due to macroscopic concentration fluctuations or would arise in a homogeneous random crystal.

Recently measurements⁷ of the critical behaviour have been performed on a sample of $\text{Fe}_{0.5}\text{Zn}_{0.5}\text{F}_2$. FeF_2 is an antiferromagnet in which the $S=2$ magnetic ions interact with Heisenberg-like exchange interactions, but the proximity of nearby crystal field levels causes a large single ion anisotropy. This anisotropy produces a large gap (6.5 meV) in the spin wave spectrum⁸ so that the critical behaviour of FeF_2 should be that of the $d=3$ Ising model and is found to be that experimentally⁹.

The sample of $\text{Fe}_{0.5}\text{Zn}_{0.5}\text{F}_2$ was found to be of excellent quality with a mosaic spread of less than 0.02 degrees and a spread in T_N of less than $2 \times 10^{-3} T_N$. These properties enabled a very detailed study of the critical properties of the disordered $d=3$ Ising model to be made. This is a particularly interesting system because α is positive for the pure $d=3$ Ising model and so the critical properties of the disordered crystal are expected to be different from those of pure FeF_2 .

The critical scattering was measured using neutron scattering techniques and was analysed assuming that the scattered intensity was given by

$$I(\vec{Q}) = \frac{AT}{\kappa^2 + q^2} + C\delta(\vec{q}) \quad (1)$$

where $\vec{Q}$ is the wavevector transfer and $\vec{q}$ is the difference between $\vec{Q}$ and the nearest reciprocal lattice vector as measured in reciprocal lattice units. The parameters A and κ were fitted to the observed critical scattering and the results for κ , and for κ^2/A are shown in fig. 1.

The results for the inverse correlation length and amplitude were fitted to power law forms;

$$\begin{aligned} \kappa(\tau) &= \kappa_0^+ \tau^{\nu_+} & T > T_N \\ \kappa(\tau) &= \kappa_0^- \tau^{\nu_-} & T < T_N \end{aligned}$$

Fig. 1. Inverse correlation length κ and inverse staggered susceptibility κ^2/A for $\text{Fe}_{0.5}\text{Zn}_{0.5}\text{F}_2$ above and below $T_N = 42.50$ K. The solid lines are fits to single power laws and $\tau = (T - T_N)/T_N$.

with $\tau = |T - T_N|/T_N$, and it was found that within error $\nu_+ = \nu_-$. In table 1, we collect the best estimates of the exponents for the correlation length, ν , the susceptibility, γ , from these experiments and of the specific heat, α , from measurements of the birefringence. Also collected in table 1 are the approximate amplitude ratios; we note that the exponents for the disordered and pure systems differ only slightly while the amplitude ratios are very significantly different. Table 1 also shows current theoretical estimates of these quantities.

This experiment very strongly suggests that the theory of the phase transitions in disordered systems is correct in predicting that even when the exponent α is negative for the pure system, the

Table 1. Exponents and Amplitude Ratios for Pure and Random $d=3$ Ising Models

	Pure Ising		Random Ising	
	Theory ¹⁰	FeF_2 ⁹	Theory ¹¹	$\text{Fe}_{0.5}\text{Zn}_{0.5}\text{F}_2$ ⁷
<u>Susceptibility</u>				
γ	1.24	1.38 ± 0.08	1.39	1.44 ± 0.06
Amplitude Ratio	5.1	6.1 ± 1.0	1.7	2.2 ± 0.1
<u>Correlation Length</u>				
ν	0.63	0.67 ± 0.04	0.70	0.73 ± 0.03
Amplitude Ratio	0.53	0.43 ± 0.07	0.83	0.73 ± 0.02
<u>Specific Heat</u>				
α	0.11	0.11 ± 0.005	-0.09	-0.09 ± 0.03
Amplitude Ratio	0.51	0.54 ± 0.02	-0.5	1.6 ± 0.3

transition is sharp but that the critical properties are altered. The smearing observed in earlier experiments⁶ is most probably due to macroscopic fluctuations in the concentrations and hence to a varying T_N throughout the crystal.

ORDERING AND RANDOM FIELDS

Theoretical Introduction

The effect of random fields on the ordering of magnetic systems was first discussed by Imry and Ma¹². They considered the Hamiltonian for a system of n -component spins as

$$H = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j - g\mu_B \sum_i \vec{H}_i \cdot \vec{S}_i \quad (2)$$

where the sum over i and j is restricted to nearest neighbours and the fields $\vec{H}_i$ are randomly directed. If it is to be energetically favourable for the system with long range order to break up into randomly oriented domains, the gain in the random field energy must outweigh the energy needed to create the domain walls. In a system of dimensionality d , the gain of random field energy in creating a domain of size L is proportional to the net magnetic field $L^{d/2}$.

In a system for which $n > 1$, the energy in creating a smooth domain wall is proportional to L^{d-2} and consequently the gain in magnetic field energy destroys the long range order for $d < d_c = 4$. In Ising systems for which $n = 1$, the domain wall energy is larger and proportional to L^{d-1} , and so Imry and Ma predicted that $d_c = 2$ for Ising systems.

Since this pioneering work of Imry and Ma there have been many theoretical treatments of this problem. Briefly renormalisation group theory and diagrammatic expansions¹³ can be performed about the upper critical dimensionality, $d = 6$. A particularly appealing approach was that of Parisi and Sourlas¹⁴ who showed by using supersymmetry that the universal properties of a system in a random field were the same as those of the corresponding pure system but in two less dimensions. This result is believed to be an exact result of the symmetry of the problem for $d > 4$, but its status for $d < 4$ is uncertain. This dimensionality shift is consistent with the arguments of Imry and Ma for the lower critical dimension of systems with more than one ($n > 1$) spin component, but is inconsistent with their predictions for $n = 1$ systems because the lower critical dimension of Ising systems in the absence of a random field is one and the dimensionality shift would then predict that in a random field, $d_c = 3$.

Since this work there have been several attempts to calculate d_c and to understand the origin of this discrepancy between the results of supersymmetry and simple domain arguments. Briefly it¹⁵ was suggested that the calculation of the domain wall energy by Imry and Ma was incorrect because it assumed there were smooth domain walls, whereas if the domain walls were rough they might better be able to take advantage of the random field energy. Calculations¹⁵ of this effect of domain wall roughening suggested that the effect could increase d_c from 2 to 3. This approach has, however, been criticised because it assumed that the domain wall energy was an analytic function of its position and could be expanded in a Taylor series. Arguments¹⁶ based on a different model of the domain wall energy gave a singular dependence of the energy on the location of the domain wall and again suggested $d_c = 2$. Consequently, at present the lower critical dimension of the Ising model in a random field is an unsolved problem.

The dimensionality shift from supersymmetry also gives¹⁵ a direct prediction for the form of the scattered intensity. The correlation function of a d dimensional Ising model is given for $T > T_c$ by;

$$\langle S_i S_j \rangle \sim R^{(1-d)/2} \exp(-\kappa R),$$

where R is the distance between the spins S_i and S_j . In the presence of a random field the dimensionality shift immediately predicts that

$$\langle S_i S_j \rangle \sim R^{(3-d)/2} \exp(-\kappa R),$$

when this form is Fourier transformed to give the scattering cross-section we obtain

$$I(\vec{Q})/|f(\vec{Q})|^2 = \frac{A}{\kappa^2 + q^2} + \frac{B}{(\kappa^2 + q^2)^2}, \quad (3)$$

where $f(\vec{Q})$ is the magnetic form factor of the ions, A and B are constants and κ is related to the size of the domains. Based on the known behaviour of κ for $d \leq d_c$ in systems without a random field it is then predicted¹⁵ that

$$\kappa \sim \langle H_i^2 \rangle^x$$

where $x = 1/(d_c - d)$ for $d < d_c$

$$\kappa \sim \exp(-a/\langle H_i^2 \rangle) \quad \text{for } d = d_c, \quad (4)$$

where a is a constant. If for small κ and $T < T_c$, the intensity (3) is to go over smoothly into the Bragg peak which arises from true long range order, then

$$B = \langle M \rangle^2 \kappa^{4-d}, \quad (5)$$

where M is the magnetisation of the system, while the constant A must tend to zero as $\kappa \rightarrow 0$.

Equation (3) together with equation (5) are consistent with the scaling relations obtained by Aharony and Pytte¹⁷ who also suggest that at the T_c of the system in the absence of the random field, then

$$\kappa \sim \langle H_i^2 \rangle^{1/\gamma},$$

and

$$I(\vec{Q}) \sim \langle H_i^2 \rangle^{-1}, \quad \text{when } \vec{q} = 0. \quad (6)$$

For several years these results¹² did not attract the attention of experimentalists because of the difficulty of producing controlled random fields. It was then pointed out by Fishman and Aharony¹⁸ that the application of a uniform field to a dilute antiferromagnet produces a random staggered field, which is then a random field conjugate to the antiferromagnetic order parameter. Fishman and Aharony initially considered an antiferromagnet with only bond disorder, whereas the experimentally realisable systems have site

disorder. In the case of site disorder there are two contributions¹⁹ to the random field. The first arises from the randomness in the magnetic moments from one cell to the next. In a site diluted antiferromagnet only one sub-lattice may be occupied in one cell whereas in another cell the other sub-lattice may be occupied, leading to a random field proportional to the applied field. In addition to the randomness in the moments the field will also produce a nearly uniform magnetisation. Due to the randomness in the exchange interactions this magnetisation will produce a random fluctuation in the local staggered magnetic field as originally described by Fishman and Aharony. This contribution is proportional to the magnetisation and hence to the product of the applied uniform field and the uniform susceptibility. Since the susceptibility is temperature dependent this can lead to a temperature dependence in the connection between the strength of the uniform field and the strength of the random field.

The above description has recently been criticised by Cardy²⁰ who argues that the strength of the random field is always proportional to the magnetisation. We believe his arguments to be in error, but further work is needed to establish the exact connection between the random field model and the realisation by a site disordered antiferromagnet in a uniform field. For example, the theory assumes that the random fields are uncorrelated, whereas there are certainly short range correlations between the random fields produced in the site diluted systems although the correlation range is much less than $1/\kappa$ in most of the experiments.

Finally it is unfortunate that the Fishman and Aharony suggestion for a realisation of random fields is applicable only to Ising systems. The application of a magnetic field to an ordered antiferromagnet with a continuous symmetry immediately causes a domain realignment in favour of the domains in which the spin directions are perpendicular to the applied field (the spin-flop phase)²¹. In most systems, there are then no components of the random fields parallel to the spin directions and the behaviour is very similar to that of a spin-flop phase in a pure antiferromagnet. In systems of sufficiently low symmetry there may be random interactions of the form $S_i S_j$; such systems may allow study of the XY model in a random field.

Neutron Scattering Results

We shall describe the results which have been obtained by applying a magnetic field to four different antiferromagnetic systems. The $\text{Rb}_2\text{Co}_x\text{Mg}_{1-x}\text{F}_4$ system is an example of a two-dimensional antiferromagnet with essentially Ising interactions²². The Co^{2+} ions have a Kramer's doublet as their ground state and the interactions

between the effective spins $S = \frac{1}{2}$ are anisotropic due to the anisotropic effects of the crystal field on the Co ions. The ions are arranged on the sites of a two dimensional square lattice and one plane of magnetic ions is sufficiently well separated from the neighbouring planes that the inter-plane magnetic interactions are negligible compared with the intra-plane interactions.

The other materials are all of the rutile structure in which the magnetic ions are arranged on a three dimensional lattice of the body centred tetragonal type. We have studied the crystals $\text{Co}_x\text{Zn}_{1-x}\text{F}_2$, $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$ and $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$. All of these materials are antiferromagnets with predominantly exchange interactions between only the nearest neighbour antiferromagnetic ions, but the interactions between the different magnetic ions are quite different. In CoF_2 the interactions are anisotropic because of the crystal field effects discussed above and result in the material having a large spin wave gap and exhibiting Ising critical behaviour^{23,6}. The interactions in FeF_2 were discussed in the preceding section, and this again is a good example of an Ising system⁸ but the anisotropy results from single ion terms in the Hamiltonian instead of anisotropic exchange. Finally in MnF_2 the exchange interactions are predominantly of Heisenberg character, but the weaker magnetic dipolar forces in the tetragonal rutile structure give rise to a small anisotropy²⁴. Consequently the MnF_2 system does belong to the Ising universality class like FeF_2 and CoF_2 , but the anisotropy is very much smaller in the MnF_2 system.

A preliminary account²⁵ of the measurements on the Co salts and on the Mn salt²⁶ have already been published and full papers on the $\text{Rb}_2\text{Co}_x\text{Mg}_{1-x}\text{F}_4$ system²⁷ and $\text{Co}_x\text{Zn}_{1-x}\text{F}_2$ system²⁸ have been submitted for publication. Consequently we shall here review only the essential features of these measurements.

One of the difficulties in working with Ising systems at low temperatures is the problem of knowing whether the system is in thermodynamic equilibrium. In the experiments on the Co and Fe salts, it was found that the results at low temperatures were dependent upon the way in which the state was prepared. For example, if the sample was cooled to low temperatures and the field then applied, the scattering was different from that obtained when the sample was cooled from above T_N in a constant field. This showed that the spins were indeed frozen at low temperatures and could not then respond to changes in the field. Reproducible results were obtained if the field was always changed at temperatures above T_N and the sample then cooled while keeping the field constant. Most of the results were therefore taken using this procedure. Although there is no guarantee that this does result in the achievement of thermodynamic equilibrium, it is the accepted way of studying spin glasses and has the merit of being a well defined procedure. We shall return to the problem of the freezing again later.

When the Co and Fe systems are cooled in the presence of a magnetic field, the scattering in the neighbourhood of the magnetic Bragg reflection is dependent upon the field. In particular it becomes progressively broader with increasing field, as shown in figs. 2 and 3. This increase in the width shows directly that the long range magnetic order is being destroyed by the application of a magnetic field. The nuclear Bragg peaks were unchanged so that the effect is not due to a change in the crystal structure. These results show directly that a random field does appear to destroy the long range order in both $d = 2$ and $d = 3$ Ising models and so the lower critical dimension d_c is apparently larger than 3.

The temperature dependence of the scattering is illustrated in fig. 4, where it is seen that the width of the scattering increases steadily with increasing temperature and that the peak intensity steadily decreases.

Fig. 2. The neutron scattering observed in $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$, a $d = 2$ Ising system, as a function of applied field.

Fig. 3. The neutron scattering observed in $\text{Co}_{0.26}\text{Zn}_{0.74}\text{F}_2$, a $d = 3$ Ising system, as a function of applied field.

Initially the experimental results were fitted to a variety of different functional forms. The scattering profiles shown in figs. 2-4 are unusual in that the wings are more intense than would be expected from a Gaussian spread of domains, but can also not be described by the usual Lorentzian form which has proved so successful in describing critical phenomena. As shown by the agreement between the solid lines and the experimental results in figs. 3 and 4, a good description of the results was obtained using eqn. (3), and by fitting the parameters A , B and κ to the experimental data. Although we cannot rule out the possibility that other functional forms would fit as well,^{27,28} we do consider that this agreement provides support for the dimensionality shift analysis described above.

The results obtained for the inverse correlation length, κ , as a function of temperature for various different fields are shown in figs. 5-7. The results show that there is a monotonic increase in κ with increasing field, but that the effect of the field is at least relatively larger at low temperatures. On cooling in an applied field, κ decreases in the neighbourhood of T_N but becomes almost constant at a temperature somewhat below T_N . This temperature

Fig. 4. The neutron scattering observed from $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$ as a function of temperature in a field of 3.5 T.

decreases with increasing field. Of particular interest is the behaviour of the inverse correlation length as a function of field and at low temperatures. This is shown in figs. 8 and 9. In the case of $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$, the $d = 2$ system, the inverse correlation length varies as the applied field to the power $2x = 1.6 \pm 0.2$. For $\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$, the data at small fields do not give a reliable estimate of κ because of experimental problems due to extinction. Fitting the data at larger fields $H > 1.5$ T we find that the inverse correlation length varies as the applied field to the power $2x = 2.1 \pm 0.2$. In contrast similar experiments on $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$ gave the power $2x = 3.6 \pm 0.2$. It is difficult to reconcile these results with the predictions given in eqn. (4). The results for $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$ and $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$ are more or less consistent with eqn. (4) if $d_c \approx 3.4$, which is higher than all the theoretical estimates, but since the $\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$ system yields a different exponent and a value of $d_c \approx 3.9$, any conclusion must be treated with caution.

The behaviour of the amplitudes A and B is very much that expected from eqns. (3) and (5). At low temperatures it is found in $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$ that the amplitude of the Lorentzian squared, B,

Fig. 5. The inverse correlation length κ as a function of temperature for various different applied fields in $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$.

is proportional to κ^2 , and in $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$ and $\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$ that B is proportional to κ , in agreement with eqn. (5). In the latter two systems the amplitude of the Lorentzian A is negligible at small fields. The behaviour of the amplitudes in the sample $\text{Co}_{0.26}\text{Zn}_{0.74}\text{F}_2$ is somewhat different. This sample has a concentration of Co ions which is very close to the percolation concentration of 0.24. On applying fields above 1.2 T, it was found that the scattering could be described by a Lorentzian profile without including the Lorentzian squared term. Also for these fields the results were independent of the prior history of the sample. The system was then a normal paramagnet, and the relatively large field had suppressed the characteristic features of the random field behaviour. In this case as the field was increased, B/κ decreased to zero at 1.2 T, and the amplitude A increased with increasing field to 1.2 T and at higher fields remained almost constant.

At temperatures well above T_N , the scattering was well described

Fig. 6. The inverse correlation length κ as a function of temperature for various applied fields in $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$.

by the normal Lorentzian profile for every system as shown at 12.5 K in fig. 4 for $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$. On cooling in a field, the profile changes continuously from a Lorentzian to a largely Lorentzian squared profile. Unfortunately, when eqn. 3 is then fitted to the results, the values of the parameters, A, B and κ , are highly correlated, and it is difficult to obtain reliable estimates. Nevertheless we show in figs. 10 and 11 the behaviour of B/κ^2 for $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$ and B/κ for $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$. They both behave very much like the square of the order parameter as predicted by eqn. 5, and a similar behaviour is found for $\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$. The amplitude of the Lorentzian steadily decreases with decreasing temperature although its behaviour close to T_N is difficult to determine. It is worthy of note that the amplitude of the Lorentzian squared is not zero at all temperatures above the break in the κ/T curves shown in figs. 2-4, but is significant for all temperatures below T_N .

The behaviour of the scattering at T_N was studied in

Fig. 7. The inverse correlation length κ as a function of temperature for various applied fields (kG) in $\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$.

$\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$, and the results for κ are illustrated in fig. 12. The inverse correlation length κ varies as the applied field to the power 0.8 ± 0.1 , and a similar analysis for the peak intensity yields it varying as the applied field to the power -1.6 ± 0.2 . As the critical exponent, η , is small for the $d = 3$ Ising model, these two results are consistent with one another but are not in good agreement with the predictions of scaling theory, eqn. (6), unless the random field is proportional to the applied field to the power 0.8.

Although many of the results described above are more or less consistent with the behaviour expected for an Ising system in a random field, there is one glaring discrepancy. The lower critical dimension is predicted to be variously 2 or 3, whereas a direct interpretation of our results suggests d_c is larger than 3. Because of this discrepancy and the implications it has for the theory as well as for the effect of random fields on the results of other experiments on three dimensional systems, we must consider the problem of the freezing at low temperatures in more detail. In particular it is possible that our results are not characteristic of the ground state of the system, but that the freezing prevents us from determining the properties of the ground state. We have performed two sets of experiments to investigate this possibility. Firstly in $\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$ we performed several experiments in which the

Fig. 8. The magnetic field dependence of the inverse correlation length and susceptibility in $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$.

field was varied while the temperature was held constant. These showed that at a temperature of 8.0 K, the spins were frozen for fields, $0 < H < 7.0$ T. At 16.0 K, however, the spins were able to follow the varying field, on a time constant of several minutes, for magnetic fields as low as 2 T. Since the scattering for fields of 2 T is almost independent of temperature below 20 K, fig. 7, this experiment strongly suggests that the spins are in equilibrium for at least part of the temperature range over which κ is almost constant in fig. 7. The break in behaviour of the κ versus temperature curve is not due to freezing at about 20 K. If however the equilibrium behaviour of the system is such that in a field of 2 T, κ is independent of temperature between 20 K and 15 K and then decreases, freezing may well prevent us from observing this decrease. This behaviour although not impossible seems unlikely to us. It was shown that $\text{Rb}_2\text{Co}_{1-x}\text{Mg}_x\text{F}_4$ was in equilibrium at all fields for $T \geq 30$ K and at least for fields greater than 4 T down to 20 K.

The second set of experiments were measurements on the $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ system. In this system the spin wave gap is much smaller

Fig. 9. The magnetic field dependence of the inverse correlation length in $\text{Fe}_{0.35}\text{Zn}_{0.65}\text{F}_2$ at 3.0 K.

and so it is to be expected that the system will remain in a thermodynamic equilibrium state down to lower temperatures. The system is, however, not a good Ising system and in particular the system has spin $S = \frac{5}{2}$ rather than $\frac{1}{2}$, and furthermore the anisotropy arises from the rather complex dipolar interactions; typically for the range of fields studied the random field energy is larger than the anisotropy.

The initial measurements were performed at Chalk River Nuclear Laboratories on a sample of $\text{Mn}_{0.78}\text{Zn}_{0.22}\text{F}_2$. The results²⁶ were surprising in that at low temperatures the magnetic Bragg reflection was unchanged in width on cooling in a magnetic field as shown in fig. 13. This shows that in $\text{Mn}_{0.78}\text{Zn}_{0.22}\text{F}_2$, long range order is not destroyed by a field unlike the cases discussed above. There was however evidence of a random field state described by a Lorentzian squared cross-section, eqn. (3), but this occurred only within about 2 K of T_N which in this case was 48 K.

More detailed measurements have now been made on a more dilute sample of $\text{Mn}_{0.65}\text{Zn}_{0.35}\text{F}_2$. For a field of about 5 T, the spin wave

Fig. 10. The integrated intensity of the Lorentzian squared in $\text{Rb}_2\text{Co}_{0.7}\text{Mg}_{0.3}\text{F}_4$, B/κ^2 , as a function of temperature for three different applied fields.

frequency becomes zero and the sample undergoes a spin-flop transition, as shown in fig. 14, to a phase in which the spins are aligned perpendicular to the c-axis. The paramagnetic phase is characterised by a Lorentzian scattering profile, and the random field phase by a Lorentzian squared profile. In the long range ordered phase the inverse correlation length, κ , is smaller than our resolution which means that κ is less than 0.0005 r.l.u. or that the domain size is in excess of 2000 lattice spacings. Finally in fig. 15 we show a plot of κ against temperature for various applied fields. The behaviour is clearly very different from that occurring in the other samples, figs. 5-7. The inverse correlation length continuously decreases with decreasing temperature and does not show the temperature independent behaviour of the other systems. We do not understand the origin of this difference in the behaviour — whether it results from the freezing although our experiments on $\text{Rb}_2\text{Co}_{1-x}\text{Mg}_x\text{F}_4$ and $\text{Fe}_{0.65}\text{Zn}_{0.35}\text{F}_2$ make this appear to be unlikely, or whether it is because $\text{Mn}_{0.35}\text{Zn}_{0.65}\text{F}_2$ is anomalous because it is not a good Ising model, has a large spin $\frac{5}{2}$, and is close to a spin-flop instability. Only further work can elucidate these questions as a function of temperature for various different applied fields.

Fig. 11. The integrated intensity of the Lorentzian squared in $\text{Co}_{0.35}\text{Zn}_{0.65}\text{F}_2$, B/K , as a function of temperature for different applied fields.

Other Measurements and Conclusions

The application of a magnetic field to a dilute antiferromagnet has been used to study the effect of random fields using several techniques other than neutron scattering. The first measurements²⁹ were susceptibility measurements on $\text{Gd}_{0.97}\text{La}_{0.03}\text{AlO}_3$ which showed that the application of a random field produced a rounding of the transition and were interpreted as showing a destruction of a long range order. Similar susceptibility measurements have been made on the $\text{Rb}_2\text{Co}_x\text{Mg}_{1-x}\text{F}_4$ systems³⁰ with $x = 0.8, 0.7$ and 0.6 and on the $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ system³¹ with $x = 0.45$ and 0.6 . The results on both of these systems also show a rounding of the transition when the field is applied. The $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ system³² was also studied for $x = 0.94$ by thermal expansion measurements and they too found a rounding of the transition was produced by the applied field.

Fig. 12. The inverse correlation length κ for $\text{Fe}_{0.65}\text{Zn}_{0.35}\text{F}_2$ as a function of field for $T = T_N$.

In contrast to these measurements specific heat and linear birefringence measurements³³ which also yield the specific heat exponent show firstly that the critical fluctuations are different in the presence of a field and secondly that the transition does remain sharp. Recent measurements on a sample of $\text{Fe}_{0.6}\text{Zn}_{0.4}\text{F}_2$ gave the results shown in fig. 16 and the transition is clearly extremely sharp. Analysis shows that the temperature derivative of the birefringence is a logarithmic function of $(T - T_N)$, which is the behaviour expected for a $d=2$ Ising and non-random system. Similar results although of not such high precision were found³³ for $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$.

The results of the susceptibility measurements are consistent with the neutron scattering measurements. There is no doubt that random fields do drastically modify the behaviour of the critical fluctuations close to T_N . There is no doubt that care must be taken in studies of critical phenomena to avoid the presence of random fields because they are relevant and do produce very large effects. In nearly all of the measurements the random field energy/site has been much less than kT_N , or the exchange interactions but there is no doubt that they have caused large effects.

The results of the specific heat measurements are more surprising because they do yield a surprisingly sharp peak as shown in

Fig. 13. The neutron scattering intensity observed along the line $(1, \xi, 0)$ at 7.0 K in $\text{Mn}_{0.78}\text{Zn}_{0.22}\text{F}_2$ for a field of 4 T (open circles) and without a field (closed circles).

fig. 16. Not surprisingly the sharpness of this peak has been interpreted as evidence that the phase transition in the $d=3$ Ising model is not destroyed by the presence of a random field. The neutron scattering measurements have been performed on the same system, $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$, however, and they show unambiguously that the systems do not have long range antiferromagnetic order. Consequently if there is a sharp transition in the presence of a field it is not a transition between a paramagnetic phase and an antiferromagnetic phase, it must be a transition to a disordered state with a presently unknown order parameter.

The measurements which are sensitive to a particular type of order, susceptibility and neutron scattering both show a smearing of the properties close to T_N , whereas the specific heat measurements are especially sensitive to the local properties. Whether the domains caused by the random field are sufficiently large that the ordering of the spins within one domain can account for the specific

Fig. 14. The phase diagram of $\text{Mn}_{0.65}\text{Zn}_{0.35}\text{F}_2$ in a field.

heat results, or whether the specific heat results do signify a new type of ordered phase only more experiments and theory will tell.

In conclusion there is no doubt that the presence of random fields does have a large effect on the critical fluctuations close to T_N . They appear to destroy the long range order in $d=3$ Ising systems although there is the possibility that the low temperature freezing of the spins may be giving problems in the interpretation of the measurements. The behaviour of the $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ system with a small gap arising from the dipolar anisotropy is different from that of the good Ising models; $\text{Co}_x\text{Zn}_{1-x}\text{F}_2$ and $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$.

Further theoretical work is needed to understand the changes in the critical fluctuations close to T_N , and to understand the freezing of the spins at lower temperatures in addition to further work on the problem of the lower critical dimension for the Ising model in a random field.

Fig. 15. Inverse correlation length in $\text{Mn}_{0.65}\text{Zn}_{0.35}\text{F}_2$ as a function of temperature for various different applied fields.

COMPETING ANISOTROPY

Systems with competing anisotropies are ones in which the spin direction of one component wishes to align along one crystallographic direction whereas for the other component it is energetically favourable for the spin to align along a different direction. There is then a competition between the anisotropy energy which favours different directions for the spins and the exchange energy which favours parallel or anti-parallel spin directions. There are several examples of systems in which this competition can be studied. The most carefully studied^{35, 36} is the $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$ system in which the single ion anisotropy energy of the Fe ion favours a spin alignment along the c axis, whereas the anisotropic Co exchange favours a spin direction perpendicular to the c-axis. Other systems are $\text{K}_2\text{Co}_x\text{Fe}_{1-x}\text{F}_4$ ³⁷, where in contrast, the anisotropic exchange between the Co ions favours alignment along the c-axis whereas the single ion Fe anisotropy favours alignment perpendicular to the c-axis and $\text{K}_2\text{Mn}_x\text{Fe}_{1-x}\text{F}_4$ where the dipolar forces favour the

Fig. 16. Measurements³⁴ on the temperature derivative of the linear birefringence in $\text{Fe}_{0.46}\text{Zn}_{0.4}\text{F}_2$.

alignment along the c-axis³⁸.

The theory of these systems within mean field³⁹ theory suggests that between the phases in which the spins are aligned parallel or perpendicular to the c-axis, there is a phase in which both the parallel and perpendicular components are ordered. The critical phenomena was then discussed by Fishman and Aharony⁴⁰ who suggested that the phase boundaries associated with the ordering of these two components of the spin were decoupled and intersected at a decoupled tetracritical point, and furthermore that the critical behaviour associated with each of the phase lines was that appropriate for the ordering of either the parallel or perpendicular components.

Although the presence of an intermediate phase has been confirmed in several different systems, detailed information on the critical

phenomena is available^{35,36} on only one system, $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$. Largely, this is because the experiments require very good single crystals with a very homogeneous concentration. In fig. 17. we show measurements of the phase diagram in $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$, showing the phases with spins ordered parallel to the c-axis, perpendicular to the c-axis and a mixed phase. The qualitative agreement with mean field theory is satisfactory. The predictions of Fishman and Aharony suggest that the phase boundary lines are decoupled and are continuous in slope at the tetracritical point. The experimental results clearly suggest that there is a discontinuity in shape, particularly in the line describing the perpendicular ordering.

The behaviour of the phase transitions was also different from that predicted as shown in fig. 18. The scattering for $\vec{Q} = (0,0,8.8)$ is the critical scattering associated with the ordering of the perpendicular component, whereas that for $\vec{Q} = (0.985,0,1)$ is largely associated with that of the parallel component. Clearly fig. 18 shows that whereas the transition at higher temperature is sharp, that at the lower temperature is rounded. Similar evidence³⁶ for this was found in studies of the temperature dependence of the ordering. There is no doubt that the ordering of $S_{||}$ and $S_{\perp}$ is coupled. There have been several suggestions put forward^{17,36} to explain this discrepancy between experiment and theory. The most appealing³⁶ is that the smearing is a result of the effect of the random fields produced as a result of the ordering at the first transition.

Fig. 17. The phase diagram of $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$ from ref. 36. The lines connecting the dashed points are the results of mean field theory and the experimental points are from susceptibility (solid) or neutron scattering (open).

Fig. 18. The neutron scattering intensity for two different wave-vector transfers in $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$ for different concentrations near the tetracritical point with $x = x_M$.

The symmetry of $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$ allows a general exchange interaction between two ions separated by $\vec{R}_{ij}$ of the form

$$\begin{aligned} \text{Hence } &= -J \vec{S}_i \cdot \vec{S}_j + \frac{K}{R^2} (\vec{R}_{ij} \cdot \vec{S}_i)(\vec{R}_{ij} \cdot \vec{S}_j) \\ &+ \frac{G}{R} \vec{S}_i \cdot (\vec{S}_j \times \vec{R}_{ij}) . \end{aligned}$$

The last term in this expression gives rise to a coupling between $S_{\parallel}$ and $S_{\perp}$ even for interactions between ions in the magnetic sheets. If either $S_{\parallel}$ or $S_{\perp}$ orders, this term generates a field on the other spin component, and due to the mixed nature of the sample the net direction of this field varies from site to site. This type of interaction was not considered by Fishman and Aharony. As we have seen in the preceding section random fields do drastically alter the critical fluctuations and in neutron scattering measurements appear to smear out the transition. Consequently this provides a ready explanation of the measurements.

If this is indeed the origin of the effect, it should be absent in, for example, the $\text{K}_2\text{Co}_x\text{Fe}_{1-x}\text{F}_4$ system because the third term in the exchange interaction is forbidden by symmetry. We must await detailed measurements on this type of system to test both the theory and the explanation of the discrepancies in $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$.

CONCLUSIONS

The first conclusion is that the study of disordered insulating magnets is a very rich field for the testing of the theories of the phase transitions in disordered systems. There is a wide variety of systems available, and experiments continue to provide a crucial test of the theories and new challenges for theoretical work.

The second main conclusion concerns the importance of random fields. Measurements have shown that relatively small random fields do produce large and dramatic effects on the ordering and critical phenomena of systems. Although, as described above, a detailed understanding of these effects is not yet available, there is no doubt that they are large and significant. It is therefore of crucial importance in studying phase transitions to ensure that impurities do not introduce random fields. We have seen above that the first detailed study of the competing anisotropy problem gave results which were not in agreement with the theory and the discrepancies probably resulted from random field effects. Similarly⁴² discrepancies between theory and experiment on tricritical points have been explained as arising from these effects. There is no doubt that they are also of importance in the study of competing interactions in metallic spin glasses and they probably also account for many of the puzzling results obtained on structural phase transitions. It is clearly of considerable importance to understand the effect of random fields in more detail, and studies of insulating disordered magnets will probably be the most fruitful line of experimentation.

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