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EXCITATIONS AND PHASE TRANSITIONS IN RANDOM ANTI-FERROMAGNETS

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ABSTRACT

Neutron scattering techniques can be used to study the magnetic excitations and phase transitions in the randomly mixed transition metal fluorides. The results for the excitations of samples with two different types of magnetic ions show two bands of excitations; each associated with excitations propagating largely on one type of ion. In the diluted salts the spectra show a complex line shape and greater widths. These results are in good accord with computer simulations showing that linear spin wave theory can be used, but have not been described satisfactorily using the coherent potential approximation. The phase transitions

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in these materials are always smeared, but it is difficult to ascertain if this smearing is due to macroscopic fluctuations in the concentration or of an intrinsic origin. Studies of these systems close to the percolation point have shown that the thermal disorder is associated with the one-dimensional weak links of the large clusters. Currently theory and experiment are in accord for the two-dimensional Ising system but features are still not understood in Heisenberg systems in both two and three dimensions.

INTRODUCTION

The transition metal fluorides are ideal systems on which to study the properties of disordered systems. Transition metal ions such as Mn^{++} , Co^{++} and Mg^{++} are chemically very similar but are magnetically very different. Consequently it is possible to grow single crystals in which magnetically very different ions are randomly distributed over the transition metal sites. It is then possible to study the excitations and phase transitions of these disordered systems in detail particularly by the use of neutron scattering techniques. The comparison of these results with theory is further facilitated because the magnetic interactions are of a relatively simple form between only near neighbours and the magnitude of these interactions is usually known from experiments on the pure materials. There are then, relatively few if any unknown parameters needed to describe the magnetic interactions in these systems and so there are few adjustable parameters which need to be introduced in confronting theory with experiment. Before 1971 most of the work on these systems had been on systems in which one of the magnetic constituents was present only in low concentration. Excellent agreement was found between the results of these experiments and theory¹. More recently experiments have been performed on more concentrated systems and in this brief review the main experimental results will be described together with an outline of the appropriate theories.

Although all the transition metal fluorides are simple anti-ferromagnets, they show a wide diversity of behaviour. They have three different crystal structures; in $RbMnF_3$, the magnetic ions, $S = \frac{5}{2}$, are arranged on a simple cubic lattice and the magnetic interactions are of Heisenberg character between nearest neighbours²

$$H_{EX} = \frac{1}{2} J \sum_i \sum_{\Delta} \vec{S}_i \cdot \vec{S}_{i+\Delta} \quad (1)$$

where Δ is a nearest neighbour to i . MnF_2 and CoF_2 have the rutile structure with the magnetic ions arranged on a body-centred tetragonal lattice. The interaction with the body-centred ions is anti-ferromagnetic and there is a weaker ferromagnetic interaction with the nearest neighbours along the c -axis. In the Mn salt both these

interactions are of Heisenberg character³ but the dipolar interactions lead to a weak anisotropy field along the unique c-axis which is consequently the spin direction;

$$H_D = - H_A \sum_i (S_i^z)^2. \quad (2)$$

In CoF_2 the effect of the orbital angular momentum is that the effective exchange within the ground state doublet, $S = \frac{1}{2}$, can be written approximately⁴ as

$$H_{AN} = \frac{1}{2} J \sum_{i\Delta} \left[S_i^z S_{i+\Delta}^z + \alpha (S_i^x S_{i+\Delta}^x + S_i^y S_{i+\Delta}^y) \right], \quad (3)$$

where α is 0.81.

The third system is the structure shown in fig. 1, K_2NiF_4 ($S=1$). The Ni ions are arranged on a square lattice with a relatively large separation and consequently little interaction between the different layers of the lattice. Although these materials order three-dimensionally, the critical scattering and magnetic excitations are characteristic of a two-dimensional system. The magnetic interactions are almost wholly between nearest neighbours and for the Mn and Ni salts of Heisenberg character⁵, eqn. 1, and for the Co salt⁶ the exchange is anisotropic eqn. 3 with $\alpha = 0.55$. The tetragonal symmetry of these materials

Fig. 1. The reciprocal lattice and crystal structure of K_2NiF_4 . The reciprocal lattice shows the scattering geometry used to determine $S(\vec{Q})$ by taking advantage of the independence of $S(\vec{Q})$ on Q_c .

leads for the Mn and Ni salts to a weak anisotropy field which aligns the spins perpendicular to the layers. The exchange interactions and dipolar fields for these systems are listed in table I for these various different systems as determined from spin wave measurements.

Table I

Dominant Exchange Constants and Anisotropy Fields deduced from linear spin wave theory.

Material	S	J(°K)	α	H _A (°K)	Reference
KMnF ₃	2.5	7.25	-	0	1
KCoF ₃	0.5	112.4	-	6.7	1
KNiF ₃	1.0	102.1	-	0	1
MnF ₂	2.5	3.57	-	0.43	1
CoF ₂	0.5	17.78	0.81	-	1
K ₂ NiF ₄	1.0	104.0	-	0.87	5
K ₂ MnF ₄	2.5	8.4	-	0.13	5
Rb ₂ MnF ₄	2.5	7.60	-	0.15	5
Rb ₂ CoF ₄	0.5	179.5	0.55	-	6

In the next section a brief description is given of the neutron scattering techniques. One of the first aspects studied in these systems was the nature of the excitations in very disordered systems. This aspect was reviewed⁷ in 1975 and so in section 3 only a brief account is presented concentrating on the more recent developments. Attention has more recently been directed to the study of the phase transitions in disordered systems. In section 4 we describe the little experimental progress which has been made in this subject. More progress has been made in the understanding of percolation as described in the final section.

NEUTRON SCATTERING

Before any experiments can be performed single crystal specimens of the mixed systems must be grown. The starting materials are carefully purified and mixed in the desired proportions. The crystals are then grown using either Bridgman or Stockbarger techniques in a manner similar to that employed for the pure materials. One of the most difficult and frustrating aspects of this work is the determination of the concentration of the constituents in the resulting crystals, and the extent to which the concentrations are uniform throughout the crystals.

Unfortunately chemical analysis involves destroying at least parts of the crystal and even then seems to give the atomic concentration, of say a 50% concentration of Mn and Mg, to only about 3%. Lattice parameter measurements and measurements of magnetic ordering temperatures are also useful indicators of the concentration.

Measurements in many of these systems have been performed to search for evidence of any chemical ordering or clustering. In none of the materials has there been any evidence of such an ordering found.

The neutron scattering measurements have all been performed with unpolarised neutrons. The incident neutron beam with wavevector $\vec{k}_I$ is scattered to give a beam with wavevector $\vec{k}_F$, and a wavevector transfer $\vec{Q} = \vec{k}_I - \vec{k}_F$. The energy transfer to the specimen is $\hbar\omega = \frac{\hbar^2}{2m_N} (k_I^2 - k_F^2)$. The cross-section for the scattering from these systems is given by;

$$\frac{d^2\sigma}{d\Omega d\omega} = C \frac{k_I}{k_F} |F(\vec{Q})|^2 \left[\cos^2\theta G_L(\vec{Q}, \omega) + (1 + \cos^2\theta) G_T(\vec{Q}, \omega) \right], \quad (4)$$

where C is a constant, $F(\vec{Q})$ the form factor of the magnetic ions, θ the angle between $\vec{Q}$ and the z axis. The spin correlation functions are given by:

$$G(\vec{Q}, \omega) = \sum_{nm} p_n \langle n | O | m \rangle \langle m | O^\dagger | n \rangle \delta(\omega - \omega_{nm}),$$

where the operator O is given for $G_L(\vec{Q}, \omega)$ by

$$O = \sum_i S_i^z \exp(i \vec{Q} \cdot \vec{R}_i),$$

and for $G_T(\vec{Q}, \omega)$ by

$$O = \sum_i S_i^x \exp(i \vec{Q} \cdot \vec{R}_i),$$

whilst n is the initial state of the system and m the final state and $\hbar\omega_{nm}$ is their energy difference.

The excitation spectra at low temperatures are obtained from measurements of the cross-section as a function of frequency transfer for various wavevector transfers. These measurements are most

conveniently performed with the aid of a triple axis crystal spectrometer which determines the energy of the incident and scattered neutrons by Bragg reflection from single crystals. The usual experimental precautions must be taken to minimize the experimental resolution while maximizing the counting rate, and to avoid the spurious scattering by the higher order neutrons reflected by the monochromators. Essentially, however, these measurements enable a quite direct measurement of $G_L(\vec{Q}, \omega)$ and $G_T(\vec{Q}, \omega)$.

The theory of phase transitions is most highly developed for the instantaneous properties of the system and much less highly developed for describing the time-dependent properties. In scattering terms it provides detailed predictions about the behaviour of the static correlation functions

$$G_T(\vec{Q}) = \int G_T(\vec{Q}, \omega) d\omega, \quad (5)$$

and

$$G_L(\vec{Q}) = \int G_L(\vec{Q}, \omega) d\omega.$$

These can be measured by measuring the differential cross-section, $G(\vec{Q}, \omega)$, and numerically performing the integrals. It is, however, more convenient to measure the static correlation function directly. In a two-axis experiment the neutrons scattered in a given direction are all recorded irrespective of their energy. Unfortunately as the energy transfer varies the wavevector transfer also varies and in the integral over ω the wavevector $\vec{Q}$ is not constant for all energy transfers. The change in wavevector for a frequency transfer $\delta\omega$ from $\omega=0$ is approximately given by

$$\delta\vec{Q} = -2\vec{k}_F \frac{\delta\omega}{E_0},$$

where E_0 is the incident energy of the neutrons. Clearly the change in the wavevector can be minimized by increasing the incident neutron energy, E_0 , to be much larger than $\delta\omega$. Unfortunately increasing E_0 also decreases the wavevector resolution. In the two-dimensional layer systems $G(\vec{Q}, \omega)$ is largely independent of the component Q_c . Consequently by performing experiments with k_F aligned along the crystallographic c axis, as shown in fig. 1, accurate measurements of $G(\vec{Q})$ can be obtained without using such high energy incident neutrons.

EXCITATIONS

In concentrated systems composed of two different magnetic

ions the excitation spectrum consists of two fairly distinct branches. This behaviour was first observed in the $\text{KMnF}_3/\text{KCoF}_3$ system⁸ but has now been observed also in $\text{MnF}_2/\text{CoF}_2$ ^{8,9}, $\text{KMnF}_3/\text{KNiF}_3$ ¹⁰ and $\text{Rb}_2\text{MnF}_4/\text{Rb}_2\text{NiF}_4$ ¹¹. The results for various concentrations of $\text{Co}_{1-c}\text{Mn}_c\text{F}_2$ are shown in fig. 2. For $c = 0.05$ there is a local mode associated with the Co ions at frequencies well above the MnF_2 host band. For $c = 0.3$ the Co band shows dispersion and considerable width and the Mn band has less

Fig. 2. Dispersion relations for the $\text{Mn}_{1-c}\text{Co}_c\text{F}_2$ system^{9,9}. The solid lines are the results of CPA calculations¹⁴ and dotted lines the dispersion relations of the pure material. The shaded region for $c = 0.3$ gives the width predicted by the calculations.

dispersion. This behaviour progresses steadily until for $c=0.95$ the the Co band is very similar to that of pure CoF_2 and there is a local mode associated with the Mn ions below the CoF_2 band.

In pure materials the frequency of the magnons at the zone boundary is given by the Ising model. In the mixed systems the Ising model suggests that the energy to create a spin deviation on an ion of type λ surrounded by cz ions of type λ and $(1 - c)z$ ions of type λ' is

$$\bar{E}_\lambda = cz J_{\lambda\lambda} + (1 - c)z J_{\lambda\lambda'} \quad (6)$$

Experiments on systems with only a small concentration of defects¹ further suggest that

$$J_{\lambda\lambda'} = (J_{\lambda\lambda} J_{\lambda'\lambda'})^{\frac{1}{2}}. \quad (7)$$

Using eqn's 6 and 7 the frequencies of the mixed systems can be calculated using the results listed in table I, as shown in table II. Clearly the agreement between experiment and theory is surprisingly good for such a simple model.

A more comprehensive theory must include a calculation of the width and wave-vector dependence of the excitations. Calculations^{12,13} for the $\text{Rb}_2\text{Mn}_c\text{Ni}_{1-c}\text{F}_4$ system using computer simulation techniques have given a good account of the experimental results confirming that the basic model for these systems is adequate and that the excitation spectra can be obtained at low temperatures by using a linear spin wave theory.

One of the most well used ways of describing the excitations in disordered systems is the coherent potential approximation or CPA. There have been several different ways developed to apply these techniques to these systems. We believe that one of the most useful approaches is that developed by Buyers et al.¹⁴. It begins with the success of the Ising model discussed above. Suppose an ion λ is surrounded by r similar ions then the frequency to create a spin deviation is

$$\bar{F}_\lambda(r) = z r J_{\lambda\lambda} + (z - r) J_{\lambda\lambda'}, \quad (8)$$

These frequencies vary from site to site with probabilities dependent upon the concentrations of the different types of ions. If the transverse part of the exchange interactions are independent of the type of ions, then the problem is formally very similar to that of random masses in the analogous phonon problem or random single site potentials in the electron problem. For these systems

Table II

The Ising frequencies (THz) in mixed antiferromagnets from reference 7.

System	Concentration	Calculation	Experiment
$\text{MnF}_2/\text{CoF}_2$	0.95	3.46	3.57 ± 0.05
		1.51	1.49 ± 0.02
	0.30	2.42	2.32 ± 0.10
		1.20	1.20 ± 0.06
	0.10	2.05	2.02 ± 0.08
		1.05	1.09 ± 0.08
$\text{KMnF}_3/\text{KCoF}_3$	0.80	1.92	1.86 ± 0.06
		1.00	0.90 ± 0.10
	0.29	6.96	6.55 ± 0.15
		2.27	2.26 ± 0.02
	0.29	7.04	6.80 ± 0.10
		2.30	2.30 ± 0.10
$\text{KMnF}_3/\text{KNiF}_3$	0.97	8.51	7.68 ± 0.10
		2.27	2.17 ± 0.05
	0.25	11.7	11.8 ± 0.5
		3.12	3.1 ± 0.15
$\text{Rb}_2\text{MnF}_4/\text{Rb}_2\text{NiF}_4$	0.5	6.81	6.48
		1.92	1.79
$\text{MnF}_2/\text{ZnF}_2$	0.78	1.18	1.19 ± 0.02
	0.69	1.04	1.05 ± 0.03
$\text{CoF}_2/\text{ZnF}_2$	0.86	1.60	1.59 ± 0.02
	0.59	1.28	1.12 ± 0.05

the single site CPA describes the scattering of the magnetic excitations by the different single site frequencies. Despite this similarity there is one difference; namely that since $E_\lambda(r)$ depends on the local environment the $E_\lambda(r)$ of nearest neighbours are not completely random but have some degree of correlation. This correlation becomes most pronounced when z is low, and we are unaware of any attempt to investigate the effects of this correlation.

The approximation that the transverse parts of the exchange interactions are independent of the ions is not usually valid. By

chance it is very nearly satisfied in $\text{MnF}_2/\text{CoF}_2$ and the results of CPA calculations for this system¹⁴ are shown in fig. 2. Clearly the agreement between experiment and theory is quite satisfactory.

In other systems various different approximations have been employed to treat the transverse part of the exchange interactions. The most successful way is to exploit the spin scaling technique of Tonegawa¹⁵ to minimize the randomness of the transverse exchange interactions. It is possible to eliminate the randomness entirely if $S_\lambda J_{\lambda\lambda'} = S_{\lambda'} J_{\lambda'\lambda}$ and $S_\lambda J_{\lambda\lambda} = S_{\lambda'} J_{\lambda'\lambda'}$. These relations are almost exactly satisfied in the $\text{KMnF}_3/\text{KCoF}_3$ and $\text{KMnF}_3/\text{KNiF}_3$ systems and the agreement between experiment and the CPA calculations^{14,10} is very satisfactory. There are then various ad hoc ways of treating further randomness and by a judicious choice of the form reasonable agreement¹⁶ can also be obtained for the $\text{Rb}_2\text{Ni/MnF}_4$ system.

The systems in which the magnetic ions are diluted with a non-magnetics have proved to be more difficult to explain in detail. The average zone boundary frequencies are given quite accurately for the Mn/ZnF_2 ¹⁷ and Co/ZnF_2 systems¹⁸ as shown in table 2. The CPA calculations, however, proved to be more unreliable because of the difficulty of treating the transverse parts of the exchange adequately. An alternative form of the CPA was, therefore, developed by Holcomb¹⁹ which treats the transverse parts of the exchange interactions adequately but at the expense of treating all the Ising parts in the same average way. The frequencies are the average frequencies of eqn. 6 instead of the $E_\lambda(r)$ of eqn. 8. There is then a difference in the predictions of these two CPA theories: the theory of Holcomb predicts a smooth distribution in frequency with a single peak at each wavevector while that of Buyers et al. predicts a multi-peaked cross-section with the peaks at least loosely associated with the different arrangements of the neighbours (values of r).

The first experiments to exhibit this fine structure were performed on the Mn/ZnF_2 system^{20,21}. They clearly showed the existence of fine structure in the differential scattering cross-section showing that a successful theory must treat the local environment of each ion in detail. More dramatic evidence of these effects has now been obtained using the two-dimensional layer materials. In this case $z=4$ and so the separation in frequency between the different $E_\lambda(r)$ is larger. In fig. 3 scattered neutron distributions²² are shown for $\text{Rb}_2\text{Co}_{0.57}\text{Mg}_{0.43}\text{F}_4$ and they clearly show the existence of four peaks corresponding to the frequencies $r = 1, 2, 3, 4$. Similar results for other concentrations in this system have been obtained by Ikeda and Shirane²³. Fig. 3 also shows that there is much less dispersion in the frequencies than in the pure material. Computer simulations of the magnetic excitations in this system performed using the techniques developed

Fig. 3. Scattered neutron distributions²² obtained from $\text{Rb}_2\text{Co}_{0.57}\text{Mg}_{0.43}\text{F}_4$ at 80 K for various wavevector transfers. The solid line is the result of a computer simulation using the techniques of Alben and Thorpe¹².

by Alben and Thorpe¹² give good agreement with the experimental results. The magnetic interactions in $\text{Rb}_2\text{Mn}/\text{MgF}_4$ are more nearly Heisenberg in character and consequently the fine structure is less marked, as shown in fig. 4. Nevertheless four peaks are observed corresponding to the four $E_\lambda(r)$ particularly for wavevectors close to the zone boundary²⁴. Also shown in fig. 4 are the results of computer simulations which give amazingly good agreement with the experimental results. This agreement shows for both of these systems that linear spin wave theory is adequate for describing the excitations and secondly enables us to determine the exchange interaction and the concentration accurately²⁴.

Fig. 4. Scattered neutron distributions²⁴ in $\text{Rb}_2\text{Mn}_{0.54}\text{Mg}_{0.46}\text{F}_4$ at 4.0 K and compared with computer simulations obtained using the techniques of Alben and Thorpe.

Calculations of these distributions using the coherent potential approximation have been performed²⁴. Clearly one of the forms of theory using the $E_{\lambda}(r)$ must be employed if the many peaked structure is to be obtained but then there is the difficulty of treating the transverse parts of the exchange interactions. At present none of the calculations have given a good account of the results shown in fig. 4.

CRITICAL PHENOMENA AT PHASE TRANSITIONS

The study of the critical phenomena at the phase transitions of the pure antiferromagnets has provided some of the most accurate measurements of the critical exponents of different types of systems. We do not, however, review all of these results because many of the classic studies such as that²⁵ of RbMnF_3 were performed nearly 10 years ago. One result which is, however, so elegant as to be worth presenting again, is that of Ikeda and Hirakawa²⁶ on K_2CoF_4 . The sub-lattice magnetisation is shown in fig. 5 and it agrees precisely with Onsager's exact solution of the two-dimensional Ising model.

The nature of the phase transitions in disordered systems has been the subject of considerable theoretical effort recently. The

Fig. 5. The sub-lattice magnetisation, $M(T)$, in K_2CoF_4 as a function of temperature. The solid line shows Onsager's exact solution of the two-dimensional Ising model.

work of Harris²⁷ suggested that if the specific heat exponent α was positive then the behaviour would be similar to that of the pure systems, but if α was negative then the concentration fluctuations would have a larger effect and might lead to a first order transition or a smeared transition or a continuous transition with different exponents from those of the pure system. Similar results²⁸ have now been obtained using renormalisation group theory and the ϵ -expansion. In the case of some systems for which α was negative

renormalisation group theory suggests that the transition is nevertheless continuous but that the values of the exponents are different²⁹. In contrast McCoy and Wu³⁰ have suggested that the phase transitions in disordered systems are smeared.

There have been two careful measurements of the critical properties of these disordered antiferromagnets published. In $\text{Rb}_2\text{Mn}_{0.5}\text{Ni}_{0.5}\text{F}_4$ the first crystal⁵ showed a smeared transition with a full width at half maximum corresponding to fluctuations in concentration of 8% and a later experiment was performed on a smaller crystal which showed concentration fluctuations of only 2%. In these two-dimensional materials the critical fluctuations are extended in

temperature for $\epsilon = \frac{T - T_N}{T_N} < 0.2$ and, since the spread in concentration corresponds to $\epsilon \sim 0.01$, it is possible to measure the properties of the critical fluctuations despite the smearing of T_C . The results were analysed by writing

$$G_T(\vec{Q}) = \frac{A_T}{K_T^2 + q^2}, \quad (9)$$

and

$$G_L(\vec{Q}) = \frac{A_L}{K_L^2 + q^2},$$

where $\vec{Q} = \vec{q} + \vec{\tau}$ and $\vec{\tau}$ is any reciprocal lattice vector of the magnetic lattice. Since in this material, the exchange interactions are of Heisenberg character, it might be expected that $G_T(\vec{Q}) = G_L(\vec{Q})$. This is not correct close to T_C as in the pure substances, because the presence of the anisotropy field causes $G_L(\vec{Q})$ to diverge for $\vec{Q} = \vec{\tau}$ while $G_T(\vec{Q})$ remains finite. In the analysis of the experimental results⁵ it is, however, necessary to include both $G_L(\vec{Q})$ and $G_T(\vec{Q})$ to obtain the four constants A_T , A_L , K_T and K_L for each temperature. In fig. 6 we show the results for the inverse correlation length, K_L , for K_2NiF_4 , K_2MnF_4 and the mixed system. Clearly the critical behaviour of all these materials is closely similar and the exponent ν is within experimental error that predicted by the exact solution of the two dimensional Ising model. These results are in accord with the theoretical predictions of renormalisation group theory ($\alpha = 0$ for the two-dimensional Ising model) provided that the smearing does result from fluctuations in the concentration.

The other study was of $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{F}_2$ by Meyer and Dietrich³¹. They found a smeared transition with the smearing corresponding to

Fig. 6. The inverse correlation length, κ_L , against $\epsilon = \frac{T - T_N}{T_N}$ for K_2NiF_4 , K_2MnF_4 and $Rb_2Mn_{0.5}Ni_{0.5}F_4$.

concentration fluctuations of 1%. In this three-dimensional system the range of the critical fluctuations in $\epsilon = \frac{T - T_N}{T_N}$ is much smaller than for the two-dimensional systems. Consequently the smearing makes the extraction of the critical exponents much more difficult. The procedure followed was similar to that used for the two-dimensional system and the results yielded exponents which are not significantly different from those obtained³² for pure MnF_2 . Since the dipolar anisotropy breaks the isotropic symmetry in MnF_2 , the critical behaviour is that of the three dimensional Ising model. This has $\alpha = -0.1$ and so the behaviour is expected to be modified by the concentration fluctuations. Renormalisation group theory predicts values of the new exponents^{28,29} but these are sufficiently close to those of pure MnF_2 that they could not have been

distinguished by the experiment.

Besides these published results similar results³³ have been found in the KMn/NiF_3 and Co/ZnF_2 systems. In both of these three-dimensional systems the smearing was sufficient to make the extraction of the exponents difficult. In conclusion, therefore, we are unable to answer what is probably the most interesting question about these phase transitions; namely whether the disorder smears the phase transition. In all the systems examined smearing has been observed but this may result from macroscopic non-uniformities in concentration and as yet it has not proved possible to decide if smearing is indeed a characteristic of uniformly random systems. If it is assumed that the smearing is due to inhomogeneities in the concentration then the exponents are consistent with those deduced using renormalisation group theory, but the accuracy of the measurements is such that this is not a very strong statement.

PERCOLATION

When the magnetic systems are diluted with non-magnetic ions the antiferromagnetic transition temperature decreases until at a critical concentration, c_p , there is no longer any long range order at $T = 0$. This critical concentration is known as the percolation point and is an example of a different type of phase transition where the lack of long range order is caused by geometrical disorder rather than thermal disorder. The properties of percolation considered as a problem in geometrical disorder have been studied³⁴ for many years. In particular for nearest neighbour interactions the critical percolation concentrations are known to be 0.59 for the square two-dimensional lattice and 0.30 for the simple cubic three-dimensional lattice. Likewise the divergence as $c \rightarrow c_p$ of the correlation functions $G_L(Q)$, have been evaluated using various techniques³⁵, and the results for the exponents describing the divergence of the correlation length, ν_G , and susceptibility, A_L/K_L^2 , γ_G , are listed in table III.

It is experimentally very difficult to perform experiments to test these exponents, not least because of the difficulties in controlling and accurately determining the concentrations of the specimens. Consequently it is much easier to determine the behaviour of the scattering as a function of temperature for certain fixed and hopefully known concentrations. Before these can be compared with theory it is, however, necessary to know the behaviour of the scattering as a function of temperature.

Following the suggestion of Stauffer³⁶, it is now generally accepted that the percolation point is an example of a multi-critical point. The behaviour as a function of temperature can then be

obtained from the behaviour as a function of concentration if the scaling fields and the cross-over exponent are known. Stauffer³⁶ and ourselves³⁷ suggested that the scaling field was not temperature but the inverse correlation length, K_1 , of a one-dimensional chain formed from the magnetic ions interacting as they do in the crystal at the percolation point. This suggestion was made partly as a result of computer simulations of clusters near to percolation which showed that they are very ramified (or one-dimensional), and secondly as an explanation for the experimental results discussed below.

The cross-over exponent can be calculated explicitly in the case of a one-dimensional chain where Thorpe³⁸ showed that as $c \rightarrow 1$ and $T \rightarrow 0$ ($c_p = 1$ for a linear chain) the inverse correlation length K is given by

$$K = K_G + K_T \quad (10)$$

where K_G is the geometrical inverse correlation length and in the

linear chain is proportional to $(c - c_p)^{\nu_G}$ with $\nu_G = 1$, while K_T is the thermal contribution to K and for the linear chain is pro-

portional to $(K_1)^{\nu_T}$ with $\nu_T = 1$. This result that $\nu_G = \nu_T$ corresponds to a cross-over exponent, $\phi = 1$. Since then Stephen and Grest³⁹ have shown for the Ising model that $\phi = 1$, in $6 - \epsilon$ dimensions, by using renormalisation group theory and the argument has been extended to all orders in ϵ by Wallace and Young⁴⁰.

Initially we discuss the experimental results for the two-dimensional Ising system²²; $\text{Rb}_2\text{Co/MgF}_4$. Four different concentrations were examined with $c = 0.55, 0.575, 0.583$ and 0.595 , and typical measurements of the total scattering cross-section as a function of Q are shown in fig. 7. The results show a peak whose width decreased with decreasing temperature and for $c = 0.595$ two-dimensional long range order developed for $T < 32$ K. The results would be accurately accounted for by eqns. 4, 5 and 9 but with $G_T(\vec{q})$ neglected. This is because Rb_2CoF_4 is an Ising-like material⁶. The experimental results at each concentration and temperature were fitted by varying A_L and K_L and as shown in fig. 7, good agreement was obtained. This shows, as was found in other systems⁴¹, that the correlation function near percolation has the form of a two-dimensional Lorentzian. In fig. 8 the results for K_L are shown plotted against the temperature. The results clearly suggest that eqn. 10 is an appropriate description of these results, for all results except for $T < 40$ K for $c = 0.595$ where the result is presumably invalid due to the development of long range order. The results can be fitted to eqn. 10 with $K_T = K_1^{\nu_T}$ with K_1 calculated from the exchange constants known from the results on the excitation

Fig. 7. Total neutron scattering intensity²² as a function of wavevector in $\text{Rb}_2\text{Co}_c\text{Mg}_{1-c}\text{F}_4$.

spectrum, fig. 3. The results shown in fig. 8 are consistent with $\nu_T = 1.33$ in agreement with the calculated value of ν_G (table III). Similar results can be obtained for the amplitude parameter A_L . Unfortunately the data analysis is complicated by a lack of knowledge of the dependence of A_L on temperature and concentration. The results suggest that the intensity $G(q^*) = \frac{A_L}{K_L^2}$ diverges at $c = c_p$ with $\gamma_T = 2.15 \pm 0.3$. As shown in table III this result is in general accord with the theoretical prediction for γ_G and a cross-over exponent, $\phi = 1$.

Similar measurements⁴¹ were made earlier on the near Heisenberg

Table III
Exponents for Systems near Percolation

	2D Square Lattice	3D Cubic Lattice
ν_G (35)	1.33 ± 0.01	0.83 ± 0.02
γ_G (35)	2.40 ± 0.03	1.68 ± 0.05
Ising System		
ν_T (22)	1.30 ± 0.05	-
γ_T (22)	2.15 ± 0.30	-
Near Heisenberg		
ν_T (41,43)	0.90 ± 0.03	0.95 ± 0.10
γ_T (41,43)	1.50 ± 0.10	1.84 ± 0.20

Fig. 8. The inverse correlation length, $K_L = K$, for four concentrations in $\text{Rb}_2\text{CoMg}_{1-c}\text{F}_4$ close to the percolation limit²².

system $\text{Rb}_2\text{Mn}_c\text{Mg}_{1-c}\text{F}_4$. In this case at high temperature $G_T(\vec{Q})$ and $G_L(\vec{Q})$ are the same but at low temperature the weak dipolar anisotropy field leads to a cross-over to Ising symmetry, and $G_L(\vec{Q})$ becomes much larger than $G_T(\vec{Q})$. This cross-over has been demonstrated experimentally⁴¹. The measurements can be analysed to give the correlation length at each temperature and the results are shown in fig. 9. Again they strongly suggest that K is the sum of a geometric and a thermal part. The temperature dependence of the one-dimensional correlation length, K_1 , was calculated including the effects of dipolar anisotropy by using the theory and program of Blume et al.⁴². The results, fig. 9, are clearly in reasonable accord with the experimental measurements. Detailed fits suggest that ν_T for this system is 0.90 ± 0.03 , considerably different from the value for the Ising system and suggesting that the cross-over exponent for the Heisenberg system is about 1.5.

Fig. 9. The correlation length K for two concentrations of $\text{Rb}_2\text{Mn}_c\text{Mg}_{1-c}\text{F}_4$. The solid line shows the Heisenberg model $(K_1)^{0.75}$ and the dotted line $(K_1)^{0.75}$ calculated including the dipolar anisotropy⁴¹.

Particularly convincing evidence of the role of the dipolar anisotropy is provided by the results of similar measurements⁴³ on the $\text{Mn}_c\text{Zn}_{1-c}\text{F}_2$ system. The tetragonal crystal structure of this material enables measurements to be made of both $G_T(\vec{Q})$ and $G_L(\vec{Q})$. The crystal had a concentration gradient along its length so that one end ordered, whereas the other did not. Consequently by making slices of the crystal it is possible to conveniently perform experiments as a function of concentration. In fig. 10 the results for K_T and K_L are shown as a function of temperature and compared with calculations of both the transverse and longitudinal correlation functions for the appropriate linear chain. Clearly the qualitative agreement with K_L and K_T is very satisfactory showing the importance of including the dipolar anisotropy.

Finally we have not as yet discussed the development of the long range order in these systems. Samples of both $\text{Rb}_2\text{Co/MgF}_4$ and $\text{Rb}_2\text{Mn/MgF}_4$ have been examined for $c > c_p$, and measurements made of the magnetisation as a function of temperature. The long range order begins at a fairly well defined temperature T_c , at which the inverse correlation length K is close to zero. The temperature dependence of the magnetisation is very sensitive to fluctuations

Fig. 10. Inverse correlation length K_L and K_T for $\text{Mn}_c\text{Zn}_{1-c}\text{F}_2$. The solid lines give the calculated inverse correlation length assuming $\phi = 1$ and $\phi = 1.4$ from ref. 43.

in the concentration and so cannot be analysed to give reliable estimates of the exponent β .

The results are less as expected in the three-dimensional systems; $\text{Mn}_c\text{Zn}_{1-c}\text{F}_2$ and $\text{KMn}_c\text{Zn}_{1-c}\text{F}_3$. We illustrate the behaviour in the latter system in fig. 11. There is a fairly well defined transition to an ordered structure at about 14 K, but unexpectedly the inverse correlation length is non-zero at this temperature and continues to decrease on further cooling, becoming almost zero at very low temperatures. Similar results were found in another sample with a lower concentration of Mn except that $T_c \approx 12$ K, the intensity of the Bragg reflection was less, and K steadily decreased with decreasing temperature but was non-zero at the lowest temperatures. A similar result, namely that K is non-zero at T_c , was also observed in the $\text{Mn}_c\text{Zn}_{1-c}\text{F}_2$ system⁴³.

A further unexpected result is also shown in fig. 11; the intensity of the Bragg reflection reaches a maximum at $T \approx 6$ K and then decreases with decreasing temperature. This feature was

Fig. 11. Bragg scattering and correlation length in $\text{KMn}_{0.33}\text{Zn}_{0.67}\text{F}_3$ as a function of temperature⁴³.

not clearly established in the other crystal of this system or for the $\text{Mn}_C\text{Zn}_{1-C}\text{F}_2$ system. We do not have a convincing explanation of either of these features. It is however worth remarking that the dipolar forces in the cubic perovskites will produce fields on the ions in different directions. Consequently there may be a complicated spin glass type of ordering at low temperatures.

We conclude that considerable progress has now been made in understanding percolation in these systems. The qualitative picture of the percolation point as a multicritical point with the temperature scale set by the one-dimensional correlation length is well established experimentally. The exponents of the two-dimensional Ising system are within experimental error in accord with a cross-over exponent of unity, but for the two-dimensional Heisenberg system the cross-over exponent of about 1.5 has not been obtained theoretically. The onset of long range order is reflected in the critical scattering for the two-dimensional systems but not for the three-dimensional ones. We are unaware of the reasons for this unusual behaviour.

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REFERENCES

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- 1. R.A. Cowley and W.J.L. Buyers, *Rev. Mod. Phys.* 44, 406 (1972).
- 2. C.G. Windsor, G.A. Briggs and M. Kestigan, *J. Phys. C* 1, 940 (1968).
- 3. O.P. Nikotin, P.A. Lindgard and O.W. Dietrich, *J. Phys. C* 2, 1168 (1969).
- 4. P. Martel, R.A. Cowley and R.W.H. Stevenson, *Can. J. Phys.* 46, 1355 (1968).
- 5. R.J. Birgeneau, J. Als-Nielsen and G. Shirane, *Phys. Rev. B* 16, 280 (1977).
- 6. H. Ikeda and M.T. Hutchings, *J. Phys. C* 11, L529 (1978).
- 7. R.A. Cowley, *A.I.P. Conf. Proc.* 29, 243 (1976).
- 8. W.J.L. Buyers, T.M. Holden, E.C. Svensson, R.A. Cowley and R.W.H. Stevenson, *Phys. Rev. Lett.* 27, 1442 (1972).
- 9. E.C. Svensson, S.M. Kim, W.J.L. Buyers, S. Rolandson, R.A. Cowley and D.A. Jones, *A.I.P. Conf. Proc.* 24, 161 (1975).
- 10. G.J. Coombs, R.A. Cowley, D.A. Jones, G. Parisot and D. Tochetti, *A.I.P. Conf. Proc.* 29, 254 (1976).
- 11. J. Als-Nielsen, R.J. Birgeneau, H.J. Guggenheim and G. Shirane, *Phys. Rev. B* 12, 4963 (1975).
- 12. R. Alben and M.F. Thorpe, *J. Phys. C* 8, L275 (1975).
- 13. S. Kirkpatrick and A.B. Harris, *Phys. Rev. B* 12, 4980 (1975).
- 14. W.J.L. Buyers, D.E. Pepper and R.J. Elliott, *J. Phys. C* 6, 1933 (1973).
- 15. T. Tonegawa, *Prog. Theor. Phys.* 51, 1293 (1974).
- 16. G.J. Coombs and R.A. Cowley, *J. Phys. C*, 8, 1889 (1975).
- 17. G.J. Coombs, R.A. Cowley, W.J.L. Buyers, E.C. Svensson, T.M. Holden and D.A. Jones, *J. Phys. C* 9, 2167 (1976).
- 18. R.A. Cowley, O.W. Dietrich and D.A. Jones, *J. Phys. C*, 8, 3023 (1975).
- 19. W.K. Holcomb, *J. Phys. C*, 7, 4299 (1974).
- 20. O.W. Dietrich, G. Meyer, R.A. Cowley and G. Shirane, *Phys. Rev. Lett.*, 35, 1735 (1975).
- 21. E.C. Svensson, W.J.L. Buyers, T.M. Holden and D.A. Jones, *A.I.P. Conf. Proc.* 29, 248 (1976).
- 22. R.A. Cowley, R.J. Birgeneau, G. Shirane, H.J. Guggenheim and H. Ikeda (unpublished).
- 23. H. Ikeda and G. Shirane (to be published).
- 24. R.A. Cowley, G. Shirane, R.J. Birgeneau and H.J. Guggenheim, *Phys. Rev. B* 15, 4292 (1977).
- 25. A. Tuccarine, H.Y. Lau, L.M. Carliss, A. Delapalme and J.M. Hastings, *Phys. Rev. B* 4, 3206 (1971).

26. H. Ikeda and K. Hirakawa, Solid State Commun. 14, 529 (1974).
27. A.B. Harris, J. Phys. C 7, 1671 (1974).
28. G. Grinstein and A. Luther, Phys. Rev. B 13, 1329 (1976).
29. D.E. Khmel'nitskii, Soviet Physics JETP 41, 981 (1975).
30. B.M. McCoy and T.T. Wu, Phys. Rev. Lett., 23, 383 (1968).
31. G.M. Meyer and O.W. Dietrich, J. Phys. C 11, 1451 (1978).
32. O.W. Dietrich, J. Phys. C 2, 2022 (1969).
M.P. Schulhof, R. Nathans, P. Heller and A. Linz, Phys. Rev. B 4, 2254 (1971).
33. R.A. Cowley and K. Carneiro (unpublished).
34. J.W. Essam, Phase Transitions and Critical Phenomena II, ed. C. Domb and M.S. Green (Academic Press, New York) (1972) p. 197.
35. H.E. Stanley, J. Phys. A 10, L211 (1977).
36. D. Stauffer, Z. Phys. B 22, 161 (1975).
37. R.J. Birgeneau, R.A. Cowley, G. Shirane and H.J. Guggenheim, Phys. Rev. Lett., 37, 940 (1976).
38. M.F. Thorpe, Journal de Physique 36, 1177 (1975).
39. M.J. Stephen and G.S. Grest, Phys. Rev. Lett. 38, 567 (1977).
40. D.J. Wallace and A.P. Young, Phys. Rev., B 17, 2384 (1978).
41. R.J. Birgeneau, R.A. Cowley, G. Shirane and H.J. Guggenheim, Phys. Rev. Lett. 37, 940 (1976) and to be published.
42. M. Blume, P. Heller and N.A. Lurie, Phys. Rev. B 11, 4483 (1975).
43. R.A. Cowley, G. Shirane, R.J. Birgeneau and E.C. Svensson, Phys. Rev. Lett. 39, 894 (1977) and to be published.