JOURNAL OF Materials CHEMISTRY

A Monte Carlo analysis of spin dynamics and Mössbauer relaxation in 2-D magnetically diluted iron oxides

Terence C. Gibb

School of Chemistry, The University, Leeds, UK LS2 9JT

Received 29th June 1999, Accepted 2nd September 1999

The spin dynamics of two-dimensional magnetically diluted iron oxides with the K_2NiF_4 structure has been studied by a Monte Carlo analysis using a simple Ising model. Below the critical temperature, antiferromagnetic domains are formed in which the domain walls are 'pinned' by the non-magnetic atoms such that increasing dilution causes substantial interpenetration of the domains. The magnetic hysteresis observed in field-cooled and zero-field-cooled magnetic measurements on $SrLaFeO_4$ diluted with a non-magnetic cation can be explained. Similarly, the observed Mössbauer relaxation can be simulated, and derives from differing relaxation rates for spins with few near neighbour spins, particularly those close to a domain boundary. The existence of 'spin clusters' which has often been assumed is not a good model. It is suggested that Ising-like behaviour in the critical region is an important aspect of these diluted Heisenberg layered systems.

Compounds with the stoichiometries ABX_3 (cubic perovskite structure) and AB_2X_4 (K_2NiF_4 structure) are of particular interest because they approximate closely to ideal 3-D and 2-D lattices for the study of magnetic superexchange interactions. Both contain linear B–X–B nearest-neighbour (nn) superexchange pathways (usually antiferromagnetic), and it is normally considered that the influence of next-nearest neighbours (nnn) is negligible. They therefore provide an excellent basis for the study of magnetic dilution in antiferromagnets. The majority of studies in depth have been carried out on transition metal fluorides (B = Mn, Fe, Co or Ni; X = F), largely because it has been possible to grow large single crystals for neutron studies.

In comparison, comparatively little work has been done using oxides because such crystals are not available. The high-spin Fe^{3+} cation has a spherical d^5 configuration, and should therefore show an uncomplicated isotropic Heisenberg behaviour in such oxides. Magnetic dilution should not influence the tendency to order antiferromagnetically. However, in a series of recent papers it has been shown that reality is much more profound. Thus Sr_2FeNbO_6 and Sr_2FeRuO_6 have been found[1,2] to be spin-glasses at low temperature, despite evidence to show that the Fe and Nb or Ru cations are disordered.[2,3] On the other hand, $SrLaFeSnO_6$ shows entirely different behaviour.[4] The random distribution of Fe and Sn on the B sites is accompanied in this case by antiferromagnetic order; the magnetic susceptibility shows hysteresis between field-cooled (FC) and zero-field-cooled (ZFC) data below 250 K, while the ^{57}Fe and ^{119}Sn Mössbauer spectra show marked magnetic relaxation to well below 150 K such that measurement of the precise ordering temperature using this technique is difficult. The oxide $SrLaFeO_4$ has the 2-D K_2NiF_4 lattice and a Néel temperature of 330 K. Magnetic dilution as in $Sr_{1+x}La_{1-x}Fe_{1-x}Sn_xO_4$ and $SrLaFe_{1-x}Ga_xO_4$ has shown similar marked hysteresis and relaxation effects.[5]

Such Mössbauer relaxation has been observed many times in diluted ferrimagnetic spinels for example, and the popular explanation, based on the work by Ishikawa,[6] is in terms of the existence of magnetic clusters. These are said to form below the critical temperature and increase in size with decreasing temperature until long-range order is achieved. However, a theoretical explanation of the behaviour of the spin system and its relationship to the observed spectra has been lacking, and the meaning of a 'cluster' has been obscure. An examination[3] of the percolation behaviour in a simple cubic 3-D perovskite lattice with 50% disordered non-magnetic substitution showed that few magnetically isolated 'clusters' as proposed by Ishikawa[6] can exist at this composition. A subsequent (unpublished) analysis developed using a combination of site percolation and bond percolation to represent thermal effects was useful but still gave no clear insight into the problem.

A more detailed interpretation of the effects of magnetic dilution in simple lattices is required. In particular, the dynamic nature of the spin system must be considered in order to give an explanation of the observed Mössbauer spectra. Published work has shown that Monte Carlo simulations can give useful results. This paper reports the results of a detailed study of relaxation in a 2-D Ising lattice. New ways of achieving a visualisation of the spin system give a much deeper understanding of the phenomena observed in diluted $SrLaFeO_4$. The results obtained provide a useful basis for continuing work on the 3-D perovskite lattice which will be reported at a later date.

Antiferromagnetic domains

One feature of these magnetically diluted systems which must be considered is the possible presence of antiferromagnetic domains. Magnetic domains are well known in ferromagnets, but the equivalent phenomena in antiferromagnets are less frequently described and more difficult to observe. They are equivalent to an anti-phase boundary. Specialised techniques such as polarised neutron topography have to be used,[7] as on single crystal MnF_2 for example. It is particularly significant that warming to just above the critical temperature, T_N, and then cooling again, restores the domain walls to almost their original positions. It is believed that impurity 'pinning' takes place, as this 'memory' is lost if the crystal is heated to a much higher temperature. There is also experimental evidence to suggest that non-magnetic impurity atoms can cause pinning of domain walls, and hence prevent the onset of long-range magnetic order in magnetically diluted rutile fluorides such as $Fe_{1-x}Zn_xF_2$. The relevance of antiferromagnetic domains in the present study will become clear.

The simulation method

In the K_2NiF_4 structure the separation between layers of magnetic ions is large so that the magnetism is very close to 2-D planar. The simplest conceptual model of the magnetism is the 2-D Ising magnet, in which each magnetic ion can adopt only two states, which for computational purposes can be designated as $+1$ and -1. This model obviously can not describe the isotropic $S=5/2$ Fe^{3+} ion accurately, but a detailed discussion of the significance of this approach will be deferred until later in the paper. It is assumed that each linear Fe–O–Fe superexchange can be represented by $Js_i^z \cdot s_j^z$ where J is the superexchange coupling constant for nn spins s_i and s_j. The thermal temperature is depicted in reduced units of kT/J where k is Boltzmann's constant. Additional interactions, which may be included as appropriate, are superexchange with 4 nnn atoms in terms of J_2, and an applied magnetic field B so that the interaction energy for each spin in an Ising model can be written as

$$E = -s_i\left(J\sum_1^4 s_j - J_2\sum_1^4 s_k\right) - Bs_i \qquad (1)$$

The simulations were all carried out using computer code written in the C language. An $N \times N$ square matrix of spins with a concentration of spins of $0 \leqslant p \leqslant 100\%$ is created at random. The matrix can be created with either random values of $s = \pm 1$ to represent a high temperature fully disordered spin system, or with alternate values of s to represent a perfect antiferromagnetic alignment. The system is then allowed to evolve using standard Monte Carlo methods.[8] A site is selected at random, and if it contains a magnetic spin the energy change for spin reversal, ΔE, is calculated. The probability of spin reversal is then calculated[9] as $P = x/(1+x)$ where $x = \exp(-\Delta E/kT)$ so that the number of attempts can be used to measure time. In order to remove edge effects, periodic boundary conditions are incorporated. Specifically, opposite edges of the square matrix are considered to be geometrically linked. One Monte Carlo cycle (MCS) corresponds to N^2 attempts at spin reversal.

A standard cooling cycle was formulated as n Monte Carlo cycles at $kT/J = 3.0$, and then repeating at temperature decrements of 0.1 until $kT/J = 0.1$. A heating cycle started similarly from $kT/J = 0.1$ and incremented by 0.1 until 3.0. In the present instance, data sets were of either 250^2 or 500^2 spins, and n was at least 1000 MCS. Typically 500 MCS were to establish approach to near equilibrium, before the next 500 MCS were used as a data collection period. In some cases $9000 + 1000$ MCS were used. Many of the simulations resulted in antiferromagnetic domain boundaries. Therefore, at the end of each data collection period the largest in-phase and out-of-phase percolation clusters[10] were determined, together with statistics regarding the numbers of spins in the bulk and in the domain boundaries, the number of spins flipped, the average value of each spin during the period, and the numbers of $s = +1$ and $s = -1$ spins. The final energy of the system was also calculated. A number of different graphical presentations were devised to display useful aspects of the data. Large numbers of simulations were carried out, but only representative examples will be discussed in detail in the description which follows.

Quenched spin systems

The dynamic evolution of a 2-D matrix of spins quenched from a high temperature random state has been studied previously,[11,12] and is briefly considered here both to indicate the differences from systems with controlled temperature change, and to establish criteria for the approach to the equilibrium state for the data sets used in the present work.

A matrix of 250^2 spins ($p = 100\%$) was created in a random state, instantaneously cooled to $kT/J = 0.5$ (well below $kT_N/J \approx 2.35$, but still with significant thermal energy), and allowed to relax towards equilibrium. The energy for a perfectly ordered state (including periodic boundary conditions) in units of J would be -1.25×10^5. Clusters of spins (both in-phase and out-of-phase) formed and grew rapidly. A two-domain state was reached within 500 MCS, and one of the domains then shrank steadily to only 15% of the total spins at 10000 MCS with a corresponding decrease in the numbers of anti-phase spins in the domain boundaries. The energy at 99.2% of ideal was still decreasing steadily, such that one can confidently envisage the ultimate formation of a single-domain state.

A similar calculation for $p = 80\%$ showed a similar rapid development of large domains at $kT/J = 0.5$, and the largest reached more than 10000 spins within 50 MCS, the total energy being 88% of the ideal. The energy continued to decrease, but only very slowly, reaching 95.7% of the ideal at 10000 MCS. The domain structure now comprised a number of large but interpenetrating domains, the primary structure of which had changed comparatively little since 1000 MCS. The largest domain which spanned the matrix now contained 23218 spins, of which 22077 were in the bulk of the domain (also containing 6803 non-magnetic atoms), with only 1141 spins in the domain wall (1077 in contact with 1, and 64 with 2 out-of-phase atoms in the neighbouring domains). A close examination of the matrix at this point reveals large numbers of non-magnetic sites along the domain boundaries, showing how they are pinning the domains, which have comparatively few contacts, and preventing rapid evolution towards an ordered state.

One consequence of this domain pinning is that meaningful 'real' systems can only be studied by allowing the temperature to change slowly so that the spin matrix can evolve over a larger length scale without 'freezing'. The rate of change of energy after 10000 MCS is so slow as to prevent any realistic determination of the final state. From the many papers on equilibrium studies using other Monte Carlo algorithms which approach equilibrium much more rapidly (at the expense of losing sight of the time variable) it is well known[8] that domain growth is strongly inhibited. It seems inevitable that the ideal ordered state can never be obtained within the limitations of the simple Ising model which allows only single spin flips, because domain growth is kinetically inhibited by the non-magnetic sites. Fortunately this is not too serious a problem in the current context in that the spin dynamics can be studied effectively without having to reach the ultimate equilibrium state.

The development of domain structures during cooling

More interest attaches to the development of the antiferromagnetic domain structure during the slow cooling of an Ising spin matrix. Various aspects of this problem have been investigated in a series of papers by Nowak and Usadel[13–18] using Monte Carlo simulations for both 2-D and 3-D systems. Their work has proved to be very useful in the present investigation, which concentrates on new aspects of the spin dynamics. Many simulations have been performed for square arrays of 250^2 and 500^2 atoms with periodic boundary conditions applied. For the smaller matrix 9000 MCS were used at each temperature step to create a near-equilibrium state, followed by another 1000 MCS for data evaluation. With the larger matrix, only $1000 + 1000$ MCS were applied. The final 'frozen' domain structure achieved at $kT/J = 0.1$ after 'slow cooling' was then examined graphically. The results from the two series were comparable, so that the features of the data which are to be considered do not appear to be unduly affected by limitations in size or timescale.

For $p = 100\%$ the spin matrix percolates below $kT/J \cong 2.35$ and rapidly develops towards a single domain structure as expected. At $p = 90\%$ the magnetic dilution causes the Néel temperature to fall, with percolation taking place below $kT/$

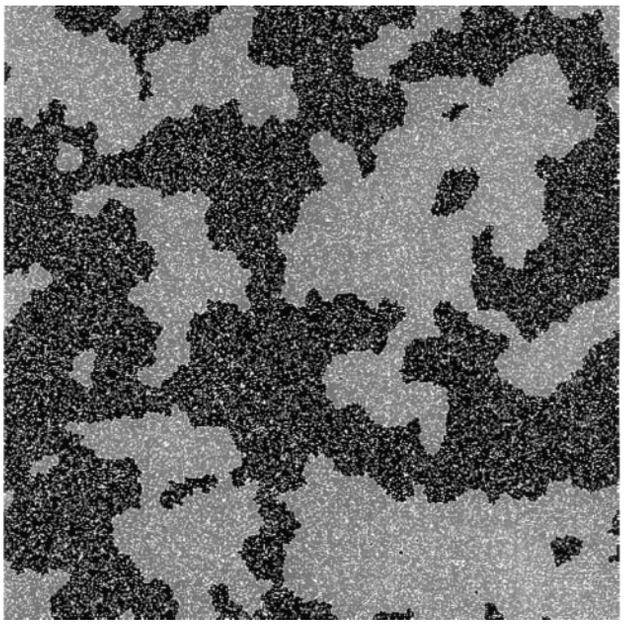

Fig. 1 The domain structure for a 2-D matrix of 500^2 atoms (with $p=80\%$, simple Ising interactions, and slowly cooled to $kT/J=0.1$ with 2000 MCS per step, as described in the text). Non-magnetic atoms are shown in white, while in-phase and out-of-phase antiferromagnetic domains are shown in black and grey respectively. Close inspection of the data shows the existence of large numbers of non-magnetic atoms along the domain boundaries.

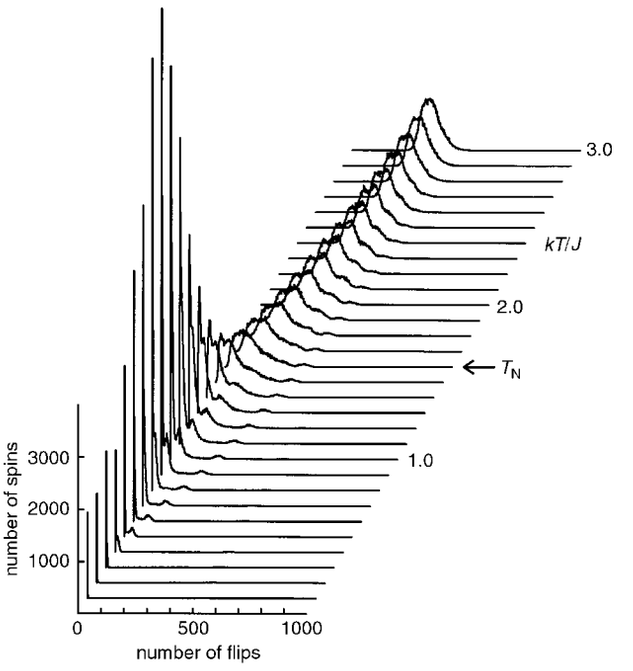

Fig. 2 The number of spin flips during 1000 MCS at each discrete temperature interval by every spin in a 250^2 matrix with $p=80\%$ shown as a histogram. Spins which do not flip at all are omitted for clarity, and values for odd and even numbers of flips are combined as the probability of odd and even numbers of flips are not the same. Below the Néel temperature there are distinct groups of spins with 0–4 nearest neighbour spins. Those spins with fewer neighbours are more prone to undergo relaxation.

$J\approx2.05$. However, the matrix becomes trapped into a two-domain structure with considerable intergrowth. Close examination reveals a large number of non-magnetic sites along the domain boundaries which are pinning the boundaries and preventing growth. Thus the main outline of the final domain structure can clearly be seen at temperatures as high as $kT/J=1.8$.

The domain behaviour observed with $p=80\%$ and 70% is similar to the 90% results except that the intergrowth becomes progressively greater, and percolation begins at $kT/J\approx1.65$ and 1.35 respectively. A typical domain structure for $p=80\%$ and 500^2 atoms is shown in Fig. 1. This style of presentation represents an instantaneous view of the dynamic spin system. The domain structure is significantly larger than in a 'quenched' simulation, but realisation of a fully ordered state is still strongly inhibited. The outlines of the main domain structure for $p=70\%$ are already apparent at $kT/J=1.1$, but the development of full percolation is also inhibited. The established percolation limit[10] for a square matrix is $p_c=59.27\%$. However, at $p=65\%$ some simulations result in percolation, while others do not, and at 60% large domains (>5000 spins) fail to develop and percolation is unlikely to be achieved. This is a natural consequence of the antiferromagnetic interactions and the domain pinning which occurs, and has implications for the nature of the magnetic structure close to p_c in that long range order cannot be achieved in such an Ising system. The kinetics of the approach to equilibrium as a function of p has not been investigated.

Spin relaxation in zero field

It is instructional to examine the fluctuation behaviour of all the spins in the matrix over a suitable time interval as a function of temperature. The number of flips at each temperature during a cooling sequence by every spin during 1000 MCS in a 250^2 matrix with $p=80\%$ is plotted as a series of histograms in Fig. 2. Spins which do not flip at all are omitted from the diagram for clarity. The values for n and $n+1$ flips are combined because the probability of an odd or even number of flips are not the same. The interaction energy for a given spin is proportional to the number of nearest neighbour (nn) spins. The very small number of spins with no magnetic nearest neighbours (and zero energy for spin reversal) flip on average 500 times, but are barely visible in Fig. 2 as a result of the choice of scale. As the temperature is raised the spins with only one nn begin to flip rapidly, and at around $kT/J=1.4$ it is possible to discern distinct groups of spins with 0, 1, 2, 3, and 4 nearest neighbour spins, despite the broadening of the distributions which will result from the finite time window. Thus one may draw the logical conclusion that the relaxation of any given spin is strongly linked to the number of nn spins, and that those with few neighbours will be more prone to showing relaxation.

For a series of values of p, a random matrix of 250^2 spins was cooled from $kT/J=3.0$ to 0.1 in steps of 0.1 with 1000 MCS per step. In a parallel series of simulations the identical spin matrix but in an initially ordered state was heated. The percolation and domain characteristics of the spin system were examined in detail. The first 500 MCS at each temperature were used to create a starting matrix, and the dynamic features were calculated on the subsequent 500 MCS. At high temperature when the spin flips are essentially random, the probability that a spin will be reversed after 500 MCS is 50%. As the spin interactions become significant compared to the thermal energy then the probability of spin reversal will decrease. The numbers of flipped spins as a function of temperature are plotted in Fig. 3 for six values of p ranging from 100% down to 60%. The results for the same cooled (triangles) and heated (circles) matrix show slight hysteresis because equilibrium is not complete. At the same time the domain sizes are larger at the lower temperatures.

The Néel temperature is judged to be the value of kT/J at which the largest domain just spans the matrix. It is difficult to determine this critical point to an accuracy of better than 0.1 from a small number of simulations on a matrix of finite size. However, a number of features were observed. In particular,

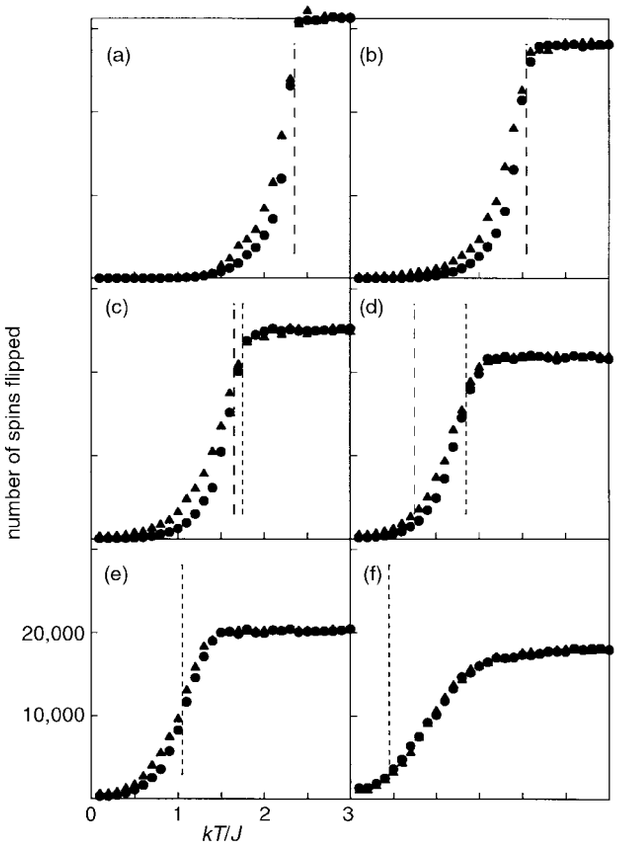

Fig. 3 The number of spins in a 250^2 matrix which have been flipped at the end of 500 MCS during cooling from a random state (triangles) and heating from an ordered state (circles) for p values of (a) 100, (b) 90, (c) 80, (d) 70, (e) 65 and (f) 60%. The Néel temperature (at which the largest domain just spans the lattice) is shown as a vertical dashed (cooling) or dotted line (heating).

the Néel temperature observed on cooling (a vertical dashed line in Fig. 3) was clearly different in some cases from that observed on heating (dotted line). For $p=100\%$ the number of spins flipped (Fig. 3) decreased very sharply at $kT/J\approx2.35$ with the simultaneous adoption of a percolating domain structure. There was no obvious distinction between cooling and heating. The residual small domains which exist above T_N are essentially dynamic so that the probability of any spin having flipped in 500 MCS remains at 50%. Immediately below T_N the domains are still dynamic, but percolation is achieved, and with decreasing temperature the system rapidly develops towards a single domain structure.

For $p=90\%$ the behaviour is very similar, apart from the domain intergrowth described above. At $p=80\%$ the cooling and heating cycles show a small separation in the apparent T_N values, and this becomes large at $p=70\%$. In the latter case the flip probability begins to slow markedly long before percolation of a single domain is achieved at $kT/J\approx0.75$ (compared to 1.35 on heating). Furthermore, for $p=65$ and 60% the matrix never develops a percolating cluster on cooling. Rather the spin matrix freezes as a consequence of the strong short range nn superexchange interaction as thermal energy is removed. This suggests the creation of a phase very similar to a spin glass.

Spin relaxation in an applied field

One of the unusual features of a diluted antiferromagnet is the observation of a magnetic memory or hysteresis in so far as the magnetism actually observed depends on the thermal history of the matrix. This has been observed[5] in both $Sr_{1+x}La_{1-x}Fe_{1-x}Sn_xO_4$ and $SrLaFe_{1-x}Ga_xO_4$. The effects of a magnetic field can be simulated by including an additional term in the energy of interaction, which can be written in relative terms using the quantity B/J. If this field is applied to a random spin system (at high temperatures) then an imbalance is created in the number of spins parallel and antiparallel to the field. For present purposes the fractional imbalance can be crudely related to the effective magnetisation, M.

There should be no difference between the magnetisation observed when the spins are (a) slowly cooled through the Néel temperature before the field is applied and the magnetisation measured during heating (a ZFC experiment), and (b) slowly cooled through the Néel temperature in the presence of the field (a FC experiment). These experiments have been simulated for different values of p using a matrix of 250^2 sites. For case (a) the spins were created as a single-domain ground state (the ideal lowest energy state in zero field) and then heated stepwise in the presence of the field to $kT/J=3.0$ in steps of 0.1 with 1000 MCS for each step. In case (b) the identical spin matrix with a random alignment was cooled similarly with the field applied.

The results are summarised in Fig. 4, which shows the ZFC (circles) and FC (triangles) simulations for six different compositions. The field was $B/J=1.0$ in all cases, the large value being chosen to compensate for the rather small size of the spin matrix. For the specific case of $p=100\%$ the ZFC and FC curves are almost identical, and any hysteresis caused by failure to reach equilibrium at each step is negligible. In the other five cases there is a marked divergence between the ZFC and FC curves below a critical temperature which is indicated approximately by the dashed vertical line. It is evident that cooling in a large field results in the formation of significantly smaller domains. Furthermore, the FC curve is always higher

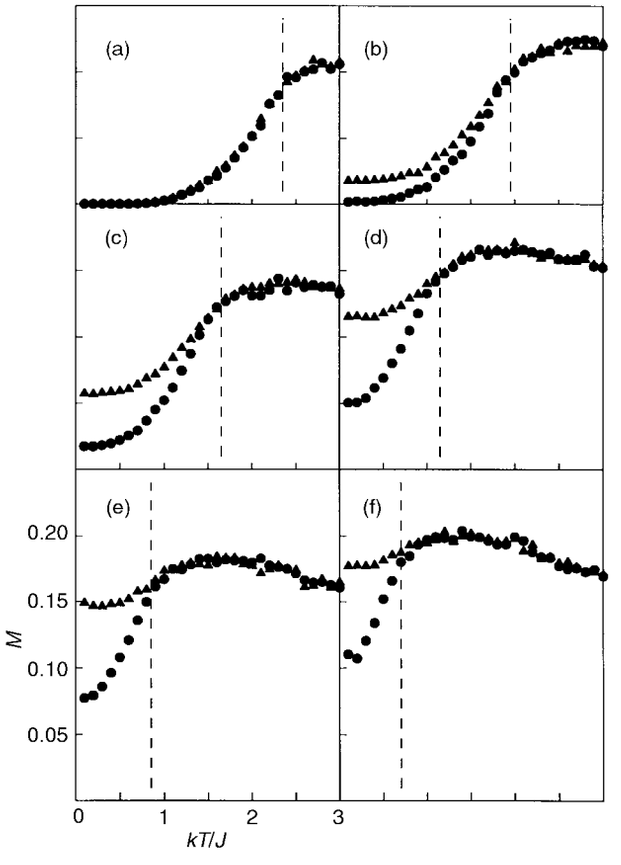

Fig. 4 The magnetisation, M, (defined in the text) induced in a matrix of 250^2 atoms in an applied field of $B/J=1.0$ for ZFC (circles) and FC (triangles) simulations with p values of (a) 100, (b) 90, (c) 80, (d) 70, (e) 65 and (f) 60%. Note the hysteresis which develops for $p<100\%$ below a critical temperature indicated approximately by the dashed vertical line.

than the equivalent ZFC curve. It is apparent that cooling in a field causes growth of field-aligned spin domains, yet inhibits the movement of domain boundaries because of pinning at non-magnetic sites, and as a result decreases the apparent value of T_N. It is believed[17,18] that the domain structure is in fact the equilibrium state for a diluted Ising antiferromagnet for any value of $B>0$.

The divergence between the FC and ZFC curves initially increases rapidly as p decreases. The domain structure which develops during FC will depend on the random nature of the spin flips, and therefore there are many apparent ground states to the system. Essentially the same result is achieved if the ZFC simulation is made using a matrix which has been cooled into a domain state, rather than the perfectly ordered matrix. The main difference is that the ZFC curve moves slightly closer to the FC curve.

For $p=65\%$ and 60% the FC simulations do not produce a domain structure in which one domain spans the matrix. The domains interpenetrate each other to a greater degree as p decreases, and long-range order is effectively lost before the percolation limit is reached. The ZFC and FC curves in Fig. 4 now resemble those found experimentally[5] for $Sr_{1+x}La_{1-x}Fe_{1-x}Sn_xO_4$ and $SrLaFe_{1-x}Ga_xO_4$ and correspond closely to similar curves observed[2] for spin-glass materials.

The energy of the simulated FC state for $p=70\%$ and 65% at $kT/J=0.1$ after 1000 MCS is actually lower than that of the ordered ZFC state after 1000 MCS in the field B at the same temperature. This is consistent with the belief[17,18] that the true ground state in an applied field is the domain state, and suggests for example that there may be no long-range magnetic order within the correlation length necessary for detection by a neutron diffraction experiment.

More distant interactions

Although the body of opinion is that next-nearest neighbour (nnn) interactions in fluorides are very small,[17] it is not entirely clear that the same will be true in oxides where the higher ionic charges and the lower electronegativity of oxygen lead to more covalency. In the K_2NiF_4 structure there are 4 nn and 4 nnn sites, while in the perovskite structure there are 6 nn and 12 nnn sites. It is believed that nnn interactions become especially relevant in the latter case. In iron oxides both interactions will be antiferromagnetic, which must result in a degree of conflict and the potential for frustration in the system as a whole.

Many of the calculations described above have been repeated allowing for an nnn interaction with $J_2/J=0.1$. The main features observed are an increased tendency to domain intergrowth and a depression of the apparent ordering temperature. However, for the 2-D oxide systems studied there is as yet no direct evidence that such effects are large in practice. Therefore a more detailed discussion will be reserved for a future paper on the 3-D lattice, where nnn interactions are especially relevant to the creation of spin glasses.

Correlation lengths

Once a spin matrix has been cooled to a very low temperature the absence of thermal energy will freeze the domain structure. Although the domains may be very large in a percolating lattice, the correlation length, λ, may become small if the domains show a significant interpenetration. Indeed the latter have been shown[15,16] to have the properties of a fractal. The 2-D staggered correlation function can be represented by

$$c(r)=\left\langle \frac{1}{2n}\sum_{i=1}^{n}(-1)^r(S_{i,n/2}S_{i,n/2+r}+S_{i,n/2}S_{i,n/2-r})\right\rangle \quad (2)$$

by observing the correlation of pairs of spins at $\pm r$ cell spacings on either side of a line of n spins. To a good approximation $c(r)\propto\exp(-r/\lambda)$ so that a plot of $\ln[c(r)]$ against r has a slope of $-1/\lambda$. Values of λ were computed for data sets with 500^2 sites cooled from $kT/J=3.0$ to 0.1 in steps of 0.1 with 10000 MCS per step. A typical plot for $p=70\%$ is shown in Fig. 5. The increasing interpenetration of the domain structure is seen as a steady decrease in λ with decreasing p, becoming very rapid below $p=70\%$. The values calculated for $p=90$, 80, 70, 65 and 60% were 54, 31, 26, 10 and 3 cell spacings, which represents a decrease in real terms from about 20000 to only 1200 pm. This would suggest that the observation of spin order by neutron measurements will be affected adversely as p decreases.

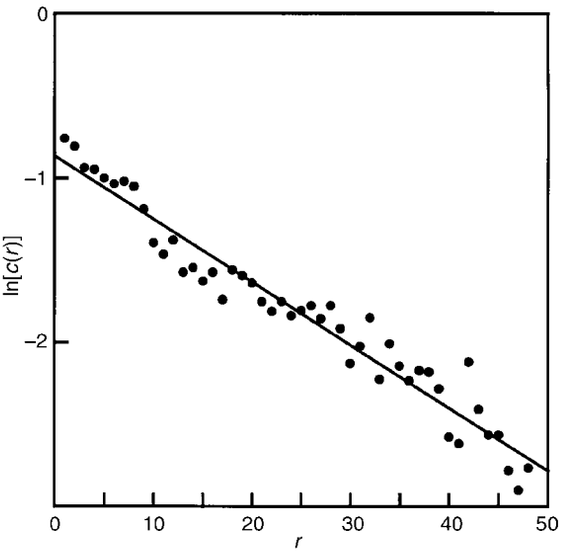

Fig. 5 A plot of $\ln[c(r)]$ against r, where $c(r)$ is the 2-D staggered correlation function, has a slope of $-1/\lambda$ where λ is the correlation length. The data shown are for $p=70\%$ after a slow-cooling simulation, and give a correlation length of about 26 cell spacings.

Dynamics of the domain boundaries

An alternative way of representing the dynamics of the spin system is to compute the average value $\langle S\rangle$ of every spin during a given time interval and to represent the results graphically. This can be done efficiently by storing the time at which each spin was last flipped and then updating the time average when the next flip takes place. The results presented here were obtained for $p=80\%$ and 250^2 sites after cooling a random array from $kT/J=3.0$ to 1.5 in steps of 0.1 with 1000 MCS per step, followed by 12000 MCS at $kT/J=1.5$ to allow equilibration, and then 10000 MCS to obtain values of $\langle S\rangle$. The ordering temperature of this matrix corresponds to $kT/J\approx1.75$, so that the calculations correspond to a reduced temperature of $T/T_N\approx0.85$.

In Fig. 6 are plotted histograms of the values of $\langle S\rangle$ for spins with from 0 to 4 nearest neighbour spins. Spins with no neighbours can flip randomly, so that $\langle S\rangle$ is close to zero. Increasing the number of neighbours reduces the probability of a spin flipping, but even with 4 nearest neighbour spins the distribution in the values of $\langle S\rangle$ is still very broad at this value of kT/J, even allowing for a degree of broadening caused by the finite size of the data set.

In Fig. 7 the domain structure for a 100×100 region of the matrix is shown by plotting the values of $\langle S\rangle$ as a vertical bar (anti-phase spins are plotted in the negative sense and shaded for emphasis). The uneven height within a domain reflects the local influence of non-magnetic neighbours on the relaxation rate of a given spin, but at the same time there is no evidence for identifiable clusters of spins in the Ishikawa description. In Fig. 8 the same plot is repeated, but the vertical bar is only

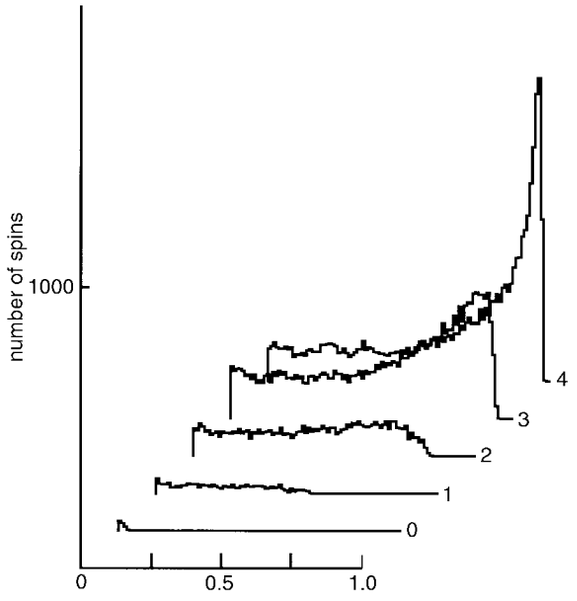

Fig. 6 Histogram of $\langle S \rangle$ for spins with from 0 to 4 nn spins at a reduced temperature of $T/T_N = 0.85$ with $p = 80\%$.

drawn if $|\langle S \rangle| < 0.25$. This dramatically shows how rapid spin relaxation is associated with spins which lie close to a domain boundary, and also indicates regions of boundary migration during the 10000 MCS of the simulation. At this fairly high reduced temperature the domain walls are still comparatively mobile, but after more than 900 actual flips per spin on average the size of the largest percolation cluster has not increased, and the decrease in energy is very small with only a slight reduction in the number of spins in the domain walls. Very similar results were obtained for $p = 70\%$ and $kT/J = 1.0$, corresponding to a reduced temperature of $T/T_N \approx 0.70$.

Relaxation in Mössbauer spectra

The final demonstration of spin dynamics concerns an attempt to simulate the observed Mössbauer spectra. The calculation of histograms of $\langle S \rangle$ has been described above. Using the hyperfine parameters observed for ^{57}Fe in $SrLaFeO_4$, and scaling the flux density of the hyperfine field B in proportion to $\langle S \rangle$, a series of 100 spectra were calculated. These were then summed with weightings from the histograms of $\langle S \rangle$. Typical calculated spectra for $p = 80\%$ after cooling a matrix of 250^2

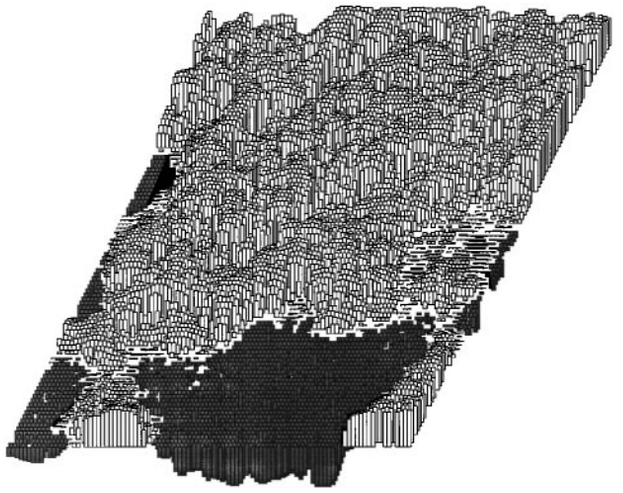

Fig. 7 A 100^2 region of the matrix used in Fig. 6 with each value of $\langle S \rangle$ plotted as a vertical bar of proportionate length. Anti-phase spins are plotted in the negative sense and shaded.

Fig. 8 The same data as in Fig. 7, but only including spins with $|\langle S \rangle| < 0.25$ Rapid relaxation is clearly associated with spins close to a domain boundary, and there is also evidence of regions of boundary migration during the 10000 MCS of the simulation.

sites to different values of kT/J in steps of 0.1 and 1000 MCS per step, with the summations being over the last 500 MCS, are shown in Fig. 9. Some broadening appears above $kT_N/J \approx 1.65$ due to the finite size of the data sets, but these results suggest that a degree of magnetic broadening could exist before long-range percolation is achieved. It is clear that the spectra develop as very broad magnetic wings emerging from the narrow central component, before sharpening into the familiar 6-line hyperfine spectrum. Similar behaviour is seen at other values of p. Despite the crudity of the simulation, this is basically the behaviour which has been observed[5] by experiment. From the previous section, it can be concluded that the appearance of a central component can be largely attributed to a combination of spins with few nearest neighbours and spins in the vicinity of a domain boundary.

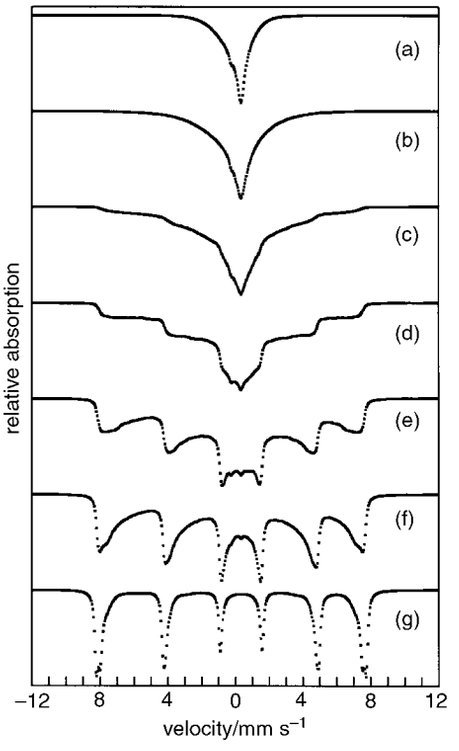

Fig. 9 Simulated Mössbauer spectra for $p = 80\%$ and values of kT/J of (a) 2.5, (b) 2.0, (c) 1.8, (d) 1.7, (e) 1.6, (f) 1.5 and (g) 1.0. Percolation is achieved at $kT_N/J \approx 1.65$.

Discussion of the relevance of the model

Any Monte Carlo simulation of a large spin system[8] suffers from the inherently slow approach to the equilibrium state. While this is a serious limitation if it is the macroscopic properties of the equilibrium state which are sought, in the present instance it has less bearing on the dynamic microscopic behaviour of individual spins. Hence meaningful results can be obtained as regards the relaxation of such spins once the system has been able to relax for a reasonable period of time.

The Ising model adopted was chosen for two main reasons. First, it is the simplest model to compute as each spin can have only two states. Secondly, the 2-D array of spins can only show long-range magnetic order in the unique case of the Ising model. While one might expect that the spins interacting in the Fe^{3+} (high-spin d^5) oxides would approximate closely to a Heisenberg model, the 2-D array of spins is then unable to achieve long-range order unless there is an additional (perhaps weak) exchange interaction in the third dimension.[20] The A_2BX_4 structure is unusual in that, for antiferromagnetic ordering, adjacent BX_2 layers show a net cancellation in the spin interaction. Thus long-range order in 3-D is only achieved by interaction between next-nearest layers which must of necessity be extremely weak. In the present instance, $SrLaFeO_4$ already has random occupation of the A sites. The local distortions created will exert a random influence on the *c*-axis exchange, but are difficult to represent in a theoretical model. In Heisenberg systems the spin-wave energy is so small that the long-range order can be expected to occur along the *c*-axis in an ordered A_2BX_4 compound, but it is to be expected that this may no longer be true in a disordered and diluted system.

The compound $SrLaFeO_4$ is known[5,21] to be an antiferromagnet below 330 K. Neutron diffraction studies[21] show that the spins are aligned in the 2D-plane (*ab*) with a moment of 4.23(5) μ_B at 4.2 K, although the precise spin arrangement remains obscure (probably because of disordered stacking along *c*). This observation is compatible[5] with the Mössbauer spectrum, although the randomisation of the A-site cations appears to result in some spin relaxation close to the critical temperature. The magnetic susceptibility also shows evidence[21] for 2-D interactions above T_N. The related compounds $SrPrFeO_4$ and $SrNdFeO_4$ (but not $SrLaFeO_4$) show[22] a discontinuous reorientation of the spins from the *ab* plane to the *c* axis in the vicinity of 80 K, which would suggest that the spin interactions are reasonably isotropic.

Magnetic dilution will have an effect on the in-plane spin interactions, but the additional consequences for the weaker *c*-axis exchange may be even more significant. The fluoride $K_2Mn_{1-x}Zn_xF_4$ ($T_N = 42$ K) makes an interesting comparison as it contains the isotropic high-spin d^5 Mn^{2+} ion. Neutron diffraction data show[23] evidence for a break-up (with dilution) of long-range order along the *c* direction (in the absence of an external magnetic field), even though the order within the layers is comparatively unaffected. Non-magnetic doping reduces correlation between layers at a greater rate than simply the percentage of dopant, since the molecular field acting on an ion from adjacent layers will be effectively randomised in sign. The observed rapid decrease in order along *c* with increase in dopant is likely to be related to such effects. However, this may not be so significant with respect to spin relaxation within a given 2-D layer for low levels of dilution, but for non-Ising interactions could lead to collapse of the spin system well before the percolation level is reached.

In $Rb_2Mn_{1-x}Mg_xF_4$ which is also a near-Heisenberg 2-D system there is a small Ising anisotropy so that the critical behaviour observed[24,25] is that of the 2-D Ising model. Similar behaviour has been found[26] in $KFeF_4$. These observations would suggest that the phase transition in diluted Heisenberg layered systems can be essentially two-dimensional in nature. Therefore cooling through T_N may establish a spin ordering based on the Ising model, and the spin-wave excitations of the Heisenberg model may be less important near to the Néel temperature. In consequence the relaxation behaviour seen in the Mössbauer spectrum might also be expected to show some of the features predicted from the 2-D Ising model. It is hoped that work in progress on Ising and Heisenberg 3-D simulations will throw additional light on this aspect.

The compound K_2FeF_4 is substantially more anisotropic because of the d^6 Fe^{2+} ion, and the spins which lie in the *ab* plane show clearly 2-D XY-like critical behaviour. However, magnetic dilution with Zn causes the Bragg intensities in the neutron scattering to rise only gradually below T_N, and there is very significant relaxation in the Mössbauer spectrum (although described in the original paper[27] as a co-existence of magnetic and paramagnetic components). An explanation is given[27] in terms of 2-D correlated regions of the order of 10 lattice spacings which fluctuate on timescales of the order of 10^{-11} (neutron) to 10^{-8} s (Mössbauer). The occurrence of similar relaxation in the Mössbauer spectra of diluted 2-D compounds with very different exchange interactions is consistent in principal with the suggested importance of a 2-D Ising-like behaviour in the critical region.

In conclusion, the present work has thrown new light on the dynamic behaviour of diluted 2-D spin systems with antiferromagnetic spin coupling. In particular, the observed magnetic hysteresis in FC and ZFC experiments and the Mössbauer relaxation in 2-D oxide systems containing Fe^{3+} can be explained by a simple Ising model for the spin system. It is suggested that Ising-like behaviour in the critical region of these crystallographically anisotropic systems is responsible for the formation of an antiferromagnetic domain structure, even though a more Heisenberg-like behaviour may prevail at lower temperatures.

References

1 R. Rodríguez, A. Fernández, A. Isalgué, J. Rodriguez, A. Labarta, T. Tejada and X. Obradors, *J. Phys. C: Solid State Phys.*, 1985, **18**, L401.
2 P. D. Battle, T. C. Gibb, C. W. Jones and F. Studer, *J. Solid State Chem.*, 1989, **78**, 281.
3 T. C. Gibb, *J. Mater. Chem.*, 1992, **2**, 415.
4 T. C. Gibb and R. J. Whitehead, *J. Mater. Chem.*, 1993, **3**, 591.
5 T. C. Gibb, A. J. Herod, S. J. Lees and P. D. Battle, *J. Mater. Chem.*, 1995, **5**, 285.
6 Y. Ishikawa, *J. Phys. Soc. Jpn*, 1962, **17**, 1835, 1877.
7 M. Schlenker, J. Baruchel and Y. Souche, *New trends in magnetism, magnetic materials, and their applications*, eds. J. L. Morán-López and J. M. Sanchez, Plenum Press, New York, 1994, p. 307.
8 H. Gould and J. Tobochnik, *An Introduction to Computer Simulation Methods*, 2nd edn., Addison Wesley, London, 1996.
9 A. R. Bortz, M. H. Kalos and J. L. Lebowitz, *J. Comput. Phys.*, 1975, **17**, 10.
10 D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd edn., Taylor and Francis, London, 1991.
11 G. J. Grest and D. J. Srolovitz, *Phys. Rev. B*, 1985, **32**, 3014.
12 G. J. Grest, C. M. Soukoulis and K. Levein, *Phys. Rev. B*, 1986, **33**, 7659.
13 U. Nowak and K. D. Usadel, *Phys. Rev. B*, 1989, **39**, 2516.
14 U. Nowak and K. D. Usadel, *Phys. Rev. B*, 1991, **44**, 7426.
15 U. Nowak and K. D. Usadel, *Phys. Rev. B*, 1991, **43**, 851.
16 U. Nowak and K. D. Usadel, *Phys. Rev. B*, 1992, **46**, 8329.
17 J. Esser, U. Nowak and K. D. Usadel, *Phys. Rev. B*, 1997, **55**, 5866.
18 M. Staats, U. Nowak and K. D. Usadel, *J. Magn. Magn. Mater.*, 1998, **177–181**, 85.
19 L. J. de Jongh and A. R. Meidema, *Adv. Phys.*, 1974, **23**, 1.
20 M. E. Lines, *J. Appl. Phys.*, 1969, **40**, 1352.
21 J. L. Soubeyroux, P. Courbin, L. Fournes, D. Fruchart and G. Le Flem, *J. Solid State Chem.*, 1980, **31**, 313.
22 M. Shimada, M. Koizumi, M. Takano, T. Shinjo and M. Takada, *J. Phys., Colloq. C2*, 1979, **40**, C2–272.

23 C. Dekker, A. F. M. Arts, H. W. de Wijn and J. K. Kjens, *Phys. Rev. B*, 1987, **35**, 7157.
24 R. A. Cowley, G. Shirane, R. J. Birgenau and H. J. Guggenheim, *Phys. Rev. B*, 1977, **15**, 4292.
25 R. J. Birgenau, R. A. Cowley, G. Shirane, J. A. Tarvin and H. J. Guggenheim, *Phys. Rev. B*, 1980, **21**, 317.
26 H. Keller and I. M. Savic, *Phys. Rev. B*, 1983, **28**, 2638.
27 B. J. Dikken, A. F. M. Arts, H. W. de Wijn, W. A. H. M. Vlak and E. Frikkee, *Phys. Rev. B*, 1985, **32**, 5600.

Paper 9/05206B