# Coexistence of Spin-Glass and Antiferromagnetic Orders in the Ising System $Fe_{0.55}Mg_{0.45}Cl_2$

Po-zen Wong,[1] S. von Molnar,[2] T. T. M. Palstra,[3] J. A. Mydosh,[3] H. Yoshizawa,[4,a] S. M. Shapiro,[5] and A. Ito[6]

[1]*Schlumberger-Doll Research, Ridgefield, Connecticut 06877*

[2]*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*

[3]*Kamerlingh Onnes Laboratorium, der Rijks-Universiteit Leiden, Leiden, The Netherlands*

[4]*Institute for Solid State Physics, University of Tokyo, Roppongi, Minatoku, Tokyo 106, Japan*

[5]*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973*

[6]*Department of Physics, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan*

(Received 13 May 1985)

The low-temperature phase of the dilute Ising antiferromagnet $Fe_{0.55}Mg_{0.45}Cl_2$ in zero field is studied by specific-heat, ac-susceptibility, and neutron-scattering experiments. We find that in this phase, spin-glass behavior and antiferromagnetic long-range order coexist. Such a mixed-order phase is predicted by the mean-field theory of reentrant spin-glasses, but has never been observed before.

PACS numbers: 75.25.+z, 75.30.Hx, 75.40.Dy, 75.50.Ee

The *coexistence* of spin-glass and ferromagnetic orderings in random alloys has been a topic of much controversy.[1-3] Despite recent advances of the mean-field theory[1] which predicted various forms of coexistence, most experiments found a *reentry* behavior, i.e., when a spin-glass state emerges from a ferromagnetic state, the long-range order of the latter is destroyed.[2] Although reentry was originally predicted by Sherrington and Kirkpatrick's mean-field theory (an infinite-range model with *Ising* spins),[4] more recent studies[1] found that coexistence generally occurs when *Heisenberg* spins are used. For example, in systems with weak uniaxial anisotropy, the longitudinal- and transverse-spin components are predicted to have separate freezing transitions, but neither destroys the spontaneous magnetization along the easy axis. For Ising-type systems, only the longitudinal component can freeze and coexist with the magnetization. Experimentally, most of the materials studied have been ferromagnetic alloys that are Heisenberg-type[2] and the situation is quite complex: While some Mössbauer studies have reported evidence for transverse freezing,[5] some neutron-scattering studies have questioned the existence of long-range order even in the supposedly purely ferromagnetic phase.[6] Antiferromagnetic alloys and Ising-type systems exhibiting spin-glass behavior have been much neglected thus far. In this paper, we present a comprehensive investigation of the Ising-type dilute antiferromagnet $Fe_{0.55}Mg_{0.45}Cl_2$, which gives clear evidence for the coexistence of longitudinal spin-glass and antiferromagnetic orders.

Pure $FeCl_2$ is a hexagonal-lattice layered compound which has ferromagnetic $a$-$b$ planes (with a triangular lattice) that stack antiferromagnetically along the $c$ axis.[7] A strong uniaxial anisotropy ($D = -17$ K) aligns the moments along the $c$ axis. The in-plane interactions are ferromagnetic for the nearest neighbors ($J_1 = 7.88$ K), but antiferromagnetic for the next-nearest neighbors ($J_2 = -1.04$ K). In diluted $Fe_{1-x}Mg_xCl_2$ crystals, one expects $J_2$ to cause frustration in the system for sufficiently large $x$, which may lead to a spin-glass phase in a manner similar to $Eu_{1-x}Sr_xS$.[6] In particular, we note that beyond the two-dimensional (2D) site-percolation threshold ($x > x_c = 0.5$), the 3D antiferromagnetic order relies on the dominance of the interplane exchange ($J' = -0.50$ K). Since this interaction is weaker than $J_2$, 3D antiferromagnetic order is likely to break down for $x > 0.5$.

Large $Fe_{1-x}Mg_xCl_2$ crystals were grown by the Bridgman technique.[7] Our neutron-scattering experiments (see below) show that there is no atomic order in the samples. Atomic absorption analysis shows that there is usually a macroscopic concentration gradient of 0.01/cm in the boule. In all of our experiments, care was taken to use small samples such that the variation in $x$ is typically less than 0.003.[7,8] This level of homogeneity is confirmed by the sharpness of the Néel transitions seen in Figs. 1–3 below. We note that a change of 0.01 in $x$ corresponds to *at least* a 0.4 K change in $T_N$ and the transitions in our samples are generally much sharper than 0.1 K.

The magnetic specific heat was measured at IBM with use of a small-sample ($\sim 5$ mg of single crystal) thermal-relaxation technique.[8] Figure 1 shows the results obtained on five samples with different concentrations and demonstrates the global effects of dilution. Strong and sharp Néel transition peaks are observed in the first three samples ($x = 0$, 0.161, 0.318). Their transition temperatures ($T_N = 23.55$, 18.0, 12.8 K, respectively) decrease linearly with increasing $x$ with a slope $dT_N(x)/dx = -1.47T_N(0)$, in agreement with Monte Carlo simulations on a 2D triangular lattice.[9] Clearly, the unsatisfied $J_2$ bonds have negligible effects in this concentration range. In the $x$

 

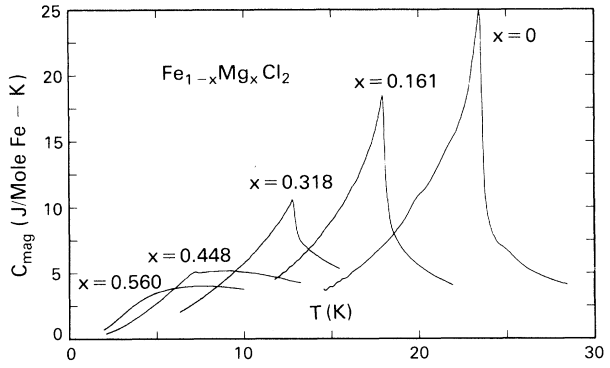


FIG. 1. Magnetic specific heat as a function of temperature for five samples with different concentrations.

$= 0.448$ ($\lesssim x_c$) sample, we see a dramatic reduction of the peak, which is barely observable near 7.0 K. In the $x = 0.560$ ($\gtrsim x_c$) sample, there is no sharp peak down to 1.9 K. Only a broad maximum, characteristic of a spin-glass, was observed. It suggests that there is no long-range antiferromagnetic order at this level of dilution.

Concurrent with our specific-heat experiments, Bertrand *et al.* independently carried out dc-magnetization measurements on a series of $Fe_{1-x}Mg_xCl_2$ samples.[10] For $x \leq 0.45$, they found $T_N$'s in excellent agreement with our data. For $x = 0.45$ and 0.55, they also found strong irreversibilities (characterized by differences between field-cooled and zero-field-cooled data) below 3.0 and 3.5 K, respectively. Since our data in Fig. 1 show no specific-heat anomalies at these temperatures, it is natural to believe that there is indeed a spin-glass phase. However, there are reservations with this interpretation because the applied field in the magnetization experiments produces site-random staggered fields, which can also cause similar irreversibilities.[8,11] Thus, it is essential to carry out careful investigations in *zero* field. We selected three representative (nominal) concentrations ($x = 0.30$, 0.45, 0.60) for detailed ac-susceptibility and neutron-scattering studies in zero field. The $x = 0.30$ sample was found to be simply antiferromagnetic. The $x = 0.60$ sample, in contrast, has no antiferromagnetic order and behaves like an ideal Ising spin-glass. It has a sharp cusp in the parallel susceptibility ($\chi_{\parallel}$) at about 3.0 K and a constant magnetic correlation length of 10 Å below it. Detailed results will be presented elsewhere. Here, we focus on the $x = 0.45$ sample which does exhibit *coexistence*.

The ac-susceptibility experiments were performed on small samples ($\sim$ 5 mg) at Leiden by use of a calibrated mutual inductance bridge with a 0.1-Oe driving field. The sample could be oriented to have its $c$ axis either parallel or perpendicular to the field direction for $\chi_{\parallel}$ and $\chi_{\perp}$ measurements. Figure 2 shows the temperature dependence of $\chi_{\parallel}$ for three frequencies:

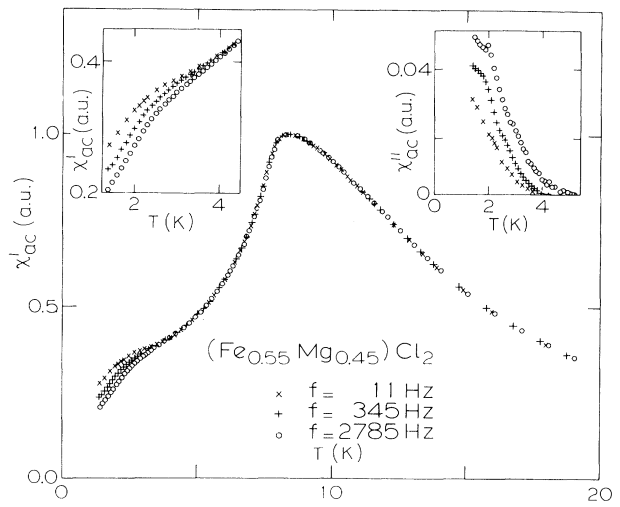


FIG. 2. Temperature dependence of the complex ac susceptibility ($\chi'_{\parallel}$ and $\chi''_{\parallel}$) measured parallel to the easy axis at three different frequencies.

11, 345, and 2785 Hz. The real part, $\chi'_{\parallel}$, is insensitive to the frequency above 5.0 K and $d(T\chi'_{\parallel})/dT$ peaks at about 7.5 K, characteristic of a Néel transition.[12] Below 5.0 K, frequency dependence gradually appears and there is a corresponding onset of the imaginary part $\chi''_{\parallel}$. Below 3.0 K, $\chi'_{\parallel}$ shows a drop and $\chi''_{\parallel}$ rises rapidly; the frequency dependence also becomes much stronger. These results imply the onset of very slow spin relaxations[13] and suggest spin-glass transitions at $T_{sg} \approx 3.0$ K.

Double axes neutron-scattering experiments were carried out at Brookhaven National Laboratory in order to measure the static structure factor $S(q)$ which is the Fourier transform of the spin-spin correlation function. Technical details and some preliminary results had been described elsewhere.[14] We recall that because the system is antiferromagnetic, the magnetic and nuclear Bragg peaks are separated in $q$ space and this allows us to study the magnetic order with little ambiguity. In principle, the scattering near the reciprocal lattice point (0,0,3) gives information about the transverse spin component and that at $(1, 0, \bar{1})$ is related to both the transverse and longitudinal components.[15] However, we find that the scattering near (0,0,3) is independent of both $T$ and $q$ which implies no transverse components. Thus only a longitudinal component is present and this is measured at $(1, 0, \bar{1})$.

In Fig. 3(a), we show the temperature dependence of the peak intensity $I(1, 0, \bar{1})$ and the diffuse scattering $I(0.98, 0, \bar{1})$, slightly off the peak. These results indicate a well-defined Néel transition at $T_N = 7.5 \pm 0.1$ K: $I(0.98, 0, \bar{1})$ reaches a peak at $T_N$ because of critical scattering, and $I(1, 0, \bar{1})$, which measures the square of the staggered magnetization, disappears above $T_N$. The value of $T_N$ agrees with the $\chi_{\parallel}$ data,

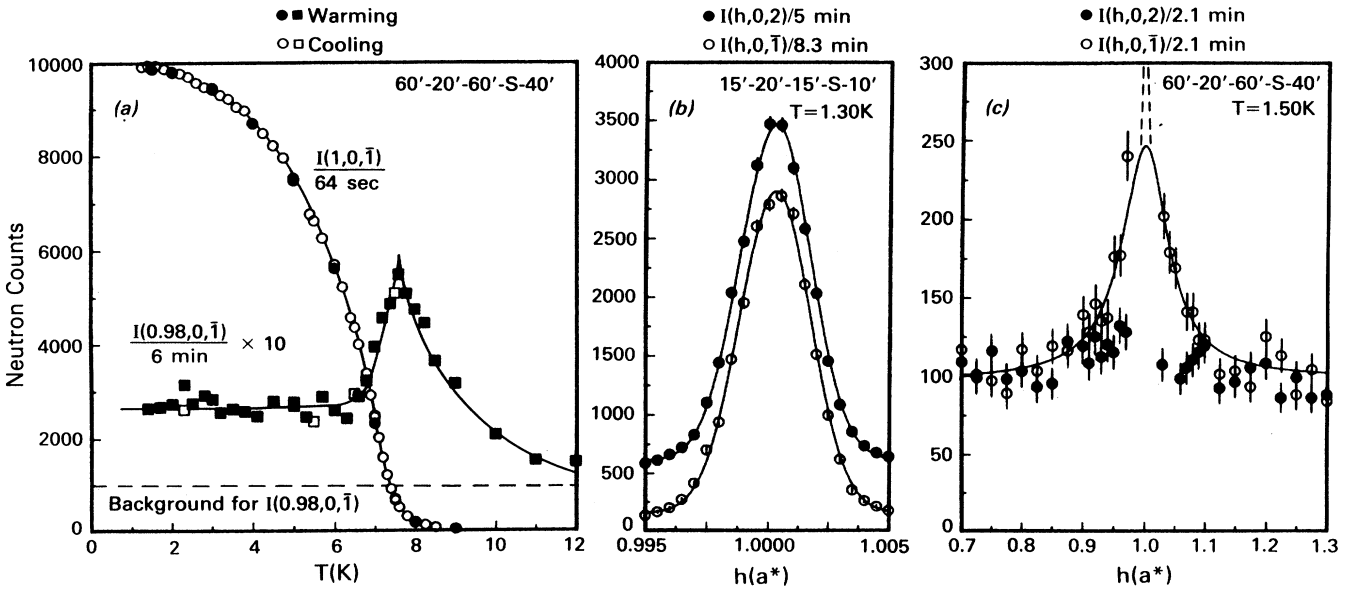


FIG. 3. (a) Temperature dependence of the magnetic Bragg scattering at $(1,0,\bar{1})$ and diffuse scattering at $(0.98,0,\bar{1})$. (b) Comparison of the $(1,0,\bar{1})$ magnetic Bragg peak and the (1,0,2) nuclear Bragg peak at $T=1.30$ K, well below $T_{sg}$. The solid lines are fits to resolution-limited Gaussians. (c) Comparison of the diffuse scattering near the $(1,0,\bar{1})$ and the (1,0,2) peaks at $T=1.50$ K. The solid line is a fit of the magnetic scattering to a Lorentzian. The dashed line represents the central Bragg component which is 3 orders of magnitude higher.

but remarkably, there are no obvious signs for a spin-glass transition at $T_{sg}\approx 3.0$ K, as seen in Fig. 2. In particular, $I(1,0,\bar{1})$ increases smoothly down to 1.2 K, suggesting that the antiferromagnetic order persists below $T_{sg}$. However, the diffuse scattering is much higher than the background at low temperatures, which implies that not all the spins are antiferromagnetically ordered as $T\rightarrow 0$. To determine if the antiferromagnetism is truly long range, we performed $(h,0,\bar{1})$ scans with a high resolution (0.0035 $\text{Å}^{-1}$ HWHM). Figure 3(b) shows a comparison between the $(1,0,\bar{1})$ magnetic Bragg peak and the (1,0,2) nuclear Bragg peak at 1.30 K, well below $T_{sg}$. Both peaks are found to be resolution-limited Gaussians. The same peak shape and peak width are observed at all temperatures below $T_N$. They imply that the antiferromagnetic order is long range ($>10^3$ Å) below $T_N$ and it is unaffected by the spin-glass transition.

In order to investigate the spin-glass nature of the system, diffuse scattering scans were made along different directions at $(1,0,\bar{1})$, (1,0,5), and $(0,0,l)$. A coarse resolution was used for higher intensity. Figure 3(c) shows an $(h,0,\bar{1})$ scan at 1.50 K ($<T_{sg}$) which exhibits a Lorentzian magnetic diffuse peak underneath the Bragg peak. The width of this peak corresponds to a correlation length $\xi$ of approximately 10 Å. Similar scans were performed at other temperatures, up to 13 K, and we find that both the width and the amplitude of the Lorentzian are constant below 6.0 K. This frozen short-range correlation is most likely the origin of the spin-glass behavior observed in the ac-susceptibility experiments. In Fig. 3(c), we also show a similar scan across the (1,0,2) nuclear peak which does not exhibit a diffuse peak. This provides a reference for the background and, more importantly, a clear demonstration that *there is no atomic clustering or short-range order in the sample.* In other words, the presence of short-range magnetic correlations cannot be attributed to some trivial microscopic sample inhomogeneities.

Our results can be summarized as follows. The peak in specific heat and $d(T\chi'_{\parallel})/dT$ above 7.0 K are signatures of a Néel transition for an antiferromagnet. The drop in $\chi'_{\parallel}$ below 3.0 K, the onset of slow relaxations in $\chi'$ and $\chi''$, and the absence of a specific-heat anomaly are all similar to the reentrant Heisenberg ferromagnets.[6,13] The most remarkable difference here is that the magnetic Bragg scattering demonstrates *directly* that the long-range antiferromagnetic order is *not* destroyed by the spin-glass transition, i.e., *the system does not reenter into a disordered phase.* In addition, the magnetic diffuse scattering shows clearly that some of the spins do not participate in the antiferromagnetic order. Instead, they have a very short correlation length that is frozen at low temperatures. Combining all these observations, along with our knowledge of the samples' concentration homogeneity, we conclude that the low-temperature phase of the system consists of both spin-glass and long-range-antiferromagnetic order. Such a *coexistence* is predicted by mean-field theory, but has never been observed experimentally. The microscopic picture of coexistence should consist

of some (perhaps the majority) spins in an infinite antiferromagnetic network and some spins frozen like a spin-glass. Whether the latter spins form isolated clusters or a large network is not known, because our experiments do not measure the *range* of the spin-glass order parameter. Computer simulations may shed some light on this question.[16]

It is natural to question why coexistence is observed in a dilute Ising antiferromagnet like $Fe_{0.55}Mg_{0.45}Cl_2$, but not in a dilute Heisenberg ferromagnet such as $Eu_{0.52}Sr_{0.48}S$.[6] Since there is no existing theory that explains this difference, we can only offer several conjectures:

(i) One possibility is related to the lower critical dimension (LCD) of spin-glasses.[17] It is well known that the mean-field theory does not consider the effects of fluctuations.[1,4] The phases predicted by such a theory are generally valid only if fluctuations are not strong enough to destroy the transitions, or in other words, the system's dimension must be above the LCD. Recent theoretical studies suggest that the LCD of spin-glasses is greater than 3 for Heisenberg systems, but less than 3 for Ising systems.[17] Hence, in 3D, the predicted phases may only exist in Ising systems and not in Heisenberg systems.

(ii) Another possibility is related to the LCD of random-field systems.[17] In their studies of reentrant ferromagnets, Maletta *et al.* and Aeppli *et al.*[6] have suggested that the freezing of frustrated spins in the systems can produce random molecular fields which act upon the unfrustrated spins in the infinite ferromagnetic network. The effect of such fields is to raise the LCD from 2 to 4 for Heisenberg systems, but only from 1 to 2 for Ising systems.[18] Since the systems in question are both 3D, this may explain the difference between the Ising and Heisenberg systems. It is also interesting to note that in $Fe_{0.70}Mg_{0.30}Cl_2$, it has been explicitly demonstrated that the antiferromagnetic long-range order is not destroyed if it is established before the random fields are applied.[11] This may be an analog of what happens at $T_{sg}$ in $Fe_{0.55}Mg_{0.45}Cl_2$.

(iii) A third possibility is related to the LCD of random-anisotropy systems. In dilute alloys, because of the lack of local symmetry around the magnetic ions, there can be random off-diagonal exchange interactions which are equivalent to random uniaxial anisotropies.[15] These can also destroy long-range order in 3D Heisenberg systems, but not Ising systems.

(iv) Finally, we remark that dipolar interactions tend to oppose ferromagnetic order but not antiferromagnetic order. Although such interactions do not destroy long-range order in pure ferromagnets, their effects might be stronger in dilute ferromagnets with frustrated bonds.

We thank J. Banavar, A. T. Ogielski, and D. Sherrington for helpful discussions. The work at Brookhaven is supported by the U. S. Department of Energy under Contract No. DE-AC02-76CH00016 and at Leiden, by the Nederlandse Stichting voor Fundamenteel Onderzoek der Materie.

[a]Temporary address: Brookhaven National Laboratory.

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