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# Observation of a disordered spin-flop phase in $Fe_{0.725}Co_{0.275}Cl_2$

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The $T$-$H$ phase diagram of the random antiferromagnet $Fe_{0.725}Co_{0.275}Cl_2$ is investigated by neutron scattering for applied field $H$ parallel to the $c$ axis (the direction of average anisotropy). We find an unusual disordered spin-flop phase in high fields in which the spins formed finite-size domains with their moments perpendicular to $H$. We argue that the disorder is a consequence of the random off-diagonal exchange interactions and the spin-flop phase is probably a realization of the three-dimensional $XY$ model in random fields.

Multicritical phenomena in uniaxial antiferromagnets have been a subject of wide interest during the last decade. Experimental studies of their phase diagrams in longitudinal magnetic fields, in particular, have produced beautiful results which confirmed many novel theoretical predictions obtained by renormalization-group calculations.[1] Generally speaking, in weak-anisotropy systems, one finds bicritical-point phase diagrams with spin-flop transitions (in which the spins' ordering direction changes from parallel to perpendicular to the easy axis) at high fields. In strong-anisotropy systems, however, one finds tricritical-point phase diagrams with spin-flip transitions (in which the spins on the two sublattices flip from antiparallel to parallel) at high fields. In more recent years, there has been considerable effort to extend these studies to random antiferromagnets. Detailed experiments have been performed on weak-anisotropy systems such as $Gd_{0.97}La_{0.03}AlO_3$ and $Mn_{1-x}Zn_xF_2$.[2-4] Preliminary data also exist for strong-anisotropy systems such as $Fe_{1-x}Mg_xCl_2$ and $Fe_{1-x}Cd_xCl_2$.[5-7] Although in each case the phase diagram appears to be of the same kind as the pure system, there are drastic differences in details which are not understood. The difficulties are most likely to be related to random-field effects.

It is by now well recognized that the longitudinal applied field generates site-random staggered fields in these systems,[7,8] and their effects are not well understood. In particular, there is a controversy on whether a true long-range-ordered (LRO) phase can exist in these systems in low fields.[9] (In pure systems, the antiferromagnetic phase is unchanged in low fields.) Without that knowledge, it is very difficult to make precise interpretations on the very delicate phase diagram and multicritical behavior. The best example of such difficulties is perhaps in the two weak-anisotropy systems mentioned above. In samples which are lightly doped ($x=0.03$ and 0.04), both Rhorer and Scheel[2] and Shapira and Oliveira[3] found that the shape of the phase boundaries near the bicritical point are similar to the pure systems, except that new values for the bicritical exponents are necessary to fit the data. More recently, however, Shapira *et al.*[3] found that in the more heavily doped samples of $Mn_{1-x}Zn_xF_2$ ($x=0.12, 0.25$), the shapes of these phase boundaries are *qualitatively* different. The first-order spin-flop line, for example, shows a negative $dH/dT$ slope near the bicritical point, which is not observed in the less diluted (or pure) samples and is unlikely to be simply a "new bicritical behavior." Similarly, in presumably pure tricritical systems, Birgeneau and Berker have also questioned the effects of random fields due to trace impurities in the samples.[10] To better understand these problems, it is essential to study carefully the nature of the ordered states in both high and low fields by neutron scattering. Although much work has been done in recent years to study the low-field phase,[9] because of its correspondence to the random-field Ising model, there has been little effort to study the ordering in the high-field phases. In this Rapid Communication, we report a neutron scattering study of the high-field phase in the random antiferromagnetic system $Fe_{0.725}Co_{0.275}Cl_2$.

Our motivation for studying $Fe_{1-x}Co_xCl_2$ is twofold. First, pure $FeCl_2$ is one of the best studied tricritical systems.[1] Random substitution of Fe ions by Co ions is known to decrease the average anisotropy of the system. In zero field, for example, the magnetic ordering changes from easy axis to easy plane when $x \gtrsim 0.307$.[11] Galam and Aharony[12] have shown by both mean-field and renormalization-group calculations that the reduction of anisotropy has the same general effects in random systems as it has in pure systems, i.e., a spin-flop (SF) phase should appear at low temperature and high field, and the phase diagram should become bicritical. However, a light scattering study on $Fe_{1-x}Co_xCl_2$ by Wood and Day[5] suggests that the phase diagram remains tricritical for $x$ as large as 0.29. A neutron scattering experiment which probes directly the spin orientation will provide the first test of the Galam-Aharony idea and clarify its disagreement with the Wood-Day experiment. Second, in the earlier study of $Fe_{1-x}Co_xCl_2$ in zero field by Wong and co-workers,[11] it was argued that there should be random off-diagonal exchange interactions between the different spin components due to the lack of local symmetry. With such interactions, a magnetization in the $c$ direction will produce random molecular fields in the $ab$ plane. Since the spin-component in the plane ($\vec{S}_\perp$) has negligible anisotropy,[11] if a SF phase occurs, it should be described by the three dimensional (3D) $XY$ model in random fields, which is generally believed to be disordered at all temperatures but has never been observed in magnetic systems. Furthermore, because we know from our previous study (see below) that the low-field phase of this system is described by the random-field Ising model,[13] it may be possible to compare the behaviors of the two random-field models in the same system.

 

Quasielastic (double axis) experiments were performed on $Fe_{0.725}Co_{0.275}Cl_2$ at the high-flux-isotope reactor of Oak Ridge National Laboratory. 14-meV neutrons from the (0,0,2) reflection of a graphite monochromator were used, along with a graphite filter to reduce high-order contamination. The sample was mounted on a displex cryostat that fits onto an electromagnet. The lowest temperature reached was 9.0 K (monitored by a calibrated carbon-glass thermometer) and the highest field was 13 kOe. The field was applied along the $c$ axis of the crystal.

In zero field, the spin component parallel to the $c$ axis ($\vec{S}_{\parallel}$) in this sample is known to order antiferromagnetically with 3D Ising characteristics.[11] In finite fields, it corresponds to the random-field Ising model.[7-9,13] In our previous study,[9,13] we found that for $H < 4$ kOe, the ordered state is unchanged (within our instrumental resolution) regardless of how the sample was cooled. Above 4 kOe, however, the system is disordered when cooled in a field, but ordered when the field is applied after cooling in zero field. Time dependence tests *suggest* that the zero-field-cooled state is the equilibrium state. We shall refer to this phase as the antiferromagnetic (AF) phase. In Fig. 1, we show the $T$-$H$ phase diagram that extends to higher fields. We find that there is a region at low temperature and high field in which $\vec{S}_{\perp}$ develops large local staggered magnetization, but without LRO. In other words, there is a *disordered* spin-flop phase. The evidence for such a phase is presented in Figs. 2–4.

In Fig. 2(a) we show the $H$ dependence of the peak intensities at the $(1,0,\bar{1})$ and (0,0,3) reflections at 11.36 K. These intensities are proportional to $(M^s_{\parallel})^2+\frac{1}{2}(M^s_{\perp})^2$ and $(M^s_{\perp})^2$, respectively,[11] where the $M^s$'s are the root-mean-square (rms) staggered magnetizations associated with $\vec{S}_{\parallel}$ and $\vec{S}_{\perp}$. The two-step behavior of $I(1,0,\bar{1})$ can be understood as the result of two successive transitions: an AF-SF transition at 7.3 kOe and a SF-PM (paramagnetic) transition near 12 kOe. The $H$ dependence of $I(0,0,3)$ is consistent with this picture. It shows $(M^s_{\perp})^2$ rises and falls rapidly between the same two fields. If we normalize $I(1,0,\bar{1})$ and $I(0,0,3)$ at 9.0 kOe, the $(M^s_{\perp})^2$ contribution can be roughly subtracted from $I(1,0,\bar{1})$ to give the $H$ dependence of $(M^s_{\parallel})^2$. The result is depicted by the dotted line in Fig. 2(a). It shows the gradual disappearance of $(M^s_{\parallel})^2$ above 7.3 kOe, consistent with a spin-flop transition. We note that the intensity at $(1,0,\bar{1})$ is due primarily to $(M^s_{\parallel})^2$ below 7.3 kOe, and to $(M^s_{\perp})^2$ above it. The hysteresis in $I(1,0,\bar{1})$ between 4 and 7.3 kOe is consistent with the behavior of $\vec{S}_{\parallel}$ observed in our previous study.[9,13] The hys-

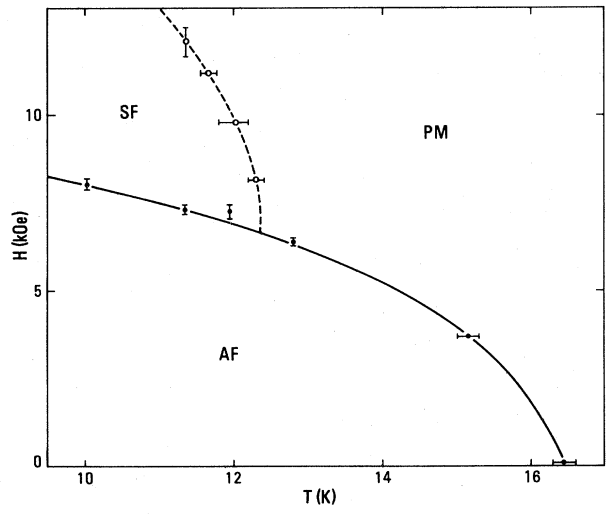


FIG. 1. The temperature-applied-field phase diagram of $Fe_{0.725}Co_{0.275}Cl_2$ for fields parallel to the $c$ axis.

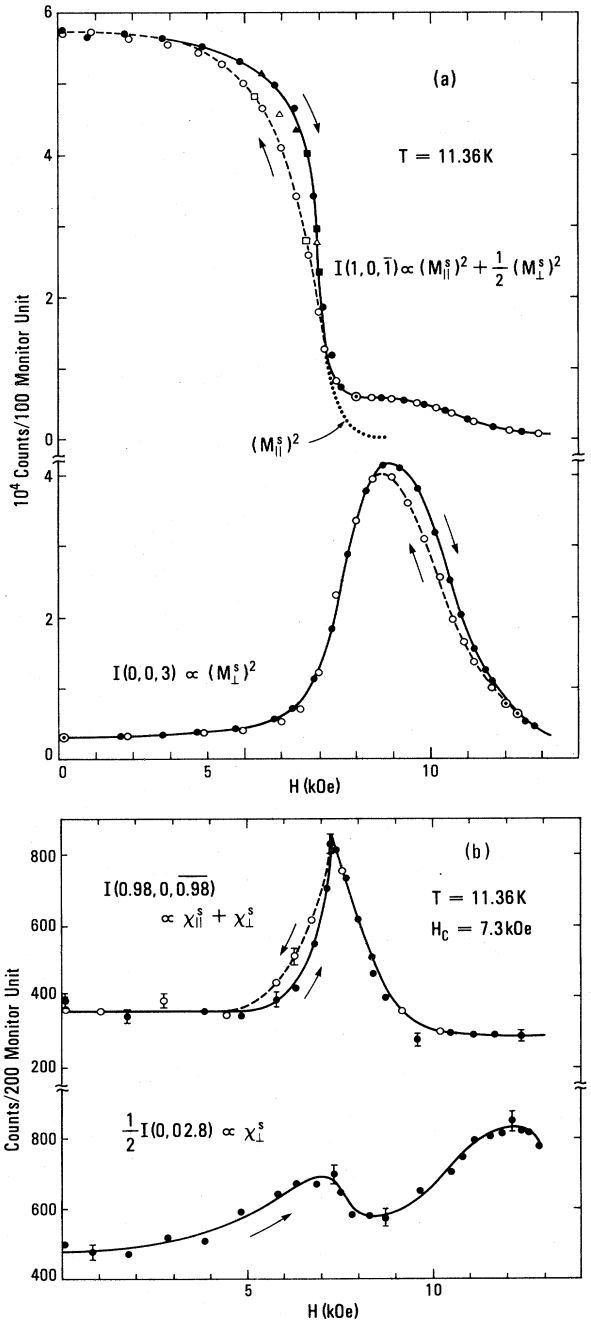


FIG. 2. Field dependence of the (a) peak intensities $I(1,0,\bar{1})$, $I(0,0,3)$ and (b) wing intensities $I(0.98,0,\overline{0.98})$, $I(0,0,2.8)$ for $T = 11.36$ K. ○ and ● denote data from the first run. In (a) ■ and □ are data from a repeat run. Δ and ▲ are obtained by reversing the direction of field change, starting from the last □ or ■, respectively.

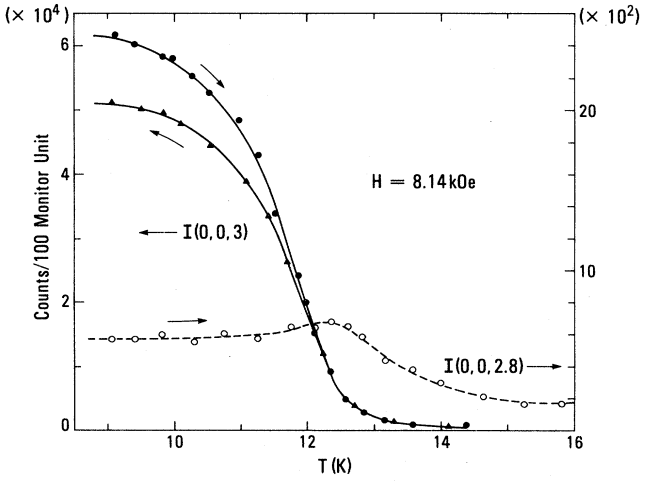


FIG. 3. Temperature depencence of $I(0,0,3)$ and $I(0,0,2.8)$ across the SF-PM boundary for $H = 8.14$ kOe.

teresis in $I(0,0,3)$, however, is quite unusual. An even more striking behavior was observed when the wing intensities at $(0.98,0,\overline{0.98})$ and (0,0,2.8) were measured as a function of $H$. They are related to $\chi^s_{\parallel}+\chi^s_{\perp}$ and $2\chi^s_{\perp}$, respectively,[11] where the $\chi^s$'s are the small-wave-vector staggered susceptibilities associated with $\vec{S}_{\parallel}$ and $\vec{S}_{\perp}$. The results, as depicted in Fig. 2(b), show a sharp peak in $I(0.98,0,\overline{0.98})$ at 7.3 kOe but two rounded peaks in $I(0,0,2.8)$ at 7.3 and 12.2 kOe. These results suggest that, at the AF-SF boundary, $\vec{S}_{\parallel}$ undergoes a second-order transition while $\vec{S}_{\perp}$ has a smeared transition. At the SF-PM boundary, the $\vec{S}_{\perp}$-transition is also ill defined. These are very different from a pure system, which has a first-order AF-SF boundary for both components and a second-order SF-PM boundary for $\vec{S}_{\perp}$.

To further characterize the SF phase, we measured $I(0,0,3)$ and $I(0,0,2.8)$ as a function of $T$ at different fields. Figure 3 depicts a set of typical results for $H = 8.14$ kOe. They again show a smeared transition for $\vec{S}_{\perp}$ at the SF-PM boundary. Thermal hystereses inside the SF phase

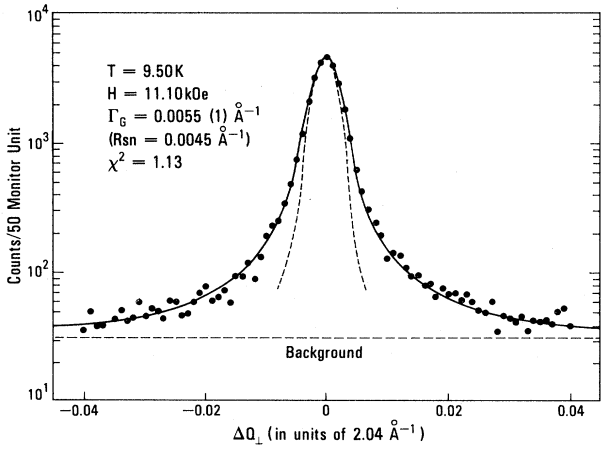


FIG. 4. Transverse scan of the $(1,0,\bar{1})$ peak in the SF phase. The sample was first cooled in zero field to 9.50 K and the field was then increased to 11.10 kOe. The procedure gives the highest peak intensity in the SF phase, but the peak width is still wider than resolution (Rsn). This implies that the SF phase does not have LRO.

were also observed. The reason for these observations became clear when the range of $\vec{S}_{\perp}$ correlation was probed by peak-shape measurements at $(1,0,\bar{1})$ and (0,0,3) as a function of $T$ and $H$. We found that both peaks were wider than our resolution limits. In Fig. 4, we show one typical scan at $(1,0,\bar{1})$ transverse to the reciprocal lattice vector. At this reflection, in zero field we have determined that a resolution limited Bragg peak can be fitted by a Gaussian plus a Lorentzian (G+L) with a Gaussian width $\Gamma_G = 0.0045(1)$ Å$^{-1}$ [half-width at half maximum (HWHM)]. The central part of such a peak is depicted by the dashed line in Fig. 4. The measured peak is clearly not resolution limited. If the scan in Fig. 4 is fitted to the same G+L form, we find $\Gamma_G = 0.0055$ Å$^{-1}$, 20% wider than the resolution limit. The G+L form is probably not the correct form for the structure factor (peak shape). At the (0,0,3) reflection, where the resolution is higher, we found that the scans can be satisfactorily fitted by a single Lorentzian term. Adding another Lorentzian or squared-Lorentzian term will improve the fit, but at the cost of additional fitting parameters. In other words, it is not possible to determine unambiguously what the correct form for the structure factor is. It is only important to mention here that regardless of what form we use to fit the data, and regardless of how the SF phase is approached, we always find that the peak is wider than our resolution, which implies that the SF phase does not have LRO. The hysteretic behaviors and the smeared $\vec{S}_{\perp}$ transitions suggest that this phase consists of frozen domains. The value of $\Gamma_G$ indicates the size of these domains are on the order of $10^3$ Å. A detailed discussion of the peak-shape analysis will be postponed until a later full length paper.

The results described above are consistent with the theoretical expectation that a SF phase should occur with the reduction of anisotropy. The quantitative predictions by Galam and Aharony[12] clearly cannot apply since the SF phase is disordered. The existence of domains in this phase also explains the light scattering phenomenon observed by Wood and Day.[5] The most likely explanation for this unusual SF phase is perhaps the one given above in terms of the random off-diagonal exchange and the random-field $XY$ model. This explanation, however, is based on the assumption that the small $\vec{S}_{\perp}$ anisotropy in the $ab$ plane is irrelevant.[11] In addition, Mukamel and Grinstein have also pointed out that the random off-diagonal exchange alone (without the random fields) may be sufficient to destroy LRO for $XY$ systems.[14] In any event, it seems most likely that the random off-diagonal exchange is responsible for the occurrence of the disordered SF phase.

As mentioned before, the AF phase is described by the random-field Ising model.[7-9,13] If we assume that the random-field $XY$ model description for the SF phase is valid, then the data presented in Fig. 2(b) would be an indication of the contrasting behaviors of the two models in the same three-dimensional system. The sharp $\vec{S}_{\parallel}$ transition, in particular, is suggestive of a true long-range-ordered AF phase, consistent with our previous finding.[9,13]

Finally, we note that in the SF phase of two other weak-anisotropy systems, $Gd_{1-x}La_xAlO_3$ and $Mn_{1-x}Zn_xF_2$,[2-4] there was no indication of disorder. The reasons, we believe, are that (i) in $Gd_{1-x}La_xAlO_3$ the SF phase has uniaxial anisotropy, and (ii) both $Gd^{3+}$ and $Mn^{2+}$ are $S$-state ions, the off-diagonal terms come mainly from dipolar interactions, which are very small.[3] In a competing-anisotropy

system such as $Fe_{1-x}Co_xCl_2$, the off-diagonal terms can be larger because of orbital contributions and the effects are more noticeable.[11,15] Nevertheless, it is interesting to observe that the negative $dH/dT$ slope of the spin-flop line near the bicritical point in $Mn_{1-x}Zn_xF_2$ (Ref. 3) is consistent with the phase diagram shown in Fig. 1. We *speculate* that this is perhaps also due to the random off-diagonal terms. Technically speaking, no matter how small these terms are, they still destroy the LRO in the SF phase (although the size of the domains can be very large and the disorder is difficult to detect). In other words, the bicritical point must be *theoretically nonexistent* when impurities are present. One possible way for this to happen is that the bicritical point turns into a tricritical point under the influence of impurities. The tricritical point joins the second-order AF-PM boundary to the first-order AF-SF boundary. The original SF-PM line disappears and the remnant transition is associated with the freezing of finite-size domains. Such a picture would be consistent with a negative $dH/dT$ slope near the "pseudobicritical" point since $dH/dT$ for the second-order AF-PM line is always negative. Experimentally, of course, the effect should only be observable when the off-diagonal terms are appreciable. The change in behavior in $Mn_{1-x}Zn_xF_2$ with increasing $x$ is consistent with such a crossover.[3] A detailed theoretical treatment of this problem will be quite interesting.

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