Competing Order Parameters in Quenched Random Alloys: $Fe_{1-x}Co_xCl_2$

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A study is reported of the magnetic properties of the random alloy $Fe_{1-x}Co_xCl_2$, which represents an archetypal example of a system with competing orthogonal spin anisotropies. Behavior similar to previous experiments and theoretical predictions is found, but with important qualitative and quantitative differences; in particular the phase transition in one variable is drastically altered by the existence of long-range order in the other variable. It is hypothesized that this is due to microscopic random-field effects.

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The physics of alloy systems with competing interactions has proven to be remarkably subtle and complex.[1,2] Perhaps the simplest nontrivial such problem is a quenched two-component alloy with constituents whose respective spin anisotropies are orthogonal.[2] For simplicity we label these two orthogonal directions $\parallel$ and $\perp$. Mean-field calculations[3] on such a system with a bilinear diagonal Hamiltonian

$$\mathcal{H}=\sum_{i,j} J_{ij}^{\parallel} S_{\parallel}(i) S_{\parallel}(j) + J_{ij}^{\perp}[\vec{S}_{\perp}(i)\cdot\vec{S}_{\perp}(j)],$$

with site random J_{ij}, yield a multicritical phase diagram with a crossover from $\parallel$ to $\perp$ ordering at some concentration x_M. More importantly, these calculations predict that in the neighborhood of x_M, two distinct phase transitions may occur in $S_{\parallel}$ and $\vec{S}_{\perp}$. Using the renormalization-group technique for the above Hamiltonian, Fishman and Aharony predict that $S_{\parallel}$ and $\vec{S}_{\perp}$ should order independently and their respective transition temperatures $T_{\parallel}$ and $T_{\perp}$, as a function of mixing concentration x, are two smooth lines on the magnetic phase diagram in the x-T plane, crossing each other at a point designated as a "decoupled tetracritical point." The prediction of decoupling is quite universal and should be valid for any two order parameters with an energy-energy coupling and finite individual ordering specific heats.

In order to explore these phenomena we have carried out a systematic study of the quenched alloy system anhydrous $Fe_{1-x}Co_xCl_2$. This system was chosen for study for a number of reasons.[4,5] Briefly, pure $FeCl_2$ and $CoCl_2$ have identical rhombohedral crystal structures with similar lattice constants and melting points. Single crystals of the random alloy $Fe_{1-x}Co_xCl_2$ can be formed at any composition x without chemical clustering. The magnetic properties of the pure compounds have been extensively characterized[4]; they have similar ordering temperatures and identical magnetic structure except for the strong anisotropy which forces the Fe spin to order along the hexagonal c axis and the Co spin to order in the a-b plane perpendicular to it. Thus, $Fe_{1-x}Co_xCl_2$ represents a simple well-characterized mixture of a three-dimensional Ising and a three-dimensional x-y antiferromagnet.

Single crystals of the alloy were prepared by standard Bridgman methods covering the entire composition range $0 \leq x \leq 1$. The composition x, as analyzed by atomic absorption spectroscopy, usually varied monotonically along the length of the cylindrical samples, sometimes by as much as 8% for a 10-g sample 5 cm long. Neutron diffraction measurements were carried out on a triple-axis spectrometer, set for elastic scattering at the high-flux beam reactor at Brookhaven Na-

tional Laboratory with use of 13.6-meV neutrons. The samples were mounted with their a^*-c^* axis in the horizontal scattering plane; this oriented the cylindrical growth axis approximately vertical. The samples were then masked such that the neutrons illuminated only a small vertical fraction of the sample; within the illuminated volume the variation in x was typically 0.5 at.%. The concentration to be studied could then be varied continuously by moving the position of the mask vertically. Bulk magnetic susceptibility parallel and perpendicular to the c axis ($\chi_{\parallel}$ and $\chi_{\perp}$) was measured by Faraday's method by use of 20-mg samples within which x also varied by no more than 0.5 at.%.

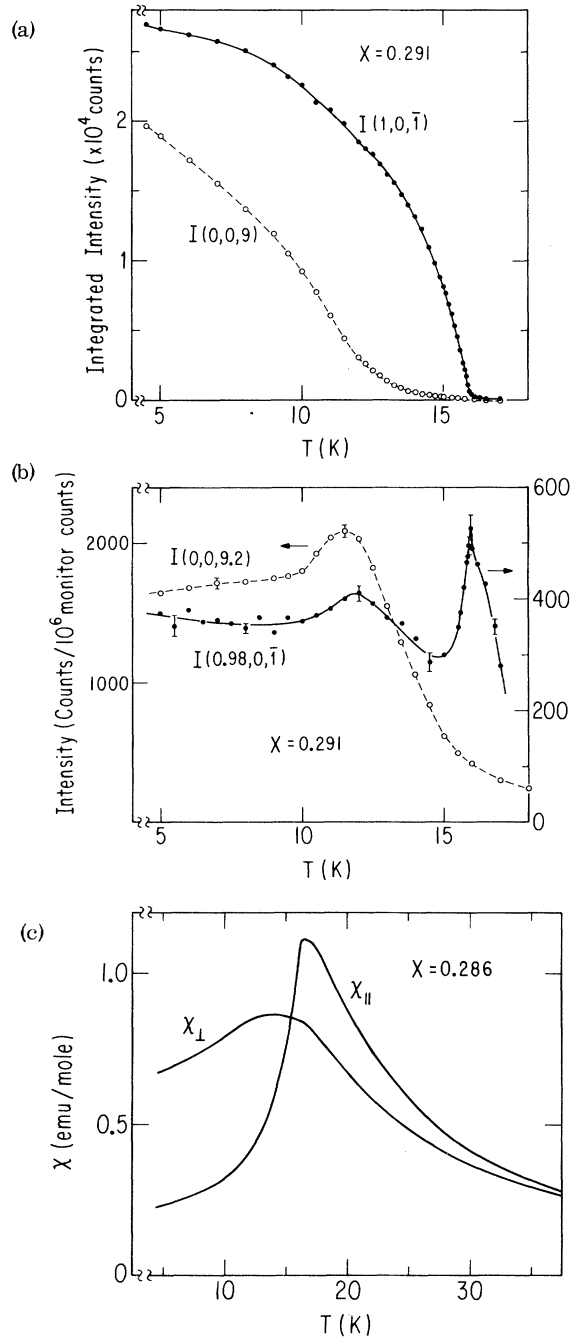

FIG. 1. (a) Temperature dependence of the magnetic scattering at the (0, 0, 9) and (1, 0, $\bar{1}$) reciprocal-lattice positions. (b) Temperature dependence of the magnetic critical scattering. (c) Temperature dependence of the static magnetic susceptibility for applied field parallel (∥) and perpendicular (⊥) to the c axis.

Typical experimental results are shown in Fig. 1(a) where we plot the magnetic intensity at the (0, 0, 9) and (1, 0, $\bar{1}$) reciprocal-lattice positions for a sample $Fe_{0.709}Co_{0.291}Cl_2$. These intensities represent the components of the sublattice magnetization $|M_{\perp}|^2$ and $0.992|M_{\parallel}|^2 + 0.505|M_{\perp}|^2$, respectively.[4] We consider first the longitudinal ordering. At the (1, 0, $\bar{1}$) position but *not* (0, 0, 9) there is a sudden onset of scattering at a temperature $T = 15.95$ K, indicating an apparently second-order transition. Further, as shown in Fig. 1(b) there is a sharp peak in the magnetic critical scattering obtained by monitoring the diffuse scattering at (0.98, 0, $\bar{1}$), slightly off the Bragg peak. Similar behavior is observed in the bulk susceptibility $\chi_{\parallel}$ [Fig. 1(c)] where a sharp peak in $d\chi_{\parallel}/dT$ is observed at 15.95 K indicating a sudden decrease in the ordering entropy. All of these features are characteristic of a well-defined second-order phase transition with order parameter $\langle S_{\parallel} \rangle$ (or $M_{\parallel}$). The smearing of this transition due to macroscopic variations in x is less than 50 mK, indicating good sample homogeneity.

The transition in the $\perp$ component is, however, fundamentally different. As noted above, the scattering around (0, 0, 9) is uniquely related to $\langle \vec{S}_{\perp} \cdot \vec{S}_{\perp} \rangle$. We see from Figs. 1(a)–1(c) that the data corresponding to $\vec{S}_{\perp}$ show markedly rounded structures at a lower temperature $T_L \cong 11.5$ K; these are not at all characteristic of a second-order phase transition. Rather they are reminiscent of behavior obtained near T_c for a ferromagnet in a weak magnetic field. We will discuss this in more detail below. In order to construct an approximate phase diagram we take as T_L for the lower transition the temperature at which each of $I(0, 0, 9.2)$, $|(d/dT)[I(0, 0, 9)]|$, and $d\chi_{\perp}/dT$ have a maximum, regardless of how rounded the maxima are. The phase diagram so obtained is shown in Fig. 2. The two upper phase lines AM and BM mark well-defined transitions from the paramagnetic phase into the $S_{\parallel}$-ordered and the $\vec{S}_{\perp}$-ordered phase, respectively. The transition lines inter-

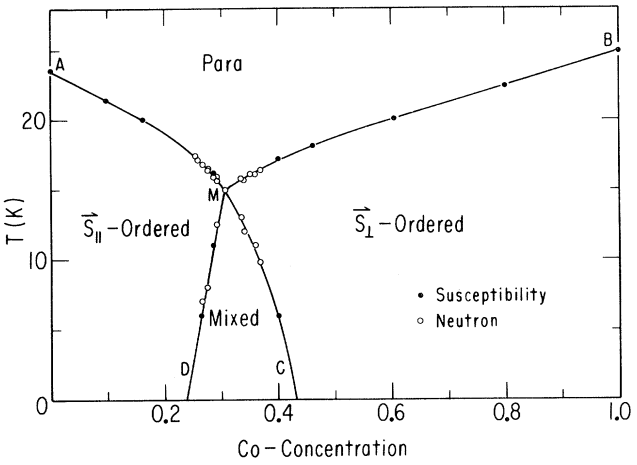

FIG. 2. Magnetic phase diagram of the $Fe_{1-x}Co_xCl_2$ system.

sect at the multicritical point M ($x_M \cong 0.307$ and $T_M \cong 14.92$ K) at large angles, in agreement with the predictions of Fishman and Aharony (FA).[2] The meaning of the lower lines CM and DM is far from clear; the nature of the "mixed phase" bounded by them is also problematic. Longitudinal scans through (0, 0, 9) and (1, 0, $\bar{1}$) show that both lines are resolution limited in the mixed phase indicating that the range of order in both $S_{\parallel}$ and $\vec{S}_{\perp}$ extends over at least several hundred angstroms. We also find that near x_M the scattering associated with the noncritical component is always close to being resolution limited below T_H.

The behavior in the immediate vicinity of the multicritical point is illustrated in Fig. 3, where we show the critical scattering for three examples with mean concentrations $x_M - 0.0025$, x_M, and $x_M + 0.0025$; with $x_M = 0.307$. At x_M (middle panel) the critical scattering associated with both $S_{\parallel}$ and $\vec{S}_{\perp}$ is relatively sharp. However, at $x_M - 0.0025$ (left panel) the phase transition associated with $\vec{S}_{\perp}$ is broadened while at $x_M + 0.0025$ (right panel) the transition associated with $S_{\parallel}$ is broadened.[6] Thus the lower transition is broadened independent of which component orders, or concomitantly, independent of whether the broken symmetry is discrete ($S_{\parallel}$) or continuous ($\vec{S}_{\perp}$).

It should be quite clear from Figs. 1–3 that $S_{\parallel}$ and $\vec{S}_{\perp}$ are not decoupled and do not behave independently: Figure 1(c) shows $\chi_{\perp}$ to have a bump at T_H, where $S_{\parallel}$ orders; Fig. 1(a) shows substantial intensity at (0, 0, 9) between T_H and T_L; Fig. 1(b) shows that the critical scattering associated with $S_{\perp}$ rises rapidly just below T_H; and Fig. 3 shows that the prior existence of long-range order in either $S_{\parallel}$ or $\vec{S}_{\perp}$ has a dramatic affect on the lower transition. Figure 2 shows that even given the uncertainities in defining T_L, the line DM is not a smooth extension of line BM, in disagreement with both the theoretical predictions of FA (Ref. 2) and the experimental conclusions of Katsumata and co-workers.[5] We note, however, that the experimental data of the latter authors are qualitatively similar to ours. Their conclusion that $S_{\parallel}$ and $\vec{S}_{\perp}$ are decoupled was based mainly on the shape of the phase boundaries which were not precisely determined in their experiments.[5]

Finally, we discuss the nature of the $S_{\parallel}$-$\vec{S}_{\perp}$

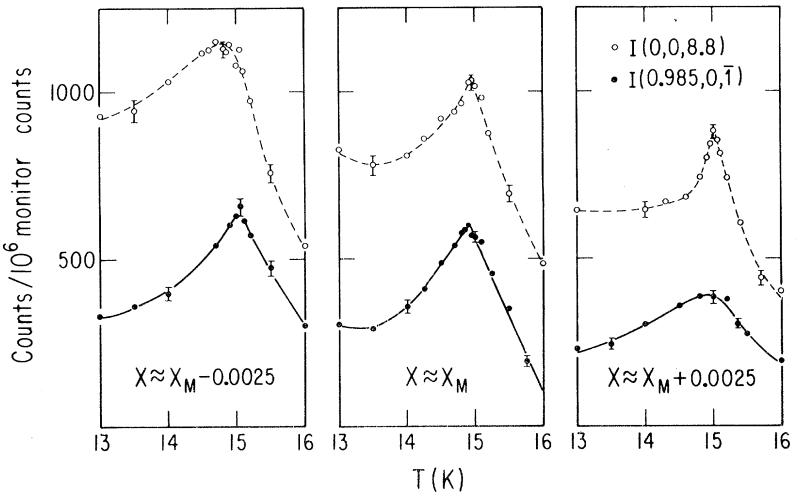

FIG. 3. Magnetic critical scattering vs temperature for concentration near the multicritical value $x_M = 0.307$.

coupling and the consequent failure of the renormalization-group predictions of FA. Both FA and previous workers have assumed a Hamiltonian which is bilinear and diagonal. As discussed in the first paragraph of this paper, this may reflect the overall macroscopic symmetry but not the correct microscopic symmetry of real alloy systems. Locally, there will be no symmetry at all so that terms of the form $J_{ij}^{\parallel,\perp} S_{\parallel}(i)[\vec{S}_{\perp}^{1}(j) + S_{\perp}^{2}(j)]$, where $J_{ij}^{\parallel,\perp}$ is site random, are allowed and are relevant. Indeed systems with large spin space anisotropies by necessity contain ions with large orbital moments; this in turn may make the off-diagonal terms as large as the diagonal terms.[7]

The presence of this cross-coupling term has at least one very important effect. The ordering of one spin component generates an effective static molecular field on the other component. Since every spin has a different local environment this molecular field is site random. Thus, the lower transitions fall in the universality class of three-dimensional (3D) Ising or XY magnets in a random magnetic field. These Hamiltonians have been studied extensively theoretically although some of the results are still controversial.[8] For continuous symmetry systems the random field is believed to shift the effective dimensionality by 2; thus a 3D XY magnet in a random field maps into a 1D XY magnet in zero field; the latter system in turn cannot have long-range order at finite temperatures. This offers an immediate explanation of why we see no sharp transition in $\vec{S}_{\perp}$ when $\langle S^{\parallel} \rangle$ is nonzero. The theoretical predictions for the 3D Ising model in a random magnetic field are less certain. In this experiment, the behavior of samples with $x > x_M$ is essentially identical to that of samples with $x < x_M$ with the role of $S_{\parallel}$ and $\vec{S}_{\perp}$ reversed. It is tempting, therefore, to infer that there is no important difference in the effects of random magnetic fields on discrete and continuous symmetry systems in three dimensions.

In conclusion, we have shown that the competition between $S_{\parallel}$ and $\vec{S}_{\perp}$ ordering in a quenched random alloy is far more interesting than the original theoretical predictions would have led us to believe. The magnetic phase diagram contains two well-defined lines of second order transitions and two more poorly defined lines which meet at a multicritical point which most certainly can not be called a "decoupled tetracritical point." Further, the low-temperature "mixed phase" most probably contains domains associated with random molecular fields. It is our belief that similar random-field effects are ubiquitous in disordered magnets.

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Note added.—D. Mukamel (to be published) has pointed out that the $FeCl_2$ symmetry allows for a term of the form $S_{\parallel}\vec{S}_{\perp}^{3}$. This term provides an alternate rounding mechanism for the Ising transition branch CM but can not cause the observed rounding of the x-y transition DM.

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