Synchrotron magnetic x-ray measurements of the order parameter in $Mn_{0.5}Zn_{0.5}F_2$

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Synchrotron magnetic x-ray scattering studies have been performed on the site-diluted antiferromagnet $Mn_{0.5}Zn_{0.5}F_2$ in zero field and in a field of 0.36 T. No hysteresis was observed in either experiment nor was any broadening due to random fields observed at the 10^{-4} Å^{-1} level in the 0.36 T external field. The sublattice magnetization was measured and the effective exponents $\beta=0.33\pm0.02$ and 0.21 ± 0.07 were extracted for 0 and 0.36 T external fields, respectively. Order-parameter curves for both fields exhibit mean-field behavior for an extended region below T_N consistent with expectations based on the Ginzburg criterion. An average over published experiments gives $\beta=0.34\pm0.01$ in good agreement with theory, for the random-exchange Ising model.

I. INTRODUCTION

Recently, there has been a reported number of experiments using high-intensity synchrotron x-ray radiation to study magnetic ordering phenomena.[1-3] In particular, Goldman *et al.*[3] studied the phase-transition behavior of MnF_2 as a test case to determine the utility of x rays in studies of magnetic critical phenomena. It was found that the antiferromagnetic order-parameter behavior could be obtained quite precisely, free of the extinction effects which dominate neutron magnetic Bragg scattering. However, the very high resolution of the synchrotron technique vitiated any studies of the critical fluctuations since only fluctuations with length scales beyond 1000 Å could be studied and these were inaccessible due to the concomitant temperature control and sample homogeneity required.

With the MnF_2 experiments as a basis, we have now applied synchrotron magnetic x-ray techniques to the phase transition in $Mn_{0.5}Zn_{0.5}F_2$. Other techniques such as NMR and the Mössbauer effect are very difficult, if not impossible, to apply in such highly diluted systems. The experiment was carried out in zero field and with a field of 0.36 T along the c axis. $Mn_{0.5}Zn_{0.5}F_2$ in zero field is a realization of the random-exchange Ising model (REIM).[4] Mitchell *et al.*[4] have studied the critical behavior of the correlation length and susceptibility in this system; our study of the critical behavior of the order parameter complements that work. As discussed extensively elsewhere,[5] $MnZnF_2$ in a uniform magnetic field is an ideal example of a random-field Ising model (RFIM), a well-studied but still largely unsolved problem. As we shall discuss below, for fields of ~0.36 T the random-field domain size is very large, of order 20 μm. This experiment thence provides information on the behavior of the order parameter and hysteresis in this very-long-length regime.

II. EXPERIMENTAL TECHNIQUE

We used the identical $Mn_{0.5}Zn_{0.5}F_2$ crystal studied by Mitchell *et al.*[4] This crystal was a $5.7\times6.4\times8.9$-mm^3 cube with one side perpendicular to an a axis polished. Scans through the Bragg peaks showed that this surface was of excellent crystallographic quality; the mosaic was less than 0.003° half width at half maximum (HWHM). Bulk concentration variations had been estimated to be at least 0.5% in the previous neutron scattering experiments done on this sample.[4] We deliberately chose a face perpendicular to the growth direction in order to minimize concentration-gradient effects. The illuminated volume for x rays was $\sim1\times3\times0.006$ mm^3 with the 0.006 mm along the growth direction. As we shall show below, the smearing of the phase transition was indeed reduced by at least an order of magnitude by this technique.

The sample was mounted in a displex cryostat with its c axis perpendicular to the scattering plane. In the $H_{ext}=0.36$ T experiment, the external field was produced by a pair of neodymium boron magnets mounted so that the field was along the c axis. Platinum resistance thermometers were used to measure and control the temperature. Absolute temperature measurement was accurate only to within 0.2 K, while temperature stability was better than 0.005 K over the period of a scan. The entire cryostat was placed in a Huber four-circle goniometer at the IBM-MIT X-20A beam line of the National Synchrotron Light Source.[6] Salient features of the beamline include a mirror for focusing the beam to a 1.1×0.7-mm^2 spot at the sample, a Si(111) double monochromator and a Si(111) analyzer. The consequent resolution was ~0.00025 Å^{-1} HWHM longitudinally; the transverse in-plane resolution was controlled by the sample mosaic.

In the geometry described above, the theoretical magnetic x-ray scattering cross section is given by[7]

$$\frac{\partial\sigma}{\partial\Omega}\sim\left[\frac{e^2}{mc^2}\right]^2\left[\frac{h\omega}{mc^2}\right]^2\frac{1}{N}[\langle S_{\parallel}(-\mathbf{Q})S_{\parallel}(\mathbf{Q})\rangle\sin^2(2\theta) + 4\langle S_{\perp}(-\mathbf{Q})S_{\perp}(\mathbf{Q})\rangle\sin^4\theta]\ , \quad (1)$$

where $\mathbf{S}(\mathbf{Q})=\sum_j e^{i\mathbf{Q}\cdot\mathbf{r}_j}\mathbf{S}_j$ and $S_\parallel$ and $S_\perp$ are components of the spin parallel and perpendicular to the crystalline c axis respectively. Here $h\omega$ is the incident photon energy, $\mathbf{S}_j$ the spin at site j, $\mathbf{Q}$ the momentum transfer, and 2θ the scattering angle. The Bragg component is given by the $(1/N)\langle S_\parallel(\mathbf{G})\rangle^2$ term in Eq. (1) with $\mathbf{G}$ a reciprocal-lattice vector while, as we shall show below, the fluctuation terms are unobservable.

As discussed by Goldman *et al.*,[3] pure magnetic scattering given by Eq. (1) should be observed at the (100) Bragg peak while pure charge scattering occurs at (200). The largest contribution to the (100) background came from multiple-scattering processes. In order to reduce this multiple scattering, the monochromator was set to scatter 6-keV x rays and the crystal rotated about $\mathbf{Q}$ until a region relatively free of multiple scattering was found. Although this multiple scattering could not be completely eliminated, the ratio of magnetic to background scattering could be made as large as 57 at low temperatures.

III. EXPERIMENTAL RESULTS AND ANALYSIS

This experiment turned out to be technically more difficult than we anticipated. Representative scans are shown in Fig. 1 for $H=0$ and $H=0.36$ T, respectively. Because of the experimental configuration, the $H=0.36$ T measurements are by necessity in the field-cooled (FC) or field-heated (FH) mode.[5] It is evident that the angular widths are remarkably narrow $\sim 0.003°$ HWHM at $H=0$ and $\sim 0.002°$ HWHM at $H=0.36$ T. In both cases we measured identical widths at the (200) charge-scattering peak position; thus the magnetic peak widths originate from the local sample mosaicity and they do not reflect underlying domain sizes. Correspondingly, the antiferromagnetic domains must exceed 4 μm in size for both $H=0$ and $H=0.36$ T. It was found, in general, that the peak intensity and width depended sensitively on the exact position on the face of the crystal which the beam hit; this is an unfortunate consequence of the extraordinarily high resolution and the near-perfection of our $Mn_{0.5}Zn_{0.5}F_2$ crystal; large mosaic crystals are generally much more forgiving. Consequently, in order to determine the temperature dependence of the peak intensity reliably it was necessary that a complete set of data be taken within a given storage ring fill; often between fills the beam position changed enough to give approximately 10% changes in the peak intensity. Different runs could, however, be normalized properly relative to each other.

Detailed fits to profiles such as those in Fig. 1 show that the width is independent of temperature to within the errors. Furthermore, at no time do we observe any critical scattering, presumably because our temperature step size and control are not fine enough. We shall discuss the significance of the widths for the 0.36-T data below.

The integrated intensities as a function of temperature over the range 14–22 K are shown in Fig. 2. In both cases, the data show an extended linear range with a crossover to critical behavior about 1K below T_N. It is evident that the transition is quite sharp with any smearing being much less than 0.05 K; as noted previously, the whole crystal exhibits a transition which is rounded by at least 0.2 K.[4] Thus by exploiting the small penetration depth of x rays and the known geometry of the concentration gradient, we have been able to reduce considerably the concentration-gradient effects.

Such extended linear behavior of the order parameter squared has been seen previously in $KMn_xZn_{1-x}F_3$ (Ref. 8) and $Co_xZn_{1-x}F_2$ (Ref. 9) for x near the percolation threshold. However, for those cases the crossover to critical behavior was masked by rounding due to concentration inhomogeneities. We believe that the linear behavior of the intensity reflects an underlying mean-field behavior. The occurrence of extended mean-field behavior in these diluted systems may be understood on the basis of the Ginzburg criterion.[10] Briefly, the crossover from mean-field to critical behavior occurs at a reduced temperature which scales like ξ_0^6, where ξ_0 is the bare length; in diluted systems ξ_0 may be much larger than a lattice constant and indeed ξ_0 diverges as x approaches the percolation concentration (x_p). Hence, one might expect a progressively longer region over which mean-field behavior obtains as $x \to x_p$.

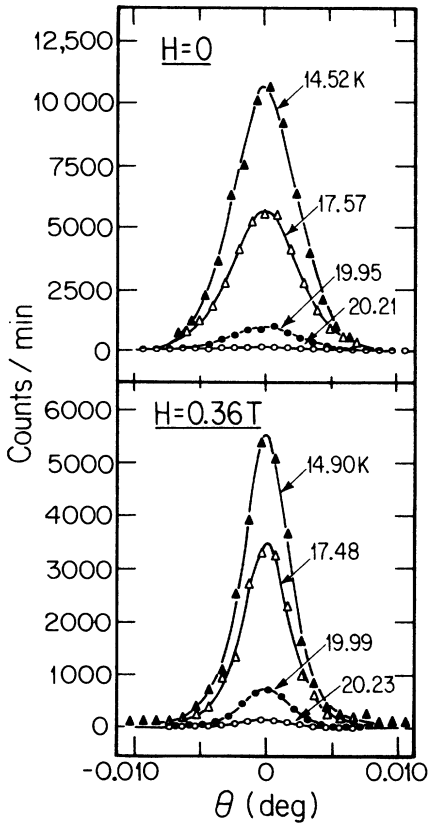

FIG. 1. Representative transverse scans through the (100) magnetic Bragg peak at $H=0$ (the solid lines are the results of fits to a combined Gaussian plus Lorentzian-squared profile) and at $H=0.36$ T (the solid lines are the results of fits to a Lorentzian-squared profile; this line shape reflects the instrumental resolution and is not a consequence of random field effects). The count rates are normalized to a ring current of 100 mA.

Before discussing the critical behavior we consider briefly the widths for the 0.36 T data. As noted above, the 0.36 T FC width is $\sim 0.002°$ HWHM or ~ 0.00005 Å^{-1} and this is determined by the sample mosaic. Previous neutron experiments[11] have shown that at a field of 2.5 T the FC width is 0.004 Å^{-1}. The neutron data also suggest that the width scales like $H^{+3.4}$ at low temperatures. With this empirical law, one predicts a width for $H=0.36$ T at low temperatures of 0.5×10^{-5} Å^{-1} which clearly would be unobservable. Future experiments with fields in excess of 1.0 T should show interesting width, line-shape, and hysteresis effects. Not surprisingly, because of the large domain sizes at 0.36 T there also are no evident hysteresis effects in the data.

We now discuss the critical behavior. As noted above, for $T > 19$ K at both fields there is a clear departure from the linear behavior in the intensity; data for temperatures greater than 19 K are shown in Fig. 3. Here we should make one parenthetical comment. In our first run with the neodymium boron magnets in place so that $H=0.36$ T, the phase-transition temperature was 19.99 K, ~ 0.16K lower than that at $H=0$; such a reduction of T_N is expected due to random-field effects.[5] However, there was then an extended shutdown of the synchrotron beam and during this period the cryostat was raised to room temperature and repumped: After this cycling of the cryostat, T_N (0.36 T) increased to 20.11 K; this increase is almost certainly an experimental artifact. The data from the first and second runs at 0.36 T superimpose absolutely provided that the temperatures for the first run are uniformly increased by 0.12 K.

We have carried out a variety of fits to the data in Figs. 1 and 3. We discuss the results for $H=0$. The data above 19.0 K are well described by a simple power law

$$I = I_0(T_N - T)^{2\beta} + I_{\mathrm{BG}} \tag{2}$$

with $\beta = 0.33 \pm 0.22$ and $T_N = 20.14 \pm 0.02$ K. The uncertainty in β arises entirely from the range of data included in the fit, that is, varying the low-T cutoff between 19.75 K and 19.0 K causes β to change by ± 0.02. Equation (2) may be generalized by including correction-to-scaling terms; however, because of the theoretical uncertainty connected with these terms, especially for random systems, their inclusion decreases rather than increases our confidence in the value of β so deduced.

Current theory predicts for the pure Ising model (Ref. 12) $\beta = 0.325$ and for the REIM (Ref. 13) $\beta = 0.34$ to 0.35 with the latter having a large but unknown theoretical uncertainty. In pure MnF_2, Goldman *et al.*[3] using synchrotron x-ray techniques find $\beta = 0.31 \pm 0.02$ in agreement with theory[12] and the more precise experiment of Heller[14] which yielded $\beta = 0.335 \pm 0.005$.

In $Fe_xZn_{1-x}F_2$ from fits of the Mössbauer hyperfine field to a single power law, Barrett[15] finds $\beta = 0.35 \pm 0.01$ and $\beta = 0.36 \pm 0.01$ in samples with $x = 0.93$ and $x = 0.83$, respectively. On the other hand, Rosov *et al.*[16] in $Fe_{0.9}Zn_{0.1}F_2$ find for fits to a single power law, $\beta = 0.33 \pm 0.01$; their experiment extends somewhat closer to T_N than Barrett's and they claim a more accurate method of data analysis. Rosov *et al.*[16] also show that by including a $(1 - T/T_N)^{0.5}$ correction-to-scaling term in the power law the best-fit β increases to $\beta = 0.35 \pm 0.01$. Apparently, inclusion of the expected $(1 - T/T_N)^{\phi}$

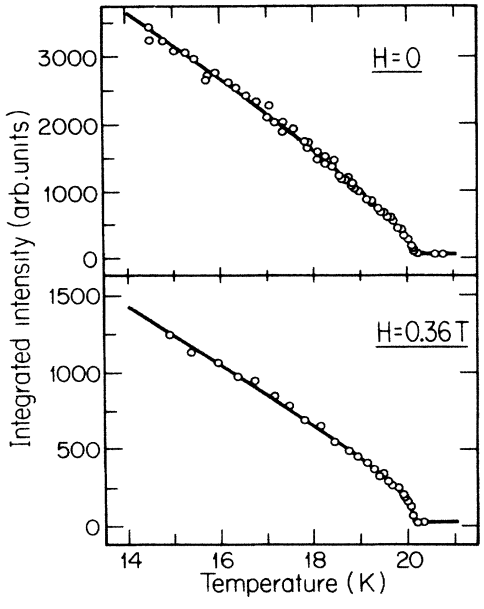

FIG. 2. Integrated intensity vs temperature for $H=0$ and $H=0.36$ T. The solid lines are the results of fits to a heuristic mean-field-critical crossover form $I = I_0[(1+[(T_N - T)/(T_N - T_{\mathrm{co}})]^{1/2\beta} - 1]^{2\beta} + I_{\mathrm{BG}}$, where T_{co} is the "mean-field-critical" crossover temperature and I_{BG} is the background intensity determined from the data for $T > T_N$. In these fits β was held fixed at the value determined from single power-law fits, Eq. (2), to the data for $T > 19K$. The crossover temperatures so-deduced are $T_{\mathrm{co}}(0) = 18.0$ K and $T_{\mathrm{co}}(0.36\ \mathrm{T}) = 18.7$ K.

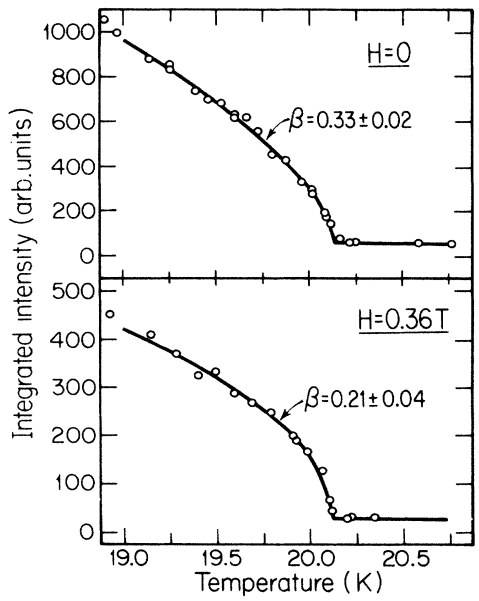

FIG. 3. Integrated intensity vs temperature in the critical region for $H=0$ and $H=0.36$ T. The solid lines are the results of fits to Eq. (2) as discussed in the text.

correction-to-scaling term[17] does not change their analysis; here $\phi \sim \alpha = 0.11$. Finally, in $Mn_{0.86}Zn_{0.14}F_2$ Dunlop and Gottlieb[18] find from fits to a single power law $\beta = 0.35 \pm 0.01$. We thus have as an average value for $MnZnF_2$ and $FeZnF_2$ for fits to a single power law

$$\beta_{\mathrm{REIM}} = 0.34 \pm 0.01 \ . \tag{3}$$

All of these experiments cover approximately the same range of reduced temperature, that is, $\sim 10^{-3}$ to $\sim 10^{-1}$, and they clearly are consistent with each other. One would have expected our $Mn_{0.5}Zn_{0.5}F_2$ experiment to show the cleanest REIM behavior since the randomness is largest in our crystal with T_N reduced by more than a factor of 3 from its pure system value. It is our view that neither our experiment nor any of the previous experiments differentiates between pure and random Ising behavior, especially if one considers the uncertainties connected with the correction-to-scaling terms. Indeed the very accurate measurements by Heller[14] in MnF_2 yield a value for β exactly intermediate between the pure and random Ising values. The experiments, however, do confirm that the critical behavior of the order parameter for the REIM and the pure Ising model are closely similar with β's within 0.03 of each other. As discussed by Mitchell *et al.*,[4] a clearer differentiation between the REIM and the pure Ising system is seen in the correlation length and susceptibility. The results of this work plus previous experiments and theory are summarized in Table I.

We now discuss the 0.36 T experiment. Previous neutron experiments have shown that when a diluted Ising antiferromagnet is cooled in a field no phase transition occurs and instead the system evolves continuously into a domain state whose length scale depends on temperature and field.[5] On reheating, the system retains the low-temperature domain size until the phase boundary is reached at which point the system transforms abruptly with increasing temperature into the paramagnetic state. This breakdown of ergodicity and the consequent hysteresis is the most dramatic manifestation of random-field behavior. All of the previous experiments have, however, been at relatively short length scales.[5]

In fact, no such hysteresis is observed in our experiment at $H = 0.36$ T. As noted previously, from the neutron experiments in $Mn_{0.5}Zn_{0.5}F_2$ one predicts a low-temperature domain size for $H = 0.36$ T of approximately 20 μm which is far beyond our resolution of (0.000 05 $\text{Å}^{-1} = 2$ μm. Thus, at this length scale the system behaves as if it is exhibiting a normal phase transition and concomitantly the measured intensity should reflect properly the order parameter squared inside of a domain. A fit of the data above 19.0 K to a single power law, Eq. (2), yields $\beta = 0.21 \pm 0.04$. However, the region over which the system should exhibit RFIM critical behavior is less than 0.2 K (the shift in T_N due to the random field). This value of $\beta = 0.21 \pm 0.04$ must therefore represent an average of the REIM and RFIM values. Current theories predict that if an equilibrium phase transition occurs in the RFIM, the transition should be either weakly first order,[19] have $\beta = 0$,[20] or have β extremely small,[21] of order 0.05. Our experiment is consistent with these varied possibilities but does not differentiate between them. Theory also predicts $\bar{\eta} = 1.1 \pm 0.1$ and $\nu = 1.4 \pm 0.1$ in agreement with results of Birgeneau *et al.*[5] but not those of Belanger *et al.*;[22] the latter also violate the rigorous inequality of Schwartz and Soffer.[23]

TABLE I. Critical exponents of the pure and random-exchange Ising model.

	Experiment	Theory	
		Random Ising[d]	Pure Ising[e]
γ	1.37±0.04[a]	1.35±0.04	1.241±0.0020
ν	0.70±0.02[a]	0.68±0.02	0.630±0.0015
α	0.09±0.07[b]	0.05±0.04	0.110±0.0045
β	0.34±0.01[c]	0.35±0.01	0.325±0.0015

[a]Reference 4.
[b]R. J. Birgeneau *et al.* Phys. Rev. B **27**, 6747 (1983). The error bar, which is larger than that in the paper, reflects the range of α found in different fits.
[c]Averaged value as discussed in the text.
[d]Average over values predicted in Ref. 13; the error bars reflect the spread in the predictions.
[e]Reference 12.

IV. CONCLUSIONS

These experiments have demonstrated that x-ray synchrotron techniques can provide precise information about the order parameter in highly disordered antiferromagnets. Such information is difficult to obtain with other techniques especially in very dilute systems. We find that in $Mn_{0.5}Zn_{0.5}F_2$, the order parameter exhibits mean-field behavior over an extended temperature range below T_N, crossing over to critical behavior for $1 - T/T_N \leq 0.06$. For $0.06 > 1 - T/T_N > 0.001$, we find $\beta = 0.33 \pm 0.02$ in agreement with theory and previous experiments. However, we conclude that no experiment to data meaningfully differentiates between pure and random Ising critical behavior for the order parameter. We find that in an applied field of $H = 0.36$ T, the overall behavior is similar to that at $H = 0$ except that β drops drastically to 0.21 ± 0.04. We suggest that this value for β is an average of the REIM and (unknown but small) RFIM values. Hysteresis effects which dominate the behavior at fields ≥ 1.5 T are not observed at 0.36 T. Clearly synchrotron x-ray experiments in the 1-T range could yield new and important information on the RFIM. Such experiments will be performed once the attendant geometrical restrictions associated with the synchrotron technique are overcome.

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