X-Ray and Neutron Scattering, Magnetization, and Heat Capacity Study of the 3D Random Field Ising Model

R. J. Birgeneau,[1] Q. Feng,[1] Q. J. Harris,[1] J. P. Hill,[2] A. P. Ramirez,[3] and T. R. Thurston[2]
[1]*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
[2]*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973*
[3]*AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974*
(Received 15 February 1995)

Magnetic x-ray and neutron scattering, SQUID magnetometry, and heat capacity measurements of $Fe_{0.5}Zn_{0.5}F_2$ in a field are presented. The zero field cooled (ZFC) x-ray results exhibit no true phase transition. Discordantly, the temperature derivative of the uniform magnetization (M) displays a peak, which has previously been interpreted as reflecting random field Ising model critical heat capacity. We demonstrate that the ZFC dM/dT peak, in common with other indirect heat capacity measurements, instead reflects the effects of nonequilibrium ZFC long range order.

PACS numbers: 75.30.Kz, 75.40.Cx, 75.50.Lk, 78.70.Ck

The problem of disorder and its role in critical phenomena has received considerable attention over the past two decades. The random field Ising model (RFIM), in particular, has inspired intense experimental and theoretical interest [1,2]. Although the ground state in three dimensions has long range order (LRO) [3], anomalously slow dynamics [4,5] prevent the formation of LRO on field cooling (FC) within experimental time scales and hamper measurements of critical phenomena. The most convenient realization of the RFIM remains random antiferromagnets in an applied field [6]. Experimentally, these systems are found to fall out of equilibrium on field cooling at a metastability temperature $T_M(H)$, forming a short range ordered domain state. On zero field cooling (ZFC) and subsequent application of a field, LRO is retained, until $T_M(H)$ is reached from below [1].

A variety of experimental probes has been applied to this system, including x-ray and neutron scattering, dilatometry, birefringence techniques, capacitance measurements, optical Faraday rotation, and SQUID magnetometry [1]. The scattering techniques measure the order parameter squared $\langle\phi\rangle^2$. Such experiments show no phase transition on warming from a ZFC state. Specifically, the correlation length does not diverge [7] and the transition broadens as the applied field is increased [8]. In particular, magnetic x-ray and neutron scattering experiments on the weakly anisotropic system, $Mn_{0.75}Zn_{0.25}F_2$ [7,8], have led to a picture in which the ZFC order is lost via the flipping of progressively larger domains. The size of these domains saturates at the FC value at $T = T_C(H)$, corresponding to the point of greatest rate of loss of LRO. $T_C(H) < T_M(H)$. Conversely, bulk thermodynamic measurements probe quantities that typically scale like the magnetic energy in zero field. Thermal derivatives of quantities such as the magnetization, the birefringences, and the length have generally been interpreted as reflecting the RFIM critical heat capacity. ZFC data from such measurements, obtained largely on the strongly anisotropic system, $Fe_{1-x}Zn_xF_2$, display a marked peak, absent in FC data, at $T_C(H)$ [1]. This peak has been interpreted as representing equilibrium critical behavior with a heat capacity exponent $\alpha_{\mathrm{RFIM}} \sim 0$, and with some dynamic rounding [9], in contrast to the "*trompe l'oeil* critical behavior" interpretation of the ZFC scattering measurements [8].

The purpose of this Letter is twofold. First, we present new x-ray scattering results on $Fe_{0.5}Zn_{0.5}F_2$ that show behavior closely analogous to that of $Mn_{0.75}Zn_{0.25}F_2$, demonstrating that the phenomena observed are general features of these RFIM systems. Second, SQUID magnetization (M) and heat capacity measurements on $Fe_{0.5}Zn_{0.5}F_2$ in a field are presented. The characteristic ZFC peak in the thermal derivative of the magnetization is observed. On general grounds one expects that for a random antiferromagnet in an applied field there will be contributions to the uniform susceptibility scaling like the energy and like the order parameter squared [6] as well as possible higher order terms. We argue that the LRO term, zero in pure systems at zero field, plays an important role in the presence of a random field. The ZFC SQUID data may then be accurately reproduced by including the LRO piece, calculated from the x-ray data, with a single adjustable parameter. Direct heat capacity measurements verify assumptions used in this model and suggest that the ZFC peak in dM/dT is solely due to the LRO term. This resolves the apparent conflict between the two classes of measurements [8,9]. Similar phenomenology will in general apply to other indirect heat capacity techniques.

$Fe_{1-x}Zn_xF_2$ is a prototypical three-dimensional (3D) random Ising system. It has a rutile-type structure and the spins, oriented along the c axis, align antiferromagnetically below $T_N(x = 0) = 77$ K. A large single ion anisotropy makes this an excellent example of a 3D Ising system. Crystals of $Fe_{0.5}Zn_{0.5}F_2$ were grown using the Czochralski method. The growth direction was along an a axis. A slice 3 mm thick was cut perpendicular

 0031-9007/95/75(6)/1198(4)$06.00 © 1995 The American Physical Society

to the growth direction and a face was polished with a 0.05 μm grit. The crystal homogeneity was evidenced by the sharpness of the zero field transition, at $T_N = 36.7$ K. The x-ray data (penetration depth of 3.7 μm) exhibited a rounding of less than 0.08 K half width at half maximum (HWHM). The x-ray measurements were performed on the IBM-MIT X20A beam line at the National Synchrotron Light Source. The x-ray spectrometer employed a doubly focusing platinum coated silicon mirror, a double bounce Ge(111) monochromator, and a flat Si(111) analyzer crystal. The sample was mounted in a split-pair superconducting magnet with the c axis aligned vertically, along the applied field. The SQUID data were taken with a Quantum Design MPMS magnetometer. Small pieces of $Fe_{0.5}Zn_{0.5}F_2$ cut from the x-ray boule were used in the SQUID and calorimetry work. All techniques measured identical zero field transition temperatures. Slight differences in $T_C(H)$ (<0.5 K) occurred at high fields due to variation in the thermometer field-dependent corrections.

Magnetic x-ray scattering was used to determine the order parameter of the ZFC state in fields up to $H = 7.0$ T. We find that, in agreement with earlier measurements on $Mn_{0.75}Zn_{0.25}F_2$ [8], the ZFC transition broadens progressively with increasing field. The x-ray peak intensity data are summarized in Fig. 1(a). The peaks are resolution limited for all temperatures and fields, and thus the peak intensities are proportional to the integrated intensity and $\langle\phi\rangle^2$. The LRO is seen to go to zero with increasing field at progressively lower temperatures in an increasingly rounded fashion. In $Mn_{0.75}Zn_{0.25}F_2$, similar behavior was characterized by a power-law decay with a Gaussian distribution of transition temperatures, of width σ_{ZFC}; this was labeled *trompe l'oeil* critical behavior [8]. We find that the same description works well here. The solid lines of Fig. 1(a) are fits by such a function with the exponent of the power law β_{ZFC} allowed to vary, $\beta_{ZFC} = 0.15 \pm 0.05$. In comparison, $\beta_{ZFC} = 0.2 \pm 0.05$ was observed in $Mn_{0.75}Zn_{0.25}F_2$. Further, as was the case in $Mn_{0.75}Zn_{0.25}F_2$, σ_{ZFC} is found to follow an H^2 law. We find $\sigma_{ZFC} = A + BH^2$ in $Fe_{0.5}Zn_{0.5}F_2$, with $B = 0.019 \pm 0.002$ K/T^2 and A representative of the small zero field rounding. The H^2 scaling of the data is graphically illustrated in Fig. 1(b). The collapse of the data is excellent for all fields. The solid line through the data is the rounded power-law function, which may now be used as a scaling function, with $\beta_{ZFC} = 0.15$. The $H = 0$ T data are included in the plot to illustrate the zero power-law behavior.

Neutron scattering measurements performed on the same sample reproduce earlier data [7] and show that $T_C(H)$ corresponds precisely to the temperature at which the correlation length of the ZFC fluctuations reaches a maximum. This correlation length is finite and equal to the FC correlation length at the same temperature. We stress that there is still LRO present at $T_C(H)$ and that the system is not in equilibrium. Equilibrium is restored

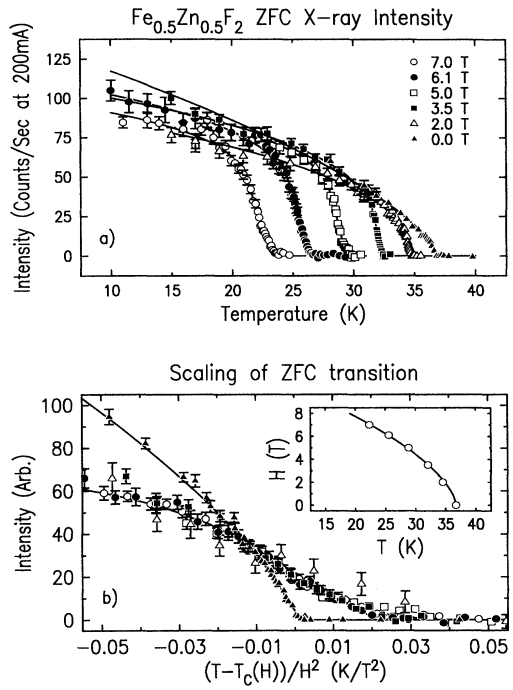

FIG. 1. (a) The ZFC order parameter as measured at the (100) Bragg peak with x rays. The solid lines represent a power law fit with a Gaussian rounding. The rounding is observed to increase as $\sim H^2$. (b) The data of (a) replotted as a function of the temperature interval away from $T_C(H)$, measured in units of H^2. The $H = 0$ data, scaled as if $H = 7.0$ T are for comparison purposes only. The inset shows the phase boundary of $Fe_{0.5}Zn_{0.5}F_2$ as measured by magnetic x-ray scattering.

at $T_M(H)$ where $T_M(H) > T_C(H)$. Thus, the picture of the disordering developed for $Mn_{0.75}Zn_{0.25}F_2$ [7,8] may be carried over in its entirety to the strongly anisotropic $Fe_{0.5}Zn_{0.5}F_2$ system. With increasing temperature, progressively larger domains are flipped, removing regions of spins from the LRO "backbone." These quasistatic fluctuations are not critical and are limited to a finite size by the slow dynamics. The maximal rate of loss of the LRO occurs at $T_C(H)$; there is no phase transition in the usual sense. This, in turn, implies that the peaked derivative of the indirect heat capacity measurements does not reflect a critical contribution to the heat capacity. We are thus faced with a discrepancy in the interpretations of the two classes of experiments. To resolve this, we reexamine the data for the susceptibility and other bulk thermodynamic quantities.

Using general arguments, Fisher [10] has shown that in an antiferromagnet with short range interactions near a phase transition $d(T\chi)/dT \sim C_m$, where χ is the $q = 0$ bulk susceptibility and C_m is the critical heat capacity. In disordered antiferromagnets in the presence of a uniform field one expects an additional term scaling like the sublattice magnetization squared, $D(H)dM_s^2/dT$ [6].

We assume for simplicity that $D(H) = D_0 + D_1 H^r$. For a conventional second order transition $M_s^2 \sim t^{2\beta}$. The LRO term is typically the stronger singularity for derivative measurements and should be especially important in the current case for which the heat capacity fluctuations are nondivergent due to the dynamics. Most importantly, the LRO term for RFIM systems will contribute to ZFC but not FC measurements.

We now discuss the SQUID data. In Fig. 2, $d(TM/H)/dT$ in the FC and ZFC states are plotted for a number of fields. As has previously been observed by Lederman *et al.* [11], a pronounced peak in the ZFC data is seen at a temperature equal within the errors to the x-ray determined $T_C(H)$. The ZFC data of Fig. 2 are in quantitative agreement with those reported in Ref. [11]. We plot in addition in Fig. 2 the temperature derivatives of the x-ray intensity scaling function at the same fields. Even with no analysis, the similarity of the central part of the peaks in the temperature derivatives of the ZFC M/H data and the temperature derivatives of the x-ray scaling function is apparent. To proceed further, we make the simplifying assumption that the thermal fluctuations in the ZFC and FC states are equal. This is validated by direct heat capacity data presented below. Thus the FC SQUID data are representative of the damped thermal fluctuations and may be taken as a first approximation to the background for the ZFC data. The component arising from dM_S^2/dT, the derivative of the x-ray scaling function, is then added to the FC results to generate the ZFC data.

The results of such a procedure are shown in Fig. 2 as the solid lines for $H = 2.5$, 4.5, and 5.5 T. Only $T_C(H)$ and the amplitude of the dM_S^2/dT term have been adjusted. The width has been held fixed at the value obtained from the H^2 scaling law of the x-ray data. The agreement between the experimental data and our simple model is very good, especially considering the simplicity of our approximation. This suggests strongly that the ZFC peak structure arises *solely* from the LRO term and not from thermal critical fluctuations. We find that the amplitude of the M_S^2 term scales like $D(H) \sim H^{2.4\pm0.4}$.

Direct heat capacity measurements of $Fe_{0.5}Zn_{0.5}F_2$ in a field on FC and ZFC provide a stringent check on these ideas. If the ZFC peak observed in the derived quantities is due to a LRO term, then it should be absent in the heat capacity data that reflect the local properties of the system. In Fig. 3(a), we present ZFC and FC data

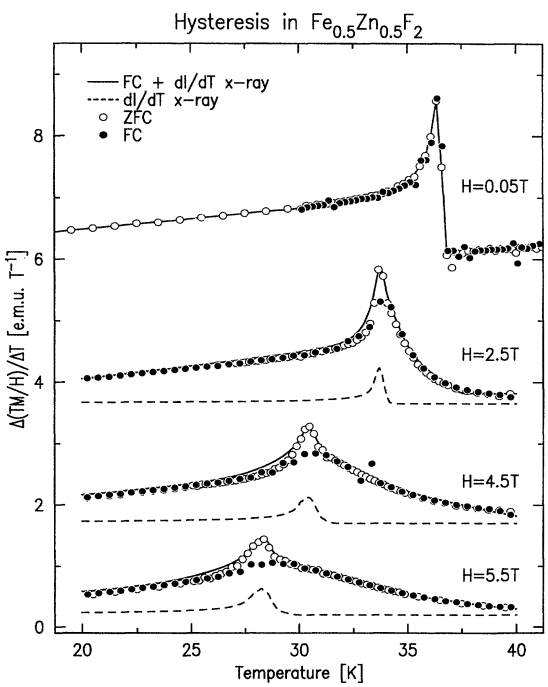

FIG. 2. The temperature derivative of the uniform ZFC and FC susceptibilities, as measured by SQUID magnetometry. The dashed line corresponds to the temperature derivative of the x-ray intensity scaling function with the intensity scaled to match the difference in the ZFC and FC results. The solid line is the sum of the FC $d(TM/H)/dT$ and $d(M_S^2)/dT$.

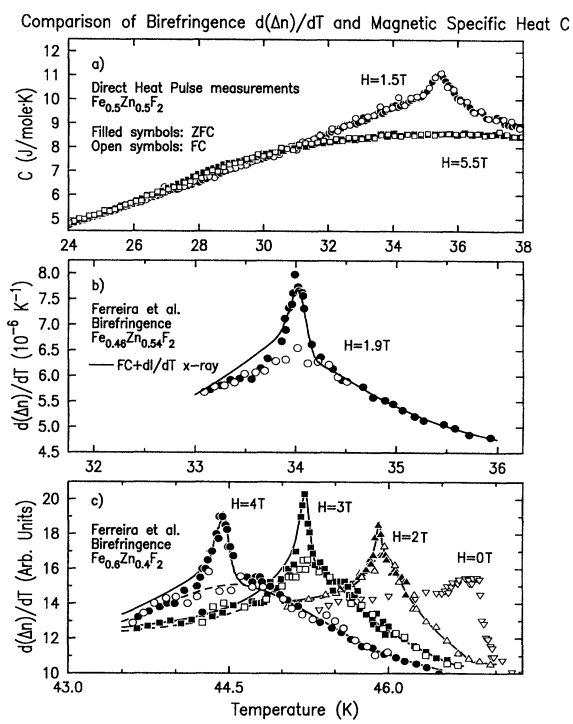

FIG. 3. (a) Heat capacity of $Fe_{0.5}Zn_{0.5}F_2$. There is no evidence of hysteresis on FC and ZFC, nor is there any sign of critical heat capacity in the ZFC data. (b) Optical birefringence data taken from Ferreira, King, and Jaccarino [9] for $Fe_{0.46}Zn_{0.54}F_2$. The closed circles are FC data; the open circles are ZFC data. The solid line is the FC data plus the contribution from the dM_S^2/dT term. (c) Similar results for $Fe_{0.6}Zn_{0.4}F_2$ [9].

taken with a standard semiadiabatic (dc) calorimeter. The time scale of each measurement is ~20 s. The results are striking. There is no evidence of an excess heat capacity in the ZFC state and little or no hysteresis in the data. This demonstrates that the FC and ZFC thermal fluctuations are closely similar. It is clear that the ZFC peak of the indirect heat capacity measurements is not indicative of the true heat capacity. The lack of hysteresis is in agreement with our own unpublished measurements on $Mn_{0.75}Zn_{0.25}F_2$ and previously published reports on $Mn_{0.5}Zn_{0.5}F_2$ [12]. In addition, no hysteresis was seen in the heat capacity of $Fe_{0.714}Co_{0.286}Cl_2$ or $Fe_{0.682}Mg_{0.318}Cl_2$ on FC and FH (field heating) [13]. However, hysteresis in the heat capacity of $Fe_{0.46}Zn_{0.54}F_2$ in a field is reported in Ref. [14]. We cannot explain these latter results.

Finally, similar arguments may be made for other indirect heat capacity measurements. For example, optical birefringence experiments measure $\Delta n^{zx} \propto \sum_r g(r)\langle s_0^z s_r^z\rangle$ in the difluorides [15]. This is proportional to the magnetic energy in a uniform system if there are only nearest-neighbor interactions or if the correlation length is large. Under such conditions $d(\Delta n)/dT \propto C_m$. However, for antiferromagnets in a random field, we expect once more that there should be a term that scales like M_S^2. In Fig. 3(b), ZFC and FC $d(\Delta n)/dT$ birefringence data from Ref. [9] are plotted. These data were taken on a sample of $Fe_{0.46}Zn_{0.54}F_2$ of very high quality. The characteristic ZFC peak is present. Taking the FC data as a measure of the noncritical background, we add to it the derivative of the x-ray scaling function measured in our sample with $T_C(H)$ adjusted slightly. In this case, the width is taken from the H^2 scaling law with $A = 0$ to account for the higher quality of the crystal used in Ref. [9]. The amplitude is then the only true adjustable parameter. Again good agreement is obtained. Finally, we show in Fig. 3(c) similar data and analysis in $Fe_{0.6}Zn_{0.4}F_2$. In this case the coefficient of the H^2 width is fitted at $H = 4$ T although the value so obtained agreed within the errors with that obtained by a simple scaling of the random filed from the $Fe_{0.5}Zn_{0.5}F_2$ results. Once more the model describes the ZFC birefrigence data very well.

In conclusion, we have shown that the *trompe l'oeil* critical behavior model of Ref. [8] describes the ZFC order parameter of $Fe_{1-x}Zn_xF_2$ in a field quite successfully. We have further shown that indirect heat capacity measurements may be readily understood using this model provided that one includes the phenomenological dM_S^2/dT term. Our results thus reconcile apparent discrepancies in the literature for the RFIM between scattering measurements of the order parameter and thermodynamic measurements. The principal challenge now for the RFIM problem is to construct a fundamental theory for the nonequilibrium behavior. A full theory for $d(T\chi)/dT$, etc., for random field systems would also be valuable.

It is a pleasure to acknowledge useful discussions with A. Aharony, J.L. Cardy, R.A. Cowley, A.B. Harris, M. Schwartz, Y. Shapira, and P.Z. Wong. The work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-76CH00016, Division of Materials Science, U.S. Department of Energy. The work at MIT was supported by the NSF under Grant No. DMR 93-15715. This research made use of MRSEC Shared Faculties supported by the NSF under Award No. DMR-9400334.

[1] R.J. Birgeneau *et al.,* Physica (Amsterdam) **137B**, 83 (1986); D.P. Belanger, Phase Transitions **11**, 53 (1988).
[2] T. Nattermann and J. Villain, Phase Transitions **11**, 5 (1988).
[3] J.Z. Imbrie, Phys. Rev. Lett. **53**, 1747 (1984).
[4] J. Villain, J. Phys. (Paris) **46**, 1843 (1985).
[5] D.S. Fisher, Phys. Rev. Lett. **56**, 416 (1986).
[6] S. Fishman and A. Aharony, J. Phys. C **12**, L279 (1979); M. Schwartz and A. Aharony (private communication).
[7] R.A. Cowley, H. Yoshizawa, G. Shirane, and R.J. Birgeneau, Z. Phys. B **58**, 15 (1984); R.A. Cowley *et al.,* Z. Phys. B **75**, 303 (1989).
[8] J.P. Hill, Q. Feng, R.J. Birgeneau, and T.R. Thurston, Phys. Rev. Lett. **70**, 3655 (1993); Z. Phys. B **92**, 285 (1993), and references therein.
[9] D.P. Belanger *et al.,* Phys. Rev. B **28**, 2522 (1983); I.B. Ferreira, A.R. King, and V. Jaccarino, Phys. Rev. B **43**, 10 797 (1991); I.B. Ferreira, Ph.D. thesis, UCSB, 1986.
[10] M.E. Fisher, Philos. Mag. **7**, 1731 (1962).
[11] M. Lederman *et al.,* Phys. Rev. Lett. **68**, 2086 (1992); Phys. Rev. B **48**, 3810 (1993).
[12] H. Ikeda and K. Kikuta, J. Phys. C **17**, 1221 (1984); H. Ikeda, J. Phys. C **19**, L811 (1986).
[13] P.Z. Wong, Phys. Rev. B **34**, 1864 (1986); this paper touches on some of the ideas explored in detail here. We thank P.Z. Wong for bringing this to our attention.
[14] K.E. Dow and D.P. Belanger, Phys. Rev. B **39**, 4418 (1989).
[15] G.A. Gehring, J. Phys. C **10**, 531 (1977); J. Ferre and G.A. Gehring, Rep. Prog. Phys. **47**, 513 (1984).