Measurement of random-exchange critical behavior in the mixed Ising system: $Fe_xCo_{1-x}F_2$

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We report on an observation of random-exchange (RE) critical behavior in a mixed three-dimensional Ising system. Using capacitance measurements, we have determined the critical-behavior universality class and the Néel temperature, $T_N(x)$, as a function of concentration x of the mixed magnetic system $Fe_xCo_{1-x}F_2$. The specific-heat critical exponent $\alpha=-0.09\pm0.06$ and the amplitude ratio $A_+/A_-=1.6\pm0.4$, are in agreement with previous experimental results on magnetically *diluted* (e.g., $Fe_xZn_{1-x}F_2$) RE systems. A mean-field interpretation of $T_N(x)$ vs x yields an Fe-Co exchange interaction $J_{\text{Co-Fe}}=13.10\pm0.30\ \text{cm}^{-1}$.

INTRODUCTION

Random-exchange (RE) behavior in the critical region has only been observed in magnetically diluted three-dimensional (3D) Ising systems[1-3] (e.g., $Fe_xZn_{1-x}F_2$). The sole mixed magnetic 3D Ising system which has been studied, in which both magnetic components exhibit 3D Ising critical behavior, was $Fe_xMn_{1-x}F_2$. Unfortunately, the effective Fe-Mn exchange interaction differs little from the almost equal Fe-Fe and Mn-Mn interactions, making the randomness very small compared to the mean exchange interaction. This being the case the critical behavior should be dominantly pure 3D Ising and, indeed, that is what has been observed.[4]

The system $Fe_xCo_{1-x}F_2$ affords one the opportunity of studying a mixed system in which both pure components (FeF_2 and CoF_2) have certified 3D Ising critical behavior,[5,6] yet have very different ordering temperatures: $T_N(FeF_2)\approx 2T_N(CoF_2)$. Hence, no matter what the Fe-Co exchange interaction may be one would expect RE critical behavior to be observable in the mixed system for x not close to either 0 or 1. Moreover, the mixed system would have the identical antiferromagnetic ordering to that of FeF_2 and CoF_2.

Since this particular mixed system has not been previously investigated, we have determined both the critical behavior universality class and the variation of $T_N(x)$ with x. From the latter we are able to obtain an estimate of the effective exchange interaction $J_{\text{Fe-Co}}$. We used a novel variation of the capacitance technique[5] to measure the critical behavior and $T_N(x)$ in single crystals of $Fe_xCo_{1-x}F_2$ grown at the University of California at Santa Barbara.

FeF_2 is a uniaxial anisotropic antiferromagnet (AF) with $T_N=78.4$ K. Below T_N the magnetization is aligned along the c axis because of its large single-ion, axial anisotropy. Hence this $S=2$ system exhibits 3D Ising critical exponent behavior. CoF_2 possesses the same magnetic ordering as FeF_2 but with $T_N\approx 38$ K. It can be described as an $S=\frac{3}{2}$ spin system with a large orbit-lattice interaction[7] or, alternatively, with an effective spin $S'=\frac{1}{2}$ and anisotropic exchange.[8] It also exhibits 3D Ising critical behavior.[6] FeF_2 and CoF_2 both have the same rutile structure, with the c and a axis differing by only 3.9% and 0.03% respectively. Hence, the mixed system $Fe_xCo_{1-x}F_2$ easily forms alloys with the same structure.

EXPERIMENTAL METHODS AND RESULTS

The $Fe_xCo_{1-x}F_2$ crystals were grown from the melt along the c axis using the Bridgeman method, a procedure which unavoidably introduces an axial gradient of concentration. Unfortunately, the boules which were of most interest for this study, those with $x\approx 0.5$, exhibited the largest axial gradients: close to 10%/cm. This large gradient even over a thin slab (0.03 cm) of sample cut perpendicular to the growth axis would result in a rounding of the transition temperature, because of the axial concentration variation, of $\delta T_N=0.12$ K. This corresponds to a rounding of the transition for reduced temperatures $t<2\times10^{-3}$, enough to preclude asymptotic critical behavior to be observed. We should also mention that radial gradients, although generally an order of magnitude smaller than the concentration variations along the growth direction, are also present. They may contribute to the rounding of the transition as would the axial gradients, given the use of large enough areas.

To minimize the effects of the gradients on the rounding of the phase transition, we have made very thin regions of crystals in the direction along the c axis. The effects of axial as well as radial gradients were minimized by optimizing a polishing technique to produce very small capacitors of $\approx$2-mm diam and 50–100-μm thickness. A very small "well" was ground in a larger slice of the boule which provided the necessary mechanical support for the thinned well. Aluminum electrodes were then deposited on both sides of the thinned well to make the capacitor. The resulting capacitance of these samples was about 10 pF. A schematic representation of the structure is shown in Fig. 1. From a comparison of the experimental data on a thinned and a "standard" capacitor from the same boule, this technique was found to provide a reduction in the rounding of the phase transition δT_N, by a factor of 7. This limited the rounding of the transition to reduced temperatures $t\leq 3\times10^{-4}$.

The concentration x of the resulting samples was determined by measuring the c-axis lattice parameter of each

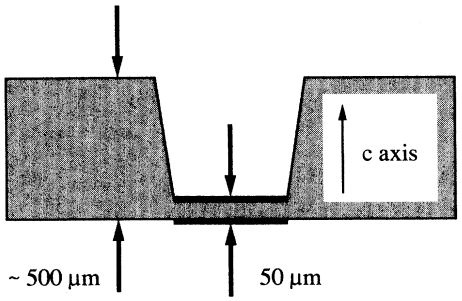

FIG. 1. Schematic representation of the cross section of a thinned capacitor of $Fe_xCo_{1-x}F_2$. The c axis is the mixed-crystal growth direction and is the one along which the maximum concentration gradient (and hence variation of T_N with distance) is expected. The black lines on both sides of the thinned well represent the Al electrodes. Care was taken to limit the electrodes to the thinned well. Electrical contacts were attached with conducting paint to the edge of the well to reduce strains.

sample by high-resolution x-ray Bragg diffraction. Assuming Vegard's law to hold for the mixed crystal, the c-axis lattice parameter will vary as

$$c(Fe_xCo_{1-x}F_2)=xc(FeF_2)+(1-x)c(CoF_2)\ , \qquad (1)$$

from which we can indirectly determine the concentration x. In the samples measured, there was no evidence in the diffraction pattern of multiple phases or crystal structures other than rutile. In addition, there was a smooth (nondiscrete) variation of the lattice parameters in the samples investigated. The well-known scattering condition is given by $2c\sin(\theta_{00l})=l\lambda$, where c is the c-axis lattice parameter, $(00l)$ is the Miller index of the Bragg plane, and λ is the wavelength of the x-ray scattered radiation.[9] By taking the *difference* between the measurements of θ_{004} and θ_{002}, the value of c can be very precisely measured. For single crystals of FeF_2 and CoF_2 we have found, using this method, $c=3.3096(2)$ and 3.179 62(3) Å respectively, in good accord, though more precise, than the reported values in the literature.[10] In fact, the final precision with which x could be measured using this technique was $\delta x\approx 0.002$ in the mixed crystals.

All critical behavior measurements were made using a three-terminal capacitance technique[5] which has been extensively used in our laboratory for critical behavior studies. For a well-defined reference capacitor, we used one made from pure FeF_2 mounted to the same heat sink as the mixed sample under study. Because $T_N(FeF_2)$ is accurately known, this also provided a secondary temperature reference, enabling us to correct for the changes in the readings of the carbon-glass thermometer from day to day.

It has been shown[5,11] that in the critical region the magnetic specific heat C_m and the capacitance C are linearly related by

$$C_m=k_1\frac{1}{C}\frac{dC}{dT}+k_2\ , \qquad (2)$$

where k_1 and k_2 are constants, and where the critical behavior of C_m is given by

$$C_m=A_{\pm}|t|^{-\alpha}+B\ . \qquad (3)$$

Here A_+ (A_-) is the amplitude above (below) the transition temperature, $t=(T-T_N)/T_N$ is the reduced temperature, α is the specific heat exponent, and B is a constant.

We chose a particular crystal ($Fe_{0.62}Co_{0.38}F_2$) that showed the least concentration gradient to probe the critical behavior of the mixed system. It satisfies the requirement that the concentration x be away from the extremes $x=1$ or 0, where 3D Ising behavior is expected. The results for $Fe_{0.62}Co_{0.38}F_2$ are shown in Fig. 2. The fit, shown by the full line, corresponds to a nonlinear least-square fit of the region $6\times10^{-4}<|t|<1\times10^{-2}$ to the specific-heat form given by Eq. (3). We obtained an amplitude ratio $A_+/A_-=1.6\pm0.4$ and a critical exponent $\alpha=-0.09\pm0.06$. The magnitude and sign of α are consistent with the RE universality class.[12] This is the first observation of RE behavior in a mixed 3D Ising system.

The above result is consistent with previously measured values[1] in the $d=3$ RE system $Fe_xZn_{1-x}F_2$, where it was found that $A_+/A_-=1.6\pm0.3$ and $\alpha=0.09\pm0.03$ and later studies[2] in which $\alpha=-0.10+0.03$. Using field theory, Jug[13] calculated for a $d=3$ diluted Ising system $\alpha=-0.034$ while Newman and Riedel,[14] using renormalization-group methods, obtained $\alpha=-0.09$. These theoretical results show that the RE specific-heat critical exponent is expected to be small and negative in good agreement with all experimental results.

It is important to mention that in the fitting procedure we also allowed for the rounding of the transition as would be caused by a *linear* variation of the Néel temperature from $T_a=\bar{T}_N-\delta T_N$ to $T_b=\bar{T}_N+\delta T_N$ according to the expression[15]

$$C_m=\begin{cases} kA_-[(T_b-T)^{1-\alpha}-(T_a-T)^{1-\alpha}]+B & \text{for } T\le T_a\ , \quad (4a)\\ k[A_+(T-T_a)^{1-\alpha}+A_-(T_b-T)^{1-\alpha}]+B & \text{for } T_a\le T\le T_b\ , \quad (4b)\\ kA_+[(T-T_a)^{1-\alpha}-(T-T_b)^{1-\alpha}]+B & \text{for } T\ge T_b\ , \quad (4c)\end{cases}$$

where $k=(\bar{T}_N)^{\alpha}/[2\delta T_N(1-\alpha)]$. When fitting the data of Fig. 2 to Eq. (4) we obtained a best-fit value $\delta T_N=0.037\pm0.002$ K. Note that this gradient-induced rounding affects the data only for $|t|<6\times10^{-4}$, a region of reduced temperature which was excluded in the determination of α and A_+/A_- in Fig. 2.

Though the amount of rounding is small for the data taken on the $Fe_{0.62}Co_{0.38}F_2$ crystal, as shown in Fig. 2,

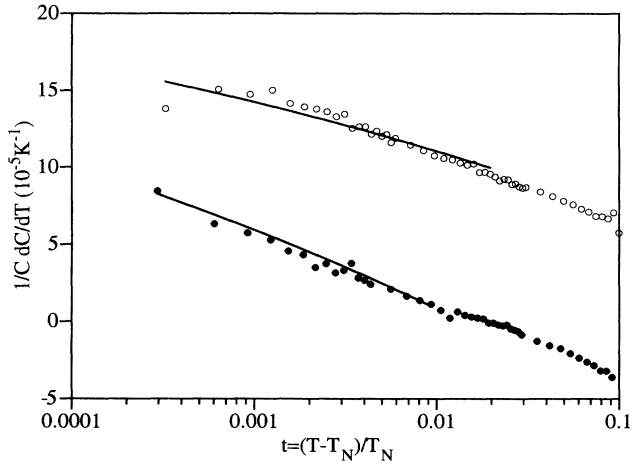

FIG. 2. $1/CdC/dT$ vs $\log_{10}|t|$, the reduced temperature, for $Fe_{0.62}Co_{0.38}F_2$. The open and closed symbols refer to $T<T_N$ and $T>T_N$, respectively. The full line corresponds to a best-fit line with $A_+/A_-=1.6\pm0.4$ and $\alpha=-0.09\pm0.06$. The region of the data where rounding due to concentration gradients occurs ($|t|<6\times10^{-4}$) was excluded from the fit.

this was not the case for other samples studied. Since $\bar{T}_N(x)$ does *not* coincide with the peak in dC/dT vs T unless the divergence is expected to be symmetric ($A_+=A_-$), it was important to include a variable δT_N to account for the observed rounding of the phase transition and obtain a more precise value of the average transition temperature, $\bar{T}_N(x)$.

In Fig. 3 we show a typical dC/dT temperature scan of an $Fe_{0.54}Co_{0.46}F_2$ sample. A least-square fit of the data to the expression in Eq. (4) in the critical region gives $\bar{T}_N=62.07\pm0.02$ K and $\delta T_N=0.08$ K. The rounding of the transition is consistent with a larger volume of the capacitor (≈1.5 times as thick as the $Fe_{0.62}Co_{0.38}F_2$ sample) in a boule characterized by large axial gradients ($\approx10\%$/cm). It was to avoid this problem that we resorted to making very small capacitors to minimize the effect of the concentration gradients. The results for $T_N(x)$ for different concentrations are plotted in Fig. 4.

For a mixed magnetic system there is not a first-principles theory to describe $T_N(x)$. In addition the new exchange interaction, J_{AB} is generally unknown. We have used a mean-field analysis for determining $J_{\text{Fe-Co}}$. In mean field, the transition temperature of a mixed system is given by[16]

$$T_N(x)=[xT_A+(1-x)T_B]/2+\{\tfrac{1}{4}[xT_A+(1-x)T_B]^2+x(1-x)(T_{AB}^2-T_AT_B)\}^{1/2}, \quad (5)$$

where

$$T_{AB}=16[S_A(S_A+1)S_B(S_B+1)]^{1/2}|J_2^{AB}|/3k_B .$$

In our case T_A and T_B are the Néel temperature of FeF_2 and CoF_2, respectively. In Eq. (5) we have assumed *only* next-nearest-neighbor (NNN) interactions between all spins, which leads to the expression of T_{AB} in terms of the $J_{\text{Fe-Co}}$ NNN exchange interaction. This is a reasonable assumption since the NN and NNN exchange interactions measured in the pure systems are about an order of magnitude smaller or more.[8,17] The full line in Fig. 4 is the best fit of the data to $T_N(x)$ given by Eq. (5) with $T_{\text{Fe-Co}}=59.61\pm1.35$ K. Considering Co as represented by an effective spin $S'=\frac{1}{2}$, and using Eq. (5), we obtain $J_{\text{Fe-Co}}=13.10\pm0.30$ cm^{-1}. This result deviates slightly from a straight line connecting $T_N(FeF_2)$ and $T_N(CoF_2)$, which would have resulted if $T_{\text{Fe-Co}}=\sqrt{T_N(FeF_2)T_N(CoF_2)}=54.43$ K.

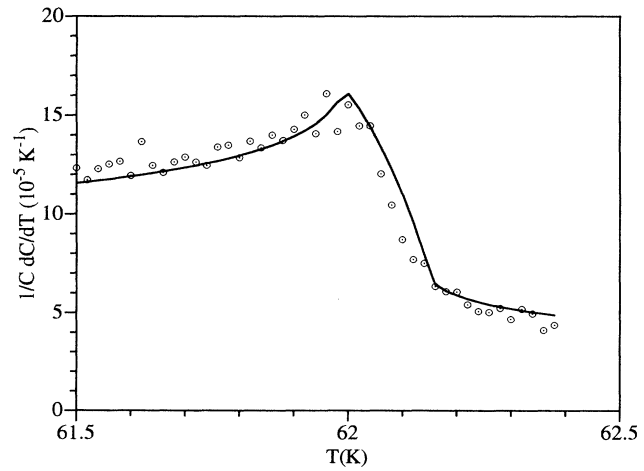

FIG. 3. $1/CdC/dT$ for $Fe_{0.54}Co_{0.46}F_2$. The solid line is a best fit to a rounded RE transition (see the text) with $T_N=62.07\pm0.02$ K and $\delta T_N=0.08\pm0.01$ K.

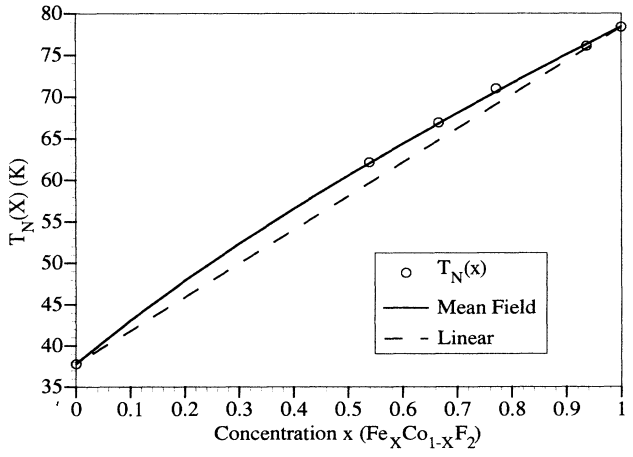

FIG. 4. Transition temperature $T_N(x)$ vs x, concentration x in $Fe_xCo_{1-x}F_2$. The solid line is a best fit of the data to Eq. (5) with $T_N(\text{Fe-Co})=59.61\pm1.35$ K. The dotted line is a linear interpolation between $T_N(CoF_2)$ and $T_N(FeF_2)$.

DISCUSSION

We have shown that a novel variation of the capacitance technique allowed us to study critical behavior in samples with exceptionally large axial gradients. In addition we have demonstrated the feasibility of using x-ray diffraction to do precise, nondestructive, *in situ* characterization of the concentration of very small single crystals of mixed constituents.

Using the advantages of the capacitance technique to study very small samples we have been able to study the critical behavior of a mixed $Fe_xCo_{1-x}F_2$ system and observe RE behavior in a *mixed* magnetic 3D Ising system. The value of the specific-heat critical exponent agrees with previous experimental results for diluted Ising antiferromagnets $Fe_xZn_{1-x}F_2$ and $Fe_xMg_{1-x}F_2$,[2,18] which are clear representatives of the RE universality class.

The measured variation of $T_N(x)$ with x allowed us to obtain J_{FeCo} using mean-field theory. Knowledge of $J_{\mathrm{Fe\text{-}Co}}$ is useful in studies of the magnetic properties of magnetic superlattices[19] of FeF_2/CoF_2, because the thermodynamic and other physical properties depend strongly on the interaction at the interface. In the limit of alternating monolayers of FeF_2 and CoF_2, the only interaction present would be the NNN Fe-Co interactions (to a first approximation). Recent experimental measurements of T_N vs n in $(FeF_2)_n(CoF_2)_n$ superlattices indicate that the extrapolated transition temperature $T_N \approx 60$ K for $n \rightarrow 1$, which is consistent with our result of $T_{\mathrm{Co\text{-}Fe}} = 59.61$ K.[11]

Perhaps the most intriguing property of a mixed magnetic system is that it would make possible a study of a new kind of random-field (RF) problem.[20] The RF problem originally considered by Imry and Ma[21] was that of a ferromagnet in a site random field. Unfortunately no realization of this is experimentally possible. The only experimental realization of the RF problem that has been found is that of the *diluted* uniaxial antiferromagnets in a uniform field,[20] as first proposed by Fishman and Aharony.[22] Here the randomness of the position of the magnetic and nonmagnetic ions in the presence of a uniform magnetic field is what gives rise to a random magnetic energy. However, there is another possibility for the generation of site random magnetic energy; namely having the moments $\mu_A \neq \mu_B$ in a random A_xB_{1-x} Ising antiferromagnet. In this case the coupling with an applied uniform magnetic field would be identical to that of the Imry-Ma problem of a ferromagnet in a site random magnetic field. Such is the case in our $Fe_xCo_{1-x}F_2$ system, where $\mu_{\mathrm{Fe}} > \mu_{\mathrm{Co}}$ and hence we expect this latter mechanism to be present and its consequences observable. A report of the experimental studies of this system[23] in a magnetic field will be published elsewhere.

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[12]The quality of the fit to this RE behavior is characterized by a sum of squares per degrees of freedom of $\chi^2 = 1.06$. For comparison we have also attempted to fit the experimental data to a pure 3D Ising behavior ($A_+/A_- = 0.53$ and $\alpha = 0.11$). In this case we obtained $\chi^2 = 5.31$, clearly indicating that random exchange gives a much better description of the critical region.

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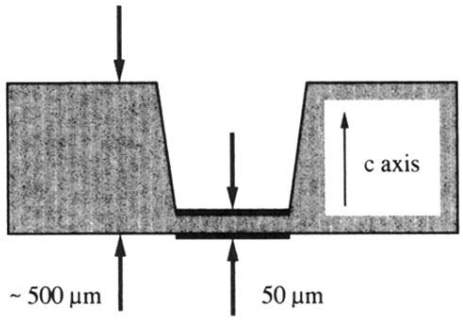

FIG. 1. Schematic representation of the cross section of a thinned capacitor of $Fe_xCo_{1-x}F_2$. The c axis is the mixed-crystal growth direction and is the one along which the maximum concentration gradient (and hence variation of T_N with distance) is expected. The black lines on both sides of the thinned well represent the Al electrodes. Care was taken to limit the electrodes to the thinned well. Electrical contacts were attached with conducting paint to the edge of the well to reduce strains.