Critical behavior of epitaxial antiferromagnetic insulators: Interdigital capacitance measurement of magnetic specific heat of FeF_2 thin films

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We have adapted the method of fabricating interdigital capacitors in the development of a technique for the measurement of magnetic specific-heat (C_m) critical behavior of micron-thick epitaxial films of antiferromagnetic insulators. This interdigital capacitance technique (ICT) was first tested on very carefully polished, bulk FeF_2 surfaces. It was then applied to a study of high-quality 3-μm epitaxial films of FeF_2 on lattice matching (001)-oriented ZnF_2 substrates. Under ideal preparatory conditions, the ICT results in both cases exhibit the divergent critical behavior of a $d=3$ Ising system; namely, $C_m = A^{\pm}|t|^{-\alpha}$ with $\alpha = 0.10 \pm 0.01$ and amplitude ratio $A^+/A^- = 0.60 \pm 0.05$.

INTRODUCTION

In an earlier study, we reported the results of antiferromagnetic resonance (AFMR) measurements of micron-thick epitaxial films of MnF_2 grown on ZnF_2 substrates.[1] Since then a considerable effort has been made to improve the quality of the epitaxy process, and to investigate other systems (e.g., FeF_2 and CoF_2 grown on ZnF_2). As before, our interest stems from the relative ease with which these closely lattice matched systems can be grown and the ultimate goal of studying superlattices of these well-characterized magnetic insulators.

One of the most fundamental properties of magnetic systems is their critical behavior in the vicinity of the phase transition. The study of the critical behavior of epitaxial films and superlattices could thus be a powerful technique for studying the properties of these structures. If one hopes to, say, measure the magnetic specific heat C_m of a magnetic superlattice, then certain formidable obstacles have to be overcome. The total volume of material contained in superlattices is conveniently no more than 10^{-4} cm^3 and is epitaxially grown on a substrate conveniently no less than 10^{-1} cm^3 in volume. Conventional specific-heat techniques would entail trying to separate the purely magnetic contribution of the layered structure from the combined phonon contributions of the superlattices plus substrate—a procedure analogous to weighing the captain and the ship and then subtracting the ship's weight to determine that of the captain.

There is a technique, however, which indirectly measures only the magnetic part of the specific heat. It has been demonstrated[2] that the temperature derivative of the capacitance, through the dielectric constant, is proportional to C_m, and this method has been applied to critical phenomena studies in both pure[2] and random[3–5] magnetic systems. However, for a thin film on a relatively thick substrate, the fractional change in the total capacitance arising from the changes in C_m of the film would be very small, if the usual disk geometry were used. In the present work we have circumvented this difficulty by using an interdigital capacitance technique in which, primarily, the dielectric properties of the film, and not the substrate, are measured.

This method has been used to study the phase transition in bulk FeF_2 single crystals, as well as in epitaxial 3-μm films of FeF_2 grown on (001) crystal faces of ZnF_2. From the results presented below, it will be apparent that a new and powerful technique has been created for investigating critical phenomena in thin films and superlattices of magnetic insulators.

INTERDIGITAL CAPACITANCE TECHNIQUE

We have adapted the method of fabricating interdigital capacitors into an interdigital capacitance technique (ICT) in order to make possible highly accurate magnetic specific-heat measurements of thin epitaxial films grown on thick dielectric substrates. The fabrication of interdigital capacitors is a well-developed process for use in semiconductor and microwave circuit elements.[6] However, to our knowledge they have never been used in magnetic insulator application or in the study of critical phenomena, magnetic or otherwise, including either bulk materials or epitaxial films.

The technique involves evaporating a pattern of interdigitated metal fingers directly onto the surface of the material to be measured. The capacitance is then measured *between* the interdigitated fingers, rather than between metal films on either face of the disk, as is conventionally done.[2] If the spacing between the interdigitated fingers is on the order of the film thickness, the measured capacitance is mostly that of the film, not that of the vacuum immediately above it, or that of the substrate. This can be seen from a calculation of the electric field in the vacuum, film, and substrate.

The electric field distribution for the ICT geometry is quite complicated, but a reasonably good approximation to it can be had from the case of two semi-infinite sheets

separated by a gap a, with one sheet at potential 0 and the other at V. This model allows us to easily map the energy density in the median plane perpendicular to the gap, and estimate an effective filling factor. For a more detailed calculation, the reader is referred to the literature[6] on the subject that exists for semiconductors. The effects of the thickness of the metal film may be neglected since it is vanishingly small, compared to the interdigital spacing. The field distribution in the dielectric is assumed to be the same in both the magnetic film and substrate, since the dielectric constants are very similar in FeF_2 and ZnF_2, and the change in ϵ of the magnetic film near the critical point is very small. Along a line midway between, and perpendicular to the sheets, we find that the electric field decreases with distance d to approximately 45% of its value at the center of the gap for $d=a$. However, the energy density of the system, and therefore the contribution to the capacitance, varies as $(\epsilon/\epsilon_0)E^2$ with $\epsilon/\epsilon_0 \cong 8$ for FeF_2. At a distance d equal to a, E^2 is approximately 20% of what it is at the center of the gap, as seen in Fig. 1. The dielectric side will contribute eight times as much to the capacitance as does the vacuum side. Therefore, the major contribution to the capacitance is contained within a layer of material of thickness a on which the interdigital is placed. The effective filling factor ν of a film of this thickness is close to unity, where ν is defined to be the ratio of the capacitance of the interdigital on the film to that of an identical interdigital on a semi-infinite slab of the same magnetic material. The filling factor ν may be estimated by comparing the effective area under the $(\epsilon/\epsilon_0)E^2$ curve for the appropriate thickness. For a 3-μm FeF_2 epitaxial film, a filling factor of $\nu=0.53$ is obtained.

The mask design used for the interdigital device pattern is shown in Fig. 2. The pattern consists of an array of 5-μm interdigitated fingers of metal separated by 5-μm spaces. The choice of 5-μm spacings was dictated by this being the smallest structure that could be easily fabricated without the use of a low-particle-count clean room. Since the pattern covers an area of 4 mm by 5 mm, and a foreign particle of a few microns anywhere in that area can cause failure, it was deemed important to choose a finger width and spacing large enough to insure good yield. With 5-μm spacings, filling factors are expected to be adequate for film thicknesses of 3 μm or more.

The interdigital pattern is formed photolithographically using the lift-off technique. The FeF_2 substrates and FeF_2 epitaxial films on ZnF_2 substrates are spin coated with Shipley 1400-25 positive photoresist, and exposed using the interdigital mask. Before developing, the samples were soaked in chlorobenzene, which hardens the surface of the photoresist. When developed, the exposed areas of photoresist are removed, and the hardened upper layer is undercut along the edges of the pattern, forming an overhang. A 1000-Å layer of titanium is deposited to insure good metalization adhesion, followed by a 2000-Å layer of gold, to obtain a low resistance. The metals were deposited by e-beam evaporation. Because of the overhang in the photoresist, there is a clean break between metal in the patterned areas and metal atop the photoresist. When the sample is placed in acetone, the photoresist dissolves and the metal on the photoresist is removed, leaving only the metal interdigital pattern. Subsequently, electrical contact to the interdigital device is made mechanically and good thermal contact to the substrate is insured by the use of thermal compound.

The most vexing problem encountered in the lithograph process is that occasional shorts would occur between the interdigitated fingers, thereby making capacitance measurements impossible. However, with all parameters in the processing optimized, we have obtained a success rate of about 70%.

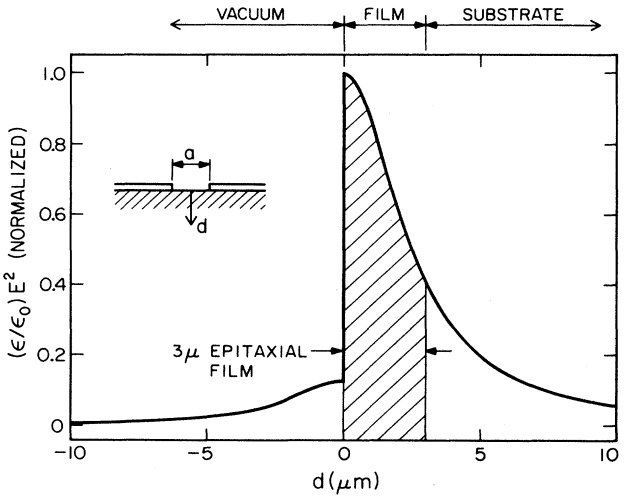

FIG. 1. Energy density distribution as a function of distance d along a line midway between, and perpendicular to, two infinitely thin conducting sheets separated by a gap $a=5$ μm. The conductors are deposited on the surface of an FeF_2 epitaxial film of 3-μm thickness grown on a thick ZnF_2. The dielectric constants of the FeF_2 and ZnF_2 are assumed to be equal.

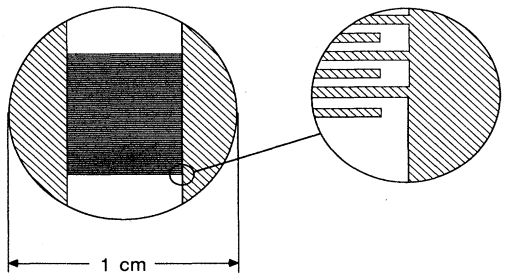

FIG. 2. Interdigital film device pattern consisting of an array of 5-μm wide interdigitated fingers of metal separated by 5-μm spaces. In the inset, the metal areas are shown shaded.

SAMPLE PREPARATION AND CHARACTERIZATION

The insulating transition-metal difluoride substrates are grown in house by the Bridgeman-Stockbarger method. They are aligned by the use of a Laue x-ray camera and cut with a diamond wire saw into 1-cm diameter by 2-mm thick disks with the c axis perpendicular to the faces.

The elaborate polishing method adopted involved a multistage grinding of the substrates which began using alumina powder on glass. This was followed by a series of successively smaller diamond grits down to $\frac{1}{4}$ μm. At each stage, the substrates were ground for a length of time that was *three* times as long as was the period necessary to remove all visible damage. The latter was verified by examination with a Normarski microscope. This procedure insured that any unseen subsurface damage introduced by the previous grinding step was completely removed. Each step was then checked by a chemical etch in a dilute solution of HCl, which selectively etches damaged areas and thus exposes any residual subsurface damage. Finally, the substrates were etch polished with a dilute solution of HCl, free etched in dilute HCl, rinsed in deionized water, and blown dry with nitrogen gas. The fact that such elaborate polishing procedures were actually necessary became evident in early ICT measurements made on a FeF_2 substrate which was prepared by polishing at each step only until the *visible* damage from the previous step was removed. Following this less elaborate procedure resulted in a marked rounding of the phase transition using the ICT, as will be discussed below.

The epitaxial films were grown in a modified Varian ultrahigh-vacuum (UHV) system. This system has been greatly improved since epitaxial films were first grown for an earlier study reporting the results of AFMR on MnF_2.[1] First, it was converted from a high vacuum (HV) system (10^{-7} Torr) to a UHV system ($<10^{-9}$). Cryoshielding has been installed to reduce the pressure increases during the heat cleaning and vaporization processes. The base pressure is $<1\times10^{-9}$ Torr with the pressure rising no higher than 2×10^{-8} Torr during all processes. All of these improvements have allowed epitaxial growth at a considerably lowered temperature, as well as extreme improvements in film quality. The ZnF_2 substrates are heat cleaned at 450 °C for 10 min. The temperature is then lowered to a growth temperature of 300 °C. The FeF_2 is evaporated from an open pyrolized graphite crucible at a rate of approximately 1 μm/h.

The epitaxial film used in this study was characterized by high-resolution double crystal diffraction (x-ray rocking curves), which provides a rapid and nondestructive means of characterizing an epitaxial layer. The details and results of this technique on various epitaxial FeF_2 and CoF_2 films will be discussed more thoroughly elsewhere.[7] The theoretical intrinsic rocking curve linewidths for films of a given thickness have been calculated using x-ray dynamical diffraction theory contained in the work of Macrander *et al.*[8] The intrinsic linewidth increases with decreasing epitaxial layer thickness because the number of scattering layers decreases.

A rocking curve linewidth (FWHM) of better than 60 arc sec was measured on the 3-μm sample (see Fig. 3). This is quite respectable, keeping in mind that the theoretical value for a FeF_2 film of this thickness is 10 arc sec. However, this was not the best epitaxial film of FeF_2 grown to date. A rocking curve linewidth of 30 arc sec was obtained on a 0.8-μm film of FeF_2 for which a linewidth of 22 arc sec was expected. In this extremely high-perfection epitaxial film, the slight discrepancy with the ideal linewidth probably results from the small ($<0.2\%$) lattice mismatch between the FeF_2 film and ZnF_2 substrate.

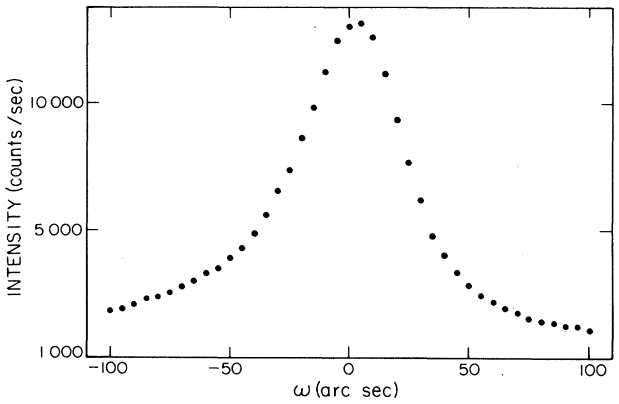

FIG. 3. X-ray rocking curve of the (002) reflection of the 3-μm FeF_2 epitaxial film used in the capacitance measurements, showing a linewidth (FWHM) of better than 60 arc sec.

EXPERIMENTAL MEASUREMENT OF C_m

A three-terminal capacitance technique was used[9] at a frequency of 1 kHz. The capacitance of the interdigital on FeF_2 was typically about 40 pF at room temperature. A 39-pF NPO capacitor was used for the reference. It was mounted in the cryostat near the interdigital capacitor, and maintained at the same temperature. The reference arm of the bridge utilized a seven-digit ratio transformer. One "step" of the ratio transformer corresponds to a change in capacitance of $\Delta C/C\sim2\times10^{-7}$. The ICT has about a quarter of the sensitivity in $1/C\ dC/dT$ as does the conventional capacitance technique. This is probably explained by the fact that in FeF_2, $1/C\ dC/dT$ is anisotropic, with a value measured with the E field parallel to the c axis which is one-third the magnitude, and of opposite sign to that obtained for $E\perp c$. In addition, there was an increase of a factor of 5 in noise over the conventional disk geometry measurements. However, the critical behavior data was of sufficiently high quality so that reasonably accurate values of the critical exponents could be determined.

The ICT was first tested on a bulk piece of FeF_2 since the critical properties of FeF_2 are well known. It was polished using the less elaborate procedures described above. The results are shown in Fig. 4(a). Instead of the expected sharp transition, we found a very noticeable

rounding of the transition became apparent at reduced temperatures less than $|t| \cong 10^{-2}$, where $t=(T-T_N)/T_N$. This can be seen more clearly by plotting $1/C\ dC/dT$ versus $\log_{10}|t|$ as shown in Fig. 5(a). This seemed odd in light of the extremely sharp transition that has been obtained in the conventional capacitance measurements[2] of thick (~ 1 mm) slabs of FeF_2. It was this result which made us suspect of our initial surface preparation methods and procedures, as discussed above.

The capacitance measurements using the ICT were then repeated on a FeF_2 substrate using the more elaborate surface preparation procedure. The results for $1/C\ dC/dT$ versus T are shown in Fig. 4(b) and in the corresponding $\log_{10}|t|$ plot in Fig. 5(b). Now the expected divergent critical behavior of a three-dimensional ($d=3$) Ising system is found with no noticeable rounding for $|t| \geq 10^{-3}$. The critical behavior of C_m is usually described by the function[10]

$$C_m=(A^+/\alpha)|t|^{-\alpha}(1+D^+|t|^{0.50})+B+Et \qquad (1)$$

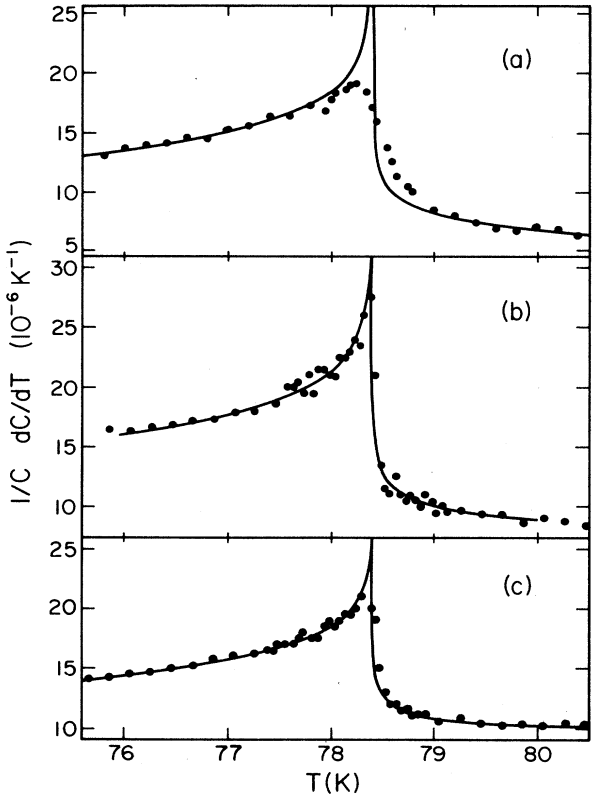

FIG. 4. (a) $1/C\ dC/dT$ vs T for the FeF_2 substrate in which the less elaborate polishing procedure was used. The solid lines in (a)–(c) represent the best fits of the data to Eq. (1). A considerable rounding of the transition is apparent. (b) $1/C\ dC/dT$ vs T for the FeF_2 substrate polished in which the elaborate surface preparation procedure was used. Note that the transition appears much sharper than in (a). (c) $1/C\ dC/dT$ vs T for the 3-μm FeF_2 epitaxial film. The transition appears to be almost as sharp as in (a).

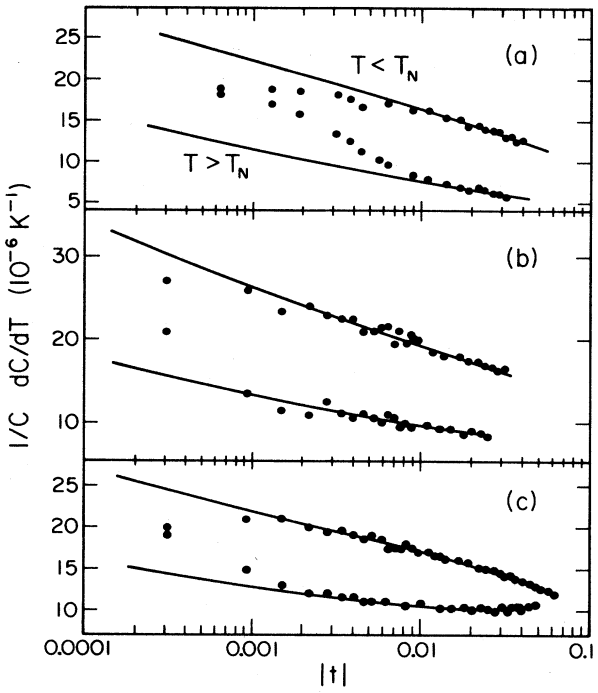

FIG. 5. (a) $1/C\ dC/dT$ vs $\log_{10}|t|$ as in 4(a). The same fits as in Fig. 4(a)–4(c) are shown as solid lines. Note that rounding occurs for $|t| \leq 10^{-2}$. (b) $1/C\ dC/dT$ vs $\log_{10}|t|$ as in 4(b). Note that rounding occurs for $|t| \leq 10^{-3}$. (c) $1/C\ dC/dT$ vs $\log_{10}|t|$ as in 4(c). Note that rounding occurs for $|t| \leq 2\times 10^{-3}$.

for $t>0$ and amplitudes A^- and D^- for $t<0$. $|t|^{-\alpha}$ is the leading singularity, with α the magnetic specific-heat critical exponent, and D is the correction to scaling term. The $B+Et$ terms are included to account for the constant and linear background. Since $dC/dT \propto C_m$, C versus t was fitted to the temperature integral of these equations using a nonlinear least-squares fitting procedure. The data was fitted for the range $10^{-3} \leq |t| \leq 3\times 10^{-2}$, including the correction to scaling. The values of $D^+/D^-=0.80$ and $D^-=0.175$ were chosen to be those previously obtained from an analysis of the bulk FeF_2 birefringence measurements.[11] All other parameters, including T_N were allowed to float. From this fitting procedure, we find $\alpha=0.10\pm0.01$ and the amplitude ratio $A^+/A^-=0.60\pm0.05$. These values are identical, within experimental error, to those previously found in capacitance[2] ($\alpha=0.110$, $A^+/A^-=0.5441\pm0.0011$) and birefringence[11] ($\alpha=0.111\pm0.007$, $A^+/A^-=0.543\pm0.020$) measurements and with the theory for the $d=3$ Ising model ($\alpha=0.110\pm0.005$,[12] $A^+/A^-=0.5$ (Ref. 13)).

Finally, a 3-μm epitaxial film of FeF_2 grown on a ZnF_2 substrate was measured using the ICT. This is the film whose double crystal diffraction characterization is shown in Fig. 3. The results for $1/C\ dC/dT$ in the critical region are shown in Figs. 4(c) and 5(c). The epitaxial

film exhibited the same $d=3$ Ising divergent critical behavior as seen on the FeF_2 substrate. The film showed signs of rounding at reduced temperatures $|t| \leq 2\times 10^{-3}$. We therefore judge the perfection of the film to be somewhat less than that of a well-polished FeF_2 surface, but much better than a poorly polished one. The nonlinear least-squares fit to the data yield $\alpha=0.10\pm 0.01$ and $A^+/A^-=0.60\pm 0.05$, in satisfactory agreement with the bulk sample and the theoretical results. To our knowledge, this is the first detailed study of the magnetic specific-heat critical behavior of an epitaxial film.

By comparing the amplitude A^- found in fitting the capacitance data of the FeF_2 substrate with that of the FeF_2 epitaxial film, a filling factor $\nu=0.69$ is obtained. This is in reasonable agreement with the estimated value of 0.53 obtained from our simplistic model; showing it is correct in predicting that most of the capacitance is measured in a layer of thickness approximately equal to the interdigital spacing.

DISCUSSION

We have developed a technique (ICT) for accurately measuring the critical behavior of the magnetic specific heat of epitaxial thin films or surfaces of insulating magnetic materials. The ICT has been demonstrated on FeF_2 bulk surfaces and on epitaxial films. Our earlier low-temperature (4 K) AFMR study of MnF_2 epitaxial films exhibited larger than expected resonance linewidths.[1] The broadening of the AFMR was interpreted as resulting from strain-induced variations in the exchange and/or anisotropy interaction in the film, to which the linewidth is extremely sensitive. But while the linewidth of the AFMR may directly correlate with the degree of perfection and the strain state of the film, it is only indirectly sensitive to the substrate surface and subsurface properties.

The ICT provides a means whereby the quality of the subsurface of a magnetic material may be judged from the sharpness of the magnetic phase transition. The arguments for this are as follows: Suppose a strain field exists in the first few microns below the surface of a crystal—as might be caused by the polishing process. Assume its normalized root-mean-square variation is $\langle (r-r_0)^2\rangle^{1/2}/r_0$, where r_0 is the equilibrium lattice constant. Since the super-exchange interaction J appears to vary roughly as r^{-12} in the transition-metal difluorides the expected rounding ΔT_N of the antiferromagnetic phase transition at T_N due to random strains would be

$$\frac{\Delta T_N}{T_N}=\frac{1}{J}\frac{\partial J}{\partial r}\langle (r-r_0)^2\rangle^{1/2}\simeq 12\frac{\langle (r-r_0)^2\rangle^{1/2}}{r_0}\ , \tag{2}$$

provided that the strain field varies on distance scales large compared to the correlation length $\xi(t)$ at a reduced temperature $|t_a|=|\Delta T/T_N|$. Put another way, by finding the reduced temperature $|t_a|$, at which the critical behavior of any thermodynamic quantity first begins to depart from its expected singular form, one would deduce that

$$\frac{\langle (r-r_0)^2\rangle^{1/2}}{r_0}\simeq\frac{|t_a|}{12}\ . \tag{3}$$

Hence, for our poorly polished FeF_2 substrate, where $|t_a|\cong 10^{-2}$, we deduce $\langle (r-r_0)^2\rangle^{1/2}/r_0\cong 10^{-3}$ in the first few microns beneath the surface.

The ICT opens the possibility of studying a wide variety of novel systems studied through their critical behavior. In the $d=3$ transition-metal difluorides, several antiferromagnets with different properties exist with good lattice matches to the nonmagnetic ZnF_2. Superlattices of magnetic-magnetic and magnetic-nonmagnetic layers are expected to exhibit a rich variety of unusual critical behavior. For example, one should be able to examine dimensional crossover from $d=3$ to $d=2$ in say a FeF_2/ZnF_2 superlattice. A crossover from critical behavior characteristic of $d=3$ to that of $d=2$ should occur at a value of $|t|$ such that the correlation length ξ in the bulk would have become approximately equal to the thickness of the magnetic layer.

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