Phenomenology, specific heat, and corrections to scaling in copper ammonium bromide

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Experimental data near the critical point for the spontaneous magnetization, the zero-field susceptibility, and the specific heat of the ($S = \frac{1}{2}$) insulating Heisenberg ferromagnet Cu $(NH_4)_2Br_4 2H_2O$ are compared with two extensions of asymptotic scaling. One is a previously described phenomenology which is equivalent to the predictions of the renormalization group (RG) when all irrelevant variables are neglected. The second results if one adds to the asymptotic scaling formulas the confluent singularities due to the leading irrelevant variable. We find that both sets of formulas are consistent with the data for all three quantities: the spontaneous magnetization, the zero-field susceptibility, and the specific heat, but that overall, the phenomenology requires fewer parameters. A discrepancy between the experimental and theoretical values for the susceptibility exponent is discussed.

I. INTRODUCTION

For small magnetic fields and temperatures close to the Curie temperature, the singular thermodynamic behavior of a ferromagnet is correctly described by the formulas of asymptotic scaling in terms of universal scaling functions and critical exponents.[1] For the spontaneous magnetization M_0, the zero-field susceptibility χ_0, and the zero-field specific heat C, asymptotic scaling yields the well-known power laws

$$M_0 = B_0|t|^{\beta}, \quad T\chi_0 = C_0|t|^{-\gamma}, \quad C = A|t|^{-\alpha}, \tag{1}$$

where $t = T/T_C - 1$ is the reduced temperature, with T the absolute temperature and T_C the Curie temperature, and where α, β, and γ are the usual critical exponents and B_0, C_0, and A are the associated amplitudes.[1] Corrections to these asymptotic scaling formulas are expected to be important outside the critical region, especially when the leading singularity is weak. For the case of the specific heat, the situation is further complicated by significant contributions from analytic background terms.[2,3]

Recently, as part of an effort to extend the asymptotic scaling formulas outside of the critical region, the present authors compared[4] experimental data for the spontaneous magnetization and the zero-field susceptibility of europium oxide and nickel with two theoretical formulas. Each of these separately takes into account one of two possible types of corrections predicted by the renormalization group[5,6] (RG). The first makes use of a phenomenology[7] which is equivalent to the predictions of the RG in the absence of irrelevant variables[8] and which includes the leading analytic corrections due to the nonlinearity of the scaling fields. The second extends the formulas of asymptotic scaling outside of the critical region by appending to the leading power laws, the lowest order confluent singularities due to the leading irrelevant variable.[5,6]

The purpose of this report is twofold. First, the phenomenology is extended to include the specific heat and the results are applied to the insulating ferromagnet copper ammonium bromide, a ($S = 1/2$) material which belongs to the same universality class ($n = 3$, $d = 3$) as do europium oxide and nickel. Second, as in the earlier analysis,[4] we compare the results of the phenomenology with the corresponding confluent singularity formulas.

II. CORRECTIONS TO SCALING

In this section, we present the correction to scaling formulas that we use to analyze the experimental data for the spontaneous magnetization, the zero-field susceptibility, and the specific heat of copper ammonium bromide.

A. Phenomenology

According to the phenomenology,[7] the spontaneous magnetization of a ferromagnet may be expressed as

$$M_0 = \frac{B_0|t|^{\beta}}{(1+at)^{\beta\xi}}, \tag{2}$$

where B_0, a, and ξ are adjustable parameters and β, as indicated above, is the usual critical exponent.[1] As in the previous study, we impose the normalization condition $M_0(T=0)=1$ and choose the slope at $T=0$ to be zero.[7] These constraints lead to the relations $B_0 = (1-a)^{\beta\xi}$ and $\xi = 1 - 1/a$, thereby reducing by 2 the number of parameters in the formula for M_0. Assuming, further, that the exponent β in Eq. (2) is fixed, either experimentally or theoretically for a given universality class, we are left with just a single free parameter.

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For the zero-field susceptibility, the corresponding formula is[7]

$$T\chi_0 = C_0|t|^{-\gamma}(1+at)^{2-\alpha-2\beta\xi} + d_0, \tag{3}$$

where γ and α are the susceptibility and specific heat exponents, respectively. Since we presume that the parameters a and ξ are fixed by the spontaneous magnetization and that the exponents γ, α, and β are known, the formula for $T\chi_0$ in Eq. (3) involves two adjustable parameters, C_0 and d_0. It should be noted that, in utilizing Eq. (3), the single constant d_0 is used to approximate terms[7,8] of the form $|t|^{1-\alpha}E_0e_0(t)$ and $D_0d_0(t)$ where E_0 and D_0 are constants and $e_0(t)$ and $d_0(t)$ are analytic functions of t normalized to unity at $t=0$. In our earlier analysis of data[4,7] for the zero-field susceptibility of Ni, it was found that this was sufficient to enable Eq. (3) to represent the data out to $3T_C$. We shall assume this approximation to be valid in the present case also so that we need not avail ourselves of the infinity of parameters implied by the missing terms.

Finally, let us consider the zero-field specific heat. The singular part of this quantity is obtained by differentiating the singular part of the free energy[7] which, in zero field, is given by

$$\frac{\mathcal{F}_{0s}}{T} = A_{F\pm}\frac{|t|^{2-\alpha}}{(1+at)^{2-\alpha}}, \tag{4}$$

where $A_{F\pm}$ are two constants with the + (−) sign referring to temperatures above (below) T_C. Differentiating $\mathcal{F}_{0s}$ twice, and adding appropriate analytic background terms, we obtain for the specific heat the formula

$$C = A_\pm\frac{|t|^{-\alpha}}{(1+at)^{4-\alpha}}(1+t)\left[1+\left(\frac{(3-\alpha)-2a}{1-\alpha}\right)t\right] + b_0 + b_1t, \tag{5}$$

where A_+ and A_- are two constants associated with the regions above and below T_C, respectively, and b_0 and b_1 are the coefficients of the analytic part. As for the susceptibility in Eq. (3), the parameter a is determined by the spontaneous magnetization so that with α fixed the specific heat C involves only the four free parameters A_+, A_-, b_0, and b_1.

B. Confluent singularities

As in the earlier analysis[4] of experimental data for europium oxide and nickel, we shall compare the results obtained from Eqs. (2), (3), and (5) with the corresponding extensions of asymptotic scaling, obtained by including the confluent singularities due to the leading irrelevant variable.[5,6] These nonanalytic corrections to scaling can be obtained by differentiating Wegner's formula for the singular part of the free energy[6] which, near the critical point, assumes the form

$$F_s = |t|^{2-\alpha}f_0\left(\frac{h}{|t|^\Delta}\right) + u_1|t|^{2-\alpha+\Delta_1}f_1\left(\frac{h}{|t|^\Delta}\right), \tag{6}$$

where f_0 and f_1 are two scaling functions, h is the magnetic field divided by k_BT, $\Delta=\gamma+\beta$, Δ_1 is the correction to scaling exponent, and u_1 is the leading irrelevant variable which remains finite at the critical point.

Making use of Eq. (6), we find that the correction to scaling formulas for the spontaneous magnetization and zero-field susceptibility are given, respectively, by

$$M_0 = B_0|t|^\beta(1+a_M|t|^{\Delta_1}) \tag{7}$$

and

$$T\chi_0 = C_0|t|^{-\gamma}(1+a_\chi|t|^{\Delta_1}), \tag{8}$$

with a_M and a_χ two parameters. Note that the susceptibility involves two free parameters, C_0 and a_χ, the same number as for the phenomenology in Eq. (3) and that for the spontaneous magnetization, there are also two free parameters B_0 and a_M, which is one more than for the phenomenology in Eq. (2).

For the zero-field specific heat, the corresponding formula is

$$C = A_\pm|t|^{-\alpha}(1+a_C^\pm|t|^{\Delta_1}) + b_0 + b_1t, \tag{9}$$

where the two analytic background terms b_0 and b_1t have been included and where, again, the + (−) sign refers to temperatures above (below) T_C. Note that in Eq. (9) there are six parameters A_+, A_-, a_C^+, a_C^-, b_0, and b_1; this is to be contrasted with the four in Eq. (5).

The inclusion of the analytic background terms b_0+b_1t in Eq. (9), it should be noted, is essentially an *ad hoc* procedure, suggested by Wegner's formula for the free energy.[6] This formula separates the free energy—and, by differentiation, the specific heat—into a singular part and an analytic part. In some studies[9] of the specific heats of ferromagnetic materials, the value of the constant b_0 has been taken to be different above and below the critical point. This implies that the background term in the specific heat is nonanalytic and requires that the number of free parameters in Eq. (9) be increased from 6 to 7.[10] The additional nonanalyticity can be understood in terms of a "jump" discontinuity, as predicted by Landau's theory,[11] and has been incorporated into RG theory by use of a crossover formalism.[12] As we shall see below, good agreement between the data and our theoretical formulas is obtained without the use of the additional degree of freedom implied by taking the value of b_0 to be different above and below T_C.

As expected, each of the above formulas in Eqs. (7), (8), and (9) reduce to the asymptotic scaling formulas when the correction amplitudes a_M, a_χ, and $a_C^\pm$ (and the background terms b_0+b_1t in the specific heat) are set to zero. Note that if $\alpha<0$, as predicted for the Heisenberg universality class,[13] the leading term in the specific heat, as $t\to0$, is the constant b_0.

III. COMPARISON WITH EXPERIMENT

In this section, we compare the above formulas with experimental data for the spontaneous magnetization,[14]

the zero-field susceptibility,[15] and the specific heat[16] of the insulating Heisenberg ferromagnet copper ammonium bromide.

In carrying out the analyses described below, we have taken the point of view[4,7] that the critical temperature, the values of the exponents α, β, γ, and the corresponding amplitudes $A_{\pm}$, B_0, and C_0 are given and that the remaining parameters in our formulas can be selected to optimize agreement with experiment. Unfortunately, for the present material, this is made awkward by an inconsistency in the value of T_C. Specifically, measurements of the spontaneous magnetization[14] yield the value $T_C = 1.735 \pm 0.002$ K, while those for the zero-field susceptibilty[15] and the specific heat[16] yield the values $T_C = 1.773 \pm 0.001$ K and $T_C = 1.795 \pm 0.002$ K, respectively. Since we have been unable to resolve this, we shall make use of the respective experimental values for T_C in each of these three cases. Our conclusions, therefore, must be viewed in light of this ambiguity.

For the Heisenberg ($n = 3$, $d = 3$) universality class, the critical and correction to scaling exponents are predicted theoretically[13] to be $\alpha = -0.13$, $\beta = 0.37$, $\gamma = 1.39$, and $\Delta_1 = 0.56$. Generally, for materials known to belong to this universality class, these theoretical values of α and β appear to be in reasonable accord with experiment.[17] On the other hand, for many of the same materials, a variety of values for the susceptibility exponent γ have been found[17] and these fall in the range 1.3–1.4. In particular, the experimental value of γ for copper ammonium bromide, is found[15] to be 1.31, which is significantly lower than the theoretical value[13] of 1.39. In view of this discrepancy between the theoretical and experimental values for γ, plus the uncertainty in the value of T_C, we shall supplement our analysis by considering also the results of fixing the critical exponents by their theoretical values. In all cases, the correction to scaling exponent will be kept at its theoretical value of $\Delta_1 = 0.56$.

A. Spontaneous magnetization

Figure 1 shows a graph of experimental data for the spontaneous magnetization[14] of copper ammonium bromide, normalized to its saturation value at $T = 0$, as a function of T/T_C for temperatures in the range $0 \leq T \leq T_C$, where $T_C = 1.735$ K. Also shown in the figure are three theoretical curves, obtained by use of Eqs. (1), (2), and (7) for the experimental value $\beta = 0.38$, a value which is in good agreement with the theoretical prediction[13] of $\beta = 0.37$ for the Heisenberg universality class.

The dotted curve in Fig. 1 represents the asymptotic scaling formula in Eq. (1) for the experimentally determined amplitude value $B_0 = 1.33$. Not unexpectedly, this formula only agrees with the data for a narrow range of temperatures close to T_C. Making use of the same value of $B_0 = 1.33$, and with $a_M = -0.1$ chosen for optimal agreement with experiment, we find that the nonanalytic correction to scaling formula in Eq. (7) is able to extend this agreement down to about $0.75T_C$. This

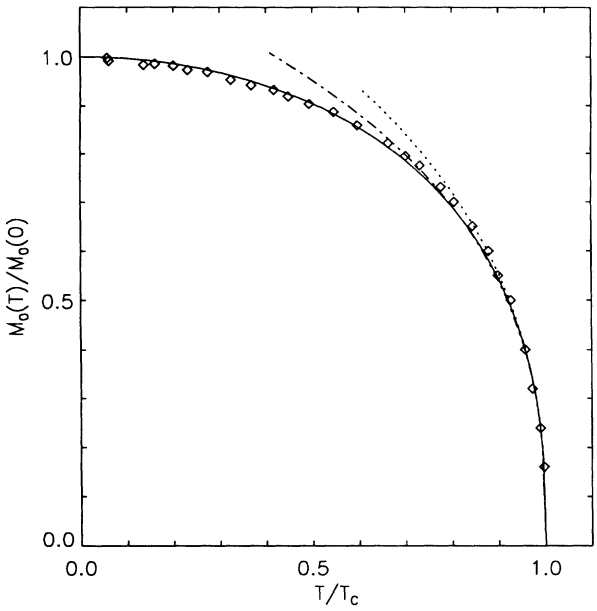

FIG. 1. The normalized spontaneous magnetization $M_0(T)/M_0(0)$ of copper ammonium bromide plotted as a function of T/T_C for $T_C = 1.735$ K and $\beta = 0.38$. The experimental points are those of Wielinga and Huiskamp (Ref. 14). The dotted curve is the power law in Eq. (1) for $B_0 = 1.33$, the solid curve is the phenomenology in Eq. (2) for $B_0 = 1.33$, $a = 0.41$, and $\xi = -1.44$, and the dot-dashed curve is the confluent singularity formula in Eq. (7) for $B_0 = 1.33$ and $a_M = -0.1$.

is represented in the figure by the dot-dashed curve. Finally, the solid curve, which is obtained by use of the phenomenology in Eq. (2), with the values $B_0 = 1.33$, $a = 0.41$, and $\xi = -1.44$, agrees with the experimental data over the *entire* range of temperatures below T_C.

Although the value $B_0 = 1.33$ is determined by experiment for small t, we find that by choosing a slightly different value, the agreement between Eq. (7) and the data can be extended to lower temperatures. Specifically, for $B_0 = 1.40$ and $a_M = -0.22$, the curve obtained by use of Eq. (7) is found to follow the data down to about $0.5T_C$. Use of this higher value for B_0 in Eq. (2), on the other hand, does not give as good agreement as does the value $B_0 = 1.33$.

B. Zero-field susceptibility

Figure 2 shows a graph of experimental data[15] for the inverse susceptibilty C/χ_0, where C is the Curie constant,[18] along with three theoretical curves obtained by use of the formulas in Eqs. (1), (3), and (8). As above, we fix the critical parameters in these formulas by use of the experimentally[15] determined values of $T_C = 1.773$ K, $\gamma = 1.31$, and $C_0 = 1.22$ K, although we find that a very slight adjustment in the value of C_0 is needed to obtain optimal agreement with experiment for the two correction to scaling formulas.

The dotted curve in Fig. 2 represents the asymptotic

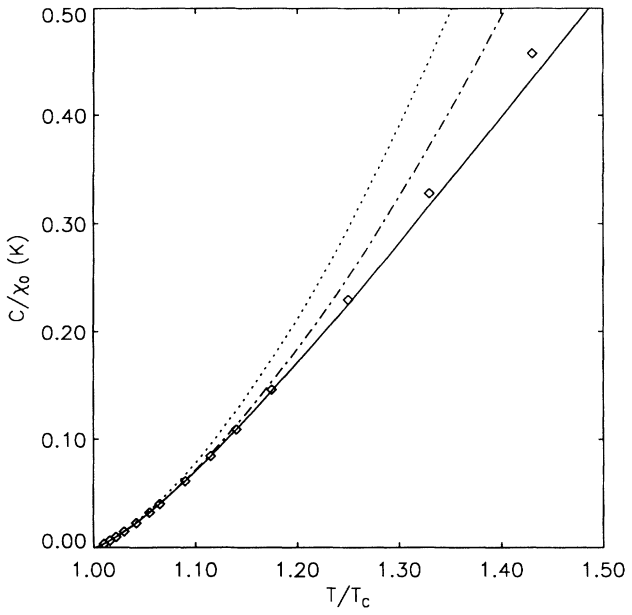

FIG. 2. The inverse susceptibility C/χ_0 of copper ammonium bromide plotted as a function of T/T_C for $T_C = 1.773$ K and $\gamma = 1.31$. The experimental points are those of De Jongh *et al.* (Ref. 15). The dotted curve is the power law in Eq. (1) for $C_0 = 1.22$ K, the solid curve is the phenomenology in Eq. (3) for $C_0 = 1.20$ K and $d_0 = -0.21$ K, and the dot-dashed curve is the confluent singularity formula in Eq. (8) for $C_0 = 1.17$ K and $a_\chi = 0.51$.

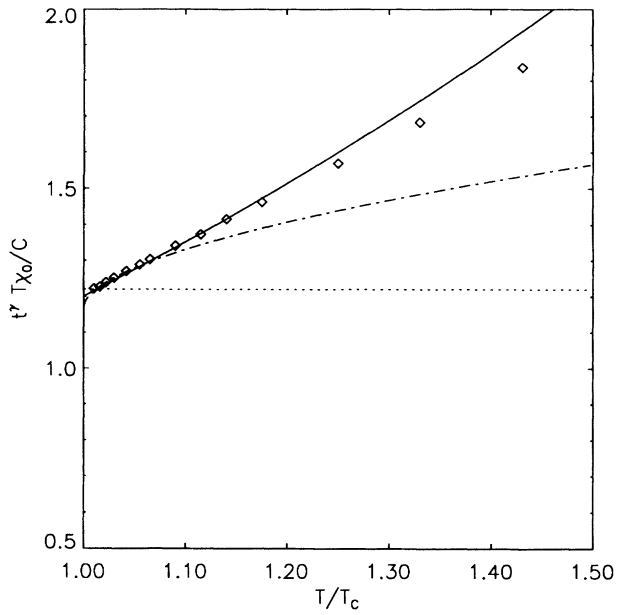

FIG. 3. Graph of the quantity $t^\gamma T\chi_0/C$ for copper ammonium bromide plotted as a function of T/T_C for $\gamma = 1.31$. The data is taken from Ref. 15. The dotted curve was obtained by use of Eq. (1), the solid curve by use of Eq. (3), and the dot-dashed curve by use of Eq. (8). Each curve was determined using the same parameter values as for Fig. 2.

scaling formula in Eq. (1). For the experimental values $\gamma = 1.31$ and $C_0 = 1.22$ K, we find that the validity of the power law is confined to the narrow range of temperatures $T_C \lesssim T \lesssim 1.07T_C$. The dot-dashed curve in the figure represents the confluent singularity formula in Eq. (8) where the choices $C_0 = 1.17$ K and $a_\chi = 0.51$ have been made to optimize the agreement with experiment. The resulting curve agrees with the data out to about $1.15T_C$. Finally, the phenomenology in Eq. (3) with $C_0 = 1.21$ K and $d_0 = -0.21$ K is represented by the solid curve and follows most of the data, with only a slight deviation from the experimental points, for temperatures above about $1.3T_C$.

An alternate and more sensitive way to compare the theoretical formulas with the data is shown in Fig. 3 where a graph of the quantity $t^\gamma T\chi_0/C$ is plotted as a function of T/T_C. The horizontal dotted line in the figure corresponds to the asymptotic scaling formula, the dot-dashed curve is a graph of the function $C_0(1+a_\chi|t|^{\Delta_1})$, as obtained from Eq. (8), and the solid curve represents the function $C_0(1+at)^{2-\alpha-2\beta\xi} + d_0t^\gamma$ which is derived from Eq. (3) of the phenomenology. Since the same parameter values are used to determine the curves in both Figs. 2 and 3, it follows that the intercepts on the vertical axis in Fig. 3 are precisely the values of C_0 used to determine each of the curves in Fig. 2. Note that the experimental points in Fig. 3 fall very nearly on a straight line.

As discussed above, it is also of interest to consider the analysis of χ_0 assuming the theoretical exponent value of $\gamma = 1.39$. The graphs in Figs. 4 and 5 are the respective

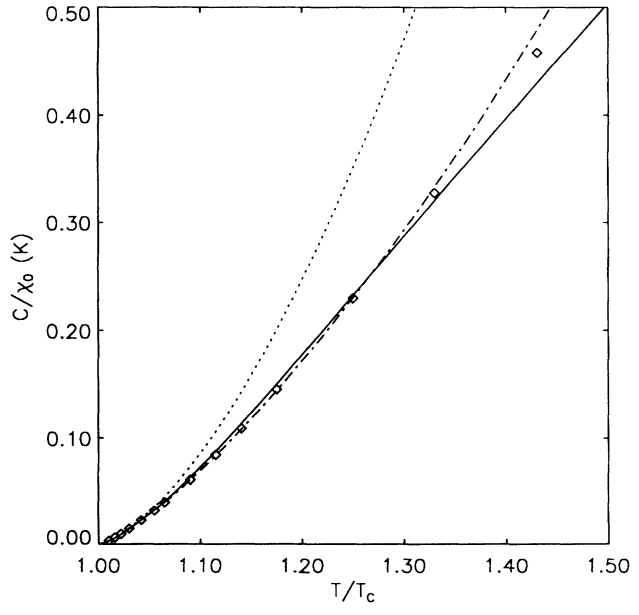

FIG. 4. The inverse susceptibility C/χ_0 of copper ammonium bromide plotted as a function of T/T_C for $T_C = 1.773$ K and $\gamma = 1.39$. The experimental points are those of De Jongh *et al.* (Ref. 15). The dotted curve is the power law in Eq. (1) for $C_0 = 0.92$ K, the solid curve is the phenomenology in Eq. (3) for $C_0 = 0.92$ K and $d_0 = 0.87$ K, and the dot-dashed curve is the confluent singularity formula in Eq. (8) for $C_0 = 0.73$ K and $a_\chi = 2.0$.

analogs for $\gamma = 1.39$ of the corresponding ones in Figs. 2 and 3 for the experimental value $\gamma = 1.31$.

The dotted curve in Fig. 4 represents the asymptotic scaling formula. In this case, the experimentally determined[15] value for the critical amplitude $C_0 = 1.22$ K turns out to be too high, given the present choice for γ. Instead, we use the value $C_0 = 0.92$ K which, as discussed below, optimizes agreement with experiment for the phenomenology. We have also considered the value $C_0 = 0.73$ K, which is the corresponding "best choice" for the nonanalytic correction formula, but we have found that the higher value of 0.92 K gives a slightly better fit to the data. The solid curve in Fig. 4 represents the phenomenology in Eq. (3) for $\gamma = 1.39$ with $C_0 = 0.92$ K and $d_0 = 0.87$ K chosen for optimal agreement with experiment. These choices for C_0 and d_0 enable the formula in Eq. (3) to follow most of the available data out to about $1.3T_C$, although the quality of the fit is not as good as for $\gamma = 1.31$.

Making use of the same value of $C_0 = 0.92$ K, we find that the confluent singularity formula in Eq. (8) with $a_\chi = 0.6$ extends the validity of the power law in Eq. (1), but only out to about $1.1T_C$. However, the agreement between Eq. (8) and the susceptibility data can be improved, if we treat both C_0 and a_χ as free parameters. In this way, we find that for $C_0 = 0.73$ K and $a_\chi = 2.0$, the agreement with experiment can be extended out to about $1.3T_C$ and this is shown by the dot-dashed curve in the figure. With this value for C_0, however, the phenomenology in Eq. (3) does not agree as well with the experimental data, no matter what value we choose for d_0. It should also be noted that the two values $C_0 = 0.92$ K and $C_0 = 0.73$ K differ substantially not only from each other but also from the value $C_0 = 1.22$ K determined experimentally[15] for $\gamma = 1.31$.

Comparison of the graphs of the quantity $t^\gamma T\chi_0/C$ for $\gamma = 1.31$ in Fig. 3 and for $\gamma = 1.39$ in Fig. 5 makes evident the differences between the two correction to scaling formulas. The most noticeable difference is the appearance in Fig. 5 of a negative curvature in the data, which becomes more pronounced as the critical point is approached. This feature, which is absent in Fig. 3, is closely matched by the dot-dashed curve, obtained by use of Eq. (8). On the other hand, the solid curve, which represents Eq. (3), shows a positive curvature which is inconsistent with the data. Comparing the two solid curves in Figs. 3 and 5, therefore, we find that the phenomenology in Eq. (3) agrees far more closely with experiment for $\gamma = 1.31$ than for $\gamma = 1.39$. By contrast, the nonanalytic correction to scaling formula in Eq. (8) is able to represent the experimental data over a much broader range of temperatures for the theoretical value of $\gamma = 1.39$ than for the experimental value of $\gamma = 1.31$.

C. Specific heat

Figure 6 shows a graph of the experimental points[16] for the zero-field specific heat C of copper ammonium bromide as a function of T/T_C for temperatures above and below T_C. Also shown are the theoretical curves obtained by use of Eqs. (5) and (9). The measured value[16] for the

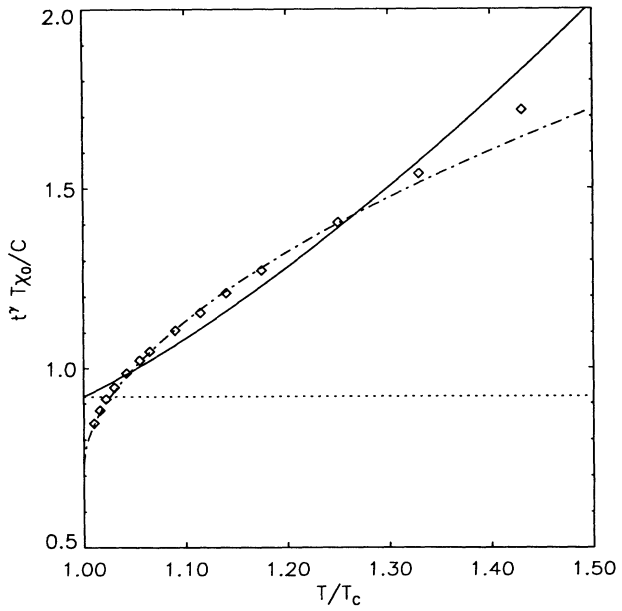

FIG. 5. Graph of the quantity $t^\gamma T\chi_0/C$ for copper ammonium bromide plotted as a function of T/T_C for $\gamma = 1.39$. The data is taken from Ref. 15. The dotted curve was obtained by use of Eq. (1), the solid curve by use of Eq. (3), and the dot-dashed curve by use of Eq. (8). Each curve was determined using the same parameter values as for Fig. 4.

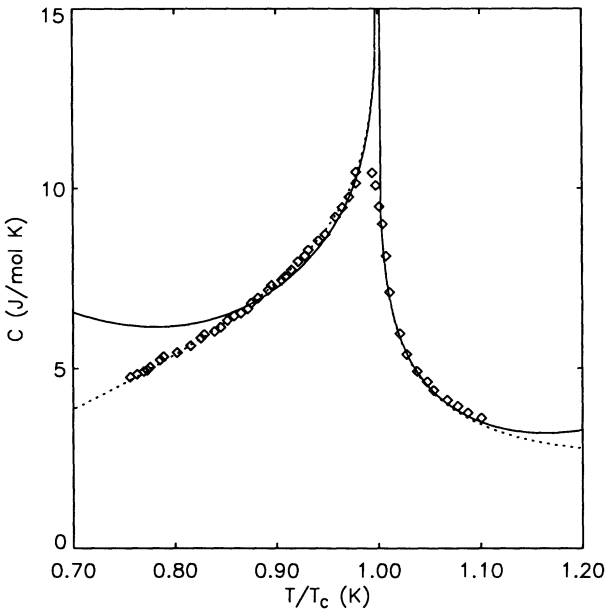

FIG. 6. The specific heat C of copper ammonium bromide plotted as a function of T/T_C for $T_C = 1.795$ K and $\alpha = -0.07$. The experimental points are those of Suzuki and Watanabe (Ref. 16). Each of the curves was determined by use of the parameter values $A_+ = -34.5$, $A_- = -28.0$, and $b_0 = 32.0$. The dotted curve was obtained by use of Eq. (9) with $a_C^\pm = 0$ and $b_1 = 8.0$, that is, the power law plus analytic background and the solid curve by use of the phenomenology in Eq. (5) with $b_1 = 47.0$.

critical temperature, in this case, is $T_C = 1.795$ K, which differs from the corresponding values of 1.735 K and 1.773 K obtained for the spontaneous magnetization[14] and the zero-field susceptibility,[15] respectively.

In the original 1970 analysis[16] of the specific heat, it was assumed that near the critical point the data could be represented by the function $A \ln|t| + B$ with both of the constants A and B free to take on different values above and below T_C. We do not use this form here since RG theory[13] predicts $\alpha = -0.13$ for the three-dimensional Heisenberg universality class and not a logarithmic divergence. We note, however, that the sharp but finite cusp, associated with a small negative value of α, can often resemble a logarithmic divergence.

In the absence of a suitable experimental value for the critical exponent α, we have chosen to fix its value, first of all, by use of the scaling relation[1,19]

$$\alpha + 2\beta + \gamma = 2, \tag{10}$$

which, for the above values $\beta = 0.38$ and $\gamma = 1.31$, gives $\alpha = -0.07$. As for the susceptibility above, we also carry out an analysis of the specific heat for the corresponding theoretical value of $\alpha = -0.13$. For both these choices of α, the six parameters A_+, A_-, b_0, b_1, and $a_C^{\pm}$ in Eqs. (5) and (9) are taken to be free, with A_+, A_-, and b_0 determined by the power law in Eq. (1) plus analytic background, that is, by Eq. (9) with $a_C^+ = a_C^- = 0$.

The dotted curve in Fig. 6 represents the asymptotic scaling formula in Eq. (1) plus analytic background for the values $A_+ = -34.5$, $A_- = -28.0$, $b_0 = 32.0$, and $b_1 = 8.0$ selected to optimize agreement with experiment. As may be seen from the graph, the resulting curve follows all of the available data. We have not included the corresponding (dot-dashed) curve for the nonanalytic correction formula since, for $a_C^+ = a_C^- = 0$, it is identical to the dotted curve in the figure. Thus for $\alpha = -0.07$ we conclude that no additional confluent singularity is needed to fit the specific heat.

The solid curve in Fig 6 represents Eq. (5) for the same values of A_+, A_-, and b_0 as for the dotted curve. This time we choose the coefficient of the linear term in the background to be $b_1 = 47.0$ with the value $a = 0.41$ in Eq. (5) fixed by the spontaneous magnetization. For these parameter values, the agreement between Eq. (5) and the experimental data, although good for temperatures above T_C, does not extend as far from the critical point below T_C as does the scaling formula without corrections. Thus, it would seem that, for $T < T_C$, the addition of correction terms to the scaling formula plus analytic background leads to a worse fit to the data. As we shall see below, this does not happen for the theoretical exponent value[13] $\alpha = -0.13$.

Finally, an important quantity to consider in the analysis of the specific heat is the amplitude ratio A_+/A_- which, like the critical exponents, is predicted to be a universal quantity.[20] Using the above values of A_+ and A_-, we find that

$$\frac{A_+}{A_-} = 1.23, \tag{11}$$

which is noticeably smaller than the value $A_+/A_- = 1.58$, obtained theoretically.[21]

Let us now reconsider the above analysis using, in place of $\alpha = -0.07$, the theoretical[13] value $\alpha = -0.13$. Figures 7 and 8 show graphs of the same experimental data as above as well as the theoretical curves obtained by use of Eqs. (5) and (9), respectively. Although the amplitudes A_+, A_-, and b_0 are free parameters, we find this time that the *same* values for these quantities can be used in both Eq. (5) *and* Eq. (9) to obtain a good fit to the data. On the other hand, the optimal value for the coefficient b_1 is again found to be quite different in the two cases.

To obtain the curves in Fig. 7, the parameters were selected to optimize agreement between the experimental data and the confluent singularity formula in Eq. (9). The resulting values are $A_+ = -22.0$, $A_- = -14.0$, $b_0 = 19.0$, $b_1 = 11.0$, and $a_C^+ = a_C^- = 0.03$ and enable Eq. (9) to follow the data over the entire range of temperatures for which it is available; this is represented in the figure by the dot-dashed curve. The dotted curve is obtained by use of Eq. (9) with the same parameter values except that $a_C^+ = a_C^- = 0$. Thus, apart from a small confluent singular correction, we find that the data is well represented by just the power law plus analytic background. However, with the same values of A_+, A_-, and b_0 and with $a = 0.41$ fixed by the spontaneous magnetization and $b_1 = 11.0$ selected optimally, we find that the solid curve, which represents Eq. (5), does not agree

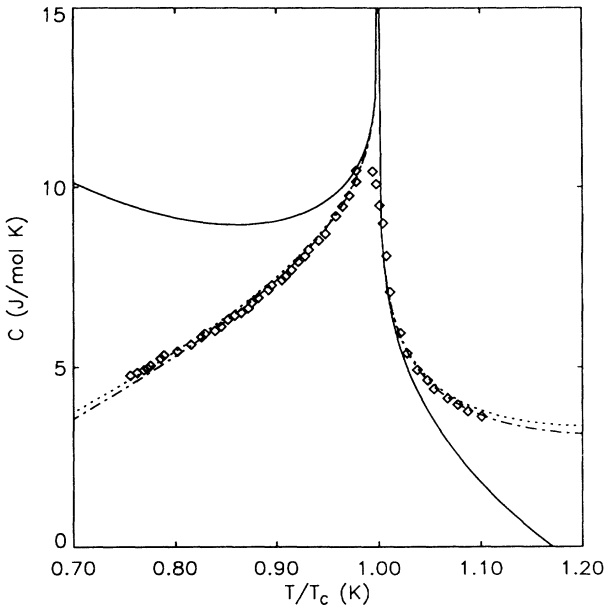

FIG. 7. The specific heat C of copper ammonium bromide plotted as a function of T/T_C for $T_C = 1.795$ K and $\alpha = -0.13$. The experimental points are those of Suzuki and Watanabe (Ref. 16). Each of the curves was determined by use of the parameter values $A_+ = -22.0$, $A_- = -14.0$, $b_0 = 19.0$, and $b_1 = 11.0$. The dotted curve was obtained using Eq. (9) with $a_C^{\pm} = 0$, that is, the power law plus analytic background, the solid curve is the phenomenology in Eq. (5), and the dot-dashed curve is the confluent singularity formula in Eq. (9) for $a_C^{\pm} = 0.03$.

as well with the experimental data.

The situation is reversed in Fig. 8, where we find that optimal agreement between experiment and Eq. (5) of the phenomenology can be obtained for the same values $A_+ = -22.0$, $A_- = -14.0$, and $b_0 = 19.0$, as above, but with the value $b_1 = 29.5$. This leads to the solid curve in the figure. The dotted curve is again obtained by use of the power law plus analytic background, while the dot-dashed curve is obtained by use of the nonanalytic correction formula in Eq. (9) with $a_C^+ = 0.23$ and $a_C^- = -0.3$, both chosen to optimize agreement with experiment. Note that for both the dotted and dot-dashed curves in Fig. 8, the same values of A_+, A_-, b_0, and b_1 as for the solid curve have been used. With these choices, we find that, except close to T_C, it is now the scaling formula plus analytic background which does not represent the data well, while the inclusion of the confluent singularity only leads to a small improvement.

We emphasize the fact that the values of the parameters A_+, A_-, and b_0 are the same for the curves in Figs. 7 and 8 and that it is only the parameter b_1 that differs, in the two cases. Furthermore, we find that it is possible to fit the data without significant use of a nonanalytic correction. Thus, it would appear that for $\alpha = -0.13$, unlike the previous choice $\alpha = -0.07$, the effects of the analytic corrections multiplying the $|t|^{-\alpha}$ term partially cancel the effects of the linear t term in the analytic background, at least over the range of temperatures considered here.

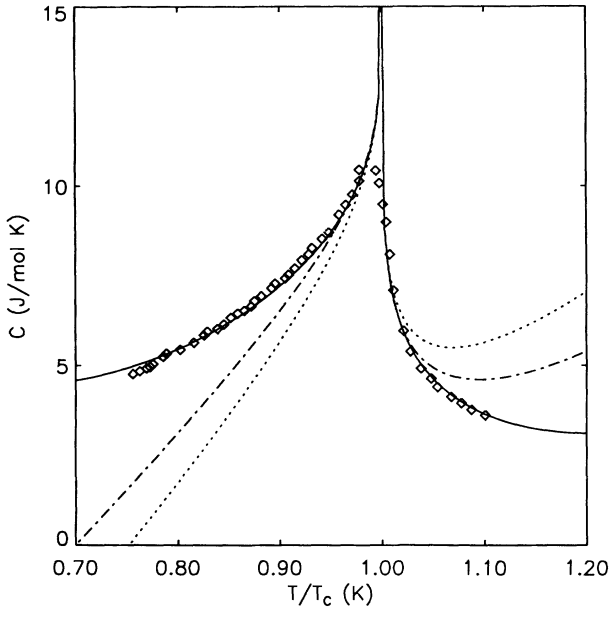

FIG. 8. The specific heat C of copper ammonium bromide plotted as a function of T/T_C for $T_C = 1.795$ K and $\alpha = -0.13$. The experimental points are those of Suzuki and Watanabe (Ref. 16). Each of the curves was determined by use of the parameter values $A_+ = -22.0$, $A_- = -14.0$, $b_0 = 19.0$, and $b_1 = 29.5$. The dotted curve was obtained by use of Eq. (9) with $a_C^\pm = 0$, that is, the power law plus analytic background, the solid curve is the phenomenology in Eq. (5), and the dot-dashed curve is the confluent singularity formula in Eq. (9) for $a_C^+ = 0.23$ and $a_C^- = -0.3$.

It is also of interest to consider the universal amplitude ratio A_+/A_- for the value $\alpha = -0.13$. Using the above values of $A_+ = -22.0$ and $A_- = -14.0$, we find that

$$\frac{A_+}{A_-} = 1.57, \tag{12}$$

which is in substantially better agreement with the theoretical[21] value $A_+/A_- = 1.58$ than the value obtained in Eq. (11) by use of the "experimental" value $\alpha = -0.07$.

Besides the critical amplitude ratio A_+/A_-, ratios formed from the correction to scaling amplitudes, a_M, a_χ, and $a_C^\pm$ in Eqs. (7), (8), and (9), are also predicted by the RG to be universal.[20] It would be of interest, therefore, to determine the values of, say, a_χ/a_M, $a_C^\pm/a_\chi$, and a_C^+/a_C^- for copper ammonium bromide and to compare these with the corresponding theoretical predictions.[20,21] Unfortunately, it appears that the presently available data do not allow an accurate determination of the values for these quantities. To obtain a good fit for the susceptibility data, for example, the value of a_χ had to be changed from 0.51 to 2.0 as the experimental value for γ was replaced by the corresponding theoretical value. Thus, for the value $a_M = -0.1$, which was used to determine the dot-dashed curve in Fig. 1, we obtain $a_\chi/a_M = -5.1$ and $a_\chi/a_M = -20.0$ for these two a_χ values.[22] Further, since it is possible to represent both the spontaneous magnetization and the specific heat data, above and below T_C, without the use of a $|t|^{\Delta_1}$ correction, it would seem that $a_C^\pm/a_\chi = 0$ and that a_C^+/a_C^- is indeterminate. This is to be compared with the values $a_C^+/a_\chi = 4.6$ and $a_C^+/a_C^- = 1.4$, which have been obtained theoretically[20,21] for the $(n = 3, d = 3)$ Heisenberg universality class. Note that for the values $a_C^+ = -0.3$ and $a_C^- = 0.23$ used in Fig. 8 we obtain $a_C^+/a_C^- = -1.3$ which is opposite in sign but close in magnitude to the theoretical value. We conclude, therefore, that reliable values for the ratios a_χ/a_M, $a_C^\pm/a_\chi$, and a_C^+/a_C^- cannot be obtained from the present data.

The above results for the specific heat of copper ammonium bromide appear to be consistent with the theoretical predictions for the Heisenberg $(n = 3, d = 3)$ universality class, and with the results of Rives *et al.*, whose measurements for this material led to the values[23] $\alpha \simeq -0.1$ and $A_+/A_- \simeq 1.5$. It should be noted, however, that these authors analyzed their data using the confluent singularity formula in Eq. (9) but with $b_1 \equiv 0$, that is, with no linear term in the analytic background. In this connection, it is of interest to note the work of Ahlers and Kornblit[9] who, in their study of the specific heat of $(S = 7/2)$ europium oxide, made use of Eq. (9) both with the constraint $a_C^+ = a_C^- = 0$ and with $a_C^\pm$ treated as adjustable parameters. While the former constraint led to the values[9] $\alpha \simeq -0.044$ and $A_+/A_- \simeq 1.22$, the latter gave $\alpha \simeq -0.1$ and $A_+/A_- \simeq 1.52$, in closer agreement with the theoretical predictions for the Heisenberg universality class. The fact that these authors make use of a nonanalytic correction in their analysis, whereas

we essentially require no term of this kind to fit the specific heat of ($S = 1/2$) copper ammonium bromide, may be significant in the light of some earlier results for certain spin-S lattice models.[24]

IV. SUMMARY AND DISCUSSION

Our main goal has been to assess the ability of two correction to scaling formulas to represent the thermodynamic behavior of the ($S = 1/2$) Heisenberg ferromagnet copper ammonium bromide in an extended region about the critical point. As in the earlier nickel and europium oxide study,[4] our general conclusion is that, for certain parameter choices, both sets of formulas can be made to agree with the experimental data, although the phenomenology provides a better fit for the spontaneous magnetization and, overall, requires fewer parameters.

In our analysis, we have made use of both experimental and theoretical values for the critical exponents. When the exponents were fixed by their theoretical values, we found that the spontaneous magnetization and the specific heat could be fitted essentially *without* the use of a confluent $|t|^{\Delta_1}$ correction. However, for the theoretical value of γ, it was found that the zero-field susceptibility data requires a significant correction term of this type to secure an optimal fit.

While experimentally measured values for the critical exponents of the specific heat and the spontaneous magnetization of other materials belonging to this universality class also appear to be in fair agreement with their theoretical[13] counterparts, experimental values for the susceptibility exponent γ are often found[17] that are lower than the theoretical value of $\gamma = 1.39$. For the present case of copper ammonium bromide, experiment seems to prefer the value $\gamma = 1.31$ for which it was found that the phenomenology provides a better representation of the data than does the confluent singularity formula. By contrast, for the theoretical value $\gamma = 1.39$ it is the confluent singularity formula that agrees better with experiment. Furthermore, by extrapolating the quantity $t^{\gamma}T\chi_0$ towards the critical point as a function of T/T_C, we found that when $\gamma = 1.39$ there appeared a distinct downward curvature in the data very close to T_C which was absent for the case $\gamma = 1.31$. Thus, it would seem that either the value $\gamma = 1.39$ is too high for this material, or considering the very good agreement between Eq. (8) and the experimental data in Fig. 5, that significant irrelevant variable effects are present in the zero-field susceptibility.

A possible explanation for some of the differences between experimental and theoretical values for γ has been suggested[25] by Herzum *et al.* These authors argue that, although theoretical calculations can be carried out for *strictly* zero magnetic field, experimental measurements of the susceptibility usually involve the use of nonvanishing magnetic fields. In some cases, it seems, the data are extrapolated to zero field whereas in others they are not. In view of this, it is worth emphasizing that the susceptibility is only truly divergent at the critical point and that, in a neighborhood about the critical point not including the phase boundary and critical isochore, even a small magnetic field will suppress the singular behavior expected at the critical point. Thus, for $T = T_C$, a weak magnetic field will leave the susceptibility large and finite whereas, for temperatures just above T_C, the susceptibility may display a weaker apparent divergence than would be observed if the magnetic field were exactly zero. In support of their argument, the above authors cite the results of two neutron scattering experiments,[26] in which the susceptibilty is obtained directly from the differential scattering cross section, thereby obviating the use of a magnetic field.

The exponent values obtained from the two experiments cited above[25] are $\gamma \simeq 1.58$ and $\gamma \simeq 1.44$. Although these are higher than the theoretical value of $\gamma = 1.39$ and differ from this value by as much as some of the lower reported values,[17] other neutron scattering experiments[26,27] carried out more recently have yielded values for the exponent γ which are much closer to the theoretical value of 1.39. A list of γ values,[26] obtained by these methods, is given in Table I for three insulating materials believed to be good realizations of the Heisenberg model. Unfortunately, to our knowledge, no such value for copper ammonium bromide has appeared in the literature.

Interestingly, values for the susceptibility exponents of magnetic metals are found[27] still to be significantly lower than the predicted value for the Heisenberg model, even when the experiments are carried out for very small fields[28] and when the data are analyzed by taking into account the leading confluent singularity; three examples[28–30] are given in Table I. Collins[27] has suggested that, because of the presence of the conduction electrons, the predictions of the Heisenberg model need not apply to these systems and that the conductors listed in Table I might even belong to a different universality class than do the insulators listed in this table.

In a more speculative vein, we note that, in general, both of the corrections to scaling considered here are expected to be present[5,6] to a greater or lesser degree. Therefore, it is of particular interest to be able to make

TABLE I. Some experimental values for the susceptibility exponent γ. Values for three insulating ferromagnets are given in the first two columns while values for three magnetic metals are given on the right. The values for EuO, EuS, $RbMnF_3$, Fe, and Co were obtained from neutron scattering experiments whereas the value for Ni is taken from the results of neutron depolarization experiments carried out by Stüsser *et al.*

Material	γ	Material	γ
EuO	1.387 ± 0.036[a]	Ni	1.32 ± 0.02[b]
EuS	1.399 ± 0.040[a]	Fe	1.344 ± 0.018[c]
$RbMnF_3$	1.366 ± 0.024[a]	Co	1.23 ± 0.05[d]

[a]Ref. 26.
[b]Ref. 28.
[c]Ref. 29.
[d]Ref. 30.

comparisons with experiment using formulas that take into account both kinds of corrections. The availability of such formulas would thus enable experimental data to be analyzed with greater confidence over a broader temperature range about the critical region. We have begun to take steps toward this goal by reformulating the phenomenology to include the confluent power law corrections and we hope to report on this in the future.

[1] M. E. Fisher, in *Lecture Notes in Physics*, edited by F. J. W. Hahne (Springer-Verlag, Berlin, 1983), Vol. 186, pps. 1–139.

[2] D. S. Greywall and G. Ahlers, Phys. Rev. Lett. **28**, 1251 (1972); G. Ahlers and A. Kornblit, Phys. Rev. B **12**, 1938 (1975); A. Aharony and G. Ahlers, Phys. Rev. Lett. **44**, 782 (1980).

[3] M. E. Fisher and H. Au-Yang, J. Phys. A **12**, 1677 (1979).

[4] S. S. C. Burnett and S. Gartenhaus, Phys. Rev. B **43**, 591 (1991).

[5] M. E. Fisher, Rev. Mod. Phys. **46**, 597 (1974).

[6] F. J. Wegner, Phys. Rev. B **5**, 4229 (1972); in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, p. 7.

[7] S. Gartenhaus, Phys. Rev. B **23**, 4541 (1981); S. Gartenhaus and W. S. McCullough, *ibid.* **35**, 3299 (1987).

[8] A. Aharony and M. E. Fisher, Phys. Rev. Lett. **45**, 679 (1980); Phys. Rev. B **27**, 4394 (1983).

[9] G. Ahlers and A. Kornblit, Phys. Rev. B **12**, 1938 (1975).

[10] According to the phenomenology, the free energy contains a singular part, which obeys asymptotic scaling in the critical region, and an additive background, which is assumed to be analytic at the critical point. Thus, it is not possible in Eq. (5) for b_0 to be different on either side of the critical point.

[11] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, New York, 1980), Pt. I, Chap. XIV.

[12] J. F. Nicoll and P. C. Albright, Phys. Rev. B **31**, 4576 (1985); **34**, 1991 (1986).

[13] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980); J. Phys. (Paris) Lett. **46**, L137 (1985).

[14] R. F. Wielinga and W. J. Huiskamp, Physica **40**, 602 (1969).

[15] L. J. De Jongh, A. R. Miedema, and R. F. Wielinga, Physica **46**, 44 (1970).

[16] H. Suzuki and T. Watanabe, J. Phys. Soc. Jpn. **30**, 367 (1970).

[17] For a compilation of critical exponents, see K. Stierstadt, R. Anders, and W. von Hörsten, Phys. Dat. **20** (1984); C. Hohenemser, N. Rosov, and A. Kleinhammes, Hyperfine Interact. **49**, 267 (1989).

[18] The experimental data, which was obtained from the column labeled H_1^α in Table II of Ref. 15, is given in terms of the dimensionless quantity $C/T\chi_0$, where C is the Curie constant. For our purposes, C is simply an unknown multiplicative factor and the quantity C/χ_0, which appears in Figs. 2 and 4, is in units of K.

[19] The validity of the scaling relation in Eq. (10) assumes, of course, that the same value of T_C is used in the determination of each of the three exponents α, β, and γ. Because of the present uncertainty in the experimentally determined value for T_C, the choice $\alpha = -0.07$ is thus somewhat ambiguous.

[20] V. Privman, P. C. Hohenberg, and A. Aharony, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic, New York, 1991), Vol. 14, p. 1.

[21] H. J. Krause, R. Schloms, and V. Dohm, Z. Phys. B **79**, 287 (1990); R. Schloms and V. Dohm, *ibid.* **42**, 6142 (1990); C. Bervillier, *ibid.* **34**, 8141 (1986).

[22] To our knowledge, no theoretical value of the ratio a_χ/a_M for the ($n = 3$, $d = 3$) Heisenberg universality class has appeared in the literature.

[23] J. E. Rives, D. P. Landau, H. P. Lung, and H. S. Chandrasekhar, Physica **86-88**, 568 (1977).

[24] W. J. Camp and J. P. Van Dyke, J. Phys. A **9**, 731 (1976); Phys. Rev. B **11**, 2579 (1975); D. M. Saul, M. Wortis, and D. Jasnow, *ibid.* **11**, 2571 (1975); W. J. Camp, D. M. Saul, J. P. Van Dyke, and M. Wortis, *ibid.* **14**, 3990 (1976).

[25] N. Herzum, K. Stierstadt, and L. Wunsch, Phys. Status Solidi A **21**, 529 (1974).

[26] J. Als-Nielsen, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5a, p. 87.

[27] M. F. Collins, *Magnetic Critical Scattering* (Oxford University Press, New York, 1989).

[28] N. Stüsser, M. Th. Rekveldt, and T. Spruijt, J. Magn. Magn. Mater. **54–57**, 723 (1986).

[29] D. Bally, M. Popovici, M. Totia, B. Grabcev, and A. M. Lungu, Phys. Lett. **26A**, 396 (1968).

[30] C. J. Glinka, V. J. Minkiewicz, and L. Passell, Phys. Rev. B **16**, 4084 (1977).