Critical behavior in ferromagnetic $Fe[S_2CN(C_2H_5)_2]_2Cl$

Gary C. DeFotis and Spencer A. Pugh*
Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185
(Received 29 July 1981)

Magnetic-susceptibility and sublattice-magnetization data are analyzed with correction-to-scaling terms included. Critical exponents $\gamma = 1.165 \pm 0.03$ and $\beta = 0.245 \pm 0.02$ are deduced, with the assumption of modified power-law expressions $\chi_0 = \Gamma t^{-\gamma}(1 + a_\chi t^\Delta)$ and $m(T/T_C) = B|t|^\beta(1 + a_M|t|^\Delta)$ with $\Delta = 0.493$, $a_\chi = 0.207$, and $a_M = 0.156$. $\Gamma = 1.47 \pm 0.07$ emu/mole, or $\Gamma_r = 1.07 \pm 0.05$ for the reduced susceptibility, and $B = 1.30 \pm 0.05$ are also determined. Γ_r is larger than most theoretical estimates for the Ising model on various three-dimensional lattices. B is smaller than theoretical results. The amplitude ratio Γ_r/B is about 0.83, larger than theoretical values for this nonuniversal but only weakly lattice-dependent quantity. Heat-capacity data are sparse and less reliably analyzed, but suggest abnormally large values of α (> 0.3) and rather small values of A (0.2 to 0.5) in $C/R = At^{-\alpha} + B'$. Including a correction-to-scaling term does not alter this conclusion. The ratio $R_C = AB^{-2}\Gamma_r$ is in the range 0.12 to 0.33, substantially less than theoretical values for this universal quantity. A straightforward explanation for the unusual critical behavior is not apparent.

The insulating compound $Fe[S_2CN(C_2H_5)_2]_2Cl$ is one of the few systems which appears to be describable as a (three-dimensional) 3D Ising ferromagnet. Evidence for this is found in the extreme anisotropy of the single crystal susceptibility,[1] in magnetization and NMR data,[2] and in heat-capacity data.[3] The detailed critical behavior is of particular interest. Susceptibility[4] and NMR[2] data appear to be consistent only with critical exponents γ and β strongly shifted from established theoretical values for the 3D Ising model. This applies also to the critical amplitudes Γ and B in the power laws

$$\chi_0 = \Gamma t^{-\gamma} , \tag{1}$$

$$m(T/T_C) = M(T)/M(0) = B|t|^\beta , \tag{2}$$

where $t = (T - T_C)/T_C$ and where χ_0 is the zero-field susceptibility corrected for demagnetization. Experimental and theoretical[5-8] values of these parameters are summarized in Table I. Possible explanations for the shifted exponents have been considered: dipole-dipole interactions, randomness, temperature-dependent effective spin value, multispin exchange interactions, and nondiverging antiferromagnetic contributions to the susceptibility.[1,2,4] In mixed crystals, $Fe[S_2CN(C_2H_5)_2]_2Cl_xBr_{1-x}$ {the diluent $Fe[S_2CN(C_2H_5)_2]_2Br$ is, when pure, paramagnetic but magnetically disordered to below 0.34 K (Ref. 9)} similar values of γ are observed.[1] The concentration dependence of the critical exponent is small and of uncertain significance. However, a randomization of exchange couplings or of single ion anisotropies in the mixed crystals could be responsible for exponent shifts relative to the pure system. The critical amplitude Γ exhibits a definite increase with decreasing chloride concentration.

Much attention has been paid recently to the effects of confluent singularities and associated correction-to-scaling (CTS) terms in the analysis of critical phenomena.[10,11] Such terms modify the asymptotic power-law behavior, and can be significant for data not very close to the critical temperature. They may be important for the data on the systems considered here. In this paper we study the effects on critical exponents and critical amplitudes in $Fe[S_2CN(C_2H_5)_2]_2Cl$ upon including CTS terms in analysis, and we compare the observed amplitudes and their ratios with existing theory. With CTS terms included Eqs. (1) and (2) become

$$\chi_0 = \Gamma t^{-\gamma}(1 + a_\chi t^\Delta) , \tag{3}$$

$$m = B|t|^\beta(1 + a_M|t|^\Delta) . \tag{4}$$

The correction exponent Δ is believed to depend only on the universality class, and the best available estimate in the case of the 3D Ising model appears to be[8] $\Delta = 0.493 \pm 0.007$. The CTS amplitudes a_χ and a_M are probably less well established. The value $a_\chi = 0.207 \pm 0.003$ for the $S = 3/2$ 3D Ising model has been obtained in one calculation.[12] Here the probably too large value $\Delta = 0.575$ was assumed, and it appears that a somewhat smaller value of a_χ would result on assuming a smaller value of Δ. CTS effects on critical exponents would probably then be less important. To estimate the value of a_M we make use of the recently established relation between the correc-

TABLE I. Data fitting for critical exponents and amplitudes in $Fe[S_2CN(C_2H_5)_2]_2Cl$, and comparison with theory.

System	γ	Γ (emu/mole)	β	B	T_C (K)	$\lvert t\rvert_{min}$	$\lvert t\rvert_{max}$
$Fe[S_2CN(C_2H_5)_2]_2Cl$, without CTS.							
Sample a	1.142 (8)[a]	1.642 (26)			2.457 (<1)	0.0041	0.301
Sample b	1.125 (6)	1.724 (22)			2.456 (<1)	0.0045	0.469
Sample c			0.265 (3)	1.432 (3)	2.457 Fixed	0.059	0.122
$Fe[S_2CN(C_2H_5)_2]_2Cl$, with CTS ($\Delta=0.493, a_X=0.207, a_M=0.156$).							
Sample a	1.175 (7)	1.426 (22)			2.457 (<1)	0.0041	0.301
Sample b	1.155 (9)	1.510 (29)			2.456 (<1)	0.0045	0.287[b]
Sample c			0.245 (3)	1.299 (3)	2.457 Fixed	0.059	0.122
$Fe[S_2CN(C_2H_5)_2]_2Cl_{0.712}Br_{0.288}$							
Without CTS	1.163 (3)	1.721 (9)			2.213 (<1)	0.012	0.398
With CTS	1.204 (4)	1.474 (9)			2.212 (<1)	0.012	0.398
3D Ising model, pure pair interactions between near neighbors; from high-T series expansions.							
	1.250 (+3, −7)[c]	1.605 (1)d[d]	0.312 (4)[e]	1.6684 (16)d[d]			
		1.449 (1)sc		1.5696 (3)sc			
		1.349 (4)bcc		1.5059 (10)bcc			
		1.330 (3)fcc		1.4861 (13)fcc			
3D Ising model, pure pair interactions between near neighbors; from renormalization group.							
	1.2402 (9)[f]		0.325 (1)[f]				

[a]Numbers in parentheses are uncertainties in last decimal place(s), from standard deviations in parameters returned by fitting programs, or uncertainties in theoretical results.
[b]A few high-temperature data points, which do not significantly affect the fit or the derived parameters, were neglected.
[c]Reference 5.
[d]Reference 6. Regarding these theoretical Γ, see text.
[e]Reference 7.
[f]Reference 8.

tion amplitudes[10]

$$a_M/a_\chi = -(\beta-\beta^0)/(\gamma-\gamma^0) \ , \tag{5}$$

where β^0 and γ^0 are mean-field theory values, $\gamma^0=1$ and $\beta^0=0.5$. There results $a_M/a_\chi=0.75$. The value $a_\chi=0.207$ will be assumed, and therefore $a_M=0.156$. In anticipation of the essential results of this report it can be observed that if CTS terms are important but neglected, then the exponents obtained from the fitting procedure are effective values, β' and γ'. These satisfy the relation[10]

$$a_M/a_\chi = -(\beta'-\beta)/(\gamma'-\gamma) \ . \tag{6}$$

Since the ratio is positive (both $a_M, a_\chi > 0$), a shift toward higher values of γ ($\gamma' < \gamma$) should be accompanied by a shift toward lower values of $\beta (\beta' > \beta)$ on incorporating CTS. For $Fe[S_2CN(C_2H_5)_2]_2Cl$ both γ' and β' are less than the theoretical values for the 3D Ising model, and a simultaneous improvement cannot be effected.

Except for the inclusion of CTS terms, the fitting procedures were similar to those previously described.[2,4] In the case of susceptibility a_χ and Δ were first assigned the fixed values referred to and optimal values for the critical exponent, critical amplitude and T_C were obtained by a nonlinear least-squares fitting program. The best parameter values for two crystals, a and b, of $Fe[S_2CN(C_2H_5)_2]_2Cl$ are given in Table I and corresponding plots exhibited in Fig. 1. Because of the presence of the CTS term, the fitted curves are not perfectly straight lines on a log χ_0 versus log t plot, but the curvature is slight. The quality of the fit is only slightly better than when CTS is neglected. Including CTS leaves T_C essentially unchanged but increases γ slightly, while decreasing Γ. The increase in γ is much less than that necessary to bring it into agreement with the 3D Ising-model theoretical value, 1.25. The consequences of allowing a_χ to vary between 0.15 and 0.35 were also investigated. No improvement in the fit results for any value of a_χ. But the parameters are highly correlated, and a theoretically unjustified $a_\chi=0.90$ leads to $\gamma \approx 1.25$, $\Gamma \approx 1.0$ emu/mole, $T_C \approx 2.45$ K, and a reasonable fit. This is not considered significant. Nor do the parameters obtained depend significantly on the range of temperature included in the fit, though there is a small tendency toward larger γ as t_{max} increases. The data are accounted for to rather large values of t and yet, as noted, γ is only slightly enhanced over its value neglecting CTS. Including a CTS term with $a_\chi=0.207$ in fitting the susceptibility of the 71% Cl mixed crystal leads to a significantly poorer quality fit, while leaving T_C essentially unchanged, decreasing Γ and increasing γ some. The latter is still much lower than the value 1.25. Absolute uncertainties in γ and Γ, from uncertainties in a_χ and other sources, are of the order 0.03 and 0.10,

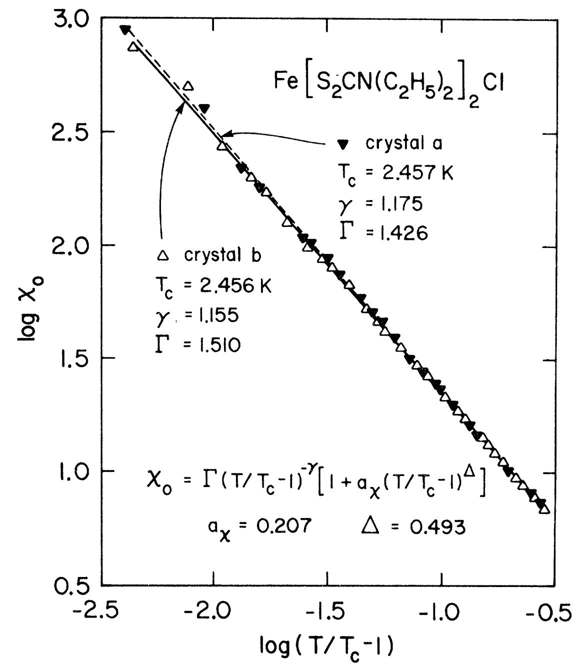

FIG. 1. Initial susceptibility of $Fe[S_2CN(C_2H_5)_2]_2Cl$ as a function of temperature, and critical parameters characterizing the data when corrections to scaling are considered. Relative experimental uncertainty is within or comparable with symbol size.

respectively, somewhat larger than the statistical uncertainties returned by the fitting program.

The NMR-derived magnetization data are exhibited graphically in Fig. 2 (see also Table I). The frequency ratio has been divided by $(1+a_M|t|^\Delta)$, with $a_M=0.156$. The slope of the straight line passing through data between 2.158 and 2.312 K is, as anticipated above, slightly less than that obtained when CTS is neglected. The exponent does not shift toward the 3D Ising-model prediction. The value of B is smaller than before. Absolute uncertainties in β and B, from uncertainties in a_M and other sources, are of the order 0.02 and 0.05, respectively. The minimum value of $|t|$ in the fitting procedure for β is, according to one criterion,[13] insufficiently small to permit a reliable exponent to be deduced. However, in fitting the magnetization data we have avoided treating T_C as a parameter, fixing it instead at a value obtained from the (completely independent) susceptibility data. The approach of the data to a straight line in Fig. 2 for $T > 2.158$ K ($|t| < |t|_{max}$) is also very clear. Deleting lower-temperature data in the temperature range of the fit (reducing $|t|_{max}$) does not significantly affect the derived exponent. As in the case of the susceptibility data, critical behavior of an essentially power-law form does appear to persist to $|t|_{max}$ values larger than usual. This may be one

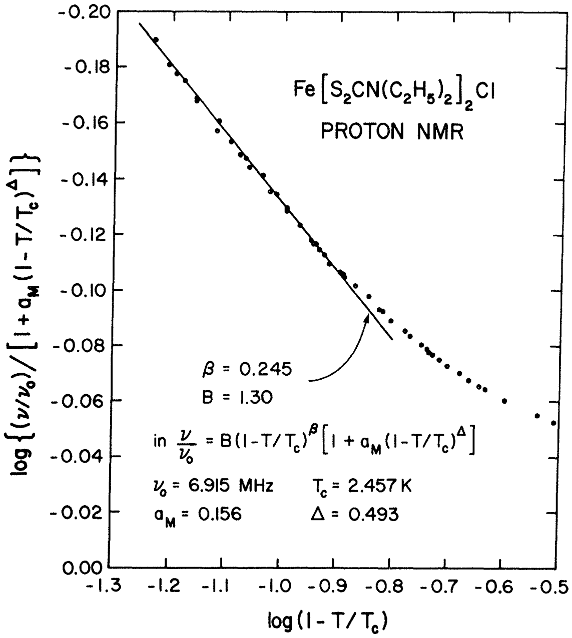

FIG. 2. Temperature dependence of reduced magnetization in $Fe[S_2CN(C_2H_5)_2]_2Cl$ from a proton resonance frequency, and critical parameters characterizing the data when corrections to scaling are considered. Relative experimental uncertainty is within or comparable with symbol size.

more indication of the unusual nature of this system.

The present results indicate that the inclusion of CTS terms in the analysis of critical behavior in $Fe[S_2CN(C_2H_5)_2]_2Cl$: (a) does not significantly improve the quality of fit beyond that obtained with the asymptotic power-law forms, (b) does not lead to exponents much more consistent with theoretical values for the simple 3D Ising model, and (c) does not (cannot) simultaneously shift both γ and β nearer such values. The critical amplitude B is substantially less than any available theoretical prediction for the Ising model on 3D lattices.[6] This is accentuated when a CTS term is introduced. The depression of B may be partly due to S being greater than one-half, but it seems unlikely that this can be responsible for the entire effect. Theoretical values for the critical amplitude of the high-temperature susceptibility[6] have been calculated using a form $\chi_r = C_0^+ t^{-\gamma}$, where $\chi_r = kT\chi_0/\mu^2$, χ_0 is the initial susceptibility per spin and μ is the moment of a single spin ($g\mu_B S$). Results are $C_0^+ = 1.1717$ (7), 1.058 (1), 0.985 (3), and 0.971 (2) on the diamond, sc, bcc, and fcc lattices, respectively. In the present work the molar initial susceptibility, $N\chi_0$, has been fitted. To compare our Γ with theoretical C_0^+ we multiply the latter by $N(3\mu_B)^2/kT = 1.37$, on taking $T = T_C \approx 2.46$ K. This gives the theoretical values of Γ in Table I. The experimental Γ are consistently larger than the theoretical except for the diamond lattice. Since the data fitting spans the range from T_C to $\sim 1.3T_C$ it may be preferable to employ a mean temperature larger than 2.46 K in this comparison. In this case all the theoretical Γ would be much less than those observed.

Theoretical discussions[14] have established the probable universality (analogous to that for exponents) of four ratios among six critical amplitudes: A/A', Γ/Γ', $R_\chi = \Gamma_r DB^{\delta-1}$, and $R_C = AB^{-2}\Gamma_r$. A is the heat-capacity amplitude and D is that for the critical isotherm, with exponent δ. Here Γ_r is the amplitude for the reduced susceptibility, corresponding to C_0^+ and not our experimental Γ. As usual primes refer to the $T < T_C$ regime for the susceptibility and the heat capacity. Γ' is not accessible in $Fe[S_2CN(C_2H_5)_2]_2Cl$ and the critical isotherm has not been measured. It is quite possible that the available heat-capacity data are insufficient for the reliable extraction of a critical exponent and critical amplitude, though we shall pursue this further on. Before making any direct comparisons with theoretical, universal, amplitude ratios we first note the following. The ratio C_0^+/B assumes the values 0.702, 0.674, 0.654, and 0.653 for the Ising model on the diamond, sc, bcc, and fcc lattices, respectively, employing the results of Ref. 6. The lattice dependence of this nonuniversal ratio appears then to be weak. Neglecting CTS the mean value of Γ for crystals a and b is 1.68, and with CTS it is 1.47. Dividing these by 1.37 (to obtain Γ_r) and by the experimental values of B, we obtain $\Gamma_r/B = 0.86$ without CTS and 0.83 with CTS. If a value of T larger than 2.46 K had been used earlier the factor 1.37 would be smaller, Γ_r larger, and Γ_r/B larger also. The experimental ratio is larger than those of the Ising model on various 3D lattices, and by more than the experimental uncertainty of about 0.07. It is also somewhat larger than ratios for the 2D Ising model[15] (0.7875 on a square lattice) and much larger than ratios for the 3D Heisenberg model[14] (0.229 on a bcc lattice).

In order to deduce the critical exponent α' for the low-temperature heat-capacity, data in a very narrow region below $T_C(|t|_{\max} = 10^{-3}$ or less) are needed. These are unavailable for $Fe[S_2CN(C_2H_5)_2]_2Cl$. The situation is more favorable above T_C, where the asymptotic critical region can extend well beyond $t_{\max} = 10^{-2}$. The present system exhibits a larger than normal critical region for χ_0 and for m, and might be expected to do so for C as well. Assuming $T_C = 2.457$ K, there are available one datum at $t = 0.003\,26$, four more data within about $t = 0.1$ of T_C and seven more within about $t = 0.23$ of T_C. Lattice and Schottky contributions can be estimated[1] and subtracted from the observed heat capacity to obtain the exchange-only, magnetic heat capacity above T_C. Assuming a power-law form $C/R = At^{-\alpha}$ and taking $T_C = 2.457$ K, one finds that the 12 data up to $t = 0.23$ are reasonably distributed about a straight line on a log C versus log t plot. Data at higher temperatures deviate systematically below this line. The resulting critical parameters are $\alpha = 0.41_7$ and $A = 0.18_2$. The three lowest-temperature data deviate most from the line, but this appears to be experimental scatter rather than a systematic effect. Theoretical values for A are in the range 1.08 to 1.13 for the 3D Ising model,[16] though here an additive constant B', of the same order of magnitude as A but negative, also appears. Alternatively, we have tried analyzing the data by assuming $T_C = 2.457$ K and the validity of the scaling condition $\alpha = 2 - 2\beta - \gamma$, yielding $\alpha = 0.34$ on employing the CTS results for γ and β, taking a mean $\gamma = 1.165$. C/R is plotted against $t^{-\alpha}$. The data are well distributed about a straight line, and the values $A = 0.29_3$ and $B = -0.15_7$ result. C is reproduced to within 2% typically between 2.707 and 3.025 K, and at 2.465 K. Data at 2.518 and 2.584 K deviate by about 11%, but oppositely so and therefore presumably due to experimental scatter. Corrections-to-scaling can be included by associating a factor with the A term, $C/R = At^{-\alpha}(1 + a_C t^{\Delta}) + B'$. From a formula analogous to Eq. (5) one calculates $a_C/a_\chi = 0.50$, and therefore $a_C = 0.104$. Proceeding as above, with $T_C = 2.457$ K and $\alpha = 0.34$ fixed, one obtains $A = 0.29_6$ and $B' = -0.18_4$. The fit is of about the same quality as without CTS. We have also attempted to analyze the data via a cubic spline approximation, followed by analytical differentiation.[17] This allows B' to be eliminated and A and α to be determined from a $\log(dC/dT)$ versus $\log t$ plot. But the sparseness of the data renders the fitting procedure and resulting derivatives rather inaccurate, and no clearly meaningful straight line of data is evident on the plot. A line corresponding to $\alpha = 0.34$ is a fair approximation in the restricted temperature interval 2.495 to 2.550 K. The corresponding amplitudes are $A = 0.52$ and $B' = -0.85$. However, only the data at 2.518 and 2.584 K are well accounted for. In the attempts at fitting the heat capacity, as with the reduced magnetization earlier, $T_C = 2.457$ K has been assumed. This is because the χ_0 analysis is believed to determine this parameter most reliably, and because it is generally advisable not to vary too many parameters at once, especially T_C, in a critical law fit. Nor in the details of the analysis did it appear that a shift in T_C would lead to better agreement. Despite the inconclusive results, indications are that α is substantially larger than the 3D Ising model value 0.125, and that the critical amplitude A is substantially smaller than theoretical predictions. If one takes the values $A = 0.18$ and $A = 0.52$ as extremes, then the ratio $R_C = AB^{-2}\Gamma_r$ is between 0.12 and 0.33 with an uncertainty of about 0.05 resulting from that in $B^{-2}\Gamma_r$. This is substantially smaller than the theoretical values 0.4748, 0.4745, 0.4735, and 0.4749 for the Ising model on the diamond, sc, bcc, and fcc lattices, obtained from the results in Refs. 6 and 16.

In view of these results, crystalline $Fe[S_2CN(C_2H_5)_2]_2Cl$ appears to present a challenge to theory, and may constitute a system in which a new universality class, related to the 3D Ising model, is realized. Of the possible sources of the unusual critical behavior, listed earlier, multispin interactions or a nondiverging antiferromagnetic contribution to the observed susceptibility initially appeared to be the most plausible. Series expansion analysis had suggested that the exponents β and γ', and presumably also γ, are shifted to lower values by such interactions, and moreover that the parametric dependence of these exponents appeared to violate universality.[18] However, these conclusions have been questioned,[19] and evidence presented[20] that multispin interactions lead to a first order rather than a continuous transition when no pair interactions are present. When pair interactions also operate they are expected to dominate the critical behavior, so that shifted exponents do not occur although amplitudes may be changed.[21] Nor is the presence of next-nearest-neighbor interactions, common in real materials and presumably present in $Fe[S_2CN(C_2H_5)_2]_2Cl$, believed to lead to shifted exponents.[22,23] However, certain 2D Ising models involving such interactions,[24] or on special lattices,[25] appear to be equivalent to models (Baxter or Ashkin-Teller) in which universality is violated and new exponents occur. Possibly the verdict in three dimensions should not be considered settled.

We had suggested[1,4] that nondiverging antiferromagnetic (AF) contributions to the susceptibility, which might arise due to the canted spin arrangement and which would tend to depress γ, could be responsible for the lowered exponent. However, it does not appear possible to construct a plausible AF-like susceptibility which can account for the shift in γ. Starting from the observed susceptibilities, rather large nondiverging contributions which increase strongly with decreasing temperature (2.8 emu/mole at 3.20 K, 5.7 emu/mole at 2.80 K, 12.1 emu/mole at 2.60 K) would need to be postulated. These do not appear reasonable. Moreover, the lowered value of β for the sublattice magnetization below T_C would remain unexplained. Nevertheless, the canted spin arrangement is a complicating feature and the model adopted in making the above estimates may be too simple. More detailed theoretical study and additional experiments (precise heat-capacity measurements near T_C and neutron scattering) would appear to be called for on this system.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research.

*Now at Department of Chemistry, Stanford University, Stanford, Cal. 94305.

[1]G. C. DeFotis, F. Palacio, and R. L. Carlin, Phys. Rev. B 20, 2945 (1979).
[2]G. C. DeFotis and J. A. Cowen, J. Chem. Phys. 73, 2120 (1980).
[3]N. Arai, M. Sorai, H. Suga, and S. Seki, J. Phys. Chem. Solids 38, 1341 (1977).
[4]G. C. DeFotis, F. Palacio, and R. L. Carlin, Physica 95B, 380 (1978).
[5]W. J. Camp and J. P. Van Dyke, Phys. Rev. B 11, 2579 (1975); see also D. S. Gaunt and M. F. Sykes, J. Phys. A 12, L25 (1979); S. McKenzie, *ibid.* 12, L185 (1979).
[6]A. J. Guttmann, J. Phys. A 8, 1249 (1975).
[7]D. S. Gaunt and A. J. Guttmann, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1974), Vol. 3, p. 223.
[8]J. C. LeGuillou and J. Zinn-Justin, Phys. Rev. Lett. 39, 95 (1977).
[9]G. E. Chapps, S. W. McCann, H. H. Wickman, and R. C. Sherwood, J. Chem. Phys. 60, 990 (1974).
[10]A. Aharony and G. Ahlers, Phys. Rev. Lett. 44, 782 (1980).
[11]J. T. Ho, Phys. Rev. B 22, 467 (1980); 23, 434 (1981).
[12]M. Ferer, Phys. Rev. B 16, 419 (1977).
[13]R. M. Suter and C. Hohenemser, J. Appl. Phys. 50, 1814 (1979).
[14]A. Aharony and P. C. Hohenberg, Phys. Rev. B 13, 3081 (1976).
[15]A. J. Guttmann, J. Phys. A 8, 1236 (1975).
[16]A. J. Guttmann, J. Phys. C 8, 4051 (1975).
[17]A. J. Guttmann, J. Phys. C 8, 4037 (1975).
[18]H. P. Griffiths and D. W. Wood, J. Phys. C 6, 2533 (1973); 7, 4021 (1974); D. W. Wood and H. P. Griffiths, *ibid.* 7, 1417 (1974).
[19]M. Gitterman and M. Mikulinsky, J. Phys. C 10, 4073 (1977).
[20]O. G. Mouritsen, S. J. Knak Jensen, and B. Brank, Phys. Rev. B 23, 976 (1981).
[21]J. Ho-Ting-Hun and J. Oitmaa, J. Phys. A 9, 2125 (1976).
[22]G. Paul and H. E. Stanley, Phys. Rev. B 5, 3715 (1972).
[23]I. C. Enting, J. Phys. C 7, 1237 (1974).
[24]K. Jüngling, J. Phys. C 9, L1 (1976).
[25]K. Jüngling, J. Phys. C 8, L169 (1975); 9, L139 (1976).