# A first-order phase transition in the face-centered-cubic Ising antiferromagnet

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The nearest-neighbor antiferromagnetic Ising model on a face-centered-cubic lattice and in zero magnetic field is investigated by the methods of series analysis. The low-temperature free-energy series is extended to seventh order. Low- and high-temperature free energies are extrapolated and their crossing locates a first-order phase transition at temperature 1.746 (±0.3%) in units of the nearest-neighbor coupling constant. The energy, susceptibility, and staggered magnetization are also investigated. A "second-order Clausius-Clapeyron" equation is derived which enables the curvature of the phase coexistence line to be determined from the above data.

## I. INTRODUCTION

The best understood first-order phase transitions are those in which the two coexisting phases are related by a symmetry operation. Such a transition occurs in, for example, a ferromagnet when the magnetic field vanishes at sufficiently low temperatures (i.e., less than the critical temperature), because the phase approached through positive fields is the mirror image of the phase approached through negative fields. This paper deals with the less well understood problem of first-order transitions which lack such symmetry. Specifically, we study the nearest-neighbor spin-$\frac{1}{2}$ Ising antiferromagnet on a face-centered-cubic lattice, which exhibits a first-order transition as temperature is varied at constant field. We attack the problem using the methods of series analysis.

The fcc Ising antiferromagnet presents interesting unsolved problems at all values of the temperature $T$ and the magnetic field $H$. However, because it is difficult to produce arbitrary-field high-temperature series expansions, our study is restricted to zero field. The $H=0$ free energy can be extrapolated from high- and low-temperature series with high precision: the estimated error is at worst 0.07%. The crossing of the high- and low-temperature free-energy curves locates the transition temperature, and once this is known other series can be extrapolated to yield any desired thermodynamic property of the transition: the change in energy, the change in susceptibility, even the curvature of the first-order line in the $(H,T)$ plane. These properties do not extrapolate as precisely as the free energy does, and their estimated errors range from 2% to 8%.

The fcc Ising antiferromagnet has been intensively studied, in part because it models such important binary alloys as copper gold. It has been subjected to such theoretical tools as the cluster variation method,[1–4] series analysis,[5–10] position-space renormalization group,[11] and Monte Carlo simulation.[12–19] (Reference 4 is a useful review. Much of this work concerns the model in general magnetic fields.) Needless to say, no exact solution has been forthcoming. Even the existence of a first-order transition, although universally accepted, remains unproven. The studies most relevant to our own are the series extrapolations of Liu *et al.*,[8] and the Monte Carlo simulations of Polgreen.[18] Liu *et al.* present a series analysis of the zero-field problem quite similar to our own work. We improve upon their study by deriving one additional term in the low-temperature free-energy expansion, by using McKenzie's additional term[20] in the high-temperature free-energy expansion, and by extrapolating the series using differential as well as Padé approximants. Liu *et al.* use only Padé (rational) approximants, which approximate the thermodynamic functions poorly near the spinodal singularity.[21] Because the first-order transition is reached long before the spinodal, this is not a serious difficulty. Nevertheless, the use of differential as well as Padé approximants increases the number of approximants obtainable from a given series, and the close agreement of many approximants increases ones confidence in the resulting estimates. Polgreen has used a special purpose computer to perform very high precision Monte Carlo simulations of the zero-field fcc Ising antiferromagnet. His estimates for the transition parameters are similar to, but inconsistent with, our own.

In outline, this paper proceeds as follows. Section II discusses the derivation of low-temperature expansions for the free energy and other thermodynamic properties. Section III uses this free-energy expansion, together with a published high-temperature expansion, to locate the transition temperature. Section IV produces numerical estimates for the thermodynamic properties of the first-order transition by comparing low- and high-temperature extrapolations. Finally Sec. V compares our results with those of other approaches. An appendix derives a Clausius-Clapeyron-like equation which permits determination of the curvature of the two phase coexistence line from zero-field thermodynamic data.

## II. DERIVATION OF LOW-TEMPERATURE EXPANSIONS

In the usual method for deriving low-temperature series (the "primitive method" of Domb[22]), one first determines the ground state and then perturbs that ground state by

 

overturning small numbers of spins. When this method is applied to the fcc Ising antiferromagnet, difficulties arise at the very first stage. If the lattice portion considered is a cube $L$ conventional unit cells on an edge (thus with $N=4L^3$ points), there are $O(2^{2L})$ different ground states.[23] Which of these many states should be perturbed to produce low-temperature expansions? A reasonable guess is that all of them should be used, and that the many resulting expansions should be averaged giving equal weight to each ground state.[6,7] This method is appealing, but it is wrong. Slawny[24] has conjectured, and Slawny and Bricmont[25] have proven, that in situations such as ours the correct expansion is produced by perturbing only those ground states which have the greatest number of low-energy excitations, the so-called "dominant" ground states.

In the case at hand, the dominant ground states are most easily described by dissecting the fcc lattice into four interpenetrating simple-cubic sublattices. In the dominant ground states two of the four sublattices are occupied by up-spins and two by down-spins. This is the metallurgist's $AB$ or $L1_0$ structure (sometimes called the $\beta$ phase[5,9]). There are six such dominant states, reflecting the $6=(4)(3)/2!$ ways of selecting two sublattices out of four. A different but equivalent description of the dominant ground states is obtained by dissecting the fcc lattice into stacked planes of square lattice. (If the fcc lattice has the conventional lattice constant $a$, then these planes have lattice constant $a/\sqrt{2}$ and are stacked with spacing $a/2$.) In this description, dominant states consist of fully magnetized planes stacked alternately (all spins up, all spins down, up, down, up, down, etc.).

Once the dominant ground state is obtained, generation of the low-temperature free-energy expansion is straightforward but extremely tedious. To fix the notation, we define the Hamiltonian

$$\mathscr{H}=J\sum_{\langle i,j\rangle}\sigma_i\sigma_j-mH_A\sum_k\sigma_k-mH_B\sum_l\sigma_l\ , \tag{1}$$

where $\sigma_i=\pm1$. The first summation extends over nearest-neighbor pairs, the second summation extends over the sites of those two sublattices which are, in the ground state, occupied by up-spins (the "up" or "$A$" sublattices), and the third over the remaining "down" (or "$B$") sublattices. Although both magnetic fields $H_A$ and $H_B$ will ultimately vanish, they are needed at this point to permit the derivation of staggered magnetizations and susceptibilities. In terms of the variables

$$x=e^{-4J/k_BT},\ y_A=e^{-2mH_A/k_BT},\ \text{and}\ y_B=e^{-2mH_B/k_BT}\ , \tag{2}$$

the free energy per site is

$$f(T,H_A,H_B)=-2J-\tfrac{1}{2}mH_A+\tfrac{1}{2}mH_B-k_BTg(x,y_A,y_B)\ , \tag{3}$$

where

$$\begin{aligned}g(x,y_A,y_B)=\ & x^2[\tfrac{1}{2}(y_A+y_B^{-1})]+x^3[4y_Ay_B^{-1}]+x^4[-\tfrac{5}{4}(y_A^2+y_B^{-2})+10(y_A^2y_B^{-1}+y_Ay_B^{-2})+2y_A^2y_B^{-2}-4y_Ay_B^{-1}]\\
&+x^5[\,8(y_A^3y_B^{-1}+y_Ay_B^{-3})+(y_A^2+y_B^{-2})+12(y_A^3y_B^{-2}+y_A^2y_B^{-3})-36(y_A^2y_B^{-1}+y_Ay_B^{-2})+4y_A^3y_B^{-3}+100y_A^2y_B^{-2}]\\
&+x^6[\,2(y_A^4y_B^{-1}+y_Ay_B^{-4})+5\tfrac{1}{6}(y_A^3+y_B^{-3})+26(y_A^4y_B^{-2}+y_A^2y_B^{-4})-104(y_A^3y_B^{-1}+y_Ay_B^{-3})\\
&\quad+(y_A^5y_B^{-4}+y_A^4y_B^{-5})+31(y_A^4y_B^{-3}+y_A^3y_B^{-4})+342(y_A^3y_B^{-2}+y_A^2y_B^{-3})+38(y_A^2y_B^{-1}+y_Ay_B^{-2})\\
&\quad+12y_A^4y_B^{-4}+204y_A^3y_B^{-3}-476y_A^2y_B^{-2}]\\
&+x^7[\,20(y_A^5y_B^{-2}+y_A^2y_B^{-5})-104(y_A^4y_B^{-1}+y_Ay_B^{-4})-8(y_A^3+y_B^{-3})\\
&\quad+4(y_A^6y_B^{-4}+y_A^4y_B^{-6})+88(y_A^5y_B^{-3}+y_A^3y_B^{-5})+437(y_A^4y_B^{-2}+y_A^2y_B^{-4})\\
&\quad+340(y_A^3y_B^{-1}+y_Ay_B^{-3})+8(y_A^6y_B^{-5}+y_A^5y_B^{-6})+108(y_A^5y_B^{-4}+y_A^4y_B^{-5})\\
&\quad+1156(y_A^4y_B^{-3}+y_A^3y_B^{-4})-2956(y_A^3y_B^{-2}+y_A^2y_B^{-3})-12(y_A^2y_B^{-1}+y_Ay_B^{-2})+60y_A^5y_B^{-5}\\
&\quad+656y_A^4y_B^{-4}+3032y_A^3y_B^{-3}+820y_A^2y_B^{-2}]+O(x^8)\ .\end{aligned} \tag{4}$$

This expansion was obtained simply by overturning spins from the dominant $L1_0$ ground state. Disconnected clusters of overturned spins were counted by hand. Connected clusters were counted by computer using a variant of the backtrack algorithm,[26] except for those few (to be precise, three) relevant connected clusters with more than ten vertices, which were counted by hand. This series was derived to order $x^6$ by Liu *et al.*,[8] and the zero-field version was independently derived (with a small error) to order $x^6$ by Mackenzie and Young.[9]

Low-temperature series for all thermodynamic properties of the model can be obtained from (4). We shall study, in addition to the free energy, the zero-field energy (all quantities are per site):

$$E(x)/J=-2+8x^2+48x^3+248x^4+1480x^5+10\,136x^6+76\,440x^7+\ldots\ , \tag{5}$$

the susceptibility

$$\chi(x)(k_BT/m^2)=4x^2+40x^4+96x^5+1316x^6+7616x^7+\ldots\ , \tag{6}$$

and the staggered magnetization

$$M^{\dagger}(x)/m \equiv -\left[\frac{\partial f}{\partial H_A}-\frac{\partial f}{\partial H_B}\right]\Big/ m = \frac{1}{N}\left\langle \sum_k \sigma_k - \sum_l \sigma_l \right\rangle$$
$$= 1-2x^2-16x^3-110x^4-792x^5$$
$$-6094x^6-49\,272x^7-\ldots . \quad (7)$$

[The first summation in (7) extends over the $A$ sublattices, the second summation extends over the $B$ sublattices, cf. Eq. (1).]

## III. LOCATION OF THE TRANSITION TEMPERATURE

The expansions of the preceding section would be directly useful if the fcc Ising antiferromagnet suffered a critical transition to the disordered phase. However, the transition is first order and must be investigated by comparing high- and low-temperature extrapolations. In particular, the transition temperature can be estimated as follows: Form approximants to the high-temperature free energy and evaluate them at a selected temperature near the transition point. Use these estimates to decide on a probable range of values for the free energy at the selected temperature, and choose an approximant at either end of the range to form effective bounds on the free energy of the disordered phase. Repeat this procedure using the low-temperature expansion to find effective bounds on the free energy of the ordered phase. Plot both pairs of bounds and use their crossing to establish the transition temperature. The remainder of this section merely details the above procedure.

The high-temperature free-energy series has been derived to 14th order by Sykes *et al.*[27] and extended to 15th order by McKenzie.[20] (Note that McKenzie presents a 14th-order series for the energy. The 15th term in the free-energy expansion can be found from these data using Eq. (1.40c) of Domb:[22] in his notation, it is $a_{15}^{(Q)}=505\,350\,753\,785\frac{3}{5}$. Although this expansion was developed with the ferromagnetic problem in mind, the free energy is analytic at $J/k_BT=0$, so it can be applied to the antiferromagnetic problem by changing the sign of $J$.

We have extrapolated the high-temperature free-energy series down to $k_BT/J=1.74$, which is near the transition temperatures reported by previous workers. Six different classes of approximants were used to effect the extrapolation. The first two are standard Dlog Padé[28] approximants and inhomogeneous differential[29] (or "integral curve"[30]) approximants (IDA's). The remaining four classes take advantage of the well-studied ferromagnetic singularity, where $f(T)\sim |T-T_c|^{2-\alpha}$. The critical temperature has been accurately located by McKenzie[31] at $\tanh(J/k_BT_c)=-0.101\,724$ (with an uncertainty of 50 parts per million), and Sykes *et al.*[27] have concluded that $\alpha=\frac{1}{8}$. While it is unlikely that this result for the exponent is exactly correct,[32,33] it is surely accurate numerically. The third and fourth classes of approximants are thus Dlog Padé approximants and IDA's with the ferromagnetic singularity fixed[29] at the above location, while the fifth and sixth classes have both $T_c$ fixed and $\alpha$ fixed at $\frac{1}{8}$.

For numerical ease, we approximate the reduced free energy (where HT denotes high temperature)

$$f_{\rm HT}^{(R)}(y)=[f/k_BT+\ln 2$$
$$+6\ln\cosh(J/k_BT)]/\tanh^3(J/k_BT)$$
$$=8-33\tanh(J/k_BT)+168\tanh^2(J/k_BT)$$
$$-930\tanh^3(J/k_BT)+\ldots \quad (8)$$

and use the variable

$$y=10\tanh(J/k_BT)\ . \quad (9)$$

The expansion for $f_{\rm HT}^{(R)}(y)$ is known to order $y^{12}$.

Some of the free-energy approximants display singularities at temperatures in the physical regime (i.e., between the ferromagnetic critical temperature $T_c<0$ and the antiferromagnetic first-order transition temperature $T_t>0$), where we have every right to expect an analytic free energy. Such approximants are rejected. Approximants displaying other signs of unexpected analytic behavior, such as a pair of poles straddling the real line in the physical regime, or very slow convergence of the numerical integration, are also rejected. Of the 44 Dlog Padé approximants considered, 10 (or 23%) were rejected. The IDA's faired much worse: of 138 approximants, 119 (or 86%) were rejected. These rejection percentages did not vary significantly between approximants with and without fixed ferromagnetic critical properties.

The estimates for the free energy at $k_BT/J=1.74$ given by the accepted approximants are displayed in the lower half of Fig. 1. Most of them cluster near the value $-2.03$ but, as expected, a few are scattered erratically and do not fit on the figure. It is interesting that 23% of the accepted Dlog Padé-approximant estimates fall off of the graph, while only 5% of the IDA estimates fall off: although many more IDA's must be rejected, those IDA's which are accepted seem to be better than the Dlog approximants. The reader is encouraged to form his own opinion, but I conclude from Fig. 1 that, at $k_BT/J=1.74$,

$$f(T)/J=-2.0295\pm 0.0015=-2.0295\ (\pm 0.07\%)\ . \quad (10)$$

Two approximants which fall near the edges of the above range are [ø/6;6] and [ø/8;4], both with a fixed ferromagnetic critical temperature.

We turn now to low-temperature series extrapolations. The low-temperature series has no physical significance at negative temperatures, so the last four of the six classes of approximants mentioned above cannot be used. On the other hand, it is now profitable to use direct Padé approximants. We approximate the function (where LT denotes low temperature)

$$f_{\rm LT}^{(R)}=-(f/J+2)(J/k_BT)e^{8J/k_BT} \quad (11)$$
$$=1+4x+15\tfrac{1}{2}x^2+74x^3+422\tfrac{1}{3}x^4+2730x^5+\ldots$$

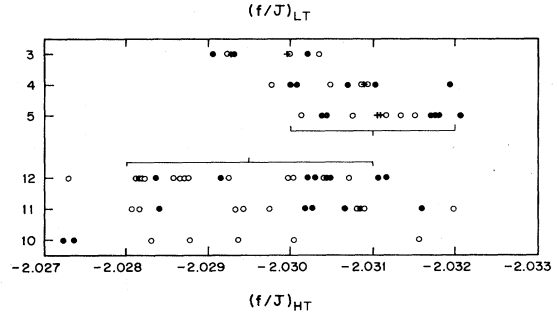


FIG. 1. Estimates for $f(T)/J$ at $k_BT/J=1.74$ produced by several approximants. Solid circles represent estimates from IDA's, open circles represent estimates from Dlog Padé approximants, and pluses represent estimates from direct Padé approximants. The lower half of the figure shows extrapolations from high-temperature series. Estimates are segregated by row according to the number of terms (10, 11, or 12) in (8) used to produce the approximant, and the overall estimate (10) is indicated by a bar. The upper half of the figure shows the same information for the low-temperature extrapolants.

using the variable

$$y=10e^{-4J/k_BT}=10x\ . \tag{12}$$

The series for $f_{\rm LT}^{(R)}(y)$ is known to order $y^5$, as shown above.

The low-temperature approximants were better behaved than their high-temperature brothers. Of 32 approximants (12 Dlog Padé approximants, 15 IDA's and 5 Padé approximants) only one (an IDA) was rejected, and all of the accepted estimates fall within the graph in the top half of Fig. 1. I conclude that, at $k_BT/J=1.74$,

$$f(T)/J=-2.0310\pm0.0010=-2.0310\ (\pm0.05\%)\ . \tag{13}$$

The "bounding" approximants are [0/3;0] and [0/1;2]. The two pairs of bounding approximants are plotted in Fig. 2. The intersection places the transition temperature at

$$k_BT_t/J=1.746\pm0.005=1.746\ (\pm0.3\%)\ . \tag{14}$$

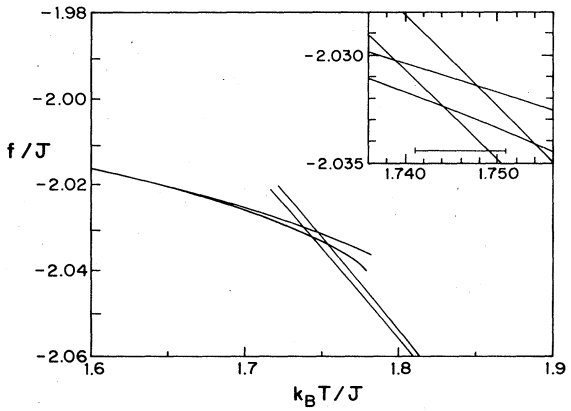


FIG. 2. Estimated bounds for the free energy. The crossing region determines the transition temperature estimate (14), which is indicated by a bar in the inset.

## IV. OTHER PROPERTIES OF THE TRANSITION

Now that the first-order transition has been located, any property of interest can be found by extrapolating the high- and low-temperature expansions for that property out to the transition point. We execute this program for some representative properties: for the energy and the staggered magnetization to allow ready comparison of our results to those of other approaches, and also for the susceptibility to allow the calculation of the curvature of the coexistence line in the $(H,T)$ plane.

The low-temperature energy expansion is given by (5), while the high-temperature energy expansion is derivable from the high-temperature free energy. These expansions are extrapolated just as described in the preceding section, except that the approximants are evaluated at $k_BT/J=1.746$ instead of 1.74. The resulting graph of energy versus temperature near the transition point is shown in Fig. 3. Taking into account both the uncertainty of the energy at a given temperature and the uncertainty of the transition temperature, I conclude that the latent heat of transition is

$$\Delta E/J=0.48\pm0.02=0.48\ (\pm4\%)\ . \tag{15}$$

It is not clear why the energy extrapolates so much less precisely than the free energy.

The low-temperature susceptibility expansion is given in (6), and a 15th-order high-temperature expansion has been derived by McKenzie.[31] The analysis of these series is a mechanical application of the techniques previously discussed, with the following result:

$$\Delta\chi(k_BT_t/m^2)=0.053\pm0.002=0.053\ (\pm4\%)\ . \tag{16}$$

The phase diagram of the fcc Ising antiferromagnet in the $(H,T)$ plane is a matter of some controversy.[4] This study can do little to clarify the matter, but we can point out that the slope, curvature, and, in fact, all derivatives of a two phase coexistence curve $T_t(H)$ at a given point

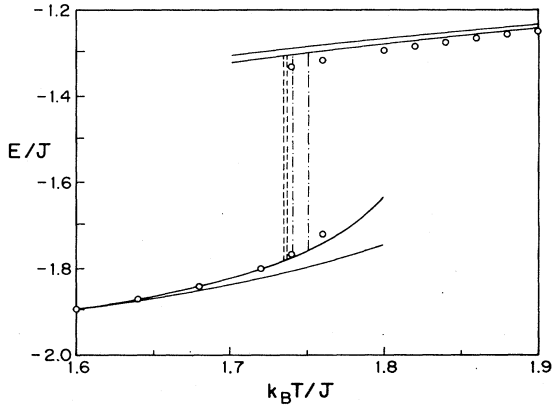


FIG. 3. Estimated bounds for the energy. The open circles are the Monte Carlo data points of Polgreen (Refs. 18 and 34). (The estimated sampling errors are smaller than the circles.) The estimate (14) for the transition temperature is marked with vertical dot-dash lines and Polgreen's estimate ($k_BT_t/J=1.736\pm0.001$) is marked with vertical dashed lines.

can be obtained from sufficiently detailed knowledge of the thermodynamic properties at that point. For the slope, this relation is nothing other than the famous Clausius-Clapeyron equation. In our case the slope of $T_t(H)$ at $H=0$ vanishes by symmetry. The curvature is obtainable from Eq. (A8):

$$\frac{d^2T_t(H)}{dH^2}=-\frac{\Delta\chi}{\Delta S}=-\frac{\Delta\chi(k_BT_t/m^2)}{(\Delta E/J)(k_BJ/m^2)} \tag{17}$$

(where $S$ is the entropy) which evaluates to

$$\frac{d^2T_t(H)}{dH^2}\left[\frac{k_BT}{m^2}\right]=-0.110\pm0.009=-0.110\ (\pm8\%)\ . \tag{18}$$

The low-temperature staggered magnetization expansion is presented in (7): in the disordered phase it of course vanishes. These data can be extrapolated in the usual manner, and the resulting bounds are graphed in Fig. 4. The jump in staggered magnetization at the transition is

$$\Delta M^{\dagger}/m=0.895\pm0.015=0.895\ (\pm2\%)\ . \tag{19}$$

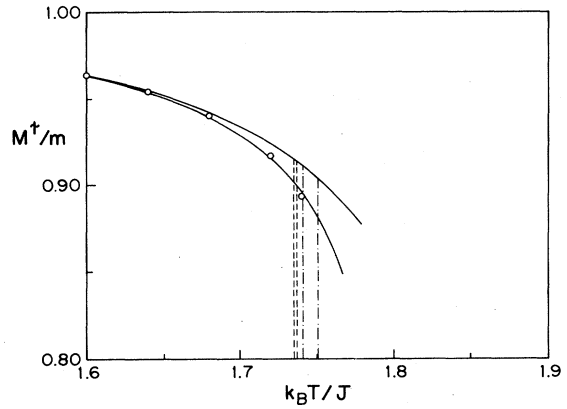


FIG. 4. Estimate bounds for the staggered magnetization. Symbols are defined as in Fig. 3.

## V. COMPARISON WITH OTHER METHODS

As mentioned in the Introduction, the fcc Ising antiferromagnet has been analyzed with a variety of techniques. Many of these extend readily to the finite-field problem, where series analysis is ineffective. The zero-field problem is thus an important proving ground where the several approximate techniques can be tested against each other. We compare several analyses taken from the literature.

Table I presents the basic comparison. Although the data speak for themselves, it is worthwhile to emphasize a few salient features. The highest transition temperatures are produced by the cluster variation method (CVM), and the improved tetrahedron-octahedron approximation of the CVM gives a lower transition temperature than the tetrahedron approximation does. Although none of the transition temperatures reported to four digits overlap with any of the others, there is nevertheless a convergence of results to the range between 1.7 and 1.8. The staggered magnetizations also behave more or less satisfactorily.

There is a much wider range in the reported latent heats: the largest is 50% greater than the smallest. To underscore this disagreement, Fig. 3 presents both the bounding approximants and the Monte Carlo data of Polgreen.[34] The disordered phase Monte Carlo data points consistently fall outside of the series estimates.

This comparison has shown that the zero-field nearest-neighbor fcc Ising antiferromagnet still deserves study with a variety of techniques, and that attention should be focused upon the thermodynamic parameters of the transition, such as its latent heat, as well as upon its location.

## ACKNOWLEDGMENTS

I am indebted to Joel L. Lebowitz for suggesting this problem to me and for constant encouragement and guidance. Several of the difficult cluster counts required for the derivation of (4) were worked out with the aid of Joseph Slawny. I was also aided in this derivation by the

TABLE I. Three parameters for the first-order transition as surmised by various workers. The parameters are the transition temperature, latent heat, and change in staggered magnetization [as defined in (7)]. The methods used are the cluster variation method [in both the tetrahedron (T) approximation and the more accurate tetrahedron-octahedron (T-O) approximation], Monte Carlo (MC) simulation and series analysis. Uncertainties in parentheses are in units of the last digit. An asterisk on a value indicates that the reference did not present this quantity as a number, but as a graph from which the value was measured.

| Method | Reference | $kT_t/J$ | $\Delta E/J$ | $\Delta M^{\dagger}/m$ |
|---|---|---|---|---|
| CVM (T) | 1, 3 | 1.8933 | 0.5029 | 0.8466 |
| CVM (T-O) | 4, 35 | 1.79 | 0.35 | 0.90* |
| MC | 13 | 1.766(4) | 0.35 | 0.88* |
| MC | 18 | 1.736(1) | 0.44* | 0.89* |
| MC | 19 | 1.706(3) | 0.454(2) | 0.9253(5) |
| Series | 8 | 1.74(5) | 0.435 | 0.92 |
| Series | This work | 1.746(5) | 0.48(2) | 0.895(15) |

unpublished thesis of C. J. Elliot,[7] a copy of which was kindly provided by D. D. Betts. I am grateful to N. D. Mackenzie for resolving the discrepancy between the expansion (4) and the one found in Ref. 9. Finally, the expansion could not have been extended to seventh order without the computing power made available to me by Dr. James Gubernatis at the Center for Materials Science of Los Alamos National Laboratory. The derivations of (5), (6), and (7) from (4) were checked using the computer algebra system MACSYMA. I have benefited from two discussions with Michael E. Fisher. Joseph Slawny and Jean Bricmont communicated a research result[25] before publication; Thomas Polgreen and Juan Sanchez graciously shared their unpublished data. It is a pleasure to acknowledge the financial support of the National Science Foundation under Grant No. DMR-81-14726.

## APPENDIX: A SECOND-ORDER CLAUSIUS-CLAPEYRON EQUATION

The Clausius-Clapeyron equation (A7) relates the slope of a first-order transition line to first derivatives of the free energy (e.g., entropy and magnetization). In this Appendix we derive a "second-order Clausius-Clapeyron" equation (A8) which relates the curvature of a first-order transition line to second derivatives of the free-energy (e.g., susceptibility and specific heat). It is clear from this derivation that the third derivative of the transition line is related to third derivatives of the free energy (e.g., $\partial\chi/\partial H$), and so on.

Suppose that two phases, $A$ and $B$, coexist in a phase diagram described by the variables $H$ and $T$. Upon an arbitrary displacement $(\delta H,\delta T)$ within a single phase the free energy $F(H,T)$ suffers a change

$$\delta F=\frac{\partial F}{\partial T}\delta T+\frac{\partial F}{\partial H}\delta H+\tfrac{1}{2}\left[\frac{\partial^2 F}{\partial T^2}(\delta T)^2+2\frac{\partial^2 F}{\partial H\,\partial T}\delta H\,\delta T+\frac{\partial^2 F}{\partial H^2}(\delta H)^2\right]+\cdots$$

$$\equiv -S\,\delta T-M\,\delta H+\tfrac{1}{2}[-(C_H/T)(\delta T)^2+2\alpha_H\,\delta H\,\delta T-\chi(\delta H)^2]+\cdots\ . \tag{A1}$$

Here, the "coefficient of thermal magnetization change" is

$$\alpha_H\equiv-(\partial M/\partial T)_H=\pm[\chi(C_H-C_M)/T]^{1/2}\ , \tag{A2}$$

where the second expression follows from a thermodynamic exercise. ($C_H$ and $C_M$ are the specific heats at constant field and magnetization, respectively.) This expression for $\delta F$ is valid even if $F(H,T)$ exhibits essential singularities[21] at the phase boundary, because the expansion (A1) is not required to converge.

If the displacement $(\delta H,\delta T)$ follows the coexistence line, then $\delta F$ for the $A$ phase must equal $\delta F$ for the $B$ phase. Defining

$$\Delta M=M_A-M_B,\quad \Delta\chi=\chi_A-\chi_B\ , \tag{A3}$$

etc., we have from (A1):

$$0=\Delta S\,\delta T+\Delta M\,\delta H+\tfrac{1}{2}[(\Delta C_H/T)(\delta T)^2-2\,\Delta\alpha_H\delta H\,\delta T+\Delta\chi(\delta H)^2]+\cdots\ . \tag{A4}$$

But if $(\delta H,\delta T)$ falls along the phase coexistence boundary $T_t(H)$, then

$$\delta T=\frac{dT_t(H)}{dH}\delta H+\frac{1}{2}\frac{d^2T_t(H)}{dH^2}(\delta H)^2+\cdots\ , \tag{A5}$$

so

$$0=\left[\Delta M+\Delta S\frac{dT_t}{dH}\right]\delta H+\frac{1}{2}\left[\Delta S\frac{d^2T_t}{dH}+\frac{\Delta C_H}{T}\left[\frac{dT_t}{dH}\right]^2-2\,\Delta\alpha_H\frac{dT_t}{dH}+\Delta\chi\right](\delta H)^2+\cdots\ . \tag{A6}$$

The value of $\delta H$ is arbitrary, so all the terms in the first set of large parentheses must vanish, whence (provided $\Delta S\neq 0$)

$$\frac{dT_t(H)}{dH}=-\frac{\Delta M}{\Delta S}\ , \tag{A7}$$

and

$$\frac{d^2T_t(H)}{dH^2}=-\frac{1}{\Delta S}\left[\Delta\chi-2\,\Delta\alpha_H\frac{dT_t}{dH}+\frac{\Delta C_H}{T}\left[\frac{dT_t}{dH}\right]^2\right]. \tag{A8}$$

This is the desired second-order Clausius-Clapeyron equation.

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