# Computer simulation study of hysteresis and free energy in the fcc Ising antiferromagnet

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A method for estimating the entropy $S$ from a Monte Carlo simulation, suggested previously by the author, is applied to the fcc Ising antiferromagnet with nearest-neighbor interactions and external magnetic field $h$. The estimated accuracy for $S$ is 0.01% to 0.5%, which is, at least, 1 order of magnitude higher than has been obtained with thermodynamic integration by Binder. Comparison of the free-energy results for the coexisting ordered and disordered phases enables us to determine with high accuracy the first-order transition points and the discontinuities in the thermodynamic functions. For the residual ground-state entropies per spin $S(0)/k_B$ at the critical fields $h_c/J=12$ and 4, we obtain 0.249 89(2) [$=0.360\,51(3)\ln 2$] and 0.239(1) [$=0.345(1)\ln 2$], respectively. The first result is significantly larger than the theoretical upper bound, $\sigma_u'=0.2398$ ($=0.3460\ln 2$), conjectured by Hadjukovic and Milošević. Our results are also significantly larger than Binder's result, $\sim\frac{1}{3}\ln 2$, obtained for both critical fields.

## I. INTRODUCTION

Identification of first-order phase transitions with computer simulation (for magnetic systems, for example) requires a calculation and comparison of the free energy for the coexisting ordered and disordered phases. Such an analysis can conveniently be carried out with the stochastic model (SM) simulation technique of Alexandrowicz,[1-3] which leads to sharp transitions and also provides the entropy and hence the free energy (see Ref. 4). On the other hand, the commonly used Metropolis Monte Carlo (MC) method[5] yields, in many cases, strong hysteresis,[6-8] and does not provide the entropy as a direct by-product of the simulation. One can obtain the entropy indirectly by carrying out a suitable reversible thermodynamic integration,[8] but this is an inefficient procedure since it requires performing *many* MC runs[8,9] for different values of a thermodynamic parameter. An alternative way is to employ a method, suggested by the author,[10] which enables one to extract the entropy from configurations obtained with *any* computer simulation technique. The method is based on a formula, in which the entropy is expressed approximately as a function of the frequency of occurrence of certain local states. These frequencies are calculated from a MC run for a *single* value of a parameter, which makes the method substantially more efficient than the thermodynamic integration procedure. Furthermore, in contrast to other methods for calculating the entropy,[11,12] the accuracy of our method actually improves with increasing system size.

So far, the method has been applied very successfully to MC simulation of several Ising lattices[10,13] and lattice-gas models;[14,15] in this paper we apply it to MC simulations of the fcc Ising antiferromagnet in order to study its phase transitions. This model is defined on a fcc lattice with $L$ cells on a side, $L^3$ cells, and $N=4L^2$ sites. On lattice site $k$, a spin variable $\sigma_k$ is defined, $\sigma_k=+1$ or $-1$. The Hamiltonian $H$ of the system is

$$H=J\sum_{\mathrm{NN}}\sigma_m\sigma_k-h\sum_{k=1}^{N}\sigma_k\ , \tag{1}$$

where $J>0$ is the antiferromagnetic interaction constant, NN denotes nearest neighbors, and $h$ denotes the magnetic field. This model also describes an $AB$ binary alloy, where $\sigma_k=1$ or $-1$ corresponds to occupation of site $k$ by atom $A$ or atom $B$, respectively. The model has been studied extensively with various approximate methods, leading to conflicting results. For $h=0$, mean field theory[16] predicts a second-order phase transition, Bethe's approximation[17] does not lead to any transition at all, and the quasichemical approximation[18] and Kikuchi's cluster-variation method each give a first-order transition.[19-23] A first-order transition has been also suggested by Lifshitz,[24,25] and recently by Mukamel and Krinsky,[26] who have carried out a renormalization-group analysis of the Landau-Ginzburg-Wilson Hamiltonians with appropriate symmetry. For nonzero fields, many ordered states and their mixtures have been shown to be stable in the ground state;[27-29] however, in the phase-diagram calculations only the three ordered states $A_3B$, $AB$, and $AB_3$, which occur in Cu-Au,[30] have been taken into account (see Fig. 1). Again, the results depend very much on the approximation: According to mean field theory,[31] all phases extend to a multicritical point, Bethe's approximation does not predict any ordering,[17] and the quasichemical approximation[18] and the cluster-variation method[19-23] each lead to a very different phase diagram. Also, a recent real-space renormalization study[32] fails to yield the ordering of the $AB$ phase and predicts the transition of the $A_3B$ phase to be of second order.

In view of these discrepancies, several groups were motivated to study the model with the MC method,[5] which, in principle, constitutes an exact procedure.[8] Indeed, such studies have been carried out by Phani *et al.*,[33,34] Binder,[35] and Binder *et al.*[36] The results give strong evidence (but not a proof) that the transitions are

 

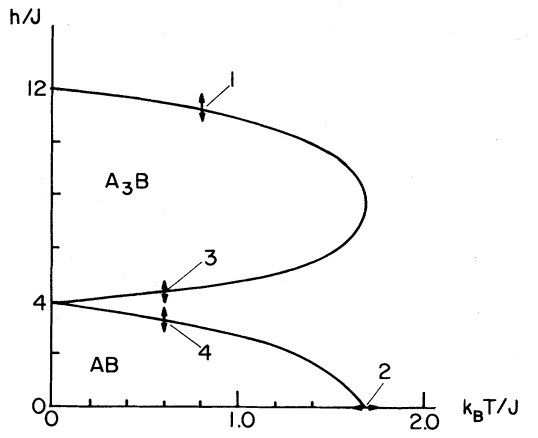


FIG. 1. Schematic $(T,h)$ phase diagram for the fcc Ising antiferromagnet at absolute temperature $T$ in the presence of a magnetic field $h$.[35] The transitions studied in this work are numbered 1–4.

always of first order. The phase diagram obtained from the MC calculations[35,36] (see Fig. 1) differs from those predicted by former studies, in that at the critical field between the two ordered phases ($h_c=4J$), the disordered phase is stable down to zero temperature. It is also predicted, in accordance with other theoretical studies,[37,38] that at this critical field and at the maximum critical field ($h_c=12J$), the ground-state entropy is finite. A MC study of the entropy (and the free energy) of this model has been carried out recently by Binder[39] using reversible thermodynamic integration. However, since this method is relatively inefficient (see previous discussion), we have decided to study the entropy of the fcc Ising antiferromagnet by applying our method to MC simulations of substantially larger lattices. Our main interest is to determine, by free-energy analysis of the hysteresis loops, the exact transition points and the discontinuities of the thermodynamic functions (which have not been provided by Binder[39]). It is also of great theoretical interest to calculate the ground-state residual entropy at $h_c=4J$ and $12J$. Finally, in order to provide a comparison of the efficiency of our method with that of the thermodynamic integration procedure, we simulate the system at four transition points that have also been studied in Ref. 39.

## II. THEORY

### A. Thermodynamic functions

We are interested in the ensemble averages (denoted by $\langle\ \rangle$) of the magnetization $M$, the internal energy $U$, the entropy $S$, and the free energy $F$ at absolute temperature $T$ and magnetic field $h$,

$$M=N^{-1}\left\langle \sum_{k=1}^{N}\sigma_k \right\rangle , \tag{2}$$

$$U=J\left\langle \sum_{\mathrm{NN}}\sigma_k\sigma_m \right\rangle -hNM , \tag{3}$$

$$F=U-TS . \tag{4}$$

As in former studies, we assume only two ordered structures, $AB$ and $A_3B$. The order parameters $\tilde{m}_{AB}$ and $\tilde{m}_{A_3B}$ for these structures are defined by the magnetization $m_\nu$ of the four simple-cubic sublattices $\nu=1,4$ (see Refs. 31 and 36),

$$m_\nu=N^{-1}\sum_{k\in\nu}\langle\sigma_k\rangle , \tag{5}$$

$$\begin{aligned}
\tilde{m}_{AB}^{(1)}&=m_1+m_2-m_3-m_4 ,\\
\tilde{m}_{AB}^{(2)}&=m_1-m_2-m_3+m_4 ,\\
\tilde{m}_{AB}^{(3)}&=m_1-m_2+m_3-m_4 ,
\end{aligned} \tag{6}$$

$$\begin{aligned}
\tilde{m}_{A_3B}^{(1)}&=m_1+m_2+m_3-m_4 ,\\
\tilde{m}_{A_3B}^{(2)}&=m_1+m_2-m_3+m_4 ,\\
\tilde{m}_{A_3B}^{(3)}&=m_1-m_2+m_3+m_4 ,\\
\tilde{m}_{A_3B}^{(4)}&=-m_1+m_2+m_3+m_4 .
\end{aligned} \tag{7}$$

### B. Monte Carlo procedure

We simulate the system with the asymmetric[5] as well as with the symmetric[40] MC procedures, which both treat one spin per MC step. Let us denote the internal energy of a configuration before and after flipping a spin $\sigma$ by $U(\sigma)$ and $U(-\sigma)$, respectively; we also define $\Delta U=U(-\sigma)-U(\sigma)$. For the asymmetric procedure, the transition probability $p(-\sigma)$ for flipping $\sigma$ is

$$p(-\sigma)=\begin{cases}1, & \Delta U\le 0\\ \exp(-\Delta U/k_BT), & \Delta U>0\end{cases} \tag{8}$$

and for the symmetric procedure,

$$p(-\sigma)=\frac{\exp(-\Delta U/k_BT)}{1+\exp(-\Delta U/k_BT)} , \tag{9}$$

where $k_B$ is the Boltzmann constant.

### C. Calculation of the entropy

Our formula for the entropy (see the Introduction) enables one to define different approximations for $S$ by taking into account different sets of local states. In this section we explain this formula and the local states in the context of the fcc Ising antiferromagnet. For the sake of simplicity we first describe the "mean-field" approximation for $S$.

#### *1. Mean-field approximation*

Assume that certain values of $m_\nu$, $\nu=1,4$ [Eq. (5)] have been obtained in an actual MC run and let us describe a procedure, different from the MC method, which enables one to construct configurations with the same values of $m_\nu$. One starts with an empty lattice and selects an empty site at random; if it belongs to sublattice $\nu$, a + spin (− spin) is determined with probability $p_{\nu,+}$ ($p_{\nu,-}$),

$$p_{\nu,+}=(1+4m_\nu)/2 , \quad p_{\nu,-}=1-p_{\nu,+} . \tag{10}$$

This procedure is continued until the entire lattice is filled

with spins. Obviously, the probability $P$ of a configuration constructed with this procedure is the product of the $p$'s [Eq. (10)] with which the $N$ spins have been chosen. For a large lattice, however, the asymptotic form of $P$ can be used,

$$P \simeq \prod_{\nu=1}^{4} p_{\nu,+}^{(N/4)p_{\nu,+}} p_{\nu,-}^{(N/4)p_{\nu,-}} , \tag{11}$$

and hence an entropy function $S_M$ ($M$ denotes mean field) is defined by

$$S_M = -k_B \ln P \simeq -k_B (N/4) \sum_{\nu} p_{\nu,+} \ln p_{\nu,+} + p_{\nu,-} \ln p_{\nu,-} . \tag{12}$$

This mean-field procedure generates configurations with the correct $m_\nu$ values, but in contrast to the MC method, it does not lead to the correct spin-spin correlations. However, one can assume, as a first approximation that the MC configurations have been *hypothetically* generated with the above mean-field procedure. Thus, the actual MC results for $m_\nu$ are interpreted with the help of Eq. (12) to obtain an approximation $S_M$ for the entropy. $S_M$, which is actually based on the assumption of random mixing of constant number of spins, constitutes an overestimation of the true entropy; it is expected to provide a good approximation only for highly ordered or disordered states. In order to obtain higher-order approximations for $S$, we shall employ a formula suggested by the author,[10] which also takes into account, in addition to the long-range order (i.e., the values of $m_\nu$), the short-range correlations between the spins.

### 2. *Higher-order approximations for the entropy*

The higher-order approximations for the entropy are based on the concepts of the SM simulation technique[1-3] mentioned in the Introduction. With this technique a configuration is obtained by filling an initially empty fcc lattice with spins with the help of a stochastic process. At the $k$th step of the process, sites $k'=1,\ldots,k-1$ have already been filled with spins, and the spin orientation at site $k$, $\sigma_{k'}$, should be determined with the help of a transition probability. It can be shown[3] that the *exact* transition probability for $\sigma_k$ depends on *all* the spins of the surface between the filled and the empty regions of the lattice. This surface (illustrated in Fig. 2) consists of the as yet "uncovered" spins of layer $l-1$ and the spins of layer $l$. Approximate transition probabilities, however, can be defined by taking into account a limited number of surface spins, which are neighbors to site $k$. For example, as a first approximation one would consider only the six nearest-neighbor spins to site $k$ (denoted by □ in Fig. 2). These six spins (called the first shell here) define $m=2^6=64$ distinct local states which are labeled $I$. One can differentiate further and define local states $I,+$ and $I,-$ by also taking into account the two possible spins at site $k$, $\sigma_k=1$, and $\sigma_k=-1$, respectively. The probability of a particular configuration constructed with the SM technique is given by the product of the transition probabilities with which the $N$ spins have been chosen. It has been shown[10] that these transition probabilities can be expressed in terms of the frequencies of occurrence $\nu_{I,+}$, $\nu_{I,-}$, and $\nu_I$ of the local states $I,+$, $I,-$, and $I$, respectively, and the entropy is given by

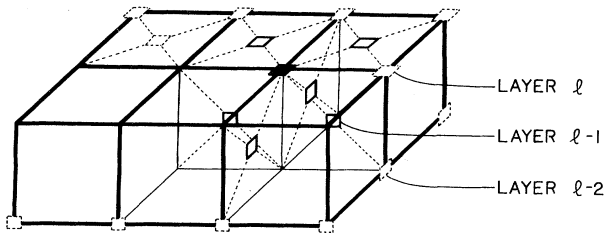


FIG. 2. A diagram illustrating the surface between the filled and the empty regions of the fcc Ising lattice at step $k$ of the $SM$ method construction. Site $k$ (denoted by a full square) is still empty. Sites from 1 to $k-1$ (on layers from 1 to $l-1$ and part of layer $l$) are already occupied with spins; they are denoted by dashed empty squares. The surface is defined by the spins of layer $l$ and the as-yet-uncovered spins of layer $l-1$. The 6 nearest neighbor spins to site $k$, which belong to the surface (first shell) are denoted by full-line empty squares.

$$S \simeq k_B N \sum_{I=1}^{m} \nu_{I,+} \ln(\nu_{I,+}/\nu_I) + \nu_{I,-} \ln(\nu_{I,-}/\nu_I) , \tag{13}$$

$$\nu_I = \nu_{I,+} + \nu_{I,-} \tag{14}$$

where $m$ is the number of local states of type $I$. Equation (13), even though based on considerations of the SM technique, can be used [ as can Eq. (12)] for estimating the entropy of configurations generated with the MC method. One has to calculate the values of $\nu_{I,+}$ and $\nu_{I,-}$ from these configurations and substitute them in Eq. (13) (see preceding discussion for the mean-field approximation, Sec. II C 1). In practice, lattice sites are visited in a predefined order, which is dictated by the SM procedure. The local states are determined and the values of $\nu_{I,+}$ are estimated by $\bar{\nu}_{I,+}$ from a sample of $n$ configurations,

$$\bar{\nu}_{I,+} = (nN)^{-1} \sum_{t=1}^{n} N_{I,+}(i(t)) , \tag{15}$$

where $N_{I,+}(i(t))$ is the number of times the local state $I,+$ appears in configuration $i$, sampled at time $t$.

Equation (13) defines approximations for the entropy which, in principle, can be systematically improved by taking into account more and more neighbors to a $k$th spin. However, in practice, the approximations are limited by the exponential increase of the number of local states. We shall now define several sets of local states for the fcc lattice.

The first set of 64 local states $I$ (based on the six NN spins of the $k$th spin) has already been described, and we denote the corresponding approximation for $S$ by $S_1$ [Eq. (13)]. The second set takes into account the six spins of the first shell and additional six spins (the second shell) defined as follows: Our $k$th spin has six empty NN sites which we call the $b$ sites here. These $b$ sites have six NN spins which belong to the surface (but not to the first shell); these six spins constitute the second shell. We

have, therefore, for the second set $m=2^{12}=4096$ local states $I$. The corresponding approximation for the entropy [Eq. (13)] is denoted by $S_2$. The third set of local states also takes into account a third shell of 13 spins, described as follows: Consider the group of empty lattice sites, which are NN's of the six $b$ sites; the 13 surface spins, which are NN's of any of the sites of this group, define the third shell. The effect of this shell, in contrast to the first two shells, is taken into account in an approximate manner. We define $a=(1-M)/3$ (where $M$ is the lattice magnetization [Eq. (2)]) and calculate the magnetization $g$ of the 13 spins of the third shell. $g$ can be located in one of six regions: $g\geq 1-a$, $1-a>g\geq 1-2a$, $1-2a>g\geq M$, $M>g\geq M-a$, $M-a>g\geq M-2a$, and $M-2a>g$. We have, therefore, $4096\times 6=24\,576$ local states for the third set; the corresponding entropy is denoted $S_3$. The fourth set of local states also takes into account the fourth shell of 16 surface spins, which is defined in the same manner as the second and third shells. For these spins, we define four local states only, using $a=(1-M)/2$; therefore, $m=98\,304$ and the approximation is denoted $S_4$.

So far, we have defined the approximations $S_1$–$S_4$ based on short-range correlations only. Now, we shall include long-range-order effects [see Eq. (12)] by considering to which sublattice $\nu$ ($\nu=1,4$), site $k$ belongs. Therefore, for the first set we have $m=64\times 4=256$, and the approximation is denoted $S_{M1}$. In the same way, we define $S_{M2}$ ($m=4096\times 4=16\,384$) and $S_{M3}$ ($m=24\,576\times 4=98\,204$). It should be pointed out that for a disordered state $S_{Mi}$ should be equal to $S_i$, since the four sublattices are equivalent. In addition, all of these approximations overestimate the true value of $S$ [see discussion for $S_M$, Eq. (12)], but they are expected to decrease monotonically as the number of local states increases.[3] One would also expect the differences, $S_{i-1}-S_i$ and $S_{M(i-1)}-S_{Mi}$, to decrease as the approximation improves, since the spin-spin correlations decay with distance and $S$ is finite. This suggests that only a limited number of shells should suffice in order to obtain good approximations for $S$.

## III. RESULTS AND DISCUSSION

We have simulated lattices of size $L=21$, $N=4\times(21)^3=37\,044$ with the "asymmetric" [Eq. (8)] as well as with the "symmetric" [Eq. (9)] MC procedures, using periodic boundary conditions. Four phase transitions have been investigated (labeled 1–4 in the phase diagram of Fig. 1); we have also calculated the ground-state residual entropy at the two critical fields $h_c=4J$ and $12J$. In order to obtain reliable statistics for the relatively large sets of local states, samples of $n=7000$ lotteries per spin have been generated. For each point $(T,h)$ studied, we have performed at least two MC runs, one starting from a completely ordered configuration (e.g., $A_3B$) and the other from a random configuration. In some cases, simulations have also been carried out which started from a completely magnetized lattice. The statistical error has been determined from several MC runs, based on different random-number sequences. The numbers $N_{I,+}$ [Eq. (15)] have been calculated every $N$ MC steps. In order to exclude the initial relaxation to equilibrium, the averaging has been started only after 1000–4000 lotteries per spin. The calculations have been carried out on the IBM 3081D computer of the Weizmann Institute of Science, Rehovot, Israel.

### A. Determination of the accuracy

First, one has to justify the approximation employed for the third shell where six local states rather than $2^{13}=8192$ have been taken into account. We have therefore defined and tested a better approximation for this shell (the entropy is denoted $S_3'$); but we have always found that $S_3=S_3'$, within the statistical error, which justifies the approximation $S_3$. We therefore *assume* that the approximation for the fourth shell (based on four local states) is also valid.

In Table I results are presented for the various approximations for $S$ obtained at the temperature $k_BT/J=0.8$ for $h/J=10.7$ (an $A_3B$ ordered state) and $h/J=11.4$ (a disordered state). These points are located in the transition region labeled 1 in Fig. 1. The two simulations have been started from a completely ordered ($A_3B$) configuration. The table shows the expected monotonic decrease of the results for $S$ as the approximation is improved. Furthermore, the differences, $S_i-S_{i+1}$ and $S_{Mi}-S_{M(i+1)}$ also decrease with increasing $i$ and become undetectable (i.e., within the statistical error) for $S_{M2}$ and $S_{M3}$ ($h/J=10.7$) and for $S_3$ and $S_4$ ($h/J=11.4$). We therefore *assume* that the decrease of the better approximations for $S$ would also be undetectable, which allows one to estimate the correct value within the statistical error of our best approximation. We obtain $S/k_B=0.040\,74(3)$ ($h/J=10.7$) and $S/k_B=0.2355(3)$ ($h/J=11.4$) (the number in parentheses denotes the statistical error; see Table I).

The accuracy obtained here is at least 1 order of magnitude better than that obtained by Binder[39] using thermodynamic integration. It should be pointed out, however, that for several simulations, starting from random configurations, the differences $S_4-S_3$ and $S_{M3}-S_{M2}$ did not converge, i.e., they were found to be larger than the statistical error. In these cases, however, one can still extrapolate the results to $S_\infty$ (see discussion in later sections). Finally, it should be noted that for the disordered phase the results satisfy $S_i=S_{Mi}$ (within the statistical error) which reflects the absence of a long-range order in the system (i.e., the four sublattices are equivalent).

### B. Analysis of hysteresis loops

Let us first analyze the transition denoted 1 in Fig. 1, where the magnetic field $h$ is varied at constant temperature $k_BT/J=0.8$. The results for the entropy $S$, the free energy $F$ [Eq. (4)], the internal energy $U$ [Eq. (3)], the magnetization $M$ [Eq. (2)], and the order parameter $\tilde{m}_{A_3B}$ [Eq. (7)] are summarized in Table II. For each of these quantities, the results appearing in the upper and lower rows are for the ordered and disordered phases, respectively. The table is divided into three sections, denoted

TABLE I. Results for the various approximations for the entropy (in units of $Nk_B$). $S_M$ is the mean-field approximation; $S_i$, $i=1,4$ are based on short-range correlations only and $S_{iM}$, $i=1,3$ also take into account the long-range order (for details see Secs. II C 1 and II C 2). $S$ is our estimate for the exact entropy. The results in the first two rows are for an ordered ($h/J=10.7$) and a disordered ($h/J=11.4$) states, close to transition 1 in Fig. 1. The results in the lower rows are for the ground-state entropy at the critical fields $h_c/J=4$ and 12. The statistical error in the last digit(s) is denoted by parentheses; for example, $0.245\,8(3)=0.2458\pm0.000\,3$.

| $\frac{k_BT}{J}$ | $h/J$ | $S_M$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_{1M}$ | $S_{2M}$ | $S_{3M}$ | $S$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.8 | 10.7 | 0.041 62(4) | 0.044 34(3) | 0.041 21(3) | 0.040 81(3) | 0.040 77(3) | 0.040 75(3) | 0.040 74(3) | 0.040 74(3) | 0.040 74(3) |
| 0.8 | 11.4 | 0.427 9(3) | 0.245 8(3) | 0.236 5(3) | 0.235 6(3) | 0.235 5(3) | 0.245 8(3) | 0.236 5(3) | 0.235 6(3) | 0.235 5(3) |
| 0 | 12.0 | 0.349 70(1) | 0.252 06(1) | 0.250 00(2) | 0.249 90(2) | 0.249 89(2) | 0.252 06(2) | 0.249 99(2) | 0.249 89(2) | 0.249 89(2) |
| 0 | 4.0 | 0.545 0(4) | 0.275 8(1) | 0.244 5(1) | 0.242 6(1) | 0.241 4(1) | 0.260 2(1) | 0.242 0(1) | 0.240 5(1) | 0.239 (1) |

TABLE II. Results obtained at $k_BT/J=0.8$ for several values of $h$ (transition 1 in Fig. 1). $S$ is the entropy; $F$, the free energy [Eq. (4)]; $U$, the internal energy [Eq. (3)]; $M$, the magnetization [Eq. (2)]; and $\tilde{m}_{A_3B}$ is the order parameter [Eq. (7)]. For each quantity the results in the upper and lower rows have been obtained from simulations starting from a completely ordered ($A_3B$) and random configurations, respectively. The values $h/J=11.21$ and 11.25 are the boundaries of the coexistence region; $h_c/J=11.21(1)$ is the critical field in which the first-order transition occurs. The statistical error is defined in the caption to Table I.

| | Order | | | Coexistence | | | Disorder | | |
|---|---|---|---|---|---|---|---|---|---|
| $h/J$ | 10.8 | 11.0 | 11.2 | 11.21($h_c$) | 11.23 | 11.25 | 11.26 | 11.3 | 11.4 |
| $S/k_BN$ | 0.049 28(5) | 0.072 17(5) | 0.111 5(3) | 0.115 9(3) | 0.123 8(7) | 0.137 (2) | | | |
| | | | | 0.208 6(5) | 0.214 0(3) | 0.218 2(3) | 0.219 7(3) | 0.225 0(2) | 0.235 6(1) |
| $-F/JN$ | 5.409 81(3) | 5.516 2(1) | 5.627 5(1) | 5.633 4(1) | 5.644 9(1) | 5.657 4(2) | | | |
| | | | | 5.634 0(4) | 5.647 3(2) | 5.660 5(1) | 5.667 1(2) | 5.693 5(1) | 5.761 4(1) |
| $-U/JN$ | 5.370 4(1) | 5.458 5(1) | 5.537 9(3) | 5.540 7(3) | 5.545 8(4) | 5.548 (1) | | | |
| | | | | 5.467 2(2) | 5.476 0(1) | 5.485 9(1) | 5.491 4(2) | 5.513 5(2) | 5.572 9(1) |
| $M$ | 0.524 4(1) | 0.540 8(1) | 0.574 9(4) | 0.578 4(4) | 0.586 1(5) | 0.598 (2) | | | |
| | | | | 0.659 7(2) | 0.665 2(2) | 0.669 7(3) | 0.671 5(2) | 0.678 6(2) | 0.694 1(2) |
| $\tilde{m}_{A_3B}$ | 0.974 9(1) | 0.956 3(2) | 0.905 (1) | 0.897 (1) | 0.880 (1) | 0.843 (8) | | | |
| | | | | 0.330 (6) | 0.332 (6) | 0.334 (4) | 0.336 (3) | 0.337 (3) | 0.347 (2) |

"order," "coexistence," and "disorder." For $h/J \geq 11.26$ (disorder), all the MC runs starting from a completely ordered ($A_3B$) configuration led to a disordered state [i.e., the values for $m_\nu$ ($\nu=1,4$) are equal and $S_i=S_{Mi}$, $i=1,3$]. Therefore, the upper row in the table for this region is empty. In the coexistence region ($h/J=11.21$ $-11.25$) the ordered and disordered phases have been obtained by starting the MC runs from a completely ordered ($A_3B$) or from a random configuration, respectively. It should be pointed out that for $h/J \leq 11.20$, we were unsuccessful in simulating the disordered phase. The table reveals that the disordered phase has lower free-energy values (i.e., higher stability) than the ordered one; the difference $\Delta F$, however, decreases from $\sim 0.0031$ to 0.0006(5) upon going from 11.25 to 11.21. We therefore define the critical field $h_c/J=11.21(1)$ at the point in which $\Delta F$ is minimal and only slightly larger than the statistical error. For $h/J \leq 11.2$ (order), results are presented only for the ordered phase (upper row) since all the MC runs that started from random configurations and showed convergence (i.e., apparent stability) led to highly ordered states with values of $U$, $S$, and $M$ close to those appearing in the table. For example, the results for $S$ deviate from the tabulated ones by less than 10%. However, the results for the order parameter $\tilde{m}_{A_3B}$ are, in most cases, significantly smaller than the values presented in the table. This stems from the fact that the lattice is not uniformly ordered (in contrast to the configurations obtained from an $A_3B$ state), but that it consists of several large ordered regions, each dominated by a different component $\tilde{m}^{(i)}_{A_3B}$ of the order parameter [Eq. (7)]. This difficulty with the MC simulation is known to occur also below the critical point of second-order transitions in ferromagnetic systems such as the square and the simple-cubic Ising lattices, where large long-lived droplets of + and − spins are generally formed.[41]

It should be pointed out that, because of the nonuniform long-range order of these structures, the approximations $S_{Mi}$ do not converge and, therefore, provide an overestimation of the correct values. Therefore, the fact that near $h_c$ the free energy of several structures has been found to be slightly below the values presented in the table should not be interpreted as higher stability of these structures. In fact, such metastable (not perfectly ordered) states have been obtained not only near $h_c$, but at much lower fields; for $h/J \leq 10.8$, however, their free energy has always been found to be larger than the free energy of the states with a uniform $A_3B$ long-range order. In our view, the formation of the metastable states far from the transition point does not reflect a physical metastability but rather has to do with the finite size of the system and the inefficiency of the MC simulation defined by Eqs. (8) and (9). In this context, it should be pointed out that, in general, the efficiency of the asymmetric [Eq. (8)] and the symmetric [Eq. (9)] MC procedures has been found to be comparable. However, for $h/J \leq 11.25$, MC runs starting from a fully magnetized state have always yielded an $A_3B$ ordered state with the asymmetric procedure, but never with the symmetric one.

To summarize this part of the work, it is clear that our results for the entropy have made it possible to very accurately determine the transition point located at the end of a narrow coexistence region of the range $\Delta h/h_c$ $=(11.25-11.21)/11.21 \sim 0.04$. In this region, the ordered state is metastable. The transition is sharp in the sense that relatively large jumps of $S$, $U$, and $\tilde{m}_{A_3B}$ (see Table IV) occur within a very small range of $h$, $h/h_c=0.1/11.21 \sim 0.001$. This provides strong evidence (but still not a proof) that the transition is of first order. In fact, former MC studies[33–36] have also predicted a phase diagram of first-order transitions but did not allow the locations of the transition points within the hysteresis loops to be determined. The location of the transition points has been determined by a recent free-energy analysis of Binder[39] (based on thermodynamic integration). This analysis, however, turns out to be less accurate than ours since it predicts $h_c/J \sim 11$, where, according to our study, the disordered state cannot be simulated at all.

In Table III results are presented at $h=0$ for several reciprocal temperatures $K=J/k_BT$ (we use $K$ rather than $1/K$ for consistency with Binder's presentation[39]). The disordered region ($K \leq 0.568$) and the $AB$ ordered region ($K \geq 0.587$) have essentially the same properties as those discussed for these regions in Table II. The table also reveals that (as in Table II) the disordered phase in the coexistence region has a lower free energy than the ordered one. The difference $\Delta F$ decreases from $\sim 0.013$ to $\sim 0.002$ upon going from $K=0.569$ to 0.586. The smallest difference 0.002 is still significantly larger than that obtained for $h_c$ in Table II. However, one should also add, to the free-enegy balance, the contribution of the ground-state entropy $S'$, which is larger than 0 for a finite lattice.[42,43] The degeneracy of the ground state is $3\times 2^{N^{1/2}}$, which for $L=21$ yields $S' \sim 0.000\,65$. The corresponding decrease in the free energy of the ordered state, $F'$, at $K=0.586$ is therefore $F'=(1/K)S'=0.0011$; this reduces $\Delta F$ to $\sim 0.0009$, which is within the statistical error. We therefore determine a critical reciprocal temperature $K_c=0.586(1)$. It should be pointed out that the range of the coexistence region, $\Delta K/K_c=0.017/0.586$ $\sim 0.03$, is larger than that observed in Table II. The jumps in $S$, $U$, and $\tilde{m}_{AB}$ (see Table IV) are also larger than those detected for the previous transition and occur within a narrow range $K/K_c=0.001/0.586 \sim 0.002$ (no intermediate states between ordered and disordered states have been obtained for $K > K_c$). This constitutes strong evidence for a first-order transition, in accord with conclusions of former studies.[18–26,33–36,39]

Our result for the critical temperature $k_BT_c/J$ $=1.706(3)$ should be compared with the value of 4 obtained by mean-field theory[16] and that of 1.46 predicted by the quasichemical approximation.[18] It is lower than the values of 1.89 and 1.766 obtained by the cluster-variation method[20–22] and the MC method,[33,34] respectively, and it is also lower than the value of 1.73 obtained by both the free-energy analysis of Binder[39] and a (2,2) Padé approximant of the specific heat.[33] Our value $\Delta S=0.267$ (Table IV) is larger than the MC estimate of Phani *et al.*[34] ($\sim 0.2$) and the cluster-variation—method prediction, $\Delta S \sim 0.25$.

We have also analyzed two other transitions (denoted 3 and 4 in Fig. 1). For transition 3 the system has been

TABLE III. Results obtained at $h=0$ for several values of the reciprocal temperature $K=J/k_BT$ (transition 2 in Fig. 1). The first-order transition occurs at $K_c=0.586(1)$, $k_BT_c/J=1.706(3)$. For details, see explanation for Table II.

| | Order | | | Coexistence | | | Disorder | |
|---|---|---|---|---|---|---|---|---|
| $K$ | 0.64 | 0.61 | 0.59 | 0.586($K_c$) | 0.582 | 0.569 | 0.565 | 0.56 | 0.55 |
| $S/k_BN$ | 0.065 2(1) | 0.090 2(1) | 0.116 7(2) | 0.123 9(3) | 0.131 9(2) | 0.178 (2) | | | |
| | | | | 0.391 0(7) | 0.398 4(5) | 0.413 8(4) | 0.417 8(4) | 0.422 7(4) | 0.431 5(4) |
| $-F/JN$ | 2.013 6(1) | 2.019 5(1) | 2.025 6(1) | 2.026 6(2) | 2.028 4(3) | 2.034 (2) | | | |
| | | | | 2.028 6(7) | 2.033 9(5) | 2.047 2(4) | 2.052 0(4) | 2.058 2(4) | 2.071 8(4) |
| $-U/Jn$ | 1.911 7(1) | 1.871 6(3) | 1.827 6(2) | 1.815 2(3) | 1.801 8(4) | 1.721 (5) | | | |
| | | | | 1.361 4(7) | 1.349 4(5) | 1.320 0(5) | 1.312 5(3) | 1.303 6(3) | 1.286 9(3) |
| $\tilde{m}_{AB}$ | 0.971 0(1) | 0.954 1(2) | 0.932 5(2) | 0.925 5(3) | 0.917 7(3) | 0.856 (4) | | | |
| | | | | 0.002 (3) | 0.002 (3) | 0.002 (3) | 0.002 (3) | 0.001 (3) | 0.002 (1) |

simulated at constant temperature $k_BT/J=0.6$ for several values of $h/J$ between 4.7 and 4. According to our results the ordered phase exists down to $h/J=4.1$, i.e., simulations starting from a completely ordered $A_3B$ state have led to a uniformly ordered configuration for $h/J\geq 4.1$, but to nonuniformly ordered ones for $h/J<4.1$. It was impossible, however, to simulate a perfectly disordered phase for $4.5\geq h/J\geq 4$, i.e., the values of $m_\nu$, $\nu=1,4$ [Eq. (5)] were always slightly different from each other. Furthermore, for these quasidisordered structures our approximations for the entropy did not converge and the correct values have been estimated by a rather crude extrapolation. We estimate $h_c/J=4.4\pm 0.1$, which is higher than the value of $\sim 4.1$ obtained in Ref. 39. The discontinuities $\Delta S$, $\Delta U$, and $\Delta\tilde{m}_{A_3B}$ (see Table IV) are significantly smaller than those observed for transitions 1 and 2; they are, however, rather inaccurate and only provide a crude estimation. It was even more difficult to analyze transition 4 (Fig. 1). Simulations, starting from a completely ordered AB state, maintained this order for $h/J\leq 3.8$; again, for higher values of $h$ only nonuniformly ordered configurations have been obtained. However, none of the MC runs, starting from a random configuration, have led to a disordered state. Therefore, our best estimation is $3.2\leq h_c/J\leq 3.8$, since for $h/J\leq 3.2$, the ordered states have always led to the lowest free energy. It should be pointed out that Binder[39] was able to determine $h_c/J\sim 3.65$.

### C. Residual ground-state entropies

We have carried out several simulations at $T=0$ for the critical fields $h_c/J=4$ (all starting from random configurations) and $h_c/J=12$ (simulations starting from random and fully magnetized configurations). The results are presented in the two lower rows of Table I. For $h_c/J=12$ the various approximations converge to the value $S(0)/k_B=0.249\,89(2)$ $[=0.360\,51(3)\ln 2]$. This highly accurate result is larger than Binder's[39] estimate of $\sim 0.2308\sim\frac{1}{3}\ln 2$ and larger than the upper-bound value $\sigma_u'=0.2398$ $(=0.3460\ln 2)$ predicted by Hadjuković and Milošević.[37] The disagreement of our result with $\sigma_u'$ does not prove that it is incorrect since one can argue that a basic assumption in the derivation of $\sigma_u'$ is not generally valid.[44] In fact, for the one-dimensional Ising antiferromagent, for $k=1000$ (where $k$ is the interaction range), the exact residual entropy 0.005 25 is *larger* than $\sigma_u'=0.004\,87$.[45]

For $h/J=4$ our appoximations for $S$ did not converge, but the differences $S_i-S_{i+1}$, $i=1,3$, decrease strongly from 0.030 to 0.0025 and 0.0012. If one *assumes* that this trend will continue also for $i\geq 4$, one can extrapolate $S(0)/k_B=0.239(1)$ $[=0.345(1)\ln 2]$, which is smaller than the result obtained for $h_c/J=12$ but larger than Binder's[39] value of $\frac{1}{3}\ln 2$.

## IV. CONCLUSIONS

Our method has yielded very accurate results (0.5–0.01 %) for the entropy of homogeneous configurations (i.e., disordered or uniformly ordered), of the fcc Is-

TABLE IV. Estimates of the discontinuities of the entropy $\Delta S$, the internal energy $\Delta U$, the magnetization $\Delta M$, and the order parameter $\Delta\tilde{m}$, obtained at transitions 1, 2, and 3, respectively (see Fig. 1). The results for transition 3 should be considered as a crude estimation. The result for $\Delta S$ for transition 2 takes into account the ground-state entropy (see Section IIIB).

| Transition number on Fig. 1 | $\Delta S/k_BN$ | $\Delta U/Nk_BT$ | $\Delta M$ | $\Delta\tilde{m}$ |
|---|---|---|---|---|
| 1 | 0.092 7(8) | 0.091 8(6) | 0.081 3(6) | 0.567(7) |
| 2 | 0.266(1) | 0.265 9(6) | | 0.925 3(5) |
| 3 | 0.006 | 0.005 | 0.00 5 | 0.66 |

ing antiferromagnet. These results are at least 1 order of magnitude more accurate than estimates for the entropy obtained with thermodynamic integration by Binder.[39] It should be pointed out, however, that Binder's results have apparently been obtained for smaller lattices and shorter MC runs than those employed here, and therefore part of our better accuracy is due to better statistics. Unfortunately, this information about the simulation is not provided in Ref. 39, which prevented us from performing a detailed comparison of the efficiency of the two methods. The accurate results for the entropy have led to accurate estimates of the free energy of the coexisting ordered and disordered phases, making it possible to determine the transition points and the discontinuities of the thermodynamic functions with high precision. The results give strong evidence that the transitions are of first order, in agreement with previous studies. We also point out the difficulties in simulating the disordered phase with the MC method (and therefore in investigating the transitions of low temperatures close to $h/J=4$). Another aspect of our study is the estimation of residual ground-state entropies. At $h_c/J=12$ we obtain an extremely accurate estimate which turns out to be significantly larger than Binder's[39] result; it is also larger than a theoretical upper-bound value for the entropy calculated by Hadjuković and Milošević.[37] However, we argue[44] that a basic assumption of their derivation should not necessarily be satisfied in general. For $h/J=4$ our result is again larger than the value obtained by thermodynamic integration.

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[44]$\sigma_u$ and $\sigma'_u$, defined in Ref. 37 do not necessarily constitute upper bounds for the entropy. Let us denote by $A(p,n\downarrow)$ the exact number of arrangements of $n\downarrow$ spins turned down such that each — spin forbids $p$ lattice sites to be occupied by any other — spin. The values of $A(p,n\downarrow)$ lead to the *correct* ground-state entropy $S$ (see Ref. 37). Obviously, any $1\leq f<p$

leads to $A(f,n\downarrow) > A(p,n\downarrow)$, and therefore to an overestimation of $S$. However, in Ref. 37, $A(f,n\downarrow)$ [for $f=r$ and $f=(3p+1)/4$] are approximated by $C(f,n\downarrow)$ [Eq. (10)] (Ref. 37), which satisfy $C(f,n\downarrow) < A(f,n\downarrow)$, since in $C(f,n\downarrow)$ the overlaps are not taken into account. Therefore, $\sigma_u(r)$ and $\sigma'_u((3p+1)/4)$ which are calculated by the $C$'s do not necessarily overestimate $S$.

[45]S. Milošević (private communication).