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Cluster-variation method applied in the pair approximation to the $S = 1$ Ising ferromagnet having additional single-ion-type uniaxial anisotropy

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In the Weiss molecular-field approximation, the $S = 1$ Ising-model ferromagnet possessing additional single-ion-type uniaxial anisotropy is known to exhibit (depending upon the ratio of anisotropy and interaction constants) both first-order (discontinuous) and second-order (continuous) magnetic phase transitions which join at a tricritical point. We further investigate the above model system in the spin-pair approximation using the cluster-variation method. Within this improved approximation, results are found for the temperature and anisotropy dependences of the thermal-average quantities $\langle S_i\rangle$, $\langle S_i^2\rangle$, $\langle S_iS_{i'}\rangle$, $\langle S_iS_{i'}^2\rangle$, $\langle S_i^2S_{i'}^2\rangle$ (i,i' are nearest-neighbor lattice sites), a better estimate for the location of the tricritical point is achieved, and the specific heat and initial paramagnetic susceptibility are calculated. To illustrate these results, the simple cubic lattice is used as an example of application.

I. INTRODUCTION

In an attempt to investigate the possibility of first-order (*discontinuous*) phase transitions in magnetic systems, Capel[1] chose to study the $S = 1$ Ising-model ferromagnet having additional single-ion-type uniaxial anisotropy. Blume[2] independently proposed an essentially equivalent model for the first-order phase transitions in UO_2. In a Weiss approximation, the above authors showed that, for certain values of the anisotropy constant relative to the exchange-interaction constant, the long-range order parameter $\langle S_z\rangle$ (i.e., the thermal average of the z component of the spin operator) can have a finite-jump discontinuity at the transition temperature, a characteristic of first-order phase transitions. For other values of the anisotropy constant relative to the exchange-interaction constant, they found that second-order (*continuous*) phase transitions appear. The point at which the line of second-order phase transitions changes into a line of first-order phase transitions has special interest and is known as a *tricritical point*, a name proposed by Griffiths[3] since such a point can also be viewed as the intersection of three lines of critical points in a suitable thermodynamic variable space (a tricritical point is a point at which three distinct phases in coexistence become identical simultaneously). The above type $S = 1$ Ising model has also been proposed by Blume, Emery, and Griffiths[4] as a model for the λ transitions and phase separations in ^{3}He-^{4}He mixtures. Within the Weiss approximation, the latter authors found qualitative agreements with many of the experimental features. The interest in the model led to the exact series analyses of Oitmaa,[5] and Saul, Wortis, and Stauffer.[6] Another application of the model for magnetic alloys can be found in the work of Bernasconi and Rys.[7]

In this paper we further study the model through use of the cluster-variation method in the spin-pair approximation. We shall focus upon the magnetic properties of the model, the application to ^{3}He-^{4}He mixtures in pair approximation having been previously published.[8] The contents of the present paper are outlined as follows. In Sec. II, we present the system Hamiltonian and identify some of its general properties and, in Sec. III, the basic equilibrium equations are derived in the pair approximation leading to results for the tricritical-point location, nearest-neighbor correlation functions, specific heat, and zero-field paramagnetic susceptibility. To illustrate these results, the simple cubic lattice is used as an example of application. Finally, a summary and discussion of the results are given in Sec. IV.

II. THE SYSTEM HAMILTONIAN

We consider the following $S = 1$ Ising Hamiltonian having crystal-field (single-ion-type) uniaxial anisotropy:

$$H = -\sum_{(i,j)} J_{ij}S_{iz}S_{jz} + \Delta\sum_{i} S_{iz}^2 , \qquad (2.1)$$

where $S_{iz} = 0, \pm 1$ is the z component of the spin operator of an ion localized upon lattice site i, $J_{ij} = J_{ji} > 0$ ($J_{ii} = 0$) denotes the strength of the ferromagnetic-interaction energy between the spins of ions at lattice sites i and j, and Δ is the uniaxial crystal-field anisotropy constant. The symbol $\sum_{(i,j)}$

indicates that the summation is taken over all distinct pairs of lattice sites. We will frequently use the following equivalent symbols interchangeably

$$\sum_{(i,j)} \leftrightarrow \sum_{i>j} \leftrightarrow \frac{1}{2} \sum_i \sum_j .$$

In our treatment, we consider a canonical ensemble of magnetic systems where each member system therefore has a fixed number N of localized ions. Due to the symmetry of the crystal field, each ionic triplet is split into a singlet $S_{iz}=0$ with zero energy and a doublet $S_{iz}=\pm 1$ with energy Δ.

As pointed out by Capel,[1] the following facts about the system Hamiltonian (2.1) can readily be observed:

(a) There are only two possibilities for the ground state of the system, namely, (i) each and every ion has $S_{iz}=1$ or each and every ion has $S_{iz}=-1$, i.e., $\langle S_z\rangle = 1$ or $\langle S_z\rangle = -1$ respectively, or (ii) each and every ion has $S_{iz}=0$, i.e., $\langle S_z\rangle = 0$. These possibilities can be shown very easily by rewriting the Hamiltonian (2.1) as follows:

$$H=\frac{1}{2}\sum_{(i,j)} J_{ij}(S_{iz}-S_{jz})^2+\sum_i\left(\Delta-\frac{1}{2}\sum_j J_{ij}\right)S_{iz}^2 . \tag{2.2}$$

For

$$\Delta<\frac{1}{2}\sum_j J_{ij},$$

the ground state is the state (i) while for

$$\Delta>\frac{1}{2}\sum_j J_{ij},$$

the ground state is the state (ii). If Δ is close to

$$\frac{1}{2}\sum_j J_{ij},$$

the ground state of the system will be almost degenerate since then the state (i) and the state (ii) have nearly the same energy. Thus, a small change in the external condition, such as the temperature of the heat bath, will give rise to a jump from a state with no magnetic ordering to a state with high magnetic ordering.

(b) Three particular cases of the Hamiltonian (2.1) are well known and easily established: (i) $\Delta=-\infty$, equivalent to the $S=\frac{1}{2}$ Ising case, with magnetic ordering at low temperatures, i.e., $\langle S_z\rangle \neq 0$, (ii) $\Delta=0$, equivalent to the $S=1$ Ising case, with magnetic ordering at low temperatures, i.e., $\langle S_z\rangle \neq 0$, (iii) $\Delta=\infty$, equivalent to the case $S=0$, with no magnetic ordering, i.e., $\langle S_z\rangle=0$.

III. SPIN-PAIR APPROXIMATION LEADING TO RESULTS FOR ORDER PARAMETERS AND TRICRITICAL PHASE DIAGRAM

In this section we apply the cluster-variation method[9-13] to the Hamiltonian (2.1),

$$\mathcal{H}=-\sum_{(i,j)} J_{ij}S_{iz}S_{jz}+\Delta\sum_i S_{iz}^2 .$$

Since we are considering an Ising-type Hamiltonian, only the z component of the spin operator appears in our discussions. Consequently, hereafter we shall simply write S_i instead of S_{iz} for notational convenience. Then, the variational free-energy function $\mathfrak{F}$ is written in a two-spin approximation as

$$\begin{aligned}\mathfrak{F}=&\sum_i \mathrm{Tr}_i\rho_i^{(1)}(i)(\Delta S_i^2)+\sum_{i>j}\mathrm{Tr}_{i,j}\rho_t^{(2)}(i,j)(-J_{ij}S_iS_j)+kT\sum_i\mathrm{Tr}_i\rho_t^{(1)}(i)\ln\rho_t^{(1)}(i)\\&+kT\sum_{i>j}[\mathrm{Tr}_{i,j}\rho_t^{(2)}(i,j)\ln\rho_t^{(2)}(i,j)-\mathrm{Tr}_i\rho_t^{(1)}(i)\ln\rho_t^{(1)}(i)-\mathrm{Tr}_j\rho_t^{(1)}(j)\ln\rho_t^{(1)}(j)] ,\end{aligned} \tag{3.1}$$

where $\rho_t^{(1)}(i)$, $\rho_t^{(2)}(i,j)$ are one- and two-site reduced trial density matrices, respectively.

In order to minimize expression (3.1), we first attempt to specify all the elements of $\rho_t^{(1)}(i)$, $\rho_t^{(2)}(i,j)$ in terms of appropriate unknown expectation values of our problem. Let us choose a representation for the operators in which each operator S_i is diagonal, i.e.,

$$S_i=\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}\equiv\mathrm{diag}(1,0,-1) ,$$

$$S_iS_j=\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}\otimes\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}$$

$$\equiv\mathrm{diag}(1,0,-1,0,0,0,-1,0,1) \quad i\neq j ,$$

where $\otimes$ designates the direct-product operation. In this representation, the Hamiltonian (2.1) is diagonal, hence all the density matrices are diagonal, i.e.,

$$\rho_t^{(1)}(i)=\mathrm{diag}[\epsilon_1(i),\epsilon_2(i),\epsilon_3(i)] , \tag{3.2}$$

$$\rho_t^{(2)}(i,j)=\mathrm{diag}[\lambda_1(i,j),\lambda_2(i,j),\ldots,\lambda_9(i,j)] . \tag{3.3}$$

The next step is to express $\{\epsilon_k(i)\}$ and $\{\lambda_l(i,j)\}$ in terms of unknown expectation values such that (a) the proper expectation value of any operator $\mathcal{O}$ is derived from the formula

$$\langle \mathcal{O} \rangle = \mathrm{Tr}(\rho \mathcal{O}) \ , \tag{3.4}$$

where ρ is the canonical density matrix of thermal equilibrium, (b) the appropriate reducibility conditions are satisfied, and (c) the normalization conditions are satisfied.

One begins with the one-spin trial density matrices $\rho_t^{(1)}(i)$. Considering the expectation values $\langle S_i \rangle$ and $\langle S_i^2 \rangle$, one has, respectively,

$$\begin{aligned}\langle S_i \rangle &= \mathrm{Tr}_i S_i \rho_t^{(1)}(i)\\ &= \mathrm{Tr}_i \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \epsilon_1(i) & 0 & 0 \\ 0 & \epsilon_2(i) & 0 \\ 0 & 0 & \epsilon_3(i) \end{pmatrix}\\ &= \epsilon_1(i) - \epsilon_3(i) \ ,\end{aligned}$$

$$\begin{aligned}\langle S_i^2 \rangle &= \mathrm{Tr}_i S_i^2 \rho_t^{(1)}(i)\\ &= \mathrm{Tr}_i \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \epsilon_1(i) & 0 & 0 \\ 0 & \epsilon_2(i) & 0 \\ 0 & 0 & \epsilon_3(i) \end{pmatrix}\\ &= \epsilon_1(i) + \epsilon_3(i) \ .\end{aligned}$$

Thus, one has

$$\begin{aligned}\epsilon_1(i) &= \tfrac{1}{2}(\langle S_i \rangle + \langle S_i^2 \rangle) \ ,\\ \epsilon_2(i) &= -\tfrac{1}{2}(\langle S_i \rangle - \langle S_i^2 \rangle) \ ,\\ \epsilon_3(i) &= 1 - \langle S_i^2 \rangle \ ,\end{aligned} \tag{3.5}$$

where the last equation is obtained from the normalization condition $\mathrm{Tr}_i \rho_t^{(1)}(i) = 1$.

In the same manner, the two-spin trial density matrices $\rho_t^{(2)}(i,j)$ are found to be

$$\begin{aligned}\lambda_1(i,j) &= \tfrac{1}{4}(\langle S_i S_j \rangle + \langle S_i^2 S_j \rangle + \langle S_i S_j^2 \rangle + \langle S_i^2 S_j^2 \rangle) \ ,\\ \lambda_2(i,j) &= \tfrac{1}{2}(\langle S_i \rangle + \langle S_i^2 \rangle - \langle S_i S_j^2 \rangle - \langle S_i^2 S_j^2 \rangle) \ ,\\ \lambda_3(i,j) &= -\tfrac{1}{4}(\langle S_i S_j \rangle + \langle S_i^2 S_j \rangle - \langle S_i S_j^2 \rangle - \langle S_i^2 S_j^2 \rangle) \ ,\\ \lambda_4(i,j) &= \tfrac{1}{2}(\langle S_j \rangle + \langle S_j^2 \rangle - \langle S_i^2 S_j \rangle - \langle S_i^2 S_j^2 \rangle) \ ,\\ \lambda_5(i,j) &= 1 - \langle S_i^2 \rangle - \langle S_j^2 \rangle + \langle S_i^2 S_j^2 \rangle \ ,\\ \lambda_6(i,j) &= -\tfrac{1}{2}(\langle S_j \rangle - \langle S_j^2 \rangle - \langle S_i^2 S_j \rangle + \langle S_i^2 S_j^2 \rangle) \ ,\\ \lambda_7(i,j) &= -\tfrac{1}{4}(\langle S_i S_j \rangle - \langle S_i^2 S_j \rangle + \langle S_i S_j^2 \rangle - \langle S_i^2 S_j^2 \rangle) \ ,\\ \lambda_8(i,j) &= -\tfrac{1}{2}(\langle S_i \rangle - \langle S_i^2 \rangle - \langle S_i S_j^2 \rangle + \langle S_i^2 S_j^2 \rangle) \ ,\\ \lambda_9(i,j) &= \tfrac{1}{4}(\langle S_i S_j \rangle - \langle S_i^2 S_j \rangle - \langle S_i S_j^2 \rangle + \langle S_i^2 S_j^2 \rangle) \ .\end{aligned} \tag{3.6}$$

One can easily verify that the normalization and reducibility conditions are indeed respectively satisfied, i.e.,

$$\mathrm{Tr}_{i,j} \rho_t^{(2)}(i,j) = \sum_{l=1}^{9} \lambda_l(i,j) = 1 \ , \tag{3.7}$$

and

$$\begin{aligned}\lambda_1(i,j) + \lambda_2(i,j) + \lambda_3(i,j) &= \epsilon_1(i) \ ,\\ \lambda_4(i,j) + \lambda_5(i,j) + \lambda_6(i,j) &= \epsilon_2(i) \ ,\\ \lambda_7(i,j) + \lambda_8(i,j) + \lambda_9(i,j) &= \epsilon_3(i) \ .\end{aligned} \tag{3.8}$$

Using the density matrices whose elements are given by (3.5) and (3.6), one can express the variational function in terms of the unknown expectation values and then perform the minimization with respect to these expectation values. To proceed along these lines, then, the variational function in the two-spin cluster approximation given by (3.1) can now be expressed as

$$\begin{aligned}\mathcal{F}(\{\langle S_i \rangle\}, \{\langle S_i^2 \rangle\}, \{\langle S_i S_j \rangle\}, \{\langle S_i S_j^2 \rangle\}, \{\langle S_i^2 S_j^2 \rangle\}) = {}& \sum_i \Delta \langle S_i^2 \rangle - \sum_{i>j} J_{ij} \langle S_i S_j \rangle + kT \sum_i \sum_{k=1}^{3} \epsilon_k(i) \ln \epsilon_k(i)\\ &+ kT \sum_{i>j} \left\{ \sum_{l=1}^{9} \lambda_l(i,j) \ln \lambda_l(i,j) - \sum_{m=1}^{3} [\epsilon_m(i) \ln \epsilon_m(i) + \epsilon_m(j) \ln \epsilon_m(j)] \right\} \ ,\end{aligned} \tag{3.9}$$

where the sets $\{\epsilon_k(i)\}$, $\{\lambda_l(i,j)\}$ are given, respectively, by (3.5) and (3.6). Minimizing the above expression (3.9) with respect to $\langle S_p\rangle$, $\langle S_p^2\rangle$, $\langle S_pS_q\rangle$, $\langle S_pS_q^2\rangle$, $\langle S_p^2S_q^2\rangle$, one obtains, respectively, the following five equilibrium equations:

$$\ln\left[\frac{\epsilon_1(p)}{\epsilon_3(p)}\right]=\sum_{j(\neq p)}\ln\left[\frac{\epsilon_1(p)}{\epsilon_3(p)}\,\frac{\lambda_8(p,j)}{\lambda_2(p,j)}\right] , \tag{3.10a}$$

$$-2\frac{\Delta}{kT}=\ln\left[\frac{\epsilon_1(p)\epsilon_3(p)}{\epsilon_2(p)^2}\right]+\sum_{j(\neq p)}\left[\ln\left[\frac{\lambda_2(p,j)\lambda_8(p,j)}{\lambda_5(p,j)^2}\right]-\ln\left[\frac{\epsilon_1(p)\epsilon_3(p)}{\epsilon_2(p)}\right]\right] , \tag{3.10b}$$

$$4J_{pq}/kT=\ln[\lambda_1(p,q)\lambda_9(p,q)/\lambda_3(p,q)\lambda_7(p,q)] , \tag{3.10c}$$

$$0=\ln\left\{[\lambda_1(p,q)\lambda_3(p,q)/\lambda_7(p,q)\lambda_9(p,q)]\frac{\lambda_8(p,q)^2}{\lambda_2(p,q)^2}\right\} , \tag{3.10d}$$

$$0=\ln\left[\frac{\lambda_1(p,q)\lambda_3(p,q)\lambda_7(p,q)\lambda_9(p,q)}{[\lambda_2(p,q)\lambda_4(p,q)\lambda_6(p,q)\lambda_8(p,q)]^2}\lambda_5(p,q)^4\right] . \tag{3.10e}$$

Let us now assume *nearest-neighbor* (nn) *range of interaction,* i.e.,

$$J_{ij}=\begin{cases} J \text{ for } i,j \text{ being a } \textit{nearest-neighbor} \text{ pair of lattice sites,}\\ 0 \text{ otherwise}. \end{cases} \tag{3.11}$$

Then, from (3.10) using (3.11), it can be shown that, provided p,q are *not* nearest-neighbor lattice sites,

$$\begin{aligned}\langle S_pS_q\rangle &= \langle S_p\rangle\langle S_q\rangle ,\\ \langle S_pS_q^2\rangle &= \langle S_p\rangle\langle S_q^2\rangle ,\\ \langle S_p^2S_q^2\rangle &= \langle S_p^2\rangle\langle S_q^2\rangle .\end{aligned} \tag{3.12}$$

Consequently, if the summation $\sum_{j(\neq p)}\cdots$ appearing in (3.10a) is split into two parts, i.e.,

$$\sum_{j(\neq p)}\cdots=\sum_{\substack{j(\neq p)\\ (j,p \text{ are nn})}}\cdots+\sum_{\substack{j(\neq p)\\ (j,p \text{ are not nn})}}\cdots ,$$

then, using (3.12), the second summation over all sites j which are not nearest neighbors of site p gives zero contribution. Hence, equation (3.10a) simplifies to

$$\ln\left[\frac{\epsilon_1(p)}{\epsilon_3(p)}\right]=z\ln\left[\frac{\epsilon_1(p)}{\epsilon_3(p)}\,\frac{\lambda_8(p,p')}{\lambda_2(p,p')}\right] , \tag{3.10a$'$}$$

where the *lattice coordination number* z is the number of nearest-neighbor lattice sites surrounding any lattice site, and p,p' are nearest-neighbor lattice sites. Similarly, Eq. (3.10b) simplifies to

$$-2\frac{\Delta}{kT}=\ln\left[\frac{\epsilon_1(p)\epsilon_3(p)}{\epsilon_2(p)^2}\right]+z\left[\ln\left[\frac{\lambda_2(p,p')\lambda_8(p,p')}{\lambda_5(p,p')^2}\right]-\ln\left[\frac{\epsilon_1(p)\epsilon_3(p)}{\epsilon_2(p)^2}\right]\right] \tag{3.10b$'$}$$

In thermal equilibrium, due to lattice translational symmetry, one defines

$$a\equiv\langle S_p\rangle,\quad b\equiv\langle S_p^2\rangle,\quad c\equiv\langle S_pS_{p'}\rangle,$$
$$d\equiv\langle S_pS_{p'}^2\rangle,\quad e\equiv\langle S_p^2S_{p'}^2\rangle , \tag{3.13}$$

whereupon one is then able to write, using (3.5), (3.6), and (3.13),

$$\begin{aligned}\epsilon_1&=\epsilon_1(p)=\tfrac{1}{2}(a+b) ,\\ \epsilon_2&=\epsilon_2(p)=1-b ,\\ \epsilon_3&=\epsilon_3(p)=\tfrac{1}{2}(-a+b)\end{aligned} \tag{3.14a}$$

and

$$\begin{aligned}\lambda_1&=\lambda_1(p,p')=\tfrac{1}{4}(c+2d+e) ,\\ \lambda_2&=\lambda_2(p,p')=\tfrac{1}{2}(a+b-d-e) ,\\ \lambda_3&=\lambda_3(p,p')=-\tfrac{1}{4}(c-e) ,\\ \lambda_4&=\lambda_4(p,p')=\tfrac{1}{2}(a+b-d-e) ,\\ \lambda_5&=\lambda_5(p,p')=1-2b+e ,\\ \lambda_6&=\lambda_6(p,p')=\tfrac{1}{2}(-a+b+d-e) ,\\ \lambda_7&=\lambda_7(p,p')=-\tfrac{1}{4}(c-e) ,\\ \lambda_8&=\lambda_8(p,p')=\tfrac{1}{2}(-a+b+d-e) ,\\ \lambda_9&=\lambda_9(p,p')=\tfrac{1}{4}(c-2d+e) .\end{aligned} \tag{3.14b}$$

After some algebraic manipulations, the five equilibrium equations (3.10) can now be written in terms of a, b, c, d, and e as follows:

$$f_1=(-a+b)^{z-1}(a+b-d-e)^{z}-(a+b)^{z-1}(-a+b+d-e)^{z}=0\ , \tag{3.15a}$$

$$f_2=(1-b)^{z-1}(c+e+2d)^{z/2}\exp(-\tfrac{1}{2}w)-2(a+b)^{z-1}(1-2b+e)^{z/2}\exp(-\gamma w)=0\ , \tag{3.15b}$$

$$f_3=(c-e)^2-(c+e+2d)(c+e-2d)\exp(-4w/z)=0\ , \tag{3.15c}$$

$$f_4=(c+e+2d)(-a+b+d-e)^2-(c+e-2d)(a+b-d-e)^2=0\ , \tag{3.15d}$$

$$f_5=(a+b-d-e)^2-(c+e+2d)(1-2b+e)\exp(-w/z)=0\ , \tag{3.15e}$$

where $w\equiv zJ/kT$, $\gamma\equiv\Delta/zJ$.

The equilibrium Helmholtz free energy F is given in terms of the parameters w, γ by

$$(NkT)^{-1}F(a(w,\gamma),b(w,\gamma),c(w,\gamma),d(w,\gamma),e(w,\gamma))=w\gamma b-\tfrac{1}{2}wc+(1-z)\sum_{k=1}^{3}\epsilon_k\ln\epsilon_k+\tfrac{1}{2}z\sum_{l=1}^{9}\lambda_l\ln\lambda_l\ , \tag{3.16}$$

where a, b, c, d, and e are the equilibrium solutions of Eqs. (3.15), which make $F=\min\mathfrak{F}$, and the quantities $\{\epsilon_k\}$ and $\{\lambda_l\}$ are given by Eqs. (3.14a) and (3.14b), respectively.

To determine the possibility of a second-order phase transition temperature T_c, first consider a temperature $T\lesssim T_c$; then, $a\gtrsim 0$ and $d\gtrsim 0$ [the fact that $d=0$ whenever $a=0$ follows from Eq. (3.15a)] whereupon one can expand (3.15a) and (3.15d) in power series of a and d, and retaining only the first-order small terms, one has

$$[(z-1)(b-e)-zb]a+(zb)d=0\ , \tag{3.17a}$$

$$(c+e)a-(b+c)d=0\ . \tag{3.17b}$$

To obtain nontrivial solutions for a and d, one must therefore have

$$\begin{vmatrix}(z-1)(b-e)-zb & zb\\ c+e & -(b+c)\end{vmatrix}=0$$

or

$$b=(z-1)c\quad (T=T_c)\ . \tag{3.18}$$

Equation (3.18) is a *necessary* condition for a second-order phase transition temperature T_c.

At $T=T_c$, the facts that $a=d=0$ result in Eqs. (3.15a) and (3.15d) becoming identities and one is left with the following forms of the remaining equations from the set (3.15):

$$(1-b)^{z-1}(c+e)^{z/2}\exp(-\tfrac{1}{2}w)-2b^{z-1}(1-2b+e)^{z/2}\exp(-\gamma w)=0\ , \tag{3.19a}$$

$$(c-e)^2-(c+e)^2\exp(-4w/z)=0\ , \tag{3.19b}$$

$$(b-e)^2-(c+e)(1-2b+e)\exp(-w/z)=0\ . \tag{3.19c}$$

From Eqs. (3.18) and (3.19), one can then derive the following relation connecting w_c $(\equiv zJ/kT_c)$ and γ for *second-order* (continuous) phase transitions:

$$w_c\gamma=z\ln[(\tfrac{1}{2}z-1)\exp(w_c/z)-\tfrac{1}{2}z\exp(-w_c/z)]+\ln 2+(z-1)\ln(z-1)+(z-1)\ln[2\sinh(w_c/z)]$$
$$-(z-1)\ln[\tfrac{1}{2}(z-2)^2\exp(2w_c/z)+(z-2)\exp(w_c/z)-z(z-2)-z\,exp(-w_c/z)+\tfrac{1}{2}z^2\exp(-2w_c/z)]\ . \tag{3.20}$$

The *first-order* (discontinuous) phase transitions can be found by equating appropriate equilibrium free energies (3.16), i.e., such transitions are characterized by

$$F(a_1,b_1,c_1,d_1,e_1,w,\gamma)=F(0,b_0,c_0,0,e_0,w,\gamma)\ , \tag{3.21}$$

where a_1, b_1, c_1, d_1, and e_1 are solutions of (3.15) and b_0, c_0 and e_0 are solutions of (3.19).

For the case of a *simple cubic* lattice ($z=6$) Eq. (3.20) has solutions only for $\gamma\leq 0.4705$; thus, for $\gamma>0.4705$, there is no second-order phase transition possible. However, as $T\rightarrow 0$, there must be complete magnetic ordering if $\gamma<\frac{1}{2}$, i.e., $\Delta<\frac{1}{2}zJ$ (cf. Sec. II). Hence, one expects (as will indeed be verified) that for $\gamma\approx 0.4705$, the second-order phase transitions change to first-order phase transitions. With the aid of a digital computer, (3.20) and (3.21) can be numerically solved resulting in the phase portrait shown in Fig. 1. As mentioned in Sec. I, the point at which the lines of second-order and first-order phase transitions meet is called a *tricritical point* since such a point can

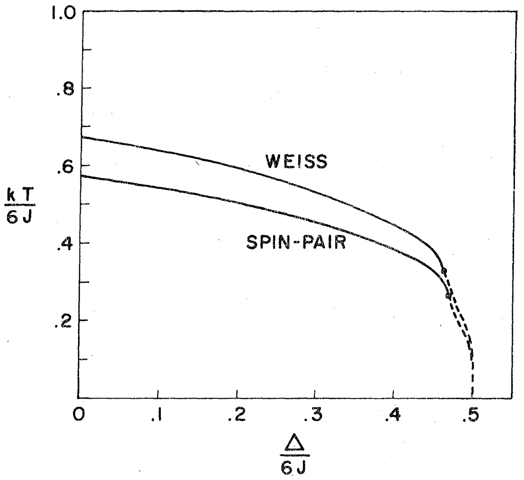

FIG. 1. Phase diagram in the T-Δ plane as found in the Weiss approximation and in the two-spin cluster approximation. The solid lines represent second-order (continuous) phase transitions and dashed lines represent those of first-order (discontinuous). The lattice structure is simple cubic ($z=6$).

also be viewed as the intersection of three lines of ordinary critical points in a suitable thermodynamic variable space, e.g., T-Δ-H space, where H is an applied uniform longitudinal magnetic field. The tricritical temperature T_t and the corresponding anisotropy constant Δ_t appearing in the phase diagram of Fig. 1 are found to be

$$kT_t/6J = 0.2715 \ , \tag{3.22a}$$

$$\gamma_t \equiv \Delta t/6J = 0.4695 \ . \tag{3.22b}$$

Thus, for the case of a simple cubic lattice ($z=6$), one concludes that, for $-\infty < \gamma < 0.4695$, one has second-order phase transitions while, for $0.4695 < \gamma < \frac{1}{2}$, one has first-order phase transitions. For this case of a simple cubic lattice ($z=6$) and for select values of the reduced anisotropy constant γ, Figs. 2(a)–2(e) display, respectively, the temperature dependencies of the thermal average quantities $a=\langle S_i\rangle$, $b=\langle S_i^2\rangle$, $c=\langle S_iS_{i'}\rangle$, $d=\langle S_iS_{i'}^2\rangle$, $e=\langle S_i^2S_{i'}^2\rangle$ (i, i' are nearest-neighbor lattice sites).

IV. SPECIFIC HEAT AND PARAMAGNETIC SUSCEPTIBILITY IN SPIN-PAIR APPROXIMATION

The specific heat at constant volume C_V of the system under study is given, using (2.1), (3.11), and (3.13), by

$$C_V = \frac{\partial\langle\mathcal{H}\rangle}{\partial T} = \frac{-w^2k}{zJ}\frac{\partial}{\partial w}\left[-\frac{NzJ}{2}c + N\Delta b\right]$$

or

$$\frac{C_V}{Nk} = -w^2\left[-\frac{1}{2}\frac{\partial c}{\partial w} + \gamma\frac{\partial b}{\partial w}\right] \ , \tag{4.1}$$

where, as previously, $w = zJ/kT$.

For $a \neq 0$, $d \neq 0$, $(\partial c/\partial w)$ and $(\partial b/\partial w)$ can be obtained in the two-spin approximation from the relation

$$\left[\frac{\partial a}{\partial w}\ \frac{\partial b}{\partial w}\ \frac{\partial c}{\partial w}\ \frac{\partial d}{\partial w}\ \frac{\partial e}{\partial w}\right]^T = -Q_5^{-1}\left[\frac{\partial f_1}{\partial w}\ \frac{\partial f_2}{\partial w}\ \frac{\partial f_3}{\partial w}\ \frac{\partial f_4}{\partial w}\ \frac{\partial f_5}{\partial w}\right]^T \tag{4.2a}$$

where $(\cdots)^T$ denotes the transpose of the row vector, the functions $f_1, \ldots, f_5$ are given by Eqs. (3.15), and Q_5^{-1} is the inverse of the Jacobian matrix Q_5 defined by

$$Q_5 \equiv \frac{\partial(f_1,f_2,f_3,f_4,f_5)}{\partial(a,b,c,d,e)} \ . \tag{4.2b}$$

For $a=d=0$, $(\partial c/\partial w)$ and $(\partial b/\partial w)$ are obtained from the relation

$$\left[\frac{\partial b}{\partial w}\ \frac{\partial c}{\partial w}\ \frac{\partial e}{\partial w}\right]^T = -Q_3^{-1}\left[\frac{\partial f_2}{\partial w}\ \frac{\partial f_3}{\partial w}\ \frac{\partial f_5}{\partial w}\right]^T \ , \tag{4.3a}$$

where the functions f_2, f_3, f_5 are given by Eqs. (3.15) with $a=d=0$ and Q_3^{-1} is the inverse of the Jacobian matrix Q_3 defined by

$$Q_3 \equiv \frac{\partial(f_2,f_3,f_5)}{\partial(b,c,e)} \ . \tag{4.3b}$$

For the case of a *simple cubic* lattice ($z=6$), Fig. 3 shows resulting specific-heat curves for select values of the reduced anisotropy constant. Peculiar features in the shapes of these curves (e.g., "bumps" and local maxima upon the shoulders) are due to the crystal-field anisotropy and its effect upon the temperature dependence of the "quadrupolar order parameter" $\langle S_i^2\rangle$ [see Eq. (4.1) and Figs. 2(b) and 2(c)]. However, such anomalous behaviors are noticeable only when the anisotropy constant is positive and the order of the exchange interaction strength.

In order to calculate the magnetic susceptibility of the system, one applies a uniform longitudinal magnetic field $H>0$. The Hamiltonian is then given by

$$\mathcal{H} = -\sum_{(i,i')} J_{ii'}S_iS_{i'} + \Delta\sum_i S_i^2 - \mu H\sum_i S_i \ , \tag{4.4}$$

where μ is the magnetic moment carried by an Ising spin. The Zeeman term in the Hamiltonian (4.4) simply adds a term $-\mu H\sum_i\langle S_i\rangle$ to the pair-approximation trial free energy (3.9) whereupon, assuming once again (3.11), minimization of the modified (3.9) then gives the following five equilibrium equations:

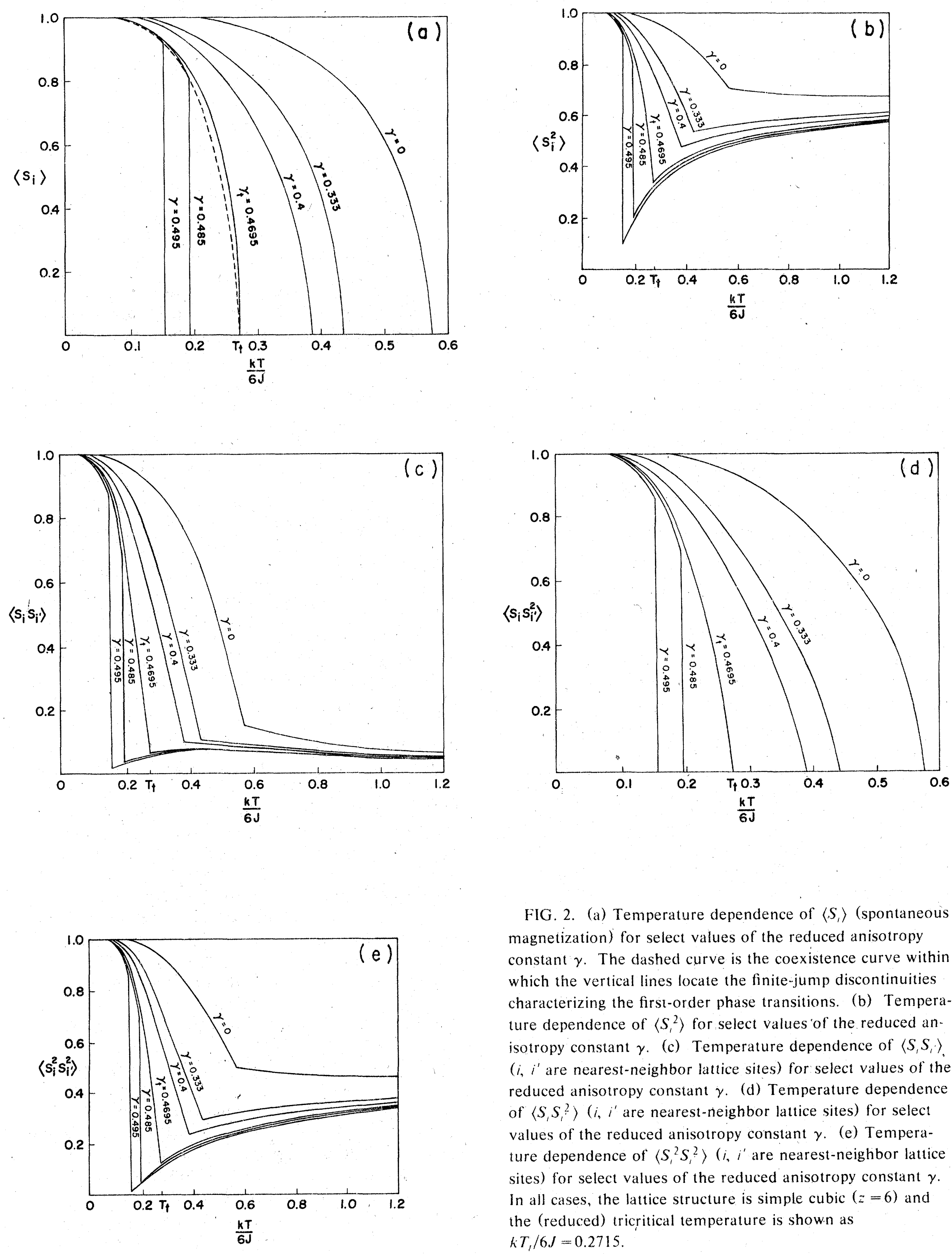

FIG. 2. (a) Temperature dependence of $\langle S_i \rangle$ (spontaneous magnetization) for select values of the reduced anisotropy constant γ. The dashed curve is the coexistence curve within which the vertical lines locate the finite-jump discontinuities characterizing the first-order phase transitions. (b) Temperature dependence of $\langle S_i^2 \rangle$ for select values of the reduced anisotropy constant γ. (c) Temperature dependence of $\langle S_i S_{i'} \rangle$ (i, i' are nearest-neighbor lattice sites) for select values of the reduced anisotropy constant γ. (d) Temperature dependence of $\langle S_i S_{i'}^2 \rangle$ (i, i' are nearest-neighbor lattice sites) for select values of the reduced anisotropy constant γ. (e) Temperature dependence of $\langle S_i^2 S_{i'}^2 \rangle$ (i, i' are nearest-neighbor lattice sites) for select values of the reduced anisotropy constant γ. In all cases, the lattice structure is simple cubic ($z=6$) and the (reduced) tricritical temperature is shown as $kT_t/6J=0.2715$.

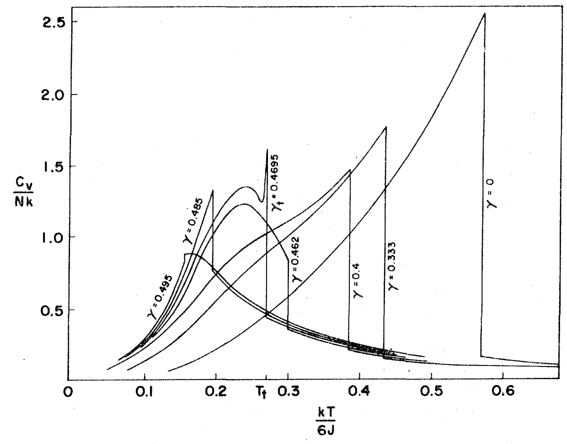

FIG. 3. Temperature dependence of the (reduced) specific heat for select values of the reduced anisotropy constant γ. The lattice structure is simple cubic ($z=6$) and the (reduced) tricritical temperature is shown as $kT_t/6J=0.2715$.

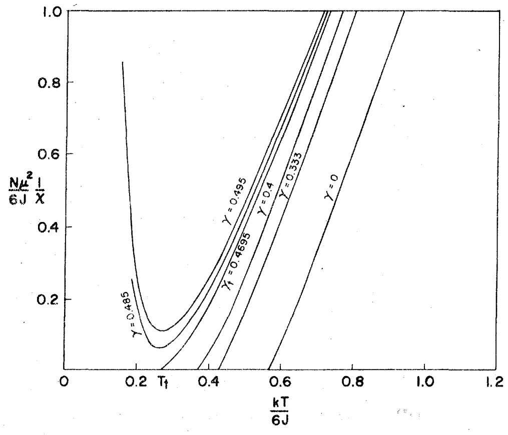

FIG. 4. Temperature dependence of the (reduced) reciprocal initial paramagnetic susceptibility for select values of the reduced anisotropy constant γ. The lattice structure is simple cubic ($z=6$) and the (reduced) tricritical temperature is shown as $kT_t/6J=0.2715$.

$$g_1=(-a+b)^{z-1}(a+b-d-e)^z\exp(-2hw)$$
$$-(a+b)^{z-1}(-a+b+d-e)^z=0\ , \tag{4.5a}$$

$$g_2=(1-b)^{z-1}(c+e+2d)^{z/2}\exp[-w(\tfrac{1}{2}+h)]$$
$$-2(a+b)^{z-1}(1-2b+e)^{z/2}\exp(-\gamma w)=0\ , \tag{4.5b}$$

$$g_3=(c-e)^2-(c+e+2d)(c+e-2d)$$
$$\times\exp(-4w/z)=0\ , \tag{4.5c}$$

$$g_4=(c+e+2d)(-a+b+d-e)^2$$
$$-(c+e-2d)(a+b-d-e)^2=0\ , \tag{4.5d}$$

$$g_5=(a+b-d-e)^2-(c+e+2d)(1-2b+e)$$
$$\times\exp(-w/z)=0\ , \tag{4.5e}$$

where $h\equiv\mu H/zJ$ and, as previously, $w=zJ/kT$. The initial magnetic susceptibility χ is defined by

$$\chi\equiv\lim_{H\to0^+}\frac{\partial(N\mu a)}{\partial H}=\frac{N\mu^2}{zJ}\lim_{h\to0^+}\frac{\partial a}{\partial h}\ , \tag{4.6}$$

where $\lim_{h\to0^+}(\partial a/\partial h)$ can be obtained from the relation

$$\lim_{h\to0^+}Q_h\left(\frac{\partial a}{\partial h}\,\frac{\partial b}{\partial h}\,\frac{\partial c}{\partial h}\,\frac{\partial d}{\partial h}\,\frac{\partial e}{\partial h}\right)^T$$
$$=-\lim_{h\to0^+}\left(\frac{\partial g_1}{\partial h}\,\frac{\partial g_2}{\partial h}\,\frac{\partial g_3}{\partial h}\,\frac{\partial g_4}{\partial h}\,\frac{\partial g_5}{\partial h}\right)^T\ , \tag{4.7a}$$

where the functions $g_1,\ldots,g_5$ are given by (4.5) and the Jacobian matrix Q_h is defined by

$$Q_h\equiv\frac{\partial(g_1,g_2,g_3,g_4,g_5)}{\partial(a,b,c,d,e)}\ . \tag{4.7b}$$

In the limit of vanishing magnetic field and for temperatures *above* the second-order phase transition temperature, one has that $a=d=0$. The first and fourth rows of (4.7a) then give, respectively,

$$[-(z-1)(b-e)+zb]\lim_{h\to0^+}\frac{\partial a}{\partial h}-zb\lim_{h\to0^+}\frac{\partial d}{\partial h}$$
$$=wb(b-e)\ , \tag{4.8a}$$

$$-2(c+e)\lim_{h\to0^+}\frac{\partial a}{\partial h}+[2(b-e)+2(c+e)]\lim_{h\to0^+}\frac{\partial d}{\partial h}=0\ . \tag{4.8b}$$

Solving the last two Eqs. (4.8), one has

$$\lim_{h\to0^+}\frac{\partial a}{\partial h}=\frac{wb(c+b)}{b-(z-1)c}\qquad T>T_c\ . \tag{4.9}$$

Hence, from (4.6), the *initial paramagnetic susceptibility* is given by

$$(zJ/N\mu^2)\chi=\frac{wb(c+b)}{[b-(z-1)c]}\qquad T>T_c\ . \tag{4.10}$$

Since, from (3.18), $b=(z-1)c$ is known to be a necessary condition for the existence of a second-order phase transition temperature T_c, one sees that the initial paramagnetic susceptibility goes to infinity at $T=T_c$. For the case of a *simple cubic* lattice ($z=6$), Fig. 4 shows resulting reciprocal initial paramagnetic susceptibility curves for select values of the reduced anisotropy constant. Once observes that the curves do not descend to a zero value for first-order phase transitions.

V. SUMMARY AND DISCUSSION

Improved results compared to those of Weiss molecular-field theory have been obtained for the equilibrium properties of the $S = 1$ Ising ferromagnet having additional single-ion-type uniaxial anisotropy. In the spin-pair approximation and for the case of a simple cubic lattice ($z = 6$), the tricritical point is located by the values $kT_t/6J = 0.2715$, $\gamma_t \equiv \Delta_t/6J = 0.4695$ as compared to the Weiss molecular-field results $kT_t^{(W)}/6J = 0.3333$, $\gamma_t^{(W)} \equiv \Delta_t^{(W)}/6J = 0.4621$. This comparison seems to indicate a feature that, although the tricritical temperature is considerably lowered from its Weiss value by improved approximations, the tricritical γ_t is only slightly altered. The spin-pair approximation results for the location of the tricritical point are comparable to those of exact series calculations[5,6] but it should be pointed out that the calculations of the present paper are for the case of a simple cubic lattice ($z = 6$) whereas those of Refs. 5 and 6 are for the case of a face-centered cubic lattice ($z = 12$). Also, within the spin-pair approximation, the temperature and anisotropy dependencies of the thermal average quantities $\langle S_i \rangle$, $\langle S_i^2 \rangle$, $\langle S_i S_{i'} \rangle$, $\langle S_i S_{i'}^2 \rangle$, $\langle S_i^2 S_{i'}^2 \rangle$ (i, i' are nearest-neighbor lattice sites) have been obtained and the specific heat and paramagnetic susceptibility have been calculated. Using the simple cubic lattice ($z = 6$) as an example of application, results are graphed for select values of the anisotropy constant. Peculiar features in the shapes of the specific heat portraits (e.g., "bumps" and local maxima upon the shoulders of the curves) can be traced to the crystal-field anisotropy and its effect upon the temperature dependence of the "quadrupolar order parameter" $\langle S_i^2 \rangle$ but such anomalous behaviors are noticeable only when the anisotropy constant is positive and the order of the exchange interaction strength.

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