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Ising model for tricritical points in ternary mixtures*†

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An Ising model with spin $S = 1$ at each lattice point which exhibits multiple tricritical points is presented. This is a generalization of the Blume-Emery-Griffiths model which was used for describing the tricritical point in He^3-He^4 mixtures. The model is solved in the molecular-field approximation. It is found that its thermodynamic behavior near the tricritical point is in qualitative agreement with the thermodynamic behavior of ternary fluids near their tricritical points.

I. INTRODUCTION

Recently, Griffiths and Widom[1,2] have pointed out that fluid mixtures which contain three or more components may exhibit phenomena which are analogous to the tricritical points observed in He^3-He^4 mixtures,[3] metamagnets,[4] NH_4Cl,[5] etc. The tricritical point in the fluid mixture is achieved when three coexisting fluid phases become identical simultaneously as some thermodynamic field variable is altered. This point is an intersection of two critical lines (in some thermodynamic field space) for which two phases become identical in the presence of a third phase. At the tricritical point of He^3-He^4 mixtures, metamagnets, etc., two of the coexisting phases are related by some symmetry transformation (e.g., for the metamagnets the symmetry operation is time reversal). This is not the case for the fluid mixtures where no symmetry transformation relates the coexisting phases. For this reason the former are called symmetric tricritical points and the later nonsymmetric tricritical points. Such nonsymmetric tricritical points have been observed experimentally and a list of references to these works is given by Griffiths and Widom.[1] Griffiths[6] used a phenomenological model of the Landau type to describe the phase diagram of three- and four-component fluid mixtures. He showed that this model is in good qualitative agreement with experiment. It would be interesting to find an explicit model which may describe the phase diagram of these mixtures.

In this work we present an Ising model with spin $S=1$ at each lattice site which may describe the phase diagram of ternary mixtures. This is a generalization of the Blume-Emery-Griffiths[7] model which was used for describing the tricritical point in He^3-He^4 mixtures.

The model and its connection with three-component fluid mixtures are described in Sec. II. In Sec. III, we present a solution of this model in the molecular-field approximation, and discuss its connection with experimental results obtained for tricritical points in ternary mixtures. It is found that the Blume-Emery-Griffiths model does exhibit three tricritical points for a certain value of the interaction parameters. This fact was overlooked by Blume-Emery-Griffiths.

II. THE MODEL

We consider a lattice-gas model with spin $S=1$ at each lattice site where the three components $S_i = \pm 1, 0$ represent the three types of molecules in the system. We do not allow for the possibility of vacancies in the model. The number of molecules of each type will be given by

$$N_+ = \frac{1}{2} \sum_{i=1}^{N} (S_i^2 + S_i) , \quad N_- = \frac{1}{2} \sum_{i=1}^{N} (S_i^2 - S_i) ,$$
$$N_0 = 1 - N_+ - N_- = \sum_{i=1}^{N} (1 - S_i^2) , \tag{1}$$

where N is the number of molecules in the system. Let us suppose now that there exists a nearest-neighbor interaction in the lattice and that the interaction energy of α- and β-type molecules ($\alpha, \beta = \pm 1, 0$) is given by $K_{\alpha\beta}$. The Hamiltonian of this system will therefore be given by

$$\begin{aligned}\tilde{\mathcal{H}} = {} & (\tfrac{1}{4}K_{++} + \tfrac{1}{4}K_{--} + K_{00} + \tfrac{1}{2}K_{+-} - K_{+0} - K_{-0}) \sum_{\langle ij \rangle} S_i^2 S_j^2 \\ & + (\tfrac{1}{4}K_{++} + \tfrac{1}{4}K_{--} - \tfrac{1}{2}K_{+-}) \sum_{\langle ij \rangle} S_i S_j \\ & + (\tfrac{1}{4}K_{++} - \tfrac{1}{4}K_{--} - \tfrac{1}{2}K_{+0} + \tfrac{1}{2}K_{-0}) \sum_{\langle ij \rangle} (S_i^2 S_j + S_i S_j^2) \\ & + z(-K_{00} + \tfrac{1}{2}K_{+0} + \tfrac{1}{2}K_{-0}) \sum_i S_i^2 \\ & + z(\tfrac{1}{2}K_{+0} - \tfrac{1}{2}K_{-0}) \sum_i S_i + K_{00} z \tfrac{1}{2} N ,\end{aligned} \tag{2}$$

where z is the number of nearest-neighbor sites of each lattice point, and $\langle ij \rangle$ means that the sum is over nearest neighbors only. The Hamiltonian (2) is the most general Hamiltonian for spin $S=1$ that includes nearest-neighbor interactions only. Since we are looking for phase transitions in systems where $\langle N_+ \rangle$, $\langle N_- \rangle$, and $\langle N_0 \rangle$ are given, it is necessary to introduce chemical potentials μ_+, μ_-, and μ_0 for the three types of molecules, and they may be incorporated into the Hamiltonian:

$$\mathcal{H} = \tilde{\mathcal{H}} - \mu_+ N_+ - \mu_- N_- - \mu_0 N_0 \ . \tag{3}$$

The Hamiltonian $\mathcal{H}$ may therefore be written in the form:

$$\mathcal{H} = -\tilde{J} \sum_{\langle ij \rangle} S_i S_j - \tilde{K} \sum_{\langle ij \rangle} S_i^2 S_j^2 - \tilde{C} \sum_{\langle ij \rangle} (S_i^2 S_j + S_i S_j^2) - H \sum_i S_i + \Delta \sum_i S_i^2 \ , \tag{4}$$

where the coefficients $\tilde{J}$, $\tilde{K}$, $\tilde{C}$, H, and Δ are linear combinations of $K_{\alpha\beta}$ and μ_α. In order to avoid breaking of the translational invariance of the system (i.e., splitting of the system into two sublattices with different $\langle N_\alpha \rangle$), we shall consider only the case where $\tilde{J}$, $\tilde{K} > 0$.

Now let us interchange the molecules $+1$ and -1. This interchange is induced by the transformation $S_i \to -S_i$ which transforms the Hamiltonian (4) to the same Hamiltonian with new parameters:

$$\begin{aligned} &J_1 = \tilde{J}, \quad K_1 = \tilde{K}, \quad C_1 = -\tilde{C}, \\ &H_1 = -H, \quad \Delta_1 = \Delta \ . \end{aligned} \tag{5}$$

Therefore, the phase diagram of the Hamiltonian (4) in the (T, Δ, H) space is the same as the phase diagram of the transformed Hamiltonian in the $(T, \Delta, -H)$ space.

In the same way one can interchange the molecules $+1$ and 0 or -1 and 0. These interchanges are induced by the transformations

$$S_i \to 1 + \tfrac{1}{2} S_i - \tfrac{3}{2} S_i^2 \tag{6}$$

and

$$S_i \to -1 + \tfrac{1}{2} S_i + \tfrac{3}{2} S_i^2 \ , \tag{7}$$

respectively. The transformed parameters will be, in these cases,

$$\begin{aligned} &J_2 = \tfrac{1}{4}(\tilde{J} + \tilde{K} - 2\tilde{C}), \\ &K_2 = \tfrac{1}{4}(9\tilde{J} + \tilde{K} + 6\tilde{C}), \\ &C_2 = \tfrac{1}{4}(-3\tilde{J} + \tilde{K} + 2\tilde{C}), \\ &H_2 = \tfrac{1}{2}(\tilde{J} - \tilde{K} + H + \Delta), \\ &\Delta_2 = \tfrac{1}{2}(3\tilde{J} + \tilde{K} + 4\tilde{C} + 3H - \Delta) \ , \end{aligned} \tag{8}$$

for the transformation (6), and

$$\begin{aligned} &J_3 = \tfrac{1}{4}(\tilde{J} + \tilde{K} + 2\tilde{C}), \\ &K_3 = \tfrac{1}{4}(9\tilde{J} + \tilde{K} - 6\tilde{C}), \\ &C_3 = \tfrac{1}{4}(3\tilde{J} - \tilde{K} + 2\tilde{C}), \\ &H_3 = \tfrac{1}{2}(-\tilde{J} + \tilde{K} + H - \Delta), \\ &\Delta_3 = \tfrac{1}{2}(3\tilde{J} + \tilde{K} - 4\tilde{C} - 3H - \Delta) \ , \end{aligned} \tag{9}$$

for the transformation (7).

In our model the number of molecules N is fixed and therefore only two fields out of the three μ_+, μ_-, and μ_0 are relevant. In fact, the μ_α's enter into the Hamiltonian (4) only through H and Δ which are given by

$$\begin{aligned} &H = \tfrac{1}{2} z K_{+0} - \tfrac{1}{2} z K_{-0} - \tfrac{1}{2}\mu_+ + \tfrac{1}{2}\mu_- \ , \\ &\Delta = -z K_{00} + \tfrac{1}{2} z K_{+0} + \tfrac{1}{2} z K_{-0} + \tfrac{1}{2}\mu_+ + \tfrac{1}{2}\mu_- - \mu_0 \ . \end{aligned} \tag{10}$$

The free energy of this model is therefore a function of three variables only, $F = F(T, \mu_+ - \mu_-, \mu_+ + \mu_- - 2\mu_0)$. One can write this alternatively as $F = F(T, \Delta, H)$.

In real ternary mixtures, unlike this model, the density is not fixed (neither the overall average density nor the densities of the separate phases), and there are three independent chemical potentials. The free energy in that case is therefore a function of four independent variables $F = F(T, \mu_1, \mu_2, \mu_3)$, where μ_i is the chemical potential of the ith component. As argued by Widom[2] one has to have at least four independent variables in the free energy in order to get a tricritical point. However, because of the special symmetry of our model [Eqs. (5), (8), (9)], it does exhibit tricritical points although its free energy is a function of only three independent variables.

In this work we discuss the phase diagram of a system described by the Hamiltonian (4) using molecular-field approximation. The phase diagram of this Hamiltonian for arbitrary $\tilde{J}$ and $\tilde{K}$ but for $\tilde{C} = 0$ was discussed by Blume, Emery, and Griffiths[7] in connection with the phase diagram of He^3-He^4 mixtures. They have found that for $\tilde{K}/\tilde{J}$ small enough, the model does exhibit one tricritical point at $H = 0$. We will show that the model does exhibit tricritical points for $\tilde{C}/\tilde{J} \neq 0$. These points are obtained by applying the transformations 8, 9 to the tricritical points at $\tilde{C}/\tilde{J} = 0$. No other tricritical points are found in this model. It is also shown that for $\tilde{C}/\tilde{J} = 0$ and $\tilde{K}/\tilde{J} = 3.0$ the model exhibits three tricritical points, one at $H = 0$ and the other two at finite values of H. This fact was overlooked by Blume, Emery, and Griffiths.

III. MOLECULAR FIELD APPROXIMATION

One can derive the molecular-field approximation of a system described by a Hamiltonian by using the variational principle for the free energy[8]

$$F \leq \phi = \mathrm{tr}\rho\mathcal{H} + (1/\beta)\,\mathrm{tr}\rho \ln\rho \ . \qquad (11)$$

In this inequality ρ is an arbitrary matrix which satisfies $\mathrm{tr}\rho = 1$, and $\beta = 1/K_B T$. The exact free energy of the system can be calculated, in principle, by minimizing the right-hand side of Eq. (11) with respect to every possible density matrix ρ. In the molecular-field approximation, however, this minimization is carried out only with respect to density matrices ρ, which can be written as a product of single-particle density matrices:

$$\rho = \prod_{i=1}^{N} \rho_i \ .$$

In order to calculate the free energy in the molecular-field approximation, we first write the most general single-particle density matrix for spin $S = 1$. This matrix has the form

$$\rho_i = e^{\beta(aS_i + bS_i^2)} / \mathrm{tr}\, e^{\beta(aS_i + bS_i^2)} \ , \qquad (12)$$

where a and b are free parameters. Inserting Eq. (12) into (11) and minimizing with respect to a and b, one obtains the free energy ϕ and the density matrix ρ in the molecular-field approximation. The result obtained in this way is

$$\begin{aligned} a &= J\,\mathrm{tr}(S_i\rho_i) + C\,\mathrm{tr}(S_i^2\rho_i) + H \ , \\ b &= K\,\mathrm{tr}(S_i^2\rho_i) + C\,\mathrm{tr}(S_i\rho_i) - \Delta \ , \end{aligned} \qquad (13)$$

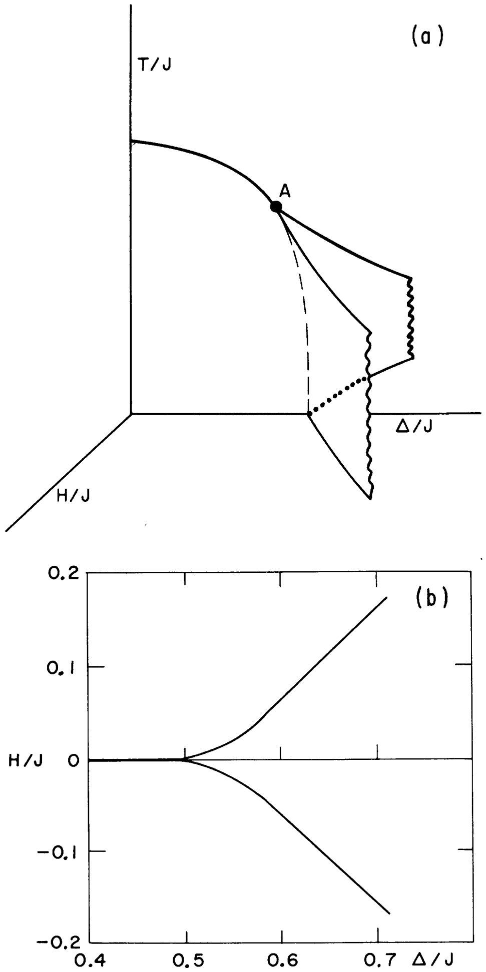

FIG. 1. Phase diagram for $K/J = 0.1$, $C/J = 0$. (a) schematic form in the H-Δ-T space. (b) projection of the critical lines on the H-Δ plane.

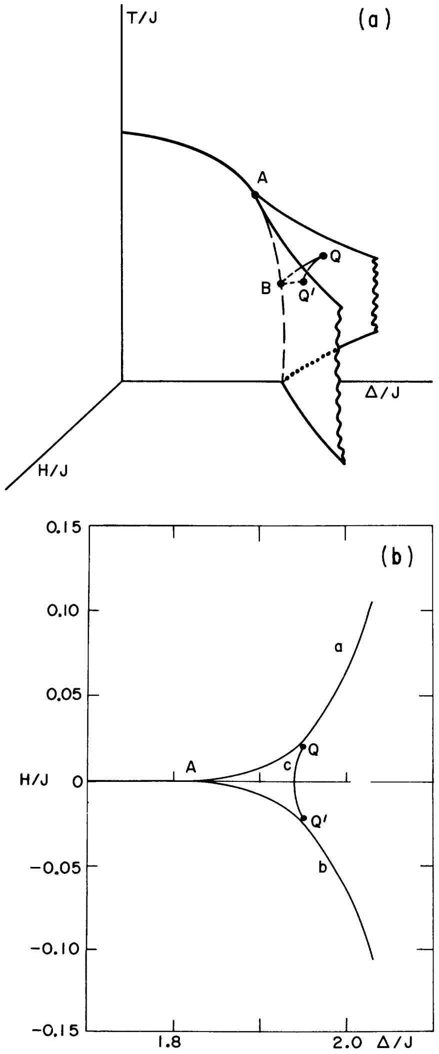

FIG. 2. Phase diagram for $K/J = 2.88$, $C/J = 0$. (a) schematic form in the H-Δ-T space. A is a tricritical point, Q and Q' are critical end points, and B is a coexistence point of four phases. (b) projection of the critical lines on the H-Δ plane.

where $J = z\tilde{J}$, $K = z\tilde{K}$, and $C = z\tilde{C}$. Let us now define

$$M = \langle N_+\rangle - \langle N_-\rangle\ , \quad Q = \langle N_+\rangle + \langle N_-\rangle\ . \tag{14}$$

M and Q will be given in this approximation by

$$M = \frac{2\sinh\beta(JM+CQ+H)}{2\cosh\beta(JM+CQ+H) + \exp[-\beta(KQ+CM-\Delta)]}\ , \tag{15}$$

$$Q = \frac{2\cosh\beta(JM+CQ+H)}{2\cosh\beta(JM+CQ+H) + \exp[-\beta(KQ+CM-\Delta)]}\ ,$$

and the free energy $\phi(H, \Delta, T)$ is given by

$$(1/N)\phi(H,\Delta,T) = \tfrac{1}{2}JM^2 + \tfrac{1}{2}KQ^2 + CMQ + (1/\beta)\ln(1-Q)\ , \tag{16}$$

where $M(H, \Delta, T)$ and $Q(H, \Delta, T)$ are given by the solutions of Eqs. (15).

In order to find the phase diagram of the system we first write down the thermodynamic potential with respect to the order parameter M:

$$A(M, \Delta, T) = \phi(H, \Delta, T) + MH\ , \tag{17}$$

where the equilibrium condition is

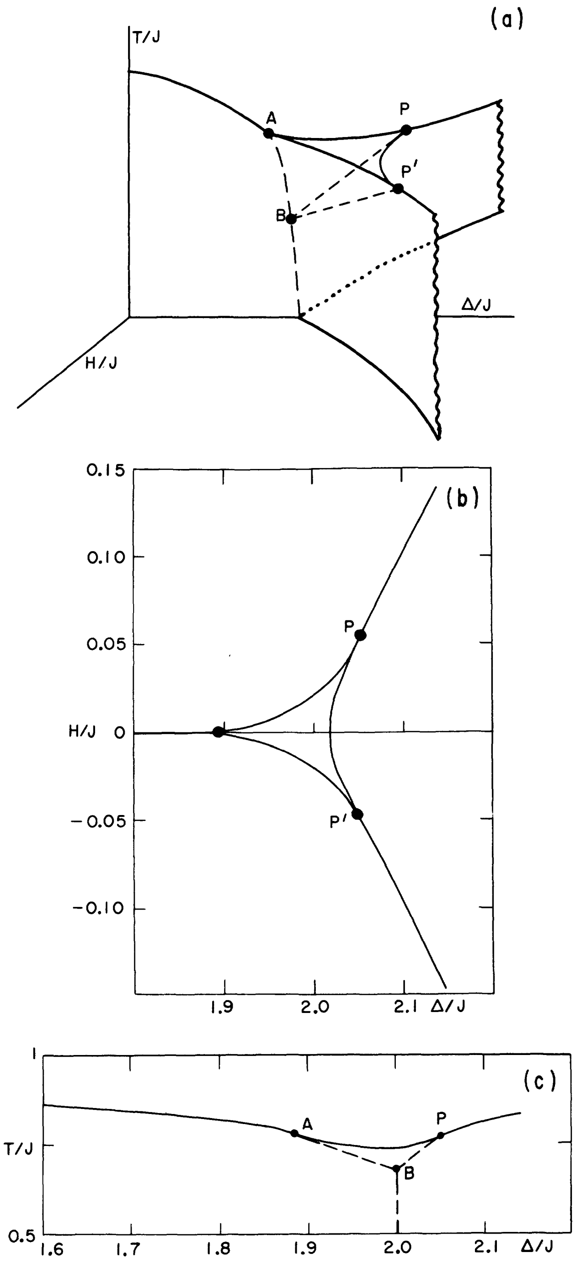

FIG. 3. Phase diagram for $K/J=3.0$, $C/J=0$. (a) schematic form in the H-Δ-T space. A, P, and P' are tricritical points and B is a coexistence point of four phases. (b) projection of the critical lines on the H-Δ plane. (c) projection of the critical lines and triple point lines on the T-Δ plane. Solid lines, critical lines; dashed lines, triple-point lines.

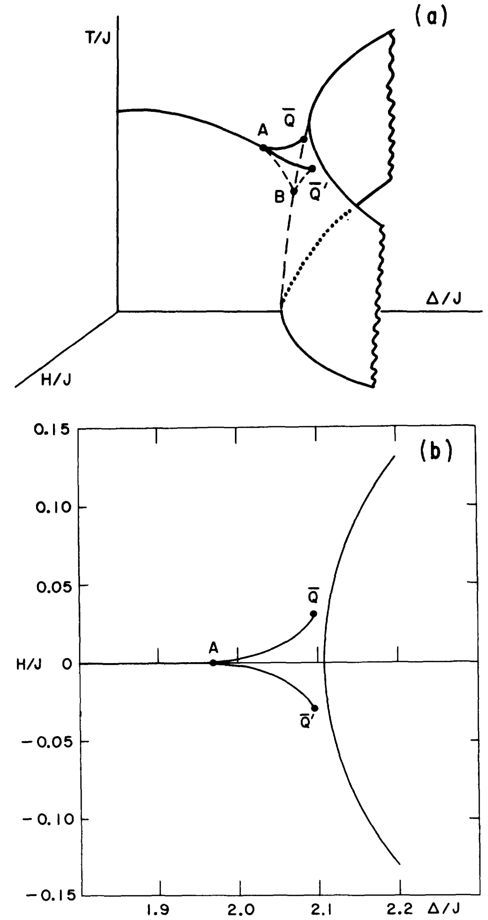

FIG. 4. Phase diagram for $K/J=3.1$, $C/J=0$. (a) schematic form in the H-Δ-T space. A is a tricritical point, $\bar{Q}$ and $\bar{Q}'$ are critical end points and B is a coexistence point of four phases. (b) projection of the critical lines on the H-Δ plane.

$$\frac{\partial A}{\partial M}=H \ . \tag{18}$$

Using this thermodynamic potential the critical points are given by

$$\frac{\partial^2 A}{\partial M^2}=\frac{\partial^3 A}{\partial M^3}=0, \ \frac{\partial^4 A}{\partial M^4}>0 \ , \tag{19}$$

and the tricritical points are given by[9]

$$\frac{\partial^2 A}{\partial M^2}=\frac{\partial^3 A}{\partial M^3}=\frac{\partial^4 A}{\partial M^4}=\frac{\partial^5 A}{\partial M^5}=0, \ \frac{\partial^6 A}{\partial M^6}>0 \ . \tag{20}$$

These equations can be derived by first solving Eq. (15) for H and Δ:

$$H=\frac{1}{2\beta}\ln\left(\frac{Q+M}{Q-M}\right)-JM-CQ \ , \tag{21}$$

$$\Delta=\frac{1}{\beta}\ln[2(1-Q)]-\frac{1}{2\beta}\ln(Q^2-M^2)+CM+KQ \ . \tag{22}$$

One can then calculate $(\partial^n H/\partial M^n)_{T,\Delta}$ from Eq. (21) using $(\partial Q/\partial M)_{T,\Delta}$ calculated from Eq. (22). The equations obtained in this way have to be solved numerically for the general case where C and H are different from zero.

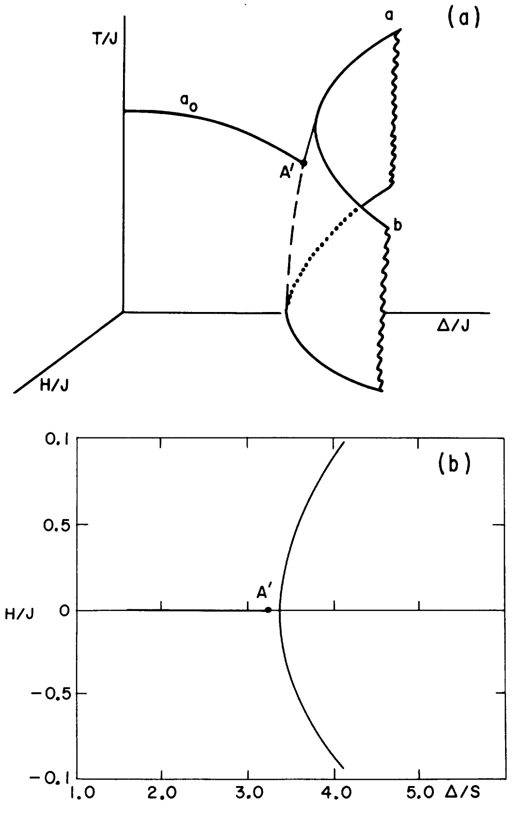

FIG. 5. Phase diagram for $K/J=5.0$, $C/J=0$. (a) Schematic form in the H-Δ-T space. A' is a critical end point. (b) The projection of the critical lines on the Δ-H plane.

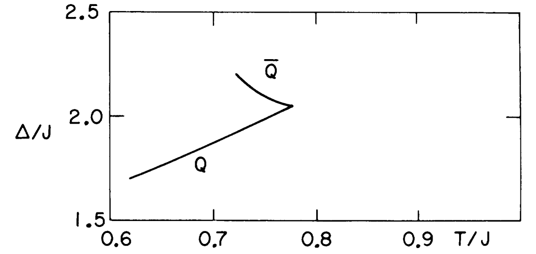

FIG. 6. Projection of the lines of critical end points $Q(K)$ and $\bar{Q}(K)$ on the T-Δ plane.

Before discussing the phase diagram for the general case where both C and H are different from zero, let us consider the case $C=0$. This case was studied by Blume, Emery, and Griffiths[7] for $H=0$. They have found that for K/J small enough, the system exhibits one tricritical point. As K/J increases beyond some value, this tricritical point becomes a critical end point. We will show that for certain value of K/J ($K/J=3.0$) the system does exhibit two tricritical points at some finite H, in addition to the tricritical point at $H=0$. The tricritical points at $H\neq 0$ are obtained from the point at $H=0$ by applying the transformations (8), (9) on it. The phase diagram of the system in the T-Δ-H space and the projection of the critical lines on the Δ-H or Δ-T planes are given for several values of K/J in Figs. 1–6.

For K/J small enough, the phase diagram is qualitatively the same as for the case $K/J=0$. This diagram for $K/J=0.1$ is given in Fig. 1. In this diagram there are three coexistence surfaces, one in the $H=0$ plane and two wings which are sym-

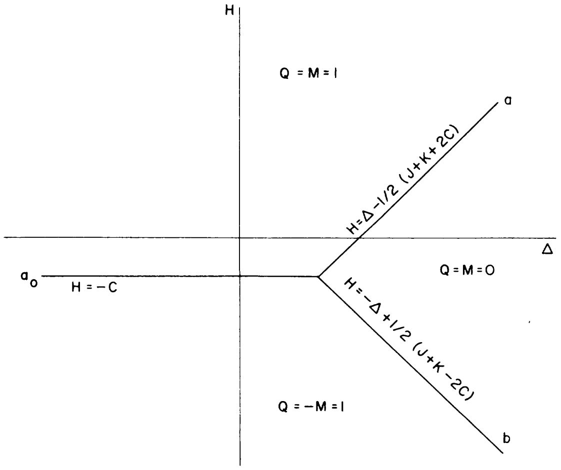

FIG. 7. Phase diagram of the system at $T=0$ for $|C|\leq\frac{1}{2}(K+J)$.

metric with respect to this plane. The three coexistence surfaces terminate in three critical lines which intersect in a tricritical point A. As K/J increases, one finds a fourth coexistence surface, and this is shown in Fig. 2, for $K/J = 2.88$. This fourth surface terminates in a critical line QQ'. The intersection points Q and Q' of this line with the two wings are critical end points. The point B where the four coexistence surfaces intersect is a coexistence point of four different phases. As K/J further increases, the critical end points Q and Q' move toward the critical wing lines, and at $K/J = 3.0$ they intersect forming two tricritical points P and P'. This is shown in Fig. 3. For this value of the parameter K/J the model coincides with the three-component Potts model discussed by Straley and Fisher.[10] The phase diagram for $K/J = 3.1$ is shown in Fig. 4. In this case the tricritical points P, P' become two critical end points $\overline{Q}, \overline{Q}'$, where the two critical lines of the wings terminate. For K/J large enough, the tricritical point A and the two critical end point $\overline{Q}, \overline{Q}'$ disappear. This is shown in Fig. 5 for $K/J = 5.0$. In this case the tricritical point A becomes a critical end point.

We have seen that the phase diagram of the Hamiltonian (4) with $C = 0$ exhibits two tricritical points P, P' at $H \neq 0$. We have also found that each of these points is an intersection of two lines of critical end points [$Q(K)$ and $\overline{Q}(K)$ or $Q'(K)$ and $\overline{Q}'(K)$]. The projection of the lines $Q(K)$ and $\overline{Q}(K)$ on the T-Δ plane near the tricritical point P is given in Fig. 6. The tricritical point occurs at a maximum in

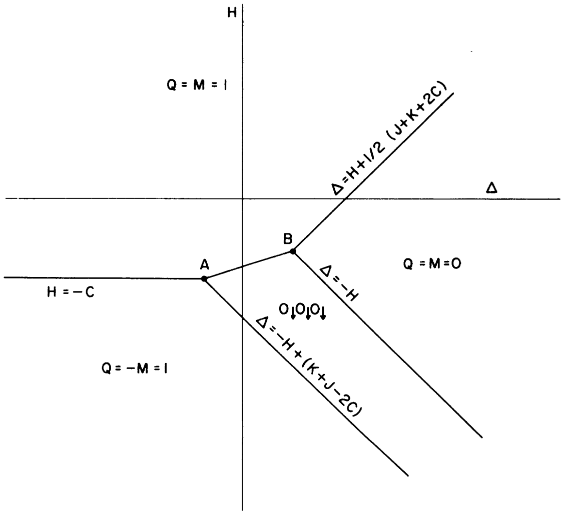

FIG. 8. Phase diagram of the system at $T = 0$ for $|C| > \frac{1}{2}(K - J)$. The region denoted by $(0{\downarrow}0{\downarrow}0{\downarrow})$ is a two sublattices region with $S_i = 0$ and $S_i = -1$ for the two sublattices.

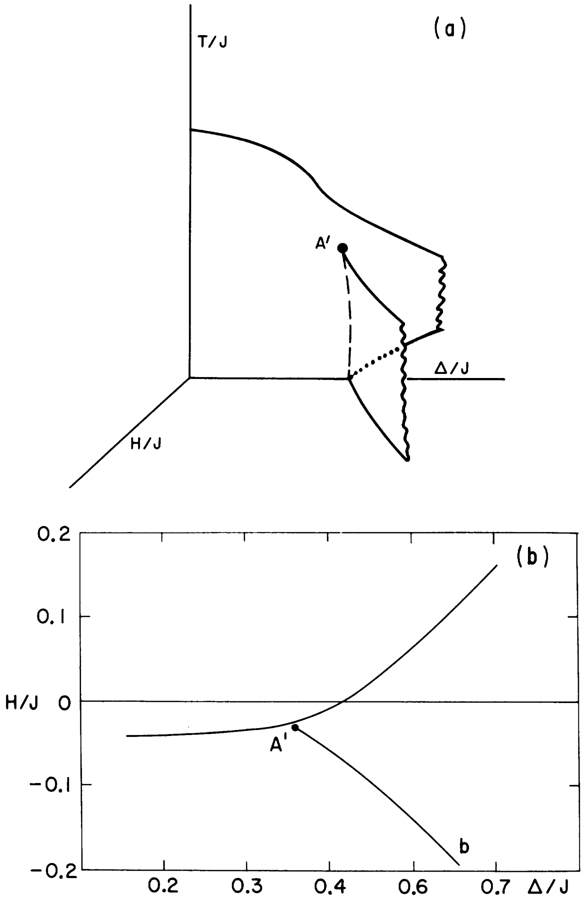

FIG. 9. Phase diagram for $K/J = 0.1$, $C/J = 0.05$. (a) Schematic form in the H-Δ-T space. A' is a critical end point. (b) Projection of the critical lines on the Δ-H plane.

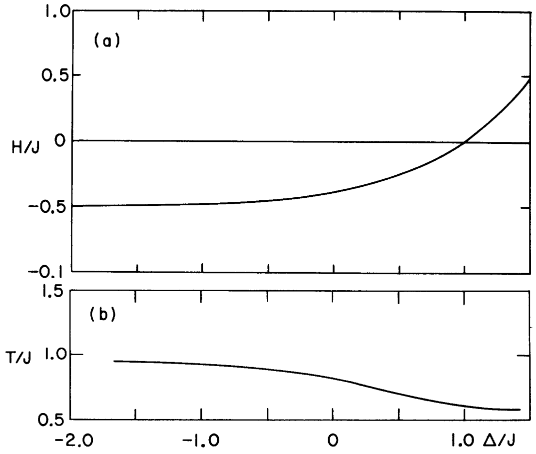

FIG. 10. The phase diagram for $K/J = 0.1$, $C/J = \frac{1}{2}(K/J + 1) = 0.55$. (a) Projection of the critical line on the H-Δ plane. (b) Same as (a) for the Δ-T plane.

temperature for both lines of critical end points. This result is in agreement with experiments[11,12] and with Griffiths' prediction based on the Landau theory.[6]

Let us now discuss the general case where both C and H are different from zero. Consider first the phase diagram at $T=0$. This diagram is given in Figs. 7 and 8 for $|C| \leqslant \frac{1}{2}(J+K)$ and $|C| > \frac{1}{2}(J+K)$, respectively. In the latter case there is a region in the H-Δ plane where the ground state of the system is not translationally invariant (even though J and K are positive). In this region the system splits into two sublattices one with $S_i = -1$ and the other with $S_i = 0$. As we are interested in fluid systems which are translationally invariant we shall discuss only the case $|C| \leqslant \frac{1}{2}(J+K)$. For $C = \frac{1}{2}(J+K)$ [or $C = -\frac{1}{2}(J+K)$] the coexistence line b (or a) in Fig. 7 occurs only at $T=0$ and it disappears for finite temperatures. It is therefore expected in this case that the phase diagram in the H-Δ-T space contains only one coexistence surface [which corresponds to the coexistence lines a(or b) and a_0 at $T=0$].

We now discuss the phase diagram of the system for $|C/J| \leqslant \frac{1}{2}(K/J+1)$ and several values of K/J. For small K/J and $C/J=0$ we have found that the system has one tricritical point at $H=0$. For finite C/J this tricritical point becomes a critical end point. The phase diagram for $K/J=0.1$ and $C/J=0.05$ is given in Fig. 9. As C/J increases, the critical line b occurs at lower and lower temperatures, and for $C/J=\frac{1}{2}(K/J+1)=0.55$ it lies in the $T=0$ plane. The phase diagram in this case contains only one coexistence surface which terminates in a critical line. The projection of the critical line on the H-Δ and T-Δ planes are given in Fig. 10.

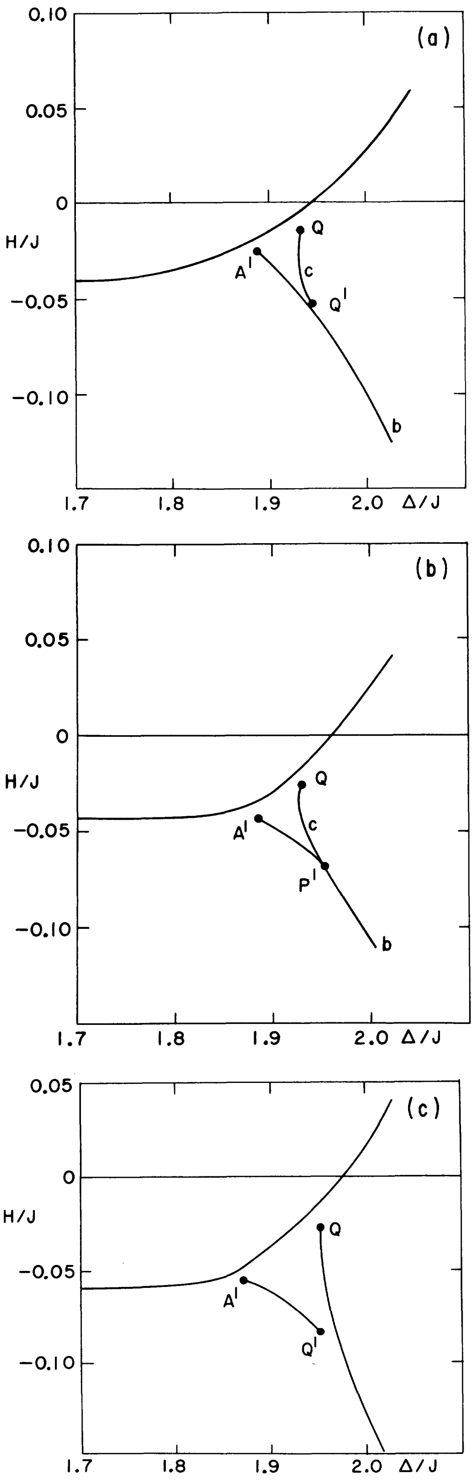

FIG. 11. (a) Projection of the critical lines on the H-Δ plane for $K/J=2.88$, $C/J=0.05$. Q, Q' and A' are critical end points. (b) The same diagram for $K/J=2.88$, $C/J=0.056$. Q and A' are critical end points; P' is a tricritical point. (c) The same diagram for $K/J=2.88$, $C/J-0.07$. A', Q', and Q are critical end points.

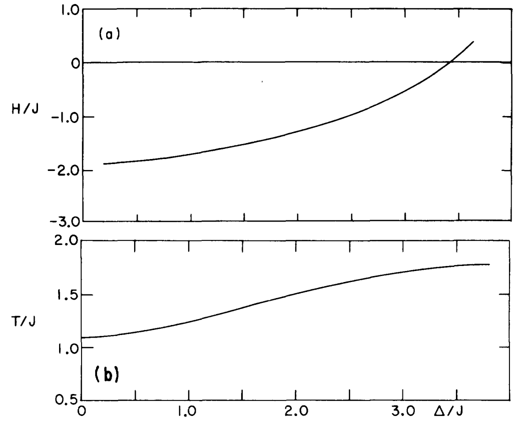

FIG. 12. Phase diagram for $K/J=2.88$, $C/J=\frac{1}{2}(K/J+1)=1.94$. (a) Projection of the critical line on the H-Δ plane. (b) Same as (a) for the T-Δ plane.

Consider now a case of higher K/J where the phase diagram for $C/J=0$ contains four coexistence surfaces and let us discuss, for example, $K/J=2.88$. The phase diagram for $K/J=2.88$ and $C/J=0$ was described in Fig. 2 and it exhibits one tricritical point A, and two critical end points Q, Q'. Taking C/J to be positive, the tricritical point becomes a critical end point and the critical end point Q' becomes closer to the critical line b. This is shown in Fig. 11(a) for $C/J=0.05$. As C/J increases, the critical lines b and c intersect, and the point Q' becomes a tricritical point, for $C/J=0.056$. This is shown in Fig. 11(b). This tricritical point may be obtained by applying the transformation (8) to one of the tricritical points at $C/J=0$. As C/J further increases, Q' becomes a critical end point as shown in Fig. 11(c) for $C/J=0.07$. For $C/J=\frac{1}{2}(K/J+1)=1.94$ the two critical lines b, c disappear (as in the case of small K/J) and the phase diagram contains only one coexistence surface which terminates in a critical line. The projections of this critical line on the H-Δ and T-Δ planes are given in Fig. 12.

The phase diagram for $K/J=5.0$ and $C/J=0$ was described in Fig. 5. As C/J is increasing, the critical line b will occur at lower temperatures until the three critical lines a_0, a, and b will intersect to form a tricritical point. Increasing C/J to the value $\frac{1}{2}(K/J+1)$ the critical line b will occur at $T=0$ and the phase diagram will contain one coexistence surface which terminates in a critical line.

IV. DISCUSSION

We have shown that the spin model presented in this work exhibits tricritical points for certain values of the interaction parameters J, K, and C. It is found that the thermodynamic behavior of this model near the tricritical points is in qualitative agreement with that of three-component fluid mixtures near their tricritical points. This model has three independent thermodynamic variables (T, Δ, H) and in order to compare it with three-component fluid systems [which have four independent thermodynamic variables (μ_1, μ_2, μ_3, T)] we used the interaction parameters K/J and C/J as extra parameters. In order to obtain full analogy with ternary mixtures one has to introduce a spin $S=\frac{3}{2}$ model (which has four independent thermodynamic variables). Such a model is now under consideration.

After this work was completed we received papers from J. Sivardiere and J. Lajzerowicz in which substantially the same calculations were performed. We thank the authors for communicating their results prior to publication. We would like to thank S. Krinsky and D. Furman for helpful discussions.

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