

## First-order phase transition in order-disorder ferroelectrics

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A four-spin coupling term is introduced to the pseudospin model Hamiltonian to account for the recently observed first-order phase transition in order-disorder ferroelectrics. The critical behavior is investigated and characteristic temperatures are calculated. We have also expressed the free energy in terms of microscopic variables and demonstrated that, in the limit of small mean spin  $\langle S^2 \rangle$ , its behavior near the critical point is identical to what is expected in thermodynamical theory.

### I. INTRODUCTION

A first-order phase transition in certain order-disorder ferroelectrics has been observed recently. The transition<sup>1</sup> of  $C_4H_2O_4$  near 373 K is just one example. It can be well understood in terms of Landau's thermodynamic theory,<sup>2</sup> especially in the neighborhood of the critical point where the theory correctly predicts characteristic temperatures of the first-order phase transition: the paraelectric phase-stability-limit temperature  $T_0$ , the critical temperature  $T_c$ , and the ferroelectric phase-stability-limit temperature  $T_0^-$ . The thermodynamic theory, however, can never interpret the observed phenomena in terms of the microscopic atomic interactions.

A pseudospin model<sup>3</sup> is able to account for the order-disorder phase-transition phenomena. The theory cannot handle the first-order phase transition by itself even though it explains the second-order phase transition quite successfully. Further work on the coupling between the pseudospin and lattice has been suggested<sup>4</sup> to discuss the phase-transition problem of order-disorder-type ferroelectrics. Again, it does not yield satisfactory results for the first-order phase transition.

It appears, therefore, necessary to examine more carefully the structure of order-disorder-type ferroelectrics in order to understand the phase-transition properties. One of the typical order-disorder ferroelectrics is potassium dihydrogen phosphate<sup>4</sup> ( $KH_2PO_4$ , KDP), in which the group  $PO_4$  forms a tetrahedron with  $P^{5+}$  at its center and the four oxygen ions at its vertices. Hydrogen bonds connect each of the vertices to other molecules on equal footing, and the potassium ion may be either above or below the tetrahedron as shown in Fig. 1. At higher temperatures, protons move back and forth along the equilibrium hydrogen bonds and the system is in a disordered state. When the phase transition occurs, the upper two protons move away from, and the lower two protons move toward, the tetrahedron. The system becomes ordered and a net dipole moment is produced along the  $c$  axis because the ion  $P^{5+}$  is pushed upward and  $K^+$  moves downward to cause the spontaneous polarization.

The squaric acid<sup>5</sup> ( $C_4H_2O_4$ ,  $H_2SQ$ ) has a layered structure, as can be seen in Fig. 2. Each molecule is a square with oxygen ions at its four vertices linked by hydrogen bonds on equal footing. At room temperature the layers are ferroelectrically ordered and antiferroelectrically stacked. Protons move randomly along the hydrogen bonds above the transition temperature, and ordered motion results at critical temperature. The net dipole moment produced in this case lies in the plane of the square, a different situation from the KDP.

From the above discussion, it is clear that in a ferroelectric material of order-disorder type, the four hydrogen bonds usually appear as a group and every one is equivalent to another. This means that the four-body interaction in such structures is generally important. In fact, Deiningham and Mehring<sup>5</sup> have pointed out the existence of four-body interaction in the  $C_4H_2O_4$  structure

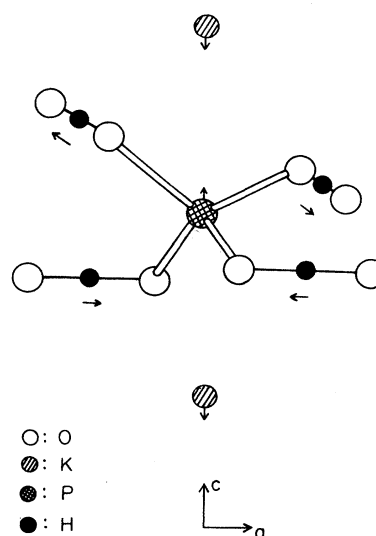


FIG. 1. Tetrahedronic structure of  $KH_2PO_4$  crystal.

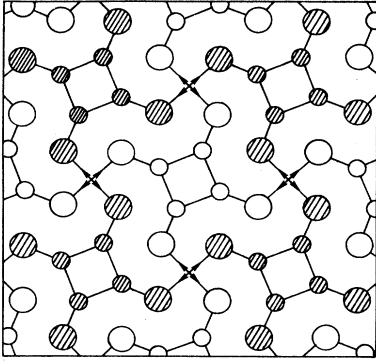


FIG. 2. Schematic diagram of the structure of squaric acid crystal cut across the layers. Different layers are denoted by open and shaded circles. Large and small circles represent O atoms and C atoms, respectively. Double arrows indicate the hydrogen bonds.

but neglected it in their actual calculation, hence, their result is still a second-order phase transition. A similar conclusion follows also from the Slater-Takagi model. Slater assumes that<sup>6</sup> only two protons can approach the tetrahedron, and his theory predicts only the second-order phase transition. On the other hand, Takagi<sup>7</sup> considers all possibilities and obtains the first-order phase transition. It is therefore necessary to include four-body interactions in the discussion of the first-order phase transition.

On the other hand, in the theoretical studies of the Ising model,<sup>8-10</sup> it has been shown that a first-order phase transition is possible only if the number of coupled spins is four or larger. But these investigations are carried out by means of either a renormalization group or finite-size scaling, and they do not involve dynamical properties.

On the basis of the pseudospin theory, we consider in this paper the four-spin interaction. The method of retarded Green's function is employed to study how the transition order is related to the coupling strength. It is found that the system exhibits a first-order phase transition when the four-body coupling strength  $J' > 4J/3$ , where  $J$  is the two-body coupling strength. The characteristic temperatures  $T_0$ ,  $T_0^-$ , and  $T_c$  are all calculated. To compare with the results of thermodynamic theory, we also derive an expression for the free energy. We find that in the limit of small mean spin  $\langle S^z \rangle$ , its behavior near the critical point is in complete agreement with predictions of the thermodynamic theory.

## II. THEORY

The order-disorder system is described by the Hamiltonian

$$H = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - \frac{1}{4} \sum_{i,j,k,l} J'_{ijkl} S_i^z S_j^z S_k^z S_l^z, \quad (1)$$

where the first two terms constitute the original pseudospin model and the third term represents the four-body

interaction.  $S_i^x$  is called the tunneling operator, which measures the tunneling power of the proton between the hydrogen double well,  $\Omega$  is the tunneling frequency, and  $S_i^z$  is half of the difference of occupation probabilities for the proton to be found in the two equilibrium positions of the hydrogen bond. The two-body coupling  $J_{ij}$  is the same for every pair of protons in KDP. In the case of  $H_2SQ$ , it represents the coupling between protons in neighboring layers as well as those in the same layer. The four-body coupling  $J'_{ijkl}$  refers to the four hydrogen bonds in the  $PO_4$  group in KDP, and in  $H_2SQ$  crystals it represents the interactions between the four hydrogen bonds in the  $C_4O_4$  group.

The retarded Green's function for any two operators  $A(t)$  and  $B(t')$  is defined by

$$\langle\langle A(t)|B(t') \rangle\rangle = -i\Theta(t-t') \langle [A(t), B(t')] \rangle, \quad (2)$$

where  $\Theta(t)$  is the step function and the commutator  $[A, B] = AB - BA$ . The Fourier component of the Green's function satisfies the equation of motion

$$\omega \langle\langle A|B \rangle\rangle_\omega = (2\pi)^{-1} \langle [A, B] \rangle + \langle\langle [A, H]|B \rangle\rangle, \quad (3)$$

where  $H$  is the Hamiltonian of the system. The correlation function  $\langle BA \rangle$  is related to the Green's function by the spectral theorem

$$\langle BA \rangle = i \int_{-\infty}^{\infty} d\omega e^{-i\omega(t-t')} \langle\langle A|B \rangle\rangle_\omega \times \frac{\langle\langle A|B \rangle\rangle_{\omega+i0^+} - \langle\langle A|B \rangle\rangle_{\omega-i0^+}}{e^{\beta\omega} - 1}, \quad (4)$$

where  $\beta = k_B T$ . It is not difficult to show from the definition (2) that the Green's function remains unchanged when the operators are changed by constants. That is,

$$\langle\langle A + \gamma | B + \gamma' \rangle\rangle = \langle\langle A | B \rangle\rangle, \quad (5)$$

where  $\gamma$  and  $\gamma'$  are arbitrary constants. But the correlation function

$$\langle (B + \gamma')(A + \gamma) \rangle \neq \langle BA \rangle. \quad (6)$$

This is evidently inconsistent with the spectral theorem (4) which implies that the correlation function does not change when constants are added to the operators. This inconsistency has been resolved by the method of undetermined constant.<sup>11</sup>

Let us choose the operators  $A = S_i^z, S_i^+, S_i^-$  and  $B = S_j^z, S_j^x$  to form Green's functions. With the Hamiltonian (1), higher-order Green's functions result from the equation of motion (3). We apply the Tyablikov scheme<sup>12</sup> to decouple the Green's functions involving two pseudospins,

$$\begin{aligned} \sum_j J_{ij} \langle\langle S_m^z S_j^z | S_n^z \rangle\rangle &\simeq \sum_j J_{ij} \langle S_j^z \rangle \langle\langle S_m^z | S_n^z \rangle\rangle \\ &= J \langle S^z \rangle \langle\langle S_m^z | S_n^z \rangle\rangle, \end{aligned} \quad (7)$$

where we have assumed for simplicity  $J = \sum_j J_{ij}$ , and  $\langle S_i^z \rangle = \langle S_j^z \rangle = \langle S^z \rangle$ . The Green's functions involving four pseudospins are decoupled according to a scheme proposed in a recent paper,<sup>13</sup> that is,

$$\sum_{j,k,l} J'_{ijkl} \langle\langle S_m^z S_j^z S_k^z S_l^z | S_n^z \rangle\rangle \simeq \sum_{j,k,l} J'_{ijkl} \langle S_j^z \rangle \langle S_k^z \rangle \langle S_l^z \rangle \langle\langle S_m^z | S_n^z \rangle\rangle = J' \langle S^z \rangle^3 \langle\langle S_m^z | S_n^z \rangle\rangle, \quad (8)$$

where  $J' = \sum_{j,k,l} J'_{ijkl}$ .

The Fourier components of the linearized Green's function satisfy the equation of motion

$$\begin{bmatrix} \omega & \Omega/2 & -\Omega/2 \\ \Omega & \omega-K & 0 \\ -\Omega & 0 & \omega+K \end{bmatrix} \begin{bmatrix} G^{zz}(\omega) \\ G^{+z}(\omega) \\ G^{-z}(\omega) \end{bmatrix} = \frac{1}{2\pi} \begin{bmatrix} 0 \\ -\langle S^+ \rangle \\ \langle S^- \rangle \end{bmatrix}, \quad (9)$$

$$\begin{bmatrix} \omega & \Omega/2 & -\Omega/2 \\ \Omega & \omega-K & 0 \\ -\Omega & 0 & \omega+K \end{bmatrix} \begin{bmatrix} G^{zx}(\omega) \\ G^{+x}(\omega) \\ G^{-x}(\omega) \end{bmatrix} = \frac{1}{2\pi} \begin{bmatrix} 0 \\ \langle S^z \rangle \\ -\langle S^z \rangle \end{bmatrix},$$

where  $K = J \langle S^z \rangle + J' \langle S^z \rangle^3$ , and  $G^{mn}(\omega) = \langle\langle S^m | S^n \rangle\rangle$ ,  $m, n = x, y, z$ . Following the procedures described in Ref. 11, we obtain, after some calculation, the following self-consistent equations:

$$[\langle S^x \rangle (J + J' \langle S^z \rangle^2) - \Omega] \langle S^z \rangle = 0, \quad (10a)$$

$$\frac{\langle S^x \rangle}{2[\langle S^x \rangle^2 + \langle S^z \rangle^2]} = \frac{\Omega}{\omega_0} \coth \frac{\omega_0}{2k_B T}, \quad (10b)$$

where

$$\omega_0 = [\Omega^2 + (J + J' \langle S^z \rangle^2)^2 \langle S^z \rangle^2]^{1/2}. \quad (11)$$

It can easily be seen that Eqs. (10) possess two sets of solutions.  $\langle S^z \rangle = 0$  corresponds to the paraelectric phase and  $\langle S^z \rangle \neq 0$  corresponds to the ferroelectric phase. In the following sections, we shall discuss the properties of these phases on the basis of (10).

### III. STABILITY-LIMIT TEMPERATURES

When the system is in the ferroelectric phase, or  $\langle S^z \rangle \neq 0$ , we have from (10a)

$$\langle S^x \rangle = \frac{\Omega}{J + J' \langle S^z \rangle^2}.$$

Substituting in (10b), we find

$$1 = \frac{J + J' \langle S^z \rangle^2}{2\omega_0} \tanh \frac{\omega_0}{2k_B T}. \quad (12)$$

For simplicity we assume  $\Omega = 0$  without loss of generality; then (12) becomes, upon substitution of (11),

$$\langle S^z \rangle = \frac{1}{2} \tanh \frac{J \langle S^z \rangle + J' \langle S^z \rangle^3}{2k_B T}. \quad (13)$$

The variation of temperature with the mean spin value  $\langle S^z \rangle$  for different ratios of the coupling strength  $J$  and  $J'$  is plotted in Fig. 3. To study the critical behavior, we have introduced a characteristic temperature  $T_0 = J/4k_B$  for the unit of temperature in the plot. The unit of  $\langle S^z \rangle$  is its value  $\langle S^z \rangle_0$  at  $T = 0$ . The three curves are for the relative coupling strengths (a)  $J' = J/3$ , (b)  $J' = 4J/3$ , and (c)  $J' = 7J/3$ .

For  $J'/J \leq 4/3$ , or cases corresponding to curves *a* and *b*, the system has two sets of solutions. When  $T \geq T_0$ , there is only one solution with  $\langle S^z \rangle = 0$  corresponding to the paraelectric phase. When  $T < T_0$ , both solutions with  $\langle S^z \rangle = 0$  and  $\langle S^z \rangle \neq 0$  are possible. As it will become clear in Sec. V, when we analyze the behavior of the free energy near  $T_0$ , the solution with  $\langle S^z \rangle = 0$  is unstable for  $T < T_0$ , and only  $\langle S^z \rangle \neq 0$  is a stable solution. This means that the system changes continuously from the paraelectric phase ( $\langle S^z \rangle = 0$ ) to the ferroelectric phase ( $\langle S^z \rangle \neq 0$ ) when its temperature decreases from above  $T_0$  to below. Thus the system exhibits a second-order phase transition with the critical temperature  $T_0$ .

For  $J'/J > 4/3$  or the case corresponding to curve *c* in Fig. 3, the system has three sets of solutions. When  $T \geq T_0^-$ , it has a paraelectric solution with  $\langle S^z \rangle = 0$ . When  $T_0^- < T < T_0^-$ , the equation has three solutions: one with  $\langle S^z \rangle = 0$  and two with  $\langle S^z \rangle \neq 0$  corresponding to the solid and dashed lines of the curve. When  $T < T_0^-$ , there are two possible solutions with  $\langle S^z \rangle = 0$  and  $\langle S^z \rangle \neq 0$ .

It is observed from Fig. 3 that  $T_0^-$  is the limiting temperature below which the system can be found in the ferroelectric phase. The value of  $T_0^-$  can be determined by the condition

$$\frac{\partial T}{\partial \langle S^z \rangle} = 0. \quad (14)$$

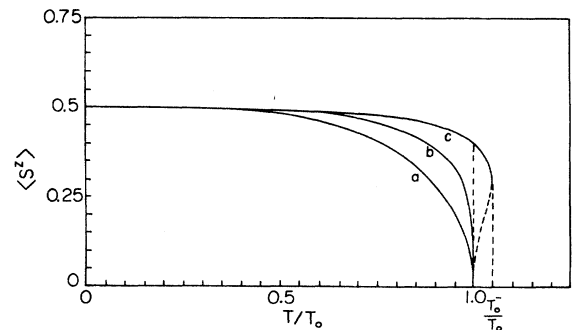


FIG. 3. Temperature dependences of  $\langle S^z \rangle$ . (a)  $J' = J/3$ , (b)  $J' = 4J/3$ , (c)  $J' = 7J/3$ .

Solving (14) we find the mean spin  $\langle S^z \rangle_-$  at  $T_0^-$ . Combining (13) and (14), we obtain

$$4k_B T_0^- = (1 - 4\langle S^z \rangle_-^2)(J + 3J'\langle S^z \rangle_-^2), \quad (15)$$

which, together with (13), yields the critical values for  $T_0^-$  and  $\langle S^z \rangle_-$ . An approximate expression can be obtained for sufficiently small  $\langle S^z \rangle_-$ . We expand (13) around  $\langle S^z \rangle = 0$  to the fourth order in  $\langle S^z \rangle$  and then combine with (15) to find

$$T_0^- = T_0 \left[ 1 + \frac{3}{16} \frac{(J'/J - 4/3)^2}{J'/J + 16/15} \right]. \quad (16)$$

Again from the analysis of the free energy in Sec. V, the ferroelectric phase is metastable but the paraelectric phase is stable in the neighborhood of  $T_0^-$ . Hence, the system remains in the paraelectric phase when the temperature drops down to  $T_0^-$ . On the other hand, the paraelectric phase is metastable and the ferroelectric phase is stable at  $T_0 + 0^+$ , or the system remains in the ferroelectric phase as the temperature increases to  $T_0 + 0^+$ . This implies that  $T_0$  is the limiting temperature for the stable paraelectric phase. Therefore, paraelectric and ferroelectric phases coexist when the temperature is within the interval  $T_0 < T < T_0^-$ . We then conclude that within this interval there exists a temperature  $T_c$  at which the stability of the two phases are equal. This is the Curie temperature of the first-order phase transition.

#### IV. DETERMINATION OF $T_c$

The critical temperature  $T_c$  and the order parameter  $\langle S^z \rangle_c$  are determined by the condition that the system possesses the same free energy in both phases. Hence, we proceed to calculate the free-energy change when the system changes phase. The Helmholtz free energy  $F$  is related to the external electric field  $E$  by

$$E = \left. \frac{\partial F}{\partial p} \right|_T, \quad (17)$$

where  $p$  stands for the polarization intensity. For the present problem, we have  $p = 2N\mu\langle S^z \rangle$ , where  $\mu$  is the effective dipole moment and  $N$  is the number of hydrogen bonds per unit volume. Equation (17) can then be put in the integral form

$$\Delta F = N \int_0^{\langle S^z \rangle} 2\mu E d\langle S^z \rangle, \quad (18)$$

which gives directly the free-energy difference between the two phases. In order to express the electric field in terms of the mean spin  $\langle S^z \rangle$ , we start with the Hamiltonian

$$H(E) = H - 2\mu E \sum_i S_i^z, \quad (19)$$

where  $H$  is given by (1). Repeating the procedures that lead to (13), we find

$$\langle S^z \rangle = \frac{1}{2} \tanh \frac{J\langle S^z \rangle + J'\langle S^z \rangle^3 + 2\mu E}{2k_B T}, \quad (20)$$

which can be rewritten as

$$2\mu E = -J\langle S^z \rangle - J'\langle S^z \rangle^3 + k_B T \ln \left[ \frac{1 + 2\langle S^z \rangle}{1 - 2\langle S^z \rangle} \right]. \quad (21)$$

Substituting (21) in (18) and integrating over  $\langle S^z \rangle$ , we obtain

$$\begin{aligned} \frac{\Delta F}{N} = & -\frac{1}{2}J\langle S^z \rangle^2 - \frac{1}{4}J'\langle S^z \rangle^4 \\ & + \frac{1}{2}k_B T \ln(1 - 4\langle S^z \rangle^2) + k_B T \ln \left[ \frac{1 + 2\langle S^z \rangle}{1 - 2\langle S^z \rangle} \right]. \end{aligned} \quad (22)$$

At the critical point,  $\Delta F = 0$  and  $\langle S^z \rangle = \langle S^z \rangle_0$ , we have

$$\begin{aligned} -\frac{1}{2}J\langle S^z \rangle_c^2 - \frac{1}{4}J'\langle S^z \rangle_c^4 + \frac{1}{2}k_B T_c \ln(1 - 4\langle S^z \rangle_c^2) \\ + k_B T_c \ln \left[ \frac{1 + 2\langle S^z \rangle_c}{1 - 2\langle S^z \rangle_c} \right] = 0, \end{aligned} \quad (23)$$

which, together with (13), can be solved for  $T_c$  and  $\langle S^z \rangle_c$ . If one assumes  $\langle S^z \rangle_c$  to be small, these equations can be expanded around  $\langle S^z \rangle_c = 0$  up to the fourth order in  $\langle S^z \rangle$  to find an approximate expression for the Curie temperature

$$T_c = T_0 \left[ 1 + \frac{1}{6} \frac{(J'/J + 1/5)(J'/J - 4/3)^2}{(J'/J + 4/5)^2} \right]. \quad (24)$$

A comparison with (16) then yields  $T_0^- > T_c > T_0$ , as expected.

#### V. FREE ENERGY NEAR THE CRITICAL POINT

Landau's thermodynamic theory of phase transition is based on the expansion of the free energy in a power series of the polarization which serves as the order parameter of the system. Thus, the free energy for the ferroelectric phase can be written as

$$F = F_0 + \frac{1}{2}a(T - T_0)p^2 + \frac{1}{4}bp^4 + \frac{1}{6}cp^6, \quad (25)$$

where  $F_0$  is the free energy for the paraelectric phase and the coefficients  $a$ ,  $b$ , and  $c$  are assumed to be temperature independent. When  $b > 0$ , the last term can be ignored and  $F$  may be employed to describe the second-order phase transition. When  $b < 0$ , only  $c > 0$  yields a stable minimum free energy. Thus the last term must be included to explain the first-order phase transition.

In order to express the quantities  $a$ ,  $b$ ,  $c$ , and  $T_0$  in terms of the microscopic parameters  $J$  and  $J'$ , we expand (22) around the critical point up to and including  $\langle S^z \rangle^6$ :

$$\begin{aligned} \frac{\Delta F}{N} = & \frac{1}{2}(4k_B T - J)\langle S^z \rangle^2 + \frac{1}{4}\left(\frac{16}{3}k_B T - J'\right)\langle S^z \rangle^4 \\ & + \frac{32}{15}k_B T\langle S^z \rangle^6. \end{aligned} \quad (26)$$

A direct comparison with (25) leads to  $T_0 = J/4k_B$ , which means that the Curie-Weiss temperature (the limiting temperature for the stable paraelectric phase) is directly proportional to the two-body coupling strength  $J$ . Since (26) is an expansion around the critical point, and since the coefficients of the second and third terms

have no singularities at  $T=T_0$ , we can replace with good approximation  $T \approx T_0 = J/4k_B$  in these terms. Thus, Eq. (26) becomes

$$\frac{\Delta F}{N} = \frac{1}{2}(4k_B T - J)\langle S^z \rangle^2 + \frac{1}{4}(4J/3 - J')\langle S^z \rangle^4 + \frac{8}{15}J\langle S^z \rangle^6. \quad (27)$$

It is observed from (27) that the coefficient  $b$  in the thermodynamical expansion (25) is proportional to  $4J/3 - J'$ . Therefore, a positive  $b$  implies  $J' < 4J/3$ , and the free energy describes a second-order phase transition. In this case, the last term of the order of  $\langle S^z \rangle^6$  can be neglected. When  $b < 0$ ,  $J' > 4J/3$ , and  $F$  describes a first-order phase transition, exactly the same as what Landau's theory concludes. The critical strength  $J' = 4J/3$  for the onset of first-order phase transition is determined approximately here by the expansion around the critical point. It is, in fact, an exact result.<sup>14</sup>

To compare, in more detail, predictions near the critical point by the microscopic model and the macroscopic theory, we plot the reduced free energy  $f = \Delta F/NJ$  calculated from (22) in Figs. 4 and 5. For the case of second-order phase transition or  $J' < 4J/3$ , Fig. 4 illustrates the behavior of  $f$  at different temperatures. Above the critical temperature  $T_0$ , the reduced free energy has only one minimum at  $\langle S^z \rangle = 0$ , as shown in 4(a), while it

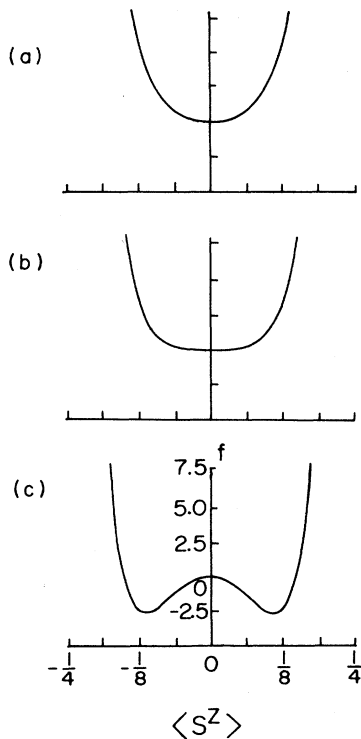


FIG. 4. Polarization dependence of the reduced free energy  $f = \Delta F/NJ$  near the second-order phase transition temperature  $T_0$ . In our numerical calculations, however, we have introduced the dimensionless temperature  $\Theta = k_B T/J$ . (a)  $T > T_0$  and  $\Theta = 0.25009$ , (b)  $T = T_0$  and  $\Theta = 0.25$ , (c)  $T < T_0$  and  $\Theta = 0.2498$ .

has two minima at  $\pm \langle S^z \rangle_m$  and a maximum at  $\langle S^z \rangle = 0$  for  $T < T_0$ , as shown in 4(c). Therefore, the paraelectric phase is unstable below the critical temperature. When  $T = T_0$ , the free energy as can be seen in 4(b) still has a minimum at  $\langle S^z \rangle = 0$ , but the curve has a flat bottom indicating a vanishing second-order derivative.

The case of first-order phase transition or  $J' > 4J/3$  is depicted in Fig. 5. The reduced free energy has two minima at  $\pm \langle S^z \rangle_m$  for  $T < T_0$  when the system is in the ferroelectric phase. This is illustrated in 5(a). Another

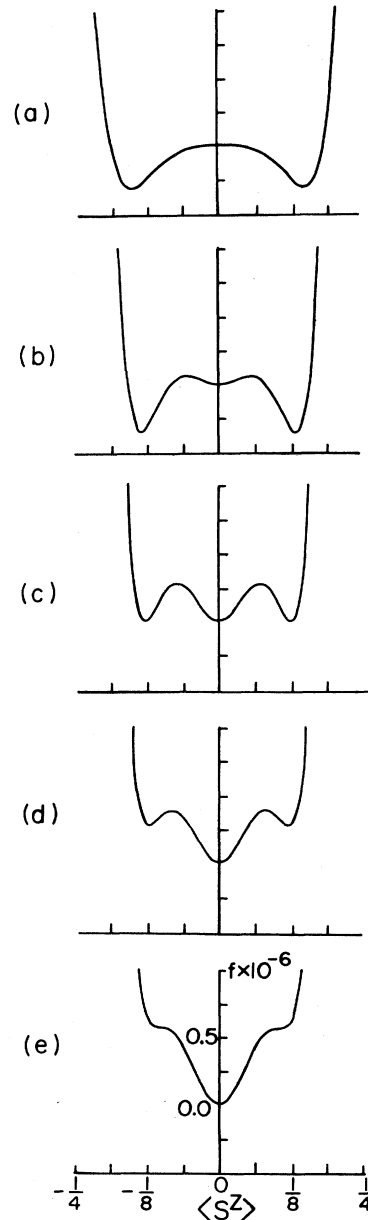


FIG. 5. Polarization dependence of the reduced free energy near the first-order phase transition temperature  $T_c$ . (a)  $T < T_0$  and  $\Theta = 0.25$ , (b)  $T_c > T > T_0$  and  $\Theta = 0.25004$ , (c)  $T = T_c$  and  $\Theta = 0.25006$ , (d)  $T_0 > T > T_c$  and  $\Theta = 0.25008$ , (e)  $T = T_0$  and  $\Theta = 0.25009$ .

minimum with larger free energy occurs at  $\langle S^z \rangle = 0$  for temperatures within the range  $T_c > T > T_0$ , as shown in 5(b). This indicates that the system may be found in the paraelectric phase, which is far less stable than the ferroelectric phase. Figure 5(c) shows the situation for  $T = T_c$  when three minima of equal free energy exist. Thus, the two phases can coexist with equal stability, as discussed in Sec. III. The order parameter changes abruptly from  $\langle S^z \rangle_c$  to zero and the transition is of the first order. When the temperature increases to above  $T_c$  but still below  $T_0^-$ , the minimum at  $\langle S^z \rangle = 0$  has lower free energy, implying a stable paraelectric phase and a metastable ferroelectric phase. Figure 5(d) illustrates this situation. When  $T = T_0^-$ , the ferroelectric phase starts to disappear, as is shown in 5(e). The system can only be in the paraelectric phase at this temperature, since it has a minimum free energy only at  $\langle S^z \rangle = 0$ .

## VI. DISCUSSION

We first showed in this article that the four-spin interaction is responsible for the first-order phase transition

observed in the order-disorder ferroelectrics. The critical four-body coupling strength  $J' = 4J/3$  was then calculated by the method of retarded Green's function. By investigating the variation of the order parameter  $\langle S^z \rangle$  with temperature, we found the conditions for the determination of the limiting temperatures  $T_0$  and  $T_0^-$  for the stable paraelectric and ferroelectric phases, respectively. For the special case in which the tunneling frequency vanishes, approximate expressions for these limiting temperatures were derived.

On the basis of the above results, the free energy of the system was expressed in terms of the microscopic parameters, and the Curie temperature  $T_c$  and the corresponding order parameter  $\langle S^z \rangle_c$  were calculated. Finally, we analyzed the critical behavior of the free energy at different temperatures. Our conclusion from this analysis is that, in the limit of small mean spin  $\langle S^z \rangle$ , the microscopic model completely predicts the same behavior of the free energy near the critical point as the macroscopic Landau theory.

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