

Theoretical Calculations of the Tricritical Point in Two Sublattice Systems

Ikuo SUZUKI

Department of Engineering Sciences

(Received July 10 1982)

Theoretical calculations of a tricritical point were derived from an energy function with two order parameters such as the Landau type free energy and the Bragg-Williams approximation energy. Several possible phase diagrams are presented as examples, for the antiferroelectric phase transition and the Rochelle salt type systems.

1. Introduction

In thermodynamic equilibrium, a physical system consists of one or more subsystems. They are characterized by the values of the extensive variables, which are determined by the values of the intensive thermodynamic variables like the temperature T , the pressure P , the electric field E etc. Griffiths et al. introduced the terms *density* and *field*, instead of the *extensive* and *intensive* variables, respectively.^{1,2)} Therefore, phases are characterized by macroscopic homogeneous values of densities.

The typical phase diagram for a pure substance in the pressure P , temperature T plane is indicated schematically in Fig. 1. The points, for which there can be coexistence of two or more phases, are called coexistence points, and the set of these points receive the name of *coexistence surface* (CXS).

A triple point (T_t , p_t) is a point where three phases coexist, and (T_c , p_c) is a critical point which is a boundary point of a first-order phase transition surface with the property that all discontinuities in densities across this surface go continuously to zero upon approaching this point. The tricritical point (TCP) is a point where three critical lines come together.

In ferroelectric and antiferroelectric phase transitions, the TCP is of great interest from a viewpoint of related anomalies observed in physical properties. When the free energy is expanded in the Landau-type

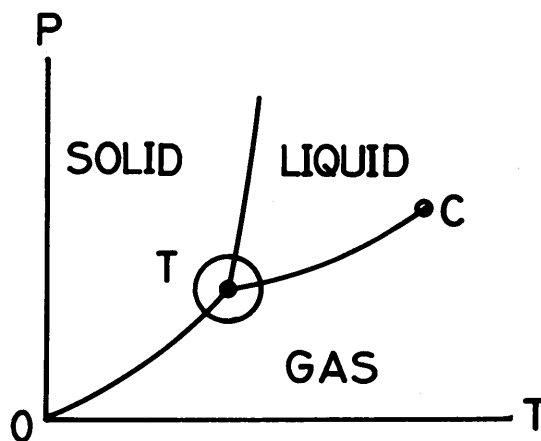


Fig. 1 Phase diagrams for typical substances. The solid lines indicate the CXS. C and T are critical and triple points.

power series in terms of a single transition parameter, the TCP is simply recognized as the point in a phase diagram, where the coefficients to the second order and fourth order terms vanish simultaneously. But, in the case where the free energy is written in terms of more than two transition parameters the situation is rather different, and the procedure for finding TCP is a little more complicated. In the present paper, we will discuss the case of the antiferroelectric phase transitions, and the ferroelectric phase transitions, on changing values of parameter in the free energy, where the free energy is given in two-sublattice polarizations.

2. Phase Diagrams

The set of all phase transition points, the phase transition surface (PS), is equal to $(FPS \cup SPS)$, where FPS and SPS are the first order and the second order phase transition surface, respectively³⁾. The set of first order phase transition surface is equal to the *coexistence surface* (CXS) and the second order phase transition surface coincides with the *critical surface* (CRS). The phase diagram is then the set (E, PS) , where E is the set of control variables.

Recently, a classification of phase diagrams was discussed on the basis of the qualitative shapes of their phase transition surfaces¹⁻⁷⁾. The critical points of the phase diagram for ferroelectrics have equal qualitative shapes around the critical points (T_c, p_c) and $(T'_c, 0)$, respectively.

In this section we introduce a general family of energy potential $V(c_1, c_2, \dots, c_k, x_1, x_2, \dots, x_n)$ depending on density variables or order parameters $x \in \mathbf{R}^n$ and k control parameters $c \in \mathbf{R}^k$. The state of the physical system is described by the value of x_i which minimizes the potential, locally. Therefore, the equilibrium and stability properties of the potential $V(c, x)$ is given ;

$$\partial V / \partial X_i = 0 \quad (1)$$

and

$$H_{ij} = \partial^2 V / \partial X_i \partial X_j > 0, \quad (2)$$

where H_{ij} is the Hessian matrix. The equilibrium points, or critical points, of a smooth potential function V are the points at which $\Delta V = 0$. The critical points at which $\det H_{ij} \neq 0$ are called isolated, non degenerate, or Morse critical points³⁾. A phase transition occurs when the point $X \in \mathbf{R}^n$ describing the state of a physical system jumps from one critical branch to another. If the *Maxwell Convention* is adopted, phase transitions will occur when the curve passes through the component of the Maxwell set on which two or more global minima are degenerate. Systematic calculations have been made by using the Catastrophe theory for one order parameter³⁻⁷⁾. In the present paper, we show an analytical method for the systems with two order parameters.

3. Antiferroelectric Phase Transition

The phenomenological theories of Antiferroelec-

tric phase transition have been developed by many investigators, in which the free energy is expanded into a power series in terms of two sublattice polarizations⁸⁻²⁰⁾. In some cases the expansion is truncated at the fourth order and then the second order transition comes out. On the other hand, the first order antiferroelectric phase transition can be obtained when the expansion is carried out to the sixth order. Moreover, the free energy with sixth order term may give rise to a qualitatively new feature, that is, appearance of a phase called a semipolar phase, which is polar from the symmetry viewpoint but has homogeneous and staggered polarization components simultaneously even at no external field¹²⁾.

When external field is applied to such a system, interesting phase diagrams are drawn in the electric field *vs.* temperature axis, for various values of the coefficients of the free energy expansion. Especially, one may encounter the case where the first order transition changes into the second order transition on applying electric field, that is to say, one may get the tricritical point (TCP) in the phase diagram.

3.1 Second Order Antiferroelectric Phase Transition

We take the Kittel's expression of free energy as a function of polarization of two sublattice P_a and P_b ;⁸⁾

$$A = f(P_a^2 + P_b^2) + gP_aP_b + h(P_a^4 + P_b^4) - E(P_a + P_b), \quad g > 0, \quad h > 0. \quad (3)$$

On introducing two new order parameters $Q = (P_a + P_b) / \sqrt{2}$ and $q = (-P_a + P_b) / \sqrt{2}$ which represent the macroscopic and staggered polarization, respectively. Eq. (3) is rewritten introducing new variables as ;

$$a = (1+t)Q^2 + tq^2 + Q^4 + q^4 + 6Q^2q^2 - eQ. \quad (4)$$

Equilibrium condition of free energy are given by

$$\partial a / \partial Q = 2Q [1 + t + 2Q^2 + 6q^2] - e = 0 \quad (5)$$

and

$$\partial a / \partial q = 2q(t + 2Q^2 + 6Q^2) = 0. \quad (6)$$

There are several physically different phases obtained and to distinguish them in this paper, we adopt the following nomenclature ;

- (I) Nonpolar (N) : $Q = 0, q = 0$,
- (II) Polar (P) : $Q \neq 0, q = 0$,
- (III) Antipolar (AP) : $Q = 0, q \neq 0$,
- (IV) Semipolar (AP) : $Q \neq 0, q \neq 0$.

We use the words '*polar*' and '*antipolar*' rather than '*ferro*' and '*antiferroelectric*', respectively. The values of Q and q are determined by the external field like the temperature and the applied field.

The stability of the equilibrium state is assured if

$$|H_{ij}| = \begin{vmatrix} \frac{\partial^2 a}{\partial p^2} & \frac{\partial^2 a}{\partial q \partial p} \\ \frac{\partial^2 a}{\partial p \partial q} & \frac{\partial^2 a}{\partial q^2} \end{vmatrix} > 0 \quad (7)$$

where the values representing the concerned equilibrium state have to be substituted for Q in $|H_{ij}|$. The second order phase transition takes place to some other phase when

$$|H_{ij}| = 0. \quad (8)$$

The phase boundary between the states $q \neq 0$ and $q = 0$ is given by eq. (8) as :

$$(1+t+6Q^2+6q^2)(t+6Q^2+6q^2)-144Q^2q^2=0. \quad (9)$$

In this equation the second order phase transition boundary is given by putting $q = 0$. The other lines indicate the spinodal lines. The second order phase boundary is determined by (5) and (9).

Let us consider the TCP where three critical lines come together. Needless to say, TCP is located on the second order transition line, where (5), (6) and (8) are satisfied.

Notice that the value of Q in the P phase is determined by (5) (but not by (6)) which is satisfied by any Q if $q = 0$, which is an even function of q , that is, $Q = Q(q^2)$, when Q and q satisfy the relation

$$g(Q(q^2), q) = \partial a / \partial Q = g(Q(0), 0) + q^2 (d^2 g / dq^2) / 2 + \dots = 0, \quad (10)$$

the continuity of Q against the change of q around $q = 0$ is broken when $d^2 g / dq^2$ changes its sign. At the tricritical point, therefore, the relation

$$\begin{aligned} \frac{d^2 g}{dg^2} &= -\frac{\partial^2 g}{\partial q^2} + 2 \frac{\partial^2 g}{\partial Q \partial q} \left(\frac{dQ}{dq} \right) \\ &+ \left(\frac{\partial^2 g}{\partial Q^2} \right) \left(\frac{dQ}{dq} \right)^2 + \frac{\partial g}{\partial Q} \left(\frac{d^2 Q}{dq^2} \right) \\ &= \frac{\partial^2 a}{\partial q^2} + \frac{\partial g}{\partial Q} \left(\frac{d^2 Q}{dg^2} \right) = 0, \end{aligned} \quad (11)$$

has to be satisfied, where it is made use of that Q is an even function of q , that is, $(dQ/dq) = 0$ at $q = 0$.

If the second order transition is determined by $\partial^2 a / \partial Q^2 = 0$ the last term of (11) is also zero, then TCP is given only by the condition $\partial g^2 / \partial q^2 = 0$. In this case $\frac{\partial^2 a}{\partial Q^2} = \frac{\partial^2 a}{\partial q^2} + 2$, then the second order phase transition is determined by $\partial^2 a / \partial q^2 = 0$. The relation (11)

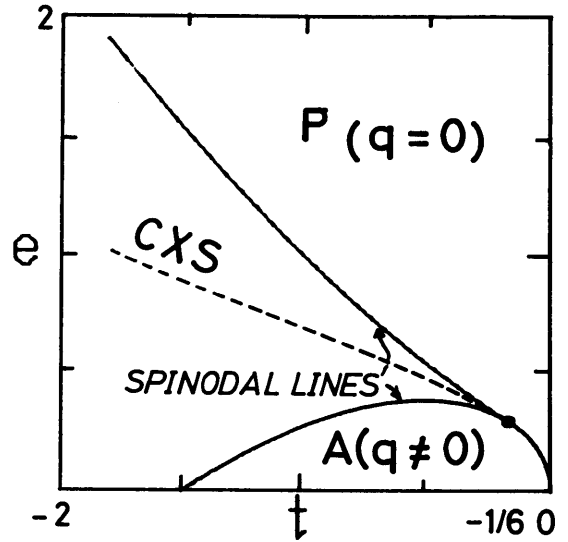


Fig.2(a) Calculated phase diagram for the second order antiferroelectric phase transition. TCP is shown in open circle.

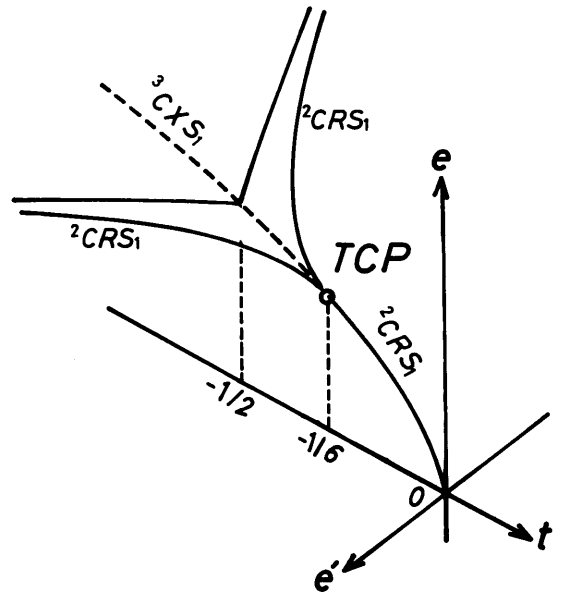


Fig.2(b) Three dimensional phase diagram.

is reduced

$$1 + t - 30Q^2 = 0, \quad (12)$$

where d^2Q/dg^2 is calculated from (6). If we put $F = t + 2q^2 + 6Q^2$, d^2Q/dq^2 is given by F_{qq}/F_q , where $F_{qq} = \partial^2 F/\partial q^2$ and $F_q = \partial F/\partial Q$. So TCP is simply calculated from (9) and (12) as²⁰⁾

$$t = -1/6. \quad (13)$$

The other critical lines should be considered, because at TCP three critical lines come together. In case of existing the staggered field e' , the equilibrium condition (6) gives the field e' as

$$e' = \partial a/\partial q = 2q(t + 6Q^2 + 2q^2). \quad (14)$$

Therefore the other two critical lines are deduced from (5), (9) and (14), which is easily calculated by determining the enveloping of the spinodal lines. The derivative (14) respect to q gives the critical lines e' in the function of q as

$$e' = [-(3 - 16q^2)q \pm q\sqrt{(3 - 16q^2)^2 + 2048q^4}]/4. \quad (15)$$

The critical lines e' are given by (14), (15) and (9). The calculated phase diagrams are shown in Fig. 2.

3.2 The First Order Antiferroelectric Phase Transition

The free energy for the first order antiferroelectric phase transition has been already given and analyzed in details^{12,14)}. Let us assume the free energy as $A = f(P_a^2 + P_b^2) + gP_aP_b + h(P_a^4 + P_b^4) + \delta P_a^2P_b^2 + \xi(P_a^2 + P_b^2)P_aP_b + j(P_a^6 + P_b^6) - E(P_a + P_b)$, ($j > 0$), (16)

where P_a and P_b are sublattice polarizations. Since the antiferroelectric phase transition is of interest now, we assume that $g > 0$. On introducing two new order parameters $Q = (P_a + P_b)/\sqrt{2}$ and $q = (-P_a + P_b)/\sqrt{2}$, eq. (16) is rewritten

$$\begin{aligned} a = & (1+t)Q^2 + tq^2 - m(Q^4 + q^4 + 6Q^2q^2) \\ & - m'(Q^4 + q^4 - 2Q^2q^2) \\ & - m''(Q^4 - q^4) + Q^6 + q^6 + 15Q^2q^2(Q^2 + q^2) \\ & - eQ. \end{aligned} \quad (17)$$

The equilibrium state can be found by solving a set of simultaneous equations :

$$\begin{aligned} \frac{\partial a}{\partial Q} = & 2(1+t)Q \\ & - 4mQ(Q^2 + 3q^2) - 4m'Q(Q^2 - q^2) - 4m''Q^3 \\ & + 6Q^5 + 60Q^3q^2 + 30Qq^4 - e = 0, \end{aligned} \quad (18)$$

$$\frac{\partial a}{\partial q} = 2tq - 4mq(q^2 + 3Q^2) - 4m'q(q^2 - Q^2)$$

$$+ 4m''q^3 + 6q^5 + 60Q^2q^3 + 30Q^4q = 0. \quad (19)$$

If q vanishes continuously on the phase boundary between the polar and semipolar, the transition is of the second order and the condition for it is expressed, using (8), as

$$\begin{aligned} \frac{1}{2} \frac{\partial^2 a}{\partial Q^2} = & 1 + t - 6(m + m' + m'')Q^2 + 15Q^4 \\ = & 0 \end{aligned} \quad (20)$$

or

$$\frac{1}{2} \frac{\partial^2 a}{\partial q^2} = t - 2(3m - m'')Q^2 + 15Q^4 = 0, \quad (21)$$

since $\partial^2 a/\partial Q\partial q = 0$ for $q=0$, where Q is obtained from (18) with $q=0$ by

$$e = 2Q [1 + t - 2(m + m' + m'')Q^2 + 3Q^4]. \quad (22)$$

If $\partial^2 a/\partial Q^2 > \partial^2 a/\partial g^2$, i.e.,

$$1 - 2(4m' + 3m'')Q^2 > 0 \quad (23)$$

the phase boundary is determined by (21) and (22), while if otherwise, by (17) and (20).

This is applied only to the second order transition. With decreasing temperature and electric field, the first order transition may take place from a polar phase to a semipolar phase when $e \neq 0$, from a nonpolar phase to an antipolar phase when $e = 0$ even if both $\partial^2 a/\partial Q^2$ and $\partial^2 a/\partial q^2$ are still positive. The determination of the phase boundary of the first order transition is usually not easy even for such a simple free energy as (17). Suzuki and Okada have already presented several diagrams which are possible for various combinations of m , m' and m'' values of the free energy (17)¹²⁾.

Let us consider the TCP related to the transition from a P phase ($Q \neq 0, q = 0$) to a SP phase ($Q \neq 0, q \neq 0$), which takes place with decreasing field e . The TCP is located on the second order transition line. The relation (11) has to be satisfied, it is made use of that Q is an even function of q , that is, $(dQ/dq) = 0$ at $q=0$. If the second order transition is determined by $\partial^2 a/\partial Q^2 = 0$ the last term of (11) is also zero, then TCP is given only by the condition $\partial^2 g/\partial q^2 = 0$. So TCP is simply calculated from (11) and (18) as

$$t = (3m - m')(3m + 7m' + 6m'') / 15 - 1 \quad (24)$$

and e is given by (22).

On the contrary, if the second order transition is determined by $\partial^2 a / \partial q^2 = 0$, the last term of (11) has a definite value. The simple calculation of (11) gives

$$[4(3m - m')^2 + 2(4m' + 3m'')(5m - 3m' + m'') - 15 - 60t] Q^2$$

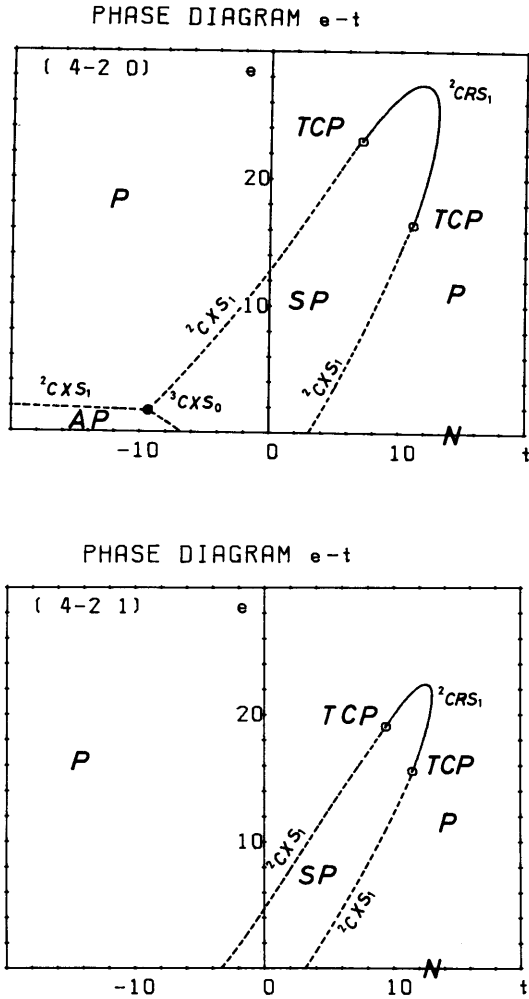


Fig. 3 Calculated phase diagrams. The adopted values of parameters (m, m', m'') are (a) $(4, -2, 0)$, (b) $(4, -2, 1)$. The open circles indicate the tricritical point and the solid and the dotted lines indicate the second and the first order phase transition lines, respectively. CRS and CXS indicate the critical surface and the coexistence surface, respectively (for details, see ref. 1).

$$+ [m + m' + m'' - 2(4m' + 3m'')t] = 0. \quad (25)$$

Calculated phase diagrams are shown in Fig.3 for various parameters.

4. Bragg-Williams Approximation Potential

We now consider the ferroelectric phase transition in a two-sublattice model whose free energy is given as²¹⁻²⁶⁾

$$a(x_1, x_2, \theta) = -\frac{1}{2}b(x_1^2 + x_2^2) - b'x_1x_2 - (x_1 - x_2) + \frac{\theta}{2} \sum \{ (1+x_i) \ln(1+x_i) + (1-x_i) \ln(1-x_i) - 2 \ln 2 \}, \quad (26)$$

where x_1 and x_2 stand for sublattice polarizations, b and b' the effective constants of interaction between dipoles belonging to the same and different sublattices, respectively, and θ represent temperature. The phase sequences to be obtained for various values of b and b' have been studied²¹⁻²⁴⁾. The coefficients b and b' can be regarded as some function of applied pressure P or concentration y in a mixed crystal system (such as $K_y(NH_4)_{1-y}NaC_4H_4O_6 \cdot 4H_2O$).

On introducing order parameters p and q as

$$p = (x_1 + x_2) / 2 \quad (27)$$

$$q = (x_1 - x_2) / 2, \quad (28)$$

representing the total and the staggered polarizations, the free energy $a(x_1, x_2, \theta)$ can be rewritten as $a(p, q, \theta)$. The equilibrium state can be found by solving

$$\frac{\partial a}{\partial p} = -\frac{b+b'}{2}p + \frac{\theta}{4} \ln \frac{(2+p+q)(2+p-q)}{(2-p-q)(2-p+q)} = 0 \quad (29)$$

$$\frac{\partial a}{\partial q} = -\frac{b-b'}{2}q - 1 + \frac{\theta}{4} \ln \frac{(2+p+q)(2-p+q)}{(2-p-q)(2+q-q)} = 0. \quad (30)$$

The paraelectric phase at high temperature is found from (29) and (30) as

$$p = 0,$$

$$(b-b')q + 1 = \theta \tanh^{-1}q, \quad (31)$$

and as is seen from (8), the second order phase transition takes at θ_0 given by

$$\frac{\theta_0}{1-q^2} = b + b' \quad (32)$$

Let us consider the TCP. Notice that the value of q in the paraelectric phase ($p=0$) is determined by (30), which is an even function of p , i.e., $q = q(p^2)$. The continuity of q against the change of p around $p=0$, where q and p satisfy

$$\frac{\partial a}{\partial q} \equiv g(p^2, q(p^2)) = 0, \quad (33)$$

is broken when $\frac{d^2g}{dp^2}$ changes its sign. Therefore at the TCP

$$\begin{aligned} \frac{d^2g}{dp^2} &= \frac{\partial^2g}{\partial p^2} + 2 \frac{\partial^2g}{\partial p \partial q} \frac{dq}{dp} + \frac{\partial^2g}{\partial q^2} \left(\frac{dq}{dp}\right)^2 + \frac{\partial g}{\partial q} \frac{d^2q}{dp^2} = 0 \end{aligned} \quad (34)$$

is satisfied. Paying attention to that q is an even function of p , we obtain from (34)

$$\frac{b'_t}{2q_t} \left[1 - \frac{4(b+b'_t)}{3\theta_t} \right] + \frac{\theta_t}{2} \frac{q_t}{(1-q_t^2)^2} = 0. \quad (35)$$

On combining this and (32), we find b'_t and θ_t satisfy the equation at TCP

$$\begin{aligned} \theta_t &= [(b-b'_t) \sqrt{\frac{b'_t}{3b} + 1}] / \tanh^{-1} \sqrt{\frac{b'_t}{3b}} \\ &= (b+b'_t) \left(1 - \frac{b'_t}{3b} \right). \end{aligned} \quad (36)$$

In Fig.4, several phase diagrams are shown in $b' - \theta$ plane.

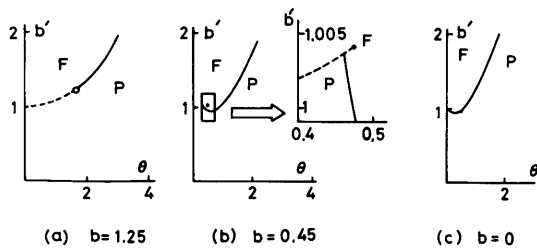


Fig. 4 Calculated $b' - \theta$ phase diagrams of the two sublattice system whose free energy is given as (1). **P** and **F** denote the paraelectric phase and the ferroelectric phase, respectively. The solid and the dotted curves indicate the second order and the first order transition lines. (a) $b=1.25$. The open circle indicates the TCP. (b) $b=0.45$. The figure in expanded scale is somewhat schematic. The solid circle indicates the critical point. (c) $b=0$.

5. Discussions

In the previous section we have shown the method for finding the TCP in the model two-sublattice system, applicable to the antiferroelectric crystals and ferroelectric phase transition. External force used to obtain TCP's is one which keeps the symmetry of systems, as the Rochelle salt type system, where TCP's have been derived with changing the parameter values representing strength of dipole interaction. So the external force inducing such changes does not break the symmetry of the system.

In contrast to the case, it should be noted that the external electric field as adopted in the antiferroelectric transition lower the symmetry of the system, and the symmetry breaking term $-eQ$ in (2) plays a substantial role in inducing TCP's. In the present paper, we showed the analytical method to get the TCP's for the systems with two order parameters. Even the free energy is not expressed by the power series, we showed that the TCP's are calculated by (11). The method showed in this paper may be powerful to derive the TCP's in different systems.

It will be of quite interest to study experimentally the physical nature of TCP's in antiferroelectric crystals of the type discussed in the present paper²⁷⁻³⁰⁾.

References

- 1) R. B. Griffiths and J. C. Wheeler : Phys. Rev. **A2** (1970)1047.
- 2) R. B. Griffiths : Phys. Rev. **B12**(1975)345.
- 3) M. C. M. Vendrik : Physica **99A**(1979)103.
- 4) R. Gilmore : *Catastrophe Theory for Scientist and Engineers* : John Wiley 1981.
- 5) A. J. Coleman and D. O'Shea : Phys. Rev. **B22** (1980)3428.
- 6) M. Golubitsky and D. Schaeffer : Commun. Pure Appl. Math. **32**(1979)21.
- 7) V. I. Arnol'd : Russ. Math. Surveys **30**(1975)1.
- 8) K. Okada : J. Phys. Soc. Jpn. **27**(1969)420.
- 10) K. Okada : *Proc. Int. Meeting Ferroelectricity, Kyoto, 1969* J. Phys. Soc. Jpn. **28**(1970)Suppl. p. 58.
- 11) K. Okada : J. Phys. Soc. Jpn. **37**(1974)1226.
- 12) I. Suzuki and K. Okada : J. Phys. Soc. Jpn. **45**

- (1978)1302.
- 13) I. Suzuki and K. Okada : J. Phys. Soc. Jpn. **47** (1979)1023.
- 14) L. Benguigui : Can. J. Phys. **46**(1968)1627.
- 15) L. Benguigui : Phys. Lett. **33A**(1970)79.
- 16) L. E. Cross : J. Phys. Soc. Jpn. **23**(1967)77.
- 17) K. Uchino and S. Nomura : Jpn. J. Appl. Phys. **18** (1979)1493.
- 18) K. Uchino, L. E. Cross and R. E. Newnham : Jpn. J. Appl. Phys. **19**(1980)L425
- 19) K. Uchino, L. E. Cross, R. E. Newnham and S. Nomura : J. Appl. Phys. **52**(1981)1455.
- 20) K. Okada : Oyo Buturi **48**(1979)645 [in Japanese]
- 21) T. Mitsui : Phys. Rev. **111**(1958)1256.
- 22) Y. Ishibashi and Y. Takagi : J. Phys. Soc. Jpn. **32** (1972)723.
- 23) Y. Ishibashi and Y. Takagi : J. Phys. Soc. Jpn. **38** (1975)1715.
- 24) Y. Ishibashi and Y. Takagi : J. Phys. Soc. Jpn. **37** (1974)1349.
- 25) K. Gesi : J. Phys. Soc. Jpn. **43**(1977)1941.
- 26) I. Suzuki and Y. Ishibashi : J. Phys. Soc. Jpn. **51** (1982)2209.
- 27) V. H. Schmidt, A. B. Western and A. G. Baker : Phys. Rev. Lett. **37**(1976)839.
- 28) P. Bastie, M. Wallade, C. Wettier and C. M. E. Zeyen : Phys. Rev. Lett. **40**(1978)337.
- 29) P. S. Peerey : Phys Rev. Lett. **35**(1975)1581.
- 30) V. K. Wadhawan and A. M. Glayer : Phase Transitions **2**(1981)75.
- 31) I. Suzuki and Y. Ishibashi : J. Phys. Soc. Jpn. **52** (1983) 187.