Theoretical investigation of the variety of first-order transitions between prototypic and ferroic phases

Kêitsiro Aizu
Hitachi Central Research Laboratory, Kokubunzi, Tokyo, Japan
(Received 30 May 1980)

Although theorists have so far investigated first-order transitions much less than second-order transitions, first-order transitions are much richer in variety. Conceivable are a first-order transition between a prototypic phase and a ferroic phase derived from it, between two ferroics derived from the same prototypic, and between a prototypic or one of its ferroics and another prototypic or one of its ferroics. The present paper deals with first-order transitions, each between a prototypic and one of its ferroics. These first-order transitions are still rich in variety. For them the concept *sense* is introduced; they are divided into second-sense transitions, third-sense transitions, and so on. First-sense transitions are also defined; they are seen to be identical with second-order transitions. The thermodynamics of sense is developed. Especially the (third) ideal case, for which all of C_k's with $k \geq 5$ and none of C_k's with $2 \leq k \leq 4$ are equal to zero (C_k is the $2k$th degree coefficient in the free-energy function), is investigated systematically, as well as the first and second ideal cases where all of C_k's with $k \geq 3$ or 4 and none of C_k's with $2 \leq k \leq 2$ or 3 are equal to zero. In the third ideal case the first, second, and third senses are possible. For experimentally discerning between the second- and third-sense transitions, several theoretically deduced relations are usable, an example of which is that $4 < \kappa_P/\kappa_F < 6$ or $6 < \kappa_P/\kappa_F < \infty$ according to the second- or third-sense transition (κ_P, κ_F are the electric susceptibilities of the prototypic and ferroic, respectively, at the transition temperature).

I. INTRODUCTION

When one phase (phase I) can be regarded as a slight distortion in atomic configuration of another phase (phase II), phase I is called a ferroic phase. (This definition of *ferroic* is substantially equivalent to the old one[1,2] which is in terms of change in orientational state. Although *ferroic* is originally[1] a unification and generalization of *ferromagnetic*, *ferroelectric*, and *ferroelastic*, the present paper is concerned only with nonmagnetic substances.) If phase II is not a slight distortion of any phase, phase II is called the prototypic phase of phase I. If phase II is a slight distortion of a third phase and this phase III is not a slight distortion of any phase, we recognize both the phases I and II as ferroic phases derived from phase III, and phase III as the common prototypic phase of phases I and II. Phase II is not recognized as prototypic for phase I. No phase can be both prototypic for one phase and ferroic for another phase. (The nuance between *prototypic phase* and *prototype* was explained in Ref. 3.)

A ferroic phase is often abbreviated to a ferroic, and a prototypic phase to a prototypic, omitting *phase*.

As is well known, phase transitions can be divided into first-order transitions and second-order transitions. So far, theorists have been interested much less in first-order transitions than in second-order transitions (as the textbook by Landau and Lifshitz[4] typifies). However, first-order transitions are much richer in variety.

The transition between two different prototypics or between a prototypic and a ferroic that is derived from another prototypic or between two ferroics derived from different prototypics cannot be second order but must be first order.

Two ferroics derived from the same prototypic are said to be conformal, lineal, or collateral to each other, according as their space groups are identical, or inter-related as proper sub- and supergroups, or otherwise.[5-7] The prototypic is lineal to any of its ferroics, since the space group of the former is a proper supergroup of the space group of the latter. The transition between two conformal, lineal, or collateral phases is said to be a conformal, lineal, or collateral transition, respectively. Every conformal or collateral transition must be first order. A lineal transition can be either first or second order. To detail further, two lineal phases are said to be immediately or mediately lineal, according as in the sequence of possible phases there is no or at least one phase whose space group is both a proper subgroup of the space group of one of those two phases and a proper supergroup of the space group of the other of those two phases. (When the transition parameter system as well as the prototype are given, the sequence of possible phases is determinate.) The transition between two mediately or immediately lineal phases is said to be a mediately or immediately lineal transition, respectively. Every mediately lineal transition must be first order. An immediately lineal transition can be either first or second order.

As examples, let us consider transitions in $BaTiO_3$, a substance familiar to many physicists.[8] The hexagonal and the cubic phase are different prototypics. The tetragonal, the orthorhombic, and the rhombohedral phase are all ferroics derived from the cubic phase. The transition between the cubic and tetragonal phases is an immediately lineal transition. The tetragonal-to-orthorhombic transition and the orthorhombic-to-rhombohedral transition are both collateral transitions. In particular the tetragonal-to-orthorhombic transition is not lineal; the symmetry of the orthorhombic phase seems to be, but is not rigorously, a proper subgroup of the symmetry of the tetragonal phase; the fact should be noted that the diad axis of the orthorhombic phase in any oriate (or orientational state) is not parallel to the tetrad axis of the tetragonal phase in any oriate. If the cubic-to-orthorhombic transition is imagined, it is an immediately lineal transition. The sequence of possible ferroics derived from the cubic phase contains also two phases that belong to point group *m* with the monoclinic unique axis along a cubic principal axis or a cubic face diagonal, respectively. If the transition from the cubic phase to either monoclinic phase is imagined, it is a mediately lineal transition. (Since the cubic-to-orthorhombic transition is immediately lineal, it, generally speaking, can be second order. But it is found not to pass a certain checkpoint for second-order transition[9]; hence as a theoretical conclusion it must be first order. The cubic-to-tetragonal transition is found to pass the same checkpoint; according to actual observation,[10] it is first order.)

In the subsequent sections we will make a more detailed investigation of immediately lineal transitions, especially from prototypics to ferroics. As has been stated, these transitions can be either first or second order. Of them the first-order ones are still rich in variety. We will introduce the concept *sense*. Then these first-order transitions are divided into second-sense transitions, third-sense transitions, and so on. (One may rename nth-sense transitions to transitions of the nth sense.) The higher in sense, the more drastic. First-sense transitions are smoothest; they are identified with second-order transitions. (No one will confuse the concept *sense* with the concept *rank* which was introduced in Refs. 5 and 6.)

II. GENERAL FOUNDATIONS: FIRST IDEAL CASE, SECOND IDEAL CASE

Let a prototype and a transition parameter system be given. For the sake of simplicity the transition parameter system is assumed to comprise only one parameter (denoted by Q) belonging to a one-dimensional nonidentity representation of the space group of the prototype. (The assumption of one-dimensional representation is not absolutely necessary; it is only for the sake of simplicity.) In the case of one-dimensional representation, all possible ferroics are conformal with one another and immediately lineal to the prototypic. We will consider one of them.

The free-energy function per unit volume Φ is assumed to be expandable into a power series in Q. Obviously,

$$\Phi = \sum_{k=0}^{\infty} C_k Q^{2k} \ , \tag{2.1}$$

where C_k's are mere coefficients. Every phase needs to satisfy the equation

$$\left(\frac{\partial \Phi}{\partial Q}\right)_s = 0 \tag{2.2}$$

and the inequality

$$\left(\frac{\partial^2 \Phi}{\partial Q^2}\right)_s > 0 \ . \tag{2.3}$$

(Subscript s means "spontaneous.") For the ferroic, since $Q_s \neq 0$, Eq. (2.2) becomes

$$\sum_{k=0}^{\infty} (k+1) C_{k+1} Q_s^{2k} = 0 \ . \tag{2.4}$$

Inequality (2.3) becomes

$$\sum_{k=0}^{\infty} (k+1)(2k+1) C_{k+1} Q_s^{2k} > 0 \ , \tag{2.5}$$

which can be rewritten to

$$\sum_{k=0}^{\infty} [\tfrac{1}{2}(k+1)(k+2)] C_{k+2} Q_s^{2k} > 0 \tag{2.6}$$

by taking account of Eq. (2.4) and the fact that $Q_s^2 > 0$.

Equation (2.4), in general, has many different solutions

$$Q_s^2 = f_1(C_1, C_2, C_3, \ldots) \ , \tag{2.7a}$$

$$Q_s^2 = f_2(C_1, C_2, C_3, \ldots) \ , \tag{2.7b}$$

$$\ldots \ ,$$

where each of the right-hand sides is a single-valued smooth real function of coefficients C_k's. Since the left-hand sides are positive, these functions need also to be positive. In the ferroic under consideration, one of Eqs. (2.7) holds. Let the equation

$$Q_s^2 = f_i(C_1, C_2, C_3, \ldots)$$

hold. We refer to this $f_i(C_1, C_2, \ldots)$ as the venule function of the ferroic under consideration. (Another ferroic conformal with the ferroic under consideration may have the same or another venule function.) We define *sense*. The venule function $f_i(C_1, C_2, \ldots)$ is said to be nth sense (or to be of the nth sense), when firstly

$$f_i(C_1, \ldots, C_n, C_{n+1}, 0, 0, \ldots)$$

(C_k's with $k \geq n+2$ are all zero) is finite for general nonzero values of $C_1, \ldots, C_n, C_{n+1}$ and secondly

$$\lim_{C_{n+1}\to 0} C_{n+1} f_i(C_1, \ldots, C_n, C_{n+1}, 0, 0, \ldots)$$

is not identically zero independently of $C_1, \ldots, C_n$. The second item, of course, implies

$$\lim_{C_{n+1}\to 0} |f_i(C_1, \ldots, C_n, C_{n+1}, 0, 0, \ldots)| = \infty \ .$$

The ferroic having the nth sense venule function is also said to be nth sense. Moreover, the transition from the prototypic to the nth sense ferroic is said to be nth sense.

For simplicity it is assumed that all C_k's except C_0 and C_1 are temperature independent and that C_1 is a monotone increasing function of temperature. If the transition is second order, then at the transition temperature the Q_s of the ferroic becomes zero and hence, according to Eq. (2.4), C_1 must become zero; in other words the transition temperature is determined as the temperature that makes $C_1 = 0$ (when C_1 as a function of temperature is given *a priori*). One necessary and sufficient condition for the transition to be second order is that the venule function of the ferroic is zero at $C_1 = 0$ independently of the other C_k's, i.e.,

$$f_i(0, C_2, C_3, \ldots) = 0 \ ;$$

the proof is easy.

We will below consider, in succession, three ideal cases where C_k's with $k \geq 3$ or 4 or 5 are all constantly zero and any other C_k is not. Conventionally, many physicists have often replaced real cases approximately by the first or second of those ideal cases.

In the first ideal case where C_k's with $k \geq 3$ are all constantly zero and any other C_k is not, Eqs. (2.1) and (2.4) reduce to

$$\Phi = C_0 + C_1 Q^2 + C_2 Q^4 \quad (C_2 > 0) \ , \qquad (2.8)$$

$$C_1 + 2C_2 Q_s^2 = 0 \ , \qquad (2.9)$$

respectively. In order that Φ is positive for great values of $|Q|$, it is necessary to assume that the coefficient in the highest degree term, i.e., C_2 is positive. Inequality (2.6) reduces to $C_2 > 0$; thus, in the first ideal case, inequality (2.6) also requires the positivity of C_2. Equation (2.9) has only one solution

$$Q_s^2 = f_1(C_1, C_2) = -C_1/2C_2 \ . \qquad (2.10)$$

Since Q_s^2 and C_2 are positive, C_1 needs to be negative. How high sense is the venule function $f_1(C_1, C_2)$? We find

$$\lim_{C_2\to 0} C_2 f_1(C_1, C_2) = -\tfrac{1}{2} C_1 \ ,$$

which is not identically zero. Therefore $f_1(C_1, C_2)$ is first sense. How high order is the transition? We see $f_1(0, C_2) = 0$. Hence the transition is second order. This exemplifies that in general a first-sense transition is second order. (Although the argument in this paragraph is not especially new, it may serve for the understanding of sense.)

In the second ideal case where C_k's with $k \geq 4$ are all constantly zero and any other C_k is not, Eqs. (2.1) and (2.4) reduce to

$$\Phi = C_0 + C_1 Q^2 + C_2 Q^4 + C_3 Q^6 \quad (C_3 > 0) \ , \qquad (2.11)$$

$$C_1 + 2C_2 Q_s^2 + 3C_3 Q_s^4 = 0 \ , \qquad (2.12)$$

respectively. C_3 needs to be positive. Inequality (2.6) becomes

$$C_2 + 3C_3 Q_s^2 > 0 \ . \qquad (2.13)$$

We assume

$$1 - 3C_1 C_3 / C_2^2 > 0 \ . \qquad (2.14)$$

Then Eq. (2.12) has two solutions

$$Q_s^2 = f_1(C_1, C_2, C_3) = -C_2/3C_3 + (C_2/3C_3)(1 - 3C_1C_3/C_2^2)^{1/2} \ , \qquad (2.15)$$

$$Q_s^2 = f_2(C_1, C_2, C_3) = -C_2/3C_3 - (C_2/3C_3)(1 - 3C_1C_3/C_2^2)^{1/2} \ . \qquad (2.16)$$

We follow the convention that $(\ )^{1/2}$ is not negative. In order that inequalities (2.13), (2.14) hold and expression (2.15) is positive, it is necessary and sufficient that

$$C_2 > 0 \ \text{and} \ C_1 < 0 \ . \qquad (2.17)$$

In order that inequalities (2.13), (2.14) hold and expression (2.16) is positive, it is necessary and sufficient that

$$C_2 < 0 \ \text{and} \ C_1 < C_2^2/3C_3 \ , \qquad (2.18)$$

the latter of which is the same as inequality (2.14). How high sense are the two venule functions? We find

$$\lim_{C_3\to 0} C_3 f_2(C_1, C_2, C_3) = -\tfrac{2}{3} C_2$$

which is not identically zero. Therefore

$f_2(C_1,C_2,C_3)$ is second sense. Expression (2.15) can be rewritten as

$$C_1/[-C_2-C_2(1-3C_1C_3/C_2^2)^{1/2}] \ . \qquad (2.19)$$

When C_3 is close to zero, expression (2.15) is equal to the power series in C_3

$$-C_1/2C_2-(3C_1^2/8C_2^3)C_3+O(C_3^2) \ . \qquad (2.20)$$

Using expression (2.19) or (2.20), we find

$$f_1(C_1,C_2,0)=-C_1/2C_2 \ , \qquad (2.21)$$

which is finite for general nonzero values of C_1, C_2. Moreover, using Eq. (2.21), we find

$$\lim_{C_2\to 0} C_2 f_1(C_1,C_2,0)=-\tfrac{1}{2}C_1$$

which is not identically zero. Therefore $f_1(C_1,C_2,C_3)$ is first sense. Comparing Eq. (2.21) with Eq. (2.10), we see

$$f_1(C_1,C_2,0)=f_1(C_1,C_2) \ . \qquad (2.22)$$

Thus $f_1(C_1,C_2,C_3)$ is an extension of $f_1(C_1,C_2)$. On the other hand, $f_2(C_1,C_2,C_3)$ is not any extension of $f_1(C_1,C_2)$. How high order are the first- and the second-sense transition? We see

$$f_1(0,C_2,C_3)=0 \ ,$$

$$f_2(0,C_2,C_3)=-2C_2/3C_3\neq 0 \ .$$

Hence the first-sense transition is second order while the second-sense transition is first order.

If the solutions to Eq. (2.12) were expressed as

$$Q_s^2=f_1(C_1,C_2,C_3)$$
$$=-C_2/3C_3+(1/3C_3)(C_2^2-3C_1C_3)^{1/2} \ , \qquad (2.23)$$

$$Q_s^2=f_2(C_1,C_2,C_3)$$
$$=-C_2/3C_3-(1/3C_3)(C_2^2-3C_1C_3)^{1/2} \qquad (2.24)$$

instead of expressions (2.15), (2.16), then the sense of $f_1(C_1,C_2,C_3)$ would not be uniquely determined; even the order of the transition to the ferroic with $f_1(C_1,C_2,C_3)$ would not be uniquely determined. Expression (2.23) turns to expression (2.15) or (2.16) depending on whether $C_2 >$ or < 0.

III. THIRD IDEAL CASE

A. Basic main part of theory

The third ideal case where C_k's with $k \geqslant 5$ are all constantly zero and any other C_k is not has never been systematically investigated by any theorist. For first-order transitions it has conventionally been assumed that C_3 is positive and the terms of degree higher than sixth have no essential effect (see, as a typical example, the theory of ferroelectricity by Devonshire[11]). However, there is *no natural reason for C_3 to be always positive.* If $C_3 < 0$, the eighth (or a higher) degree term has an essential effect and its neglect is not permitted.

The third ideal case will be investigated below. (The reader is assumed to be, to some extent, familiar with the mathematics of cubic equations.) Equations (2.1), (2.4) become

$$\Phi=C_0+C_1Q^2+C_2Q^4+C_3Q^6+C_4Q^8 \ \ (C_4>0) \ , \qquad (3.1)$$

$$C_1+2C_2Q_s^2+3C_3Q_s^4+4C_4Q_s^6=0 \ , \qquad (3.2)$$

respectively. C_4 needs to be positive. Note that Eq. (3.2) can be rewritten as

$$-2q-3px+x^3=0$$

by putting

$$x=Q_s^2+C_3/4C_4 \ ,$$

$$p=(C_3/4C_4)^2(1-8C_2C_4/3C_3^2) \ , \qquad (3.3)$$

$$q=-(C_3/4C_4)^3(1-4C_2C_4/C_3^2+8C_1C_4^2/C_3^3) \ . \qquad (3.4)$$

Three cases, viz., case α, case β, and case γ are distinguished. Case γ is where $p<0$, i.e.,

$$C_2>3C_3^2/8C_4 \ . \qquad (3.5)$$

(In this case it follows that $p^3-q^2<0$.) Case β is where $p>0$ and $p^3-q^2<0$, i.e.,

$$C_2<3C_3^2/8C_4 \qquad (3.6)$$

and

$$(1-8C_2C_4/3C_3^2)^3<(1-4C_2C_4/C_3^2+8C_1C_4^2/C_3^3)^2 \ ; \qquad (3.7)$$

the latter inequality is equivalent to the inequality

$$1-\frac{3C_1C_3}{C_2^2}-\frac{32C_2C_4}{9C_3^2}+\frac{12C_1C_4}{C_2C_3}-\frac{12C_1^2C_4^2}{C_2^2C_3^2}<0 \qquad (3.8)$$

since the left-hand side minus the right-hand side of inequality (3.7) is equal to the left-hand side of inequality (3.8) multiplied by

$$16C_2^2C_4^2/3C_3^4 \ .$$

Case α is where $p^3-q^2>0$, i.e.,

$$(1-8C_2C_4/3C_3^2)^3>(1-4C_2C_4/C_3^2+8C_1C_4^2/C_3^3)^2 \qquad (3.9)$$

or

$$1-\frac{3C_1C_3}{C_2^2}-\frac{32C_2C_4}{9C_3^2}+\frac{12C_1C_4}{C_2C_3}-\frac{12C_1^2C_4^2}{C_2^2C_3^2}>0 \ . \qquad (3.10)$$

(In this case the inequality $p > 0$ follows naturally.) If in inequality (3.10) we put $C_4=0$, we get the same as inequality (2.14); thus inequality (3.10) is an extension of inequality (2.14). On the other hand, inequality (3.8) is not. In cases α and β, we define A_+ and A_-:

$$A_+=(C_3^3/8C_4^2)[4C_2C_4/C_3^2-1+(1-8C_2C_4/3C_3^2)^{3/2}] , \quad (3.11)$$

$$A_-=(C_3^3/8C_4^2)[4C_2C_4/C_3^2-1-(1-8C_2C_4/3C_3^2)^{3/2}] . \quad (3.12)$$

Obviously, $A_+ >$ or $< A_-$ according as $C_3 >$ or <0. Of A_+, A_-, we denote the greater by $\max(A_+,A_-)$ and the lesser by $\min(A_+,A_-)$. Then inequality (3.7) can be rewritten as

$$C_1 > \max(A_+,A_-) \quad \text{or} \quad < \min(A_+,A_-) , \quad (3.13)$$

and inequality (3.9) as

$$\min(A_+,A_-) < C_1 < \max(A_+,A_-) . \quad (3.14)$$

In case γ, Eq. (3.2) is found to have the only solution

$$Q_s^2=f^{\gamma}(C_1,C_2,C_3,C_4) = -\frac{C_3}{4C_4}-\frac{C_3}{2C_4}\left[\frac{8C_2C_4}{3C_3^2}-1\right]^{1/2}\sinh\tfrac{1}{3}\gamma , \quad (3.15)$$

where

$$\sinh\gamma=\left[\frac{8C_2C_4}{3C_3^2}-1\right]^{-3/2}\left[1-\frac{4C_2C_4}{C_3^2}+\frac{8C_1C_4^2}{C_3^3}\right] . \quad (3.16)$$

In case β, Eq. (3.2) is found to have the only solution

$$Q_s^2=f^{\beta}(C_1,C_2,C_3,C_4) = -\frac{C_3}{4C_4}-\frac{C_3}{2C_4}\left[1-\frac{8C_2C_4}{3C_3^2}\right]^{1/2}\sigma\cosh\tfrac{1}{3}\beta , \quad (3.17)$$

where

$$\sigma\cosh\beta=\left[1-\frac{8C_2C_4}{3C_3^2}\right]^{-3/2}\left[1-\frac{4C_2C_4}{C_3^2}+\frac{8C_1C_4^2}{C_3^3}\right] \quad (3.18)$$

and $\sigma=+1$ or -1. Since $\cosh\beta$ and $(1-8C_2C_4/3C_3^2)^{-3/2}$ are positive, the value of σ is determined by only the sign of the expression

$$1-4C_2C_4/C_3^2+8C_1C_4^2/C_3^3 : \quad (3.19)$$

We have $+1$ if positive, and -1 if negative. Though the sign of β is not determined, it is no matter; we agree that $\beta \geqslant 0$.

In case α, Eq. (3.2) is found to have the three solutions

$$Q_s^2=f_n^{\alpha}(C_1,C_2,C_3,C_4) = -\frac{C_3}{4C_4}-\frac{C_3}{2C_4}\left[1-\frac{8C_2C_4}{3C_3^2}\right]^{1/2}\cos\frac{\alpha+2n\pi}{3} \quad (n=0,1,2) , \quad (3.20)$$

where

$$-\pi<\alpha<\pi , \quad (3.21)$$

$$\cos\alpha=\left[1-\frac{8C_2C_4}{3C_3^2}\right]^{-3/2}\left[1-\frac{4C_2C_4}{C_3^2}+\frac{8C_1C_4^2}{C_3^3}\right] , \quad (3.22)$$

$$\sin\alpha=(4C_2C_4/\sqrt{3}C_3^2)(1-8C_2C_4/3C_3^2)^{-3/2} \times\left[1-\frac{3C_1C_3}{C_2^2}-\frac{32C_2C_4}{9C_3^2}+\frac{12C_1C_4}{C_2C_3}-\frac{12C_1^2C_4^2}{C_2^2C_3^2}\right]^{1/2} . \quad (3.23)$$

According to Eq. (3.23) and inequality (3.21), α is of the same sign as C_2. If in Eq. (3.20) we put $n=3$, we see $f_3^{\alpha}=f_0^{\alpha}$; thus symbol f_0^{α} may be replaced by f_3^{α}.

The temperatures with which we are concerned are restricted to those not much lower than the temperature making $C_1=0$. On unlimited cooling, the ferroic succeeding the prototypic directly might not continue most stable but get changed to another ferroic (of a different sense) at a certain temperature. In the present paper we do not deal with such ferroic-to-ferroic transitions.

For a while we consider case α. How high sense are the three venule functions? The bringing of C_4 close to zero does not break inequality (3.10), even if $C_1=0$. When C_4 is close to zero, we find, from Eq. (3.23) and inequality (3.21),

$$\alpha=(4C_2C_4/\sqrt{3}C_3^2)(1-3C_1C_3/C_2^2)^{1/2}+O(C_4^2) . \quad (3.24)$$

By use of Eq. (3.24), Eq. (3.20) can be rewritten as

$$f_n^{\alpha}(C_1,C_2,C_3,C_4) = -\frac{C_3}{4C_4}(1+2\cos\tfrac{2}{3}n\pi)+\frac{2C_2}{3C_3}\cos\tfrac{2}{3}n\pi + \frac{2C_2}{3^{3/2}C_3}\left[1-\frac{3C_1C_3}{C_2^2}\right]^{1/2}\sin\tfrac{2}{3}n\pi+O(C_4) . \quad (3.25)$$

From Eq. (3.25) we find

$$\lim_{C_4\to 0} C_4 f_0^{\alpha}(C_1,C_2,C_3,C_4)=-\tfrac{3}{4}C_3 \quad (3.26)$$

which is not identically zero, and

$$f_1^\alpha(C_1,C_2,C_3,0) = -\frac{C_2}{3C_3} + \frac{C_2}{3C_3}\left[1 - \frac{3C_1C_3}{C_2^2}\right]^{1/2}, \tag{3.27}$$

$$f_2^\alpha(C_1,C_2,C_3,0) = -\frac{C_2}{3C_3} - \frac{C_2}{3C_3}\left[1 - \frac{3C_1C_3}{C_2^2}\right]^{1/2}, \tag{3.28}$$

which are both finite for general nonzero values of C_1, C_2, C_3. Therefore $f_0^\alpha(C_1, \ldots, C_4)$ [or $f_3^\alpha(C_1, \ldots, C_4)$] is concluded to be third sense, while $f_1^\alpha(C_1, \ldots, C_4)$ and $f_2^\alpha(C_1, \ldots, C_4)$ must be lower sense. Comparing Eqs. (3.27), (3.28) with Eqs. (2.15), (2.16), we see

$$f_1^\alpha(C_1,C_2,C_3,0) = f_1(C_1,C_2,C_3),$$

$$f_2^\alpha(C_1,C_2,C_3,0) = f_2(C_1,C_2,C_3).$$

Thus $f_1^\alpha(C_1, \ldots, C_4)$ is an extension of $f_1(C_1,C_2,C_3)$, and $f_2^\alpha(C_1, \ldots, C_4)$, of $f_2(C_1,C_2,C_3)$. Since in Sec. II it has been proved that $f_1(C_1,C_2,C_3)$ is first sense and $f_2(C_1,C_2,C_3)$ second sense, it is now evident that $f_1^\alpha(C_1, \ldots, C_4)$ is first sense and $f_2^\alpha(C_1, \ldots, C_4)$ second sense.

How high order is each of the first-, second-, and third-sense transitions? When $C_1=0$, Eq. (3.2) becomes

$$Q_s^2(2C_2+3C_3Q_s^2+4C_4Q_s^4)=0, \tag{3.29}$$

which is found to have the three solutions

$$Q_s^2 = g_0(C_2,C_3,C_4) = 0, \tag{3.30}$$

$$Q_s^2 = g_1(C_2,C_3,C_4) = -3C_3/8C_4 + (3C_3/8C_4)(1-32C_2C_4/9C_3^2)^{1/2}, \tag{3.31}$$

$$Q_s^2 = g_2(C_2,C_3,C_4) = -3C_3/8C_4 - (3C_3/8C_4)(1-32C_2C_4/9C_3^2)^{1/2}. \tag{3.32}$$

Note that when $C_1=0$, inequality (3.10) becomes

$$1-32C_2C_4/9C_3^2 > 0 \tag{3.33}$$

whose left-hand side is the same as the content of $(\ )^{1/2}$ in expressions (3.31), (3.32). The set of $g_n(C_2,C_3,C_4)$ $(n=0,1,2)$ should be identical with the set of $f_n^\alpha(0,C_2,C_3,C_4)$ $(n=0,1,2)$. Which element is identical with which element? From Eqs. (3.30), (3.31), (3.32) we find

$$g_0(C_2,C_3,0)=0, \tag{3.34}$$

$$g_1(C_2,C_3,0) = -2C_2/3C_3, \tag{3.35}$$

$$\lim_{C_4\to 0} C_4 g_2(C_2,C_3,C_4) = -3C_3/4. \tag{3.36}$$

On the other hand, Eqs. (3.26), (3.27), (3.28), if we put $C_1=0$, become

$$\lim_{C_4\to 0} C_4 f_0^\alpha(0,C_2,C_3,C_4) = -3C_3/4, \tag{3.37}$$

$$f_1^\alpha(0,C_2,C_3,0)=0, \tag{3.38}$$

$$f_2^\alpha(0,C_2,C_3,0) = -2C_2/3C_3. \tag{3.39}$$

Comparing Eqs. (3.34), (3.35), (3.36) with Eqs. (3.37), (3.38), (3.39), we conclude that

$$f_0^\alpha(0,C_2,C_3,C_4) = g_2(C_2,C_3,C_4), \tag{3.40}$$

$$f_1^\alpha(0,C_2,C_3,C_4) = g_0(C_2,C_3,C_4), \tag{3.41}$$

$$f_2^\alpha(0,C_2,C_3,C_4) = g_1(C_2,C_3,C_4). \tag{3.42}$$

Substituting Eqs. (3.30), (3.31), (3.32) into the right-hand sides of Eqs. (3.40), (3.41), (3.42), we obtain

$$f_0^\alpha(0,C_2,C_3,C_4) = -\frac{3C_3}{8C_4} - \frac{3C_3}{8C_4}\left[1 - \frac{32C_2C_4}{9C_3^2}\right]^{1/2}, \tag{3.43}$$

$$f_1^\alpha(0,C_2,C_3,C_4)=0, \tag{3.44}$$

$$f_2^\alpha(0,C_2,C_3,C_4) = -\frac{3C_3}{8C_4} + \frac{3C_3}{8C_4}\left[1 - \frac{32C_2C_4}{9C_3^2}\right]^{1/2}. \tag{3.45}$$

Thus it turns out that the first-sense transition is second order while the second- and third-sense transitions are first order. Equations (3.43), (3.44), (3.45) can also be deduced from Eqs. (3.20)–(3.23), but this method is less simple than that described above.

What is the equation determining the first-, second-, or third-sense transition temperature? At this temperature, what is the expression for the Q_s of the ferroic? We obviously have $C_1=0$ and $Q_s=0$ for the first-sense transition. For the second- or third-sense transition, since it is first order, the Q_s of the ferroic is nonzero even at the transition temperature. From this fact and Eq. (3.1), it follows that at the transition temperature the equation

$$C_1+C_2Q_s^2+C_3Q_s^4+C_4Q_s^6=0 \tag{3.46}$$

must be satisfied. Of course, Eq. (3.2) also must be satisfied. Subtracting Eq. (3.46) from Eq. (3.2) and dividing the resultant equation by Q_s^2, we get the equation

$$C_2+2C_3Q_s^2+3C_4Q_s^4=0. \tag{3.47}$$

We assume

$$1-3C_2C_4/C_3^2 > 0. \tag{3.48}$$

Then Eq. (3.47) is found to have the two solutions

$$Q_s^2(\text{second}) = g_4(C_2,C_3,C_4) = -C_3/3C_4 + (C_3/3C_4) \times (1-3C_2C_4/C_3^2)^{1/2} , \quad (3.49)$$

$$Q_s^2(\text{third}) = g_5(C_2,C_3,C_4) = -C_3/3C_4 - (C_3/3C_4) \times (1-3C_2C_4/C_3^2)^{1/2} . \quad (3.50)$$

Obviously,

$$g_4(C_2,C_3,0) = -C_2/2C_3 ,$$

$$\lim_{C_4\to 0} C_4 g_5(C_2,C_3,C_4) = -2C_3/3 .$$

Hence the Q_s^2 given in Eq. (3.49) pertains to the second-sense transition, and that in Eq. (3.50) to the third-sense transition. Substituting Eq. (3.49) or (3.50) into Eq. (3.46), we obtain

$$C_1 + \frac{2C_3^3}{27C_4^2}\left[1 - \frac{9C_2C_4}{2C_3^2} \mp \left(1 - \frac{3C_2C_4}{C_3^2}\right)^{3/2}\right] = 0 , \quad (3.51)$$

which is the equation determining the transition temperature; of the double sign $\mp$, let the upper or lower part be taken according to the second- or third-sense transition.

At the first-sense transition temperature, since $C_1 = 0$, inequality (3.10) becomes inequality (3.33). At the second- or third-sense transition temperature, since C_1 satisfies Eq. (3.51), the left-hand side of inequality (3.10) becomes

$$\frac{22C_3^4}{243C_2^2C_4^2}\left(1 - \frac{3C_2C_4}{C_3^2}\right) \times \left[1 - \frac{105C_2C_4}{22C_3^2} + \frac{72C_2^2C_4^2}{11C_3^4} \mp \left(1 - \frac{36C_2C_4}{11C_3^2}\right)\left(1 - \frac{3C_2C_4}{C_3^2}\right)^{1/2}\right] . \quad (3.52)$$

Remember that we have assumed inequality (3.48). Let us put

$$(1-3C_2C_4/C_3^2)^{1/2} = L ; \quad (3.53)$$

then the content of the large brackets in expression (3.52) can be rewritten as

$$\tfrac{1}{22}(1 \mp L)^2[2 + (1 \pm 4L)^2] .$$

Therefore inequality (3.48) ensures the holding of inequality (3.10).

If inequality (3.33) holds then inequality (3.48) holds; but the converse is not true. For the second- or third-sense transition, inequality (3.48) is absolutely necessary, but inequality (3.33) is not. For $f_2^\alpha(C_1, \ldots, C_4)$ or $f_0^\alpha(C_1, \ldots, C_4)$, the domain of C_1 need not contain point $C_1 = 0$. Equation (3.45) or (3.43) is not absolutely necessary. Even if inequality (3.33) does not hold, inequality (3.48) ensures the holding of inequality (3.10) at the transition temperature.

In the present ideal case, the $(\partial^2\Phi/\partial Q^2)_s$ of the ferroic is calculated as

$$\left(\frac{\partial^2\Phi}{\partial Q^2}\right)_s = 8(C_2Q_s^2 + 3C_3Q_s^4 + 6C_4Q_s^6) . \quad (3.54)$$

At the first-sense transition temperature, since $Q_s = 0$, we have $(\partial^2\Phi/\partial Q^2)_s = 0$. At the second- or third-sense transition temperature, by substituting Eq. (3.49) or (3.50) into Eq. (3.54), we get

$$\left(\frac{\partial^2\Phi}{\partial Q^2}\right)_s = \frac{16C_3^3}{9C_4^2} \times \left[-\left(1 - \frac{3C_2C_4}{C_3^2}\right) \pm \left(1 - \frac{3C_2C_4}{2C_3^2}\right)\left(1 - \frac{3C_2C_4}{C_3^2}\right)^{1/2}\right] . \quad (3.55)$$

We consider again the first-sense transition temperature. At this, although Q_s and $(\partial^2\Phi/\partial Q^2)_s$ are zero,

$$\frac{\partial Q_s^2}{\partial C_1} \quad \text{and} \quad \frac{\partial}{\partial C_1}\left(\frac{\partial^2\Phi}{\partial Q^2}\right)_s$$

are nonzero. Differentiating Eq. (3.2) with respect to C_1, we get

$$\frac{\partial Q_s^2}{\partial C_1} = -\frac{1}{2C_2} . \quad (3.56)$$

Differentiating Eq. (3.54) with respect to C_1 and using Eq. (3.56), we get

$$\frac{\partial}{\partial C_1}\left(\frac{\partial^2\Phi}{\partial Q^2}\right)_s = -4 . \quad (3.57)$$

On cooling, which transition is actualized, the first- or second- or third-sense transition? For the first-sense transition to be actualized, it is necessary that the right-hand sides of Eqs. (3.56), (3.57) are both negative. The set of these two inequalities is, obviously, equivalent to the single inequality

$$C_2 > 0 . \quad (3.58)$$

For the second-sense transition to be actualized, it is necessary that the right-hand side of Eq. (3.49) is real and positive, or in other words, inequality (3.48) holds and the right-hand side of Eq. (3.49) is positive. It is, moreover, necessary that the right-hand side of Eq. (3.55) with the upper part of the double sign ± is positive. The set of these three inequalities is found to be equivalent to the set of two inequalities

$$C_2 < 0, \quad C_3 > 0 \ . \tag{3.59}$$

For the third-sense transition to be actualized, it is necessary that inequality (3.48) holds, the right-hand side of Eq. (3.50) is positive, and the right-hand side of Eq. (3.55) with the lower part of the double sign is positive. The set of these three inequalities is found to be equivalent to the set of two inequalities

$$1 - 3C_2C_4/C_3^2 > 0, \quad C_3 < 0 \ , \tag{3.60}$$

the former of which is the same as inequality (3.48). The set of inequalities (3.59) is not compatible with inequality (3.58) nor with the set of inequalities (3.60). On the other hand, inequality (3.58) and the set of inequalities (3.60) are compatible.

It is convenient to first make a broad classification according to the sign of C_3 and second a subdivision according to the value of C_2. When $C_3 > 0$, the first- or second-sense transition is actualized according as $C_2 >$ or < 0; this is obvious. When $C_3 < 0$, the first- or third-sense transition is actualized according to whether C_2 is greater or less than a certain value, which we will clarify. It is immediately found that if $C_2 > C_3^2/3C_4$ the first-sense transition is actualized, and if $C_2 < 0$ the third-sense transition. Now let C_2 be intermediate, i.e., let

$$0 < C_2 < C_3^2/3C_4 \ . \tag{3.61}$$

(We assume that C_2 is not exactly equal to 0 nor to $C_3^2/3C_4$.) As is already known, the equations determining the first- and third-sense transition temperatures are, respectively, $C_1 = 0$ and Eq. (3.51) with the lower part of the double sign. Therefore the first- or third-sense transition is actualized according to

$$1 - 9C_2C_4/2C_3^2 + (1 - 3C_2C_4/C_3^2)^{3/2} < \text{ or } > 0 \ . \tag{3.62}$$

This inequality is found to be equivalent to the inequality[12]

$$C_2 > \text{ or } < C_3^2/4C_4 \ . \tag{3.63}$$

Thus, if

$$C_3^2/4C_4 < C_2 < C_3^2/3C_4 \ ,$$

the first-sense transition is actualized, and if $0 < C_2 < C_3^2/4C_4$, the third-sense transition. Table I summarizes the conclusions.

When $C_3 > 0$ and $C_2 < 0$, we find[12]

$$1 - 9C_2C_4/2C_3^2 - (1 - 3C_2C_4/C_3^2)^{3/2} < 0 \ . \tag{3.64}$$

TABLE I. The conditions determining whether the first-, second-, or third-sense transition should be actualized, in the third ideal case where C_k's with $k \geqslant 5$ are all constantly zero and any other C_k is not.

If	and if	then the transition to be actualized is
$C_3 > 0$	$C_2 > 0$	First sense
	$C_2 < 0$	Second sense
$C_3 < 0$	$C_2 > C_3^2/4C_4$	First sense
	$C_2 < C_3^2/4C_4$	Third sense

Hence it turns out that if the second-sense transition is actualized, the transition temperature is higher than the temperature making $C_1 = 0$. When $C_3 < 0$ and $C_2 < C_3^2/4C_4$, we find

$$1 - 9C_2C_4/2C_3^2 + (1 - 3C_2C_4/C_3^2)^{3/2} > 0 \tag{3.65}$$

even if C_2 is not inside interval (3.61) but negative. Therefore it turns out that if the third-sense transition is actualized, the transition temperature is higher than the temperature making $C_1 = 0$.

Although it has been stated earlier that for the second- or third-sense transition inequality (3.33) is not absolutely necessary, it is seen that inequality (3.33) holds naturally when $C_3 > 0$ and $C_2 < 0$ or when $C_3 < 0$ and $C_2 < C_3^2/4C_4$. Since inequality (3.33) holds, the domain of C_1 for $f_2^a(C_1, \ldots, C_4)$ or $f_0^a(C_1, \ldots, C_4)$ contains point $C_1 = 0$, and Eq. (3.45) or (3.43) holds. The additional condition that the second- or third-sense transition be actualized is important.

As has been stated, at the first-sense transition temperature we have $Q_s = 0$, $C_1 = 0$, and $(\partial^2\Phi/\partial Q^2)_s = 0$. At the second- or third-sense transition temperature, the expressions for Q_s, C_1, and $(\partial^2\Phi/\partial Q^2)_s$ are given in Eqs. (3.49) or (3.50), (3.51), and (3.55), respectively; in particular, $(\partial^2\Phi/\partial Q^2)_s > 0$. We are now interested in the temperature that makes $(\partial^2\Phi/\partial Q^2)_s = 0$ for the second- or third-sense transition. At this temperature, what are the expressions for Q_s and C_1? After intermediate calculations we find

$$Q_s^2(\text{second}) = -\frac{C_3}{4C_4} + \frac{C_3}{4C_4}\left[1 - \frac{8C_2C_4}{3C_3^2}\right]^{1/2} \ , \tag{3.66}$$

$$Q_s^2(\text{third}) = -\frac{C_3}{4C_4} - \frac{C_3}{4C_4}\left[1 - \frac{8C_2C_4}{3C_3^2}\right]^{1/2} \ , \tag{3.67}$$

$$C_1(\text{second}) = A_+, \quad C_1(\text{third}) = A_- \ , \tag{3.68}$$

where A_+ and A_- are the same as defined in Eqs.

(3.11) and (3.12). The inequality

$$1-8C_2C_4/3C_3^2>0 \tag{3.69}$$

is requisite, and the right-hand sides of Eqs. (3.66), (3.67) need to be positive. When $C_3>0$ and $C_2<0$, inequality (3.69) surely holds and the right-hand side of Eq. (3.66) is surely positive. When $C_3<0$ and $C_2<C_3^2/4C_4$, inequality (3.69) surely holds and the right-hand side of Eq. (3.67) is surely positive. The domain of C_1 for the second- or third-sense venule function is

$$C_1<A_+ \quad\text{or}\quad C_1<A_- \ , \tag{3.70}$$

respectively. When $C_3>0$ and $C_2<0$, we find

$$A_-<0<A_+ \ . \tag{3.71}$$

When $C_3<0$ and $C_2<C_3^2/4C_4$, we find

$$A_+<0<A_- \ . \tag{3.72}$$

Precisely speaking, inequality (3.72) should be replaced by $A_+\leq 0<A_-$, because if $C_2=0$ then $A_+=0$. But we assume $C_2\neq 0$. As has been stated, the temperatures with which we are concerned are restricted to those not much lower than the temperature making $C_1=0$. Let the domain of C_1 for the second- or third-sense venule function be restricted to the interval

$$A_-<C_1<A_+ \quad\text{or}\quad A_+<C_1<A_- \tag{3.73}$$

which contains point $C_1=0$ because of inequalities (3.71) or (3.72). Inequality (3.73) is the same as inequality (3.14) so that the condition for case α is satisfied.

The domain of C_1 for the first-sense venule function is $C_1\leq 0$. When $C_1=0$, inequality (3.10) becomes inequality (3.33), or equivalently, $C_2<9C_3^2/32C_4$. If this inequality holds, inequality (3.10) holds not only at point $C_1=0$ but in a certain neighborhood of it. Let the domain of C_1 be restricted to this neighborhood. Then the condition for case α is satisfied. We will make the neighborhood clearer. When $C_3>0$ and $0<C_2<9C_3^2/32C_4$, we find $A_-<0<A_+$; hence the neighborhood is $A_-<C_1\leq 0$. When $C_3<0$ and

$$C_3^2/4C_4<C_2<9C_3^2/32C_4 \ ,$$

we find $A_+<0<A_-$; hence the neighborhood is $A_+<C_1\leq 0$.

If $C_2>9C_3^2/32C_4$, the condition for case α is not satisfied. Especially if

$$9C_3^2/32C_4<C_2<3C_3^2/8C_4 \ , \tag{3.74}$$

inequality (3.6) holds and inequality (3.8) holds in a certain neighborhood of point $C_1=0$. Let the domain of C_1 be restricted to this neighborhood. Then the set of conditions for case β is satisfied. We will make the neighborhood clearer. When $C_3<0$ [and inequality (3.74) holds], we find $A_+<A_-<0$; hence the neighborhood is $A_-<C_1\leq 0$ [remember inequality (3.13)]. When $C_3>0$, we find $0<A_-<A_+$; hence the neighborhood is $C_1\leq 0$ with no definitely determined lower end. In the present case the first-sense venule function is not $f_1^\alpha(C_1,\ldots,C_4)$ but $f^\beta(C_1,\ldots,C_4)$; the latter is thought to be the continuation of the former as C_2 increases (of course, *not* with temperature). When $C_3<0$ and $A_-<C_1\leq 0$ [and inequality (3.74) holds], we find $\sigma=-1$. When $C_3>0$ and $C_1\leq 0$, we also have $\sigma=-1$. Whether $C_3>$ or <0, we find

$$A_-\to 0 \ , \quad A_+\to C_3^3/32C_4^2 \quad \text{as } C_2\to 9C_3^2/32C_4 \ . \tag{3.75}$$

From this it follows that, as $C_2\to 9C_3^2/32C_4$, the interval $A_-<C_1\leq 0$ tends to contract into point $C_1=0$. (The interval $A_-<C_1\leq 0$ appears also in case α.) Since Eq. (3.44) holds and $f^\beta(C_1,\ldots,C_4)$ is the continuation of $f_1^\alpha(C_1,\ldots,C_4)$, $f^\beta(0,C_2,C_3,C_4)$ should be zero. We will confirm this. The equation

$$4(\cosh\tfrac{1}{3}\beta)^3-3\cosh\tfrac{1}{3}\beta-\cosh\beta=0 \tag{3.76}$$

holds whatever value β takes on. When $C_1=0$, Eq. (3.18) becomes

$$\cosh\beta=(1-8C_2C_4/3C_3^2)^{-3/2}(4C_2C_4/C_3^2-1) \ . \tag{3.77}$$

By the right-hand side of this equation we replace $\cosh\beta$ in Eq. (3.76). It is not difficult to solve the resultant equation cubic with respect to $\cosh\frac{1}{3}\beta$. The solutions are

$$\cosh\tfrac{1}{3}\beta=\tfrac{1}{2}(1-8C_2C_4/3C_3^2)^{-1/2}$$

and

$$\cosh\tfrac{1}{3}\beta=\left(1-\frac{8C_2C_4}{3C_3^2}\right)^{-1/2}\times\left[-\frac{1}{4}\pm\frac{3}{4}\left(1-\frac{32C_2C_4}{9C_3^2}\right)^{1/2}\right] \ .$$

Because of inequality (3.74), the first solution is real and the two others are imaginary. Thus the first solution is the true value of $\cosh\frac{1}{3}\beta$. Putting this value into Eq. (3.17), we obtain

$$f^\beta(0,C_2,C_3,C_4)=0 \ . \tag{3.78}$$

It can also be deduced from Eqs. (3.20), (3.17) that $\partial f_1^\alpha/\partial C_1$ and $\partial f^\beta/\partial C_1$ at $C_1=0$ are isomorphous functions of C_2 (with different domains of C_2)

$$\frac{\partial f_1^\alpha}{\partial C_1}=-\frac{1}{2C_2},\quad \frac{\partial f^\beta}{\partial C_1}=-\frac{1}{2C_2} \ . \tag{3.79}$$

The right-hand side $-1/2C_2$ is the same as the right-hand side of Eq. (3.56) which was deduced by a different method.

If C_1 is negative and close to zero, positivity of f^β is found from Eqs. (3.78), (3.79). Even if C_1 is not very close to zero, positivity of f^β is proved as follows. Let β_0 stand for the β when $C_1=0$ or the β satisfying Eq. (3.77). We assume $C_1<0$. If $C_3>0$, then $\cosh\beta > \cosh\beta_0$, $\beta>\beta_0$, $\frac{1}{3}\beta > \frac{1}{3}\beta_0$, and hence $\cosh\frac{1}{3}\beta > \cosh\frac{1}{3}\beta_0$. If $C_3<0$, then $\cosh\beta<\cosh\beta_0$, $\beta<\beta_0$, $\frac{1}{3}\beta<\frac{1}{3}\beta_0$, and hence $\cosh\frac{1}{3}\beta < \cosh\frac{1}{3}\beta_0$. Therefore, whether $C_3>$ or <0, we see

$$-C_3/4C_4+(C_3/2C_4)(1-8C_2C_4/3C_3^2)^{1/2}\cosh\tfrac{1}{3}\beta$$
$$> -C_3/4C_4+(C_3/2C_4)(1-8C_2C_4/3C_3^2)^{1/2} \times \cosh\tfrac{1}{3}\beta_0 = 0 \ .$$

We find

$$A_- \to \frac{C_3^3}{16C_4^2}\ ,\quad A_+ \to \frac{C_3^3}{16C_4^2}\quad \text{as}\quad C_2 \to \frac{3C_3^2}{8C_4}-0\ . \tag{3.80}$$

Thus the interval (A_-,A_+) or (A_+,A_-) tends to one point $C_3^3/16C_4^2\,(\neq 0)$.

If $C_2>3C_3^2/8C_4$, we are in case γ. Whether $C_3>$ or <0, the domain of C_1 is $C_1\leq 0$ with no lower end. $f^\gamma(C_1,\ldots,C_4)$ is thought to be the continuation of $f^\beta(C_1,\ldots,C_4)$ as C_2 increases. We can prove

$$f^\gamma(0,C_2,C_3,C_4)=0 \tag{3.81}$$

in the same manner as that for Eq. (3.78). As $C_2\to 3C_3^2/8C_4+0$, we find (irrespective of whether $C_1=$ or $\neq C_3^3/16C_4^2$)

$$|\gamma|\to\infty,\quad (\sinh\tfrac{1}{3}\gamma)/(\sinh\gamma)^{1/3}\to 2^{-2/3}\ ,$$

$$f^\gamma(C_1,C_2,C_3,C_4) = -\frac{C_3}{4C_4}-\frac{C_3}{2C_4}\left(1-\frac{4C_2C_4}{C_3^2}+\frac{8C_1C_4^2}{C_3^3}\right)^{1/3} \times \frac{\sinh\frac{1}{3}\gamma}{(\sinh\gamma)^{1/3}}$$
$$\to -C_3/4C_4+(C_3/4C_4)(1-16C_1C_4^2/C_3^3)^{1/3}\ . \tag{3.82}$$

As $C_2\to 3C_3^2/8C_4-0$, we find in the same manner that $f^\beta(C_1,C_2,C_3,C_4)$ tends to the same limit (3.82). Thus f^β and f^γ conjoin with each other at $C_2=3C_3^2/8C_4$. It is obvious that, whether $C_3>$ or <0, expression (3.82) is positive when $C_1<0$ and zero when $C_1=0$. The positivity of f^γ when $C_2>3C_3^2/8C_4$ and $C_1<0$ can be proved in the same manner as that for the positivity of f^β.

B. For experimental discernment

How can the first-, second-, and third-sense transitions be experimentally discerned from one another? Since the first-sense transition is second order and the others are all first order, it is easy to discern the first-sense transition from the others. If the ferroic phase is ferroelectric or ferroelastic, the second- and third-sense transitions are easy to discern from each other by observing the temperature dependence of electric susceptibility or elastic compliance near the transition point. Theoretically, what differences should the second- and third-sense transitions exhibit?

We assume that Q can be identified with a component of electric polarization P. Since the second- or third-sense transition is first order, we have two electric susceptibilities, that of the prototypic and that of the ferroic, at each temperature near the transition point; they are denoted by κ_P and κ_F. At the transition point we find

$$\frac{1}{\kappa_P}=2C_1=-\frac{4C_3^3}{27C_4^2}\left[1-\frac{9C_2C_4}{2C_3^2}\mp\left(1-\frac{3C_2C_4}{C_3^2}\right)^{3/2}\right] \tag{3.83}$$

using Eq. (3.51), and

$$\frac{1}{\kappa_F}=-\frac{16C_3^3}{9C_4^2}\left[1-\frac{3C_2C_4}{C_3^2}\mp\left(1-\frac{3C_2C_4}{2C_3^2}\right)\left(1-\frac{3C_2C_4}{C_3^2}\right)^{1/2}\right] \tag{3.84}$$

directly from Eq. (3.55); of the double sign $\mp$, let the upper or lower part be taken according to the second- or third-sense transition. Equations (3.83), (3.84) can be rewritten as

$$1/\kappa_P=(2C_3^3/27C_4^2)(1\pm 2L)(1\mp L)^2\ , \tag{3.85}$$

$$1/\kappa_F=(8C_3^3/9C_4^2)(\pm L)(1\mp L)^2\ ; \tag{3.86}$$

for the meaning of L, see Eq. (3.53). Dividing Eq. (3.86) by Eq. (3.85), we obtain

$$\kappa_P/\kappa_F=6/(1\pm 1/2L)\ . \tag{3.87}$$

For the second-sense transition, $1<L<\infty$ and so

$$4<6/(1+1/2L)<6\ ;$$

thus

$$4<\kappa_P/\kappa_F<6\ . \tag{3.88}$$

For the third-sense transition, $\frac{1}{2}<L<\infty$ and so

$$6<6/(1-1/2L)<\infty\ ;$$

thus

$$6<\kappa_P/\kappa_F<\infty\ ; \tag{3.89}$$

note that $\kappa_P \to \infty$, $\kappa_F \to -C_4^2/C_3^3$ $(<\infty)$ as $L \to \frac{1}{2}+0$, i.e., as $C_2 \to C_3^2/4C_4 - 0$. Relations (3.88), (3.89) are usable for experimentally discerning between the second- and third-sense transitions; the two intervals inside which κ_P/κ_F should be do not overlap each other.

Let T_c stand for the transition temperature, T_0 the temperature at which $1/\kappa_P$ becomes zero, and T_1 the temperature at which $1/\kappa_F$ becomes zero. We assume that C_1 depends linearly on temperature T. Then the following can be proved: For the second-sense transition

$$\tfrac{4}{3} < (T_1 - T_0)/(T_c - T_0) < \sqrt{2} \ , \tag{3.90}$$

and for the third-sense transition

$$\sqrt{2} < (T_1 - T_0)/(T_c - T_0) < \infty \ . \tag{3.91}$$

The proofs are given in the Appendix. It is easy to rewrite inequalities (3.90), (3.91) to

$$\sqrt{2}+1 < (T_c - T_0)/(T_1 - T_c) < 3 \ , \tag{3.92}$$

$$0 < (T_c - T_0)/(T_1 - T_c) < \sqrt{2}+1 \ , \tag{3.93}$$

respectively. Relations (3.90)–(3.93) are usable for experimentally discerning between the second- and third-sense transitions; the two intervals inside which the ratio of $T_1 - T_0$ to $T_c - T_0$ or of $T_c - T_0$ to $T_1 - T_c$ should be do not overlap each other.

In addition to the two above-mentioned criteria

$$\kappa_P/\kappa_F$$

and

$$(T_1 - T_0)/(T_c - T_0)$$

or

$$(T_c - T_0)/(T_1 - T_c) \ ,$$

some other criteria are conceivable, but we omit their description.

By the way it is easily found that in the second ideal case we have, for the second-sense transition,

$$\kappa_P/\kappa_F = 4 \ , \tag{3.94}$$

$$(T_1 - T_0)/(T_c - T_0) = \tfrac{4}{3} \ , \tag{3.95}$$

$$(T_c - T_0)/(T_1 - T_c) = 3 \ , \tag{3.96}$$

instead of inequalities (3.88), (3.90), (3.92); the intervals $(4,6)$, $(\frac{4}{3},\sqrt{2})$, $(\sqrt{2}+1,3)$ contract into the points 4, $\frac{4}{3}$, 3 which are the extremities of these intervals opposite to the boundaries between these intervals and the intervals for the third-sense transition.

Let us consider $BaTiO_3$. As has been mentioned in Sec. I, the cubic phase is prototypic, the tetragonal phase is one of its ferroics, and the transition between them (at about 120 °C) is a first-order immediately lineal transition. The transition parameters belong to the three-dimensional zero-wave-number representation T_{1u} and hence can be identified with the three components of electric polarization P_x, P_y, P_z. This transition parameter system theoretically generates, from the $m3m$ prototypic, altogether six ferroics nonconformal with one another (see the right column, p. 2, Ref. 13). In the tetragonal phase, one of P_{xs}, P_{ys}, P_{zs} is nonzero and the two others are zero. Possible are altogether six oriates (or orientational states) which are distinguished according to which of P_{xs}, P_{ys}, P_{zs} is nonzero and according to whether the nonzero component is positive or negative. Let us restrict our consideration to the cubic-to-tetragonal transition and those two oriates of the tetragonal phase in which $P_{xs} = P_{ys} = 0$, $P_{zs} \neq 0$, and assume that in the free-energy function Φ the variables P_x and P_y are constantly zero. Then Φ is a function of only one parameter P_z. This function as a power series in P_z is easily found to be of the same form as expression (2.1). Thus the present general theory is applicable to the cubic-to-tetragonal transition of $BaTiO_3$. Is this transition second or higher sense? We assume that $BaTiO_3$ has $C_4 > 0$, and apply relations (3.88), (3.89). According to the measurement by Merz,[14] κ_P/κ_F is evaluated as

$$\kappa_P/\kappa_F = 10\,000/1500 = 6.7 \ .$$

Therefore the transition seems to be third sense. However, the value 6.7 is not distinctly greater than the boundary value 6; its accuracy is not very high. In view of these, the possibility of second-senseness is not perfectly rejected. The author will in future search the literature for transitions with great values of κ_P/κ_F or $(T_1 - T_0)/(T_c - T_0)$.

Finally we add a consideration of the first-sense venule function in the nonideal case where no C_k is constantly zero. This function $f_1(C_1, C_2, C_3, \ldots)$, as in the ideal cases, has the characteristics that the domain of C_1 is $C_1 \leq 0$ and that $f_1 = 0$ at $C_1 = 0$. $f_1(C_1, C_2, C_3, \ldots)$ is expected to be expansible into a power series in $b = -C_1$ with a wide region of convergence. From Eq. (2.4) we find

$$\begin{aligned} f_1(C_1, C_2, C_3, \ldots) &= (1/2C_2)b - [3C_3/(2C_2)^3]b^2 \\ &\quad + [2(3C_3)^2/(2C_2)^5 - 4C_4/(2C_2)^4]b^3 \\ &\quad + \left[-\frac{5(3C_3)^3}{(2C_2)^7} + \frac{5(3C_3)(4C_4)}{(2C_2)^6} - \frac{5C_5}{(2C_2)^5} \right] b^4 \\ &\quad + O(b^5) \ . \end{aligned} \tag{3.97}$$

This expansion was useful in previous theories by Aizu (Ref. 9) and others (though there only the concept of order existed and the concept of sense, especially, sense higher than second did not), and will also be useful in the future.

APPENDIX

The proofs of inequalities (3.90), (3.91) are presented here. C_1 can be expressed as

$$C_1=\Lambda(T-T_0) \tag{A1}$$

with a positive constant Λ. The C_1's in Eqs. (3.68) are the same as $\Lambda(T_1-T_0)$, while the C_1 in Eq. (3.51) is the same as $\Lambda(T_c-T_0)$. Thus

$$\Lambda(T_1-T_0)=\frac{C_3^3}{8C_4^2}\left[\frac{4C_2C_4}{C_3^2}-1\pm\left(1-\frac{8C_2C_4}{3C_3^2}\right)^{3/2}\right] , \tag{A2}$$

$$\Lambda(T_c-T_0)=\frac{2C_3^3}{27C_4^2}\left[\frac{9C_2C_4}{2C_3^2}-1\pm\left(1-\frac{3C_2C_4}{C_3^2}\right)^{3/2}\right] . \tag{A3}$$

Let us put

$$C_2C_4/C_3^2=J ,$$
$$(1-3J)^{1/2}=L ,$$
$$(1-\tfrac{8}{3}J)^{1/2}=M . \tag{A4}$$

Then Eqs. (A2), (A3) can be rewritten as

$$\Lambda(T_1-T_0)=(C_3^3/16C_4^2)(1\mp M)^2(1\pm 2M) , \tag{A5}$$

$$\Lambda(T_c-T_0)=(C_3^3/27C_4^2)(1\mp L)^2(1\pm 2L) . \tag{A6}$$

Division of Eq. (A5) by Eq. (A6) gives

$$\frac{T_1-T_0}{T_c-T_0}=\frac{27(1\mp M)^2(1\pm 2M)}{16(1\mp L)^2(1\pm 2L)} . \tag{A7}$$

The right-hand side can be regarded as a function of J. Differentiation with respect to J gives

$$\frac{d}{dJ}\frac{T_1-T_0}{T_c-T_0}=\frac{27(1\mp M)(1\pm 8L\mp 9M)}{16(1\mp L)^3(1\pm 2L)^2} . \tag{A8}$$

For the second-sense transition we have $J<0$, $L>M>1$, and so $1-L<0$, $1+2L>0$, $1-M<0$. Thus the right-hand side of Eq. (A8) is of the same sign as its factor $1+8L-9M$. We find

$$1+8L-9M=-24J[1/(1+L)-1/(\text{i}+M)]<0 .$$

Hence expression (A8) is negative. In orther words expression (A7) is a monotone decreasing function of J. As $J\to-\infty$, we find $1/L\to 0$, $M/L\to 2\sqrt{2}/3$, and so

$$(T_1-T_0)/(T_c-T_0)\to\sqrt{2} .$$

As $J\to 0$, we find $L\to 1$, $M\to 1$, $(1-M)/(1-L)\to\frac{8}{9}$, and so

$$(T_1-T_0)/(T_c-T_0)\to\tfrac{4}{3} .$$

After all, inequality (3.90) is concluded.

For the third-sense transition we have $J<\frac{1}{4}$, $L>\frac{1}{2}$, $M>3^{-1/2}$. Hence the right-hand side of Eq. (A8) is of the same sign as its factor $1-8L+9M$. We put $1-8L+9M=\psi(J)$ (a function of J). $\psi(J)$ is, obviously, continuous in the interval $(-\infty,\frac{1}{4})$. It is easily found that the equation $\psi(J)=0$ has no solution. Hence $\psi(J)$ has a definite sign. Obviously, $\psi(0)=2>0$. Thus $\psi(J)$ must be positive in the interval $(-\infty,\frac{1}{4})$. This statement amounts to the statement that expression (A8) must be positive in the interval $(-\infty,\frac{1}{4})$, and further, to the statement that expression (A7) must be a monotone increasing function of J. As $J\to-\infty$, we find $1/L\to 0$, $M/L\to 2\sqrt{2}/3$, and so

$$(T_1-T_0)/(T_c-T_0)\to\sqrt{2} .$$

As $J\to\frac{1}{4}$, we find $L\to\frac{1}{2}$, $M\to 3^{-1/2}$, and so

$$(T_1-T_0)/(T_c-T_0)\to\infty .$$

After all, inequality (3.91) is concluded.

[1]K. Aizu, Phys. Rev. B 2, 754 (1970).
[2]K. Aizu, J. Phys. Soc. Jpn. 32, 1287 (1972).
[3]K. Aizu, J. Phys. Soc. Jpn. 44, 683 (1978).
[4]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1958).
[5]K. Aizu, J. Phys. Soc. Jpn. 38, 1592 (1975).
[6]K. Aizu, J. Phys. Soc. Jpn. 42, 424 (1977).
[7]K. Aizu, J. Phys. Soc. Jpn. 46, 384 (1979).
[8]F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962), Chap. IV.
[9]K. Aizu, J. Phys. Soc. Jpn. 47, 1773 (1979).
[10]L. E. Cross, Philos. Mag. 44, 1161 (1953).
[11]A. F. Devonshire, Philos. Mag. 40, 1040 (1949).

[12]Toward the proof it is helpful to know

$$1-9C_2C_4/2C_3^2\mp(1-3C_2C_4/C_3^2)^{3/2}=-(1\mp L)^2(\tfrac{1}{2}\pm L) ,$$

where $L=(1-3C_2C_4/C_3^2)^{1/2}$.

[13]K. Aizu, J. Phys. Soc. Jpn. 41, 1 (1976).
[14]W. J. Merz, Phys. Rev. 76, 1221 (1949).