AIP Journal of Applied Physics

Elastic anomalies of barium titanate

B. Subramanyam and K. S. Viswanathan

Citation: Journal of Applied Physics **74**, 945 (1993); doi: 10.1063/1.354836
View online: http://dx.doi.org/10.1063/1.354836
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/74/2?ver=pdfcov
Published by the AIP Publishing

Elastic anomalies of barium titanate

B. Subramanyam and K. S. Viswanathan
Department of Physics, Indian Institute of Technology, Madras 600 036, India

(Received 28 July 1992; accepted for publication 29 March 1993)

The anomalies of the second-, third-, and fourth-order elastic constants have been derived for barium titanate and related compounds for the phase transition from cubic to tetragonal and from the tetragonal to the orthorhombic phases. The equilibrium values of the three components of the order parameter and the strain variables in the two phases have been obtained from the stability conditions. The fluctuations in the order parameter in the two phases have been derived from the Landau–Khalatnikov equations. Expressions have been given for the shift in the zero point energy in the tetragonal and orthorhombic phases, and these are shown to be proportional to $(T-T_c)^2$. The anomalies for all the second-order elastic constants have been derived for both phases, and relations among them have been reported. It is shown that the elastic anomalies suffer a discontinuity at the transition temperature for both the phases. Our expressions give the temperature variation of the third-order elastic and fourth-order elastic constants for the phase transition from the tetragonal to the orthorhombic phase.

I. INTRODUCTION

Barium titanate is a classical example of a substance undergoing a first-order phase transition. The optical, dielectric, piezoelectric, elastic, and other properties of $BaTiO_3$ and similar ferroelectric compounds have been reviewed in several articles and monographs.[1–14] $BaTiO_3$ is paraelectric and has a cubic $pm\bar{3}m(0_h^1)$ perovskite structure above the Curie temperature of 120 °C. At the Curie point, the crystal becomes polar and its structure changes from cubic to tetragonal. The resulting space group is $p4mm$ (C_{4v}^1), a subgroup of $pm\bar{3}m$. Below the Curie point, the vector of spontaneous polarization is directed along the (001) direction. On lowering the temperature, the dipole moment increases and the crystal becomes correspondingly more tetragonal, with an increase in the lattice constant along the polar direction (tetragonal c axis) and a decrease in a direction (a axis) perpendicular to it.

$BaTiO_3$ undergoes two other displacive phase transitions on cooling. Below 5 °C the spontaneous polarization points in the (011) direction. The point group symmetry is $mm2$ (C_v), and the crystal system is orthorhombic. This group is not a subgroup of the tetragonal phase above ($P4.mm$) but is a subgroup of the parent phase above ($pm\bar{3}m$). Finally, on cooling further below -70 °C, $BaTiO_3$ undergoes a further phase transition from orthorhombic to the rhombohedral R_{3m} (C_{3v}^5) phase, in which the polarization vector is directed along the (111) direction. This too is not a subgroup of the orthorhombic phase but is a subgroup of the parent group $pm\bar{3}m$. All three phase transitions cannot be described by a continuous second-order phase transition, but are first-order phase transitions. There is no piezoelectric effect above the Curie 120 °C point in $BaTiO_3$.

The temperature variations of the elastic contants and the consequent anomalies have been investigated by several authors.[8–12] Variation of C_{11} and C_{44} was measured[4] in the vicinity of the upper transition at $T_c=401$ K. C_{11} was found to vary as $C_{11}(T)=C_{11}^0-A_1(T-T_0)^{-\mu}$ with a critical exponent $\mu=0.41$, where T_0 is the paraelectric/Curie temperature (lower stability limit).

There are other ferroelectrics[14] like $KNbO_3$ ($T_c=435$ °C), $KTaO_3$ ($T_c=-260$ °C), and $PbTiO_3$ ($T_c=490$ °C), which are chemically similar to $BaTiO_3$ and whose dielectric and structural properties are almost identical. The theory given in this paper will apply equally well to these ferroelectrics.

In this paper, we study systematically the anomalies of the second-, third-, and fourth-order elastic constants arising from the phase transitions from the cubic to the tetragonal phase, and from the tetragonal to the orthorhombic phase, respectively. In order to limit the length of the paper, we reserve the results of the phase transition to the rhombohedral phase to a subsequent paper. The equilibrium values of the components of the order parameter and the strain variables in the two phases are obtained from the stability conditions while the fluctuations in the order parameter in the two phases are derived from the Landau–Khalatnikov equations. In Sec. IV, we give an expression for all the second-order elastic (SOE) anomalies in a single formula for the tetragonal phase. Relations among the anomalies of the SOE constants have been derived. It is shown that the SOE constants are temperature dependent, showing a discontinuity at the transition temperature. In Secs. IV C and IV D we give expressions for the anomalies in the third-order and fourth-order elastic constants as well as the relations among them. In Sec. V we give expressions for the anomalies of the second-, third-, and fourth-order elastic constants in the orthorhombic phase and discuss their temperature variations.

II. EQUILIBRIUM VALUES OF THE ORDER PARAMETERS AND THE STRAIN

The free energy F of the system is a sum of the elastic energy, the Landau energy, and the coupling energy between the components of the order parameters and the strain variables. The latter two have been given by Fatuzzo and Merz[14] for the phase transition of barium titanate and similar compounds. We have

$$F=\frac{1}{2}\sum_{ij}C_{ij}\eta_i\eta_j+\cdots+\frac{a}{2}(P_x^2+P_y^2+P_z^2)+\frac{b}{4}(P_x^4+P_y^4+P_z^4)$$
$$+C(P_x^2P_y^2+P_y^2P_z^2+P_z^2P_x^2)+g_{11}(\eta_1P_x^2+\eta_2P_y^2+\eta_3P_z^2)$$
$$+g_{12}[\eta_1(P_z^2+P_y^2)+\eta_2(P_z^2+P_x^2)+\eta_3(P_x^2+P_y^2)]$$
$$+g_{44}(\eta_4P_yP_z+\eta_5P_zP_x+\eta_6P_xP_y), \quad (1)$$

where

$$a=a'(T-T_c), \quad (1a)$$

a' being a constant. The coefficients b and C are constants, more or less independent of temperature. Further, g_{11}, g_{12}, and g_{44} are coupling constants and η_i (i=1–6) are the six components of the strain tensor. P_x, P_y, and P_z are the three components of the order parameter. It can be shown that the corrections brought about by the third-order and fourth-order deformation energies to the equilibrium values (of the order parameter and the strain variables) are smaller by a factor $Q_{30}^2C_{ijk}/C_{ij}$ in comparison with the contribution from second-order deformation energy. We shall therefore neglect them in future calculations. The equilibrium values of the order parameter components as well as the strain variables can be obtained from the stability conditions: these are

$$(\partial F/\partial P_i)_0=0 \quad \text{for } i=x,y,z,$$
$$(\partial F/\partial \eta_i)_0=0 \quad \text{for } i=1\text{–}6. \quad (2)$$

For the sake of convenience, these equations are given in Appendix A. There are four different kinds of solutions, depending on the symmetry of the crystal phase of $BaTiO_3$:

Case 1. In the cubic phase above 120 °C, barium titanate is paraelectric: The simplest solutions of Eqs. (2) are given by

$$P_x=P_y=P_z=0. \quad (3)$$

The solutions of the set of nine equations in (2) lead to the following equilibrium values for the order parameter and strain variables:

$$P_x=P_y=P_z=0 \quad (4)$$

and

$$\eta_{10}=\eta_{20}=\eta_{30}=\eta_{40}=\eta_{50}=\eta_{60}=0. \quad (5)$$

Case 2. Barium titanate undergoes a phase transition from a cubic to a tetragonal structure as it is cooled through 120 °C. In the tetragonal phase, it is ferroelectric with an electrical polarization along the c axis. It can be seen that the set of Eqs. (2) admits another solution, in which

$$P_x=P_y=0; \quad P_z\neq 0. \quad (6)$$

This solution corresponds to the ferroelectric tetragonal phase. When (6) holds, the equilibrium values of the strain variables and electrical polarization for the tetragonal phase are given by

$$\eta_{10}=\eta_{20}=\frac{x+y}{3}P_{z0}^2, \quad (7)$$

$$\eta_{30}=\frac{x-2y}{3}P_{z0}^2, \quad (8)$$

where

$$x=-\frac{g_{11}+2g_{12}}{C_{11}+2C_{12}} \quad (9a)$$

and

$$y=\frac{g_{11}-g_{12}}{C_{11}-C_{12}}, \quad (9b)$$

$$\eta_{40}=\eta_{50}=\eta_{60}=0. \quad (10)$$

Further, the equilibrium value of the electrical polarization is described by

$$P_{z0}^2=-aP, \quad (11a)$$

where

$$P=1\bigg/b-\frac{2(g_{11}+2g_{12})^2}{3(C_{11}+2C_{12})}-\frac{4(g_{11}-g_{12})^2}{3(C_{11}-C_{12})}. \quad (11b)$$

It is seen from (7) and (8) that the lattice deformations are proportional to the square of the spontaneous electrical polarization, in agreement with the experimental results.

Case 3. The set of nine equations (2) admits another solution in which

$$P_x=0; \quad P_y=P_z\neq 0. \quad (12)$$

This solution is the theoretical counterpart of the orthorhombic phase transition when the crystal $BaTiO_3$ is cooled below 5 °C. By solving Eqs. (2) it can be seen that the equilibrium values of the strain variables and components of the order parameter in the orthorhombic phase are given by

$$\eta_{10}=(2/3)(x+y)P_{z0}^2, \quad (13)$$

$$\eta_{20}=\eta_{30}=(P_{y0}^2/3)(2x-y), \quad (14)$$

$$\eta_{40}=(g_{44}/C_{44})P_{z0}^2, \quad (15)$$

$$\eta_{50}=\eta_{60}=0, \quad (16)$$

$$P_{y0}^2=P_{z0}^2=-Ka, \quad (17a)$$

where

$$K=1/[b+2C-(g_{44}^2/C_{44})-\tfrac{4}{3}(g_{11}+g_{12})^2(C_{11}+2C_{12})^{-1}$$
$$-\tfrac{2}{3}(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}]. \quad (17b)$$

It is seen that in this phase too, the lattice deformations are proportional to the square of the spontaneous electrical polarization.

Case 4. Equations (2) admit yet another solution in which $P_x=P_y=P_z\neq 0$. This corresponds to the rhombohedral phase transition that takes place at $-70\,°C$. In order to keep the length of the paper within resonable limits, we shall not consider this case in this paper and we relegate it to a separate paper.

III. THE LANDAU–KHALATNIKOV EQUATIONS

The LK equation relates the regression in the fluctuations of the order parameter towards equilibrium to the thermodynamic restoring force. While the stability conditions give the equilibrium values of the components of the order parameter, the LK equation gives expressions for the fluctuations of the order parameter from its equilibrium value.

The LK equations for the three components of the order parameter can be written as

$$\dot{P}_x=-\Gamma_1(\partial F/\partial P_x), \quad (18a)$$

$$\dot{P}_y=-\Gamma_2(\partial F/\partial P_y), \quad (18b)$$

$$\dot{P}_z=-\Gamma_3(\partial F/\partial P_z), \quad (18c)$$

where Γ_1, Γ_2, and Γ_3 are the kinetic coefficients.

A. Case 2: The tetragonal phase

We shall first consider the solution of the LK equation for the ferroelectric phase between 120 and 5 °C. To solve these equations, we shall write

$$P_x=P_{x0}+P_x^*,\ P_y=P_{y0}+P_y^*,\ P_z=P_{z0}+P_z^*,$$

and

$$\eta_i=\eta_{i0}+\eta_i^*. \quad (18d)$$

Symmetry of the tetragonal structure requires that

$$\Gamma_1=\Gamma_2. \quad (19)$$

By expanding $\partial F/\partial P_i$ ($i=x$, y, z) about the equilibrium values of the components of the order parameter and the strain variables, and ignoring product terms of higher orders, one obtains

$$\frac{\partial F}{\partial P_i}=\left(\frac{\partial F}{\partial P_i}\right)_0+\sum_j\left(\frac{\partial F}{\partial P_i\partial P_j}\right)_0 P_j^*+\sum_j\left(\frac{\partial F}{\partial P_i\partial \eta_j}\right)_0\eta_j^*. \quad (20)$$

Further, by writing P_i^* proportional to $e^{i\Omega t}$ we see that the LK equations reduce to

$$[i\Omega+\Gamma_1(\partial^2F/\partial P_x^2)_0]P_x^*+\Gamma_1(\partial^2F/\partial P_x\partial P_y)_0P_y^*$$
$$+\Gamma_1(\partial^2F/\partial P_x\partial P_z)_0P_z^*=-\Gamma_1\sum_i(\partial^2F/\partial P_x\partial\eta_i)_0\eta_i^*, \quad (21a)$$

$$[i\Omega+\Gamma_1(\partial^2F/\partial P_y^2)_0]P_y^*+\Gamma_1(\partial^2F/\partial P_y\partial P_x)_0P_x^*$$
$$+\Gamma_1(\partial^2F/\partial P_y\partial P_z)_0P_z^*=-\Gamma_1\sum_i(\partial^2F/\partial P_y\partial\eta_i)_0\eta_i^*, \quad (21b)$$

$$[i\Omega+\Gamma_3(\partial^2F/\partial P_z^2)_0]P_z^*+\Gamma_3(\partial^2F/\partial P_z\partial P_y)_0P_y^*$$
$$+\Gamma_3(\partial^2F/\partial P_z\partial P_x)_0P_x^*-\Gamma_3\sum_i(\partial F/\partial P_z\partial\eta_i)_0\eta_i^*. \quad (21c)$$

By differentiating the free energy twice with respect to P_x, P_y, and P_z, and making use of the expressions for the equilibrium values of the parameters given by Eqs. (7)–(11) we find that

$$(\partial^2F/\partial P_x^2)_0=(\partial^2F/\partial P_y^2)_0$$
$$=a[1-2CP+\tfrac{2}{3}P(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}$$
$$-\tfrac{2}{3}P(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}], \quad (22a)$$

$$(\partial^2F/\partial P_z^2)_0=a[1-3b+\tfrac{2}{3}P(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}$$
$$+\tfrac{4}{3}P(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}]. \quad (22b)$$

In the same way, the equilibrium values of $(\partial^2F/\partial P_i\partial P_j)_0$ and $(\partial^2F/\partial P_i\partial\eta_j)_0$ can be evaluated. These are listed in Appendix B. We find that the fluctuations of the order parameter about the equilibrium values reduce to the form

$$P_x^*=A\eta_5^*, \quad (23)$$

$$P_y^*=A\eta_4^*, \quad (24)$$

$$P_z^*=\sum_{i=1}^{6}\alpha_i\eta_i^*, \quad (25)$$

where

$$A=-\Gamma_1(g_{44}P_{z0})/P_1, \quad (26a)$$

$$\alpha_1=\alpha_2=-2\Gamma_3(g_{12}P_{z0})/P_3, \quad (26b)$$

$$\alpha_3=-2\Gamma_3(g_{11}P_{z0})/P_3, \quad (26c)$$

$$\alpha_4=\alpha_5=\alpha_6=0. \quad (26d)$$

Further,

$$P_1=i\Omega+\Gamma_1(\partial^2F/\partial P_x^2)_0, \quad (27a)$$

$$P_3=i\Omega+\Gamma_3(\partial^2F/\partial P_z^2)_0. \quad (27b)$$

B. Case 3: The orthorhombic phase

For the orthorhombic phase, the equilibrium values of the components of the order parameter and the strain variables are given by Eqs. (13)–(17). The equilibrium values of the second derivatives of the free energy with respect to P_i and η_i are listed in the Eqs. of Appendix B. From the symmetry of the orthorhombic phase one can assume

$$\Gamma_1\neq\Gamma_2=\Gamma_3. \quad (28)$$

Using these in the LK equations (18), we find that the fluctuations of the components of the order parameter from their mean values are given by

$$P_x^* = \sum_i \alpha_{xi} \eta_i^*, \tag{28a}$$

$$P_y^* = \sum_i \alpha_{yi} \eta_i^*, \tag{28b}$$

$$P_z^* = \sum_i \alpha_{zi} \eta_i^*, \tag{28c}$$

where

$$\alpha_{x1} = \alpha_{x2} = \alpha_{x3} = \alpha_{x4} = 0, \tag{29a}$$

$$\alpha_{x5} = \alpha_{x6} = -\Gamma_1 g_{44} P_{z0} / P_1, \tag{29b}$$

$$\alpha_{y1} = \alpha_{z1} = (\Gamma_2^2 \bar{P} - \Gamma_2 P_2) 2 g_{12} P_{z0} (P_2^2 - \Gamma_2^2 \bar{P}^2)^{-1}, \tag{30a}$$

$$\alpha_{y2} = \alpha_{z3} = (\Gamma_2^2 \bar{P} g_{12} - \Gamma_2 P_2 g_{11}) 2 P_{z0} (P_2^2 - \Gamma_2^2 \bar{P}^2)^{-1}, \tag{30b}$$

$$\alpha_{y3} = \alpha_{z2} = (\Gamma_2^2 \bar{P} g_{11} - \Gamma_2 P_2 g_{12}) 2 P_{z0} (P_2^2 - \Gamma_2^2 \bar{P}^2)^{-1}, \tag{30c}$$

$$\alpha_{y4} = \alpha_{z4} = (\Gamma_2^2 \bar{P} - \Gamma_2 P_2) g_{44} P_{z0} (P_2 - \Gamma_2^2 \bar{P}^2)^{-1}, \tag{30d}$$

$$\alpha_{y5} = \alpha_{y6} = \alpha_{z5} = \alpha_{z6} = 0, \tag{30e}$$

where we write

$$P_1 = i\Omega + \Gamma_1 (\partial^2 F / \partial P_x^2)_0, \tag{31a}$$

$$P_2 = i\Omega + \Gamma_2 (\partial^2 F / \partial P_z^2)_0, \tag{31b}$$

and

$$\bar{P} = 4 C P_{z0}^2 + g_{44} \eta_{40} = K_a (-4C + g_{44}^2 / C_{44}). \tag{32}$$

IV. THE ELASTIC ANOMALIES IN THE TETRAGONAL PHASE

A. The free energy and zero point energy in the tetragonal phase

Substituting Eqs. (7) to (11) and 18(d) in the equation for the free energy, we find that

$$F = \frac{1}{2} \left(\sum_{ij} C_{ij} (\eta_{i0} + \eta_i^*)(\eta_{j0} + \eta_j^*) + \frac{1}{6} \sum_{ijk} C_{ijk} \cdots \right) + \frac{a}{2} [P_x^{*2} + P_y^{*2} + (P_{z0} + P_z^*)^2] + \frac{b}{4} [P_x^{*4} + P_y^{*4} + (P_{z0} + P_z^*)^4]$$
$$+ C[P_x^{*2} P_y^{*2} + (P_x^{*2} + P_y^{*2})(P_{z0} + P_z^*)^2] + g_{11}[(\eta_{10} + \eta_1^*) P_x^{*2} + (\eta_{20} + \eta_2^*) P_y^{*2} + (\eta_{30} + \eta_3^*)(P_{z0} + P_z^*)^2]$$
$$+ g_{12}\{(\eta_{10} + \eta_1^*)[P_y^{*2} + (P_{z0} + P_z^*)^2] + (\eta_{20} + \eta_2^*)[P_x^{*2} + (P_{z0} + P_z^*)^2] + (\eta_{30} + \eta_3^*)(P_x^{*2} + P_y^{*2})\}$$
$$+ g_{44}[(\eta_{40} + \eta_4^*) P_y^* (P_{z0} + P_z^*) + (\eta_{50} + \eta_5^*) P_x^* (P_{z0} + P_z^*) + (\eta_{60} + \eta_6^*) P_x^* P_y^*]. \tag{33}$$

In the above expression for free energy, the linear terms in η_i^* vanish in view of the stability conditions. We denote by F_0, F_2, F_3, and F_4 respectively, the terms of orders zero, two, three, and four in the strain variables. The zero-order term F_0 gives the shift in the zero point energy at the transition temperature. Its derivative with respect to temperature will give the specific heat anomaly at the transition temperature. In fact,

$$F_0 = \frac{1}{2} \sum_{ij} C_{ij} \eta_{i0} \eta_{j0} + \frac{a}{2} P_{z0}^2 + \frac{b}{4} P_{z0}^4 + g_{11} \eta_{30} P_{z0}^2$$
$$+ g_{12} P_{z0}^2 (\eta_{10} + \eta_{20}). \tag{34}$$

By substituting the values of P_{z0}^2, η_{i0}, etc. in the above expression and simplifying we find that

$$F_0 = -a^2 P/4 = -(a'^2/4) P (T - T_c)^2. \tag{35}$$

The change in the zero point energy is proportional to $(T - T_c)^2$ near the phase transition; consequently the change in specific heat proportional to $(T_c - T)$ is given by the formula

$$\Delta C_V = (\partial F_0 / \partial T)_V = (a'^2 P/2)(T_c - T). \tag{36}$$

B. Anomalies in the second-order elastic (SOE) constants

By collecting all the terms which are quadratic in strain variables, we can write the expression for the second-order deformation energy as

$$F_2 = \frac{1}{2} \sum_{ij} C_{ij}^* \eta_i^* \eta_j^*, \tag{37}$$

where C_{ij}^* represent the modified SOE constants. Let us write

$$C_{ij}^* = C_{ij} + \Delta C_{ij}^*, \tag{38}$$

ΔC_{ij}^* then gives the anomalies in SOE constants arising from the phase transition. Now

$$F_2=\frac{1}{2}\sum_{ij}C_{ij}\eta_i^*\eta_j^*+\Delta F_2$$

$$=\frac{1}{2}\sum_{ij}C_{ij}\eta_i^*\eta_j^*+\frac{a}{2}\{P_x^{*2}+P_y^{*2}+P_z^{*2}\}+\frac{3b}{2}\{P_{z0}^2P_z^{*2}\}+CP_{z0}^2(P_x^{*2}+P_y^{*2})+g_{11}(\eta_{10}P_x^{*2}+\eta_{20}P_y^{*2}+\eta_{30}P_z^{*2}+2P_{z0}\eta_3^*P_z^*)$$

$$+g_{12}[\eta_{10}(P_y^{*2}+P_z^{*2})+\eta_{20}(P_z^{*2}+P_x^{*2})+\eta_{30}(P_x^{*2}+P_y^{*2})+2P_{z0}(\eta_1^*P_z^*+\eta_2^*P_z^*)]+g_{44}P_{z0}(\eta_4^*P_y^*+\eta_5^*P_x^*). \quad (39)$$

Substituting the expressions for P_x^*, P_y^*, P_z^* from (23) to (25) and collecting all terms containing η_i^* η_j^* in this expression, we find that

$$\Delta C_{ij}^*/2=A^2(\delta_{i5}\delta_{j5}+\delta_{i4}\delta_{j4})[a/2+CP_{z0}^2+g_{12}(\eta_{10}+\eta_{30})+g_{11}\eta_{10}]+\alpha_i\alpha_j(a/2+\tfrac{3}{2}P_{z0}^2+g_{11}\eta_{30}+2g_{12}\eta_{10})$$

$$+2P_{z0}(g_{12}\alpha_i\delta_{j1}+g_{12}\alpha_i\delta_{j2}+g_{11}\alpha_i\delta_{j3})+g_{44}P_{z0}A(\delta_{i4}\delta_{j4}+\delta_{i5}\delta_{j5}). \quad (40)$$

The above equation gives the anomalies for all the SOE constants in a single formula. By giving integral values for the indices i and j ranging from 1 to 6, we can obtain anomalies for the individual SOE constants. The existence of elastic anomalies shows that the velocities of sound waves undergo a change during the phase transition. In view of the complex nature of ΔC_{ij}^*, the waves are attenuated in this region.

The following relations among the elastic anomalies can easily be verified:

$$\Delta C_{11}^*=\Delta C_{12}^*=\Delta C_{22}^*, \quad (41a)$$

$$\Delta C_{13}^*=\Delta C_{23}^*, \quad (41b)$$

$$\Delta C_{44}^*=\Delta C_{55}^*. \quad (41c)$$

The anomalies in the individual SOE constants are given by

$$\Delta C_{11}^*=-8\Gamma_3^2g_{12}^2a^2/P_3^2[-3bP^2/2+(P^2/3)(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}+P/2+(2P^2/3)(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}]$$
$$+8\Gamma_3g_{12}^2Pa/P_3, \quad (42a)$$

$$\Delta C_{33}^*=-8\Gamma_3^2g_{12}^2a^2/P_3^2[-3bP^2/2+(P^2/3)(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}+P/2+(2P^2/3)(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}]$$
$$+8\Gamma_3g_{11}^2Pa/P_3, \quad (42b)$$

$$\Delta C_{13}^*=-8\Gamma_3^2g_{11}g_{12}/P_3^2[-3bP^2/2+(P^2/3)(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}+P/2+(2P^2/3)(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}]$$
$$+8a\Gamma_3g_{12}g_{11}P/P_3, \quad (42c)$$

$$\Delta C_{44}^*=-2\Gamma_1^2g_{44}^2a^2/P_1^2[-CP^2/2+(P^2/3)(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}+P/2-(P^2/3)(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}]$$
$$+2\Gamma_1^2g_{44}^2Pa/P_1. \quad (42d)$$

We shall now define the relaxation time τ for the system by the relation

$$\tau=[\Gamma_3(\partial^2F/\partial P_z^2)_0]^{-1}=[\Gamma_1(\partial^2F/\partial P_x^2)_0]^{-1}. \quad (43)$$

For simplicity, we assume that the relaxation time is isotropic. Then Eqs. (27a) and (27b) become

$$P_1=\Gamma_1q_1a(1+i\Omega\tau), \quad (27c)$$

$$P_3=\Gamma_3q_3a(1+i\Omega\tau), \quad (27d)$$

where q_1a and q_3a are given by Eqs. (22a) and (22b), respectively.

Now the relaxation time has a temperature dependence given by Lemanov[6]:

$$\tau=\tau_0/|T_c-T|, \quad (44)$$

where τ_0 has a value of order 10^{-11}–10^{-10} sK. Under most experimental conditions, the acoustic frequency is chosen in the range 10^8–10^9 Hz. Hence $\Omega\tau_0$ has a value of the order of 10^{-2}–10^{-3}.

Substituting (27c) and (27d) in Eqs. (42a)–(42d), we find that all the elastic anomalies have the form

$$\Delta C_{ij}^*=F_{ij}(A_{ij}-iB_{ij}\Omega\tau)(1+i\Omega\tau)^{-2}, \quad (45)$$

where F_{ij}, A_{ij}, and B_{ij} are constants that can easily be determined from these equations (42a)–(42d). Further, the real part of the constants is given by

$$R(\Delta C_{ij}^*)=F_{ij}[A_{ij}-\Omega^2\tau^2(A_{ij}+2B_{ij})](1+\Omega^2\tau^2)^{-2}. \quad (46a)$$

When $T=T_c$, $\Omega\tau\to\infty$ and it follows that $R(\Delta C_{ij}^*)\to 0$. When $|T-T_c|=\Omega\tau_0=10^{-2}$, we have $\Omega\tau=1$ and

$$R(\Delta C_{ij}^*)=-F_{ij}B_{ij}/2. \quad (46b)$$

We further see that the stationary point for the expression on the right-hand side of (46) is reached for the value $\Omega^2\tau^2=1+2A_{ij}/(A_{ij}+2B_{ij})$ and for this value,

$$R(\Delta C_{ij}^*)=-F_{ij}(A_{ij}+2B_{ij})^2/8(A_{ij}+B_{ij}). \quad (46c)$$

When $\Omega\tau\to 0$, $R(\Delta C_{ij}^*) = F_{ij}A_{ij}$. This is the asymptotic value of the elastic anomalies in the low symmetry phase.

The temperature dependence of the elastic anomalies can now be easily understood. It follows that the elastic constants $C_{ij}^* = C_{ij} + R(\Delta C_{ij}^*)$ have a dip at the transition temperature of order $-F_{ij}\ (A_{ij}+2B_{ij})^2/8(A_{ij}+B_{ij})$. Within a temperature range of the order 10^{-1} K, the elastic constants reach their low symmetry value of

$$C_{ij}+F_{ij}A_{ij}. \quad (46d)$$

C. Anomalies in the TOE constants

The expression for F_3 in the free energy contains cubic terms in the order parameter and the strain variables. Let us write

$$C_{ijk}^*=C_{ijk}+\Delta C_{ijk}^*, \quad (47)$$

$$F_3=\frac{1}{6}\sum_{ijk} C_{ijk}^*\eta_i^*\eta_j^*\eta_k^*=\frac{1}{6}\sum_{ijk} C_{ijk}\eta_i^*\eta_j^*\eta_k^*+\Delta F_3,$$

where

$$\Delta F_3=\frac{1}{6}\sum_{ijk}\Delta C_{ijk}^*\eta_i^*\eta_j^*\eta_k^*$$
$$=bP_z^{*3}+2CP_{z0}P_z^*(P_x^{*2}+P_y^{*2})+g_{11}(\eta_1^*P_x^{*2}+\eta_2^*P_y^{*2}+\eta_3^*P_z^{*2})+g_{12}[\eta_1^*(P_y^{*2}+P_z^{*2})+\eta_2^*(P_z^{*2}+P_x^{*2})+\eta_3^*(P_x^{*2}+P_y^{*2})]$$
$$+g_{44}(\eta_4^*P_y^*P_z^*+\eta_5^*P_z^*P_x^*+\eta_6^*P_x^*P_y^*). \quad (48)$$

Substituting for P_x^*, P_y^*, and P_z^* from (23) to (25), we obtain

$$\frac{1}{6}\sum_{ijk}\Delta C_{ijk}^*\eta_i^*\eta_j^*\eta_k^*=bP_{z0}\Big(\sum_i\alpha_i\eta_i^*\Big)^3+2CP_{z0}A^2\Big(\sum_i\alpha_i\eta_i^*\Big)(\eta_4^{*2}+\eta_5^{*2})+g_{11}\Big[A^2(\eta_1^{*2}\eta_5^{*2}+\eta_2^{*2}\eta_4^{*2})+\Big(\sum_i\alpha_i\eta_i^*\Big)^2\eta_3^*\Big]$$
$$+g_{12}\Big[A^2(\eta_1^{*2}\eta_4^{*2}+\eta_2^{*2}\eta_5^{*2})+\Big(\sum\alpha_i\eta_i^*\Big)^2(\eta_1^*+\eta_2^*)+A^2(\eta_4^{*2}+\eta_5^{*2})\eta_3^*\Big]$$
$$+g_{44}\Big[A(\eta_4^{*2}+\eta_5^{*2})\Big(\sum_i\alpha_i\eta_i^*\Big)+A^2\eta_4^*\eta_5^*\eta_6^*\Big]. \quad (49)$$

The third-order elastic anomalies can now be obtained immediately by comparing the coefficients of the various cubic terms in the left-hand and right-hand sides. We find that

$$\Delta C_{111}^*=\Delta C_{222}^*=\Delta C_{112}^*=\Delta C_{122}^*, \quad (50a)$$

$$\Delta C_{111}^*/g_{12}^3=\Delta C_{333}^*/g_{11}^3, \quad (50b)$$

$$\Delta C_{113}^*=\Delta C_{223}^*, \quad (50c)$$

$$\Delta C_{113}^*/g_{12}=\Delta C_{133}^*/g_{11}, \quad (50d)$$

$$\Delta C_{144}^*=\Delta C_{255}^*, \quad (50e)$$

$$\Delta C_{155}^*=\Delta C_{244}^*, \quad (50f)$$

$$\Delta C_{344}^*=\Delta C_{355}^*. \quad (50g)$$

The actual expressions for the independent TOE constants can be found to be

$$\Delta C_{111}^*/6=-4\{\Gamma_3^2g_{12}^3Pa/P_3^2\}(1+2b\Gamma_3Pa/P_3), \quad (51a)$$

$$\Delta C_{133}^*/2=-\{12g_{11}\Gamma_3^2g_{12}^2Pa/P_3^2\}(1+2b\Gamma_3Pa/P_3), \quad (51b)$$

$$\Delta C_{144}^*/2=-\{\Gamma_1g_{44}^2g_{12}Pa/P_1P_3\}\{2\Gamma_3+(\Gamma_1/P_1)(P_3+4C\Gamma_3Pa)\}, \quad (51c)$$

$$C_{344}^*/2=-\{\Gamma_1g_{44}^2Pa/P_1P_3\}[2\Gamma_3g_{11}+(4C\Gamma_3Pag_{11}+P_3g_{12})\Gamma_1/P_1], \quad (51d)$$

$$C_{456}^*/6=-\{\Gamma_1^2g_{44}^3Pa\}/P_1^2. \quad (51e)$$

Substituting (27c) and (27d) in (51a), we find that ΔC_{111}^* can be rewritten as

$$\Delta C_{111}^*=-4g_{12}^3P\{1+2bP[q_3(1+i\Omega\tau)]^{-1}\}\times[q_3^2a(1+i\Omega\tau)^2]^{-1}. \quad (52a)$$

The presence of the factor $a=a'(T-T_c)$ in the denominator might suggest a singularity of order $|T-T_c|^{-1}$, but this singularity is in fact removed by the strong attenuation through the factor $(1+i\Omega\tau)^2$ in the denominator. Now

$$R(\Delta C_{111}^*)$$
$$=-(4g_{12}^3P\Omega\tau/q^2a'\Omega\tau_0)\{(1-\Omega^2\tau^2)(1+\Omega^2\tau^2)^{-2}+2bP(1-3\Omega^2\tau^2)[q_3(1+\Omega^2\tau^2)^3]^{-1}\}. \quad (52b)$$

In the low symmetry regime, $R(\Delta C^*_{1111})$ increases initially within a temperature range $|T_c-T|=10^{-2}$ K, then falls down to negative values, and finally reaches the asymptotic value of zero.

D. Anomalies in the FOE constants

Let us write

$$C^*_{ijkl}=C_{ijkl}+\Delta C^*_{ijkl}. \tag{53}$$

It is then seen that

$$\Delta F_4=\frac{1}{24}\sum_{ijkl}\Delta C^*_{ijkl}\eta_i^*\eta_j^*\eta_k^*\eta_l^*$$

$$=\frac{b}{4}\alpha_i\alpha_j\alpha_k\alpha_l\eta_i^*\eta_j^*\eta_k^*\eta_l^*+CA^2(\eta_4^{*^2}+\eta_5^{*^2})\alpha_i\alpha_j\eta_i^*\eta_j^*$$

$$+CA^4\eta_4^{*^2}\eta_5^{*^2}+\frac{b}{4}A^4(\eta_4^{*^4}+\eta_5^{*^4}). \tag{54}$$

Comparing the coefficients of the various terms on both sides, we first arrive at the following relations between the FOE anomalies:

$$\Delta C^*_{1111}=\Delta C^*_{2222}=\Delta C^*_{1122}, \tag{53a}$$

$$\frac{\Delta C^*_{1111}}{g_{12}^4}=\frac{\Delta C^*_{3333}}{g_{11}^4}=\frac{\Delta C^*_{1133}}{g_{11}^2g_{12}^2}=\frac{\Delta C^*_{2233}}{g_{11}^2g_{12}^2}, \tag{53b}$$

$$\Delta C^*_{4444}=\Delta C^*_{5555}, \tag{53c}$$

$$\frac{\Delta C^*_{4444}}{6b}=\frac{\Delta C^*_{4455}}{4C}=A^4. \tag{53d}$$

The actual expressions for the FOE anomalies are given by

$$\Delta C^*_{1111}=96\frac{b\Gamma_3^4g_{12}^4P^2a^2}{P_3^4}, \tag{54a}$$

$$\Delta C^*_{4444}=6\frac{b\Gamma_1^4g_{44}^4P^2a^2}{P_3^4}. \tag{54b}$$

From (54a) it follows that

$$R(\Delta C^*_{1111})=96bg_{12}^4P^2\tau^2(1-6\Omega^2\tau^2+\Omega^4\tau^4)$$
$$\times[a'^2\tau_0^2q_3^4(1+i\Omega\tau)^4]^{-1}. \tag{55}$$

In the absence of attenuation, FOE constants should suffer a singularity of order $|T_c-T|^{-2}$, but damping at the transition temperature removes this singularity. One can see that $R(\Delta C^*_{1111})$ initially increases with decreasing temperature and thereafter decreases asymptotically to zero.

V. ELASTIC ANOMALIES FOR THE ORTHORHOMBIC PHASE

As the crystal is cooled through 5 °C, barium titanate remains ferroelectric but its structure changes from tetragonal to orthorhombic until a temperature of −70 °C is reached. Between 5 and −70 °C the polarization is along the [011] direction. In this case, $P_x=0$, $P_y=P_z\neq 0$.

The stability conditions yield a second set of solutions, which correspond to the orthorhombic structure of the crystal. The equilibrium values of the strain variables as well as the components of the order parameter have already been listed in Eqs. (13)–(17) of Sec. II for this phase.

Again, the fluctuations of the components of the order parameter, as derived from the LK equations, have the form

$$P_x=P_{x0}+P_x^*, \tag{56a}$$

$$P_y=P_{y0}+P_y^*, \tag{56b}$$

$$P_z=P_{z0}+P_z^*, \tag{56c}$$

where P_x^*, P_y^*, P_z^* are linear functions of the strain variables, given by Eqs. (28)–(30).

Substituting (56) in (1), we find that the expression for the free energy becomes

$$F=\frac{1}{2}\sum_{ij}C_{ij}(\eta_{i0}+\eta_i^*)(\eta_{j0}+\eta_j^*)+\frac{1}{6}\sum_{ijk}C_{ijk}\cdots+\frac{a}{2}[P_x^{*^2}+(P_{z0}+P_y^*)^2+(P_{z0}+P_z^*)^2]+\frac{b}{4}[P_x^{*^4}+(P_{z0}+P_y^*)^4+(P_{z0}+P_z^*)^4]$$
$$+C[P_x^{*^2}(P_{z0}+P_y^*)^2+P_x^{*^2}(P_{z0}+P_z^*)^2+(P_{z0}+P_y^*)^2(P_{z0}+P_z^*)^2]+g_{11}[(\eta_{10}+\eta_1^*)P_x^{*^2}+(\eta_{20}+\eta_2^*)(P_{z0}+P_y^*)^2$$
$$+(\eta_{30}+\eta_3^*)(P_{z0}+P_z^*)^2]+g_{12}\{(\eta_{10}+\eta_1^*)[(P_{z0}+P_z^*)^2+(P_{z0}+P_y^*)^2]\}+(\eta_{20}+\eta_2^*)[P_x^{*^2}+(P_{z0}+P_z^*)^2]$$
$$+(\eta_{30}+\eta_3^*)[P_x^{*^2}+(P_{z0}+P_z^*)^2]+g_{44}\{(\eta_{40}+\eta_4^*)(P_{z0}+P_y^*)(P_{z0}+P_z^*)+\eta_5^*(P_{z0}+P_y^*)P_x^*+\eta_6^*P_x^*(P_{z0}+P_y^*)\}. \tag{57}$$

As before, we neglect the contributions to the zero point energy, SOE, TOE, and FOE constants arising from the third-order and fourth-order terms in the elastic deformation energy.

The zero point energy in this phase is given by

$$F_0=\frac{1}{2}\sum_{ij}C_{ij}\eta_{i0}\eta_{j0}+aP_{z0}^2+\frac{b}{2}P_{z0}^4+CP_{z0}^4+g_{11}P_{z0}^2(\eta_{20}+\eta_{30})$$
$$+g_{12}P_{z0}^2(2\eta_{10}+\eta_{20}+\eta_{30})+g_{44}P_{z0}^2\eta_{40}. \tag{58}$$

On substituting the values for the above parameters from (13) to (17), we find that

$$F_0=\frac{Ka'^2(T-T_c)^2}{2}. \tag{59}$$

Hence the specific heat is given by

$$C_V = Ka'^2(T_c - T). \quad (60)$$

The difference ΔC_v in the specific heat between the orthorhombic and tetragonal phases is given by

$$\Delta C_V^* = a'^2(T_c - T)(K - P/2). \quad (61)$$

A. SOE anomalies in the orthorhombic phase

We shall adopt the same procedure as in the previous section and for the sake of brevity, give only the important equations for evaluating the elastic anomalies. It can be seen from (54) that the expression for ΔF_2 is given by

$$\begin{aligned}\Delta F_2 &= \frac{1}{2} \sum_{ij} \Delta C_{ij}^* \eta_i^* \eta_j^* \\ &= \sum_{ij} (\alpha_{yi}\alpha_{yj} + \alpha_{zi}\alpha_{zj}) \left(\frac{a}{2} + \frac{3bP_{z0}^2}{2} + CP_{z0}^2 + g_{11}\eta_{20} + g_{12}(\eta_{10} + \eta_{20}) \right) \eta_i^* \eta_j^* + \left(\frac{a}{2} + 2CP_{z0}^2 + g_{11}\eta_{10} \right. \\ &\left. + 2g_{12}\eta_{20} \right) \sum_{ij} \alpha_{xi}\alpha_{xj}\eta_i^*\eta_j^* + \sum_{ij} 2g_{11}P_{z0}(\alpha_{yi}\eta_i^*\eta_2^* + \alpha_{zi}\eta_i^*\eta_3^*) + \sum_{ij} (4CP_{z0}^2 + g_{44}\eta_{40})\alpha_{yi}\alpha_{zj}\eta_i^*\eta_j^* \\ &+ \sum_{ij} 2g_{12}P_{z0}(\alpha_{yi}\eta_i^*\eta_1^* + \alpha_{zi}\eta_i^*\eta_1^* + \alpha_{zi}\eta_i^*\eta_2^* + \alpha_{yi}\eta_i^*\eta_3^*) + \sum_{ij} g_{44}P_{z0}(\alpha_{yi}\eta_i^*\eta_4^* + \alpha_{zi}\eta_i^*\eta_4^* + \alpha_{xi}\eta_i^*\eta_5^* + \alpha_{xi}\eta_i^*\eta_5^*).\end{aligned} \quad (62)$$

By writing $\eta_1^* = \delta_{1i}\eta_i^*$, etc., we can obtain a single formula for all the elastic anomalies in terms of the Kronecker delta functions. There are eight independent elastic anomalies. Besides, there are several relations among them. They are given by

$$\Delta C_{22}^* = \Delta C_{33}^*, \quad (63a)$$

$$\Delta C_{55}^* = \Delta C_{66}^* = \Delta C_{56}^*, \quad (63b)$$

$$\Delta C_{12}^* = \Delta C_{13}^*, \quad (63c)$$

$$\Delta C_{24}^* = \Delta C_{34}^*. \quad (63d)$$

The expressions for the elastic anomalies are

$$\Delta C_{11}^* = 4\alpha_{y1}^2 a L_1 + 2\alpha_{y1}^2 Ka(g_{44}^2/C_{44} - 4C) + 8g_{12}\alpha_{y1}(-Ka)^{0.5}, \quad (64a)$$

$$\Delta C_{22}^* = 2(\alpha_{y2}^2 + \alpha_{y3}^2) a L_1 + 2\alpha_{y2}\alpha_{y3} Ka(g_{44}^2/C_{44} - 4C) + 4(g_{11}\alpha_{y2} + g_{12}\alpha_{y3})(-Ka)^{0.5}, \quad (64b)$$

$$\Delta C_{44}^* = 4\alpha_{y4}^2 a L_1 + 2\alpha_{y4}^2 (g_{44}^2/C_{44} - 4C) Ka + 4g_{44}\alpha_{y4}(-Ka)^{0.5}, \quad (64c)$$

$$\Delta C_{55}^* = 2\alpha_{x5}^2 a L_2 + 2g_{44}\alpha_{x5}(-Ka)^{0.5}, \quad (64d)$$

$$\Delta C_{12}^* = 2\alpha_{y1} a L_1(\alpha_{y2} + \alpha_{y3}) + \alpha_{y1}(\alpha_{y2} + \alpha_{y3})(g_{44}^2/C_{44} - 4C) \times -Ka + 2[g_{11}\alpha_{y1} + g_{12}(\alpha_{y1} + \alpha_{y2} + \alpha_{y3})] \times (-Ka)^{0.5}, \quad (64e)$$

$$\Delta C_{14}^* = 4\alpha_{y1}\alpha_{y4} a L_1 + 2\alpha_{y1}\alpha_{y4}(g_{44}^2/C_{44} - 4C)Ka + 2(2g_{12}\alpha_{y4} + g_{44}\alpha_{y1})(-Ka)^{0.5}, \quad (64f)$$

$$\Delta C_{23}^* = 4\alpha_{y2}\alpha_{y3} a L_1 + (\alpha_{y2}^2 + \alpha_{y3}^2)(g_{44}^2/C_{44} - 4C)Ka + 4(g_{11}\alpha_{y3} + g_{12}\alpha_{y2})(-Ka)^{0.5}, \quad (64g)$$

$$\Delta C_{24}^* = 2\alpha_{y4}(\alpha_{y2} + \alpha_{y3}) a L_1 + \alpha_{y4}(\alpha_{y2} + \alpha_{y3})(g_{44}^2/C_{44} - 4C) \times Ka + (2g_{11}\alpha_{y4} + 2g_{12}\alpha_{y4} + g_{44})(\alpha_{y2} + \alpha_{y3}) \times (-Ka)^{0.5}, \quad (64h)$$

where

$$L_1 = \tfrac{1}{2} - \tfrac{3}{2}Kb - CK + (\tfrac{2}{3}K)(g_{11} + 2g_{12})^2(C_{11} + 2C_{12})^{-1} + (\tfrac{1}{3}K)(g_{11} - g_{12})^2(C_{11} - C_{12})^{-1}, \quad (65a)$$

$$L_2 = \tfrac{1}{2} - 2CK + (\tfrac{2}{3}K)(g_{11} + 2g_{12})^2(C_{11} + 2C_{12})^{-1} + (-\tfrac{2}{3}K)(g_{11} - g_{12})^2(C_{11} - C_{12})^{-1}. \quad (65b)$$

The temperature dependence of these elastic constants can be evaluated as in the previous case.

B. TOE anomalies in the orthorhombic phase

By collecting terms of order 3 of the form $\eta_i^*\eta_j^*\eta_k^*$, we find that the expressions for the anomalies for the TOE constants can be obtained from the following equation:

$$\frac{1}{6}\sum_{ijk}\Delta C^*_{ijk}=bP_{z0}\sum_{ijk}(\alpha_{yi}\alpha_{yj}\alpha_{yk}+\alpha_{zi}\alpha_{zj}\alpha_{zk})\eta^*_i\eta^*_j\eta^*_k+2CP_{z0}\sum_{ijk}(\alpha_{xi}\alpha_{xj}\alpha_{yk}+\alpha_{yi}\alpha_{yj}\alpha_{zk}+\alpha_{xi}\alpha_{xj}\alpha_{zk}+\alpha_{yi}\alpha_{zj}\alpha_{zk})\eta^*_i\eta^*_j\eta^*_k$$

$$+g_{11}\sum_{ij}(\alpha_{xi}\alpha_{xj}\eta^*_1+\alpha_{yi}\alpha_{yj}\eta^*_2+\alpha_{zi}\alpha_{zj}\eta^*_3)\eta^*_i\eta^*_j+g_{12}\{\eta^*_1(\alpha_{yi}\alpha_{yj}+\alpha_{zi}\alpha_{zj})+\eta^*_2(\alpha_{zi}\alpha_{zj}+\alpha_{xi}\alpha_{xj})$$

$$+\eta^*_3(\alpha_{xi}\alpha_{xj}+\alpha_{yi}\alpha_{yj})\}\eta^*_i\eta^*_j+g_{44}\sum_{ij}(\alpha_{yi}\alpha_{zj}\eta^*_4+\alpha_{zi}\alpha_{xj}\eta^*_5+\alpha_{xi}\alpha_{xj}\eta^*_6)\eta^*_i\eta^*_j. \quad (66)$$

From this, one can verify that

$$\Delta C^*_{222}=\Delta C^*_{333}, \quad (67a)$$

$$\Delta C^*_{555}=\Delta C^*_{666}=0, \quad (67b)$$

$$\Delta C^*_{122}=\Delta C^*_{133}. \quad (67c)$$

The expression for some of the principal TOE elastic anomalies are as follows:

$$\Delta C^*_{111}/6=2bP_{z0}\alpha^3_{y1}+4CP_{z0}\alpha^3_{y1}+2g_{12}\alpha^2_{y1}, \quad (68a)$$

$$\Delta C^*_{222}/6=bP_{z0}(\alpha^3_{y2}+\alpha^3_{y3})+2CP_{z0}\alpha_{y2}\alpha_{y3}(\alpha_{y2}+\alpha_{y3})+g_{12}\alpha^2_{y3}+g_{11}\alpha^2_{y2}, \quad (68b)$$

$$\Delta C^*_{444}/6=2bP_{z0}\alpha^3_{y4}+4CP_{z0}\alpha^3_{y4}, \quad (68c)$$

$$\Delta C^*_{456}=8CP_{z0}\alpha^2_{x5}\alpha_{y4}+2g_{44}\alpha_{x5}\alpha_{y4}. \quad (68d)$$

C. FOE anomalies in the orthorhombic phase

The fourth-order elastic anomalies are derivable from the equation

$$\frac{1}{24}\sum_{ijkl}\Delta C^*_{ijkl}\eta^*_i\eta^*_j\eta^*_k\eta^*_l=\frac{b}{4}(\alpha_{xi}\alpha_{xj}\alpha_{xk}\alpha_{xl}+\alpha_{yi}\alpha_{yj}\alpha_{yk}\alpha_{yl}+\alpha_{zi}\alpha_{zj}\alpha_{zk}\alpha_{zl})\times\eta^*_i\eta^*_j\eta^*_k\eta^*_l+C(\alpha_{xi}\alpha_{xj}\alpha_{yk}\alpha_{yl}+\alpha_{yi}\alpha_{yj}\alpha_{zk}\alpha_{zl}+\alpha_{zi}\alpha_{zj}\alpha_{xk}\alpha_{xl})\eta^*_i\eta^*_j\eta^*_k\eta^*_l. \quad (69)$$

By giving individual values ranging from 1 to 6 to i, j, k, l, the various FOE constants can be evaluated.

APPENDIX A

The stability conditions $\partial F/\partial P_i=0$ ($i=x,y,z$) and $\partial F/\partial\eta_i=0$ ($i=1$–6) can be explicitly written as

$$(\partial F/\partial P_x)=aP_x+bP^3_x+2CP_x(P^2_y+P^2_z)+2g_{11}\eta_1P_x+2g_{12}P_x(\eta_2+\eta_3)+g_{44}(\eta_6P_y+\eta_5P_z)=0, \quad (A1)$$

$$(\partial F/\partial P_y)=aP_y+bP^3_y+2CP_y(P^2_z+P^2_x)+2g_{11}\eta_2P_y+2g_{12}P_y(\eta_3+\eta_1)+g_{44}(\eta_4P_z+\eta_6P_x)=0, \quad (A2)$$

$$(\partial F/\partial P_z)=aP_z+bP^3_z+2CP_z(P^2_x+P^2_y)+2g_{11}\eta_3P_z+2g_{12}P_z(\eta_1+\eta_2)+g_{44}(\eta_4P_y+\eta_5P_x)=0, \quad (A3)$$

$$(\partial F/\partial\eta_1)=C_{11}\eta_1+C_{12}(\eta_2+\eta_3)+g_{11}P^2_x+g_{12}(P^2_y+P^2_z)=0, \quad (A4)$$

$$(\partial F/\partial\eta_2)=C_{11}\eta_2+C_{12}(\eta_3+\eta_1)+g_{11}P^2_y+g_{12}(P^2_z+P^2_x)=0, \quad (A5)$$

$$(\partial F/\partial\eta_3)=C_{11}\eta_3+C_{12}(\eta_1+\eta_2)+g_{11}P^2_z+g_{12}(P^2_x+P^2_y)=0, \quad (A6)$$

$$(\partial F/\partial\eta_4)=C_{44}\eta_4+g_{44}P_yP_z=0, \quad (A7)$$

$$(\partial F/\partial\eta_5)=C_{44}\eta_5+g_{44}P_zP_x=0, \quad (A8)$$

$$(\partial F/\partial\eta_6)=C_{44}\eta_6+g_{44}P_xP_y=0. \quad (A9)$$

When combined with (A7), (A8), and (A9), it can be seen that Eqs. (A1), (A2), and (A3) have factors P_x, P_y, and P_z, respectively.

It follows that Eq. (A1)–(A3) have the following types of solutions:

(1) $P_x=P_y=P_z=0$,
(2) $P_x=P_y=0$, $P_z\neq 0$,
(3) $P_x=0$, $P_y=P_z\neq 0$,
(4) $P_x=P_y=P_z\neq 0$.

Equations (4) and (5) represent the solution of Eqs. (A1)–(A9) for case (1). Equations (7)–(11) yield the solution of case (2), while the solution of case (3) is given by Eqs. (13)–(17). In writing Eq. (A1) to (A9) we have neglected the third- and fourth-order terms in the deformation energy F_{ela} as they are of smaller order.

APPENDIX B

In this appendix we give the equilibrium values of the second derivatives of F with respect to the nine parameters for the tetragonal and orthorhombic phases.

A. Tetragonal phase

We have given in Eqs. (22a) and (22b) the values of $(\partial^2F/\partial P^2_i)$ for $i=x$, y, and z.

It can be seen by direct differentiation and substitution of the equilibrium values that the equilibrium values of the other second-order derivatives of F are as follows:

$$(\partial^2F/\partial P_x^2)_0=a+2CP_{z0}^2+2g_{11}\eta_{10}+2g_{12}(\eta_{20}+\eta_{30}), \quad \text{(B1)}$$

$$(\partial^2F/\partial P_y^2)_0=a+2CP_{z0}^2+2g_{11}\eta_{20}+2g_{12}(\eta_{30}+\eta_{10}), \quad \text{(B2)}$$

$$(\partial^2F/\partial P_z^2)_0=a+3bP_{z0}^2+2g_{11}\eta_{30}+2g_{12}(\eta_{10}+\eta_{20}), \quad \text{(B3)}$$

$$(\partial^2F/\partial P_x\partial P_y)_0=(\partial^2F/\partial P_x\partial P_z)_0=(\partial^2F/\partial P_y\partial P_z)_0=0, \quad \text{(B4)}$$

$$(\partial^2F/\partial P_x\partial\eta_i)_0=0 \quad \text{for } i=1,2,3,4, \text{ and } 6,$$

$$(\partial^2F/\partial P_x\partial\eta_5)_0=g_{44}P_{z0}, \quad \text{(B5)}$$

$$(\partial^2F/\partial P_y\partial\eta_i)_0=0 \quad \text{for } i=1,2,3,5, \text{ and } 6, \quad \text{(B6)}$$

$$(\partial^2F/\partial P_y\partial\eta_4)_0=g_{44}P_{z0}, \quad \text{(B7)}$$

$$(\partial^2F/\partial P_z\partial\eta_i)_0=0 \quad \text{for } i=4,5, \text{ and } 6, \quad \text{(B8)}$$

$$(\partial^2F/\partial P_z\partial\eta_1)_0=(\partial^2F/\partial P_z\partial\eta_2)_0=2g_{12}P_{z0}, \quad \text{(B9)}$$

$$(\partial^2F/\partial P_z\partial\eta_3)_0=2g_{11}P_{z0}. \quad \text{(B10)}$$

B. Orthorhombic phase

For the orthorhombic phase, we have the following expressions:

$$(\partial^2F/\partial P_x^2)_0=a[1-4CK+\tfrac{4}{3}K(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1} -(4/3)K(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}], \quad \text{(B11)}$$

$$(\partial^2F/\partial P_y^2)_0=(\partial^2F/\partial P_z^2)_0 =a[1-3bK+\tfrac{4}{3}K(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1} -\tfrac{2}{3}K(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}], \quad \text{(B12)}$$

$$(\partial^2F/\partial P_x\partial P_y)_0=(\partial^2F/\partial P_x\partial P_z)_0=0, \quad \text{(B13)}$$

$$(\partial^2F/\partial P_y\partial P_z)_0=4CP_{z0}^2+g_{44}\eta_{40}, \quad \text{(B14)}$$

$$(\partial^2F/\partial P_x\partial\eta_i)_0=0 \quad \text{for } i=1,2,3, \text{ and } 4, \quad \text{(B15)}$$

$$(\partial^2F/\partial P_x\partial\eta_5)_0=(\partial^2F/\partial P_x\partial\eta_6)_0=g_{44}P_{z0}, \quad \text{(B16)}$$

$$(\partial^2F/\partial P_y\partial\eta_1)_0=(\partial^2F/\partial P_y\partial\eta_3)_0=2g_{12}P_{z0}, \quad \text{(B17)}$$

$$(\partial^2F/\partial P_y\partial\eta_2)_0=2g_{11}P_{z0}, \quad \text{(B18)}$$

$$(\partial^2F/\partial P_y\partial\eta_4)_0=g_{44}P_{z0}, \quad \text{(B19)}$$

$$(\partial^2F/\partial P_y\partial\eta_5)_0=(\partial^2F/\partial P_y\partial\eta_6)_0=0, \quad \text{(B20)}$$

$$(\partial^2F/\partial P_z\partial\eta_1)_0=(\partial^2F/\partial P_z\partial\eta_2)_0=2g_{12}P_{z0}, \quad \text{(B21)}$$

$$(\partial^2F/\partial P_z\partial\eta_3)_0=2g_{11}P_{z0}, \quad \text{(B22)}$$

$$(\partial^2F/\partial P_z\partial\eta_4)_0=g_{44}P_{z0}, \quad \text{(B23)}$$

$$(\partial^2F/\partial P_z\partial\eta_5)_0=(\partial^2F/\partial P_z\partial\eta_6)_0=0. \quad \text{(B24)}$$

[1] C. W. Garland, in Physical Acoustics, edited by W. P. Mason and R. N. Thruston, Vol. VII, 1970.
[2] Sh. Kashida, I. Hatta, A. Ikushima, and Y. Yamada, J. Phys. Soc. Jpn. **34**, 997 (1973).
[3] P. A. Fleury and K. Lyons, in *Structural Phase Transitions*, edited by K. A. Muller and H. Thomas (Springer, Berlin, Heidelberg, New York, 1981), pp. 9–91.
[4] B. Luthi and W. Rehwald, in *Structural Phase Transitions*, edited by K. A. Muller and H. Thomas (Springer, Berlin, Heidelberg, New York, 1981).
[5] A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor & Francies, London, 1981), pp. 2–110.
[6] V. V. Lemanov, Proceedings of the Second International Conference on Condensed Matter Physics, 1982.
[7] W. Rehwald, Adv. Phys. **22**, 721 (1973).
[8] D. Berlin Court and H. Jaffe, Phys Rev. **111**, 161 (1958).
[9] E. J. Huibregtesem, W. H. Bressey, and M. E. Drougard, J. Appl. Phys. **30**, 899 (1959).
[10] S. Fushimi and T. Ikeda, Rev. Elec. Comm. Lab (Tokyo) **14**, 161 (1966).
[11] T. F. Heuter and D. P. Neuhaus, J. Acoust. Soc. Am. **27**, 292 (1955).
[12] T. Ikeda, J. Phy. Soc. Jpn. **13**, 809 (1957).
[13] R. Blinc and B. Zeks, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).
[14] E. Fatuzzo and W. J. Merz, *Ferroelectricity* (North-Holland, Amsterdam, 1967).