Second order elastic anomalies in barium titanate from cubic to tetragonal phase transition

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Abstract. The anomalies of the second order elastic constants have been derived for barium titanate for the phase transition from cubic to tetragonal. The equilibrium values of the components of the order parameter and the strain variables have been obtained from the stability conditions. The fluctuations in the order parameter have been derived from the Landau–Khalatnikov equations. Expression for the shift in the zero point energy in the tetragonal phase is obtained and is shown to be proportional to $(T - T_c)^2$. The anomalies for all the second order elastic constants have been derived and relations among them reported. It is shown that the second order elastic anomalies suffer a discontinuity at the transition temperature.

Keywords. Elastic anomalies; phase transition; barium titanate.

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1. 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 $pm\bar{3}m(O_h^1)$ perovskite structure above the Curie temperature of 120°C. At the Curie point, the crystal becomes polar and its structure changes from cubic to a tetragonal phase. 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 a subgroup of the parent group $pm\bar{3}m$. All the 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 variation of the elastic contants and the consequent anomalies have been investigated by several authors [1, 6, 8–10]. Variation of C_{11} and C_{44} were measured by Luthi and Rehwald [13] 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 $\mu = 0.41$ and T_0 is paraelectric Curie temperature (lower stability limit).

There are other ferroelectrics [4] 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 also.

In this paper, we study systematically the anomalies of the second order elastic (SOE) constants arising from the phase transition from the cubic to the tetragonal phase. The equilibrium values of the components of the order parameter and the strain variables in the two phases are obtained from the stability conditions [15] while the fluctuations in the order parameter in the two phases are derived from the Landau–Khalatnikov equations. The strains developed during a phase transition are infinitesimal and the third order deformation energy is one order smaller than the second order deformation energy. Hence the corrections brought about by third and fourth order deformation energies to the equilibrium values are negligible in comparison with second order deformation energy. We shall therfore neglect them in future calculations. In § 4, we give an expression for all the 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.

2. The equilibrium values of the order parameters and the strain variables

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 [4] for the phase transition of barium titanate and similar compounds. We have

$$F = (1/2)\sum_{ij} C_{ij}\eta_i\eta_j + (a/2)(P_x^2 + P_y^2 + P_z^2) + (b/4)(P_x^4 + P_y^4 + P_z^4)$$

$$+ C(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2) + g_{11}(\eta_1 P_x^2 + \eta_2 P_y^2 + \eta_3 P_z^2)$$

$$+ g_{12}\{\eta_1(P_z^2 + P_y^2) + \eta_2(P_z^2 + P_x^2) + \eta_3(P_x^2 + P_y^2)\}$$

$$+ g_{44}(\eta_4 P_y P_z + \eta_5 P_z P_x + \eta_6 P_x P_y) \tag{1}$$

where $a = a'(T - T_c)$, 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 $\eta_i(i = 1$ to $6)$ are the six components of the strain tensor. P_x, P_y and P_z are the three components of order parameter. The equilibrium values of the order parameter components as well as the strain variables can be obtained from the stability conditions: These are

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

$$(\partial F/\partial \eta_i)_0 = 0 \quad (\text{for } i = 1 \text{ to } 6). \tag{2}$$

In the cubic phase above 120°C, barium titanate is paraelectric: The simplest solution of equations (2) are given by

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

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

$$P_{xo} = P_{yo} = P_{z0} = 0 \qquad (4)$$

and

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

Barium titanate undergoes a phase transition from cubic to 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 equations (2) admit another solution, in which

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

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

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

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

where

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

and

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

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

Further the equilibrium value of the electrical polarization is described by

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

where

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

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

3. The Landau – Khalatnikov (LK) 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

$$\dot{P}_x = -\Gamma_1(\partial F/P_x), \tag{12a}$$

$$\dot{P}_y = -\Gamma_2(\partial F/P_y), \tag{12b}$$

$$\dot{P}_z = -\Gamma_3(\partial F/P_z), \tag{12c}$$

where Γ_1 Γ_2 and Γ_3 are the kinetic coefficients.

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

$$P_x = P_{x0} + P_x^*; \quad P_y = P_{y0} + P_y^*; \quad P_z = P_{z0} + P_z^* \text{ and } \eta_i = \eta_{i0} + \eta_i^*. \tag{13}$$

Symmetry of the tetragonal structure ensures that

$$\Gamma_1 = \Gamma_2. \tag{14}$$

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

$$\partial F/\partial P_i = (\partial F/\partial P_i)_0 + \sum_j (\partial^2 F/\partial P_i \partial P_j)_0 P_j^* + \sum_j (\partial^2 F/\partial P_i \partial \eta_j)_0 \eta_j^*. \tag{15}$$

Further by writing P_i^* proportional to $e^{i\Omega t}$ (Ω is the angular frequency of the acoustic wave) we see that the LK equations reduce to

$$\{i\Omega + \Gamma_1(\partial^2 F/\partial P_x^2)_0\} P_x^* + \Gamma_1(\partial^2 F/\partial P_x \partial P_y)_0 P_y^* + \Gamma_1(\partial^2 F/\partial P_x \partial P_z)_0 P_z^*$$

$$= -\Gamma_1 \sum_i (\partial^2 F/\partial P_x \partial \eta_i)_0 \eta_i^*, \tag{16a}$$

$$\{i\Omega + \Gamma_1(\partial^2 F/\partial P_y^2)_0\} P_y^* + \Gamma_1(\partial^2 F/\partial P_y \partial P_x)_0 P_x^* + \Gamma_1(\partial^2 F/\partial P_y \partial P_z)_0 P_z^*$$

$$= -\Gamma_1 \sum_i (\partial^2 F/\partial P_y \partial \eta_i)_0 \eta_i^* \tag{16b}$$

$$\{i\Omega + \Gamma_3(\partial^2 F/\partial P_z^2)_0\} P_z^* + \Gamma_3(\partial^2 F/\partial P_z \partial P_y)_0 P_y^* + \Gamma_3(\partial^2 F/\partial P_z \partial P_x)_0 P_x^*$$

$$= -\Gamma_3(\partial^2 F/\partial P_z \partial \eta_i)_0 \eta_i^*. \tag{16c}$$

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 equations (7) to (11) we find that

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

$$- (2/3)P(g_{11} - g_{12})^2(C_{11} - C_{12})^{-1}\}, \tag{17a}$$

$$(\partial^2 F/\partial P_z^2)_0 = a\{1 - 3b + (2/3)P(g_{11} + 2g_{12})^2(C_{11} + 2C_{12})^{-1}$$

$$+ 4/3P(g_{11} - g_{12})^2(C_{11} - C_{12})^{-1}\}. \tag{17b}$$

In the same way, the equilibrium values of $(\partial^2 F/\partial P_i \partial P_j)_0$ and $(\partial^2 F/\partial_i \partial \eta_j)_0$ can be evaluated. The following relations only exist with others equal to zero.

$$(\partial^2 F/\partial P_x \partial \eta_5)_0 = (\partial^2 F/\partial P_y \partial \eta_4)_0 = g_{44} P_{z0}, \tag{18a}$$

$$(\partial^2 F/\partial P_z \partial \eta_1)_0 = (\partial^2 F/\partial P_z \partial \eta_2)_0 = 2g_{12} P_{z0}, \tag{18b}$$

$$(\partial^2 F/\partial P_z \partial \eta_3)_0 = 2g_{11} P_{z0}. \tag{18c}$$

Substituting (18) and (17) in (16) the fluctuations of the order parameter about the equilibrium values reduce to the form

$$P_x^* = A\eta_5^* \tag{19}$$

$$P_y^* = A\eta_4^*, \tag{20}$$

$$P_z^* = \sum_{i=1}^{6} \alpha_i \eta_i^*, \tag{21}$$

where

$$A = -(\Gamma_1 g_{44} P_{z0})/P_1, \tag{22a}$$

$$\alpha_1 = \alpha_2 = -2(\Gamma_3 g_{12} P_{z0})/P_3, \tag{22b}$$

$$\alpha_3 = -2(\Gamma_3 g_{11} P_{z0})/P_3, \tag{22c}$$

$$\alpha_4 = \alpha_5 = \alpha_6 = 0. \tag{22d}$$

Further

$$P_1 = i\Omega + \Gamma_1 (\partial^2 F/\partial P_x^2)_0, \tag{23a}$$

$$P_3 = i\Omega + \Gamma_3 (\partial^2 F/\partial P_z^2)_0. \tag{23b}$$

4. The elastic anomalies in the tetragonal phase

Substituting equation (13) in (1) for the free energy, we find that

$$F = (1/2)\left\{ \sum_{ij} C_{ij}(\eta_{i0} + \eta_i^*)(\eta_{j0} + \eta_j^*) \right\}$$

$$+ (a/2)\{P_x^{*2} + P_y^{*2} + (P_{z0} + P_z^*)^2\} + (b/4)\{P_x^{*4} + P_y^{*4} + (P_{z0} + P_z^*)^4\}$$

$$+ C\{P_x^{*2} P_y^{*2} + (P_x^{*2} + P_y^{*2})(P_{z0} + P_z^*)^2\}$$

$$+ g_{11}\{\eta_{10} + \eta_1^*)P_x^{*2} + (\eta_{20} + \eta_2^*)P_y^{*2} + (\eta_{30} + \eta_3^*)(P_{z0} + P_z^*)^2\}$$

$$+ g_{12}\{(\eta_{10} + \eta_1^*)[P_y^{*2} + (P_{z0} + P_z^*)^2]$$

$$+ (\eta_{20} + \eta_2^*)[P_x^{*2} + (P_{z0} + P_z^*)^2] + (\eta_{30} + \eta_3^*)(P_x^{*2} + P_y^{*2})\}$$

$$+ g_{44}\{(\eta_{40} + \eta_4^*)P_y^*(P_{z0} + P_z^*) + (\eta_{50} + \eta_5^*)P_x^*(P_{z0} + P_z^*)$$

$$+ (\eta_{60} + \eta_6^*)P_y^* P_x^*\} \tag{24}$$

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,

$$F_0 = (1/2)\sum_{ij} C_{ij}\eta_{i0}\eta_{j0} + (a/2)\,P_{z0}^2 + (b/4)P_{z0}^4 + g_{11}\eta_{30}P_{z0}^2$$

$$+ g_{12}P_{z0}^2(\eta_{10} + \eta_{20}). \tag{25}$$

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

$$F_0 = -a^2 P/4 = -(a'^2/4)P(T - T_c)^2 \tag{26}$$

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

$$C_v = (\partial F_0/\partial T)_V = (a'^2 P/2)(T_c - T). \tag{27}$$

4.1 *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

$$F_2 = (1/2)\sum_{ij} C_{ij}^*\eta_i^*\eta_j^* \tag{28}$$

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

$$C_{ij}^* = C_{ij} + \Delta C_{ij}^* \tag{29}$$

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

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

$$= (1/2)\sum_{ij} C_{ij}\eta_i^*\eta_j^* + (a/2)\{P_x^{*^2} + P_y^{*^2} + P_z^{*^2}\} + (3b/2)\{P_{z0}^2 P_z^{*^2}\}$$

$$+ CP_{z0}^2(P_x^{*^2} + P_y^{*^2}) + g_{11}(\eta_{10}P_x^{*^2} + \eta_{20}P_y^{*^2} + \eta_{30}P_z^{*^2} + 2P_{z0}\eta_3^*P_z^*)$$

$$+ g_{12}\{\eta_{10}(P_y^{*^2} + P_z^{*^2}) + \eta_{20}(P_z^{*^2} + P_x^{*^2}) + \eta_{30}(P_x^{*^2} + P_y^{*^2})$$

$$+ 2P_{z0}(\eta_1^*P_z^* + \eta_2^*P_z^*)\} + g_{44}P_{z0}(\eta_4^*P_y^* + \eta_5^*P_x^*\}. \tag{30}$$

Substituting the expressions for P_x^*, P_y^*, P_z^* from (19) to (21) and collecting all terms containing $\eta_i^*\eta_j^*$ in this expression, we find that

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

$$+ \alpha_i\alpha_j(a/2 + (3b/2)P_{z0}^2 + g_{11}\eta_{30} + 2g_{12}\eta_{10})$$

$$+ 2P_{z0}(g_{12}\alpha_i\delta_{j1} + g_{12}\alpha_i\delta_{j2} + g_{11}\alpha_i\delta_{j3})$$

$$+ g_{44}P_{z0}A(\delta_{i4}\delta_{j4} + \delta_{i5}\delta_{j5}). \tag{31}$$

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 one to six, 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.

$$\Delta C_{11}^* = \Delta C_{12}^* = \Delta C_{22}^* \tag{32a}$$

$$\Delta C_{13}^* = \Delta C_{23}^* \tag{32b}$$

$$\Delta C_{44}^* = \Delta C_{55}^* \tag{32c}$$

The anomalies in the individual SOE constants are given by

$$\Delta C_{11}^* = -8\Gamma_3^2 g_{12}^2 a^2/P_3^2\{-3bP^2/2 + (P^2/3)(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}$$
$$+ P/2 + (2P^2/3)(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}\}$$
$$+ 8\Gamma_3 g_{12}^2 Pa/P_3 \tag{33a}$$

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

$$\Delta C_{13}^* = -8\Gamma_3^2 g_{11}g_{12}/P_3^2\{-3bP^2/2 + (P^2/3)(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}$$
$$+ P/2 + (2P^2/3)(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}\}$$
$$+ 8\Gamma_3 g_{12}g_{11} Pa/P_3 \tag{33c}$$

$$\Delta C_{44}^* = -2\Gamma_1^2 g_{44}^2 a^2/P_1^2\{-CP^2/2 + (P^2/3)(g_{11}+2g_{12})^2(C_{11}+2C_{12})^{-1}$$
$$+ P/2 - (P^2/3)(g_{11}-g_{12})^2(C_{11}-C_{12})^{-1}\}$$
$$+ 2\Gamma_1 g_{44}^2 Pa/P_1 \tag{33d}$$

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

$$\tau = \{\Gamma_3(\partial^2 F/\partial P_z^2)_0\}^{-1} = \{\Gamma_1(\partial^2 F/\partial P_x^2)_0\}^{-1}. \tag{34}$$

For simplicity, we assume that the relaxation time is isotropic. Then equations (23a) and (23b) become

$$P_1 = \Gamma_1 q_1 a(1 + i\Omega\tau) \tag{35a}$$

$$P_3 = \Gamma_3 q_3 a(1 + i\Omega\tau) \tag{35b}$$

where $q_1 a$ and $q_3 a$ are given by (23a) and (23b) respectively.

Now the relaxation time has a temperature dependence given by Lemanov [12] as

$$\tau = \tau_0/|T_c - T| \tag{36}$$

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 (35a) and (35b) in (33a) to (33d), we find that all the elastic anomalies have the form

$$\Delta C_{ij}^* = \frac{F_{ij}(A_{ij} - B_{ij}i\Omega\tau)}{(1 + i\Omega\tau)^2} \tag{37}$$

where F_{ij}, A_{ij} and B_{ij} are constants that can easily be determined from (33a)–(33d). Further, the real parts of these constants are given by

$$R(\Delta C_{ij}^*) = F_{ij}\{A_{ij} - \Omega^2\tau^2(A_{ij} + 2B_{ij})\}(1 + \Omega^2\tau^2)^{-2} \tag{38a}$$

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

$$R(\Delta C_{ij}^*) = \frac{-F_{ij}B_{ij}}{2}. \tag{38b}$$

We further see that the stationary point for the expression on the RHS of (38a) is reached for the value of $\Omega^2\tau^2 = 1 + 2A_{ij}/(A_{ij} + 2B_{ij})$ and for this value,

$$R(\Delta C_{ij}^*) = -F_{ij}(A_{ij} + 2B_{ij})^2/\{8(A_{ij} + B_{ij})\} \tag{38c}$$

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 10^{-1} K the elastic constants reach their low symmetry value of

$$C_{ij} + F_{ij}A_{ij}. \tag{38d}$$

We conclude that the SOE anomalies are temperature dependent, showing a discontinuity at the transition temperature.

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