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Second order elastic anomalies in barium titanate from orthorhombic to rhombohedral phase transition

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Abstract. The anomalies in second order elastic constants have been derived for barium titanate for the phase transition from orthorhombic to rhombohedral state. The equilibrium values of order parameter, strain variables and fluctuations in order parameter have been derived using stability conditions and Landau-Khalatnikov equations respectively. Expression for shift in specific heat is obtained. All the anomalies in second order elastic constants have been derived and relations among them reported. The numerical values of anomalies in the individual constants are calculated and their variation is represented graphically. Changes in elastic constants occur over a range of temperature of the order 10^{-2} K.

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 author in an earlier communication studied systematically [1] the anomalies of the second, third and fourth-order elastic constants arising from the cubic to the tetragonal phase and from tetragonal to the orthorhombic phase. Barium titanate undergoes yet another phase transition on cooling further below -70 C from orthorhombic to the rhombohedral $R_{3m}(C_{3v}^5)$ phase in which the polarization vector is directed along the [111] direction. This group is a subgroup of the parent (cubic) phase.

In this paper, the anomalies of the second-order elastic constants arising from the phase transition from the orthorhombic to rhombohedral phase are reported. The equilibrium values of the order parameter components and the strain variables are obtained from the stability conditions while the fluctuations in the order parameter are derived from Landau–Khalatnikov equation. In § 2 expressions for the equilibrium values of order parameter and strain variables are derived. In § 3 expressions for fluctuations in order parameter in terms of strain variables using Landau–Khalatnikov equations are obtained. Section 4 gives a single formula for all the second order elastic (SOE) anomalies in the rhombohedral phase. Relations among the SOE anomalies have been derived. The numerical equations for the anomalies of the individual SOE constants are given and their temperature variation is discussed.

2. Equilibrium values of the order parameters and the strain variables

The free energy of the crystal is given by

$$F = F_{ela} + F_L + F_c \tag{1}$$

where F_{ela} is the elastic energy, F_L is Landau energy and F_c is coupling energy. The expressions for the various energies are taken from the earlier publication [1]. In the present case $P_x = P_y = P_z \neq 0$. For the stability of the crystal, the partial derivatives of F with respect to strain variables and order parameter components must vanish. Using the expression for free energy and solving the nine equations for the stability of the crystal the equilibrium values of strain variables $\eta_{i0}(i = 1 \text{ to } 6)$ and order parameter components are obtained. They are

$$\eta_{10} = \eta_{20} = \eta_{30} = X_1 P_{z0}^2 \tag{2}$$

$$\eta_{40} = \eta_{50} = \eta_{60} = Z_1 P_{z0}^2 \tag{3}$$

where

$$P_{x0}^2 = P_{y0}^2 = P_{z0}^2 = \frac{-a}{b + 4C - 2X - 2Z} = -aP, \tag{4a}$$

$$X_1 = -\frac{g_{11} + 2g_{12}}{C_{11} + 2C_{12}}, \tag{4b}$$

$$Z_1 = -\frac{g_{44}}{C_{44}}, \tag{4c}$$

$$X = \frac{(g_{11} + 2g_{12})^2}{(c_{11} + 2c_{12})}, \tag{4d}$$

$$Z = \frac{g_{44}^2}{c_{44}}, \tag{4e}$$

$$a = a''(T - T_c). \tag{4f}$$

1 = In the above equations (2) to (4) a'', b, C, g_{11}, g_{12} and g_{44} are constants. The numerical values of above constants except a'' and for the elastic constants C_{11}, C_{12} and C_{44} are taken as given by Devonshire [2] who first applied Landau theory to barium titanate. They are

$$b = 65{\cdot}6 \times 10^{-12}, C = -0{\cdot}1 \times 10^{-12}, g_{11} = -11{\cdot}2$$

$$g_{12} = 0{\cdot}8,\ g_{44} = -8,\ C_{11} = 6{\cdot}0 \times 10^{12}\,\text{dyne/cm}^2$$

$$C_{44} = C_{12} = 3{\cdot}0 \times 10^{+12}\,\text{dyne/cm}^2. \tag{5}$$

From the above numerical values we find that

$$P = +0{\cdot}151 \times 10^{12}, \tag{6a}$$

$$X = 7{\cdot}68 \times 10^{-12}, \tag{6b}$$

$$Z = 21{\cdot}6 \times 10^{-12}, \tag{6c}$$

3. Landau–Khalatnikov equations

As explained in an earlier communication [1] the three LK equations are

$$\dot{P}_x = -\Gamma_1 \frac{\partial F}{\partial P_x}, \tag{7a}$$

$$\dot{P}_y = -\Gamma_2 \frac{\partial F}{\partial P_y}, \tag{7b}$$

$$\dot{P}_z = -\Gamma_3 \frac{\partial F}{\partial P_z}. \tag{7c}$$

The symmetry of the rhombohedral phase requires $\Gamma_1 = \Gamma_2 = \Gamma_3 = \Gamma$. 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 by ignoring product terms of higher order derivatives and further by writing P_i^* to be proportional to $e^{i\Omega t}$ where Ω is angular frequency of acoustic wave we arrive at the following expressions for the various derivatives

$$\left(\frac{\partial^2 F}{\partial P_k^2}\right)_0 = aP' \quad (k = x, y, z) \tag{8a}$$

where

$$P' = a(1 - 3bP - 4CP + 2PX] \tag{8b}$$

$$\left(\frac{\partial^2 F}{\partial P_x \partial P_y}\right)_0 = \left(\frac{\partial^2 F}{\partial P_y \partial P_z}\right)_0 = \left(\frac{\partial^2 F}{\partial P_z \partial P_x}\right)_0 = aP[Z - 4C] \tag{8c}$$

$$\left(\frac{\partial^2 F}{\partial \eta_1 \partial P_x}\right)_0 = \left(\frac{\partial^2 F}{\partial \eta_2 \partial P_y}\right)_0 = \left(\frac{\partial^2 F}{\partial \eta_3 \partial P_z}\right)_0 = 2g_{11}(-aP)^{1/2} \tag{8d}$$

$$\left(\frac{\partial^2 F}{\partial \eta_i \partial P_x}\right)_0 = \left(\frac{\partial^2 F}{\partial \eta_j \partial P_y}\right)_0 = \left(\frac{\partial^2 F}{\partial \eta_k \partial P_z}\right)_0 = 2g_{12}(-aP)^{1/2}$$

for

$$i = 2 \text{ and } 3 \text{ for } j = 1 \text{ and } 3 \text{ for } k = 1 \text{ and } 2 \tag{8e}$$

$$\left(\frac{\partial^2 F}{\partial \eta_i \partial P_x}\right)_0 = \left(\frac{\partial^2 F}{\partial \eta_j \partial P_y}\right)_0 = \left(\frac{\partial^2 F}{\partial \eta_k \partial P_z}\right)_0 = g_{44}(-aP)^{1/2}$$

and

$$\text{for } i = 5 \text{ and } 6 \text{ for } j = 4 \text{ and } 6 \text{ for } k = 4 \text{ and } 5 \tag{8f}$$

and all other second order derivatives are zero.

By substituting above relations in LK equations and solving for the fluctuations in order parameter components in terms of strain variables the following relations are obtained.

$$P_k^* = \alpha_{ki} \eta_i^*, \; k = x, y, z \text{ and } i = 1 \text{ to } 6. \tag{9}$$

The values of

$$\alpha_{x1} = \alpha_{y2} = \alpha_{z3} = -\frac{\Gamma P_{z0} A}{(a' - b')(a' + 2b')}, \tag{10a}$$

$$\alpha_{x2}=\alpha_{x3}=\alpha_{y1}=\alpha_{y3}=\alpha_{z1}=\alpha_{z2}=-\frac{\Gamma P_{z0}B}{(a'-b')(a'+2b')}, \tag{10b}$$

$$\alpha_{x4}=\alpha_{y5}=\alpha_{z6}=\frac{2\Gamma P_{z0}g_{44}b'}{(a'-b')(a'+2b')}, \tag{10c}$$

$$\alpha_{x5}=\alpha_{x6}=\alpha_{y4}=\alpha_{y6}=\alpha_{z4}=\alpha_{z5}=-\frac{\Gamma P_{z0}g_{44}a'}{(a'-b')(a'+2b')} \tag{10d}$$

where

$$a'=aP'\Gamma(1+i\Omega\tau], \tag{11a}$$

$$b'=aP\Gamma[-Z+4C], \tag{11b}$$

$$A=2g_{11}a'+2g_{11}b'-4g_{12}b', \tag{11c}$$

$$B=2g_{12}a'-2g_{11}b'. \tag{11d}$$

The relaxation time

$$\tau=\left[\Gamma\left(\frac{\partial^2 F}{\partial P_z^2}\right)_0\right]^{-1}. \tag{11e}$$

4. Elastic anomalies in rhombohedral phase

Substituting $\eta_i=\eta_{i0}+\eta_i^*$ and $P_j=P_{j0}+P_j^*$ ($i=1$ to 6 and $j=x,y$ and z), the expression for free energy becomes,

$$\begin{aligned}
&1/2C_{ij}(\eta_{i0}+\eta_i^*)(\eta_{j0}+\eta_j^*)+\frac{a}{2}[(P_{z0}+P_x^*)^2+(P_{z0}+P_y^*)^2+(P_{z0}+P_z^*)^2]\\
&+\frac{b}{4}[(P_{z0}+P_x^*)^4+(P_{z0}+P_y^*)^4+(P_{z0}+P_z^*)^4]\\
&+C[(P_{z0}+P_x^*)^2(P_{z0}+P_y^*)^2+(P_{z0}+P_y^*)^2(P_{z0}+P_z^*)^2\\
&+(P_{z0}+P_z^*)^2(P_{z0}+P_x)^2]\\
&+g_{11}[(\eta_{10}+\eta_1^*)(P_{z0}+P_x^*)^2+(\eta_{20}+\eta_2^*)(P_{z0}+P_y^*)^2\\
&+(\eta_{30}+\eta_3^*)(P_{z0}+P_z^*)^2]\\
&+g_{12}[(\eta_{10}+\eta_1^*)\{(P_{z0}+P_y^*)^2+(P_{z0}+P_z^*)^2\}\\
&+(\eta_{20}+\eta_2^*)\{(P_{z0}+P_z^*)^2+(P_{z0}+P_x^*)^2\}\\
&+(\eta_{30}+\eta_3^*)\{(P_{z0}+P_x^*)^2+(P_{z0}+P_y^*)^2\}]\\
&+g_{44}[(\eta_{40}+\eta_4^*)(P_{z0}+P_y^*)(P_{z0}+P_z^*)\\
&+(\eta_{50}+\eta_5^*)(P_{z0}+P_z^*)(P_{z0}+P_x^*)+(\eta_{60}+\eta_6^*)(P_{z0}+P_x^*)(P_{z0}+P_y^*)]
\end{aligned} \tag{12}$$

In the above expression for free energy the linear terms in η_i^* vanishes in view of the stability conditions. F_0 and F_2 correspond to terms of order zero and two in the strain variables respectively. F_0 gives the shift in zero point energy at the transition temperature. Its derivative with respect to temperature will give the specific heat anomaly at the transition temperature.

$$F_0 = -\frac{3}{4}a^2 P = -\frac{3}{4}[a''^2(T - T_c)^2]P, \tag{13}$$

$$\Delta C_v = \left(\frac{\partial F_0}{\partial T}\right)_v = -\frac{3}{2}a''^2 P(T - T_c)$$
$$= -0{\cdot}227a''^2(T - T_c) \times 10^{12}. \tag{14}$$

The change in specific heat is proportional to $(T - T_c)$.

By collecting all the terms which are quadratic in strain variables, the expression for F_2 is

$$F_2 = \frac{1}{2}\sum_{ij} C^*_{ij}\eta^*_i\eta^*_j \tag{15}$$

where C^*_{ij} represents the modified SOE constants.

Let us write

$$C^*_{ij} = C_{ij} + \Delta C^*_{ij} \tag{16}$$

ΔC^*_{ij} then gives the anomalies in SOE constants arising from the phase transition. Substituting the expressions for $P^*_k(k = x, y, z)$ in (12) from (9) and (10) and collecting all terms containing $\eta^*_i\eta^*_j$ the expression for SOE anomalies is

$$\begin{aligned}\frac{\Delta C^*_{ij}}{2}\eta^*_i\eta^*_j &= (\alpha_{xi}\alpha_{xj} + \alpha_{yi}\alpha_{yj} + \alpha_{zi}\alpha_{zj})P^2_{z0}\left[\frac{a}{2P^2_{z0}} + \frac{3b}{2} + 2C - X\right]\eta^*_i\eta^*_j\\
&+ (\alpha_{xi}\alpha_{yj} + \alpha_{yi}\alpha_{zi} + \alpha_{zi}\alpha_{xj})P^2_{z0}(4C - Z)\eta^*_i\eta^*_j\\
&+ 2P_{z0}g_{11}[\alpha_{xi}\eta^*_1\eta^*_i + \alpha_{yi}\eta^*_2\eta^*_i + \alpha_{zi}\eta^*_3\eta^*_i]\\
&+ [2P_{z0}g_{12}(\eta^*_1 + \eta^*_2) + g_{44}P_{z0}(\eta^*_4 + \eta^*_5)]\alpha_{zi}\eta^*_i\\
&+ [2P_{z0}g_{12}(\eta^*_3 + \eta^*_1) + g_{44}P_{z0}(\eta^*_4 + \eta^*_6)]\alpha_{yi}\eta_i\\
&+ [2P_{z0}g_{12}(\eta^*_2 + \eta^*_3) + g_{44}P_{z0}(\eta_5 + \eta_6)]\alpha_{xi}\eta^*_i.\end{aligned} \tag{17}$$

The following relations among the elastic anomalies can easily be verified by giving integral values for the indices i and j ranging from 1 to 6

$$\Delta C^*_{11} = \Delta C^*_{22} = \Delta C^*_{33}, \tag{18a}$$

$$\Delta C^*_{44} = \Delta C^*_{55} = \Delta C^*_{66}, \tag{18b}$$

$$\Delta C^*_{12} = \Delta C^*_{13} = \Delta C^*_{23}, \tag{18c}$$

$$\Delta C^*_{14} = \Delta C^*_{25} = \Delta C^*_{36}, \tag{18d}$$

$$\Delta C^*_{15} = \Delta C^*_{16} = \Delta C^*_{24} = \Delta C^*_{26} = \Delta C^*_{34} = \Delta C^*_{35}, \tag{18e}$$

$$\Delta C^*_{45} = \Delta C^*_{46} = \Delta C^*_{56}. \tag{18f}$$

The anomalies in SOE constants show that the velocities of the sound waves undergo a change during the phase transition. The complex nature of the anomalies indicates

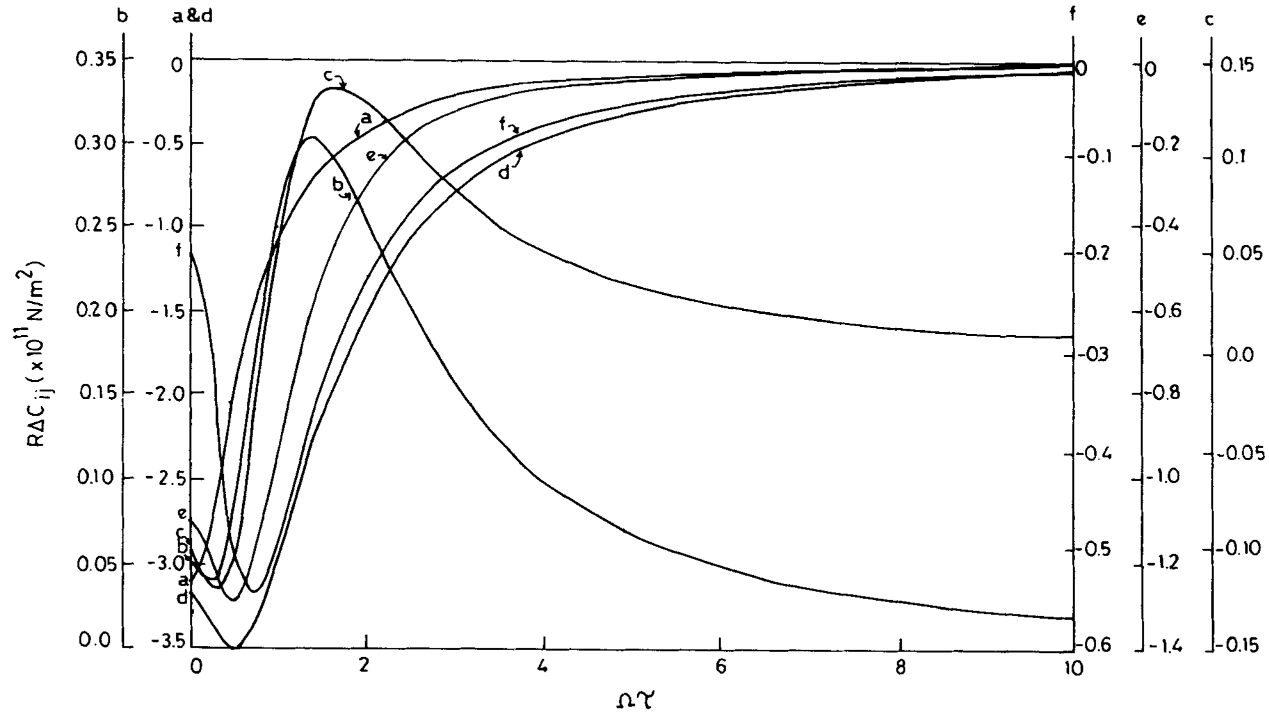

Figure 1. Variation of real part of $\Delta C_{ij}^* = R\Delta C_{ij}^*$ with respect to product of circular frequency and relaxation time $\Omega\tau$ according to Landau theory. a) $R\Delta C_{44}^*$ vs $\Omega\tau$; b) $R\Delta C_{12}^*$ vs $\Omega\tau$; c) $R\Delta C_{14}^*$ vs $\Omega\tau$; d) $R\Delta C_{11}^*$ vs $\Omega\tau$; e) $R\Delta C_{15}^*$ vs $\Omega\tau$; f) $R\Delta C_{45}^*$ vs $\Omega\tau$.

that the waves are attenuated in this region. Using the numerical values of the different constants given in (8) the real part of the anomalies in the individual SOE constants are given by

$$R\Delta C^*_{11} = -\frac{[3{\cdot}18 + 20{\cdot}17\Omega^2\tau^2 + 33{\cdot}44\Omega^4\tau^4 + 17{\cdot}8\Omega^6\tau^6]}{[1 + 2{\cdot}6\Omega^2\tau^2 + 1{\cdot}44\Omega^4\tau^4]^2} \times 10^{12}, \quad (19a)$$

$$R\Delta C^*_{44} = -\frac{[3{\cdot}1 + 7{\cdot}7\Omega^2\tau^2 + 10{\cdot}2\Omega^4\tau^4 + 4{\cdot}5\Omega^6\tau^6]}{[1 + 2{\cdot}6\Omega^2\tau^2 + 1{\cdot}44\Omega^4\tau^4]^2} \times 10^{12}, \quad (19b)$$

$$R\Delta C^*_{12} = +\frac{[0{\cdot}05 - 0{\cdot}15\Omega^2\tau^2 + 3\Omega^4\tau^4 + 3{\cdot}9\Omega^6\tau^6]}{[1 + 2{\cdot}6\Omega^2\tau^2 + 1{\cdot}44\Omega^4\tau^4]^2} \times 10^{12}, \quad (19c)$$

$$R\Delta C^*_{14} = +\frac{[-0{\cdot}1 - 1{\cdot}8\Omega^2\tau^2 + 1{\cdot}06\Omega^4\tau^4 + 2{\cdot}125\Omega^6\tau^6]}{[1 + 2{\cdot}6\Omega^2\tau^2 + 1{\cdot}44\Omega^4\tau^4]^2} \times 10^{12}, \quad (19d)$$

$$R\Delta C^*_{15} = -\frac{[1{\cdot}1 + 8\Omega^2\tau^2 + 12{\cdot}5\Omega^4\tau^4 + 1{\cdot}65\Omega^6\tau^6]}{[1 + 2{\cdot}6\Omega^2\tau^2 + 1{\cdot}44\Omega^4\tau^4]^2} \times 10^{12}, \quad (19e)$$

$$R\Delta C^*_{45} = -\frac{[0{\cdot}2 + 3{\cdot}7\Omega^2\tau^2 + 6\Omega^4\tau^4 + 2{\cdot}4\Omega^6\tau^6]}{[1 + 2{\cdot}6\Omega^2\tau^2 + 1{\cdot}44\Omega^4\tau^4]^2} \times 10^{12}. \quad (19f)$$

The relaxation time τ has a temperature dependence given by Lemanov [3]

$$\tau = \tau_0/|T_c - T| \quad (20)$$

where τ_0 has a value of the order 10^{-11} to 10^{-10}sK. Under experimental conditions the acoustic frequency Ω is chosen in the range 10^8–10^9Hz. Hence $\Omega\tau_0$ has a value of the order of 10^{-2} to 10^{-3}. The temperature dependence of anomalies can now be easily understood by writing $C^*_{ij} = C_{ij} + R\Delta C^*_{ij}$. The variation of real part of the anomalies is shown in figure 1. At $T = T_c$, $\tau \to \infty$ and all the anomalies vanish. It is seen from figure that the anomalies occur over a range of temperature 10^{-2}K below the transition temperature. The real part of ΔC^*_{44} falls to the value in rhombohedral phase. On the other hand the real parts of ΔC^*_{12} and ΔC^*_{14} reach maximum values and have a dip and rise again to the values in the rhombohedral phase. The real parts of ΔC^*_{11}, ΔC^*_{15} and C^*_{45} have a dip and rise again to the values in the rhombohedral phase. Unfortunately no experimental data are available as yet for comparison. Hopefully the present work will stimulate experimental investigations.

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