# Landau expansion parameters for BaTiO3

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# Landau expansion parameters for $BaTiO_3$

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The 6th order Taylor expansion of the free energy in terms of the order parameter has been generally accepted to describe first order structural phase transitions. In recently years, some researchers added the 8th order terms in order to explain the two branches in dielectric loops observed in the $BaTiO_3$ single crystal. We show that the Landau free energy terminated at the 6th orders is sufficient to fit the experimental observations if the rich information in the field-induced phase transitions is explored. By using the typical characteristics of ferroelectric and dielectric double loops above the Curie temperature $T_c$, the temperature-dependent expansion coefficients can be determined with high accuracy. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4838456]

## I. INTRODUCTION

Landau phenomenological theory is commonly accepted to describe and predict ferroelectric phase transition and temperature dependence of material properties.[1–3] Although without much details in the microscopic scale, the theory with the free energy simply expanded in powers of order parameters, such as polarization and strain, can explain a lot of macroscopic phenomena based on thermodynamic concepts. Predictions for single crystals,[4–6] ceramics,[7,8] and films[9–12] agreed well with experimental observations and gave valuable guidance for material fabrications and applications. With the decrease of system size, phenomenological theories with modified free energy considering the effects of strain, surface, size, defect, and electrodes were also adopted for nanoscale materials based on the free energy of the bulk counterparts,[13–15] and have demonstrated great success. For example, critical thickness was predicted to be several atomic layers for $BaTiO_3$ and $PbTiO_3$,[15–17] which agreed well with the first principle's calculations[18] and synchrotron radiation detections.[19]

The Landau theory was first used for second order phase transitions with a basic assumption that the transition between the high and low temperature phases takes place continuously at a given temperature.[20] Since most of the structural transitions and a number of magnetic transitions were found to be discontinuous, the validity of the Landau theory was checked in various systems with first-order phase transition.[21] Under rigid symmetry framework relating to the form of interaction between various degrees of freedom, the 6th order Taylor series expansions were commonly accepted as the basic free energy format describing the first order paraelectric-ferroelectric phase transition in $BaTiO_3$ single crystal. Recently, the 8th order nonlinear polarization terms were adopted to describe the existence of monoclinic and triclinic phases in the $Pb(Zr,Ti)O_3$ system,[22] which could be explained also by the existence of local field induced by space charges. The role of the 8th order terms was also considered necessary in the $BaTiO_3$ system with a large external strain and using a free energy with only the first second order term to be temperature-dependent.[23] However, it was shown that higher order expansion coefficients are actually temperature dependent in Ref. 24, and the 8th orders were adopted to explain the electric induced polarization loops and complex dielectricity nonlinearity in high temperatures.

From the point view of mathematics, polynomial with higher-order expansion terms will give higher accuracy, especially at very low temperatures, but may induce more fluctuations. On the other hand, simplicity is also very important for a theoretical model. The number of terms in the expansion should be as less as possible, so long as all phenomena can be described. Most importantly, all expansion coefficients need to have physical meanings and correspond to measurable quantities in order to be determined uniquely. Usually, the free energy curve for a system much below the phase transition temperature is a simple double well without too much information about higher order polynomials to fit the expansion coefficients. One possible way is to use the temperature dependent X-ray data accompanied with the phase boundaries in the phase diagram.[25] Since the order parameter fluctuation near the Curie temperature has rich information of all polynomials, such as the double loops[26,27] and triple loops,[28] another way is to use emerged typical critical points (zero points and inflection points) in the polynomials and their corresponding derivatives. The first, second, and third derivatives of the free energy with respect to the polarization are directly related to the polarization-electric field loop, dielectric-electric field loop, and the dielectric stiffness properties, respectively. Typical points in these curves can be used to extract the Landau expansion coefficients up to the 6th order.[29] However, higher order terms, such as the 8th order expansions, require additional information and their physical meaning is unclear so that direct measurement is not possible.

In this work, theoretical analyses of the existence of complex polarization-electric field and dielectric-electric field

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loops in temperatures around the Curie temperature were carried out and compared with experimental results. The unusual dielectric double loop, which was considered as a clue for adding the 8th order expansion terms, was illustrated by using only a 6th order expansion. A method to find and check the whole set of Landau parameters for bulk single ferroelectric crystals with first order phase transition was given under the frame work of Landau theory with free energy expansion up to the 6th order in terms of the order parameter.

## II. SIXTH-ORDER THERMODYNAMIC POTENTIAL

In macroscopic level, the considered material is treated as a continuum without considering the underlying atomic structures. A dielectric system can be described by three independent variables, chosen from the conjugate pairs (temperature $T$, entropy $S$), (stress $\mathbf{X}$, strain $\mathbf{x}$), and (electric field $\mathbf{E}$, electric displacement $\mathbf{D}$). According to Lines and Glass,[30] electric displacement $\mathbf{D}$ should be chosen as the order parameter rather than the polarization $\mathbf{P}$ because the electrostatic work function is actually expressed in terms of the Maxwell electric field $\mathbf{E}$ and electric displacements $\mathbf{D}$. However, for experimental convenience and historical customary, polarization $\mathbf{P}$ is usually chosen as the order parameter since $\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P}$ with the term $\varepsilon_0\mathbf{E}$ ($\varepsilon_0 = 8.85 \times 10^{-12}$) to be negligibly small in ferroelectric materials. Without electric field, the electric displacement equals to the polarization which is known as the spontaneous polarization. However, with the existence of electric field, including applied external electric field, depolarization field, and electric fields induced by defects and space charges, the polarization $\mathbf{P}$ should be regarded as the total polarization.

The equilibrium state corresponds to the minimum of the Gibbs free energy $G$ with respect to all its independent variables. Under quasi-static and adiabatic condition (no change of Enthalpy), the change of $G$ for bulk ferroelectric materials with small deviations from the prototype equilibrium state can be expressed as a Taylor series of $D_i$ and $X_i$

$$G - G_0 = \frac{\partial G}{\partial X_i}X_i + \frac{\partial G}{\partial D_i}D_i + \frac{1}{2}\frac{\partial^2 G}{\partial X_i X_j}X_i X_j + \frac{1}{2}\frac{\partial^2 G}{\partial D_i D_j}D_i D_j + \frac{1}{2}\frac{\partial^2 G}{\partial X_i D_j}X_i D_j \ldots \quad (1)$$

Under zero stress ($X_i = 0$), the free energy of ferroelectrics, with centrosymmetric paraelectric state as the prototype, can be expressed as a simple polynomial terminated in the six-order term for a one dimensional system

$$\Delta G = \alpha D^2 + \beta D^4 + \gamma D^6, \quad (2)$$

where $\alpha = \frac{1}{2}\partial^2 G/\partial D^2$, $\beta = \frac{1}{4!}\partial^4 G/\partial D^4$, $\gamma = \frac{1}{6!}\partial^6 G/\partial D^6$ are the dielectric stiffness coefficients. As stated above, at temperatures far away from the transition points, typical features of higher order terms are buried. Whereas, at temperatures near the Curie temperature $T_c$, the features related with higher order terms can emerge, i.e., the electric field induced phase transition exists (Double loops). It is also an obvious hint for dielectricity with two branches, which was the main argument to adopt the 8th order terms.[24]

For a clear illustration, we will use dimensionless functions following Merz[26] to show the rich information in the electric induced double loops and the dielectric behaviors around the Curie temperature. We assumed that the total polarization $P \approx D$ for ferroelectrics. With dimensionless variables $p = (-3\gamma/\beta)^{1/2}P$, $t = 3\alpha\gamma/\beta^2$, $e = (-27\gamma^3/\beta^5)^{1/2}E$, and $f = -9\gamma^2/\beta^3\delta G$, the Gibbs free energy and the dielectric equation of state can be normalized as dimensionless forms as $f = tp^2 - p^4 + \frac{1}{3}p^6$ and $e = 2tp - 4p^3 + 2p^5$, respectively.

Polynomial curves can be recognized by those typical points, i.e., zero points and inflection points. As shown in Fig. 1, there are four typical dimensionless temperatures:

(1) $t = t_0 = 0$, corresponding to the Curie-Weiss temperature $T_0$. $f = 0$ has only one positive root $p = \sqrt{3}$, and $e = 0$ has one positive root $p = \sqrt{2}$ corresponding to the minimum point of $f$.
(2) $t = t_c = 3/4$, known as the Curie temperature and derived from the determinant $\Delta_f = 1 - 4t/3 = 0$ of function $f = 0$ with Vieta's theorem. $f = 0$ has one positive root besides the zero one. This is also the direct hint of first order phase transition where the polarization jumps to a non-polar state without the change of free energy and a bifurcation exists.
(3) $t = t_1 = 1$, derived from the determinant $\Delta_e = 0$ of function $e = 0$. $f = 0$ has no positive root, but one pair of inflection points, which corresponds to the positive root of $e = 0$, indicating the initiation of the double loop.

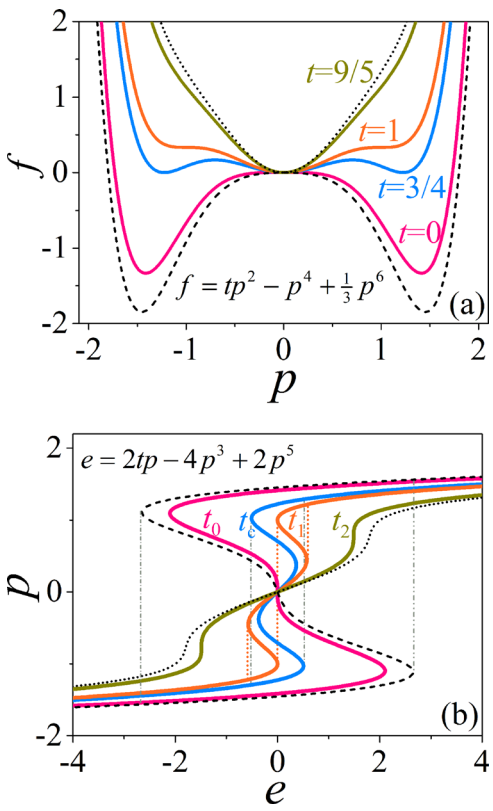



FIG. 1. Dimensionless (a) Landau free energy $f$ and (b) polarization $p$ with respect to electric field $e$.

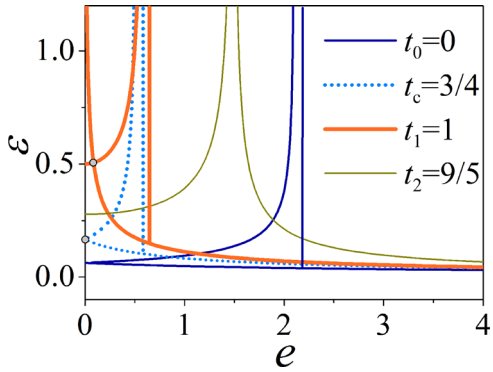



FIG. 2. Dimensionless dielectricity loop vs. electric field under typical temperatures.

(4) $t = t_2 = 9/5$, derived from $\Delta_{\partial e/\partial p} = 0$. Both equations $f = 0$ and $e = 0$ have no positive root, while the function of $e$ has one pair of inflection points and function of $\partial e/\partial p$ has only one positive root besides the zero one.

The dimensionless dielectricity can be derived as $\varepsilon = \partial e/\partial p = 2t - 12p^2 + 10p^4$. The inflections in the $p$-$e$ loops always correspond to the infinity of $\varepsilon$. For temperatures lower than $t_0$ and higher than $t_2$, in the ferroelectric and paraelectric states, respectively, $\varepsilon - e$ curves are only with one pair of infinite peaks as expected. For temperature between $t_0$ and $t_2$, zigzag $p - e$ curve has more than one pair of dielectric infinities overlapped. As shown in Fig. 2, two branches of the dielectricity cross each other at $E = 0$ when $t = t_c$. This point shifts away until the temperature reaches $t_2$, at which double loop disappears and no cross-point exists in the permittivity vs. the electric field curve.

The dielectric loops for temperature $t_c < t < t_1$ and $t_1 < t < t_2$ are particularly interesting. For temperature range of $t_c < t < t_1$, the $p - e$ loop exists an overlap, resulting the dielectric response with double peaks in each side of electric field as shown in Fig. 3. Unfortunately, this phenomenon has not been observed. With the increase of temperature, the overlap hysteresis loops depart from each other, and become two separated loops as shown in the inset of Fig. 3. The dielectric response turns out to be a significantly different shape from that in Fig. 3. Luckily, this phenomenon was captured in the experiment described in Ref. 24. However, it was used as the reason for the need of 8th order expansions. Due to the complex nature of the ferroelectric and dielectric behaviors under electric field, it is obvious that Landau parameters cannot be fitted only by using one section of the curve as practiced in Ref. 24. We also noted that, near the tetragonal to orthorhombic phase transition, triple loops exist, corresponding with more complex dielectric loops.[28]

## III. TYPICAL POINTS TO FIT THE LANDAU PARAMETERS

With the rich information in electric induced double loops and dielectric loops, the polynomial coefficients can be theoretically determined. In fact, some of these typical characteristics were clearly observed and used to find the parameters of the polynomial.[29] The critical conditions and the corresponding critical temperatures were listed in Table I.

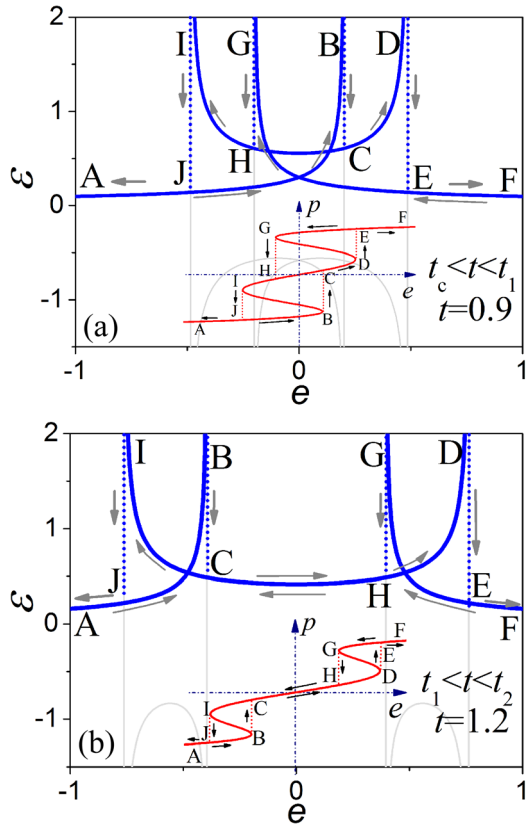



FIG. 3. Dielectric response (a) in temperature range of $t_c < t < t_1$ and (b) in temperature range of $t_1 < t < t_2$. Inset is the corresponding $p$-$e$ loop.

Some of them were calculated by using the existing parameters of free energy up to the 6th order explanations. As stated in Table I, the observed $t_0$ increases with the published years. This is not surprising because of the improvement in fabrication method and quality of crystals. Since the Curie and Curie Weiss temperatures are highly related with the composition, the stoichiometry, defects, electric and mechanical boundary conditions, the extracted parameters will vary with such factors and probably cannot agree exactly with each other.[31]

Actually, it is not difficult to extract the parameter based on the above theory. The whole quadratic coefficients and higher order coefficients of the Landau free energy can be derived by cutting the crystal in [001], [011], and [111] directions. Starting from the work of Devonshire, the Gibbs free energy is only composed of the Landau-type free-energy density functional $f_L$ written as systematic-expansion $O_h$-symmetry-invariant terms in components of polarization $P_i (i = 1,2,3)$

TABLE I. Critical conditions and typical temperatures (Unit in °C).

| $T_0(t_0 = 0)$ | $T_c(t_c = 3/4)$ | $T_1(t_1 = 1)$ | $T_2(t_2 = 9/5)$ | References |
|---|---|---|---|---|
| 96.5[a] | 107.5[a] | | | Merz[26] |
| 108[a] | 108.64 | 108.83 | 109.37 | Buessem *et al.*[33] |
| 100.8[a] | 111.6[a] | 115.4[a] | 126.4[a] | Gonzalo and Rivera[29] |
| 108[a] | 119.28 | 121.98 | 128.57 | Bell and Cross[4] |
| 110[a] | 115.26 | 116.69 | 120.51 | Pertsev *et al.*[9] |
| 118[a] | 130[a] | <135[a] | >135[a] | Wang *et al.*[24] |

[a]Experimental data.

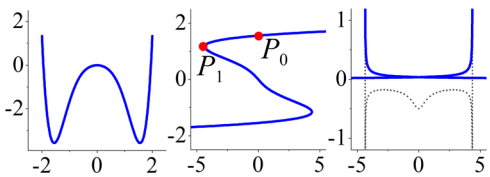
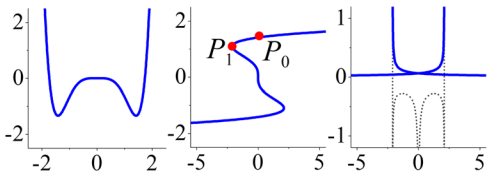
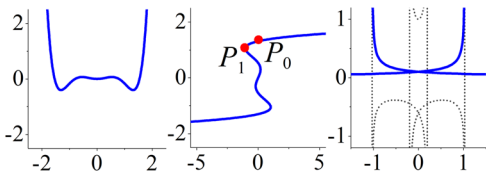
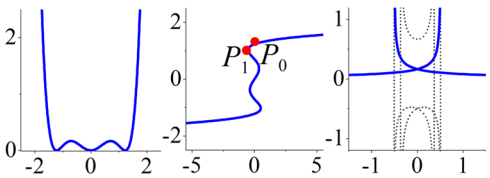
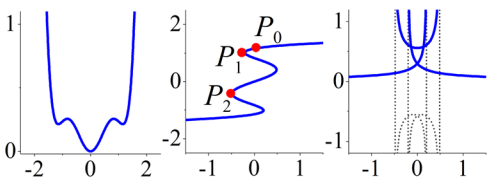
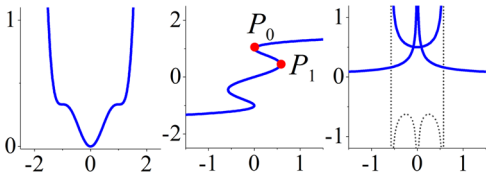
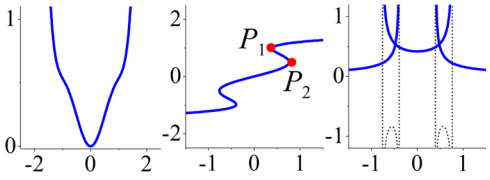
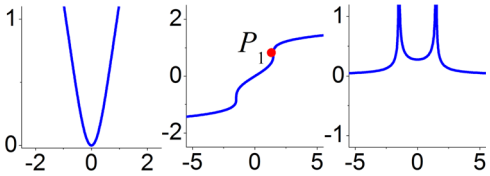
$$f_L = \alpha_1(P_1^2+P_2^2+P_3^2)+\alpha_{11}(P_1^4+P_2^4+P_3^4)+\alpha_{12}(P_1^2P_2^2+P_2^2P_3^2+P_3^2P_1^2)+\alpha_{111}(P_1^6+P_2^6+P_3^6)$$
$$+\alpha_{112}[P_1^2(P_2^4+P_3^4)+P_2^2(P_3^4+P_1^4)+P_3^2(P_1^4+P_2^4)]+\alpha_{123}P_1^2P_2^2P_3^2. \quad (3)$$

The change of the Gibbs free energy under external electric field will be

$$\Delta G = f_L - E_1P_1 - E_2P_2 - E_3P_3. \quad (4)$$

For field-induced phase transition from cubic directly to tetragonal, orthorhombic, and rhombohedra in crystals with crystal direction of [001], [011], and [111], respectively, the

TABLE II. Temperature-dependent Landau parameters from experiment. $\alpha = \alpha_0(T - T_c)$ and $\alpha_0 = 1/(C\varepsilon_0)$ with $C$ the Curie-Weiss constant determined from the inverse-dielectric property with respect to temperature. $\varepsilon$ is the dielectric susceptibility at $E = 0$. $P_0$ is the polarization under zero electric field, and $P_1$ and $P_2$ are polarizations in the reflection points.

| Temperature | $f-p, p-e$ and $\varepsilon - e$ curves | Temperature dependent parameters |
|---|---|---|
| $t=-1$ |  | $\beta = \frac{-\alpha}{2P_0^2P_1^2}\frac{(P_0^4-5P_1^4)}{(3P_0^2-5P_1^2)}$<br>$\gamma = \frac{\alpha}{3P_0^2P_1^2}\frac{(P_0^2-3P_1^2)}{(3P_0^2-5P_1^2)}$ |
| $T_0(t_0=0)$ |  | $\beta = \frac{-1}{8\varepsilon P_0^2}, \gamma = \frac{1}{12\varepsilon P_0^4}$ |
| $t=0.5$ |  | $\beta = \frac{-\alpha}{2P_0^2P_1^2}\frac{(P_0^4-5P_1^4)}{(3P_0^2-5P_1^2)}$<br>$\gamma = \frac{\alpha}{3P_0^2P_1^2}\frac{(P_0^2-3P_1^2)}{(3P_0^2-5P_1^2)}$ |
| $T_c(t_c=3/4)$ |  | $\beta^2 = 4\alpha\gamma, \beta = \frac{-2\alpha}{P_0^2}, \gamma = \frac{\alpha}{P_0^4}$ |
| $t=0.9$<br>$T_c<T<T_1$ |  | $\beta = \frac{-\alpha}{2P_0^2P_1^2}\frac{(P_0^4-5P_1^4)}{(3P_0^2-5P_1^2)}$<br>$\gamma = \frac{\alpha}{3P_0^2P_1^2}\frac{(P_0^2-3P_1^2)}{(3P_0^2-5P_1^2)}$ |
| $T_1(t_1=1)$ |  | $\beta^2 = 3\alpha\gamma, \beta = \frac{-\alpha}{P_0^2}, \gamma = \frac{\alpha}{3P_0^4}$ |
| $t=1.2\ T_1<T<T_2$ |  | $\beta = \frac{-\alpha(P_1^2+P_1^2)}{6P_1^2P_2^2}$<br>$\gamma = \frac{\alpha}{15P_1^2P_2^2}$ |
| $T_2(t_2=9/5)$ |  | $3\beta^2 = 5\alpha\gamma, \beta = \frac{-\alpha}{3P_1^2}, \gamma = \frac{\alpha}{15P_1^4}$ |

free energy with respect to polarization of $P_3$, $P_{011} = \sqrt{2}P_3$, and $P_{111} = \sqrt{3}P_3$ under electric fields of $E_3$ along the [001] direction, $E_{011} = \sqrt{2}E_3$ along the [011] direction, and $E_{111} = \sqrt{3}E_3$ along the [111] direction can be described by the following equations, respectively,

$$\Delta G_{001} = \alpha_1 P_3^2 + \alpha_{11} P_3^4 + \alpha_{111} P_3^6 - E_3 P_3, \quad (5a)$$

$$\Delta G_{011} = \alpha_1 P_{011}^2 + \alpha_{11}^{O} P_{011}^4 + \alpha_{111}^{O} P_{011}^6 - E_{011} P_{011}, \quad (5b)$$

$$\Delta G_{111} = \alpha_1 P_{111}^2 + \alpha_{11}^{R} P_{111}^4 + \alpha_{111}^{R} P_{111}^6 - E_{111} P_{111}, \quad (5c)$$

where $\alpha_{11}^{O} = \frac{1}{2}\alpha_{11} + \frac{1}{4}\alpha_{12}$, $\alpha_{111}^{O} = \frac{1}{4}(\alpha_{111} + \alpha_{112})$, $\alpha_{11}^{R} = \frac{1}{3}(\alpha_{11} + \alpha_{12})$, and $\alpha_{111}^{R} = \frac{1}{27}(3\alpha_{111} + 6\alpha_{112} + \alpha_{123})$. By using the typical points listed in Table II together with the temperature-dependent inverse dielectricity, the parameters for single crystal in [001] direction can be easily obtained and be verified as temperature dependent. Consequently, the parameters in [011] and [111] directions can be derived.

Based on the phenomenological theory of ferroelectricity in barium titanate by Devonshire,[32] the parameters for this crystal have been modified a lot based on several basic experimental observations, such as the double loop[26] and triple loop.[28] Buessem, Cross, and Goswami (BCG)[33] summarized some important observations[28,34] and gave a set of temperature-dependent coefficients. Later on, Bell and Cross,[4] and Pertsev *et al.*[9] also give a modified parameters based on Ref. 31 without too much explanation. Several most popular Landau parameters for $BaTiO_3$ single crystal were collected and listed in Table III for comparison, including the 6th order expansions by Merz,[26] BCG,[33] Bell and Cross,[4] Pertsev *et al.*,[9] and 8th order expansions by Li *et al.*[23] and Wang *et al.*[24] The problem for the temperature-dependent 6th order expansion is the application for ultrathin films with large compression as mentioned by Li *et al.*[23] Since $\alpha_{111}$ is temperature-dependent, the solution for the polarization will have a singularity at $\alpha_{111} = 0$, corresponding to a temperature of 170 °C. For ultrathin film, the singularity point can be smaller than the phase transition temperature postulated by large compressions based on the linear elasticity assumption. However, in film with strain of about 3%, the nonlinear elasticity could dominate, which may modify the 6th order terms and push the singularity point to a higher temperature. Besides, other factors, such as the surface, interface, depolarization field, may also contribute to the 6th order terms. Piezoelectric effect should also be considered because of the existing depolarization field and bias electric field induced by the asymmetry structure. The parameters modified by Pertsev *et al.*[9] were commonly accepted and can be used for the ultrathin film even with large strain since the temperature-dependent property of $\alpha_{111}$ was transformed to $\alpha_{123}$. However, the change of the coefficient has no experimental support up to date.

## IV. SUMMARY AND DISCUSSION

In recent years, some researchers introduced the 8th order terms in the free energy expansion of the Landau theory. Such practice introduced more number of undetermined coefficients, which have no direct physical meaning and not have corresponding measureable quantities for their unique determination. We studied the typical characteristics around the Curie temperature by using the Landau free energy expansion terminated at the 6th order for a first order structure phase transition in ferroelectrics. Double dielectric-electric loops emerge at temperatures a little higher than the Curie temperature, which indicates that the introduction of

TABLE III. Existing expansion parameters of the Landau polynomial for $BaTiO_3$ single crystal (all in SI units).

| References | $a_1, a_{11}, a_{111}$ | $a_{12}, a_{112}, a_{123}$ | $a_{1111}, a_{1112}, a_{1122}, a_{1123}$ |
|---|---|---|---|
| Merz (Ref. 26) | $3.3 \times 10^5 (T-368.5)$<br>$1.37 \times 10^8$<br>$2.76 \times 10^9$ | —— | —— |
| Buessem *et al.* (Ref. 31) | $3.3 \times 10^5 (T-381)$<br>$4.69 \times 10^6 (T-393)$<br>$-5.38 \times 10^7 (T-393) + 2.68e9$ | $3.23 \times 10^8$<br>$4.36 \times 10^9$<br>—— | —— |
| Bell and Cross (Ref. 4) | $3.34 \times 10^5 (T-381)$<br>$4.69 \times 10^6 (T-393) - 2.02 \times 10^8$<br>$-5.52 \times 10^7 (T-393) + 2.76 \times 10^9$ | $3.23 \times 10^8$<br>$4.47 \times 10^9$<br>$4.91 \times 10^9$ | —— |
| Pertsev *et al.* (Ref. 9) | $3.33 \times 10^5 (T-383)$<br>$3.6 \times 10^6 (T-448)$<br>$6.6 \times 10^9$ | $4.9 \times 10^8$<br>$2.9 \times 10^9$<br>$7.6 \times 10^7 (T-393) + 4.4 \times 10^{10}$ | —— |
| Li *et al.* (Ref. 23) | $4.124 \times 10^5 (T-388)$<br>$-2.097 \times 10^8$<br>$1.294 \times 10^9$ | $7.974 \times 10^8$<br>$-1.950 \times 10^9$<br>$-2.500 \times 10^9$ | $3.863 \times 10^{10}$<br>$2.529 \times 10^{10}$<br>$1.637 \times 10^{10}$<br>$1.367 \times 10^{10}$ |
| Wang *et al.* (Ref. 24) | $3.61 \times 10^5 (T-391)$<br>$-1.83 \times 10^9 + 4 \times 10^6 T$<br>$1.39 \times 10^{10} - 3.2 \times 10^7 T$ | $-2.24 \times 10^9 + 6.7 \times 10^6 T$<br>$-2.2 \times 10^9$<br>$5.51 \times 10^{10}$ | $4.84 \times 10^{10}$<br>$2.53 \times 10^{11}$<br>$2.80 \times 10^{11}$<br>$9.35 \times 10^{10}$ |

8th orders for such phenomena is not necessary for $BaTiO_3$ single crystal. The whole set of the 6th order polynomial coefficients can be obtained from those typical points of electric-field-induced phase transitions around the Curie temperature for single crystals with [001], [011], and [111] orientations, and most of the nonlinear parameters are temperature-dependent as shown in experiments. Existing Landau parameters in the literature were collected and compared. Based on our evaluation, the Landau parameters given by BCG[33] and modified by this research group in 1984[4] were more reasonable for single bulk crystal. However, to study the thin film under large strain, parameters given by Pertsev *et al.*[9] can be adopted. More accurate parameters for bulk and reasonable model for ultrathin films under large strain still need further investigation.

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