Landau thermodynamic potential for BaTiO$_3$

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In this paper the description of the dielectric and ferroelectric properties of BaTiO$_3$ single crystals using the Landau phenomenological thermodynamic potential was addressed. Our results suggest that when using the sixth-power free energy expansion of the thermodynamic potential, remarkably different values of the fourth-power coefficient, β (the coefficient of P_i^4 terms), are required to adequately reproduce the nonlinear dielectric behavior of the paraelectric phase and the electric field induced ferroelectric phase ($E_b \parallel [001]$), respectively. In contrast, the eighth-power expansion with a common set of coefficients enables a good description for both phases at the same time. These features, together with the data available in literature, strongly attest to the necessity of the eighth-power terms in Landau thermodynamic potential of BaTiO$_3$. In addition, the fourth-power coefficients, β and ξ (the coefficient of $P_i^2 P_j^2$ terms), were evaluated from the nonlinear dielectric responses along [001], [011], and [111] orientations in the paraelectric phase. Appreciable temperature dependence was evidenced for both coefficients above T_C. Further analysis on the linear dielectric response of the single domain crystal in the tetragonal phase demonstrated that temperature dependent anharmonic coefficients are also necessary for an adequate description of the dielectric behavior in the ferroelectric phase below T_C. As a consequence, an eighth-power thermodynamic potential, with some of the anharmonic coefficients being temperature dependent, was proposed and compared with the existing potentials. In general the potential proposed in this work exhibits a higher quality in reproducing the dielectric and ferroelectric properties of this prototypic ferroelectric substance. © *2007 American Institute of Physics.*
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I. INTRODUCTION

Structural phase transformation phenomena are an important issue in solid state physics. Both phenomenological and microscopical approaches have been playing comparable roles in understanding the phase transition nature of the magnetics, superconductors, and ferroelectrics. Particularly for ferroelectrics, considerable attention is paid to the phenomenological Landau-Devonshire theory in parallel with advancing techniques of first-principle calculations. In the phenomenology of ferroelectrics, the issue recently attracting attention was the role of high-order anharmonic polarization terms in the Landau free-energy expansion.[1,2] In these works, the terms containing eighth (or higher) power of polarization, traditionally neglected in the phenomenological framework, was demonstrated to be vitally important for the description of the phase diagrams of perovskite ferroelectrics (e.g., for the recently discovered monoclinic phase of some complex perovskites in the vicinity of the morphotropic phase

boundary).[3] The physics behind this effect is the need of high-order terms for adequate description of the symmetry of the problem. Another demarche in the field has been recently undertaken by Li *et al.*, who have revisited the phenomenological theory of classical ferroelectric BaTiO$_3$.[4] These authors suggested the incorporation of the eighth power terms in the Landau expansion of BaTiO$_3$ in order to eliminate the temperature dependence of the anharmonic coefficients and to adapt the description to the situation of large compressive strains. In contrast to Refs. 1 and 2, here no symmetry arguments have been involved. The message by Li *et al.* was that the Landau expansion containing eighth power terms (with temperature independent anharmonic coefficients) is as efficient in the description of many properties of BaTiO$_3$ as the traditional sixth-order expansion with the temperature dependent anharmonic terms.[5,6] This conjecture is of the interest since the strong temperature dependence of the anharmonic coefficients in the BaTiO$_3$ Landau expansion is in conflict with the displacive nature of ferroelectricity in the material, at least under the common assumption that the critical fluctuations are weak in this system.[7,8] Interestingly, in their

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analysis of the Landau potential using first-principles calculations, Iniguez *et al.* obtained that the sixth-order expansion accounts for the main features of the BaTiO$_3$ phase diagram, but that all coefficients in the expansion have nontrivial temperature dependences.[9]

All in all, these results pose two questions. First, are higher than sixth power terms in the BaTiO$_3$ Landau expansion really needed for the correct physical description and are not just a matter of convenience? Second, does the incorporation of such terms enable elimination of the strong temperature dependence of the anharmonic coefficients in the BaTiO$_3$ Landau expansion? Addressing these questions, the present paper demonstrates by analyzing the dielectric response that, both the eighth-power terms and the temperature dependence of the anharmonic coefficients (at least of the quartic coefficients) are essential for the adequate description of the thermodynamic behavior of BaTiO$_3$, especially on crossing the cubic-tetragonal phase transition. Including these necessities, an improved Landau phenomenological potential is proposed and compared with the existing models. Preliminary results on this subject have been published elsewhere.[10]

II. IMPORTANCE OF THE EIGHTH-POWER TERMS

A. The effect of the eighth-power terms on dielectric nonlinearity

Besides the phase stability, the nonlinear dielectric behavior is another characteristic that directly evidences the contributions of the anharmonic terms in the Landau thermodynamic potential. To demonstrate the crucial role of the eighth-power term in the Landau expansion we first address a simple case, namely the dielectric nonlinearity of BaTiO$_3$ with respect to the electric field E applied along the [001] axis, in the vicinity of the cubic/tetragonal phase transition temperature, T_C. In this case only the [001] component of the polarization, $P = P_3$, is involved, so that the Landau expansion of the Gibbs potential containing the eighth-power term reads

$$\Delta G = \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 + \frac{1}{8}\delta P^8 - EP. \tag{1}$$

Accordingly we have for the equation of state and c axis permittivity ε_c

$$E = \alpha P + \beta P^3 + \gamma P^5 + \delta P^7, \tag{2}$$

$$\varepsilon_c^{-1} = \alpha + 3\beta P^2 + 5\gamma P^4 + 7\delta P^6. \tag{3}$$

These equations provide a description of the nonlinear dielectric response of BaTiO$_3$ in terms of the eighth-power expansion. One can compare this description with that in terms of the sixth-power expansion

$$E = \alpha P + \beta' P^3 + \gamma' P^5, \tag{4}$$

$$\varepsilon_c^{-1} = \alpha + 3\beta' P^2 + 5\gamma' P^4, \tag{5}$$

which have been traditionally used in the field. These descriptions are clearly different. Formally, as one can readily check, the situation described by the expansion, Eqs. (2) and
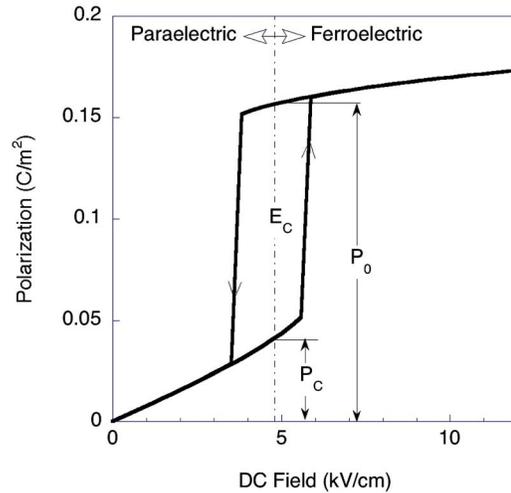

FIG. 1. (Color online) Schematic of the phase transition induced by an electrical field applied along [001] axis above T_C for BaTiO$_3$ single crystal. In paraelectric phase the polarization varies with field below P_C, while in ferroelectric phase the polarization sits in the interval above P_0.

(3) with the polarization-independent coefficients β, γ, and δ corresponds to polarization-dependent coefficients β' and γ' in Eqs. (4) and (5):

$$\beta' = \beta - \delta P^4, \quad \gamma' = \gamma + 2\delta P^2. \tag{6}$$

In general, the consideration of the polarization-dependent anharmonic coefficients in the Landau expansion has no physical sense. However, if a not too wide interval of polarization variation is experimentally addressed with a finite measurement accuracy, coefficients β' and γ' defined by Eq. (6) can be considered as polarization-independent when fitting the dielectric nonlinearity. At the same time, serious problems may arise in situations when a large variation of polarization is involved, e.g., the "jump" of the polarization on crossing the first-order phase transition. To verify this point we consider the case just above T_C, where the ferroelectric phase can be induced by an electrical field. As is schematized by the $E \geq 0$ segment of the "double hysteresis loop" in Fig. 1, the polarization jumps at the critical field E_C, whereas below or above this value the polarization varies slowly with the bias field. At electric fields corresponding to the paraelectric phase, the polarization varies from zero to the critical value P_C. Consequently the contributions of the polarization dependent terms can be estimated from Eq. (6) to be not more than δP_C^4 and $2\delta P_C^2$ to β' and γ', respectively. In contrast, at electric fields corresponding to the ferroelectric phase, the polarization ranges in a much higher interval of not less than P_0, the minimum value of polarization in ferroelectric phase. Accordingly the polarization dependent correction terms in Eq. (6) will be expected to be not less than δP_0^4 and $2\delta P_0^2$, respectively. In Table I, we list the numerical values of the polarization dependent terms in both phases and the typical values of the corresponding coefficients. The value of δ follows the suggestion of Li *et al.*[4] Apparently the values of the polarization dependent terms strongly depend on the interval over which the polarization varies. In the ferroelectric phase, the values of the "correction" terms are comparable to the typical values of the cor-

TABLE I. Estimated values of the polarization dependent terms in Eq. (6) and typical values of the corresponding coefficients. The value of δ is taken from Ref. 4.

Quantities	Paraelectric	Ferroelectric	Units
P	≤ 0.04	≥ 0.16	(C/m^2)
δP^4	$\leq 5 \times 10^4$	$\geq 2 \times 10^8$	(V m^5 C^{-3})
$2\delta P^2$	$\leq 2 \times 10^8$	$\geq 1.5 \times 10^{10}$	(V m^9 C^{-5})
$-\beta$		$(6-9) \times 10^8$	(V m^5 C^{-3})
γ		$(1-2) \times 10^{10}$	(V m^9 C^{-5})

TABLE II. Anharmonic coefficients determined from the field dependence of dielectric permittivity shown in Fig. 2. The values proposed by Li *et al.* are also listed for comparison.

Order	Phase(s)/Author	$-\beta$ (V m^5 C^{-3})	γ (V m^9 C^{-5})	δ(V m^{13} C^{-7})
6	Paraelectric	8.6×10^8	1×10^{10} [a]	0
6	Ferroelectric	18.7×10^8	8.2×10^{10}	0
8	Both	8.6×10^8	0.8×10^{10}	3.4×10^{11}
8	Li *et al.* (Ref. 4)	8.4×10^8	0.77×10^{10}	3.0×10^{11}

[a]The value of γ in paraelectric phase cannot be determined only by fitting the electric field dependence of the permittivity. The present value is estimated by combining the dielectric nonlinearity and the position of the critical field E_C.

responding coefficients, whereas they are negligible in the paraelectric phase.

Thus from the above analysis, we conclude that if the coefficients of the eighth-power terms have a value of the order of that suggested by Li *et al.*, the anharmonic polarization coefficients β' and γ' of BaTiO$_3$ estimated in terms of the sixth-power expansion should exhibit appreciable jumps on crossing the field induced phase transition. Such "phase sensitivity" of the nonlinear coefficients of the sixth-power expansion enables the detection of the eighth-power terms, suggesting a simple and direct way to assess the role of the eighth-power terms.

Keeping this in mind, we studied the nonlinear dielectric behavior of BaTiO$_3$ single crystals in paraelectric phase and in electric field induced ferroelectric phase (E_b//[001]) at a temperature a few degrees higher than T_C. The experimental details can be found in our previous work.[10] Figure 2 shows the experimental data measured at 135 °C (for this crystal, the phase transition temperature $T_C=130$ °C). Little hysteresis effect related to the relaxation phenomena is found within either phase, indicating the high insulating quality of the crystal and the space charge free state of the crystal-
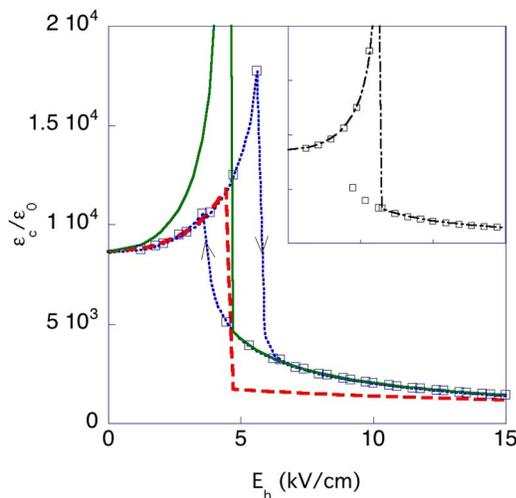
electrode interface.[11] The sixth-order expansions, Eqs. (4) and (5), are used to fit the curves with the common value of α, and remarkably different β are obtained for either phase, as listed in Table II. As for γ, we cannot determine it exclusively from the nonlinear dielectric behavior of the paraelectric phase. The position of E_C, where the ferroelectric phase is induced by the bias field, is used to obtain an estimate, which differs considerably from that derived in the ferroelectric phase. The ferroelectric-phase coefficients have a serious problem in describing the dielectric properties of the paraelectric phase, and vice versa. As illustrated in the inset of Fig. 2, the eighth-order expansion with a common set of coefficients enables a good fit in both phases at the same time. As-estimated values of β, γ, and δ, agree well with the set suggested by Li *et al.*[4]

Furthermore this approach is extended to a wider temperature interval around T_C. As shown in Fig. 3, the quartic coefficient determined with the sixth-power expansion exhibits strong phase dependence, characterized by a "jump" on crossing the phase transition no matter whether this transition is induced by electric field or temperature. In contrast the values determined with the eighth-power expansion are phase independent as the Landau theory coefficients must
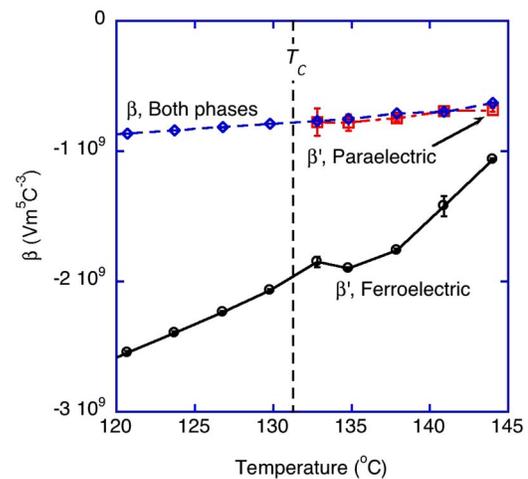

FIG. 2. (Color online) Field dependence of the dielectric permittivity for BaTiO$_3$ single crystal at 135 °C. The open squares represent the measured values, and the dotted line (blue) is to guide the eyes. Remarkably different β are obtained for either phase when fitting with Eqs. (4) and (5), as listed in Table I. The dashed (red) and solid (green) lines are calculated with the coefficients derived from the paraelectric and ferroelectric data, respectively. The ferroelectric coefficients have a serious problem in describing the dielectric properties of the paraelectric phase, and vice versa. The inset shows the much better fit quality (black dashed-dotted line) of an eighth-order expansion for both phases.

FIG. 3. (Color online) The quartic coefficient determined with sixth- and eighth-power expansions in the vicinity of T_C. Phase dependent β' values are derived when using sixth-power expansion, whereas phase independent β can be obtained with the eighth-power expansion. The β values below T_C are estimated by fitting the dielectric nonlinearity with constant γ and δ. However, this is less convincing since the temperature dependence of γ and δ have been arbitrarily omitted.

TABLE III. Literature available values of the anharmonic coefficients for BaTiO$_3$ determined with the sixth-power expansion in the vicinity of T_C.

Authors	$-\beta$ (V m^5 C^{-3})	γ (V m^9 C^{-5})	Principles of the determination
Merz (Ref. 15)	5.4×10^8	1.7×10^{10}	Instability of the paraelectric phase under bias field
Drougard (Ref. 12)	$(4-8) \times 10^8$	NA	Polarization dependence of the dielectric permittivity in paraelectric phase
Meyerhofer (Ref. 14)	$(7-10) \times 10^8$	$(2-2.5) \times 10^{10}$	Field dependence of the polarization in paraelectric phase
Kaczmarek (Ref. 13)	6×10^8	NA	Field dependence of the dielectric permittivity in paraelectric phase
Gonzalo (Ref. 16)	$(15-20) \times 10^8$	$(5-10) \times 10^{10}$	Instability of the paraelectric and ferroelectric phase above T_C [a]

[a]In this work, the critical polarization (or the polarization at the destabilizing electric field) of either phases, were determined from double hysteresis loops. These values in practice strongly depend on the measuring and sample conditions, e.g., the switching frequency and electrode/crystal interface natures. Even though, the differences are appreciable when comparing with those determined from paraelectric properties.

behave. The "phase sensitivity" of β determined by the sixth-power expansion, and its elimination by the incorporation of the eighth-power term, strongly attest to the essentiality of the eighth-power terms in the BaTiO$_3$ Landau expansion.

B. Literature available evidence

In the preceding section, we show that the eighth-power terms are essential for the adequate description of the dielectric nonlinearity of BaTiO$_3$, especially in the ferroelectric region in the vicinity of the cubic-tetragonal phase transition temperature. Interestingly, this point was not realized for a long time. The probable reason was that the anharmonic coefficients were in most cases determined by dealing with the properties (e.g., dielectric permittivity,[12,13] birefringence,[14] and phase instability[15]) of the paraelectric phase using the sixth-power expansion, whereas the dielectric behavior or the polarization of the ferroelectric phase were not considered. In these cases the contribution of the eighth-power terms is negligible and cannot be detected. Values of the coefficients reported in these early studies are actually equivalent to our nonlinear coefficients determined from the paraelectric phase only, as explained above. When the properties of the ferroelectric phase, particularly the very high polarization are involved in determining the anharmonic coefficients of the sixth-power expansion, quite different values for the fourth- and sixth-order coefficients can be obtained according to our preceding discussion. Actually this divergency can be found in the work of Gonzalo *et al.*,[16] where the critical polarization values, at which the paraelectric or the ferroelectric phase loose their stability, have been employed in evaluating the anharmonic coefficients. The values of their coefficients are nearly the same as our coefficients determined from the ferroelectric phase. In Table III we collected values of the coefficients available from the literature, which were determined in the vicinity of T_C. The method of determining coefficients is briefly described for each case. Appreciable difference can be found when comparing data from Gonzalo *et al.* and those derived from the properties of the paraelectric phase. Unfortunately this difference of

$\sim$100% in magnitude for β and $\sim$300% for γ were ignored by the authors though it provides a strong signal that the eighth-power terms cannot be neglected.

Additional evidences for the necessity of the eighth-power terms can be found from the linear dielectric responses on crossing the cubic-tetragonal phase transition. At the first-order phase transition temperature T_C, under zero bias field, we have

$$\Delta G(P_S) = \frac{1}{2}\alpha P_S^2 + \frac{1}{4}\beta P_S^4 + \frac{1}{6}\gamma P_S^6 + \frac{1}{8}\delta P_S^8 = 0, \tag{7}$$

$$E(P_S) = \alpha P_S + \beta P_S^3 + P_S^5 + \delta P_S^7 = 0, \tag{8}$$

$$\varepsilon_{c,T}^{-1} = \alpha + 3\beta P_S^2 + 5 P_S^4 + 7\delta P_S^6, \tag{9}$$

$$\varepsilon_{c,C}^{-1} = \alpha = \alpha_0(T_C - T_0), \tag{10}$$

where P_S is the spontaneous polarization of the tetragonal phase at T_C. $\varepsilon_{c,C}$, and $\varepsilon_{c,T}$ represent the c axis dielectric permittivity of the cubic and the tetragonal phase on crossing the phase transition, respectively. $\alpha_0 = 1/(C\varepsilon_0)$ is the temperature derivative of α and C, T_0 is the Curie-Weiss constant and Curie-Weiss temperature, respectively.

Accordingly, two quantities, namely the variation of the dielectric permittivity and the variation of the temperature derivative of the inverse permittivity along c axis on crossing the ferroelectric phase transition, can be analytically derived as

$$R = \frac{\varepsilon_{c,C}}{\varepsilon_{c,T}} = 4 + \frac{\delta P_S^6}{\alpha}, \tag{11}$$

$$R' = -\frac{\mathrm{d}(1/\varepsilon_{c,T})/\mathrm{d}T}{\mathrm{d}(1/\varepsilon_{c,C})/\mathrm{d}T}$$

$$= 8 + \frac{18\delta P_S^2}{4\gamma + 9\delta P_S^2} - 3\frac{P_S^2}{\alpha_0}\frac{\mathrm{d}\beta}{\mathrm{d}T} - 5\frac{P_S^4}{\alpha_0}\frac{\mathrm{d}\gamma}{\mathrm{d}T} - \cdots. \tag{12}$$

Using the coefficients values and their temperature derivatives of the existing Landau potentials,[4–6] we can estimate the numerical values for the two quantities. Table IV lists the numerical results calculated by the analytical derivations

TABLE IV. Analytical calculated and experimentally determined values of R and R' for BaTiO$_3$ single crystals. The anharmonic coefficients and their temperature derivatives are taken from literature (Refs. 4–6). The spontaneous polarization are taken from literature (Ref. 15).

Quantities	Sixth-power expansion	Eight-power expansion	Experimental data
R	4	5.3	6.2,[b] 7.3,[c] 3.3,[d] 6.1,[e] 5.2,[f]
R'	7.9[a]	9.3	12,[g] 9.4[f]

[a]As can be seen, the contributions by the temperature dependence of the anharmonic coefficients to R' are quite weak and in an opposite direction in comparison to that by the eighth-power term.
[b]Reference 15.
[c]Reference 19.
[d]Reference 14.
[e]Reference 20.
[f]This work.
[g]Reference 17.

with sixth- and eighth-power expansions. In case of the sixth-power expansion, namely $\delta=0$, $R=4$, and $R'\sim 8$. In contrast, the existence of δ that has a value of the order of that suggested by Li *et al.*, leads to appreciable larger values for both quantities. Available experimental data are also collected for comparison. Apparently most of the experimental values are considerably larger than those derived by the sixth-power expansion. Considering the possible experimental inaccuracy in determining the lattice permittivity in the ferroelectric phase due to the not fully eliminated domain contribution, the real values of R is expected to be even larger. The deviations of experimentally determined R and R' from those calculated from the sixth-power expansion, affords additional evidence for the essentiality of the eighth-power term.

In summary the necessity of the eighth-power terms in the BaTiO$_3$ Landau expansion is demonstrated by our dielectric nonlinearity measurements and literature available data. Keeping in mind that the existence of the eighth-power terms leads to the polarization dependence of the anharmonic coefficients in the sixth-power expansion according to Eq. (6), the temperature dependence of the quartic coefficients, which was usually determined with the sixth-power expansion,[12,14] might be logically ascribed to the eighth-power terms as the polarization around T_C is strongly temperature dependent. In the next section we will address the temperature dependence of the anharmonic coefficients in the presence of the eighth-power terms and show that the incorporation of the eighth-power terms cannot eliminate the temperature dependence of the fourth-order anharmonic coefficients.

III. TEMPERATURE DEPENDENCE OF THE ANHARMONIC COEFFICIENTS

A. Temperature dependence of the quartic coefficients

Though the existence of the nonzero eighth-power terms leads to polarization dependent corrections to the quartic and sextic coefficients, however, these corrections are negligible in the paraelectric phase regime, where the contribution of the anharmonic terms is dominated by the quartic terms.[10] Consequently the values determined with the sixth-power expansion of paraelectric properties have a high accuracy. As

can be seen from Fig. 3, the quartic coefficient determined by the sixth-power and eighth-power expansion agree well when only paraelectric data are considered. Therefore, we cannot disregard the temperature dependence of β suggested by Drougard[12] and Meyerhofer[14] according to the nonlinear dielectric or birefringence behavior of the paraelectric phase. A linear temperature dependence was independently revealed for β at temperatures above but not far above T_C. Figure 4(a) illustrates the quartic coefficient β as a function of temperature in the vicinity of T_C. An apparent temperature dependence can be found in the paraelectric phase, well agreeing with Drougard and Meyerhofer's results. Linearly extrapolating to higher temperatures shows that β vanishes at around 185 °C which, however, is inconsistent with our previous observations of around 165 °C.[10] The difference in the zero cross-over temperature of β may be influenced by many factors, e.g., the conductivity, charge accumulating at the oxide-electrode interface, and processing history of the sample, all of which can strongly affect the accuracy of the nonlinear measurements. It is important, however, that both our previous and present work show qualitatively the same behavior of β, which is temperature dependent and changes sign at some temperature well above T_C. In the ferroelectric phase, the β values determined with the eighth-power expansion and temperature independent γ and δ exhibit a continuous and similar temperature dependence as in paraelectric phase (see Fig. 3). However this temperature dependence is, by itself, not convincing since we cannot extract sufficient information to verify the temperature dependence of the higher-than-fourth power anharmonic coefficients merely from the dielectric nonlinearity measurements. The necessity of the temperature dependent anharmonic coefficients in the ferroelectric phase will be demonstrated in the next subsection.

The value of another quartic coefficient, ξ [see Eq. (13)], can be evaluated by combining the nonlinear dielectric responses along [001], [011], and [111] orientations of the paraelectric phase. In this case the anharmonic contributions are dominated by the quartic terms, and the higher-than-fourth-power terms can be omitted.[10] The free energy expression can be simplified as

$$\Delta G = \frac{1}{2}\alpha\left(P_1^2 + P_2^2 + P_3^2\right) + \frac{1}{4}\beta\left(P_1^4 + P_2^4 + P_3^4\right)$$
$$+ \frac{1}{2}\xi\left(P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2\right) - E_1 P_1 - E_2 P_2 - E_3 P_3,$$

(13)

where P_1, P_2, P_3 and E_1, E_2, E_3 are Cartesian components of polarization and electric field, respectively. The nonlinear dielectric response along three orientations can be deduced by successive differentiation[21]:

$$E_{hkl} = \alpha P_{hkl} + \beta_{hkl} P_{hkl}^3,$$

(14)

$$\varepsilon_{hkl}^{-1} = \alpha + 3\beta_{hkl} P_{hkl}^2,$$

(15)

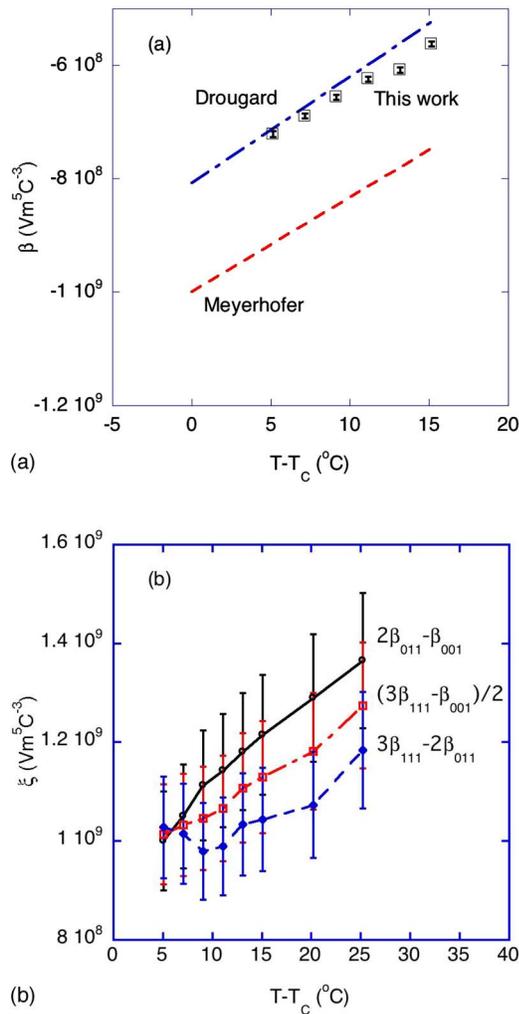where the effective nonlinear coefficients β_{hkl} are linear combinations of β and ξ

FIG. 4. (Color online) Temperature dependence of the quartic coefficients β (a) and ξ (b). The values of ξ are determined by combining the dielectric nonlinearity measurements along [001], [011], and [111] orientations, and the values and temperature derivatives calculated from three combinations agree well with each other.

$$\beta_{001} = \beta,$$

$$\beta_{011} = \frac{1}{2}(\beta + \xi),$$

$$\beta_{111} = \frac{1}{3}(\beta + 2\xi) \tag{16}$$

Figure 4(b) illustrates the values of ξ as a function of temperature. The values determined from various combinations agree with each other with an accuracy of 10% and show consistent temperature dependence over the studied temperature interval. However, our results determined from dielectric nonlinearity are quite different from those proposed in Ref. 14, where the values of ξ were directly estimated by fitting the electric field dependence of the induced polarization of the paraelectric phase. Both the value itself and its temperature derivative have opposite signs in comparison with those reported by Meyerhofer[14] in the vicinity of T_C. We believe that our positive ξ values are correct for the following reasons. Both [011] and [111] oriented crystals exhibit a de-

creasing electric field dependence of the dielectric permittivity, suggesting positive values of the effective nonlinear coefficients, β_{011} and β_{111}. In contrast, a negative ξ definitely results in negative β_{011} and β_{111}, which is opposite to our experimental data. A negative value of ξ suggested in Ref. 14 is actually in contradiction with the birefringence measurements reported in the same paper.[22] Finally, ξ must exhibit a value larger than the absolute value of β to fit the positive β_{011}. A smaller value of ξ, as was implicitly assessed by fitting the tetragonal/orthorhombic phase transition temperature with the sixth-power expansion,[5,6,23] cannot describe the dielectric nonlinearity of [011] crystals in the paraelectric phase.

Therefore, we show that even in the presence of eighth-power terms, which are actually not important for the paraelectric phase, both of the quartic coefficients definitely have to be temperature dependent, at least above T_C. The temperature dependence of the higher-power coefficients, however, cannot be precisely determined merely from dielectric nonlinearity results. More measurements, e.g., the polarization as a function of electric field, are needed to clarify this point.

B. Temperature dependence of the anharmonic coefficients in tetragonal phase

In ferroelectric phases below T_C, the contributions of the terms higher than quartic are comparable to those of the quartic terms.[10] Neither the coefficients themselves nor their temperature dependence can be determined from dielectric nonlinearity in a reasonable accuracy. Here we propose a simple way to cross-check the necessity of the temperature dependent anharmonic coefficients in tetragonal phase. First we assume that the Landau coefficients are temperature independent except the quadratic coefficient, α, which is linearly temperature dependent following the Curie-Weiss law. The equation of state and c axis permittivity ε_c of the tetragonal phase can be simplified as

$$E = \alpha_0(T - T_0)P + g(P), \tag{17}$$

$$\varepsilon_c^{-1} = \alpha_0(T - T_0) + g'(P), \tag{18}$$

where $g(P)$ summarizes all the contributions from the higher order anharmonic terms. Under zero electric field, $E = 0$, $P = P_S$. Assuming that the only temperature dependence in g comes from P_S, one can readily derive

$$\frac{dE}{dT} = 0 = \alpha_0 P_S + [\alpha_0(T - T_0) + g'(P_S)]\frac{dP_S}{dT}. \tag{19}$$

Thus we have

$$g'(P_S) = -\frac{\alpha_0 P_S}{dP_S/dT} - \alpha_0(T - T_0). \tag{20}$$

Combining Eq. (18) and (20), we get

$$\varepsilon_{r,c} = -\frac{1}{\alpha_0 \varepsilon_0}\frac{d \ln P_S}{dT} = -C\frac{d \ln P_S}{dT}, \tag{21}$$

where $\varepsilon_{r,c}$ represents the relative dielectric permittivity along the direction of the spontaneous polarization P_S in tetragonal
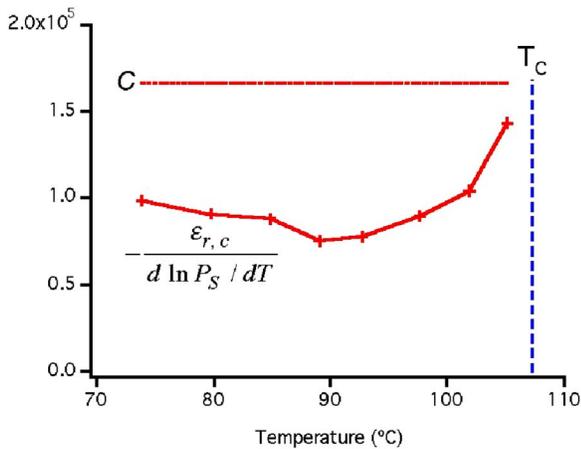
FIG. 5. (Color online) Divergency between the quantity $\varepsilon_{r,c}/(d \ln P_S/dT)$ and C in the ferroelectric tetragonal phase. The values of dielectric permittivity and spontaneous polarization are extracted from literature (Ref. 15).

temperature in the tetragonal phase. The experimental data are extracted from Ref. 15, where the measurements were performed on identical single domain BaTiO$_3$ crystals. Appreciable difference ($\sim$50% of C) can be found between these two quantities, attesting to the invalidity of the temperature independent assumption. Namely, in ferroelectric phase, the temperature dependent anharmonic coefficients are indeed necessary for an adequate description of the thermodynamics of BaTiO$_3$. However, detailed information about the temperature dependence of each coefficient cannot be obtained by this simple method.

IV. IMPROVED THERMODYNAMIC POTENTIAL FOR BATIO$_3$ SINGLE CRYSTALS

In the preceding sections we demonstrate that not only the eighth-power terms, but also the temperature dependent anharmonic coefficients (at least temperature dependent quartic coefficients), are essential in BaTiO$_3$ Landau thermodynamic potential. Hereinafter we propose the following improved potential for this prototype substance by introducing temperature dependent coefficients into the eighth-order expansion. For convenience we use the same notations as in Ref. 4

phase. Thus by comparing the quantity $-\varepsilon_{r,c}/(d \ln P_S/dT)$ with C, we can readily verify the validity of the temperature independent assumption.

In Fig. 5 we compare the two quantities as a function of

$$
\begin{aligned}
\Delta G =\ & \alpha_1\left(P_1^2 + P_2^2 + P_3^2\right) + \alpha_{11}\left(P_1^4 + P_2^4 + P_3^4\right) + \alpha_{12}\left(P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2\right) + \alpha_{111}\left(P_1^6 + P_2^6 + P_3^6\right) \\
& + \alpha_{112}\left[P_1^2\left(P_2^4 + P_3^4\right) + P_2^2\left(P_3^4 + P_1^4\right) + P_3^2\left(P_1^4 + P_2^4\right)\right] + \alpha_{123}P_1^2 P_2^2 P_3^2 + \alpha_{1111}\left(P_1^8 + P_2^8 + P_3^8\right) \\
& + \alpha_{1112}\left[P_1^6\left(P_2^2 + P_3^2\right) + P_2^6\left(P_3^2 + P_1^2\right) + P_3^6\left(P_1^2 + P_2^2\right)\right] + \alpha_{1122}\left(P_1^4 P_2^4 + P_2^4 P_3^4 + P_3^4 P_1^4\right) \\
& + \alpha_{1123}\left(P_1^4 P_2^2 P_3^2 + P_1^2 P_2^4 P_3^2 + P_1^2 P_2^2 P_3^4\right) - E_1 P_1 - E_2 P_2 - E_3 P_3,
\end{aligned}
\tag{22}
$$

where the coefficients α_1, α_{11}, α_{12}, α_{111}, and α_{1111} corresponding to the preceding notations $\frac{1}{2}\alpha$, $\frac{1}{4}\beta$, $\frac{1}{2}\xi$, $\frac{1}{6}\gamma$, and $\frac{1}{8}\delta$, respectively. The temperature dependent α_1, α_{11}, and α_{12}, are directly determined from our linear and nonlinear dielectric measurements above T_C. The linear dependences are simply extrapolated down to low temperatures. The temperature dependence of α_{111} is estimated by fitting the spontaneous polarization of the tetragonal phase, with a temperature independent α_{1111} that is evaluated from the dielectric nonlinearity above T_C. A linear dependence is revealed for α_{111} and extrapolated to low temperatures. The rest of the coefficients are assumed to be temperature independent. α_{112} and α_{1112} are estimated by fitting the dielectric permittivity perpendicular to the spontaneous polarization, ε_a, as a function of temperature in the tetragonal phase. α_{1122} is evaluated to fulfill the tetragonal/orthorhombic phase transition temperature. α_{123} and α_{1123} are adjusted to fit the orthorhombic/rhombohedral phase transition temperature and its field dependence.[24] The numerical values of the nonlinear coefficients described above are listed in Table V. For comparison those of the two existing potentials proposed by Bell[5] and Li *et al.*[4] are also presented.

In the first glance, our model is just a combination of

those proposed by Li *et al.* and Bell.[4,5] However, it should be kept in mind that (i) the eighth-power terms used in Li *et al.* potential are not just a convenience but an essentiality in eliminating the "phase sensitivity" of the anharmonic coefficients of the sixth-power expansion; (ii) even with the eighth-power expansion, the temperature dependence of the anharmonic coefficients cannot be disregarded, as has been generally demonstrated by the dielectric properties of the tetragonal phase (Fig. 5), and directly revealed by our dielectric measurements for the two quartic coefficients (Fig. 4). Disregarding these temperature dependence of the quartic coefficients and the eighth-order terms leads to an inadequate description of the dielectric behavior, even in a qualitative way. In contrast, incorporating these changes, a high quality in reproducing the dielectric behavior of BaTiO$_3$ single crystals is achieved, particularly in the vicinity of the cubic-tetragonal phase transition. First, above T_C our model is capable in quantitatively fitting the dielectric nonlinearity as a function of temperature and crystallographic orientation (see Figs. 2 and 4), which in principle cannot be well described by either of the other potentials. Second, in the tetragonal phase the linear dielectric constant and the spontaneous polarization can be precisely reproduced. Figure 6 compares

TABLE V. Coefficients of BaTiO$_3$ Landau thermodynamic potential in Eq. (22), where T is temperature in K.

Coefficients	This work	Li *et al.*[a]	Bell and Cross[b]	Units
α_1	$3.61\times10^5(T-391)$	$4.124\times10^5(T-388)$	$3.34\times10^5(T-381)$	V m C^{-1}
α_{11}	$-1.83\times10^9+4\times10^6\,T$	-2.097×10^8	$-2.045\times10^9+4.69\times10^6T$	V m^5 C^{-3}
α_{12}	$-2.24\times10^9+6.7\times10^6\,T$	7.974×10^8	3.23×10^8	V m^5 C^{-3}
α_{111}	$1.39\times10^{10}-3.2\times10^7\,T$	1.294×10^9	$2.445\times10^{10}-5.52\times10^7T$	V m^9 C^{-5}
α_{112}	-2.2×10^9	-1.950×10^9	4.47×10^9	V m^9 C^{-5}
α_{123}	5.51×10^{10}	-2.500×10^9	4.91×10^9	V m^9 C^{-5}
α_{1111}	4.84×10^{10}	3.863×10^{10}	0	V m^{13} C^{-7}
α_{1112}	2.53×10^{11}	2.529×10^{10}	0	V m^{13} C^{-7}
α_{1122}	2.80×10^{11}	1.637×10^{10}	0	V m^{13} C^{-7}
α_{1123}	9.35×10^{10}	1.367×10^{10}	0	V m^{13} C^{-7}

[a]Reference 4.
[b]References 5 and 6.

the experimentally measured and the theoretically calculated $1/\varepsilon_{c,r}$ as a function of temperature around the paraelectric/ferroelectric phase transition. In spite of the great difference existing among the investigated crystals (e.g., the T_C varies from 108 °C for Merz's crystal[15] to 130 °C of our crystal), the measured dielectric permittivity concide on departing from T_C. The curve calculated with the potential proposed in this work agrees well with the experimental data, whereas those calculated with Li *et al.* and Bell's coefficients show remarkable divergence with the experimental values in tetragonal phase. Note that when determining the anharmonic coefficients we have never used the experimental ε_c data measured below T_C.

The low temperature ferroelectric properties are also calculated with the three potentials listed in Table V. The three consecutive phase transition temperatures are yielded with the current potential as 404, 284, and 189 K, respectively. In Fig. 7, we present the spontaneous polarization along pseudo cubic [001] of BaTiO$_3$ as a function of temperature. Some of the experimental data available in literature are also presented for comparison. In the tetragonal phase, the three potentials have similar quality in reproducing the spontaneous

polarization, both in its absolute value and in its temperature dependence. In the orthorhombic phase none of these models can well describe the temperature dependence of the spontaneous polarization. The existing potentials (Li *et al.* and Bell's) give better estimations of the average value of the spontaneous polarization. In the rhombohedral phase, however, our potential exhibits a better accuracy than the other two potentials. Again we emphasize that the experimentally measured polarization values of the rhombohedral phase have not been used in determining the anharmonic coefficients. As for the dielectric properties of the low temperature ferroelectric phases, experimental data available in literature are rather scattered and sometimes are not self-consistent.[15,23,25] Tentatively we measured a poled [111] crystal at cryogenic temperatures. At 20 K the relative dielectric constant is about 40. Considering the possible incompletely eliminated domain contributions, the real value seems to be even less. The corresponding calculations give 30, 81, and 68 when using our, Li *et al.* and Bell's potentials, respectively. Apparently the thermodynamic potential proposed in this work exhibits a better accuracy.
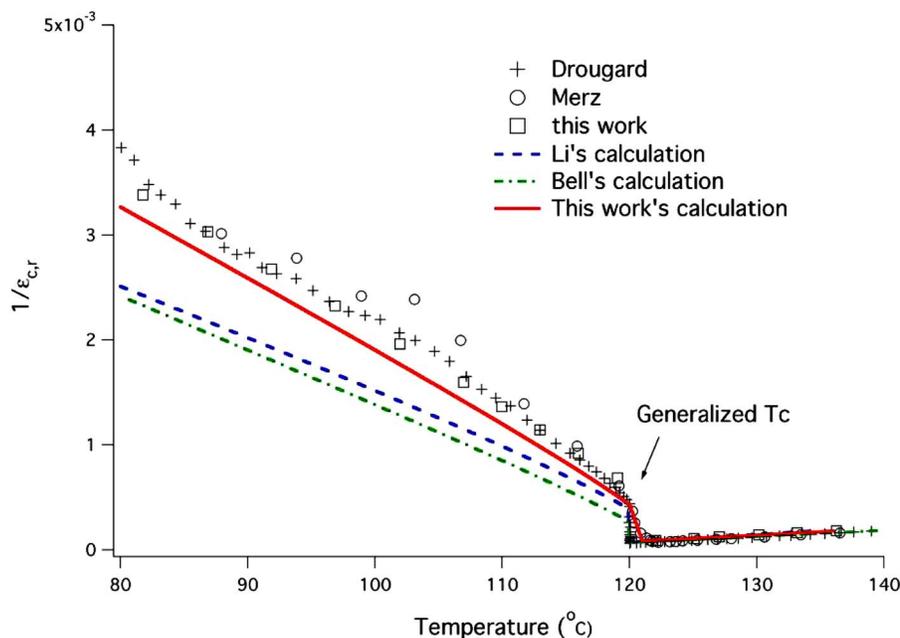

FIG. 6. (Color online) Inverse dielectric permittivity along the spontaneous polarization in the vicinity of T_C, a comparison between the calculations and the experimental data. For convenience the phase transition temperatures are normalized to 120 °C. The scattered dark marks are experimentally measured by different researchers on different crystals: + by Drougard (Ref. 19), ○ by Merz (Ref. 15), and □ in this work. The dashed (blue), dash-dotted (green), and solid (red) lines are calculated with Li *et al.*, Bell, and the proposed potential in this work, respectively. Note that despite the great difference in the source sample, the permittivity exhibits tremendous consistence on departing from T_C. This potential has a much better quality in fitting the experimental data than the two existing potentials do.
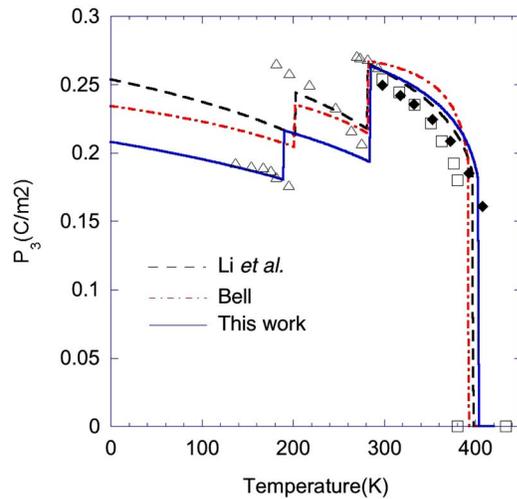
FIG. 7. (Color online) Spontaneous polarization along pseudo cubic [001] of BaTiO$_3$, a comparison between the calculations and the experimental data. The scattered marks represent the experimental data: $\square$, $\triangle$, and $\blacklozenge$ are extracted from literature (Refs. 15, 25, and 26), respectively. The dashed (dark), dash-dotted (red), and solid (blue) lines are calculated with Li *et al.*, Bell, and the proposed potential in this work, respectively. The polarization values of the rhombohedral phase are exactly reproduced by the improved thermodynamic potential.

V. CONCLUSIONS

In conclusion, we demonstrate by analyzing the dielectric nonlinearity that both the eighth-power terms and the temperature dependent anharmonic coefficients are necessary in BaTiO$_3$ Landau phenomenological potential for the adequate description of the thermodynamic behavior of this substance. Accordingly, an improved Landau potential, characterized by an eighth-order Landau expansion with some temperature dependent anharmonic coefficients, is proposed and compared with the existing potentials. In general the proposed potential exhibits a higher quality in reproducing the dielectric and ferroelectric properties of this prototype ferroelectric substance.

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