Phenomenological thermodynamic potential for CaTiO$_3$ single crystals

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(Received 17 October 2011; published 23 February 2012)

DOI: 10.1103/PhysRevB.85.064117 PACS number(s): 77.80.B−, 64.60.Ej

I. INTRODUCTION

The ideal perovskite structure, described as a simple cubic network of corner linked BO$_6$ octahedra with A atoms occupying 12-fold oxygen coordinated sites, is inherently unstable and can exhibit a variety of distortions. These include polar distortions, dominated by off-centering of the B cation in its oxygen octahedron, and tilts and rotations of the oxygen octahedron network. The polar distortions lead to the presence of dipoles and to ferroelectric and antiferroelectric behavior in several well-known perovskite compounds, such as BaTiO$_3$, PbTiO$_3$, PbZrO$_3$, and BiFeO$_3$. Oxygen octahedron rotations produce a variety of nonpolar phases, the phase transitions of which are called antiferrodistortive (AFD) phase transitions. The same compound can show instabilities to both distortions in the cubic phase, in which case they usually compete. Strontium titanate (SrTiO$_3$) is a good example of such compounds. Although SrTiO$_3$ has a ferroelectric instability, it is paraelectric all the way down to 0 K. Its ferroelectric transition is weakened along the direction of AFD tilt. 2,3 With a sufficiently large epitaxial strain, SrTiO$_3$ becomes ferroelectric even at room temperature. 5

At ambient temperature and pressure, calcium titanate (CaTiO$_3$) has the orthorhombic distorted-perovskite structure with space group $Pbnm$, a structure common to many perovskite oxides. Disregarding the distortion of TiO$_6$ octahedra, the structure of CaTiO$_3$ can be illustrated as a combination of two kinds of TiO$_6$ octahedron tilts: two out-of-phase tilts along $x_1$ and $x_2$ directions, and one in-phase tilt along $x_3$ direction (Fig. 1). With the standard Glazer’s notation, 5 it can be expressed as $a$−$a$−$c^{+}$. These two kinds of tilts can also be used to characterize the AFD transitions in CaTiO$_3$. We will discuss it in more details later.

The AFD transition sequence of CaTiO$_3$ is complicated. From high to low temperature, CaTiO$_3$ transforms from cubic ($Pm\bar{3}m$) to tetragonal ($I4/mcm$) at about 1600 K, and from tetragonal ($I4/mcm$) to orthorhombic at about 1500 K. 6−11 The later transition or transitions is quite controversial. Ali and Yashima 10,11 proposed a direction transition from $I4/mcm$ to $Pbnm$ by the Rietveld analysis of high-temperature x-ray and neutron diffraction data. Also by the analysis of high-temperature neutron diffraction data, Kennedy et al. 5 found there might be an intermediate phase with $Cnmc$ structure between the transition from $I4/mcm$ to $Pbnm$. And the transition temperature from $Cnmc$ to $Pbnm$ is around 1380 K, which agrees with both the drop-calorimetry measurements of Guyot et al. 7 and the Raman spectroscopy observation of Gillet et al. 8 On the other hand, Carpenter theoretically investigated the structural transitions of CaTiO$_3$ using Landau theory, and he concluded that in order to get a stable $Pbnm$ structure, there must be some intermediate structure between $I4/mcm$ and $Pbnm$. However, he proposed an $I4/mcm \rightarrow Imma \rightarrow Pbnm$ transition sequence.

Despite of the complicity and discrepancy, none of the above-mentioned structures is polar or ferroelectric at ambient pressure. However, CaTiO$_3$ has a ferroelectric soft mode as manifested by a high dielectric constant at low temperature 13 and later first-principles calculations. 14 Experiments also show frequency independence of CaTiO$_3$ dielectric constants, which makes it a high-quality microwave material. Therefore, similar to SrTiO$_3$, CaTiO$_3$ is also an incipient ferroelectric, 15 and the extrapolated ferroelectric transition temperature is about −111 K. 13,15 It is natural to consider the ferroelectricity of CaTiO$_3$ as an analog to that of SrTiO$_3$, which is weakened by AFD, but can be induced by applied strain. 2,5−6,14 In addition, some other perovskites with $Pbnm$ structures, including CaMnO$_3$, 17 SrZrO$_3$, 18 etc., 19 are possible to exhibit strain-induced ferroelectricity. Recently, by first-principles calculations, Eklund et al. 20,21 predicted that 1.5% epitaxial tensile strain can indeed lead to ferroelectric transition. Experimentally, Vlahos 22 found spontaneous polarization in the CaTiO$_3$/NdGaO$_3$ film system with a tensile constraint strain of 1.15%. Thus, ferroelectricity in CaTiO$_3$ can be induced by a sufficiently large tensile strain.

In addition to the strain-induced ferroelectric behavior of thin films, the twin walls of CaTiO$_3$ have been extensively investigated, including trapping of oxygen vacancies, 23,24 the
activation energy for twin-wall motion,\textsuperscript{25} and the intrinsic elasticity of the twin walls.\textsuperscript{26} By theoretical simulations, Goncalves-Ferreira \textit{et al.}\textsuperscript{27} showed that the CaTiO\textsubscript{3} ferroelastic twin walls exhibit sizeable spontaneous polarization due to the vanishing of octahedra tilt and the decrease of the material density. Further experiments show that the twins of CaTiO\textsubscript{3} are ferroelectric themselves.\textsuperscript{22} Since the formation of twins is usually to lower the total strain energy, the twins themselves are usually strained. Therefore, the discovered ferroelectricity of CaTiO\textsubscript{3} twin domains may also be due to strain effect.

In order to control and manipulate its properties with an applied external strain, it is necessary to understand the thermodynamics of CaTiO\textsubscript{3}. Carpenter \textit{et al.}\textsuperscript{28,29} proposed a Landau expansion to describe the AFD transitions in (Ca, Sr)TiO\textsubscript{3}. Although he made a systematic analysis of the stability of all the possible structures, the ferroelectric transition is not considered, and coefficients were not determined. In this paper, we construct a phenomenological thermodynamic potential for a CaTiO\textsubscript{3} single crystal, which incorporates both the AFD transitions and the ferroelectric transitions with different stress and strain conditions. This potential can therefore be employed to analyze all the important phase transitions and their dependence on stress and strain conditions. In the following section, we’ll introduce the phenomenological model and convert all the parameters determined from first-principles calculations to this model. In the third section, all the temperature-dependent coefficients will be determined, and some of the parameters from first-principles calculations will be revised from fitting the experimental data. Finally, we’ll use a dielectric constant to validate our model and then investigate the competition mechanism of AFD and ferroelectric transitions in the CaTiO\textsubscript{3} thin film phase diagram.

II. PHENOMENOLOGICAL DESCRIPTION

The phase transitions in CaTiO\textsubscript{3} can be described with a single Landau free energy expansion in terms of $\varepsilon_1$, $P_t$, and $q_i$. Here, $\varepsilon_i$ ($i = 1−6$) are the strain components following Voigt’s convention; $P_t$ ($i = 1, 2, 3$) represent three components of the spontaneous polarization in the Cartesian coordinate system; and $q_i$ ($i = 1, 2, 3$) represent the linear oxygen displacement that corresponds to simultaneous out-of-phase tilt of TiO\textsubscript{6} octahedra. Similarly, $q_i$ ($i = 4, 5, 6$) represent the oxygen displacement of simultaneous in-phase tilt of TiO\textsubscript{6} octahedra. The relationship between order parameter $q_i$ and octahedral tilt angles is explained in the Appendix. In terms of soft modes, $P_1$, $q_i$ ($i = 1, 2, 3$), and $q_i$ ($i = 4, 5, 6$) correspond to the $\Gamma_4^−, R_4^+, M_3^+$ modes, respectively. The total free energy has following form:

$$F = F_{\text{Polar}} + F_{\text{OPT}} + F_{\text{IPT}} + F_{\text{Elastic}} + F_{\text{Coupling}}.$$  (1)

The first three terms on the right-hand side of Eq. (1) describe contributions from spontaneous polarization, out-of-phase tilt, and in-phase tilt:

$$F_{\text{Polar}} = \alpha_1(T)(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^2 + P_2^2 + P_3^2)^2 + \alpha_{12}(P_1^2 + P_2^2 + P_3^2) + \alpha_{111}(P_1^2 + P_2^2 + P_3^2)^3 + \alpha_{112}(P_1^2 + P_2^2 + P_3^2)(P_1^4 + P_2^4 + P_3^4) + \alpha_{122}(P_1P_2P_3)^2,$$  (2)

$$F_{\text{OPT}} = \beta_1(T)(q_1^2 + q_2^3 + q_3^2) + \beta_{11}(q_1^2 + q_2^3 + q_3^2)^2 + \beta_{12}(q_1^4 + q_2^4 + q_3^4) + \beta_{111}(q_1^2 + q_2^2 + q_3^2)^3 + \beta_{112}(q_1^2 + q_2^2 + q_3^2)(q_1^4 + q_2^4 + q_3^4) + \beta_{122}(q_1q_2q_3)^2,$$  (3)

$$F_{\text{IPT}} = \gamma_1(T)(q_1^2 + q_2^3 + q_3^2) + \gamma_{11}(q_1^2 + q_2^3 + q_3^2)^2 + \gamma_{12}(q_1^4 + q_2^4 + q_3^4) + \gamma_{111}(q_1^4 + q_2^4 + q_3^4)^3 + \gamma_{112}(q_1^2 + q_2^2 + q_3^2)(q_1^4 + q_2^4 + q_3^4) + \gamma_{122}(q_1q_2q_3)^2,$$  (4)

where $\alpha$, $\beta$, and $\gamma$ are constants. Only the coefficients of the second-order terms are assumed to be temperature dependent, i.e.

$$\alpha_i(T) = \alpha_{10}\Theta_{S1} \left[ \coth \left( \frac{\Theta_{S1}}{T} \right) - \coth \left( \frac{\Theta_{S1}}{T_1} \right) \right],$$

$$\beta_i(T) = \beta_{10}\Theta_{S2} \left[ \coth \left( \frac{\Theta_{S2}}{T} \right) - \coth \left( \frac{\Theta_{S2}}{T_2} \right) \right],$$

$$\gamma_i(T) = \gamma_{10}\Theta_{S3} \left[ \coth \left( \frac{\Theta_{S3}}{T} \right) - \coth \left( \frac{\Theta_{S3}}{T_3} \right) \right],$$  (5)

where $T_1$, $T_2$, and $T_3$ are Curie temperatures, and $\Theta_{S1}$, $\Theta_{S2}$, and $\Theta_{S3}$ are saturation temperatures. The strain contribution to the total free energy can be written as

$$F_{\text{Elastic}} = \frac{1}{2}C_{11}(\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2) + C_{12}(\varepsilon_1\varepsilon_2 + \varepsilon_3\varepsilon_2 + \varepsilon_1\varepsilon_3) + \frac{1}{2}C_{44}(\varepsilon_1^4 + \varepsilon_2^4 + \varepsilon_3^4),$$  (6)

where $C_{11}$, $C_{12}$, and $C_{44}$ are elastic stiffness constants, and $\varepsilon_1−\varepsilon_6$ are strain components. The coupling energy among
different-order parameters and strains is written as
\[ F_{\text{Coupling}} = -t_{11}(P_1^2 q_1^2 + P_2^2 q_2^2 + P_3^2 q_3^2) - t_{12} \left[ P_1^2 (q_1^2 + q_3^2) + P_2^2 (q_2^2 + q_3^2) + P_3^2 (q_1^2 + q_2^2) \right] \\
- t_{44}(P_1 P_2 q_1 q_2 + P_1 P_3 q_1 q_3 + P_2 P_3 q_2 q_3) - \kappa_{11}(P_1^2 q_1^2 + P_2^2 q_2^2 + P_3^2 q_3^2) \\
- \kappa_{12}[P_1^2 (q_2^2 + q_3^2) + P_2^2 (q_1^2 + q_3^2) + P_3^2 (q_1^2 + q_2^2)] - \kappa_{44}(P_1 P_2 q_1 q_2 + P_1 P_3 q_1 q_3 + P_2 P_3 q_2 q_3) \\
- \mu_{11}(q_1^2 q_2^2 + q_2^2 q_3^2 + q_3^2 q_1^2) - \mu_{12}[(q_2^2 + q_3^2) q_2^2 + (q_2^2 + q_3^2) q_3^2 + (q_2^2 + q_3^2)] - g_{11}(P_1^2 q_1^2 + P_2^2 q_2^2 + P_3^2 q_3^2) \\
- g_{12}[(q_1^2 + q_3^2) + q_2^2 (P_1^2 + P_2^2) + \varepsilon_5 (P_1^2 + P_2^2)] - g_{44}(P_1 P_2 q_1 q_2 + P_1 P_3 q_1 q_3 + P_2 P_3 q_2 q_3) - \lambda_{11}(q_1^2 q_1^2 + q_2^2 q_2^2 + q_3^2 q_3^2) \\
- \lambda_{12}[q_1^2 (q_2^2 + q_3^2) + q_2^2 (q_1^2 + q_3^2) + q_3^2 (q_1^2 + q_2^2)] - \lambda_{44}(q_1^2 q_1^2 + q_2^2 q_2^2 + q_3^2 q_3^2) \\
- \zeta_{12}[q_1^2 (q_2^2 + q_3^2) + q_2^2 (q_1^2 + q_3^2) + q_3^2 (q_1^2 + q_2^2)] - \zeta_{44}(q_1^2 q_1^2 + q_2^2 q_2^2 + q_3^2 q_3^2), \quad (7) \]

where \( t_{ij}, \kappa_{ij}, g_{ij}, \mu_{ij}, \lambda_{ij}, \) and \( \zeta_{ij} \) are coupling coefficients. The 33 parameters appearing in Table I were determined from a series of first-principles total-energy calculations on distorted perovskite structures. Detailed information of the first-principles calculations and the approach to determining these coefficients can be found in Refs. 20 and 21. The parameters (in SI unit) converted from first-principles calculations are listed in the Table I.

### III. RESULTS AND DISCUSSION

#### A. AFD transitions

For the AFD transition with only one in-phase TiO\(_6\) octahedron tilt and two out-of-phase TiO\(_6\) octahedron tilts, i.e. \( P_1 = P_2 = P_3 = q_1 = q_2 = q_3 = 0 \), we have

\[ F = \beta_{10} \Theta_{32} \left[ \coth \left( \frac{\Theta_{32}}{T} \right) - \coth \left( \frac{\Theta_{32}}{T} \right) \right] (q_1^2 + q_2^2) \]

\[ + \gamma_{10} \Theta_{33} \left[ \coth \left( \frac{\Theta_{33}}{T} \right) - \coth \left( \frac{\Theta_{33}}{T} \right) \right] q_3^2 \]

\[ + \beta_{11}(q_1^2 + q_2^2)^2 + \beta_{12}(q_1^2 + q_2^2)^2 + \beta_{14}(q_1^2 + q_2^2)^3 \]

\[ + \beta_{12}(q_1^2 + q_2^2)(q_1^4 + q_2^4) + (\gamma_{14} + \gamma_{12}^* q_3^2) q_3^2 \]

\[ + (\gamma_{11} + \gamma_{12}) q_3^2 - \mu_{12}^*(q_1^2 + q_2^2) q_3^2, \quad (8) \]

where \( \beta_{ij}^{*,*} \), \( \mu_{ij}^{*,*} \), and \( \gamma_{ij}^{*,*} \) are normalized coefficients with stress-free boundary conditions (see Appendix for details). The order parameters and free energies of different structures are summarized in Table II.

According to experimental results, as discussed in the introduction, we can conclude that there are at least two AFD transitions, i.e. \( Pm\overline{3}m \) to \( I4/mcm \) and another transition to \( Pbnn \). The latter cannot be a direct transition from \( I4/mcm \) to \( Pbnn \), if the energy of \( Imma \) or \( Cmcm \) is higher than \( Pbnn \). As compared in Table II, appropriate selection of coefficients can generate different possibilities for the latter AFD transition sequence, such as \( I4/mcm \rightarrow Imma \rightarrow Pbnn \), \( I4/mcm \rightarrow Cmcm \rightarrow Pbnn \), etc. Carpenter\(^{20}\) analyzed the energy difference between these structures and proposed an \( I4/mcm \rightarrow Imma \rightarrow Pbnn \) transition sequence. It should be noted that the \( Imma \) structure was not observed experimentally. Here, we propose another scenario for the transformation sequence, \( I4/mcm \rightarrow Cmcm \rightarrow Pbnn \), although the existence of \( Cmcm \) structure is still controversial in this system.\(^7,9-11\) However, only this transition sequence can account for both the transition temperature of about 1380 K, which was determined by Guyot et al.\(^7\) and Gillet et al.\(^{12}\), respectively, and Kennedy et al.'s neutron diffraction results.\(^9\) According to Guyot et al.'s heat capacity measurement,\(^7\) both \( I4/mcm \rightarrow Cmcm \) and

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**Table I.** The parameters converted from first-principles calculations\(^4\) (Ref. 21; energy density unit: J/m\(^3\)).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1 )</td>
<td>(-3.56 \times 10^{10})</td>
</tr>
<tr>
<td>( \alpha_{11} )</td>
<td>(3.70 \times 10^{10})</td>
</tr>
<tr>
<td>( \alpha_{12} )</td>
<td>(9.72 \times 10^{10})</td>
</tr>
<tr>
<td>( \alpha_{111} )</td>
<td>(-1.18 \times 10^{10})</td>
</tr>
<tr>
<td>( \alpha_{112} )</td>
<td>(-5.94 \times 10^{10})</td>
</tr>
<tr>
<td>( \alpha_{122} )</td>
<td>(-2.68 \times 10^{10})</td>
</tr>
<tr>
<td>( \beta_1 )</td>
<td>(-2.05 \times 10^{10})</td>
</tr>
<tr>
<td>( \beta_{11} )</td>
<td>(1.20 \times 10^{10})</td>
</tr>
<tr>
<td>( \beta_{12} )</td>
<td>(3.62 \times 10^{10})</td>
</tr>
<tr>
<td>( \beta_{111} )</td>
<td>(-2.89 \times 10^{10})</td>
</tr>
<tr>
<td>( \beta_{112} )</td>
<td>(-2.31 \times 10^{10})</td>
</tr>
<tr>
<td>( \beta_{122} )</td>
<td>(-4.92 \times 10^{10})</td>
</tr>
<tr>
<td>( \gamma_1 )</td>
<td>(-1.85 \times 10^9)</td>
</tr>
<tr>
<td>( \gamma_1 + \gamma_2 )</td>
<td>(1.48 \times 10^9)</td>
</tr>
<tr>
<td>( \gamma_{11} + \gamma_{12} )</td>
<td>(-2.31 \times 10^9)</td>
</tr>
<tr>
<td>( \gamma_{12} )</td>
<td>(-6.79 \times 10^9)</td>
</tr>
<tr>
<td>( \mu_{11} )</td>
<td>(3.29 \times 10^{10})</td>
</tr>
<tr>
<td>( \mu_{11}^{<em>,</em>} )</td>
<td>(4.03 \times 10^{11})</td>
</tr>
<tr>
<td>( C_{11} )</td>
<td>(1.07 \times 10^{11})</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>(9.99 \times 10^{10})</td>
</tr>
<tr>
<td>( t_{11} )</td>
<td>(-1.53 \times 10^{10})</td>
</tr>
<tr>
<td>( t_{12} )</td>
<td>(-7.79 \times 10^{10})</td>
</tr>
<tr>
<td>( t_{44} )</td>
<td>(2.34 \times 10^{10})</td>
</tr>
<tr>
<td>( \kappa_{11} )</td>
<td>(-1.43 \times 10^{10})</td>
</tr>
<tr>
<td>( \kappa_{12} )</td>
<td>(-5.02 \times 10^{10})</td>
</tr>
<tr>
<td>( \kappa_{44} )</td>
<td>(-2.10 \times 10^{10})</td>
</tr>
<tr>
<td>( \gamma_{11} )</td>
<td>(-8.76 \times 10^{10})</td>
</tr>
<tr>
<td>( \gamma_{12} )</td>
<td>(-1.24 \times 10^{10})</td>
</tr>
</tbody>
</table>

\(^{a}R^+_{91}\) mode is neglected.

\(^{b}\)Normalized by eliminating \( X^+_2 \) mode.
$Pm\bar{3}m$ transitions are of the first order. For the $Pm\bar{3}m \rightarrow 14/mcm$ transition at about 1600 K, there is no or very small latent heat, which may be buried by the broad calorimetric peak of the previous transition.\textsuperscript{7} Therefore, this transition may be of the second order or weakly first order. However, the tilt angles-vs-temperature diagram from the x-ray diffraction and neutron diffraction results\textsuperscript{9,11} shows discontinuity near the transition temperature, a characteristic feature of a first-order transition.

In this paper, we adopted Guyot et al.’s\textsuperscript{5} measured data of the transformation latent heat and assumed that the $Pm\bar{3}m \rightarrow 14/mcm$ transition is also of first order with a small latent heat of 1.0 kJ/mol. The saturation temperatures were estimated from the (Ca,Sr)TiO$_3$ phase diagrams.\textsuperscript{30} The calculated values of $\beta_{10}$ and $\gamma_{10}$ by first principles show good agreement with the measured latent heat. So we simply adopted them to make the whole set of parameters consistent. The other parameters were determined by fitting Kennedy et al.’s\textsuperscript{8} and Yashima et al.’s\textsuperscript{11} neutron diffraction and x-ray diffraction data. A comparison between the fitted parameters and those from first principles is shown in Table III.

As shown in Table III, the fitted parameters deviate from those calculated by first principles. Both signs and magnitudes are different in almost every case. However, this can be expected because the first principles is for 0 K, and our fits are from the whole temperature range. The validity of the first-principles calculations can be tested by comparing the total free energy at 0 K from both sets of parameters. Actually, the difference is about 6.5% of the total free energy. Considering the possible errors and approximations made during the two calculations, this difference is small. In addition, the discrepancy is only confined to the parameters of the fourth- and sixth-order terms. The nice agreement between our fitted plot and the measured values (Fig. 2) indicates the accuracy of the parameters of the second-order terms and coupling terms from first principles. As shown in Fig. 2, the fitted plot not only reproduces three first-order transitions but also shows the saturation of tilt angles at very low temperature. We also compared the free energy of these structures to study the phase stabilities, as plotted in Fig. 3. Although the differences between $14/mcm$ and Imma and between Cmcm and Pbnm are very small, the relative phase stability of different structures is just as we expected. And the small energy difference between Cmcm and Pbnm indicates the difficulty to get stable Cmcm phase during in-situ x-ray diffraction and neutron diffraction experiments.

### Table II. The order parameters and free energies of different structures of AFD transitions.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Order parameters</th>
<th>Energy expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pm\bar{3}m$</td>
<td>$q_i = 0, (i = 1, 2, 6)$</td>
<td>$F_{14/mcm} = \beta_4 q_1^2 + (\beta_{111} + \beta_{112}) q_1^2$</td>
</tr>
<tr>
<td>$I4/mcm$</td>
<td>$q_i = q_i \neq 0$</td>
<td>$F_{Imma} = 2\beta_4 (q_1^2) + (4 \beta_{111} + 2 \beta_{112}) (q_1^2) + (8 \beta_{111} + 4 \beta_{112}) (q_1^2)$</td>
</tr>
<tr>
<td>Cmcm</td>
<td>$q_i \neq q_i \neq 0$</td>
<td>$F_{Cmcm} = \beta_4 q_1^2 + (\beta_{111} + \beta_{112}) q_1^2 + (\beta_{111} + \beta_{112}) q_1^2 + (4 \gamma_{111} + 8 \gamma_{112}) q_1^2$</td>
</tr>
<tr>
<td>Cmcm</td>
<td>$q_i \neq q_i \neq 0$</td>
<td>$F_{Cmcm} = \beta_4 q_1^2 + (\beta_{111} + \beta_{112}) q_1^2 + (\beta_{111} + \beta_{112}) q_1^2 + (8 \beta_{111} + 4 \beta_{112}) (q_1^2) + (4 \gamma_{111} + 8 \gamma_{112}) (q_1^2) + (8 \gamma_{111} + 4 \gamma_{112}) (q_1^2)$</td>
</tr>
<tr>
<td>Pbnm</td>
<td>$q_i = q_i \neq 0, q_i \neq 0$</td>
<td>$F_{Pbnm} = 2\beta_4 (q_1^2) + (4 \beta_{111} + 2 \beta_{112}) (q_1^2) + (8 \beta_{111} + 4 \beta_{112}) (q_1^2) + (4 \gamma_{111} + 8 \gamma_{112}) (q_1^2) + (8 \gamma_{111} + 4 \gamma_{112}) (q_1^2) + (8 \gamma_{111} + 4 \gamma_{112}) (q_1^2) + (4 \gamma_{111} + 8 \gamma_{112}) (q_1^2) + (8 \gamma_{111} + 4 \gamma_{112}) (q_1^2)$</td>
</tr>
</tbody>
</table>

### Table III. Parameters from fitting and their counterparts from first-principles calculations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$T_2$ (K)</th>
<th>$T_1$ (K)</th>
<th>$\Theta_{q_2}$ (K)</th>
<th>$\Theta_{q_3}$ (K)</th>
<th>$\beta_{10}$</th>
<th>$\gamma_{10}$</th>
<th>$\beta_{11}$</th>
<th>$\beta_{111}$</th>
<th>$\beta_{112}$</th>
<th>$\gamma_{11}$</th>
<th>$\gamma_{111}$</th>
<th>$\gamma_{112}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>From fitting</td>
<td>1285 1590 274 345</td>
<td>$-1.41 \times 10^{68}$</td>
<td>$1.45 \times 10^{69}$</td>
<td>$-3.59 \times 10^{68}$</td>
<td>$1.15 \times 10^{69}$</td>
<td>$-3.38 \times 10^{68}$</td>
<td>$1.15 \times 10^{70}$</td>
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</tr>
<tr>
<td>From first principles</td>
<td>$1.54 \times 10^{26}$</td>
<td>$1.68 \times 10^{26}$</td>
<td>$1.10 \times 10^{29}$</td>
<td>$-2.89 \times 10^{27}$</td>
<td>$2.64 \times 10^{29}$</td>
<td>$-2.31 \times 10^{28}$</td>
<td>$1.27 \times 10^{30}$</td>
<td>$-2.31 \times 10^{28}$</td>
<td></td>
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</tbody>
</table>
Experimentation shows that the intensity of the optical second harmonic generation (SHG) of CaTiO$_3$ thin film changes continuously as a function of temperature, which indicates the ferroelectric transition of CaTiO$_3$ may be of the second order. However, the defects in the thin films, including strain inhomogeneity, domain structures, and so on, may make a first-order transformation look like a second-order one. Further studies are needed to understand the nature of ferroelectric transition in CaTiO$_3$. In this paper, we assume the ferroelectric transformation of CaTiO$_3$ is second order. According to Devonshire’s theory, the dielectric constant of a second-order transformation can be written as

$$\varepsilon_{ij} = \frac{1}{\varepsilon_0} \alpha_{ij} (i,j = 1,2,3),$$

where $\varepsilon_0$ is the vacuum permittivity, and $\alpha_{ij}$ is the coefficient of $P_i P_j$, where $i,j = 1,2,3$. Thus, $P_1 = P_2$, so it is easy to get $\varepsilon_{11} = \varepsilon_{22}$. The calculated dielectric constants are shown in Fig. 4. The total dielectric constant ($\sqrt{2\varepsilon_{11}^2 + \varepsilon_{33}^2}$) is 300 at 0 K, and 144 at room temperature. They are quite close to the measured values 331 and 168, which indicate good accuracy for both the $\alpha_1$ value from first-principles calculations and the Curie temperature $T_1$ from this calculation.

With all the temperature-dependent coefficients, we can investigate the phase stability under different boundary conditions. Here, we will calculate the temperature-constraint strain phase diagram of (001) CaTiO$_3$ thin film as an example.

For the stable structures of strained (001) CaTiO$_3$ thin films, Eklund et al. reported two possible ferroelectric structures on the tensile strain side, $Pmc_{21}$ and $Pmn_{21}$, among which the $Pmn_{21}$ structure has slightly lower free energy. Also from first-principles calculations, Bousquet showed that $Pmc_{21}$ is stable. On the compressive side, $Pnma_{21}$ is the stable structure. In the following calculations, we will only consider these three structures.

Firstly, we renormalized the free energy expression with the thin film boundary condition (see Appendix for detail). By...
minimizing the total free energy with respect to \( q_1 \) and \( q_6 \), respectively, we get

\[
\beta_1'(T) + (2\beta_{11} + \beta_{12})q_1^2 + 6(2\beta_{111} + \beta_{112})q_1^4 - \mu_{13}q_6^2 = 0, \\
\gamma_3'(T) + 2\gamma_{33}q_6^2 + 3(\gamma_{111} + \gamma_{112})q_6^4 - 2\mu_{13}q_1^2 = 0,
\]

(11a)

(11b)

where \( \beta_{ij}' \), \( \mu_{ij}' \), and \( \gamma_{ij}' \) are normalized coefficients. Combining Eqs. (11a) and (11b) with the equation from the coefficient of \( P_1^2 \),

\[
2\alpha'_1(T) - (2t_{11} + 2t_{12} + t_{44})q_1^2 - 2\kappa_{13}q_6^2 = 0,
\]

(12)

we can get the phase boundary between \( Pbnm \) and \( Pmc_{21} \) structures. It should be mentioned here, from our potential, the stable structure on the tensile side is \( Pmc_{21} \), not \( Pmn_{21} \). Similarly, for the phase boundary of \( Pbnm \rightarrow Pna_{21} \) transition,

![FIG. 5. (Color online) The temperature-constraint strain phase diagram of (001) CaTiO\(_3\) (a) with AFD and (b) without AFD. The transition point shown in (a) is measured by SHG experiment.\(^\text{22}\)](image)
we need to solve Eqs. (11a) and (11b) and the equation from the coefficient of $P_3^2$

$$2\alpha_3(T) - 2\alpha_1^2 q_1^2 - 2\kappa_{33} q_6^2 = 0. \tag{13}$$

The calculated phase diagram is asymmetric, as shown in Fig. 5(a). The minimum tensile strain to induce the ferroelectric transition is about 1.5%, which agrees well with the prediction from the first-principles calculations. On the compressive side of the diagram, about 13% compressive strain is needed to induce a $Pbnm \rightarrow Pna_2_1$ transition. This value is so huge that it exceeds the limit of substrate constraint strain. In other words, it is impossible to have a $Pna_2_1$ structure in (001) CaTiO$_3$ thin films. The temperature-constraint strain phase diagram of (001) CaTiO$_3$ thin film without AFD [Fig. 5(b)] was calculated by setting $q_i = 0$ ($i = 1$–6) and solving

$$\begin{bmatrix}
\frac{\partial^2 F}{\partial P_1^2} & \frac{\partial^2 F}{\partial P_1 \partial P_2} & \frac{\partial^2 F}{\partial P_1 \partial P_3} \\
\frac{\partial^2 F}{\partial P_2 \partial P_1} & \frac{\partial^2 F}{\partial P_2^2} & \frac{\partial^2 F}{\partial P_2 \partial P_3} \\
\frac{\partial^2 F}{\partial P_3 \partial P_1} & \frac{\partial^2 F}{\partial P_3 \partial P_2} & \frac{\partial^2 F}{\partial P_3^2}
\end{bmatrix}
\begin{bmatrix}
\frac{\partial P}{\partial P_1} \\
\frac{\partial P}{\partial P_2} \\
\frac{\partial P}{\partial P_3}
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}. \tag{14}$$

Comparing Figs. 5(a) and 5(b), we can easily find the asymmetry of the temperature-constraint strain phase diagram comes from the effect of AFD. Also the ferroelectric transition temperature of CaTiO$_3$ is greatly suppressed by AFD. A similar but weaker effect was also found in SrTiO$_3$. The substantial effect of AFD on ferroelectricity in SrTiO$_3$ is attributed to the competitive anharmonic couplings between AFD mode and the ferroelectric mode and their mutual coupling to the elasticity. In our phenomenological model of CaTiO$_3$, the stability of different structures is strongly dependent on the coupling coefficients among $P_i$, $q_i$, and $\varepsilon_i$, which can be easily seen from Eqs. (11a), (11b), (12), and (13). This indicates that the competition mechanism between AFD and ferroelectricity is essentially the same as that of SrTiO$_3$.

By minimizing the total free energy, we also calculated the polarization of (001) CaTiO$_3$ thin film as a function of in-plane constraint tensile strain at different temperatures. As shown in Fig. 6, the ferroelectric transition temperature increases with in-plane tensile strain. At 0 K, the minimum tensile strain needed to induce the ferroelectric transition is about 1.5%. At 200 K, the critical tensile strain increases to about 4%, indicating the difficulty to obtain strain-induced ferroelectricity at elevated temperature. The calculated polarization of 4% tensile strain at 0 K is 0.61 C/m$^2$, which is more than twice that of BaTiO$_3$. The polarization also exhibits saturation near the transition point and becomes linearly dependent on tensile strain in a large strain region. As compared in the figure, our result of 0 K is a little larger than the first-principles calculations. The discrepancy may rise from different selection of stable structures. In the first-principles calculation, the stable structure used is $Pmn2_1$, whereas we computed the polarization of $Pmm2_1$.

### IV. CONCLUSIONS

A phenomenological thermodynamic potential is developed for CaTiO$_3$ single crystals. The coefficients of the potential are determined from first-principles calculations and neutron diffraction and x-ray diffraction data. This potential effectively coupled the AFD transitions and strain-induced ferroelectric transitions. Several experimental observations, including transition temperatures, transition latent heat, dielectric constant, and tilt angles of TiO$_6$ octahedron, are successfully reproduced. Then the temperature-constraint strain single-domain phase diagram of (001) CaTiO$_3$ is constructed. The dependence of Curie temperature on constraint strain is quite asymmetric, i.e. only tensile strain can induce ferroelectric transition. Comparing the phase diagrams with and without AFD, we conclude that the asymmetry is not inherited from the ferroelectric transition itself but attributed from the AFD suppression.

### ACKNOWLEDGMENTS

Y. Gu would like to thank Z. G. Mei for useful discussions. This work is supported by the NSF MRSEC under Grant No. DMR-0820404 and DMR-0908718.

### APPENDIX

#### 1. Relationship between order parameter $q$ and octahedral tilt angles

For an infinitesimal angle, there is no octahedron distortion during tilting. In the 10-atom supercell, there are four atoms (all oxygen) that displace by equal amounts. The amplitude of $q_i = 1$ means each atom moves 1 Å along $x_i$ direction. Then in a simplified diagram of TiO$_6$ octahedron tilt, we have

$$\tan \theta_i = \frac{2 \times (q_i \times 0.5)}{d_0} = \frac{q_i}{d_0} (i = 1, 2, 3), \tag{A1}$$
where $\theta_i$ is the in-phase tilt angle, and $\omega_0$ is the lattice parameter of the 5-atom cell. Similarly, we have the relationship for out-of-phase tilt
\[ \tan \varphi_i = \frac{q_i}{a_0} \quad (i = 4, 5, 6), \quad \text{(A2)} \]
where $\varphi_i$ is the in-phase tilt angle.

2. Normalizing the total free energy with stress-free boundary condition

With the stress-free boundary condition, we have
\[ \frac{\partial F}{\partial \epsilon_{ij}} = \sigma_{ij} = 0. \quad \text{(A3)} \]

Then we can rewrite the expression for the total free energy as
\[ F = \alpha_{10} \Theta_{S1} \left[ \coth \left( \frac{\Theta_{S1}}{T} \right) - \coth \left( \frac{\Theta_{S1}}{T_1} \right) \right] \left( P_2^2 + P_2^3 + P_3^2 + \alpha_{11}^* (P_1^2 + P_2^3 + P_3^2)^2 + \alpha_{12}^* (P_1^4 + P_2^4 + P_3^4) \right) \\
+ \alpha_{11} (P_1^2 + P_2^3 + P_3^2)^3 + \alpha_{12} (P_1^2 + P_2^3 + P_3^2) (P_1^4 + P_2^4 + P_3^4) + \alpha_{122} (P_1 P_2 P_3)^2 \\
+ \beta_{10} \Theta_{S2} \left[ \coth \left( \frac{\Theta_{S2}}{T} \right) - \coth \left( \frac{\Theta_{S2}}{T_2} \right) \right] \left( q_1^2 + q_2^2 + q_3^2 \right) + \beta_{11}^* (q_1^4 + q_2^4 + q_3^4) + \beta_{12}^* (q_1^2 + q_2^2 + q_3^2)^2 \\
+ \gamma_{10} \Theta_{S3} \left[ \coth \left( \frac{\Theta_{S3}}{T} \right) - \coth \left( \frac{\Theta_{S3}}{T_3} \right) \right] \left( q_1 + q_2 + q_3 \right) + \gamma_{11}^* (q_1^2 + q_2^2 + q_3^2)^2 + \gamma_{12}^* (q_1^4 + q_2^4 + q_3^4) \\
+ \gamma_{11} (q_1^2 + q_2^2 + q_3^2)^3 + \gamma_{11} (q_1^2 + q_2^2 + q_3^2) (q_1^4 + q_2^4 + q_3^4) + \gamma_{12} (q_1^2 + q_2^2 + q_3^2) (q_1^4 + q_2^4 + q_3^4) + \gamma_{12} (q_1^4 + q_2^4 + q_3^4) \\
- \mu_{11}^* (q_1^2 + q_2^2 + q_3^2)^3 - \mu_{12}^* (q_1^2 + q_2^2 + q_3^2)^2 - \mu_{12}^* (q_1^4 + q_2^4 + q_3^4) - \mu_{12}^* (q_1^4 + q_2^4 + q_3^4) \\
- \kappa_{11}^* (P_1^4 + P_2^4 + P_3^4) + \kappa_{12}^* (P_1^2 + P_2^2 + P_3^2) + \kappa_{12}^* (P_1^4 + P_2^4 + P_3^4) - \frac{\xi_{44}^4 \xi_{44}}{C_{44}} (q_1^2 q_2^2 q_3^2 + q_1 q_2 q_3 + q_1 q_2 q_3), \quad \text{(A4)} \]

where the * sign designates the renormalized coefficients, i.e.

\[ \alpha_{11}^* = \alpha_{11} - \frac{C_{11} (g_{12}^2 + 2g_{12} g_{12}) - C_{12} (g_{12}^2 + 2g_{12})}{2(C_{11} - C_{12})(C_{11} + 2C_{12})}, \quad \alpha_{12}^* = \alpha_{12} - \frac{g_{12}^2}{4C_{44}}, \quad \alpha_{12}^* = \alpha_{12} - \frac{(g_{11} - g_{12})^2}{2(C_{11} - C_{12}) + \frac{g_{12}^2}{4C_{44}}} \\
\beta_{11}^* = \beta_{11} - \frac{C_{11} (\lambda_{12}^2 + 2\lambda_{12} \lambda_{12}) - C_{12} (\lambda_{12}^2 + 2\lambda_{12})}{2(C_{11} - C_{12})(C_{11} + 2C_{12})}, \quad \beta_{12}^* = \beta_{12} - \frac{(\lambda_{11} - \lambda_{12})^2}{2(C_{11} - C_{12}) + \frac{\lambda_{12}^2}{4C_{44}}} \\
\gamma_{11}^* = \gamma_{11} - \frac{C_{11} (\zeta_{12}^2 + 2\zeta_{12} \zeta_{12}) - C_{12} (\zeta_{12}^2 + 2\zeta_{12})}{2(C_{11} - C_{12})(C_{11} + 2C_{12})}, \quad \gamma_{12}^* = \gamma_{12} - \frac{(\zeta_{11} - \zeta_{12})^2}{2(C_{11} - C_{12}) + \frac{\zeta_{12}^2}{4C_{44}}} \\
\mu_{11}^* = \mu_{11} + \frac{C_{11} (\lambda_{11} S_{11} + 2\lambda_{12} S_{12}) - C_{12} (\lambda_{11} S_{11} - 2\lambda_{11} S_{11} - 2\lambda_{12} S_{11})}{(C_{11} - C_{12})(C_{11} + 2C_{12})}, \quad \mu_{12}^* = \mu_{12} - \frac{C_{12} (\lambda_{11} S_{11} + 2\lambda_{12} S_{12}) - C_{11} (\lambda_{12} S_{11} + \lambda_{11} S_{12})}{(C_{11} - C_{12})(C_{11} + 2C_{12})} \\
\nu_{11}^* = \nu_{11} + \frac{C_{11} (\lambda_{11} S_{11} + 2\lambda_{12} S_{12}) - C_{12} (\lambda_{11} S_{11} - 2\lambda_{11} S_{11} - 2\lambda_{12} S_{11})}{(C_{11} - C_{12})(C_{11} + 2C_{12})}, \quad \nu_{12}^* = \nu_{12} - \frac{C_{11} (\lambda_{12} S_{12} + 2\lambda_{12} S_{12}) - C_{12} (\lambda_{11} S_{12} - 2\lambda_{11} S_{12} - 2\lambda_{12} S_{12})}{(C_{11} - C_{12})(C_{11} + 2C_{12})} \\
\nu_{11}^* = \nu_{11} + \frac{\xi_{44}^4 \xi_{44}}{C_{44}}, \quad \kappa_{11}^* = \kappa_{11} + \frac{C_{11} (\xi_{11} S_{11} + 2\xi_{12} S_{12}) - C_{12} (\xi_{11} S_{11} - 2\xi_{11} S_{11} - 2\xi_{12} S_{11})}{(C_{11} - C_{12})(C_{11} + 2C_{12})}, \quad \kappa_{12}^* = \kappa_{12} - \frac{C_{12} (\xi_{12} S_{12} + 2\xi_{12} S_{12}) - C_{11} (\xi_{12} S_{12} - 2\xi_{12} S_{12} - 2\xi_{12} S_{12})}{(C_{11} - C_{12})(C_{11} + 2C_{12})}. \quad \kappa_{11}^* = \kappa_{11} + \frac{\xi_{44}^4 \xi_{44}}{C_{44}}. \quad \kappa_{12}^* = \kappa_{12} - \frac{C_{44} \xi_{44}}{C_{44}}.
3. Normalizing the total free energy with thin film boundary condition

The thin film boundary condition is a mixed set of strain and stress boundary conditions. For (001) CaTiO$_3$ thin film, there is a biaxial strain in the $x_1$-$x_2$ plane, and all the stress components associated with $x_3$ direction are equal to zero, i.e.

\[
\begin{align*}
\epsilon_{11} &= \epsilon_{22} = \epsilon_S, \\
\epsilon_{12} &= \epsilon_{21} = 0, \\
\sigma_{13} &= \sigma_{23} = \sigma_{31} = \sigma_{32} = \sigma_{33} = 0,
\end{align*}
\]

where $\epsilon_S$ is the constraint strain. To satisfy the above stress-free condition it requires that

\[
\frac{\partial F}{\partial \epsilon_{ij}} = \sigma_{ij} = 0 \quad (i,j = 13, 23, 31, 32, 33).
\]

So we have

\[
F = \alpha'_1(T)(P_1^2 + P_2^2) + \alpha'_2(T)P_2^3 + \alpha'_{11}(P_1^3 + P_2^3) + \alpha'_{13}P_3^3 + \alpha'_{12}P_1^2P_2^2 + \alpha'_{13}(P_1^2 + P_2^2)P_3^2 + \alpha_{111}(P_1^2 + P_2^2 + P_3^2)^3
\]

\[
+ \alpha_{112}(P_1^3 + P_2^3 + P_3^3) + \alpha_{122}(P_1P_2P_3)^2 + \beta'_1(T)(q_1^2 + q_2^2 + q_3^2) + \beta'_1(q_1^4 + q_2^4) + \beta'_3q_3^4
\]

\[
+ \beta'_1q_1^2q_2^2 + \beta'_3(q_1^2 + q_2^2 + q_3^2)^3 + \beta_{12}(q_1^2 + q_2^2 + q_3^2)(q_1^2 + q_2^2 + q_3^2)^2 + \beta_{122}(q_1q_2q_3)^2
\]

\[
+ \gamma'_1(T)(q_1^2 + q_2^2) + \gamma'_1(q_1^2 + q_3^2) + \gamma'_2q_3(q_1^2 + q_3^2) + \gamma'_3q_1(q_1^2 + q_3^2) + \gamma'_3q_2(q_1^2 + q_3^2) + \gamma'_1(q_2^2 + q_3^2)^3
\]

\[
+ \gamma'_1(q_2^2 + q_3^2) + \gamma'_2(q_2^2 + q_3^2) + \gamma'_3q_1(q_2^2 + q_3^2) + \gamma'_3q_2(q_2^2 + q_3^2)
\]

\[
- \mu'_1(q_1^2 + q_2^2)(q_1^2 + q_3^2) - \mu'_1(q_2^2 + q_3^2)(q_1^2 + q_3^2) - \mu'_1(q_1^2 + q_2^2)(q_1^2 + q_3^2)
\]

\[
- \kappa'_1(P_1^2 + P_2^2)q_3^2 - \kappa'_1(q_1^2 + q_3^2)P_3^2 - \kappa'_4(P_1^2 + P_2^2 + P_3^2)^2
\]

\[
+ \left(\frac{C_{11} + 2C_{12}}{C_{11}} - \frac{C_{12}}{C_{11}}\right)q_3^2,
\]

where the $'$ sign represents the renormalized coefficients with thin film boundary condition, i.e.

\[
\alpha'_1(T) = \alpha_1(T) - \left(\frac{g_{11} + g_{22} - \frac{2C_{12}}{C_{11}}g_{12}}{12} \right) \epsilon_S, \quad \alpha'_3(T) = \alpha_3(T) - \left(\frac{g_8}{2C_{11}} - \frac{2C_{12}}{C_{11}}g_{11}\right) \epsilon_S, \quad \alpha'_1 = \alpha_{11} + \alpha_{12} - \frac{g_{12}^2}{2C_{11}},
\]

\[
\alpha'_{13} = \alpha_{13} + \alpha_{12} - \frac{g_{13}^2}{2C_{11}}, \quad \alpha'_{12} = 2\alpha_{11} - \frac{g_{12}^2}{C_{11}}, \quad \alpha'_{13} = 2\alpha_{11} - \left(\frac{g_{13}^2}{C_{11}} + \frac{g_{12}^2}{2C_{11}}\right),
\]

\[
\beta'_1(T) = \beta_1(T) - \left(\frac{\lambda_1 + \lambda_2 - \frac{2C_{12}}{C_{11}}\lambda_{12}}{2C_{11}} \right) \epsilon_S, \quad \beta'_3(T) = \beta_3(T) - \left(\frac{2\lambda_2 - \frac{2C_{12}}{C_{11}}\lambda_{12}}{2C_{11}} \right) \epsilon_S, \quad \beta'_1 = \beta_{11} + \beta_{12} - \frac{\lambda_{12}}{2C_{11}},
\]

\[
\beta'_{13} = \beta_{13} + \beta_{12} - \frac{\lambda_{12}}{2C_{11}}, \quad \beta'_{12} = 2\beta_{11} - \frac{\lambda_{12}}{C_{11}}, \quad \beta'_{13} = 2\beta_{11} - \left(\frac{\lambda_{12}}{C_{11}} + \frac{\lambda_{12}}{2C_{11}}\right),
\]

\[
\gamma'_1(T) = \gamma_1(T) - \left(\frac{\xi_1 + \xi_2 - \frac{2C_{12}}{C_{11}}\xi_{12}}{C_{11}} \right) \epsilon_S, \quad \gamma'_3(T) = \gamma_3(T) - \left(\frac{2\xi_2 - \frac{2C_{12}}{C_{11}}\xi_{12}}{C_{11}} \right) \epsilon_S, \quad \gamma'_1 = \gamma_{11} + \gamma_{12} - \frac{\xi_{12}}{2C_{11}},
\]

\[
\gamma'_{13} = \gamma_{13} + \gamma_{12} - \frac{\xi_{12}}{2C_{11}}, \quad \gamma'_{12} = 2\gamma_{11} - \frac{\xi_{12}}{C_{11}}, \quad \gamma'_{13} = 2\gamma_{11} - \left(\frac{\xi_{12}}{C_{11}} + \frac{\xi_{12}}{2C_{11}}\right),
\]

\[
\mu'_{11} = \mu_{11} + \frac{\xi_{12}\lambda_{12}}{C_{11}}, \quad \mu'_{33} = \mu_{33} + \frac{\xi_{12}\lambda_{12}}{C_{11}}, \quad \mu'_{12} = \mu_{12} + \frac{\xi_{12}\lambda_{12}}{C_{11}}, \quad \mu'_{13} = \mu_{12} + \frac{\xi_{12}\lambda_{12}}{C_{11}}, \quad \mu'_{31} = \mu_{12} + \frac{\xi_{12}\lambda_{11}}{C_{11}},
\]

\[
t'_{11} = t_{11} + \frac{\xi_{12}\lambda_{12}}{C_{11}}, \quad t'_{33} = t_{11} + \frac{\xi_{12}\lambda_{11}}{C_{11}}, \quad t'_{12} = t_{12} + \frac{\xi_{12}\lambda_{12}}{C_{11}}, \quad t'_{13} = t_{12} + \frac{\xi_{12}\lambda_{11}}{C_{11}}, \quad t'_{14} = t_{44} + \frac{\xi_{12}\lambda_{14}}{C_{11}},
\]

\[
t'_{31} = t_{12} + \frac{\xi_{12}\lambda_{12}}{C_{11}}, \quad t'_{44} = t_{44} + \frac{\xi_{12}\lambda_{14}}{C_{11}}, \quad t'_{44} = t_{44} + \frac{\xi_{12}\lambda_{14}}{C_{11}}, \quad \kappa'_{11} = \kappa_{11} + \frac{\xi_{12}\xi_{11}}{C_{11}}, \quad \kappa'_{33} = \kappa_{11} + \frac{\xi_{12}\xi_{11}}{C_{11}}, \quad \kappa'_{12} = \kappa_{12} + \frac{\xi_{12}\xi_{12}}{C_{11}}, \quad \kappa'_{13} = \kappa_{12} + \frac{\xi_{12}\xi_{11}}{C_{11}}, \quad \kappa'_{31} = \kappa_{12} + \frac{\xi_{12}\xi_{11}}{C_{11}}, \quad \kappa'_{44} = \kappa_{44} + \frac{\xi_{12}\lambda_{14}}{C_{11}},
\]

\[
(A9)
\]
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