Devonshire-Landau free energy of BaTiO₃ from first principles

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We have studied the Devonshire-Landau potential underlying the phase transition sequence of BaTiO₃ using the first-principles effective Hamiltonian of Zhong, Vanderbilt, and Rabe [Phys. Rev. Lett. **73**, 1861 (1994)], which has been very successful in reproducing the phase transitions and the dielectric and piezoelectric properties of this compound. The configuration space (determined by the polarization **P** as order parameter) was explored with the help of auxiliary electric fields. We show that the typically assumed form of the potential, a sixth-order expansion in **P** around the paraelectric cubic phase, properly accounts for the behavior of the system, but we find a nontrivial temperature dependence for all the coefficients in the expansion, including the quadratic one, which is shown to behave nonlinearly. Our results also prove that the sixth-order terms in the free-energy expansion (needed to account for the first-order character of the transitions and the occurrence of an orthorhombic phase) emerge from an interaction model that only includes terms up to the fourth order.

I. INTRODUCTION

From a phenomenological point of view, the behavior of a system in the vicinity of a phase transition can be described in the framework of Landau theory.[1] In this scheme, one begins by identifying the so-called order parameter, a (in general multidimensional) variable **Q** that characterizes the symmetry change in the transition, and then constructs the Landau free-energy function $F(\mathbf{Q};T)$, with the property that the equilibrium value of **Q** as a function of temperature is that which minimizes F. Formally, the Landau free energy is an incomplete thermodynamic potential, which in principle, could be calculated as:

$$F(\mathbf{Q};T) = -k_B T \ln \sum_{j/\mathbf{Q}} e^{-U_j/k_B T}, \quad (1)$$

in analogy with the procedure to obtain the standard free energy in terms of the partition function. Here, the sum is only over those states with the given value of **Q**. In a Landau phenomenological treatment, one just assumes that $F(\mathbf{Q};T)$ exists, and that it can be represented as a simple power series in **Q** in the vicinity of the transition:

$$F(\mathbf{Q};T) = F_0(T) + A(T)Q^2 + B \sum_{\beta} f_{\beta}^{(4)}(\mathbf{Q}) + \dots, \quad (2)$$

where $f_{\beta}^{(j)}$ are invariants of order j constructed from **Q**. The quadratic coefficient A is assumed to vary linearly with temperature in the form $A(T) = \alpha(T - T_0)$, in such a way that T_0 is the transition temperature (for a second-order transition) or the lower metastability limit of the upper phase (for a first-order one). These assumptions are known to break down in the critical region close to the transition point of continuous phase transformations, but they are valid when describing the approximate behavior of the system in wider temperature intervals around the transition temperature. Classical Landau theory ignores any temperature variation of the higher-order

coefficients in the expansion. Nevertheless, it has been applied quite successfully to the analysis of many materials in wide temperature ranges.[2] Nowadays, Landau theory is the most common approach to study the phenomenology of any symmetry-breaking structural phase transition.

One of the early successes of this phenomenological approach to phase transitions was the description by Devonshire[3] of the sequence of transitions in barium titanate (BaTiO₃), a sequence that spans a temperature interval of more than 200 degrees. This material exhibits, at high temperatures, a paraelectric cubic perovskite structure and, as temperature decreases, it undergoes three successive first-order transitions to ferroelectric phases with tetragonal, orthorhombic, and rhombohedral symmetries. In these phases, the polarization **P** points along one of the $\langle 1,0,0 \rangle$, $\langle 1,1,0 \rangle$, and $\langle 1,1,1 \rangle$ cubic directions, respectively.[4] The polarization **P** can be identified as the (three-dimensional) order parameter, and the Devonshire-Landau potential (per unit volume) written as:

$$F = F_0 + \tfrac{1}{2} a P^2 + u P^4 + v(P_x^4 + P_y^4 + P_z^4) + h_1 P^6$$
$$+ h_2(P_x^6 + P_y^6 + P_z^6) + h_3[P_x^4(P_y^2 + P_z^2) + P_y^4(P_z^2 + P_x^2)$$
$$+ P_z^4(P_x^2 + P_y^2)], \quad (3)$$

where F_0 is the free energy of the reference cubic phase and P^2 stands for $P_x^2 + P_y^2 + P_z^2$ (the notation is taken from the review paper by Cowley[5]). This is the complete expansion of F up to the sixth order, and its relatively simple form is due to the high symmetry of the system. The sixth-order terms in **P** in the expansion are needed to account for the first-order character of the transitions (to model nonequivalent coexisting free-energy minima). Moreover, it can be seen that one needs anisotropic sixth-order terms in F to account for the orthorhombic phase of BaTiO₃.[6] Devonshire showed that by assuming a linear temperature dependence for a and suitable

constant values for the rest of the coefficients, it is possible to qualitatively reproduce the transition sequence, as well as the dielectric properties of the system.[7]

After Devonshire's work, the use of an expansion like that of Eq. (3) has become the standard way to model the thermodynamic properties of ferroelectric perovskites, even though the correctness of the assumption of constant high-order coefficients was questioned early on. Drougard *et al.* and Huibregtse and Young[8] studied BaTiO$_3$ at temperatures just above the cubic to tetragonal transition and in the orthorhombic phase, respectively; they assumed the existence of a Devonshire-Landau potential but showed that there should be a significant temperature dependence of the fourth-order terms.[9] It has since been shown that there is a relatively large latitude to produce Devonshire-like models that lead to qualitatively sensible predictions for the transition sequence, divergence of the dielectric constants, etc., even though these models may not be *realistic* when confronted with other experimental evidence.[10] On the other hand, it could be questioned whether such a relatively simple free-energy expansion as that in Eq. (3) exists at all. For instance, Nakamura and Kinase have worked on a different approach to the problem in which a nonpolynomical form of the free energy is used; they also discuss the connection of their work to the Devonshire theory.[11]

In the past decade, first-principles methods based on density-functional theory have demonstrated to be accurate enough to reproduce and predict structural phase transitions in perovskite oxides.[12] In particular, the phase-transition sequence and other properties of BaTiO$_3$,[13,14] PbTiO$_3$,[15] and KNbO$_3$ (Ref. 16) have been studied using the so-called *effective Hamiltonian* approach. An *ab initio* effective Hamiltonian H_{eff} is a mechanical model that includes the relevant microscopic degrees of freedom of the system and is constructed on the basis of first-principles calculations. This model can then be analyzed by statistical methods (typically, Monte Carlo or molecular dynamics) to explore the finite-temperature behavior of the system. Monte-Carlo simulations with an *ab initio* effective Hamiltonian for BaTiO$_3$ have been extremely successful, replicating approximately the experimental transition sequence[13] and succeeding in reproducing the main features of the dielectric and piezoelectric properties of the real system.[14]

A natural question to ask then, is to what extent the thermal behavior resulting from these *ab initio* effective Hamiltonians is compatible with the Devonshire-Landau framework. In this paper we show that a Devonshire-Landau expansion of the form of Eq. (3) does indeed emerge from detailed Monte Carlo simulations with the *ab initio* effective Hamiltonian for BaTiO$_3$ of Ref. 13, with the important qualification that the coefficients in the expansion have a nontrivial temperature dependence. In particular, we show that the sixth-order terms in $F(\mathbf{P};T)$ are nonzero only in the temperature range in which the transitions occur. Moreover, it becomes clear that these sixth-order coefficients appear as products of the statistical fluctuations of a Hamiltonian that only includes terms up to the fourth order in the polar degrees of freedom.

II. METHOD AND TECHNICAL DETAILS

Zhong, Vanderbilt, and Rabe[13] constructed their effective Hamiltonian for BaTiO$_3$ retaining as relevant degrees of freedom of the system a local polar distortion $\mathbf{u}_i$ in each cell, the homogeneous strain η, and an inhomogeneous strain represented by a second set of local vectors $\mathbf{v}_i$. The H_{eff} has the form:

$$
H_{\text{eff}} = \sum_{i,j;\alpha,\beta} J(i,j;\alpha,\beta)u_{i\alpha}u_{j\beta} + \sum_{i;\alpha,\beta} \Gamma(\alpha,\beta)u_{i\alpha}^2 u_{i\beta}^2
$$

$$
+ \sum_{i;\alpha,\beta;l} B(i;\alpha,\beta;l)u_{i\alpha}u_{i\beta}\eta_l + \sum_{l,h} B(l,h)\eta_l\eta_h,
$$

$$(4)$$

where, for clarity, we have not written the terms associated to the inhomogeneous strain. Here, i and j range over the cells in the system, α and β are cartesian indexes, and l and h refer to tensor components in Voigt notation. For the local polar modes, the H_{eff} contains harmonic couplings $J(i,j;\alpha,\beta)$ (on site, $i=j$, and between modes in different cells up to the third nearest neighbors) that reproduce the instabilities of the cubic phase of BaTiO$_3$,[17] and fourth-order on-site terms $\Gamma(\alpha,\beta)$ that define the low-symmetry minima and stabilize the system. The effect of strain is included through the standard elastic energy and through the coupling coefficients $B(i;\alpha,\beta;l)$, which account for the spontaneous strain in the low-symmetry phases. This model is probably the simplest one that captures the essential physics of the system. As mentioned in the Introduction, H_{eff} is fourth-order in the $\{\mathbf{u}_i\}$ variables, whose simulation-box average $\mathbf{u} = 1/N\Sigma\mathbf{u_i}$ determines the polarization through $\Omega\mathbf{P}=Z^*\mathbf{u}$, where Ω is the cell volume and Z^* the local-mode effective charge (see Ref. 13).

A direct link between this H_{eff} and the phenomenological potential of Eq. (3) can be established in the very low-temperature limit $T\rightarrow 0$. Eq. (1) shows that $F(\mathbf{P};0)$ is just the energy of the lowest-lying state with polarization $\mathbf{P}$. In BaTiO$_3$, for $\mathbf{P}$ around the equilibrium value, this state exhibits homogeneously polarized cells with the global strain adjusted so as to minimize the energy (the inhomogeneous strain is zero). Hence $F(\mathbf{P};0)$ can be identified in this region with the energy $U(\mathbf{P})$ resulting from H_{eff} for such a homogeneous configuration. As the homogeneous strain is proportional to the square of the polarization (see Ref. 18), this energy is fourth-order in the polarization, and can be described, in principle, by an expansion of the type of Eq. (3). This means that $h_1=h_2=h_3=0$ in the low-temperature limit. Using the H_{eff} parameters, we obtain the rest of the coefficients of $F(\mathbf{P};0)$: $a=-4/3$, $u=0.094$, and $v=0.051$. Here, units have been chosen so that the first-octant rhombohedral ground state minimum is located at $\mathbf{P}=(1,1,1)$ and its energy per unit volume with respect to the cubic phase is -1. (This election fixes the value of a and the relation $9u+3v=1$; i.e., $F(\mathbf{P};0)$ is determined only by one coefficient.) We have plotted this 0 K free-energy map in Fig. 1(h), which shows the cubic phase as a local free-energy maximum, te-
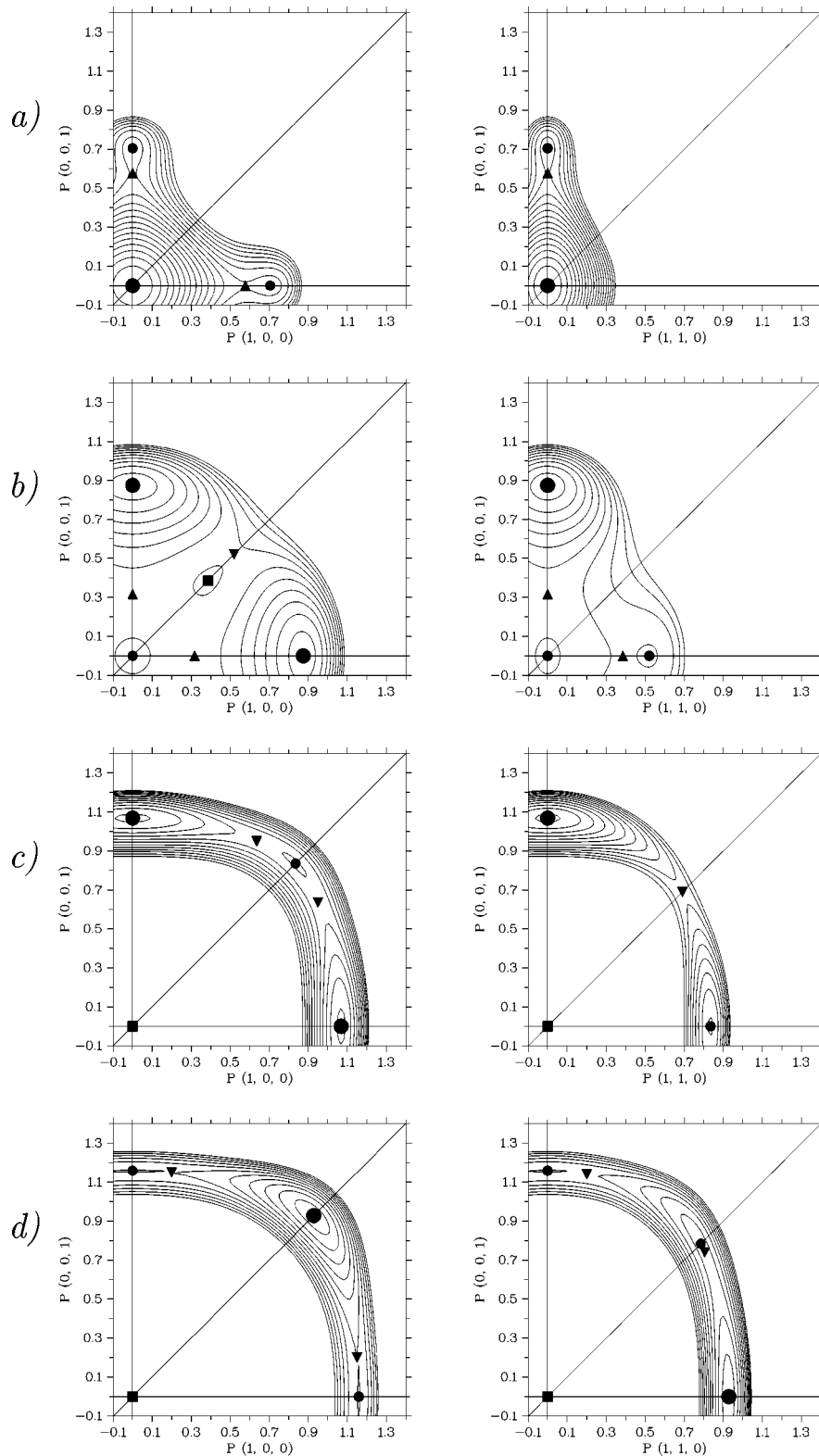
FIG. 1. Free-energy maps of BaTiO$_3$ at several temperatures. Panel (a): 300 K, (b): 290 K, (c): 250 K, (d): 220 K, (e): 210 K, (f): 190 K, (g): 100 K, and (h): 0 K. For each temperature we show the (010) and ($1\bar{1}0$) planes of the order-parameter configuration space, with contour lines depicted only in the low free-energy regions. Symbols characterize the relative stability of the critical points with respect to displacements within a given plane: circles for free-energy minima (a bigger circle corresponds to the stable-equilibrium state), squares for free-energy maxima, and triangles for saddle points [''up'' (resp. ''down'') triangles for points that are maxima (resp. minima) along the radial direction]. Note that critical points with orthorhombic symmetry may need to be represented by two different symbols in the (010) and ($1\bar{1}0$) planes [see panel (b)].
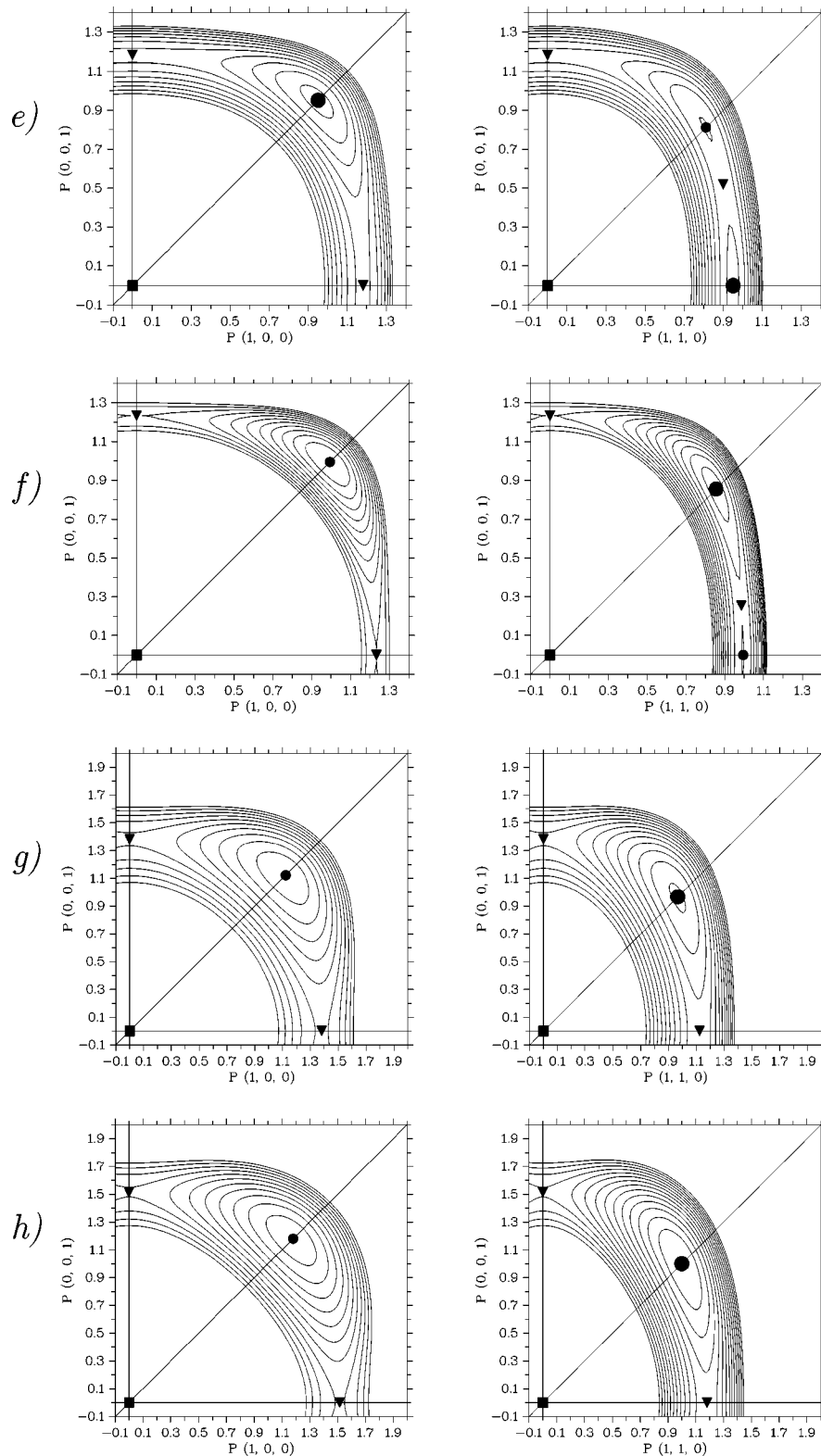
FIG. 1. (*Continued*).

tragonal, and orthorhombic saddle points (both stable in the radial direction), and the rhombohedral global minima.

Now we tackle the calculation of F at finite temperatures.[19] A straightforward approach to obtain information about the Landau potential from the results of Monte Carlo[20] simulations was presented by Radescu *et al.*[2] in the context of a three dimensional Φ^4 model. From Eq. (1) it is easy to show that there exists a relation between the probability distribution of the order parameter $\mathcal{P}(\mathbf{Q};T)$ and the corresponding Landau potential $F(\mathbf{Q};T)$:

$$F(\mathbf{Q};T) - F_{eq}(T) = -k_B T \ln[\mathcal{P}(\mathbf{Q};T)], \qquad (5)$$

where $F_{eq}(T)$ is the equilibrium free energy of the system at the temperature considered. This procedure, which can be quite efficiently applied to relatively simple cases such as the Φ^4 model (one-dimensional order parameter, a single second-order phase transition), is not well suited for our problem. We have to study a three-dimensional free-energy map with coexisting nonequivalent minima. A typical Monte Carlo simulation gives information only about one free-energy minimum (usually, the one corresponding to the stable-equilibrium state of the system), with a poor sampling of the order-parameter probability-distribution function in other regions. On the other hand, more sophisticated sampling strategies would be very demanding from the computational point of view.

This problem can be overcome, and $F(\mathbf{P};T)$ computed in an efficient manner, by modifying the effective Hamiltonian so as to include the effect of an external electric field $\mathbf{E}$:[14]

$$H'_{\text{eff}} = H_{\text{eff}} - \mathbf{E} \cdot Z^* \sum_i \mathbf{u}_i, \qquad (6)$$

where Z^* is the Born effective charge associated to the local polar distortions. As the quantity multiplying the electric field is just the total dipole moment of the system, the new Landau potential is simply $F'(\mathbf{P};T,\mathbf{E}) = F(\mathbf{P};T) - \mathbf{EP}$. An applied electric field changes the location (and possibly the symmetry) of the stable-equilibrium state. The new location can be determined by a Monte Carlo (MC) simulation of the modified effective Hamiltonian ($\mathbf{P}_{eq} = \langle \mathbf{P} \rangle$) and also computed directly from F'. The idea can be mathematically expressed as:

$$\left[\frac{\partial F'(\mathbf{P};T,\mathbf{E})}{\partial \mathbf{P}} \right]_{\mathbf{P}_{eq}(T,\mathbf{E})} = \mathbf{0}. \qquad (7)$$

The left-hand side of this equation depends linearly on the coefficients of F and on the electric field. Thus, for a given temperature, we can consider several electric fields, perform MC runs to obtain the equilibrium values $\mathbf{P}_{eq}$,[21] and then find the best solution of an overdetermined set of linear equations of the form of Eq. (7) to get the coefficients of the expansion of F.

For each temperature, we first performed a zero-field calculation to obtain a snapshot of the stable-equilibrium configuration. We then used this configuration as the starting point for the runs with electric field applied. In order to illustrate the kind of information we were pursuing, consider T such that the stable-equilibrium state of the system is orthorhombic with $\mathbf{P}_{eq} = P_{eq}(1,1,0)$. In this case, we would first use fields of the form $(E,E,0)$ to obtain information about the response of the system within the orthorhombic phase. Fields of the forms $(E,0,0)$, $(0,0,E)$, and (E,E,E) would probe the relative stability of minima with different symmetries. Finally, general fields leading to $P_{x,eq} \neq P_{y,eq} \neq P_{z,eq} \neq P_{x,eq}$, would explore in detail the intermediate regions of the configuration space. In our Monte Carlo simulations we used a $14 \times 14 \times 14$ supercell (which corresponds to 13 720

atoms) with periodic boundary conditions; we typically performed 15 000 MC sweeps for the thermalization of the system and 35 000 more to calculate the averages of the polarization (these are very well-converged calculation conditions, as can be checked in Refs. 13–15). For each temperature, we considered around one hundred different electric fields and constructed a largely overdetermined system of equations for the coefficients in F, which could then be reliably fitted.

III. RESULTS AND DISCUSSION

The data from our Monte Carlo simulations can indeed be represented by a Landau free energy in the form of Eq. (3) in a wide-temperature interval that includes all the transitions. [The transition temperatures predicted by the effective Hamiltonian are $T_{c1} = 297$ K (cubic to tetragonal), $T_{c2} = 230$ K (tetragonal to orthorhombic), and $T_{c3} = 200$ K (orthorhombic to rhombohedral), respectively.[22]] Our results show that the coefficients in the expansion of F have a significant and nontrivial temperature dependence.

Before discussing in detail the behavior of the coefficients, it is helpful to present the shape of the free energy they determine at a few temperatures in the range of the phase transitions. Figure 1(a) (300 K) shows how tetragonal local minima appear just above the first transition, while the absolute minimum of F is still located at $\mathbf{P}=0$ in the cubic well. Panels (b) and (c) correspond to 290 and 250 K, respectively, i.e., temperatures in the range of stability of the tetragonal phase. We see that the tetragonal wells are indeed the global free-energy minima, and that the orthorhombic and rhombohedral wells nucleate in the form of saddle points that are unstable with respect to a tetragonal distortion (in the rhombohedral case, the saddle points are unstable with respect to an orthorhombic distortion also). Panels (d) and (e) refer to 220 and 210 K, respectively, i.e., temperatures in the orthorhombic range. The tetragonal wells become metastable with respect to the orthorhombic ones, which are now the free-energy global minima. At the same time, rhombohedral local minima appear. Finally, panels (f) and (g) correspond to 190 and 100 K, respectively, both in the rhombohedral temperature range. Here we see that the rhombohedral minima have finally become the deepest ones. It is clear that the sequence converges to the free-energy map given by the effective Hamiltonian itself [panel (h)]. For all the transitions, the coexistence of different free-energy minima in the figures evidences their first-order character.

Our method to explore the F landscape has a limitation when probing the vicinity of the cubic phase. After the point $\mathbf{P}=0$ becomes a local free-energy maximum a few degrees below T_{c1}, it is no longer possible to sample the region around it using auxiliary electric fields: the cubic structure is already unstable and thus no longer useful as a starting point for the simulations, and attempts to steer a system in a tetragonal, orthorhombic, or rhombohedral well towards $\mathbf{P}=0$ only succeed in landing it in the corresponding symmetry-inverted domain. As the behavior of F around $\mathbf{P}=0$ is basically determined by the quadratic coefficient a of the Devonshire-Landau expansion, the value assigned to this co-
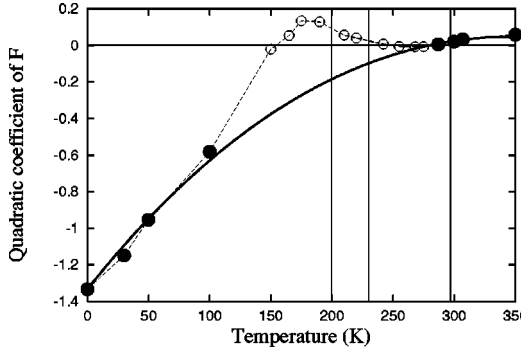
FIG. 2. Temperature behavior of the quadratic coefficient (a) of the Devonshire-Landau potential: The dashed line connects the values obtained from a direct fit to MC data, the solid line shows the interpolated $a(T)$, and the solid circles are the points used to fit the interpolating polynomial (see text). The transition temperatures are marked with vertical lines.

efficient by a fit of the simulation data should be considered suspect. (This problem pertains only to the region near $\mathbf{P}=0$). Information about the relative stability of tetragonal, orthorhombic, and rhombohedral phases is available at any temperature, since it is always possible to apply fields that lead the system to each of these symmetries.)

As shown in Fig. 2, at temperatures around and above T_{c1}, the behavior of a is fairly reasonable. It is positive at high temperatures, becoming negative a few degrees below T_{c1}, as corresponds to a first-order transition. For very low temperatures, a also behaves well, tending smoothly to its 0 K value. This is because, in this region, the underlying Landau potential is simple (the thermal fluctuations are relatively small and the sixth-order terms almost negligible). However, in the intermediate region (from 150 to 250 K), a turns positive again, which would mean that the cubic phase becomes metastable in a wide temperature interval. This metastability is explicitly ruled out within our model by zero-field MC simulations starting from a cubic phase, in which we found no trace of it, which illustrates the fact that the fitted a is not guaranteed to be valid within the unexplored region close to $\mathbf{P}=0$. We thus reconsidered the fitting of our data, imposing a smooth temperature evolution of a: we assumed that in the intermediate-temperature range $a(T)$ is given by a simple interpolation (Fig. 2) between the high-temperature region, where we can reliably sample it, and the low-temperature limit determined directly by the convergence to the effective Hamiltonian (a third-order polynomial suffices for our purposes). With this from for $a(T)$ fixed, our MC data are still well fitted to the Landau potential of Eq. (3). For instance, at 190 K, the relative error obtained when $a(T)$ is freely fitted is 2.2%, and when $a(T)$ is fixed by the interpolation, the error is still very small: 3.6%. This clearly shows that, in the intermediate-temperature region, our Monte Carlo data contain little information about the value of a. Higher-order terms were tried but found to play no role in the fit, so they can be excluded from the potential. Our final results are shown in Fig. 3.
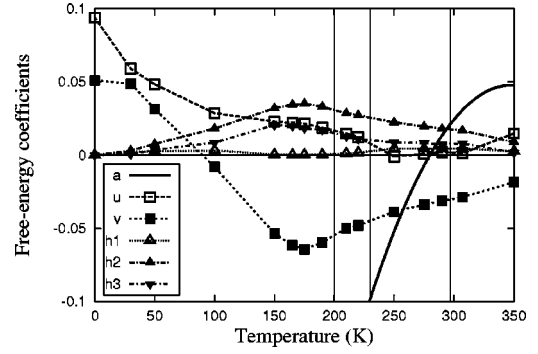

FIG. 3. Free-energy coefficients fitted to MC data assuming $a(T)$ is given by the solid line in Fig. 2. The transition temperatures are marked with vertical lines.

At very low temperatures a, u, and v tend to their 0 K values and the sixth-order terms go to zero. On the other hand, at temperatures well above the first transition ($T > 350$ K) we find the MC data are properly fitted to a fourth-order Landau potential, so the sixth-order terms can again be excluded from the model. The sixth-order terms then occur only in the temperature range in which the transitions take place (as plainly shown in Fig. 3). It is also remarkable that the fourth-order terms exhibit a very strong temperature dependence. Particularly, the anisotropic term v changes sign at around 90 K and takes large negative values all through the intermediate-temperature range. So, apart from the influence it has, together with h_2 and h_3, in determining the transition sequence, we find that a negative v is responsible for the first-order character of the cubic to tetragonal transition.

In Fig. 4 we have plotted our coefficients near the cubic to tetragonal transition temperature together with the available experimental results.[8,9] (We have changed the temperature scale to make the experimental T_{c1} coincide with the theoretical one.) The agreement is only qualitative, but as good as could be expected given the simplifying assumptions involved in the experimental work of Ref. 8 (the coefficients are restricted to be constant or to depend linearly on tempera
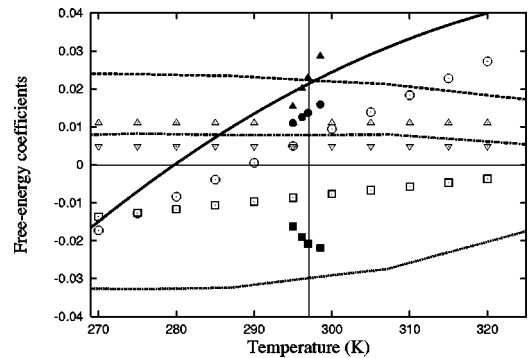

FIG. 4. Comparison of our free-energy coefficients (lines) with the experimental values of Refs. 8 (open symbols) and 9 (solid symbols): solid line and circles for a, dotted line and squares for $u+v$, dashed line and ''up'' triangles for h_1+h_2, and dash-dotted line and ''down'' triangles for h_3. The vertical line marks the cubic-tetragonal transition temperature.

ture) and the fact that the differences among the two experiments are comparable to those between experiment and theory.

Our work strongly suggests that the phase transitions of BaTiO$_3$ can be described in terms of a single Landau potential F with the form of Eq. (3). Despite what is assumed in most of the previous work on this problem, the quadratic parameter a is found to exhibit a strongly nonlinear temperature dependence. This is clear because we can reliably calculate a at high (over T_{c1}) and very low temperatures, and the two regions cannot be joined linearly. We show that all the high-order terms in F present a very significant evolution with temperature. This conclusion is essentially opposed to the temperature-independent behavior that is still assumed by some authors (see, for example, Ref. 10). It is also very remarkable that the two features of BaTiO$_3$ that require the inclusion of sixth-order terms in the Landau potential, i.e., the first-order character of the transitions and the occurrence of an orthorhombic phase, have been reproduced using a fourth-order effective Hamiltonian.[23] This piece of information should be taken into account when constructing mechanical models to study the finite-temperature behavior of BaTiO$_3$ or similar compounds. For instance, the authors of Ref. 11 included sixth-order terms in the underlying interaction model for BaTiO$_3$ with the explicit aim to account for the first-order character of the transitions; our results indicate that those terms should be unnecessary.

IV. SUMMARY

We have studied the Devonshire-Landau potential underlying the phase transition sequence of BaTiO$_3$ using the first-principles effective Hamiltonian parametrized by Zhong, Vanderbilt, and Rabe. The order-parameter configuration space was explored with the help of auxiliary electric fields that change the location and relative stability of the free-energy minima. Our results show that the typically assumed form of the potential, an expansion up to the sixth order in the polarization from the paraelectric cubic phase, properly accounts for the behavior of the system. But, despite what is usually presumed, we find a nontrivial temperature dependence for all the coefficients in the expansion, including the quadratic term a, which is shown to behave nonlinearly. Our work also shows that the sixth-order terms in polarization needed to explain basic features of BaTiO$_3$ in a Devonshire-Landau approach (the first-order character of the transitions and the occurrence of an orthorhombic phase) are properly accounted for by an interaction model that only includes terms up to the fourth order.

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[1] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958).

[2] S. Radescu, I. Etxebarria, and J. M. Perez-Mato, J. Phys.: Condens. Matter **7**, 585 (1995).

[3] A. F. Devonshire, Philos. Mag. **40**, 1040 (1949); **42**, 1065 (1951); Adv. Phys. **3**, 85 (1954).

[4] See, for example: F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, England, 1962; reedition by Dover Publications, Inc., New York, 1993) or M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectric Materials* (Clarendon, Oxford, 1977).

[5] R. A. Cowley, Adv. Phys. **29**, 1 (1980).

[6] For a discussion of the conditions that a Devonshire-Landau potential must fulfill to account for phases of a given symmetry, see D. Vanderbilt and M. H. Cohen, cond-mat/0009337 (unpublished).

[7] In the second article in Ref. 3, Devonshire extended the theory to consider the strain and gave a proper account for the elastic and piezoelectric properties of the system.

[8] M. E. Drougard, R. Landauer, and D. R. Young, Phys. Rev. **98**, 1010 (1955); E. J. Huibregtse and D. R. Young, *ibid.* **98**, 1562 (1956).

[9] A temperature dependence of the sixth-order terms in F was reported by J. A. Gonzalo and J. M. Rivera, Ferroelectrics **2**, 31 (1971).

[10] See the discussion in Ref. 5 and that by K. Fujita and Y. Ishibashi, Jpn. J. Appl. Phys., Part 1 **36**, 254 (1997).

[11] K. Nakamura and W. Kinase, J. Phys. Soc. Jpn. **61**, 4596 (1992); **61**, 2114 (1992).

[12] See the short review by D. Vanderbilt, Curr. Opin. Solid State Mater. Sci. **2**, 701 (1997) and references therein.

[13] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. Lett. **73**, 1861 (1994); Phys. Rev. B **52**, 6301 (1995).

[14] A. García and D. Vanderbilt, Appl. Phys. Lett. **72**, 2981 (1998); *Proceedings of the First-Principles Calculations for Ferroelectrics: Fifth Williamsburg Workshop*, edited by R. E. Cohen, AIP Conf. Proc. No. 436 (AIP, Woodbury, NY, 1998), p. 53.

[15] U. V. Waghmare and K. M. Rabe, Phys. Rev. B **55**, 6161 (1997).

[16] H. Krakauer, R. Yu, C. Z. Wang, and C. Lasota, in *Proceedings of the 1997 Williamsburg Workshop on Ferroelectrics*, edited by H. Chen [Ferroelectrics **206**, 133 (1998)].

[17] The dispersion curves associated to the harmonic effective system are essentially those of the unstable band calculated by Ghosez *et al.* [Ph. Ghosez, E. Cockayne, U. V. Waghmare, and K. M. Rabe, Phys. Rev. B **60**, 836 (1999)].

[18] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **49**, 5828 (1994).

[19] For a determination of $F(T)$ for an idealized model of a structural phase transition, see A. P. Giddy, M. T. Dove, and V. Heine, J. Phys.: Condens. Matter **1**, 8327 (1989).

[20] Although our emphasis is on Monte Carlo simulations, the discussion applies also to molecular dynamics methods.

[21] From a MC simulation we typically obtain $\langle \mathbf{P} \rangle$ corresponding to the stable-equilibrium state of the system. Eq. (7) can be used

also if the system gets stuck in a metastable-equilibrium state, but not if the simulation alternates from one free-energy minimum to another, giving a spurious $\langle \mathbf{P} \rangle$.

[22] The experimental transition temperatures for $BaTiO_3$ are $T_{c1} = 403$ K, $T_{c2} = 278$ K, and $T_{c3} = 183$ K.

[23] For $Pb(Zr_xTi_{1-x})O_3$, a similar fourth-order effective Hamiltonian reproduces a monoclinic phase [see L. Bellaiche, A. Garcia, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000)], and thus would formally lead to eighth-order terms in the Devonshire-Landau potential. See Ref. 6 and references therein.