Electromechanical Behavior of $BaTiO_3$ from First Principles

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Using an effective Hamiltonian parametrized from first-principles, Monte Carlo simulations are performed in order to study the piezoelectric response of $BaTiO_3$ in the ferroelectric tetragonal phase as a function of temperature. The effect of an electric field on the phase behavior is also illustrated by a simulation of the transformation of a rhombohedral domain into a tetragonal one under a strong field.

One of the earliest technological applications of ferroelectric materials was in the area of electromechanical transducers, the physical basis of which is the piezoelectric effect. The piezoelectric coefficients characterize the (linear) change in polarization in the presence of an external stress, or equivalently, a change in shape under the application of an external electric field. While a phenomenological, descriptive framework for such electromechanical effects has been available for a long time, a quantitative microscopic understanding of the response of individual materials is lacking, and further technical development has to proceed largely by trial and error. The importance of obtaining a deeper understanding has been highlighted by recent reports [1] of giant piezoelectric response in single crystals of relaxor perovskites of the form PMN-PT and PZN-PT. The structural complexity of these materials and the variety of phenomena that might be involved make it rather difficult to offer a clear understanding of their observed properties.

It is in this context that first-principles calculations can help. They can be used to selectively "turn off" features of the system and study its response in conditions that are very difficult or impossible to realize in the laboratory. Besides, they can provide a microscopic view of the materials properties. So far, the primary uses of first-principles calculations relevant to this area have been calculations of piezoelectric coefficients for simple materials at zero temperature [2]. In this work, as a step towards the theoretical treatment of the electromechanical response of complex systems, we present the first calculations of the piezoelectric response as a function of temperature for $BaTiO_3$, an important member of the perovskite family of ferroelectric compounds. We also illustrate the influence of electric fields on the phase behavior of $BaTiO_3$. We base our approach on a scheme which has proven very successful [4] in the description of the rich phase diagrams of perovskite oxides: an effective Hamiltonian which contains the physically relevant degrees of freedom of the structure (notably the "soft mode") is constructed on the basis of high-quality first-principles calculations, and the statistical mechanics of the system is then studied by Monte Carlo simulation. The usefulness of the method is not restricted to the calculation of piezoelectric coefficients and the study of generalized phase diagrams. Indeed, the elastic and dielectric response can be similarly computed, and it can form the basis for an analysis of non-linear effects [5].

The appropriate thermodynamic identity for a crystal in the presence of a (possibly anisotropic) stress and an electric field is [6]

$$dU = TdS + \sigma_\nu d\eta_\nu + E_i dD_i \quad . \tag{1}$$

Here U is the internal energy of the crystal (per unit volume), T and S are the temperature and entropy, σ_ν and η_ν are the components of the stress and strain tensors in the Voigt notation [7], E_i is the ith component of the macroscopic electric field, and D_i is the corresponding component of the electrical displacement vector (in SI units, $\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P}$).

We parametrize the energy U of the system by means of an effective Hamiltonian $H_{\rm eff}$ which represents a Taylor expansion of the energy surface around the high-symmetry cubic perovskite structure. $H_{\rm eff}$ is written in terms of the dynamical variables which are relevant to the low-energy distortions: the amplitudes $\{\mathbf{u}\}$ of the local modes (three degrees of freedom per unit cell) which represent the "soft" transverse optical phonon and are directly related to the polarization of the crystal [$\mathbf{P} = (Z^*/V)\sum\mathbf{u}$, where Z^* is the mode effective charge and V is the cell volume]; a set $\{\mathbf{v}\}$ of displacement variables representing the acoustic modes; and the six components of the homogeneous strain η. The parameters of the energy expansion, including the on-site local-mode self-energy, the interaction between local modes (both short-range and dipole-dipole), the elastic energy, and the local mode-elastic coupling, are computed using highly accurate first-principles LDA calculations with Vanderbilt ultrasoft pseudopotentials [3]. More details about the construction of the effective Hamiltonian are given in Ref. [4], where the method is shown to provide a good account of the phase transition sequence in $BaTiO_3$ within the limitations of an approach based on low-energy distortions. The extension of the standard Metropolis Monte Carlo algorithm to include the effects of stress and electric field involves replacing the Boltzmann probability factor $\exp(-\beta U^j)$ by $\exp[-\beta(U^j - \sigma_\nu \eta_\nu^j - E_i P_i^j)]$ in the acceptance criterion for state j. For a given temperature, stress, and field, the strain η and the mode variables are allowed to fluctuate, their average values determining the shape and net polarization of the system.

As an important application of the method, we compute the piezoelectric response of the tetragonal (ferroelectric) phase of $BaTiO_3$ (point group $4mm$), which is stable from approximately 278K to 403K and exhibits a spontaneous polarization that we take to be along the z axis. The relevant coefficients are

$$d_{i\nu} = \left(\frac{\partial \eta_\nu}{\partial E_i}\right)_\sigma = \left(\frac{\partial P_i}{\partial \sigma_\nu}\right)_E = \beta \langle \Delta P_i \Delta \eta_\nu \rangle \tag{2}$$

where $\Delta X = X - \langle X \rangle$ and the averages are computed using the extended Boltzmann factor defined above [8]. These equations suggest three different ways to calculate the response: direct calculations of the average strain as a function of applied field, or the average polarization as a function of (anisotropic) stress, and computation of the statistical correlation between polarization and strain. The latter is conceptually the simplest, although relatively long simulations (on the order of 100000 Monte Carlo sweeps (MCS) [9]) are needed to obtain good statistics. Of the direct approaches, the field-strain calculations are the most efficient as only one series of calculations for varying E_3 is needed to compute the most common coefficients d_{31} and d_{33} (representing respectively the transverse contraction and the longitudinal expansion under the application of a field parallel to the ferroelectric axis).

An effective Hamiltonian based on a finite Taylor expansion of the energy should not be expected to reproduce perfectly the behavior of the material at relatively high temperatures. In particular (see Ref. [4]) the theoretical transition temperatures are progressively shifted downwards with respect to the true ones [11]. In order to provide a better comparison of our results for d_{31} and d_{33} to experiment (Fig. 1), we have therefore rescaled linearly the theoretical temperatures so that the end points of the range of stability of the tetragonal phase coincide. The agreement with the available experimental data is very good, and the general trend of the temperature dependence (upward tendency in d_{33}, downward in d_{31}) corresponds to the pseudo-divergent behavior observed experimentally near the tetragonal-to-cubic transition [12]. In the thermodynamic limit, the correlation and field-strain approaches should be completely equivalent. Since we use finite runs and finite simulation boxes ($12 \times 12 \times 12$ or 1728 unit cells for the correlation analysis and $10 \times 10 \times 10$ or 1000 unit cells for the field-strain calculations), the results are similar but not identical.

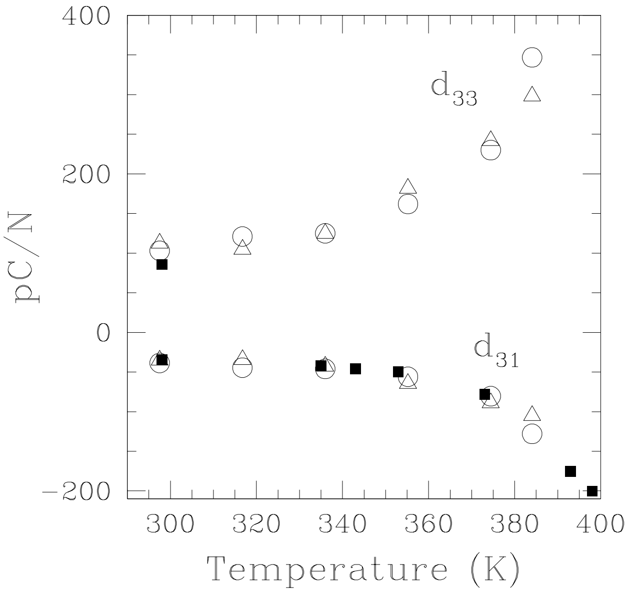

FIG. 1. Piezoelectric coefficients as a function of temperature in the tetragonal phase. Open triangles and circles represent values computed from the strain response to an electric field and from polarization-strain correlations, respectively. Solid squares show experimental data points (Ref. [10]).

Our method can also be applied to the study of the stability of the different phases as a function of the external field and stress. As an illustration of the influence of electric fields on the phase diagram, we performed a simulation of the effect of a strong field on the strain and electrical polarization of a $BaTiO_3$ sample in the rhombohedral (R) phase. This phase, with point group $3m$, is stable at temperatures below 183K, and exhibits a spontaneous polarization along one of the original $\langle 111 \rangle$ cubic directions, and a corresponding strain deformation with respect to the cubic phase satisfying $\eta_1 = \eta_2 = \eta_3$ and $\eta_4 = \eta_5 = \eta_6$. Choosing a simulation temperature of 100K, we applied an electric field along the cubic z axis, progressively increasing the strength of the field up to a maximum value of 5×10^3 kV/cm. The evolution of the strain and polarization as a function of the field is shown in Figs. 2 and 3, respectively. The rhombohedral symmetry is immediately broken by the field, as can be seen by the $\eta_1 = \eta_2 \neq \eta_3$ splitting (and the analogous one among the polarization components). In the approximate range $2 - 2.5 \times 10^3$ kV/cm, there is a noticeable split in η_1 and η_2, all the off-diagonal components of the strain save η_4 ($2\eta_{23}$ in the standard tensor notation) fall to zero, and P_1 falls to nearly zero. Thus, this range corresponds to an orthorhombic phase with the polarization in the yz plane (different simulations "pick" at random between the yz and the xz planes). For larger fields, the equality between η_1 and η_2 is restored, all the off-

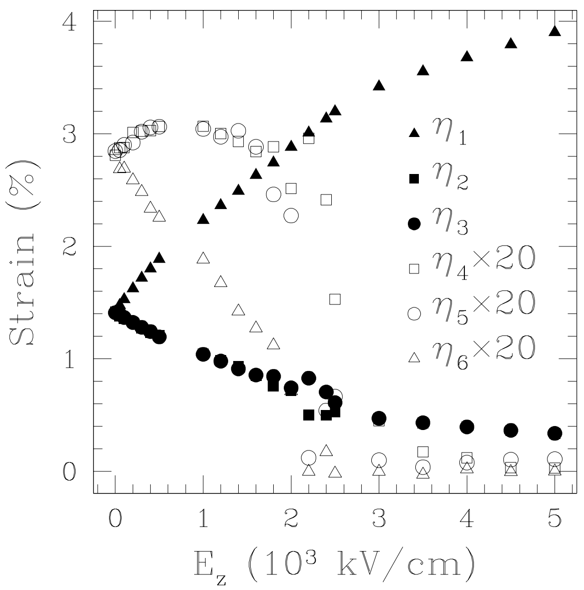

FIG. 2. Strain vs. field for the phase transformation from rhombohedral to tetragonal under a strong field. Off-diagonal strain components are magnified for clarity.

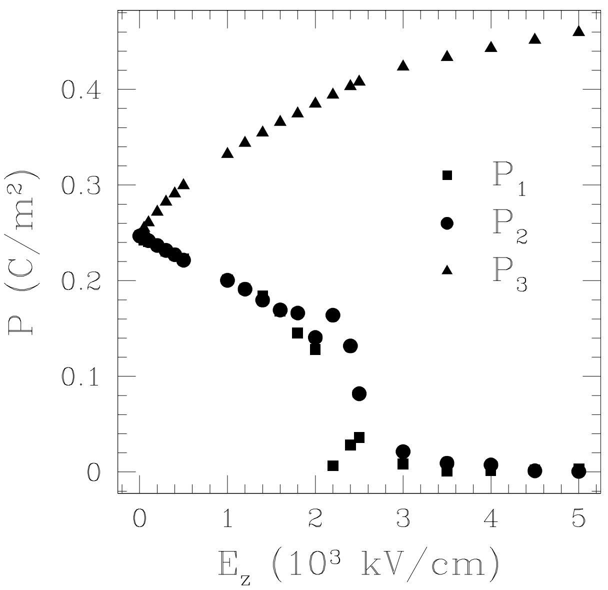

FIG. 3. Polarization vs. field for the phase transformation from rhombohedral to tetragonal under a strong field.

diagonal strain components fall to zero, and P_2 follows P_1 in its earlier drop. The resulting phase is tetragonal, with **P** along the [001] direction. The behavior emerging from our simulation parallels that seen experimentally [1] in the PMN-PT and PZN-PT giant-response materials: individual domains are in a rhombohedral structure, and as an electric field is applied and progressively increased along z, the polarization rotates from a [111] direction to a [001] direction.

In conclusion, we have shown how the electromechanical response of a system can be computed from first principles using an effective Hamiltonian suitably augmented by terms representing the influence of applied (anisotropic) stresses and electric fields. As an application, we have presented the first calculations of the piezoelectric response of ferroelectric tetragonal $BaTiO_3$ as a function of temperature. We have also performed simulations illustrating the effect of electric fields on the phase behavior of this material.

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[6] See, for example, M.E. Lines and A.M. Glass, *Principles and Applications of Ferroelectric and Related Materials* (Clarendon Press, Oxford, 1977).

[7] In what follows, Greek subscripts run from 1 to 6 (Voigt scheme).

[8] The relationship between $d_{i\nu}$ and the strain and polarization correlations can be simply obtained by differentiation of the expression $\Lambda\langle X\rangle = \sum_j X^j \mathrm{Prob}_j$, where Prob_j is the extended Boltzmann factor and Λ is the extended partition function.

[9] A Monte Carlo sweep is completed after each local variable is considered for a "flip attempt" and each component of the homogeneous strain suffers $2L+1$ attempted changes, where L is the linear size of the simulation box.

[10] *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology* New Series,Vol. III/11, (Springer, 1989).

[11] For the rhombohedral to orthorhombic to tetragonal to cubic transition sequence, the experimental T_c's are respectively 187K, 278K, and 403K, while the theoretical ones are 197K, 230K, and 295K.

[12] See, for example, M.E. Lines and A.M. Glass, *op. cit.*; F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, 1962).