A Microscopic Model of Ferroelectricity in Stress-free PbTiO₃ Ultrathin Films

Ph. Ghosez^{a)} and K. M. Rabe
Department of Applied Physics, Yale University, P.O. Box 208284, New Haven, CT 06520-8284, USA.

(February 26, 2018)

The ground-state polarization of PbTiO₃ thin films is studied using a microscopic effective Hamiltonian with parameters obtained from first-principles calculations. Under short-circuit electrical boundary conditions, (001) films with thickness as low as three unit cells are found to have a perpendicularly polarized ferroelectric ground state with significant enhancement of the polarization at the surface.

Ferroelectricity is a collective phenomenon and, as such, it is expected to be strongly influenced by surfaces and finite size effects [1,2]. It has been generally thought that decreasing the thickness of thin films of perovskite ABO₃ compounds suppresses ferroelectricity and eliminates it altogether at a nonzero critical thickness. In PbTiO₃, this critical size has been estimated as 7-10 nm [3–5]. However, recently synthesized high quality films of PbZr_xTi_{1-x}O₃ have been observed to exhibit a stable perpendicularly polarized ferroelectricity down to and possibly even below a thickness of 40 Å [6]. This suggests that the earlier observations could stem from variations in electrical and mechanical boundary conditions or from extrinsic effects associated with defects and impurities.

In this Letter, we address the question of the intrinsic ferroelectricity of PbTiO₃ thin films using a first-principles effective Hamiltonian (\mathcal{H}_{eff}) based on that previously developed for studies of the finite-temperature ferroelectric transition in the bulk [7]. This approach combines the advantages of phenomenological models, which are physically transparent, with those of first-principles simulations, which yield highly accurate material-specific microscopic information. We find that PbTiO₃ films exhibit a ferroelectric instability which is even greater than that of the bulk, and identify the reason for this within the model. Further, we analyze the spatial variation of the polarization within the film, showing that polarization is significantly enhanced over the bulk value in a single surface layer.

We consider symmetrically TiO_2 terminated (001) slabs of PbTiO_3 , under stress-free and short-circuit boundary conditions. The latter are imposed by the presence of perfectly conducting sheets positioned at a distance $a_0/4$ above and below the top and bottom surfaces of the slab, where a_0 is the experimental lattice constant of bulk PbTiO_3 ($a_0 = 3.97 \text{ Å}$).

As for the bulk [7], for the thin films, \mathcal{H}_{eff} is constructed by projecting the full interionic Hamiltonian into a subspace which contains the relevant degrees of freedom. These are the localized atomic displacement patterns $(\vec{\xi_i})$ centered around each unit cell i, determined by the lattice Wannier function method [12], and the homogeneous strain tensor $e_{\alpha\beta}$. The form of the resulting model is

$$\mathcal{H}_{eff} = (\mathcal{H}_{dipolar} + \mathcal{H}_{sr}) + \mathcal{H}_{anharm} + \mathcal{H}_{strain}$$

where the harmonic part is separated into a long-range dipolar term, $\mathcal{H}_{dipolar}$, and short-range corrections, \mathcal{H}_{sr} . \mathcal{H}_{anharm} represents the anharmonic couplings and \mathcal{H}_{strain} combines the elastic energy and the lowest order coupling of $\vec{\xi}_i$ to $e_{\alpha\beta}$. The local dipole per unit cell is $\vec{p_i} = Z_i^* e a_0 \vec{\xi}_i$ where Z_i^* is the Born effective charge associated with $\vec{\xi}_i$.

The present construction, based on projection from a thin-film interionic Hamiltonian, is substantially refined over that presented previously [8], which was a simple slab truncation of the bulk \mathcal{H}_{eff} . However, in order to avoid computationally intensive first-principles slab calculations [9–11], we use an approximate interionic Hamiltonian, obtained by transfer of microscopic information available for the bulk to the thin film geometry. The associated modifications include termination of the interatomic short-range force constants at the surface [13], change in the effective dipole-dipole interaction resulting from the perfectly conducting plates which implement the short-circuit boundary conditions, and corrections to preserve global translational symmetry and charge neutrality [14]. The projection is then performed using the same basis functions as for the bulk, with minor modifications for the unit cells at the surface. The anharmonic and strain terms are, for simplicity, assumed to be the same as in the bulk. Further details will be given in Ref. [15].

The minimum of \mathcal{H}_{eff} for in-plane and perpendicularly polarized films is reported for different thicknesses in Table I. The polarization is assumed to be uniform within each layer. The mechanical boundary conditions are taken as stress free, so that the strain relaxes to its optimum value. At each thickness, perpendicular polarization is seen to be most favorable, with stabilization relative to the paraelectric state increasing with decreasing thickness. The corresponding layer-by-layer polarization profiles are shown in Fig. 1. While in the interior the polarization approaches the bulk value even for very thin films, it is significantly enhanced at the surface. In fact, unpolarized films are unstable

against polarization of only the two surface layers. The enhancement of the average polarization couples to the strain, resulting in a c/a ratio that increases slightly with decreasing thickness.

To understand the ferroelectric instability and surface polarization enhancement in perpendicularly polarized films, we consider \mathcal{H}_{eff} specialized to the case of perpendicular polarization, constant in each layer. The computed parameters are both layer and thickness dependent, approaching bulk values in the interior of the film. As illustrated in Table I and in Figure 1, this behavior can be closely reproduced by assigning bulk values to all parameters except the onsite interaction in the surface layer and the quadratic interaction between the surface and its neighboring layer, and by approximating the dipolar interaction matrix as described below. This corresponds to the following *simplified* model with parameters reported in Table II. The short-range and anharmonic part take the form:

$$\mathcal{H}_{sr} + \mathcal{H}_{anharm} = \sum_{n=1}^{N} (A_l \, \xi_n^2 + B \, \xi_n^4 + C \, \xi_n^6 + D \, \xi_n^8) + \sum_{n=1}^{N-1} a \, \xi_n \, \xi_{n+1} + \sum_{n=1}^{N-2} b \, \xi_n \, \xi_{n+2} + \Delta A_l \, (\xi_1^2 + \xi_N^2) + \Delta a \, (\xi_1 \, \xi_2 + \xi_{N-1} \, \xi_N).$$

where A_l, B, C, D, a and b are directly related to bulk \mathcal{H}_{eff} parameters, while ΔA_l and Δa arise from changes at the surfaces and are, to a good approximation, independent of the thickness.

The dipolar contribution, computed using the Ewald summation technique including the effect of the metallic plates, is accurately represented (to within 0.1%) by the expression

$$\mathcal{H}_{dipolar} = \frac{1}{2\epsilon_{\infty}} \left[\frac{4\pi u_{conv}}{a_0(N+1/2)} \left(\sum_{n=1}^{N} Z_n^* \xi_n \right)^2 + u_{self} \sum_{n=1}^{N} Z_n^{*2} \xi_n^2 \right.$$

$$\left. + u_{sur} \left(Z_1^{*2} \xi_1^2 + Z_N^{*2} \xi_N^2 \right) + u_{nn} \sum_{n=1}^{N-1} Z_n^* Z_{n+1}^* \xi_n \xi_{n+1} \right].$$

$$(1)$$

where the optical dielectric constant, ϵ_{∞} , is taken equal to 8.24 [7,13] and Z^* is +10.218 at the surface and +10.056 elsewhere.

Finally, the terms which represent the coupling of the polarization to homogeneous strain are derived directly from the corresponding bulk terms:

$$\mathcal{H}_{strain} = \frac{N}{2}C_{11}\sum_{\alpha}e_{\alpha\alpha}^2 + NC_{12}\sum_{\alpha<\beta}e_{\alpha\alpha}e_{\beta\beta} + (\sum_{n=1}^N \xi_n^2)(g_0\sum_{\alpha}e_{\alpha\alpha} + g_1e_{33}).$$

Within this simplified model, the origin of the enhancement of the ferroelectric instability in thin films over the bulk can be readily identified. The model can be obtained from a reference model which has the uniform bulk ferroelectric ground state by modifying three terms as follows: (i) changing the dipolar contribution by moving the perfectly conducting plates, at the level of the model, outward by $a_0/4$ from where the array of dipoles combined with their images forms an infinite simple cubic lattice; (ii) suppressing the periodic boundary conditions on the short-range terms, that is, eliminating the coupling of layers 1 and 2 to layers N and N+1, and (iii) including the short-range surface corrections ΔA_l and Δa . We can introduce these modifications of the bulk model separately.

By examining first the effects of term (i), we can qualitatively understand how the electrical boundary condition plays a crucial role in determining the thin film ground state [16]. The change in the dipolar contribution from the bulk to the thin film significantly suppresses the perpendicular polarization. This is not surprising as motion of the plates outward from the slab decreases the compensation of the depolarization field. In contrast, starting from the bulk and truncating the antiferroelectric short-range couplings at the surface (term (ii)) leads to a large energy gain, a large enhancement of the surface polarization, and a somewhat lesser enhancement of the polarization of the interior layers which is close to constant starting with the second layer. Examining the effects of the short-range surface terms ΔA_l and Δa (term (iii)), we find similar behavior, except that the polarization in the second layer, while still greater than its bulk value, is suppressed relative to that of the interior layers.

In the full thin film model, the combined effects of terms (ii) and (iii) compete with the suppression of ferroelectricity by the dipolar contribution of term (i). The surface enhancement and characteristic shape of the polarization profile is preserved by the inclusion of term (i), while the magnitude of the overall enhancement is lowered, so that the values of polarization in the interior approach the bulk value.

When comparing to observations on ultrathin PbTiO₃ films, several factors must be taken into account. First, substrates will generally induce epitaxial stress, which can significantly change the ferroelectric state of the film [17].

The screening of the depolarization field by surface charges can be expected to be less effective than for the ideal case of perfectly conducting plates considered here, which would act to reduce the polarization enhancement [18]. Finally, the finite conductivity of PbTiO3 could lead to the creation of a depletion layer and related effects [19] not included in this model. Nevertheless, the plausibility of surface polarization enhancement warrants further investigation.

In conclusion, we have constructed a microscopic \mathcal{H}_{eff} for the study of PbTiO₃ thin films under stress-free and short-circuit boundary conditions. This model shows that (001) PbTiO₃ films as thin as three unit cells exhibit a perpendicularly polarized ferroelectric ground state, with significant enhancement of the polarization at the surface. The ferroelectric instability is consistent with recent observations, suggesting further theoretical and experimental investigation.

Acknowledgements

We thank Ch. Ahn, M. Buttiker, S. Desu, R. Ramesh, J. F. Scott, J.-M. Triscone and T. Tybell for stimulating discussions. We acknowledge the Aspen Center for Physics and the support of ONR Grant N00014-97-0047.

- a) Present address: Département de Physique, Université de Liège, Bât. B5, B-4000 Sart Tilman, Belgium; e-mail: Philippe.Ghosez@ulg.ac.be
- [1] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
- [2] J. F. Scott, Ferroelectrics Review 1, 1 (1998).
- K. Ishikawa, T. Nomura, N. Okada, K. Takada, Jpn. J. Appl. Phys. (part 1) 35, 5196 (1996).
- [4] S. Li, J. A. Eastman, J. M. Vetrone, C. M. Foster, R. E. Newnham and L. E. Cross, Jpn. J. Appl. Phys. (part 1) 36, 5169 (1997).
- [5] T. Maruyama, M. Saitoh, I.Sakay and T. Hidaka, Appl. Phys. Lett. 73, 3524 (1998).
- [6] T. Tybell, C. Ahn and J.-M. Triscone, Appl. Phys. Lett. 75, 856 (1999).
- [7] U. V. Waghmare and K. M. Rabe, Phys. Rev. B 55, 6161 (1997).
- [8] K. M. Rabe and Ph. Ghosez, J. Electroceram., in press.
- [9] R. E. Cohen, Ferroelectrics **194**, 323 (1997).
- [10] J. Padilla and D. Vanderbilt, Phys. Rev B 56, 1625 (1997); J. Padilla and D. Vanderbilt, Surface Science 418, 64 (1998);
 B. Mayer and D. Vanderbilt, unpublished.
- [11] L. Fu, E. Yaschenko, L. Resca and R. Resta, in "First-Principles Calculations for Ferroelectrics", edited by R. E. Cohen, AIP Conf. Proc. No. 436 (AIP, Woodbury, 1998), p. 107.
- [12] K. M. Rabe and U. V. Waghmare, Phys. Rev. B 52, 13236 (1995).
- [13] Ph. Ghosez, E. Cockayne, U. V. Waghmare and K. M. Rabe, Phys. Rev. B 60, 836 (1999).
- [14] A. Ruini, R. Resta and S. Baroni, Phys. Rev. B 57, 5742 (1998).
- $\left[15\right]$ Ph. Ghosez and K. M. Rabe, in preparation.
- [16] For a fully quantitative assessment of the effects of electrical boundary conditions, it is necessary to move the plates at the level of the interionic Hamiltonian, before the projection. This would also lead to slight modifications of the short-range surface parameters.
- [17] N. A. Pertsev, A. G. Zembilgotov and A. K. Tagantsev, Phys. Rev. Lett. 80, 1988 (1998).
- [18] K. Binder, Ferroelectrics 35, 99 (1981); R. Kretschmer and K. Binder, Phys. Rev. B20, 1065 (1979).
- [19] Y. Watanabe, Phys. Rev. **B57**, 789 (1998).

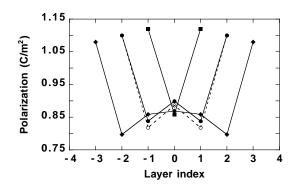


FIG. 1. Layer-by-layer profiles of the polarization for films of thickness N=3 (squares), N=5 (solid circles) and N=7 (diamonds). The polarization profile for the simplified model for N=5 is shown by the open circles and dashed line. For the bulk, the computed polarization in the tetragonal phase is equal to 0.83 C/m^2 .

TABLE I. Energy per unit cell in eV (in reference to the paraelectric state) and macroscopic strain as a function of thickness (N) for perpendicularly (\bot) and in-plane (\parallel) polarized films. The last column refers to the *simplified* model (see text). For comparison, in the tetragonal bulk phase: E = -0.086 eV, $\epsilon_{xx} = \epsilon_{yy} = -0.015$ and $\epsilon_{zz} = 0.064$.

N	E_{tot}^{\parallel}	$\epsilon_{xx}^{\parallel}=\epsilon_{zz}^{\parallel}$	$\epsilon_{yy}^{\parallel}$	E_{tot}^{\perp}	$\epsilon_{xx}^{\perp} = \epsilon_{yy}^{\perp}$	ϵ_{zz}^{\perp}	E_{model}^{\perp}
3	-0.110	-0.017	0.071	-0.320	-0.023	0.098	-0.309
5	-0.076	-0.014	0.061	-0.217	-0.020	0.084	-0.210
7	-0.072	-0.014	0.060	-0.163	-0.018	0.076	-0.172

TABLE II. Parameters of the simplified \mathcal{H}_{eff} when energies are in eV, lengths in Å and ξ_n is normalized to a_0 .

$\overline{A_l}$	-66.2664	a	+118.046	u_{conv}	-14.3997	C_{11}	+117.9
B	$+6.906 \times 10^{3}$	b	+14.718	u_{self}	+32.7745	C_{12}	+51.5
C	-1.658×10^5	ΔA_l	-46.866	u_{surf}	-0.0472	g_0	-107.7
D	$+9.630 \times 10^{6}$	Δa	+26.598	u_{nn}	-2.3788	g_1	-790.3