Surface reconstruction and ferroelectricity in PbTiO$_3$ thin films

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Surface and ferroelectric properties of PbTiO$_3$ thin films are investigated using an interatomic potential approach with parameters computed from first-principles calculations. We show that a model developed for the bulk describes properly the surface properties of PbTiO$_3$. In particular, the antiferrodistortive surface reconstruction, recently observed from X-ray scattering, is correctly reproduced as a result of the change in the balance of long-range Coulombic and short-range interactions at the surface. The effects of the surface reconstruction on the ferroelectric properties of ultrathin films are investigated. Under the imposed open-circuit electrical boundary conditions, the model gives a critical thickness for ferroelectricity of 4 unit cells. The surface layer, which forms the antiferrodistortive reconstruction, participates in the ferroelectricity. A decrease in the tetragonality of the films leads to the stabilization of a phase with non-vanishing in-plane polarization. A peculiar effect of the surface reconstruction on the in-plane polarization profile is found.

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I. INTRODUCTION

One fascinating feature of perovskites is that they exhibit a large variety of structural phase transitions. The variety of transition behavior and low-temperature distorted structures depend on the individual compound. Among the perovskites one finds ferroelectric (FE) crystals such as BaTiO$_3$, K$_2$Ti$_3$O$_7$ (displaying three phase transitions), and PbTiO$_3$ (displaying only one transition), antiferroelectrics such as PbZrO$_3$, and materials such as SrTiO$_3$ that exhibit other non-polar antiferrodistortive (AFD) instability involving the rotation of the oxygen octahedra.

With the rapidly advancing miniaturization of ferroelectric devices and the use of thin films, attention is focusing on the role played by surfaces and interfaces in the overall performance of the materials. The effects of surfaces on the structural phase transitions have become an issue of significant importance because the surface can affect the structural behavior of the perovskites by modifying the strength of various instabilities. Lead titanate is a clear example. In PbTiO$_3$ (PT), ferroelectricity is due to the condensation of a $\Gamma_{15}$ unstable phonon in which the oxygen octahedra shift against the Pb sub-lattice. The ground state consists of shifts along (001) accompanied by a tetragonal lattice strain which stabilizes this direction. However, complete phonon dispersions for the ideal perovskite structure PbTiO$_3$ as determined by density functional calculations show ferroelectric ($\Gamma_{15}$) and also rotational antiferrodistortive ($R_{35}$ type) instabilities. In bulk, the FE and AFD instabilities compete with each other and the FE lattice distortion suppresses the AFD distortion, but the proximity to a surface modifies that balance. Recently, an antiferrodistortive reconstruction of the PbTiO$_3$ (001) surface has been found using grazing incidence X-ray scattering. The atomic structure of the surface consist of a single layer of an AFD structure with oxygen cages rotated by 10° around the [001] axis through the Ti ions. Latter on, the AFD reconstruction at the PbO-terminated (001) surface was reproduced by Bungaro and Rabe using ab-initio calculations. They also found for in-plane polarized films that the FE and AFD distortions coexist in the proximity of the surface. Regarding device applications, out-of-plane polarized films are more relevant. Therefore, it is worth investigating also the effects of the surface reconstruction on the out-of-plane ferroelectricity, since it was speculated that the AFD reconstruction may be related to the dead layer often postulated to explain the observed decrease in ferroelectric character in thin films.

The realistic simulation of PT thin-films is a theoretical challenge due to the interplay of polar and non-polar instabilities at the surface. Although first-principles methods are extremely precise and include thoroughly electronic effects, they are quite computer demanding. So, these calculations are restricted to the investigation of zero-temperature properties of perovskites involving a rather small number of atoms. For the study of the thermal behavior, or to handle larger system sizes, other methods are necessary. During the last years, the effective Hamiltonian approach has been used for the investigation of thin film properties. However, for the simulation of Pb-based perovskite thin-films the coexistence of rotational and FE distortions should be explicitly considered. Atomistic simulations based on interatomic potentials can account naturally for the presence of competing instabilities. However, the validity of any atomistic simulation study depends to considerable extent on the quality of the potentials used. The interatomic potential approach firmly grounded by having its parameters fitted against results of first-principles calculations is a promising technique for investigating...
thin-film properties of Pb-based perovskites. In this paper we investigate the ferroelectric properties of PT thin films using a shell model developed completely from first-principles calculations. We investigate first if the model developed for the bulk describes properly surface properties. Then the ferroelectric behavior of ultrathin films under open-circuit electrical boundary conditions are investigated.

II. MODEL AND COMPUTATIONAL DETAILS

The approach we follow in this work is based on the atomistic modeling using interatomic potentials. We indeed found that the shell model approach does provide computationally efficient and confident methodology for the simulation of ferroelectric perovskites, including bulk properties of pure crystals, superlattices, and solid solutions, and solid solutions, and solid solutions, and thin films properties. In the shell model, each atom is represented by a massive core coupled to a massless shell, and the relative core-shell displacement describes the atomic polarization. The model contains coulombic long-range and pairwise short-range interactions. In the present study we use the model developed in Ref which contains order core-shell couplings and short-range interactions described by two different types of potentials. A Rydberg potential \( V(r) = (a + br) \exp(-r/\rho) \) is used for the Pb-Ti, Pb-O and Ti-O pairs, and a Buckingham potential \( V(r) = a \exp(-r/\rho) + cr^{-6} \) is used for O-O interactions. The model was developed completely from first-principles calculations within the Local Density Approximation (LDA). The parameters were adjusted to reproduce a wide number of LDA results, including lattice dynamics and total energy calculations. The resulting model was able to reproduce delicate properties of PT in good agreement with LDA results. However, as a consequence of the LDA, volume and volume dependent properties are underestimated with respect to experimental values. For example, the model gives a tetragonal ground state with a lattice parameter \( a = 3.859 \AA \), a tetragonal distortion \( c/a = 1.043 \), and a spontaneous polarization \( P = 54 \mu C/cm^2 \), while the experimental data are \( a = 3.90 \AA, c/a = 1.065 \), and \( P = 75 \mu C/cm^2 \). The underestimate of the static structural properties is translated via the adjusted model to the finite temperature behavior. Molecular dynamics simulations showed a cubic-tetragonal transition at \( T_C = 450K \), 300K below the experimental value. Nevertheless, the qualitative temperature behavior of lattice parameters and polarization was correctly reproduced. See Reference for more details.

The investigation of the surface properties is carried out using an isolated slab geometry with periodic boundary conditions in the x-y plane. The long ranged electrostatic energy and forces are calculated by a direct sum method. The equilibrated zero-temperature structure of the slabs was determined by a zero-temperature quench until the force on each individual ion was less than 0.001 eV/Å. To mimic the two dimensional clamping and straining of the film due to the presence of a substrate, we force the simulation cell to be square in the x-y plane.

III. RESULTS AND DISCUSSION

A. Surface effects in non-polar slabs. Validation of the model

The parameters of the model were derived to describe perfect crystal properties, and it is not guaranteed that the same potentials are suitable to describe the surface properties of PT. In the bulk, the underlying potential surface is a result of a delicate balance between long range Coulomb, short range, and core-shell interactions. Such balance could change significantly at the surface, where the atomic environment changes due to the discontinuity of the crystal. So, it is important to check if the model developed for the bulk proves also successful for describing surface properties.

A first-principles study for (001) surfaces of cubic PT has been performed by Meyer, Padilla and Vanderbilt using \( c(1 \times 1) \) surface periodicity. As a first step, we take these first-principles calculations as benchmark results to compare with. To this end we determined the atomic equilibrium position for both PbO- and TiO- symmetrically terminated 7-layer periodic slabs. We set the in-plane lattice parameter to the cubic equilibrium value yielded by the model in bulk, \( a = 3.887 \AA \), and we relaxed the atomic positions from the ideal positions only in the direction perpendicular to the surface. The results obtained for the atomic relaxations for both slabs are listed in Table whereas the values for the interlayer distances and rumplings are listed in Table Ab-initio results are shown in parenthesis as reference. The model reproduces satisfactorily the relaxation direction of the atoms, the change in the interlayer distances, and atomic rumplings. For the case of the PbO surface, the equilibrium termination for PT, the numerical values are in very good agreement with the ab-initio ones. The average surface relaxation energy obtained by the model \( \Delta E_{relax} = 0.237 eV \) is also in quite good agreement with the ab-initio result of 0.210 eV.

The recent pseudopotential study of the AFD surface reconstruction in PbTiO\(_3\) slabs provides reliable additional information to validate the model. In Table we show structural parameters of the relaxed \( c(2 \times 2) \) 11-layer PbO terminated slab. The overall agreement with the ab-initio results is very good. The model reproduces the main differences between the \( c(2 \times 2) \) and \( (1 \times 1) \) surface periodicities, that is the presence of an AFD reconstruction with a reduction of rumplings and interlayer distances. Regarding the AFD surface reconstruction, the rotation angles are slightly overestimated with respect to the pseudopotential calculations; the experimentally determined rotation angle for the surface
layer is $10^\circ$. The energy gain associated with the octahedra rotations is 0.32 eV per surface unit cell, which is approximately one order of magnitude larger than the bulk ferroelectric well depth.

It was pointed out that the enhancement of the AFD distortion at the PbO surface is a consequence of the particular chemistry of Pb, due to its tendency to move off-center and form strong covalent Pb-O bonds. We have demonstrated that this electronic effect, which has been showed to be an important factor for ferroelectricity in PbTiO$_3$, can be mimicked at the atomic level by a shell model. In this less-sophisticated approach, the AFD surface reconstruction is obtained just as a result of the change in the balance of long-range Coulombic and short-range interactions at the surface.

| Atom       | $\delta_x$ | Atom     | $\delta_x$ |
|------------|------------|----------|------------|
| Pb(1)      | -3.45 (-4.36) | Ti(1)    | -4.17 (-3.40) |
| O$_{I11}$  | -0.27 (-0.46) | O$_I$    | -2.94 (-0.34) |
| Ti(2)      | 3.19 (2.39)  | O$_{I11}$| -2.94 (-0.34) |
| O$_I$      | 1.65 (1.21)  | Pb(2)    | 1.58 (4.53)   |
| O$_{I11}$  | 1.65 (1.21)  | O$_I$    | -0.34 (0.43)  |
| Pb(3)      | -0.78 (-1.37)| Ti(3)    | -0.98 (-0.92) |
| O$_{I11}$  | 0.33 (-0.20) | O$_I$    | 0.56 (-0.27)  |
|           |            | O$_{I11}$| 0.56 (-0.27)  |

TABLE I: Atomic relaxations perpendicular to the surface ($\delta_x$) of the PbO (left panel) and the TiO$_2$ (right panel) terminated surface in the cubic phase. $\delta_x$ are given as percent of the theoretical unit cell parameter $a$. For comparison, ab-initio results (Ref. [18]) are shown in parentheses.

| PbO surface | TiO surface |
|-------------|-------------|
| $\Delta d_{12}$ | -4.04 (-4.2) -4.17 (-4.4) |
| $\Delta d_{23}$ | 2.34 (2.6) +0.83 (+3.1) |
| $\Delta d_{34}$ | -0.02 (-0.8) -0.21 (-0.6) |
| $\nu_1$ | 3.02 (3.9) 1.22 (3.1) |
| $\nu_2$ | 1.85 (1.2) 1.93 (4.1) |
| $\nu_3$ | 0.96 (1.2) 1.54 (0.7) |

TABLE II: Change in the interlayer distance ($\Delta d$) and layer rumpling ($\nu$) for the PbO (left panel) and the TiO$_2$ (right panel) terminated surface in the cubic phase, given as percent of the theoretical unit cell parameter $a$. For comparison, ab-initio results (Ref. [18]) are shown in parentheses.

### B. Ferroelectric behavior in polar slabs

We use the atomistic model to explore zero-temperature ferroelectric properties in PT ultrathin films. We consider only PbO-terminated surfaces because they are the most stable ones. The simulation cell contains 10 × 10 unit cells with periodic boundary conditions along the $x-y$ plane. The in-plane lattice parameter was set and clamped to the model equilibrium value for the tetragonal bulk $a=3.859\text{Å}$. Since this value is close to the lattice parameter of SrTiO$_3$, this clamped condition simulates the strain effect of a SrTiO$_3$ substrate.

We have performed standard-atomic relaxation methods to determine the zero temperature structure in slabs from 2 to 10 unit cells thick that contains from 1200 to 5200 atoms, respectively. In each case, the relaxation started with atoms slightly displaced from their ideal cubic positions. After a first quenching, the system is iteratively warmed-up and quenched again in order to eliminate possible metastable configurations. To analyze the results, we define the cell parameter $c$ as the distance between two consecutive PbO planes, and the local polarization is defined as the polarization of a Ti-centered unit cell.

A decrease in tetragonality is an important effect produced by the presence of the surface. Figure 1 provides detailed microscopic information about the average cell-by-cell tetragonal distortion $c/a$ for a 10-unit cells thick slab. It can be seen that the tetragonality of all unit cells in the slab is considerably lower than in the bulk ($c/a = 1.043$ for the bulk). The stronger reduction is observed for the surface cells which are practically cubic ($c/a = 1.005$) while the tetragonality increases towards the interior of the slab reaching the value $c/a = 1.032$. As the imposed in-plane lattice parameter corresponds with the one of ferroelectric bulk PT, we can expect that the tetragonality gradually converges to the bulk value when the film thickness increases. In fact, we have obtained that, while the tetragonality of the outermost layer practically does not depend on film thickness (surface relaxation effects are predominant for these layers), the inner cells display a thickness dependence. Figure 2 shows the evolution of the $c/a$ ratio with film thickness for cells in the middle of the slab. We can roughly estimate from the extrapolation of Figure 2 that $d = 86\text{Å} (\approx 22$ unit cells) is the lower-bond estimate of the slab thickness required to reach the tetragonality of the bulk in the center of the film. The strong thickness dependence of tetragonality is in qualitative agreement with recent experimental measurements which showed that the average $c/a$ ratio decreases substantially for films thinner than 200Å.

In slabs under ideal open-circuit electrical boundary conditions, as we are considering here, out-of-plane ferroelectricity manifests above a critical thickness, through the formation of stripe domains of alternating polarity. These domains are effective in neutralizing the depolarized field and stabilizing the ferroelectric phase, even

### Interlayer

| Interlayer | $\Delta d_{12}$ | $\Delta d_{23}$ | $\Delta d_{34}$ | $\Delta d_{45}$ | $\Delta d_{56}$ |
|------------|----------------|----------------|----------------|----------------|----------------|
|            | -3.3 (-3.4)    | +2.1 (+2.9)    | -0.1 (-0.9)    | +0.3 (+0.4)    | +0.1 (-0.1)    |
| $\nu_1$    | -1.4 (-1.4)    | +1.3 (+0.9)    | -1.4 (-2.0)    | +0.5 (+0.4)    | +0.2 (-0.2)    |
| $\nu_2$    | -0.9 (-1.2)    | +1.7 (-2.9)    | +0.8 (3.9)     | +1.7 (1.0)     | +0.3 (0.3)     |
| $\nu_3$    | -1.7 (-1.9)    | +0.8 (3.9)     | +1.7 (1.0)     | +0.3 (0.3)     | +0.3 (0.3)     |
| $\theta_{bulk}$ | 6.0 (3.3)    | 6.0 (3.3)     | 6.0 (3.3)      | 6.0 (3.3)      | 6.0 (3.3)      |

TABLE III: Change in the interlayer distance ($\Delta d$), layer rumpling ($\nu$) and rotation angle of oxygen octahedra ($\theta$) for the PbO terminated surface at $d_{bulk}$ in a 11-layer non-polar PbTiO$_3$ slab. For comparison, ab-initio results (Ref. [18]) are shown in parentheses.
tions, the model gives a critical thickness ($d_c$) for ferroelectric domains below the ferroelectric transition in epitaxial PbTiO$_3$ ultrathin films on SrTiO$_3$ substrates was reported from X-ray scattering, and the ferroelectric phase was found to be stable for thickness down to 3 unit cells. Figure 3 shows the cell-by-cell out-of-plane polarization profile of a chain perpendicular to the surface of slabs of 4 and 5 unit cell width. It is clear that under the imposed stress and electrical boundary conditions, the model gives a critical thickness ($d_c$) for ferroelectricity of 4 unit cells ($d_c$ is defined as the maximum thickness at which polarization is zero). In the 4-cell slab the surface cells develop a small inward polarization of $\approx 3 \mu C/cm^2$ due to surface atomic relaxations (see Table I) while the polarization of the two inner cells is practically zero. In the 5-cell slab, individual chains have a net out-of-plane polarization but the average polarization of the slab is zero due to the development of stripe domains (the evolution of the polarization at the center of the slab with film thickness is shown in Figure 2). The inner cells display a local polarization of $\approx 18 \mu C/cm^2$, that is 0.33 of the bulk value. The surface cells present an even stronger reduction of polarization. It is very important to point out, however, that the polarization of the surface cells in the 5-cell ferroelectric slab is considerable larger than in the 4-cell non-ferroelectric one, it increases from $\approx 3 \mu C/cm^2$ to $\approx 10 \mu C/cm^2$. This polarization enhancement indicates that the surface layer, which forms an AFD reconstruction, also participates in the ferroelectricity. We note that the value of $d_c$, obtained with the model is two unit cells larger than the experimental one reported in Ref. [21]. This difference could arise from the fact the model was developed to reproduce the LDA ground state of bulk PT, and consequently the ferroelectric instability is underestimated. Another possibility is that we are not explicitly simulating the presence of a substrate (although we are considering its strain effects) which modifies the boundary condition at one face of the film. Atomistic investigations of the substrate effects on the critical thickness are in progress.

In the simulations, the in-plane lattice parameter was set to the tetragonal bulk value a=$3.859\text{Å}$, so a vanishing in-plane polarization component could be expected. However, this is not the case and the slabs develop a polarization component along the (110) direction. For the bulk, the coupling of the ferroelectric soft mode with strain is the main driving force for the stabilization of the (001)-polarized tetragonal phase over the (111)-polarized rhombohedral one. In films, the decrease in tetragonality favors the stabilization of a phase with a non-vanishing in-plane polarization component, above and also below the critical thickness. Figure 4 shows the change of the average in-plane polarization with film thickness. The reduction of tetragonality produces that the in-plane polarization increases when the film thickness decreases. Locally, a strong increment of the in-plane polarization at the surface is observed (see the profile in the inset of Figure 4). The polarization decreases towards the interior of the slab. For thick enough films, it is expected that the interior of the slab reaches the vanishing in-plane polarization of the bulk.

We showed above that non-polar slabs displayed an AFD surface reconstruction. Polar slabs show a surface reconstruction with a similar rotation angle which is independent on the slab thickness. However, one difference is that neighboring planes of octahedra along the rotation axis rotates in-phase instead of out-of-phase. In fact, for the polar slabs, $\theta_2 = 13.5^\circ$, $\theta_4 = 4.5^\circ$ and $\theta_6 = 7.3^\circ$ for

FIG. 1: Average cell-by-cell tetragonal distortion $c/a$ for a 10-unit cells thick slab.

FIG. 2: Thickness dependence of the tetragonal distortion (for the inner cells) and the spontaneous out-of-plane polarization of the ferroelectric domains.

without electrodes. The observation of stripe domains below the ferroelectric transition in epitaxial PbTiO$_3$ ultrathin films on SrTiO$_3$ substrates was reported from X-ray scattering, and the ferroelectric phase was found to be stable for thickness down to 3 unit cells. Figure 3 shows the cell-by-cell out-of-plane polarization profile of a chain perpendicular to the surface of slabs of 4 and 5 unit cell width. It is clear that under the imposed stress and electrical boundary conditions, the model gives a critical thickness ($d_c$) for ferroelectricity of 4 unit cells ($d_c$ is defined as the maximum thickness at which polarization is zero). In the 4-cell slab the surface cells develop a small inward polarization of $\approx 3 \mu C/cm^2$ due to surface atomic relaxations (see Table I) while the polarization of the two inner cells is practically zero. In the 5-cell slab, individual chains have a net out-of-plane polarization but the average polarization of the slab is zero due to the development of stripe domains (the evolution of the polarization at the center of the slab with film thickness is shown in Figure 2). The inner cells display a local polarization of $\approx 18 \mu C/cm^2$, that is 0.33 of the bulk value. The surface cells present an even stronger reduction of polarization. It is very important to point out, however, that the polarization of the surface cells in the 5-cell ferroelectric slab is considerable larger than in the 4-cell non-ferroelectric one, it increases from $\approx 3 \mu C/cm^2$ to $\approx 10 \mu C/cm^2$. This polarization enhancement indicates that the surface layer, which forms an AFD reconstruction, also participates in the ferroelectricity. We note that the value of $d_c$, obtained with the model is two unit cells larger than the experimental one reported in Ref. [21]. This difference could arise from the fact the model was developed to reproduce the LDA ground state of bulk PT, and consequently the ferroelectric instability is underestimated. Another possibility is that we are not explicitly simulating the presence of a substrate (although we are considering its strain effects) which modifies the boundary condition at one face of the film. Atomistic investigations of the substrate effects on the critical thickness are in progress.

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the first, second and third layers, respectively. We note that unstable modes at the M and R points, which are associated with oxygen rotation instabilities, have similar frequencies and compete to each other in the cubic bulk [3]. For the bulk, the model yields to an energy difference of only 2 meV per unit cell between the M and R distortions ($\Delta E = 1.2$ meV per unit cell from ab-initio calculations [3]). The presence of the polarized surface affects these two competing structural instabilities stabilizing M-type distortions at the surface.

Finally, we show a peculiar effect of the AFD surface reconstruction on the in-plane polarization profile. Although the average in-plane polarization is oriented along the (110) direction, unit cells are not uniformly polarized along that direction. This can be visualized by the top view of the surface showed in Figure 5. We will consider the displacements of the Pb atoms to make the description simpler. It is clear from the figure that the Pb atoms displace mainly along (100) directions (see the arrows) in such a way that half of the Pb atoms are displaced along a (100) direction, and the other half along a (010) direction. Although the effect is much stronger at the surface, this local behavior is observed throughout the ultrathin film. This polarization profile, which produces an average in-plane polarization along the (110) direction, is a consequence of the oxygen octahedra rotation plus the tendency of Pb to move off-center shortening Pb-O bonds.

In summary, we have shown that the delicate balance of lattice strain and polar and non-polar instabilities, which is responsible for the observed tetragonal ground-state of bulk PbTiO$_3$ and the AFD structure of the surface, is accurately simulated by an interatomic potential approach with parameters computed from first-principles calculations. In ultrathin films, a remarkable decrease in tetragonality leads to the stabilization of a phase with non-vanishing in-plane polarization, above and also below the critical thickness ($d_c$) for ferroelectricity. Under the imposed stress and electrical boundary conditions, $d_c$ was found to be 4 unit cells. The surface layer, which forms an AFD reconstruction, also participates in the ferroelectricity.

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FIG. 5: Top view of the antiferrodistortive surface reconstruction. The arrows indicate the displacements of the Pb atoms which produce an average in-plane polarization oriented along the (110) direction.

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