Absence of Critical Thickness in an Ultrathin Improper Ferroelectric Film

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We study the ferroelectric stability and surface structural properties of an oxygen-terminated hexagonal $YMnO_3$ ultra-thin film using density functional theory. Under an open circuit boundary condition, the ferroelectric state with the spontaneous polarization normal to the (0001) surface, is found to be metastable in a single domain state despite the presence of a depolarizing field. We establish a connection between the result and the role of improper ferroelectric transition. Our results imply that improper ferroelectric ultrathin films can have rather unique properties that are distinctive from those of very thin films of ordinary ferroelectrics.

The integration of ferroelectric oxide materials into existing microelectronic device architectures is currently of much interest as they hold promise for a wide range of potentially new applications [1, 2]. This has generated an enormous effort to understand the properties of ferroelectric perovskite ultrathin films, such as $BaTiO_3$, where it has been shown that electrical boundary conditions [3, 4, 5, 6], surface and interface properties [7, 8, 9, 10], as well as epitaxial strain [11, 12] all play an important role. Although there appears to be no fundamental size limit below which ferroelectricity disappears, ultrathin ferroelectric films with the polarization normal to the surface remain a challenge. This is because the depolarization field arising from the accumulated charges at the surfaces, if not screened, can strongly suppress the instability towards a single-domain ferroelectric state. This is indeed what happens in a material displaying a proper ferroelectric transition (note, henceforth we refer to such materials as proper ferroelectrics), namely one where the primary order parameter is the electrical polarization, e.g., $BaTiO_3$. The depolarizing field contributes to the free energy a positive term quadric in the polarization thereby re-normalizing the soft-mode energy and stabilizing the paraelectric phase. Even in a system with metallic electrodes, which can provide the necessary screening in most cases, when the thickness of the ferroelectric film becomes comparable to the effective screening length of the metal, the screening is incomplete resulting in a reduced polarization [5, 7, 13], an increased coercive field [14], and in some case suppress the tendency towards (single-domain) ferroelectricity completely.

It would clearly be advantageous, if not at least fundamentally interesting, to consider the surface properties of ultrathin films of materials in which ferroelectricity did not originate from a polar instability, but rather from an improper ferroelectric transition – i.e., one where the spontaneous polarization does not drive the transition but instead is a slave to some other primary order parameter. As pointed out decades ago by Levanyuk and San-
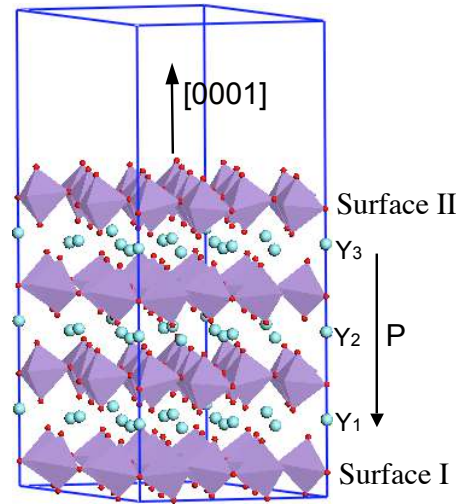

FIG. 1: Side view of $YMnO_3$ (0001) thin film slab two unit-cells thick symmetrically terminated with apical oxygens. The three Y (large blue circles) planes are indicated. Small red circles and polyhedra represent oxygens and MnO_5 cages. The polarization of the unrelaxed FE structure pointing from surface II to surface I is indicated.

nikov in a series of papers [15, 16], an instability towards a single-domain ferroelectric state in a improper ferroelectric is still possible even if the depolarization field remains unscreened, e.g., under open circuit boundary conditions.

In this letter we study for the first time finite size effects in an improper ferroelectric from first principles. We use hexagonal $YMnO_3$ [17, 18, 19, 20], which was recently predicted [21] and subsequently experimentally confirmed [22, 23] to display an improper ferroelectric transition as an example. We investigate the intrinsic properties of isolated thin films of $YMnO_3$ with (0001) orientation and a clean oxygen terminated surface *in the absence of an external field or electrode* and determine the influence of the surface on the ferroelectric state. Despite the growth of $YMnO_3$ thin films on a wide range

of substrates [24], the structural properties of the surface have not been extensively studied previously. We show that contrary to the case of a thin film proper ferroelectric, e.g., $BaTiO_3$ or $PbTiO_3$ [4, 5, 7], the polarization persists in a single domain $YMnO_3$ film to approximately two unit cells thick (the smallest size in which a bulk region can be defined), i.e., the relaxation of the $YMnO_3$ slab *does not result in a paralectric structure.*

We carry out the first-principles study of $YMnO_3$ thin films using density functional theory as implemented in the VASP code [25] and projected augmented wave pseudopotentials. The Hubbard correction to the local density approximation (LDA+U) is applied to the Mn $3d$ orbitals to account for the correlation effect. We use $U = 6.0$ eV and $J = 0.9$ eV which was previously shown [21, 26] to yield a band gap and lattice parameters close to the experiments. We start with a slab composed of two unit cells, stacked along the hexagonal axis, of the bulk ferroelectric $YMnO_3$ structure, terminating symmetrically on the apical oxygens with a vacuum layer of ~ 10 Å added as shown in Fig. 1. This is the minimum thickness for a $YMnO_3$ film for which a "bulk" region can be defined. We fully relax the atomic positions of the slab while keeping the in-plane lattice constants fixed at the theoretical bulk ferroelectric equilibrium values (i.e., $a = 6.09$ Å and $c = 11.36$ Å). The planewave cutoff energy is 500 eV and a Monkhorst-Pack $4 \times 4 \times 1$ k-point mesh is used for the Brillouin zone integration. We have applied collinear approximation to describe the antiferromagnetic spin ordering while neglecting spin-orbital coupling and magnetic anisotropy, which was previously found to be small compared to the structural energetics [21].

Previous theoretical work has shown that the chemical bonding in rare-earth based hexagonal manganites such as $YMnO_3$ plays a very minor role in the origin of ferroelectricity [20], unlike that of conventional perovskite ferroelectrics where covalency effects between the cations and oxygens are crucial [27]. The difference in the nature of bonding from that of perovskites also affects the geometric relaxation and surface band structure as we will show next.

The geometric relaxation normal to the surface is illustrated in Fig. 2, where I and II denote the same surfaces as in Fig. 1. At both surfaces, the surface apical (O_A) oxygens sitting atop the MnO_5 cages move substantially inward relative to their unrelaxed positions, toward the bulk region, with a displacement ranging between 0.25 Å and 0.33 Å. The displacements are larger than those reported for, e.g., $BaTiO_3$ surface [28], which measure of ~ 0.1 Å. This is unsurprising as there are no metal cations that bond with the apical oxygens in the common surface plane in $YMnO_3$. Instead, the surface oxygens bond strongly with the Mn atoms in the next atomic plane. The surface relaxation should thus be more significant than that found in perovskites. In the next layer
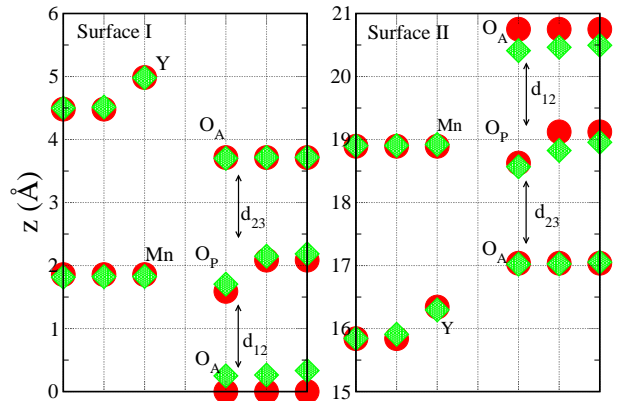

FIG. 2: Geometric relaxation of the bottom and top four surface atomic planes in the $YMnO_3$ slab along the surface normal direction. Circles and diamonds depict the unrelaxed and relaxed z-coordinates, respectively, for the surface MnO_5 and Y planes.

down, the Mn atoms move towards the surface on average by 0.03 Å and 0.02 Å, while the oxygens (O_P) move towards the bulk region by 0.08 Å and 0.17 Å for surfaces I and II, respectively. The apical oxygens (O_A) and Y layer below the surface plane have negligible relaxation (≤ 0.01 Å). Overall, the interplane distance (calculated from position averaged for each layer) at surface I between the first two surface planes d_{12} reduces by 0.23 Å and between the second and third planes d_{23} has reduced by 0.02Å. Similarly, a reduction of d_{12} by 0.21 Å and d_{23} by 0.08 Å is found at surface II.
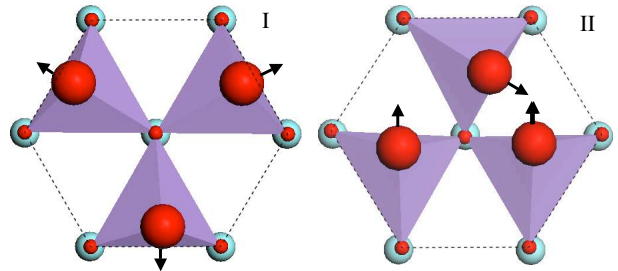

FIG. 3: Top view of the in-plane positions of the surface apical oxygens (large red circles) relative to the MnO_5 polyhedra for surfaces I and II. The blue medium circles depict Y atoms near the surface. The arrows depict the in-plane relaxation direction relative to the initial positions.

Surface I and II differ significantly with respect to their in-plane relaxation as shown in Fig. 3. Three apical oxygens move outward along the in-plane unit-cell axis by about 0.38, 0.4, and 0.47 Å at surface I, displaying a tendency to compensate the shortened Mn-O_A bond along the c axis. At surface II, two of the three apical oxygens (in the unit cell) display a tendency to dimerize, yielding a O-O bond of 2.23 Å, 3.14 Å, and 3.59 Å (the length is 3.22 Å, 3.67 Å, and 3.67 Å in the bulk). The
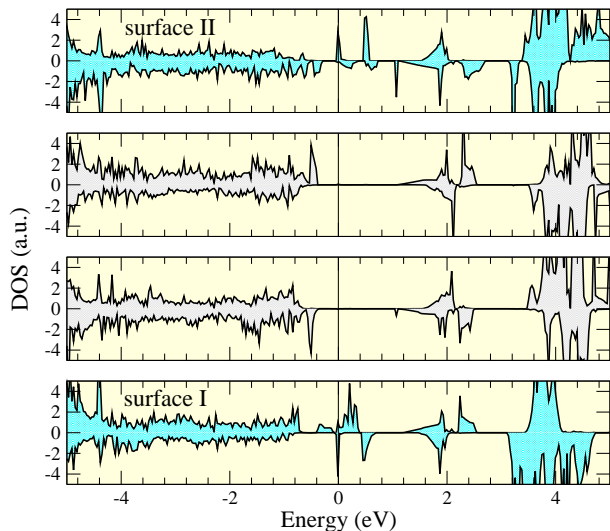
FIG. 4: The projected density of states for each MnO_5 plane along the $YMnO_3$ thin film c axis as in Fig 1. The top and bottom panels correspond to surface II and I. The polarization points from the top to the bottom surface. The Fermi level is marked at $E = 0$.

non-equivalence between the two surfaces evident from the in-plane relaxation arises from the presence of the ferroelectric polarization as we show below.

Fig. 4 shows the projected density of states (PDOS) for each MnO_5 plane along the c axis of the film. Like the geometric relaxation, the electronic structure of the interior layers rapidly converges to that of bulk $YMnO_3$ where a band gap about 1.4 eV has been reported [29]. The top of the valence bands on the surfaces shows more changes than the conduction bands with respect to the bulk, as the valence band is partially composed of O 2p of apical oxygens lying in the surface plane. There are surface states that lie deep near the center of the gap which pin the Fermi level in the gap. These states are primarily of the O $2p$ character admixed with the Mn $3d$ and are localized at the surface plane of the oxygen terminated surface. This is somewhat different from a perovskite such as $BaTiO_3$, where surface states were found to intrude only into the lower part of the gap as a result of the strong hybridization between Ti and O [28]. Quantitatively, the band structure of the $YMnO_3$ film relaxed in the FE structure looks similar to that obtained for a paraelectric structure (not shown), however, one can notice a slight asymmetry in the relaxed FE structure between the two surface states, namely, a slight excess of electrons at surface I and excess of holes at surface II. As we will show the asymmetry can be traced to the polarization across the film normal to its surface.

By determining the potential drop across the fully relaxed $YMnO_3$ film in our calculation, we evaluate the depolarizing field E_d of 0.025 eV/Å across the film [30]. This electric field in the $YMnO_3$ slab is approximately

an order of magnitude smaller than that of an isolated $PbTiO_3$ slab [7] (the latter can be calculated by artificially imposing a constraint on the ions so that the structure does not relax back to a paraelectric state) and is of course consistent with the fact that the ferroelectric Berry phase polarization [32] in bulk $YMnO_3$ of 6.5 $\mu C/cm^2$ is approximately one order of magnitude smaller than the bulk polarization in $PbTiO_3$.

The magnitude of the field in a $YMnO_3$ film appears to indicate that not only does a spontaneous polarization exist in an isolated slab of $YMnO_3$ but that the value is comparable to that in the bulk. Next we calculate, albeit approximately, the polarization in the $YMnO_3$ slab via ionic displacements from a paraelectric reference structure to the relaxed ferroelectric structure, $\mathbf{u}$, and Born effective charges, $\mathbf{Z}$, where $P \approx \mathbf{Z} \cdot \mathbf{u}$ [33]. The resulting polarization equals to ~ 6.1 $\mu C/cm^2$ which is only slightly smaller than the bulk polarization.

So why does an uncompensated single domain slab of $BaTiO_3$ (or $PbTiO_3$ for that matter) remains paraelectric yet a slab of $YMnO_3$ under similar conditions becomes ferroelectric? The simplest way to understand this difference is to investigate a phenomenological free energy. In materials that display a proper ferroelectric transition such as $BaTiO_3$, the free energy can be expanded in terms of the polarization:

$$\mathcal{F}(P) = 1/2\alpha P^2 + 1/4\beta P^4 + \mathcal{O}(P^6)$$

where the ferroelectric transition occurs when $\alpha = 0$ (for purposes of illustration we are only discussing second order phase transitions). In the case of an uncompensated film a depolarizing field, $\vec{E}_d \propto -\vec{P}$, adds a positive term to the free energy, $\mathcal{F}_d \sim P^2$, renormalizing α to α', where due to the comparatively large depolarization energy, $\alpha' > 0$ at all temperatures, suppressing the ferroelectric transition into a single domain state. The polarization charges on the surface must be compensated by free charges provided by, e.g., external electrodes, to preserve the polarization.

In contrast, $YMnO_3$ was shown to display an improper ferroelectric transition where the polarization arises due to a non-trivial coupling to a zone-boundary lattice instability, the K-mode. A simplified free energy is given by:

$$\mathcal{F}(P,K) = \alpha_{02}P^2 + \alpha_{20}K^2 + \beta_{40}K^4 + \beta_{31}K^3P + ...$$

where K corresponds to the primary order parameter associated with the zone boundary K_3 phonon mode (accounting for the transition $\sim 1200K$) and P is the polarization [21]. Here the quadratic coefficient of the polarization, α_{02}, does not soften to zero at the ferroelectric transition [34], i.e., $\alpha_{02} > 0$ at any temperature, and the spontaneous polarization arises because of the β_{31} coupling, where for small K, $P \sim K^3$. Physically this

coupling acts like a field, where K_3 "pushes" the equilibrium value of the single minimum potential well of the polar mode to nonzero value. The energy associated with this field, as previously calculated in bulk YMnO$_3$ ($\sim 5 \times 10^{-4}$ eV/Å^3, or 0.06 eV per formula unit), turns out roughly 6 times larger than the depolarizing energy. For an uncompensated film in this situation, the effect of the depolarization field is to stiffen the already "hard" quadratic coefficient α_{02}, which can effectively lower the equilibrium value of the polarization (see Ref. 21) but in principle does not suppress the instability to a single domain ferroelectric state.

We have studied the ferroelectricity and surface relaxation of oxygen terminated YMnO$_3$ thin films. Using ultrathin films of YMnO$_3$ as an example, we show that in improper ferroelectrics, the instability to a single domain ferroelectric state does not vanish even when the depolarization field remains unscreened, i.e., in the absence of electrodes or external field. Our results are applicable for all materials that display an improper ferroelectric transition, whether the polarization is induced by structural changes, like the case we considered here, or by for example a spin ordering. This has potential exciting applications given that a wide class of perovskite nanostructures have been recently found to display improper ferroelectricity [35].

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[30] There is also a small field of 0.0056 eV/Å in the vacuum region pointing in the opposite direction arising from the periodic boundary condition applied to the supercell. Note that we did not apply an external field [4] because we do not intend to simulate a situation of "idealized electrodes" or a short circuit condition. Instead we have applied a dipole correction [31] which removes the field in the vacuum region by introducing a small potential discontinuity.
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[34] The coefficients in the free energy model obtained for bulk YMnO$_3$ in Ref. 21 are (in eV unit) $\alpha_{02} = 0.016$, $\beta_{04} = 0.002$, $\alpha_{20} = -1.279$, $\beta_{40} = 0.813$, $\beta_{22} = 0.155$ and $\beta_{31} = -0.334$.
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