First-principles study of high-field piezoelectricity in tetragonal PbTiO$_3$

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We calculate from first principles the nonlinear piezoelectric response of ferroelectric PbTiO$_3$ for the case of a polarization-enhancing electric field applied along the tetragonal axis. We focus mainly on the case of fixed in-plane lattice constants, corresponding to epitaxially constrained thin films. We find that the dependence of the c/a ratio on electric field is almost linear in the range up to 500 MV/m, with little saturation. This result contrasts with expectations from Landau-Devonshire approaches based on experimental results obtained at lower fields, but is in qualitative agreement with a recent experiment in which higher fields were attained using pulsed-field methods. We also study cases in which the in-plane epitaxy constraint is removed, or an artificial negative pressure is applied, or both. These calculations demonstrate that PbTiO$_3$ can show a strikingly non-linear piezoelectric response under modified elastic boundary conditions.

I. INTRODUCTION

Piezoelectricity was discovered in the late nineteenth century and has been successfully described at the phenomenological macroscopic level since the early twentieth century. Piezoelectric materials find a variety of technological uses including sonar detection, electromechanical actuators and resonators, and high-precision applications such as in microbalances and scanning-probe microscopes. Most of these conventional applications depend on the linearity of the strain response to the applied electric field or vice versa. Application of large strains or strong electric fields may, however, generate a nonlinear response. Such nonlinearities are less well characterized and understood, despite the fact that they may have important practical implications for degrading or improving device performance.

The intrinsic nonlinear piezoelectric properties of a material may be difficult to access experimentally for two reasons. First, application of large stresses or strains may cause cracking or other forms of mechanical failure, while application of strong electric fields may cause dielectric breakdown, leading in either case to a limited ability to access the nonlinear regime. Second, most strong (and strongly nonlinear) piezoelectrics are ferroelectrics, whose spontaneous polarization is strongly modified by applied strains or fields. Real samples of ferroelectric materials usually break up into domains having different directions of the spontaneous polarization, and the observed piezoelectric response may be dominated by extrinsic processes associated with changes in domain populations under applied strain or field. Studies of single-domain samples are difficult; even if such a sample is obtained, the domain may tend to reorient under applied strain or field. In the case of a strong applied electric field, one expects that the sample will eventually be poled into a single-domain state, so that a subsequent increase of the field strength will access the intrinsic piezoelectric response. However, one must still overcome the problems associated with dielectric breakdown mentioned earlier.

In the last two decades or so, predictive quantum-mechanical descriptions based on first-principles electronic-structure calculations have been successfully developed and applied to piezoelectric and ferroelectric materials (see Ref. [1] for a recent review). These methods allow one to isolate the intrinsic contributions to the nonlinear piezoelectric behavior of a material by calculating the response explicitly. We apply such methods here to the study of tetragonal PbTiO$_3$ (PT) thin films under a strong electric field applied parallel to the polarization direction.

Our work is motivated in part by recent experimental and modeling studies of PT and PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) thin films.[2,3,4] Based on experimental measurements[2] on PT and PZT films in fields up to $\sim$50 MV/m, Landau-Devonshire models were developed to systematize the data and extrapolate to higher fields.[3] For pure PT, these papers show d_{33} dropping by about 16% and 10% as the electric field is increased to 50 MV/m for the cases of free-stress and epitaxially-constrained samples respectively. (For the latter, the in-plane lattice constant was constrained to that of the SrTiO$_3$ substrate.) These results are roughly in agreement with previous results of a first-principles calculation[5] for the free-stress case, although the methods used there involved approximations that are removed in the present work.

More recently, Grigoriev et al.[4] measured the piezoelectric response of epitaxially constrained PZT 20/80 (i.e., $x=0.2$) films using a novel approach in which dielectric breakdown was avoided by the use of ultrashort electric-field pulses in a thin-film geometry. This allowed access to much larger electric fields than previously possible, up to about 500 MV/m compared with $\sim$50 MV/m studied in the earlier experiments. The strain response showed almost no saturation up to the highest fields reached in the experiment, around 500 MV/m, con-

trasting with the conclusions of Refs. [2,3]. These results may suggest that the previous work, limited as it was to smaller fields and longer time scales, may have been more sensitive to extrinsic effects such as incomplete poling of the domains.

Clearly, information from predictive first-principles calculations would be very useful here. A preliminary application of such methods to the case of stress-free PT under strong applied electric fields[6] showed not only a lack of saturation, but even an enhancement of the piezoelectric response, with d_{33} increasing up to fields of about $550\,MV/m$. This unexpected[2,3] enhancement was ascribed to a field-induced structural transition in which the PT crystal adopts a supertetragonal state at high fields, with an extreme axial c/a ratio of 1.2-1.3. Such a supertetragonal state was first identified theoretically by Tinte *et al.*,[7] who predicted its occurrence in PT under conditions of fictitious negative pressure. Interestingly, a similarly strong tetragonal distortion was recently reported for other materials, e.g. $BiCoO_3$ in its bulk ground state[8] and $BiFeO_3$ films under a compressive epitaxial strain.[9] These results suggest that the peculiar electromechanical response of PT reported in Ref. 6 might be a rather general property of many perovskite materials. In particular, it is not unreasonable to think that, by understanding the interplay of composition, epitaxial strain, pressure and applied external fields, one might be able to *control* the crossover between the competing "normal" and "supertetragonal" phases in a given Pb- or Bi-based compound. This might produce exciting and unusual effects, such as giant piezoelectric responses and radical magnetoelectric couplings (for example, a magnetic moment collapse and insulator-to-semimetal transition under pressure was recently reported for $BiCoO_3$[10]), with a wide range of implications for technology and fundamental science.

To help shed light on the above issues, in this work we extend the analysis of Ref. 6 to study the impact of the elastic boundary conditions on the electromechanical response of PT. In particular, we address here the case of epitaxially constrained or stress-free films, with or without external pressure, and in a wide range of applied electric fields. For the case of an epitaxially constrained film, our first-principles calculations indicate that d_{33} of PT monotonically decreases with field, but only slowly: by about 2-3% up to $50\,MV/m$, 11-14% at $500\,MV/m$, and 40-50% at $1500\,MV/m$. Our results thus suggest that, based on intrinsic material properties, the strain enhancement can continue to quite large fields, with only a very slow saturation of d_{33}, at variance with previous expectations[2,3] and strengthening the findings in Ref. 4. In the absence of an epitaxial constraint, we confirm the previous results of Ref. [6], finding a maximum of d_{33} around $550\,MV/m$ and then a gentle drop-off to about a third of its highest value at $1400\,MV/m$. We further investigate the field-induced strain response of the system under the application of a fictitious negative pressure.

In comparing our work with experimental studies, it is useful to keep in mind the context and implicit assumptions of our calculations. Following the standard framework of density-functional theory, we treat pure defect-free PT in perfect tetragonal symmetry at zero temperature, with and without in-plane epitaxial constraint. We preserve the primitive periodicity, so that domain formation is excluded. We study the response of the system on a time scale on which lattice and strain response can occur, but domain dynamics cannot occur. We can go to much larger fields than can be accessed even by the pulsed-field methods,[4] limited only by the intrinsic breakdown fields associated with our method for treating the electric field.[11,12] We thus study a regime of intrinsic behavior that, we believe, is closer to that of Ref. [4] than that of Refs. [2,3].

The paper is organized as follows. We briefly describe the computational details in Sec. II. We then present the results of our calculations in Sec. III and compare them with experiment. We also describe further investigations of the system as we go beyond the experimental conditions, and discuss the implications of the work. We then summarize in Sec. IV.

II. COMPUTATIONAL METHODS

The calculations are performed using density-functional theory with two *ab-initio* computer code packages, ABINIT[13] and LAUTREC.[14] We use the Ceperley-Alder[15,16] exchange-correlation, implemented in the Perdew-Zunger[17] and Perdew-Wang[18] parameterizations for ABINIT and LAUTREC respectively. For ABINIT we use norm-conserving pseudopotentials generated using the method of Ramer and Rappe[19] as implemented in the OPIUM package,[20] while in LAUTREC we use projector augmented-wave (PAW) potentials.[21] In both cases, the semicore $3s$ and $3p$ orbitals of Ti, and the $5d$ orbitals of Pb are treated as valence electrons. Plane-wave cutoffs of 50 and 30 Hartree are chosen for ABINIT and LAUTREC respectively (the PAW potentials being softer than the norm-conserving ones). The Brillouin zone is sampled by a $4 \times 4 \times 4$ Monkhorst-Pack[22] k-point mesh for ABINIT and a $6 \times 6 \times 6$ mesh for LAUTREC. A stress threshold of 2×10^{-2} GPa is used for cell relaxation,[23] and forces on ions are converged below 2.5×10^{-3} eV/Å.

In ABINIT the electric polarization is calculated using the Berry-phase approach[24] and is coupled to a fixed electric field E.[25,26] In LAUTREC the electric polarization is computed using the centers of the "hermaphrodite" Wannier orbitals[26,27] and the electric displacement field D is used as the independent electrical variable.[6,26] In either case, the appropriate E or D field is applied, and the internal coordinates and unconstrained lattice constants are allowed to relax within the constraints of the enforced $P4mm$ tetragonal symmetry. In both cases, the results are presented as a function of E; for the case of LAUTREC, this is determined at each D from the com-
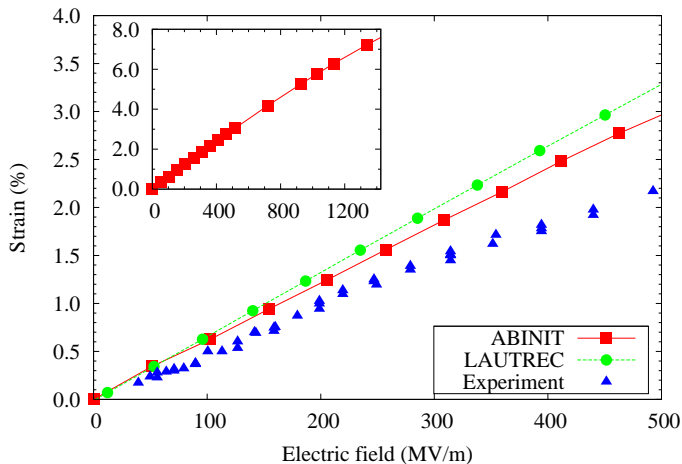
FIG. 1: Out-of-plane strain response to applied electric field, relative to zero-field ferroelectric state, under in-plane epitaxial constraint. Experiment: data of Grigoriev et al.[4] for several PZT 20/80 capacitors of varying thickness. Theoretical points with fitted lines: computed results for pure PbTiO$_3$ using two computer codes. Inset shows the ABINIT results over a more extended range of fields.

puted polarization using $E = D - 4\pi P$.

As we shall see, the results obtained using ABINIT and LAUTREC are generally consistent, but with some quantitative differences between them. Tests indicated that the codes produce almost identical results when using the same potentials, so we can ascribe these differences almost entirely to the different potentials used (norm-conserving for ABINIT vs. PAW for LAUTREC).

III. RESULTS

A. Piezoelectric response with epitaxy constraint

Both the ABINIT and LAUTREC computer codes were used to compute the response of the PT system to electric fields up to $1400 \, \mathrm{MV/m}$ applied parallel to the polarization (along the tetragonal axis). The epitaxy constraint was enforced by fixing the in-plane lattice constant a to remain at a value 1.14% smaller than the computed equilibrium a_0 of bulk tetragonal PT; this factor was chosen to facilitate comparison with the experiments of Grigoriev et al.[4] in which the PZT 20/80 film was compressively strained by 1.14% relative to its bulk equilibrium in-plane lattice constant by its epitaxial coherence with the SrTiO$_3$ (ST) substrate. Having computed the equilibrium a_0 to be 3.892 and 3.854 Å using ABINIT and LAUTREC respectively, we therefore set the constrained a to be 3.848 and 3.811 Å for the two codes respectively. (We have traced the shift of lattice constant between codes to the choice of Ti pseudopotential, but trends are well reproduced. For example, the respective c/a ratios for the two codes are 1.085 and 1.083 at the constrained a, and 1.047 and 1.044 at the

equilibrium a_0.) For each value of the applied field, we computed the relaxed structure subject to the epitaxial constraints, and computed the strain $\eta_3 = (c - c_0)/c_0$, where c is the z lattice constant at the given field and c_0 is the zero-field value.

The main panel of Fig. 1 shows the results in the range up to $500 \, \mathrm{MV/m}$, together with a comparison with the experimental data of Grigoriev et al.[4] on PZT 20/80, while the inset shows the computed behavior over the full range. The higher fields, above $\sim 500 \, \mathrm{MV/m}$, are still outside the range that is achievable experimentally, even with pulsed-field techniques. We find that the strain increases monotonically over the entire range up to $1400 \, \mathrm{MV/m}$, with only a small tendency to begin saturating at the highest fields. In the range up to $500 \, \mathrm{MV/m}$, the results look very nearly linear. We obtain an excellent fit to the results with a simple quadratic form $\eta(E) = a_1 E + a_2 E^2$ (where $\eta_3 = \eta$ and $E_3 = E$ henceforth). We obtain fitted values of $a_1 \simeq 0.063 - 0.071 \, \mathrm{m/GV}$ and $a_2 \simeq -0.01 \, (\mathrm{m/GV})^2$, where the quoted range reflects the choice of computer code.

The slopes of the curves in Fig. 1 are, of course, related to the piezoelectric response of the material. At finite field it is possible to define two slightly different piezoelectric coefficients $\tilde{d}_{33} = d\eta/dE$ and $d_{33} = dc/dV$, where $V = cE$ is the potential drop across a unit cell; from $d\eta = c^{-1} dc$ it follows that the definitions are related by $d_{33}^{-1} = \tilde{d}_{33}^{-1} + E$. We report d_{33} values here, consistent with the conventions of Ref. 4. However, the two definitions coincide at $E = 0$ and differ by only about 2% at $500 \, \mathrm{MV/m}$, so the difference is not significant in what follows. The results are presented in Fig. 2(a); we find a monotonically decreasing trend with electric field for both ABINIT and LAUTREC. However, the fall-off is quite slow, decreasing by only about 2-3% up to a field of $50 \, \mathrm{MV/m}$.

Other properties of PT under applied field show a similar, nearly linear behavior. In Fig. 2(b) we present the variations of the internal coordinates as a function of applied field (here computed using ABINIT, but similar results are obtained with LAUTREC). As expected, Pb and Ti ions, being positively charged, displace along the direction of the applied electric field, while O atoms displace in the opposite direction, thus increasing the ferroelectric mode amplitude. The Born effective charges Z^*, shown in Fig. 3(a), are almost independent of field, with only a mild reduction in their magnitudes with increasing field. However, at zero field the Z^* values under the epitaxial constraint are noticeably smaller in magnitude than their free-stress counterparts.[28] Since the Z^*'s are almost constant, we expect the electric polarization to increase with field in proportion to the displacements shown in Fig. 2(b), and Fig. 3(b) shows that this is indeed the case. A satisfactory fit of the form $P(E) = c_0 + c_1 E + c_2 E^2$ is obtained with $c_0 = 0.94 \, \mathrm{C/m^2}$, $c_1 = 0.39 \, \mathrm{C/(GV)m}$ and $c_2 = -0.072 \, \mathrm{C/(GV)^2}$. None of these quantities show any anomalous change with electric field.
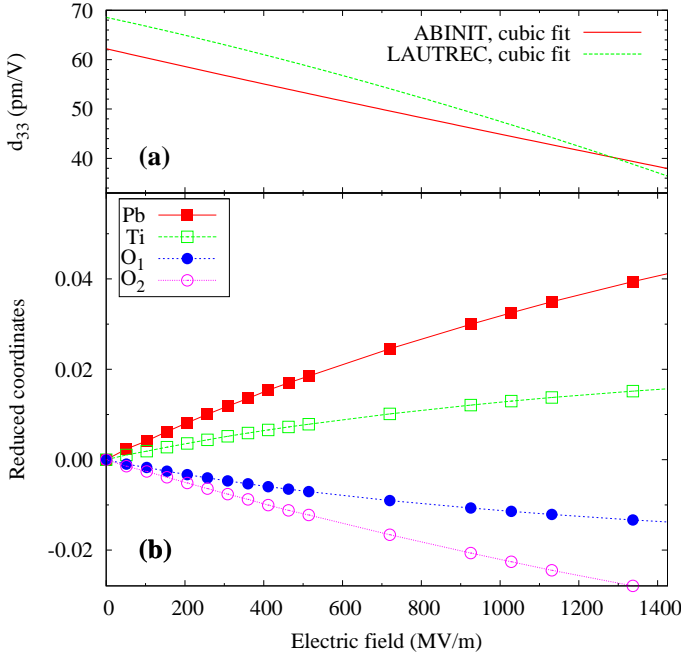
FIG. 2: Variation of properties of tetragonal PbTiO$_3$ with electric field under in-plane epitaxial constraint. (a) Piezo-electric coefficient d_{33} (calculated with both codes). (b) Out-of-plane displacements of ions from zero-field positions (calculated with ABINIT).

We now return to a discussion of the strain response. Our theory is in qualitative agreement with the recent pulse-field data,[4] which show a nearly linear behavior similar to that predicted theoretically. The theory has a somewhat larger slope; our zero-field d_{33} of $\sim$68 pm/V can be compared with their 45 pm/V. The agreement seems reasonable given that the materials are different (PT vs. PZT 20/80). Hints of a hump-like nonlinearity in the experimental data of Ref. 4 around 200 MV/m are not supported by the theory; if such a feature is really present, we would argue that it must arise from extrinsic effects not considered by the theory.

Our zero-field d_{33} is also significantly larger than the value of 45 pm/V obtained by the Landau-Devonshire theory for PZT 20/80,[3] which is in reasonable agreement with the zero-field value of Grigoriev et al. (For detailed comparisons, it should be kept in mind that the misfit of -0.5% reported in Ref. 3 is only about half of that in Ref. 4.) However, our theoretical curves and the experimental data of Grigoriev et al. both show a much slower saturation of the strain response with field than was found by the Landau-Devonshire approach, where d_{33} was predicted to fall by about 15% already at 50 MV/m for PZT 20/80 with epitaxy constraint. Our d_{33} falls by only about 2-3% over the same range. The lack of saturation means that we predict large strains of about 3.0% at fields of around 500 MV/m, and we also predict a large polarization of about 1.10 C/m^2 at such fields. Possible reasons for the discrepancies between our results and those of the Landau-Devonshire theory will be discussed
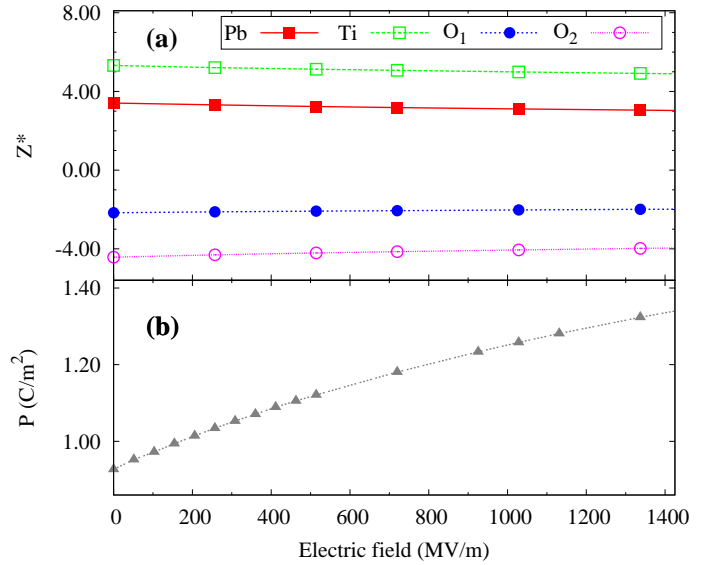

FIG. 3: Variation of properties of tetragonal PbTiO$_3$ with electric field under in-plane epitaxial constraint, calculated with ABINIT. (a) Born effective charges. (b) Polarization.

further in Sec. III C.

The Landau-Devonshire theory[3] also provided a zero-field value of 31 pm/V, falling by about 10% at 50 MV/m, for pure PT on an ST substrate. Recall that our calculations above were carried out at an in-plane lattice constant that was reduced by 1.14% relative to that of PT in order to model the strain state of PZT 20/80 in coherent epitaxy on a ST substrate. Therefore, in order to obtain a more direct comparison for the pure PT case, where the epitaxy with the ST substrate is almost perfect, we repeated our calculations with the in-plane lattice constant fixed to the theoretical equilibrium lattice constant of PT, finding a zero-field d_{33} of 50 pm/V. This is reduced somewhat from our value of 68 pm/ at -1.14% misfit, but still quite a bit larger than their value of 31 pm/V. Again, we find a very slow saturation (even slower that for the smaller in-plane lattice constant), in disagreement with the Landau-Devonshire theory.

B. Application of negative pressure and removal of epitaxy constraint

In this section we present the results of further investigations of the behavior of the system under modified elastic boundary conditions that are not directly relevant to the thin-film experiments. These investigations are motivated in part by previous ab initio calculations of Tinte et al.,[7] who showed that the c/a ratio and polarization of PT undergo an anomalous and strongly nonlinear variation as a function of an artificial applied negative pressure. The c/a ratio was found to increase gradually until the negative pressure reached about -4.8 GPa, where the c/a ratio rapidly increases to $\sim$1.20, with a subsequent
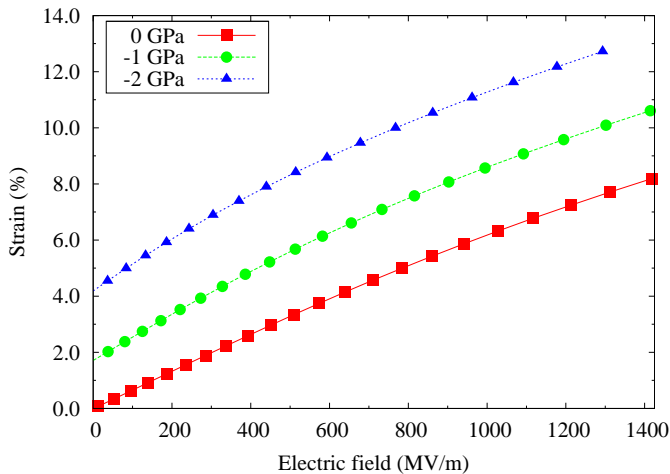
FIG. 4: Field-induced strain, relative to zero-field zero-pressure state, for tetragonal PbTiO$_3$ under in-plane epitaxial constraint, calculated with LAUTREC.
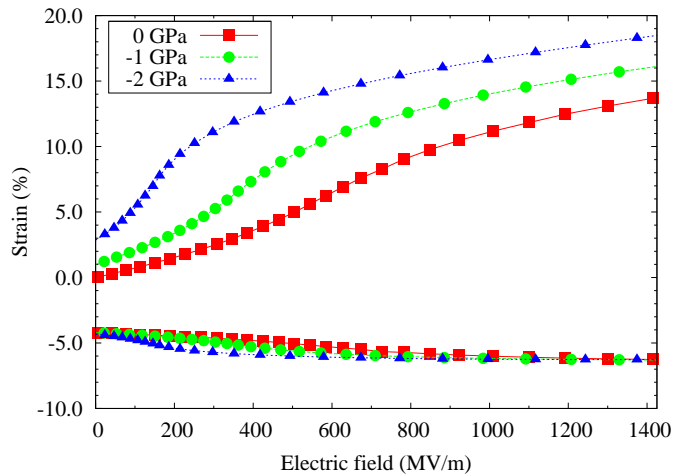

FIG. 5: Field-induced strain, relative to out-of-plane lattice constant of zero-field zero-pressure state, for tetragonal PbTiO$_3$ under free-stress (0 GPa) and negative-pressure (-1 and -2 GPa) boundary conditions, calculated with LAUTREC. Top curves: out-of-plane strain. Bottom curves: in-plane strain.

slower increase up to ~ 1.25 at -7 GPa. Neither an electric field nor an epitaxy constraint were applied in that calculation, but the results nevertheless hint at a possible supertetragonal state of PT that might be accessed under unusual boundary conditions. We also note that negative pressure is sometimes used to simulate the effect of chemical substitution, and that such an approach may be relevant here for providing hints about the behavior of PZT solid solutions. Zr and Ti belong to the same column of the Periodic Table, but Zr has a larger effective radius and will therefore tend to expand the lattice constant of PZT relative to pure PT; from the point of view of a Ti ion, this could produce a similar effect as is obtained from application of a negative pressure to pure PT.

Here, we explore the strain response as a function of both electric field and negative pressure, with and without the epitaxial constraint. The exercise is carried out in three steps. First, we apply a negative pressure in the presence of the epitaxial constraint, obtaining the strain response as a function of electric field. (In this case only the zz component of the stress tensor is relevant, and we could equally well say that we are applying a tensile uniaxial stress along c.) Second, we remove the negative pressure and repeat the calculations presented in Sec. III A, but without epitaxial constraint, so that the crystal is free to relax its in-plane lattice constants in response to the applied field. Finally, we combine the two steps described above and study the behavior as a function of electric field and negative hydrostatic pressure in the absence of any epitaxial constraint. Some results of this kind, both at zero and negative pressure, have already been presented in Ref. 6.

Our present results for the application of negative pressure in the presence of the epitaxial constraint are shown in Fig. 4, where the strain plotted on the vertical axis is defined as relative to the c lattice constant at zero

pressure and zero field. In this and subsequent figures we present calculations performed with the LAUTREC package. The zero-pressure curve duplicates the data presented in Fig. 1, while the ones at -1 and -2 show the enhancement in the strain caused by the negative pressure, which shifts the curves by about 2% per GPa. Otherwise they look rather similar, except that there is slightly more nonlinearity in the curves as the pressure becomes more negative.

The removal of the epitaxial constraint causes a much more drastic change in behavior, however, as shown by the square symbols (red curves) in Fig. 5. Both in-plane and out-of-plane strains are defined relative to the c lattice constant at zero field. As expected, the enhanced polarization and enhanced tetragonality induced by the field cause the out-of-plane lattice constant to grow, and the in-plane one to shrink, with increasing field. However, this variation shows an anomalous behavior: the change in strain starts out slowly at lower fields, accelerates and occurs most rapidly at a characteristic field $E_{\text{anom}} \simeq 550$ MV/m, and then slows again at higher fields. This anomalous behavior is most evident in the curve for the out-of-plane strain, but is also visible for the in-plane strain. The anomaly also shows up clearly in the behaviors of the piezoelectric coefficient and internal displacements, presented in Fig. 6(a) and (b) respectively.

Finally, the remaining curves in Fig. 5 show how this behavior evolves as a negative pressure is applied. The anomaly becomes more pronounced as the pressure becomes more negative, with E_{anom} shifting to lower fields of about 375 and 150 MV/m at -1 and -2 GPa respectively. (This behavior was also presented in Ref. 6 in terms of reduced electrical coordinates.) Very large strains (with c/a ratios approaching 1.25) occur at the largest fields and strongest negative pressures considered.
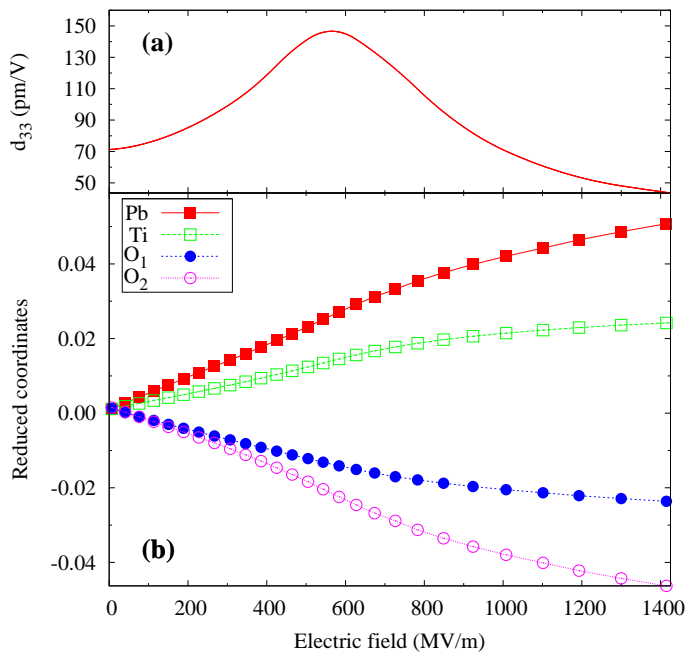
FIG. 6: Variation of properties of tetragonal PbTiO$_3$ with electric field under free-stress boundary conditions, calculated with LAUTREC. (a) Piezoelectric coefficient d_{33}. (b) Out-of-plane displacements of ions from zero-field positions.

The behaviors are similar to those already reported in Ref. 7 as a function of negative pressure alone, but here we find that the application of an electric field works cooperatively with the negative pressure to induce the crossover into the supertetragonal state.[6]

Returning to the zero-pressure results, we can now compare these more directly with previous works in which the epitaxy constraint was absent. As was shown in Fig. 6(a), we find that d_{33} starts at about 70 pm/V at zero field, increases up to about 140 pm/V near $E_{anom} = 550$ MV/m, and then falls again at higher fields. The results of Ref. 5 instead show d_{33} starting at 39 pm/V and decreasing monotonically as the field is increased. The discrepancy with respect to our results may be attributed to the more approximate methods used in Ref. 5, where the electric field was applied in an approximation in which extra forces appear on the atoms in proportion to the Born effective charges computed at zero field.[5,29] The Landau-Devonshire results of Ref. 3 also show d_{33} decreasing monotonically with field, but starting from a zero-field value of 79 pm/V that is closer to ours. The comparison between their work and ours deserve further comment, as will be provided in the next section.

C. Discussion

In this section we discuss some of the factors that need to be considered when comparing our theoretical calculations with previous theory and experiment. We focus first on three important considerations, namely, the elas-

tic boundary conditions (epitaxial vs. free-stress), the reference in-plane lattice constant, and the Zr content. We then discuss several other factors that may also play a significant role. Some comparisons have already been made along these lines in Sec. III A, but we concentrate here on possible mechanisms and physical explanations for the observed trends.

1. Reference in-plane lattice constant

When applying the epitaxial constraint, we have a choice of which in-plane lattice constant a to use for the comparison. As explained earlier, most of our results are reported for a value of a that is 1.14% smaller than the equilibrium lattice constant of PT, to facilitate comparison with the experiment of Grigoriev et $al.$[4] on PZT 20/80. If instead we repeat the calculations by fixing a to be that of tetragonal PT at its theoretical equilibrium lattice constant, as mentioned earlier near the end of Sec. III A, we find a zero-field d_{33} of about 50 pm/V, to be compared with the value of about 68 pm/V obtained at the smaller lattice constant with LAUTREC code. This trend is understandable since one may expect a larger d_{33} in a more tetragonal material. It is also consistent with the trend shown in Fig. 4(a) of Chen et $al.$, where d_{33} increases from 39 to 58 pm/V when the epitaxy constraint is made 1% more compressive.

2. Epitaxial vs. free-stress boundary conditions

Our work reinforces the expectation that the choice of epitaxial vs. free-stress elastic boundary conditions plays a crucial role in the piezoelectric response. This is true already at zero field, but the effect becomes enormous for elevated fields.

At zero field, one expects the free-stress d_{33} to exceed the epitaxial one, other things being equal. This can be understood as follows. If we start from the relaxed tetragonal ferroelectric PT crystal and apply an enhancing electric field along z with the in-plane a fixed, we can decompose the response according to a two-step process. First, we apply the field while allowing a and c to relax. We expect the degree of tetragonality to increase along with P, so that a shrinks while c grows, as confirmed by Fig. 5. Second, we enlarge a back to its zero-field value, again while allowing c to relax; since the Poisson ratio is positive, this should cause c to shrink. Thus, d_{33} should be smaller in the epi-constrained case. This is true in the work of Chen et $al.$[3], where for example the zero-field d_{33} decreases from 79 to 31 pm/V for pure PT, and from 87 to 45 pm/V for PZT 20/80, when going from free-stress to epi-constrained boundary conditions. It is also confirmed in our calculations on pure PT; we find that the zero-field d_{33} decreases from 71 to 50 pm/V (LAUTREC values) in going from the free-stress to the epi-constrained case.

As indicated earlier, we find a drastic difference in the *non-linear* response when we remove the epitaxy constraint, with the smooth decrease of d_{33} in Fig. 2(a) replaced by the rapid increase and peak around $550\,\mathrm{MV/m}$ in Fig. 6(a). This peak is clearly a signature of the crossover into the supertetragonal state.

3. Zr content

Of course, it is important to keep track of the differences between pure PT and PZT with different Zr concentrations, as we have tried to do consistently above. As is well known, PZT is often preferred as a more practical material for experimental purposes and for applications because of reduced leakage currents and other beneficial properties. The work of Chen *et al.*[3] reports d_{33} increasing from 79 to 87 pm/V in going from pure PT to PZT 20/80 in the free-stress case, and from 31 to 39 pm/V in the epi-constrained case at zero misfit. If this trend is correct, it is in the wrong direction to explain the difference between our theory and the experiment of Grigoriev *et al.*[4], since our d_{33} values for pure PT are larger than theirs for PZT 20/80. Other factors may be responsible for this discrepancy, as discussed in the next subsection. Ideally it would be advantageous if the pulsed-field experiments could be carried out on a series of samples of varying Zr content so that an extrapolation could be made to the pure-PZ case, allowing a more direct comparison with theory.

4. Other factors

Here we comment briefly on a number of other factors that might play a role when comparing our results with experiment. Our theory is purely a zero-temperature theory, and also completely neglects the effects of disorder arising from Zr configurations in PZT, or from defects such as oxygen vacancies even in pure PT. Both disorder and thermal fluctuations may tend to cause the local polarization direction to fluctuate about the global tetragonal axis, and it is well known that polarization rotation can generate large electromechanical responses in this class of materials.[30] At larger length scales, it is also possible that the samples might not be in a perfect single-domain state, with the incomplete switching being caused by defects, roughness, or other imperfections in the thin-film samples. In such a case, the intrinsic piezoelectric response would be underestimated, while extrinsic contributions associated with domain-wall motion might also be present. For ultrathin films, depolarization effects and the influence of the perovskite-electrode interfaces[31,32] will also play an important role. We expect that these issues will be clarified as improved methods of sample preparation become available, and as systematic studies are done to see how the piezoelectric responses depend on film thickness and other properties.

IV. SUMMARY

In summary, we have studied the piezoelectric response of $PbTiO_3$ to a polarization-enhancing electric field applied along the tetragonal axis under several kinds of mechanical boundary conditions. In the epitaxially constrained regime we find hardly any saturation of the piezoelectric coefficient d_{33} up to a field of $500\,\mathrm{MV/m}$, in agreement with recent experimental measurements and in contrast with the predictions of Landau-theory expansions. With the removal of the epitaxial constraint we find a remarkable non-linear effect, with d_{33} rising to twice its zero-field value at $\sim 550\,\mathrm{MV/m}$ and then decreasing again for higher applied fields.

The comparison between ABINIT and LAUTREC shows fairly good agreement. Some quantitative discrepancies do exist (e.g., in equilibrium lattice constants); these can be traced to the sensitivity of $PbTiO_3$ to the choice of pseudopotentials. Nevertheless, the trends in the two calculations are very similar. Moreover, extensive tests show that the dissimilarities in the finite-field techniques (constrained-E with Berry phase in ABINIT vs. constrained-D with Wannier functions in LAUTREC) have little or no impact on the calculated properties, once the subtleties in the treatment of the electrical and strain variables have been properly accounted for.

Quantitative comparisons with experiment still present a formidable challenge, in part because it remains difficult to characterize the precise sample conditions underlying a given electrical measurement. However, significant progress has now been made on the theoretical side, and experimental control of film properties continues to improve. Thus, we hope that direct comparisons between theory and experiment regarding nonlinear piezoelectric behavior will provide an increasingly fruitful avenue for future investigations.

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