Ferroelectric properties of K\textsubscript{NbO\textsubscript{3}}/K\textsubscript{TaO\textsubscript{3}} superlattices by atomic-level simulation

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We use atomic-level simulation methods to determine the zero-temperature structure and properties of coherent K\textsubscript{NbO\textsubscript{3}}/K\textsubscript{TaO\textsubscript{3}} superlattices. We find that the in-plane behavior is essentially bulk-like with an abrupt jump in the polarization at the interfaces. By contrast, the polarization in the modulation direction is continuous through the interfaces with the interior of the K\textsubscript{TaO\textsubscript{3}} layers remaining polarized for modulation lengths of up to 160 unit cells. The zero-frequency dielectric constant in the modulation direction has a similar magnitude to that of K\textsubscript{NbO\textsubscript{3}}. An investigation of the switching behavior shows that for modulation lengths greater than 24 unit cells, each K\textsubscript{NbO\textsubscript{3}} layer behaves essentially independently. For modulation lengths of less than 12 unit cells, the K\textsubscript{NbO\textsubscript{3}} layers interact so strongly with each other that the superlattice essentially behaves as a single artificial structure. © 2001 American Institute of Physics. [DOI: 10.1063/1.1410329]

I. INTRODUCTION

The perovskite oxides (general formula ABO\textsubscript{3}) are widely exploited for their ferroelectric, piezoelectric, and dielectric properties. In particular, because single-component bulk materials cannot always provide the desired response, multicomponent perovskites in the form of solid solutions and heterostructures have attracted much attention. For example, the temperature at which the peak in the dielectric properties of multicomponent perovskites in the form of solid solutions cannot always provide the desired response, especially because single-component systems are widely exploited for their ferroelectric, piezoelectric, and dielectric properties. In particular, changing \(T_c\) increases monotonically with decreasing \(L\); a similar increase in the in-plane dielectric constant of \(\chi_{xx}\) is seen in K\textsubscript{TiO\textsubscript{3}}/Pb\textsubscript{1-\(x\)}La\textsubscript{\(x\)}TiO\textsubscript{3} superlattices.\textsuperscript{2} Erbil and co-workers\textsuperscript{3,4} found a low-frequency in-plane dielectric constant of \(\chi_{xx}\approx420,000\) in Pb\textsubscript{TiO\textsubscript{3}}/Pb\textsubscript{1-\(x\)}La\textsubscript{\(x\)}TiO\textsubscript{3} superlattices.

Among the most extensively investigated multilayer systems is K\textsubscript{NbO\textsubscript{3}}/K\textsubscript{TaO\textsubscript{3}} (KNO/KTO) on a K\textsubscript{TaO\textsubscript{3}} substrate.\textsuperscript{5} KNO/KTO is a particularly clean system for study since the lattice mismatch is only \(-0.8\)% and thus, as shown by Christen et al., it forms coherent epitaxial interfaces.\textsuperscript{6} They found that for large modulation lengths \(\Lambda\), the Curie temperature, \(T_c\), decreases with decreasing \(\Lambda\). They interpreted this result as the thickness dependence of the ferroelectric properties of independent, uncoupled KNO layers. However, for \(\Lambda<12\) the value of the Curie temperature was found to be \(\Lambda\) independent and similar to that of a K\textsubscript{TaO\textsubscript{3}} Nb\textsubscript{0.5}O\textsubscript{2} random-alloy film.\textsuperscript{6} This effect was ascribed to “long-range ferroelectric interactions,”\textsuperscript{6} the nature of which remains unclear. If we assume that the ferroelectric properties of the heterostructure are determined by the ferroelectric component, then these results suggest that for small \(\Lambda\) the ferroelectric layers are strongly coupled through the nonferroelectric layer, that the superlattice as a whole behaves like a single structure. Moreover, the existence of regimes of uncoupled and strongly coupled layers also suggest that there should be an intermediate regime in which, although interacting with each other, the properties of individual KNO layers remain distinct.

Given this experimental background, theoretical and simulation investigations of the properties of ferroelectric heterostructures are highly desirable. Indeed, there is already significant literature in this area in the context of the Ginzburg–Landau–Devonshire (GLD) theory.\textsuperscript{7–10} Such calculations are not entirely straightforward, however. In particular, it is necessary to define the boundary conditions on superlattices.\textsuperscript{2}
the polarization at the interfaces between layers. While some authors (Schwenk et al. and Li et al.) assumed that the polarization is continuous at the interfaces between layers, Glinchuk et al. assumed that the polarization at the interfaces is zero; Qu et al. discuss the properties of a superlattice as a function of the strength of the coupling at the interfaces. Which, if any, of these choices of boundary conditions is most appropriate for a specific multilayer structure is unclear.

Atomic-level simulations are ideal for the study of multilayers because the simulations can be studied on the same length scale as the experimental systems. Moreover, the crystallography of the multilayer can be defined and the position of every ion determined, thereby providing atomic-level information on the ferroelectric and dielectric properties. Furthermore, once the nature of the interactions between ions and the crystallographic structure of the interface are defined, the atomic-level simulations will determine the local atomic structure and polarization at the interfaces. This may provide insights into the appropriate choice of boundary conditions for GLD-based studies of this kind of superlattice.

In this article we present the results of systematic atomic-level simulations of the zero-temperature structure, ferroelectric, and dielectric properties of KNbO3/KTaO3 (ferroelectric/paraelectric) superlattices. We choose this material system both because it is experimentially well-characterized and because the size of simulation cell required to model coherent interfaces is small compared to that for incoherent interfaces probably present in less well lattice matched materials. Moreover, we have previously developed good atomic-level descriptions of KNO and KTO. We characterize in detail the polarization in these heterostructures, show that the in-plane and out-of-plane polarizations are largely decoupled, and determine the dielectric and switching properties. Analysis of these results provides a physically consistent view of the superlattice behavior. A brief summary of some aspects of this work has appeared elsewhere.

The rest of this article is organized as follows. In Sec. II, we present the details of the simulation methods, the setup of the simulation cell, and briefly review the basic properties of KNO and KTO. In Sec. III, we explore the spatial dependence of the structure and polarization of superlattices of various modulation lengths; we determine their dielectric properties and switching characteristics in Sec. IV. Section V contains our conclusions.

II. SIMULATION DETAILS

In this section, we gather together all of the relevant technical details of how the simulations were performed and analyzed.

A. Shell-model description of KNO and KTO

Atomic-level simulation methods involving pair potentials with either a rigid-ion model or a shell model have long been used with considerable success to describe the finite temperature and defect properties of many ionic systems. In the shell model, atomic polarizability is accounted for by defining a core and a shell for each ion (representing the ion core with the closed shells of electrons and the valence electrons, respectively), which interact with each other through a harmonic spring (characterizing the ionic polarizability), and interact with the cores and shells of other ions via Coulombic interactions. The interactions among the valence electrons are characterized by a repulsive, exponentially decaying, pair-potential interaction between shells (the Born–Mayer term). These interactions are usually only included for cation–anion (A–O and B–O) and anion–anion (O–O) interactions; the cation–cation (A–A, B–B, and A–B) interactions are assumed to come solely from Coulombic effects. Covalency effects, such as Born effective charges, are at least qualitatively accounted for in the shell model through the ionic polarizabilities, whose magnitudes may be considered to include the effects of hybridization. Covalency effects are also included by setting the ion charges to values less than the formal valence, and by adding a van der Waals 1/r6 attractive term to the O–O shell–shell repulsion. This combination of the Born–Mayer term and the van der Waals interaction is known as the Buckingham potential.

Building on the insights gained from electronic-structure calculations and from experience obtained with an anisotropic shell-model approach, we have previously developed a Buckingham potential with an isotropic shell model which also describes the phase behavior of KNO. From a technical standpoint, this isotropic shell model differs from the anisotropic one in that a fourth-order core–shell interaction for the Nb ions is incorporated in addition to that for the O ions. This both stabilizes the ferroelectric phases and prevents the very large local electric fields associated with the breaking of the cubic symmetry from making the core–shell displacements too large. The isotropic model has the conceptual advantage of allowing the simulation of structurally disordered systems, which cannot be simulated within the anisotropic model. Using the isotropic interatomic potential, we have accurately reproduced the solid phase diagram of KNO, obtaining the correct sequence of phases (rhomboedral, orthorhombic, tetragonal, and cubic) with transition temperatures accurate to ~25 K and lattice parameters correct to ~1%. We have also constructed a potential that accurately describes the structure and dielectric properties of KTO, which remains cubic and paraelectric throughout the solid phase.

The simulation of systems containing both KNO and KTO requires the definition of no additional interatomic–interaction terms because the only interaction in the mixed systems that does not occur in the one-component systems are the interactions between Nb and Ta cations which, as is usual, are assumed to be purely Coulombic. This consideration is actually very important since otherwise data from systems containing both Nb and Ta would also have to be used in the parameterization of the potentials for multicomponent systems. Using this same assumption with a somewhat different shell model, the lattice dynamics of KT$_{x}$Nb$_{1-x}$O$_{3}$ (KTN) solid solutions in the paraelectric phase was well reproduced for the whole range of Nb concentration and with temperature. Moreover, a recent first-principles, force-constant calculation on various perovskites
suggested pair potentials of pure systems may be used to predict the properties of solid solutions without the need for any additional terms. Finally, we have explicitly demonstrated that the parameterization for KTO and KNO provides also a good description of the mixed KTN system. Taken together, these show the reliability of the use of the two potentials in combination to study not only random solid solutions but also systems where microstructural ordering plays an important role, such as the superlattices considered here.

The Ewald method has long been the method of choice for the calculation of the Coulomb energy and the corresponding forces and stresses in three-dimensionally periodic ionic solids and liquids. The physical interpretation of the Ewald method is not obvious, however, and it is computationally expensive, scaling with system size \( N \) as \( N^{3/2} \) at best. This has prompted attempts to replace it with computationally less expensive and physically more intuitive methods. In this article we use the method of Wolf et al. in which the \( r^{-1} \) Coulomb pair potential is summed in a direct and physically intuitive way. The key observation underpinning this method is that the large fluctuations in the naive \( r^{-1} \) Coulomb sum are a direct consequence of the fact that when summing the energy out to some cutoff distance \( R_c \), the system summed over is hardly ever neutral. It was found that by compensating for the excess charge within the truncation sphere of each ion with an exactly equal and opposite charge at \( R_c \), the perfect-crystal energy converges to the Madelung constant even for rather small values of \( R_c \). To also allow the more computationally efficient simulation of interfacial systems, the \( r^{-1} \) potential was multiplied by the damping function \( \text{erfc}(-\alpha r_{ij}) \), where \( \text{erfc} \) denotes the complementary error function and \( \alpha \) is the damping constant; this functional form for the damping was chosen because of its close connection with the Ewald method, and for the ease by which the necessary mathematical manipulations can be carried out. For ionic crystals with rocksalt structure and for ionic liquids, the resulting damped, charge-neutralized, direct-summation method was shown to give energies, forces, and stresses of interfacial systems which converge with decreasing \( \alpha \) to values as close to those obtained from the Ewald method as desired. This damped charge-neutralized, direct-summation method is straightforward to implement and has a computational load that scales linearly with \( N \).

We have verified that the temperature dependence of the lattice parameters, unit-cell angles and polarization of KNO and KTO, determined using the direct-summation method can be made arbitrarily close to those obtained using the Ewald method. For all of our simulations, we chose \( \alpha = 0.35 \text{ Å}^{-1} \) and \( R_c = 9.0 \text{ Å} \), which provides both very satisfactory agreement with the Ewald results and good computational efficiency. Most importantly, this choice of parameters reproduces rather precisely the \( T = 0 \text{ K} \) energy differences between the four phases of KNO calculated by the Ewald method. At \( T = 0 \text{ K} \), we find that KNO is rhombohedral with a lattice parameter of 4.034 Å and a rhombohedral angle of 89.3°; we have determined the zero-temperature lattice dielectric constant to be \( \varepsilon_{33}^{0}(\text{KNO}) = 50 \).

By contrast, KTO is cubic at all temperatures with a \( T = 0 \text{ K} \) lattice parameter of 4.005 Å and a zero-temperature dielectric constant of \( \varepsilon_{33}^{0}(\text{KTO}) = 3000 \). This calculated \( T = 0 \text{ K} \) lattice mismatch of 0.7% is similar to the experimental room-temperature value of 0.8%. All results shown in the rest of this article were obtained using the direct summation method and these parameters.

We have also previously verified that the model reproduces satisfactorily the values of the Born effective ionic charges obtained from \textit{ab initio} electronic calculations, both for KNO and KTO. This is important for an adequate description of the dielectric properties. (Note that in Ref. 11, the values of the two components of the Born effective charges for the oxygen ions are mistakenly reversed.)

### B. Simulation cell setup

The simulation cell consists of alternating KNO and KTO layers of thickness \( \Lambda/2 \) (measured in unit cells). Thus the thickness of a KNO/KTO bilayer, known as the modulation length, is \( \Lambda \). The modulation direction is taken to be the \( z \) direction; thus, the \( x-y \) plane is parallel to the interfaces between layers. The \((001)\) directions of the crystallographic unit cells in the two layers are aligned with the \( x, y, \) and \( z \) directions in the simulation cell (see Fig. 1). The interfaces between layers are chosen to be coherent, as is observed in experiments on KNO/KTO heterostructures, and consist of a KO plane common to neighboring KNO and KTO layers. Periodic border conditions are applied to the simulation cell in all three directions. In the \( x-y \) plane, these correspond to the simulation of an infinite monodomain structure. The imposition of periodicity in the \( z \) direction can be interpreted physically as the simulation of a section of a superlattice in a region far from either the surface or the substrate, neither of which is explicitly simulated.

We have used standard atomic-level relaxation methods to determine the zero-temperature structure and properties in unit-cell-thick slices through superlattices (i.e., in the \( z \) direction) for modulations lengths ranging from \( \Lambda = 2 \) to \( \Lambda = 48 \). All the ions were initially placed at positions corresponding...
to those in the perfect crystal at zero temperature. The equilib-
ibrated zero-temperature structure was then determined by a
zero-temperature quench until the force on each individual
core and shell was less than 0.05 eV Å
. Since the simul-
ations were intended to model a superlattice on a KTO sub-
strate, the in-plane lattice parameter was fixed to that of KTO
at zero temperature; however since the heterostructure is not
under any constraint in the modulation direction, the length
of the simulation cell in the z direction was allowed to ex-
pand or contract to reach zero stress. The polarization was
determined from the core–shell displacements and the dis-
placements of the ions from their centrosymmetric positions.
The KTO substrate does not produce any strain within the
KTO layers; however, it does place the KNO layers under a
compressive strain.

We chose a periodic simulation cell containing a total of
four layers (KNO/KTO/KNO/KTO; see Fig. 2) rather than
only two layers (KNO/KTO) because we want to investigate
the interaction between KNO layers in the superlattice,
which would not be possible with a two-layer system. This
four-layer arrangement offers, in addition, the computational
benefit of allowing a tetragonal simulation cell despite the
rhombohedral and cubic symmetries of the KNO and KTO
unit cells (see Fig. 1). The simulation cells consisted of 6 × 6 unit
cells in the plane and up to 96 unit cell in the z
direction. The largest simulation thus involved 17 280 ions.

The fundamental output of our simulations are the $T$
=0 K positions of the cores and shells of every ion. For the
purposes of analysis, however, it is more useful to average
this information on core and shell positions over stoichio-
metric unit cells. Moreover, because of the planar structure
of these multilayers, it is natural to further average the prop-
erties over unit-cell thick slices.

C. Determination of the polarization and dielectric
properties

Polarization only makes sense when defined in terms of
the displacement of ions summed over a neutral stoicho-
metric unit, the smallest of which is a single crystallographic
unit cell. The $\alpha$ Cartesian component of the polarization of
unit cell $n$, $P_{\alpha n}$, is defined as

$$P_{\alpha n} = \sum_i \sum_{\nu=1}^2 q_{\nu n} r_{i\nu an},$$  \hspace{1cm} (1)

where the sum on $i$ runs over the ions in the stoichiometric
unit cell $n$ and $\nu=1$ and $\nu=2$ correspond to the core and
shell, respectively, of a given ion. The neutral stoichiometric
unit cell over which the sum is performed can be defined in a
number of different ways. The most natural definition for
systems containing KNbO$_3$ and KTaO$_3$ consists of the unit
cell centered at the Nb and Ta ions. Such a unit cell has an
oxygen ion on each of the six faces, which are assumed to be
shared equally with the neighboring cells, and a K ion at
each of the eight corners, which are assumed to be shared
equally among eight unit cells. Within this definition the di-
pole moment of the undistorted cubic phase is zero.

By determining the electric-field dependence of the po-
larzation we can determine the dielectric and susceptibility
tensors ($\varepsilon = \chi + 1$). In continuum electrodynamics, the sus-
pceptibility tensor is defined by the linear relation

$$\chi_{\alpha\beta} = \frac{1}{\varepsilon_0} \frac{\partial P_{\alpha}}{\partial E_{\beta}},$$  \hspace{1cm} (2)

where $P_{\alpha}$ and $E_{\beta}$ are the components of polarization and
electric field in the $\alpha$ and $\beta$ Cartesian directions, respec-
tively, and $\varepsilon_0$ is the permittivity of free space. To simulate an
imposed external electric field we impose a force $F_{i\nu a}$ of
magnitude

$$F_{i\nu a} = q_{\nu i} E_{a}$$ \hspace{1cm} (3)
on the core and shell ($\nu=1,2$) of each ion $i$. The polarization
is calculated from Eq. (1) and then used to determine the
dielectric constants via Eq. (2). The superlattices can be fer-
roelectrically switched by imposing a sufficiently large elec-
tric field in the direction opposite to the polarization.

III. FERROELECTRIC PROPERTIES

In order to understand the basic properties of these co-
herent ferroelectric/paraelectric superlattices, we first exam-
isne in some detail the case of $\Lambda = 36$ on the KTO substrate.
By systematically studying multilayers with modulation
lengths ranging from $\Lambda = 2$ to $\Lambda = 48$, we then explore the
interactions between neighboring KNO and KTO layers, and
between KNO layers. Finally to examine the effects of strain,
we compare the $\Lambda = 36$ superlattice on a KNO substrate with
the $\Lambda = 36$ superlattice on a KTO substrate.

A. Structure and polarization

We characterize the structure of the superlattices in
terms of the variation of the lattice parameter in the modu-
lation direction $c(z)$. We define $c(z)$ as the separation of
neighboring K ions; this is, perhaps, the most natural choice
since the K ions only weakly couple to the ferroelectric dis-
tortion. Using this definition, Fig. 3 shows that there is an
~2% variation in $c(z)$ through the $\Lambda = 36$ superlattice. In a
separate simulation of a perfect crystal of KNO, we have
determined the spacing of KO layers under these in-plane
strain conditions; this and the lattice parameter of KTO are
shown in Fig. 3 as dotted lines. We can see that in the center
of the KNO layers, $c(z)$ converges to the perfect-crystal val-
ues. However, $c(z)$ in the KTO layers (4.015 Å) is 0.25%
larger than the perfect-crystal value of 4.005 Å; as we shall see below, this arises from the strong coupling between polarization and strain in the system.

Interestingly, Fig. 3 clearly shows that there are two structurally distinct interfaces in the superlattice, there being a slightly larger jump in the lattice parameters at one interface than the other. These two interfaces, which we denote type I and type II (see Fig. 2), correspond to the KNO layer polarization at the interfaces pointing into and out of the KTO layer, respectively. However, because the profiles of $c(z)$ defined in terms of the spacing of the Ta and Nb ions and in terms of the O$_i$ ions (in the KO planes) and O$_h$ ions (in the Nb$_2$O$_5$ and Ta$_2$O$_5$ planes) do not show such strong differences between the two interfaces, we may regard this difference as a secondary effect.

Before examining the polarization in the superlattice, it is useful to determine as a reference the effects of the strain on the polarization in the KNO layers. The in-plane compressive strains in the KNO layer produced by the KTO substrate break the strict rhombohedral symmetry of the polarization, resulting in a reduction of the components of polarization in the x–y plane ($P_x$, $P_y$) compared to the unstrained state and producing a corresponding enhancement in the component of polarization in the modulation direction, $P_z$ (see Table I and the arrows in Fig. 4).

Figure 4 shows the components of polarization in unit-cell-thick slices through the $\Lambda=36$ superlattice. As it is physically much simpler, we first examine the in-plane polarization $P_x = P_y$. The KTO layers of the superlattice are under zero in-plane strain when placed on a KTO substrate; thus, as expected for a paraelectric, we find that $P_x = 0$ in the KTO layer interiors. We find that in the interiors of the KNO layers $P_x = 33.4 \mu C/cm^2$, which is the same as that determined for a perfect crystal under the same strain conditions (see Table I). Moreover, as is evident from Fig. 4, the change in $P_x$ at the interface is almost atomically abrupt, with the polarization reaching the values in the interior of layer over only two or three lattice parameters. This indicates that the coupling of $P_x$ across the interfaces is weak. This rather abrupt change in $P_x$ is similar to the situation of the 180° domain wall, at which the polarization rapidly reaches bulk values on either side.

The profile of $P_z$ in Fig. 4 displays a very different behavior from that of $P_x$, being essentially continuous through the layer interiors and the interfaces; in this regard it is rather similar to the variation in $c(z)$. As we saw for $P_x$, the value of $P_z$ in the interior of the KNO layer reaches the value for a perfect crystal under the same strain conditions (see arrow and Table I). Moreover, this value is attained within a only few unit cells of the KNO/KTO interface. The behavior in the KTO layer is rather more interesting; in particular, even at the center of the KTO layer, $P_z$ does not reach the value of zero one would expect for a paraelectric under zero in-plane strain. As we discuss below, the strong electric fields induced in the KTO layer due to the polarization of the KNO layers are responsible for both this polarization in the layer interior and the associated piezoelectric strain seen in Fig. 3.

An understanding of the marked difference in the behavior of $P_z$ and $P_x$ through the interfaces comes from a consideration of the anisotropy in the correlation of the polarization dipoles in ABO$_3$ perovskite ferroelectrics. This, so-

![FIG. 3. Lattice parameter $c(z)$ in the $z$ direction for unit-cell thick layers through a $\Lambda=36$ superlattice on a KTO substrate as determined from the spacing between K ions. The dotted lines are the lattice parameters in the $z$ direction for KNO and KTO at the same in-plane strain.](image)

![FIG. 4. Components of polarization, $P_x$ (open circles) and $P_z$ (solid circles), in unit-cell-thick slices through the $\Lambda=36$ superlattice on the KTO substrate. The upper arrow marks $P_x$ for a KNO perfect crystal under this strain (see also Table I); the other arrows are $P_z$ for a KNO perfect crystal.](image)
called Lorentz field\(^2\) arises from the significant mutual enhancement of dipole moments on a single B–O chain lying along the direction of polarization, compared with the rather weak coupling of dipole moments on different B–O chains along the polarization direction. As a consequence, strongly correlated chains of polarization tend to form with only rather weak correlations in the direction normal to the chains. This anisotropy in the Lorentz field manifests itself in these superlattices as the long-ranged correlations in \(P_z\) across the interfaces and only very short-ranged correlations in \(P_x\).

### B. KTO layers and KNO/KTO interfaces

The above analyses of \(P_z\) show that there is both significant interaction across the KNO/KTO interfaces and a significant penetration of \(P_z\) into the KTO layer. To quantify these effects, we have simulated a series of superlattices with modulation lengths ranging from \(\Lambda = 2\) to \(\Lambda = 48\).

Figure 5 shows the \(z\) component of the polarization in the unit cells at either side of the two different KNO/KTO interfaces, \(P_z\). The rather weak dependence of \(P_z\) on \(\Lambda\) indicates that the ferroelectric structure of the interface does not change substantially with modulation length and that the interfaces may be considered to have certain intrinsic properties. However, the type I interfaces have slightly larger values of \(P_z\) than the type II interfaces.

We have determined the length scale over which the polarization converges to the value in the layer interior from the value at the interface \(P_z\) by fitting \(P_z\) to the exponential form: \(P_z - P_{\text{bulk}} = (P_z - P_{\text{bulk}}) \exp(-z/\lambda)\), where \(\lambda\) is the extrapolation length. As shown in Fig. 6, for the KNO layer \(\lambda \sim 2\) and is essentially independent of the modulation length. By contrast, for the KTO \(\lambda\) appears to increase linearly with the modulation length \(\Lambda\). This increase indicates that even the longest modulation length we have simulated (\(\Lambda = 48\)) is not sufficient to obtain the equilibrated transition from the interface to the interior of the KTO layer. Consistent with the above, we find that the polarization in the interior of the KTO layers is strongly \(\Lambda\) dependent, while in the KNO layer it is essentially independent of \(\Lambda\).

We have attempted to estimate the modulation length \(\Lambda_{\infty}\) required for the structure and properties of the interior of the KTO layer to reach the values for the perfect crystal under the same strain conditions. Figure 7 shows the value of the \(z\) component of polarization at the center of the KTO layer \(P_z\) and the \(z\) component of lattice strain at the center of the KTO layer \(s_z\) as a function of \(1/\Lambda\). Clearly for small enough \(1/\Lambda\) (\(\Lambda > 16\)), \(s_z\) displays linear behavior, from which we extrapolate a value for \(\Lambda_{\infty} \sim 160\). However, the nonlinear dependence of \(P_z\) vs \(1/\Lambda\) even for these rather large values of \(\Lambda\) in Fig. 7 makes it impossible to estimate a value for \(\Lambda_{\infty}\).
from the polarization data. We therefore take the value of \( L' = 160 \) as a lower-bound estimate of the modulation length required for \( P_z \) to reach zero in the center of a KTO layer.

It is important to understand the origin of this penetration of the polarization into the KTO layers. We recall from Fig. 3 that \( c(z) \) in the KTO layers is larger than that of the perfect crystal. Such a lattice expansion could arise from the piezoelectric response of the KTO under an electric field. For a KTO perfect crystal under the in-plane strain conditions present in the superlattice, we have determined the polarization associated with a range of values of strain in the \( z \) direction; these are the open symbols in Fig. 8. Plotted as the solid squares in Fig. 8 is the strain dependence of the polarization in the superlattice, determined from the data in Figs. 4 and 7. The excellent agreement between the superlattice data and the calculation for the perfect crystal indicates that the polarization and lattice expansion in the interior of the KTO layers are the same as those of a perfect crystal under an external electric field. Although the system is not under an external electric field, the polarization in the KNO layers does produce an electric field in the KTO layers; presumably it is this internal electric field which produces the observed piezoelectric response and polarization.

C. Effects of strain

The above analyses have shown that the internal electric fields arising from the ferroelectric behavior of the KNO layer are important in determining the response of the KTO layer. To explore the effects of strain we have repeated the simulations for the \( \Lambda = 36 \) superlattice under the conditions of an in-plane imposed strain corresponding to a cubic KNO substrate.

Again, as a reference, we have simulated a KTO perfect crystal under this in-plane tension and consequent out-of-plane compression. We find that the strain induces an in-plane orthorhombic polarization; the polarization in the \( z \) direction remains zero.

Because when grown on a KNO substrate both the KNO and KTO layers are polarized, there is now a richer possible arrangement of polarizations than in the case of the KTO substrate. In particular, as shown in Fig. 9, there are two possible arrangements of in-plane components of polarization in the KNO and KTO layers. (If we considered a simulation cell with more layers, there would be an even larger number of possibilities.) Again, within a single superlattice there are two types of interfaces depending on whether \( P_z \) at the interface of the KNO layer is pointing into or out of the layer.

Figure 10 shows \( P_x \) and \( P_z \) for the two different cases shown in Fig. 9. We first note that the profiles in \( P_z \) for the two cases are indistinguishable, further evidence for the coupling between \( P_z \) and \( P_z \) being very weak. Moreover, the value of \( P_z = 26.2 \mu \text{C/cm}^2 \) at the center of the KNO layer is the same as that of a strain-free perfect crystal (see Table I).
However, even under these strain conditions the value of $P_z$ still does not quite reach zero at the center of the KTO layer, again illustrating the effects of the electric field arising from the KNO layers.

At first glance, the two profiles for $P_x$ in Fig. 10 appear to be very different from each other. Actually, however, one is essentially a mirror image in the $z$ direction of the other translated by a layer. Indeed, this is exactly what one would expect if the effects of $P_z$ could be ignored—see Fig. 9. They are not quite identical at the interfaces however; compare the open squares close to $z=36$ with the stars close to $z=54$, again illustrating that although weak, there is some residual coupling between $P_x$ and $P_z$.

It is clear from this analysis that, while the substrate strain changes the values of polarization in the layer interiors, it does not qualitatively change the behavior in the interface regions. To this degree the effects of strain and the interface-induced electric fields are essentially decoupled.

IV. DIELECTRIC AND SWITCHING BEHAVIOR

The utility of ferroelectric materials generally arises not from the polarizations themselves but from the ability to significantly change the polarization by the application of an electric field; i.e., their high dielectric constants, and their ability to switch polarization in a large enough electric field. Therefore in this section, we explore in some detail both the dielectric and switching behavior of these superlattices under an electric field applied in the modulation direction.

A. Dielectric constants of KNO/KTO superlattice

We recall from Sec. II that the zero-field dielectric constants of unstrained KNO and KTO are $\varepsilon_{zz}$(KNO)$\approx 50$ and $\varepsilon_{zz}$(KTO)$\approx 3000$. Naively, we would expect the dielectric constant through a superlattice to span approximately this range. The solid circles in Fig. 11 are the layer-by-layer values of dielectric constant $\varepsilon_{zz}$ calculated by the direct imposition of an electric field (see Sec. II) to the $\Lambda = 36$ superlattice on the KTO substrate. While the dielectric constant in the KNO layer lies in the range of 30–50, consistent with the above expectation, the dielectric constant in the KTO layer reaches a peak of only $\approx 120$, only $\approx 3\%$ of the corresponding perfect-crystal value.

This large apparent discrepancy arises because the KTO layer is neither unstrained nor, more importantly, under zero electric field. Figure 12 shows the electric-field dependence of $P_z$ for perfect crystals of KNO and KTO under the in-plane strain conditions of a KTO substrate. The polarization for KNO does not depend quite linearly on the electric field except at the smallest fields, indicating a weakly electric-field independent dielectric constant. However, KTO shows a very strongly nonlinear electric-field dependence with the dielectric constant decreasing markedly with increasing electric field. To demonstrate how this is important to the dielectric properties of the superlattices, we have used the slopes of the data in Fig. 12 to determine the field-dependent dielectric constants for perfect crystals at the same values of polarization as in the profiles in Fig. 4. These estimated dielectric constants are plotted in Fig. 11 as the open diamonds. We see that in the KNO layer, the simulated and estimated values are almost identical, indicating that the KNO layer responds in a manner consistent with that of a perfect crystal under strain and finite electric field. More importantly, while the estimated values for the dielectric constant in the KTO layer are up to 50% larger than the simulated values, they are still only a very small fraction of the zero-field dielectric constant of perfect-crystal KTO. Thus, the rather low values for $\varepsilon_{zz}$ of these superlattices obtained from simulation are entirely consistent with the response of strained perfect crystals under the combination of an applied electric field and an internal electric field.
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B. Switching behavior of KNO/KTO superlattices

Just as the KNO layers significantly modify the dielectric response of the KTO layers, we can expect them to play an even more important role in the switching behavior. In this subsection we address two particular questions associated with the ferroelectric switching of these superlattices: (i) what is the nature of response of the KTO layers to an applied electric field? and (ii) how are the KNO layers coupled to each other through the intervening KTO layers?

To address these questions, we have determined the ferroelectric switching behavior of superlattices of various modulation lengths. Shown in Fig. 13 are hysteresis curves for the representative examples of \( \Lambda = 6 \) and \( \Lambda = 36 \). These coercive fields were calculated for the unit-cell thick slice at the center of each KNO and KTO layer. For \( \Lambda = 6 \), we see that the polarization in the KTO layers is almost as large as in the KNO layers; moreover, the coercive fields for the KNO and KTO layers are identical. This single value for the coercive fields and the weak spatial variation in the polarization indicates that the entire superlattice is essentially acting as a single structure, with properties different from either of its components.

For \( \Lambda = 36 \), Fig. 13 shows that the KNO layer has a square hysteresis loop characteristic of a good ferroelectric; the polarization and coercive field are larger than for \( \Lambda = 6 \), consistent with more bulk-like behavior of a thicker KNO layer. The KTO layer also displays hysteretic behavior. However, by contrast with the \( \Lambda = 6 \) superlattice, the coercive field for the KTO layers is much smaller than for the KNO layer, indicating that the KNO and KTO layers are much more weakly coupled than in the \( \Lambda = 6 \) superlattice.

The hysteresis loop for the KTO layers resembles the response of a poor ferroelectric; however as we now demonstrate it is actually the response of a paraelectric material under the combination of the applied electric field and the internal field produced by the polarized KNO layers. Figure 14 shows the polarization of one of the KTO layers when the electric field is applied to it but not to the surrounding KNO layers. The resulting \( P - E \) curve is completely reversible and nonhysteretic; i.e., it displays the response of a paraelectric material. Consistent, with the response seen in Fig. 13, this \( P - E \) curve passes through \( E_c = 0.6 \times 10^6 \) V/cm rather than \( E = 0 \), because of the electric field arising from the ferroelectric polarization within the KNO layers. The hysteretic behavior seen in Fig. 12 is therefore not an intrinsic property of the KTO layer but arises from the switching of the KNO layers under the large external electric field which, in turn, switches the sign of the internal field on the KTO layers.

While the above results show the effects on the KTO layers of the ferroelectricity within the KNO layers, they do not address the issue of any KTO mediated ferroelectric coupling between the KNO layers themselves. To investigate this coupling we have examined the properties of superlattices in which \( P_z \) in the KNO layers take opposite signs. Figure 15(a) compares the polarization through the \( \Lambda = 36 \) superlattices in which \( P_z \) in the KNO layers are parallel (solid circles, see also Fig. 4) and antiparallel (open circles). The two sets of data are essentially identical in one of the KNO layers, indicating that there is very weak coupling between the KNO layers; in the other KNO layer they are identical in magnitude, but opposite in sign. By contrast for \( \Lambda = 12 \) in Fig. 15(b), the magnitude of \( P_z \) in the KNO layers is substantially smaller with the antiparallel arrangement of polarizations. This is a signature of the strong coupling between the KNO layers, mediated through the dielectric response of the KTO layers. We do not show the results for \( \Lambda = 6 \) because the coupling is so strong that the antiparallel orientation of KNO polarizations is unstable and spontaneously switches to the parallel arrangement.

The coercive fields \( E_c \) from Fig. 13 (and corresponding figures for other values of \( \Lambda \)) and the data for the switching field \( E_s \) for the antiparallel arrangement of KNO polarizations have been compiled in Fig. 16. A consistent picture of

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**FIG. 13.** Calculated hysteresis loops show that for \( \Lambda = 6 \) the superlattice responds as a single artificial structure, while for \( \Lambda = 36 \) the KNO and KTO layers have markedly different behaviors.

**FIG. 14.** \( P_z \) in the KTO layer of the \( \Lambda = 36 \) superlattice as a function of electric field \( E_z \) applied to the KTO layer only is completely reversible, characteristic of paraelectric behavior under an internal electric field.
the ferroelectric interactions emerges from this figure. We may broadly divide the behavior into regimes of strong coupling ($\Lambda < 12$), intermediate coupling ($12 < \Lambda < 24$), and weak coupling ($\Lambda > 24$).

The presence of these regimes can be understood in terms of the competition between two different effects present in these symmetric superlattices. First, as the modulation length increases, the properties of the KNO layers tend to converge toward the properties of a bulk (strained) perfect crystal. Second, a consequence of increasing the thickness of the individual layers is that the coupling between KNO layers through the KTO layers decreases. This decrease in the KNO–KNO coupling has the tendency to lower the coercive field.

As we have discussed above, for the smallest modulation lengths, $\Lambda < 12$, the interaction between KNO layers is so strong that the multilayer behaves as a single artificial material with the KNO layers locked to each other, resulting in $E_c$ for the KNO and KTO layers being identical. The strong coupling between the KNO layers is attested to by the further observation that the antiparallel arrangement of $P_z$ is spontaneously unstable, i.e., $E_s = 0$.

For intermediate modulation lengths, $12 < \Lambda < 24$, the competition between the decrease in $E_c$ due to the increased thickness of the KTO layers separating the KNO layers, on the one hand, and the increase in $E_c$ due to the increased thickness of the KNO layers, on the other, is finely balanced. This results in a continued increase in $E_c$ up to $\Lambda = 18$, above which it decreases. This corresponds to the intermediate coupling regime.

For long modulation length, $\Lambda > 24$, $E_c$ and $E_s$ are almost equal, reflecting the increasing freedom in the response of the interior of KNO layer; this indicates that the system is in the weak coupling regime. In this regime the values of $E_c$ converges monotonically to their asymptotic perfect-crystal values of $2.5 \times 10^6$ V/cm for KNO and 0 for KTO.

A direct manifestation of the weak coupling between the KNO layers can be seen in Fig. 15(a), in which we saw that the profile of $P_z$ in the KNO layers is independent of the sign of $P_z$ in the neighboring layer. Moreover, this independence in the behavior of the KNO layers indicates that for these modulation lengths the KNO/KTO interface on one side of a KTO layer does not affect the properties of the interface on the other side. This observation allows us to make an estimate of the modulation length required for the KNO layer to be independent of each other. We define the “penetration length” $\delta$ through the gradient of $P_z$ at the interface [see Fig. 15(a)] according to

$$\frac{\partial P_z}{\partial z}|_{\text{int}} + P_{\text{int}} / \delta = 0.$$  

We find that for large modulation lengths this has a constant value, $\delta \sim 6$. Thus, if the thickness of a single KTO layer is
2δ = 12, the KNO/KTO interfaces do not overlap and the KNO layers do not interact. This corresponds to a modulation length of L = 24 and defines the onset of the weak coupling regime (see Fig. 16).

In Sec. III B, we determined that the minimum modulation required for \( P_z \) in the interior of the KTO layers to reach zero to be \( \Lambda \sim 160 \). These two calculations are not inconsistent since, while one (\( \Lambda = 24 \)) measures the interface effect only, the other (\( \Lambda = 160 \)) is a measure of the very soft dielectric response in the interior of the KTO layer, where small electric fields can induce significant polarization with almost no energy cost.

Because of the competition between the thickness of individual layers and their separation, it is likely that the ranges of \( \Lambda \) over which these three regimes exist will be considerably different in asymmetric superlattices (in which the thicknesses of the KNO and KTO layers are unequal) and in different materials systems.

V. CONCLUSIONS

One of the motivations for choosing this particular materials system for study was the existence of experimental data on the properties of KNO/KTO superlattices. The key experimental result is that the Curie temperature is independent of \( \Lambda \) for \( \Lambda < 12 \). The interpretation of this was that for these short modulation lengths the superlattice effectively behaves as a single artificial structure; this behavior was attributed to “long-ranged ferroelectric interactions.” While we have not yet determined the Curie temperatures for these superlattices, Fig. 16 does give a very related measure of the coupling within the system. Our finding that \( E_c \) for the KNO and KTO layers are identical and only weakly \( \Lambda \) dependent for \( \Lambda < 12 \) is quantitatively consistent with the experimental findings of a constant \( T_c \) for \( \Lambda < 12 \). Moreover, our analyses show that there can be significant ferroelectric interactions between the KNO layers mediated through the intervening KTO layers. We found that for this particular system, these interactions are present for \( \Lambda < 24 \), for which modulation lengths the KNO/KTO interface on one side of a KTO layer modifies the structure and properties of the interface on the other side. For much smaller lengths (\( \Lambda < 12 \)), however, the ferroelectric interactions are so strong that the polarizations in the two KNO layers in our model superlattices are locked to each other. Presumably at a rather similar value of \( \Lambda \), all the KNO layers in a superlattice containing large number of KNO and KTO layers would be likewise locked to each other. In this sense, for these modulation lengths the ferroelectric interactions would, indeed, be long-ranged. This agreement with experiment provides a strong a posteriori validation of our approach to the simulation of ferroelectric/paraelectric heterostructures.

The traditional theoretical approach to the study of ferroelectrics using the GLD theory has been very successful in describing the bulk properties of ferroelectrics. A number of additional complications arise, however, when the GLD theory is applied to heterostructures. First, typically, only the component of polarization in the modulation direction is treated. Our simulations show that this is, indeed, a good approximation for this coherent perovskite superlattice since \( P_x \) and \( P_z \) are essentially decoupled. Second, as discussed in Sec. I, it is necessary to define boundary conditions on the polarization at the interface. Our simulation results show that in this coherent paraelectric/ferroelectric heterostructure, \( P_z \) and its derivative are continuous. Because the heterostructures simulated in this article are perhaps the simplest interfacial systems (they are made from two compounds differing only by the homovalent substitution of the atom B in perovskite \( \text{ABO}_3 \)), this seems quite reasonable. Indeed, this continuity condition was adopted by Schwenk et al.\textsuperscript{7} and by Li et al.\textsuperscript{8} As for the interface itself, from the data in Fig. 5 we conclude that \( P_{\text{int}} \) is a well-defined quantity independent of the modulation length. The boundary conditions appropriate to other kinds of heterostructures may, of course, be very different from this and will have to be determined on a case-by-case basis.

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