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FERROELECTRICITY

Quasi-Two-Dimensional Ferroelectricity in $KNbO_3/KTaO_3$ Superlattices

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Abstract—First-principles density functional theory is used to calculate the phonon spectrum in the paraelectric phase, the ground-state structure and polarization distribution in the polar phase, and energies of ferro- and antiferroelectrically ordered phases of free-standing $(KNbO_3)_1(KTaO_3)_n$ ferroelectric superlattices with $n = 1–7$. It is established that quasi-two-dimensional ferroelectricity with polarization oriented in the layer plane, which weakly interacts with polarization in neighboring layers, appears in potassium niobate layers with a thickness of one unit cell in the superlattices. The possibility of using of such ferroelectric superlattices as a medium for three-dimensional information recording is shown.

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The problem of critical size of ferroelectric particles and critical thickness of ferroelectric thin films, at which ferroelectricity disappears in them, is of fundamental and practical importance. The first studies of ferroelectric nanoparticles showed that ferroelectricity disappears at a particle diameter of ~100 Å. However, further experiments on ultrathin films [1] and first-principles theoretical calculations [2–6] showed that a nonzero polarization normal to the film surface is retained in films with a thickness up to 3–6 unit cells if the depolarizing field is compensated. In films of PVDF-TrFE copolymer, an organic ferroelectric, switchable polarization was observed in films of two monolayers (10 Å) thick [7]. The ferroelectric state with polarization parallel to layers was established in $BaTiO_3$ and $PbTiO_3$ films with a thickness of three unit cells [8, 9] and zirconate–titanate films with a thickness of one unit cell [10]. An unstable ferroelectric mode with polarization in the layer plane is also characteristic for $PbB'_{1/2}B''_{1/2}O_3$ solid solution films with a thickness of one unit cell [11]. In all the above cases, the transition to two-dimensional ferroelectricity resulted from the physical reduction of the sample size in one direction. In this work, we demonstrate that *arrays of nearly independent ferroelectrically ordered quasi-two-dimensional layers*—the structures which can be used as a medium for three-dimensional information recording—can be formed in $KNbO_3/KTaO_3$ superlattices.

Ferroelectric phenomena in $KTa_{1-x}Nb_xO_3$ solid solutions have been studied for a long time. Experiments show that a polar phase appears in samples at $x > x_c = 0.008$ [12], the properties of which near the critical concentration x_c are characterized by manifestations of quantum effects and local disorder (dipolar glass). To explain the peculiarities of the system behavior near x_c, a number of models were proposed [13, 14], including the hypothesis of off-centering of Nb atoms in $KTaO_3$ [15–19]. However, as shown in [20], the single-well shape of the local potential of Nb atom in the solid solution excludes the possibility of its off-centering (this was confirmed by the present calculations). Properties of ferroelectric superlattices (SLs) in the $KNbO_3/KTaO_3$ system have been studied in [21–30]; the manifestations of antiferroelectricity in them were observed in [27, 29]. Calculations of phonon frequencies at the Γ point in the paraelectric phase of $(KNbO_3)_1(KTaO_3)_7$ SL [31] detected weak ferroelectric instability with polarization in the layer plane at the lattice parameter equal to the $KTaO_3$ lattice parameter. However, the nature of this instability and the possibility of its observation in other conditions (in particular, in SLs with other periods) were not analyzed in that paper.

The objective of this work is to study the evolution of ferroelectric instability in free-standing $(KNbO_3)_1(KTaO_3)_n$ SLs with increasing n. These studies were motivated by the disagreement between the results of our previous calculations of the ground-state structure of SLs with $n = 1$ and 3 [30] and the results of [29]. Furthermore, the conclusion about the tendency of Nb atoms in $KTa_{1-x}Nb_xO_3$ solid solution to clustering, based on the calculations of [31], seemed to be somewhat strange because the energy gain was observed only in structures with Nb atoms ordered in planes and was absent in structures with Nb atoms ordered in chains.

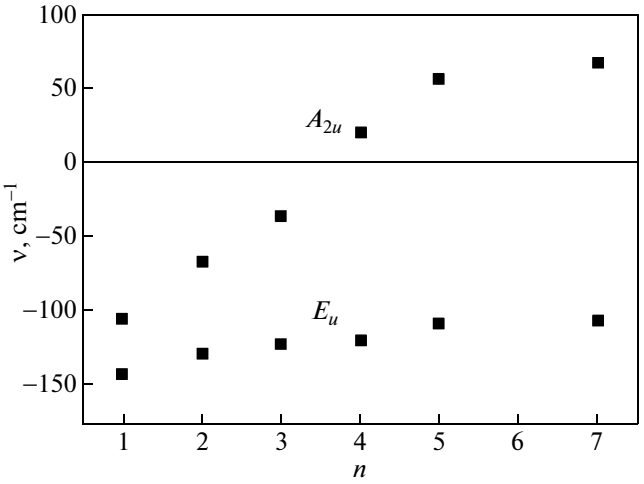

Fig. 1. Dependence of the energy of polar optical A_{2u} and E_u modes in the paraelectric $P4/mmm$ phase on the thickness of potassium tantalate layer in $(KNbO_3)_1(KTaO_3)_n$ superlattices.

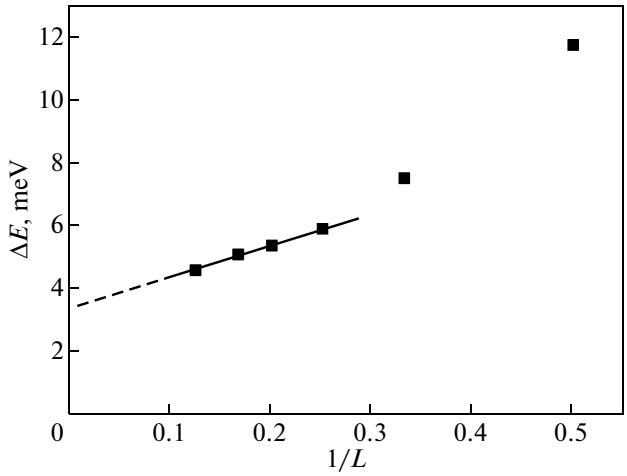

Fig. 2. Ferroelectric ordering energy per niobium atom as a function of the inverse period $L = n + 1$ of the $(KNbO_3)_1(KTaO_3)_n$ superlattices.

The $(KNbO_3)_1(KTaO_3)_n$ superlattices considered in this work were periodic structures grown in [001] direction and consisted of a $KNbO_3$ layer with a thickness of one unit cell and a $KTaO_3$ layer with a thickness of n unit cells ($1 \le n \le 7$). These structures were simulated on supercells of $1 \times 1 \times (n + 1)$ unit cells. In addition, properties of $2 \times 2 \times 2$ and $4 \times 2 \times 1$ supercells containing one niobium atom were studied.

The calculations were performed using first-principles density functional theory with pseudopotentials and wave functions expanded in plane waves as implemented in the ABINIT program [32]. As in [30], the exchange-correlation interaction was described in the local density approximation (LDA). Optimized separable nonlocal pseudopotentials constructed using the OPIUM program and complemented by a local potential to improve transferability were used as pseudopotentials. The parameters used to construct pseudopotentials and other calculation details are given in [30, 33]. The maximum energy of plane waves was 40 Ha (1088 eV); integration over the Brillouin zone was performed using Monkhorst–Pack grids of $8 \times 8 \times 4$, $8 \times 8 \times 2$, and $6 \times 6 \times 2$ size for SLs with $n =$ 1 and 2, $n = 3$ and 4, $n = 5$ and 7, respectively. Atomic positions and lattice parameters were relaxed until the Hellmann–Feynman forces become smaller than 5×10^{-6} Ha/Bohr (0.25 meV/Å). Phonon spectra were calculated within the density functional perturbation theory. Spontaneous polarization was calculated using the Berry phase method.

The $KNbO_3$ and $KTaO_3$ structure calculated using the described approach is in good agreement with experiment. For example, the lattice parameters of cubic $KNbO_3$ and $KTaO_3$ are equal to 3.983 and 3.937 Å and differ from the experimental values (4.016 and 3.980 Å) by 0.81 and 1.07%, respectively (the small underestimate of the lattice parameters is typical for LDA approximation). The calculated ratio c/a in the $KNbO_3$ tetragonal phase is 1.0197 whereas the experimental value is 1.0165; the calculated spontaneous polarization in the tetragonal phase of $KNbO_3$ is 0.372 C/m^2 (the experimental values are 0.37–0.39 C/m^2 [34]).

The calculated frequencies of two lowest-energy optical modes in the paraelectric $P4/mmm$ phase of free-standing $(KNbO_3)_1(KTaO_3)_n$ SLs with $n = 1$–7 are shown in Fig. 1. In the SL with $n = 1$, both ferroelectric modes with A_{2u} and E_u symmetry, which genetically arise from unstable TO-phonon at the center of the Brillouin zone of the perovskite structure, are unstable. As n increases, the A_{2u} mode becomes stable, and only one unstable E_u phonon remains in the phonon spectrum. The search for an equilibrium structure shows that the ground state for SL with $n = 1$ is the Cm phase [30]; for other SLs (despite the existence of unstable A_{2u} mode in the $P4/mmm$ phase for SLs with $n \le 3$) the $Amm2$ phase is the ground state.[1] The polarization vector in this phase is in the layer plane and is oriented along the [110] direction.

As follows from Fig. 2, the energy gain resulting from the ferroelectric distortion of the structure does not decrease to zero with increasing n. Along with the existence of unstable phonons in the paraelectric phase, this indicates the stability of the ferroelectric ground state in $KNbO_3$ layers of minimum possible

[1] As follows from calculations of the phonon spectra in the paraelectric $P4/mmm$ phase of SLs with $n \le 3$, along with the ferroelectric instability, unstable phonons at Z, X, and R points at the boundary of the Brillouin zone are observed. Among correspondingly distorted phases, the lowest energy is inherent to the polar $Amm2$ phase in which all phonons are stable at all points of the Brillouin zone.

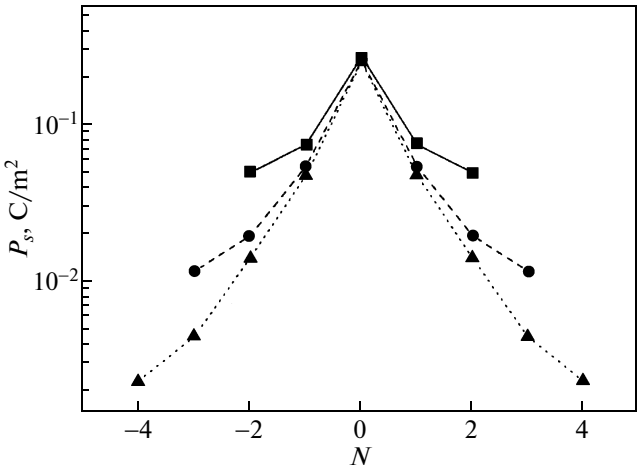

Fig. 3. Polarization profiles in $(KNbO_3)_1(KTaO_3)_n$ superlattices with $n = 3$, 5, and 7. $N = 0$ corresponds to the potassium niobate layer.

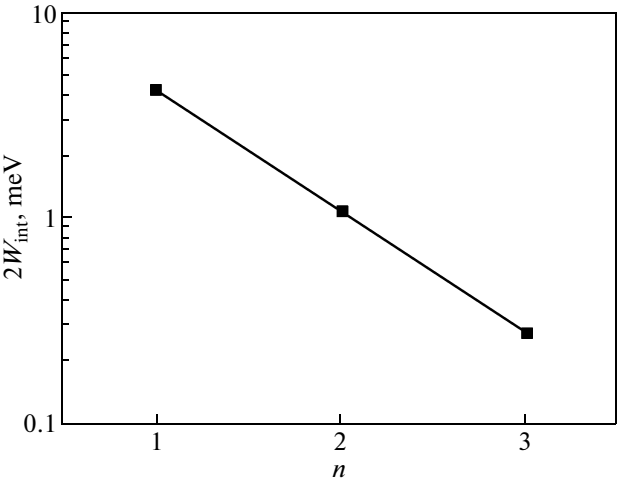

Fig. 4. Energy difference of ferroelectric and antiferroelectric ordering as a function of the thickness of potassium tantalate layer in $[(KNbO_3)_1(KTaO_3)_n]_2$ superlattices.

thickness (one unit cell) enclosed between thick $KTaO_3$ layers.

The polarization profiles in superlattices were calculated by the approximate formula $P_s = (e/\Omega)\Sigma_i w_i Z_i^* u_i$, where Ω is the unit cell volume of the layer under consideration, u_i is the displacement of the ith atom with respect to its position in the nonpolar structure, Z_i^* is the effective charge of this atom,[2] and w_i is the weight factor equal to unity for Nb(Ta) and O atoms lying in the Nb(Ta)–O layer, equal to 1/2 for K and O atoms lying in two nearest K–O planes, and equal to zero for other atoms. The dependences of P_s on the layer number in SLs with $n = 3$, 5, and 7 are shown in Fig. 3. One can see that in the region between $KNbO_3$ layers the polarization decreases approximately exponentially with a characteristic decay length of ~3 Å. This result indicates strong polarization localization in the potassium niobate layer and proves the *quasi-two-dimensional nature of ferroelectricity* in the structures under consideration. The polarization in the $KNbO_3$ layer monotonically decreases from 0.279 to 0.257 C/m^2 when going from SL with $n = 3$ to SL with $n = 7$ (for comparison, in bulk orthorhombic $KNbO_3$ the calculated P_s value is 0.418 C/m^2). The total polarization of SL calculated using the Berry phase method coincides within 3% with the sum of polarizations of the layers.

To determine the interaction energy W_{int} between neighboring polarized $KNbO_3$ layers separated by $KTaO_3$ layers, the energy of $[(KNbO_3)_1(KTaO_3)_n]_2$ superlattices with doubled period and antiferroelectric ordering of neighboring potassium niobate layers was calculated. The energy difference of ferroelectrically and antiferroelectrically ordered structures per niobium atom is shown in Fig. 4. One can see that the dependence of the difference between these energies on the $KTaO_3$ layer thickness is exponential with a characteristic decay length of 2.9 Å.

The criterion of polarization stability in quasi-two-dimensional layer with respect to spontaneous reversal of polarization is the condition $2W_{int} < U$, where W_{int} is the interlayer interaction energy and U is the height of the potential barrier between different orientational states of polarization in the layer. The factor 2 in the formula corresponds to the worst case where the polarization in the layer under consideration is antiparallel to the polarization direction in neighboring layers. In the studied structures, the easiest way to reorient polarization is its rotation in the layer plane; thus, U is equal to the energy difference between structures polarized along the [110] and [100] directions. According to calculations, $U = 1.84$ meV for SL with $n = 2$ and 1.69 meV for SL with $n = 3$. A comparison of U and $2W_{int}$ (Fig. 4) shows that the polarization stability criterion is satisfied at $n \geq 2$. A comparison of the data shown in Figs. 2 and 4 enables to conclude that the interaction energy between spontaneously polarized layers in superlattices with $n \geq 3$ is less than 10% of the ordering energy. This gives reasons to consider such superlattices as *arrays of nearly independent spontaneously polarized layers*, with satisfied conditions of quasi-two-dimensional ferroelectricity in each of them.

A comparison of energies of $2 \times 2 \times 2$, $4 \times 2 \times 1$, and $1 \times 1 \times 8$ supercells with the same concentration but different niobium atom ordering patterns (they correspond to the absence of pairs of nearest Nb atoms, linear chains of Nb atoms, and planes of Nb atoms) show any evidence of niobium clustering in planes: the energies of relaxed paraelectric phases of $4 \times 2 \times 1$ and

[2] In the calculation, the effective charges obtained for the $P4/mmm$ phase of SL with $n = 1$ were used; the effective charges in SL with $n = 2$–7 differed slightly from the used ones.

Frequencies of unstable phonons at high-symmetry points of the Brillouin zone for *P*4/*mmm* phase of $(KNbO_3)_1(KTaO_3)_n$ superlattices with $n = 1$, 2, and 3

n	Phonon frequencies, cm^{-1}			
	Γ (0, 0, 0)	*Z* (0, 0, 1/2)	*X* (1/2, 0, 0)	*R* (1/2, 0, 1/2)
1	143*i*	126*i*	71*i*	61*i*
2	118*i*	114*i*	50*i*	50*i*
3	114*i*	113*i*	46*i*	45*i*

$1 \times 1 \times 8$ supercells (eight perovskite molecules) are higher than the energy of the $2 \times 2 \times 2$ supercell (containing no nearest Nb atom pairs) by 3.0 and 8.9 meV, respectively. The tendency to the short-range ordering was observed only in structures in which Nb and Ta atoms alternated in chains: e.g., the energy of the paraelectric phase of $(KNbO_3)_1(KTaO_3)_1$ and $(KNbO_3)_1(KTaO_3)_2$ SLs grown in the [111] direction was lower by 14.0 and 18.8 meV, respectively, than the energy of the paraelectric phase of SLs of the same composition, but grown in the [001] direction.

The results obtained in this study are in agreement with the results of atomistic simulation of $KNbO_3/KTaO_3$ superlattices [24, 25]. According to these works, the polarization component parallel to layers decreased by a factor of 3–4 at a distance of one lattice period (in contrast to the polarization component normal to layers). Our results on the instability of phonon with A_{2u} symmetry in SL with $n \le 3$ agree with the data of [29] only partially: in [29], the stable polar phase with the *P*4*mm* symmetry was obtained only in SLs with $n \le 2$. However, despite the qualitative agreement of results of this and previous studies, the physical conclusions of this work differ significantly.

First, as shown above, the *P*4*mm* phase is not the ground-state structure in any considered $KNbO_3/KTaO_3$ SLs. The cause why the *Cm* or *Amm*2 phases are the ground state in considered SLs is the discovered in [30] tendency of the polarization rotation toward the layer plane, which enables to lower the electrostatic and mechanical energy in the structure.

Second, the retention of stable polarization in $KNbO_3$ layer with a thickness of one unit cell and highly inhomogeneous distribution of polarization, with the interaction between neighboring polarized layers that exponentially decreases with increasing distance between them, leads to a new previously unknown feature of the ground-state structure of $(KNbO_3)_1(KTaO_3)_n$ SLs—the formation of an array of nearly independent quasi-two-dimensionally polarized layers in the bulk of the superlattice.

As for the above-mentioned simultaneous presence of unstable phonons at the center of the Brillouin zone and at its boundary (with antiferroelectric character of the eigenvector) in the phonon spectra of paraelectric phase of SL, from the Table it follows that the frequencies of two pairs of unstable modes (at points Γ and *Z*, *X* and *R*) converge as the potassium tantalate layer thickness *n* increases. This means that when the interaction between layers weakens, the tendency of the system to ferroelectric ordering in planes cease to depend on whether the polarization in neighboring layers is oriented parallel or antiparallel. This supports the conclusion about the independence of quasi-two-dimensional ferroelectrically ordered planes in SLs with thick $KTaO_3$ layers.

We discuss now some possible applications of the discovered phenomenon. At first sight, the fact that the polarization in considered SLs is in the layer plane may seem uninteresting. So far, when discussing the ferroelectricity in thin films, the main attention was paid to films in which polarization is normal to their surfaces, as they are more suitable for practical applications. However, the physical interactions responsible for the formation of quasi-two-dimensional ferroelectric ground state in $KNbO_3/KTaO_3$ SLs are the factors which transform the superlattice into the array of nearly independent polarized planes. These structures can be used as a medium for *three-dimensional* information recording. Accepting that the lateral size of ferroelectric domains that have long-term stability with respect to spontaneous reversal of polarization is 250 Å [35], the potential volume information density is $\sim 10^{18}$ bit/cm^3 at an interlayer distance of 16 Å (corresponding to the period of the SL with $n = 3$). This value exceeds the volume information density achieved in modern optical storage devices by six orders of magnitude.

It should be added that the two-component order parameter, which describes polarization in $KNbO_3$ layers and enables the polarization rotation by 90°, offers one more interesting opportunity. In ferroelectric memory devices (FeRAM) with polarization normal to the film surface the surface charge screening resulting from leakage currents and film conductivity is the main obstacle for implementing the nondestructive read-out method. The systems with the polarization rotation by 90° have a property which in principle can help to overcome the disadvantage: nondestructive read-out using the anisotropy of dielectric constant in the layer plane can be implemented in them. For example, in $(KNbO_3)_1(KTaO_3)_n$ SL with $n = 2$ calculated dielectric constants in the plane parallel and perpendicular to polarization are 142 and 188; in SL with $n = 3$ these values are 225 and 281.

Finally, we note that similar phenomena were observed in two more ferroelectric superlattices, $BaTiO_3/BaZrO_3$ and $BaTiO_3/BaSnO_3$. In contrast to the $KNbO_3/KTaO_3$ SL considered in this work, the ferroelectric interaction in $BaTiO_3$ layers with a thickness of one unit cell and the interlayer interaction in titanate-based superlattices are complicated by the structural instability with respect to octahedra rota-

tion, which competes with the ferroelectric instability. In one more studied SL, $BaTiO_3/SrTiO_3$, the interlayer interaction is too strong and prevents the formation of the quasi-two-dimensional ground state. The results of the study of these superlattices will be published in a separate paper.

In conclusion, the ground-state structure and properties of ferroelectric $(KNbO_3)_1(KTaO_3)_n$ superlattices with $n = 1–7$ were calculated within the density functional theory. It was shown that the tendency to ferroelectric ordering is retained in $KNbO_3$ layers of minimum thickness (one unit cell) whereas the interaction energy between neighboring layers exponentially decreases with increasing n. An analysis shows that quasi-two-dimensional ferroelectricity with polarization oriented in the layer plane, which weakly interacts with polarization in neighboring layers, appears in potassium niobate layers in studied superlattices. In superlattices with $n \geq 3$, the array of nearly independent ferroelectrically polarized planes becomes the ground state. The use of such arrays as a medium for three-dimensional information recording enables to achieve the volume information density of the order of 10^{18} bit/cm^3. The results obtained in this work show that in complex systems the polarization calculated using the Berry phase method should not always be interpreted as a bulk property. Changes in polarization in a supercell can be so large that the ferroelectric system acquire properties of two-dimensional systems.

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