=== **FERROELECTRICITY** ===

Properties of BaTiO₃/BaZrO₃ Ferroelectric Superlattices with Competing Instabilities

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Abstract—Properties of $(BaTiO_3)_1/(BaZrO_3)_n$ ferroelectric superlattices (SLs) with $n = 1$–7 grown in the [001] direction are calculated from first principles within the density functional theory. It is revealed that the quasi-two-dimensional ferroelectricity occurs in these SLs in the barium titanate layers with a thickness of one unit cell; the polarization is oriented in the layer plane and weakly interacts with the polarization in neighboring layers. The ferroelectric ordering energy and the height of the barrier separating different orientational states of polarization in these SLs are sufficiently large to provide the formation of an array of independent polarized planes at 300 K. The effect of the structural instability on the properties of SLs is considered. It is shown that the ground state is a result of simultaneous condensation of the Γ_{15} polar phonon and phonons at the M point (for SLs with even period) or at the A point (for SLs with odd period); it is a polar structure with out-of-phase rotations of the octahedra in neighboring layers, in which highly polarized layers are spatially separated from the layers with strong rotations. The competition between the ferroelectric and structural instabilities in biaxially compressed SLs manifests itself in that the switching on of the octahedra rotations leads to an abrupt change of the polarization direction and can cause an improper ferroelectric phase transition to occur. It was shown that the experimentally observed z-component of polarization in the SLs can appear only as a result of the mechanical stress relaxation.

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1. INTRODUCTION

Ferroelectric superlattices (SLs) represent a new class of artificial materials whose properties, such as the Curie temperature and spontaneous polarization, often exceed those of bulk ferroelectrics [1, 2]. An analysis of properties of ten ferroelectric SLs with the perovskite structure grown in the [001] direction has shown that they are ferroelectrics at low temperatures, no matter whether they are composed of two ferroelectrics, a ferroelectric and a paraelectric, or even two paraelectrics [3]. One of the possible applications of SLs can be non-volatile ferroelectric random access memory (FRAM) devices in electronics.

The recent studies of the ferroelectric instability in free-standing $(KNbO_3)_1(KTaO_3)_n$ superlattices grown in the [001] direction showed that, with increasing n, the tendency to the ferroelectric ordering is retained in $KNbO_3$ layers with a thickness of one unit cell while the interaction energy between neighboring $KNbO_3$ layers exponentially decreases [4, 5]. It was shown that at $n \geq 2$ the ground state of the SLs is an array of ferroelectrically polarized planes whose polarization is concentrated in the $KNbO_3$ layer, is parallel to the [110] direction, and weakly interacts with polarization in neighboring layers. The use of such arrays of quasi-two-dimensional ferroelectric planes as a medium for the three-dimensional data recording can make it pos-

sible to achieve a volume recording density of $\sim 10^{18}$ bit/cm³.

Unfortunately, the implementation of the above-described ground state in the $(KNbO_3)_1(KTaO_3)_n$ SLs requires very low temperatures (~ 4 K) because of the low ferroelectric ordering energy and low height of the potential barrier separating different orientational states of polarization. That is why one of the aims of this work was to study the feasibility of similar quasi-two-dimensional structures and the ways to improve their characteristics in $BaTiO_3/BaZrO_3$ ferroelectric superlattices with an active layer of barium titanate.

In $BaTiO_3/BaZrO_3$ superlattices, the tension of the $BaTiO_3$ layers as a result of the epitaxial matching with the $BaZrO_3$ layers having a larger lattice parameter should stabilize the $Amm2$ ground state necessary to implement the quasi-two-dimensional structure [4] in the $BaTiO_3$ layers. However, since the simultaneous compression of the $BaZrO_3$ layers can cause the polarization normal to the interface to occur in them [6], the search for the ground-state structure in these SLs requires a detailed analysis. Furthermore, the instability of the $BaZrO_3$ structure with respect to the octahedra rotation [7–9] can result in the competition of the ferroelectric and structural instabilities in the SLs, and this problem also calls for a detailed study.

The properties of BaTiO$_3$/BaZrO$_3$ SLs have been studied previously both experimentally [10−15] and theoretically [3]. The initial interest to these SLs was caused by giant dielectric constants observed in them [10]. Room-temperature observations of ferroelectric hysteresis loops in the SLs [11, 13, 15] suggested that the ferroelectric transition temperature is them exceeds 300 K. The spontaneous polarization non-monotonically varied with the period of SLs and depended on the electrode configuration (in short-period SLs with electrodes on both sides of the film, hysteresis loops were absent [13]). These features have already been discussed in [3] and were explained by the rotation of the polarization to the layer plane. The recent study of Raman spectra and dielectric properties of BaTiO$_3$/BaZrO$_3$ SLs revealed the appearance of the z-component of polarization in barium titanate layers in the SLs grown on MgO substrates [15]. Interpretation of these results requires the study of the influence of substrate-induced strain on the ground-state structure of the SLs.

2. CALCULATION TECHNIQUE

The (BaTiO$_3$)$_1$(BaZrO$_3$)$_n$ superlattices considered in this work are periodic structures grown in the [001] direction and consisting of the BaTiO$_3$ layer with a thickness of one unit cell and the BaZrO$_3$ layer with a thickness of n unit cells ($1 \leq n \leq 7$). These SLs were modeled on supercells of $1 \times 1 \times L$ unit cells, where $L = n + 1$ is the SL period; in modeling the structures generated by instabilities at the M and A points at the boundary of the Brillouin zone, the primitive cell volume was doubled. In this work, particular attention was paid to free-standing SLs. In addition, a number of calculations were performed for biaxially compressed (BaTiO$_3$)$_1$(BaZrO$_3$)$_1$ and (BaTiO$_3$)$_2$(BaZrO$_3$)$_2$ SLs and for free-standing (BaTiO$_3$)$_n$(BaZrO$_3$)$_n$ SLs with $n = 2$, 3, and 4.

The calculations were performed using the density functional theory with pseudopotentials and wave function expansion in plane waves as implemented in the ABINIT code [16]. As in the earlier study of these SLs [3], the exchange−correlation interaction was described in the local density approximation (LDA). As pseudopotentials, the optimized separable nonlocal pseudopotentials constructed using the OPIUM program [17] were used; the local potential correction was added to them to improve the transferability. The parameters used for constructing the pseudopotentials and other calculation details are given in [3, 18]. The cut-off energy for the plane waves was 30 Ha (Hartree) (816 eV); the integration over the Brillouin zone was performed using the $8 \times 8 \times 4$ Monkhorst−Pack mesh for SLs with $n = 1$ and 2 and the $8 \times 8 \times 2$ one for SLs with $n = 3-7$. The relaxation of the lattice parameters and atomic positions was performed until the Hellmann−Feynman forces became less than $5 \times$

10^{-6} Ha/Bohr (0.25 meV/Å). In the case of biaxially compressed SLs, the in-plane lattice parameter was fixed equal to $0.97a_0$, $0.98a_0$, and $0.99a_0$, where $a_0 = 7.7182$ Bohr (4.0843 Å) is the in-plane lattice parameter for the $P4/mmm$ phase of the free-standing (BaTiO$_3$)$_1$(BaZrO$_3$)$_1$ SL. The phonon spectra were calculated using the equations obtained from the density functional perturbation theory. The total spontaneous polarization in the SLs was calculated by the Berry phase method; its distribution over layers was calculated using the formula $P_\alpha = \sum_i w_i Z^*_{i,\alpha\beta} u_{i,\beta}$ from displacements u_i of atoms obtained in the polar phase and tensors of their effective Born charges $Z^*_{i,\alpha\beta}$ in the paraelectric phase; here w_i are the weight factors equal to unity for atoms in the Ti−O or Zr−O layer under consideration, 1/2 for atoms in neighboring Ba−O layers, and zero for other atoms.

The properties of BaTiO$_3$ obtained using the described approach were published previously [18] and are in good agreement with experiment.

3. RESULTS

3.1. Structure of BaZrO$_3$

The structure of BaZrO$_3$ calculated using the described approach is in good agreement with experiment and results of earlier calculations [7−9]. For example, the lattice parameter in cubic BaZrO$_3$ is 7.8724 Bohr (4.1659 Å) and differs from the experimental value (4.191 Å at 2 K [7]) by 0.60% (the small underestimate of the lattice parameters is characteristic of the used LDA approximation). As in earlier studies [7−9], the calculations of the phonon spectrum of cubic BaZrO$_3$ reveal an unstable phonon mode at the R point at the boundary of the Brillouin zone with a frequency of $81i$ cm^{-1} (Fig. 1). The unstable phonon at the M point observed in [9] is absent in our calculations.

However, the instability of the phonon spectrum of BaZrO$_3$ at the R point has not yet been confirmed experimentally. One of the possible causes of disagreement between experiment and theory can be quantum fluctuations [7] which can destroy the long-range order in rotations of the oxygen octahedra.[1] According to our calculations, the ground-state structure of BaZrO$_3$ is $I4/mcm$. This result differs from predictions of [8], in which the $P\bar{1}$ structure was considered to be equilibrium. In the present study, it was shown that the $P\bar{1}$ structure is nonequilibrium and slowly relaxes to

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[1] EXAFS measurements of the Debye−Waller factor for Ba−O bonds in BaZrO$_3$ revealed its anomalously high values at 300 K, corresponding to the amplitude of the local rotations of ~4 degrees. In our opinion, this gives an evidence of the instability under consideration. The results of these studies will be published elsewhere.
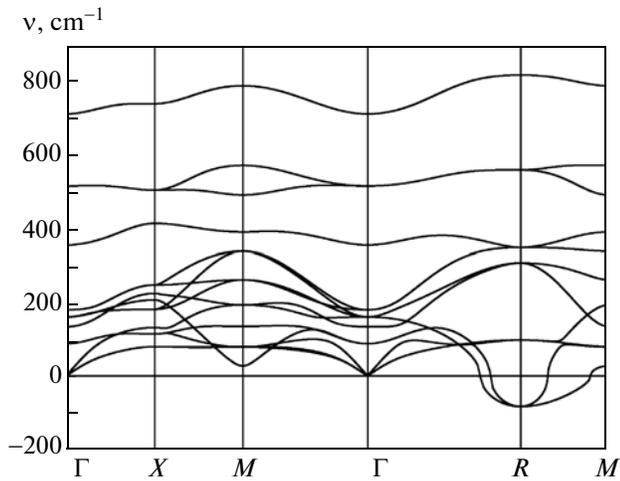
Fig. 1. Phonon spectrum of the BaZrO$_3$ crystal in the cubic phase.

the *I*4/*mcm* structure. The calculated static dielectric constant of barium zirconate in the ground state is $\varepsilon_{xx} = \varepsilon_{yy} = 58.8$, $\varepsilon_{zz} = 53.3$ (the experimental value is 47 [7]).

3.2. BaTiO$_3$/BaZrO$_3$ Superlattices

The phonon spectra of different phases of the free-standing (BaTiO$_3$)$_1$(BaZrO$_3$)$_3$ superlattice are shown in Fig. 2. One can see that two types of instability are observed in the phonon spectrum of the paraelectric *P*4/*mmm* phase (Fig. 2a): the ferroelectric instability and the structural instability associated with the oxygen octahedra rotation. The phonon frequencies at high-symmetry points of the Brillouin zone in the paraelectric phase of superlattices with $n = 1, 2$, and 3 are given in Table 1.

The instability region appearing as a band of imaginary phonon frequencies along the path Γ–Z–R–X–Γ (imaginary frequencies are presented as negative numbers in the figure) is caused by the ferroelectric instability of ...–Ti–O–... chains, which was established for the first time in [19]. An analysis of the eigenvectors of phonons related to this instability region shows that out-of-phase transverse Ti and O atomic displacements in the *xy* plane in chains propagating in the [100] and [010] directions dominate in these eigenvectors at all points of the Brillouin zone; at the Brillouin zone center, this displacement pattern corresponds to the doubly degenerate ferroelectric E_u mode. For out-of-phase atomic displacements in the chains propagating in the [001] direction and consisting of alternating titanium and zirconium atoms (...–Ti–O–Zr–O–...), the lowest-energy ferroelectric A_{2u} mode at the Γ point is always stable; its frequency increases from 37 cm^{-1} for $n = 1$ to 85 cm^{-1} for $n = 3$. A similar instability region along the path
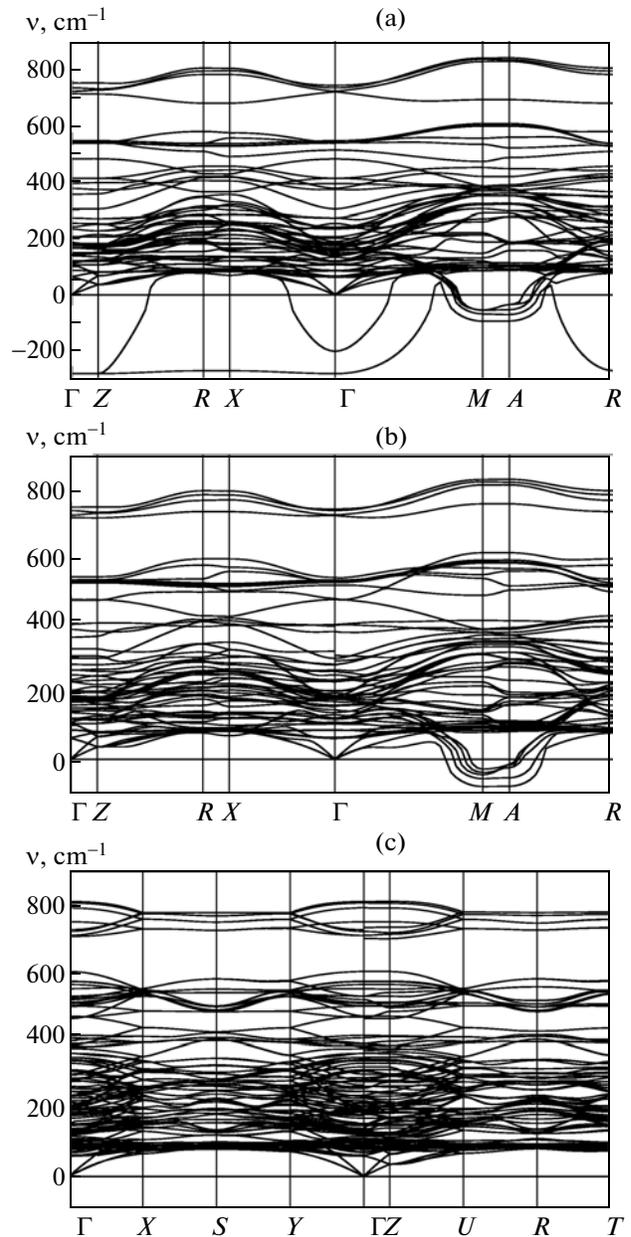

Fig. 2. Phonon spectra of the free-standing (BaTiO$_3$)$_1$(BaZrO$_3$)$_3$ superlattice in (a) *P*4/*mmm*, (b) *Amm*2, and (c) *Pmc*2$_1$ phases.

Γ–Z–R–X–Γ was observed in KNbO$_3$/KTaO$_3$ superlattices [5].

Among the possible polar phases resulting from the condensation of the unstable E_u mode at the Γ point, the *Amm*2 phase with polarization along the [110] direction has the lowest energy in (BaTiO$_3$)$_1$(BaZrO$_3$)$_n$ SLs with $n = 1$–7. However, the phonon spectra of this phase (Fig. 2b) show that phonons at the *M* and *A* points at the boundary of the Brillouin zone remain unstable, which indicates the instability of the *Amm*2 structure with respect to the oxygen octahedra rota-

Table 1. The lowest frequencies of optical phonons at high-symmetry points of the Brillouin zone in $P4/mmm$ and $Amm2$ phases and in the ground state ($Pmc2_1$) of free-standing $(BaTiO_3)_1(BaZrO_3)_n$ superlattices with $n = 1, 2$, and 3

| n	Phonon frequencies, cm^{-1}					
	$\Gamma(0, 0, 0)$	$Z(0, 0, \frac{1}{2})$	$X(\frac{1}{2}, 0, 0)$	$R(\frac{1}{2}, 0, \frac{1}{2})$	$M(\frac{1}{2}, \frac{1}{2}, 0)$	$A(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
			$P4/mmm$ phase			
1	248i	243i	233i	228i	90i	86i
2	269i	268i	257i	257i	88i, 65i	90i, 63i, 21i
3	279i	279i	268i	268i	92i, 66i, 54i, 53i	91i, 68i, 51i, 34i
			$Amm2$ phase			
1	91	66	87	89	60i	54i
2	76	46	84	79	69i, 39i	72i, 41i
3	61	36	68	77	79i, 58i, 46i, 38i, 25i	79i, 53i, 20i, 16i
	$\Gamma(0, 0, 0)$	$Z(0, 0, \frac{1}{2})$	X/Y	U/T	S	R
			$Pmc2_1$ phase			
1	84	66	70/76	78/82	86	89
3	60	35	67/73	68/74	80	81

tion.[2] This instability of the polar $Amm2$ phases is characteristic of SLs with all periods (see Table 1). Thus, the $Amm2$ phase is not a true ground-state structure for the SLs under consideration.

As follows from Table 1, the frequencies of two unstable phonons at the M and A points for the $Amm2$ phase of the superlattices with different periods are very close. Therefore, to search for the true ground state, it is necessary to compare the energies of all structures resulting from the condensation of these two phonons.

An analysis of the eigenvectors of unstable phonons at the M point shows that the most unstable phonons are characterized by out-of-phase rotations of octahedra in neighboring layers. In SLs with even period ($L = 2, 4$), the rotation angle is small in the BaTiO$_3$ layers and large in the BaZrO$_3$ layers (Figs. 3a and 3c); in SLs with odd period ($L = 3$), the rotation angle is zero in the BaTiO$_3$ layers and is large in the BaZrO$_3$ layers (Fig. 3b). Modes with lower instability (Table 1) include modes with other combinations of rotations in layers (in particular, in-phase rotations in BaZrO$_3$ layers and strong out-of-phase rotations in every second BaZrO$_3$ layer) and a doubly degenerate mode with a complex combination of distortion and tilting of the oxygen octahedra (for $L = 4$).

An analysis of the eigenvectors of unstable phonons at the A point shows that in SLs with even period ($L = 2, 4$), the most unstable phonons are characterized by the out-of-phase rotations in neighboring BaZrO$_3$ layers and the absence of rotations in the BaTiO$_3$ layers
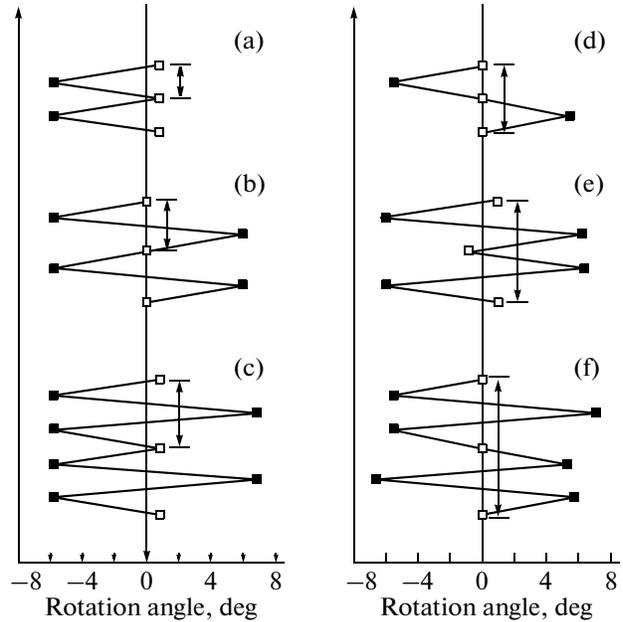
Fig. 3. Octahedra rotation angles in the ground state of $(BaTiO_3)_1(BaZrO_3)_n$ superlattices corresponding to the phonon condensation at points (a–c) M and (d–f) A. (a, d) $n = 1$ ($L = 2$), (b, e) $n = 2$ ($L = 3$), (c, f) $n = 3$ ($L = 4$). BaTiO$_3$ and BaZrO$_3$ layers are denoted by open and filled squares, respectively. Vertical lines with arrows indicate the physical periods of the resulting structures.

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[2] Hereafter, we shall use the notation of the points in the Brillouin zone of the tetragonal paraelectric structure for their notation in the low-symmetry structures.

Table 2. Lattice parameters in the paraelectric $P4/mmm$ phase of free-standing $(BaTiO_3)_1(BaZrO_3)_n$ superlattices with $1 \leq n \leq 7$, the energy of the ferroelectric ground state ΔE_1 ($Amm2$ phase), the energy ΔE_2 of the $I4/mcm$ or $P4/mbm$ phases with pure rotations, the energy of the true ground state ΔE_3 ($Ima2$ and $Pmc2_1$ phases), and the polarization in the ferroelectric ground (P_{s1}) and true ground (P_{s3}) states

Parameter	n					
	1	2	3	4	5	7
a_0, Bohr	7.7182	7.7747	7.8009	7.8160	7.8258	7.8379
c_0, Bohr	15.3298	23.1923	31.0604	38.9304	46.8013	62.5443
ΔE_1, meV	−72.7	−101.0	−115.1	−123.6	−129.3	−136.2
ΔE_2, meV	−21.3	−34.6	−46.7	−57.7	−68.3	−
ΔE_3, meV	−78.3	−116.8	−142.3	−161.5	−177.8	−
P_{s1}, C/m^2	0.2755	0.2024	0.1568	0.1273	0.1070	0.0809
P_{s3}, C/m^2	0.2591	0.1859	0.1445	0.1113	0.0984	−

(Figs. 3d and 3f). In SLs with odd period ($L = 3$), out-of-phase rotation angles are large in the BaZrO$_3$ layers and small in the BaTiO$_3$ layers (Fig. 3e). In both cases, the *physical period* of SLs is doubled in comparison with the period L specified by the layer sequence. Modes with lower instability (Table 1) are qualitatively similar to the above-described modes at the M point.

An abrupt change in the rotation angle in going from the BaTiO$_3$ layer to the BaZrO$_3$ layer and its weak dependence on the period of SL correlate with the small change of the unstable phonon frequency along the $M-A$ line, which indicates a strong localization of these rotations in the layers.

To search for the ground state of SLs, the oxygen octahedra rotations corresponding to the least stable

phonons at the M and A points of the Brillouin zone were added to the polar $Amm2$ structure. A comparison of the total energies of the structures resulting from simultaneous condensation of the "rotational" and ferroelectric modes shows that the ground-state structure depends on the superlattice period L: for odd L, it is described by the space group $Ima2$ and results from the condensation of the unstable "rotational" mode at the A point; for even L, it is described by the space group $Pmc2_1$ and results from the condensation of the unstable "rotational" mode at the M point. The energy difference of the structures resulting from the condensation of phonons at the M and A points is rather small (1.6−1.9 meV). The energies of the structures corresponding to the ferroelectric ground state and to the true ground state, as well as to nonpolar structures with pure octahedra rotations (space group $I4/mcm$ for odd L and $P4/mbm$ for even L) are given in Table 2.[3] An increase in all three energies with increasing n is due to two effects: (i) an increase in the BaZrO$_3$ volume fraction in the structure, which results in an increase of the instability of SLs with respect to the octahedra rotation; (ii) an increase in biaxial tension of the BaTiO$_3$ layers (as a consequence of an increase in the in-plane lattice parameter), which enhances the ferroelectric instability. The corresponding change in the frequencies of unstable phonons at the Γ point can be seen in Table 1.

The polarization profiles in the obtained ground states for SLs with $n = 1$, 3, and 5 are shown in Fig. 4. One can see that the polarization is concentrated in the barium titanate layer and almost exponentially decreases with distance with a characteristic length scale of ~2.0 Å. It is interesting that the spontaneous polarization in the true ground state is lower than the polarization in the ferroelectric ground state by only

Fig. 4. The polarization distribution between the layers in the ground-state structure of $(BaTiO_3)_1(BaZrO_3)_n$ superlattices with $n = 1$, 3, and 5. The layer number $N = 0$ corresponds to the BaTiO$_3$ layer.

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[3] The ferroelectric ground state is a structure with a minimum energy obtained by taking into account only the ferroelectric unstable mode.
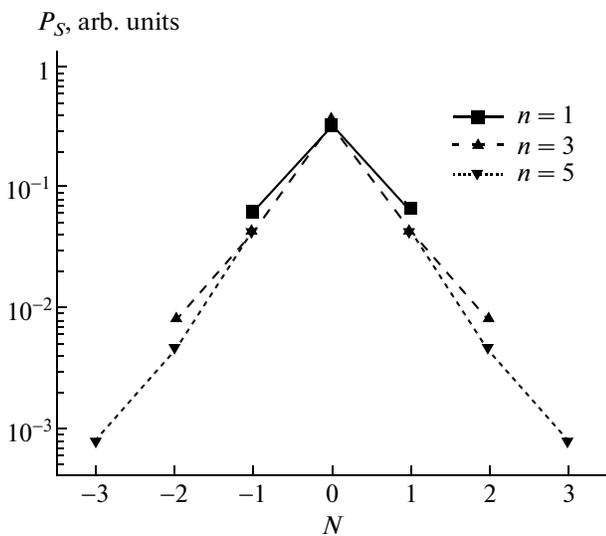
6–12% (Table 2). This indicates the weak effect of the octahedra rotations on the spontaneous polarization in SLs.[4] We explain this by the fact that regions with high polarization in the SLs under consideration are spatially separated from regions with strong octahedra rotations, and thus the competition between the structural and ferroelectric instabilities becomes significantly decreased. This feature essentially distinguishes the superlattices from such crystals as CaTiO$_3$ and PbTiO$_3$ with competing instabilities in the cubic phase. In the former case, the structural distortions completely suppress ferroelectricity; in the latter case, an opposite effect occurs.

To test the possibility of forming the arrays of quasi-two-dimensional polarized planes in the ground state of (BaTiO$_3$)$_1$(BaZrO$_3$)$_n$ SLs, we estimated the interlayer interaction energy. The energy $2W_{int}$ (the energy corresponding to two domain walls) was calculated as the difference of the total energies of ferroelectrically and antiferroelectrically ordered SLs with a doubled period in a similar way as in [4]; in this calculation, the octahedra rotations were neglected. The value of $2W_{int}$ was 7.46 meV for $n = 1$, 1.505 meV for $n = 2$, and 0.420 meV for $n = 3$, and decreased almost exponentially with increasing n. For all n, this energy was much lower than the energy gain resulting from the ferroelectric ordering ΔE_1 (Table 2), which ensures almost independent polarizations in the quasi-two-dimensional layers and the formation of the arrays of independent polarized planes similar to those observed in [4]. The potential barrier height ΔU for reorientation of the polarization, which occurs in the SLs under consideration by rotating the polarization vector in the layer plane, was 22.9 meV (per Ti atom) for $n = 1$, 33.2 meV for $n = 2$, and 38.3 meV for $n = 3$. The obtained potential barrier heights and ferroelectric ordering energies are much higher than those for the KNbO$_3$/KTaO$_3$ SLs considered in [4, 5]. In our opinion, these values are sufficiently large to provide stable polarization in the arrays of quasi-two-dimensional polarized planes at 300 K.

4. DISCUSSION

We start the discussion with an analysis of possible polar structures in (BaTiO$_3$)$_1$(BaZrO$_3$)$_n$ SLs. The ferroelectric instability in the ...−Ti−O−... chains can lead not only to the ferroelectric ordering, but also to the formation of antiferroelectric structures resulting from the condensation of unstable phonons at Z, R, and X points at the boundary of the Brillouin zone. Three types of the polarization ordering in the chains, which result from the condensation of these unstable
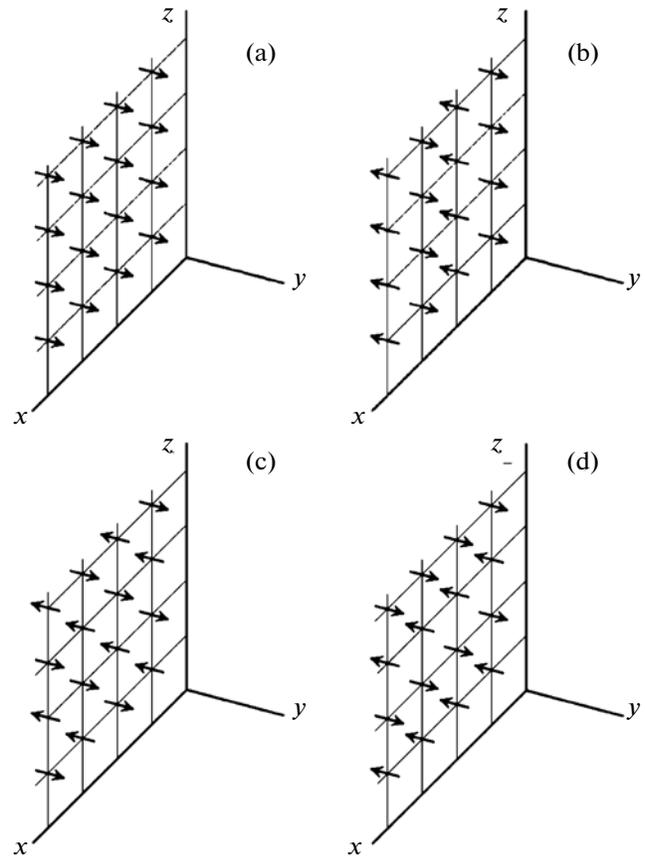
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[4] An additional cause of the decrease in the polarization in free-standing SLs when the octahedra rotations are switched on can be a systematic decrease (by 0.02–0.03 Bohr) in the in-plane lattice parameter.

Fig. 5. Schematics of the polarization ordering in the ...−Ti−O−... chains propagating along the y axis which accompanies the condensation of unstable phonons at points (a) Γ, (b) X, (c) R, and (d) Z.

phonons in the paraelectric $P4/mmm$ phase, are shown in Fig. 5. It is seen that these structures differ only in the relative orientation of polarization in neighboring chains. For example, for the phonon condensation at the X point, the antiferroelectric $Pmma$ phase appears in the SLs; the modulation wave vector in this phase is directed along the x axis, whereas the out-of-phase displacements of Ti and O atoms forming the chains are directed along the y axis (Fig. 5b). It is remarkable that this phase still exhibits the ferroelectric instability with respect to the polar displacements along the x axis and finally transforms to the polar Pm ($Pmc2_1$ for $n = 1$) phase being *ferrielectric*. Similarly, the antiferroelectric $Cmma$ phase with the modulation described by the phonon at the R point and with out-of-phase displacements along the y axis (Fig. 5c) also is ferroelectrically unstable and finally transforms to the *ferrielectric Abm*2 phase. In contrast to non-degenerate unstable phonons at the X and R points, the unstable phonon at the Z point is doubly degenerate, and its condensation can lead to two antiferroelectric phases, $Pmma$ (Fig. 5d) and $Cmcm$, with displacements in one or both ...−Ti−O−... chains,

Table 3. Energies of the antiferroelectric phases appearing as a result of the condensation of unstable phonons at the boundary of the Brillouin zone and of the ferroelectric *Amm*2 phase in free-standing $(BaTiO_3)_1(BaZrO_3)_n$ superlattices with $n = 1, 2,$ and 3 (the energy of the paraelectric *P*4/*mmm* phase is taken as the energy reference)

Unstable phonon	$n = 1$		$n = 2$		$n = 3$	
	phase	E, meV	phase	E, meV	phase	E, meV
X	*Pmma*	−37.3	*Pmma*	−52.1	*Pmma*	−59.8
	*Pmc*2₁	−68.1	*Pm*	−95.2	*Pm*	−109.0
R	*Cmma*	−33.7	*Cmma*	−51.1	*Cmma*	−59.7
	*Abm*2	−64.9	*Abm*2	−94.3	*Abm*2	−108.8
Z	*Pmma*	−41.9	*Pmma*	−60.7	*Pmma*	−69.6
	Cmcm	−68.9	*Cmcm*	−100.3	*Cmcm*	−114.9
Γ	*Amm*2	−72.7	*Amm*2	−101.0	*Amm*2	−115.1

respectively. These displacements result in the in-plane microscopic polarization directed along [100] and [110]. It was the latter of these two phases which was considered above in the calculation of the interlayer interaction energy.

The ferroelectric instability of the intermediate *Pmma* and *Cmma* phases is easily understandable: in these two phases, the structural relaxation occurs in only one of two ferroelectrically unstable ...−Ti−O−... chains propagating in the [100] and [010] directions, and so the structure retains the ferroelectric instability in the second chain. In the *Pmc*2₁, *Pm*, *Abm*2, and *Cmcm* phases, the structural relaxation occurs simultaneously in both chains; this is why these structures are stable (metastable). In all cases, the obtained intermediate and *ferrielectric* phases have higher energies in comparison with the ferroelectric *Amm*2 phase (Table 3).

Now we discuss the structure of rotations in the SLs under consideration. A comparison of the frequencies of unstable phonons corresponding to various combinations of rotations in the layers of SLs with the same period shows that phonons with out-of-phase rotations in neighboring layers are energetically least stable. These rotations are fully consistent with the instability at the *R* point in the parent cubic BaZrO₃ (Fig. 1). The main difference between the two rotation systems corresponding to unstable phonons at the *M* and *A* points is the relation between rotations in the *neighboring periods* of the superlattice: for the phonon condensation at the *M* point, when the structure is translated by one SL period, the octahedra are rotated in phase; in the case of the phonon condensation at the *A* point, they are rotated out of phase. It can be seen that the ground state of the SL always corresponds to such a rotation system in which the octahedra are rotated out of phase in any pair of neighboring layers, i.e., the *M* phonon is condensed in the SLs with even period and the *A* phonon is condensed in the SLs with odd period.

One more subject for discussion is the comparison of the obtained results with the experimental data of [15]. According to the X-ray data from this work, the spontaneous polarization in SLs is predominantly oriented in the layer plane; however, the line narrowing and an increase in the frequency of the soft *E*-mode in Raman spectra indicate the monoclinic distortion of the structure and the appearance of the *z*-component of polarization in BaTiO₃ layers. The *z*-component of polarization determined from the hysteresis loops nonmonotonically depends on the superlattice period. The authors of [15] supposed that the appearance of the polarization component normal to the film is caused by the ferroelectric phase transition predicted in [6] in biaxially compressed BaZrO₃ layers.

The calculations performed in the present work showed that the A_{2u} phonon is indeed unstable in biaxially compressed BaZrO₃ (space group *P*4/*mmm*) with the in-plane lattice parameter equal to the lattice parameter of the free-standing $(BaTiO_3)_1(BaZrO_3)_1$ SL ($a_0 = 7.7182$ Bohr) (according to our data, the critical lattice parameter at which the instability of this phonon appears is ~7.735 Bohr and notably exceeds the value of 7.425 Bohr specified in [6]). However, the instability of the A_{2u} phonon in biaxially stretched BaTiO₃ with the lattice parameter equal to a_0 is absent (the phonon frequency is 45 cm⁻¹). Therefore, the appearing of the *z*-component of polarization in SLs needs a more detailed analysis.

As we have shown previously [3], the A_{2u} mode (which is responsible for the appearance of the *z*-component of polarization) is stable (37 cm⁻¹) in the paraelectric *P*4/*mmm* phase of the free-standing $(BaTiO_3)_1(BaZrO_3)_1$ SL. The calculations of the phonon frequencies for the *P*4/*mmm* phase of $(BaTiO_3)_n(BaZrO_3)_n$ SLs with $n = 2, 3,$ and 4 performed in this work showed that the frequency of this mode rapidly decreases with increasing n (28.5 cm⁻¹ for $n = 2$ and 17 cm⁻¹ for $n = 3$) and becomes unstable at $n = 4$ (7i cm⁻¹). However, the instability of the A_{2u}

phonon in the paraelectric phase does not mean that the z-component of polarization will appear in the ferroelectric ground state. The in-plane spontaneous polarization, which appears due to the strong instability of the E_u phonon, abruptly increases the frequency of the corresponding mode (B_1 or B_2) in the $Amm2$ phase, and this phase becomes stable with respect to the appearance of the z-component of polarization.

This stability reduction of the A_{2u} phonon with increasing n recalls the results obtained for the (BaTiO$_3$)$_m$(BaO)$_n$ Ruddlesden–Popper SLs [20]. In these SLs, a similar decrease in the A_{2u} phonon frequency with increasing the BaTiO$_3$ layer thickness was observed; at $m \geq 8$, it became unstable. However, already at $m = 4$, the instability at the X point appearing in the SLs resulted in the formation of domain-like structure, since it was energetically more favorable to form a structure with a z-component of polarization periodically varying in space, rather than to uniformly polarize the BaO layer having a low dielectric constant. The macroscopic z-component of polarization is absent in such a structure.

Another possible cause for the appearance of the z-component of polarization can be a substrate-induced strain in the superlattice (in [15], the SLs were grown on MgO substrate). Calculations show that in (BaTiO$_3$)$_n$(BaZrO$_3$)$_n$ SLs with $n = 1$ and 2, for the in-plane lattice parameter equal to $a = 0.99a_0$ and $0.98a_0$ (a_0 is the in-plane lattice parameter of the free-standing SL) and the disabled octahedra rotations, the polarization vector is rotated by ~38° and ~67° from the layer plane (the space group of the ferroelectric ground state is Cm); for $a = 0.97a_0$ and disabled rotations, the vector is rotated by 90° (the space group of the ferroelectric ground state is $P4mm$). However, when the octahedra rotations are enabled, in all SLs we see an unexpected result: the z-component of polarization disappears in SLs with $a = 0.99a_0$ and $0.98a_0$ (space group of the ground state is $Pmc2_1$ for $n = 1$ and $Pnc2$ for $n = 2$), whereas in the SL with $a = 0.97a_0$, the polarization rotates toward the layer plane by ~24° (the space group of the ground state is Pc).

The competition between the ferroelectric and structural instabilities in crystals with the perovskite structure has been known for a long time [21, 22]; however, the fact that the octahedra rotations can have such a strong effect on the polarization seems to be observed for the first time. This finding can be important for the following reason. In the SLs under consideration, the energy gain resulting from the structural distortions is less than the energy gain resulting from the ferroelectric ordering (compare the energies ΔE_1 and ΔE_2 in Table 2). This leads us to expect that, as the temperature increases, the structural phase transition in the SLs will occur at a lower temperature than the ferroelectric phase transition. Then, since the disappearance of the octahedra rotations results in the onset

of the z-component of polarization, the situation is possible that an improper ferroelectric phase transition accompanied by the appearance of a nonzero z-component of polarization can occur in the SLs when the structural phase transition temperature is approached from below (when the octahedra rotation angle rapidly decreases). The abrupt rotation of the polarization vector as the temperature varies can result in the appearance of a number of physical property anomalies resembling the anomaly in the piezoelectric coefficients near the morphotropic phase boundary. However, currently, it is not clear whether the structural phase transition occurs in BaZrO$_3$. Nevertheless, even if the establishment of the long-range order in the octahedra rotations in BaZrO$_3$ is impossible for some reason, the changes in the local angles of the rotations with temperature can have a significant effect on the z-component of polarization.

The above-considered attempts to explain the appearance of the z-component of polarization, which were based on the assumption of a uniformly strained BaTiO$_3$/BaZrO$_3$ SL, were not successful (the strong biaxial substrate-induced in-plane compression of the SL cannot be retained in a thick SL). It seems that the only way to explain this phenomenon is to consider the stress relaxations occurring in SLs with thick layers. This idea has already been used to explain the appearance of the z-component of polarization in BaTiO$_3$/BaZrO$_3$ SLs with large periods in [3, 13]. Our calculations show that the critical in-plane lattice parameter at which the z-component of polarization appears in BaTiO$_3$ is ~7.565 Bohr; in this case, the out-of-plane lattice parameter is $c \approx 7.471$ Bohr. If we take into account the systematic error (−0.7%) in the prediction of the lattice parameters for BaTiO$_3$, the experimental parameter $c = 3.981$ Å in the BaTiO$_3$ layer should correspond to this situation. According to the X-ray data [15], such a relaxation of mechanical stress already appears in the SL with a period of $L = 32$ Å. So, this relaxation explains the appearance of the z-component of polarization in SLs with the specified and larger periods.

The first-principles calculations allow us to understand why the quality of short-period BaTiO$_3$/BaZrO$_3$ and BaTiO$_3$/Ba(Ti,Zr)O$_3$ SLs grown in the [001] direction is not very good [15, 23]. This is because of the tendency of BaTi$_{1-x}$Zr$_x$TiO$_3$ solid solutions to three-dimensional chessboard-type ordering of cations at the B sites. The calculations show that the energy of the paraelectric phase of the (BaTiO$_3$)$_1$(BaZrO$_3$)$_1$ SL with the elpasolite structure (space group $Fm3m$), which appears when growing the SL in the [111] direction, is by 83 meV (per formula unit) lower than the energy of the same SL but grown in the [001] direction. It is possible that defects generated during the stress relaxation in SLs grown in the [001] direction become the nucleation centers of three-dimensional chessboard-type ordered inclu-

sions. Furthermore, the possible electrical activity of these defects can be a factor which changes the electrostatic boundary conditions at the heterointerface and stabilizes the polar state in the $BaTiO_3$ layer without inducing an appreciable electric field and polarization in the $BaZrO_3$ layer.

5. CONCLUSIONS

The properties of $BaTiO_3$/$BaZrO_3$ superlattices with competing ferroelectric and structural instabilities were calculated from first principles within the density functional theory. It was established that the quasi-two-dimensional ferroelectricity with the polarization oriented in the layer plane, which weakly interacts with the polarization in neighboring layers, occurs in SLs grown in the [001] direction with one-unit-cell thick barium titanate layer. It was shown that the energy gain from the ferroelectric ordering and the height of the potential barrier separating different orientational states of polarization are sufficiently large to observe the formation of an array of independent polarized planes at room temperature. The effect of the structural instability on the properties of SLs was considered. It was shown that the ground state is a result of simultaneous condensation of the ferroelectric Γ_{15} mode and phonons at the M point (for SLs with even period) or at the A point (for SLs with odd period). Thus, the ground state is a structure with out-of-phase rotations in neighboring layers, in which highly polarized layers and layers with strong octahedra rotations are spatially separated. This significantly reduces the influence of structural distortions on the spontaneous polarization. It was shown that the switching on of the octahedra rotations in biaxially compressed $BaTiO_3$/$BaZrO_3$ SLs with an in-plane strain of $1-3\%$ results in an abrupt change in the polarization direction. This suggests that an improper ferroelectric phase transition accompanied by the appearance of a nonzero z-component of polarization can occur in these SLs with increasing temperature.

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