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Comparative study of [001] surface relaxations of perovskite titanates

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Abstract

Surface relaxations of the cubic perovskite SrTiO_3 and BaTiO_3 crystals have been studied in the framework of the shell model. The positions of atoms in several surface layers embedded into the electrostatic field of the remainder of the crystal were calculated. Ti^{4+} , Sr^{2+} , Ba^{2+} and O^{2-} ions in six near-surface layers are displaced differently from their crystalline sites. Such effects create the so-called surface rumpling, a dipole moment and the electric field in the near-surface region. Calculated atomic displacements were compared with the LEED experimental data and showed good agreement. Our simulations have demonstrated that the cubic perovskite SrTiO_3 crystals reveal surface polarization and accompanied by the presence of relevant electric field. This arises due to a disturbed force balance accompanying the surface creation and affect 5–6 planes below the surface. In other words, the surface can serve as important factor imposing a long-range order in paraelectric SrTiO_3 . As discussed in the literature, the [001] surface turns out to be ferroelectric with properties different from the bulk material. © 1998 Elsevier Science S.A.

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1. Introduction

The size effect on phase transitions in perovskites is the phenomenon which is known from the middle of 1950s [1–3]. Nevertheless, recently, it has attracted an intent attention because of the development of thin films and composite materials. Large capacity memory devices put this phenomenon into the group of the hot topics in modern solid state physics [4]. The discrepancy of experimental results on the influence of the size of thin films or particles of perovskites [5–9] may be affected by the surface preparation of the samples. Although there were some theoretical efforts to study the defects in perovskites (see, for example, Refs. [10–15]) they were devoted mainly to the investigation of point defects, for example, doped or undoped bulk materials. At the same time, surface represents the defect that may lead to unusual behavior of perovskites, which may be realized in the changes of the thermodynamic and kinetic properties of first-order phase transitions. The relaxation of the surface may be sufficient in thin films as well as in small particles and may shift the

thermodynamic parameters which are usually used in characterization of phase transitions in the film/particle-based devices. The aim of this paper is to demonstrate the effect of the surface relaxation on the polarization of the layers of paraelectric phase in the vicinity of the [001] surface in SrTiO_3 and to compare it with the surface relaxation in BaTiO_3 . These simulations give sense to the estimation of phenomenological parameters which could be utilized in the framework of the phenomenological phase transition theory. This concerns especially the extrapolation length for the polarization [16]. The sign of this value is crucial in predicting the influence of the surface on phase transformations. The phenomenological Landau theory was recently applied to the investigation of asymmetric behaviour in ferroelectric films [17].

The strontium titanate compound (SrTiO_3) exhibits one of the best-behaved and thoroughly investigated displacive phase transitions [18]. At high temperatures (above 103 K), the structure is precisely cubic perovskite with symmetry $m3m$ and it exhibits paraelectric properties. Its dielectric constant follows a Curie–Weiss law and it increases with the decrease of the temperature as high as 10^4 at $T \sim 4$ K. This is related to a low-lying transverse optic (TO) mode at the Γ -point. At temperatures below the second-order

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phase transition, the structure changes because of small cooperative atomic displacements. The distortion of SrTiO_3 is precisely tetragonal for all temperatures below the phase transition, which is not ferroelectric. The order parameter is represented by the angle of rotation of TiO_6 octahedra around one of the axes of the original cubic cell. The symmetry of the tetragonal phase is associated to rotation of the octahedra around the cubic c -axis. SrTiO_3 is a superconducting material [19].

Although the ab initio calculations represent more consistent procedure to study the properties of oxides [20,21] its application is restricted by relatively small number of surface layers. This is why to study the above mentioned phenomenon, we used the shell-model technique [22,23]. This technique was previously successfully applied to the investigation of the defects in a lot of ionic crystals including perovskites [10–15].

2. Simulations

In the present simulation, we kept cubic perovskite structure for the bulk SrTiO_3 and BaTiO_3 crystals. To study the surface relaxation, we optimized the positions of several (from 1 to 10) surface layers situated in the field of the remainder of the crystal. Six additional layers modelled the remainder of the crystal. Ions in these layers were fixed in lattice sites. The number of additional layers was chosen to reach a convergency of the crystal field at the surface layers.

The interatomic interaction is chosen in the spirit of core–core, core–shell and shell–shell pair potentials, representing the shell-model. In this approach, each ion is represented by charged core and shell. The sum of the core

and the shell charges is equal to the charge of the corresponding ideal ion. Interactions between the cores and between cores and shells of different ions include only Coulombic interaction. At the same time, the interactions between the shells of different ions besides of Coulombic part can contain the short-range potentials to account for the effects of exchange repulsion of the ions as well as Van-der-Waals attraction between them. All simulations were made by MARVINS code [24]. This code realizes the shell-model technique for simulation of the surface structures.

3. Results and discussion

Our calculations for SrTiO_3 show that Ti^{4+} , Sr^{2+} and O^{2-} ions move differently from their crystal sites. This leads to the creation of a dipole moment at the surface. The induced dipole moment in both possible cases (Ti- and Sr-containing top layer) is perpendicular to the surface. It is because all ions move only along the surface perpendicular and their movement during relaxation do not break the surface symmetry. The induced dipole moment oscillates at the beginning during growth of the number of relaxed layers. These oscillations practically vanish when the number of relaxed layers reaches six. The same number of layers was necessary to reach convergency of the crystal field in the surface region. Thus, the influence of surface extends on 5–6 ion layers inside SrTiO_3 crystal. Finally, the value of the surface dipole moment converges to -0.167 e \AA in the case of the Sr-containing top layer and to -0.447 e \AA for the Ti-containing top layer.

In SrTiO_3 crystal, the dipole moment is directed inside the crystal (has the negative sign) in both variants of the

Table 1

Relaxation of the first four layers for Sr- or Ba-terminated surfaces in strontium and barium titanates, respectively. Coordinates and displacements are in the lattice parameters of the unrelaxed lattice

No. of layer	Type	Coordinate, z	Ion	SrTiO_3 displacement	Ion	BaTiO_3 displacement
1	core	–0.5	Sr^{2+}	–0.0710	Ba^{2+}	–0.0372
	shell			–0.0503		–0.0343
	core		O^{2-}	0.0115	O^{2-}	0.0099
	shell			–0.0315		–0.0276
2	core	–1.0	Ti^{4+}	0.0157	Ti^{4+}	0.0125
	shell			0.0153		0.0123
	core		O^{2-}	0.0087	O^{2-}	0.0076
	shell			0.0121		0.0103
3	core	–1.5	Sr^{2+}	–0.0142	Ba^{2+}	–0.0051
	shell			–0.0110		–0.0048
	core		O^{2-}	0.0007	O^{2-}	0.0016
	shell			–0.0058		–0.0026
4	core	–2.5	Ti^{4+}	0.0019	Ti^{4+}	0.0020
	shell			0.0018		0.0019
	core		O^{2-}	0.004	O^{2-}	0.0011
	shell			0.0010		0.0015

top layer. The same direction of the surface dipole moment was obtained independently on the number of relaxed surface layers. In Tables 1 and 2, we listed the displacements of ions' cores and shells for four top layers at the surface. These tables show movement of ions in the case when the largest set of the relaxed layers was accounted for in our calculations (10 relaxed layers). Table 1 contains the displacements of ions for the case of Sr/Ba-containing top layer, and Table 2 contains the displacements for the case of Ti-containing top layer. In both cases—Sr-terminated top layer or Ti-terminated top layer in SrTiO₃—we can see displacements of ions in the top layer inwards the crystal and their displacements in the second layer outwards the crystal.

For the case of Sr-containing top layer, the surface Sr ions move inwards on 7% of the bulk (nondisturbed) lattice constant (a_0), and in the third layer, the displacements of Sr ions are reduced to 1.4% of a_0 . Ti ions move in SrTiO₃ outwards the crystal on $\sim 1.6\%$ of a_0 in the second layer and eight times less in the fourth layer. Cores of oxygen ions move outwards and shells move inwards in Sr-containing layers. Both oxygen cores and shells relax outwards in the Ti-containing layers. Magnitudes of ions displacements fall down essentially in the following layers, except for the Sr ions in the third layer. The last still is more than 1% of a_0 .

The very similar trends in ions displacements are observed in the case of Ti-containing top layer in SrTiO₃. Displacements of the surface Ti ions are $\sim 3\%$ of a_0 inwards the crystal, and displacements of Sr ions in the second layer are outwards for roughly 3% of a_0 . Oxygen ions move inwards in the top layer and again we can see opposite movement of oxygen cores and shells in Sr-containing layers. Displacements of ions in following layers fall down in approximately six times and practically vanish at the 5–6 layers.

In the case of the Ti-containing top layer, the negative sign of the surface dipole moment is determined by relatively more significant movement of Ti⁴⁺ ions in comparison with the displacements of two O²⁻ ions inwards the crystal at the surface layers. Opposite movement of Sr²⁺ ions only partly reduces the large dipole moment created by Ti-containing layers. If the top layer is Sr-containing, then the displacements of Sr are so large, that the opposite displacements of Ti ions cannot change the dipole moment sign. In both cases, we can observe large polarization of ions in the first two layers at the surface. It exhibits itself in large differences between displacements of cores and shells of ions. Although differences between cores' and shells' displacements of Ti ions sometimes look very small, we have to remember, that the charge of the Ti's shell is very large in the employed shell-model parameters. This leads to the large dipole moment of Ti ions, even at a relatively small shift of its shell from the core position. The large polarization of the ions in SrTiO₃ crystal is the evidence of large electric field at the surface layers.

The analogous calculations were performed for [001] BaTiO₃ surface with Ba- or Ti-terminated surface layers. The corresponding data are also presented in Tables 1 and 2. The induced dipole moment also oscillates at the beginning during the growth of the number of relaxed layers. These oscillations practically vanish when the number of relaxed layers reaches six that corresponds with SrTiO₃ calculations. The same number of layers was necessary to reach convergency of the crystal field at the surface region. All these evidences show that the influence of surface extends on 5–6 ion layers inside BaTiO₃ crystal. Finally, the value of the surface dipole moment converges to 0.271 e Å for the Ba-containing top layer and to -0.755 e Å in the case of Ti-terminated surface.

In contradiction to SrTiO₃, the sign of the dipole moment on [001] surface in BaTiO₃ depends on the type of

Table 2

Relaxation of the first four layers for Ti-terminated surfaces in strontium and barium titanates. Coordinates and displacements are in the lattice parameters of the unrelaxed lattice

No. of layer	Type	Coordinate, z	Ion	SrTiO ₃ displacement	BaTiO ₃ displacement
1	core	-0.5	Ti ⁴⁺	-0.0296	-0.0272
	shell			-0.0288	-0.0266
	core		O ²⁻	-0.0173	-0.0094
	shell			-0.0240	-0.0175
2	core	-1.0	Sr ²⁺ /Ba ²⁺	0.0346	0.0219
	shell			0.0263	0.0209
	core		O ²⁻	-0.0021	0.0017
	shell			0.0134	0.0104
3	core	-1.5	Ti ⁴⁺	-0.0060	-0.0033
	shell			-0.0059	-0.0032
	core		O ²⁻	-0.0029	-0.0001
	shell			-0.0043	-0.0014
4	core	-2.5	Sr ²⁺ /Ba ²⁺	0.0049	0.0039
	shell			0.0037	0.0031
	core		O ²⁻	-0.001	0.0002
	shell			0.0014	0.0016

the top layer. If the top layer contains Ba ions, then induced dipole moment is positive. On the contrary, in the case of the Ti-containing top layer, the surface has negative dipole moment. The same signs of the surface dipole moment were obtained independently on the number of the relaxed surface layers.

We can see in Table 1 the displacements of ions in the top layer inside and in the second layer outside the crystal. The same results were obtained for Ba- and Ti-containing surfaces (compare with Table 2).

The positive sign of the surface dipole moment for Ba-containing surface appears because of large displacements of negative O^{2-} ions in the top layer inside and positive Ti^{4+} ions in the second layer outside the crystal. Ba^{2+} ions have twice less charges. Their movement inside the crystal cannot compensate the dipole moment, created the movement of Ti^{4+} and the surface O^{2-} ions.

4. Conclusions

For Ba- and Ti-terminated surfaces of $BaTiO_3$, we observe large polarization of ions in the first two layers of surface. Calculations show large differences between displacements of cores and shells of ions. This difference reaches about 3% of the lattice parameter for O^{2-} ions, which belong to the surface of Ba-terminated crystal. Although the differences between core and shell displacements for Ti-ions occasionally look very small, we have to remember that the charge of the Ti's shell is very large in the employed shell-model parameters. This immediately leads to the large dipole moment of Ti ions, even with a relatively small shift of its shell from the core position.

Our simulations demonstrate that polarization of the surface in $SrTiO_3$ and $BaTiO_3$ crystals is determined by three main factors: (1) Large field appears at the surface because of destroyed force balance with the creation of the surface. It pushes the ions of the top layer inwards the crystal and pull outwards the ions of the second layer; (2) Difference in ionic radii of ions leads to different displacements (different places, where ions will be stopped by their neighbours); (3) A large difference in ionic charges of cations (Ti^{4+} , Sr^{2+} , and Ba^{2+}) and large ionic radii do not allow to compensate the dipole moment created by Ti-displacement. There is no complete compensation, even because of opposite displacements of both types of ions.

This means that the surface layers are polarized and that starting from the definite size of the sample, the surface effects may induce spontaneous polarization in nonferroelectric strontium titanate. However, if the interaction length is comparable with sample sizes, the ferroelectric

phase can disappear even for sufficiently small sizes of the sample. The surface can therefore assist the onset of long-range order in nonferroelectric $SrTiO_3$ intervening the competition between inter- and intra-molecular interactions. Thus, the surface of $SrTiO_3$ turns out to be an excellent variable for tuning the balance between the competing interactions involved.

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