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LETTER TO THE EDITOR

Atomistic simulation of $SrTiO_3$(001) surface relaxation

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Abstract. The (001) surface relaxation of the cubic perovskite $SrTiO_3$ crystal has been studied using the shell model. The positions of atoms in several surface layers embedded in the electrostatic field of the remainder of the crystal are calculated. We show that Ti^{4+}, Sr^{2+}, and O^{2-} ions in six near-surface layers are displaced differently from their crystalline sites which leads to the creation of so-called surface rumpling, a dipole moment, and an electric field in the near-surface region. Calculated atomic displacements are compared with LEED experimental data.

Strontium titanate, $SrTiO_3$, has been studied extensively because of its electronic properties, including semiconductivity and superconductivity [1–3]. In fact, this is the first ternary oxide found to be a superconductor (at $T \leqslant 1$ K). At high temperatures (above 103 K) $SrTiO_3$ has a cubic perovskite structure; at all temperatures, bulk $SrTiO_3$ exhibits paraelectric properties.

The $SrTiO_3$(001) surface is widely used as a substrate for epitaxial growth of high-T_c superconductors, in particular $YBaCu_3O_7$. The structure of the substrate surface affects the quality of the epitaxial films [4]. Recently, a low-energy-electron diffraction (LEED) study of a $SrTiO_3$(001) surface has been published [5] where the relaxation of surface metal and oxygen atoms in opposite directions (the so-called rumpling) from their perfect-plane sites was estimated. As is known, this effect can be quite considerable in oxide crystals. For instance, an *ab initio* Hartree–Fock study of O relaxation on MgO(110) surface estimates it to be as large as 7% of the interlayer distance [6]. The oxide surface relaxation can even reach 68% (for the Al-terminated corundum surface [7]).

Although there have been some theoretical efforts to study defects in perovskites (see, for example, [8–11]) they were devoted mainly to the investigation of point defects. At the same time, any surface is nothing but a 2D defect, which may lead to unusual behaviour of perovskite films and nanocrystals, including the changes of the thermodynamic and the kinetic properties in first-order phase transitions. The relaxation of the surface atoms may turn out to be large enough to affect the thermodynamic parameters characterizing the phase transitions, as compared with their bulk values. In particular, structure modification near to the surface of a paraelectric crystal like $SrTiO_3$ may result in its ferroelectric reconstruction at finite temperatures, as suggested in reference [5].

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The aim of this letter is to study in detail the surface relaxation of a large (up to ten planes) near-surface region and to demonstrate on the basis of this the presence of a considerable *surface polarization* even in paraelectric cubic $SrTiO_3$. Although the above-mentioned *ab initio* calculations are known to be efficient in the study of the properties of oxides (see also [12]), their use is substantially restricted by the relatively small number of surface layers which can be realistically handled. This is why in this letter a simpler *shell-model* technique is used [13]. This approach was previously successfully applied to the investigation of defects in numerous ionic crystals including perovskites [8–11]. Its great advantage is that the shell model is well suited for the treatment of the polarization effects which are a central issue of our study. Despite there being several previous *ab initio* papers [14, 15] devoted to a study of the surface relaxations and surface dynamics of $SrTiO_3$ [100] slabs, we decided here to focus on calculations of the surface polarization. The latter is closely related to the methodological problems of the convergency of the atomic relaxation as a function of the number of near-surface crystalline layers taken into account. The advantage of our study was the application of the model of a semi-infinite crystal. In the framework of this approach it was possible to look for a polarization change not only for a few surface layers as in previous studies but also to increase the number of near-surface crystalline planes until the results converged. For this purpose we have used modern shell-model potentials combined with modern GULP [17] and MARVINS [18] codes, which allowed us to study the defect properties of complicated perovskite and oxide structures.

In the present simulations we have studied a periodic two-dimensional slab of cubic $SrTiO_3$. To study the surface relaxation, we have optimized the atomic positions in several (varied from one to ten) (100) surface planes placed in the electrostatic field of the remainder of the crystal (simulated by six additional planes whose atoms were fixed at their perfect-lattice sites). The number of these additional planes was chosen to achieve convergency of the crystalline field in the surface planes.

The interatomic interactions are described by the core–core, core–shell, and shell–shell pair potentials, representing the shell model. In this approach each ion has a charged core and electronic shell. The sum of the core and shell charges is equal to the charge of the corresponding ideal ion. The spring constant k connects the core and the shell of the same ion. The value of this spring coefficient and the shell charge Y are chosen to describe correctly the polarizability α of the ion in the crystal:

$$\alpha = Y^2/k. \tag{1}$$

The interactions between the cores and between cores and shells of different ions are of entirely Coulombic nature. At the same time, the interactions between the shells of different ions, besides the Coulombic part, also contain short-range potentials accounting for the effects of the exchange repulsion together with the van der Waals attraction between them. The short-range potential is

$$W_{sh} = A\exp(-r/\rho) - C/r^6. \tag{2}$$

The parameters A, ρ, and C depend on the nature of the interacting ions and on the crystalline environment. The use of integer ionic charges does not imply restriction to ionic materials: in fact the short-range potential in equation (2) effectively takes into account covalency and charge-transfer effects. A detailed description of the shell model used here can be found in [13]. The relevant shell-model parameters were earlier carefully fitted to the lattice constant of cubic bulk $SrTiO_3$.

Of great importance for reliable surface and defect calculations is a method's ability to reproduce not only the equilibrium bulk structure, but also the elastic properties and

bulk modulus. For the potentials used, these elastic constants are: $C_{11} = 30.15$ (33.0), $C_{12} = 13.74$ (10.10), $C_{44} = 13.78$ (12.40) [9]; all of these constants are in units of 10^{11} dyn cm^{-2}. These values are in a good agreement with the relevant experimental values given in brackets, and give confidence in the use of the shell model in surface relaxation study. Agreement with experiment of theoretical values for low/high-frequency dielectric constants obtained in the framework of the shell-model potentials [9] proves the applicability of the method in perovskite studies. Lastly, the good quality of the potentials used in this letter is also indicated by the agreement between the calculated and experimental phonon frequencies (in units of 10^{12} s^{-1}): 8.50 (7.95) at the Γ_{25} point of the BZ and 13.03 (13.40) at R_{12} (the experimental values, from reference [16], are given in brackets).

The calculations of the phonon frequencies were carried out using the GULP computer code [17], whereas the surface relaxation was found by means of the MARVINS computer code [18]. This code effectively realizes the shell-model technique for simulations of the surface structures. In our slab calculations we simulated both Ti- and Sr-terminated (100) surfaces.

Our calculations show that Ti^{4+}, Sr^{2+}, and O^{2-} ions reveal very different displacements from their perfect-crystalline sites. This leads to the creation of a *dipole moment* at the surface. The induced dipole moment is in both cases (Ti and Sr termination) perpendicular to the surface. This is the case because all of the ions are displaced only along the z-axis, perpendicular to the surface. (That is, the atomic relaxation does not violate the surface symmetry.)

In figure 1 the values of the surface dipole moments for different numbers of relaxed layers are plotted. One can see that the induced dipole moment *oscillates* as the number

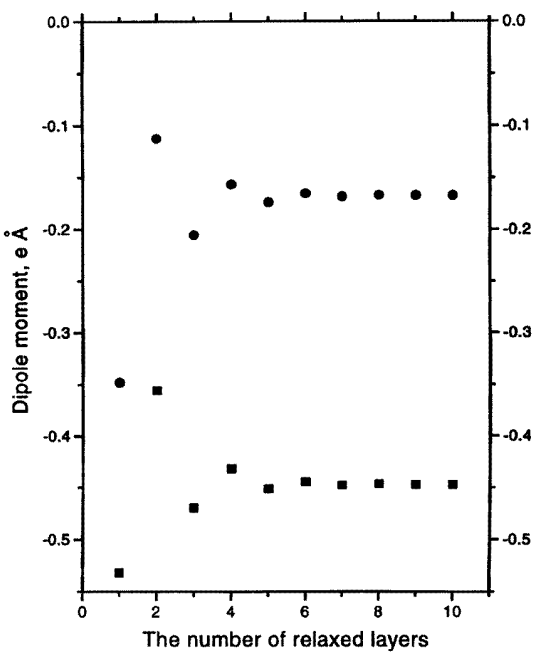

Figure 1. The dependence of the (001) surface dipole moment in cubic $SrTiO_3$ on the number of relaxed layers, for the cases of Ti termination (bold squares) and Sr termination (bold circles). The dipole moments are in units of e Å.

of relaxed near-surface layers increases from one to six. For a larger number of relaxed layers these oscillations practically vanish, and the dipole moment saturates. Note that the same number of layers (six) was found to be necessary to reach convergency for the crystalline field in the surface region. These results show that influence of the (100) surface extends to 5–6 atomic layers inside the $SrTiO_3$ crystal. The values of the surface dipole moments saturate at -0.167 e Å (for the Sr-terminated surface) and at -0.447 e Å (for the Ti-terminated surface). Note that, in both cases, irrespective of the number of relaxed layers, the dipole moments are negative, i.e. directed to the crystalline bulk.

Table 1. The relaxation of the uppermost six layers in the Sr-terminated surface. In total, ten near-surface (100) planes were allowed to relax. The z-coordinate refers to that in a perfect crystal, in units of $a_0 = 3.9$ Å (the bulk crystal lattice parameter).

Layer	Ion	Type	z-coordinate	Δz
1	Sr^{2+}	Core	−0.5	−0.0710
		Shell	−0.5	−0.0503
	O^{2-}	Core	−0.5	0.0115
		Shell	−0.5	−0.0315
2	Ti^{4+}	Core	−1.0	0.0157
		Shell	−1.0	0.0153
	O^{2-}	Core	−1.0	0.0087
		Shell	−1.0	0.0121
3	Sr^{2+}	Core	−1.5	−0.0142
		Shell	−1.5	−0.0110
	O^{2-}	Core	−1.5	0.0007
		Shell	−1.5	−0.0058
4	Ti^{4+}	Core	−2.0	0.0019
		Shell	−2.0	0.0018
	O^{2-}	Core	−2.0	0.0004
		Shell	−2.0	0.0010
5	Sr^{2+}	Core	−2.5	−0.0028
		Shell	−2.5	−0.0023
	O^{2-}	Core	−2.5	−0.0003
		Shell	−2.5	−0.0013
6	Ti^{4+}	Core	−3.0	0.0000
		Shell	−3.0	0.0000
	O^{2-}	Core	−3.0	−0.0003
		Shell	−3.0	−0.0002

Tables 1 and 2 give the displacement magnitudes for atomic cores and shells for six top layers near to the surface (in total, up to ten layers were relaxed in the calculations). From this, one can see the difference between the Sr- and Ti-terminated surfaces. However, in both cases the surface ions are displaced inwards, whereas the ionic displacements in the second layer point outwards from the crystal.

For the case of the Sr-terminated surface, the surface ions shift inwards by 7% of the bulk lattice constant ($a_0 = 3.9$ Å), whereas in the third layer the displacements of Sr ions are reduced to 1.4%. Ti ions are displaced outwards from the crystal by ≈1.6% in the second layer and by eight times less in the fourth layer. The cores of O ions displace outward but their shells displace inwards on the Sr-terminated surface. In turn, *both* O cores and shells relax outwards on the Ti-terminated surface. The magnitudes of the ionic displacements fall

Table 2. As table 1, but for the Ti-terminated surface.

Layer	Ion	Type	z-coordinate	Δz
1	Ti^{4+}	Core	−0.5	−0.0296
		Shell	−0.5	−0.0288
	O^{2-}	Core	−0.5	−0.0173
		Shell	−0.5	−0.0240
2	Sr^{2+}	Core	−1.0	0.0346
		Shell	−1.0	0.0263
	O^{2-}	Core	−1.0	−0.0021
		Shell	−1.0	0.0134
3	Ti^{4+}	Core	−1.5	−0.0060
		Shell	−1.5	−0.0059
	O^{2-}	Core	−1.5	−0.0029
		Shell	−1.5	−0.0043
4	Sr^{2+}	Core	−2.0	0.0049
		Shell	−2.0	0.0037
	O^{2-}	Core	−2.0	−0.0010
		Shell	−2.0	0.0014
5	Ti^{4+}	Core	−2.5	−0.0014
		Shell	−2.5	−0.0013
	O^{2-}	Core	−2.5	−0.0008
		Shell	−2.5	−0.0010
6	Sr^{2+}	Core	−3.0	0.0005
		Shell	−3.0	0.0003
	O^{2-}	Core	−3.0	−0.0005
		Shell	−3.0	−0.0001

off significantly for the deeper layers, except those of the Sr ions in the third layer, which still exceed 1%.

Very similar trends in ionic displacements are observed for the Ti-terminated surface. The inward displacements of the surface Ti ions are ≈3%, and the outward displacements of the Sr ions in the second layer have nearly the same magnitude. The O ions are displaced inwards in the top layer; again we can see opposite displacement directions for the O cores and shells on the Sr-terminated surface. The displacements of ions in deeper layers decrease by approximately a factor of six, and practically vanish beyond 5–6 layers.

For the Ti-terminated surface, the negative sign of the surface dipole moment comes from a larger inward displacement of Ti^{4+} ions, in comparison with those for the O^{2-} ions. The opposite direction of the displacement of Sr^{2+} ions in the second layer only partly reduces the large dipole moment created by Ti displacements. For the Sr-terminated surface the displacements of Sr ions are so large (7.1%) that the opposite displacements of Ti ions in the second layer cannot change the resulting sign of the surface dipole moment.

In both cases a large *polarization* of ions in the near-surface layers takes place; it manifests itself through the large difference in displacements of cores and shells of the same ions. (Although these differences for Ti ions sometimes look quite small, recall that the effective charge of the Ti shell is very large.) This leads to the large dipole moment of Ti ions, even for the relatively small relative core–shell shifts. The observed large polarization of the ions in $SrTiO_3$ crystal indicates the existence of a *strong electric field* near the surface of this paraelectric crystal.

We also performed calculations of the *surface energy*, E_S, for the relaxed surfaces. In the case of a Sr-terminated surface ($E_S = 17.119$ J m^{-2}) it is only slightly less than for the Ti-terminated case (17.163 J m^{-2}). This tiny difference of 0.04 eV/cell appears to be entirely due to the difference between the relaxation energies of the surfaces in the two cases. It looks like the Ti-terminated surface is slightly more stable than the Sr-terminated surface. But, anyway, the difference is very small, and therefore the two types of surface could coexist in reality, which is confirmed experimentally [5].

To summarize, our simulations have demonstrated that cubic perovskite $SrTiO_3$ crystals reveal surface polarization, accompanied by the presence of the relevant electric field. This arises due to a disturbed force balance accompanying the surface creation, and affects 5–6 planes below the surface. In other words, the surface can serve as an important factor in imposing a long-range order in paraelectric $SrTiO_3$. As discussed in reference [5], this surface turns out to be ferroelectric with properties different from those of the bulk material.

The calculated relative Me–O (Me = Sr, Ti) displacements on the two surfaces—0.32 Å for Sr terminations and 0.05 Å for Ti terminations—should be compared with the experimental LEED results [5]: 0.16 ± 0.08 Å and 0.08 ± 0.08 Å, respectively.

Table 3. Relative displacements of atoms from their sites in three near-surface planes (in % of the interlayer distance $d_0 = 1.95$ Å). 'Experiment' indicates results from reference [5].

	Sr-terminated surface	
Planes	Theory	Experiment
1–2	−17	-10 ± 2
2–3	+6	$+4 \pm 2$

The LEED study also contains estimates of the relative displacements of the second plane with respect to the first, and the third plane with respect to the second. In table 3 they are compared with our calculations. The agreement between theory and experiment encourages us to make more extensive use of the shell model in surface studies. In conclusion, it should be stressed that the relaxation (surface) energy dealt with here is much larger than the energy differences that are associated with subtle phase transition effects, and thus the demands placed on the shell-model parameters are much less tough.

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