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Surface rumpling of cubic $CaTiO_3$ from density functional theory*

Yang Kun(杨 鲲)†, Wang Chun-Lei(王春雷), Li Ji-Chao(李吉超), Zhang Chao(张 超), Wu Qing-Zao(吴清早), Zhang Yan-Fei(张艳飞), Yin Na(尹 娜), and Liu Xue-Yan(刘雪燕)

School of Physics and Microelectronics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

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In this paper, the structure of cubic $CaTiO_3$ (001) surfaces with CaO and TiO_2 terminations has been studied from density functional calculations. It has been found that the Ca atom has the largest relaxation for both kinds of terminations, and the rumpling of the CaO-terminated surface is much larger than that of TiO_2-terminated surface. Also we have found that the metal atom relaxes much more prominently than the O atom does in each layer. The CaO-terminated surface is slightly more energetically favourable than the TiO_2-terminated surface from the analysis of the calculated surface energy.

Keywords: surface rumpling, perovskite, density functional theory
PACC: 6820, 7300, 7115M

1. Introduction

Perovskite ABO_3 thin films have been extensively studied since they have many important applications, such as in catalysis, non-volatile memory cells, substrates for high-T_c superconducting growth, etc.[1−3] In these applications, surface structure and properties play important roles. It can be regarded that perovskite ABO_3 is composed of neutral AO- and BO_2- alternate layers in the $< 001 >$ direction, thus the (001) surface could be terminated by either AO- or BO_2- plane. After successful applications of first principles calculations to study the electronic structure of perovskite oxides,[4,5] several first principles calculations have been carried out on the (001) surface properties of $SrTiO_3$, $BaTiO_3$ and $PbTiO_3$ recently. It has been found that for $SrTiO_3$ and $BaTiO_3$, SrO- or BaO-terminated surface is thermodynamically equally stable as the TiO_2-terminated surface.[6−9] For $PbTiO_3$, controversial results have been obtained as to whether the PbO- or TiO_2-terminated surface is more energetically favourable.[6,9,10] The surface rumpling of SrO-terminated $SrTiO_3$ surface has been found to be larger than that with TiO_2 termination,[7,9,11] while the surface rumpling of TiO_2-terminated $BaTiO_3$ surface has been predicted to be larger than that with BaO termination.[8,9] However, $PbTiO_3$ demonstrates almost equal surface rumpling for both kinds of terminations.[9,10] Perovskite $CaTiO_3$ has been widely used in microwave communication systems as well as in immobilizing high-level radioactive waste. More recently, $CaTiO_3$ has been adopted as compositional modification in $SrTiO_3/CaTiO_3/BaTiO_3$ ferroelectric superlattices, and it has been found to be polarized in spite of its non-ferroelectric nature.[12] An orthorhombic Pbnm to tetragonal I4/mcm phase transition occurs for $CaTiO_3$ at 1498 ± 25 K, and another transformation from the tetragonal I4/mcm to cubic $Pm\bar{3}m$ phase occurs at 1634 ± 13 K.[13]

In this paper, the cubic $CaTiO_3$ (001) surface properties, including relaxations of atoms and rumpling of the surfaces as well as surface energy, band structures and density of states, are studied from first principles density functional theory (DFT).

2. Computational details

First principles DFT calculations are carried out by using CASTEP code,[14] which is based on the total energy plane-wave pseudopotential methods. Vander-

*Project supported by the National Natural Science Foundation of China (Grant No 10474057).
†E-mail: yangk@mail.sdu.edu.cn

bilt ultra-soft pseudopotentials[15] and local density approximation (LDA) within the CA-PZ form[16,17] are employed. The plane-wave energy cutoff is 340 eV for all calculations and the Brillouin zone integration is performed by using the Monkhorst–Pack scheme[18] with Ca (3s, 3p, 4s), Ti (3s, 3p, 3d, 4s), and O (2s, 2p) treated as valence. The geometry optimization is finished when the remaining forces become smaller than 0.03 eV/Å and the displacements of the atoms are less than 0.001 Å.

At first step, optimized lattice constant of 3.829 Å has been obtained for cubic bulk $CaTiO_3$ with an (8×8×8) k-point mesh. The theoretical lattice constant is very close to the previously computed value from LDA,[19] and is slightly smaller than the experimental value of 3.897 Å.[13] This underestimation of lattice constant is typical of LDA calculations. We use this theoretical lattice constant in all calculations presented here. Two symmetrical repeat-slab surface models with CaO and TiO_2 terminations are used for the calculations. For each unit slab, there are seven alternating CaO and TiO_2 layers and a vacuum region. The thickness of the vacuum region is set to be 7.658 Å, which is equal to two theoretical lattice constants, in order to minimize possible interactions between layers of neighbouring slabs. The change of the calculated structure parameters is less than 0.3% by further increasing the thickness of vacuum region to three theoretical lattice constants. So a vacuum region of two theoretical lattice constants is large enough. The unit slabs representing both kinds of terminations are depicted in Fig.1. These model structures have tetragonal symmetry with space group P4/mmm. For the CaO-terminated surface, the unit slab consists of four CaO and three TiO_2 layers, so that the slab is terminated with CaO layer on either surface. For the TiO_2-terminated slab, there are three CaO and four TiO_2 layers in the unit slab, so we have a slab with TiO_2 layers terminated on both outmost surfaces. The in-plane lattice constant of the slabs is set to the computed cubic equilibrium value. The atomic displacements perpendicular to the surface are fully relaxed by using an (8×8×2) k-point mesh, which corresponds to 10 k-points in the irreducible Brillouin zone.

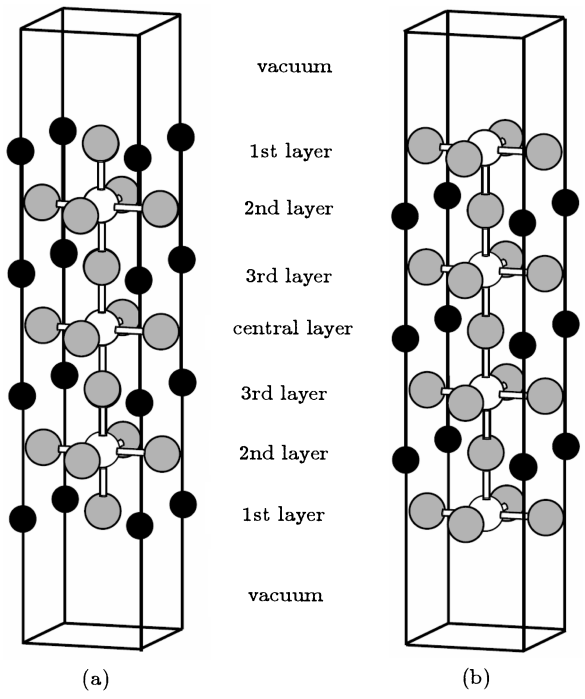


Fig.1. Unit slab for (a) CaO-terminated and (b) TiO_2-terminated surface structures of cubic $CaTiO_3$. The solid, grey and open circles represent the Ca, O and Ti atoms respectively.

3. Results and discussion

Due to the symmetry, there is a mirror reflection on the central layer of each slab, thus the relaxations of the atoms on top and bottom layers are of the same amplitude but along opposite directions, and so are other symmetrical layers. The atomic displacements δz of the outmost three layers are listed in Table 1. We can see from Table 1 that for both kinds of terminations, all the surface layer atoms move inward (toward the central layer). For CaO-terminated surface, the surface layer Ca atom has the largest relaxation, which moves inward by 10.7% of the bulk lattice constant. However, for the TiO_2-terminated surface, the largest relaxation is not on the surface layer atoms but on the second layer Ca atom, which relaxes outward (toward the surface) by 5.5%. For both kinds of surface terminations, the second layer metal atom and O atom relax in opposite directions, i.e. the metal atom moves outward and the O atom moves inward. For the third layer, all the atoms relax inward for both cases. It should be pointed out that the metal atom relaxes much more remarkably than O atom in all layers. Also, the displacements of Ca atoms are much larger than those of Ti atoms in both cases, which indicates that the Ca atom is much easier to relax than the Ti atom.

Table 1. Atomic displacements (relative to ideal positions) of the top three layers of CaO- and TiO_2-terminated $CaTiO_3$ surfaces. Units are percentages of theoretical lattice constant (a=3.829 Å), and positive values refer to displacements towards the surface.

Layer	CaO-terminated		TiO_2-terminated	
	Atom	δz	Atom	δz
1	Ca	−10.7	Ti	−3.7
	O	−0.7	O	−2.0
2	Ti	1.0	Ca	5.5
	O	−0.7	O	−0.2
3	Ca	−2.9	Ti	−1.0
	O	−0.6	O	−0.7

The surface relaxation parameters are listed in Table 2. Surface rumpling parameter s measures the outward displacement of the surface layer O atom with respect to the surface layer metal atom. Δd_{12} is the change of the first interlayer spacing, as measured from the surface to the second layer metal atom z-coordinate, and Δd_{23} is similar to Δd_{12} but between the second and the third layers. From Table 2 we can see that the rumpling of CaO-terminated surface is much greater than that of TiO_2-terminated surface. This is mainly because of the much larger displacement of the surface layer Ca atom of CaO termination than that of the surface layer Ti atom of the TiO_2 termination. This result suggests that the $CaTiO_3$ (001) surface could be rougher if it is terminated with CaO rather than TiO_2. Parameter Δd_{12} is negative for both kinds of terminations, which means that the distance between first layer and the second layer becomes smaller by comparison with its bulk value. The absolute value of Δd_{12} for CaO-terminated surface is larger than that of TiO_2-terminated surface, it suggests that the distance between the surface layer and the second layer is much more reduced for CaO-terminated surface. On the contrary, the distance between the second layer and the third layer expands for both terminations since parameter Δd_{23} is positive for both cases, and the expansion is larger for TiO_2-terminated surface than for CaO-terminated surface.

Table 2. Surface relaxation parameters (in percent of theoretical lattice constant a=3.829 Å) for CaO- and TiO_2-terminated $CaTiO_3$ surfaces.

Surface	s	Δd_{12}	Δd_{23}
CaO-terminated	9.9	−11.7	3.9
TiO_2-terminated	1.7	−9.2	6.5

Surface energy is calculated by following the approach in Ref.[7]. The surface energy E_s is defined as the sum of the cleavage energy (E_{cle}) and relaxation energy (E_{rel}). Since surfaces with the two terminations emerge simultaneously under cleavage, it is assumed that the relevant cleavage energy is the same for both terminations:

$$E_{cle} = \frac{1}{4}[E_{slab}^{unrel}(CaO) + E_{slab}^{unrel}(TiO_2) - 7E_{bulk}], \quad (1)$$

where $E_{slab}^{unrel}(CaO)$ and $E_{slab}^{unrel}(TiO_2)$ are the energies for unrelaxed CaO- and TiO_2-terminated slabs respectively, E_{bulk} is the bulk unit cell energy. The factor 1/4 is due to the fact that four surfaces are created

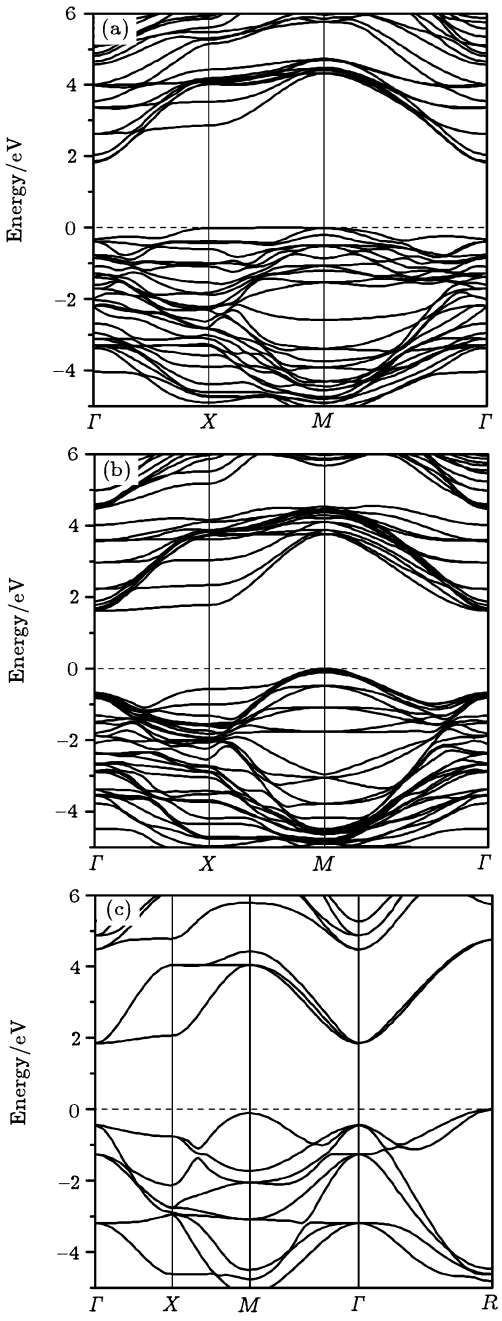


Fig.2. Band structures of $CaTiO_3$: (a) CaO-terminated surface, (b) TiO_2-terminated surface and (c) cubic bulk.

during the cleavage, and the factor 7 is introduced because the two seven-layer slabs represent seven bulk unit cells. The relaxation energy is defined as the energy change after relaxation:

$$E_{\rm rel}({\rm I}) = \frac{1}{2}[E^{\rm rel}_{\rm slab}({\rm I}) - E^{\rm unrel}_{\rm slab}({\rm I})], \qquad (2)$$

where $E^{\rm rel}_{\rm slab}({\rm I})$ is the slab energy after relaxation, index 'I' in the parentheses stands for CaO or TiO_2 termination. Since both top and bottom surfaces of the slab are relaxed, a factor 1/2 is introduced in Eq.(2). The surface energy we obtained for CaO-terminated structure is 0.92 eV, which is slightly lower than that of 1.16 eV for TiO_2-terminated surface. The surface energy difference between CaO- and TiO_2-terminated $CaTiO_3$ (001) surface is 0.24 eV. While for $SrTiO_3$ (001) surface, the energy of SrO-terminated surface is only $0.04 \sim 0.08$ eV smaller than that of TiO_2-terminated surface.[7,9] This means that there is less energy preference for the two kinds of $SrTiO_3$ (001) surfaces, but slight energy favouring occurs for $CaTiO_3$ (001) surface with CaO termination. In other words, there is nearly equal opportunity for either SrO or TiO_2 termination for the $SrTiO_3$ (001) surface, whereas there could be more CaO on the $CaTiO_3$ (001) surface.

Figure 2 shows the band structures of CaO- and TiO_2-terminated relaxed surfaces along the typical 2D Brillouin zone direction $\Gamma - X - M - \Gamma$, and band structure of bulk $CaTiO_3$ is also presented for comparison. The top valence band is very flat for CaO-terminated surface, it can be seen from Fig.2(a), especially between X and M points. The band gap obtained for CaO-terminated surface is 1.83 eV. This gap value shows almost no reduction with respect to its bulk band gap value 1.85 eV. From Fig.2(b) of the band structure of the TiO_2-terminated surface, we can see that there is a tendency of the upper valence band states to intrude upward, especially near the M point. The calculated band gap for the TiO_2-terminated surface is 1.62 eV, which is more reduced from its bulk value than that of the CaO-terminated surface.

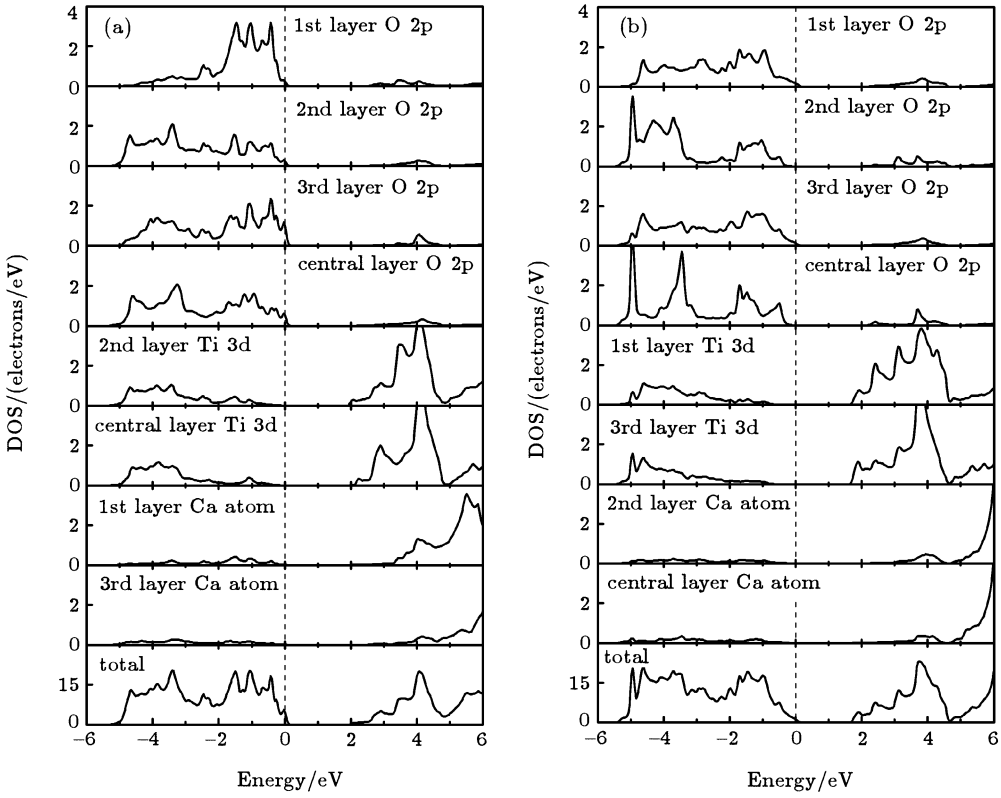


Fig.3. Total and projected DOS for (a) CaO-terminated surface and (b) TiO_2-terminated surface of $CaTiO_3$.

Total and projected density of states (DOS) for CaO- and TiO_2-terminated surfaces are shown in Fig.3. For both kinds of surface terminations, the top of valence bands are mainly composed of O 2p states, the lowest conduction bands are occupied by Ti 3d states. From Fig.3(a) for DOS of CaO-terminated surface, we can find that the O 2p states of all layers present peaks in the top valence region, which corre-

sponds to the flat top valence bands. In Fig.3(b) for DOS of TiO_2-terminated surface, we see that the O 2p states in the top valence region are lowered and expanded, especially for the O 2p states of the surface and the third layers, which accords with the intrusion of the upper valence bands.

4. Summary

From DFT calculations we find that the surface rumpling of CaO-terminated cubic $CaTiO_3$ (001) surface is larger than that of TiO_2-terminated surface. Ca atom has the largest relaxation for both kinds of surface termination. Therefore the largest relaxation is on the outmost surface layer atom for CaO termination. However, for the TiO_2 termination, the largest relaxation is not on the surface layer Ti atom, but on the second layer Ca atom. Surface energy calculations reveal that the CaO-terminated surface is slightly easier to form than the TiO_2-terminated surface. The band gap is reduced more for TiO_2 surface termination than CaO termination. The reduction of band gap of TiO_2-terminated surface with respect to the bulk is mainly due to the upward intrusion of the upper valence band states near the M point.

References

[1] Scott J F 2000 *Ferroelectric Memories* (New York: Dekker)

[2] Kajiyoshi K and Yanagisawa K 2004 *J. Phys.: Condens. Matter* **16** S1351

[3] Zhai J W, Chen H, Colla E V and Wu T B 2003 *J. Phys.: Condens. Matter* **15** 963

[4] Wang Y X, Zhong W L, Wang C L, Zhang P L and Su X T 2002 *Chin. Phys.* **11** 714

[5] Xue W D, Chen Z Y, Yang C and Li Y R 2005 *Acta Phys. Sin.* **54** 0857 (in Chinese)

[6] Mayer B, Padilla J and Vanderbilt D 1999 *Faraday Discuss.* **114** 395

[7] Heifets E, Eglitis R I, Kotomin E A, Maier J and Borstel G 2001 *Phys. Rev.* B **64** 235417

[8] Xue X Y, Wang C L and Zhong W L 2004 *Surf. Sci.* **550** 73

[9] Piskunov S, Kotomin E A, Heifets E, Maier J, Eglitis R I and Borstel G 2005 *Surf. Sci.* **575** 75

[10] Lazaro S, Longo E, Sambrano J R and Beltran A 2004 *Surf. Sci.* **552** 149

[11] Padilla J and Vanderbilt D 1998 *Surf. Sci.* **418** 64

[12] Lee H N, Christen H M, Chisholm M F, Rouleau C M and Lowndes D H 2005 *Nature* **433** 395

[13] Ali R and Yashima M 2005 *J. Solid State Chem.* **178** 2867

[14] Segall M D, Lindan P L D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.: Condens. Matter.* **14** 2717

[15] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892

[16] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566

[17] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048

[18] Monkhorst H J and Pack J D 1977 *Phys. Rev.* B **16** 1748

[19] Dieguez O, Rabe K M and Vanderbilt D 2005 *Phys. Rev.* B **72** 144