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Ab initio study of the $SrTiO_3$, $BaTiO_3$ and $PbTiO_3$ (0 0 1) surfaces

R.I. Eglitis [a,*], S. Piskunov [a], E. Heifets [b], E.A. Kotomin [c], G. Borstel [d]

[a] Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany
[b] California Institute of Technology, MS 139-74, Pasadena, CA 91125, USA
[c] Institute of Solid State Physics, University of Latvia, Kengaraga 8, LV- 1063 Riga, Latvia
[d] Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

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Abstract

The results of first-principles calculations of the two possible terminations of (0 0 1) surfaces of $SrTiO_3$ (STO), $BaTiO_3$ (BTO) and $PbTiO_3$ (PTO) perovskites are presented. Surface atomic structures and their electronic configurations have been calculated using ab initio density functional theory (DFT) combined with hybrid (B3PW) exchange-correlation technique. Our results are compared with previous quantum mechanical calculations and available experimental data. Surface relaxations and the electronic states near valence band gap are discussed in details for all three perovskites.

Keywords: $SrTiO_3$; $BaTiO_3$; $PbTiO_3$; Single crystal surfaces; Surface relaxation; Electronic structure; Ab initio calculations
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1. Introduction

The surfaces of ABO_3 perovskite materials are intensively investigated because of their importance for high temperature oxygen sensors, in photo-catalysis, as substrates for high-T_c superconductors and as dielectric materials [1,2]. During the last years the electronic properties and atomic structure of many ABO_3-type perovskite thin films have been extensively studied both experimentally [3–7] and theoretically [8–12]. Inspite great physical importance of all these studies, calculations have been carried out, mostly, using local density approximation (LDA) method. It is well-known fact that in the DFT-LDA calculations the band gap could underestimate the experimental one by a factor of two. This greatly limits the proper theoretical description of surface properties depending on the excited electron states, such as optical adsorption. On the other hand, band gap obtained through the pure-HF calculations greatly overestimates the experimental value [13]. A possible solution of this problem is the use of so-called "*hybrid*" functionals (a combination of the non-local HF exchange, DFT exchange, and generalized gradient approximation (GGA) correlation functional). Examples are so-called B3LYP and B3PW which are extremely popular in quantum chemistry of molecules and recently have been applied to periodic-structure ab initio calculations on a wide range of crystalline materials [14], including perovskites and their surfaces [15,16]. In all cases, the hybrid functional technique shows the best agreement with experimental data for both bulk and optical properties of materials under investigation. In the present paper, in order to analyze the surface electronic states near band gap region, we present a consistent comparison of calculated by means DFT-B3PW method atomic structure and electronic properties for surfaces of three similar perovskites, accounting data existing in literature.

The ABO_3 (0 0 1) surfaces have been modelled considering crystals as a set of crystalline planes perpendicular to the given surface, and cutting out 2D slab of a finite thickness, periodic in *x*–*y* plane. The slabs containing seven layers could be treated thick enough since the convergence of calculated slab total energy per ABO_3 unit is achieved. This energy differs less than 0.0005 Hartree for seven- and nine-layered slabs for all three perovskites. To provide the most-qualitative analyze of perovskite surfaces, we model perovskites in their high-symmetry cubic ($Pm3m$) phase. It

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* Corresponding author. Tel.: +49-541-969-2667; fax: +49-541-969-2351.
E-mail address: reglitis@uos.de (R.I. Eglitis).

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allows us to keep all computational conditions simple and identical.

To perform first-principles DFT-B3PW calculations on surfaces the linear combination of atomic orbitals (LCAO) method implemented in CRYSTAL'98 computer code [13,17] has been used in present study. This is the periodic-structure computer program that uses localized Gaussian type functions (GTF) localized at atoms as the basis for expansion of the crystalline orbitals. The ability to calculate the electronic structure of materials within both HF and Kohn-Sham Hamiltonians and implementation of purely 2D slab model are the main advantages of this code. However, in order to employ the LCAO-GTF method, it is necessary to optimize the basis sets (BS), which would be suitable for the electronic structure computations of crystals under study. Such BS's optimization for all three perovskites is discussed in [15].

The calculated lattice constants are (in Å): $a = 3.90$ (STO), $a = 4.01$ (BTO), and $a = 3.93$ (PTO), in the perfect agreement with experiment.

2. Surface structure

In present simulations we allowed to relax atoms of two outermost surface layers along the z-axis for each structure. By symmetry, surfaces of perfect cubic crystals have no forces along x- and y-axes. Displacements of third layer atoms are negligibly small. The optimization of atomic coordinates has been done through the slab total energy minimization using our own small computer code implements conjugated gradients optimization technique with numerical computation of derivatives.

In order to compare the calculated surface structures with available experimental results, the amplitudes of surface rumpling s (the relative displacement of oxygen with respect to the metal atom in the surface layer) and the changes in interlayer distances Δd_{ij} (i and j are the numbers of layers) are presented in Table 1. Our calculations of the interlayer distances are based on the positions of relaxed *metal* ions, which are known to be much stronger electron scatterers than oxygen ions [3]. The agreement is quite good for all theoretical methods, which give the same sign for both the rumpling and change of interlayer distances. The amplitude of surface rumpling of SrO-terminated STO is predicted much larger in comparison to that for TiO_2-terminated STO surface, when the rumpling of BTO TiO_2-terminated surface is twice larger than that for BaO-terminated surface, and PTO demonstrates practically equal rumpling for both terminations. As one can see from Table 1, all surfaces display the reduction of interlayer distance d_{12} and expansion of d_{23}. The calculated surface rumpling amplitudes agree quite well with the LEED, RHEED and MEIS experiments [3–5] which are available for only STO surfaces. Nevertheless, the calculated changes in interlayer distances d_{12} are mostly in disagreement with LEED experimental data. As an example, the LEED experiments show unlike RHEED the d_{12} expansion for TiO_2-terminated STO, but all calculations, on the contrary, demonstrate the *reduction* of this magnitude. Moreover, it is well seen from Table 1 that experiments contradict each other in the sign of Δd_{12} and Δd_{23} for SrO-terminated surface as well as for Δd_{23} of TiO_2-terminated STO. Another problem is that the LEED, RHEED and MEIS experiments demonstrate that the topmost oxygen always move outward from the surfaces whereas all calculations predict for the TiO_2-terminated STO surface that oxygen goes

Table 1
Surface rumpling s, and relative displacements of the three near-surface planes for AO- and TiO_2-terminated surfaces Δd_{ij} (in percent of lattice constant)

	AO-terminated			TiO_2-terminated		
	s	Δd_{12}	Δd_{23}	s	Δd_{12}	Δd_{23}
STO						
This study	5.66	−6.58	1.75	2.12	−5.79	3.55
Ab initio[16]	4.9	−5.5		1.3	−4.4	
Ab initio[9]	5.8	−6.9	2.4	1.8	−5.9	3.2
Ab initio[11]	7.7	−8.6	3.3	1.5	−6.4	4.9
Shell model [18]	8.2	−8.6	3.0	1.2	−6.4	4.0
LEED experiment [3]	4.1 ± 2	−5 ± 1	2 ± 1	2.1 ± 2	1 ± 1	−1 ± 1
RHEED experiment [4]	4.1	2.6	1.3	2.6	1.8	1.3
MEIS experiment [5]				1.5 ± 0.2	0.5 ± 0.2	
SXRD experiment [6]	1.3 ± 12.1	−0.3 ± 3.6	−6.7 ± 2.8	12.8 ± 8.5	0.3 ± 1	
BTO						
This study	1.37 (1.40)	−3.74 (−3.79)	1.74 (1.70)	2.73 (2.69)	−5.59 (−5.57)	2.51 (2.54)
Ab initio [8]	1.39	−3.71	0.39	2.26	−5.2	2.06
Shell model [12]	0.37	−2.42	2.39	1.4	−6.5	3.17
Shell model [18]	4.72	−4.97	1.76	1.78	−4.91	2.52
PTO						
This study	3.51 (3.78)	−6.89 (−7.03)	3.07 (3.01)	3.12 (3.58)	−8.13 (−8.28)	5.32 (5.44)
Ab initio [10]	3.9	−6.75	3.76	3.06	−7.93	5.45

inwards. Even more important is the contradiction between three above mentioned experiments and recent SXRD [6] where oxygen atoms are predicted to move inwards for *both* surface terminations reaching rumpling amplitude up to 12.8% for TiO_2 terminated surface. Up to now, the reason for such discrepancies between the different experimental data is not clear and discussed in [6,9]. Thus, the disagreement between theoretical and experimental data cannot be taken too seriously, till the conflict between experimental results will be resolved.

3. Electronic structures

The calculated by means of the DFT-B3PW optical band gaps for surfaces and the bulk of all three perovskites are given in Table 2. It is well seen the good agreement with experiment is achieved. The band structure for SrO-terminated surface demonstrates practically the same flatness of upper valence bands (VB) as the bulk STO with the VB top at the M point of the Brillouin zone and the bottom of conduction band (CB) at Γ point. The optical band gap for SrO-terminated surface becomes smaller with respect to the band gap of the bulk STO. The smallest indirect gap is between the M and Γ points. This gap is equal to 3.3 eV, compare with the smallest gap in the bulk, 3.63 eV (see Table 2). The analysis of the density of states (DOS) calculated for SrO-terminated surface demonstrates no contribution of the surface O 2p electronic states to the VB top which mainly consists of the central oxygen orbitals. The main contribution into the CB bottom comes from the 3d titanium electronic states from the Ti from the second layer nearest to the surface.

The band structure calculated for TiO_2-terminated surface of STO demonstrates that the VB top is less flat as compared with SrO-termination. The indirect optical band gap (M–Γ) becomes even smaller, 3.17 eV. For the TiO_2-terminated STO surface, the main contribution into the top of VB make the electrons from the $2p_x$ and $2p_y$ orbitals which are perpendicular to Ti–O–Ti bridge, whereas the main contribution to the CB bottom make the 3d states of Ti from the third layer, the electronic states of surface Ti atom lie a little bit higher in energy. The calculated STO DOS are in a good agreement with the MIES and UPS spectra recently reported on TiO_2-terminated TO (0 0 1) surface by Maus-Friedrichs et al. [7]. The band structures calculated for the cubic BTO (0 0 1) surfaces demonstrate practically the same behavior as in STO case. Nevertheless, the split of upper VB band is better pronounced (is larger) for the TiO_2-terminated BTO in comparison with STO surface.

Due to hybridization of Pb 6s and O 2p orbitals in PTO, the calculated band structure and DOS of this perovskite differ slightly from the those calculated for STO and BTO. The smallest gaps for the bulk and surface band structures lies between X and Γ points of the Brillouin zone. In the bulk, VB top is formed significantly by the Pb 6s orbitals, which also make the main contribution into the VB bottom. The CB bottom in the PTO bulk is formed by Ti 3d orbitals, the same as in other perovskites. The optical band gap for PbO-terminated surfaces is not smaller as in the case of BTO and STO, but even a little bit increases up to 2.96 eV (with respect to the 2.87 in the bulk). The VB top in the PbO-termination consists of a mixture of Pb 6s and O 2p orbitals from the third layer, whereas the CB bottom is formed by Ti 3d orbitals from the subsurface layer. The VB top for the TiO_2-terminated PTO (0 0 1) surface at the X point consists surprisingly of a mixture of O 2p and Pb 6s states from the surface and central layers. Moreover, main contribution make the orbitals of central atoms. The CB bottom for the TiO_2-terminated PTO consists mainly of Ti 3d orbitals from the third layer. The calculated band gaps of PbO- and TiO_2-terminated PTO (0 0 1) surface are practically the same, 2.96 and 2.98 eV, respectively. The different behavior of the electronic properties of the (0 0 1) surfaces of PTO and other perovskite under study can be explained by hybridization of Pb 6s and O 2p and a weak covalency of the Pb–O bond.

4. Conclusions

We calculated the surface atomic relaxation and the electronic structure of two possible terminations of the (0 0 1) surfaces for STO, BTO and PTO crystals. We used the

Table 2
The calculated optical gap (in eV) for the bulk [15] and surface-terminated perovskites

Optical gap	STO			BTO			PTO		
	Bulk	SrO	TiO_2	Bulk	BaO	TiO_2	Bulk	PbO	TiO_2
Γ–Γ	3.96	3.72	3.95	3.55	3.49	2.96	4.32	3.58	3.18
X–X	4.53	4.37	4.04	4.39	4.22	3.63	3.02	3.79	3.10
M–M	5.70	5.62	5.17	5.39	5.40	4.17	5.55	5.37	5.01
R–R	6.47			6.12			5.98		
X–Γ	4.39	3.55	3.92	4.20	3.49	3.41	2.87	2.96	2.98
M–Γ	3.71	3.30	3.17	3.60	3.32	2.33	3.66	3.55	3.19
R–Γ	3.63			3.50			3.66		
Experiment	3.75—direct gap			3.2			3.4		
	3.25—indirect gap [21]			[19]			[20]		

DFT-B3PW method employed *hybrid* exchange-correlation technique. The data of our surface structure calculations are in good agreement with theoretical results published previously and partly with experimental data. The absence of the surface electronic states in the upper valence bands for the AO-terminated (0 0 1) surfaces of all perovskites and presence of Pb 6s orbitals in the VB top of PTO could be important for the further treatment of the electronic structure of surface defects on perovskite surfaces as well as for the adsorption and surfaces diffusion of atoms and small molecules relevant for catalysis.

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