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The electronic and atomic structure of $SrTiO_3$, $BaTiO_3$, and $PbTiO_3(0\,0\,1)$ surfaces: Ab initio DFT/HF hybrid calculations

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Abstract

In our first-principles study, the electronic properties of the (0 0 1) surfaces of three key perovskite crystals, namely $SrTiO_3$ (STO), $BaTiO_3$ (BTO), and $PbTiO_3$ (PTO), have been calculated by means of the density functional theory (DFT) using the exchange-correlation functional containing *"hybrid"* of the non-local Hartree–Fock (HF) exchange, DFT exchange, and Generalized Gradient Approximation (GGA) correlation functionals, commonly known as B3PW. Such a technique allows us to get the optical bulk band gap very close to experiment unlike previous calculations of perovskites. Special attention is paid to careful calculations of the surface rumpling and change of the distances between three near-surface planes. We compare results with available experimental data. The calculated electronic band structures for relaxed surfaces show no splitting of surface electronic states from the upper valence bands for the AO-terminated (0 0 1) surfaces (consisting of Ti 4d and O 2p orbitals) and the presence of Pb 6s orbitals in the top of the $PbTiO_3$ valence band. This is important for the treatment of the electronic structure of surface defects on ABO_3 perovskite surfaces as well as for adsorption and surface diffusion of atoms and small molecules (e.g. O, O_2), relevant for catalysis and fuel cell applications.

Keywords: ABO_3 perovskites; Single crystal surfaces; Surface relaxation; Electronic structure; Ab initio calculations

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1. Introduction

The surfaces of ABO_3 perovskites are intensively investigated because of their importance for high temperature oxygen sensors, in photocatalysis, as substrates for high-T_c superconductors and as high k dielectric materials for nanoelectronics [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 impor-

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tance 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 about two. This greatly limits the proper theoretical description of such properties as optical adsorption and defects. On the other hand, band gap obtained through the pure-HF calculations typically 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 methods 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 DFT-B3PW-calculated atomic structure and electronic properties for surfaces of three similar perovskites, accounting for the experimental data existing in literature.

2. Computational details

To perform the first-principles DFT-B3PW calculations, the CRYSTAL'98 computer code [13,17] was used. This code uses Gaussian-type functions (GTF) localized at atoms as the basis set for an expansion of the crystalline orbitals. The ability to calculate the electronic structure of materials within both the HF and Kohn–Sham (KS) Hamiltonians and implementation of isolated 2D slab model without its artificial repetition along the z axis, are the main advantages of this code. However, in order to employ the LCAO-GTF method, it is desirable to optimize the basis sets (BS), necessary for the electronic structure computations. Such BS's optimization for all three perovskites is developed and discussed by us in Ref. [15]. Unlike the standard BS [18], we added the polarized O d orbitals, replaced the Ti inner core orbitals by the small-core Hay–Wadt presudopotentials, and consistently used the two diffuse s and p Gaussians as the separate basis orbitals on the Ti, Ba, Sr and Pb.

Our calculations were performed using the hybrid exchange-correlation B3PW functional involving a hybrid of non-local Fock exact exchange and Becke's three-parameter gradient corrected exchange functional [19] combined with the non-local gradient corrected correlation functional by Perdew and Wang [20,21]. The Hay–Wadt small-core ECP's [22–24] were adopted for Ti, Sr, and Ba atoms [22–24]. The "small-core" ECP's replace only inner core orbitals, but orbitals for outer core electrons as well as for valence electrons are calculated self-consistently. Light oxygen atoms were left with the full electron BS. The BSs were adopted in the following forms: O—8-411(1d)G (the first shell is of s-type and is a contraction of eight Gaussian type functions, then there are three sp-shells and one d-shell), Ti—411(311d)G, Sr and Ba—311(1d)G; see Ref. [15] for more details.

The reciprocal space integration was performed by the sampling the Brillouin zone of the unit cell with the $8 \times 8 \times 1$ Pack–Monkhorst net [25], which provides the balanced summation in direct and reciprocal lattices [26]. To achieve high accuracy, large tolerances of 7, 8, 7, 7, 14, (i.e. the calculation of integrals with an accuracy of 10^{-N}) were chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, the first exchange pseudo-overlap, and for the second exchange pseudo-overlap respectively [17].

The $ABO_3(001)$ surfaces were 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 the 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. These energies (per unit cell) differ less than 0.0005 Hartree for seven- and nine-layered slabs for all three perovskites.