

## Highly Confined Spin-Polarized Two-Dimensional Electron Gas in SrTiO<sub>3</sub>/SrRuO<sub>3</sub> Superlattices

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(Received 5 August 2011; published 8 March 2012)

We report first-principles characterization of the structural and electronic properties of (SrTiO<sub>3</sub>)<sub>5</sub>/(SrRuO<sub>3</sub>)<sub>1</sub> superlattices. We show that the system exhibits a spin-polarized two-dimensional electron gas, extremely confined to the 4*d* orbitals of Ru in the SrRuO<sub>3</sub> layer. Every interface in the superlattice behaves as a minority-spin half-metal ferromagnet, with a magnetic moment of  $\mu = 2.0\mu_B/\text{SrRuO}_3$  unit. The shape of the electronic density of states, half-metallicity, and magnetism are explained in terms of a simplified tight-binding model, considering only the *t*<sub>2g</sub> orbitals plus (i) the bidimensionality of the system and (ii) strong electron correlations.

DOI: 10.1103/PhysRevLett.108.107003

PACS numbers: 74.70.Pq, 73.20.At, 75.10.-b, 75.70.-i

The family of ABO<sub>3</sub> perovskite compounds is really prominent among all the complex oxides. The delicate interaction between their electronic, spin, lattice, and orbital ordering degrees of freedom, whose respective energy couplings are all of the same order of magnitude [1], gives rise to a wide variety of ground states and phenomena [2]. These compounds typically exhibit exceptional functional properties that, moreover, can be finely tuned by playing with temperature and/or electrical (screening) [3], mechanical (strain) [4], and chemical (doping) [5] boundary conditions.

At the bulk level, ABO<sub>3</sub> compounds cover the whole spectrum of conducting properties, ranging from good insulators and semiconductors to metals and even superconductors [2]. Moreover, it has recently been shown that their conducting behavior can also drastically change at surfaces [6] and interfaces [7]. The possibility to create highly confined two-dimensional electron gases (2DEGs) at oxide interfaces has also been demonstrated and has generated much excitement.

The most widely studied system is certainly the 2DEG formed at the LaO/TiO<sub>2</sub> polar interface between LaAlO<sub>3</sub> (LAO) and SrTiO<sub>3</sub> (STO) [8], two good band insulators at the bulk level. Although the mechanism at the origin of the transfer of charges remains partly controversial, the 2DEG is formed by the accumulation of electrons in the Ti 3*d* states of STO over a thickness of a few nanometers near the interface and exhibits interesting exotic properties. In a different context, when looking for oxides with enhanced thermoelectric properties, Ohta *et al.* [9] highlighted the possibility to create a highly confined 2DEG in [(STO)<sub>*m*</sub>/(SrTi<sub>0.8</sub>Nb<sub>0.2</sub>O<sub>3</sub>)<sub>*n*</sub>]<sub>*p*</sub> superlattices. Since Nb-doped STO is a well-known conducting electrode material [10], such a superlattice can be viewed as the limiting case

of ultrathin metal oxide layers embedded in an insulating STO matrix. The 2DEG arises from the doping produced by the Nb atoms so, alternatively, the system can also be interpreted as a *partial* doping of a STO matrix at the *B* site. Very recently, the formation of a 2DEG has been achieved through a related route: the doping of the *A* site of the STO matrix. The Sr atoms of a single SrO layer of STO are partially [11] or completely [12] replaced by a rare-earth element, *R*, which provides additional electrons. In this case, the conduction electrons provided by the substitutional layer are transferred to the STO matrix but stay near the *RO* layer due to Coulomb attractions, and possibly also to the large dielectric constant of STO [13].

In this Letter, we predict from first-principles calculations the appearance of a highly confined 2DEG in (STO)<sub>5</sub>/(SrRuO<sub>3</sub>)<sub>1</sub> superlattices (STO/SRO). This system is to some extent related to those previously considered. SRO is a well-known conductive material so that STO/SRO present similarities with (STO)<sub>*m*</sub>/(SrTi<sub>0.8</sub>Nb<sub>0.2</sub>O<sub>3</sub>)<sub>*n*</sub> superlattices [9]. Also, STO/SRO can be seen as a STO matrix in which a TiO<sub>2</sub> layer is periodically replaced by a single RuO<sub>2</sub> layer, appearing as a variant of the work of Jang *et al.* [12]. However, contrary to all recent examples of 2DEGs in perovskites previously discussed, that confine the conducting electrons in Ti 3*d* orbitals of STO, the conducting electrons in STO/SRO are localized *exclusively* in Ru 4*d* orbitals. We will show that this gives rise to new and unexpected features. Contrary to current thought regarding SRO *thin films* [14–16], and *finite period* superlattice [17], our infinite period superlattices exhibit an extremely confined half-metallic ferromagnetic (FM) 2DEG, very promising for spintronic devices [18].

For this study, we perform first-principles simulations of STO/SRO superlattices using two complementary

approaches. Unless otherwise stated, all the calculations presented here have been performed within the local spin density approximation (LSDA) to the density functional theory using the SIESTA code [19]. An extra Hubbard- $U$  term is included to account for the strong electron correlations, with a  $U_{\text{eff}}$  of 4.0 eV applied only to the  $d$  orbitals of Ru. The robustness of the results presented below have been double-checked using the CRYSTAL09 code [20] within the B1-WC hybrid approach [21] that mixes the generalized gradient approximation functional of Wu and Cohen [22] with 16% of exact exchange within the B1 scheme [23]. Hybrid functionals are well known to provide improved description of magnetic and highly correlated oxides, and B1-WC appeared recently as a successful approach to describe 2DEG at the LAO/STO interface [24]. The excellent agreement between the results obtained independently within both approaches strongly supports our predictions. The procedure to fit the  $U_{\text{eff}}$  and other technicalities can be found in Discussions 1 and 2 of the Supplemental Material [25]. Both spin orderings in the SRO layers, FM and antiferromagnetic (AFM), where the up and down spins of the RuO<sub>2</sub> layer are ordered in a checkerboard arrangement, are simulated.

In the most stable phase, that turns out to have FM order, our simulations predict a  $P4/mbm$  space group. Oxygen octahedra rotate changing the phase from layer to layer, as shown in Fig. 1(b). This pattern of rotation shares some similitudes with the  $a^0a^0c^-$  Glazer notation of the STO matrix, but now the module of the rotation angles around the  $z$  axis are not the same from one octahedra to the adjacent one. The angle of rotation of the RuO<sub>6</sub> octahedra,  $\theta_{\text{SRO}} = 11.6^\circ$ , is roughly the same as in bulk tetragonal SRO under the same strain condition in the basal plane ( $\theta_{\text{SRO}}^{\text{bulk}} = 11.4^\circ$ ). The rotations of the TiO<sub>6</sub> octahedra rapidly converge to the bulk LDA value of STO ( $\theta_{\text{STO}}^{\text{bulk}} = 4.3^\circ$ ), indicating that the rotations are functions of the local chemical environment [26]. Taking into account that bulk SRO crystallizes within the GdFeO<sub>3</sub> structure ( $Pnma$  space group), with  $a^-b^+a^-$  Glazer notation, we have explored the possibility of the existence of out-of-plane tiltings in SRO. However, under the epitaxial configuration considered here, we have checked that they disappear. This supports that the single unit cell of SRO in our superlattices are stabilized in a pseudocubic perovskite structure [27]. As shown in Fig. 1(c), both the rumplings and the changes in interplanar spacing with respect to the ideal (nonrelaxed) structure are very small.

Figure 2 shows the projected density of states (PDOS) on the atoms at the different SrBO<sub>3</sub> unit cells (where  $B$  is Ti or Ru), within the LDA +  $U$  [Fig. 2(a)] and B1-WC hybrid functional [Fig. 2(b)]. The physical conclusions that can be drawn are robust, independently of the theoretical framework used. In particular, (i) remarkably the system presents a 2DEG, strictly confined in the SRO layer. The electronegativity of Ru (2.20), larger than the one for Ti (1.54), is

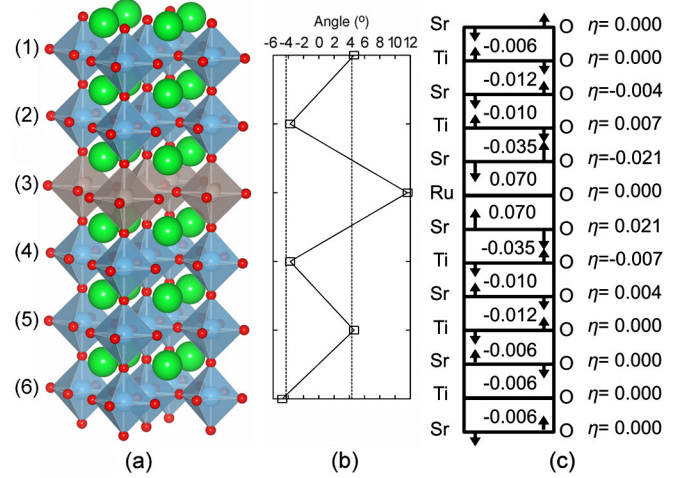


FIG. 1 (color online). Schematic representation of the relaxed structure of STO/SRO superlattices with LDA +  $U$ . (a) Unit cell periodically repeated in space. O atoms (in red) are located at the vertex of the octahedra, while Sr (in green) are at the interstices between them and Ti (in blue) and Ru (in gray) are situated at the center according to the layer labeling. (b) Rotation angle of the oxygen octahedra,  $\theta$ , around the [001] direction ( $z$  axis). Squares represent  $\theta$  for the corresponding octahedra at the same height as in (a). Dotted lines are the theoretical value of  $\theta$  for bulk STO. (c) Layer-by-layer rumpling,  $\eta_i = [z(M_i) - z(O_i)]/2$ , where  $z(M_i)$  is the position of the cation and  $z(O_i)$  is the position of O, in a given layer  $i$ . Atoms in layer  $i$  move in the direction indicated by the arrows. Black lines represent the mean position of each atomic layer. Numbers inside the structure are the change in the interplanar distance between consecutive planes with respect to the ideal unrelaxed structure (half of the bulk value of STO,  $a = 3.874$  Å). Similar results are obtained within the B1-WC functional (see Discussion 3 of the Supplemental Material [25]). Units in Å.

the main candidate to be the driving force for the electron localization. This localization resembles that recently found on the  $d$  orbitals of V in SrVO<sub>3</sub>/Nb:SrTiO<sub>3</sub> quantum wells [28]. (ii) The electronic states around the Fermi level are fully spin polarized, with only the minority-spin electrons involved in the charge transport [18]. (iii) The 2DEG exhibits ferromagnetism, with a magnetic moment of  $\mu = 2.0\mu_B/\text{SRO}$  formula unit. Integrating the spin-polarized charge density on spheres surrounding the atoms (in SIESTA) or analyzing the Mulliken spin population within B1-WC (in CRYSTAL), we see that the magnetic moment is mostly due to the Ru atoms,  $\mu_{\text{Ru}} = 1.4\mu_B$ , within the range of measured magnetic moments in single crystals [29] and polycrystalline samples [30]. The same value of  $\mu_{\text{Ru}}$  is obtained in the AFM configuration. The remaining magnetic moment in the FM configuration comes from the oxygen atoms. These results are robust with respect to pseudopotentials, basis set, functional, and inclusion of spin-orbit coupling (Discussion 4 of the Supplemental Material [25]). Interestingly, the electronic structure at the interface inherits some of the particularities

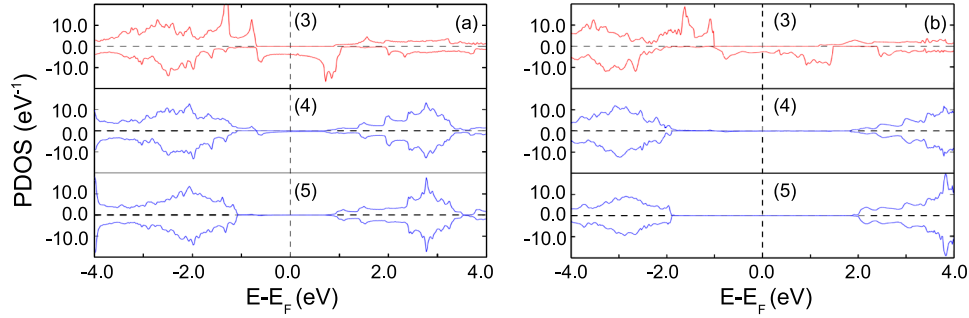


FIG. 2 (color online). Layer-by-layer PDOS on the atoms at the  $\text{SrBO}_3$  layers ( $B = \text{Ti}$  or  $\text{Ru}$ ), within (a) the LSDA +  $U$  and (b) the B1-WC hybrid functional, for the corresponding relaxed STO/SRO superlattice. Each panel represents the PDOS of a unit cell, numbered as in Fig. 1(a). Corresponding layers in the upper half of the structure are equivalent by symmetry. Majority (minority) spin is represented in the upper (lower) half of each panel.

theoretically predicted in *bulk* SRO when the electronic correlations are properly included [as in LDA +  $U$  [31], pseudo-self-interaction correction [32], or B1-WC hybrid functional (Discussion 5 in the Supplemental Material [25]). Between these properties, we might cite the half-metallicity [31] or the saturation of the magnetic moment [32]. Experimental observation of the half-metallicity remains a challenge, mostly due to the large magnetic fields required to overcome the high magnetic anisotropy barriers and fully magnetize the samples.

Regarding the band shape, we observe in Fig. 3 that the bands with Ru- $d_{xy}$  character are significantly different from the degenerate Ru- $d_{xz,yz}$  bands. While the PDOS of Ru- $d_{xy}$  resembles that usually found in bulk  $t_{2g}$  bands [33], the double peaked shape [peaks marked with arrows in Fig. 3(b)] for Ru- $d_{xz,yz}$  is similar to that of a 1D metal. It is also significant that the relative position of these bands for the majority and minority spins is different, an effect attributable to the strong electronic correlations in the system, enhanced with respect to bulk due to the two dimensionality of the system (see below). Indeed, to study the effect of the Hubbard- $U$  in our calculations we carried out a plain LSDA simulation (without  $U$  corrections) and plotted the PDOS (Discussion 2 in the Supplemental Material [25]). The *shape* of the Ru- $d_{xy}$  and Ru- $d_{xz,yz}$  is the same as when the Hubbard- $U$  term is considered. However, the position of the bands is shifted to almost the same energy range for both spin channels, destroying the half-metallicity.

If the half-metallicity can be attributed to the electronic correlation, the shape of the bands can only be explained through the 2D character of the electron gas. To check this point, we have made use of a tight-binding model, where only the  $t_{2g}$  states are retained in the basis set. Qualitatively, the shape of the  $t_{2g}$  bands is found to be the same for all perovskites including transition metal ions in the  $B$  position. Assuming cubic symmetry, the PDOS associated with these bands for a full three-dimensional solid is shown in Fig. 4(a). Using this model we then

simulate the changes in the PDOS when the system is bidimensional, extended periodically through the  $xy$  plane. In Fig. 4(b) we can see that, while  $d_{xy}$  band remains unaltered, the  $d_{xz,yz}$  ones now present two peaks in good agreement with the ones in the full first-principles

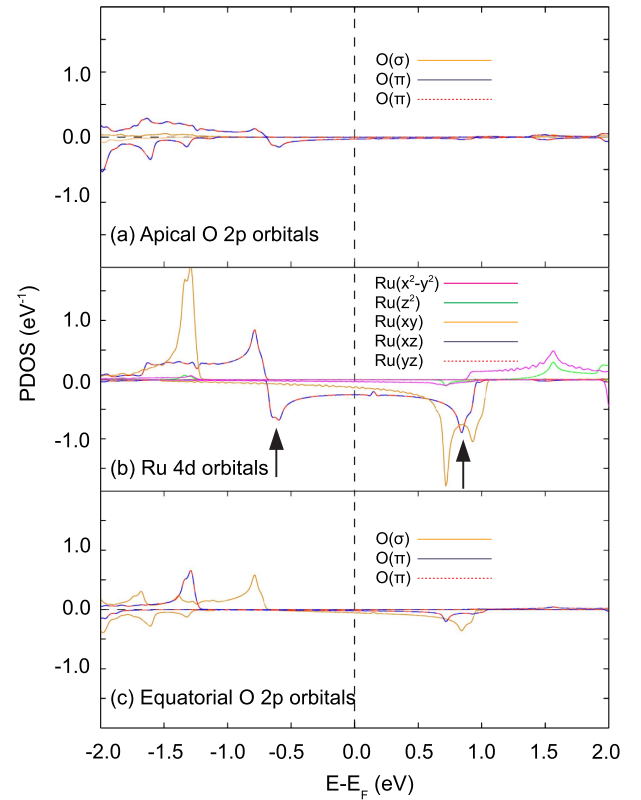


FIG. 3 (color online). PDOS on the atoms at the central SRO layer, projected on the orbitals of (a) an apical O atom, (b) the Ru atom, and (c) an equatorial O atom. In the DOS projections corresponding to oxygen, the 2p orbital directed towards the transition metal ions is denoted by O( $\sigma$ ), while the two quasi-degenerate orbitals perpendicular to this bond direction are O( $\pi$ ). The arrows in (b) mark the position of the peaks for the Ru- $d_{xz,yz}$  orbitals (see text).

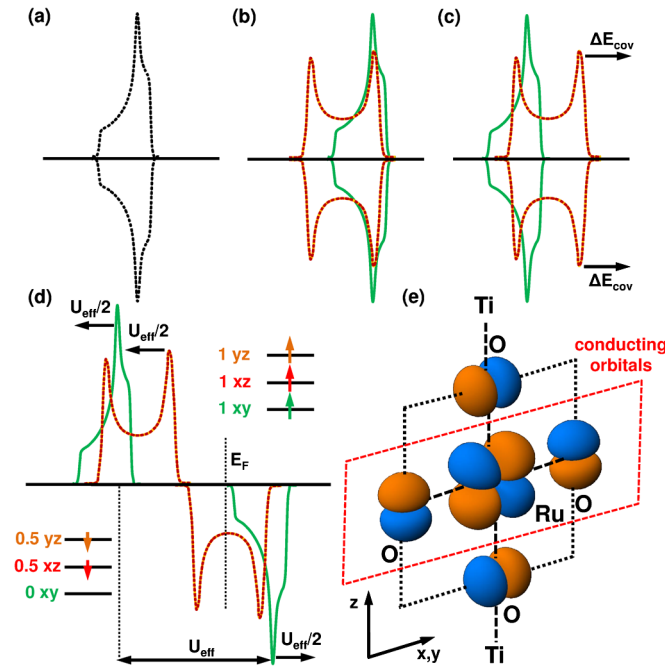


FIG. 4 (color online). Result of the tight-binding model used to interpret the DOS of  $t_{2g}$   $d$  orbitals. Our model shows the transformation from (a) the three-dimensional bulk to (b) a two-dimensional structure. Refinements of the model to include, first, covalent bonding effects in plane and out of plane (c), and second, shifts of the bands due to strong electronic correlation via a Hubbard- $U$  term (d), are required to reproduce the first-principles band structure. Dotted black lines in (a) represent the  $d_{xy,xz,yz}$  manifold, degenerated in energy. Once the symmetry is broken, the  $d_{xy}$  state is represented by a solid green line and the degenerated  $d_{xz,yz}$  orbitals by dotted red lines. Panel (e) illustrates the orbitals used in the tight-binding model and differences of in-plane and out-of-plane bonding for  $d_{xz}$  orbitals (identical sketch can be done for the  $d_{yz}$  orbitals).

calculations [arrows in Fig. 3(b)]. In particular, the PDOS of bidimensional  $d_{xz,yz}$  levels closely resembles that of textbook one-dimensional electron gas [33] due to the negligible interactions of  $d_{xz,yz}$  wave functions in the  $xy$  plane with other than first neighbors. However, we can observe that the LDA +  $U$  bands are shifted with respect to the ones obtained in our tight-binding model. These shifts are due to (i) the difference in bonding of the orbitals with in-plane and out-of-plane neighbors and (ii) the Hubbard- $U$  correction. To take into account the first effect we note that the  $d_{xy}$  wave functions only interact strongly with in-plane neighbors which are all functions centered around  $\text{Ru}^{4+}$  ions. In contrast,  $d_{xz,yz}$  wave functions interact in plane with centers around  $\text{Ru}^{4+}$  ions while out of plane they interact with functions centered on  $\text{Ti}^{4+}$  ions mediated by O atoms [see Fig. 4(e)]. Since  $\text{Ru}^{4+}$  ions are more electronegative than  $\text{Ti}^{4+}$  ones, the apical oxygens are polarized towards the  $\text{Ru}^{4+}$ . This translates into an increase of covalency and, therefore, a decrease in the energy of the bonding states and an increase of the

antibonding levels, denoted as  $\Delta E_{\text{cov}}$  in Fig. 4(c). Finally, we include the effect of the  $U_{\text{eff}}$  value to take into account magnetism. LDA +  $U$  theory predicts that orbital energies are shifted by  $U_{\text{eff}}(1/2 - \lambda)$  where  $\lambda$  is the occupation of the orbital. Using this formula, and assuming that the majority spin  $t_{2g}$  levels are full, while the minority spin  $d_{xz}$ ,  $d_{yz}$ , and  $d_{xy}$  contain, respectively, 0.5, 0.5, and 0.0 electrons, we find the shifts depicted in Fig. 4(d). Qualitatively, we find the bands to be in good agreement with those obtained in the full first-principles calculations [see Fig. 3(b)].

In summary, our first-principles simulations predict the appearance of a two-dimensional, half-metallic, ferromagnetically ordered electron gas at the insulator-ultrathin-metal-film interfaces in  $(\text{STO})_5/(\text{SRO})_1$  superlattices. The 2DEG is extremely confined at Ru  $4d$  orbitals. At odds with previous realizations of 2DEG, where the main mechanism behind localization is of electrostatic nature [13,24], we propose the larger electronegativity of Ru to be the main cause for the extreme confinement. The half-metallic properties and the concomitant FM is an intrinsic property due to enhanced electron correlation, and not to extrinsic properties (O vacancies) as postulated in LAO/STO 2DEG [34]. Our results encourage experimental verification, to check the usefulness of these superlattices in magnetoresistance or spintronic devices.

Financial support from Grant No. FIS2009-12721-C04-02, European FP7 project OxIDES (No. CP-FP 228989-2), ARC project TheMoTher, and IAP project P6/42 from the Belgian state-Belgian Science Policy. Ph. G. also acknowledges financial support through a Research Professorship from the Francqui Foundation. D. I. B. acknowledges financial support from the grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, Project No. PN-II-RU-TE-2011-3-0085. We acknowledge the computer resources, technical expertise, and assistance provided by the Red Española de Supercomputación. Other calculations were performed on the computers at the ATC group and on the Nic3 at ULg.

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