Highly-confined spin-polarized two-dimensional electron gas in SrTiO$_3$/SrRuO$_3$ superlattices

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We report first principles characterization of the structural and electronic properties of (SrTiO$_3$)$_m$/SrRuO$_3$$_n$ 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$_3$ layer. Every interface in the superlattice behaves as a minority-spin half-metal ferromagnet, with a magnetic moment of $\mu = 2.0 \mu_B$/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 $t_{2g}$ orbitals plus (i) the bi-dimensionality of the system, and (ii) strong electron correlations.

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The family of ABO$_3$ 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$_3$ 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 behaviour can also drastically change at surfaces [6] and interfaces [7]. The possibility to create highly-confined electron gas (2DEGs) at oxide interfaces has also been demonstrated and generated a huge excitement.

The most widely studied system is certainly the 2DEG formed at the LaO/TiO$_2$ polar interface between LaAlO$_3$ (LAO) and SrTiO$_3$ (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)$_m$(SrTi$_{0.8}$Nb$_{0.2}$O$_5$)$_n$$_p$ 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)$_5$/SrRuO$_3$$_1$ superlattices (STO/SRO). This system is to some extent related to those previously considered. SRO is a well-known conductive material so that STO/SRO present similarities with (STO)$_m$/SrTi$_{0.8}$Nb$_{0.2}$O$_5$$_n$ superlattices [9]. Also, STO/SRO can be seen as a STO matrix in which a TiO$_2$ layer is periodically replaced by a single RuO$_2$ 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 though regarding SRO thin films [14][16], and finite period superlattice [17], our infinite period superlattices exhibits 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 doubled checked using the CRystAL09 code [20] within the B1-WC hybrid scheme [21]. 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 [22]. 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 the Discussion 1 and 2 of the Supplemental materials [23]. Both spin-orderings in the SRO layers, FM and antiferromagnetic (AFM), where the up and down spins of the RuO\(_2\) layer are ordered in a checkerboard arrangement, are simulated.

Oxygen octahedra rotate changing the phase from layer to layer, as shown in Fig. 1(b). This pattern of rotation shares some similarities with the \( a^0_b^0c^- \) Glazer rotation 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\(_2\) 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 (\( \theta_{\text{bulk}} = 11.4^\circ \)). The rotations of the TiO\(_2\) octahedra rapidly converge to the bulk LDA value of \( \theta_{\text{SRO}} = 4.3^\circ \), indicating that the rotations are functions of the local chemical environment [24]. Taking into account that bulk SRO crystallizes within the GdFeO\(_3\) structure (\( Pnma \) space group), with \( a^-b^+a^- \) Glazer rotation, 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 [25]. As shown in Fig. 1(c), both the rumplings, and the changes in inter-planar spacing with respect to the ideal (non-relaxed) structure, are very small.

Figure 2 shows the projected density of states (PDOS) on the atoms at the different SrBO\(_3\) unit cells (where B is Ti or Ru), within the LDA+U [panel (a)], and B1-WC hybrid functional [panel (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 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\(_3\)/Nb:SrTiO\(_3\) quantum wells [26]. (ii) The electronic states around the Fermi level are fully spin-polarized, with only the minority-spin electrons involved in the charge transport [15]. (iii) The 2DEG exhibits ferromagnetism, with a magnetic moment of \( \mu = 2.0 \mu_B \)/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 [27], and polycrystalline samples [28]. 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 [23]). Interestingly, the electronic structure at the interface inherits some of the particularities theoretically predicted in bulk SRO when the electronic correlations are properly included [as in LDA+U [29], pseudo self-interaction correction [30], or

In the most stable phase, that turns out to have FM order, our simulations predict a \( P4/mnbm \) space group.
B1-WC hybrid functional (Discussion 5 in the Supplemental materials [23]). Between these properties, we might cite the half-metallicity [29] or the saturation of the magnetic moment [30]. 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. 5 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 [31], the double peaked shape [peaks marked with arrows in Fig. 5(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 materials [23]). 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 to these bands for a full three-dimensional solid is shown in Fig. 4(a). Using this model

![Figure 2](image-url) (color online) Layer-by-layer PDOS on the atoms at the SrBO\(_2\) layers (B = Ti or 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. 4(a). Corresponding layers in the upper-half of the structure are equivalent by symmetry. Majority/minority spin are represented in the upper/lower halves of each panel, respectively.

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 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 [31] due to the negligible interactions of \(d_{xz,yz}\) wavefunctions 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 \(d_{xy}\) wavefunctions only interact strongly with in-plane neighbors which are all functions centered around Ru\(^{4+}\) ions. In contrast, \(d_{xz,yz}\) wavefunctions interact in-plane with centers around Ru\(^{4+}\) ions while out-of-plane they interact with functions centered on Ti\(^{4+}\) ions mediated by O atoms [see Fig. 4(e)]. Since Ru\(^{4+}\) ions are more electronegative than Ti\(^{4+}\) ones, the apical oxygens are polarized towards the 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 \(\Delta E_{covan}\) in Fig. 4(c). Finally, we include the effect of the \(U_{eff}\) value to take into account magnetism. LDA+U theory predicts that orbital energies are shifted by \(U_{eff}(1/2 - \lambda)\) 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 pre-
dict the appearance of a two-dimensional, half-metallic, ferromagnetically ordered electron gas at the insulator/ultrathin-metal-film interfaces in (STO)$_5$/(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, 22], 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 [32]. Our results encourage experimental verification, to check the usefulness of these superlattices in magnetoresistance or spintronic devices.

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**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 panel (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. Black lines in (a) represent the $d_{xy,zz,yy}$ manifold, degenerated in energy. Once the symmetry is broken, the $d_{xy}$ state is represented by a green line, and the degenerated $d_{xz,yz}$ orbitals by red lines. (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).

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