Charge origin and localization at the *n*-type $SrTiO_3/LaAlO_3$ interface

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We report a first-principles study of $(LaAlO_3)_m/(SrTiO_3)_n$ heterostructures using density-functional theory at the LDA+U level. Our results support the original explanation of Ohtomo and Hwang [Nature (London) **427**, 423 (2004)] that the charge at the *n*-type interface may be due to electrostatic doping. The internal electric field in the $LaAlO_3$ layer is calculated to be 0.24 V/Å. Though it is not sufficient to cause the dielectric breakdown in a wide band-gap La aluminate, it causes charge transfer into the adjacent narrower gap $SrTiO_3$ layer. The quasi-two-dimensional nature of the charge distribution is caused by a combination of the crystal-field effect, pseudo-Jahn-Teller distortion, and interface chemistry. Our theoretical estimate suggests that the interfacial carrier density of about 2×10^{13} cm^{-2} can be easily achieved.

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Recent experiments on (001)-oriented perovskite heterostructures grown by molecular-beam epitaxy and pulsed laser deposition suggest the possibility of creating high mobility two-dimensional (2D) electron gas (2DEG) localized at the oxide/oxide interface.[1–7] In particular, Ohtomo and Hwang[1] reported the growth of atomically precise lattice matched superlattices comprised of alternating layers of $LaAlO_3$ (LAO) and $SrTiO_3$ (STO). They discovered metallic conductivity at the interface between the two oxides and found that depending on the interface stoichiometry, i.e., TiO_2/LaO or SrO/AlO_2, it could be *n* or *p* type, respectively. For the *n*-type interface they reported high electron mobility measured by the Hall effect. However, the *p*-type interface is found to quickly become insulating, presumably, due to the charge compensation.[2] In a follow-up study of the STO/LAO system Thiel *et al.*[3] reported the steplike change in the two-dimensional carrier sheet density and sheet conductance plotted as a function of the LAO layer thickness. When the film thickness exceeds the critical value of four LAO unit cells the conductivity increases by 5 orders of magnitude. What makes these findings especially remarkable is the fact that both STO and LAO are wide band-gap insulators with the band gaps of 3.2 and 5.6 eV, respectively.

These curious results have generated an intense debate about the origin of charge in the conducting layer. Both "extrinsic" 4×10^{16} cm^{-2}–7×10^{20} cm^{-3} (e.g., due to oxygen vacancies[6,7]) and "intrinsic" 10^{13} cm^{-2} carrier density (related to the "polar catastrophe" or electrostatic doping[1,3,8]) mechanisms have been discussed. In this Brief Report we present theoretical calculations in support of the electrostatic doping model for the *n*-type LAO/STO interface and offer a consistent picture explaining the origin of charge and its localization at the interface. We find that the charge accumulates on the STO side of the interface once the intrinsic electric field in the polar LAO layer reaches a critical value. In contrast with the polar catastrophe, instead of the dielectric breakdown, the internal field in the polar material causes charge transfer to the conduction band of the adjacent layer of a different material with a lower band gap (STO). We show that the localization of charge in close proximity of the interface originates on a split-off t_{2g} state of interface Ti and is caused by a combination of three different effects: (i) the crystal filed induced symmetry lowering, (ii) the pseudo-Jahn-Teller (JT) effect, and (iii) the interface chemistry. The calculated strength of the internal electric field, the critical thickness of LAO, and interfacial carrier density are found to be 0.24 V/Å, four to five unit cells of LAO, and 2×10^{13} cm^{-2}, respectively, in close agreement with experiment. Taking the JT energy as a rough measure of the electron-phonon coupling we estimate the superconducting transition temperature to be around 200 mK in qualitative agreement with the recent report by Reyren *et al.*[9]

All calculations are carried out using density-functional theory with the plane-wave based Vienna *ab initio* package (VASP).[10,11] We use the projector-augmented wave (PAW) method of Blöchl[12] in the implementation of Kresse and Joubert.[13] The local-density approximation (LDA) is employed for $LaAlO_3$ with the Ceperley-Alder exchange-correlation functional[14] as parametrized by Perdew and Zunger.[15] As it will become clear having the correct experimental band gap of $SrTiO_3$ in these calculations is essential. We achieve that by using LDA+U with $U_{eff}=8.5$ eV, this results in the 3.2 eV band gap and 3.89 Å lattice constant in good agreement with experiment. A similar value was used by Pentcheva and Pickett.[16] $LaAlO_3$ is treated at the LDA level. This inconsistency brings some uncertainty to the value of the bonding/antibonding splitting of the La d/O $2p$ states forming the band edges. The effect however is small judging by the change in the band offset and does not affect the main findings of this Brief Report. Plane waves are included up to the kinetic-energy cutoff of 600 eV. For the Brillouin-zone integration an $8\times8\times8$ Monkhorst-Pack special k point grid is used for bulk $SrTiO_3$ and $LaAlO_3$ and a $6\times6\times2$ grid for LAO/STO heterostructures. The calculations are converged in energy to 10^{-6} eV/cell and the structures are relaxed until the forces are less than 10^{-2} eV/Å. We use slab geometry; the $(LAO)_m(STO)_n(LAO)_m$ ($n=4.5$, $m=3,5$ unit cells) slabs are separated by 20 Å of vacuum to eliminate the spurious slab-slab interaction. We will describe the simulation cells in more details in what follows.

The most intriguing question about the STO/LAO interface is, of course, the very origin of the interfacial charge and the mechanism of its localization. To date, most theoretical calculations have been done using symmetric supercells owing to the use of the periodic boundary conditions.[16–18]

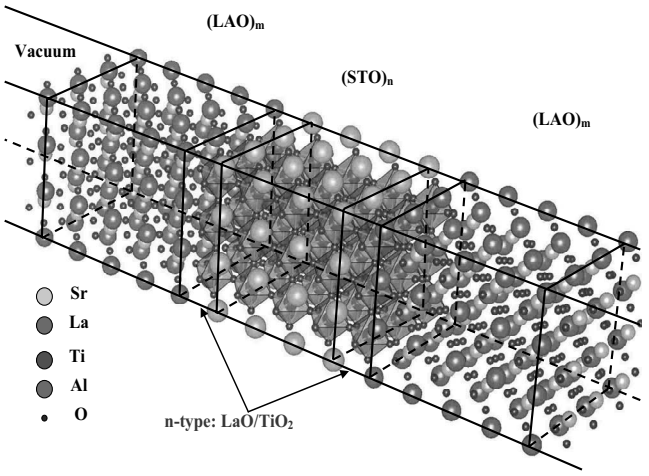

FIG. 1. The symmetric vacuum terminated $(LAO)_m(STO)_n(LAO)_m$ slab with two identical n-type interfaces.

However, in this geometry the extra electron is introduced somewhat artificially due to the stoichiometry violation in the LAO layer (both sides of it are chosen to be LaO terminated). In a symmetric supercell there are two identical interfaces and each gets a half of an electron as was originally discussed by Ohtomo and Hwang.[1] Thus, we argue, these calculations can only explain what the charge might do once it is introduced into the system but cannot shed light on the possible origin of the charge itself. To avoid this difficulty and still be able to use the periodic boundary conditions, we construct a symmetric vacuum slab with two identical n-type interfaces as shown in Fig. 1. The LAO film is AlO_2 terminated on the vacuum side and LaO terminated on the STO side, thus the LAO layer is stoichiometric (experimentally both surfaces of LAO can be stabilized[4,19]). The atomic relaxation is very important when one deals with the ionic system under strain, and a few words are in order describing how to build a slab, such as shown in Fig. 1, properly. When we build a slab we assume the STO layer to be a substrate and its lateral dimensions define those of the simulation cell. That results in 2.4% tensile strain in the LAO layer. This is a theoretical value; the experimental value is 3.5%. In a separate slab calculation (LAO layer plus vacuum) we determine the elastic response of LAO to this strain. The contraction in the z direction gives $c=3.64$ Å. If LAO is treated at the LDA+U level the estimated correction to the LDA result is less than 1%. Next, we build a LAO/STO/LAO slab with a symmetric TiO_2-terminated STO layer and 20 Å of vacuum. Freezing initially the atomic coordinates, the LaO/TiO_2 interplanar distance is optimized (we obtain 1.96 Å), and finally the full geometric relaxation of the structure is performed. The largest $m=5$, $n=4.5$ slab considered has dimensions of $55\times3.89\times3.89$ Å^3. As expected, the final rearrangement takes place mostly the vicinity of the interface. Such structures allow using the periodic boundary conditions in polar cases at the expense of essentially doubling the problem size.

We now analyze the electronic properties of the system for $n=4.5$, $m=3$, and $m=5$. In Fig. 2(a) we show the plane-averaged electrostatic potential plotted as a function of the

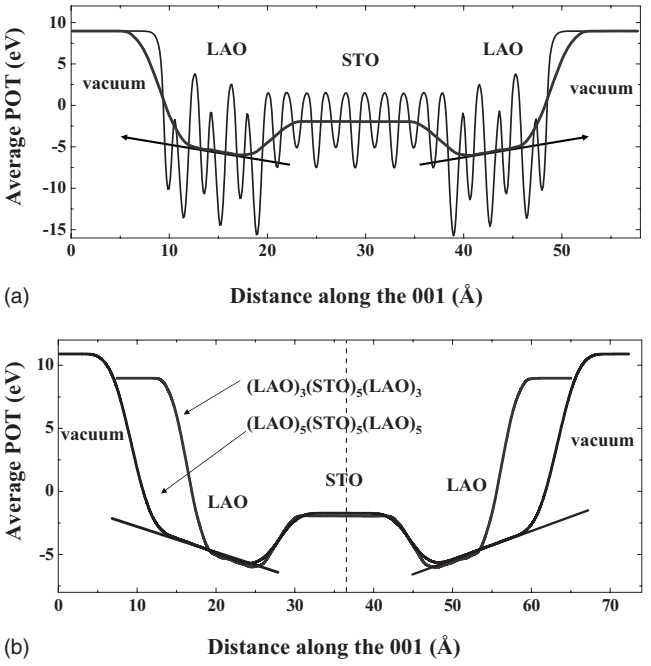

FIG. 2. (a) The xy-averaged electrostatic potential across the $(LAO)_3(STO)_{4.5}(LAO)_3$ simulation slab. The field is estimated to be 0.24 V/Å. (b) Comparison of the electrostatic potential in precritical $(LAO)_3(STO)_{4.5}(LAO)_3$ and postcritical $(LAO)_5(STO)_{4.5}(LAO)_5$ structures.

position in the direction normal to the surface, and its macroscopic average with the oscillations on the scale of a unit cell integrated out[20] for $n=4.5$, $m=3$. The internal electric field as discussed in the context of the polar catastrophe in the case of polar semiconductors by Harrison *et al.*[21] is clearly seen. In Fig. 2(b) we show the results for two structures that differ in the thickness of the LAO layer; the intrinsic electric field is on the order of 0.24 V/Å. The experimental band gap of LAO is 5.6 eV, and in a freestanding film this electric field would result in the dielectric breakdown if the film thickness exceeds 23 Å. The situation is changed dramatically, however, by the presence of an STO layer since the band gap of $SrTiO_3$ is only 3.2 eV. Taking into consideration the LAO/STO valence-band offset [calculated value of 0.1 eV (Ref. 22)] to gain this energy it takes only three and a half unit cells or about 13 Å of LAO. Obviously this distance is sufficiently small for electron tunneling to occur; thus the critical thickness for charge transfer is about four LAO layers

In Fig. 3(a) we plot the partial density of states (DOS) projected onto atomic planes in the STO and LAO across the precritical $(LAO)_3(STO)_{4.5}(LAO)_3$ structure. The potential drop due to the intrinsic electric field is clearly seen in the LAO layer, however, the field is not strong enough to cause any charge transfer at this thickness. In Fig. 3(b) we show the DOS projected onto atomic planes in the LAO and STO for a $(LAO)_5(STO)_{4.5}(LAO)_5$ structure. The critical LAO thickness is now exceeded, and the charge is transferred from the top of the LAO valence band near the vacuum surface to the conduction band of STO at the LAO/STO interface. Note that the bulk region of STO remains insulating as the charge

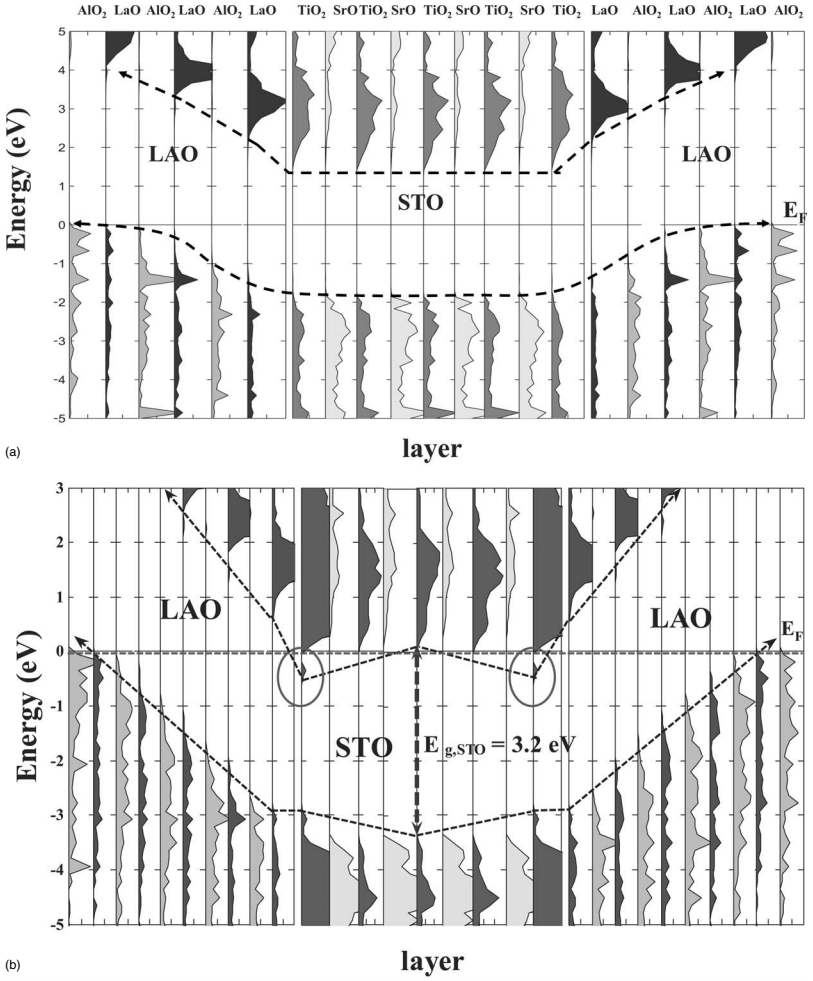

FIG. 3. (a) The density of states projected onto atomic planes across the $(LAO)_3(STO)_{4.5}(LAO)_3$ simulation cell. (b) The density of states projected onto atomic planes across the $(LAO)_5(STO)_{4.5}(LAO)_5$. The 2D electron-gas regions are clearly seen at both interfaces. The extent of the 2DEG region is about 1 nm. Note that the thickness of the LAO layer in (b) is larger than that in (a).

is localized in approximately two unit cells adjacent to the interface. This is consistent with the internal field of 0.24 V/Å estimated from Fig. 2. This critical value agrees very well with that experimentally observed by Thiel *et al.*[3] This result indicates that, at least in principle, the electrostatic doping can be responsible for the charge found at the *n*-type STO/LAO interface. We still, however, need to explain the charge localization. If we decompose the partial density of states projected onto the interface Ti atom into orbital contributions as shown in Fig. 4, it is clear that the charge is localized in a split-off d_{xy} orbital. The origin of this splitting is somewhat complicated, and we carefully explore it. Pentcheva and Pickett[16,17] discussed the crystal-field-like effect due to the symmetry lowering at the interface, and the Jahn-Teller effect has been suggested.[23] Also, Duan *et al.*[24] discussed the chemical effect (the bond-length difference) as the origin of the interfacial Ti displacement at the $Fe/BaTiO_3$ interface which results in the symmetry lowering. Indeed, all three mechanisms possibly play a role. We estimate the crystal-field splitting performing a calculation for a $Q=+1$ state of a short period symmetric supercell. The charge state is chosen so there is no additional electron in the conduction band of STO due to the stoichiometry violation discussed earlier, and thus there is no Jahn-Teller distortion. We indeed observe a splitting of the t_{2g} manifold on the interface Ti atom but it is only 0.01 eV. Accordingly, it almost cannot be seen in the atomic plane projected DOS plot for the $(LAO)_3(STO)_{4.5}(LAO)_3$ structure in Fig. 3(a), though the symmetry is obviously broken at the interface. A large 0.4 eV splitting is clearly seen in Fig. 3(b). It is important to note

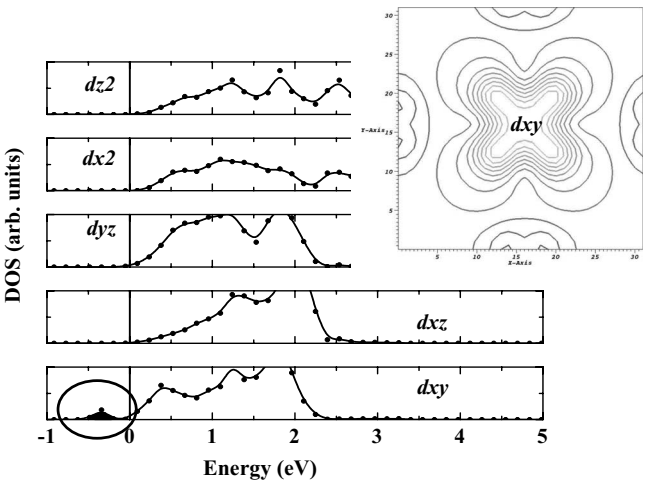

FIG. 4. The partial density of states projected onto the interfacial Ti atom. The d_{xy} orbital is split and is occupied (the Fermi energy is set to zero). Integration of the charge density gives the value of 10^{13} cm^{-2} (see text). The charge distribution in the interface plane strongly resembles the d_{xy} orbital (inset).

that this crystal-field splitting of Ti t_{2g} occurs in the interface plane only. Ti atoms further from the interface still feel a cubic crystal field. The chemical effect would be due to a shorter Al-O bond which would pull the interface Ti atom toward LAO. The actual Ti displacement is in the opposite direction. The detail analysis of the displacement pattern will be published elsewhere. It suffices to say that it is not caused by the bond-length difference. We therefore argue that a pseudo-Jahn-Teller effect is at play here. The initial crystal-field splitting is increased dramatically to 0.4 eV once the charge is transferred into STO by the internal field of the LAO layer with above critical thickness. This large Jahn-Teller splitting is indicative of a strong electron-phonon coupling in the interface layer.[25] The integration of the square of the wave function over the energy window from the bottom of the split-off band to the Fermi level gives the charge corresponding to this occupied band; the charge-density contour plot in the interface plane is shown in the inset of Fig. 4. The charge extends over approximately two STO unit cells but viewed as the interface charge corresponds to the charge density of 1.2×10^{13} cm^{-2} in excellent agreement with experimental values of Thiel *et al.*[3] and Huijben *et al.*[4]

In summary we present theoretical results in support of electrostatic doping as the possible source of the electric charge at the *n*-type STO/LAO interface.[1,8] Our results clearly show the existence of the internal electric field of 0.24 V/Å in the LAO layer resulting in the critical thickness of four unit cells necessary to generate the interface charge in STO.[3] We find that the localization of this charge in close proximity to the interface is caused by a combination of the crystal filed and pseudo-Jahn-Teller effects. Although we cannot exclude the oxygen vacancy contribution[6,7] to the two-dimensional electron gas, the calculation supports the electrostatic doping model[1,3,8] in that the intrinsic field alone can produce the lowest observable value of the charge density.[3,4]

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