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Magnetism of LaAlO₃/SrTiO₃ superlattices

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First-principles electronic structure calculations are performed to elucidate magnetic properties of LaAlO₃/SrTiO₃ heterostructures. We find that TiO₂-terminated interfaces are *n*-type conducting which is consistent with experimental observations. In a (LaAlO₃)₃/(SrTiO₃)₃ superlattice, this interface is magnetic with a magnetic moment on the Ti³⁺ atom of 0.2μ_B, as revealed by the spin-polarized calculations within the local density approximation (LDA). For thicker SrTiO₃ layers the magnetic moment decreases and eventually disappears because the electron gas spreads over more than one unit cell, making the electron delocalized across the superlattice and violating the Stoner criterion for magnetism. Thus, magnetization in these superlattices is due to geometric confinement of the electron gas. The inclusion of electron correlations via the LDA+*U* approximation with *U*=5 eV on the Ti atoms makes the two-dimensional electron gas half-metallic and enhances and stabilizes the interface magnetization. © 2008 American Institute of Physics. [DOI: 10.1063/1.2829244]

Recent advances in thin-film deposition techniques, such as molecular beam epitaxy and pulsed laser deposition, have allowed manufacturing oxide-based superlattices with atomically abrupt interfaces. Some of these heterostructures exhibit novel physical properties that are not present in the respective bulk constituents. In particular, it was demonstrated experimentally that polar discontinuities cause the interface between two common wide-gap insulating oxides LaAlO₃ and SrTiO₃ to become conducting.^{1,2} The quasi-two-dimensional electron gas (2DEG) forming at the interface has extremely high carrier mobility and an electron density that is larger by an order of magnitude than the density of 2DEG at known semiconductor interfaces. This phenomenon is interesting due to possible application in all-oxide high-electron mobility field-effect transistors.³ Very recently, the evidence of magnetism at the interface between these nonmagnetic oxides was found which may open exciting perspectives for spintronics applications.⁴

Perovskite oxides exhibit a wide variety of valence states which can be described with the expression A^{X+}B^{Y+}O₃²⁻, where X+Y=6. In the (001) direction, the solid consists of alternating planes of A^{X+}O₂⁻ and B^{Y+}O₃²⁻ which can be charged. Polar discontinuities at the interface between two different oxides can lead to interface reconstruction. Mixed valence oxides allow for the possibility of charge (rather than ion) redistribution. This is the case for LaAlO₃/SrTiO₃(001) heterostructure, where La³⁺Al³⁺O₃²⁻ consists of alternating (LaO)⁺ and (AlO₂)⁻ planes and Sr²⁺Ti⁴⁺O₃²⁻ consists of alternating (SrO)⁰ and (TiO₂)⁰ planes, leading to a polar interface according to the bulk valence. However, due to accessible mixed valence of Ti, allowing for its reduction toward Ti³⁺, half an electron per two-dimensional unit cell can be transferred across the interface to compensate for the electrostatic potential divergence.⁵ Thus, there are uncompen-

sated *n*-type carriers at the (LaO)⁺/(TiO₂)⁰ interface and *p*-type carriers at the (AlO₂)⁻/(SrO)⁰ interface, which are supposed to make these interfaces conductive. The *n*-type conductance has indeed been confirmed experimentally for the (LaO)⁺/(TiO₂)⁰ interface, but the (AlO₂)⁻/(SrO)⁰ interface was found to be insulating.^{1,3} First-principles calculations of LaAlO₃/SrTiO₃ superlattices, based on density functional theory within the local density approximation⁶ (LDA) and the LDA+*U* approximation,⁷ have been performed. Calculations essentially confirm the presence of charge carriers in both *n*-type ($\frac{1}{2}$ electron on the interface Ti 3*d* band) and *p*-type interfaces ($\frac{1}{2}$ hole on the interface O 2*p* band).

Recently, it was demonstrated that the interface between the nonmagnetic LaAlO₃ and SrTiO₃ becomes magnetic at low temperatures.⁴ This was attributed to ferromagnetic alignment of the induced electrons on the Ti 3*d* conduction band. This behavior is corroborated by spin-polarized first-principles calculations of LaAlO₃/SrTiO₃ interface,⁷ as well as LaTiO₃/SrTiO₃ interfaces.⁸

In this paper, we use first-principles calculations based on density functional theory to elucidate the origin of the magnetism at LaO/TiO₂ interfaces of (LaAlO₃)_{*m*}/(SrTiO₃)_{*n*} superlattices (where *n* and *m* is the number of monolayers of the respective compounds). Within LDA, for the thinnest SrTiO₃ layer considered (*n*=3), we find that the interface Ti atoms have a magnetic moment of 0.2μ_B. This magnetic moment disappears as the electron gas delocalizes when the SrTiO₃ slab becomes thicker. A model based on the Stoner criterion for magnetism suggests that the magnetization in these superlattices is due to geometric confinement of the electron gas. The inclusion of electron correlations, via the LDA+*U* approximation with *U*=5 eV on the Ti atoms, makes the two-dimensional electron gas half-metallic and enhances and stabilizes the interface magnetization.

Density functional calculations of the electronic and atomic structure of (LaAlO₃)_{*m*}/(SrTiO₃)_{*n*} superlattices are performed using the projector augmented wave method

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TABLE I. Magnetic moments on the interface Ti atom (m_{Ti}), the total moment of the unit cell (m_{total}), the exchange splitting (Δ), and the parameter $I\rho(E_F)$ entering the Stoner criterion [Eq. (4)] for $(\text{LaAlO}_3)_3/(\text{SrTiO}_3)_n$ superlattices with different SrTiO_3 layer thickness (n) calculated within LDA ($U=0$).

n	m_{Ti} (μ_B)	m_{total} (μ_B)	Δ (eV)	$I\rho(E_F)$
3	0.21	0.53	0.29	1.17
5	0.07	0.22	0.10	0.53
7	0.023	0.10	0.03	0.34
9	0.016	0.07	0.02	0.35

implemented in the Vienna *ab initio* simulation package (VASP).⁹ We consider structures with $m=3$ and $n=3, 5, 7,$ and 9 , in which both interfaces are $(\text{LaO})^+/(\text{TiO}_2)^0$ type.¹⁰ The in-plane lattice constant is chosen to be the average value of the experimental lattice constants of LaAlO_3 (3.789 Å) and SrTiO_3 (3.905 Å). The resulting supercell is tetragonal with $a=b=3.847$ Å and $c/a=(n+m)/2$. Within this cell the ionic positions are fully relaxed. Due to the large lattice mismatch between the bulk lattice constants of LaAlO_3 and SrTiO_3 , the resulting lattice has a tetragonal distortion of both compounds. There is also a substantial buckling of the atoms at the interface due to ionic relaxation. These results are similar to the relaxations reported previously for smaller superlattices.⁶

First, we consider the electronic structure of the paramagnetic 2DEG at the LaO/TiO_2 interface as a function of the SrTiO_3 thickness. We find that the conduction band is partially occupied, suggesting that the LaO/TiO_2 interface becomes metallic with n -type carriers. This is consistent with experimental findings¹ and theoretical calculations.^{6,7} The number of conduction electrons is 0.5 electrons per interface, as obtained from the integrated density of states. These electrons occupy mainly the Ti 3*d* conduction band that proves the validity of the simple ionic model, in which half of electron per interface is transferred from LaAlO_3 to unoccupied Ti band in the SrTiO_3 .⁵ Perhaps surprisingly, we find that, as thickness of SrTiO_3 increases, the conduction electrons are distributed to all Ti atoms inside the SrTiO_3 slab, rather than being confined only to the Ti atoms at interfaces. This behavior is different from that in $(\text{LaTiO}_3)_m/(\text{SrTiO}_3)_n$ superlattices where the electron gas was found to be localized within a couple of monolayers near the interface.¹¹

The partial occupation of the Ti 3*d* band in SrTiO_3 necessitates the proper treatment of electron-electron correlations. We, therefore, performed electronic structure calculations for the $\text{LaAlO}_3/\text{SrTiO}_3$ superlattices using LDA+*U* method.¹² It appears that the inclusion of moderate U up to 5 eV on Ti *d* states does not result in the localization of the electrons close to the interface.

It is found experimentally that Ti 3*d* electrons localized at the $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces align ferromagnetically leading to magnetic behavior at low temperatures.⁵ In order to understand the origin of the magnetism, we perform spin-polarized calculations of the electronic structure of $(\text{LaAlO}_3)_m/(\text{SrTiO}_3)_n$ superlattices having LaO/TiO_2 interfaces. For $n=3$ SrTiO_3 film, we find within LDA that the 2DEG becomes magnetic, with a magnetic moment of $0.2\mu_B$ on Ti atoms. However, as is evident from Table I, with in-

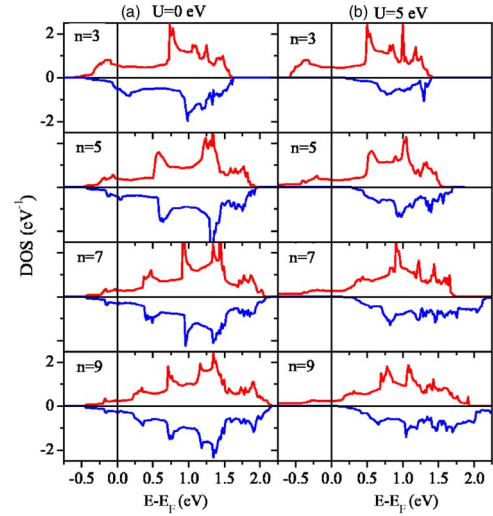


FIG. 1. (Color online) Density of states for majority- and minority-spin electrons on the Ti atom at the interface for $(\text{LaAlO}_3)_3/(\text{SrTiO}_3)_n$ superlattices: (a) $U=0$ and (b) $U=5$ eV. The Fermi energy is denoted by the vertical solid line.

creasing the SrTiO_3 thickness this magnetic moment decreases and disappears.

Figure 1(a) shows the LDA majority- and minority-spin densities of states (DOSs) for the Ti atom at the interface for different thicknesses of SrTiO_3 . As is seen, the exchange splitting Δ decreases rapidly with SrTiO_3 thickness: it has a maximum $\Delta=0.29$ eV for 3 ML and practically vanishes for 7 ML of SrTiO_3 (see Table I). In order to understand this behavior, we employ the Stoner model for itinerant magnetism.¹³

The basic idea of the Stoner model is as follows. Due to the localized nature of *d* electrons, two *d* electrons experience a strong Coulomb repulsion provided that they have antiparallel spins and occupy the same orbital. To reduce the energy, it is advantageous for the *d* electrons to have parallel-oriented spins because the Pauli exclusion principle does not permit two electrons with the same spin to approach each other closely (i.e., occupy the same orbital) and hence the Coulomb interaction is reduced. Therefore, the Coulomb repulsion in conjunction with the Pauli principle leads to the ferromagnetic exchange interaction which favors the exchange splitting Δ of the spin bands and the formation of a spontaneous magnetic moment,

$$m = \int_{E_F+\Delta/2}^{E_F+\Delta/2} \rho(E)dE - \int_{E_F-\Delta/2}^{E_F-\Delta/2} \rho(E)dE. \quad (1)$$

Here, E_F is the Fermi energy and $\rho(E)$ is the DOS of a paramagnetic state. This leads to the gain in the exchange energy given by

$$\varepsilon_{\text{ex}} = -\frac{1}{2} I m^2, \quad (2)$$

where I is the Stoner parameter (exchange constant). However, putting electrons into states with the same spin direction enhances the kinetic energy,

$$\varepsilon_{\text{kin}} = \int_{E_F+\Delta/2}^{E_F+\Delta/2} \rho(E)E dE + \int_{E_F-\Delta/2}^{E_F-\Delta/2} \rho(E)E dE, \quad (3)$$

TABLE II. Magnetic moments on the interface Ti atom (m_{Ti}), the total moment of the unit cell (m_{total}), the exchange splitting (Δ), and the parameter $U\rho(E_F)$ entering criterion (7) for $(\text{LaAlO}_3)_3/(\text{SrTiO}_3)_n$ superlattices with different SrTiO_3 layer thicknesses (n) calculated with $U=5$ eV.

n	m_{Ti} (μ_B)	m_{total} (μ_B)	Δ (eV)	$U\rho(E_F)$
3	0.41	0.996	1.17	7.56
5	0.26	0.999	0.87	3.44
7	0.17	0.995	0.75	2.24
9	0.16	1.006	0.57	2.31

the increase being larger the wider the d band or lower the d -band DOS. There are, therefore, two competing tendencies, which have to be balanced in order to find whether ferromagnetic ordering is favored. The condition which has to be satisfied for the appearance of ferromagnetism is the Stoner criterion,

$$I\rho(E_F) > 1, \quad (4)$$

where $\rho(E_F)$ is the DOS of a paramagnetic state at the Fermi energy. If the Stoner criterion is satisfied, then the ferromagnetic state is favorable. Within the approximation of $\rho(E)$ being symmetric around E_F in energy interval Δ , it is easy to find by minimizing the total energy $\varepsilon = \varepsilon_{\text{kin}} + \varepsilon_{\text{ex}}$ that the Stoner parameter is related to the exchange splitting by the equation

$$I = \frac{\Delta}{m}. \quad (5)$$

Using Eq. (5) and values of Δ and m obtained from the first-principles calculation for the $(\text{LaAlO}_3)_3/(\text{SrTiO}_3)_3$ superlattice, we find $I=0.725$ eV. Assuming that this value is independent of SrTiO_3 thickness in the superlattice, the parameter $I\rho(E_F)$ entering the Stoner criterion [Eq. (4)] can then be calculated for each thickness of SrTiO_3 . The results are shown in Table I. It is seen that the decay of magnetism in the system is associated with the violation of the Stoner criterion. Thus, the disappearance of the magnetic moment on the Ti atoms, with the increasing SrTiO_3 thickness, is caused by the delocalization of the electron gas that is spread over all the Ti atoms in the SrTiO_3 , resulting in the decrease of $\rho(E_F)$.

The Ti $3d$ bands play an essential role in conducting and magnetic properties of $\text{LaAlO}_3/\text{SrTiO}_3$ superlattices. Due to the localized nature of the $3d$ states, a proper treatment of the on-site Coulomb interaction between electrons is required. Using the LDA+ U approximation, we find that the inclusion of the on-site Coulomb interaction with a moderate value of $U=5$ eV leads to half-metallicity of the 2DEG in the heterostructures. This is evident from Fig. 1(b) which shows the spin-dependent DOS on the interface Ti atom for different thicknesses of SrTiO_3 , indicating a zero minority-spin DOS at the Fermi energy. In addition, the on-site Coulomb interaction stabilizes magnetism. As is seen from Table II, for all SrTiO_3 thicknesses, the calculated LDA+ U magnetic moment of the unit cell is about $1\mu_B$.

In order to understand the magnetism of the 2DEG in the presence of electron correlations, we apply the Hubbard model.¹³ The electron correlations add to the energy a term

$U\sum n_{i\uparrow}n_{i\downarrow}$, where in the mean-field approximation, $\langle n_{i\uparrow} \rangle = n/2 + m$ and $\langle n_{i\downarrow} \rangle = n/2 - m$. The total energy for the Hubbard model is then

$$\varepsilon = \varepsilon_{\text{kin}} + U\left(\frac{n^2}{4} - m^2\right), \quad (6)$$

where n is the total number of electrons in the system. Minimizing the energy gives a condition for magnetism analogous to the Stoner criterion,

$$U\rho(E_F) > 1. \quad (7)$$

This suggests that the electron correlation U is additive to the Stoner parameter I , which is the origin of the 2DEG magnetization stabilization in the presence of the on-site Coulomb interaction.

In conclusion, we have studied magnetism and conducting properties of $\text{LaAlO}_3/\text{SrTiO}_3(001)$ superlattices for different thicknesses of SrTiO_3 . We found that the polarization discontinuity at the LaO/TiO_2 interface causes a partial occupation of the Ti $3d$ conduction band in SrTiO_3 . For the smallest SrTiO_3 thickness, the system becomes magnetic, however, the magnetism disappears as the thickness of SrTiO_3 increases. The Stoner model predicts that the delocalization of the electron gas over the SrTiO_3 thickness reduces the magnetic moment. Taking into account electron-electron correlations within the LDA+ U method, we found that the on-site Coulomb interaction stabilizes the magnetization and makes the 2DEG half-metallic.

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