University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Evgeny Tsymbal Publications | Research Papers in Physics and Astronomy

2012

Magnetic and superconducting phases at the $LaAlO_3/SrTiO_3$ interface: The role of interfacial Ti 3*d* electrons

N. Pavlenko
Institute for Condensed Matter Physics

Thilo Kopp
Universitat Augsburg, thilo.kopp@physik.uni-augsburg.de

Evgeny Y. Tsymbal
University of Nebraska-Lincoln, tsymbal@unl.edu

George A. Sawatzky
University of British Columbia, sawatzky@physics.ubc.ca

Jochen Mannhart
Max Planck Institute for Solid State Research, j.mannhart@fkf.mpg.de

Follow this and additional works at: http://digitalcommons.unl.edu/physicstsymbal

 Part of the Condensed Matter Physics Commons

Pavlenko, N.; Kopp, Thilo; Tsymbal, Evgeny Y.; Sawatzky, George A.; and Mannhart, Jochen, "Magnetic and superconducting phases at the $LaAlO_3/SrTiO_3$ interface: The role of interfacial Ti 3*d* electrons" (2012). *Evgeny Tsymbal Publications*. 39.
http://digitalcommons.unl.edu/physicstsymbal/39

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Evgeny Tsymbal Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

PHYSICAL REVIEW B **85**, 020407(R) (2012)

Magnetic and superconducting phases at the $LaAlO_3/SrTiO_3$ interface: The role of interfacial Ti 3*d* electrons

N. Pavlenko,[1,2] T. Kopp,[2] E. Y. Tsymbal,[3] G. A. Sawatzky,[4] and J. Mannhart[5]

[1]*Institute for Condensed Matter Physics, 79011 Lviv, Ukraine*

[2]*EKM and Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany*

[3]*Department of Physics and Astronomy, Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588-0299, USA*

[4]*Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T1Z1*

[5]*Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany*

(Received 28 December 2011; published 19 January 2012)

Ferromagnetism and superconductivity are, in most cases, adverse. However, recent experiments reveal that they coexist at interfaces of $LaAlO_3$ and $SrTiO_3$. We analyze the magnetic state within density functional theory and provide evidence that magnetism is not an intrinsic property of the two-dimensional electron liquid at the interface. We demonstrate that the robust ferromagnetic state is induced by the oxygen vacancies in $SrTiO_3$ or in the $LaAlO_3$ layer. This allows for the notion that areas with increased density of oxygen vacancies produce ferromagnetic puddles and account for the previous observation of a superparamagnetic behavior in the superconducting state.

DOI: 10.1103/PhysRevB.85.020407 PACS number(s): 74.81.−g, 73.20.Mf, 74.45.+c, 74.78.Fk

The formation of a metallic state at the interface of the bulk insulators $LaAlO_3$ and $SrTiO_3$ (Ref. 1) has become a prototype for the reconstruction of electronic states in systems with artificially reduced dimensionality. This two-dimensional (2D) electronic system is affected by sizable electronic correlations which allow characterizing the extended interface electronic states as an electron liquid.[2,3] The correlations not only induce a superconducting state[4] but also support magnetism.[5] An unexplained phenomenon is the coexistence of magnetism and superconductivity[6,7] in the 2D electron liquid.

Recent measurements by Dikin *et al.*[6] demonstrate a hysteretic behavior in the field dependences of magnetoresistance and critical temperature which suggests the existence of ferromagnetism in the superconducting samples of $LaAlO_3$ (LAO) grown on $SrTiO_3$ (STO). Moreover, Dikin *et al.* take the viewpoint that two distinct electronic systems are associated with the antagonistic superconducting and ferromagnetic properties: The electrons that are generated by the polar catastrophe mechanism are suggested to be related with magnetism, while superconductivity is associated with the charge carriers induced by the presence of oxygen vacancies. The concept of two different types of charge carriers which could contribute to the interface electrical transport has been discussed also in Refs. 8–11.

Very recently, Li *et al.*[7] probed magnetism through torque magnetometry, which allows detecting directly the magnetic moment of the interface in an external magnetic field H. They found a strong superparamagnetic torque signal in the superconducting state. With the assumption that the signal originates from the STO layer next to the interface, they obtained a magnetic moment M of 0.3–0.4μ_B per unit cell and a collective magnetic moment of the superparamagnetic grains of the order of 1000μ_B. The observation of a superparamagnetic $M(H)$ indicates that ferromagnetic grains form even in the superconducting state. Magnetic oxygen sites at the AlO_2 surface (cf. Ref. 12) and the buildup of triplet coupling of Ti 3*d* states through the oxygen bonds (or possibly vacancies) in the TiO_2 interface plane (cf. Ref. 13) have been proposed[7] as scenarios for the formation of a magnetic state.

The interpretation of the experimental results asks a compelling question: Can the Ti 3*d* orbitals that were identified in the previous band-structure calculations (see, e.g., Refs. 14–22) be responsible both for the metallic and magnetic states coexisting at the same interface? In this Rapid Communication, we present the results of density functional studies which support the existence of a robust ferromagnetic state at the LAO/STO interface induced by oxygen vacancies. We demonstrate that both the magnetism and conductivity occur involving the Ti 3*d* electrons, but the magnetism is due to rather confined electrons around O vacancies while the conductivity is a result of the 2D electron gas caused by electronic reconstruction. We argue that this behavior is a prerequisite of the coexistence of magnetism and superconductivity which are observed at low temperatures.

To explore whether a ferromagnetic state is induced at these interfaces, we consider oxygen vacancies as a mechanism responsible for magnetism. We generate a number of supercells which consist of two symmetric LAO/STO parts, where each part contains a stack of 4-unit-cell (u.c.)-thick LAO layers deposited on a STO slab of a thickness varying between 1.5 and 6 u.c. The interfacial configuration is considered as TiO_2/LaO. The LAO-STO-LAO parts are separated by a 13-Å-thick vacuum sheet. Oxygen vacancies are assumed to lie in the first interfacial TiO_2 layers or in one of the AlO_2 layers of the LAO film. A cell with an oxygen vacancy in MO_2 (M = Ti,Al) is sketched in Fig. 1(b). The vacancy is introduced by excluding the oxygen atom O($a/2$, $b/2$) in the center of the M_2O_4 plaquette. The location of the vacancy at the interface is motivated by the experimental evidence of O vacancies present in STO in samples grown at oxygen pressures below 10^{-5} mbar.[23,24]

Density functional calculations are performed using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof pseudopotential implementation[25] in the

 ©2012 American Physical Society

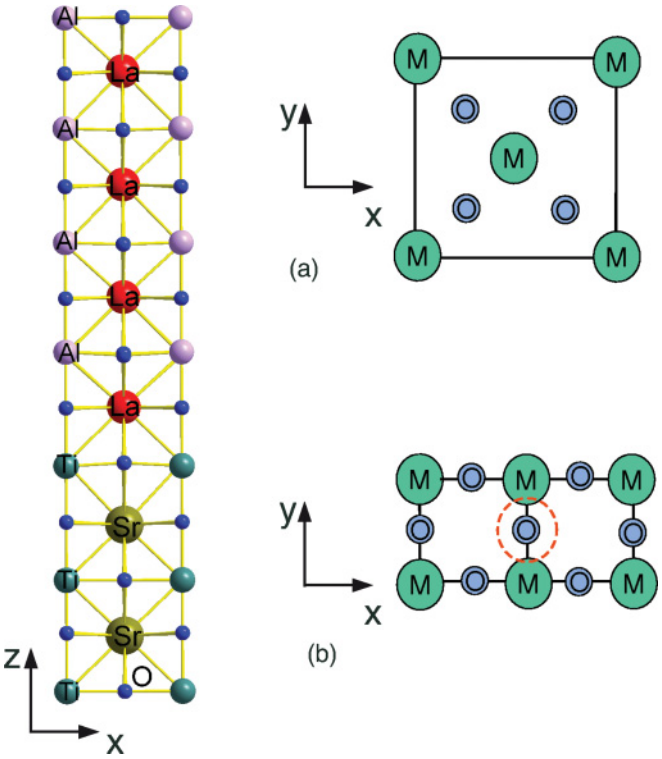

FIG. 1. (Color online) Schematic view of the $SrTiO_3/LaAlO_3$ heterostructure. The supercell contains a 4-unit-cell-thick $LaAlO_3$ layer deposited on a 2.5-unit-cell-thick $SrTiO_3$ slab. The full supercell consists of two symmetric parts of the depicted structure and a vacuum layer of 13 Å. The structures on the right-hand side show (a) a projection of the supercell of STO/LAO on the (x,y) plane of TiO_2, and (b) a M_2O_4 (M = Ti, Al) plaquette generated for the study of the system with O vacancies. The position of an O vacancy is identified by a red dashed circle.

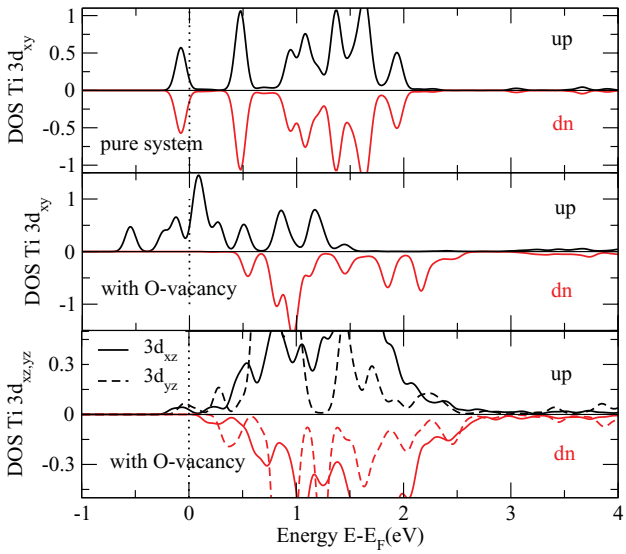

FIG. 2. (Color online) Projected DOS (in eV^{-1}) for $3d$ (t_{2g}) states of the interfacial Ti in the supercell containing 4-unit-cell-thick $LaAlO_3$ layers and a 4-unit-cell-thick $SrTiO_3$ layer. DOS in the pure system and in the system with one O vacancy (25%) per supercell area in the interfacial TiO_2 layer are shown for comparison. The vertical gray line denotes the Fermi level.

QUANTUM ESPRESSO (QE) package.[26] We use a kinetic energy cutoff of 640 eV and the Brillouin zone of the 106- to 166-atom supercells sampled with $5\times5\times1$ to $9\times9\times1$ $\boldsymbol{k}$-point grids. An increase of the $\boldsymbol{k}$-point mesh from $(5\times5\times1)$ to $(7\times7\times1)$ leads to a negligibly small change of the total energy by 0.005 Ry and to an increase of the Ti magnetic moments by small values of $\sim0.05\mu_B$ in the presence of O vacancies. The difference between the Ti magnetic moments for the two different $(2n\times2n\times1)$ and $(n\times2n\times1)$ $\boldsymbol{k}$ meshes for $n=4$ is $\sim0.02\mu_B$, which is a negligibly small value. In our calculations we account for a local Coulomb repulsion of Ti $3d$ electrons by employing a GGA + U approach with $U_{\mathrm{Ti}}=2$ eV.[2] First, we consider pure stoichiometric TiO_2/LaO interfaces as references for the oxygen-doped interfaces. The supercells which contain (2×2) planar unit cells have been structurally relaxed along the z axis by a combination of the optimization procedures of the full potential WIEN2K package and the pseudopotential QE package.[26,27] The in-plane lattice constants have been fixed to their bulk-STO cubic values ($a_{\mathrm{STO}}=b_{\mathrm{STO}}=3.905$ Å). Similar to the previous calculations,[14–19] we find that a metallic state is produced at the LAO/STO interface due to the electronic reconstruction.

Figure 2 presents the projected Ti $3d$ densities of states (DOS) for both spin directions in a system with supercells containing 4 LAO u.c. and 4 STO u.c. along the z direction (the full supercell contains twice the number of LAO unit cells). The difference in the spin-projected DOS implies a nonzero spin polarization. For a pure system without oxygen vacancies, the occupancies of the spin-up and spin-down $3d$ states are almost identical. The maximal magnetic moments of the interface Ti are $\sim0.005\mu_B$ and the polarization from the more distant TiO_2 planes is negligible. The calculated magnetic moment per (1×1) unit cell of the LAO/STO interface is $0.03\mu_B$, which originates mostly from the surface oxygen sites. This polarization is too small to support a robust ferromagnetic state, suggesting that magnetism is not due to the pure interface electron gas.

The situation with O vacancies is different. An oxygen vacancy adds two extra electrons at the interface to preserve charge neutrality. The two electrons are most likely localized in the vicinity of the O vacancy, as found for CaO by Elfimov *et al.*[12] As shown below, this enhances the charge density and increases the exchange splitting of the spin bands; consequently, O vacancies stabilize the ferromagnetic order.

First, we assume that the oxygen vacancy lies within the TiO_2 plane at the interface. In the oxygen-deficient system, we find sizable Ti magnetic moments at the interfacial TiO_2 plane (see Fig. 3). The magnetic moment of the Ti atoms next to the O vacancy is $\sim0.33\mu_B$ and that of the more distant Ti(0,0) atoms at the interfacial plane is $\sim0.34\mu_B$. Magnetic moments on Ti atoms away from the interface are negligible (Fig. 3). We also find a sizable magnetic moment on the AlO_2 surface plane of $\sim-0.18\mu_B$ aligned antiparallel to the magnetic moment of the interface Ti atoms. Needless to say, the concentration of O vacancies in these model structures is far higher than the average density in the experimentally investigated heterostructures. Nevertheless, it is evident that a triplet coupling is induced between the nearest-neighbor Ti

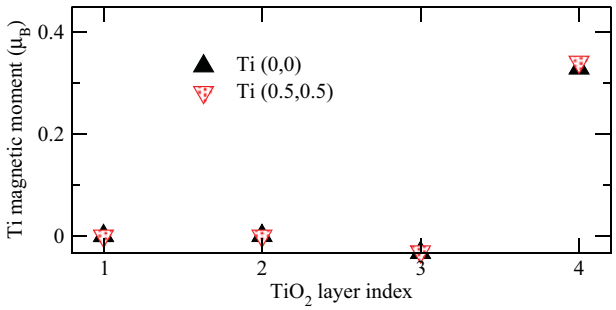

FIG. 3. (Color online) Magnetic moments of Ti atoms in different TiO_2 layers in the (4 u.c.) $SrTiO_3$/(4 u.c.) $LaAlO_3$ structures for the structure with one O vacancy in the interfacial TiO_2 layer. The black up and red down triangles correspond to the two Ti atoms with the planar coordinates (0,0) and ($0.5a$,$0.5a$) in a doubled unit cell of $SrTiO_3$. The TiO_2 layer 4 is the layer next to the interface.

sites and that ferromagnetism is enhanced in O-vacancy-rich regions of the interfacial plane.

The elimination of the central oxygen in the (2×1) configuration results in the formation of stripes of O vacancies along the y direction, characterized by two vacancies near Ti ($0.5a$,0) and no vacancies near the Ti (0,0) atom. To test the stability of such an "inhomogeneous" distribution of O vacancies, we have also performed GGA + U calculations of a supercell with an ordered "homogeneous" arrangement of the vacancies corresponding to exactly one vacancy per each Ti atom. This can be obtained by elimination of one oxygen in the square $(\sqrt{2} \times \sqrt{2})$ supercell shown in Fig. 1(a). The comparison of the calculated total energy with the energy for that of the (2×1) supercell [Fig. 1(b)], both containing a 4-u.c.-thick STO layer, gives an energy gain of ~0.25 eV per interface unit cell, which indicates a tendency toward an inhomogeneous spatial distribution of oxygen vacancies in LAO/STO.

It is expected that areas with an increased density of oxygen vacancies allow for the formation of ferromagnetic puddles, as was recently observed by Bert *et al.*[28] Their respective collective magnetic moments are a likely candidate for the source of the superparamagnetic behavior observed by Li *et al.*[7] As compared to the ferromagnetically ordered structure, the total energy of the (2×1) configuration with an antiferromagnetically ordered interface increases by 0.36 eV/u.c., which implies a high stability of the ferromagnetic state.

The ferromagnetic ordering can be examined in the framework of the Stoner model for ferromagnetism. This model treats the stabilization of the ferromagnetic state as a result of the difference between the reduction of the Coulomb interaction for the $3d$ electrons with parallel spins of neighboring Ti ions and the increase of the kinetic energy caused by the widening of the $3d$ bands for the electrons of the same spin.[21] The condition for the appearance of ferromagnetism is based on the Stoner criterion $I\rho(\varepsilon_F) > 1$. The interaction $I = \Delta/m$ parametrizes the exchange splitting Δ, and m is the magnetic moment of Ti in the ferromagnetic state (per μ_B); $\rho(\varepsilon_F)$ is the paramagnetic density of states at the Fermi level. The parameters appearing in the Stoner criterion are derived from the results of the GGA + U calculations and are presented in Table I. The Stoner condition is satisfied irrespective

TABLE I. Calculated magnetic moments of interface Ti ions nearest to the O vacancy, the exchange splitting (Δ), and the parameter $I\rho(\varepsilon_F)$ of the Stoner criterion for $(LaAlO_3)_4/(SrTiO_3)_n$ heterostructures with different n.

n	m_{Ti} (μ_B)	Δ (eV)	$I\rho(\varepsilon_F)$
1.5	0.31	1.15	3.89
2.5	0.33	0.82	1.26
3.5	0.34	0.98	1.64

of the thickness of the STO layer, which implies that the ferromagnatic state is favorable in these systems, although the magnetic moment and exchange splitting slightly decrease with increasing STO thickness, consistent with Ref. 21. The excess $3d$ charge in the vacancy-doped supercells leads to a substantial increase of $\rho(\varepsilon_F)$ up to ~1.5–1.8 eV^{-1} as compared to the pure systems with $\rho(\varepsilon_F) \approx 0.5$–$0.7$ eV^{-1}. The enhanced $\rho(\varepsilon_F)$ contributes to the strong increase of the Ti magnetic moments in the oxygen-deficient systems.

O vacancies strongly influence the electronic structure of the Ti $3d$ states: The excess charge originating from the eliminated O atom in the interfacial TiO_2 plane leads to a redistribution in the occupancy of the five $3d$ orbitals. The contribution of the $3d$ e_g orbitals to the magnetic moment formation is rather insignificant. In contrast, a substantial amount of excess electron charge is transferred to the t_{2g} spin-up orbitals (Fig. 2). In a (2×1) unit cell, the location of the O vacancy along the y direction between the two Ti atoms [see Fig. 1(b)] leads to symmetry breaking, splitting the two t_{2g} ($3d_{yz}$ and $3d_{xz}$) orbitals. Due to the random distribution of O vacancies along the x and y directions in LAO/STO samples, the electron charge is assumed to occupy both the $3d_{yz}$ and the $3d_{xz}$ state, yet the dominant contribution to the magnetic moment has to be ascribed to the $3d_{xy}$ spin-up occupancy.

Oxygen vacancies may appear not only at the interfacial TiO_2 layer but also on the surface and in the bulk of the LAO layer. Consistent with previous calculations,[29] we find that the lowest total energy is achieved with the vacancy located in the top AlO_2-surface layer [Fig. 4(b)], with an energy gain of ~1.5 eV as compared to a vacancy in the interface TiO_2 layer. The 25% concentration of surface vacancies produces two electrons per (2×1) unit cell, with one electron transferred to the interface and another one hybridized at the AlO_2 surface close to a central O vacancy, similarly to Ref. 12. Our calculations show that the placement of an O vacancy in the AlO_2 planes of the LAO layer still induces a significant magnetic moment on the interface Ti atoms [Fig. 4(a)]. This magnetic moment originates from the spin polarization of the occupied Ti $3d$ states due to the electron charge transferred from the O-vacancy site. Interestingly, when the O vacancy lies close to the surface of LAO, we find a sizable magnetic moment in the AlO_2 layer with the O vacancy [Fig. 4(a)], similarly to that obtained when the O vacancy is placed in the interfacial TiO_2 layer. This magnetic moment is due to the exchange splitting of the not fully occupied local oxygen-vacancy-centered state of a mixed Al s-p character which produces quasi-one-dimensional electronic bands and

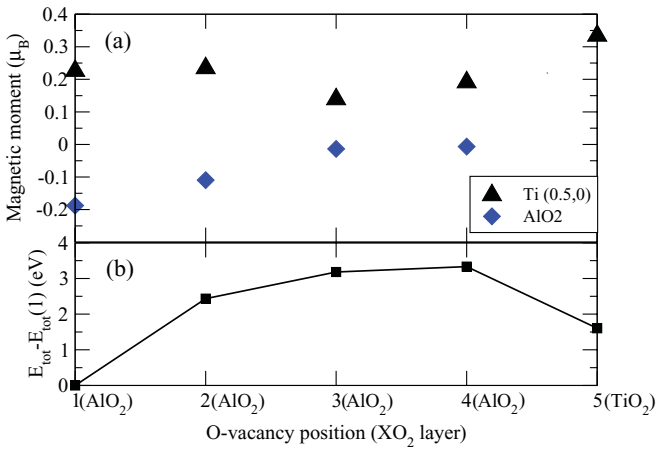

FIG. 4. (Color online) (a) Magnetic moments of the interface Ti and AlO_2 layer (per u.c.) in (2 STO)/(4 LAO) supercells with a change of the position of the O vacancy along the (001) direction between the top AlO_2 layer (left) and interface TiO_2 (right). (b) Variation of the total energy $E_{tot} - E_{tot}(1)$ with the change of the position of the O vacancy along the (001) direction. Here $E_{tot}(1)$ is the total energy for the system with an O vacancy located in the top AlO_2 surface.

ferromagnetic moments in the AlO_2 layer antiparallel to that of the interface Ti atom.[30]

Recent studies of the LAO/STO interfaces distinguish two different types of charge carriers in terms of the interfacial localized Ti 3*d* electrons and the mobile $3d_{xy}$ electrons of several distant Ti layers,[10] or they relate magnetism to the interfacial electrons produced by the electronic reconstruction and associate superconductivity to the charge carriers induced by O vacancies.[6] Our findings offer the perspective that both the magnetism and the superconductivity are due to the interfacial Ti 3*d* electrons. The magnetism, however, is a result of the spin splitting of the populated electronic states induced by O vacancies, while the metallic behavior of the interface results from the 2D electron liquid caused by the electronic reconstruction. The metallic state has been related to a superconducting state below 300 mK, and the predicted scenario suggests that the corresponding charge carriers move in regions of small or vanishing O-vacancy concentrations.

Note added. After the submission of the manuscript, we were informed that Bert *et al.*[28] had in fact observed submicrometer puddles of ferromagnetism in the presence of the superconducting state at the $LaAlO_3/SrTiO_3$ interface. An alternative scenario has been proposed recently by Michaeli *et al.*,[31] who suggest a homogeneously polarized interface layer which is magnetically coupled to a second superconducting layer.

The authors acknowledge helpful discussions with R. Ashoori, I. S. Elfimov, S. S. Jaswal, Lu Li, L. Klein, I. V. Stasyuk, and S. Seri. This work was supported by the DFG (TRR 80), the EC (oxIDes), Nebraska MRSEC (NSF DMR-0820521), NSF-EPSCoR (EPS-1010674), the A. von Humboldt Foundation, and the Ministry of Education and Science of Ukraine (Grant No. 0110U001091). Financial support from the CFI, NSERC, CRC, and the Max Planck-UBC Centre for Quantum Materials are gratefully acknowledged. Grants of computer time from the Leibniz-Rechenzentrum München through the HLRB project h1181 are thankfully acknowledged.

[1] A. Ohtomo and H. Hwang, Nature (London) **427**, 423 (2004).
[2] M. Breitschaft, V. Tinkl, N. Pavlenko, S. Paetel, C. Richter, J. R. Kirtley, Y. C. Liao, G. Hammerl, V. Eyert, T. Kopp, and J. Mannhart, Phys. Rev. B **81**, 153414 (2010).
[3] H. W. Jang, D. A. Felker, C. W. Bark, Y. Wang, M. K. Niranjan, C. T. Nelson, Y. Zhang, D. Su, C. M. Folkman, S. H. Baek, S. Lee, K. Janicka, Y. Zhu, X. Q. Pan, D. D. Fong, E. Y. Tsymbal, M. S. Rzchowski, and C. B. Eom, Science **331**, 886 (2011).
[4] N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, Science **317**, 1196 (2007).
[5] A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, Nat. Mater. **6**, 493 (2007).
[6] D. A. Dikin, M. Mehta, C. W. Bark, C. M. Folkman, C. B. Eom, and V. Chandrasekhar, Phys. Rev. Lett. **107**, 056802 (2011).
[7] Lu Li, C. Richter, J. Mannhart, and R. C. Ashoori, Nat. Phys. **7**, 762 (2011).
[8] S. S. A. Seo, Z. Marton, W. S. Choi, G. W. J. Hassink, D. H. A. Blank, H. Y. Hwang, T. W. Noh, T. Egami, and N. H. Lee, Appl. Phys. Lett. **95**, 082107 (2009).
[9] T. Fix, F. Schoofs, J. L. MacManus-Driscoll, and M. G. Blamire, Phys. Rev. Lett. **103**, 166802 (2009).
[10] Z. S. Popovic, S. Satpathy, and R. M. Martin, Phys. Rev. Lett. **101**, 256801 (2008).
[11] Ariando, X. Wang, G. Baskaran, Z. Q. Liu, J. Huijben, J. B. Yi, A. Annadi, A. R. Barman, A. Rusydi, S. Dhar, Y. P. Feng, J. Ding, H. Hilgenkamp, and T. Venkatesan, Nat. Commun. **2**, 188 (2011).
[12] I. S. Elfimov, S. Yunoki, and G. A. Sawatzky, Phys. Rev. Lett. **89**, 216403 (2002).
[13] B. Lau, M. Berciu, and G. A. Sawatzky, Phys. Rev. Lett. **106**, 036401 (2011).
[14] R. Pentcheva and W. E. Pickett, Phys. Rev. B **74**, 035112 (2006); Phys. Rev. Lett. **102**, 107602 (2009).
[15] N. Pavlenko and T. Kopp, Surf. Sci. **605**, 1114 (2011).
[16] Z. S. Popovic and S. Satpathy, Phys. Rev. Lett. **94**, 176805 (2005).
[17] S. Okamoto, A. J. Millis, and N. A. Spaldin, Phys. Rev. Lett. **97**, 056802 (2006).
[18] J. Lee and A. A. Demkov, Phys. Rev. B **78**, 193104 (2008).
[19] K. Janicka, J. P. Velev, and E. Y. Tsymbal, Phys. Rev. Lett. **102**, 106803 (2009).
[20] I. Gonzales, S. Okamoto, S. Yunoki, A. Moreo, and E. Dagotto, J. Phys. Condens. Matter **20**, 264002 (2008).
[21] K. Janicka, J. P. Velev, and E. Y. Tsymbal, J. Appl. Phys. **103**, 07B508 (2008).
[22] Z. Zhong and P. J. Kelly, Europhys. Lett. **84**, 27001 (2008).

[23]G. Herranz, M. Basletic, M. Bibes, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzic, J.-M. Broto, A. Barthelemy, and A. Fert, Phys. Rev. Lett. **98**, 216803 (2007).

[24]A. Kalabukhov, R. Gunnarsson, J. Borjesson, E. Olsson, T. Claeson, and D. Winkler, Phys. Rev. B **75**, 121404(R) (2007).

[25]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[26]P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys. Condens. Matter **21**, 395502 (2008).

[27]P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Wien, TU Wien, Austria, 2001).

[28]J. A. Bert, B. Kalisky, C. Bell, M. Kim, Y. Hikita, H. Y. Hwang, and K. A. Moler, Nat. Phys. **7**, 767 (2011).

[29]L. Zhang, X. F. Zhou, H. T. Wang, J. J. Xu, J. Li, E. G. Wang, and S. H. Wei, Phys. Rev. B **82**, 125412 (2010).

[30]The details of the spin and charge distribution will be published separately.

[31]K. Michaeli, A. C. Potter, and P. A. Lee, e-print arXiv:1107.4352.