# Magnetic and superconducting phases at the $LaAlO_3$–$SrTiO_3$ interface

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The formation of a metallic state at the interface of the bulk insulators $LaAlO_3$ and $SrTiO_3$ [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. The correlations not only induce a superconducting state but also support magnetism. An unexplained phenomenon is the coexistence of magnetism and superconductivity in the 2D electron liquid.

Recently, Li *et al*. [2] 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 $SrTiO_3$ layer next to the interface, they obtained a magnetic moment $M$ of 0.3–0.4 $\mu_B$ per unit cell and a collective magnetic moment of the superparamagnetic grains of the order of 1000 $\mu_B$. 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 and the buildup of triplet coupling of Ti 3$d$ states through the oxygen bonds (or possibly vacancies) in the $TiO_2$ interface plane have been proposed as scenarios for the formation of a magnetic state.

The interpretation of the experimental results leads to a compelling question: Can the Ti 3$d$ orbitals that were identified in the previous band-structure calculations be responsible both for the metallic and magnetic states coexisting at the same interface? To answer this question, we performed density-functional studies. These support the existence of a robust ferromagnetic state at the $LaAlO_3$–$SrTiO_3$ interface induced by oxygen vacancies. We demonstrate that both the magnetism and conductivity occur by 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 liquid 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 considered oxygen vacancies as a mechanism responsible for magnetism [3]. We generated a number of supercells which consist of two symmetric $LaAlO_3$–$SrTiO_3$ parts, where each part contains a stack of 4-unit-cell (u.c.)-thick $LaAlO_3$ layers deposited onto a $SrTiO_3$ slab of a thickness varying between 1.5 and 6 u.c. The interfacial configuration is considered as $TiO_2$–LaO (see Fig. 1). The $LaAlO_3$–$SrTiO_3$–$LaAlO_3$ 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 $LaAlO_3$ 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 choice of the vacancy location at the interface is motivated by the experimental evidence of oxygen vacancies present in $SrTiO_3$ samples grown at oxygen pressures below $10^{-5}$ mbar.

Density-functional calculations were performed using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof pseudopotential implementation in the QUANTUM ESPRESSO package [3]. We use a kinetic energy cutoff of 640 eV and the Brillouin zone of the 106 to 166-atom supercells sampled with 5×5×1 to 9×9×1 $k$-point grids. In our calculations we account for a local Coulomb repulsion of Ti 3$d$ electrons by employing a GGA+$U$ approach with $U_{Ti}$ = 2 eV. 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. The in-plane lattice constants have been fixed to their bulk-$SrTiO_3$ cubic values ($a_{SrTiO3}$ = $b_{SrTiO3}$ = 3.905 Å). Similar to the previous calculations, we find that a metallic state is produced at the $LaAlO_3$–$SrTiO_3$ interface due to the electronic reconstruction [3].

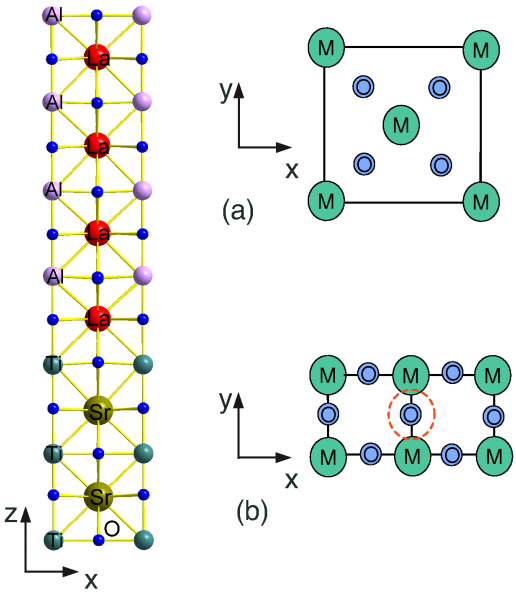


Figure 1: Schematic view of the $SrTiO_3$–$LaAlO_3$ heterostructure. The supercell contains a 4-unit-cell-thick $LaAlO_3$ layer deposited on a 2.5-unit-cell-thick $SrTiO_3$ slab. The full supercell consists of two symmetric parts of the depicted structure and a vacuum layer of 13 Å. The structures on the right-hand side show (a) a projection of the supercell of $SrTiO_3$–$LaAlO_3$ 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 (from [3]).

Figure 2 presents the projected Ti 3*d* density-of-states (DOS) for both spin directions in a system with supercells containing four $LaAlO_3$ and four $SrTiO_3$ unit cells along the $z$ direction (the full supercell contains twice the number of $LaAlO_3$ unit cells). The difference in the spin-projected DOS implies a non-zero spin polarization. For a pure system without oxygen vacancies, the occupancies of the spin-up and spin-down 3*d* states are almost identical. The maximal magnetic moments of the interface Ti are ~0.005 $\mu_B$ and the polarization from the more distant $TiO_2$ planes is negligible. The calculated magnetic moment per (1×1) unit cell of the $LaAlO_3$–$SrTiO_3$ 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 oxygen 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 oxygen vacancy. As shown below, this enhances the charge density and increases the exchange splitting of the spin bands; consequently, oxygen vacancies stabilize the ferromagnetic order [3].

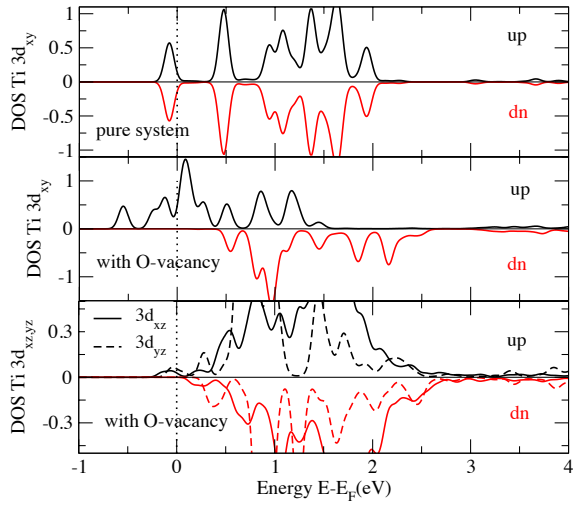


Figure 2: Projected DOS (in $eV^{-1}$) for 3*d* ($t_{2g}$) states of the interfacial Ti in the supercell containing 4-unit-cell-thick $LaAlO_3$ layers and a 4-unit-cell-thick $SrTiO_3$ layer. DOS in the pure system and in the system with one O vacancy (25%) per supercell-area in the interfacial $TiO_2$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

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 oxygen vacancy is ~ 0.33 $\mu_B$ and that of the more dis-

tant Ti (0,0) atoms at the interfacial plane is ~ 0.34 $\mu_B$. 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 ~ -0.18 $\mu_B$ aligned antiparallel to the magnetic moment of the interface Ti atoms. Needless to say, the concentration of oxygen 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 sites and that ferromagnetism is enhanced in oxygen-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 oxygen vacancies along the $y$ direction, characterized by two vacancies near Ti (0.5 $a$, 0) and no vacancies near the Ti (0, 0) atom. To test the stability of such an "inhomogeneous" distribution of oxygen 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 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 $SrTiO_3$ 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 $LaAlO_3$–$SrTiO_3$.

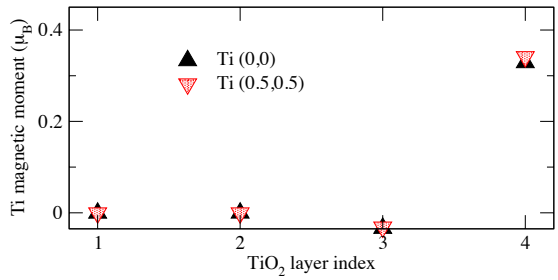


Figure 3: Magnetic moments of Ti atoms in different $TiO_2$ layers in the (4 u.c.) $SrTiO_3$–(4 u.c.) $LaAlO_3$ structures for the structure with one O vacancy in the interfacial $TiO_2$ layer. The black up and red down triangles correspond to the two Ti atoms with the planar coordinates (0, 0) and (0.5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

Oxygen vacancies strongly influence the electronic structure of the Ti 3$d$ states: The excess charge originating from the eliminated oxgen atom in the interfacial $TiO_2$ plane leads to a redistribution in the occupancy of the five 3$d$ orbitals. The contribution of the 3$d$ $e_g$ orbitals to the magnetic moment formation is rather insignificant. In contrast, the dominant contribution to the magnetic moment has to be ascribed to the $t_{2g}$ 3$d_{xy}$ spin-up occupancy.

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 oxygen 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 oxygen-vacancy concentrations.

**References:**

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[3] *Pavlenko, N., T. Kopp, E.Y. Tsymbal, G.A. Sawatzky, and J. Mannhart.* Physical Review B **85**, 020407(R) (2012).

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