Oxygen vacancy clustering and pseudogap behaviour at the LaAlO$_3$/SrTiO$_3$ interface

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Abstract

The two-dimensional electron gas at the LaAlO$_3$/SrTiO$_3$ interface promises to add a new dimension to emerging electronic devices due to its high degree of tunability. Defects in the form of oxygen vacancies in titanate surfaces and interfaces, on the other hand, play a key role in the emergence of the ordered states and their tunability at the interface. On the basis of an effective model, we study the influence of oxygen vacancies on the superconductivity and ferromagnetism at the LaAlO$_3$/SrTiO$_3$ interface. Using the Bogoliubov–de Gennes formulation in conjunction with Monte Carlo simulation, we find a clustering of the oxygen vacancies at the interface that favours the formation of coexisting ferromagnetic puddles spatially separated from the superconductivity. We also find a carrier freeze-out at low temperatures, observed experimentally in a wide variety of samples. A sufficiently large amount of oxygen vacancies leads to pseudogap-like behaviour in the superconducting state.

Keywords: superconducting film, disorder effects, pseudo-gap superconductivity

(Some figures may appear in colour only in the online journal)

1. Introduction

The discovery of a two-dimensional electron gas (2DEG) at the (001) interface of two oxide insulators, SrTiO$_3$ and LaAlO$_3$ [1], is hailed as unique, due to the gamut of novel properties that it has thrown up: low temperature superconductivity (below 200 mK) [2, 3], coexistence of superconductivity and ferromagnetism [4, 5], electric field-induced metal–insulator transition [6–8] and superconductor–insulator transition [9]. The 2DEG at the interface is formed as a result of an intrinsic electronic transfer process, known as the polar catastrophe mechanism, occurring to nullify a charge discontinuity at the interface [10–12]. The 2DEG is lying in a material which is more complex than simple semiconductors and thus the ground state phase diagram consists of several competing phases which can be turned ON or OFF by changing some external parameters such as the gate voltage or magnetic field. The excellent tunability of the 2DEG makes the LaAlO$_3$/SrTiO$_3$ interface an important material for future electronic devices [13–15]. However intrinsic defects such as the oxygen vacancies, created during the deposition process, can influence several properties and thus deserve serious attention while designing such devices. The oxygen vacancies contribute electrons to the interface [16–18] that are responsible for metallic conduction for amorphous samples [19, 20]. Annealing in the presence of oxygen destroys these vacancies, degrading the mobility of carriers, while both crystalline and amorphous samples which are not annealed show a carrier freeze-out below 100 K [19, 21]. The critical LaAlO$_3$ thickness (four unit cells for crystalline samples) for the appearance of metallicity decreases with increase in the oxygen vacancies [19].

Besides the modulation of electronic properties, the oxygen vacancies have a significant influence on the magnetic properties as well. Density functional theory suggests that magnetism is not an intrinsic property of the interface electrons; it is caused by the spin-splitting of the populated electronic states induced by the oxygen vacancies in the SrTiO$_3$ or LaAlO$_3$ layer [22]. Oxygen annealing results in a quenching of the magnetic moment, observed in
Figure 1. (a) Initial and (b) final vacancy configurations with vacancy concentration \( f = 0.1 \) (left column) and \( f = 0.2 \) (right column). (c) and (d) show the profiles of the local pairing amplitude and on-site magnetization respectively. Parameters used: \( \mu = 0 \), \( \alpha = 0.8 \) and \( H_x = 0.5 \).

x-ray magnetic circular dichroism (XMCD) measurements [23]—an indication that the electrons donated by oxygen vacancies are essentially localized at the interface. According to Pavlenko et al [24], the oxygen vacancies at the interface lead to an interplay of ferromagnetic order in the itinerant \( t_{2g} \) bands and complex magnetic oscillations in the orbitally reconstructed \( e_g \) bands.

However, it is important to study the effect of oxygen vacancies on the superconducting state as well, since a competing ferromagnetic order is present with non-zero vacancy concentration.

Our analysis, based on a BdG formalism, followed by Monte Carlo simulation for the superconducting state, reveals a clustering of oxygen vacancies in the two-dimensional (2D) plane at very low temperatures. Superconductivity is affected by the oxygen vacancies in a non-trivial way. In the clustered regions, superconductivity is destroyed locally and ferromagnetic puddles are formed. As we argue here, the carrier freeze-out effect observed in the samples might be related to the clustering of the vacancies within the interface. The local density of states (LDOS) shows a strong dependence on the vacancy concentration along with the emergence of a pseudogap-like behaviour.

2. The model and method

The 2DEG is formed via the polar catastrophe mechanism in the terminating TiO\(_2\) layer at the interface. The interface electrons occupy the \( t_{2g} \) bands of Ti atoms and are responsible for the ferromagnetism and superconductivity at the interface. The \( d_{xy} \) band has a bandwidth twice that of \( d_{xz} \) or \( d_{yz} \) and is located lower in energy, at the \( \Gamma \) point. Hence electrons occupying this band are expected to be localized due to the Coulomb repulsion at the interface. These localized electrons interact with the conduction electrons via a ferromagnetic exchange, modelled by a Zeeman field parallel to the interface plane [25, 26]. In fact, recent spectroscopic studies revealed direct evidence for ferromagnetism of \( d_{xy} \) character in the plane [25].

Superconductivity originates from the usual phonon-mediated electron–electron pairing as in doped SrTiO\(_3\) substrates [27, 28]. The highly broken inversion symmetry at the interface plane leads to a large Rashba spin–orbit (SO) interaction which modifies the electronic bands and pairing symmetry of the superconducting state [26]. The in-plane Zeeman field brings about an asymmetry in the two-sheeted Fermi surface (created by the SO interaction) and favours a finite-momentum pairing of the electrons.

Motivated by this phenomenology and electronic structure, we consider the following Hamiltonian for a Rashba SO coupled superconductor in the presence of a uniform in-plane Zeeman field and oxygen vacancies [25, 26]:

\[
\mathcal{H} = -t \sum_{i,j>\sigma} (c_i^\dagger \sigma c_{j\sigma} + h.c.) - \sum_{i,\sigma} (\mu - V \delta_i) c_i^\dagger \sigma c_i^\sigma \\
- H_x \sum_{i,\sigma,\sigma'} (\sigma_i^\sigma \sigma_i^{\sigma'} c_{i\sigma}^\dagger d_{i\sigma'} + \sum r (c_{r\sigma}^\dagger d_{i\sigma r}) + h.c.) \\
- \frac{\alpha}{2} \sum_{i,j>\sigma,\sigma'}(\sigma_i^\sigma \sigma_j^{\sigma'}) c_i^\dagger \sigma c_j^\sigma
\]

where \( t \) is the hopping amplitude (set to 1 as the unit of energy) on a 2D square lattice, \( H_x \), chosen along the \( x \) direction without loss of generality, is the in-plane Zeeman field, \( \alpha \) is the Rashba SO coupling strength, \( d_{ij} \) is a vector connecting sites \( i \) and \( j \), and the \( \sigma \) are the Pauli matrices. The parameter \( \delta_i \) represents the location of oxygen vacancies, being 1 for sites with an oxygen vacancy and 0 otherwise, with a defect state described as a local shift \( V \) in the chemical potential \( \mu \). Since the oxygen vacancies are predominantly pinned at the interface TiO\(_2\) layer due to energy balance, it is reasonable to ignore the small level of three-dimensional diffusion of the vacancies and study the dynamics of the vacancies in the 2D plane only. In the following analysis, we work at half-filling, as superconductivity has maximum stability there (we checked other fillings). It is also assumed that the effect of the oxygen vacancy is the same at all vacancy sites and take \( V = 2 \) throughout. We checked that the underlying physics, under the approximations, remains qualitatively similar for a range of
values of \( V \). The local superconducting pairing amplitude is defined as \( \Delta(r_i) = -(c_{i\uparrow}c_{i\downarrow}) \).

The Hamiltonian (2) is diagonalized using a spin-generalized Bogoliubov–Valatin transformation \( \tilde{c}_{n\sigma}(r_i) = \sum_{i,a} u_{n\sigma}(r_i) \tilde{f}^\dagger_{n\sigma} + v_{n\sigma}(r_i) \tilde{f}_{n\sigma}^\dagger \), which gives the local pairing gap in terms of Bogoliubov amplitudes \( u_{n\sigma}(r_i) \) and \( v_{n\sigma}(r_i) \) as

\[
\Delta(r_i) = -\sum [u_{n\uparrow}(r_i)u_{n\downarrow}^*(r_i)(1-f(E_n)) + u_{n\downarrow}(r_i)u_{n\uparrow}^*(r_i)f(E_n)]
\]

where \( f(x) = 1/(1 + e^{x/T}) \) is the Fermi function at temperature \( T \). The in-plane magnetization density and occupation number are obtained via

\[
m(r_i) = \frac{1}{2} \{ c_{i\uparrow}^\dagger c_{i\uparrow} + c_{i\downarrow}^\dagger c_{i\downarrow} \} = \sum_{n,\sigma} u_{n\sigma}^* u_{n\sigma} f(E_n)
\]

\[
n(r_i) = \sum_{\sigma} \{ c_{i\sigma}^\dagger c_{i\sigma} \} = \sum_{n,\sigma} \{ (u_{n\sigma}^2 f^2(E_n) + v_{n\sigma}^2(1-f^2(E_n))) \}.
\]

The quasiparticle amplitudes \( u_{n\sigma}(r_i) \) and \( v_{n\sigma}(r_i) \) are determined by solving the BdG equations

\[
\mathcal{H} \phi_n(r_i) = \epsilon_n \phi_n(r_i)
\]

where \( \phi_n = [u_{n\uparrow}(r_i), u_{n\downarrow}(r_i), v_{n\uparrow}(r_i), v_{n\downarrow}(r_i)] \).

The local order parameters are solved self-consistently on a finitely large square lattice with periodic boundary conditions and finally the average values are calculated. The oxygen vacancy configuration is annealed via a Monte Carlo simulation, starting from a high temperature, in which the free energy is updated using the eigenvalues of the BdG Hamiltonian. As temperature went down, a larger number of Monte Carlo steps were performed, each step allowing one oxygen vacancy to move to one of its nearest neighbours non-vacant sites, following the standard Metropolis algorithm (with charged impurities, long-range transfer of vacancies is highly unlikely, even at higher temperatures).

Each MC step then involves solving of the BdG equations, followed by a random change in vacancy configuration as above. For low temperatures, the superconducting and ferromagnetic properties are calculated.

3. Results and discussion

The Monte Carlo annealing shows a tendency towards bunching of the oxygen vacancies, as shown in figure 1, panels (a) and (b), which turns out to be crucial in establishing a ferromagnetic order.

One oxygen vacancy adds two additional electrons to the interface which are then pinned near the vacant sites. However, a considerable concentration of vacancies is required for the emergence of overall ferromagnetism [24, 26]. Such defect-induced ferromagnetism is also observed in bulk SrTiO\(_3\) substrate, attesting to the connection between the level of impurity and the observed ferromagnetism [29, 30]. In the clustered regions, the pairing gap collapses due to large fluctuations in the local electron density, and the localized moments, originating from the oxygen vacancies, order to form ferromagnetic puddles, as shown in figures 1(c) and (d). The clustering of vacancies implies a spatial phase separation of the superconductivity and ferromagnetism, allowing them to coexist at the interface [31], and can be detected by positron annihilation spectroscopy [32] or NMR experiments [33].

The oxygen vacancies disrupt the lattice and effectively act as localized centres with enhanced scattering of electrons, which is stronger at higher temperatures. At high temperatures, predictably, there is no evidence of ordering or bunching of the vacancies.

At low temperatures, the vacancies tend to form clusters as depicted in figure 2, where we plot the temperature variation of the nearest neighbour vacancy–vacancy correlation function \( D_{NN} = \frac{1}{N} \sum_{\langle ij \rangle} V_i V_j \), where \( V_i, V_j \) are impurity potentials at sites \( i, j \) respectively. This behaviour is more prominent with a sufficiently large number of vacancies. Mannhart et al [34] found, from a second-harmonic generation experiment, that the impurity signal maximizes for LaAlO\(_3\) film of the thickness of one unit cell, and proposed a possible explanation via uncompensated polar distortion. The above results show that a clustering of the oxygen vacancies may be possible within the two-dimensional TiO\(_2\) layer even without a polar distortion. With increasing vacancy concentration \( f \), the mean pairing gap reduces while the average magnetic moment increases, as shown in figure 3.

At a finite vacancy concentration, both the superconducting pairing (figure 3(a)) and the ferromagnetic order (figure 3(b)) are quite sensitive to the Rashba SO interaction, since the spin precession due to Rashba coupling is strongly affected by scattering from the defects created by the oxygen vacancies. The temperature dependence of the superconductivity and ferromagnetism with changing oxygen vacancy level is shown in figure 4. Below a superconducting transition at \( T_c = 0.8 \), superconductivity and ferromagnetic order coexist.
The average magnetization shows a peak at $T_c$ which is determined by the interplay of superconductivity and ferromagnetism, and reflects an electronic phase separation. Below $T_c$, there is an inhomogeneous mixture of superconductivity and ferromagnetism in mutually excluded regions in the plane, and magnetism appears in the form of robust ferromagnetic puddles in the regions of the clustering of oxygen vacancies, where the superconductivity has been degraded. Thus the average moment increases with increasing vacancy concentration. On the other hand, beyond $T_c$, the in-plane Zeeman field gives rise to a ferromagnetic order which pervades the two-dimensional plane. The long tail in figure 4(c) implies that the ferromagnetism is extended up to temperatures well beyond $T_c$, which has also been reported experimentally [5].

Both crystalline and amorphous interfaces, as well as oxygen-deficient SrTiO$_3$ substrates, exhibit a carrier freeze-out below $\sim 100$ K [19, 35, 36] following the empirical relation $n \propto e^{-\epsilon/k_B T}$, up to very low temperatures, where $\epsilon$ is the activation energy for oxygen vacancy formation (about 4.2 meV for oxygen-deficient SrTiO$_3$ and 0.5 meV for an oxygen-annealed LaAlO$_3$/SrTiO$_3$ interface). This carrier freezing effect is very important and sometimes leads to a metal–insulator transition [21]. We observe a similar behaviour for the carrier concentration in our analysis as the temperature is lowered, shown in figure 4(b). Clearly, the $T = 0$ value of the carrier concentration is strongly defect-limited as well.

The superconducting properties depend sensitively on the stoichiometry and subsequent ordering of oxygen vacancies, as reported from some earlier experimental studies [37, 38]. Oxygen vacancies destroy the superconducting order locally (figure 1(c)). In figure 5, we show the density of states of the system for a range of vacancy concentrations. As the oxygen vacancy concentration is increased gradually, the superconducting energy gap closes and a pseudogap-like feature shows up. Recent tunnelling spectra measurements [39] revealed a pseudogap behaviour of the interface superconductivity similar to that for the high $T_c$ cuprates. Since oxygen vacancies are an inalienable part of SrTiO$_3$ substrates, the pseudogap is expected to be present in any SrTiO$_3$-based interface superconductor with broken inversion symmetry. With increasing vacancy concentration, there is a pile-up of the states at around $-2$ eV (figure 5), reflecting the pinning at the vacancy potential; oxygen vacancies affect all vacancy sites uniformly in our model (2). There is a gradual shift of the states to lower energies with increasing oxygen vacancy level, and in realistic situations the peak around $-2$ eV will get broadened due to the spread in the vacancy potential.

4. Conclusion

Oxygen vacancies at the interface constitute a key ingredient of the LaAlO$_3$/SrTiO$_3$ interface and play a major role in the
emergence of coexisting ferromagnetism and superconductivity. The Monte Carlo method coupled to the BdG mean-field formalism captures the essential features of the inhomogeneous system. The Rashba SO interaction, originating from the highly broken inversion symmetry, creates helical bands in which the electron spins are aligned to essentially render the superconductivity a chiral $p_x \pm ip_y$-wave one. Following Michaeli et al [40], we assume that there are localized electrons from the $d_{xy}$ band acting as localized moments and interacting with the conduction electrons via a ferromagnetic exchange (modelled as a uniform Zeeman field parallel to the interface plane). The conventional wisdom is that electrons cannot be both ferromagnetically ordered and superconducting simultaneously. Here, the defects in the form of oxygen vacancies play a crucial role in stabilizing a robust ferromagnetism and, hence, the coexistence of the two competing orders. Although there can certainly be effects of oxygen vacancies at the layers just above or below the interface plane which is TiO$_2$ terminated, our calculations show that a clustering of the vacancies in the 2D plane at very low temperatures is possible, with significant implications. This helps to establish long-range ferromagnetic order in the regions where superconductivity is locally degraded. It also sheds light on the carrier freeze-out effect observed experimentally as the temperature is reduced. With increasing vacancy concentration, pseudogap states appear in the properties of field-effect devices fabricated using LaAlO$_3$/SrTiO$_3$ heterostructures.

Although the formation of the 2DEG is analogous to that in semiconductor heterostructures by modulation doping, the physics at the interfaces of perovskite compounds is much richer than that at semiconductor interfaces due to the correlated nature of the electrons. In the LaAlO$_3$/SrTiO$_3$ interface, the nominal pair of electrons coming from each oxygen vacancy is localized near the Ti ions due to Coulomb correlation and gives rise to a finite magnetic moment at the interface. As we have shown in the calculation, the clustering of the vacancies leads to the formation of ferromagnetic puddles, which makes the LaAlO$_3$/SrTiO$_3$ interface very special and different from other interfaces. However, we expect similar clustering effects in other SrTiO$_3$-based interfaces like LaTiO$_3$/SrTiO$_3$ or GdTiO$_3$/SrTiO$_3$ where a similar 2DEG has been reported to be present.

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