

Toward High Temperature Quasi-two-dimensional Superconductivity

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The demonstration of a quasi-two-dimensional electron gas (2DEG) and superconducting properties in LaAlO₃/SrTiO₃ heterostructures has stimulated intense research activity in recent ten years. The 2DEG has unique properties that are promising for applications in all-oxide electronic devices. The superconductivity in such heterostructures has been observed below 300 mK. For superconductivity applications it is desirable to have more wide temperature of the existence range and the ability to control superconductivity properties by external stimulus. Based on first-principles calculations and theoretical consideration we show that all-oxide heterostructures incorporating ferroelectric constituent, such as BaTiO₃/La₂CuO₄, allow creating 2DEG. We predict a possibility of a high temperature quasi-two-dimensional superconductivity state. This state could be switchable between superconducting and conducting states by ferroelectric polarization reversal. We also discuss that such structures must be more simple for preparation. The proposed concept of ferroelectrically controlled interface superconductivity offers the possibility to design novel electronic devices.

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The creation of quasi-two-dimensional superconducting states at the interface and the ability to control such states by magnetic and electric fields is impossible without the use of new materials and without the development of new design interfaces. Unique properties of functional materials are achieved due to the effects associated with the complex composition of the interface structure. Such new materials include oxide heterointerfaces between two nonconducting oxides in which, owing to strong electronic correlations, unique transport properties are observed. A quasi-two-dimensional electron system (2DEG) has been discovered [1] at the interface between two oxide insulators, LaAlO₃ (LAO) and SrTiO₃ (STO) by Ohtomo and Hwang [1], and it has attracted significant attention [1–9] due to a wide range of other physical phenomena observed in LAO/STO. High carrier mobility and high electron density of the 2DEG were demonstrated [1, 3, 7–9], which makes it promising for applications in all-oxide field-effect devices. Subsequently, the coexistence of a two-dimensional electron superconductivity and ferromagnetism was discovered in this system [3, 4]. It was found [3] that the system passes into the superconducting state below 300 mK. The density of the charge carriers in such a heterostructure reaches the value of $3 \cdot 10^{13} \text{ cm}^{-2}$.

The most common mechanism for describing these phenomena is the polarization catastrophe model [1, 10]. The polar discontinuity at the interface leads to the divergence of the electrostatic potential. Along the [001] direction, LAO can be considered as an alternation of the differently charged layers of (LaO)⁺¹ and (AlO₂)⁻¹. As it was shown experimentally, in the heterostructure with the TiO₂ interface layer the electric potential along the [001] direction appears due to the polarity disruption at the interface. Thus, the atomically flat quality of the

interface between two components is utterly necessary since the effect is related to the strictly defined sequence of layers inside each slab. A transition to the superconducting state is observed at very low temperatures. That is why it is essential to develop technical approaches to create quasi-two-dimensional superconductivity at higher temperatures and it is also important to study the processes of switching superconductivity.

We present the results of the *ab-initio* calculation of the structural and electronic properties of the heterostructure consisting of ferroelectric material and parent compound of high temperature superconductor (PCHTSC) of BaTiO₃/La₂CuO₄ (BTO/LCO) heterostructure. We consider a possibility of a high temperature quasi-two-dimensional superconductivity (HT2DSC) state appearance in that heterostructure. We discuss the Kosterlitz-Thouless critical temperature T_{KT} for the transition to the superconducting state due to preformed Cooper pairs. We also show that such structures must be more simple for preparation.

For densities of states calculations and structural optimization we have used density functional theory (DFT) [11]. Exchange and correlational effects were accounted by generalized gradient approximation (GGA) [12]. Kohn-Sham equations were solved using the plane-wave basis set (PAW) [13], realized within the VASP code [14], which is a part of the MedeA[®] software of Materials Design [13]. The cut-off energy was chosen to be 400 eV. The force tolerance was 0.05 eV/Å and the energy tolerance for the self-consistency loop was 10^{-5} eV. The Brillouin zones were sampled including $5 \times 5 \times 1$ \mathbf{k} -points. Since there is a strong correlation between d and f -electrons in our system the GGA+ U correction were included to our computational scheme [15]. The U parameter was added to La $4f$, Ti $3d$ and Cu $4d$ orbitals

($U=8\text{eV}$, 2eV and 10eV , respectively). The choice of U for Ti and La values was based on our previous research [16]. The choice of U for Cu was based on comparison with LSDA+ U calculations and experimental data for band gap and Cu local magnetic moment (Table 2 from [17] and [18]).

We study the heterostructure components separately. The structure optimization has been performed for the bulk BTO with quasi-cubic tetragonal structure and for the bulk LCO with orthorhombic structure. Cell parameters obtained after optimization were $a=b=4.00\text{ \AA}$, $c=4.02\text{ \AA}$ for BTO and $a=5.42\text{ \AA}$, $b=5.42\text{ \AA}$, $c=13.23\text{ \AA}$ for LCO (experimental values: $a=b=3.999\text{ \AA}$, $c=4.022\text{ \AA}$ and $a=5.331\text{ \AA}$, $b=5.339\text{ \AA}$, $c=13.150\text{ \AA}$, respectively [19]). In Fig. 1 (a) the density of states spectrum of the bulk BTO material is presented. The obtained band gap is somewhat lower than experimental value of 3.2eV [20]. In order to determine the electronic properties of the studied structure the density of states (DOS) spectrum has been calculated taking into account magnetic properties of LCO. Fig. 1b shows the atom-resolved DOS for La, Cu and O. It is seen that the band gap of bulk LCO is approximately 1.55eV .

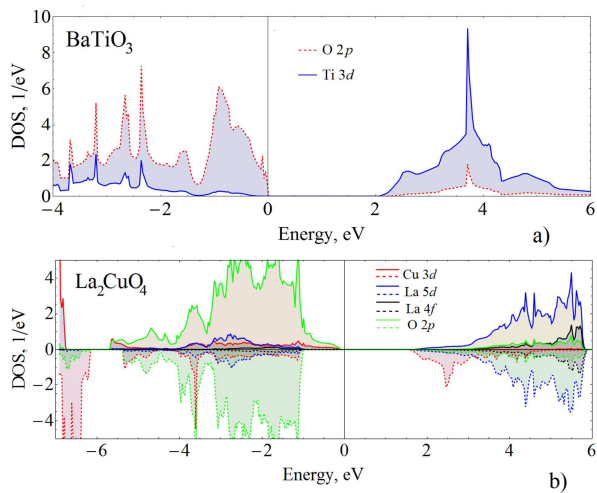


FIG. 1: The density of states of the bulk BaTiO_3 in the tetragonal phase (a) and La_2CuO_4 in the orthorhombic phase (b)

In Fig. 2a half of the unit cell of the studied system BTO/LCO with BaO interface layer is presented whereas the second part is a mirror copy with respect to the central LaO layer. For modeling the heterostructure the LCO central slab was enlarged by a factor of 1.5 and bounded by a varying number of BaTiO_3 layers with interface BaO or TiO_2 layers on both sides. Such a unit cell guarantees the absence of the dipole moment and additional polarity which might arise due to non-symmetric structure. In order to avoid interaction of the surfaces and slabs with their periodic images, a 20 \AA vacuum region was added. In plane a and b cell parameters were fixed, whereas atom positions were allowed to relax dur-

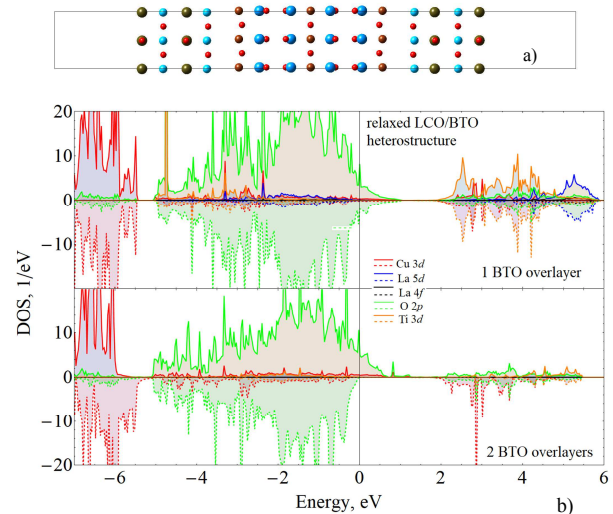


FIG. 2: The unit cell of the heterostructure $\text{BaTiO}_3/\text{La}_2\text{CuO}_4$ (a) and their density of states (b)

ing the optimization procedure.

After the optimization of both interface types (first corresponds to BaO interface layer, second – to the TiO_2 layer) it was found that in the first case, the total energy of the system is lower, meaning that the structure is more stable. That is why all further reasoning will be presented for the most stable configuration. It is seen from Fig. 2a that in the near-surface TiO_2 layer the Ti atoms move out of the oxygen planes by $a \approx 0.15\text{ \AA}$. That leads to a dipole moment induction towards the interface. Calculations involving higher number of the BTO layers are required to get a full picture of structural distortions, what will be done in our further publications.

In order to determine the electronic properties of the studied structure the density of states (DOS) spectrum has been calculated taking into account magnetic features of LCO. Fig. 2b show the atom-resolved DOS for Cu, La and Ti for 1 and 2 BTO overlayers. It is seen that already with one BTO layer the band gap is closed. Cu atomic orbitals cross the Fermi-level. Besides, the total magnetic moment induction takes place which is mainly corresponds to Cu atoms forms.

Let us analyze the results and perform some estimates of the parameters of the arising state. We could estimate the width of the area with metallic conductivity as $0.7\text{-}3\text{ nm}$. Then for a two dimensional density n_s we got the value: $n_s \approx 10^{14} - 4 \cdot 10^{14}\text{ cm}^{-2}$. Thus we expect that the system will become superconducting. Taking into account that the thickness of the of the conducting layer is small the superconducting properties are governed by the Kosterlitz-Thouless transition. The temperature of the transition is defined as

$$T_{KB} = \frac{A\hbar^2 n_s}{4k_B m^*}, \quad (1)$$

where m^* is the effective mass of the current carriers, A

is a coefficient ($A \approx 0.9$ for two dimensional case) [21]. Taking into account that 2D density is $n_s = 10^{14} \text{ cm}^{-2}$ and assuming that $m^* = 3m_e$ [22], where m_e is the free electron mass, we obtain $T_{BK} \approx 70K$. Note, that this temperature is higher than the mean field critical temperature of the bulk LCO with optimal doping ($T_c \approx 40K$). It means that the critical temperature of the interface will be determined by the mean field critical temperature of LCO with optimal doping.

Let us consider the effect of application of an external magnetic field to SC leads. First of all note that the effective penetration depth will be enhanced $\lambda_{eff} = \lambda^2/d$ (d is the effective thickness of the interface layer). Therefore the lower critical field will be strongly reduced. Depending on the intensity of the magnetic field H , it either penetrates or does not penetrate into the SC. The field does not penetrate into the SC at fields below H_{c1} . Above H_{c1} , the field begins to penetrate into the SC in the form of vortices, while the volume around the vortices remains in the SC state. Fields above H_{c2} completely penetrate the sample, the magnetic field in the sample becomes uniform, and the SC completely collapses. In the case of a thin SC film or a thin SC layer, there will be the feature, primarily associated with a demagnetizing factor. When the field is applied perpendicularly to the SC layer the field at the film boundary increases greatly by a factor of K ($K \approx 2 - 10 \cdot 10^6$ for a 1-5 nm thick film [23]) due to a large demagnetizing factor. As a result, when the field at the boundary $H_1 = K H$ exceeds H_{c1} , magnetic field vortices begin to penetrate the sample. Thus, the value of the external magnetic field at which the field begins to penetrate into SC is $H_{c1,eff} = H_{c1}/K$, where H_{c1} is the value for the bulk sample (in fact H_{c1} for films is smaller than that for bulk due to a transmission coefficient being bigger for films. But the coefficient K is so huge, that $H_{c1,eff}$ is very small in any case). Thus, the value of $H_{c1,eff}$ for a thin SC layer turns out to be $H_{c1,eff} \approx 0$ ($\ll 1$ G). The value of H_{c2} for a thin SC layer is the same as that for a bulk. The value of H_{c2} for a thin SC layer is still large (for example, $H_{c2} \approx 390000$ G for $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$). Therefore, it is necessary to expect the appearance of flux flow resistivity in our heterostructure in any arbitrarily small fields, due to the scattering of the superconducting current by flowing vortices.

It is supposed that the appearance of interface conductivity is related to the structural and, consequently, electronic reconstructions. The layers $(\text{BaO})^0$ and $(\text{TiO}_2)^0$ are "electrically neutral" in the simplest ionic limit, but there is a ferroelectric polarization due to the Ti^{+4} atoms displacements out of octahedron center in the BTO. The direction of such a polarization can be switched by an external electric field. That is impossible to do in the case of LAO slab, because an external influence cannot change the sequence of $(\text{LaO})^{1+}$ and $(\text{AlO}_2)^{1-}$ layers. Moreover it is very important that in this case there is no need to make a very high-quality interface boundary, because the

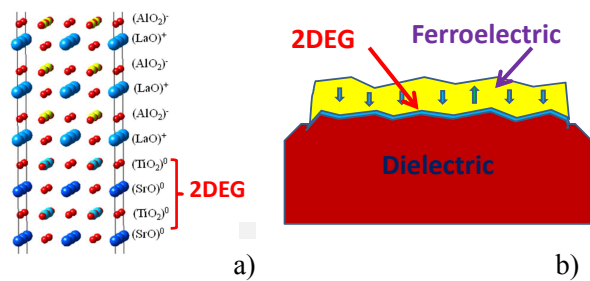


FIG. 3: The heterostructure LAO/STO, interface area (a) and schematic illustration of the ferroelectric/dielectric with non-flat interface boundary (b)

polarization arises in the volume of the ferroelectric. This differs from the case of LAO where, for the appearance of polarization on the interface, it is necessary to obey strictly the sequence of $(\text{LaO})^{+1}$ and $(\text{AlO}_2)^{-1}$ layers. Besides, the BTO/LCO system attracts the interest because it contains antiferromagnetic insulator La_2CuO_4 , which can be transferred to conducting and superconducting state by increasing the concentration of the free carriers [24, 25]. That was realized by doping of the LCO by Sr or Ca [24, 25]. It can be further expected that increasing the free charge carriers can lead to the 2D superconductivity in a system with 2DEG. Therefore, there is an opportunity to switch both conductivity and superconductivity by an electric field in the heterostructures similar to BTO/LCO.

Recently, we have experimentally observed the occurrence of a quasi-two-dimensional state with a metallic character of the temperature behavior of the conductivity at the boundary of the ferroelectric $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ and the antiferromagnet LaMnO_3 [26]. A distinctive feature of these experiments was that the 2DEG state occurs under conditions where the boundary between regions with different components at the interface in the heterostructure is not ideally flat. In LAO/STO 2DEG formation requires the atomically flat boundary and, in addition, a certain sequence of layers of LaO and AlO_2 . Earlier it was predicted [6, 27] that 2DEG can arise when a ferroelectric film is applied to an insulator. In this paper, we present an idea that two-dimensional superconductivity at relatively high temperatures can arise when a ferroelectric film is grown at the an insulator substrate which could become a superconductor after doping.

The work [26] was the first research in the low interface quality systems. Thus the proposed heterostructure seems to be exceptionally crucial. Firstly, we investigate the emergence of a quasi-two-dimensional electron gas at a new type of $\text{BaTiO}_3/\text{La}_2\text{CuO}_4$ heterostructure interface in which there is neither LaAlO_3 nor SrTiO_3 . Secondly, PSHTSC can transform into a superconductor state with an increase in the number of carriers, so new physics and new possibilities appear here. And the most

importantly, thirdly, the use of a ferroelectric makes it possible to avoid the necessity of an extremely high quality of the interface, because the polarization in BaTiO₃ allow the polarization catastrophe to occur at any interface quality. The possibility of a quasi-two-dimensional electron gas creation under less stringent conditions for the interface quality of the heterostructure and the realization of multifunctional conductivity switching regimes and magnetization can substantially increase the possibility of utilization these systems in the mass production of technical devices based on such heterostructures.

Earlier, in the work of Bozovic group the giant proximity effect in cuprate superconductors had been observed [28]. Later, in Goldmann's work [29] the switching-off of the superconductivity when an electric field is applied to a sample with superconducting properties through an ionic conductor was considered. In our investigation, we propose the creation of a superconducting state due to the proximity effect with a ferroelectric, therefore turning it off and turning it on with electric or magnetic fields, by changing the direction of polarization in the ferroelectric film, or by changing the magnetic properties of the substrate, respectively. We also emphasize that when ferroelectric films are used in heterostructures, the less stringent requirements are imposed on the quality of the emerging interfaces. Therefore, the suggested interfaces with ferroelectric films are a completely new approach to the creation of 2DEG, which we have already tested [26]. And the idea of creating on the basis of such 2DEG states of two-dimensional superconductivity at the interface with LCO is even more unique proposal, which has no analogues in the world.

In conclusion, in our paper we have presented the calculations of the structural and electronic properties of the ferroelectric/PCHTSC (BaTiO₃/La₂CuO₄) heterostructure. After the epitaxial ferroelectric BaTiO₃ film was deposited on the LCO sample using, for example, the magnetron sputtering technique we can get HT2DSC in the interphase.

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