Proximity induced superconductivity in monolayer CuO$_2$ on the cuprate substrates

Guo-Yi Zhu$^1$, Fu-Chun Zhang$^{2,3}$, and Guang-Ming Zhang$^{1,4}$

$^1$State Key Laboratory of Low-Dimensional Quantum Physics and Department of Physics, Tsinghua University, Beijing 100084, China.
$^2$Department of Physics, Zhejiang University, Hangzhou 310027, China.
$^3$Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China.
$^4$Collaborative Innovation Center of Quantum Matter, Beijing 100084, China.

(Dated: April 3, 2018)

To understand the recently observed high temperature superconductivity in the monolayer CuO$_2$ grown on the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ substrates, we propose a two band model of the hybridized oxygen $p_x$ and $p_y$ orbitals with the proximity effect of the substrate. We demonstrate that both the nodal and nodeless superconducting states can be induced by the proximity effect, depending on the strengths of the pairing parameters.

PACS numbers: 74.20.Rp, 74.72.-h, 74.45.+c, 74.20.Mn

INTRODUCTION

High transition temperature ($T_c$) superconductivity in cuprates remains one of the most challenging topics in condensed matter physics$^{[1,4]}$. Despite world-wide efforts in the past 30 years, the physics community has still not reached a consensus what causes $T_c$ so high. All the high $T_c$ superconducting copper oxides have layered structures, the superconducting layers CuO$_2$ are sandwiched by non-conducting charge reservoir layers. Modulation of charge carriers in the CuO$_2$ planes is realized through substitution of chemical elements in non-conducting planes, a key parameter in study of the high $T_c$ superconductors.

Recently, Zhong, et. al., reported that a monolayer CuO$_2$ is successfully grown on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) substrates via molecular beam epitaxy (MBE)$^3$. Their result is interesting and important$^6$. Unlike the sandwiched CuO$_2$ layers in the bulk Bi-2212, a monolayer CuO$_2$ is on the BiO surface of the top substrates, which opens a new route for most direct probe such as scanning tunneling microscopy (STM) on the high $T_c$ copper oxides. Two distinct and spatially separated energy gaps are observed on the films: the V-shaped gap is similar to the gap observed on BiO layer, and the U-shaped gap is of superconducting nature and is nodeless. The latter is also immune to scattering by K, Cs, and Ag atoms. The observed U-like gap is in striking contrast with the nodal gap in the $d_{xy}-y^2$-wave pairing symmetry which is well established in the bulk cuprates$^{[2,4]}$. The reported superconductivity in the monolayer CuO$_2$ raises two important questions. One is the nature of its superconductivity: is it the same as the superconductivity of the Bi-2212 substrates, or a new superconducting state? The other is its pairing symmetry.

We begin with a brief summary of the electronic structure of the high $T_c$ superconducting copper oxides. The parent compounds of the copper oxides are anti-ferromagnetic Mott insulator, and superconductivity arises upon chemical doping, which introduces charge carriers in the CuO$_2$ planes. The layers in cuprates are generally charged, either with positive charge such as in the BiO layer in Bi-2212 or with negative charge such as in the sandwiched CuO$_2$ layer. The charge carriers on the CuO$_2$ plane in the parent compound is $-2e$ per unit cell consisting of one copper and two oxygen atoms. The copper has a valence of 2+ and is in 3d$^9$ configuration with a single hole of $d_{x^2-y^2}$ orbital, and oxygen has a valence of 2- and is in configuration of 2p$^6$. Due to the strong on-site Coulomb repulsion, each Cu-atom is occupied with a single 3d hole carrying spin-1/2 moment. Chemical doping introduces additional holes into CuO$_2$ plane. These additional holes primarily reside on the oxygen sites, forming the Zhang-Rice spin singlets, which move through the square lattice of Cu-ions by exchanging with neighboring Cu spin-1/2 moment. This leads to an effective two-dimensional t-J model or large on-site repulsive Hubbard model$^{[10]}$. This model describes some of elementary low-temperature physics in hole doped cuprates. In the relevant parameter region, the carrier density introduced by doping is typically 0.1 $\sim$ 0.25 hole per unit cell in bulk superconducting cuprates.

We now turn to examine the electronic structure of the MBE grown monolayer CuO$_2$ on the top of a BiO layer, which is the surface plane of charge neutral Bi-2212 substrate. If we neglect the charge transfer from the monolayer CuO$_2$ to the inner planes, the monolayer CuO$_2$ is charge neutral as required by total charge neutrality. Therefore, the Cu ion has valence of 2+, or 3d$^9$ configuration, while the oxygen-ion has valence of 1- and is hence in configuration of 2p$^6$ in the monolayer CuO$_2$. The charge carriers in the CuO$_2$ monolayer thus have additional two holes in average on the oxygen-ions per unit cell, which is in contrast with the bulk superconducting cuprates. It is expected that some charge carriers on the monolayer CuO$_2$ may be transferred to the inner planes of the substrate Bi-2212, so that the actual charge carriers on the oxygen-ions will be slightly reduced. With
such a large charge carrier concentration, we expect the CuO$_2$ monolayer itself to be a good metal, whose low energy physics is totally different from the cuprates near a Mott insulator.

In this paper we propose that the superconductivity observed in the CuO$_2$ monolayer is proximity induced superconductivity from the substrate cuprate. The primary reason in support of this scenario is that the transition temperature of the superconductivity in the monolayer is essentially the same as that of the Bi-2212 substrates as reported in Ref. [5]. The challenge to this scenario is to explain the U-shaped superconducting gap in the monolayer. We shall examine a two-band model for the monolayer, which is coupled to the d-wave superconducting substrate by proximity effect. We show that in certain parameter region, a two-band d-wave proximity induced superconductivity may be gapful with U-shaped gap. We expect the monolayer to exhibit a lower T$_c$ if the substrate has a lower T$_c$ or non-superconducting if the substrate is non-superconducting. So the present theory can be tested and distinguished in experiments.

The rest part of the paper is organized as follows. In the next section, we present a model Hamiltonian for proximity induced superconductivity in monolayer CuO$_2$. In the third section, we discuss the possible nodeless superconducting gap of the model and present numerical results for the phase diagram on the nodal or nodeless superconducting phases. The paper ends with a short summary and discussion.

**TWO-BAND MODEL FOR MONOLAYER CuO$_2$ AND ITS PROXIMITY EFFECT INDUCED D-WAVE SUPERCONDUCTIVITY**

In this section, we propose a two-band model for the monolayer CuO$_2$ on the Bi-2212 substrate and examine the proximity effect induced d-wave superconductivity. We first discuss the Hamiltonian part without the pairing, i.e., a non-interacting electron system on a square lattice with oxygen orbitals of either 2p$_x$ or 2p$_y$ as shown in Fig. 1, whose Hamiltonian is given by

$$H_0 = \sum_{k\sigma} \left( c_{1,k\sigma}^\dagger \right) \left( \begin{array}{cc} \epsilon_x & \epsilon_{xy} \\ \epsilon_{xy} & \epsilon_y \end{array} \right) \left( \begin{array}{c} c_{1,k\sigma} \\ c_{2,k\sigma} \end{array} \right),$$  (1)

where

$$\begin{align*}
\epsilon_x &= -2(t_x \cos k_x + t_y \cos k_y) - \mu, \\
\epsilon_y &= -2(t_y \cos k_x + t_x \cos k_y) - \mu, \\
\epsilon_{xy} &= -4t_{xy} \cos \frac{k_x}{2} \cos \frac{k_y}{2},
\end{align*}$$  (2)

and $t_x$, $t_y$, and $t_{xy}$ are assumed to be positive parameters, and characterize the nearest neighbor intra- and inter-orbital hopping terms, respectively. More accurate description for the monolayer would also include Cu-3d$_{x^2-y^2}$ orbital. The holes on the O-site ($2p_x$ and $2p_y$) are strongly coupled to the localized Cu-3d$_{x^2-y^2}$ spin, and the system may be described by the Kondo lattice model with two conduction bands [11]. Roughly speaking, the holes on the Cu-site lead to a renormalization of the two conduction bands of O-orbitals as in the usual Kondo lattice problem. From this point of view, the non-interacting two-band model described in Eq.(1) is a simplified model for the monolayer with the understanding that the conduction bands are renormalized ones [11].

The inter-orbital hopping term hybridizes the two orbitals into two bands with dispersion

$$\epsilon_{\pm}(k) = \frac{\epsilon_x + \epsilon_y}{2} \pm \sqrt{\left(\frac{\epsilon_x - \epsilon_y}{2}\right)^2 + \epsilon_{xy}^2}. \quad (3)$$

The model is symmetric under reflection with respect to x-axis or y-axis (Cu-O bonds), and has $C_4$ rotational symmetry:

$$\begin{align*}
\epsilon_x(k_x, k_y) &= \epsilon_y(k_y, -k_x), \\
\epsilon_{\pm}(k_x, k_y) &= \epsilon_{\pm}(k_y, -k_x).
\end{align*}$$

To describe the proximity effect of the cuprate substrate with d-wave superconductivity, we introduce d-wave pairings for the carriers on the oxygen 2p$_x$ and 2p$_y$ orbitals as shown in Fig.1. In the momentum space, the full model Hamiltonian can be written as

$$H = \sum_{k} \Psi_k^\dagger H(k) \Psi_k, \quad (4)$$

where the Nambu spinor has been introduced as $\Psi_k^\dagger = \left( c_{1,k\uparrow}^\dagger \ c_{2,k\downarrow}^\dagger \ c_{1,-k\downarrow} \ c_{2,-k\uparrow} \right)$, and the Hamiltonian matrix is given by

$$H(k) = \begin{pmatrix}
\epsilon_x & \epsilon_{xy} & \Delta_{xx}(k) & \Delta_{xy}(k) \\
\epsilon_{xy} & \epsilon_y & \Delta_{yx}(k) & \Delta_{yy}(k) \\
\Delta_{xx}(k) & \Delta_{yx}(k) & -\epsilon_x & -\epsilon_{xy} \\
\Delta_{xy}(k) & \Delta_{yy}(k) & -\epsilon_{xy} & -\epsilon_y
\end{pmatrix}, \quad (5)$$

FIG. 1: The monolayer CuO$_2$ on the cuprate Bi-2212 substrate and our effective two-band model with all possible d-wave proximity pairings.
with
\[
\Delta_{xx}(k) = \Delta_0 + 2(\Delta_y \cos k_y + \Delta_z \cos k_z),
\]
\[
\Delta_{yy}(k) = -\Delta_0 - 2(\Delta_x \cos k_x + \Delta_z \cos k_z),
\]
\[
\Delta_{xy}(k) = 4\Delta_{xy} \sin \frac{k_x}{2} \sin \frac{k_y}{2}.
\] (6)

Note that the d-wave pairing symmetry of the substrates requires
\[
\Delta_{xx}(k) = -\Delta_{yy}(k), \Delta_{xy}(k) = -\Delta_{yx}(k),
\]
where \( \bar{k} = (k_y, -k_x) \). By transforming the gap function matrix for \( p_z \) and \( p_y \) orbitals into the hybridized band basis, we arrive at
\[
\bar{\Delta}_k(k) = \begin{pmatrix} \Delta_{++}(k) & \Delta_{+-}(k) \\ \Delta_{-+}(k) & \Delta_{--}(k) \end{pmatrix},
\]
with
\[
\Delta_{++}(k) = \Delta_d(k) + \Delta_s(k) \cos \theta_k + \Delta_{xy}(k) \sin \theta_k,
\]
\[
\Delta_{--}(k) = \Delta_d(k) - \Delta_s(k) \cos \theta_k - \Delta_{xy}(k) \sin \theta_k,
\]
\[
\Delta_{-+}(k) = -\Delta_d(k) \sin \theta_k + \Delta_{xy}(k) \cos \theta_k,
\]
\[
\Delta_{+\bar{y}}(k) = \Delta_0 + (\Delta_x + \Delta_y)(\cos k_x + \cos k_y),
\]
\[
\Delta_d(k) = (\Delta_x - \Delta_y)(\cos k_x - \cos k_y),
\]
where \( \theta_k = \tan^{-1} \frac{k_y}{k_x} \) in the range of \([0, \pi]\). It shows that the hybridized bands of \( p_x \) and \( p_y \) orbitals are subjected to mixture of s-wave and d-wave pairings together with \( \Delta_{xy}(k) \), which is neither s- nor d-wave symmetry due to the mirror reflection symmetry breaking with regards x- or y-axis. For consideration of mirror symmetry, we will set \( \Delta_{xy} = 0 \) in what follows. Actually an analysis of the proximity pairing for the monolayer on top of the substrate Bi-2212 suggests the leading order in \( \Delta_{xy} \) vanishes \cite{12}. Neglect of this term does not seem to change qualitative physics we wish to address. Therefore the intra-band pairings \( \Delta_{++} \) and \( \Delta_{--} \) are dominated by d-wave symmetry with a correction of modulated s-wave component. Under the limit \( \varepsilon_{xy} >> |\varepsilon_x - \varepsilon_y| \), we have \( \bar{k} \rightarrow \pi/2 \), the s-wave correction vanishes, and the intra-band pairings are pure d-wave symmetric, which is actually no surprise due to the proximity effect. However, the inter-band pairing \( \Delta_{-+} \) is pure s-wave symmetric, which plays a key role in opening the nodal gap for d-wave pairing.

By diagonalizing the Hamiltonian matrix, we obtain the superconducting quasiparticle spectrum. The quasiparticle dispersion takes the simple form
\[
E_{\pm}(k) = \sqrt{A_k \pm \sqrt{A_k^2 - 4B_k}},
\] (7)
where
\[
A_k = \varepsilon_x^2 + \varepsilon_y^2 + 2\varepsilon_{xy} + \Delta_{xx}^2 + \Delta_{yy}^2,
\]
\[
B_k = (\varepsilon_{xy} + \varepsilon_x) \varepsilon_y + 2\Delta_{xx}\Delta_{yy}\varepsilon_{xy} + \Delta_{xx}\varepsilon_y^2 + \Delta_{yy}\varepsilon_x^2.
\] (8)

Two quasiparticle bands \( E_+(k) \) and \( E_-(k) \) are separated, and \( E_-(k) \) corresponds to the lower one.

With the expression for the quasiparticle spectra, we are in good position to examine the gap nodes and the STM probe of the gap. The d-wave pairing in the bulk cuprates has the form of \( \Delta_d(k) \propto (\cos k_x - \cos k_y) \), and there are four nodes along the lines of \( k_x = \pm k_y \), which are crossing points of the lines with the Fermi surface. As the intra-band pairing is dominated by d-wave pairing, it is expected that gap nodes in quasi-particle excitations are very likely to occur. However, the mixture with s-wave pairing could potentially open the gap nodes as long as the s-wave component is relatively strong enough e.g. if \( t_{xy} \) is small, and \( \Delta_0 \) is large. The exact criterion is given by the zeroes of \( B_k \), which will be discussed in the next section.

**NODELESS GAP FUNCTION IN TWO-ORBITAL MODEL**

In this section, we examine the possibility of nodeless gap in the two-orbital d-wave superconductivity in the previous section. From Eqs. (7), (8), the condition for zeroes of the quasiparticle is given by \( B_k = 0 \). This depends on the hopping and pairing parameters. To illustrate the possible nodeless gap, let us first consider a special case: \( \epsilon_{xy}(k) = 0 \), namely the inter-orbital hopping vanishes. In this case, \( B_k = 0 \) requires both \( \epsilon_x(k) = \epsilon_y(k) = 0 \) and \( \Delta_{xx}(k) = 0 \) or \( \Delta_{yy}(k) = 0 \). These conditions cannot be satisfied in general except on some discrete parameter space points. This simple example clearly demonstrates the possible nodeless gap in the two-orbital d-wave superconductivity. Actually this corresponds to the limit without hybridization, and the intra-band pairing \( \Delta_{xx}(k) \) and \( \Delta_{yy}(k) \) are effectively \( C_4 \) anisotropic extended s-wave pairing. In passing, we note that the d-wave gap function in a two orbital model allows a \( k \)-independent term in intra-orbital pairing, and the d-wave symmetry only requires the opposite signs of this term for the two different orbitals, as explicitly shown in Eq.(6).

Next, unlike the limit case we demonstrated above, we show that a weak coupling pairing theory does not lead to a gapful d-wave state when \( t_{xy} >> |t_x - t_y| \). This condition is more physically relevant since \( t_{xy} \) is the nearest neighbor hopping. Within the weak coupling theory, we may consider only intra-band pairing and neglect the inter-band pairing since the two bands are not degenerate in the presence of the inter-orbital hopping. Since then the intra-band pairing is almost pure d-wave symmetric, the nodal structure in the d-wave pairing therefore remains in two-orbital bands within the weak coupling theory. This shows that the vanishing of the gap nodes requires a strong pairing coupling, comparable to the energy splitting of the two bands. Below we shall consider a
interesting to note that the gap property only depends on $\Delta_x + \Delta_y$ instead of each of them in separate forms. At small values of $\Delta$’s, the gap has nodes, consistent with the weak coupling pairing analyses. Note that $B_k$ is non-negative, which is required for the quasiparticle solutions as implied in Eq. (7). It can be seen that the nodeless phase only occurs at large values of the on-site pairing strength $\Delta_0$. Qualitatively, we may understand this result as that the gapless phase requires strong interband pairing comparable to the band splitting.

In the nodeless superconducting phase with $\Delta_x = 0.6$, $\Delta_y = 0.3$, $\Delta_0 = 2.1$, and $\mu = 0.2$, the lower quasiparticle band $E_-(k)$ in the Brillouin zone is calculated and displayed in Fig. 5a. This quasiparticle band has dramatic changes, very different from the corresponding band without the pairing. The local density of states, which is proportional to the local differential tunneling conductance STM probes, can be calculated by using the quasiparticle dispersion and is plotted in Fig.5b. Although there appears a U-shaped mini-gap in the lower energy regime, the resonant peak does not reside exactly on the edge of the mini-gap, rather different from the conventional single band model, because the resonant peak still has its origin from d-wave pairing. As a comparison, we also give rise to the results for the nodal superconducting phase with $\Delta_x = 0.6$, $\Delta_y = 0.3$, $\Delta_0 = 0.9$, and $\mu = 0.2$, and the corresponding results are displayed in Fig.5c and 5d.

## SUMMARY AND DISCUSSIONS

In summary, the successful growth of the monolayer CuO$_2$ on Bi-2212 reported by Zhong et al. [5] has provided a new material, as a complement to bulk cuprates,
to study physics in copper oxides. Motivated by their new finding, we have proposed that the observed high $T_c$ superconductivity with nodeless gap is proximity induced superconductivity and that the normal state of the monolayer is described by a two-orbital model. We have further examined the superconducting gap functions in a two-orbital model and demonstrated a mixture of d-wave and s-wave pairing, which may explain the observed U-shaped gap in the experiment. In our calculations, the nodeless gap phase in the two-orbital model occurs in the region where the on-site pairing coupling is strong and comparable to the energy splitting in the two bands.

We wish to point out that the non-interacting two-orbital model we used in the paper is a simplified model and the coupling between the O-2p bands and the localized spin on the Cu sites has the Kondo coupling, which is expected to greatly reduce the band widths of the O-orbitals near the Fermi level. From this point of view, the nodeless gap phase may be realized in the monolayer CuO$_2$. While our theory is more closely related to the monolayer CuO$_2$, our results may be relevant to nodeless d-wave superconductivity in heavy fermion superconductor CeCu$_2$Si$_2$, where the superconductivity is believed to have d-wave symmetry, recent specific heat data and superfluid density indicates a full gap in its low-energy excitations.

After finishing this paper, we noted that nodeless excitation spectrum in a two-orbital model with d-wave symmetry was previously discussed in the context of iron based superconductivity. The reason for gapful excitations is due to the lack of intersection of the Fermi surfaces and the line nodes of the superconducting gap function, similar to the limiting case with vanishing inter-orbital hopping term we discussed in the beginning of the third section in this paper. More physically relevant case we discussed in this paper as illustrated in Fig. 2 to Fig. 5 has a large inter-orbital hopping integral, and the gapful excitation is resulted in the large inter-band pairing.

ACKNOWLEDGMENT

We thank Qi-Kun Xue and his group members for stimulating discussions on their experiments. We also thank W. Q. Chen for helpful discussions, especially on the proximity induced pairing strength including the on-site pairing. GMZ acknowledges the support of NSF-China through Grant No.20121302227, and FCZ is supported in part by National Basic Research Program of China (under grant No.2014CB921203) and NSFC (under grant No.11274269).

[1] J. P. Bednorz and K. A. Muller, Z. Phys. B 64, 189 (1986).
[2] P. W. Anderson, Science 235, 1196 (1987).
[3] P. W. Anderson, P. A. Lee, M. Randeria, T. M. Rice, N. Trivedi, and F. C. Zhang, J. Phys. Condens. Matter 16, R755 (2004).
[4] P. A. Lee, N. Nagaosa, and X. G. Wen, Rev. Mod. Phys. 78, 17 (2006).
[5] Y. Zhong, Y. Wang, S. Han, Y. F. Lv, W. L. Wang, D. Zhang, H. Ding, Y. M. Zhang, L. L. Wang, K. He, R. D. Zhong, J. A. Schneeloch, G. D. Gu, C. L. Song, X. C. Ma, Q. K. Xue, Science Bulletin 61, 1239 (2016), arXiv:1607.01852.
[6] F. C. Zhang, Science Bulletin 61, 1236 (2016).
[7] Z. X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitulnik, P. Dickinson, S. Doniach, J. DiCarlo, T. Loeser, and C. H. Park, Phys. Rev. Lett. 70, 1553 (1993).
[8] D. A. Wollman, D. J. Van Harlingen, W. C. Lee, et al., Phys Rev Lett. 71, 2134 (1993).
[9] C. C. Tsuei, J. R. Kirtley, C. C. Chi, L. S. Yujahnes, A. Gutpa, T. Shaw, J. Z. Sun, and M. B. Ketchen, Phys. Rev. Lett. 73, 593 (1994).
[10] F. C. Zhang, and T. M. Rice, Phys. Rev. B 37, 3759 (1988).
[11] G. M. Zhang, et. al., in preparation.
[12] W. Q. Chen, private communications (2016).
[13] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, A. Kapitulnik, P. Dickinson, S. Doniach, J. DiCarlo, T. Loeser, and C. H. Park, Phys. Rev. Lett. 70, 1553 (1993).
[14] G. M. Zhang, et. al., in preparation.
[15] W. Q. Chen, private communications (2016).
[16] E. M. Nica, R. Yu, and Q. Si, arXiv:1505.04170.