Electronic structure and superconductivity in unconventional cuprates Ba$_2$CuO$_{3+\delta}$

Congcong Le$^{1,2,3}$ Kun Jiang$^{1,3}$ Yinxiang Li$^3$, Shengshan Qin$^{1,3}$
Ziqiang Wang$^4$, Fuchun Zhang$^{1,2}$ and Jiangping Hu$^{3,5,1}$

$^1$Kavli Institute of Theoretical Sciences, University of Chinese Academy of Sciences, Beijing, 100190, China
$^2$Chinese Academy of Sciences Center for Excellence in Topological Quantum Computation, University of Chinese Academy of Sciences, Beijing 100190, China
$^3$Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
$^4$Department of Physics, Boston College, Chestnut Hill, MA 02467, USA
$^5$Collaborative Innovation Center of Quantum Matter, Beijing, China

(Dated: September 30, 2019)

We study the recently discovered 73K high-$T_c$ superconductor Ba$_2$CuO$_{3+\delta}$ at $\delta \simeq 0.2$ grown under high pressure. Neutron experiments find that the polycrystal exhibits a structure similar to La$_2$CuO$_4$, but with dramatically different lattice parameters due to the CuO$_6$ octahedron compression. The resulting crystal field leads to an inverted Cu 3d $e_g$ complex with the $d_{z^2-r^2}$ orbital sitting below the $d_{x^2-y^2}$ orbital and an electronic structure highly unusual compared to the conventional cuprates. We conjecture that the material realizes a new path of in-plane positional oxygen doping, where the doped oxygens create matrices of compressed Ba$_2$CuO$_4$ embedded in Ba$_2$CuO$_3$. Constructing a strongly correlated two-orbital model at hole doping $x = 2\delta$ of the Cu $d^9$ state, we show that the spin-orbital exchange interactions lead to a multiband antiphase $d$-wave superconducting state, i.e. a nodal $d_{\pm}$ pairing state. These findings suggest that the class of unconventional cuprates with liberated orbitals as doped two-band Mott insulators can be a direction for realizing high-$T_c$ superconductivity with enhanced transition temperature $T_c$.

The current understanding of high-$T_c$ cuprate superconductors$^1$ crucially relies on the crystal field due to the Jahn-Teller distortion of the elongated CuO$_6$ octahedra. The topmost Cu 3d-electron $e_g$ states split accordingly into well separated lower $d_{3z^2-r^2}$ ($d_{z^2}$) and upper $d_{x^2-y^2}$ ($d_{z^2}$) orbitals (Fig. 1(a)). In the parent compound, such as the prototypical single-layer La$_2$CuO$_4$ (La214), the Cu$^{2+}$ is in the 3$d^9$ configuration with a fully occupied $d_{z^2}$ orbital and an active $d_{x^2}$ orbital partially occupied by one electron. The strong correlation produces a spin-$\uparrow$ antiferromagnetic (AF) Mott insulator. Hole doping leads to an effective one-band model of Zhang-Rice singlets formed by the hole in the $d_{z^2}$ orbital and a doped hole in the planar oxygen $2p^5$ orbitals$^2$. The AF exchange interactions give rise to nodal $d$-wave high-$T_c$ superconductivity in the CuO$_2$ planes$^3$. Such a picture describes the vast majority of the conventional cuprates, where the dormant $d_{z^2}$ orbital plays only a minor role$^4$.

The recent discovery of high-$T_c$ superconductor Ba$_2$CuO$_{3+\delta}$ at $\delta \simeq 0.2$$^8$ highlights a class of “unconventional” cuprates where the different crystal field distributions lead to electronic structures with liberated $d_{z^2}$ orbital$^8$. The polycrystal samples have been synthesized under high pressure in a strongly oxidizing environment and at high temperatures. Extraordinary properties were observed by a combination of magnetization, specific heat, neutron scattering, x-ray absorption spectroscopy (XAS), and $\mu$ spin-rotation ($\mu$SR) experiments:

(i) The polycrystalline BCO$_3$ has an atomic structure similar to La214, but with dramatically different lattice parameters due to the octahedral compression, leading to inverted $d_{z^2}$ and $d_{z^2}$ orbitals as shown in Fig. 1(b); (ii) The extra $O_\delta$ occupy the oxygen sites in the CuO$_{1+\delta}$ planes with no evidence of ordering; (iii) Despite the large hole doping concentration reflected in the Cu $L_3$ spectrum, the O K-edge XAS shows spectral the weight transfer similar to optimally doped La214, indicative of the presence of strong Mott-Hubbard local correlations$^{10,11}$; and remarkably, (iv) The superconducting (SC) transition temperature $T_c \simeq 73K$, which is nearly twice that of the conventional cuprates in the La214 family, and the SC volume fraction is close to 40% in the low temperature limit. The focus of this work is to provide a theoretical description of the crystal and electronic structure, and the nature of the SC state for these experimental findings. In doing so, we find that the cuprate phenomenon is enriched due to the liberated $d_{z^2}$ orbital and the two-band doped Mott insulator with strongly orbital dependent correlation effects may provide a mechanism for the dramatic $T_c$ enhancement.

Based on the neutron and $\mu$SR measurements, it is instructive to consider Ba$_2$CuO$_{3+\delta}$ (Ba213$\delta$) at $\delta \simeq 0.2$ as having the extra $O_\delta$ oxygenated into the copper-oxygen chain plane of the stoichiometric Ba$_2$CuO$_3$ (Ba213)$^{12,13}$, which would have two domains with Cu-O chains along either the $x$ or the $y$ directions. Intriguingly, Ba$_2$CuO$_4$ (Ba214), which is isostructural to La214, materializes locally around the domain boundary as illustrated in Fig. 1(c) for a diagonal domain wall. It is thus conceivable that the Ba214 would be clustered around the randomly distributed domain walls, such that Ba213$\delta$
can be viewed as $\delta$-Ba214$\oplus$(1 - $\delta$)-Ba213, i.e. a matrix of Ba214 with CuO$_2$ planes embedded in the background of Ba213 with Cu-O chain planes. This aligns with $\mu$SR experiments that find no evidence for in-plane ordered oxygen superstructures. Since the Cu$^{4+}$ (3$d^0$) in Ba214 is not a stable ionization state, self-doping by charge transfer takes place with the Cu$^{2+}$ in Ba213. Thus, Ba213$\delta$ represents a new path of in-plane positional $\delta$-oxygen doping, in sharp contrast to conventional cuprates where doping is achieved by either substitutional or interstitial dopants, all residing outside the CuO$_2$ plane.

Measuring the doping concentration referenced to the $3d^9$ configuration in both Ba214 and Ba213 by $x$ and $x'$, we have the relation: $\delta x + (1 - \delta)x' = 2\delta$. Since the $\mu$SR experiments did not observe apparent charge disproportionation, we take the Cu atoms to be of equal valence in the Ba213 and Ba214 regions, resulting in a common heavily overdoped hole concentration $x = x' = 2\delta \approx 40\%$. Note that if the entire Ba$_2$CuO$_{3+\delta}$ were viewed as Ba214 with randomly distributed oxygen vacancies in the plane, one would arrive at the same value of $x$ and the electronic structure to be discussed below provided that the vacancy potential is ignored. However, the high density of such vacancies ($\sim 40\%$) makes the predication of the SC state less reliable.

Using the structure parameters measured by neutron scattering (Table S1), we carried out density functional theory (DFT) calculations for stoichiometric Ba213 and Ba214 using the Vienna $ab$ initio simulation package (VASP) [14][16]. The details are described in the supplementary material (SM) [13]. The corresponding band structures are calculated with the generalized gradient approximation (GGA) [17]. For Ba213, there is a single 1D band at low energy near the Fermi level, resulting in two 1D Fermi surface sections in the Brillouin zone (Fig. S2). The primary $d$-electron content is $d_{z^2}$ for the Cu-O chains along the $x$-direction, which is a linear combination of the $d_{x^2}$ and $d_{y^2}$ orbitals. We expect 40% hole-doping of such a single-band to give a correlated metallic state. In the rest of the paper, we focus on the compressed Ba214 and show that despite the heavy hole-doping, a new two-band antiphase $d$-wave SC state emerges due to the multi-orbital correlated electronic structure and the spin-orbital exchange interactions.

For compressed Ba214, the obtained DFT band structure is shown in Fig. 1(d). There are two bands crossing the Fermi level, originating predominately from the Cu $3d_{x^2}$ and $3d_{y^2}$ orbitals. Since the distorted CuO$_6$ octahedron has a shorter distance connecting the Cu to the apical oxygens than to the planar oxygen (Table S1), the $d_{x^2}$ orbital couples strongly with the apical oxygen $p_z$ orbital. The inverted crystal field pushes the atomic energy of the $d_{z^2}$ orbital to be $\sim 0.93$eV above the $d_{x^2}$ orbital. Thus the atomic limit of the $3d^9$ configuration has one electron in the $d_{x^2}$ orbital while the $d_{y^2}$ orbital is occupied by two electrons (Fig. 1(b)), in contrast to conventional cuprates. Upon crystallization, although the much smaller hopping integrals of the out of plane $d_{z^2}$ orbital produce a narrow band, the $d_{z^2}$ orbital generates a much wider band through the larger hopping integrals via the planar oxygen such that the two bands overlap near the Fermi level (Fig. 1(d)). Thus, we propose that the compressed Ba214 is an unconventional cuprates where both the $d_{x^2}$ and $d_{y^2}$ orbitals of the $e_g$ sector contribute to superconductivity. Although multi-orbital superconductivity has been studied extensively for the $t_{2g}$ electrons in the iron pnictides and chalcogenides superconductors [15][22], it is new for the $e_g$ electrons in the cuprates. Remarkably, in the presence of strong on-site Coulomb repulsion, we find that a strong-coupling theory for the electronic structure predicts a nodal $d$-wave superconductor with antiphase pairing gaps on the two Fermi surfaces at the high doping $x = 0.4$ achieved experimentally.

To this end, we construct an effective two-orbital model on the Cu square lattice $H = H_I + H_f$, where $H_I$ describes the DFT band structure near the Fermi level and $H_f$ the electron correlations. The model is equivalent to a generalization of the Zhang-Rice singlet construction where the charge degrees of freedom on the oxygen sites have been integrated out, and the Cu$^{4+}$ in the $3d^8$ configuration includes the spin singlets of a hole (3$d^9$) on Cu-site and a hole (2$p^5$) on its neighbouring O-sites with compatible symmetries to $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ [2]. Denoting a
spin-$\sigma$ electron in the effective $d_{z^2}$ - and $d_{x^2-y^2}$ -like orbitals by $d_{\alpha\sigma}$, $\alpha = x, z$ respectively, we have
\[
H_I = \sum_{k\sigma} \varepsilon_k^\sigma d_{k\sigma}^\dagger d_{k\sigma} + \sum_{k\sigma} \epsilon_{\alpha} d_{k\alpha\sigma}^\dagger d_{k\alpha\sigma}, \tag{1}
\]
where $\epsilon_{\alpha}$ is the crystal field energy of each orbital.

The lattice structure of Ba214 belongs to the $D_{4h}$ point group. The intra and interorbital hoppings can be expressed in terms of the lattice harmonics of $A_{1g}$ symmetry: $\gamma_k = \cos k_x + \cos k_y$, $\alpha_k = \cos k_x \cos k_y$, and $\gamma_k' = \cos 2k_x + \cos 2k_y$, and $B_{1g}$ symmetry: $\beta_k = \cos k_x - \cos k_y$ and $\beta_k' = \cos 2k_x - \cos 2k_y$, for up to third nearest neighbor hopping.

The corresponding expression for the hopping energies in Eq. (1) is given by $\varepsilon_k^{\alpha\beta} = -2t_{\alpha\gamma} - 4t_{\alpha\beta}^\alpha - 2t_{\beta\gamma}^\beta$ and $\varepsilon_k^{x\beta} = 2t_{x2\beta}^\xi + 2t_{x2\beta}^\gamma$, where the values of the hopping parameters are given in Table S2 together with $\epsilon_{\alpha}$ in the SM [13]. The band structure of the two-orbital TB model is shown in Fig. 1(e). It faithfully represents the low energy DFT band structure in Fig. 1(d), including the orbital contents, as a two-band system with a bandwidth $W \simeq 4eV$. Since the interorbital mixing $\varepsilon_k^{x\beta}$ carries the $B_{1g}$ harmonics, the band structure along the nodal direction ($\Gamma \rightarrow M$) is orbital diagonal. Moreover, the interband mixing is also weak along the $\Gamma \rightarrow X$ direction because of the large band energy separation. However, the two bands hybridize strongly when the band energies are close, as seen along $X \rightarrow M$. Reproduced in Fig. 2(a), the Fermi levels are indicated by the dashed black line for the $d_{\alpha\beta}$ configuration with $n_e = 3$ electrons, i.e. the undoped case at $x = 0$ with orbital occupations $n_x^d \simeq 1.3$ and $n_{x+}^d \simeq 1.7$; and by the blue dashed line for the experimentally realized doped level $x = 0.4$, where the bare occupations change to $n_x^d = 1.04$ and $n_{x+}^d = 1.56$. There are two Fermi surfaces (FSs), one electron-like of dominant $d_{z^2}$ character around $\Gamma$ and a much smaller hole-like $d_{x^2-y^2}$ FS around $M$. We next turn to the correlation effects beyond the band description.

The correlation part of the Hamiltonian $H_I$ follows from the standard two-orbital Hubbard model [23,24] for the $c_g$ complex
\[
H_I = U \sum_{i,\alpha} \hat{n}_{i\alpha\uparrow} \hat{n}_{i\alpha\downarrow} + \left( U' - \frac{1}{2} J_H \right) \sum_{i,\alpha < \beta} \hat{n}_{i\alpha\uparrow} \hat{n}_{i\beta\downarrow} \tag{2}
\]
\[
- J_H \sum_{i,\alpha \neq \beta} \mathbf{S}_{i\alpha} \cdot \mathbf{S}_{i\beta} + J_H \sum_{i,\alpha \neq \beta} d_{i\alpha\downarrow}^\dagger d_{i\beta\uparrow}^\dagger d_{i\alpha\uparrow} d_{i\beta\downarrow},
\]
where the intra and interorbital repulsion $U$ and $U'$ are related to Hund’s rule coupling $J_H$ by $U = U' + 2J_H$. We will set $U = 7eV$ and hence $U/W \simeq 1.8$, and $J_H = 0.1U$ in the rest of the paper. The strong correlated effects can be studied using the multiorbital Gutzwiller projection method [24,25]: $H_I + H_I \rightarrow H_G = P_G H_I P_G$, where $P_G$ is the finite-$U$ projection operator that reduces the statistical weight of the Fock states with multiple occupations.

The projection can be conveniently implemented using the Gutzwiller approximation (GA) [26,27] developed to study the multiorbital cobaltates [24], Fe-pnictides [28], and the monolayer CuO$_2$/Bi2212 [9],
\[
H_G = \sum_{k\sigma\beta} g_{k\beta\sigma}^\alpha \varepsilon_k^{\alpha\beta} d_{k\alpha\sigma}^\dagger d_{k\beta\sigma} + \sum_{k\sigma} (\epsilon_{\alpha} + \lambda_{\sigma}^\alpha) d_{k\alpha\sigma}^\dagger d_{k\alpha\sigma}, \tag{3}
\]
where the orbital dependent hopping and crystal field renormalizations $g_{k\beta\sigma}^\alpha$ and $\lambda_{\sigma}^\alpha$ are determined self-consistently. We first study the undoped case at $x = 0$ and $n_e = 3$. The Gutzwiller solution shows that the ground state is an antiferromagnetic (AF) insulator. It is remarkable that the AF order is orbital selective, i.e. the electron correlation induces the interorbital carrier transfer [26] and drives the $d_{z^2}$ band to half-filling with $n_z = 1$. The paramagnetic interacting band dispersions are shown in Fig. 2(b) at $U = 4.4eV$, exhibiting a half-filled $d_{z^2}$ band, while the $d_{x^2-y^2}$ band is pushed below the Fermi level and completely filled. An insulating gap opens up with AF ordered moments coming from the localized $d_{z^2}$ electrons.

For large hole doping at $x = 0.4$ and $n_e = 2.6$ relevant for the experiments, the correlation renormalized band dispersions in the paramagnetic state is shown in Fig. 2(c) and the FSs in Fig. 2(d). Interestingly, while the correlation induced interband carrier transfer is small with orbital occupations $n_z = 1.02$ and $n_x = 1.58$ close to their bare values, the band narrowing effect is strong and orbital-dependent. The strongly correlated $d_{z^2}$ band remains close to half-filling and narrows significantly by a factor $g_{zz} = 0.33$ while the $d_{x^2-y^2}$ band only narrows by a factor $g_{xx} = 0.87$. It is thus rather natural to consider a picture of two-orbital doped Mott insulator where the
SC state arises from the spin-orbital superexchange interactions of the Kugel-Khomskii type \cite{4, 23, 25}. In the spin-orbital basis \((d_{x^2}, d_{y^2}, d_{z^2})^T\), the fermion bilinears at each site can be represented as a tensor product \(T^\mu_i S^\mu_i\), where \(S^\mu_i\) and \(T^\mu_i\), \(\mu = x, y, z\) are one half of the identity and Pauli matrices acting in the spin and orbital sectors, respectively. For example, \(d_{x^2}^\dagger \cdot d_{x^2} = T_i^+ S_i^-\), where \(T_i^\pm = T_i^x \pm i T_i^y\) and \(S_i^\pm = S_i^x \pm i S_i^y\). The spin-orbital superexchange interactions can thus be derived and written as

\[
H_{J-K} = \sum_{\langle ij \rangle} \left[ J S_i \cdot S_j + \sum_{\mu, \nu} I_{\mu \nu} T_i^\mu T_j^\nu \right] + \sum_{\mu, \nu} K_{\mu \nu}(S_i \cdot S_j)(T_i^\mu T_j^\nu)
\]

where the \(J\)-term is the SU(2) invariant Heisenberg spin exchange coupling, while the terms proportional \(I_{\mu \nu}\) and \(K_{\mu \nu}\) describe the anisotropic orbital and spin-orbital entangled superexchange interactions, respectively, since the orbital rotation symmetry is broken by the lattice in \(H_0\). In Ref. \cite{9}, it was shown that despite the orbital \(T^z\) order induced by the crystal field splitting, the transverse orbital \(T^x, T^y\) fluctuations contribute to SC pairing. Thus, including all contributions to spin-singlet pairing represented by \(\Delta_{ij}^{\alpha \beta} = d_{\alpha \alpha}^{\dagger} d_{\beta \beta} - d_{\alpha \beta}^{\dagger} d_{\alpha \beta}\) in the spin and spin-orbit entangled quadruple exchange interactions in Eq. \((4)\), we arrive at the effective Hamiltonian describing the possible SC ground states in the strongly correlated two-orbital model

\[
H = P_G H_t P_G - \sum_{\langle ij \rangle} \left[ J_s \sum_{\alpha \beta} \Delta_{ij}^{\alpha \beta} \Delta_{ij}^{\alpha \beta} \right] + \frac{K}{2} \sum_{\alpha \neq \beta} \left( \Delta_{ij}^{\alpha \alpha} \Delta_{ij}^{\beta \beta} + \Delta_{ij}^{\alpha \beta} \Delta_{ij}^{\beta \alpha} \right)
\]

The couplings \((J_s, K)\) are explicit functions of \(t_{\alpha \beta}, U\), and \(J_H\) \cite{2}, but will be considered as phenomenological parameters in our effective theory.

In the following, we set \(J_s = 200\) meV and \(K = 80\) meV, and study the emergent SC states in such a two-band doped Mott insulator at high doping \(x = 0.4\) relevant for the experiments. To this end, we determine the expectation values of the nearest neighbor pairing fields

\[
\langle \Delta_{ij}^{\alpha \beta} \rangle = \frac{1}{N_s} \sum_{k, \alpha \beta} b_{\alpha \beta}^{\dagger}(k)e^{ik(r_i-r_j)}
\]

self-consistently in the Gutzwiller approximation, where \(N_s\) is the number of lattice sites and \(b_{\alpha \beta}(k)\) the form factors of different symmetries in the \(D_{4h}\) point group of the crystal; \(b_{\alpha \alpha}(k) = \gamma_k\) and \(b_{\alpha \beta}(k) = \beta_k\) in the \(A_{1g}\) and \(b_{\alpha \beta}(k) = \beta_k\) and \(b_{\beta \beta}(k) = \gamma_k\) in the \(B_{1g}\) channel. Remarkably, we find that the ground state is a prominent superconductor with \(B_{1g}\) symmetry. In Fig. 3(a) and 3(b), the gap functions are plotted along the FSs, which exhibit a two-band \(d_{\pm}\)wave structure with 8 nodes (4 on each FS) and an overall sign-change between the two FSs. This is a strong coupling \(d\)-wave analogy of the proposed \(s_{\pm}\) pairing gap function in Fe-based superconductors. We stress that the new mechanism of doping an orbital-selective Mott insulator in the two-band unconventional cuprate is crucial for the emergent high-\(T_c\) SC state in the highly overdoped region. The close to half-filled, strongly correlated \(d_{z^2}\) band is responsible for the large pairing gap (\(\sim 25\) meV). The highly overdoped wider \(d_{z^2}\) band develops a smaller (\(\sim 9\) meV) antiphase gap, but can nevertheless boost the superfluid density. Thus, such a two-band superconductor can provide both a large pairing amplitude and a substantial superfluid density for phase coherence, which are necessary for producing high-\(T_c\) superconductivity in doped Mott insulators \cite{3}. It is conceivable that this mechanism provides an explanation for the nearly doubled \(T_c\) compared the isostructural single-band La214. The calculated orbital resolved local density of states, \(N_{\alpha \sigma}(\omega) = \sum_{\mathbf{k}, \mathbf{\tau}} \text{Im} \int_0^\infty e^{i\omega \tau} \langle T_{\tau} d_{\mathbf{k} \alpha \sigma}(\mathbf{r}) d_{\mathbf{k} \alpha \sigma}^\dagger(0) \rangle\), is shown in Fig. 3(c), exhibiting the mixing of two \(d\)-wave gap functions and the dominate spectral weight from the \(d_{z^2}\) band. We also find that increasing the \(\delta\)-oxygen density to \(\delta = 0.45\) leads to a different SC state of \(A_{1g}\) symmetry near the \(d^8\) configuration with a two-band \(s_{\pm}\) gap function \cite{8}, in qualitatively agreement with the recent weak-coupling RPA calculations \cite{30}. 

![Figure 3](image-url)
In summary, we presented a theoretical description of the atomic and electronic structure, and the emergence of superconductivity of the newly discovered 73K high-$T_c$ Ba$_2$CuO$_{3+y}$ at $\delta = 0.2$ \cite{[44]}. The key difference to the conventional cuprates is that the high pressure and oxygenation growth stabilized polycrystals isostuctural to La214, but with an inverted crystal field due to the compressed octahedron that activates both the $d_{z^2}$ and $d_{s^2}$ orbitals highly overdoped ($x = 0.4$) from the $d^9$ configuration. This is complimentary to the CuO$_2$ monolayer grown on Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ \cite{[51]}, where the liberation of the $d_{z^2}$ orbital and nodeless two-band superconductivity have been argued to arise from the crystal field of the unbalanced octahedron and the heavy hole-doping through interface carrier transfer \cite{[9]}. Constructing a minimal two-orbital Hubbard model using the DFT band structure, we found that the correlated electronic states can be described by a novel doped two-orbital Mott insulator and materialize a new two-band high-$T_c$ SC state with $d_{z^2}$-wave gap functions through the spin and spin-orbit exchange interactions. The multiband and the orbital selectivity are crucial for the $T_c$ enhancement at such high dopings via a combination of strong pairing interaction and the large superfluid density. The basic prediction of $d_{z^2}$ orbital libration and two-band superconductivity should be amenable to experimental tests for two pairing gaps in the heat capacity, NMR, and tunneling measurements in the current polycrystal samples. While further experimental and theoretical studies are necessary, the present theory offers a conjecture that Ba$_2$CuO$_{3+y}$ highlights a class of unconventional cuprates, including the 95K Sr$_2$CuO$_3$+δ \cite{[22],[34]}, where in-plane positional δ-oxygen doping under high-pressure can serve as a route toward higher $T_c$ by utilizing the electrons partially occupying both the 3d $e_g$ orbitals.

We thank C.Q. Jin and S. Uchida for useful discussions. The work is supported in part by the Ministry of Science and Technology of China 973 program (No. 2017YFA0303100, No. 2015CB921300), National Science Foundation of China (Grant No. NSFC-1190020, 11534014, 11334012), and the Strategic Priority Research Program of CAS (Grant No. XDB07000000); and the U.S. Department of Energy, Basic Energy Sciences Grant No. DE-FG02-99ER45747 (K.J and Z.W). Z.W. thanks the Institute of Physics, CAS for hospitality. The first two authors (C. Le and K. Jiang) contributed equally.

\[1\] J.G. Bednorz, K.A. Muller, Z. Phys. B 64, 189 (1986).
\[2\] F. C. Zhang and T. M. Rice, Phys. Rev. B 37, 3759(R) (1988).
\[3\] Patrick A. Lee, Naoto Nagaosa, and Xiao-Gang Wen, Rev. Mod. Phys. 78, 17 (2006).
\[4\] C.-C. Chen, et. al. Phys. Rev. Lett. 105, 177401 (2010).
\[5\] X. Wang, H.T. Dan, and A.J. Millis, Phys. Rev. B 84, 014530 (2011).
\[6\] H. Sakakibara, H. Usui, K. Kuroki, R. Arita, and H. Aoki, Phys. Rev. Lett. 105, 057003 (2010).
\[7\] H. Sakakibara, H. Usui, K. Kuroki, R. Arita, and H. Aoki, Phys. Rev. B 85, 064501 (2012).
\[8\] W. M. Li, et al., PNAS 116, 12156 (2019).
\[9\] K. Jiang, X. Wu, J. Hu and Z. Wang, Phys. Rev. Lett. 121, 227002 (2018).
\[10\] D. C. Peets, D. G. Hawthorn, K. M. Shen, Y.-J. Kim, D. S. Ellis, H. Zhang, S. Komiyab, Y. Ando, G. A. Sawatsky, R. Liang, D. A. Bonn, and W. N. Hardy, Phys. Rev. Lett. 103, 087402 (2009).
\[11\] Xin Wang, Luca de Medici, and A. J. Millis, Phys. Rev. B 81, 045452 (2010).
\[12\] Kai Liu, Zhong-Yi Lu, Tao Xiang, Phys. Rev. Materials 3, 044802 (2019).
\[13\] See Supplemental Material for more detailed discussions.
\[14\] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
\[15\] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
\[16\] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169(1996).
\[17\] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
\[18\] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
\[19\] S. Graser, T. A. Maier, P. J. Hirschfeld, and D. J. Scalapino, New J. Phys. 11, 025016 (2009).
\[20\] F. Wang, H. Zhai, Y. Ran, A. Vishwanath, and D. Lee, Phys. Rev. Lett. 102, 047005 (2009).
\[21\] A. Chubukov, D. Efremov, and I. Eremin, Phys. Rev. B 78 134512 (2008).
\[22\] K. Seo, B. Bernevig, and J. Hu, Phys. Rev. Lett. 101, 206404 (2008).
\[23\] C. Castellani, C.R. Natoli, and J. Ranninger, Phys. Rev. B 18, 4945 (1978).
\[24\] A. Georges, L. de Medici, and J. M. Raveja, Annu. Rev. Condens. Matter Phys. 4, 137 (2013).
\[25\] K. I. Kugel and D. I. Khomskii, Sov. Phys. JETP 37, 725 (1973); K. I. Kugel and D. I. Khomskii, Sov. Phys. Usp. 25, 231 (1982).
\[26\] J. Bunemann, W. Weber, and F. Gebhard, Phys. Rev. B 67, 6898 (1998).
\[27\] F. Lechermann, A. Georges, G. Kotliar, and O. Parcollet, Phys. Rev. B 76, 155102 (2007).
\[28\] S. Zhou, Z. Wang, Phys. Rev. Lett. 105, 096401 (2010).
\[29\] Sen Zhou, Meng Gao, Hong Ding, Patrick A. Lee, and Ziqiang Wang, Phys. Rev. Lett. 94, 206401 (2005).
\[30\] T. A. Maier, T. Berlijn, and D. J. Scalapino, Phys. Rev. B 99, 224515 (2019).
\[31\] Y. Zhong, Y. Wang, S. Han, Y. Lv, W. Wang, D. Zhang, H. Ding, Y. Zhang, L. Wang, K. He, R. Zhong, J. A. Schneeloch, G. Gu, C. Song, X. Ma, Q. K. Xue, Science Bulletin 61, 1239 (2016).
\[32\] T. H. Geballe and M. Marcezi, Physica C 469, 680 (2009).
\[33\] Q. Q. Lin, H. Yang, X.M. Qin, Y.Yu, L.X. Yang, F.Y.Li, R.C.Yu, C.Q.Jin, S.Uchida, Phys. Rev. B 74, 100506 (2006).
\[34\] Z. Hiroi, M. Takano, M. Azuma, Y. Takeda, Nature 364, 315 (1993).
TABLE S1. Experimental determined crystal Structure of Ba$_2$CuO$_{3+\delta}$ in space group $I4/mmm$ with lattice constant $a = 4.003\,\AA$ and $b = 12.942\,\AA$.

| Atom | site | x   | y   | z     | occupancy |
|------|------|-----|-----|-------|-----------|
| Ba   | 4e   | 0   | 0   | 0.35627 | 1         |
| Cu   | 2a   | 0   | 0   | 0     | 1         |
| O$_1$| 4e   | 0   | 0   | 0.1438 | 1         |
| O$_2$| 4c   | 0   | 0.5 | 0     | 0.592     |

SUPPLEMENTAL MATERIAL

A. Density functional calculations

Our calculations are performed using density functional theory (DFT) employing the projector augmented wave (PAW) method encoded in the Vienna ab initio simulation package (VASP) [1–3]. Generalized-gradient approximation (GGA) [4] for the exchange correlation functional is used. Throughout the work, the cutoff energy is set to be 500 eV for expanding the wave functions into plane-wave basis. In the calculation, the Brillouin zone (BZ) is sampled in the $k$ space within Monkhorst-Pack scheme [5]. On the basis of the equilibrium structure, the $k$ mesh used is $10 \times 10 \times 4$. In our calculation, we adopt the experimental parameters listed in Table S1 [6] and use the stoichiometric formula Ba$_2$CuO$_4$ (Ba214) and Ba$_2$CuO$_3$ (B213), whose crystal structures are shown in Fig. S1(a) and Fig. S2(a). The calculated band structures are shown in Fig. S1(c) and Fig. S2(c) for Ba214 and Ba213 respectively. Note that the convention of BZ using the BCO primitive unit cell is slightly different than the normal cuprate convention. To be consistent with other cuprates, we use the common convention of cuprates. As can be seen from Fig. S2, Ba213 has 1D Cu-O chain planes. We choose the chain to be along the $x$ direction. As a result, the hopping in the $y$ direction is greatly reduced due to the lack of oxygen on the bond, leading to an 1D band with two 1D Fermi surface sections shown in Fig. S2(b) and (c), which are consistent with the calculations in Ref. [7].

B. Orbital construction and Tight-binding model parameters

To construct an effective model describing the band structures near Fermi level, we can analyze orbital characters of the electronic structure. The $d_{x^2-y^2}$ orbital mixed with the anti-symmetric combination of the in-plane oxygen $p_x$ and $p_y$ orbitals is similar to the Zhang-Rice singlet of common cuprate contributing a hole pocket around the M point. Due to the compressed octahedron, the $d_{z^2}$ orbital strongly hybridizes with the $p_z$ orbital from the top apical oxygen (O$_A$) and bottom apical oxygen (O$_B$), as shown in the left side of Fig. S1(b).

FIG. S1. (a) Crystal structure of Ba$_2$CuO$_4$. (b) Effective molecular orbital through hybridization between $d_{x^2}$ and apical oxygen $p_z$ orbitals. Right side is the schematic molecular orbital $\phi_1$. (c) Calculated DFT band structure.

FIG. S2. (a) Crystal structure of Ba$_2$CuO$_3$ with Cu-O chain in $x$ direction. (b) The Fermi surface of Ba$_2$CuO$_3$. (c) Calculated DFT band structure.

One can consider a local molecular model describing this hybridization. Taking $p^A_x$, $d_{x^2}$, $p^B_z$ as the basis, the effective Hamiltonian of the molecular model can be writ-
The corresponding eigenvectors are

$$\phi_1 = -p_x^A + p_z^B - \frac{1}{2t}(\epsilon_1 + \epsilon_2 + \sqrt{8t^2 + (\epsilon_1 - \epsilon_2)^2})d_{z^2}$$

$$\phi_2 = p_x^A + p_z^B$$

$$\phi_3 = -p_x^A + p_z^B - \frac{1}{2t}(\epsilon_1 + \epsilon_2 - \sqrt{8t^2 + (\epsilon_1 - \epsilon_2)^2})d_{z^2}.$$

The schematic molecular orbital $\phi_1$ is plotted in right side of Fig. S1(b). From Fig. S1(c), we can also find that $\phi_1$ and $\phi_3$ are located around Fermi level and -4.5eV respectively. $\phi_2$ is entirely attributed to O$_{A/1}$/p$_z$ orbitals and distributes around -2.6eV. Hence, $\phi_1$ with the $d_{z^2}$ like bonding orbital and Zhang-Rice singlet with the $d_{z^2}$ like bonding orbital dominate the electronic structure around the BCO Fermi level. Based on the DFT results and orbital fields, we construct a two-orbital tight-binding (TB) model of Cu $e_g$ complex for the BCO. The Hamiltonian is given in Eq. (1) in the main text. Denoting $d_{\alpha\sigma}$, $\alpha = x(d_{x^2}), z(d_{z^2})$

$$H_t = \sum_{k\sigma} \varepsilon_{k\sigma}^x d^\dagger_{k\sigma} d_{k\sigma} + \sum_{k\sigma} \frac{\varepsilon_{k\sigma}}{2} (d^\dagger_{k\sigma} d_{k\sigma} + h.c.) + \sum_{k\sigma} \varepsilon_{k\sigma}^{z} d^\dagger_{k\sigma} d_{k\sigma} + \sum_{k\sigma} \varepsilon_{k\sigma}^{1} d^\dagger_{k\sigma} d_{k\sigma} \tag{S3}$$

where $\varepsilon_{\alpha\beta}$ is the kinetic energy due to intra and interorbital hopping, and $\varepsilon_{\alpha}$ is the on-site energy of $d_{z^2}$ and $d_{z^2}$ orbitals. Up to third nearest neighbor hopping, we have

$$\varepsilon_{k}^{xx} = -2t_x \gamma_k - 4t_x' \alpha_k - 2t_y' \gamma_k$$

$$\varepsilon_{k}^{zz} = -2t_z \gamma_k - 4t_z' \alpha_k - 2t_y' \gamma_k$$

$$\varepsilon_{k}^{zz} = 2t_{\gamma z} \beta_k + 2t_{\gamma x} \alpha_k \gamma_k \tag{S4}$$

where the intraorbital hopping involves lattice harmonics of $A_1$ symmetry $\gamma_k = \cos k_x + \cos k_y$, $\alpha_k = \cos k_x \cos k_y$, and $\gamma'_k = \cos 2k_x + \cos 2k_y$, and the interorbital hopping involves $B_1$ harmonics $\beta_k = \cos k_x - \cos k_y$ and $\beta'_k = \cos 2k_x - \cos 2k_y$. The hopping parameters for the $1st$ ($t$), $2nd$ ($t'$), and $3rd$ ($t''$) nearest neighbors are listed in Table S2. The on-site energy of $d_{x^2}$ and $d_{z^2}$ are $e_x = 2.275eV$ and $e_z = 3.2035eV$.

References:

1. G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
2. G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
3. G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169(1996).
4. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
5. H. J. Monkhorst and J. Pack, Phys. Rev. B 13, 5188 (1976).
6. W. M. Li, et al., PNAS 116, 12156 (2019).
7. Kai Liu, Zhong-Yi Lu, Tao Xiang, Phys. Rev. Materials 3, 044802 (2019).