# Non-Zhang-Rice Singlet Character of the First Ionization State of T-CuO

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(Received 2 June 2015; revised manuscript received 27 October 2015; published 25 February 2016)

We argue that tetragonal CuO (T-CuO) has the potential to finally settle long-standing modeling issues for cuprate physics. We compare the one-hole quasiparticle (qp) dispersion of T-CuO to that of cuprates, in the framework of the strongly correlated ($U_{dd} \to \infty$) limit of the three-band Emery model. Unlike in $CuO_2$, magnetic frustration in T-CuO breaks the $C_4$ rotational symmetry and leads to strong deviations from the Zhang-Rice singlet picture in parts of the reciprocal space. Our results are consistent with angle-resolved photoemission spectroscopy data but in sharp contradiction to those of a one-band model previously suggested for them. These differences identify T-CuO as an ideal material to test a variety of scenarios proposed for explaining cuprate phenomenology.

DOI: 10.1103/PhysRevLett.116.087002

*Introduction.*—Understanding the high-temperature superconductivity in cuprates [1] is one of the biggest challenges in condensed matter physics. These layered materials contain two-dimensional (2D) $CuO_2$ layers which exhibit antiferromagnetic (AFM) order when undoped, and host superconductivity upon doping. Consequently, it is widely believed that understanding the behavior of a doped $CuO_2$ layer is the key to understanding the unusual properties of these materials.

The first step is to understand the nature of the quasiparticle (qp) that forms when a hole is doped into a $CuO_2$ layer. Despite many efforts, this issue is not yet settled.

The Cu $3d_{x^2-y^2}$ and ligand O $2p$ are the most relevant orbitals, and their appropriate model is the three-band Emery Hamiltonian [2]. Zhang and Rice argued that its quasiparticle is a Zhang-Rice singlet (ZRS) hopping on the Cu sublattice, well described by the (relatively) simpler one-band $t$-$J$ or Hubbard Hamiltonians [3–5]. Significant effort focusing on these one-band models followed. In the absence of exact solutions or accurate approximations, progress came from numerical studies of finite-size clusters and from cluster dynamical mean-field theory [6]. These showed that the qp dispersion is strongly influenced by the quantum fluctuations of the AFM background [7], and that longer-range hopping is necessary for quantitative agreement with experimental measurements [8–11]. The longer-range hoppings required to achieve this agreement agree with those calculated theoretically [12,13]. This was taken as proof that these extended one-band models are correct, and the focus shifted to studying them at finite doping [14]. While much work was done in the past two decades, the lack even of consensus that they support robust, high-temperature superconductivity raises doubts about how appropriate they are to describe the hole-doped cuprates [15].

There are two reasons why one-band models might fail to capture the desired physics at finite doping. (i) They may describe the qp correctly yet fail to appropriately model the effective interactions between qp's, responsible for pairing. This was shown to occur when degrees of freedom from different sublattices are mapped onto an effective one-band model [16]. Because in cuprates the doped holes reside on oxygen whereas the magnons reside on Cu [17], a one-band model may similarly fail to mimic their full interaction. (ii) They may predict the correct qp dispersion for the wrong reasons. Support for the latter view comes from our recent work on the $U_{dd} \to \infty$ limit of the Emery model; the resulting Hamiltonian has spins at the Cu sites and doped holes on the O sublattice [17]. In stark contrast to one-band models where spin fluctuations are key to obtaining the correct qp dispersion, here this is found even in their absence [18]. This qualitative difference shows that although these qp's have similar dispersion, it is controlled by different physics [19].

To fully decide whether these one- and three-band models are equivalent, one must compare them for a material like $CuO_2$, so that it is described by similar Hamiltonians, however, one where they give different predictions. In this Letter we show that tetragonal CuO (T-CuO) is precisely this material whose investigation can finally resolve these fundamental modeling issues.

Thin films of T-CuO were recently grown epitaxially on $SrTiO_3$ [20]. They consist of stacks of weakly interacting CuO layers, whose structure has two intercalated $CuO_2$ lattices (sharing the same O), see Fig. 1(a). Figure 1(b) shows a $CuO_2$ layer. Because Cu $3d_{x^2-y^2}$ orbitals only hybridize with their ligand O $2p$ orbitals, shown in the same color in Fig. 1, the two $CuO_2$ sublattices would be effectively decoupled if $pp$ hopping between the two sets of O $2p$ orbitals was absent [21]. In this case, a hole doped into one sublattice would evolve just like in a $CuO_2$ layer, and the same (but doubly degenerate) qp dispersion would be predicted by both one- and three-band models, as discussed.

However, the $CuO_2$ sublattices are coupled by $pp$ hopping, which lifts this degeneracy. The resulting qp dispersion was measured by angle resolved photoemission spectroscopy (ARPES) [22]. It seems to be quite similar to that of $CuO_2$ and was argued to be well described by the $t - t' - t'' - J$ model [22]. As we show next, this is opposite to what we find for the $U_{dd} \to \infty$ limit of the three-band model. We predict qualitatively different dispersions for T-CuO and $CuO_2$; however, their differences are hidden in magnetically twinned samples. We present our results next and then explain why they cannot be reproduced by one-band models.

*Model.*—We study the $U_{dd} \to \infty$ limit of the Emery model, with spins at the Cu sites and a single doped hole on the O sublattice. This limit is justified because $U_{dd}$ is the largest energy scale [23]. The corresponding Hamiltonian, see Fig. 1(b), is [17]

$$\hat{H} = \hat{T}_{pp} + \hat{T}_{\mathrm{swap}} + \hat{H}_{J_{pd}} + \hat{H}_{J_{dd}}. \tag{1}$$

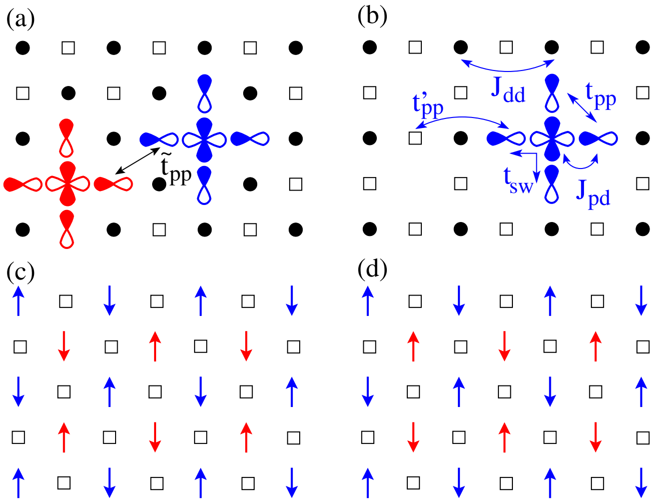

FIG. 1. Structure of a layer of (a) T-CuO, and (b) $CuO_2$. Full circles are Cu, empty squares are O. The Cu $3d_{x^2-y^2}$ orbitals are drawn at a few sites, with white (dark) lobes showing our choice for positive (negative) signs. The corresponding ligand O $2p$ orbitals are also indicated on neighboring O sites. The T-CuO layer can be thought of as two intercalated $CuO_2$ layers sharing common O. The coppers of the two sublattices hybridize with different O $2p$ orbitals. Panels (c) and (d) show the two degenerate ground states of the undoped T-CuO layer. Different colors are used for the Cu spins on the two sublattices for better visibility.

$\hat{T}_{pp} = \sum_{i \neq j \in \mathrm{O}, \sigma} t_{i-j} p^{\dagger}_{i,\sigma} p_{j,\sigma}$ describes next-nearest (NN) $t_{pp}$, and second NN $t'_{pp}$ hopping of the hole between ligand O $2p$ orbitals; the latter is restricted to oxygens bridged by a Cu. For technical details see the Supplemental Material [24] and Ref. [25]. $T_{\mathrm{swap}}$ describes Cu-mediated hopping accompanied by a spin swap. Specifically, the hole at a Cu site adjacent to the doped hole hops to another neighbor O, followed by the doped hole falling into the vacated Cu orbital. Because the original doped hole replaces the Cu hole, their spins are swapped. Thus $T_{\mathrm{swap}} = -t_{sw} \sum_{i \in \mathrm{Cu}, \mathbf{u} \neq \mathbf{u}', \sigma, \sigma'} s_{\mathbf{u}-\mathbf{u}'} p^{\dagger}_{i+\mathbf{u},\sigma} p_{i+\mathbf{u}',\sigma'} |i_{\sigma'}\rangle\langle i_{\sigma}|$, where $\mathbf{u}, \mathbf{u}' = (\pm 0.5, 0), (0, \pm 0.5)$ are the distances between Cu and its NN O sites. It shows the change of the Cu spin located at $\mathbf{R}_i$ from $\sigma$ to $\sigma'$ as the doped hole changes its spin from $\sigma'$ to $\sigma$ while moving to another O. The sign $s_{\boldsymbol{\eta}} = \pm 1$ comes from overlaps of the orbitals involved [24]. $\hat{H}_{J_{pd}} = J_{pd} \sum_{i,\mathbf{u}} \mathbf{S}_i \cdot \mathbf{s}_{i+\mathbf{u}}$ is generated when the Cu hole hops onto the O hosting the doped hole, followed by one of the two holes returning to the Cu. This gives rise to AFM exchange between the spins $\mathbf{s}_{i+\mathbf{u}}$ of the doped hole and $\mathbf{S}_i$ of its neighbor Cu. Finally, $\hat{H}_{J_{dd}} = J_{dd} \sum_{\langle i,j \rangle'} \mathbf{S}_i \cdot \mathbf{S}_j$ is the AFM coupling between NN Cu spins, except on the bond blocked by the doped hole. Its energy scale $J_{dd} \sim 150$ meV is taken as the unit of energy, in terms of which $t_{pp} = 4.1$, $t'_{pp} = 0.6 t_{pp}$, $t_{sw} = 3.0$ and $J_{pd} = 2.8$ [23]. The Hubbard repulsion $U_{pp}$ is not included in Eq. (1) because we consider only the case of a single doped hole.

In $CuO_2$ the ligand orbitals are the important ones, but it is straightforward to also include the in-plane non-ligand orbitals. These do not hybridize with Cu $3d_{x^2-y^2}$ so their addition does not affect $\hat{T}_{\mathrm{swap}}$, $\hat{H}_{J_{pd}}$ or $\hat{H}_{J_{dd}}$, which arise from such hybridization. Only $\hat{T}_{pp}$ must be supplemented accordingly. By symmetry, NN hopping between two nonligand orbitals is the same $t_{pp}$ as for ligand orbitals, with signs dictated by the lobes' overlap. Hopping between ligand and non-ligand orbitals, denoted $\hat{T}_{\mathrm{mix}}$ and shown by the arrow in Fig. 1(a), has magnitude $\tilde{t}_{pp}/t_{pp} = (t_{pp,\sigma} - t_{pp,\pi})/(t_{pp,\sigma} + t_{pp,\pi}) = 0.6$ because $t_{pp,\sigma} = 4 t_{pp,\pi}$ [26]. For $CuO_2$, inclusion of the non-ligand orbitals has a minor effect on the qp dispersion [18].

The Hamiltonian for T-CuO is a straightforward generalization of Eq. (1). Hole hopping is described by the same $\hat{T}_{pp} + \hat{T}_{\mathrm{mix}}$. Because of the two Cu sublattices, however, there are two sets of terms $\hat{T}_{\mathrm{swap}}$, $\hat{H}_{J_{pd}}$ and $\hat{H}_{J_{dd}}$ which couple Cu spins on each sublattice to each other and to the doped hole, when it occupies a $2p$ orbital with ligand character for that sublattice. We use the same parameters for T-CuO as for $CuO_2$ (the results remain qualitatively similar if the parameters are varied within reasonable ranges) and focus on the effect of $\hat{T}_{\mathrm{mix}}$, which moves the hole between the two sets of $2p$ orbitals and changes to which Cu sublattice it is coupled [21].

*Variational approximation.*—We extract the qp dispersion $E_{\rm qp}(\mathbf{k})$ from the one-hole propagator computed variationally in a restricted Hilbert space that allows up to $n_m$ magnons to be created by the doped hole through $\hat{T}_{\rm swap}$ and $\hat{H}_{J_{pd}}$ processes, assuming that it was injected in a Néel-like background [18,24]. Of course, in reality there are spin fluctuations in the AFM background, but because their energy scale $J_{dd}$ is small, they are slow and have little effect on the qp: the hole creates and moves its magnon cloud on a time scale faster than that controlling the spin fluctuations, so the latter can be ignored [18,19]. If the T-CuO energy scales are similar, and given the weak coupling between the two Cu sublattices, this approximation should remain valid.

In undoped T-CuO each Cu sublattice has AFM order due to its $\hat{H}_{J_{dd}}$ term. Any weak coupling $\tilde{J}_{dd}$ between the two Cu sublattices is therefore fully frustrated: any spin interacts with equal numbers of up and down spins from the other sublattice. Nevertheless, order by disorder selects one of the two degenerate states depicted in Figs. 1(c) and 1(d) as the ground state of the undoped system [27]. Because they have FM chains running along the $x = \pm y$ diagonals, they are related by a $C_4$ rotation so it suffices to study one case. Thus for T-CuO in either of these states, the quasiparticle dispersion $E_{\rm qp}(\mathbf{k})$ is not invariant to $C_4$ rotations, only to $C_2$ ones.

*Results.*—Figures 2(a)–2(c) show $E_{\rm qp}(\mathbf{k})$ from the variational method with $n_m = 1$, 2, 3, respectively, for the magnetic order of Fig. 1(c). The Brillouin zone (BZ) is displayed in Fig. 2(d). Full (dashed) lines are for T-CuO ($\rm CuO_2$).

In $\rm CuO_2$, at the points marked by circles and squares there are identical, nearly isotropic minima [10,11]. With increasing $n_m$, the bandwidth narrows and the dispersion flattens below the polaron + one magnon continuum (both are standard polaronic effects [18]) but the shape is unchanged. The results are nearly converged at $n_m = 3$ for $\rm CuO_2$, with a bandwidth of $\sim 2J_{dd}$ in agreement with exact diagonalization results and experimental data [18]).

In T-CuO, we verified that for $\hat{T}_{\rm mix} = 0$ the same (but now doubly degenerate) dispersion is obtained. When $\hat{T}_{\rm mix}$ is turned on, this degeneracy is lifted. Only the low-energy eigenenergy is shown in Fig. 2. Again, results are essentially converged for $n_m = 3$. As expected, the dispersion loses its invariance to $C_4$ rotations because the qp now moves in a magnetic background that lacks this symmetry. In the $k_x = -k_y$ quadrants, $E_{\rm qp}(\mathbf{k})$ again displays deep, isotropic minima around $\pm[(\pi/2), -(\pi/2)]$ (full squares) and is thus similar to $\rm CuO_2$. The difference, however, is significant in the $k_x = k_y$ quadrants near the $\pm[(\pi/2), (\pi/2)]$ points (circles). Not only are energies here higher than at the $\pm[(\pi/2), -(\pi/2)]$, but these minima are shifted toward the $\Gamma$ point. Note that the BZ corners (empty squares) still mark local minima, but they lie at high energies just below the polaron + one magnon continuum.

We now prove that this unusual dispersion for T-CuO involves physics beyond the Zhang-Rice singlet. As such, it cannot be described by one-band models obtained through a projection onto these states.

We start by estimating the effect of $\hat{T}_{\rm mix}$ on the $\rm CuO_2$ degenerate eigenstates that appear in its absence, whose energy $E_0(\mathbf{k})$ is shown by dashed lines in Fig. 2. Especially near $[\pm(\pi/2), \pm(\pi/2)]$, the $\rm CuO_2$ qp indeed has a large overlap with a ZRS Bloch state [19], and the hole occupies the $x^2 - y^2$ linear combination of O $2p$ ligand orbitals sketched for two NN sites in Fig. 2(e). For T-CuO, these degenerate states combine into one Bloch state $|d, \mathbf{k}\rangle$ with momentum $\mathbf{k}$ in its bigger BZ. If we use $|d, \mathbf{k}\rangle$ as an

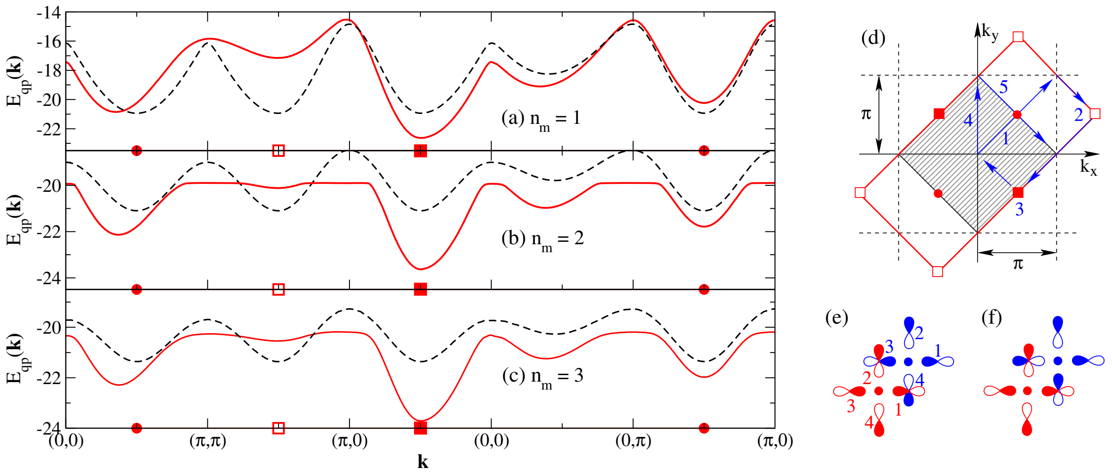

FIG. 2. qp dispersion in units of $J_{dd}$ for (a) $n_m = 1$, (b) $n_m = 2$, and (c) $n_m = 3$ with full (dashed) lines for T-CuO ($\rm CuO_2$). The Brillouin zone for the magnetic order of Fig. 1(c) is shown in red in (d). The shaded area is the smaller BZ for $\rm CuO_2$. The points marked by circles and empty or full squares are equivalent in $\rm CuO_2$ but not in T-CuO. (e) Hopping between two adjacent ZRSs, and (f) between a ZRS (red) and one with $x - y$ symmetry (blue). See text for more details.

approximation for the low-energy eigenstate, then the T-CuO dispersion becomes $E_{\mathrm{qp}}(\mathbf{k}) \approx E_0(\mathbf{k}) + \delta E(\mathbf{k})$, where $\delta E(\mathbf{k}) = \langle d, \mathbf{k}|\hat{T}_{\mathrm{mix}}|d, \mathbf{k}\rangle$ is

$$\delta E(\mathbf{k}) = -\tilde{t}_{pp} \cos\frac{k_x + k_y}{2}[1 - \cos(k_x - k_y)].$$

The cosines are a geometric factor from the Bloch states' phase differences between neighboring Cu sites [24].

Because $\delta E(k_x = -k_y) = -2\tilde{t}_{pp} \sin^2 k_x$ and $\delta E(k_y = k_x \mp \pi) = \pm 2\tilde{t}_{pp} \sin(k_x)$, minima at $\pm[(\pi/2), -(\pi/2)]$ (full squares) move to lower energies while minima at the BZ corners (empty squares) move up. This agrees with the results of Fig. 2.

However, because $\delta E(k_x = k_y) = 0$, the dispersion near $\pm[(\pi/2), (\pi/2)]$ (circles) should remain unchanged instead of these minima moving toward the $\Gamma$ point. Moreover, we find that the overlap between the T-CuO qp and $|d, \mathbf{k}\rangle$ *vanishes* at $\mathbf{k} = \pm[(\pi/2), (\pi/2)]$. These facts clearly prove that the changes near the $\pm[(\pi/2), (\pi/2)]$ points cannot be due to Zhang-Rice singlet physics.

Indeed, $\hat{T}_{\mathrm{mix}}$ hopping between $x^2 - y^2$ linear combinations centered at NN Cu sites is suppressed, see Fig. 2(e): e.g., a hole at site 1 of the lower Cu (red) hops into $p_1^\dagger + p_3^\dagger$ of the upper Cu (blue), which is orthogonal to its $x^2 - y^2$ linear combination. Instead, hopping between adjacent $x^2 - y^2$ and $x - y$ combinations is enhanced, see Fig. 2(f). The shift of the $\pm[(\pi/2), (\pi/2)]$ minima toward $\Gamma$ is due to a large mixing of the singlet with $x - y$ symmetry into the quasiparticle eigenstate, which thus loses its ZRS nature (for more details see the Supplemental Material [24]). Note that experiments like Refs. [28], which are sensitive only to the local singlet character, cannot distinguish a ZRS singlet from one with such mixed symmetry.

We checked that adding terms like $\tilde{J}_{dd}$ and $\tilde{J}_{pd}$ [21] has no qualitative effects on the dispersion. This is expected because their matrix elements are small and/or featureless near $[\pm(\pi/2), \pm(\pi/2)]$. We are therefore confident that our prediction is robust.

ARPES finds the T-CuO qp dispersion to obey $C_4$ symmetry and to have a large BZ, corresponding to a unit cell containing one Cu and one O atom [22]. Both features are very surprising for the long-range magnetic orders of Figs. 1(c) and 1(d), which break the $C_4$ symmetry. Moreover, any AFM-type order has at least two magnetically nonequivalent Cu atoms so its BZ is like in Fig. 2(d) or smaller, never larger. Our results become consistent with ARPES if we assume the presence of domains in both ground states, so that their average is measured experimentally. Indeed, as shown in the Supplemental Material [24], averaging $E_{\mathrm{qp}}(\mathbf{k})$ of Fig. 2(d) with its counterpart rotated by 90° leads to an apparent doubling of the BZ and a new pattern of minima with two different energies, in agreement with those found experimentally.

We predict that a dispersion like in Fig. 2 appears in the ARPES of "magnetically untwinned" T-CuO films in the insulating limit. This is very different and thus easily distinguishable from the one-band model prediction [22]. The observation of this pattern, with shallower displaced minima in two quadrants, will provide a clear proof of low-energy physics beyond the ZRS, and of the superiority of three-band models to model such materials. If T-CuO films can be doped, this new pattern of minima will open extraordinary opportunities to test many ideas relating the shape of the Fermi surface, location of "hot spots" and possibility of nesting, to much of the cuprate phenomenology, including the symmetry of the superconducting gap, formation of stripes, appearance and relevance of various other ordered phases, etc.

We note that ARPES measurements on untwinned pnictides have been successfully performed (see, e.g., Ref. [29]). It is therefore reasonable to expect that similar measurements for T-CuO are feasible. An important lesson from this study is that low-energy physics of a non-ZRS nature can arise in T-CuO and similar materials in suitable circumstances or symmetries. The presence of disorder, of other nearby quasiparticles, of stripes, charge-density wave, or other ordered phases may have a similar effect in $\mathrm{CuO}_2$ layers.

We thank G. Koster and M. Grioni for useful discussions. Work was supported by NSERC, QMI, CIFAR, SNF, and a UBC 4Y Fellowship (CA).

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