X-Ray Absorption Spectra Reveal the Inapplicability of the Single-Band Hubbard Model to Overdoped Cuprate Superconductors

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X-ray absorption spectra on the overdoped high-temperature superconductors $Tl_2Ba_2CuO_{6+\delta}$ and $La_{2-x}Sr_xCuO_{4\pm\delta}$ reveal a striking departure in the electronic structure from that of the underdoped regime. The upper Hubbard band, identified with strong correlation effects, is not observed on the oxygen K edge, while the lowest-energy prepeak gains less intensity than expected above $p \sim 0.21$. This suggests a breakdown of the Zhang-Rice singlet approximation and a loss of correlation effects or a significant shift in the most fundamental parameters of the system, rendering single-band Hubbard models inapplicable. Such fundamental changes suggest that the overdoped regime may offer a distinct route to understanding in the cuprates.

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The greatest unsolved problem in correlated electron physics is high-temperature superconductivity in the cuprates. As holes are doped into their Mott-insulating parent compound, a plethora of new electronic phases emerge [1], but for only the undoped Mott insulator does an agreed-upon microscopic picture exist. The remaining phases are characterized by unusual electronic structure—the Fermi surface may consist of remnant arcs [2–4] or pockets enclosing little of the Brillouin zone [5–8], superconductivity with unconventional $d_{x^2-y^2}$-symmetry pairing emerges [9–11], and a nonsuperconducting ''pseudogap'' state exhibits a gap reminiscent of superconductivity.

Past optimal doping, where the superconducting transition temperature T_c peaks, the materials behave more like conventional metals. This ''overdoped'' side's resistivity approaches the Fermi liquid T^2 power law [12,13], while the Fermi surfaces of $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) [14–16] and $La_{2-x}Sr_xCuO_{4\pm\delta}$ (LSCO) [17] closely resemble those from band structure calculations. Understanding this evolution may prove key to understanding the cuprates' phase diagram.

An undoped CuO_2 plane's copper atoms have the electronic configuration $[Ar]3d^9$, with one hole in each Cu $3d_{x^2-y^2}$ orbital; although band structure calculations in the local density approximation (LDA) predict metallic behavior, it is instead a charge transfer insulator with a 2–3 eV gap—strong correlation effects produce upper and lower Hubbard bands, electron addition and removal states of the system, respectively, separated in energy by U, with an oxygen band between them. Hole doping manifests as a transfer of spectral weight from the Hubbard bands into states near the Fermi energy, often labeled the ''Zhang-Rice singlet band'' [18]. Both one- and three-band models calculate this transfer to be roughly proportional to doping [19–22], in agreement with oxygen K-edge x-ray absorption spectra (probing O $2p$ unoccupied states) on underdoped and optimally doped cuprates [21,23–25]. Measurements on a handful of overdoped LSCO samples [23,24], however, suggested the low-energy spectral weight to plateau on further doping, and optical measurements have also observed changes [26]. Since preparing overdoped LSCO crystals without oxygen deficiencies or inhomogeneity is difficult, it is tempting to attribute this to poor sample quality. If verified, however, these results could herald significant changes in the cuprates' physics and a fundamental breakdown of the approaches commonly used to model them.

Although the doped holes occupy oxygen orbitals, they can save energy by hybridizing with a Cu spin to form a $d_{x^2-y^2}$-symmetry Zhang-Rice singlet [18,27]. Each doped hole locally compensates a Cu spin, mimicking a doped hole in a single-band Hubbard model with $3d_{x^2-y^2}$ symmetry, as opposed to a three-band model comprising Cu $3d_{x^2-y^2}$ and O $2p_{x,y}$ states. This effective single-band description underpins the widely used t-J model of the cuprates.

In this Letter, we report new x-ray absorption spectroscopy (XAS) measurements at the oxygen K edge in over-

doped LSCO and Tl-2201, comparing them to underdoped $YBa_2Cu_3O_x$ (YBCO). We confirm the weakening of low-energy spectral weight transfer at higher dopings; that this is observed in both families indicates it to be generic to overdoped cuprates. These results point to a fundamental change in electronic structure, suggesting the inapplicability of a Zhang-Rice description or any model based upon it, and implying uncharted theoretical territory beyond optimal doping. These changes may help explain the overdoped regime's comparative normalcy, and suggest that it may offer a new and distinct starting point for understanding in the cuprates.

$Tl_2Ba_2CuO_{6+\delta}$ single crystals were grown by a self-flux technique [15], annealed under controlled oxygen partial pressures, etched using dilute bromine in anhydrous ethanol to ensure high-quality surfaces, and masked with gold to eliminate any spurious contributions. Crystals were kept in H_2O- and CO_2-free environments to prevent surface damage. Tl-2201's doping was estimated using Presland's phenomenological formula [28],

$$1 - \frac{T_c}{T_c^{\max}} = 82.6(p - 0.16)^2, \quad (1)$$

with $T_c^{\max} = 94$ K, which has proven consistent with dopings determined from the Luttinger theorem and measurements of the Fermi surface area in heavily overdoped Tl-2201 crystals by angular magnetoresistance oscillations [14] and angle-resolved photoemission spectroscopy [15].

Samples of La_2CuO_4 [29] and LSCO were grown by the traveling solvent floating zone technique, cut to expose the ac plane, polished with 0.05 μm alumina grit, and etched with dilute Br prior to measurement. Samples of YBCO were detwinned, oxygen-annealed self-flux-grown single crystals [30] with polished and etched ac or as-grown ab plane surfaces; doping was determined as in Ref. [31].

Oxygen K-edge x-ray absorption spectra were measured at beam line 8.0.1 of the Advanced Light Source [32], with an energy resolution of 0.40 eV, via total fluorescence yield (significantly less surface-sensitive than total electron yield), and normalized by incident intensity. Tl-2201 spectra were collected at room temperature on overdoped crystals with T_cs of 9.5, 60, and 69 K for $E \perp c$; a $T_c = 60$ K crystal measured with a 40° angle between E and a, such that all features were visible, showed no change to 91 K. LSCO and YBCO were measured at normal incidence with $E \parallel a$.

To account for variations in signal strength (e.g., less of the beam strikes smaller samples), the spectra were further normalized against each other using energy ranges below and well above the main edge. Small shifts in the beam line's energy calibration precluded an overall calibration; instead, the spectra's main absorption edges were matched to earlier work [23,25,33]. The key results reported in this Letter are insensitive to the transitions' absolute energies,

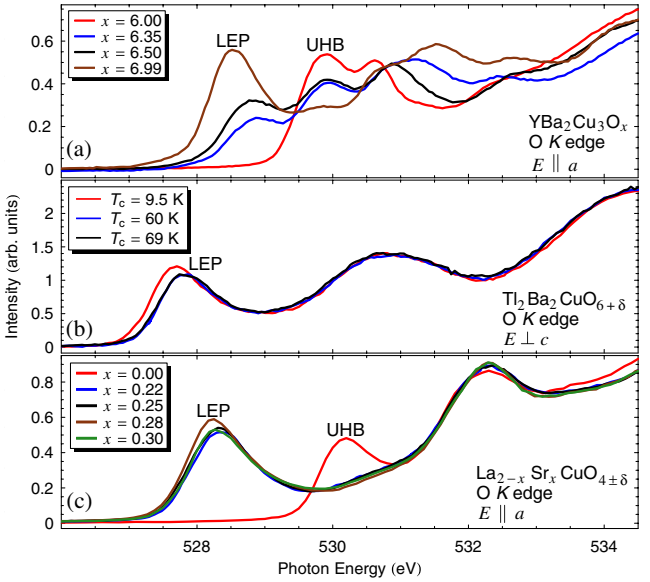

FIG. 1 (color online). Doping dependence, O K edge, $E \parallel a$ (to avoid YBCO CuO chain features): (a) YBCO shows typical underdoped cuprate behavior—the lowest-energy prepeak (LEP), absent in the undoped ($x = 6.00$) cuprate, grows rapidly and shifts to lower energy as doping increases; the next prepeak (UHB), identified with the upper Hubbard band, is suppressed, but remains clearly visible to light overdoping ($x = 6.99$). (b) Tl-2201's UHB is not observed, while its LEP exhibits only minor doping dependence. (c) Overdoped LSCO's doping dependence resembles Tl-2201's; undoped $x = 0$ provides a reference point.

which are a function of the initial core level's energy and can vary by crystallographic site and orbital symmetry.

YBCO, Tl-2201, and LSCO in-plane oxygen K-edge spectra are shown in Fig. 1. From undoped ($x = 6.00$) to slight overdoping ($x = 6.99$), YBCO's lowest-energy pre-edge peak (prepeak) at ~528.3 eV decreases in energy and strengthens while the next prepeak (~529.8 eV, identified with the upper Hubbard band) weakens, consistent with theoretical expectations and previous measurements [24,25]. Tl-2201's lowest-energy prepeak is only visible for $E \perp c$, identifying it as an extension of that in YBCO; it continues to increase in intensity and decrease in energy with doping, although its intensity changes more gradually. Similar behavior is seen in LSCO. The remaining prepeaks in Tl-2201 are attributed to the BaO and primarily the Tl_2O_2 layers, by their polarization dependence and by comparison to LDA band structure calculations (not shown). The upper Hubbard band, ubiquitous in underdoped cuprates and clearly observed in YBCO, is absent or weak and nearly doping-independent in the overdoped materials' oxygen edges.

The lowest-energy prepeak's doping dependence is shown in Fig. 2 for Tl-2201, YBCO, and LSCO; previous measurements are included. Integration windows were

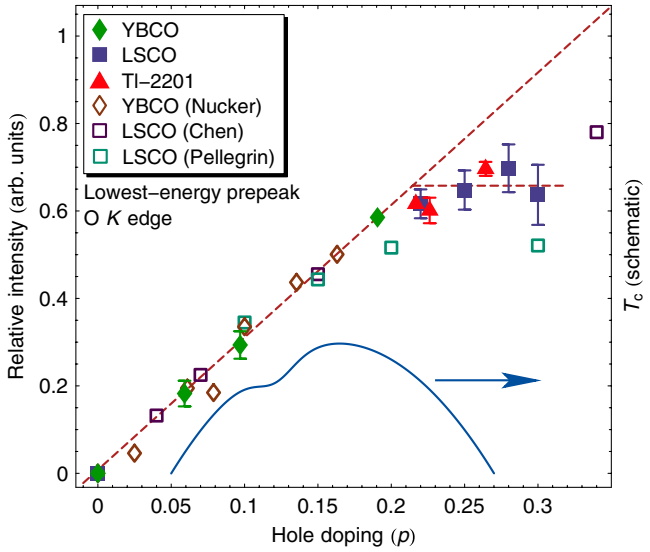

FIG. 2 (color online). Doping dependence of lowest-energy O K-edge prepeak ($E \parallel a$); data from Nücker *et al.* [25], Chen *et al.* [23], and Pellegrin *et al.* [24] are included and the superconducting dome is provided for reference. The weight closely tracks p up to and past optimal doping ($p = 0.16$), but deviates from this trend around $p = 0.21$, exhibiting much weaker doping dependence in the strongly overdoped regime.

526.75–529.25 eV (YBCO), 526.7–529.4 eV (LSCO), and 525.6–529.4 eV (Tl-2201); weights were normalized by assuming LSCO and YBCO follow the same line in the underdoped regime and by equating the $x = 0.22$ LSCO and Tl-2201 $p = 0.217$ ($T_c = 69$ K) weights. That YBCO, a bilayer material, should exactly track single-layer LSCO is not obvious, but this is immaterial to the overdoped trends discussed below. A small offset of ~0.02 due to nonzero weight in the undoped spectra was subtracted from the LSCO and YBCO weights, which assumes a linear doping dependence of the Hubbard band. The prepeak's intensity increases roughly linearly with doping over much of the doping range, consistent with one- or three-band Hubbard descriptions of XAS [19–22]. However, overdoped Tl-2201 and LSCO deviate from this trend around $p = 0.21$, exhibiting weaker doping dependence and possibly even decreasing at the highest LSCO doping. While changes in the cuprates' physical properties have been observed in this doping range [34,35], x-ray absorption directly reveals the underlying fundamental change in the electronic structure that is likely responsible. The prepeak's doping dependence, apparently generic to overdoped cuprates, conflicts with the basic description of the cuprates in a doped one- or three-band Hubbard model; indeed, it more closely resembles that of a simple band metal, with one new Fermi level hole state per doped hole rather than the two derived from spectral weight transfer. Together with the missing upper Hubbard band, these results indicate a clear change in the nature of the electronic structure.

These changes likely mark a fundamental breakdown of the Zhang-Rice singlet model at high dopings and with it the applicability of single-band Hubbard or t-J models. At $p = 0.25$, the probability for nearest neighbor Zhang-Rice singlets reaches unity. These share a common oxygen atom, making them nonorthogonal and costing the O $2p$ on-site repulsion U_{pp}. With Zhang-Rice singlets thus unstable at high dopings and inapplicable as a basis state, one key question is what takes their place. This limitation of the theory may be obvious, at least in retrospect, but very little theoretical work has considered it, and what could extend or supplant the current single-band Hubbard approaches remains unanswered.

In a correlated picture, at high doping levels the high O $2p$ hole density would increase the influence of U_{pp} (~5 eV [36] and similar to the O $2p$ bandwidth), reducing Cu–O covalency in the ground state [37]. This would *intensify* strong correlation effects for Cu $3d$ holes and further stabilize local Cu spins. The upper Hubbard band is only visible on the oxygen edge due to strong Cu $3d$–O $2p$ mixing, and would quickly vanish if covalency fell—Eskes showed the low-energy dynamical spectral weight transfer to depend strongly on the covalency t_{pd}/Δ_{pd} (the ratio of the intersite hopping parameter to the charge transfer energy) [19,38]. Leaving the region where Zhang-Rice singletlike states are stable, the system may enter the region of free O $2p$ holes in a Cu ($S = 1/2$) lattice background [27]. The greater role for U_{pp} would increase the charge transfer energy and introduce correlation effects to the oxygen bands. Oxygen holes would retain their mainly p_x and p_y character (these states remain atop the O $2p$ bands), but Zhang-Rice singlets would no longer enforce $d_{x^2-y^2}$ symmetry. The loss of covalency would greatly reduce superexchange, and with little change expected in U_{dd}, copper atoms would behave more like isolated spins. Data suggestive of such behavior have been reported in overdoped LSCO [39].

The absence of spectral features associated with the strong correlation effects ubiquitous in the underdoped regime signals a fundamental change in the cuprates' electronic structure around $p = 0.21$, although the nature of this change is unclear and further work will be required to determine its origin, full properties, exact location, and whether this location varies by material. These changes suggest the breakdown of single-band Hubbard approaches as holes cease to be dilute. The overdoped cuprates may behave as simple, ordinary band metals, with the underdoped regime's Fermi arcs and other curious electronic structure features being signatures of strong correlations that only arise for low dopings. The correlations could instead survive, masked from the oxygen K edge by reduced covalency, with an increased role for U_{pp} and significant doping-dependent shifts in fundamental parameters of the system such as the charge transfer energy and p–d hopping terms (different parameters are already

required for electron- and hole-doped cuprates [19]). The latter explanation suggests Fermi-liquid-like O $2p$ holes weakly coupled to a Cu $3d$ spin bath, reminiscent of the heavy fermion superconductors. Both explanations are inconsistent with the Zhang-Rice singletlike states underpinning single-band Hubbard models; fundamentally new theoretical approaches will be required to successfully model the full superconducting dome. Ultimately, these results may tie into the trend toward more conventional Fermi-liquid-like behavior as T_c decreases in the overdoped cuprates, and may open a fruitful new route to understanding in these otherwise enigmatic materials.

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Note added in proof.—It has been brought to the authors' attention that a saturation in prepeak intensity on overdoping has also been reported in single-layer bismuth-based cuprates [40].

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