

# Doping evolution of Zhang-Rice singlet spectral weight: A comprehensive examination by x-ray absorption spectroscopy

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The total spectral weight  $S$  of the emergent low-energy quasiparticles in high-temperature superconductors (HTSCs) is explored by x-ray absorption spectroscopy. In order to examine the applicability of the Hubbard model, regimes that cover from zero doping to overdoping are investigated. In contrast to results of mean-field theory, we found that  $S$  deviates from linear dependence on the doping level  $p$ . The slope of  $S$  versus  $p$  changes continuously throughout the whole doping range with no sign of saturation up to  $p = 0.23$ . Therefore, the picture of the Zhang-Rice singlet remains intact within the most prominent doping regimes of HTSCs.

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## I. INTRODUCTION

The high-temperature superconductors (HTSCs) still attract intensive research attention in condensed matter physics even nearly three decades after their discovery. In some respects, understanding of HTSCs is even more elusive nowadays due to very recent experimental endeavors and controversies. For examples, issues such as the possible Fermi surface reconstruction<sup>1</sup> and a new competing order of charge ordering<sup>2</sup> are reshaping our understanding of HTSCs. More fundamentally, the appropriate picture of doped quasiparticles in HTSCs and their orbital character has not completely emerged yet. Many believe that the central piece of these issues lies in the elucidation of the doped Mott insulator. The general consensus has been that the parent compound of HTSCs is a Mott insulator and the doped holes can be described by an effective Hubbard model or the  $t$ - $J$  model projecting out the double occupancy. As holes are doped into the oxygen orbital in HTSCs, they hybridize with Cu spins to form Zhang-Rice singlets<sup>3</sup> (ZRSs) residing between the upper (UHB) and the lower (LHB) Hubbard band.

However, these foundations in our understanding of HTSCs have been challenged for the past several years.<sup>4</sup> A noticeable case from x-ray absorption spectroscopy (XAS) was proposed by Peets *et al.*<sup>5</sup> By compiling available XAS data for different cuprates, they claimed that the spectral weight of ZRSs was saturated for the hole doping level  $p \geq 0.21$ . (Also, see an earlier statement of saturated ZRS weight with  $p > 0.16$  in Ref. 6.) This surprising finding of saturation in XAS explicitly indicated the breakdown of ZRSs. Moreover, this early saturation, if it holds, actually indicates a failure of the three-band model of cuprates, as was later pointed out.<sup>7</sup> Partly stimulated by this unexpected breakdown of the fundamental frame of Mott physics for HTSCs, very recently there have been many reports using modern theoretical techniques to reinvestigate this issue.<sup>7-11</sup> Despite these new theoretical efforts, the conclusions drawn from these calculations are

not entirely consistent with each other. Therefore, a new and more comprehensive experimental examination of Zhang-Rice-singlet XAS is certainly indispensable.

In this work, we examine the XAS at the O  $K$  and Cu  $L$  edges using well-(001)-oriented  $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$  thin films within the 123 family to avoid any possible discrepancy due to different cuprate systems. By analyzing the total spectral weight revealed in the Zhang-Rice band of the O  $K$  edge and ligand holes in the Cu  $L$  edge, we show that, consistently with theoretical calculations, both spectral weights show clear deviations from simple linear dependence on the doping level  $p$ . In addition, we find that the slope of  $S$  versus  $p$  changes continuously throughout the whole doping range without any sign of saturation up to  $p = 0.23$ . *Our results show the validity of Zhang-Rice singlets within the most intensively studied doping regimes of HTSCs.* In addition, the present results might not be in conflict with the work of Peets *et al.*, since the highest doping  $p = 0.23$  in this paper only slightly overlaps the saturation regime reported in Ref. 5.

## II. EXPERIMENTS

We start by characterizing the samples and measurements used in this work. Highly oriented (001)  $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$  (Ca-YBCO;  $x = 0, 0.3$ , and  $0.4$ ) thin films were deposited on (100) SrTiO<sub>3</sub> substrates by the pulsed laser deposition (PLD) method. A KrF excimer laser ( $\lambda = 248$  nm) operating at a repetition rate of 5 Hz with an energy density of  $\sim 5$  J/cm<sup>2</sup> was used for Ca-YBCO film growth in the optimal growth conditions of 740–770 °C substrate temperatures and 0.26–0.3 Torr oxygen partial pressures. The electrical resistivity as a function of temperature  $\rho(T)$  was measured by a standard four-probe method. The oxygen content of the films can be repeatedly changed by the controlling temperatures and oxygen pressures inside the quartz tube surrounded by the furnace.<sup>12</sup> XAS at the O  $K$  and Cu  $L$  edges was performed in fluorescence mode using synchrotron radiation from the 6 m

high-energy spherical monochromator (HSGM) beamline at the National Synchrotron Radiation Research Center in Taiwan. Details of the XAS experiments can be found elsewhere.<sup>13,14</sup> All the thin films were about 300 nm thick to avoid an absorption contribution from the oxide substrates. Self-absorption corrections were applied to these spectra to correct the saturation effects. The energy resolution of the monochromator was set to  $\sim 0.1$  eV for the O  $K$  edge range and  $\sim 0.2$  eV for the Cu  $L$  edge.

The doping level  $p$  was determined with special care. For superconducting samples, the estimated value of  $p$  was derived from  $1 - T_c/T_{c,\max} = 82.6(p - 0.16)^2$ ,<sup>15</sup> where  $T_{c,\max}$  is the maximum transition temperature at the optimum doping in each system. For heavily underdoped thin films of  $p = 0.02$ – $0.05$  with no  $T_c$ ,  $p$  was determined from the value of the thermoelectric power (TEP) at room temperature.<sup>15</sup> The  $p$  values of several superconducting underdoped or overdoped samples were cross-checked by both  $T_c$  and the thermoelectric power. The results for  $p$  were found to be consistent between these two methods. For TEP measurements, the magnitude of the temperature gradient was maintained below 1 K and the sample space was maintained in a good vacuum ( $10^{-4}$  Torr). Due to the high resistivity in the extremely underdoped regime of Ca-YBCO, the  $p$  value of the sample with second-lowest doping was assessed to be about 0.012 from the interpolation of the peak intensity of the UHB in the O  $K$  edge XAS.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows  $\rho(T)$  of representative samples from underdoping to overdoping. The  $T$  dependence and the values of  $\rho(T)$  both demonstrate the high quality of the thin films, nearly as good as that of single crystals. Figure 1(b) shows the corresponding O  $K$  edge XAS spectra of YBCO and Ca-YBCO samples in Fig. 1(a). XAS provides information

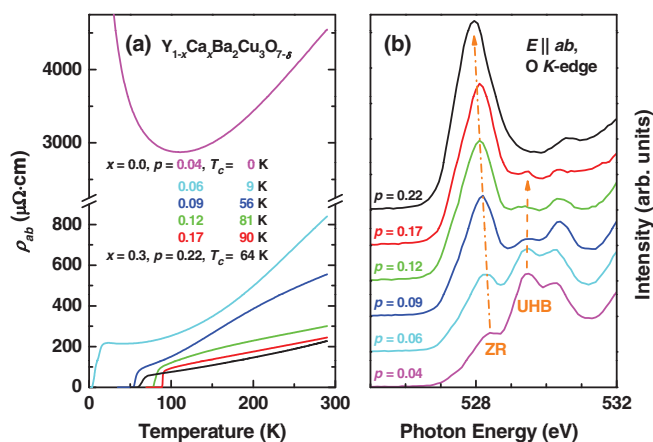


FIG. 1. (Color online) (a) The temperature dependence of in-plane resistivity ( $\rho_{ab}$ ) for YBCO ( $x = 0$ ) thin films with various hole concentrations ( $p = 0.04, 0.06, 0.09, 0.12$ , and  $0.17$ ) and Ca-YBCO ( $x = 0.3$ ) thin film for  $p = 0.22$ . (b) The polarized ( $E \parallel ab$ ) XAS of the O  $K$  edge of YBCO and Ca-YBCO thin films measured at room temperature. The yellow dashed and dash-dotted lines are guides to eyes to depict that the ZRS and UHB are moving away from each other in energy as  $p$  increases.

about the unoccupied states near the Fermi energy  $E_F$ , and is considered as one of the most appropriate tools to explore doped Mott insulators. Actually, early seminal XAS work helped to establish the ZRS picture in HTSCs.<sup>16,17</sup> The features of the O  $K$  edge XAS around  $E = 527.5, 528.2$ , and  $529.4$  eV are attributed to the CuO chain holes, ZRSs, and UHB, respectively. The ZR band and the UHB are not rigid and are correlated with each other. Removing  $p$  electrons from a Mott insulator in the atomic limit should increase the ZRS spectral weight by  $2p$  at the expense of UHB spectral weight by  $p$ , as qualitatively shown in Fig. 1(b). (The LHB also loses spectral weight of  $p$ , which cannot be detected by XAS.) The peaks of the ZRSs and UHB evolve away from each other with increasing  $p$  as suggested by some calculations that the UHB shifts away from  $E_F$  when  $p$  becomes larger.<sup>7,8,11</sup>

The main theme of the present work is the  $p$  dependence of the ZRS spectral weight  $S$ . Figure 2(a) shows  $S(p)$  from  $p = 0$  to  $0.23$ , covering both the underdoped and overdoped regimes. The open red circles denote the experimental spectral weight as illustrated by the inset of Fig. 2(a). (The data point at  $p = 0$  came from the zero ZRS spectral weight of a sample rather than the extrapolation.) Earlier calculations have pointed out that the spectral weight  $S$  should be linear with respect to the doping level  $p$  in the present doping range.<sup>18,19</sup> However, a recent experimental XAS study claimed saturation of  $S$  for  $p \geq 0.21$ .<sup>5</sup> As seen in Fig. 2(a), our results do show a weak slope change in  $S$  throughout the whole doping range, but no sign of saturation was observed. The recent calculations via the two-dimensional one-band Hubbard model<sup>8</sup> (black solid line) and three-orbital Hubbard model<sup>11</sup> (blue solid triangles) are also depicted in Fig. 2(a). It is seen that both the one-band and three-orbital Hubbard models capture the trend of  $S(p)$  with impressive accuracy. According to Ref. 11, this slope change is due to the combined effects of core-hole interaction and weakened correlation with doping. The doping levels from  $p = 0$  to  $0.23$  are the regimes that host superconductivity and other competing orderings like the pseudogap for HTSCs. Therefore, the Hubbard model and ZRSs seem to be good (at least to the first order) approximations to describe the intriguing nature of HTSCs. For the presently studied doping regimes, the one-band and the three-orbital Hubbard models lead to almost the same results [see Fig. 2(a)]. In principle, the three-orbital Hubbard model would go beyond the one-band Hubbard model and predict a smaller  $S$  at higher doping than the one-band model does.<sup>11</sup> In principle, an effectively doping-dependent Hubbard  $U(p)$  is needed to fit the spectra weight.<sup>11,20</sup> Further comprehensive examinations at higher doping levels are certainly desirable.

Moreover, in the low-doping regimes  $S$  also shows features other than a simple linear behavior with respect to the doping level  $p$  [see Fig. 2(a)]. Explicitly, there exists an unexpected kink at  $p \approx 0.02$  in  $S(p)$ . The slope of  $S(p)$  suddenly changes to a smaller value for  $p > 0.02$ . Experimentally, this kink might manifest the interplay between O  $2p$  and Cu  $3d$  states as will be discussed later. Interestingly, the one-band model appears to capture the kink feature as indicated by the black solid line in Fig. 2(a).<sup>8</sup> More theoretical studies are needed to fully identify the origin of the surprising slope change at such a low doping level.

There has been concern that different integration energy windows might lead to different conclusions.<sup>5,7–11</sup> We also

tried a  $\pm 0.5$  eV integration window and basically obtained the same  $p$  dependence of  $S(p)$  (results not shown). Furthermore, as shown in Fig. 2(b),  $S(p)$  of the ZRS band was obtained from a Gaussian multipeak fit. Experimentally, the integration window should not be a major factor since the spectra inevitably have suffered instrumental broadening.  $S(p)$  from the Gaussian peak fit is nearly identical to that from the energy window integration as seen in Figs. 2(a) and 2(b). To avoid being biased by existing theoretical calculations, a phenomenological two-slope fit was further used to analyze the data as shown in Fig. 2(c). In this two-slope fit,  $p_c$  is the doping level at which the slope changes. The blue solid line in Fig. 2(c) represents the optimal two-slope analysis with  $p_c = 0.11$ . While the fitting quality of the two-slope analysis is inferior to that of Liebsch’s curve as shown in the Fig. 2(c) inset, in either case it suggests that the slope of  $S(p)$  changes within the present doping regimes.

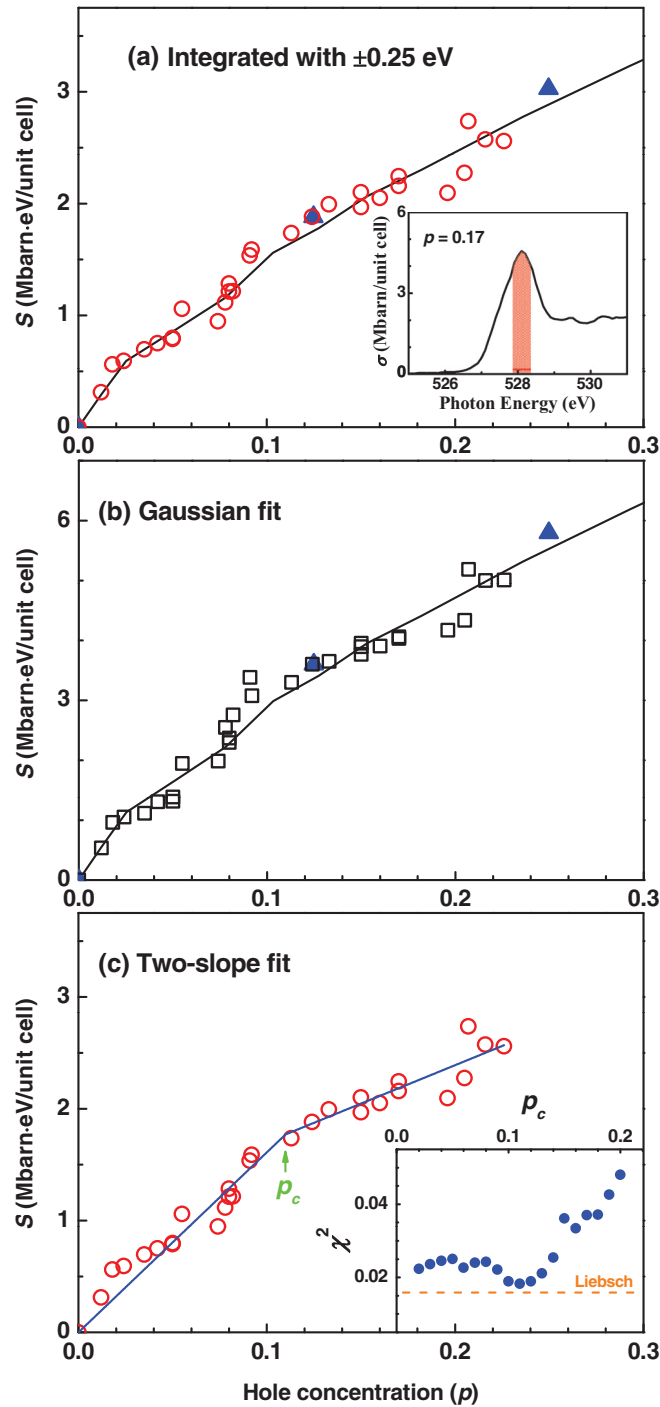


FIG. 2. (Color online) (a) The doping  $p$  dependence of the spectral weight  $S$  of the ZRS (red open circles) from the integration within  $\pm 0.25$  eV of the ZRS peak energy. The red area shown in the inset is an example integration for  $p = 0.17$  YBCO. The black curve was calculated by Liebsch (Ref. 8). Theoretical calculations (blue triangles) from Chen *et al.* (Ref. 11) normalized at  $p \sim 0.125$  are also depicted. (b)  $S(p)$  (black open squares) from the multipeak Gaussian fit. (c)  $S(p)$  analyzed by the two-slope fit. The inset shows the  $\chi^2$  distribution with the turning point ( $p_c$ ) as well as the  $\chi^2$  value from the curve fit of Liebsch (the orange dashed line).

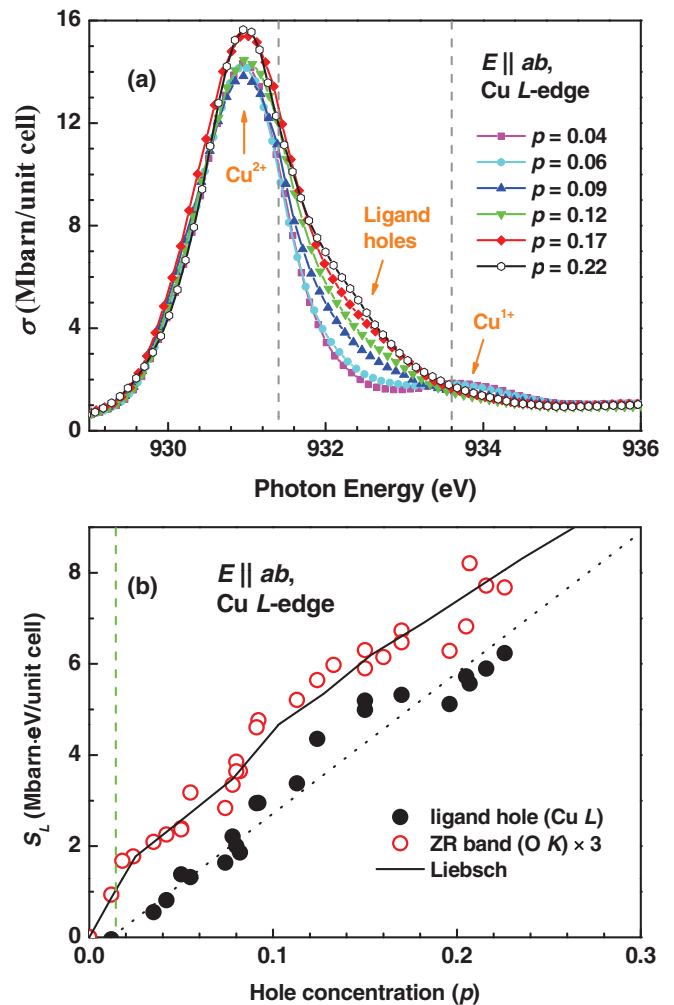


FIG. 3. (Color online) (a) The polarized ( $E \parallel ab$ ) Cu  $L$  edge XAS of YBCO and Ca-YBCO thin films measured at room temperature. The spectra consist of a main peak near 931 eV (associated with  $\text{Cu}^{2+}$ ), a broad peak near 932 eV (ligand holes), and a small peak near 934 eV (related to  $\text{Cu}^{1+}$  on empty Cu-O chains). (b) The spectra weight  $S_L$  of the ligand hole as a function of  $p$  was estimated by integrating the area within the two gray dashed lines [as shown in (a)]. The black dotted line is the linear fit of  $S_L(p)$ . The green dashed line indicates the doping level below which  $S_L(p)$  is negligible.

Figure 3(a) shows the corresponding Cu  $L$  edge XAS of the YBCO and Ca-YBCO samples in Fig. 1(a). It is noted that Cu  $L$  edge XAS with selective  $p$  samples is shown here. In addition to the  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$  features, in between them there exists an extra spectral weight. This feature has also been considered to be relevant to ZRSs and attributed to the ligand-hole states in the  $\text{CuO}_2$  planes.<sup>16,21</sup> The spectral weight  $S_L(p)$  was extracted by integration of  $\sigma_{\text{Cu}}(p) - \sigma_{\text{Cu}}(p=0)$  between  $E = 931.4$  and  $933.6$  eV as denoted by two vertical dashed lines in Fig. 3(a).  $S_L(p)$  was further corrected to the Gaussian fit of the  $\text{Cu}^{1+}$  feature and plotted in Fig. 3(b). The subsequent  $S_L(p)$  was plotted together with  $S(p)$  of the O  $K$  edge in Fig. 2(a) for comparison. At  $p = 0.012$ , the ZRS band possesses significant spectral weight, while  $S_L$  is still near zero. This indicates that the doped holes exclusively enter O  $2p$  states at a very small doping. It is noticed that the spectral weight  $S_L(p)$  shows a nonzero value when the doping level  $p > 0.02$ , presumably due to the fact that doped holes start entering Cu  $3d$  states. Consequently, the Néel temperature  $T_N$  significantly decreases to zero for  $p > 0.02$  since the long-range antiferromagnetic order is frustrated by the neighboring unoccupied sites. The evolution of the orbital character of the doped holes with  $p$  has been recently demonstrated by Compton scattering.<sup>22</sup> Therefore, the experimental reason for the kink at  $p \approx 0.02$  and the slope change of  $S(p)$  for the entire doping regime could be that the O  $2p$  states lose part of their spectral weight to Cu  $3d$  states due to the stronger Cu  $3d$  character of doped holes with increasing  $p$ . Comparing the linear fit of the  $S_L$  data (black dotted line) with the solid

line in Fig. 3(b),  $S_L(p)$  has a weaker slope change than does  $S(p)$ . This observation is also consistent with the stronger Cu character of the doped holes with increasing  $p$  in the YBCO system.

#### IV. CONCLUSIONS

To conclude, the Hubbard model and Zhang-Rice singlets describe the spectral weight of doped quasiparticles  $S(p)$  well in high-temperature superconductors for a wide doping range. This doping regime, as presented in this study, covers almost all interesting states in high-temperature superconductors including antiferromagnetism, superconductivity, the pseudogap, the (field-induced charge or magnetic) stripe phase,<sup>23–25</sup> and charge ordering. To distinguish the validity of the three-orbital Hubbard model from that of the one-band model and to explore the claimed saturation regime, x-ray absorption spectroscopy measurements with even higher doping levels are needed.

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