Electron Correlation and Charge Transfer in $[(Ba_{0.9}Nd_{0.1})CuO_{2+\delta}]_2/[CaCuO_2]_2$ Superconducting Superlattices

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We use x-ray spectroscopy to examine the electronic structure of high-temperature superconducting superlattices $[(Ba_{0.9}Nd_{0.10})CuO_{2+\delta}]_2/[CaCuO_2]_2$. The O $2p$ density of states reveals the insulating character of the individual component layers and the metallic character of the superlattices. We report the first direct observation of Zhang-Rice singlets in artificial high-temperature superconducting hetero-epitaxial structures. The experimental findings in the superlattices and its component layers offer evidence of charge transport from the so-called charge reservoir layer to the superconducting infinite layer. This suggests a strong link between superconductivity and both electron correlation and charge transfer within the superlattices.

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The mechanism describing high-temperature superconductivity (HTSC) among cuprates is still highly controversial. Although it is widely accepted that HTSC occurs primarily within Cu-O planes of cuprates [1], there is still contention concerning the low-energy physics of these planes [2]. It was recognized shortly after the discovery of HTSC that superconducting superlattices (SL), possessing a fundamentally planar character, could be used to investigate the physics of atomic planes in high-T_c compounds. These superlattices were first grown as auxiliaries to cuprates in an effort to understand high-T_c superconductivity [3]. Since then, there has been a great amount of investigation of these structures. Much of this work has dealt with the foremost question posed by these systems; i.e., what is the relationship between geometrical structure and superconductivity? Early efforts to determine this focused on the relation of T_c to the thickness variation of insulating layers between superconducting layers [4–6], and the thickness of SL component layers versus interlayer coupling, and carrier doping [4,5]. Recently Bozovic *et al.* [6] varied the geometry of $La_{1.85}Sr_{0.15}CuO_4/La_2CuO_4$ superlattices to study the interplay of antiferromagnetism and superconductivity.

While the variation of superconductive properties with layer thickness in SL is a natural choice of investigation, it is highly appealing to employ the planarity of SL to probe the in-plane physics. To do so, one can utilize artificial HTSC heterostructures grown by alternately depositing two different, juxtaposed insulating cuprates. One insulator, the charge reservoir (CR), stores charge carriers; the other, called the infinite layer (IL), supports the superconductive planes. Therefore, the artificial high-T_c SL allows an important approach in studying Cu-O plane physics; each functional block may be separately interrogated and subsequently compared to the other and the superlattice.

Such high-T_c SL, schematically shown in Fig. 1, are grown by pulsed laser deposited molecular beam epitaxy (MBE) in which superconducting SL can be fabricated in an atomic layer-by-layer fashion [7,8]. Using methods discussed elsewhere [9], 2×2 $[(Ba_{0.9}Nd_{0.1})CuO_{2+\delta}]_2/[CaCuO_2]_2$ [10] superconducting superlattices with low interface roughness, good crystallinity, and a T_c of 65 K were fabricated. Measurements of transport properties were performed with a standard four-probe technique by varying the magnetic field up to 8 T over a temperature range of 4.2 to 300 K.

An increasing amount of work has been performed on these artificial HTSC SL. Balestrino demonstrated that

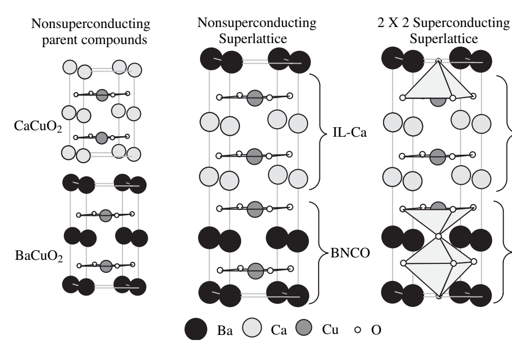

FIG. 1. Schematic of the (a) $[(Ba_{0.9}Nd_{0.1})CuO_{2+\delta}]_2$ and $(CaCuO_2)_2$ parent compounds, and unit cells for (b) nonsuperconducting and (c) superconducting $[(Ba_{0.9}Nd_{0.1})CuO_{2+\delta}]_2/(CaCuO_2)_2$ superlattices epitaxially grown by pulsed laser MBE starting from the parent compounds. IL-Ca and BNCO indicate the Ca and Ba-based layers, respectively. CR represents the charge reservoir.

superconductivity occurs only within the infinite layer and not the charge reservoir [11]. Colonna *et al.* [12] performed extended x-ray absorption fine structural analysis on $(BaCuO_2)_2/(CaCuO_2)_2$ superlattices. They investigated the SL structure and observed an oxygen doping mechanism similar to that of $YBa_2Cu_3O_{7-x}$. Raman spectroscopy [13] was performed on $SrCuO_2/BaCuO_2$ SL in order to investigate the role of apical oxygen atoms in the SL. However, there has been no effort to determine the electronic structure of these superconducting superlattices.

The electronic structure can be probed with x-ray emission (XES) and x-ray absorption (XAS) spectra, which reflect the partial density of states of valence band and conduction band, respectively. XAS [14] and XES can be combined to detect electronic density of states across the Fermi level, while resonant inelastic x-ray scattering (RIXS) is a powerful technique [15] to probe the low-energy electronic structure of cuprate planes. Already Guo [16] and Duda [17] showed that RIXS can shed light on cuprate energetics. By performing x-ray emission, resonantly excited at the absorption edges, we have probed the low-energy electronic excitations of the SL and its component layers. Charge transfer excitations were observed in the (CR) film but not in the IL film or superlattice, suggesting charge is transferred from the CR to the IL in the superlattice. In addition, we present direct evidence of the Zhang-Rice singlets (ZRS) in the IL and superlattice. To the best of our knowledge, this is the first observation of the ZRS in an artificial HTSC compound.

The experimental work was performed at the Advanced Light Source in Berkeley. At Beamline 7.0.1, the undulator and monochromator produced an intense x-ray beam with a spot size of 100 μm and energy resolution of 0.2 and 0.5 eV for XAS and XES, respectively. The O 1s absorption spectra were measured at an incident angle of 70° to the sample surface. Resonant soft x-ray emission spectra were exclusively recorded using a grazing-incidence spectrometer with a two-dimensional detector with a resolution of 0.35 eV. The spectrometer was situated in a horizontal plane and positioned 90° with respect to the incoming photon beam.

The XAS and XES spectra reflecting the unoccupied and occupied density of states are displayed in Fig. 2. The $CaCuO_2$ and $(Ba_{0.9}Nd_{0.1})CuO_{2+\delta}$ films show an open gap between the top of their valence bands and the bottom of their conduction bands because of their insulating characters. The SL possesses an overlap between the valence and conduction bands, or continuous density of states across the Fermi level, suggesting a metallic character. The insulating band gap closing is seen as the bottom of the conduction band is shifted into the band gap region while the top of the valence band remains unchanged. Such conduction band lowering is the direct evidence of hole doping in the superlattice.

Figure 3(a) shows XES spectra of BNCO thin film recorded at selected photon energies. The peaks A and B reflect the O 2p bands, which can be understood within the

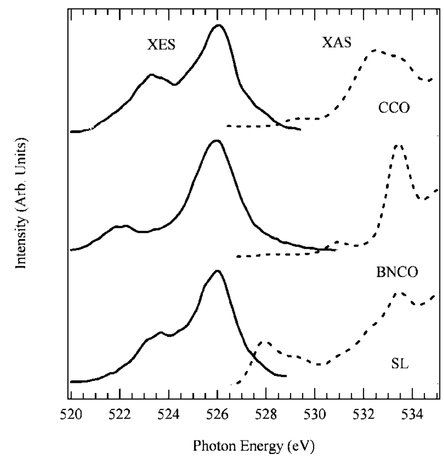

FIG. 2. XES (solid lines) and XAS (dashed lines) of the charge reservoir, infinite layer, and the superlattice reflect occupied and unoccupied densities of states near the Fermi level, respectively.

band structure description. Peak A is usually called the O 2p "main-band" peak. Peak B, located at 522 eV, is due to the covalent mixing states of O 2p-Cu 3d bonding. The arrows indicate the elastic peaks. The feature labeled *CT* is due to charge transfer excitations, which refers to the excitation of an electron from the O 2p band to the Cu 3d band, thereby producing a ligand hole in the O 2p band. This process is written as $d_j^9 \leftrightarrow d_j^{10}\underline{L}$, where $\underline{L}$ denotes a ligand hole. In the spectrum excited at 530.9 eV a low-energy excitation appears next to the elastic peak. This can be assigned to Cu *dd* excitations, which have been previously predicted [18–20] and recently identified in O 1s XES of insulating cuprates [16]. The *dd* excitation and *CT* features appear significantly at the specific photon energy of 530.9 eV. The appearance of the strongly weighted *CT* peak shows that resonant XES is strongly dependent on incident x-ray energy [20] and may indicate the quasi-one-dimensional nature for $(Ba_{0.9}Nd_{0.1})CuO_{2+\delta}$.

$CaCuO_2$ (CCO) shows a similar two-band spectral shape in Fig. 3(b), where the separation is only 3 eV between the O 2p main-band peak A and the band peak B. Noted in the spectrum excited at 529.3 eV is the small shoulderlike feature 527.5 eV attributable to *dd* excitations by virtue of its position [15]; 1.8 eV from the elastic peak. The two-band spectral profile of CCO, containing no *CT* peaks, is in excellent agreement with previous XES results [21]. Attention is called to the small spectral weight that persists at 528 eV independent of the variation of incident photon energy. These nonshifting, inelastic, low-energy features have been discussed in theoretical and experimental investigations and are attributed to ZRS [21,22]. The ZRS is the coupled state of an O 2p hole and a Cu 3d hole on a CuO_4 plaquette. Zhang and Rice proposed that a Cu hole could couple to an O 2p hole as it moves in a CuO_2 plane. They sought the ground state of a half-filled CuO_2 plane with one extra hole. A two-band Hubbard Hamiltonian model was constructed including hybridization between Cu 3d, O 2p_x, and O 2p_y orbitals, and strong Cu on-site Coulomb repul-

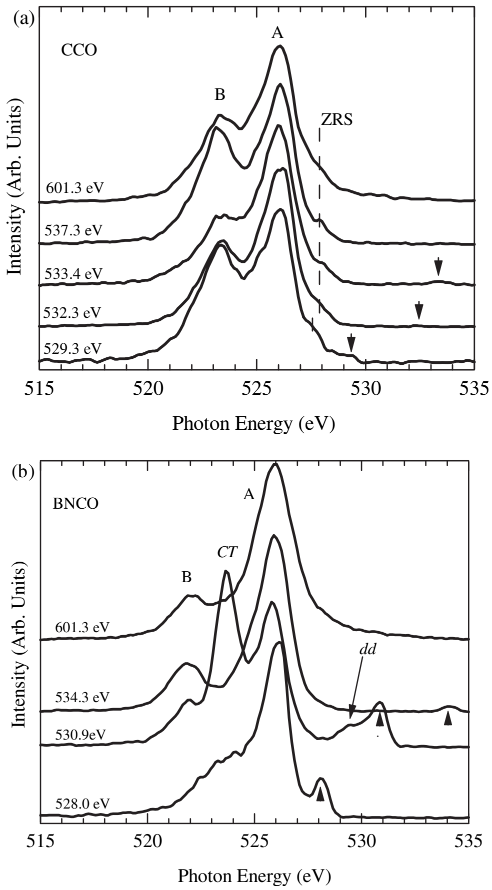

FIG. 3. XES spectra of $(Ba_{0.9}Nd_{0.1})CuO_{2+\delta}$ thin film (a) and $CaCuO_2$ thin film (b) recorded at selected excitation energies. *CT* and *dd* energy loss excitations are observed in BNCO, and the Zhang-Rice singlet is observed in the CCO film.

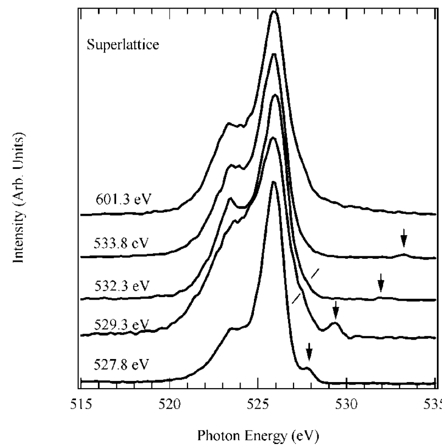

FIG. 4. XES spectra of $(Ba_{0.9}Nd_{0.1}CuO_2)_2/(CaCuO_2)_2$ superconducting superlattice recorded at selected excitation energies. Slanted lines indicate the ZRS features.

sion U. Zhang and Rice showed that the ground state of the hole-doped CuO_2 plane is the ZRS. Because it is possible to add the extra hole by three methods, doping, photoemission, or XES, we are able to investigate the electronic structure of doped cuprates.

O K x-ray emission spectra representing the total oxygen density of states due to nonbonding O $2p$ bands of the SL are displayed in Fig. 4. The separation of the main band and hybridized band structure is about 3 eV, similar to the IL layer. Features A and B represent the total oxygen density of states due to nonbonding O $2p$ bands. The major peaks match predicted [23] and measured spectral character of other high-T_c cuprates. The change in spectral shape with incident energy is likely due to contributions from different oxygen sites as the probe energy is changed [16] above. Similar to the $CaCuO_2$ film, the features at 528 eV are due to ZRS excitations as this spectral weight cannot be identified as *dd* excitations due to their fluorescent nature. The small intensity of the ZRS features is due to the reduction of the Zhang-Rice band resulting from the transfer of spectral weight from the SL upper Hubbard band (UHB) to the lower Hubbard band (LHB) [14]. Evidence of spectral weight transfer is seen in Fig. 4 where the UHB (at 529.3 eV) is weaker than the LHB (at 528 eV). It is important to distinguish the ZRS excitations in RIXS from those obtained by photoemission. We note that the existence of the ZRS is expected to be generally observable in insulating and high-T_c cuprates, and has been reported in photoemission work on CuO and a $Bi_2Sr_2CaCu_2O_{8+\delta}$ [24,25]. In photoemission, ZRS spectral weight is the result of an electron removal process. However, in RIXS, the ZRS state is the result of an electron excitation from the O $2p$ to Cu $3d$, forming an O $2p$ hole. Subsequently, an electron from a nearest neighbor Cu atom occupies (hole formation) the hole in the O $2p$ level. This nonlocal exchange of electrons between Cu ions is, by definition, accompanied by an exchange of holes (which form the ZRS). Therefore the RIXS spectral weight ascribed to Zhang-Rice singlets originate from O $2p$ to O $1s$ and Cu $3d$ to O $2p$ electronic transitions. The latter transition involves the Cu $3d$ states in the UHB, and the former yields information on the electronic states very close to the Fermi level. A reduction of the UHB lessens the low-energy spectral intensity. It has been suggested that ZRS states are split off from the valence band upon doping. While the ZRS reported here are not strictly split off from the valence band, the features are located at the top of the valence band supporting the general understanding that the ZRS band should occupy the so-called charge transfer gap.

We now discuss the occurrence or absence of the *CT* excitation in all three studied systems. The concurrence of *CT* and *dd* excitations in the CR is a characteristic of cuprates [26,27]. However, the incorporation of extra oxygen atoms in the Ba plane during growth of the SL leaves CR film charge unbalanced with O deficiencies in the CuO_2 plane [28], which may explain the observation of the *CT* excitation in BNCO and not in CCO. The absence of charge transfer features in the $CaCuO_2$, which is consistent with spectra from similar samples [21], represents a charge transfer asymmetry between the two constituent layers of superlattices. The asymmetry gives indirect evidence of unidirectional charge transport between layers, namely, from the CR to the IL. This is qualitatively understandable in the context of valence considerations, where charge is transferred from the CR to the IL in order to preserve the charge balance of the superlattices.

The disappearance of the in-plane *CT* feature in the SL can be understood in the following way: the high-T_c SL has two extra oxygen atoms [12], not possessed by the BNCO region of a nonsuperconducting SL, that are apical to Cu in the CuO plane. These oxygen atoms are shifted, giving a pyramidal coordination around Cu near the Ba-Ca interface and a distorted octahedral cage around Cu within the BNCO unit cell. The Jahn-Teller distortion of the CuO_6 octahedron gives a d_{z^2} character to doping holes on apical oxygen atoms. As a result, the BNCO *CT* excitation involving planar Cu $d_{x^2-y^2}$ hole is delocalized as the newly formed hole state couples to the CCO region. Hole doping necessarily proceeds from the CR to the IL through the apical oxygens [29]. We propose that these holes are transported into the superconducting region where they may form the ZRS. Thus, the experimental findings lead to a possible mechanism of high-T_c superconductivity, namely, the hole doping of an antiferromagnetic insulator in which ZRS singlets are already present. The movement of the ZRS [22] is predicted by the *t-J* model to lead to superconductivity by breaking the antiferromagnetic order.

In conclusion, we report the first direct observation of Zhang-Rice in artificial heteroepitaxial high-temperature superconductors. The electronic structure studies reveal the insulating to metallic transitions from individual IL and CR layers to SL. We have shown that charge transfer occurs from the charge reservoir to the infinite layer, which leads to the understanding of high-T_c superconductivity in the superlattices. The present study shows promise of RIXS being used as an insightful probe of superconducting superlattices and the utility of heteroepitaxial artificial structures in understanding the behavior of other hole-doped high-T_c superconductors.

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