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# Energy band structure of the high $T_c$ superconductors

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*In honor of Martin Peter's 60th birthday.*

**Abstract.** High resolution results on the electronic band structure and properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $\text{YB}_2\text{Cu}_3\text{O}_6$ ,  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  as obtained from highly precise state-of-the-art local density calculations demonstrate the close relation of the band structure to the structural arrangements of the constituent atoms and provide an integrated chemical and physical picture of the interactions and their possible relation to superconductivity. The ionic character of the Y is proven by similar detailed highly precise local density calculations for high  $T_c$   $\text{GdBa}_2\text{Cu}_3\text{O}_7$  and explain the coexistence of magnetism and superconductivity in the high  $T_c$  rare-earth superconductors. Surprising features are the low DOS at  $E_f$ , especially for  $\delta \geq 0.1$  which is lower per Cu atom than that in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  – in agreement with experiment and a relatively large magnetic Stoner factor. Strong indications are demonstrated for the inadequacy of a conventional phonon mechanism for obtaining the higher  $T_c$ . Charge transfer excitations of occupied Cu1–O dp $\pi$  anti-bonding orbitals into their empty Cu1–O dp $\sigma$  anti-bonding orbital partners, result in poorly screened ‘ $\text{Cu}^{3+}$ – $\text{Cu}^{4+}$ ’-like charge fluctuations. These charge transfer excitations (excitons) thus lead to strong polarization effects in these poorly screened (highly ionic) materials and induce attractive interactions among the 2D electrons. Thus, these interactions via exchange of excitons enhance the electron pairing and serve to enhance the  $T_c$  proposed for the quasi 2D superconductors.

## I. Introduction

It is fitting for this Festschrift to honor Prof. Martin Peter by focussing on two of the scientific subjects to which he has made important contributions – band structure and superconductivity. The work discussed below illustrates the role of band structure in providing unique information about the ground state of the new superconductors and how this information may provide clues to the mechanism(s) which give rise to their high  $T_c$ .

The discovery of the high  $T_c$  superconductors  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ [1] and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [2] has generated excitement among scientists and technologists on an unprecedented scale. It has also led to considerable effort to understand the mechanism giving rise to their superconductivity. One of the starting points is certainly a detailed picture of the electronic structure of the compound, a goal

which is achieved by present day supercomputers in combination with highly precise numerical methods to solve the local density (LD) Kohn–Sham equations in a self-consistent way. Even today, the origin of superconductivity in the new metallic oxides remains a challenge despite some intriguing hints obtained from experiment and electronic structure calculations. Still, it is now quite apparent that understanding the electronic structure and properties of the new high  $T_c$  superconductors is emerging. This is an important step toward achieving an understanding of the origin of their superconductivity. Detailed high resolution local density band structure results have served to demonstrate what has been our major emphasis, namely the close relation of the physics (band structure) and chemistry (bonds and valences) to the structural arrangements of the constituent atoms, and may provide insight into the basis mechanism of their superconductivity. Results obtained on the systems we have studied –  $\text{La}_2\text{CuO}_4$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , and  $\text{GdBa}_2\text{Cu}_3\text{O}_7$  indicate a number of common chemical and physical features, especially the role of oxygens (and oxygen vacancies), which bear further scrutiny. In this paper, we provide a brief summary of the results on the detailed electronic structures of the  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  and  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$  systems, compare them, and point out their relations to charge transfer excitations as a possible mechanism of superconductivity.

## II. Electronic structure and properties of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$

In  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  ( $\text{M} = \text{Sr}, \text{Ba}$ ) [3], the results of highly precise all-electron local density full potential linearized augmented plane wave [4] (FLAPW) calculations of the energy band structure, charge densities, Fermi surface, etc., demonstrated: (i) that the material consisted of metallic Cu–O(1) planes separated by insulating (dielectric) La–O(2) planes and (ii) that this 2D character and alternating metal/insulator planes would have, as some of their most important consequences, strongly anisotropic (transport, magnetic, etc.) properties. Thus, the calculated band structure along high symmetry directions in the Brillouin zone shows only flat bands, i.e., almost no dispersion, along the  $c$  axis, demonstrating that the interactions between the Cu, O(2) and La atoms are quite weak. However, along the basal plane directions there are very strong interactions between the Cu–O(1) atoms leading to large dispersions and a very wide bandwidth ( $\sim 9$  eV).

The band structure near  $E_F$  has a number of interesting features. What is especially striking is that, in contrast to the complexity of its structure, only a single free electron-like band crosses  $E_F$  (cf., Fig. 1) and gives rise to a simple Fermi surface. Since this band  $A$  in Fig. 1 originates from the Cu  $d_{x^2-y^2}$ –O(1)  $p_{x,y}$  orbitals confined within the Cu–O(1) layer, it exhibits clearly all the characteristics of a two dimensional electron system. Particularly striking is the occurrence of a van Hove saddle point singularity (SPS). Such an SPS is expected, and found, to contribute strongly, via a singular feature, to the density of states (DOS). As we shall see, this dominance of the DOS near  $E_F$  by the SPS

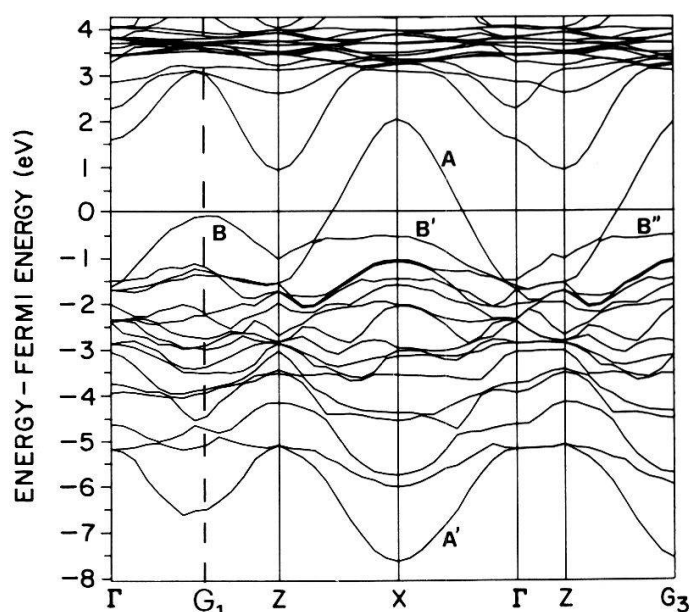


Figure 1

Band structure of  $\text{La}_2\text{CuO}_4$  along symmetry lines in the extended Brillouin zone. (See Ref. [3] for the notation used.)

contribution is responsible for many of the striking properties of this material with  $M_x$  additions.

The remarkable 2D nature of the electronic structure leads to a simple picture of the conductivity confined essentially to the metallic Cu–O(1) planes separated by insulating (ionic) planes of La–O(2). This picture is strongly confirmed by independent calculations [5] which model  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  as a single slab consisting of a Cu–O(1) layer sandwiched by one La–O(2) layer on each side. (Note that such a slab has the correct stoichiometry and is charge neutral.) The electronic structure near  $E_F$  is dominated by the same single band of 2D  $p$ – $d$  bonding character; the nesting feature [6] (with zone boundary spanning vector) and the van Hove SPS in the DOS are reproduced with this slab approach. In the band structure shown in Fig. 1, the strongly dispersed band *A* along the  $\Gamma$ –*X* (110) direction has only a Cu  $d_{x^2-y^2}$ –O(1)  $p_{x,y}$  component, while band *B* along the  $\Gamma$ – $G_1$ –*Z* (100) direction, especially at  $G_1$  (i.e. the van Hove SPS point), is a mixture of Cu  $d_{x^2-y^2}$ –O(1)  $p_{x,y}$  and Cu  $d_{z^2}$ –O(2)  $p_z$  orbitals. Another notable feature in the band structure of  $\text{La}_2\text{CuO}_4$  is that the character of the bonding partner (band *A'*) of the anti-bonding Cu  $d_{x^2-y^2}$ –O  $p_{x,y}$  band *A* consists not only of the Cu  $d_{x^2-y^2}$ –O  $p_{x,y}$  orbitals but has a large contribution from Cu  $sp$  orbitals, as also described by others [7]. (Note that these results are significantly different from the two dimensional tight binding model of Mattheiss [8], where the anti-bonding band *A* and *B*, as well as the bonding band *A'*, were regarded as having the same Cu  $d_{x^2-y^2}$ –O  $p_{x,y}$  orbital character.)

The quasi-2D properties of the electronic structure are also supported by plots of the charge densities of electrons at  $E_F$  (cf. Fig. 2). This charge density consists mainly of Cu  $d_{x^2-y^2}$  and O(1)  $p_{x,y}$  hybridized orbitals in the plane with some additional contribution of the Cu  $d_{z^2}$  and O(2)  $p_z$  components. There is



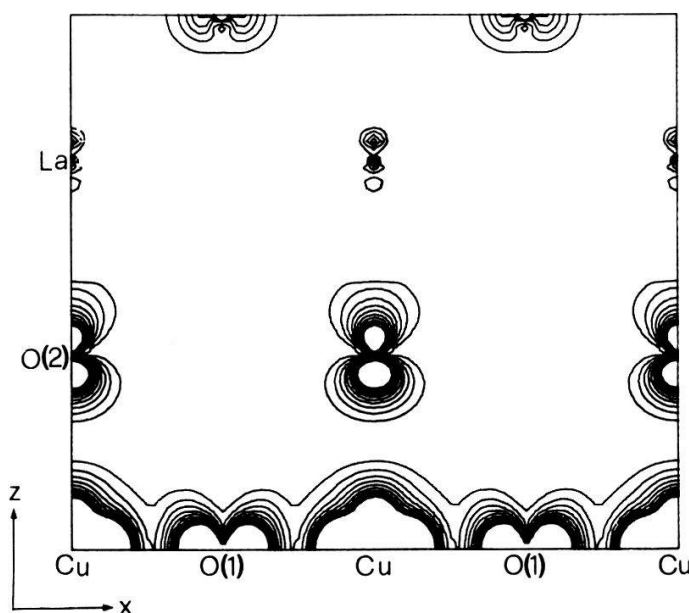


Figure 2  
Contour plot in the  $xz$  vertical plane of valence the charge density at  $E_F$  for  $\text{La}_2\text{CuO}_4$ .

essentially no electron density around the La site at  $E_F$ . This means that the La atoms do not contribute directly to the dynamical processes involving electrons near  $E_F$ . Further, an analysis of the band structure shows that the  $5d$  level of La lies more than 1 eV above  $E_F$ ; the  $5p$  levels of La were found [3] to lie far below  $E_F$  ( $\sim 15$  eV). Thus, it is a fairly good approximation to consider the La atoms to be described in chemical terms as  $\text{La}^{3+}$  ions.

In view of the results presented above, we would expect – as a first approximation – that the introduction of divalent elements (e.g.,  $\text{M} = \text{Ba}$ ,  $\text{Sr}$ , etc.) as substitutional replacements for La would not change any major feature of the band structure, charge density, DOS, etc.. Thus, the use of a rigid band approximation to treat the case of alloys,  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ , may be considered as a quite good first approximation when  $x$  is small ( $\leq 0.3$ ). (This has been confirmed by independent virtual crystal approximation calculations [5]). Hence, in this spirit, the variation of composition  $x$  in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  can be taken into account simply as a change in the position of  $E_F$ , that is  $E_F = E_F(x)$ . Further, since  $E_F$  lies very close to the SPS,  $N(E_F)$  is extremely sensitive to the position of  $E_F$  relative to the singular point. As a function of  $x$ ,  $N(E_F)$  varies from 1.2 states/eV-cell at  $x = 0$  to 1.9 states/eV-cell at  $x = 0.16$ . This large variation in  $N(E_F)$  will immediately affect a number of properties such as the magnetic susceptibility, specific heat, etc.

One major effect of the van Hove singularity on the properties of the system is the anomalous behavior of  $T_c$  with varying composition  $x$  in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ . With increasing  $x$ , the superconducting critical temperature  $T_c$  increases rapidly from 14 K for  $x \approx 0.05$  to a maximum of 37 K for  $x \approx 0.2$  but then drops sharply for larger  $x$  values. Under the condition that the pairing potential  $V$ , in the pairing interaction parameter  $\lambda = N(E_F)V$ , is constant, the change in  $T_c$  with the composition  $x$  is associated with a change of  $N(E_F)$ . In fact, recent reports [9]

show a large variation of  $T_c$  vs.  $x$  which rise sharply from 0 K at  $x < 0.03$  to 22 K at  $x = 0.08$ , hits a maximum at  $x \approx 0.15$  and then drops off sharply. These results are very consistent with our picture. Thus, it is clear that the strong variation in  $N(E_F)$ , derived from the quasi-2D van Hove singularity, plays a dominant role in the anomalous behavior of  $T_c$  as a function of  $x$ .

In total energy frozen phonon calculations [5] on  $\text{La}_{2-x}\text{M}_x\text{Cu}_4$ , the role and effect of the optical breathing mode turned out to be significant. Since the breathing phonon mode involves the motion of oxygen atoms against the directional bonding of Cu  $d$ -O  $p$  in the plane, the in-plane Cu  $d_{x^2-y^2}$ -O(1)  $p_{x,y}$  states of the 2D conduction bands are strongly affected by the breathing displacement. On the other hand, the out-of-plane Cu  $d_{z^2}$ -O(2)  $p_z$  orbitals, which are quite localized in the plane, are not much affected by the same breathing mode. But, because of the relative change of the Cu  $d_{x^2-y^2}$ -O(1)  $p_{x,y}$  and Cu  $d_{z^2}$ -O(2)  $p_z$ , the charge fluctuations between Cu atoms, which can be as large as 0.3 electrons at the maximum of the O displacement, lead to transitions of the out-of-plane Cu  $d_{z^2}$ -O(2)  $p_z$  into the in-plane Cu  $d_{x^2-y^2}$ -O(1)  $p_{x,y}$ . Since the out-of-plane (anti-bonding) Cu  $d_{z^2}$ -O(2)  $p_z$  states near  $E_F$  are localized, we expect that the localized Cu  $d_{z^2}$ -O(2)  $p_z$  states, introduced by the charge fluctuation, may couple to the delocalized conduction electrons of the in-plane Cu  $d_{x^2-y^2}$ -O(1)  $p_{x,y}$  orbital and possibly to form an excitonic state [5]. Thus, a key role in possible charge transfer excitations (CTE) is played by excitations between occupied localized Cu  $d_{z^2}$ -O(2)  $p_z$  and empty itinerant Cu  $d_{x^2-y^2}$ -O(1)  $p_{x,y}$  states. We emphasized that these could couple resonantly with natural 'Cu<sup>2+</sup>-Cu<sup>3+</sup>-like' charge fluctuations which exist in the  $x > 0$  compounds, with important consequences for the superconductivity.

### III. Electronic structure and properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$

For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , we presented [10, 11] detailed high resolution results on the electronic band structure and density of states derived properties as obtained from the same highly precise state-of-the-art local density approach. These results demonstrated the close relation of the band structure to the structural arrangements of the constituent atoms and have helped to provide an integrated chemical and physical picture of the interactions.

The important structural features of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds arise from the fact that  $(2 + \delta)$  oxygen atoms are missing from the perfect triple perovskite,  $\text{YCuO}_3(\text{BaCuO}_3)_2$ . These vacancies arise from a total absence of O atoms in the Y-O planes (which seems to separate the Cu-Cu interactions across the Y plane) and an absence of O atoms in the Cu planes between the Ba-O planes (which leads to the formation of linear chains of Cu-O-Cu). As a result, there are two Cu ions (called Cu2) in five-coordinated positions – as shown in Fig. 3. Since the interatomic distance Cu2-O4 (2.303 Å) is much larger than Cu1-O4 (1.850 Å) [12], the Cu1 ions have a rather weak interaction with the Cu2 ions. The Cu2 ions are in the locally very strong tetragonal distortion and this yields a 2D structure

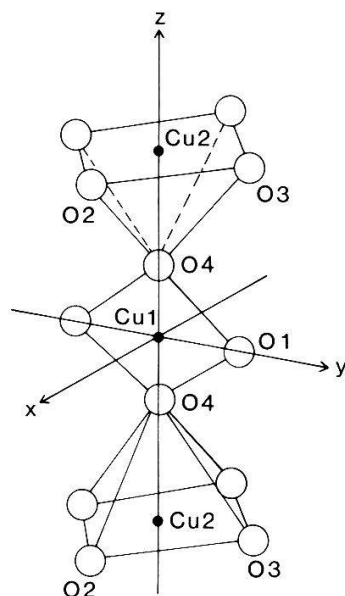


Figure 3  
A local environment for the Cu1 and Cu2 atoms in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , following the Y–Cu2–Ba–Cu1–Ba–Cu2–Y ordering along  $z$ .

for these planes similar to that of  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ . The additional distortions of the O2 and O3 ions (the so-called ‘dimpling’) arises from the absence of O ions in the adjacent Y–O plane. From the contour plots of the valence charge density of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  on two vertical planes cutting the Cu–O bonds, it is apparent that there is an overall two-dimensionality to this system; the three horizontal Cu planes of the unit cell form, in fact, separated entities which do not interact with the neighboring entities along the  $c$  axis.

The calculated valence band structure of stoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_7$  along high symmetry directions in the bottom ( $k_z = 0$ ) plane of the orthorhombic BZ is shown in Fig. 4. The very close similarity in the band structure for the  $k_z = 0$  and  $k_z = \pi/c$  planes [10] indicates the highly 2D nature of the band structure.

It is seen from Fig. 4 that, as in the case of  $\text{La}_2\text{CuO}_4$ , a remarkably simple band structure near  $E_F$  emerges from this complex set of 36 bands originating (from three Cu (3d) and seven O (2p) atoms). Four bands – two each consisting of Cu2 (3d)–O2 (p)–O3 (p) orbitals and Cu1 (d)–O1 (p)–O4 (p) orbitals – cross  $E_F$ . Two strongly dispersed bands C ( $S'_1$  and  $S_4$  in Fig. 4; the labelling is given by their character at  $S$ ) consist of Cu2 ( $d_{x^2-y^2}$ )–O2 ( $p_x$ )–O3 ( $p_y$ ) combinations and have the 2D character which proved so important for the properties of  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ . The symmetry allowed interactions of the Cu2 bands with the Cu1 band results in a complicated dispersion for the Cu2 bands (as occupied bands) along  $\Gamma$ –X and  $\Gamma$ –Y. Note that the  $S_1$  and  $S'_1$  states have the same symmetry and so can interact (anticrossing) and disperse along the  $S$ –Y direction. Significantly, the Cu1 ( $d_{z^2-y^2}$ )–O1 ( $p_y$ )–O4 ( $p_z$ ) anti-bonding band A ( $S_1$  in Fig. 4) shows the (large) 1D dispersion expected from the Cu1–O1–Cu1 linear chains but is almost entirely unoccupied. This band is in sharp contrast to the  $\pi$ -bonding band B (formed from the Cu1 ( $d_{zy}$ )–O1 ( $p_z$ )–O4 ( $p_y$ ) orbitals) which is almost entirely occupied in the stoichiometric ( $\delta = 0$ ) compound and becomes fully occupied for the superconducting materials ( $\delta \geq 0.1$ ). We will soon see that since this almost flat  $\pi$ -bonding band B (the state  $S_5$  in Fig. 4) lies just below and crosses  $E_F$  (for

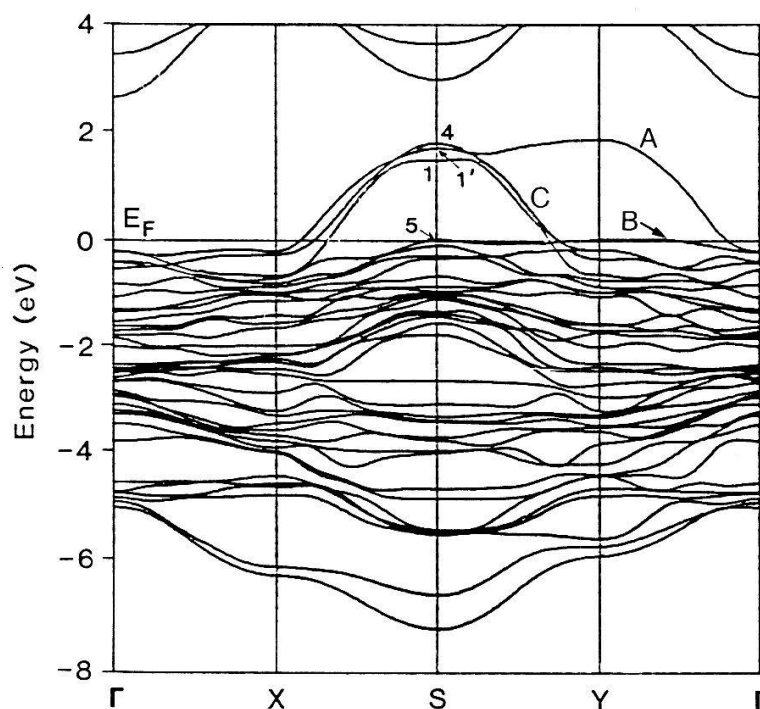


Figure 4  
Band structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  along symmetry directions in the  $k_z = 0$  plane of the orthorhombic Brillouin zone.

$\delta = 0$ ) along S–Y, it gives rise to peaks in the DOS near  $E_F$  making the DOS at  $E_F$  sensitive to the position of  $E_F$  (i.e., to  $\delta$ ).

In our calculation for  $\delta = 0$ , the DOS at  $E_F$ ,  $N(E_F)$ , is 1.13 states/eV Cu-atom, which is comparable to the 1.2 and 1.9 states/eV Cu-atom found earlier for  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  at  $x = 0$  and at the peak at  $x = 0.16$ , respectively. For increasing  $\delta$  values (hence increasing  $E_F$ ),  $N(E_F)$  decreases sharply. Thus, for  $\delta = 0.1$ ,  $N(E_F) = 0.87$  states/eV Cu-atom while, for  $\delta = 0.2$ ,  $N(E_F) = 0.52$  states/eV Cu-atom (after which the DOS remains roughly constant). This means that the  $N(E_F)$  per Cu atom values in the high  $T_c$  superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , are significantly lower than was found earlier (either experimentally or theoretically) for the (lower) high  $T_c$  superconductor,  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ . This result – which agrees with the conclusion of a recent experiment [13] – has a number of important possible consequences for DOS derived properties and superconductivity, including: reduced screening, an increased role for the polarization of ionic constituents, lowered conductivity (and reduced superconducting current carrying capacity), etc.

Charge density calculations [10, 11], both for the total valence charge and for the individual states crossing  $E_F$ , reflect the structural properties of the material. Charge density plots for the individual states near  $E_F$  demonstrate the 2D nature of Cu2–O2–O3 dp $\sigma$  bands and the 1D nature of the Cu1–O1–O4 dp $\sigma$  bands. The ionic Y (or R = rare earth) atoms act as electron donors and do not otherwise participate. Also, the partial DOS at  $E_F$  for Y give extremely low values for the conduction electrons (the same is true for Gd). These results give an immediate explanation for the observed [14] coexistence of the high  $T_c$  SC and magnetic

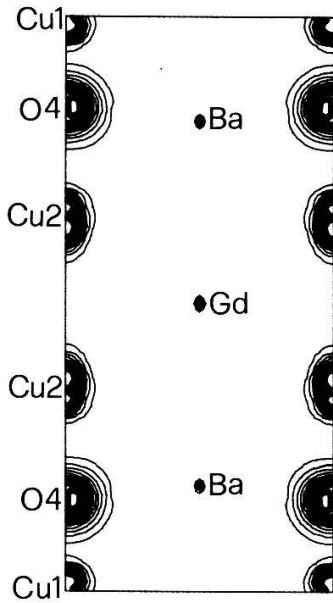


Figure 5  
Contour plots in the [110] plane of valence charge density near  $E_F$  (within  $\sim 0.2$  eV) of  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ .

ordering in the  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  structures. The lack of conduction electron density around the R-site (cf. Fig. 5) [15] means that the unpaired rare-earth  $f$ -electrons are decoupled from the Cooper pairs (i.e., magnetic isolation) and so cannot pair-break.

#### IV. $\text{YBa}_2\text{Cu}_3\text{O}_7$ vs. $\text{YBa}_2\text{Cu}_3\text{O}_6$ : chains vs. planes

Recently, several neutron experiments [16] showed that the oxygen vacancies concentrate on the O1 sites and change the composition and symmetry from orthorhombic (in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ) to tetragonal (in  $\text{YBa}_2\text{Cu}_3\text{O}_6$ ). The absence of oxygens on the O1 site destroys the 1D chain structure in the  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . The additional oxygen vacancies, therefore, change the local symmetry as well as the electronic configuration around the Cu1 sites. In this geometry, each Cu1 ion would be completely isolated from the other Cu1 ions in the Cu1 plane (having no oxygens lying between the Cu1's) and remain as  $\text{Cu}^+$  ions with a completely filled  $d$ -shell. Hence, the  $d$ -orbital states of Cu1 are expected to be very localized in the Cu1 plane. One notable consequence of the change of structure is that the Cu1–O4 distance in  $\text{YBa}_2\text{Cu}_3\text{O}_6$  is even shorter than in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

To examine these expectations and to provide insight into the possible role [11] of the CTE in the 1D chains of  $\text{YBa}_2\text{Cu}_2\text{O}_{7-\delta}$ , we compare the results of calculations [17] for both  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , focussing on the role of chains vs. planes. The calculated band structures (near  $E_F$ ) of both tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are shown in Fig. 6. Both band structures have in common two 2D-conduction bands arising from the Cu2–O planes. In Fig. 6(a), the 2D bands  $D_4$ ,  $D_1$  and  $C_4$ ,  $C_1$  of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  consist mainly of Cu2 ( $d_{x^2-y^2}$ )–O2 ( $p_x$ )–O3 ( $p_y$ ). Similarly, in Fig. 6(b), the bands  $Y_4$ ,  $Y_1$  and of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  come from Cu2( $d_{x^2-y^2}$ )–O2( $p_x$  or  $p_y$ ). As seen in the charge density plot of the 2D state, all the components are lying within the 2D Cu–O



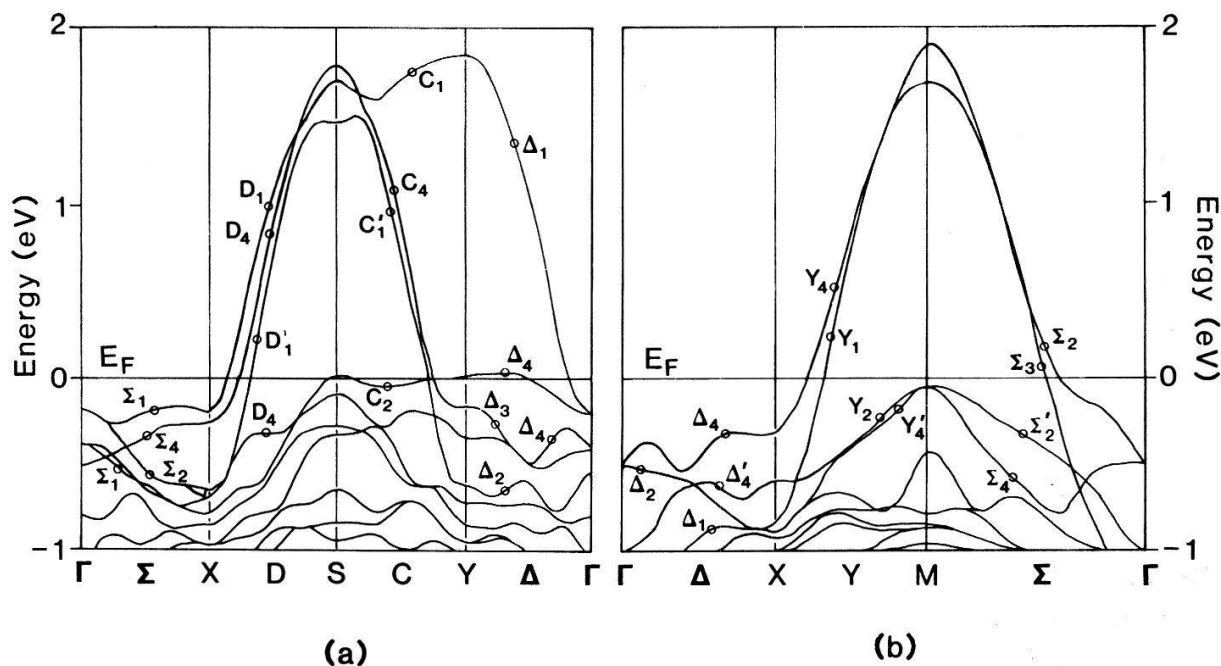


Figure 6  
Energy bands near  $E_F$  of (a)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and (b)  $\text{YBa}_2\text{Cu}_3\text{O}_6$ .

planes. In addition, there are small contributions of O  $s$ - and  $p_z$ -components as shown in Fig. 3 of the reference [11]. These arise from the 'dimpling' distortions of the Cu2–O planes, which result in the significant polarization of O ions. Aside from small polarization terms, the 2D conduction bands are well characterized by  $dp\sigma$  anti-bonding states of Cu  $d_{x^2-y^2}$  and O  $p_x, p_y$  orbitals.

While both  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$  have 2D Cu–O  $dp\sigma$  bands in common, the electronic structure involving Cu1–O1–O4 1D-complex are drastically different. First, in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the Cu1 ( $d_{z^2-y^2}$ )–O1 ( $p_y$ )–O4 ( $p_z$ ) anti-bonding  $dp\sigma$  band shows a strong 1D dispersion, which comes from the hybridization of Cu1–O1 orbitals in the chains. As shown in Fig. 6(a), the 1D  $dp\sigma$  band ( $D_1$ – $C_1$ – $\Delta_1$ ) is almost empty. As the Cu1–O1 chain is destroyed in  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , the anti-bonding bands are lowered well below  $E_F$ , and do not contribute any more to the states near  $E_F$ . Instead of having  $dp\sigma$  bands at the top of the valence bands from Cu1–O4–O1 complex, anti-bonding ( $\Delta_2, \Delta_4$  and  $Y_2, Y_4$  in Fig. 6(b))  $dp\pi$  bands of Cu1 ( $d_{zy}, d_{zx}$ )–O4 ( $p_y, p_x$ ) are lying near  $E_F$ . These  $dp\pi$  bands of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  have the same character as the  $dp\pi$  band of Cu1 ( $d_{zy}$ )–O1 ( $p_z$ )–O4( $p_y$ ) ( $C_2$ – $\Delta_4$ ) in Fig. 6(a) with missing O1 component, but those in the tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  are doubly degenerate at  $\Gamma$  and M symmetry points due to their crystal symmetry. The results indicate that the orthrhombic-to-tetragonal transition does not alter the 2D electronic structure near  $E_F$ , but affect significantly the 1D electronic structure near  $E_F$ .

As we discussed, the primary role of vacancies introduced in the Cu1–O chains is the change of 1D electronic structure. In  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , there is an almost empty  $dp\sigma$  band and an almost filled  $dp\pi$  band, both of which originate from the Cu1–O1–O4 chain complex. On the contrary, all the Cu1 and O4 bands in  $\text{YBa}_2\text{Cu}_3\text{O}_6$  are completely occupied. When we consider the 'formal' valence of



Cu1, therefore, additional vacancies in the chain induce  $\text{Cu}^{1+}$  from ' $\text{Cu}^{3+}$ '. What we mean by ' $\text{Cu}^{3+}$ ' is only a formal correspondance of a Cu orbital state to the configuration of Cu1–O1–O4 hybridizations. In fact, due to the strong covalent hybridization between Cu  $d$  and O  $p$  orbitals, the pure ionic picture is not valid any more for these Cu-oxides superconductors. Hence, the real valence of Cu must be reduced by the amount of hybridization with oxygen atoms. Therefore, we can conclude that the introduction of vacancies, or the change of O contents in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , concerns primarily with the 1D chain electronic configuration.

In fact, almost all the samples of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  are obtained via quenching at high temperature [18] (around 900 C) or non-equilibrium methods [19]. So to speak, those tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  are thermodynamically in a metastable state. Regarding the change of oxygen contents as a doping process, we have to distinguish the doping processes in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ . In the case of divalent ion doping in the pure  $\text{La}_2\text{CuO}_4$ , the La ion and divalent ion M are very ionic and do not participate in the valence band electronic structure. Thus, as a first approximation, the substitution of La by M (Sr, Ba, . . .) may lead to the change of the chemical potential of conduction electrons in the 2D Cu–O band. However, in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , there are two different types of Cu atoms. As we discussed, the oxygen vacancies introduced in the chains are only effective on the 1D electronic structure induced by the Cu–O1–O4 chain structure. Since the change of oxygen contents affects only the 1D electronic structure, therefore, the 2D conduction bands are almost irrelevant to the vacancies in the chain.

More specifically, if we look at the Cu–O  $p$ DOS at  $E_f$  of both  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , there is very little change in the DOS distribution over Cu and O ions in the 2D Cu–O plane. The most dominant contributions are from Cu- $d$  and O- $p$  states as expected from a strong hybridization of Cu and O in the plane. In addition to the 2D hybridization, the small ( $\sim 5\%$ ) contributions of O  $s$ -components are noted. This admixture of O  $s$ - and  $p$ -components arises from the 'dimpling' of oxygens and results in the polarization of oxygen vertical to the Cu2–O plane. After all, these polarized oxygens O2, O3 are in a thermodynamic stable configuration regardless of the change of oxygen contents, while the unpolarized O1 in the chains are in a much more unstable configuration.

From the comparative study of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , it is noted that the oxygens (e.g. O1 and O4) in the 1D chains are extremely important for electronic structure of the compounds. The magnetically and electronically active oxygens in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  suggests that the new Cu-oxides superconductors are qualitatively different from usual transition metal oxides in their electronic structures. First of all, a systematic (perturbative) theory of superexchange starting from the localized limit of cation  $d$  orbitals would be difficult, otherwise impossible, to be used because the interaction (hybridization) between Cu  $d$  orbitals and O  $p$  orbitals is so strong that the O  $p$  orbital states give a large contribution to the DOS at  $E_f$  and the perturbative treatment, based upon the closed-shell O  $p$  orbital states far below  $E_f$ , may diverge or not work. Second, there is a conceptual difficulty in understanding the interplay between the on-site Coulomb repulsion on Cu-sites and the strong hybridization of Cu  $d$ –O  $p$  orbitals

which leads to an  $\sim 9$  eV separation of  $dp\sigma$  bonding and anti-bonding states. Since the  $dp\sigma$  hybridization energy is certainly larger than the on-site Coulomb energy, the on-site repulsion may not be large enough to result in an expected dynamical localization.

## V. Comparison of the electronic structures of $\text{La}_2\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$

By comparing the electronic structure near  $E_F$  of  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , we found similarities as well as different characteristics. First, the dominant electronic structure near  $E_F$  is the presence of very strongly dispersed conduction bands crossing  $E_F$  and almost 'flat' bands. Both  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  have 2D bands composed of Cu  $d_{x^2-y^2}$ -O(1)  $p_{x,y}$  in  $\text{La}_2\text{CuO}_4$  and Cu<sub>2</sub> ( $d_{x^2-y^2}$ )-O2 ( $p_x$ )-O3 ( $p_y$ ) in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . All of these 2D bands are strongly dispersed conduction bands. Second, however, the character of the localized states just below  $E_F$  is quite different. For  $\text{La}_2\text{CuO}_4$ , the strong tetragonal distortion of the  $\text{CuO}_6$ -octahedra leads to the splitting of the  $d_{x^2-y^2}-p_{x,y}$  and  $d_{z^2}-p_z$  levels. Combined with the quasi-2D  $\text{K}_2\text{NiF}_4$  structure, the in-plane  $d_{x^2-y^2}-p_{x,y}$  states form a strongly dispersed conduction band; on the other hand, the out-of-plane  $d_{z^2}-p_z$  states remain localized. As shown in Fig. 1, the bands  $B'$ ,  $B''$ , which are formed from Cu  $d_{z^2}$ -O  $p_z$  orbitals, are located about 0.5 eV below  $E_F$  and show little dispersion. Also, as mentioned before, the band  $B$  is a mixture of two types of in-plane  $d_{x^2-y^2}-p_{x,y}$  and out-of-plane  $d_{z^2}-p_z$  orbitals, because both belong to the same symmetry representation along  $\Gamma$ - $G_1$ - $Z$ .

As is now well-known, there are two types of Cu-atoms in the unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The Cu2 in the 2D plane has a square pyramidal coordination of oxygens due to the missing oxygen in the Y-plane. From this structure, we expect that the Cu2  $d_{x^2-y^2}$  and Cu2  $d_{z^2}$  energy levels are further apart than those in  $\text{La}_2\text{CuO}_4$ . Further, the distance between the Cu1 and O4 atoms in the chains is unusually short. Therefore, in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the flat bands near  $E_F$  (band  $B$  in Fig. 4) dominantly have the character of the  $dp\pi$  antibonding state of Cu(1)  $d_{zy}$ -O(1)  $p_z$ -O(4)  $p_y$  orbitals rather than of the Cu2  $d_{z^2}$ -O(4)  $p_z$  states in the 2D conduction plane. In addition to the flat  $dp\pi$  bands, the 1D chain structure provides, as a partner, a strongly dispersed  $dp\sigma$  band composed of Cu(1)  $d_{z^2-y^2}$ -O(1)  $p_y$ -O(4)  $p_z$  orbitals, which is similar to the 2D  $d_{x^2-y^2}-p_{x,y}$  in the case of  $\text{La}_2\text{CuO}_4$ .

We can draw an analogy between the electronic structures near  $E_F$  of  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ; we find the electronic structure of a well dispersed  $d_{x^2-y^2}-p_{x,y}$  band and a fairly localized  $d_{z^2}-p_z$  state in the 2D Cu-plane of  $\text{La}_2\text{CuO}_4$  corresponding to that of a strongly dispersed Cu1-O1-O4  $dp\sigma$  band and a localized Cu1-O1-O4  $dp\pi$  state in the 1D chain of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . In fact, the 2D  $dp\sigma$  conduction bands in the Cu2-plane of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are well separated at  $E_F$  from 1D bands, while the 2D conduction bands of the  $d_{x^2-y^2}-p_{x,y}$  orbitals in  $\text{La}_2\text{CuO}_4$  show a hybridization with the localized  $d_{z^2}-p_z$  orbitals along the (100) direction.

## VI. Mechanism of superconductivity

We have made crude estimates [11] of the electron-phonon interaction in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , using the rigid muffin-tin approximation (RMTA) [20] to calculate the McMillan-Hopfield constant  $\eta$  and the electron-phonon coupling constant,  $\lambda$ . Surprisingly, by far the largest contribution to  $\eta$  comes from the O1 atoms, again indicating the important role played by the ‘metallized’ oxygens. We find that the calculated  $T_c$ , even for the assumed Debye temperature  $\theta_D = 100$  K, cannot exceed the value of  $\sim 32$  K – a similar limit found previously in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  [21]. Despite the crudeness of the RMTA approach, it is expected that this estimate cannot be so far off (i.e., a factor of three) and so casts doubt on a purely electron-phonon explanation of the observed high  $T_c$ .

Many authors have discussed the excitonic mechanism [22] of superconductivity, in which the effective attractive interaction between conduction electrons originates from virtual excitations of excitons rather than phonons. The basic idea of the models proposed is that conduction electrons residing on the conducting filament (or plane) induce electronic transitions on nearby easily polarizable molecules (or complexes), which result in an effective attractive interaction between conduction electrons. As perhaps a striking realization of the excitonic mechanism of superconductivity,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has two 2D conduction bands and additional highly polarizable 1D electronic structure between the two conduction planes.

We previously discussed the importance of ‘ $\text{Cu}^{2+}-\text{Cu}^{3+}$ ’-like charge fluctuations in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  and the 1D feature in the electronic structure near  $E_F$  of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , pointing out the possible role played by charge transfer excitations (‘excitons’) of occupied (localized)  $\text{Cu1-O}$   $\text{dp}\pi$  orbitals into their empty (itinerant)  $\text{Cu1-O}$   $\text{dp}\pi$  anti-bonding partners. As shown schematically in Fig. 7, we can characterize the 1D electronic structure with two types of electronic states in it, one free-electron-like (the well-dispersed  $\text{dp}\sigma$  band) and the other localized (the almost flat  $\text{dp}\pi$  state). When the localized hole is created (effectively a ‘ $\text{Cu}^{4+}$ -complex’) due to the excitation, a strong attractive correlation between the hole and excited electron may lead to an electron-hole bound state (‘exciton’). Hence, this excitation of the localized  $\text{dp}\pi$  with the electron-hole correlation in the 1D electronic structure will give rise to a strong polarization in the 1D chains between two conduction planes and couple to the 2D conduction electrons, which carry most of the superconductivity.

Finally, we should note that while we discussed the charge transfer excitation (CTE) based upon the excitations of occupied *localized*  $\text{dp}\pi$  states into the empty *itinerant*  $\text{dp}\sigma$  anti-bonding band, Varma *et al.* [23] proposed a charge transfer resonance mechanism by considering excitations of the bonding  $\text{Cu } d_{x^2-y^2}-p_x-p_y$   $\text{dp}\sigma$  state ( $\beta$ ) and into its anti-bonding (conduction)  $\text{dp}\sigma$  band ( $\alpha$ ) partner. Starting from the particle-hole excitation  $\beta \rightarrow \alpha$ , they argued that a sharp excitonic resonance from the  $\alpha\beta$  transitions can happen if the  $\alpha\beta$  particle-hole have Coulomb attractions strong enough to cancel the  $\alpha\beta$  interband transition gap, which is more than 6 eV. However, it appears unreasonable to neglect the

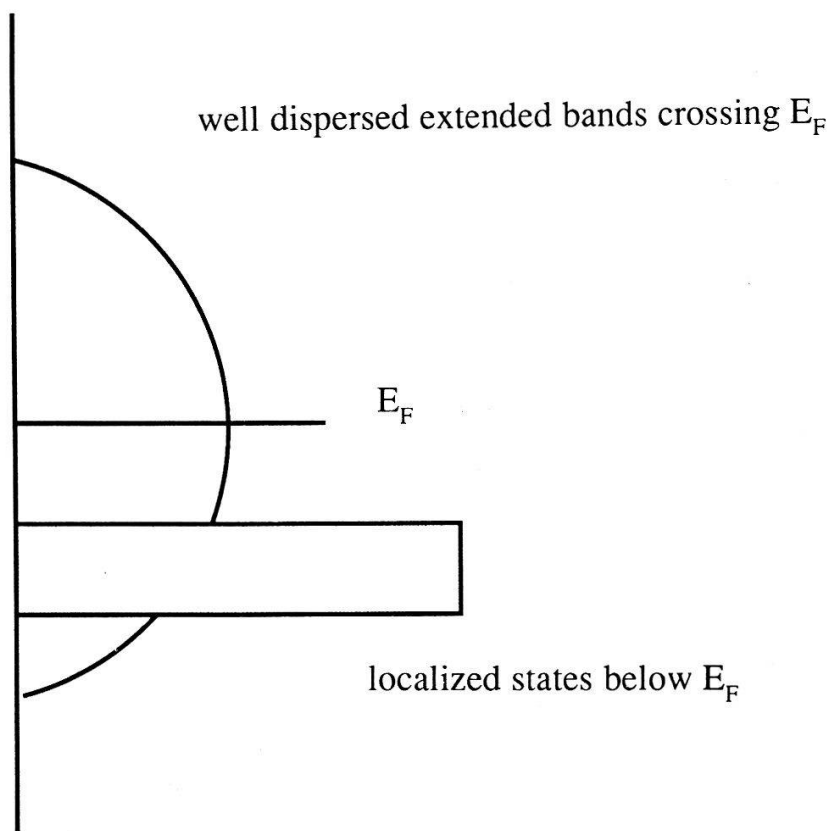
Electronic Configuration

Figure 7  
Schematic drawing of the 1D electronic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

presence of the  $\text{dp}\pi$  orbital states which lie near  $E_F$ , and hence  $\text{dp}\pi \rightarrow \text{dp}\sigma$  particle-hole excitation must be included in the CTE model. We again note that similarly in the case of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , the ' $\text{Cu}^{2+}-\text{Cu}^{3+}$ '-like resonant charge fluctuations induced by the optic breathing mode were shown [5] to lead to transitions between the in-plane  $d_{x^2-y^2}$  orbitals and localized out-of-plane  $d_{z^2}$  orbital states located just below  $E_F$  to the itinerant in-plane  $d_{x^2-y^2}$  orbitals. The crucial role of O  $p$  electrons involved in the photoemission process (which may relate to the excitonic mechanism) has been discussed in detail by Redinger et al. [24].

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