Electron-energy-loss studies of core edges in \((\text{Tl}_{0.5}\text{Pb}_{0.5})(\text{Ca}_{1-x}\text{Y}_x)\text{Sr}_2\text{Cu}_2\text{O}_7-\delta\)

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Superconductivity is observed in the \((\text{Tl}_{0.5}\text{Pb}_{0.5})(\text{Ca}_{1-x}\text{Y}_x)\text{Sr}_2\text{Cu}_2\text{O}_7-\delta\) system in the composition range \(0 \leq x < 0.6\), with a maximum \(T_c\) of 108 K at \(x \sim 0.2\). For \(x \geq 0.6\), the material becomes semiconducting. We have investigated the electronic structure of these materials using transmission electron-energy-loss spectroscopy on individual crystallites, over the entire composition range, \(0 \leq x \leq 1\). In the semiconducting end of the composition range, the material already shows a pre-edge feature in the O 1s absorption edge, which we attributed to an empty density of states in the conduction band containing O 2p character. This feature therefore should not be used as a direct measure of the hole concentration in the material. We found that the holes associated with superconductivity do give rise to a secondary pre-edge feature, about 1.5 eV lower in energy. The emergence of this feature also correlates with that of another secondary feature in the copper \(L_3\) edge, suggesting a strong covalency between oxygen and copper in the \(\text{CuO}_2\) plane. Evidence is also presented for the existence of holes responsible for normal conductivity but not for superconductivity.

I. INTRODUCTION

Following the first experiment by Nücker et al., who demonstrated a correlation between the pre-edge structure of the oxygen K (1s) absorption and the degree of hole doping and, hence, superconductivity in \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) and \(\text{YBa}_2\text{Cu}_3\text{O}_7\), electron-energy-loss spectroscopy (EELS) has become a widely used tool for the investigation of electronic structure of high-temperature superconducting materials. Nücker et al. concluded that the valence band is made up of O 2p orbitals and that the intensity of the pre-edge peak may be correlated with the number of holes introduced into this band. Other authors have applied the same analysis to other high-temperature superconducting systems. However, a similar pre-edge peak has since been observed in electron-doped superconducting materials, calling into question this simple correlation. We present our results on a study of the near-edge structure of copper \(L_3\), calcium \(L_{2,3}\), and oxygen K absorption edges in a range of materials in the \((\text{Tl}_{0.5}\text{Pb}_{0.5})(\text{Ca}_{1-x}\text{Y}_x)\text{Sr}_2\text{Cu}_2\text{O}_7-\delta\) system as a function of \(x\). We observe a pre-edge peak in the oxygen K absorption even in semiconducting samples of this series, giving further evidence that this structure cannot be simply related to the hole concentration. However, we will show that oxidation of the copper oxide sheets due to the partial substitution of \(Y^{3+}\) by \(Ca^{2+}\) does modify the shape of this peak, and a measure of the hole concentration can still be obtained from a fine-structure analysis.

The synthesis and the structure determination of \((\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CaCu}_2\text{O}_7-\delta\) were reported by Subramanian et al., with a \(T_c \sim 85\) K. Recently, Liu and coworkers have reported bulk superconductivity up to 110 K in the \((\text{Tl}_{0.5}\text{A}_{0.5})(\text{Ca}_{0.2}\text{R}_{0.2})\text{Sr}_2\text{Cu}_2\text{O}_7-\delta\) system \((A = \text{Pb or Bi}, \text{R} = \text{Y or rare-earth elements})\). The structure of these high-temperature superconductors is similar to that of \(\text{TlCaBa}_2\text{Cu}_2\text{O}_{7-\delta}\). A partial substitution of \(\text{Tl}\) by \(\text{Pb}\) seems to be necessary in order to stabilize the structure when \(\text{Ba}\) is totally replaced by \(\text{Sr}\). This structure can be described in terms of an intergrowth of double rock-salt-type \(\text{[Tl(A)O][SrO]}\) layers with double oxygen-deficient perovskite \(\text{[Sr}_x\text{Ca}_y\text{R}_z\text{Cu}_2\text{O}_6]}\) layers formed by two sheets of corner-sharing \(\text{CuO}_3\) pyramids interleaved with calcium and/or rare-earth ions. The structure of \((\text{Tl}_{0.5}\text{A}_{0.5})(\text{Ca}_{1-x}\text{R}_x)\text{Sr}_2\text{Cu}_2\text{O}_{7-\delta}\) also resembles that of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) with the \((\text{Tl},\text{A})\)-O square lattice replacing the \(\text{CuO}_2\) chain layer, \(\text{Sr}\) atoms replacing \(\text{Ba}\) atoms, and \(\text{Ca}\) atoms partially substituting for \(\text{Y}\) or the rare-earth atoms. Neutron-diffraction measurements (unpublished results and see Ref. 8) show that the oxygen atoms in the \((\text{Tl},\text{Pb})\)-O layer have large and anisotropic mean-square amplitude deviations, suggesting possible disorder in the local chemical bonding. A model for \((\text{Tl}_{0.5}\text{Pb}_{0.5})(\text{Ca}_{1-x}\text{Y}_x)\text{Sr}_2\text{Cu}_2\text{O}_7-\delta\) is shown on Fig. 1 in which the symmetrical position drawn for \(O\) in the \(\text{Tl}\)-O layer merely represents a statistical average. The great attraction of such materials lies in the possibility of controlling the doping of the \(\text{CuO}_2\) sheets with a simple chemical substitution involving other layers in the unit cell, in principle leaving the oxygen stoichiometry unchanged. This has an advantage over previous experi-
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II. EXPERIMENT

\((Tl_{0.3}Pb_{0.7})(Ca_{1-x}Y_x)Sr_2CuO_7-x\) has been prepared by a solid-state reaction method which has been described in detail elsewhere. Briefly, samples covering the whole composition range \((0 \leq x \leq 1)\) were prepared by mixing and grinding high-purity powders of \(CaCO_3\), \(Y_2O_3\), \(SrCO_3\), and \(CuO\) in stoichiometric proportions. The mixtures were calcined in air at \(970^\circ C\) for 12 h, then ground and mixed with stoichiometric proportions of \(Tl_2O_3\) and \(PbO\), and die-pressed into pellets. These were wrapped in gold foil to alleviate loss of \(Tl\) and \(Pb\) during the high-temperature processing. The pellets were reacted for 3 h at \(950^\circ C\) in flowing oxygen, then cooled to room temperature at a rate of \(2-5^\circ C/min\) or by quenching in air. The resultant materials are single phase as checked by x-ray diffraction (XRD) and energy-dispersive x-ray spectroscopy (EDX). Superconductivity was measured by a standard four-point electrical resistivity probe, and the phase diagram deduced from these measurements is plotted in Fig. 2 as a function of compositional parameter \((1-x)\).

For the EELS investigation, each sintered sample was crushed between glass microslides. The resulting powder was spread onto an electron microscope grid covered with a hole carbon film. The grid was quickly transferred into the vacuum chamber of a VG-HB501 scanning transmission electron microscope (STEM) where EELS measurements were carried out. Spectra were collected, with a defocused electron probe covering areas from a few nm in diameter upwards, only from electron transparent regions of individual particles exhibiting a single-

FIG. 1. The idealized crystal structure for \((Tl_{0.3}Pb_{0.7})(Ca_{1-x}Y_x)Sr_2CuO_7-x\). All the atoms are drawn to scale with regard to the unit cell, but with their radii halved in order to show each of them clearly. The \(Pb\) and \(Y\) are one of the smaller ions in their respective positions.

that the pre-edge structure is mostly of oxygen \(2p_{x,y}\) character, although it is worth pointing out that the energy resolution in these studies is only about 2 eV, so some details in the edge structure may have been lost.

FIG. 2. The phase diagram for \((Tl_{0.3}Pb_{0.7})(Ca_{1-x}Y_x)Sr_2CuO_7-x\) deduced from the electrical measurement.
crystal diffraction pattern. The estimated film thickness was approximately 500–1000 Å. The incident electron has an energy of 100 keV \((k_0 = \lambda^{-1} = 27 \text{ Å}^{-1})\) and a convergence semiangle of about 8 mrad \((\Delta k = 0.2 \text{ Å}^{-1})\). The collection semiangle was set to about 32 mrad \((\Delta k = 0.9 \text{ Å}^{-1})\). Given that the mean values of the core-orbital radius of the O 1s and Cu 2p wave functions are both about 0.1 Å, the electron transitions from the core levels should follow the dipole selection rule to a good approximation. However, the effect of crystal anisotropy is strongly suppressed under such conditions because \(\Delta k\) is large enough to sample a substantial fraction of the Brillouin zone. Typical spectral acquisition times are of the order of 5 sec with the use of a newly constructed CCD-based parallel detection system. The beam current is of the order of 0.1 nA. The data is collected with an energy scale about 0.2 eV/channel and the spectrometer has a resolution of about 0.7 eV, measured as the FWHM of the zero-loss peak. The absolute energy of the various peaks is calibrated with respect to the pre-edge peak of the carbon K edge of the supporting evaporated amorphous carbon film, the latter is taken to be 285.0 eV. Any systematic error due to the nonlinearity in the bias voltage supply is corrected by calibrating with the known energy positions of the oxygen K and copper L3 absorption spectra in CuO.

The probable error in absolute energy determination is about 0.5 eV. Note that, in this work, no use is made of the high spatial resolution of which the focused electron probe of the STEM is capable, other than to select good single-crystal areas from which the spectra are acquired.

![Copper L3 absorption edges](image1)

**FIG. 3.** Copper L3 absorption edges of \((\text{TLbo.5Pb0.5})_{x}(\text{Ca}r-x)_{y} \text{Sr}_{2} \text{Cu}_{3} \text{O}_{7-\delta} \).  

![Oxygen K absorption edges](image2)

**FIG. 4.** Oxygen K absorption edges of \((\text{TLbo.5Pb0.5})_{x}(\text{Ca}r-x)_{y} \text{Sr}_{2} \text{Cu}_{3} \text{O}_{7-\delta} \).

### III. RESULTS

The copper L3 absorption edges of \((\text{TLbo.5Pb0.5})_{x}(\text{Ca}r-x)_{y} \text{Sr}_{2} \text{Cu}_{3} \text{O}_{7-\delta} \) are shown in Fig. 3. The intensities of the spectra are normalized with respect to the main peak (535.5 eV) of the oxygen K edges (Fig. 4). For \(x=1\), i.e., for the end member in the semiconducting range, the copper L3 edge is a narrow peak (FWHM \(\approx 1.7 \text{ eV}\)) with a binding energy of 931.5 eV. This is very close to the L3 peak (at 931.2 eV) observed in CuO under similar conditions and is attributed to the simple transition from the Cu 2p \(3d^9\)–O 2p \(6\) ground-state configuration to the excited Cu 2p \(3d^9\)–O 2p \(6\) state. For samples with decreasing \(x\) (increasing \([\text{Ca}]/[\text{Y}]\) ratio), a new feature appears to develop at the high-energy side of the main peak. From the difference spectra, the new feature is found to center at about 933.4 eV. A similar feature has also been observed in the superconducting compounds \(\text{YBa}_2 \text{Cu}_3 \text{O}_{7-\delta}\), but barely so in \(\text{Bi}_2 \text{CaSr}_2 \text{Cu}_3 \text{O}_{8+\delta}\). Our observations are believed to be the first example of the evolution of such a feature as a function of doping over a compositional range.

Oxygen K absorption edges of \((\text{TLbo.5Pb0.5})_{x}(\text{Ca}r-x)_{y} \text{Sr}_{2} \text{Cu}_{3} \text{O}_{7-\delta} \) are shown in Fig. 4. The spectra for compounds with different \(x\) values are normalized to have the same height at the main peak at 535.5 eV. The spectrum for the sample with \(x=1\) consists of a narrow pre-edge peak centered at about 528.7 eV and a broad main peak at about 535.5 eV. As \(x\) decreases (the \([\text{Ca}]/[\text{Y}]\) ratio increases), the energy position of the main peak remains the same. The pre-edge feature
broadens but is initially still centered at about 528.7 eV. For \( x \leq 0.3 \), however, an additional low-energy feature appears clearly at \( \sim 527 \) eV. The intensity of this new feature increases in a nonlinear manner with increasing Ca doping, first rapidly for \( x \) between 0.3 and \( \sim 0.1 \), then saturating towards \( x = 0 \). It should be pointed out that the system goes through a phase transition from a semiconductor to a metal-superconductor at \( x = 0.6 \) (Fig. 2), although the intensity of the pre-edge feature at 528.7 eV remains nearly the same throughout the whole compositional range, in contrast to the earlier finding on \( \text{Tl}(\text{Ca}_{1-x} \text{Y}_x)\text{Ba}_2\text{Cu}_2\text{O}_{x-\delta} \) (\( x = 0, 0.8, 1.0 \)).

Some of calcium \( L_{2,3} \) absorption edges of \( \text{Tl}(0.5\text{Pb}_{0.5})(\text{Ca}_{1-x}\text{Y}_x)\text{Sr}_2\text{Cu}_2\text{O}_{x-\delta} \) are shown in Fig. 5. The overall shape of the absorption features is the same for compounds with different \( x \) values, but the intensity changes roughly in line with the Ca content in the compound. The absorption mainly consists of two strong lines, separated by about 3.5 eV. These are identified as "excitonic" peaks associated with transitions from the spin-orbit split Ca \( 2p_{1/2}, 2p_{3/2} \) states into the empty \( d \) states. Another minor feature located at 345.5 eV has also been observed, as in the spectra of metallic Ca. This feature has been attributed to the effect of exchange and Coulomb interactions as the result of the \( 2p-3d \) coupling, and is not an indication of the presence of non-equivalent sites for the Ca ions.

In the course of data acquisition, we also observed some effects due to prolonged exposure to the high-energy electrons. Figure 6 shows a sequence of oxygen K-edge spectra for \( \text{Tl}(0.5\text{Pb}_{0.5})(\text{Ca}_{0.9}\text{Y}_{0.1})\text{Sr}_2\text{Cu}_2\text{O}_{x-\delta} \) as a function of the electron exposure (in sec), showing the effect of the high-energy electron irradiation on the electronic structure of the material.

**IV. DISCUSSION**

The oxygen K edges display the \( p \)-projected density of states in the unoccupied bands. The most striking aspect of the data shown in Fig. 4 is the existence of the pre-edge feature in samples with \( x \geq 0.6 \), which are semiconducting. The height of this feature remains approximately unchanged with Ca substitution for Y, even for materials in the metallic range (\( x \leq 0.6 \)). This demonstrates clearly that the pre-edge feature in the oxygen K absorption edge is not simply related to holes, induced by cationic substitution, which appears to be so vital to superconductivity. At the moment, we lack photoemission data for this series of compounds in order to obtain information about the binding energies of the various oxygen...
1s states in the unit cell. However, for most CuO-based superconductors, the lowest binding energies for the oxygen 1s state have been found to be between 528.5–529.0 eV. 30–32 It is reasonable to assume that the lowest binding energy for the O 1s state in these compounds is also in the same range. Thus, the pre-edge feature observed in the O 1s absorption peak for the sample with \( \chi = 1 \) (centered at 528.7 eV) probably reflects the fact that above the semiconducting gap, the conduction-band states must have considerable oxygen p character. The core-hole effect can be neglected as the peak is not greatly modified by the metal-insulator transition.

The oxygen p orbital character, seen in the empty conduction-band states, may originate from hybridized orbitals between any one of the three nonequivalent oxygen ions and its nearest-neighbor metal ions in the unit cell. In the SrO compound, because of a covalent mixture between O 2p and Sr 4d states, a strong excitonic peak is observed at around 534 eV. 21 The feature observed at about 528.7 eV in the oxide superconductors is unlikely to have the same origin because the Sr empty d states as well as other empty d states of Ca and Y are located at least about 5–10 eV above the Fermi level \( (E_F) \), as determined by inverse photoemission experiments. 31 In fact, the transition to these empty \( p-d \) hybridized states is more likely to be responsible for the main absorption peak at 535.5 eV. One possible contribution to the pre-edge absorption in the yttrium-rich samples is the transition to states in the Ti (Pb) -O hybridized orbitals, which have been found close to \( E_F \) in the related Ti\( _2 \)Ba\( _2 \)Ca\( _4 \)Cu\( _2 \)O\( _8 \) and Ti\( _2 \)Ba\( _2 \)Ca\( _2 \)Cu\( _3 \)O\( _10 \) compounds. 16,31,35 Meyer III et al. 31 attribute them to be Ti 6p – O 2p hybridized states crossing the Fermi surface. This is consistent with the x-ray-absorption near-edge structure (XANES) result which shows that Ti is in a mixed “valence” state of 1+ and 3+. 15 In the (Ti\( _{0.9} \)Pb\( _{0.1} \))\( _2 \)YSr\( _2 \)Cu\( _2 \)O\( _7 - \delta \) compound, we would expect (Ti,Pb) 6sp – O 2p antibonding states to contribute to the empty conduction band. But unlike the double Ti layer compounds, 16,31,33 this conduction band does not cross the Fermi level because the material is nonconducting (\( \chi = 1 \)). According to the band-structure calculations, the conduction band may also contain some Ti 5d – O 2p antibonding states due to the small Ti-O separation along the c-axis. 34,35 Another possible final state associated with the pre-edge transitions is the upper Hubbard band of the strongly correlated Cu 3d states highly hybridized with the O 2p states. Such a band has always been assumed to exist since the “parent” compounds of the CuO-based superconducting materials are known to be antiferromagnetic insulators, with strong on-site correlation on the copper sites. 36 However, it has never been positively identified either in absorption spectra 1 or in inverse photoemission spectroscopy. 37 At this stage, without a further detailed analysis, it is difficult to decide whether the hybridized O p character in the conduction band giving rise to the pre-edge absorption peak in the nonsuperconducting Y-rich compounds originates from the (Ti,Pb) – O or from the Cu – O bond. Further experiments are needed to investigate this structure.

The effect of replacing Ca by Y in this series of compounds is most strongly felt in modifying the fine structure of the O 1s absorption edge (Fig. 4). This shows up as a broadening of the pre-edge feature and the growth of a new peak below 528 eV (i.e., at the Fermi level) in the Ca-rich materials. These features have been analyzed by fitting three Gaussians to each spectrum up to 540 eV [Fig. 7(a)]. The integrated intensity of the two pre-edge features G1 and G2, having been normalized against the intensity of G3, are plotted as a function of composition in Figs. 8(b) and 8(c), where G1, G2, and G3 correspond to peaks around 527, 528.7, and 535.5 eV, respectively. The lower-energy feature G1, whose intensity closely correlates with the compositional variation of \( T_c \) [shown in Figs. 8(a) and 8(c)], can be attributed to transitions originating from the CuO\( _2 \) plane. Its intensity initially increases with the Ca doping, indicating that the effect of the Ca substitution for Y is to induce hole states near the Fermi level. In this respect, the compounds are typical of a \( p \)-type CuO-sheet-based superconductor. 1,3,4 Towards the high end of the Ca concentration, the superconduct-

FIG. 7. The modeling of the near-edge structure in the oxygen K (a) and copper L\( _1 \) (b) absorption spectra which are used to estimate the oscillator strength of various features present. The oxygen K edge is fitted by three Gaussians (G1, G2, and G3); the copper L\( _1 \) edge is fitted by two Lorentz oscillators (P1 and P2) plus an arctangent energy-dependent background (C) to account for the transition into the continuum.
ing transition temperature goes through a maximum [Fig. 8(a)], which is mimicked by the variation of $G_1$ [Fig. 8(c)]. The latter suggests a possible saturation of the hole concentration in the CuO$_2$ plane, although measurements of the normal resistivity show a continuous increase of overall carrier concentration with increasing Ca. In contrast, the renormalized intensity of $G_2$ increases monotonically with the Ca concentration [Fig. 8(b)]. This gives evidence in support of the suggestion that, while the lower-energy feature $G_1$ comes from the CuO$_2$ plane, the main pre-edge peak $G_2$ originates from different O sites, possibly those bonded to the (Ti,Pb) ions. This separation of the pre-edge feature is also observed in the related Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_8$ compound where the low-energy pre-edge peak centered at 528 eV has O $p_{x,y}$ symmetry and the higher-energy pre-edge peak located at about 529.5 eV has predominantly O $p_z$ symmetry. By considering the $G_2$ plot in terms of a constant background plus a variation induced by the Ca substitution [Fig. 8(b)], we suggest that holes produced in the O orbitals outside the CuO$_2$ plane appear to contribute to the normal conduction but not to the superconductivity.

Because of the strong excitonic effect associated with the allowed dipole transition from Cu 2$p$ to 3$d$ states, the copper $L_3$ spectra are dominated by matrix element effects and details about the density of states cannot be resolved. However, the line-profile analysis of the excitonic peak has revealed the effect of substituting Ca by Y in this series of compounds. The higher-energy shoulder (at $\sim$ 933.4 eV) is only significant in the Ca-rich samples. This is demonstrated by the curve in Fig. 8(d) where the area under this high-energy shoulder, normalized against the area under the main peak (at $\sim$ 931 eV), is plotted as a function of the composition parameter $(1-x)$. The areas estimated by fitting the main peak and the shoulder by two Lorentz oscillators, and an arctangent energy dependence for the continuum absorption [Fig. 7(b)].

The curve in Fig. 8(d) resembles the behavior shown in Fig. 8(c) for the lower pre-edge peak in the O 1$s$ absorption band. It has been suggested that this high-energy structure may be the result of a hole in the O 2$p$ states and is associated with transitions from the Cu 2$p^3 3d^9\rightarrow O 2p^5$ ground state to the Cu 2$p^4 3d^{10}\rightarrow O 2p^6$ excited state. On the other hand, Zaanen et al. have argued that this high-energy feature observed in YBa$_2$Cu$_3$O$_7$, is due to the van Hove singularity in the band structure of the Cu-O chains, despite the strong core-hole effects. Since there is only one type of a Cu site in the unit cell for the series of compounds investigated here, namely the Cu in the CuO$_2$ sheet which is common to all cuprate superconductors, this high-energy feature can be unambiguously identified with the consequence of doping the CuO$_2$ sheet brought about by substitution of calcium for yttrium.

In such a complex structure, some unintentional cation substitution may be possible, particularly in view of the fact that the ionic radii of Sr$^{2+}$, Ca$^{2+}$, Tl$^{3+}$ are rather similar. It has been reported that about 15% of Tl is substituted by Ca in Tl$_2$Ca$_2$Ba$_2$Cu$_3$O$_{10}$. Various degrees of intermixing between Sr and Ca have also been reported in Bi$_2$Ca$_{1+\delta}$Sr$_{2-\delta}$Cu$_2$O$_{8+\delta}$.

In the case of Ca substituting at a Sr site, the binding energy of the Ca 2$p$ state will be increased by about 2 eV and thus will be very obvious in our Ca 2$p$ absorption spectra. Since we only observe very well-defined Ca 2$p$ doublets, we may conclude that Ca
only replaces Y in our samples. Our EDX results did not
detect any unintentional cation substitution, indicative of
the high quality of the samples prepared.

V. CONCLUSIONS

With the synthesis of good quality samples over the
whole compositional range, the effect of the substitution of
Ca for Y in the homologous series of compounds
(Tl$_{0.5}$Pb$_{0.5}$)[Ca$_{1-x}$Y$_x$]$_2$Cu$_2$O$_{2-y}$ has been studied using
transmission electron-energy-loss spectroscopy. It is
found that unwanted cation intermixing is negligible.
The effect on the electronic structure of the material is to
introduce empty states into the O p band in the CuO$_2$
layer at the Fermi level, giving rise to a new pre-edge feature
for $x \leq 0.6$, and probably responsible for inducing a tran-
sition from a semiconductor to a metal. The supercon-
ducting transition temperature ($T_c$) is found to correlate
with the intensity of this transition. Our results also sug-
gest that strong covalent mixing occurs between Cu and
O orbitals near the Fermi level, and this must be taken
into account by any theoretical models for high-$T_c$
superconductivity. In the O 1s absorption spectra, another set
of empty density of states is observed above $E_F$, even in
the semiconducting samples. The origin of these states
may lie either with the antibonding orbitals of (Tl,Pb)—O
bonds or with the localized Cu-O orbitals. Because of
this, the intensity of the whole pre-edge feature cannot be
used as a measure of the hole concentration, nor should it
be directly correlated with superconductivity. On the
other hand, there is an additional contribution to the
main pre-edge peak from holes in orbitals outside the
CuO$_2$ plane which may contribute to the normal conduc-
tivity but not to the superconductivity.

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1N. Nücker, J. Fink, B. Renker, D. Ewert, C. Politis, J. W. P.
Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman,

P. Kuper, G. Kruijzinga, J. Ghijsen, M. Grioni, P. J. Wejs, F.
M. F. de Groot, G. A. Sawatzky, H. Verweij, L. F. Feiner, and
H. Petersen, Phys. Rev. B 38, 6483 (1988); P. Kuper, M.
Grioni, G. A. Sawatzky, D. B. Mitzi, A. Kapitulnik, A. San-
tantiello, P. De Padova, and P. Thiry, Physica C 157, 260
(1989).

Shindo, H. Sato, G. L. Liedl, D. Perry, K. Hiraga, M. Hir-
abayashi, S. Nakajima, M. Kikuchi, Y. Syono, K. Hojou,

4D. Shindo, K. Hiraga, S. Nakajima, M. Kikuchi, Y. Syono, N.
Kobayashi, K. Hojou, T. Soga, S. Furuno, and H. Otsu, Phys-

5D. Shindo, K. Hiraga, S. Nakajima, M. Kikuchi, Y. Syono, K.
Hojou, T. Soga, S. Furuno, and H. Otsu, Physica C 165, 321

6N. Nücker, P. Adelmann, M. Alexander, H. Romberg, S.
Nakai, J. Fink, H. Rietschel, G. Roth, H. Schmidt, and H.

7T. Takahashi, H. Katayama-Yoshida, and H. Matsuyama, Z.

8M. A. Subramanian, C. C. Torardi, J. Gopalakrishnan, P. L.

9R. S. Liu, J. M. Liang, S. F. Wu, Y. T. Huang, P. T. Wu, and

10P. T. Wu, R. S. Liu, J. M. Liang, Y. T. Huang, S. F. Wu, and

11M. Liang, R. S. Liu, Y. T. Wang, S. F. Wu, P. T. Wu, and

12Y. T. Huang, R. S. Liu, W. N. Wang, and P. T. Wu, Jpn. J.

13R. Raveau, C. Michel, M. Hervieux, D. Groult, and J. Provost,

14F. Studer, D. Bourgault, C. Martin, R. Retoux, C. Michel, B.
Raveau, E. Dartyge, and A. Fontaine, Physica C 159, 609
(1989).

15T. Suzuki, M. Nagoshi, Y. Fukuda, S. Nakajima, M. Kikuchi,
Y. Syono, and M. Tachiki, Physica C 162-164, 1387 (1989); T.
Suzuki, M. Nagoshi, Y. Fukuda, Y. Syono, M. Kikuchi, N.


17R. S. Liu, P. P. Edwards, Y. T. Huang, S. F. Wu, and P. T.

18D. McMullan, J. M. Rodenburg, Y. Murooka, and A. J.

19The energy position of the pre-edge peak in the C 1s absorp-
sion spectrum of an evaporated amorphous carbon film has
been measured to be 285.5 eV [S. D. Berger, D. R. McKenzie,
eV [J. Fink, T. Müller-Heinzlerling, J. Pfluger, A. Buaben,
P. Koidl, and G. Creecelius, Solid State Commun. 47, 687
(1983)] for our calibration purpose, an average value is taken.


21S. Nakai, T. Mitsuishi, H. Sugawara, T. Matsukawa, S. Mi-

22M. Grioni, J. B. Goedkoop, R. Schoorl, W. M. F. de Groot, J.
C. Fuggle, F. Schafers, E. E. Koch, G. Rossi, J. -M. Esteva,

23A. Bianconi, A. Congiu Castellano, M. De Santis, P. Rudolf,
P. Lagarde, A. M. Flank, and A. Marcelli, Solid State Com-
mun. 63, 1009 (1987).

24D. D. Sarma, O. Strebel, C. T. Simmons, U. Neukirch, and G.

25N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer,

26O. Strebel, P. Sladeczek, M. Asensio, C. Laubschat, A. Kolod-

The term “excitonic” here does not necessarily imply a bound final state which is extrinsic to the band structure, but a transition to empty states in the narrow d band, strongly modified by core-hole effects.


J. R. Cooper (unpublished).


