

XPS studies of the Bi-Sr-Ca-Cu-O ceramics at temperatures near T_c

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Ceramic samples of the oxide superconductor $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, with $x=0, 0.2$, and 0.3 have been prepared and studied by x-ray-photoelectron spectroscopy. A comparison of the Cu $2p$, Bi $4f$, and O $1s$ spectra of undoped and doped samples from ambient temperature down to 96 K near the critical temperature suggests the formation of dimer oxygen species in the superconducting state. A mechanism of charge transfer between CuO_2 and BiO planes is proposed to explain this possibility, which is suggested to be related to the change of the conductivity of the ceramics.

I. INTRODUCTION

Bi-Sr-Ca-Cu-O ceramics form an important class of high- T_c superconductor materials. It was found that several phases can be obtained from these ceramics depending on the preparation conditions.¹ These phases are the following: 2:2:0:2 ($T_c \sim 22$ K), 2:2:1:2 ($T_c \sim 80$ K), and 2:2:2:3 ($T_c \sim 110$ K). It has also been observed that mixtures of these phases are usually obtained and some techniques have been elaborated, aiming to purify the materials and select the highest proportion of the 2:2:2:3 phase.² The most studied method consists of doping the ceramic by lead adjunction. It was found that with controlled lead concentration, the 2:2:2:3 phase could be stabilized.³ However, there is still some controversy on the elaborating technique and even on the nature of the doped ceramics.

We can make some generalizations about the copper oxide superconductors:^{4,5}

(i) Superconduction occurs within two-dimensional CuO_2 planes and in compounds exhibiting mixed-valence copper.

(ii) The CuO_2 planes in perovskite-like structure are not initially conducting. They need to be charged with injected carriers.

(iii) Superconducting CuO_2 planes are separated by charge-reservoir layers.

(iv) The charge transport occurs via electrons or holes belonging to the Cu($3d$) and O($2p$) bands, and probably originates in the CuO_2 planes.

(v) The electronic band at the Fermi level is strongly hybridized due to the similarity in energy between the Cu $3d$ and O $2p$ states.

(vi) The superconduction appears in all cases at the doping level for which the antiferromagnetic insulator loses its local moment to become metallic.

(vii) The bismuth sites are distorted (mismatched) not only electrostatically but also for electronic reasons. In fact, the Bi layer is the only one that could accept the electrons from the CuO_2 planes.

In a previous work on Bi-Sr-Ca-Cu-O ceramics,⁶ we

have shown that with optimum lead doping level (0.2–0.3), the 110 K phase was greatly ($\sim 50\%$) stabilized with substitution of Bi by Pb atoms. X-ray-photoelectron-spectroscopy (XPS) experiments performed on samples with different doping levels show that the Pb IV oxidation state increases with that of Bi V. A broadening of the Cu $2p$ line was also observed. However, the Cu oxidation state could not be clearly established. We suggest that both Cu II and Cu III states are present in doped samples. Since these states have much bearing on the mechanism of superconduction, we have carried out a temperature-dependent XPS study of both copper and oxygen species in Bi-Sr-Ca-Cu-O ceramics and propose an explanation of the charge-carrier process.

II. EXPERIMENT

The ceramics were synthesized with the nominal composition $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, with x varying from 0 to 0.3. The preparation method has been described in detail in a previous paper.⁷

A SQUID (superconducting quantum interference device) magnetometer with a maximum field of 55 kG was used for magnetic measurements. The resistivity measurement was performed by the standard four-probe ac method on bars cut from the pellets. XPS experiments were carried out on a ESCA LEYBOLD LH 12 (Université de Nantes-CNRS) using Mg $K\alpha$ radiation at 1253.6 eV. Binding-energy data were referenced to the Au $4f_{7/2}$ line (84 eV) from a gold plate fixed on the sample holder. The analyzed surface was about 1 mm^2 with an effective depth of about 100 Å. The XPS samples were pressed pellets with no epitaxy, which were scraped with a steel blade to expose new surface. The data were analyzed with a computer program which performs satellite and background subtraction, smoothing, and deconvolution to obtain the different components of the spectra.

III. RESULTS

Using both magnetic and resistivity measurements, we find the superconducting transition at 80 K for undoped

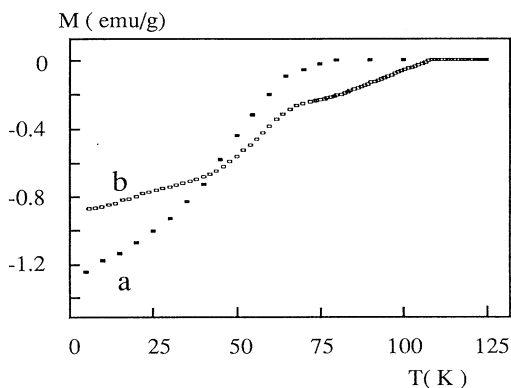


FIG. 1. Zero-field-cooled magnetization curves at 50 G for Bi compounds: (a) for undoped and (b) for 0.3 Pb-doped samples.

samples and at 110 K for 0.3 Pb-doped samples (Fig. 1). Furthermore, a comparison of M/H (after zero-field cooling of the sample) with $1/4\pi$ indicates that approximately 25% of the doped sample is superconducting below 110 K and 70% of it is superconducting below 80 K.

The XPS spectra then were obtained for the 0.3 Pb-doped sample. Figure 2 shows the O 1s spectra at various temperatures from (a) 296 K and (d) 96 K. We can see that they present two peaks (denoted as O_I and O_{II} , respectively) located at 532 and 529 eV at room temperature. While the O_{II} peak is clearly established to be related to the oxygen in the ceramic,⁸ the peak found at 532

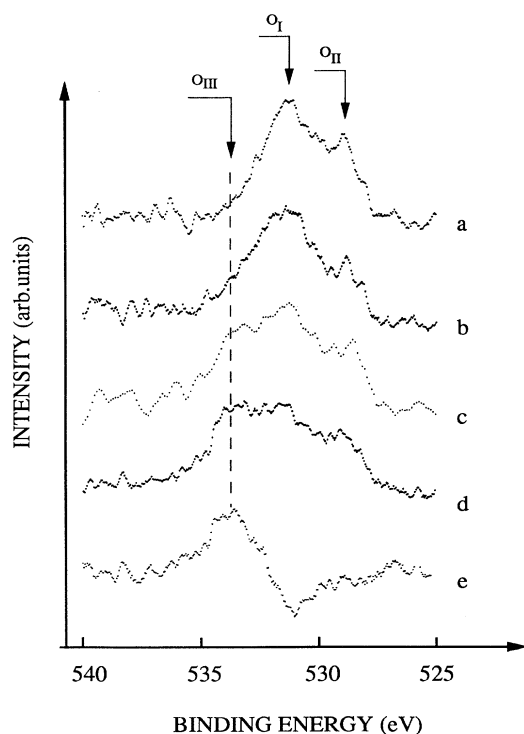


FIG. 2. XPS spectra of O 1s for 0.3 Pb-doped samples: (a) $T=296$ K, (b) $T=130$ K, (c) $T=110$ K, (d) $T=96$ K, (e) the $d - a$ difference spectrum.

eV is suggested to be due to carbonate contamination of the surface⁹ and disappears after oxygen annealing.¹⁰ In our experiments on freshly cut ceramic surfaces, the contamination effects seem to be negligible and the surfaces are found to be free of carbon (within experimental sensitivity). Hence, the two observed peaks would correspond to oxygen in the ceramic systems. When cooling the samples at just below their critical temperatures [3(c) and 3(d)], we observe that, whereas the peaks O_I and O_{II} do not change, a shoulder appears at the high-binding-energy side of the spectra. By subtracting curve d from curve a , we can see that a new peak, denoted as O_{III} , is situated at 534 eV near the sample critical temperature and remains approximately constant for temperatures lower than T_c (110 K). This peak decreases and vanishes when bringing the sample back to room temperature.

Figure 3 shows the Cu 2p spectra of these samples at the same temperatures along with a CuO sample at 296 K. At room temperature, the Cu spectrum of the sample [3(a)] has a full width at half maximum (FWHM) of 3.8 eV with a peak located at 933.6 eV. In a previous study, considering the large value of the FWHM together with the apparent shakeup satellites located at about 943 eV, we have established⁶ that the Cu 2p line is composed principally of Cu II and for a lesser extent, of Cu III oxidation states. When the sample is cooled to 96 K, we note a decrease of the FWHM of the spectrum resulting from a decrease in its intensity at 934 eV [shown by 3(e) resulting from the difference between 3(a) and 3(d)]. This binding

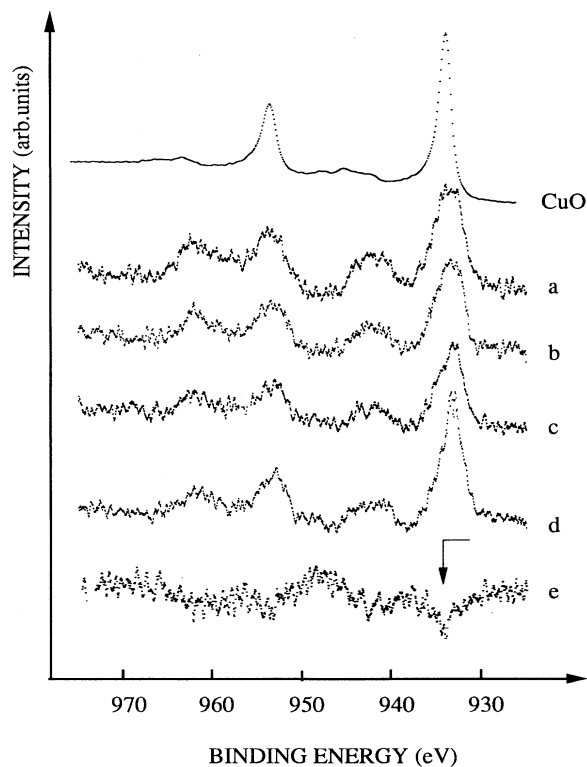


FIG. 3. XPS spectra of Cu 2p for CuO and 0.3 Pb-doped samples: (a) $T=296$ K, (b) $T=130$ K, (c) $T=110$ K, (d) $T=96$ K, (e) the $d - a$ difference spectrum.

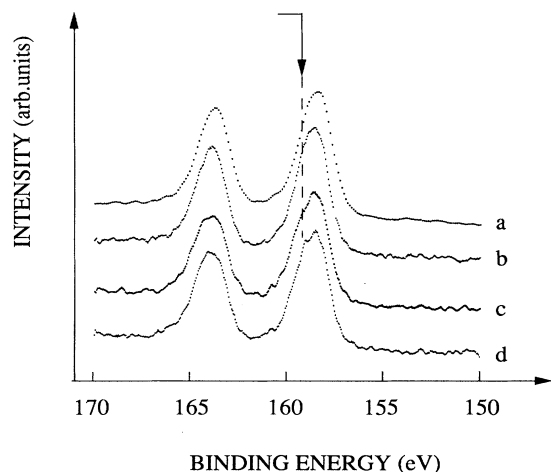


FIG. 4. XPS spectra of Bi $4f$ for 0.3 Pb-doped samples: (a) $T=296$ K, (b) $T=130$ K, (c) $T=110$ K, (d) $T=96$ K.

energy is found to correspond to the Cu II oxidation state as shown by the CuO spectrum. Further proof of this diminution can be observed by the decrease in intensity of the shakeup satellites in 3(c) and 3(d) [also in 3(e)] which are also attributed to the Cu II state.¹¹ Again, the observed changes in the Cu spectrum disappear upon heating the sample to ambient temperature.

Simultaneously, changes are observed in Bi $4f$ spectra (Fig. 4) at 110 and 96 K. The intensity of the peak remains constant but the shape shows a virtual growth at the low-binding-energy side and a shoulder is seen at the high-binding-energy side in the spectra 4(c) and 4(d). Using results already obtained on Ba-Bi-O₃ (Ref. 6), we deconvoluted these spectra into Bi III (peak position at 159 eV) and Bi V components (peak position at 158.2 eV) as shown in Fig. 5. The FWHM of these components is about 1.4 eV and shows little variation in all cases. It appears clearly from this spectral decomposition that Bi oxidation states have changed in the superconducting state; the diminution of the positive charge of the Bi V com-

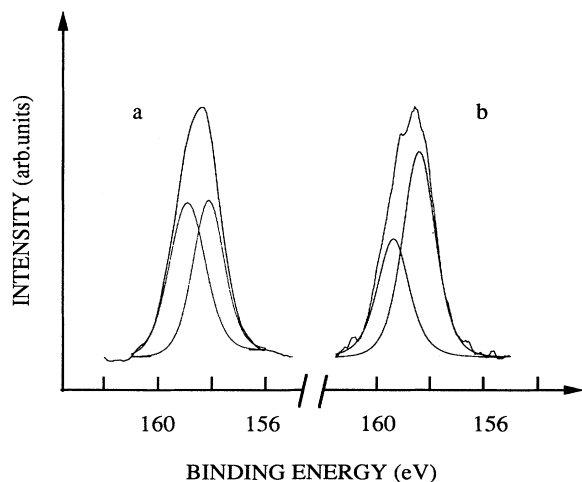


FIG. 5. Deconvoluted spectra of the Bi $4f_{7/2}$ line into Bi III and Bi V components: (a) $T=296$ K, (b) $T=96$ K.

ponent indicates that BiO planes should be enriched with electrons coming from other planes of the structure.

The evolution of the O $1s$, Cu $2p$, and Bi $4f$ spectra in the 0.2 Pb-doped sample is very similar to that observed above. On the contrary, within the same range of temperature, no noticeable evolution of these spectra was observed in the undoped sample. Unfortunately, the ESCA analyzer used could not access temperatures below 94 K, so the evolution of the spectra at the critical temperature could not be studied for these samples.

IV. DISCUSSION

The above observations are consistent with the earlier XPS study on YBa₂Cu₃O₇ (Ref. 12), where it was shown that the intensity around 533 eV of the O $1s$ line increases on lowering the temperature to the superconducting state. This peak is attributed to the presence of the dimer oxygen species formed by dimerization of the O¹⁻ species following $2O^{1-} \rightarrow O_2^{2-}$; this means that the electrons would have been generated in the creation of O¹⁻ holes from O²⁻. Furthermore, it has been shown in these compounds¹³ that on cooling, the d^{10} state of the copper (Cu I) is found to increase significantly suggesting that holes are on the oxygen rather than on the copper sites. The change in the valence state of copper is, moreover, confirmed in an XPS study on similar superconductors¹⁴ where it was found that the d^9/d^{10} ratio of copper states decreases when going from the superconducting to the nonsuperconducting state. These observations can be understood considering that the oxygen sites in the Cu-O chains are only partially filled, resulting in broken chains along the b axis. In Bi₂Sr₂CaCu₂O₈, angle-resolved resonant photoemission experiments¹⁵ have confirmed the dominant O $2p$ character in the states at the Fermi level. The result simply implies that the metallic conduction would occur at the oxygen band and the pair formation would be achieved with the oxygen holes.

To account for the above results, we now shall consider the superconduction transition mechanism in ceramics. Previous results of spin-density measurements in YBa₂Cu₃O₇ (Ref. 16) have shown that the magnetization of both the copper and the oxygen atoms decrease appreciably in the transition from the normal to the superconducting state. For Cu atoms, the magnetization varies from $2 \times 10^{-3} \mu_B$ at 120 K to $0.6 \times 10^{-3} \mu_B$ at 30 K, while the moment of oxygen atoms becomes zero in the superconducting state. This reduction of magnetization is attributed to spin pairing.¹⁶ Such a decrease can be favored by the dimer oxygen formation, $2O^{2-} \rightarrow O_2^{2-} + 2e$ with an excess of electrons. On the other hand, the superconducting behavior is linked with hole creation in the oxygen-copper layer so the excess electrons of this plane should be transferred elsewhere in the structure. A copper dimer formation following $2Cu^{2+} + 2e \rightarrow Cu_2^{2+}$ would lead to an increase of Cu I states to the detriment of Cu II ones. This is just what we observe on the 934 eV component [Fig. 3(e)] when cooling the sample below its transition temperature. But we

also note that the Bi planes seem to be the most suitable ones to collect these electrons since they are electrostatically mismatched.⁵ The change in Bi spectra suggests that Bi atoms would be enriched with electrons from the Cu-O planes. In fact, we observe a redistribution of the Bi III and Bi V states in the superconducting state with the Bi III component increasing to the detriment of the Bi V one; $\text{Bi}^{5+} + 2e \rightarrow \text{Bi}^{3+}$. The reduction of Bi appears, hence, as a further proof of the possibility of dimer oxygen formation and the existence of charge transfer between superconducting CuO_2 planes and reservoir BiO ones in the superconducting state.

V. CONCLUSION

In summary, we have performed photoemission measurements on the Bi-Sr-Ca-Cu-O ceramics (undoped and doped with lead) from 296 K to temperatures close to T_c . The changes observed in the oxygen spectra of the doped samples suggest that there is formation of the dimer oxygen species, taking into account the decrease of the Cu II state and the reduction of Bi V to Bi III oxidation states. The charge transfer between CuO_2 planes and reservoir BiO ones is suggested to be in strong relation with the modification of the surface conductivity of the ceramics.

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