



1988

XPS DOS Studies of Oxygen-Plasma Treated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Surfaces as a Function of Temperature


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Conard, T., Vohs, J.M., Pireaux, J.J., and Caudano, R. (1988). XPS DOS Studies of Oxygen-Plasma Treated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Surfaces as a Function of Temperature. In Margaritondo, G., Joynt, R., and Onellion, M. (Eds.), *High T_c Superconducting Thin Films, Devices, and Applications*, pp. 240-247. American Institute of Physics.

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Abstract

Monochromatized $\text{AlK}\alpha$ XPS has been used to monitor changes in the electronic structure of 123 sintered pellets as a function of temperature (90-650K). Since 123 surfaces are known to lose oxygen and react with water, a novel procedure was used to prepare the material surface that would be representative of the bulk material. In contrast with published results, we observed drastic DOS modification (i.e. the appearance of a new peak close to the Fermi level at low temperature).

Disciplines

Biochemical and Biomolecular Engineering | Chemical Engineering | Engineering | Engineering Science and Materials | Materials Science and Engineering

XPS DOS STUDIES OF OXYGEN-PLASMA TREATED $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$
SURFACES AS A FUNCTION OF TEMPERATURE.

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ABSTRACT

Monochromatized AlK_{α} XPS has been used to monitor changes in the electronic structure of 123 sintered pellets as a function of temperature (90-650K). Since 123 surfaces are known to lose oxygen and react with water, a novel procedure was used to prepare the material surface that would be representative of the bulk material. In contrast with published results, we observed drastic DOS modification (i.e. the appearance of a new peak close to the Fermi level at low temperature).

INTRODUCTION

Since the discovery of high temperature superconductivity in the perovskites $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ¹ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ², there have been numerous experimental investigations of their physical properties, including a number of photoemission studies using ultraviolet, X-ray, or synchrotron radiation. This work is of great importance in the understanding of the temperature dependence in the electronic structure of these compounds.

It is now well known that the perovskite superconductors easily lose oxygen at their surfaces, even at room temperature. Several methods have been used to analyse compounds with a correct (i.e. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) oxygen composition such as annealing in oxygen³ or scraping the superconductor at low temperature⁴. The present work used a novel procedure to prepare surfaces representative of the bulk oxygen stoichiometry by applying in situ an oxygen plasma discharge.

In this study, we have measured the density of states (DOS) of an YBaCuO sintered pellet in the valence band between the Fermi level and 50eV below it, over a wide temperature range (90 - 650 K). While doing this, we have also monitored the core levels of the oxygen, copper, and barium atoms. In contrast with published results^{4,5}, we observed drastic changes in the DOS close to the Fermi level.

EXPERIMENTAL DETAILS

YBaCuO samples were powders prepared according to the original recipe². For the photoemission experiments they were prepared as disks of approximately 10 mm in diameter and 1 mm thick. They were stored in air at room temperature.

The photoemission measurements were performed in a HP5950A spectrometer with hemispherical analyser. Monochromatic AlK_α X-rays (1486.6 eV) were used as exciting radiation and the base pressure in the analysis chamber fluctuated between 1.10^{-9} to 10^{-8} Torr depending on the sample temperature treatment. Indeed, the sample holder could be cooled with liquid nitrogen to a temperature of about 90 K and heated resistively to 650 K. The temperature was maintained in all this range by a thermoresistance temperature controller.

Initially, we recorded XPS spectra of the core levels without any sample treatment. Then the sample was brought out the ultrahigh vacuum chamber and severely scraped with a stainless steel blade. It was then rapidly reintroduced in the chamber and scraped again in vacuo with a diamond file. The aim of this surface treatment was to obtain a surface of the ceramic with a composition as close as possible to that of the bulk. The sample was then treated with an oxygen plasma discharge. Figure 1 shows the

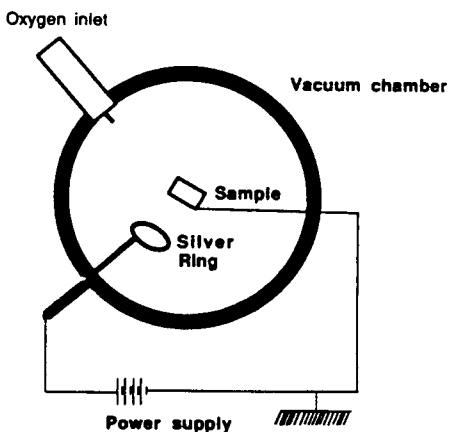


Fig. 1: Principle scheme of the oxygen plasma discharge

principle scheme of this discharge: A high purity silver ring was maintained at 500 V above the sample for twenty minutes in a pressure of 10^{-2} mbar of oxygen. The discharge current was approximately 0.7 mA: as a result, a blue glowing discharge bombarded the sample with ionized oxygen atoms. This procedure was used to restore the sample surface with the correct oxygen composition (i.e. YBa₂Cu₃O₇). After this surface treatment we began the temperature dependent analysis.

The core level spectra of all the constituent atoms exhibited more than

one component. Curve fitting routines were used to distinguish them: a background proportional to the surface of the peaks, and gaussian-lorentzian mixed functions were used to reproduce the shape of the recorded spectra.

RESULTS AND DISCUSSION

CORE LEVEL SPECTRA

For all samples and stages of treatment, even after the severe scraping, significant contamination by carbon species was evident. There were two kinds of carbon species in the C1s spectra. One at approximately 289 eV which is at the same binding energy as the C1s peak for BaCO_3 , one of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ precursors. This peak could be due to unreacted precursor but is more probably due to reaction between the ceramic and some component of air like CO_2 ^{6,7}. The other component at 284.7 eV is attributed to hydrocarbon contamination and was used to calibrate all the spectra. In contrast with other results⁸ we could not

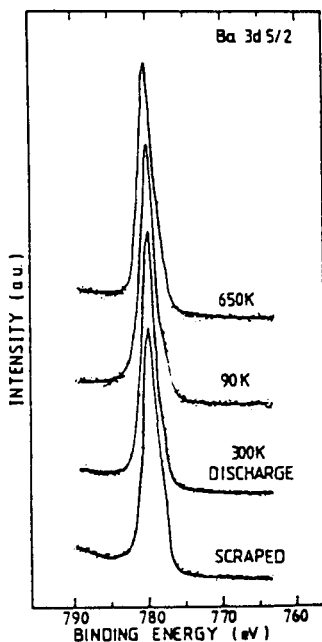


Fig. 2: Spectra of Ba 3d5/2 level: after scraping and after discharge in oxygen at room temperature, at 90K and 650K

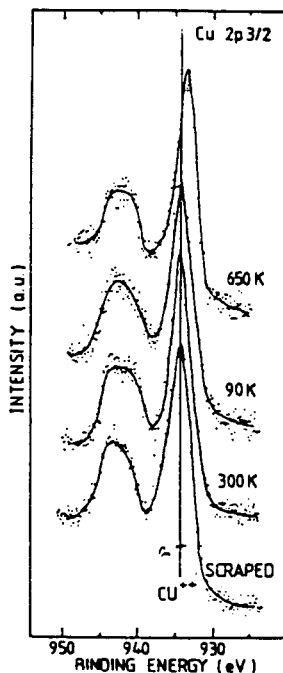


Fig. 3: Spectra of Cu 2p3/2 level: after scraping and after discharge in oxygen at room temperature, at 90K and 650K

eliminate this component after scraping: this peak is an indication of a large contamination in and around the micrograins in the ceramic.

The barium 3d_{5/2} spectra did not exhibit any change as a function of treatment procedure or sample temperature. Therefore, the barium peak was used as a reference in this work to calculate the atomic ratio of the other constituents. The Ba3d_{5/2} spectra are displayed in figure 2.

Figure 3 shows the spectra of the 3/2 component of the Cu2p doublet. These spectra exhibit a broad satellite structure near 940 eV typical of the Cu⁺⁺ shake-up. No significant changes were observed in these spectra after scraping, oxygen plasma discharge and at low temperature. However, when the sample was heated, the Cu2p_{3/2} peak shifted to lower binding energy. The origin of this displacement can be attributed to reduction of copper from Cu⁺⁺ to Cu⁺. This could be clearly seen after computer curve resolution. This is also confirmed by the fact that the intensity ratio between the satellite peak and the main peak strongly decreased as the temperature was increased.

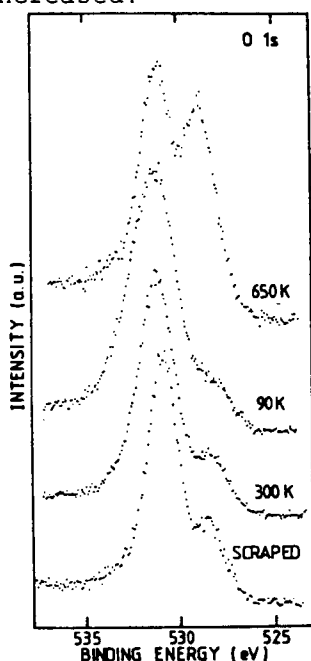


Fig. 4: Spectra of O 1s level: after scraping and after discharge in oxygen at room temperature, at 90K and 650K

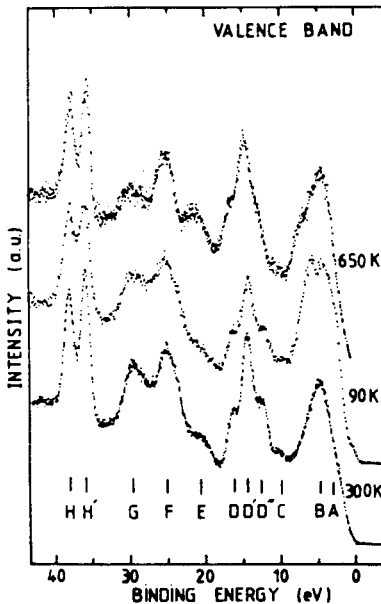
Figure 4 displays the O1s spectra; the calculated atomic ratios are listed in table I. After scraping, the amount of oxygen present at the surface decreased significantly, suggesting that these ceramics were highly contaminated in the surface region. After the O₂ discharge treatment there was no major modification in the room temperature spectra, however, the surface atomic concentrations were close to the bulk stoichiometry. At low temperature, the total amount of oxygen present at the surface increased significantly. This increase can be attributed to water contamination resulting from adsorption from the background gas. The component corresponding to O1s in water at about 533 eV increased and now represents a significant portion of the oxygen 1s signal. The high temperature spectra shows also significant modification that can be attributed to water desorption.

YBa ₂ Cu ₃ O _{7-δ}		
Sample treatment	Cu	O
untreated	4.3	14.1
scraped	4.2	6.5
discharge	2.7	7.0
low temp.	3.1	11.2
high temp.	1.8	4.4

Table I: Sample atomic ratios referred to barium. Note: the first two ratios for copper were obtained from a separate sample

VALENCE BAND SPECTRA

Figure 5 displays three valence band spectra recorded after the O₂ discharge at 300 K and subsequent cooling and heating to 90 and 650 K respectively. Table II lists the assignments of the main features of the room temperature spectra in accordance with recently published results⁹. In all these spectra, and even for other samples, we observed the presence of a W4f doublet at 36 and 38,5 eV which is likely due to bulk tungsten contamination resulting from the YBaCuO synthesis in a tungsten



Structure	Origin
A	Cu3d-O2p
B	Hybrid state
C	O2p satellite
D	Ba3d _{1/2}
D'	Ba3d _{1/2}
	Ba3d _{3/2}
D''	Ba3d _{3/2}
E	O2s
F	Y4p _{1/2}
	Y4p _{3/2}
G	Ba5s
H	W4f _{5/2}
H'	W4f _{7/2}

Table II : Valence band structure attribution. (Adapted from ref 9)

Fig. 5: Valence band spectra of oxygen plasma discharge pellet at room temperature, 90K and 650K

crucible. No significant contribution of the W signal is expected at binding energies close to the Fermi level.

At low temperature (approximately 90 K), we observed drastic modification in the DOS (fig. 6). At 6 eV, a new strong feature (Y) is clearly apparent. This new peak can be explained if we recall that water adsorption is probably contaminating the sample surface at liquid nitrogen temperature. Another group¹⁰ has reported similar DOS changes when they intentionally adsorbed H₂O on YBa₂Cu₃O₇. This interpretation is also consistent with changes we observed in the O1s spectra.

Another clearly visible change at low temperature is an increase in the DOS very near the Fermi level (structure X). This increase can not be explained by the presence of water/ice at the surface^{10,11} as ice only contributes at higher binding energies and not at the Fermi level. This is the first time, to our knowledge, that such a temperature dependence in the DOS of YBaCuO has been observed by XPS. A similar modification in the DOS of the Bi₄Ca₃Sr₃Cu₄O_{16+x} compound at low temperature has recently been reported¹² (fig.7) : it was measured by angle integrated ultraviolet photoemission and has been interpreted as the consequence of the opening of a superconductor gap. Another angle resolved UPS study¹³ on YBa₂Cu₃O₇ also shows a modification in the DOS near the

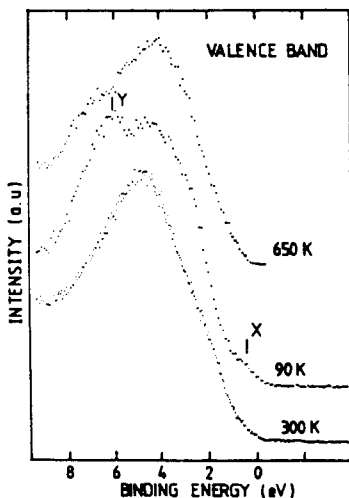


Fig. 6: Valence band spectra of oxygen plasma discharge pellets at room temperature, 90K, and 650K

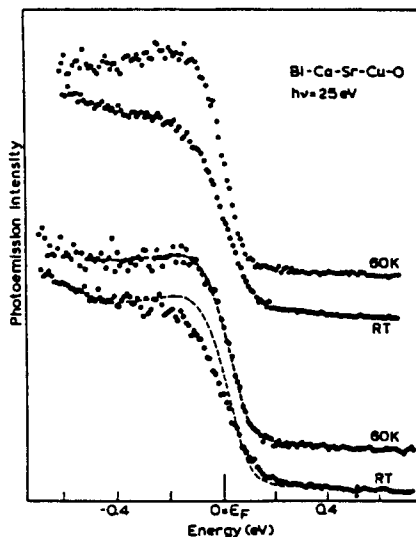


Fig. 7: Photoemission spectra taken at room temperature and at 60K for Bi₄Ca₃Sr₃Cu₄O_{16+x} (ref 12)

Fermi level for certain direction of the Brillouin zone and for certain photon energy. In the present study, the fact that we are working in angle integrated mode allows us to exclude such an origin. This conclusion is reinforced by the fact that this modification is a temperature dependent structure since it does not appear in the room and high temperature spectra.

When the temperature of the superconductor was increased to 650 K, the structure at 6 eV is partially removed. This is interpreted as water desorption. However, there was still a strong shoulder at this energy, suggesting a reaction between this ceramic and the water previously adsorbed at the surface and formation of hydroxide species at the surface. This interpretation is consistent with the study of Kurtz et al.⁷ which shows that another superconducting ceramic ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) is highly reactive with the different components of air (O_2 , H_2O , CO_2 , CO). The other modification at high temperature is the disappearance of structure X at the Fermi edge.

CONCLUSION

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples whose surfaces has been treated in situ in an oxygen plasma discharge showed for the first time DOS modification close to the Fermi level, at liquid nitrogen temperature. This observation is consistent with the fact that the sample stoichiometry has been restored by the preparation process, and also probably with the fact that XPS, when induced by a monochromatized AlK_{α} source, is certainly less surface and grain boundary sensitive than previously published synchrotron photoemission results. As a consequence, we attribute the new DOS structure appearing at the Fermi level at 90K to an oxygen related band in the superconductor

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