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XPS Study of the Dependence on Stoichiometry and Interaction with Water of Copper and Oxygen Valence States in the $YBa_2Cu_3O_{7-x}$ Compound

P. SALVADOR* AND J. L. G. FIERRO

Instituto de Catálisis y Petroleoquímica, CSIC, Serrano, 119 28006 Madrid, Spain

AND J. AMADOR, C. CASCALES, AND I. RASINES

Instituto de Ciencia de Materiales, CSIC, Serrano, 113-28006 Madrid, Spain

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In order to elucidate the valence states of both copper and oxygen in $YBa_2Cu_3O_{7-x}$ as a function of the oxygen content, their O_{1s} and Cu_{2p} core-level X-ray photoelectron spectra were studied at room temperature for $0.9 \geq x \geq 0.1$. No evidence of the Cu^{3+} (i.e., $3d^8$) configuration was found for the ground state of a superconducting sample ($x \simeq 0.1$). Rather, the ground state for this composition can be described as a mixture of two configurations: mainly $3d^9KL$ (i.e., Cu^{2+}–O^- hybridization), where K represents an electron of the conduction band and L stands for a hole in the oxygen bonded to a virtually divalent copper, and some $3d^{10}$ (i.e., Cu^+). The amount of monovalent copper was found to increase with x, as oxygen (O^- species) from Cu_1–O chains parallel to the crystallographic b axis leave the lattice and electrons are transferred to the adjacent Cu^{2+} ions. Simultaneously, the concentration of holes delocalized in the oxygen valence band decreases, the Fermi level goes upward, and the material's behavior at room temperature changes from quasi-metallic (degenerated p-type semiconductor) to p-type semiconducting. For $x \simeq 0.9$ the amount of Cu^+ predominates over that of Cu^{2+}. The high reactivity of the superconducting material with water is evidenced by the special characteristics of its O_{1s} core-level spectrum. The presence of OH^- ions indicates dissociative adsorption of water molecules from the air. The XPS signal due to OH^- species is higher than that of the O^{2-} lattice ions, even when the sample was preserved from exposure to air. Moreover, when the superconducting sample was contaminated by prolonged exposition to air, the O^{2-} signal could hardly be observed. These results are consistent with the existence of delocalized holes in O_{2p} orbitals. In fact, the O^- lattice species strongly react with water molecules to produce more stable OH^0 radicals, which further recombine to generate H_2O_2 whose decomposition is catalyzed by Cu^{2+} ions. As a result, molecular oxygen from lattice O^- species is evolved. Charge neutrality in the superconductor lattice is preserved by filling O^- vacancies with OH^- groups, which became coordinated to Ba^{2+} ions as inferred from the analysis of the Ba_{3d} XPS spectrum.

Introduction

A full understanding of the superconductivity mechanisms in the $RBa_2Cu_3O_{7-x}$ (R = Y, La, lanthanide) oxides requires a fair knowledge of the local electronic configuration of Cu and oxygen ions. The transition at room temperature from the semiconducting ($x \gtrsim 0.5$) to the metallic phase ($0.5 > x > 0$), which shows superconductivity at temperatures near that of liquid nitrogen, is

* To whom correspondence should be addressed.

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governed by the oxygen content, x, and, therefore, by the formal oxidation state of Cu atoms. Assuming a fixed integer valence for the remaining atoms, i.e., 2 for oxygen and barium and 3 for yttrium, the formal valence for copper should be 2.3 for $x = 0$, 2 for $x = 0.5$, and 1.7 for $x = 1$. Therefore, a mixture of Cu^{2+} and Cu^{3+} ions should be expected for $x < 0.5$.

The crystal structure of $YBa_2Cu_3O_{7-x}$ has been established by X-ray diffraction (*1*), neutron diffraction (*2*), and high-resolution transmission electron microscopy (*3*). The orthorhombic unit cell for $0 \lesssim x \lesssim 0.5$ contains two copper atoms, Cu_2, with a square pyramidal coordination to 5 oxygen atoms, and one copper atom, Cu_1, surrounded by 4 oxygens in square planar coordination, forming Cu_1–O chains along the b axis. Pyramidal coordination is frequent for Cu(II); thus, the valence of Cu_2 atoms is assumed to be 2. On the other hand, from neutron diffraction experiments it is now well known that the oxygen sites of the Cu_1–O chains are practically emptied when x increases from 0 to 0.5, and the orthorhombic crystal structure becomes tetragonal. In this case, it must be concluded that Cu_1 atoms are progressively reduced from Cu^{3+} ($x = 0$) to Cu^{2+} ($x = 0.5$). Because the superconductivity decreases or even vanishes when x increases, it is inferred that the presence of Cu^{3+} at Cu_1 sites is essential for superconducting properties. The valence of copper in these oxides has been investigated mainly by X-ray absorption (*4–11*) and photoemission (*12–15*). While some authors claim the existence of Cu^{3+} (*4, 6, 9, 10, 14*), others do not find any evidence of this valence state (*5, 7, 8, 12, 13, 15*). Lengeler *et al.* (*11*) recently concluded that $YBa_2Cu_3O_{6.9}$ ($x = 0.1$) contains two divalent Cu_2 ions with a K-edge similar to those present in the green semiconductor Y_2BaCuO_5, consisting in 0.84 Cu^{3+} as in $KCuO_2$ and in 0.16 Cu^{1+} as in Cu_2O. Formally, Cu^{3+} can have two different configurations at the ground state, i.e., $3d^8$ and $3d^9$ L, where L stands for a hole in the oxygen ligand. While $3d^8$ is characteristic of the ionic bond between copper and oxygen, $3d^9L$ indicates strong covalency in the Cu–O bond. The well-known electronic structure of the superconducting compound implies a strong mixing of Cu_{3d} and O_{2p} orbitals, favoring the $3d^9L$ configuration. Moreover, holes in the O_{2p}-derived valence band have been directly observed by core-level excitation of oxygen 1s electrons into empty p-states of the Fermi level, E_F, via electron energy loss spectroscopy (*16*). Inverse photoemission measurements also show the existence of unoccupied O_{2p} orbitals just above the top of the valence band (*17*). From high-energy inelastic electron spectroscopy measurements, Kamaras *et al.* (*18*) have shown that the density of empty O_{2p} states close to E_F increases with x. Moreover, all spectroscopic investigations have failed to reveal pure $3d^8$ configurations, either in $YBaCu_2O_{7-x}$ superconducting materials or in compounds like $NaCuO_2$ (*19*) and KCu(biuret)$_2$ (biuret = $NH_2CONHCONH_2$) (*7*), where a pure formal valency of 3 is expected.

On the other hand, the existence of delocalized holes in the O_{2p} energy levels should involve the existence of stable O^- species in the superconductor lattice. This explains the unusual release of oxygen from the superconductor when it is in contact with water (*20*), suggesting interesting catalytic properties for these new superconducting materials, for instance in the formation of CH_3 radicals from methane. However, this is far from the scope of this paper and will be considered elsewhere (*21*). Here we have used X-ray photoelectron spectroscopy (XPS) to study not only the dependence on x of the actual valence of copper and oxygen in $YBa_2Cu_3O_{7-x}$ but also the effect that the interaction of the superconductor with water has on both the copper oxidation state and the lattice stability.

Experimental

$YBa_2Cu_3O_{7-x}$ ceramics were prepared by homogeneously mixing analytical grade Y_2O_3, BaO_2, and CuO powders. The mixture was pressed into pellets and heated to 975°C in air for 48 hr. This process was repeated twice after regrinding. The material prepared in this way was monophasic, orthorhombic, and served as the starting material for obtaining samples with three different oxygen contents via annealing treatments under controlled temperature and atmosphere (*22*), as indicated in Table I.

The pellets used for XPS measurements were surface cleaned by scraping them with a hard metallic knife before the annealing treatments. In order to avoid contamination of the pellets during air exposure, especially from water vapor, they were removed from the furnace at ~150°C and immediately transferred into the vacuum chamber of the XPS spectrometer under a residual pressure of ca. 10^{-5} Torr. Conductivity measurements performed at the temperature of liquid nitrogen confirmed that the sample 4-O_2 was superconducting, whereas the samples 4-H_2 and 8-N_2 were not and showed *p*-type semiconducting behavior at room temperature. For comparative purposes the XPS spectra of the contaminated 4-O_2 sample were also studied. With this aim, the sample was left in contact with the air for several days after the annealing treatment at 400°C in O_2 (see Table I).

TABLE I

PREPARATIVE CONDITIONS AND CHARACTERISTICS OF $YBa_2Cu_3O_{7-x}$ SAMPLES[a] WITH DIFFERENT OXYGEN CONTENTS

Sample	Temperature (°C)	Time (hr)	Atmosphere	x	Present phase
4-O_2	400	24	Flushing O_2	~0.1	Orthorhombic
4-N_2	400	24	Flushing N_2	~0.5	Orthorhombic
8-N_2	800	24	Flushing N_2	~0.9	Tetragonal

[a] All the samples were heated at 2°C min^{-1} and cooled to ~150°C at the same rate.

XPS spectra were obtained with a Leybold Heraeus LHS 10 spectrometer, working in the ΔE = constant mode at a pass energy of 20 eV. The spectrometer was provided with a hemispherical electron analyzer and a Mg$K\alpha$ anode X-ray source (Mg$K\alpha$ = 1253.6 eV). Samples 3 mm thick were mounted on a long rod placed in an introduction chamber, and outgassed to ca. 10^{-5} Torr for 5 min before the samples were moved into the turbopumped analysis chamber. The pressure in this chamber was maintained below 3×10^{-9} Torr during data acquisition. Either 20 or 50 eV energy regions of the photoelectrons of interest at the pass energy selected were chosen as a compromise, enabling acceptable energy resolution to be obtained within reasonable data acquisition times. Each spectral region was signal averaged to a number of scans to provide a good signal-to-noise ratio. Although surface charging was observed on all samples, accurate binding energies (BEs) could be determined by charge referencing with the adventitious C_{1s} line arising from oil vapor contamination in the initial outgassing step at BE = 284.6 eV.

Results and Discussion

Cu_{2p} Core-Level Spectra and Copper Oxidation States

Figure 1 shows the Cu_{2p} spectra of the three samples obtained under the experimental conditions shown in Table I, with oxygen contents per formula of 6.9, 6.5, and 6.1 ($x \simeq 0.1, 0.5, 0.9$), respectively. The spectra of the sample 4-O_2, which was exposed to the air for several days, and those of a CuO reference sample are also shown in Fig. 1.

The XPS spectrum of CuO (Fig. 1a) presents the typical $Cu_{2p_{3/2}}$ and $Cu_{2p_{1/2}}$ lines separated by 20 eV, as reported in the liter-

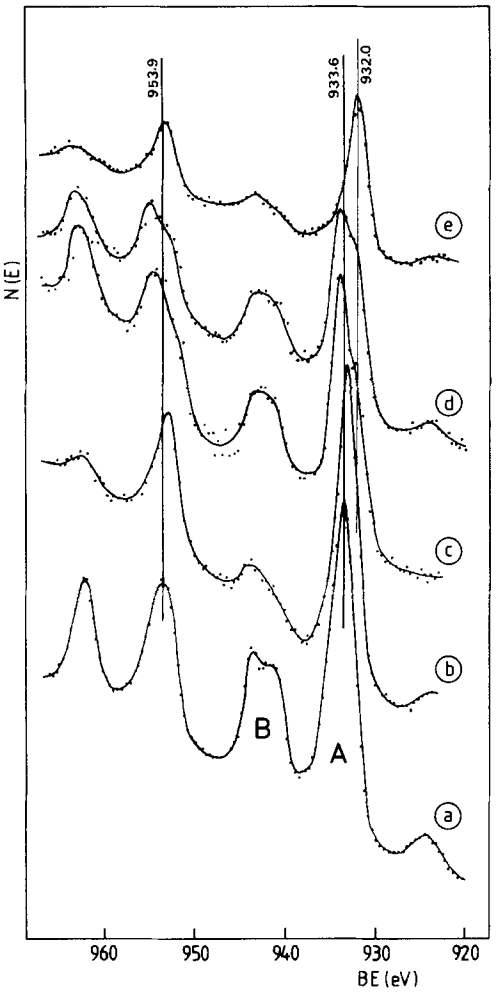

FIG. 1. Room-temperature XPS Cu_{2p} core-level spectra of the $Ba_2Cu_3YO_{7-x}$ sample subjected to various pretreatments: (b) exposed to air at room temperature; (c) oxidized in an oxygen flow at 400°C; (d) reduced in a nitrogen flow at 400°C; (e) reduced in a nitrogen flow at 800°C. For comparative purposes, the Cu_{2p} core-level spectrum of the CuO reference compound (a) is also included. All the spectra show whole spin–orbit splitting with intense final-state satellites.

ature (*23*). Each core level shows two lines, *A* and *B*, which are associated with the $2p3d^{10}L$ and $2p3d^9$ final states, respectively (*24*). The *B* peak is characteristic of Cu^{2+} compounds. The $2p3d^{10}L$ final state, where *L* stands for a ligand hole, involves charge transfer from the O_{2p}-derived valence band levels to the Cu_{3d} orbitals. The spectra of $YBa_2Cu_3O_{7-x}$ (Figs. 1b–1e) show important differences compared with those of CuO, and are very sensitive to the value of x. For the superconducting sample, i.e., the most oxidized ($x \simeq 0.1$, Fig. 1c), the *A* peak appears shifted toward higher binding energies (BE = 934.1 eV) than those in CuO (BE = 933.6 eV). Moreover, an incipient shoulder centered at ~932 eV is present. The *B*/*A* intensity ratio is also lower in $YBa_2Cu_3O_{6.9}$ (0.37) than in CuO (0.49). For $x = 0.5$ (Fig. 1d) the position of the *A* peak and the *A*/*B* ratio do not practically change, while the shoulder at ~932 eV becomes more intense than that for $x = 0.1$. Finally, for $x = 0.9$ (Fig. 1e) the *A* peak almost disappears (only a small shoulder can be observed) and the shoulder appearing at ~932 eV for $\simeq 0.5$ and $x = 0.1$ becomes a well-defined peak. Moreover, the *B* peak decreases considerably.

It is especially interesting to compare the spectrum of the orthorhombic superconducting sample, $YBa_2Cu_3O_{6.9}$ (Fig. 1c), with that corresponding to its air-exposed counterpart (Fig. 1b). Three main features characterize the spectrum of the latter: (a) the setting of the *A* peak at BE = 933.4 eV, very near that corresponding to the Cu spectrum; (b) the disappearance of the shoulder at BE $\simeq$ 932 eV; and (c) the lowering of the intensity of the $2p3d^9$ final state (*B* peak), which gives a ratio $B/A = 0.2$, considerably lower than that for the noncontaminated sample ($B/A = 0.37$). Table II summarizes the main spectral features of the different XPS spectra.

According to recent X-ray absorption results reported by Lengeler *et al.* (*11*), the superconductor $YBa_2Cu_3O_{6.9}$ contains two Cu^{2+} ions per formula, with a *K*-edge similar to that of semiconducting Y_2BaCuO_5 but different from that in CuO, which contains 0.84 Cu^{3+} ions, like those present in $KCuO_2$, and 0.16 Cu^+ ions as in Cu_2O. Like

TABLE II

BINDING ENERGIES[a] (eV) OF SEVERAL ATOMIC LEVELS

Sample	Pretreatment	O_{1s}	Ba_{4d} 3/2	Ba_{4d} 5/2	Cu_{2p} 1/2	Cu_{2p} 3/2
$Ba_2Cu_3YO_{7-x}$	None	531.2 (528.7)	795.8	780.6	953.3	933.4
$Ba_2Cu_3YO_{7-x}$	Oxidized in O_2 at 400°C	532.0 (530.3)	795.4	779.6	954.3	934.1 (932.0)
$Ba_2Cu_3YO_{7-x}$	Annealed in N_2 at 400°C	531.9 (530.5)	795.0	779.1	954.6	934.1 (932.0)
$Ba_2Cu_3YO_{7-x}$	Annealed in N_2 at 800°C	532.3 (530.0)	794.6	777.8	952.3	931.8 (934)
CuO	None	(531.5) 529.5	—		953.9	933.6

Note. BE of less intense lines are indicated in parentheses.

[a] Referenced to C_{1s} line at BE = 284.6 eV.

other authors, Lengeler *et al.* (*11*) think that Cu^{2+} ions should occupy Cu_2 sites in the orthorhombic unit cell, while Cu^{3+} and Cu^{1+} probably occupy Cu_1 sites. Also according to Lengeler *et al.* (*11*), the formal trivalency of copper in the superconductor cannot be understood as actual Cu^{3+} with $3d^8$ ground-state configuration, but rather as a valence state represented by the configuration $Cu_{3d^9}O_{2p^5}$. Therefore, the main difference between this configuration and that of formal $Cu^{2+}_{3d^9}O_{2p^6}$ is the existence of a hole in the ligand O_{2p}-derived band. Bianconi *et al.* (*13*) have studied the differences between the XPS Cu_{2p} spectrum of the di- and trivalent copper compounds K_2Cu^{2+}(biuret)$_2$ and KCu^{3+}(biuret)$_2$, respectively, and have not found evidence of Cu^{3+} ions with $2p3d^8$ final states in the trivalent compound. On the other hand, the main difference between both spectra lies in the shape of the *B* peak associated with the $2p_{3/2}3d^9$ final state in the divalent copper compound, and the $2p_{3/2}3d^9L$ final state corresponding to the $3d^9L$ configuration in the ground state for the trivalent compound. Steiner *et al.* (*19*) compared the XPS $Cu_{2p_{3/2}}$ spectra of $NaCuO_2$, with formally Cu^{3+} ions, and those of CuO. They found that the peak intensity ratios *A*/*B* increased considerably in the trivalent compound, while the BE of the $2p3d^{10}L^2$ final state (*A* peak in $NaCuO_2$) was about 1.5 eV higher than that of the $2p3d^{10}L$ final state (*A* peak in CuO).

On the basis of these statements, the spectral features of Fig. 1 can be interpreted as follows. The existence of Cu^{2+} ions in the sample of $YBa_2Cu_3O_{6.9}$ (Fig. 1c) is confirmed by the presence of a relatively high *B* peak at BE $\simeq$ 942 eV, associated with the $2p3d^9$ final-state configuration. However, the appearance of the *A* peak at a BE = 934.1 eV, higher than in CuO, seems to indicate that some Cu^{2+} ions with a $Cu_{3d^9}O_{2p^5}$ configuration in the ground state are also present. Moreover, the incipient shoulder at a BE $\simeq$ 932 eV reveals the existence of a very small proportion of Cu^+ ions. This could be expected taking into account that oxygen vacancies are generated at the Cu_1–O chains as x increases. In fact, the release of O^- species coordinated to Cu_1 atoms in the Cu_1–O chains parallel to the *b* axis should be accompanied by the reduction of the copper ions, according to

$$Cu_1^{2+}\text{–}O^- \rightarrow Cu_1^+ - \square + \tfrac{1}{2}O_2^{\uparrow}, \qquad (1)$$

where $\square$ represents an O^- vacancy.

In the ideal superconducting sample (x = 0), all the oxygen positions in the Cu_1–O chains are filled and the material behaves like a metal (degenerated *p*-type semicon-

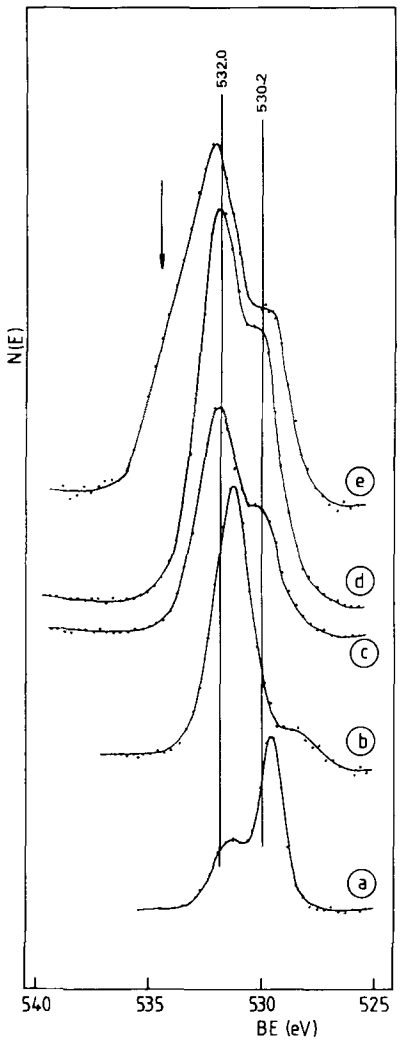

FIG. 2. Room-temperature XPS O_{1s} core-level spectra of the $YBa_2Cu_3O_{7-x}$ sample subjected to the same pretreatments as in Fig. 1.

ductor) at room temperature. The predominance of the electronic configuration $3d^9L$ in this case produces, as already stated, a downward shift of the Fermi level, which invades the O_{2p} valence band. The oxygen energy levels below E_F then become empty (holes associated with O^- species) and form a thin band for conduction of thermally excited electrons from the filled energy level below E_F. When x increases, O^- vacancies are generated and electrons are transferred from O^- sites to adjacent copper ions, as Eq. (1) indicates. In this way, copper decreases its valence state and reaches the $3d^{10}$ configuration. At the same time the number of holes in the upper part of the O_{2p}-derived valence band drastically diminishes and E_F moves up. At $x \gtrsim 0.5$ the material reaches the electronic configuration typical of a p-type semiconductor, with E_F just above the upper limit of the valence band, and loses its superconducting properties.

Figure 2 shows the O_{1s} core-level spectra for the same samples as in Fig. 1. A well-defined couple of peaks characterize these spectra at binding energies of $\simeq$530 and $\simeq$532 eV, respectively. The exact position and relative intensity of both peaks strongly depend on the sample (see Table II). According to literature data about 1s core-level spectra in metal oxides, the lower binding energy peak corresponds to species with two negative charges, O^{2-}, while the higher energy peak is associated with oxygen species having only one negative charge, which include O^-, O_2^{2-}, and OH^- species (*25*). In the case of CuO, the higher BE peak at 351.5 eV is due to hydroxyl groups resulting from the dissociative adsorption of water molecules. This peak is considerably less intense than that associated with O^{2-} species appearing at lower BE which indicates a relatively weak surface hydration of CuO. This is not the case for the $YBa_2Cu_3O_{7-x}$ samples, in which the higher BE peak is much more intense than that at lower BE, which indicates a high contamination of OH^- species despite the experimental precautions taken to avoid the hydration of the samples (see Experimental). This effect is especially important for the sample exposed to air for several days, where the peak associated with OH^- species has dramatically increased, while that due to O^{2-} ions has almost disappeared.

The high reactivity of $YBa_2Cu_3O_{7-x}$ with water can be attributed (*20*) not only to the high hydration energy of Ba^{2+} ions but also to the existence of O^- and/or O_2^{2-} lattice species which are extremely reactive. In fact, these species are responsible for the spontaneous release of molecular oxygen from the superconductor's lattice when put in contact with water, probably according to the reactions (*20*)

$$2O^-(L) + 2H_2O \rightarrow \tfrac{1}{2}O_2^{\uparrow}(L) + 2OH^- + H_2O(L) \quad (2)$$

$$O_2^{2-}(L) + 2H_2O \rightarrow \tfrac{1}{2}O_2^{\uparrow}(L) + 2OH^- + H_2O(L), \quad (3)$$

where (L) represents lattice species.

Both reactions should involve the generation of H_2O_2 molecules, which further decompose into oxygen and water, a reaction which is catalyzed by $Cu^{2+}(L)$ ions:

$$O_2^{2-}(L) + 2H_2O \rightarrow H_2O_2(L) + 2OH^- \quad (4)$$

$$H_2O_2(L) \xrightarrow{Cu^{2+}} H_2O + \tfrac{1}{2}O_2^{\uparrow}(L) \quad (5)$$

The same should be valid for $O^-(L)$ species through the generation of more stable OH^0 radicals from which H_2O_2 is formed:

$$O^-(L) + H_2O \rightarrow OH^0(L) + OH^- \quad (6)$$

$$OH^0(L) + OH^0(L) \rightarrow H_2O_2(L) \quad (7)$$

During reactions (2) and (3) the lattice loses two negative charges; charge neutrality is preserved because O^- vacancies in the Cu_1–O chains are filled by OH^- ions, which become very strongly coordinated to Ba^{2+} lattice ions. Consequently, the chemical bonds between Cu_1 and OH^- groups are broken and the solid decomposes to give $Ba(OH)_2$, CuO, and semiconducting Y_2BaCuO_5 (*26*).

The identification of O^- and/or O_2^{2-} species in the O_{1s} spectrum of superconducting $YBa_2Cu_3O_{6.9}$ is ambiguous because of the presence of a strong signal due to OH^- ions at a BE very close to that of O^- (*25*). In fact, the O_{1s} spectra of 4-N_2 and 8-N_2 samples, which should not contain O^- species, are very similar to those of the superconducting sample, 4-O_2. Gourieux *et al.* (*27*) compared the spectra corresponding to clean surfaces, obtained by scramping *in situ* samples of composition $YBa_2Cu_3O_{6.76}$, with the spectra of the same samples highly contaminated, and claimed to be able to distinguish a peak at BE $\simeq$ 532 eV due to contaminants (OH^- probably) from another peak at 530–531 eV due to singly charged oxygen species (probably O^- and/or O_2^{2-}). However, these results must be taken cautiously because of the difficulties in obtaining fully water-free surfaces, even under the experimental conditions used by Gourieux *et al.*

On the other hand, the peak corresponding to OH^- species in the most reduced sample, $YBa_2Cu_3O_{6.1}$, shows a clear asymmetry toward higher BE due to the presence of a weak component, which may be attributed to water molecules nondissociatively adsorbed on $Cu^+(L)$ ions. Typical O_{1s} spectra of hydrogen-bonded water molecules show in fact one peak at BE between 533 and 535 eV (*25, 27*).

Figure 3 shows the Ba_{3d} spectra for the various samples used in this study. Two well-differentiated spectral features can be observed in the highly hydroxylated sample. The very intense peak centered at about 781 eV should correspond to the $Ba_{3d_{5/2}}$ signal of the $Ba(OH)_2$ phase formed during the decomposition of the superconductor by reaction with water (*26*). The small shoulder between 777 and 778 eV must be associated with Ba^{2+} ions coordinated to O^{2-} species in the superconductor's lattice. The spectra corresponding to the samples 4-O_2 ($x \simeq 0.1$) and 4-N_2 ($x \simeq 0.4$) are very similar and show a peak centered at ~779 eV, which suggests the existence of only one type of Ba^{2+} ions (those present in the superconductor) and, therefore, the absence of the $Ba(OH)_2$ phase. It

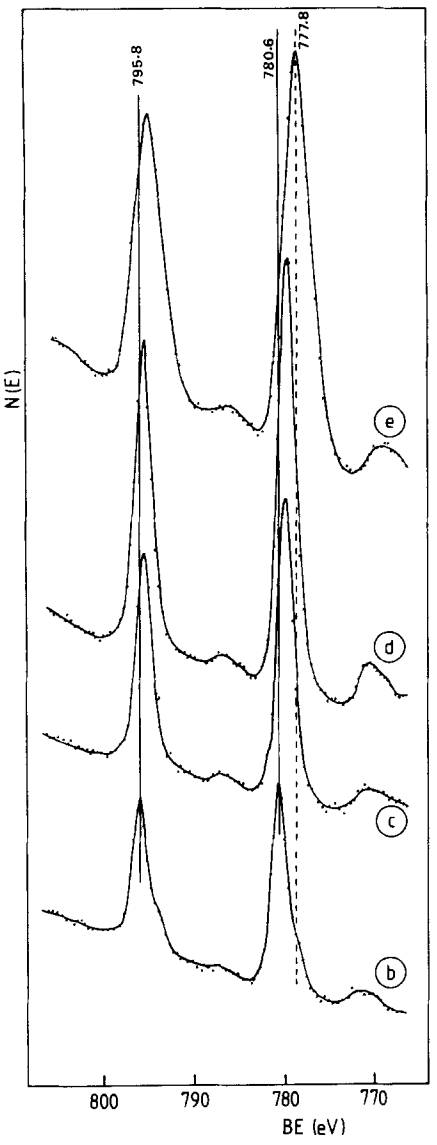

FIG. 3. Room-temperature XPS Ba_{4d} core-level spectra of the $YBa_2Cu_3O_{7-x}$ sample subjected to the same pretreatments as in Fig. 1. All the spectra again show whole spin–orbit splitting.

is worth noting that in the most reduced sample ($x = 0.9$) the $Ba_{3d_{5/2}}$ signal appears shifted toward lower BE by about 1 eV. A possible reason for this is the drastic changes occurring in the lattice positions surrounding the Ba ions. These changes mainly concern the Cu_I–O chains parallel to the b axis. In fact, for low values of x (superconducting sample) Ba ions are screened by O^- species in those chains. However, when x increases these species are lost, divalent Cu_I ions are reduced to Cu^+ and the screening effect disappears.

Conclusions

The room-temperature XPS study of the $YBa_2Cu_3O_{7-x}$ compound for different values of x ($0.9 \geq x \geq 0.1$) shows that the copper ground-state electronic configuration for $x \simeq 0.1$ (superconducting composition) is not $3d^8$ but rather $3d^9KL$, where K represents an electron of the conduction band and L stands for a hole in the oxygen bonded to a virtually divalent copper. Therefore, one can reasonably assume a strong Cu^{2+}–O^- hybridization in the superconducting sample. As x increases the amount of monovalent copper ($3d^{10}$ ground-state configuration) is found to increase. It can be assumed that, under sample reduction, O^- species from Cu_I–O chains parallel to the crystallographic b axis leave the lattice, electrons being transferred to adjacent Cu^{2+} ions. For $x \simeq 0.9$ the amount of Cu^+ clearly predominates over that of Cu^{2+}.

The special features of the O_{1s} core-level spectra show the high reactivity of the superconducting material with water vapor from the air. The XPS signal due to adsorbed OH^- species is higher than that of O^{2-} lattice ions, even if precautions are taken in order to avoid sample contamination. These results are consistent with the existence of delocalized holes in O_{2p} orbitals. O^- lattice species strongly react with H_2O molecules producing OH^0 radicals ($O^-(L) + H_2O \rightarrow OH^0(L) + OH^-$), which further recombine to generate more stable H_2O_2 species. Lattice Cu^{2+} ions then catalyze H_2O_2 decomposition and molecular oxygen is evolved. In order to preserve charge neutrality O^- vacancies are filled by

OH^- ions from water molecules. These OH^- groups become preferentially coordinated to Ba^{2+} ions as inferred from the Ba_{3d} XPS spectrum. Consequently, chemical bonds between Cu_I and OH^- groups are broken and the solid decomposes.

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