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Symmetry of the $3d^9$ ligand hole induced by doping in $YBa_2Cu_3O_{7-\delta}$

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Polarized Cu L_3-edge x-ray absorption spectra of a single crystal of $YBa_2Cu_3O_{6.8}$ have been measured to determine the symmetry of the orbital of the electronic holes induced by doping. The states induced by doping in $YBa_2Cu_3O_{7-\delta}$ ($0<\delta<\sim 0.5$) have been found to be ligand holes $\underline{L}^*$, giving the $3d^9\underline{L}^*$ configuration, and their weight is correlated with T_c. The polarization dependence shows that the hole $\underline{L}^*$, induced by doping, is found to be mainly in the Cu-O orbital oriented along the **c** axis involving the O $2p_z$ orbital of the O(4) atom in the Ba plane and the Cu $3d_{z^2}$ orbitals. This result indicates the important role of BaO layers and shows that theories of high-T_c superconductivity have to take account of a second band with different symmetry, beyond the single band (the two-dimensional band derived from the Cu $3d_{x^2-y^2}$ and O $2p_x$,$2p_y$ orbitals in the **a**-**b** plane of the CuO_2 layers) usually considered in models of the electronic structure of high-T_c superconductors.

Core-level spectroscopy provides a direct tool to investigate the electronic structure and the charge carriers in high-T_c superconducting materials.[1–16] X-ray photoemission[7–11] probes the occupied electronic states, while core-level x-ray-absorption spectroscopy (XAS) (Cu K edge,[1–6] Cu L_3 edge,[12–15] and oxygen K edge[16]) probes the unoccupied electronic states of angular moment $l'=l\pm 1$ at selected atomic sites. Moreover, polarized XAS spectra probe the orientation of the unoccupied orbital. Thus L_3-edge polarized XAS spectrometry of a single crystal is a suitable probe to determine experimentally the symmetry of the orbital where the electronic holes induced by doping are formed.

The $YBa_2Cu_3O_{7-\delta}$ material[17,18] exhibits a tetragonal-to-orthorhombic transition at $\delta \sim 0.6$[19–23] with antiferromagnetic insulating behavior for $1>\delta>\sim 0.6$,[24,25] as in La_2CuO_{4-y} (Ref. 26) for $y>0$, and superconducting behavior for $\sim 0.6>\delta>0$.[27,28] The electronic structure of the formally divalent Cu compounds La_2CuO_4 and $YBa_2Cu_3O_{\sim 6.5}$ is characteristic of charge-transfer insulators, with the Coulomb repulsion energy between the $3d$ holes $U_{dd}>\Delta E$ where ΔE is the charge-transfer energy.[29,30] This electronic structure is described by configuration interaction between $3d^9$ and $3d^{10}\underline{L}$ configurations (where $\underline{L}$ stands for the ligand hole in the oxygen-$2p$-derived valence band), where a single hole fluctuates between the Cu $3d$ and the ligand orbitals. No evidence of a two-hole configuration Cu $3d^8$ was found in the doped superconducting compounds with formal Cu valence $v>2$. Indication that electronic holes, induced by doping, should be in the O-$2p$-derived band was given by several groups.[1,5–8]

L_3 x-ray-absorption spectroscopy has been able to give direct experimental evidence that the states induced by increasing oxygen content for $\sim 0.5>\delta>0$ in $YBa_2Cu_3O_{7-\delta}$ and by Sr doping of La_2CuO_4 have the $3d^9\underline{L}^*$ configuration (where $\underline{L}^*$ indicates a hole in a ligand orbital induced by doping).[12–15] It was shown that the $3d^9\underline{L}^*$ states are formed in the gap between the $3d^9$ and $3d^{10}\underline{L}$ configuration of the divalent compound.[13] Direct evidence that the additional holes are in the oxygen-$2p$-derived band has been given by oxygen K-edge XAS spectroscopy measured by electron energy loss.[16] The presence of the $3d^9\underline{L}^*$ configuration has been recently confirmed in L_3 XAS spectra[31] and by an accurate analysis of the line shape of the Cu $2p$ core-level XPS spectra.[10,11] Here we have determined by L_3 XAS the correlation of the weight of the $3d^9\underline{L}^*$ states with the superconducting critical temperature for $\delta<0.5$.

It is well known that band-structure calculations show that the upper valence band, called here σ_1, is formed by the antibonding Cu-O orbitals Cu $3d_{x^2-y^2}$, O $2p_x$,$2p_y$. This two-dimensional band in the **ab** plane of the CuO_2 layers is expected to be at the origin of the antiferromagnetic order observed in the insulating phase. The opening of a gap due to the antiferromagnetic exchange interaction at the Fermi energy has been found recently by Andersen and co-workers.[32] Several theories for high-T_c superconductivity taking into account the formation of additional holes only in this σ_1 band have been proposed, but up to now no experimental method has been able to give a precise assignment of the orbitals where the additional

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holes are formed.

In this experiment we have investigated the symmetry of the holes in the $3d^9\underline{L}^*$ configuration by polarized L_3 XAS spectroscopy on a single crystal. The results show that the electronic holes $\underline{L}^*$ are mainly formed in a band (σ_2) which involves the capping O(4) atom in the Ba-O plane according to the notation of Ref. 19 and is in a Cu-O bond along the direction of the **c** axis which at the Cu(2) site has Cu $3d_{3z^2-r^2}$ symmetry.

The L_3 x-ray-absorption experiment has been carried out at de Laboratoire de l'Accélérateur Linéaire (ACO) storage ring synchrotron radiation facility Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) at Orsay. A double-crystal $10\bar{1}0$ beryl monochromator with an energy resolution about 0.35 eV at 900 eV has been used. The absorption coefficient has been measured by total-electron-yield method. The thickness of the probed surface layer is about 100 or 200 Å. The crystal has the **c** axis along the surface normal and it has been mounted with the **c** axis along the horizontal plane. The polarized spectra of the single crystal with several incidence angles between the photon beam and the sample surface normal have been recorded by rotating the direction of the **c** axis of the sample.

The polarized spectra changing the incident angle between the electric field ε and the **c** axis of the crystal from nearly normal incidence $\alpha = 15°$, where α is also the angle between the electric field ε and the **ab** plane (i.e., ε nearly perpendicular **c**), to grazing incidence $\alpha = 85°$, i.e., nearly ε parallel to the **c** axis, have been measured using polarized synchrotron radiation.

Single superconducting crystals were prepared at the Tohoku University. The resistivity plot of the single crystal shows zero resistance at 82.5 K. The experiment has been repeated with a different crystal on the new storage ring Super ACO at LURE and similar results have been obtained. The superconducting ($T_c = 92$ K) $YBa_2Cu_3O_{\sim 7}$ pellets have been prepared by successive grounding and firing in an oxygen atmosphere. Three sets of samples have been prepared with different losses of oxygen δ in $YBa_2Cu_3O_{7-\delta}$. Each set of samples with different values δ have been obtained from the same (formally $YBa_2Cu_3O_7$) sample, used as a reference for $\delta = 0$, which has been cut in several parts. The spectrum of the single crystal recorded at 40° incident angle, close to the magic angle 36°, is similar to the L_3 XAS spectrum of polycrystalline $YBa_2Cu_3O_{6.8}$ showing that the oxygen content in the probed surface layer of the crystal corresponds to this stoichiometry, in good agreement with the results of bulk resistivity and magnetic susceptibility.

In Fig. 1 the Cu L_3 XAS spectra of polycrystalline samples $YBa_2Cu_3O_{7-\delta}$ for $\delta = 0.45$ ($T_c = 48$ K); $\delta = 0.3$ ($T_c = 60$ K); $\delta = 0.15$ ($T_c = 85$ K); and $\delta = 0$ ($T_c = 92$ K) are reported. The pre-edge-absorption background has been subtracted. The absorption-edge jump, i.e., the variation of the absorption coefficient from below to above the white-line energy (which is only 3% of the white-line intensity) has been subtracted. Increasing the oxygen content (decreasing δ) the white line at 931.1 eV is practically unchanged and the new feature at 932.5 eV appears. The new peak is assigned to the electronic transition from the $3d^9\underline{L}^*$ to the $\underline{2p}3d^{10}\underline{L}^*$ final state. This peak lies in the energy range between the white line at 931.1 and 934 eV and its maximum is at about 1.4 eV above the $\underline{2p}3d^{10}$ white line of divalent Cu compounds.

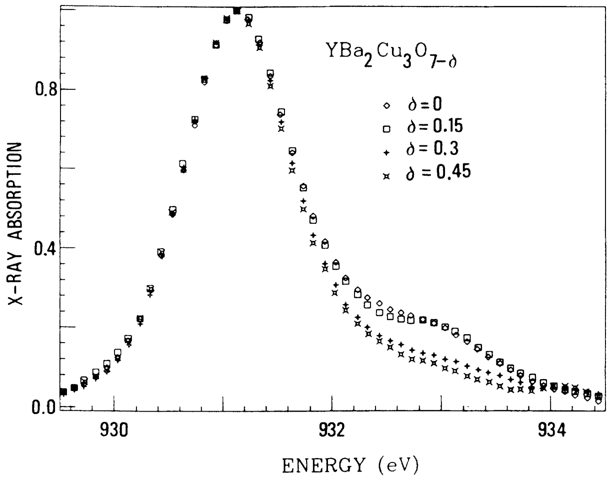

FIG. 1. Cu L_3 XAS spectra of $YBa_2Cu_3O_{7-\delta}$ for $\delta = 0.45$, 0.3, 0.15, and 0. The peak at about 932.5 eV increases with an increase of oxygen content.

This shift is nearly the same shift between the main line of the Cu $2p$ core level in x-ray photoemission spectra (XPS) of the same sample $YBa_2Cu_3O_{\sim 6.5}$ due to the $\underline{2p}3d^{10}\underline{L}$ state, and the shoulder at about 1.5 eV higher binding energy observed in the samples with $\delta < 0.6$ is in agreement with recent results.[10,11] This has been associated with the $\underline{2p}3d^{10}\underline{L}\underline{L}^*$ final state induced by doping. Assuming that 1.5 eV is a measure of the shift of the binding energy of the Cu $2p$ initial state induced by doping, the final state in XAS at 932.5 eV is close to the Fermi level. The increase, with oxygen content, of the weight of the final states $\underline{2p}3d^{10}\underline{L}^*$ is related to the increase of the weight of the $\overline{3d}^9\underline{L}^*$ configuration in the initial state. Therefore the weight of the $3d^9\underline{L}^*$ follows the increase of the critical temperature.

In Fig. 2 the difference spectra between the L_3 XAS spectra of $YBa_2Cu_3O_{7-\delta}$ for $\delta = 0$, 0.15, 0.3, and the spectrum of $YBa_2Cu_3O_{6.55}$ are reported. The white line does not exhibit any appreciable variation with δ, therefore in the difference spectra it is completely suppressed. The peak $\underline{2p}3d^{10}\underline{L}^*$ at 932.5 eV exhibits a weak change between $\delta = 0$ and $\delta = 0.15$ in agreement with the fact that T_c remains in the range 80–90 K. A large decrease is observed going from $\delta = 0.15$ to 0.3 in agreement with the drop of T_c from 90 to about 50 K whereas a smaller decrease has been found going from the $\delta = 0.3$ sample to the $\delta = 0.45$ one. Therefore from the unpolarized data it is found that the oxidation of the $YBa_2Cu_3O_{\sim 6.5}$ sample gives the states $3d^9\underline{L}^*$ in a divalent substrate described by mixing of the $3d^9$ and $3d^{10}\underline{L}$ configuration. The weight of the $3d^9\underline{L}^*$ state follows T_c and therefore it can be associated with the charge carriers which give the high-T_c superconductivity.

Figure 3 shows the polarized L_3 x-ray absorption spectra for the two extreme incidence angles $\alpha = 85°$ and

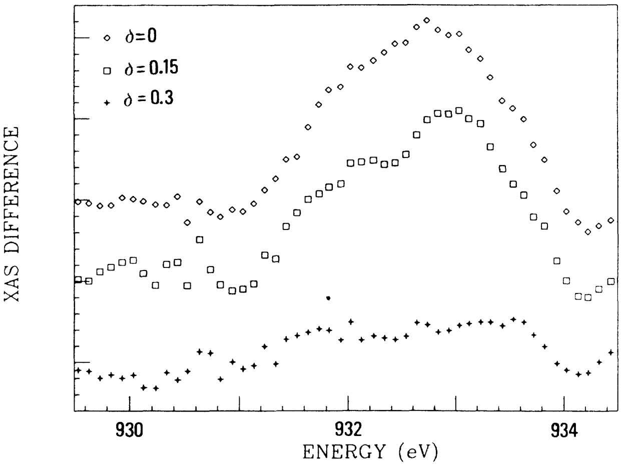

FIG. 2. Difference spectra between the L_3 XAS spectra of $YBa_2Cu_3O_{7-\delta}$ for $\delta=0$, 0.15, 0.3, and the spectrum of $YBa_2Cu_3O_{6.55}$.

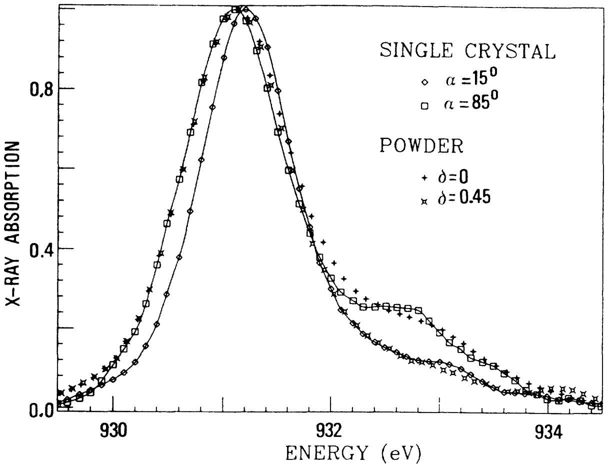

FIG. 3. Polarized Cu L_3 XAS spectra for the $YBa_2Cu_3O_{6.8}$ single crystal (points joined by solid curves) with the two different polarizations. The shoulder at 932.5 eV is nearly suppressed for $\alpha=15°$ which is the angle between the electric field ε and the **ab** plane and it is strongly enhanced in the spectrum $\alpha=85°$, i.e., with nearly $\varepsilon \| c$ configuration. The polarized spectra are compared with the spectra of two polycrystalline samples: $YBa_2Cu_3O_{6.55}$ and $YBa_2Cu_3O_7$. The spectra are normalized at the white-line maxima.

$\alpha=15°$ that we have recorded. The spectra have been normalized to the maximum of the white line. The electric field ε is nearly parallel to the **c** axis for the incidence angle 85°. For this polarization a shoulder at 932.5 eV is clearly observed and it disappears going toward the polarization with the electric field ε nearly parallel to the **ab** plane (or nearly perpendicular to **c**).

The white line is at 931.1 eV for $\alpha=85°$ and it is at 931.2 eV for $\alpha=15°$. The peak at 931.2 eV is therefore mainly due to the core transition from Cu 2p to the Cu $3d_{x^2-y^2}$ orbital in the Cu(2) site. It is interesting to remark that the peak at 931.2 eV is exactly the same as the peak of CuO (Ref. 12) in energy position and full width at half maximum (which is 0.95 eV confirming our assignment). The white line of the polycrystalline sample $YBa_2Cu_3O_{\sim 6.5}$ is larger than each white line of the polarized spectra, showing that it is given by the sum of the two contributions observed in the two polarization directions. Therefore the main white line of the L_3 XAS spectra shows one component observed with $\varepsilon \| c$ polarization and the other one for $\varepsilon \perp c$. By fitting the spectra recorded at different incident angles θ, we have obtained the extrapolated spectra for $\theta=0$ and $\theta=90$. The intensity ratio between the white lines in the $\theta=90$ ($\varepsilon \| c$) and $\theta=0$ ($\varepsilon \perp c$) spectra is found to be $I(90)/I(0)=0.68\pm0.12$. The maximum of the ($\varepsilon \| c$) spectrum is at 110 ± 20 meV lower energy than that of ($\varepsilon \perp c$) spectrum.

The interpretation of the XAS spectrum is complicated by the fact that it is determined by the sum of the spectrum due to the absorbing Cu(2) site and that due to the Cu(1) site. Therefore assuming that the Cu(2) site absorption spectrum gives a contribution to the white line for both polarizations, the single Cu 3d hole in the divalent substrate will have both $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ symmetries in agreement with the vibronic mixing of the a_1 and b_1 orbitals due to the pseudo-Jahn-Teller effect in the Cu square pyramid coordination. On the other hand, the Cu(1) site absorption spectrum could contribute to the white line for the ($\varepsilon \| c$) polarization because the Cu 3d hole is expected to be in the $3d_{x^2-z^2}$ orbital of the Cu(1) square plane units in the **bc** plane.

The XAS peak due to $2p^5 3d^{10}\underline{L}^*$ final state at 932.5 eV is characteristic of the superconducting state and it is observed only in the $YBa_2Cu_3O_{7-\delta}$ systems with $\sim 0.5 < \delta < 0$. The polarization dependence of this peak shows that its intensity is greater in the $\varepsilon \| c$ polarized spectrum than in the $\varepsilon \perp c$ polarized spectrum, therefore the initial state will be $\underline{3d}_{3z^2-r^2}\underline{L}^*$ (where $\underline{3d}_{3z^2-r^2}$ indicates a hole in the Cu $3d_{3z^2-r^2}$ orbital) if this transition takes place at the Cu(2) site. On the other hand, if this transition takes place at the Cu(1) site it will be determined by the initial state $\underline{3d}_{z^2-y^2}\underline{L}^*$.

There are two possible configurations for the $3d^9\underline{L}^*$ states: Cu(2) $3\underline{d}_{3z^2-r^2}\underline{L}^*$ if this peak is due to the Cu(2) site and/or Cu(1) $\underline{3d}_{z^2-y^2}\underline{L}^*$ if the absorbing atom is the Cu(1) atom. Although this experiment is not able to distinguish between these two possibilities the following conclusions are valid in both cases.

First, the holes are induced by doping in an orbital involving a Cu—O bond oriented along the **c** axis, i.e., in a direction orthogonal to the direction of higher conductivity in the single crystal $YBa_2Cu_3O_{6.8}$.

Second, the O(4) ion, following the notation of Ref. 19, contributes with its O $2p_z$ orbital to the orbital where the ligand hole $\underline{L}^*$ is formed. This is the only oxygen ion between the four different types of oxygen ions in the unit cell O(1), O(2), O(3), O(4) that has the O $2p_z$ pointing toward both Cu(1) and Cu(2) ions.

Finally this experiment shows that the ligand hole is mainly present in the O(4) sites. The determination of the probability of the $3d^9\underline{L}^*$ configuration with 3d hole, with Cu $3d_{x^2-y^2}$ character requires further experimental investigation. The additional holes are mainly formed in the σ_2 band which at the Cu(2) site crossing the CuO_2 antiferromagnetic layers should have a component in the **z** direction, i.e., Cu $3d_{3z^2-r^2}$ molecular symmetry. It is clear that the role of Ba ions appears to be very important in the conductivity mechanism in these perosvkites both because the O(4) ion is in the BaO plane and because Ba should play a key role in lowering the energy of the states derived by Cu $3d_{3z^2-r^2}$ orbital at the Cu(2) site.

As a consequence the theories for pairing of the holes giving high-T_c superconductivity should include an additional itinerant *quasi*-two-dimensional band where the holes induced by doping are formed in the gap between the bonding and antibonding Cu $3d_{x^2-y^2}$ band as discussed by Castellani.[33] The present experimental results have several implications for the microscopic mechanism of pairing in high-T_c materials, in fact, the localization of the itinerant hole $\underline{L}^*$ in the O(4) atom implies that mainly only few optical phonons are coupled with the itinerant hole in agreement with recent results of infrared photoinduced absorption.[34] The role of the drastic reduction of number of phonon modes that are involved in the formation of Cooper pairs for increasing T_c has been recently proposed by F. De Martini.[35] Preliminary results of this work have been published elsewhere.[36]

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