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**Cu 3d⁹ – LIGAND HOLE CONFIGURATION IN YBa₂Cu₃O₇₋ₓ BY X-RAY SPECTROSCOPIES**


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**Abstract:** Cu K edge and L₃ edge x-ray absorption near edge structure (XANES) and Cu L₃ x-ray photoelectron spectroscopy (XPS) of YBa₂Cu₃O₇ have been measured to determine the local electronic structure. The K-edge XANES have been interpreted by multiple scattering approach. The data show the formation of the 3d⁹ configuration (where L is a hole in the oxygen derived band, ligand hole) many body configuration in the initial state of the superconducting oxide.

**INTRODUCTION** - Recent experimental results obtained by x-ray spectroscopies have shown that in the new high Tc superconducting oxides the Cu 3d states are localized in the sense that the intra-atomic Coulomb repulsion $U_{dd} \approx 6$ eV is greater than the band width. Therefore the strong correlation effects induce a distortion of the calculated one-electron density of states and they will influence the electronic properties of the new high Tc superconducting oxides. The preliminary point to be establish is therefore the origin of conductivity in these unusual metallic ceramic materials. In high correlated oxides with high electronic correlation like NiO, CuO (and CeO₂ and PrO₂, where the localized states are the 4f states) systems the first available state above the ground state $3d^0$ is the $3d^{n+1}L$ configuration (where L is a hole in the oxygen derived valence band, ligand hole). Therefore the gap in insulating systems is not of the standard Mott-Hubbard type (from $3d^n$ to $3d^{n+1}$, $3d^{n-1}$) but of charge transfer type. The energy separation $\Delta E$ between the two ionic (without including the hybridization V) configuration $3d^n$ and the $3d^{n+1}L$ is therefore smaller than $U_{dd}(\Delta E < U_{dd})$. The $3d^{n+1}L$ configuration has a large width due to the convolution of the oxygen valence band with the metal localized narrow level. The presence of a large covalent bond between the metal ion and the oxygen ligands is indicated by the large value of the hybridization $V$ of the same order of magnitude as $\Delta E$ which determines the strong mixing between the two configurations i.e. the interatomic intermediate valent state of these systems.

YBa₂Cu₃O₆.₅₊ₓ for x=0 is a semiconductor with formally bivalent Cu ions. The transition from the semiconducting to metallic phase is observed for x larger than zero and the superconductivity critical temperature increases with x for 0<x<0.5.

In the many body description YBa₂Cu₃O₆.₅ (x=2) is expected to be a mixture of 3d⁹ and 3d¹⁰ configuration for the local cluster (CuO₄)²⁻. The additional oxygen x in YBa₂Cu₃O₆.₅₊ₓ should induce new states $3d^8$ and...
3d^9_L, if the hole is created at the Cu or at the oxygen site respectively and 3d^{10}_L^2 if both holes are in the oxygen site for the cluster (CuO_4)^5. The weight of these configurations depends on their relative energy position and hybridization.

We report evidence for:

a) no evidence of Cu 3d^8 configuration from Cu K-edge XANES

b) the formation of states due to a many body configuration with itinerant holes in the oxygen valence band coupled with localized 3d electrons on the Cu sites (called 3d^9_L) in the superconducting phase of YBa_2Cu_3O_7;

The conductivity in this highly correlated system is assigned to the presence of the electron-hole configuration 3d^9_L at the Fermi level and superconductivity to pairing of the oxygen holes. Recently non conventional BCS theories of the high T_c oxides have been put forward^19-26. Our findings give experimental support to the description of the superconductivity as pairing of oxygen holes^25,26.

**EXPERIMENTAL** - The samples have been prepared by starting from powder of ultra pure Y_2O_3, BaCO_3 and CuO using the standard procedure. The K-edge XANES experiment was performed at the Frascati synchrotron radiation facility using ADONE 1.5 GeV storage ring using a Si(220) monochromator. The L_{2,3} XANES experiment has been carried out using as x-ray source the ACO storage ring LURE synchrotron radiation facility in Orsay. A double crystal Beryl 1010 monochromator has been used. The x-ray absorption has been measured by detecting the emitted electrons by a channeltron in the total yield mode. The Cu 2p XPS spectra have been recorded using a Vacuum Generator ESCA LAB MKII system and the Mg Kα line as x-ray source.

![Cu L3 absorption spectra](image_url)

**RESULTS** - a) Evidence of 3d^9-ligand-hole configuration - Fig. 1 shows the Cu L_3 absorption spectrum of a bulk YBa_2Cu_3O_{6.7} sample and its Cu 2p_{3/2} XPS spectrum. The Cu 2p_{3/2} XPS spectra of YBa_2Cu_3O_{6.7} shows two lines A and B, as in bivalent Cu compounds, assigned mainly to 2p_3d^9 and 2p_3d^{10}_L.
final states respectively. The white line maximum at the L₂ absorption edge is found at 931.1 eV. The full width at half high is $\Gamma = 1.25$ eV. The white line is assigned to Cu 2p3d₁⁰ final state for the Cu 3d⁹ initial state. A broad shoulder indicated by the arrow in Fig.1 appears at about 933 eV on the high energy side of the white line. The L₂ edge shows a similar feature at about 1.8 eV above the white line.

This feature is characteristic of superconducting materials and it is at about the same energy, ~933 eV, as the peak B in XPS spectrum due to 2p3d₁⁰_L₂ final state. Therefore this peak is assigned to the transition from 3d⁵_L₂ initial state to a final state 2p3d₁⁰_L₂ indicating the formation of 3d⁵_L₂ state in the ground state. The energy separation between the two final state configurations 2p3d₁⁰ and 2p3d₁⁰_L₂ gives the ligand ionization energy. For the metallic superconductors no gap is observed between the two final states. The lack of a gap indicates that there are ligand holes close to the Fermi energy.

Fig.2- Cu K-edge XANES spectrum of YBa₂Cu₃O₇ upper curve and calculated XANES spectrum using the multiple scattering approach from the two clusters having as central atom the four fold coordinated Cu¹ (curve a) and the five-fold coordinated Cu² in the CuO₂ layers normal to the c-axis (curve b) and their weighted sum (curve c).

b) Lack of 3d⁸ (Cu³⁺) configuration- The high oxidation state of Cu ions in YBa₂Cu₃O₇ is usually expected to give Cu³⁺, 3d⁸ states in the ground state. This configuration should give a 2p3d⁹ final state in the Cu L₂ XANES expected at 942 eV. In fact the energy of this final state should be close to that of the peak A, 2p3d⁹, in the XPS spectrum. The absence of a peak at 942 eV in the XANES spectrum indicates the absence of Cu 3d⁸ states (Cu³⁺) in the ground state.

Cu K-edge XANES of (La₁₋ₓSrₓ)₂CuO₄ ²⁷-³⁰ and of YBa₂Cu₃O₇ ³¹-³⁵ have been measured by several groups. Controversial interpretations of the data have been reported in order to extract the Cu valence state. The main point is if the presence of Cu³⁺ (Cu 3d⁸) can be inferred from this spectrum. We have performed a
one-electron multiple scattering calculation in order to determine the role of the multiple scattering signal determined by the complex crystalline structure which can provide an explanation for the various spectral features observed in the spectra. XANES calculations have been carried out using the multiple scattering program\(^{36}\) and the coordinates given by x-ray diffraction data\(^{37-39}\). Previous K-XANES calculations for the La\(_2\)CuO\(_4\)\(^{29}\) were limited to a small cluster of two neighbor shells around the central atom. We have extended the calculation to the Y-Ba-Cu oxide taking into account the orthorombic distorsion and the presence of two different Cu sites. A cluster of 40 atoms including four shells has been used in the calculation. In Fig. 2 we report the experimental Cu K-edge XANES spectrum (upper curve) and the calculation for the Cu\(_1\) and Cu\(_2\) sites and the weighted sum to be compared with the experimental spectrum. In fig. 3 the non self-consistent XANES calculations for the site Cu2 are reported showing the effect of the size of the cluster.

![Graph showing XANES calculations](image)

Fig. 3- XANES calculations of the Cu2 site in YBa\(_2\)Cu\(_3\)O\(_7\) by increasing the size of the cluster with central Cu ion, from a single shell cluster (lower curve) to a cluster of four shells (upper curve). Curve 1 : CuO\(_5\). Curve 2 : CuO\(_5\)Ba\(_4\)Y\(_4\). Curve 3 : CuO\(_5\)Ba\(_4\)Y\(_4\)Cu\(_6\). Curve 4 : CuO\(_5\)Ba\(_4\)Y\(_4\)Cu\(_6\)O\(_20\).

It is clear that increasing the size of the cluster the agreement between the calculations and the experiment increases. Similar results have been obtained by P.J. Durham et al. using self-consistent calculations.\(^{40}\) The agreement remains qualitative however the calculation gives account for all experimental features, therefore no peak can be associated with the presence of Cu\(^{3+}\) ions. These results are confirmed by the observed spectral changes obtained by varying oxygen concentration.

**DISCUSSION.** - This experiment gives direct evidence that increasing oxygen content \(x\leq 0\) in YBa\(_2\)Cu\(_3\)O\(_6.5+x\) does not give Cu\(^{3+}\) ions with Cu 3d\(^8\) configuration but gives the 3d\(^9\) electronic configuration. These many body states have an energy width of about 2 eV being determined by the convolution of the oxygen 2p
band and the Cu 3d states. These states fill the gap between the 3d⁹ and the 3d¹⁰ configuration of the bivalent compound YBa₂Cu₃O₆.₅. In conclusion in order to interpret the x-ray spectroscopies of the superconducting copper oxides it is necessary to describe the ground state by many body configurations as shown in fig. 4.

\[ \Psi = a \, 13d^9 + b \, 13d^{10}_L \]
\[ \Psi^1 = a \, 13d^9 + b \, 13d^{10}_L \]
\[ \Psi^2 = a \, 13d^9_L + b \, 13d^{10}_L^2 + c \, 13d^8 \]

Fig. 4 - Schematic picture of the many body configurations for a (CuO₄)⁶⁻ cluster in a bivalent Cu compound (left side) and for YBa₂Cu₃O₇ (right side) where additional states 3d⁹, 3d¹⁰ and 3d⁸ (dashed lines) for a cluster (CuO₄)⁶⁻ are formed.

Our results show that the itinerant states are not 3d holes in Cu sites, as assumed in the Anderson model, but are holes in the oxygen band. These holes are coupled with the localized Cu 3d electrons giving a single 3d⁹ configuration. The high Hubbard correlation energy indicates the presence of local moments in the Cu sites that can give local antiferromagnetic order in the CuO₂ planes which could induce the pairing between two holes.

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