Cu 3d⁹ - LIGAND HOLE CONFIGURATION IN YBa₂Cu₃O₇ BY X-RAY SPECTROSCOPIES

A. BIANCONI, A. CLOZZA, A. CONGIU CASTELLANO, S. DELLA LONGA, M. DE SANTIS, A. DI CICCIO, K. GARG, P. DELOGU*, A. GARGANO*, R. GIORGI*, P. LAGARDE**, A.M. FLANK** and A. MARCELLI***

Dipartimento di Fisica, Università degli Studi di Roma "La Sapienza", I-00185 Roma, Italy

**ENEA, Centro Ricerche Casaccia, Laboratorio Superfici e Metallurgia Fisica, Via Anguillarese 301, I-00060 Roma, Italy*

***LURE, CNRS-CEA-MEN, Bât. 209C, Université Paris-Sud, F-91405 Orsay Cedex, France*

****INFN, Laboratori Nazionali di Frascati, I-00044 Frascati, Italy*

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 3d⁹L̄ (where L̄ 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 T_c superconducting oxides¹⁻³ the Cu 3d states are localized in the sense that the intra-atomic Coulomb repulsion U_{dd}~6 eV is greater than the band width⁴⁻⁹. Therefore the strong correlation effects induce a distortion of the calculated one-electron density of states¹⁰⁻¹⁴ and they will influence the electronic properties of the new high T_c 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 3dⁿ is the 3dⁿ⁺¹L̄ configuration (where L̄ is a hole in the oxygen derived valence band, *ligand hole*).¹⁵⁻¹⁸ Therefore the gap in insulating systems is not of the standard Mott-Hubbard type (from 2 x 3dⁿ to 3dⁿ⁺¹, 3dⁿ⁻¹) but of charge transfer type. The energy separation ΔE between the two ionic (without including the hybridization V) configuration 3dⁿ and the 3dⁿ⁺¹L̄ is therefore smaller than U_{dd} (ΔE < U_{dd}). The 3dⁿ⁺¹L̄ 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 ΔE which determines the strong mixing between the two configurations i.e. the interatomic intermediate valent state of these systems.

YBa₂Cu₃O_{6.5+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 YBa₂Cu₃O_{6.5} (v=2) is expected to be a mixture of 3d⁹ and 3d¹⁰L̄ configuration for the local cluster (CuO₄)⁻⁶. The additional oxygen x in YBa₂Cu₃O_{6.5+x} should induce new states 3d⁸ and

$3d^9L$, 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 $3d^9L$) 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 $3d^9L$ 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 forward¹⁹⁻²⁶. 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 $K\alpha$ line as x-ray source.

Fig. 1 - Cu $2p_{3/2}$ XPS spectrum of $YBa_2Cu_3O_{7-x}$ (dotted line) and the Cu $2p_{3/2}$ XANES spectrum of $YBa_2Cu_3O_{7-x}$ (solid line). The white line is due to the $2p3d^{10}$ final state and a new feature at ~933 eV the same energy as the peak B in XPS spectrum $2p3d^{10}L$ is observed.

The presence of this XANES peak is associated with $2p3d^{10}L$ final state i.e. to the formation of $3d^9L$ configuration in the ground state.

The absence of a peak $2p3d^9$ at 942 eV in the XANES spectra indicates the absence of $Cu\ 3d^8$ in the ground state.

RESULTS - a) Evidence of $3d^9$ -ligand-hole configuration - Fig. 1 shows the Cu L_3 absorption spectrum of a bulk $YBa_2Cu_3O_{7-x}$ sample and its Cu $2p_{3/2}$ XPS spectrum. The Cu $2p_{3/2}$ XPS spectra of $YBa_2Cu_3O_{7-x}$ shows two lines A and B, as in bivalent Cu compounds, assigned mainly to $2p3d^9$ and $2p3d^{10}L$

final states respectively. The white line maximum at the L_3 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 $2p3d^{10}$ final state for the Cu $3d^9$ 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 L_2 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 $2p3d^{10}\bar{L}$ final state. Therefore this peak is assigned to the transition from $3d^9\bar{L}$ initial state to a final state $2p3d^{10}\bar{L}$ indicating the formation of $3d^9\bar{L}$ state in the ground state. The energy separation between the two final state configurations $2p3d^{10}$ and $2p3d^{10}\bar{L}$ 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 $YBa_2Cu_3O_7$ 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 CuO_2 layers normal to the c-axis (curve b) and their weighted sum (curve c).

b) **Lack of $3d^8$ (Cu^{3+}) configuration-** The high oxidation state of Cu ions in $YBa_2Cu_3O_7$ is usually expected to give Cu^{3+} , $3d^8$ states in the ground state. This configuration should give a $2p3d^9$ final state in the Cu L_3 XANES expected at 942 eV. In fact the energy of this final state should be close to that of the peak A, $2p3d^9$, in the XPS spectrum. The absence of a peak at 942 eV in the XANES spectrum indicates the absence of $Cu 3d^8$ states (Cu^{3+}) in the ground state.

Cu K-edge XANES of $(La_{1-x}Sr_x)_2CuO_4$ ²⁷⁻³⁰ and of $YBa_2Cu_3O_7$ 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 Cu^{3+} ($Cu 3d^8$) 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 program³⁶ and the coordinates given by x-ray diffraction data³⁷⁻³⁹. Previous K-XANES calculations for the La_2CuO_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 orthorhombic distortion 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 Cu1, and Cu2 sites and the weighed 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.

Fig.3- XANES calculations of the Cu2 site in $\text{YBa}_2\text{Cu}_3\text{O}_7$ 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 : $\text{CuO}_5\text{Ba}_4\text{Y}_4$. Curve 3 : $\text{CuO}_5\text{Ba}_4\text{Y}_4\text{Cu}_6$. Curve 4 : $\text{CuO}_5\text{Ba}_4\text{Y}_4\text{Cu}_6\text{O}_{20}$.

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 $x > 0$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ 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 $3d^9$ and the $3d^{10}\underline{L}$ configuration of the bivalent compound $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$. 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.

Fig. 4 - Schematic picture of the many body configurations for a $(\text{CuO}_4)^{6-}$ cluster in a bivalent Cu compound (left side) and for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (right side) where additional states $3d^9\underline{L}$, $3d^{10}\underline{L}^2$ and $3d^8$ (dashed lines) for a cluster $(\text{CuO}_4)^{5-}$ are formed.

Our results show that the the itinerant states are not 3d hole in Cu sites, as assumed in the Anderson model^{20,21}, but are holes in the oxygen band. These holes are coupled with the localized Cu 3d electrons giving a single $3d^9\underline{L}$ many body configuration. The high Hubbard correlation energy U_{dd} indicates the presence of local moments in the Cu sites that can give local antiferromagnetic order in the CuO_2 planes which could induce the pairing between two holes^{25,26}

Acknowledgments - We would like to thank A. Kotani, G.A. Sawatzky and A. Fontaine for stimulating discussions and A. Scacco, C. Sanipoli and F. Stazi for technical help. This experiment has been partially supported by CEE contract STP-0040-1-(CD).

REFERENCES

1. J.C. Bednorz and K.A. Muller *Z. Physik B Condensed Matter* **64**, 189 (1986)
2. M.K.Wu, J.R.Ashburn, C.J.Torng, P.H.Hor, R.L.Meng, L.Gao, Z.J.Huang, Y.Q.Wang, and C.W.Chu *Phys. Rev. Lett.* **58**, 908 (1987)

3. R.J. Cava, B. Batlogg, R.B. van Dover, D.W. Murphy, S. Sunshine, T. Siegrist, J.P. Remeika, E.A. Rietman, S. Zahurak, and G.P. Espinosa *Phys. Rev. Lett.* **58**, 1676 (1987)
4. A. Bianconi, A. Congiu Castellano, M. De Santis, C. Politis, A. Marcelli, S. Mobilio, A. Savoia *Z. Physik B Condensed Matter* **67**, 307 (1987)
5. A. Bianconi, A. Congiu Castellano, M. De Santis, P. Rudolf, P. Lagarde, and A.M. Flank, *Solid State Commun.* **63**, 1009 (1987)
6. A. Bianconi, A. Congiu Castellano, M. De Santis, P. Delogu, A. Gargano, R. Giorgi *Solid State Commun.* **63**, 1135 (1987)
7. A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai *Phys. Rev. B* **35**, 8814 (1987)
8. A. Fujimori, E. Takayama-Muromachi, Y. Uchida, *Solid State Commun.* **63**, 857 (1987)]
9. A. Bianconi, A. Clozza, A. Congiu Castellano, S. Della Longa, M. De Santis, A. Di Cicco, K. Garg, P. Delogu, A. Gargano, R. Giorgi, P. Lagarde, A. M. Flank, and A. Marcelli "Proceedings of the Adriatic Research Conference on High Temperature Superconductors" Trieste, Italy 6-8 July 1987 edited by Y.Lu, M.Tosi and E.Tosatti, World Scientific, Singapore
10. L.F. Mattheis *Phys. Rev. Lett.* **58**, 1028 (1987)
11. J. Yu, A.J. Freeman, and J.-H. Xu *Phys. Rev. Lett.* **58**, 1035 (1987)
12. W.M. Temmerman, G.M. Stocks, P.J. Durham, and P.A. Sterne *J. Phys. F* **17**, L135 (1987)
13. S. Massida, J. Yu, A.J. Freeman and D.D. Koelling *Phys. Lett.* **122**, 198 (1987)
14. J. Yu, S. Massida, A.J. Freeman and D.D. Koelling *Phys. Lett.* **122**, 203 (1987)
15. J. Zaanen, G.A. Sawatzky and J.W. Allen *Phys. Rev. Lett.* **55**, 418 (1985)
16. A. Bianconi, A. Marcelli, H. Dexpert, R. Karnatak, A. Kotani, T. Jo, and J. Petiau *Phys. Rev. B* **35**, 806 (1987) and references cited therein
17. T. Jo, and A. Kotani, *Solid State Commun.* **54**, 451 (1985)
18. A. Fujimori, F. Minami, and S. Sugano *Phys. Rev. B* **29**, 5225 (1984)
19. D.J. Scalapino, E. Loh, Jr., and J.E. Hirsch *Phys. Rev. B* **35**, 6694 (1987) and H.B. Schuttler, J.D. Jorgensen, D.G. Hinks, D.W. Capone, and D.J. Scalapino to be published
20. P.W. Anderson *Science* **235**, 1196 (1987)
21. P.W. Anderson, G. Baskaran, Z. Zou, and T. Hsu *Phys. Rev. Lett.* **58**, 2790 (1987); G. Baskaran, Z. Zou, P.W. Anderson, *Solid State Commun.* **63**, 973 (1987)
22. M. Cyrot *Solid State Commun.* **62**, 821 (1987) and *Solid State Commun.* **63**, 1015 (1987)
23. C. Noguera, and P. Garoche *Solid State Commun.* (1987) to be published
24. P.A. Lee and N. Read *Phys. Rev. Lett.* **58**, 2691 (1987)
25. V.J. Emery *Phys. Rev. Lett.* **58**, 2794 (1987)
26. J.E. Hirsch *Phys. Rev. Lett.* **59**, 228 (1987)
27. H. Oyanagi, H. Ihara, T. Matsubara, T. Matsushita, T. Tokumoto, M. Hirabayashi, N. Terada, K. Senzaki, Y. Kimura, and T. Yao, *Jpn. J. Appl. Phys.* **26**, L488, (1987)
28. J.M. Tranquada, S.M. Heald, A.R. Moodenbaugh and M. Suenaga *Phys. Rev. B* **35**, 7187 (1987)
29. E.E. Alp, G.K. Shenoy, D.G. Hinks, D.W. Capone II, L. Soderholm, H.B. Schuttler, J. Guo, D.E. Ellis, P.A. Montano, and M. Ramanathan *Phys. Rev. B* **35**, 7199, (1987)
30. Y.B. Boyce, F. Bridges, T. Claeson, T.H. Geballe, C.W. Chu, J.M. Tarascon *Phys. Rev. B* **35**, 7203 (1987)
31. A. Bianconi, A. Congiu Castellano, M. De Santis, C. Politis, A. Marcelli, S. Mobilio, A. Savoia *Z. Physik B Condensed Matter* **67**, 307 (1987)
32. H. Oyanagi, H. Ihara, T. Matsubara, T. Matsushita, T. Tokumoto, M. Hirabayashi, N. Terada, K. Senzaki, Y. Kimura, and T. Yao, *Jpn. J. Appl. Phys.* **26**, L638, (1987)
33. F. Baudalet, G. Collin, E. Dartyge, A. Fontaine, J.P. Kappler, G. Krill, J.P. Itie, J.J. egoudez, M. Maurer, P. Monod, A. Revcolevschi, H. Tolentino, G. Tourillon, and M. Verdaguer *Z. Physik B Condensed Matter* to be published
34. H. Oyanagi, H. Ihara, T. Matsubara, T. Matsushita, M. Hirabayashi, M. Tokumoto, K. Murata, N. Terada, K. Senzaki, T. Yao, H. Iwasaki, and Y. Kimura *Jpn. Journ. Appl. Phys.* **26**, L1233, (1987)
35. Lyttle *Phys. Rev. B* to be published
36. P.J. Durham, J.B. Pendry, C.H. Hodges, *Comput. Phys. Commun.* **25**, 193, (1982)
37. J.J. Capponi, C. Chaillout, A.W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J.L. Soubeyroux, J.L. Tholence, and R. Tournier *Europhysics Lett.* **3**, 1301 (1987)
38. W.I.F. David et al. *Nature* **327**, 310 (1987)
39. G. Caletani, C. Rizzoli *Nature* **328**, 606 (1987)
40. P.J. Durham, W.M. Temmerman and G.M. Stocks, proceedings of the 14th International Conference on x-ray and inner-shell processes, Paris, September 14-18, 1987 (France). *Jour. de Physique*, to be published.