SOFT X-RAY ABSORPTION AND EMISSION SPECTRA AND THE ELECTRONIC STRUCTURE OF THE Ba2 YCu3 O7-x SUPERCONDUCTOR

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JOURNAL DE PHYSIQUE
Colloque C9, supplément au n°12, Tome 48, décembre 1987

SOFT X-RAY ABSORPTION AND EMISSION SPECTRA AND THE ELECTRONIC STRUCTURE OF THE $Ba_2YCu_3O_{7-x}$ SUPERCONDUCTOR

K.-L. TSANG, C.H. ZHANG, T.A. CALLCOTT, L.R. CANFIELD*, D.L. EDERER*, J.E. BLENDELL*, C.W. CLARK*, N. WASSDAHL**, J.E. RUBENSSON**, G. BRAY**, N. MORTENSSON**, J. NORDGREN**, R. NYHOLM*** and S. CRAMM****

University of Tennesse, Knoxville, TN 37966, U.S.A.
**National Bureau of Standards, Gaithersburg, MD 20899, U.S.A.*
***University of Uppsala, Uppsala, S-751 21 Uppsala, Sweden*
****University of Lund, Lund, Sweden*
*****Universität Hamburg, Hamburg, F.R.G.*

Résumé

Nous présentons des spectres d'émission dans les X mous, du $Ba_2YCu_3O_{7-x}$ supraconducteur, excité par des faisceaux d'électrons, ainsi que les spectres du rendement total de photoélectrons du même materiau excité par des photons d'énergie comprise entre 20 et 600 eV. Nous confirmons, par la mesure de ce rendement, que le cuivre a une valence +2 dans ce composé. L'émission de rayons X mous fourni, par l'étude du spectre $N_{4,5}$ du barium, du spectre $M_{4,5}$ de l'yttrium et du spectre K de l'oxygène, une mesure de la densité d'états partielle de type p (p-PDOS) localisée sur chacun des sites atomiques respectifs. Dans chaque cas cette densité d'états est très petite à l'énergie de Fermi, et a un premier pic situé entre 3.5 et 4 eV en dessous du niveau de Fermi. L'étude du spectre K de l'oxygène confirme l'interprétation selon laquelle les structures observées dans les mesures de photoémission sont associées aux orbitales 2p de l'oxygène. Enfin nous n'avons observé aucun changement entre les spectres enregistré au dessus ou au dessous de la température critique T_c.

Abstract

We present e-beam excited soft x-ray emission spectra and total photoelectron yield spectra in the 20-600 eV photon energy range for the $Ba_2YCu_3O_{7-x}$ superconductor. We confirm the 2+ valency of Cu in the compound by total yield measurements. In soft x-ray emission, the $N_{4,5}$ spectrum of Ba, the $M_{4,5}$ spectrum of Y, and the K spectrum of O provide measures of the p-type partial density of states (p-PDOS) localized on the respective atomic sites. In each case the p-PDOS is very small at the Fermi energy with the first peak in the p-PDOS lying 3.5 to 4 eV below the Fermi energy. The K spectra of O confirm the interpretation that the structure observed in the photoemission measurements are associated with the O 2p orbitals. Finally no changes are observed between spectra taken above and below T_c.

Interest in the scientific community has been raised to a fever pitch by the recent discovery of high-temperature superconductors.[1-3] The exact mechanism mediating electron pairing is still unknown, and, at least for the compound discussed in this paper, the relevance of the standard BCS mechanism has been cast in doubt by the absence of an isotope effect.[4] Several alternative mechanisms have been proposed[5,6] and the electronic structures have been calculated by several authors.[7-10] These calculations have been tested to a degree by photoemission measurements [11-13] of the total density of states in the valence band.

We present measurements of soft x-ray emission and total photoelectron yield of $Ba_2YCu_3O_{7-x}$ that complement previous experimental work. Our total photoelectron yield measurements near the 3p ionization threshold in Cu support the contention that Cu is in the +2 valence state.[11-14] We have used electron-beam excited soft x-ray emission spectra to measure the p-type partial density of states (p-PDOS) localized on O, Ba, and Y sites. For the elements (Y, Ba, and O) the major peak in the soft x-ray emission spectra lies about 3.4 to 4.0 eV below ε_F rather than at the ~ 2 eV that would be expected from p-PDOS derived from ground state band

structure calculations.[7-10] This finding is in qualitative agreement with earlier photoemission measurements.[11-13] We have also observed the $L_{2,3}$ emission spectrum of Cu in $Ba_2YCu_3O_{7-x}$, which maps out valence states of d symmetry. The maximum in the PDOS lies about 2.5 eV. below ε_F. These observations place the d and p bands about 2 eV. and 4 eV. below ε_F respectively. The present measurements have been made both at room temperature and at 85 K. No difference in the p-PDOS was observed at the two temperatures. This is consistent with observations that $Ba_2YCu_3O_{7-x}$ does not undergo a structural phase change between T_c and room temperature.[15]

The samples were prepared at the National Bureau of Standards by combining $BaCO_3$, CuO, and Y_2O_3 in the appropriate proportions by weight. Superconductivity was verified by a.c. magnetic susceptibility measurements. The transition temperature measured was 90 K and the transition temperature zone had a width of a few degrees.

The results of the total quantum yield and the electron beam-excited soft x-ray emission measurements are shown in Figs. 1a and 1b respectively for the photon energy range 50-175eV. The detected x-ray fluorescence spectrum is shown in Fig. 1b.

Fig. 2 is a plot of region A in Fig. 1a on an expanded scale. The upper curve was obtained on a sample of $Ba_2YCu_3O_{7-x}$. The lower curve was obtained three months later after the sample was irradiated by electrons at the NSLS facility and by x-rays at the Hamburg Synchrotron Radiation (HASY) Laboratory. The small change in the absolute yield shows there has been no gross contamination of the bulk of the sample.The positions of the yield maxima correspond exactly to the energy positions of maxima observed in the partial cross section involving the excitation of a 3p core electron resonantly yielding a satellite about 9.4 eV below the Fermi energy.[17] The position of the double peaked structure in Cu, CuO, and Cu_2O is appropriately labelled and identified by arrows. This observation adds confidence to the interpretation that most of the Cu is in the +2 oxidation state. Our x-ray emission measurement of the L spectrum of Cu, shown in Fig. 4, gives additional confirmation of this interpretation.

Figure 1:

a) Total quantum yield for superconducting $Ba_2YCu_3O_{7-x}$ as a function of the photon energy. A defines the energy region corresponding to that required for the promotion of a 3p core electron in Cu to the conduction band. The energy band denoted by B is the absorption by 4d core electrons in Ba.

b) Intensity of soft x-ray fluorescence excited by 2 keV electrons vs. photon energy. C denotes the energy position of the $N_{2,3}M_{4,5}$ transition in Y in second order reflection from the grating; F is the first order signal of this transition. D is the energy region corresponding to Ba inner shell transitions $O_{2,3}N_{4,5}$ and transitions between the valence electrons and the Ba 4d hole states.

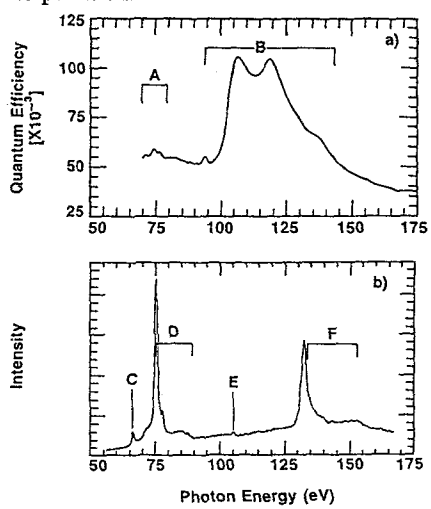
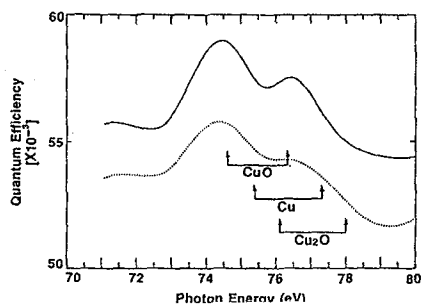


Figure 2:

The quantum efficiency (QE) curve of region A in Fig. 1a with both axes expanded. The solid line shows the QE obtained in April 1987; the dotted line is the QE obtained from the same sample three months later after study in several laboratories. The energy positions of the double peaked absorption structures for CuO, Cu, and Cu_2O are shown by the arrows (from Ref. 17).



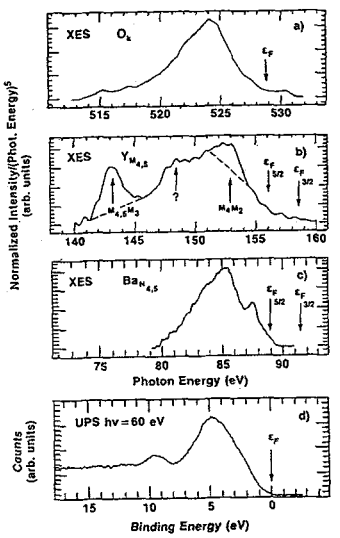
The K spectrum of O, the $M_{4,5}$ spectrum of Y, and the $N_{4,5}$ spectrum of Ba are shown in Figs. 3a-c. These spectra were obtained by subtracting a background which includes a smooth extrapolation of the strong (n+1)p to nd inner core transitions (n=3,4 for Ba and Y respectively) lying at immediately lower energy levels. In Fig. 3b there are spectral features at 143.2 and 148.2 eV. The feature at 143.2 eV is identified[18] as an $M_{4,5}M_3$ transition of Y. The spectral feature at 148.2 eV coincides with a line identified[18b] as the Y M_4M_2 transition. This identification is inconsistent with those of other compilations[18a,c] that place the M_4M_2 transition at about 152 eV. We believe the feature at 148.2 eV is most probably due to an impurity or perhaps to structure in the valence band, and that the M_4M_2 transition occurs at 152.5 eV. We have suggested a subtraction of these interfering transitions by a dashed curve in Fig. 3b.

In Fig 3 we compare the PDOS of p symmetry for O, Y, and Ba (or mostly p-like symmetry in the case of Ba and Y) with the total DOS obtained by photoelectron spectroscopy[11-13] at a photon energy of 60 eV. The UPS measurements sample all the symmetries in the band, and a comparison of UPS and x-ray emission spectra provides information about the energy of bands not projected out by dipole selection rules. Each spectrum has been adjusted so that our best estimate of the photon energy corresponding to the Fermi energy ε_F is aligned with the ultraviolet photoelectron spectrum (UPS) zero binding energy. The photon energy for a transition between ε_F and the 1s core hole in O was based on the energy (529 eV) of the near-edge structure in O 1s obtained by electron energy loss spectra (EELS) measured in CuO.[19] We make this choice by arguing that L shell edge energies obtained from our soft x-ray excited L emission spectra for CuO and Cu metal have approximately the same chemical shift between the oxide and metal (about -1.5 eV), and are in good absolute agreement (1 eV) with the corresponding L edge energies derived from EELS.[20]

Figure 3:

a-c) X-ray fluorescence spectra of transitions of valence electrons of p symmetry localized at the atomic site to core states of O, Y, and Ba respectively. The spectra were corrected for background and normalized according to a proceedure given in the text. The spectra are aligned so that the Fermi energies ε_F associated with the highest core hole state (respectively O ^2S, Y $^2D_{5/2}$, Ba $^2D_{5/2}$) coincide in each case. Interfering $M_{4,5}M_3$ and M_4M_2 transitions in Y are indicated. The dashed line is the valence band spectrum after the removal of these discrete lines.

d) Photoemission spectrum obtained at a photon energy of 60 eV, showing the DOS of the valence band (courtesy R. L. Kurtz and R. L. Stockbauer, ref. 11).



The transition energy between ε_F and the 3d and 4d core holes in Y and Ba shown in Fig.3b and 3c respectively is obtained in a more straightforward manner. Our measurements of the photon energy of the inner core transitions for Ba and Y differ by only a few tenths of an eV from those found in the metallic state. Furthermore, the binding energies of the 5p (4p) electron in Ba (Y) obtained from photoelectron spectroscopy[11-13] should be an excellent approximation to the x-ray binding energy since the difference in sceening between the UPS and x-ray transitions should be nearly the same for the valence and the first lower core level. Thus we add 14.3 eV[12] to our inner core transition energy of 75.0 eV and obtain 89.3 eV for the energy difference between ε_F and the 4d $^2D_{5/2}$ core hole (N_5 edge) of Ba. The same argument applied to Y yields 156.3 eV for the energy difference between ε_F and the 3d $^2D_{5/2}$ hole in Y (the M_5 edge). For Y and Ba , ε_F is identified in Fig. 3 for both the nd $^2D_{5/2}$ and the nd $^2D_{3/2}$ core holes. The spectra are aligned to the more intense nd $^2D_{5/2}$ level. The structure in Ba at 87.4 eV can be attributed to transitions between the valence band and the $^2D_{3/2}$ core hole (N_4 edge). These valence $\rightarrow$ core hole transitions can also be masked by O K radiation diffracted in 6th order .

In Figure 4 we present measurements made at the Hamburg synchrotron, using monochromatized synchrotron radiation for excitation. Figure 4a is an oxygen K spectrum taken at the photon excitation energies of 570 eV and 535.4 eV, just above the ionization threshold. At an excitation energy of 570 eV there is an enhancement in the PDOS just below ϵ_F due to shake up excitations. The spectrum obtained with an excitation energy of 570 eV is very similar to the spectrum obtained by electron bombardment (Fig. 3a). The low energy O K spectrum provides evidence of a low PDOS at ϵ_F. Figure 4b shows the $L_{2,3}$ x-ray emission spectrum for pure copper and for the high T_c compound. The spectra were obtained with excitation just above the $L_{2,3}$ ionization energy. We note that the peak of the spectrum obtained from the high T_c compound occurs at an energy about 2.5 eV below the L_3 ionization energy derived from the EELS data[20] for CuO. This suggests that the maximum in the PDOS of d symmetry localized at the Cu site is approximately 2.5 eV below ϵ_F.

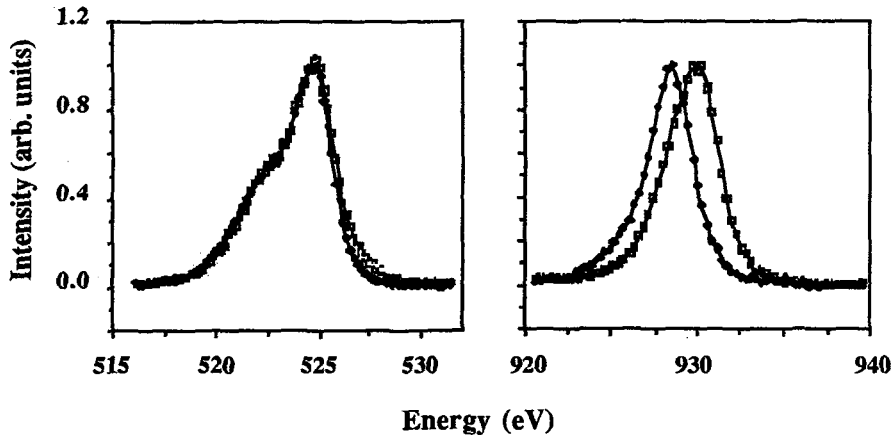


Figure 4:

a) Oxygen K emission spectra excited by photons of 570 eV (open squares), and by photons of 535 eV (filled triangles).

b) Copper $L_{2,3}$ emission spectra excited by photons of 935 eV. Spectrum of pure copper (open squares) and of copper in the high T_c superconductor (filled triangles).

Photoemission measurements [11-13] show the maximum intensity in the DOS to be about 4.5 eV below ϵ_F with an enhancement at 2.5 eV below ϵ_F. These results are consistent with theoretical evidence [9,10] Our measurements suggest that states of p symmetry are located at BE= 4.5 eV and those of d symmetry with copper bonding may have an enhancement at about 2.5 eV. This experimental evidence is supported more strongly by a tight binding calculation [10] of the band structure and the DOS than by a local density band study [9] where the O p states have a large DOS at 2 eV BE and are embedded in the copper d bands which have the largest DOS at about 4 eV.

The authors are grateful to Dr. L. Bennett of the Alloy Physics Division at the National Bureau of Standards for verifying the superconducting nature of the samples. The authors also thank R. Stockbauer and R.Kurtz of NBS for the spectrum shown in Fig. 3d, and M. Stocks for helpful suggestions. We also appreciate the hospitality shown us at the Hamburg Synchrotron radiation source, and we are grateful to C. Kunz for the use of his monochromator. Assistance from the operating staff of the NBS-SURF II synchrotron light source is gratefully acknowledged. This research is supported by NSF grant DMR-8593541 (UT), by the Science Alliance grant from the state of Tennessee (UT), by USDOE contract DE-AC05-84OR21400 (ORNL), and by the U. S. Air Force Office of Scientific Research under contract ISSA87-0050 (NBS). The research was carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory, supported by USDOE contract DE-AC02-76CH00016.

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