# Observation of Strong Electron Correlations in $YBa_2Cu_3O_{7-\delta}$ by *hv*-Dependent Photoelectron Spectroscopy

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# Observation of Strong Electron Correlations in $YBa_2Cu_3O_{7-\delta}$ by $h\nu$-Dependent Photoelectron Spectroscopy.

P. THIRY (*), G. ROSSI (*), Y. PETROFF (*), A. REVCOLEVSCHI (**) and J. JEGOUDEZ (**)

(*) *Laboratoire pour l'Utilisation du Rayonnement Electromagnétique CNRS-CEA-MEN, Université Paris-Sud, 91405 Orsay, France*

(**) *Laboratoire de Chimie des Solides, Université Paris-Sud, 91405 Orsay, France*

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**Abstract.** – We present photoemission spectra from single-phase $YBa_2Cu_3O_{7-\delta}$ which have been measured in the photon energy range $(17 \div 130)$ eV, at $T = 80$ K, $T = 300$ K and intermediate temperatures using synchrotron radiation. Intense satellites associated with the Cu $3d$ and O $2p$ bands are observed to undergo resonances at the Cu $3p$ and O $2s$ core level excitation thresholds, respectively, indicating the presence of holes in the Cu and O hybrid bands on both Cu and O sites. The strong correlation effects for the valence electrons suggest that one-electron calculations may not be appropriate for a detailed description of the electronic properties of this material.

Since the discovery of high-$T_c$ superconductors by Bednorz and Müller [1], there have been a very large number of experiments on these materials. Although very few concern the electronic properties, studies of this kind can be important for determining whether the superconductivity is phonon mediated [2] or it can be understood in connection with strong electron correlations [3].

In this paper we report photoemission measurements on the compound $YBa_2Cu_3O_{7-\delta}$, where $\delta \simeq 0.1$. This phase has been recently identified as an oxygen-deficient perovskite ($\sim 2.1$ vacancies) [4].

Samples of nominal composition $YBa_2Cu_3O_{7-\delta}$ were prepared by mixing and thoroughly grinding appropriate amounts of $BaCO_3$, $Y_2O_3$ and CuO powders. After compression in parallel bars, the samples were heated in air at 950 °C for 15 hours, then cooled for a few hours to room temperature. X-ray diffraction at this stage indicated that there was full reaction between the starting compounds. The diffraction lines are consistent with an orthorhombic unit cell having parameters $a = 3.83$, $b = 3.88$, $c = 11.69$ Å. Samples were subsequently annealed in oxygen at 900 °C for 6 hours and then slowly cooled down to room temperature. When the samples are broken or cleaved, several mirrorlike surfaces of the order of 1 mm$^2$ can be obtained. The photoemission experiments were performed at the French Synchrotron Radiation Center (LURE) using a set-up described earlier [5]. The pressure in the chamber was of the order of $1 \cdot 10^{-10}$ mbar. The samples were cleaved or

broken at $T = 300$ K and at $T = 80$ K. No contamination was observed while the measurements were performed on 7 different samples. The relative intensities of the peaks vary from sample to sample depending on the properties of the microcrystals at the surface.

The electronic structure of $YBa_2Cu_3O_{6.9}$ has been recently calculated by Mattheiss and Hamann [6] and by Massidda *et al.* [7]. The calculated density of states [6] contains two peaks located at $-0.8$ eV and $-3.7$ below $E_F$ corresponding to the hybridized Cu $3d$-O $2p$ bands. The O $2s$ bands are centred at $-16$ eV and the Ba $5p$ bands at $-10$ eV. However, as shown in table I these energies are quite different with respect to our experimental measurements. We do not observe the large number of peaks in the energy region between the Fermi level and $-2$ eV. It appears that both band structure calculations have overestimated the density of states in the region from $E_F$ to $-2$ eV.

TABLE I. – *Binding energies of the different structures observed by photoemission spectra of* $YBa_2Cu_3O_{7-\delta}$. *The energy to the peak D, corresponding to the* Cu $3d$ *satellite, changes at resonance from* $-11$ *to* $-12$ eV. *This shift has also been observed in the case of* Ni [8], *and is understood in terms of a branching ratio between the triplet and singlet satellite terms.*

| Structure | Origin | Energy (eV) | Theory [6] (eV) |
|---|---|---|---|
| $A'$ | Cu $3d$-O $2p$ | $-1.5$ | |
| $A$ | Cu $3d$-O $2p$ | $-3$ | $-0.8$ |
| $B$ | Cu $3d$-O $2p$ | $-4.5$ | $-3.7$ |
| $C$ | $2p$ satellite / $3d$ satellite ($^3F$) | $-9$ | |
| $D$ | $3d$ satellite ($^1G$) (at resonance) | $-12$ | |
| $E$ | Ba $5p_{3/2}$ | $-13.7$ | $-10$ |
| $E'$ | Ba $5p_{1/2}$ | $-15.5$ | |
| | O $2s$ | $-19.7$ | $-16$ |
| $G$ | Y $4p_{3/2}$ | $-24$ | |
| $G'$ | Y $4p_{1/2}$ | $-25.2$ | |
| | Ba $5s$ | $-27.5$ | |
| $I$ | Ba $4d_{5/2}$ | $-89.1$ | |
| $I'$ | Ba $4d_{3/2}$ | $-91.4$ | |
| $J$ | Ba $4d$ satellites | $-96.6$ | |
| $J'$ | Ba (at $T = 80$ K) | $-98.9$ | |

Photoemission spectra taken at $h\nu = 40$ eV and $T = 300$ K for four samples of $YBa_2Cu_3O_{7-\delta}$ are shown on fig. 1. The spectrum for sample (1) contains the sharpest structures, probably because of the larger grain surfaces exposed ([1]). Some samples showed a weak Fermi edge. On one of the cleaves a sharp edge was observed at $T = 80$ K (see the inset of fig. 1). We emphasize that because the samples are polycrystalline it is difficult to determine accurately the density of states close to $E_F$. The experimental spectra show a low density of states due to the orientational average of the polycrystals. However, for some direction of the Brillouin zone, a high density of states could be present; single crystals studies are required to determine this property.

([1]) The experimental chamber was baked at $T = 200$ °C for 24 hours after each sample change: no effect on the superconductivity of the samples was observed.

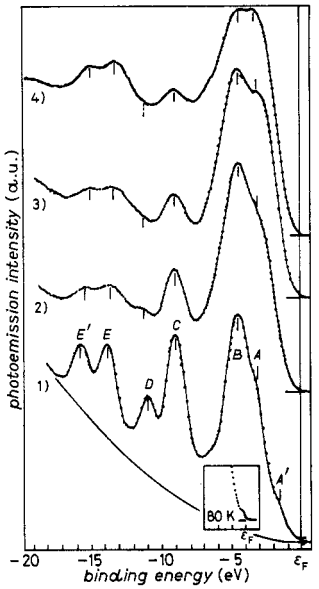


Fig. 1.

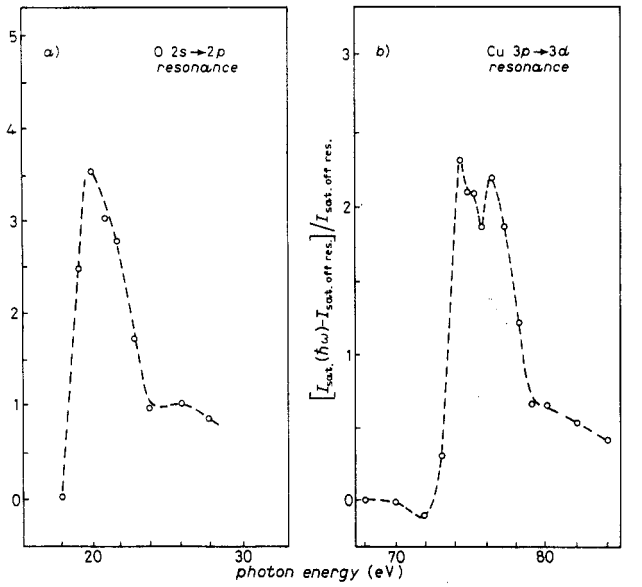


Fig. 2.

Fig. 1. – Photoemission spectra of four samples of $YBa_2Cu_3O_{7-\delta}$ obtained at $h\nu = 40$ eV and $T = 300$ K. The polycrystalline samples are cleaved or broken under vacuum ($1 \cdot 10^{-10}$ mbar). Sample one shows the sharpest structures. The insert shows a very sharp Fermi edge observed at $T = 80$ K on one of the cleavage of sample 2: it has not been reproduced.

Fig. 2. – *a*) O satellite (peak *C*) intensity profile *vs.* the exciting photon energy in the range (18 ÷ 28) eV, $T = 300$ K. *b*) Satellite ($^1G$) (peak *D*) intensity profile *vs.* the exciting photon energy in the range (68 ÷ 84) eV, $T = 300$ K. The resonance energy is $h\nu = 74$ eV (Cu $3p_{3/2}$ core level) like in CuO [9]. The second peak is due to the $3p_{1/2}$ core level component.

The main band is composed of a peak *B* at $-4.4$ eV with respect to $E_F$ which has a large Cu $3d$-like contribution, and two shoulders *A* and *A'* which appear to have dominant O $2p$-like character. Peaks *C* and *D* both contain satellites of the Cu $3d$-O $2p$ valence bands. Peak *D* is one component of a Cu $3d^8$ final-state satellite similar to that observed in Ni [10, 11] and in CuO [9]. The *D* satellite undergoes a sharp resonance (fig. 2*b*)) at the Cu $3p$ core level excitation threshold, with a maximum at $h\nu = 74$ eV (like CuO, but unlike $Cu_2O$). At resonance, the $^1G$ component is strongly enhanced, while the $^3F$ multiplet contributes to the intensity of peak *C* also off resonance. From the photoemission data in Cu vapour [12] the $^3F$ multiplet off resonance has an intensity which is roughly one-half of that of the $^1G$ at resonance. An increase of the *B*/*A* branching ratio is observed at the resonance of the *D* satellite. From recent data [13] peak *C* has been attributed to carbon impurities, but from our data a large fraction of peak *C* appears to be a satellite associated with the O $2p$ states. This result is supported by two observations: 1) the intensity of peak *C* is inversely proportional to the intensity of peaks *AA'* which contain the shallower part of the occupied O $2p$-like hybrid states; 2) peak *C* undergoes a sharp resonance at the O $2s$ threshold which we attribute to dipole coupling of O $2s$ and empty O $2p$-like states (fig. 2*a*)). An increase of the *A'*/*B* branching ratio is observed at the *C* satellite resonance [14]. The Cu-related satellite (peak *D*) can be understood as a $d^8$ final state like in the case of Ni and of CuO. Figure 3 shows the photoemission spectrum at resonance for the Cu $3d$-like states ($\hbar\omega = 74$ eV) and the curve measured at $T = 80$ K, where a puzzling increase of the intensity

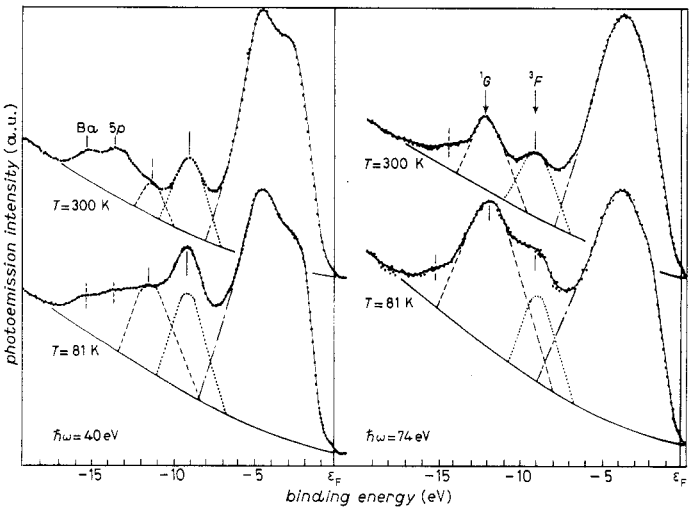


Fig. 3. – Photoemission spectra for $YBa_2Cu_3O_{7-\delta}$ at resonance for $T = 300$ K and $T = 81$ K. The dashed areas emphasize the satellite contribution which undergoes the largest resonance. The relative amplitude of the Cu $^1G$ satellite and the valence band changes dramatically with $T$.

of the satellite relative to the $d$ band is observed. The oxygen-related satellites implies that the O $2p$-like states are not fully occupied. The large variations of the $C/A$ peak intensity from sample to sample, and as a function of the temperature, indicates that the filling of the hybrid Cu $3d$-O $2p$ band states is very sensitive to sample order, defects, and $T$.

A widely adopted approach in the discussion of the electronic properties of the high-$T_c$ superconductor Cu-oxydes is the definition of the formal valence of all constituent ions. Assuming that the O $2p$ derived states were fully occupied would force one to conclude that there is one $Cu^{3+}$ ion for every two $Cu^{2+}$ ions. Our data show that the O $2p$ states are not fully occupied, since the satellite resonance can only occur in the presence of O $2p^5$ or lower ion configurations. This removes the need for $Cu^{3+}$, in agreement with the experimental results of Yarmoff *et al.* and Bianconi *et al.* [13]. The remarkable effects seen in the photoemission at $T = 80$ K are the decrease of peak $A$ with respect to peak $B$, the increase of the oxygen-related satellite that contributes to peak $C$, and the increase of the Cu satellite $D$, in particular at the $3p$-$3d$ resonance. Charge redistribution in the hybrid valence states suggest that larger electron correlation effects will also have consequences for the core level photoemission of the other constituent atoms: Y and Ba. The Ba $4d$ core level lineshape at $T = 81$ K, and lower $T$, shows an intense shake-up doublet at 7.5 eV lower final-state energy and other changes with respect to the high-temperature (*i.e.* $T > (130 \pm 10)$ K) photoemission lineshape. The low-temperature Ba $4d$ spectrum is compared in fig. 4 with the atomic phase spectrum [15] (all Ba $4d$ spectra have been aligned to the same energy of the main doublet). The 7.5 eV shake-up compares well with the atomic shake-up ($6s \rightarrow 7s$) [15] and also the broadening of the $4d_{3/2}$ component of the main doublet could be associated with the smaller atomic shake-up's ($6s \rightarrow 5d$). The low-temperature photoemission effects turn on progressively when lowering the sample temperature below $(130 \pm 10)$ K.

Summarizing our results and interpretation, we find that:

1) $YBa_2Cu_3O_{7-\delta}$ is a material whose electron states are strongly correlated. This observation alone has important consequences and it makes it difficult to compare the spectroscopic results on $YBa_2Cu_3O_{7-\delta}$ to the ground-state band structure calculations, but the very large energy and density of states differences between the experiments and

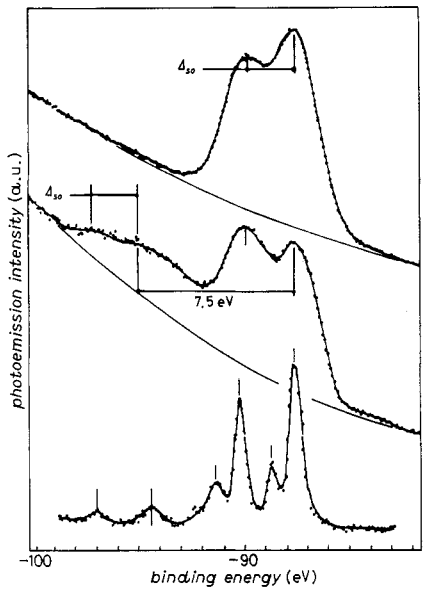


Fig. 4. – Ba $4d$ core level photoemission from $YBa_2Cu_3O_{7-\delta}$ ($\hbar\omega = 130$ eV) at 300 K (top curve), at 81 K (central curve, qualitatively identical also at 20 K), and for atomic Ba [14] (bottom curve). The three curves have been aligned at the binding energy of the Ba $4d_{5/2}$ peak of the 300 K $YBa_2Cu_3O_{7-\delta}$ in order to compare the lineshapes.

theory [13, 18] clearly show that strong electron-electron correlation must be accounted for even in the ground-state, and this is not the case for one-electron theories.

2) The presence of the large satellite $C$ which undergoes a resonance at the O $2s$ excitation threshold is a measure of the existence of empty O $2p$ states in the ground-state.

3) By lowering the sample temperature below $(130 \pm 10)$ K (and down to 20 K) the photoemission from both Cu and O related satellites increases in intensity, while the photoemission intensity of the main Cu $3d$-O $2p$ valence bands decreases with a relative stronger decrease of the $AA'$ peaks with respect to the $B$ peak. These observations indicate that charge redistribution occurs at low temperature with a selective decrease in the intensity of the shallower states. The appearance of strong shake-up satellites of the Ba $4d$ also indirectly indicates that the charge redistribution involves the whole crystal and not just the Cu and O sites.

4) The Coulomb interaction between band electrons described by the $U$ parameter can hardly be determined in the absence of a full experimentally determined band structure. What should be stressed though, is that the $U$ value is similar for both Cu $3d$ and O $2p$ electrons (it would be of the order of $(3 \div 5)$ eV in atomic limit), since the satellite energies with respect to the valence state energies are quite similar.

The relationship between our findings and the superconducting phase transition ($T_c \sim 90$ K for our materials) poses an interesting question which is under investigation [16].

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