Soft-x-ray absorption and emission spectra and the electronic structure of the $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ superconductor

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We present e -beam-excited soft-x-ray emission spectra and total-photoelectron-yield spectra in the 20–600 eV photon energy range for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$. In soft-x-ray emission, the $N_{4,5}$ structure of Ba, the $M_{4,5}$ spectrum of Y, and the K spectrum of O provide a direct measure 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 ϵ_F . The maximum in the O K spectrum is 2.6 ± 0.5 eV below ϵ_F . This result provides direct confirmation that the shoulder previously found at $\epsilon_F - 2.3$ eV in photoelectron emission spectra is associated with O p orbitals. No changes are observed between spectra taken above and below T_c .

Interest within 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, for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ the relevance of the 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^{11–14} of the total density of states (DOS) in the valence band.

Total-photoelectron-yield spectroscopy and soft-x-ray emission spectroscopy are less surface sensitive than photoelectron spectroscopy, and one expects them to provide a better representation of the bulk properties of the samples, the surfaces of which have been shown to be sensitive to loss of O.¹² In addition, both techniques provide spectra which are selected for chemical species and angular momentum states and thus provide more detailed information than is available from photoemission alone.

We used e -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. The peak in the p -PDOS derived from the O K emission spectrum was 2.6 ± 0.5 eV below ϵ_F . This result agrees with the expected p -PDOS derived from ground-state band-structure calculations^{7–10} and provides direct evidence that the shoulder observed 2.3 eV below ϵ_F in the photoemission spectra is associated with p orbitals on the oxygen sites. For Ba and Y the maximum in the p -PDOS was about 4 eV below ϵ_F . The

present measurements were 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 $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ does not undergo a structural phase change between T_c and room temperature.¹⁵

The samples were prepared according to an established procedure.⁴ Superconductivity was verified by ac magnetic-susceptibility measurements. The transition temperature measured was 90 K and the transition temperature zone had a width of a few degrees.

Total-yield measurements were made at the beginning and end of a sequence of x-ray emission measurements. The samples were studied in a facility that was developed for the measurement of total quantum yields to calibrate standard photodiodes.¹⁶ The oxygen K , barium $N_{4,5}$, and yttrium $M_{4,5}$ x-ray emission spectra [Fig. 1(b)] were obtained by bombarding the sample with a 2-kV, 100- μA electron beam pulse. The fluorescence was detected by a high-sensitivity spectrometer.¹⁷

The results of the total-quantum-yield and the soft-x-ray emission measurements are shown in Figs. 1(a) and 1(b), respectively, for the photon energy range 50–175 eV. In Fig. 1(a) the spectral band with the two small peaks, shown as A , is near the $3p$ ionization threshold energy of Cu (the $M_{2,3}$ absorption edge). The two small peaks are associated with Cu $3p$ core electrons making transitions to the conduction band. The energy position of this structure is an important indicator of the valence of the Cu ion.¹⁸ The spectral region B contains the most

FIG. 1. (a) Total quantum yield for superconducting $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ as a function of the photon energy. The energy bands denoted by the letters are defined in text. (b) Intensity of soft-x-ray fluorescence excited by 2 keV electrons vs photon energy.

prominent features in the figure, which arise from excitation of a Ba $4d$ electron ($N_{4,5}$ absorption). These features, along with the small peak at a photon energy of 95 eV, are associated with localized finite states that are similar in atomic and metallic Ba, and in BaF_2 , BaCl_2 , and BaBr_2 .¹⁹ As the valence of Ba in the halide compounds increases to +2 (i.e., $\text{Br} \rightarrow \text{F}$), the first large peak at 106 eV exhibits structure attributable to $4d^9$ nf excitons, which becomes more pronounced as the valence increases.¹⁹ The relatively weak excitonic structure visible here is similar to that encountered in the least ionic of these compounds, BaBr_2 , and is suggestive that some fraction of the barium valence electrons are localized at the

barium site. A previous report¹² of photoelectron yield compared the 1:2:3 compound to BaF_2 , and concluded that Ba in the 1:2:3 compound has a valency of +2.

The detected x-ray fluorescence spectrum is shown in Fig. 1(b). The intense spectral feature at a photon energy of 132 eV is emission associated with Y $4p \rightarrow 3d$ ($N_{2,3}M_{4,5}$) transitions. The grating also diffracts radiation in higher order, and the small peak C at 66 eV arises from these same transitions observed in second order. The most prominent feature in the spectrum is due to $5p \rightarrow 4d$ ($O_{2,3}N_{4,5}$) transitions of Ba. At slightly higher photon energies, contained in the region bounded by D, valence band $\rightarrow$ core hole transitions are found. The small feature E is the valence band $\rightarrow 1s$ transition of O appearing in the fifth order of diffraction (these transitions occur in an energy band around 525 eV). Finally, the energy region bounded by F includes the valence $\rightarrow 3d$ transitions localized on the Y atom. Transitions between the valence band and $3p$ holes in Cu are masked by the intense inner core transitions of Ba that occur in the same spectral region. The energy position of these transitions for this compound is tabulated in Table I.

Figure 2 is a plot of region A in Fig. 1(a) on an expanded scale. The upper curve is for a sample of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$. The lower curve was obtained after the sample was irradiated both by electrons and by x rays. The small change in the absolute yield shows there has been no gross contamination of the bulk of the sample. The energy position of the two yield maxima did not change after two months of exposure in different environments at different laboratories. This observation suggests that the bulk material is stable and the Cu valence is not easily changed by exposure to radiation and different vacuum environments. 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.¹⁸ This observation adds confidence to the interpretation²⁰ that most of the Cu is in the +2 oxidation state, though it does not exclude the possibility that a small fraction of Cu atoms have +3 valence. Our x-ray emission measurement of the L spec-

TABLE I. Soft-x-ray transition energies for Y and Ba in the metallic form (columns 3–5) and in $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ (column 6). The most intense lines of a group are denoted by *. Uncertain classifications are indicated by ?.

Element	Transition	Ref. 25(a)	Photon energy (eV)			This work
			Ref. 25(b)	Ref. 25(c)		
Y*	$M_{4,5}N_{2,3}$	132.8	132.48	132.7 133.3 134.6		132.4(1)
Y	$M_{4,5}M_3$	143.4	142.0	141.0 143.0		143.2(2)
Y	M_4M_2	152.2	148.5?	152.9		152.5(2)
Ba*	N_5O_3	75.30	75.33	75.1		75.2(1)
Ba*	N_4O_2	75.90	75.95	75.6		75.8(1)
Ba	N_4O_3	77.96	77.95	77.8		77.8(1)

FIG. 2. The quantum efficiency (QE) curve of region A in Fig. 1(a) with both axes expanded. The solid line shows the initial QE; 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 Cu₂O are shown by the arrows (from Ref. 18).

trum of Cu (Ref. 21) gives additional confirmation of this interpretation.

We now turn to the regions D and F in Fig. 1(b). These regions are relevant because they provide an insight into the *p*-PDOS localized at the atoms of Ba and Y. Since the transition is between the valence band and the 4*d* core hole in Ba (respectively, 3*d* core hole in Y), dipole selection rules select out valence states of *p* or *f* symmetry. We believe that the majority of the states will have *p* symmetry because states of *f* symmetry lie high up in the conduction band. The *K* spectrum of O, the *M*_{4,5} spectrum of Y, and the *N*_{4,5} spectrum of Ba are shown in Figs. 3(a)–3(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. This normalizes the data to unit energy and makes it proportional to the product of the transition-matrix element and the density of states of the proper symmetry.²² The data were further normalized to unit area so that they could be compared to other spectra.

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 spectroscopy¹¹ at a photon energy of 60 eV. The ultraviolet photoemission spectrum (UPS) measurements sample all the symmetries in the band, and a comparison of UPS and x-ray emission spectra will provide 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 UPS zero binding energy.

The photon energy for a transition between ϵ_F and the 1*s* core hole in O is based on the curve crossover point of the emission spectrum [solid line in Fig. 3(a)] and the total-yield spectrum¹⁴ [dashed lined in Fig. 3(a)]. The total-yield spectrum provides a measure of the absorption

FIG. 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 are corrected for background and normalized according to a procedure 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. The dashed curve in (a) is the total-yield curve for O obtained from Ref. 14. Interfering *M*_{4,5}*M*₃ and *M*₄*M*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 Kurtz and Stockbauer, Ref. 11).

cross section and yields the lowest photon energy for transitions between 1*s* core states and unoccupied levels in the conduction band. The spectrum was excited by a 2-keV electron beam and is broadened near ϵ_F by shakeup processes. The crossover point of the curves depends to some extent on the amplitude of the emission spectrum relative to the absorption spectrum. We chose this ratio of amplitudes by considering the calculated¹⁰ partial densities of occupied and unoccupied states. The crossover energy is 527.0 ± 0.5 eV, where the uncertainty is due to broadening of the emission spectrum by shakeup and the uncertainty in the ratio of the densities of occupied and unoccupied states. Calculations,⁹ inverse photoemission measurements,¹⁴ and total-yield measurements¹⁴ show that there are unoccupied oxygen 2*p* orbitals just above the top of the conduction band.

The transition energy between ϵ_F and the $3d$ and $4d$ core holes in Y and Ba shown in Figs. 3(b) and 3(c), respectively, is obtained with the help of photoemission spectroscopy (PES) results. From Table I we note that 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 spectroscopy¹¹⁻¹⁴ should be an excellent approximation to the x-ray binding energy since the difference in screening between the UPS and x-ray transitions should be nearly the same for the valence and the first lower core level. Thus we obtain 89.3 eV and 153.6 eV, respectively, for the energy difference between ϵ_F and the $4d^2D_{5/2}$ core hole (N_5 edge) of Ba 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 may be associated with transitions between the valence band and the $2D_{3/2}$ core hole (N_4 edge), but also corresponds to the energy position of O K radiation diffracted in sixth order [note the presence of fifth-order O K radiation in Fig. 1(b)].

In Fig. 3(b) there are spectral features at 143.2, 148.2, and 152.5 eV. The feature at 143.2 eV is identified²³ as an $M_{4.5}M_3$ transition of Y (see Table I). The spectral feature at 148.2 eV coincides with a line identified^{23(b)} as the Y M_4M_2 transition. This identification is inconsistent with those of other compilations^{23(a),23(c)} that place the M_4M_2 transition at about 152 eV (Table I). The feature at 148.2 eV may therefore be due to an impurity or perhaps to structure in the valence band. The M_4M_2 transition most likely occurs at 152.5 eV.

For each element studied, the p -PDOS at ϵ_F is small. Barium and yttrium have maxima in their p -PDOS about 4 eV below ϵ_F . The calculated PDOS localized at Ba and Y extend from ϵ_F to about 5 eV below ϵ_F , and is in good qualitative agreement with our measurements. The max-

imum in the p -PDOS localized at the O sites at about 2.6 ± 0.5 eV below ϵ_F provides direct evidence that the feature observed at 2.3 eV in the UPS spectrum can be attributed partially to oxygen $2p$ orbitals. The agreement between the calculated O K spectrum¹⁹ and the measurement is very good. The measured band width is about 7 ± 1 eV while the calculated width is about 6 eV. The maximum in the calculated O K spectrum is found 1.6 eV below ϵ_F and about 1 eV higher in the valence band than our results. The PDOS localized at O computed by the authors of Ref. 10 has a width of 7 eV and a maximum about 3 eV below ϵ_F , which is in even better agreement with our results.

We conclude that our measurements are in good semi-quantitative agreement with several calculations. We also see evidence that barium may have electronic charge localized near it. This provides an alternate suggestion to the proposal that some copper might have +3 valence^{7,10} or that one of the oxygen might be in the 1^- oxidation state.¹⁴

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