PHYSICAL REVIEW B VOLUME 52, NUMBER 13 1 OCTOBER 1995-I

Barium contributions to the valence electronic structure of $YBa_2Cu_3O_{7-\delta}$, $PrBa_2Cu_3O_{7-\delta}$, and other barium-containing compounds

D. R. Mueller and J. S. Wallace
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

J. J. Jia, W. L. O'Brien, Q.-Y. Dong, and T. A. Callcott
University of Tennessee, Knoxville, Tennessee 37996

K. E. Miyano* and D. L. Ederer
Tulane University, New Orleans, Louisiana 70118

(Received 13 February 1995)

Monochromatic photon beams were used to excite barium $N_{\mathrm{IV,V}}$ soft x-ray emission spectra from $YBa_2Cu_3O_{7-\delta}$, $PrBa_2Cu_3O_{7-\delta}$, BaF_2, and $BaTiO_3$. Near threshold excitation was used to demonstrate that small contributions to the barium N_{V} and N_{IV} emission spectra in the energy region above the $5p \rightarrow 4d$ core-core transitions do not arise as satellite emission from transitions in multiply excited atoms but rather occur as a result of transitions from the valence states. The emission spectrum of $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ reveals a contribution to the electronic density of states at the barium site in the region near the Fermi level. The $YBa_2Cu_3O_{7-\delta}$ compound is a superconductor and $PrBa_2Cu_3O_{7-\delta}$ is an insulator. It has been proposed that the difference between them is due to mixing of praseodymium and barium among the sites occupied by yttrium and barium, with an accompanying change in electronic structure. However, our measurements indicate that the barium partial density of states for the two compounds are essentially identical.

INTRODUCTION

In studies of the electronic structure of high-T_c cuprates, attention has been directed mainly toward the copper-oxygen planes. It is generally assumed that the alkaline-earth elements in high-T_c compounds do not contribute to the valence electronic structure in these materials or to the valence bands of insulating barium compounds. There is, however, some evidence that the alkaline-earth ions also play a role in determining the superconducting properties. Ronay and Newns[1] have pointed out the importance of the alkaline-earth species in determining the transition temperature in the 1:2:3, 2:2:1:2, and 2:2:2:3 families of high-T_c superconductors. Substitution of strontium for barium in these compounds reduces the transition temperatures by approximately 20%. The failure of $PrBa_2Cu_3O_{7-\delta}$ to superconduct in spite of its orthorhombic crystal structure has also attracted much attention. Yang and co-workers[2,3] measured a shift of the barum core-level binding energy as Pr is substituted for Y or Eu in $Y_{1-x}Pr_xBa_2Cu_3O_7$ or $Eu_{1-x}Pr_xBa_2Cu_3O_7$. A similar binding-energy change was observed by these authors as a function of oxygen content in $YBa_2Cu_3O_{7-\delta}$. They ascribe the core-level binding energy shifts to initial state changes in the charge at the Ba site that occurs as a result of changes in the Ba-O(4) overlap as a function of Pr concentration or oxygen deficiency. In particular they cite charge transfer between localized Ba $5d$–O $2p$ states and Ba $6s$–O $2p$ bands in the vicinity of the Fermi level as the mechanism responsible for the barium core-level binding-energy shifts.

Soft x-ray emission spectra are sensitive to local electronic structure. We have examined the barium $N_{\mathrm{IV,V}}$ emission spectra of $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ to test these ideas. The dipole selection rule limits the states contributing to the x-ray emission to those of p-type and f-type symmetry at the barium site. Note however that the f states are rather far into the conduction band[4] and thus are unlikely to hybridize significantly with the valence states and contribute to the measured emission. Although the measurements are not directly sensitive to states of d-type or s-type symmetry at the barium site, overlap with states at adjacent sites or hybridization with states of p-type symmetry at the barium can result in contributions to the $N_{\mathrm{IV,V}}$ emission which we have observed. Hybridization effects and cross transitions are important in defining x-ray emission spectra of various materials. Note for example the mostly silicon $2p$ derived states in the upper part of the valence band that appear in silicon $L_{\mathrm{II,III}}$ emission spectra[5] and the valence emission bands in the $M_{\mathrm{IV,V}}$ emission spectra of early $4d$ transition metals.[6]

It has been generally assumed that the alkaline-earth elements in the high-T_c compounds do not contribute to the valence electronic structure in these materials or to the valence band in other insulating compounds. However, evidence from soft x-ray emission spectroscopy and calculations[7] shows that alkaline-earth species make small but measurable contributions to the valence electrons density of states. In previous publications we presented electron-beam-excited soft x-ray emission spectra for $YBa_2Cu_3O_{7-\delta}$ (Ref. 8) and $Bi_2Sr_2CaCu_2O_{8-\delta}$ (Ref. 9) which clearly show a distinctive barium contribution to the valence density of states. This paper deals with soft x-ray emission from barium in several compounds by

0163-1829/95/52(13)/9702(7)/$06.00

a monochromatic photon beam near the barium 4*d* threshold in energy. This mode of excitation has been used to eliminate the possibility that transitions in multiply excited atoms contribute to the emission data and is also useful in separating the $N_{\rm IV}$ and $N_{\rm V}$ contributions to the emission spectra. In particular we have observed the soft x-ray emission spectrum of barium in $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ which reveals a contribution to the electronic density of states at the barium site in the region near the Fermi level. It has been proposed[2,3] that the difference between them is due to mixing of praseodymium and barium among the sites occupied by yttrium and barium, with an accompanying change in the electronic structure. In fact our measurements indicate that the barium *p*-type partial density of states for the two compounds is nearly identical, which suggests that charge transfer from other sites either does not exist or does not have *p*-type symmetry. The x-ray emission spectrum suggests that both compounds have the same energy separation between the valence band and the 5*p* core level. Data for $BaTiO_3$ and BaF_2 are presented for comparison.

In x-ray emission spectroscopy an electron or a photon beam is used to generate vacancies in the core levels of atoms within a specimen. The energy distribution of the x-rays emitted as electrons drop into core-level vacancies from occupied valence states depends upon the product of the matrix element connecting the initial core vacancy with the valence states and upon the local density of electronic states at the site of the initial core vacancy. The x-ray emission process obeys the dipole selection rule; consequently an x-ray emission spectrum also resolves the angular momentum of the electronic states. Aside from a factor of photon energy cubed (which arises from the photon density of states and the dipole approximation) the matrix element connecting the initial and final states is often only weakly energy dependent over the limited energy extent of the valence band, particularly when the measurement is sensitive to valence levels of only one angular momentum symmetry.

X-ray emission spectra excited with energies well above threshold often include satellite contributions from transitions in multiply excited atoms.[10] Satellite contributions can occur with intensities that are a significant fraction (up to 30%) of the total emission intensity. The multiply excited atoms may be generated via Auger decay of a deeply bound core level into a spectator vacancy and a vacancy in a level that is subsequently involved in radiative decay.[11] Use of a monochromatized photon beam to generate the core vacancies facilitates excitation at energies below those required to excite more tightly bound core levels thereby eliminating the Auger mechanism of spectator vacancy generation. Excitation near threshold can also eliminate the possibility that direct multiple excitation or overlapping features from transitions involving more tightly bound states contribute to the emission spectra.

EXPERIMENT

The soft x-ray emission experiments were performed on beamline U-10A at the National Synchrotron Light Source at Brookhaven National Laboratory. The apparatus installed there incorporates facilities to generate core vacancies within a sample employing either an incident electron beam (0.5–5 keV), white light, or monochromatized synchrotron radiation. The monochromator is based on a variable-line-spaced grating design,[12] and is tunable in the range from 40 to 280 eV. For typical operating conditions a photon flux of $\sim 2\times 10^{13}$ photons/sec is delivered in a 2 mm^2 spot on the sample. The monochrometer band width for this flux was about 1 eV.

Light emitted from the sample was energy analyzed by a grating spectrometer and a computer-interfaced multichannel detector. The instrumentation has been described in more detail elsewhere.[12–14] The spectrometer resolution employed in the present work was 0.2 eV. The pressure in the sample chamber was below 10^{-7} Pa during the measurements.

The BaF_2 was a commercially available single crystal. The $BaTiO_3$ sample was a single crystal prepared at Louisiana State University. The $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ samples were pressed or sintered polycrystalline pellets that were scraped immediately before insertion into the vacuum chamber. $YBa_2Cu_3O_{7-\delta}$ samples from several sources were examined. $PrBa_2Cu_3O_{7-\delta}$ samples were prepared at the National Institute of Standards and Technology by solid-state reaction of Pr_6O_{11}, $BaCO_3$, and CuO powders. The Pr_6O_{11} and $BaCO_3$ were commercial powders and the CuO was prepared by decomposing basic cupric carbonate (malachite, nominally $CuCO_3$-$Cu(OH)_2$) at 500 °C in air. The powders were mixed using a high speed dry mixer and pellets of 12.7 mm diameter and approximately 2 mm thick were uniaxially pressed at 100 MPa. These pellets were heated to 920 °C for 12.5 h then were removed from the hot furnace and allowed to air quench to room temperature. The resulting pellets gave x-ray-diffraction spectra which appeared to be single phase, with peaks corresponding to those found by Okai *et al.*[15]

The vacuum chamber was baked at a temperature of 150 °C for 12 h prior to the measurements. This procedure is not expected to modify the sample stoichiometry because out diffusion of oxygen is not measurable at temperatures below 350 °C.[16] The fluoride and titanate samples are stable to higher temperatures. The experiments were conducted with the samples at room temperature. There was no evidence of sample decomposition induced by the incident photon beam. The energy calibration of the spectrometer was verified by examining the position of the Fermi edge in $L_{\rm II,III}$ emission spectra from a piece of aluminum foil mounted on the sample manipulator (Fermi edge to $L_{\rm III}$ transition energy: 72.8 eV). Multiple order diffraction features for emission from Y metal were used to verify that the spectrometer calibration uncertainty was less than 0.2 eV over the entire energy range (50–200 eV) of the 600 line/mm grating.

Because photons rather than low-energy electrons are detected, soft x-ray emission is insensitive to sample charging which can complicate photoelectron studies of insulating samples. Because photons have a longer absorption length in solids than the mean free path of low-energy electrons, x-ray emission spectroscopy is less surface sensitive than photoelectron spectroscopy. At the soft x-ray energies examined in this study atomic absorption data[17] may be used to estimate the average depth of sample probed:

$$z_{\mathrm{ave}}=\cos(\theta_i)\cos(\theta_o)\int_0^{\infty} z\exp[(-\mu_i-\mu_o)z]dz\bigg/\int_0^{\infty}\exp[(-\mu_i-\mu_o)z]dz\ .$$

Here z is the vertical distance below the surface of the sample, μ_i and μ_o are the absorption coefficients of the ingoing and outgoing radiation, while θ_i and θ_o are the angles the incident and outgoing photon beams make with respect to the surface normal. The average depth was evaluated from the absorption data found in Ref. 17, using values of 45° and 15° for θ_ι and θ_o, respectively. The barium $N_{\mathrm{IV,V}}$ emission spectra presented in this paper originate within the samples from an average depth of ~ 150 Å.

RESULTS

Figure 1 illustrates the soft x-ray emission spectrum of $\mathrm{YBa_2Cu_3O_{7-\delta}}$. The spectrum is dominated by the $5p_{3/2}\rightarrow 4d_{5/2}$, and $5p_{1/2}\rightarrow 4d_{3/2}$ core-core emission features with transition energies of 75.3 and 75.9 eV, respectively. In addition the $\Delta J=0$ $5p_{3/2}\rightarrow 4d_{3/2}$ core-core transition is evident at 77.9 eV. In the energy range from approximately 81 to 90 eV weak emission features are apparent. These are also shown on an expanded intensity scale in the figure. The data were obtained using a monochromatic photon beam as the excitation source.

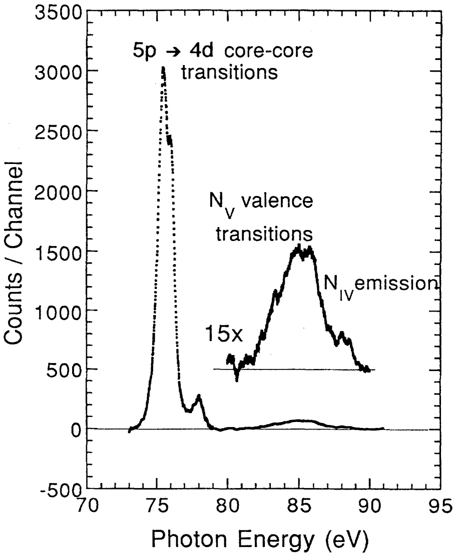

FIG. 1. Soft x-ray emission from $\mathrm{YBa_2Cu_3O_{7-\delta}}$ in the energy region of the barium $N_{\mathrm{IV,V}}$ transitions. Note the weak emission features in the energy range from 81 to 90 eV. The emission in this energy range is also shown on an expanded intensity scale offset along the vertical axis. The spectrum is shown following subtraction of a flat background of approximately 1000 counts per channel due to scattered light and detector dark counts. The spectrum was excited by a 110 eV photon beam.

Weak emission features are also evident at energies above those of the $5p\rightarrow 4d$ core-core transitions in the emission spectrum of barium fluoride. For this compound the features are narrow enough to clearly resolve the N_{V} and N_{IV} contributions.

Figure 2 illustrates soft x-ray emission from barium fluoride. The two spectra illustrated were excited by monochromatic photon beams with photon energies of 102 and 138 eV. We note that the spectra are identical except for the relative intensity of features arising from transitions into initial $4d_{3/2}$ and $4d_{5/2}$ vacancies. The intensity changes presumably reflect the photon energy dependence of the $4d_{3/2}$:$4d_{5/2}$ photoionization cross section ratio. The barium fluoride soft x-ray emission shows weak emission features near 82 and 85 eV. In the present experiment we can rule out the possibility that these features are multiple excitation satellites. High-energy satellites to emission lines are often generated by transitions in multiply excited atoms. Such multiply excited atoms may be generated via Auger decay of a more tightly bound core state, or by direct shakeup excitation. The Auger decay mechanism is unavailable for both spectra illustrated here because the spectra were excited with incident photon energies well below the threshold of the next most tightly bound barium core level. At 102 eV the incident photons are not energetic enough to produce multiple excitation (e.g., $4d^9 5p^5$ configurations) by a direct shakeup mechanism either.

Figure 3 shows the valence-to-core transition region for barium fluoride in greater detail. The spectrum is shown following division by a factor of photon energy

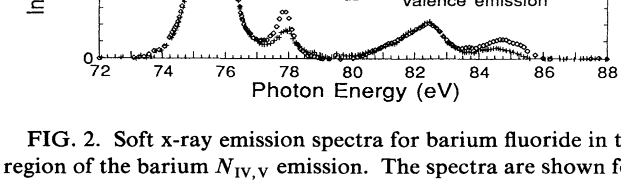

FIG. 2. Soft x-ray emission spectra for barium fluoride in the region of the barium $N_{\mathrm{IV,V}}$ emission. The spectra are shown following subtraction of a flat background of approximately 1000 counts per channel due to scattered light and detector dark counts, and have been normalized to have the same $5p_{3/2}\rightarrow 4d_{5/2}$ transition intensity. The spectra were excited by monochromatic 102 and 138 eV photon beams.

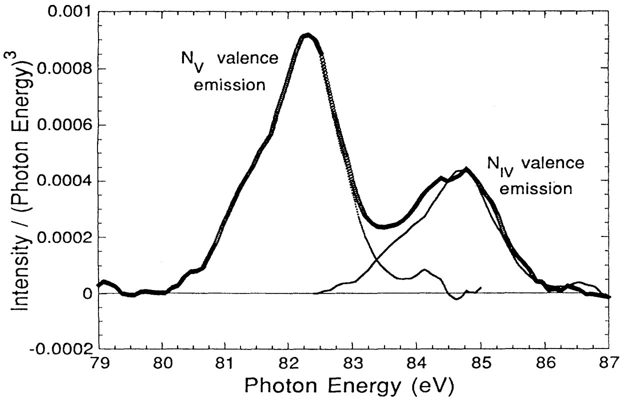

FIG. 3. Barium fluoride soft x-ray emission in the valence region is shown in more detail. Separation of the emission spectrum into its N_{IV} and N_V components is illustrated. The data has been divided by a factor of photon energy cubed. Photons of 110 eV were used to excite the spectrum.

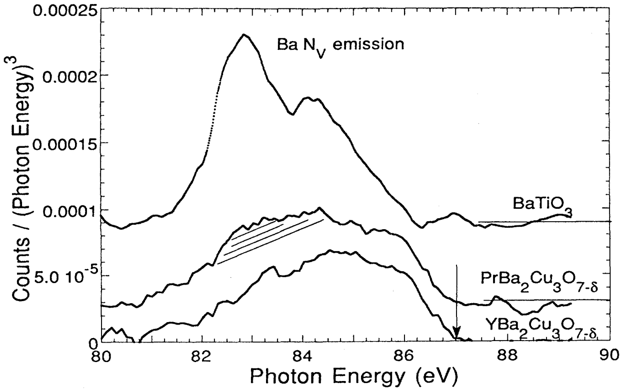

FIG. 4. Soft x-ray emission spectra for $YBa_2Cu_3O_{7-\delta}$, $PrBa_2Cu_3O_{7-\delta}$, and $BaTiO_3$. The closed arrow indicates the binding energy (from Ref. 18) of the N_V level with respect to the Fermi level for $YBa_2Cu_3O_{7-\delta}$. To facilitate comparison with partial density of states information the spectra have been divided by photon energy cubed and only the N_V component of the emission is shown. The shaded region indicates a shift in emission intensity away from the Fermi level in $PrBa_2Cu_3O_{7-\delta}$. For clarity the spectra have been offset along the vertical axis.

cubed to take into account the final-state photon density of states in the dipole approximation. To separate the N_{IV} and N_V contributions we used the raw data to estimate the intensity ratio for transitions into N_{IV} and N_V vacancies. The spin-orbit splitting for the barium $4d$ states is 2.6 eV. Because the N_V level is less tightly bound the lowest energy 2.6 eV segment over which the intensity is nonzero may be attributed to N_V emission alone. A fraction (48% in the example illustrated in Fig. 3) of the intensity measured in this lowest energy region was subtracted from the next lowest 2.6 eV segment of the spectrum to take into account the N_{IV} contribution. The subtraction yields the N_V spectrum in the next lowest 2.6 eV wide segment of the spectrum. This procedure was repeated until the entire spectrum was decomposed into its N_V and N_{IV} components. An incorrect estimate of the N_{IV}:N_V intensity ratio yields N_V and N_{IV} components that are not consistent with the measured emission profile.

A procedure based on the excitation energy dependence of the valence-to-core transitions was also used to separate the N_{IV} and N_V contributions to the emission spectrum. Note that subtraction of spectra obtained at different photon energies, but scaled to have the same N_V emission intensity (as in Fig. 2), yields the N_{IV} emission profile. The N_{IV} profile may be rescaled and subtracted from the data to determine the N_V contribution. The decomposition of the emission spectrum into its N_V and N_{IV} components using the two methods produced very similar results.

Photon-excited soft x-ray emission spectra were also collected for $BaTiO_3$, the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$, and the nonsuperconductor $PrBa_2Cu_3O_{7-\delta}$. The $5p \rightarrow 4d$ core-core transitions occur with the same transition energies in all these compounds. The shapes and locations of the valence bands for these materials differ from each other and those of barium fluoride. Figure 4 shows the barium p-type (and f-type if there are such contributions in the valence region) partial density of states for the valence bands of $BaTiO_3$, $YBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$. The partial density of states information was derived from data of the type shown in Fig. 1 by dividing the experimental spectrum by the photon energy cubed and separating the N_V and N_{IV} contributions to the emission. For both $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ the ratio of the valence transition intensity to that of the $5p \rightarrow 4d$ core-core transitions is less than that for barium titanate or barium fluoride, and the valence emission is spread over a larger energy range.

Parmigiani *et al.*[18] have determined that the binding energies for the barium $5p_{3/2}$ and $4d_{5/2}$ levels in orthorhombic $YBa_2Cu_3O_{7-\delta}$ are 12.0 and 87.0 eV, respectively. Similar results were obtained by Yang and coworkers.[2,3] The valence emission occurs in the region 6–12 eV above the $5p_{3/2} \rightarrow 4d_{5/2}$ core-core transition. Because the binding energy of the $5p_{3/2}$ state is 12.0 eV, the N_V valence emission represents a contribution to the density of states in the energy range from 0 to 6 eV in binding energy provided that there is no relaxation shift between the photoelectron data and the x-ray emission spectrum. The same binding energy is assigned to the valence soft x-ray emission if the data are referred to the binding energy of the $4d_{5/2}$ level—that is, if the binding energies are determined by subtracting the transition energies from the 87 eV binding energy of the $4d_{5/2}$ state.

Note that the relaxation shifts due to the response of other electrons, or the lattice, to the creation and annihilation of core vacancies may in general displace soft x-ray emission spectra toward lower energy with respect to binding energies determined on the basis of photoelectron measurements. For Al_2O_3, MgO, and SiO_2 the $L_{II,III}$ soft x-ray emission spectra are displaced toward lower energies by up to 1.2 eV with respect to the valence photoelectron spectra when referenced to the $L_{\mathrm{II,III}}$ core-level photoelectron binding energies.[19] This displacement is due to the generation of phonons in response to the creation of the core vacancies prior to their annihilation by radiative decay. If such phonon relaxation effects are operative prior to the valence $N_{\mathrm{IV,V}}$ transitions described here, they must result in an effect of smaller magnitude because in these compounds, the Fermi level occurs at the top of the soft x-ray emission band at an emission energy of 87 eV, which corresponds to the observed 4*d* binding energy.[2,3,18] The lack of a large phonon relaxation shift in the present example might be a consequence of the short lifetime of barium 4*d* core holes relative to those of Mg, Al, or Si 2*p* vacancies in the oxides of these elements. Decreased core-vacancy lifetime has also been offered as an explanation for the absence of a stokes shift in the emission spectra of elemental Mg, Al, and Si.[19]

Large displacements of the soft x-ray emission spectrum due to an electronic screening mechanism are also eliminated because population of such screening states also shifts the x-ray emission data toward smaller transition energies relative to photoelectron data. For boron in BN, for example, a 1.8 eV shift in the emission spectrum is observed at excitation energies tuned to populate the core exciton.[20] Similarly, a large shift of the measured spectrum toward lower transition energy due to such a relaxation effect would imply that the Fermi level lies in the emission band.

While a change in the binding energy of the $4d_{5/2}$ electron in $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ relative to that of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ has been suggested by the authors of Ref. 3 and explained by them as arising from a change in the initial state of the photoemission process, our measurements are consistent with no shift in the binding energy, at least for valence electrons of *p*-type symmetry. However, there appears to be a slight redistribution of intensity toward lower energy in the emission spectrum of $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ relative to that of $\mathrm{YBa_2Cu_3O_{7-\delta}}$. This intensity redistribution is suggested by the shading of the $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ spectrum shown in Fig. 4.

DISCUSSION

Several phenomena can alter or complicate the interpretation of x-ray emission spectra. Among these are: the energy dependence of the spectrometer response, reabsorption of radiation emitted within the sample (self-absorption), satellite emission features, and mulitplet splitting arising from spin-orbit interaction between open subshells.

The spectra presented here have been corrected for the energy dependence of the spectrometer sensitivity which was determined by comparing the bremsstrahlung profile in electron-beam-excited spectra from Al and Cu samples with literature reports[21] of these profiles. In any event the spectrometer response varies smoothly by less than 10% over the relatively narrow energy range of the valence emission and the shape of the measured valence emission band is relatively insensitive to errors in the spectrometer response correction that we have carried out.

The emission spectra presented here have not been corrected for sample self-absorption. An energy-dependent estimate of the absorption coefficient within the compound can be made using atomic photoionization cross-section data[17] and the sample density. A correction factor to take into account the reabsorption of soft x rays within the sample can be expressed in terms of the absorption coefficients of the ingoing and emitted radiation and geometrical factors:

$$I_{\mathrm{corrected}} = I_{\mathrm{measured}}\{1+[\mu_o \sec(\theta_o)/\mu_i \sec(\theta_i)]\}\ .$$

Where θ_i is the angle between the sample's surface normal and the incident radiation beam, θ_o is the angle between the normal and the detector, and μ_i and μ_o are, respectively, the absorption coefficients for the incoming and outgoing radiation beams. Over the energy range of the valence $\rightarrow$Ba 4*d* transitions this correction factor varies only slightly ($\sim 5\%$) because the absorption coefficient does not change strongly below the barium absorption edge.

Multiplet splitting can, in general, greatly complicate the interpretation of soft x-ray emission spectra. For barium in ionic compounds (or in barium metal for that matter) there is little electron population in open subshells and multiplet splitting is unimportant. Evidence of this is provided by the triplet of diagram lines that is characteristic of the $5p \rightarrow 4d$ core-core transition. The diagram lines for the compounds examined here are much sharper in energy than valence band features. Multiplet splitting would greatly broaden the transitions. This is the case for the lanthanide elements for which the $5p \rightarrow 4d$ transitions are broadened by interactions with the open 4*f* subshell.[22]

Another question that arises in the interpretation of soft x-ray emission spectra is whether the emission is sensitive to the presence of the initial core-level vacancy. X-ray emission requires the presence of an initial core vacancy; nevertheless the emission spectrum often closely follows the ground-state density of states distribution rather than calculations of the valence density of states around an atom including a core-level vacancy. For simple metals it has been demonstrated theoretically[23] that the x-ray emission spectrum closely follows one-particle calculations of the spectrum in the absence of the core vacancy as a consequence of many-body effects in the decay of the core vacancy. This is the so-called "final-state rule" (since the final state in the emission process contains no core vacancy). We note that x-ray emission spectra from CuO, $\mathrm{Cu_2O}$, and $\mathrm{Bi_2Sr_2CaCu_3O_8}$ (Ref. 24) also follow the relevant ground-level density of states. We also note that the observed energies of the $5p \rightarrow 4d$ transitions are consistent with the final-state rule. Recall that the observed photoelectron binding energies of the Ba $4d_{5/2}$ and $5p_{3/2}$ levels in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ are 87.0 and 12.0 eV, respectively.[18] A $5p_{3/2} \rightarrow 4d_{5/2}$ transition energy of 75.0 eV is thus expected on the basis of these binding energies. This value agrees with the observed $5p_{3/2} \rightarrow 4d_{5/2}$ transition energy of 75.3 to within the experimental error of a few tenths of an eV in both photoelectron and soft x-ray emission results. If the energy levels appropriate to determination of the transition energy were those in the presence of the core vacancy, a transition energy of ~ 79.4 eV $[=\{(102.5+89.9)/2\}-16.8$ eV] would be expected. Here we have made use of the equivalent cores approximation in estimating the binding energy of the 4*d* and 5*p* levels of barium in the presence of a 4*d* level vacancy, and have made use of tabulated values of the photoelectron binding energies in lanthanum and barium metal.[25] Note that the chemical shift on compound formation should be nearly the same for the 4*d* and 5*p* core levels and does not enter into the calculation.

Several observations demonstrate that the weak features observed in the emission spectra at transition energies greater than those of the $5p \rightarrow 4d$ core-core transitions arise from transitions of valence electrons into the initial core-level vacancies: (i) two emission features corresponding to transitions into $4d_{5/2}$ and $4d_{3/2}$ vacancies appear and are separated by the spin-orbit splitting of the 4*d* level; (ii) the photon energy dependence of the relative intensity of the valence features reflects the photon energy dependence of the relative intensity of the corresponding $4d \rightarrow 5p$ core-core transitions; (iii) for barium fluoride photoemission measurements of the valence region are available,[26,27] and indicate that the valence soft x-ray emission features coincide in energy (relative to the 5*p* core levels) with the barium fluoride valence band; (iv) the weak emission features differ in shape and transition energy for the various compounds; (v) the features cannot be explained as short-wavelength satellite emission.

The soft x-ray valence emission can, in principle, be interpreted in two ways: the emission may reveal hybridization of barium *p* states (5*p* or 6*p*) with the valence band; or the radiation might arise from cross transitions between states centered on adjacent atoms and the barium core vacancy. Similar questions on the origin of emission features have come up in the interpretation of emission spectra from various oxides, nitrides, and fluorides including BeO and AlN. In general the radiative intensity arising from transitions between states centered at one atomic site and a core state at a different atomic site is too weak to account for the observed emission.[28] The distinction is somewhat a matter of semantics and depends on how valence electron populations are assigned.

For barium titanate several electronic structural calculations have been reported.[29,30] Nemoshkalenko and Timosheusii[29] present a calculated barium N_{V} valence emission spectrum. The calculated N_{V} valence emission is ascribed to barium *p* and *f* states mixing with the oxygen 2*p* bands. The measured emission spectrum differs from the calculation both in its form and its energy position. The measured emission spectrum indicates a contribution to the partial density of states at the barium site extending over the energy range from 6 to 11 eV above the $5p_{3/2}$ state. According to x-ray photoemission spectroscopy measurements the binding energy of the barium $5p_{3/2}$ state is 14.3 eV.[31] The barium contribution to the valence band thus occurs with binding energies from ~ 3.3 to ~ 8.3 eV (in the absence of relaxation shifts). The calculated emission spectrum is broader than the measurements, with intensity extending up to the top of the valence band.

We are not aware of calculations of the barium $N_{\mathrm{IV,V}}$ emission spectrum for $\mathrm{YBa_2Cu_3O_{7-\delta}}$ or $\mathrm{PrBa_2Cu_3O_{7-\delta}}$. Richert and Allen[32] have however calculated strong *d*-states peaks for Y and Ba 5 eV above the Fermi level. A small barium contribution to the intensity of states is also apparent in their calculations in the region from zero to 5 eV below the Fermi level. The revelation of a small barium contribution to the electronic density of states in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ near the Fermi level may indicate a role for the alkali-earth ions in determining the properties of high-T_c cuprates. Similarly, Hamada *et al.*[7] have calculated the barium contribution to the electronic structure in $\mathrm{Ba_{1-x}K_xBiO_3}$. In their calculations the calculated intensity of the x-ray emission from the barium was small and showed a maximum in intensity about 3 eV above the Fermi energy. In discussions of the structural chemistry of high-T_c superconductors it has been suggested that the layers between the copper-oxygen planes in high-T_c cuprates serve as charge reservoir states.[33] In $\mathrm{YBa_2Cu_3O_{7-\delta}}$ it is believed that the copper-oxygen chains serve this role. The proximity of the barium-derived states to the Fermi level however suggests the possibility that they might also be important as charge reservoir states. The emission spectra of barium titanate and barium fluoride differ from those of the cuprates in that they indicate barium contributions to the density of states well below the Fermi energy.

The data presented in Fig. 4 strongly suggests that the Fermi level for valence band states of $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ and $\mathrm{YBa_2Cu_3O_{7-\delta}}$ of *p* symmetry have the same binding energy and the barium *p*-type partial density of states for the two compounds is almost identical, which suggest that charge transfer from other sites either does not exist or does not have *p*-type symmetry. According to the explanation offered by Yang and co-workers[2,3] the binding-energy change reflects changes in the relative population of a band derived from barium 5*d* levels localized at the barium site, and a delocalized band derived from barium 6*s* and oxygen 2*p* states. For $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ evidence of electron transfer to states less localized at the barium site was sought by comparing the ratio of the valence emission intensity to the $5p \rightarrow 4d$ core-core emission intensity for the $\mathrm{YBa_2Cu_3O_{7-\delta}}$ and $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ spectra. Note that the core-core emission intensity serves as a convenient means of normalizing the valence emission data. No significant change in the valence emission relative to the core-core emission intensity was noted. Two factors may contribute to the failure to observe a change. The measurements are sensitive to states of *p*-type symmetry at the Ba site. The bands involved in Yang's model are derived from barium 6*s* and 5*d* states. We are uncertain how much *p*-type character (at the Ba site) is mixed with the two bands. Furthermore, it may be that the amount of charge transfer is smaller than what the present experiment can detect.

The observation of barium contributions to the density of states in proximity to the Fermi energy in itself provides some support for Yang's model in that his model supposes barium-derived bands crossing the Fermi level. In addition there appears to be some slight redistribution of intensity toward lower energy in the emission spectrum of $PrBa_2Cu_3O_{7-\delta}$ which may indicate a shift in the energy of a barium-derived band when Pr is substituted for Y in $YBa_2Cu_3O_{7-\delta}$. It would be of interest to measure the fluorescence due to transitions into barium 5*p* vacancies. The measurements in this case would be directly sensitive to barium 6*s* and 5*d* levels.

SUMMARY

Photon-excites for x-ray emission has been used to obtain satellite free barium N_V and N_{IV} emission spectra. Weak features in the energy region above the $5p \rightarrow 4d$ core-core transitions arise due to transitions from states of the valence band. The barium $N_{IV,V}$ emission data were used to derive the barium *p*-type density of states distributions for BaF_2, $BaTiO_3$, $YBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$. We observed no significant shift in energy position or intensity distribution of the valence band. Neither did we observe a significant change in the valence emission relative to the core-core emission intensity. However, both the $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ emission data indicate a barium contribution to the occupied electronic density of states in the region immediately below the Fermi level. Our measurements indicate that the difference between the superconducting nature of $YBa_2Cu_3O_{7-\delta}$ compound and the insulating nature of $PrBa_2Cu_3O_{7-\delta}$ is not due to the *p*-like character of the barium partial density of states for the two compounds.

ACKNOWLEDGMENTS

These measurements were supported at the University of Tennessee and at Tulane University by National Science Foundation Grant No. DMR-8715430 and by a Science Alliance Center of Excellence Grant from the University of Tennessee. The National Synchrotron Light Source is supported by the DOE through Contract No. DE-AC02-CH00016. The authors would like to thank D. Temple of the Louisiana State University for providing the barium titanate single-crystal sample.

---

*Present address: Physics Department, Brooklyn College, Brooklyn, NY 11210.

[1] M. Ronay and D. M. Newns, Phys. Rev. B **39**, 819 (1989).
[2] I-S. Yang, A. G. Schrott, and C. C. Tsuei, Phys. Rev. B **41**, 8921 (1990).
[3] I-S. Yang, A. G. Schrott, C. C. Tsuei, G. Burns, and F. H. Dacol, Phys. Rev. B **43**, 10 544 (1991).
[4] T. Miyahara, T. Hanyu, H. Ishii, M. Yanagihara, T. Kamada, H. Kato, K. Naito, and S. Suzuki, J. Phys. Soc. Jpn. **55**, 408 (1986).
[5] R. D. Carson III, Ph.D. thesis, University of Virginia, 1989.
[6] A. Meisel, G. Leonhardt, and R. Szargan, *X-Ray Spectra and Chemical Binding* (Springer-Verlag, Berlin, 1989), p. 260.
[7] N. Hamada, S. Massidda, A. J. Freeman, and J. Redinger, Phys. Rev. B **40**, 4442 (1989).
[8] K-L. Tsang *et al.*, Phys. Rev. B **37**, 2293 (1988).
[9] D. R. Mueller *et al.*, Phys. Scr. **41**, 979 (1990).
[10] Reference 6, p. 42.
[11] N. Wassdahl, J.-E. Rubensson, G. Bray, P. Glans, P. Blekert, R. Nyholm, S. Cramm, N. Martensson, and J. Nordgren, Phys. Rev. Lett. **64**, 2807 (1990).
[12] T. A. Callcott, W. O'Brien, J. Jia, Q.-Y. Dong, D. L. Ederer, R. N. Watts, and D. R. Mueller, Nucl. Instrum. Methods Phys. Res. Sect. A **319**, 128 (1992).
[13] T. A. Callcott, K. L. Tsang, C. H. Zhang, D. L. Ederer, and E. T. Arakawa, Rev. Sci. Instrum. **57**, 2680 (1986).
[14] T. A. Callcott, C. H. Zhang, D. L. Ederer, D. R. Mueller, J. E. Rubensson, and E. T. Arakawa, Nucl. Instrum. Methods Phys. Res. Sect. A **291**, 13 (1990).
[15] B. Okai, K. Takahashi, H. Nozaki, M. Kosuge, and M. Ohta, Jpn. J. Appl. Phys. Lett. **26**, L1648 (1987).
[16] K. N. Tu, N. C. Yeh, S. I. Park, and C. C. Tsuei, Phys. Rev. B **39**, 304 (1989).
[17] E. B. Saloman, J. H. Hubbell, and J. H. Scofield, At. Data Nucl. Data Tables **38**, 1 (1988).
[18] F. Parmigiani, G. Pacchioni, C. R. Brundle, D. E. Fowler, and P. S. Bagus, Phys. Rev. B **43**, 3695 (1991).
[19] W. L. O'Brien, J. Jia, Q-Y. Dong, T. A. Callcott, K. E. Miyano, D. L. Ederer, D. R. Mueller, and C-C. Kao, Phys. Rev. B **47**, 140 (1993).
[20] W. L. O'Brien, J. Jia, Q.-Y. Dong, T. A. Callcott, K. E. Miyano, D. L. Ederer, D. R. Mueller, and C-C. Kao, Phys. Rev. Lett. **70**, 238 (1993).
[21] T. J. Peterson, Jr. and D. H. Tomboulian, Phys. Rev. **125**, 235 (1962).
[22] T. M. Zimkina, V. A. Fomichev, and S. A. Gribovskii, Sov. Phys. Solid State **15**, 1786 (1974).
[23] U. Barth and G. Grossmann, Solid State Commun. **32**, 645 (1979).
[24] D. R. Mueller, J. Wallace, D. L. Ederer, J. Jia, W. L. O'Brien, Q.-Y. Dong, and T. A. Callcott, Phys. Rev. B **46**, 11 069 (1992).
[25] *Center for X-ray Optics X-ray Data Booklet*, edited by D. Vaughan (Lawrence Berkeley Laboratory, University of California, Berkeley, 1986).
[26] W. Pong, C. S. Inouye, and S. K. Okada, Phys. Rev. B **18**, 4422 (1978).
[27] R. T. Poole, J. Szajman, R. C. G. Leckey, J. G. Jenkin, and J. Liesegang, Phys. Rev. B **12**, 5872 (1975).
[28] Reference 6, p. 276.
[29] V. V. Nemoshkalenko and A. N. Timoshevsii, Phys. Status Solidi B **127**, 163 (1985).
[30] V. R. Marathe, S. Lauer, and A. Trautwein, Ferroelectrics **25**, 367 (1980).
[31] L. T. Hudson, R. L. Kurtz, S. W. Robey, D. Temple, and R. L. Stockbauer, Phys. Rev. B **47**, 10 832 (1993).
[32] B. A. Richert and R. E. Allen, Phys. Rev. B **37**, 7869 (1988).
[33] R. J. Cava, Science **247**, 656 (1990).