Chemical composition and electronic structure of high-temperature superconductors: $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

Ming Tang, Y. Chang, M. Onellion, J. Seuntjens, D. C. Larbalestier, and G. Margaritondo
*Department of Physics, Material Science Program and Synchrotron Radiation Center,
 University of Wisconsin, Madison, Wisconsin 53706*

N. G. Stoffel and J. M. Tarascon

Bell Communications Research, 331 Newman Springs Road, Red Bank, New Jersey 07701

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We have studied the electronic structure of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0-0.15$) with synchrotron-radiation photoemission and electron-energy-loss spectroscopy. The results were compared to those previously obtained on $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$. The observed photoemission resonances are consistent with a prevailing Cu^{2+} valence state for copper. Partial-yield spectra of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ indicate that the valence state of Eu is Eu^{3+} , and that of Ba is Ba^{2+} , similar to the corresponding elements in $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$. From the energy-loss spectra, we derived plasmon energies and indications for peaks in the density of unoccupied states. The change in x for the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples only causes rigid shifts of the photoemission spectra.

I. INTRODUCTION

In recent months, the discovery of high-temperature superconductivity has stimulated unprecedented interest in transition-metal and rare-earth oxides such as $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$, and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.¹ The electronic properties of these materials are one key factor² for the explanation of the superconducting mechanism. Among the most important questions is the effect of the chemical composition on the electronic structure. In fact, several workers³ have reported that even small changes in the chemical composition strongly affect the transport properties.

We performed a systematic study of the effects of chemical composition on the electronic properties of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$, and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The experimental techniques were different modes of photoemission spectroscopy with synchrotron radiation and electron-energy-loss spectroscopy. The results discussed here, on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$, were obtained at room temperature. However, our previous studies of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ across the critical temperature did not reveal detectable changes in the spectra.⁴

Y and Eu compounds were selected for direct comparison since they exhibit some of the highest critical temperatures, and because of the interest in the effects of substituting trivalent Y with a rare earth like Eu, which can be either divalent or trivalent. As far as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is concerned, Sr substitution of La has been previously reported to affect the critical temperature,⁵ with the highest value occurring for $x=0.15$.

The main result of our study is that the valence electronic structure of these materials appears remarkably independent of the chemical composition. For example, only rigid shifts in energy were observed in the photoemission spectra of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ when x was changed. Likewise, the valence spectra of the Eu and Y compounds are very similar to each other, and also similar to those of

the La-Sr compounds. In particular, they confirm that the density of states is very low near the Fermi level for these high-temperature superconductors. The Cu-satellite photoemission resonances are, for all compounds, consistent with a Cu^{2+} valence state—although we cannot rule out a trivalent state due to the lack of information about the corresponding spectral features. The bulk plasmon energies are also remarkably close for $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$. The photoemission spectra taken in the partial-yield mode identify the valence state of Eu as primarily trivalent, and that of Ba as divalent.

II. METHODOLOGY

The samples, in the form of sintered pellets, were mounted on a copper holder using a conductive, ultra-high-vacuum compatible glue (ohmex), and cleaned with a diamond grinder under ultrahigh vacuum. Photoemission spectra were taken with a double-pass cylindrical mirror electron energy analyzer, using photons produced by the Grasshopper Mark V and the General Motors-Wisconsin ERG beamlines of the Wisconsin Synchrotron Radiation Center. Electron-energy-loss spectra were taken on the $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ samples in the negative second-derivative mode. The electron beam was produced by a coaxial electron gun within the cylindrical mirror analyzer. The same gun was used for Auger analysis.

The above processing method has been extensively used to produce clean polycrystalline surfaces of many different kinds of materials, suitable for electron spectroscopy experiments. In the present case, we did not find evidence for substantial spectral contributions from carbon contamination. Some question exists about the possible carbon-related origin of a photoemission feature found for all materials approximately 9.5–9.7 eV below the Fermi level. However, in preliminary tests on sintered and

single-crystal carbon-free samples of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, we still found such a feature, therefore its carbon-related origin is not demonstrated. The results were carefully monitored for changes with time, and such changes were observed in some cases. The spectra presented here are, to our best knowledge, free from these problems. In particular, the working pressures in the low- 10^{-10} Torr range or below were sufficient to keep the clean surfaces immune from contamination over many hours.

In previous experiments on Y compounds,⁴ we found that unmonochromatized synchrotron radiation can cause changes in oxygen composition similar to those induced by thermal annealing. These experiments enabled us, in particular, to identify the spectral features which are changed upon oxygen depletion. We were careful in avoiding accidental depletion of oxygen, and in fact our spectra are consistent with those obtained for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ samples not affected by such a depletion.

III. EXPERIMENTAL RESULTS

Figure 1 shows a series of valence-band photoemission energy distribution curves, taken at different photon energies on $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$. The photon energies include values close to the Ba $5p$ resonance, triggered by the Ba $4d$ optical absorption threshold ($h\nu=100$ and 105 eV

FIG. 1. Photoemission energy distribution curves (EDC's) taken on the high-temperature superconductor $\text{Ba}_2\text{EuCu}_3\text{O}_{7+x}$ at room temperature and for different photon energies. Notice the photoemission resonances, discussed in the text. The EDC's were normalized to the intensity of the main peak.

spectra), and the Cu satellite resonance at the Cu $3p$ threshold ($h\nu=74$ and 76 eV spectra).

The spectra of Fig. 1 are quite similar to those we reported for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ in Ref. 4. These similarities are interesting because of the possibility of a different valence state for Eu with respect to trivalent Y—this point will be discussed in detail later. Note, in particular, the low density of states near the Fermi energy, E_F , in Fig. 1, very similar to that reported in Ref. 4. Likewise, the feature closest to E_F , i.e., the oxygen-derived shoulder most easily observed at the lowest photon energies, is equally prominent for the Eu and Y compounds, and the main valence-band feature, at -5.1 eV, is essentially the same for both materials. This latter feature is predominantly Cu derived. The similarity between the $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ spectra is also present for the next feature at -9.7 ± 0.2 eV. As we already mentioned, this feature is attributed by some authors to carbon contamination, but we did not reach conclusive evidence about its origin from experiments on nominally C-free samples.

The Cu-satellite resonant feature is clearly visible in Fig. 1 at -12.7 eV. This feature is again quite similar to that observed⁶ for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, after eliminating second-order signal which affected some of the early data.⁴ Finally, there is a very strong photoemission resonance in Fig. 1 for the Ba $5p$ doublet at -14.3 and -16.0 eV, the same binding energies observed for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$.

A more complete assessment of the effects of substituting Y with Eu was made by performing photoemission experiments in the partial-yield mode of photoemission spectroscopy. As it is well known, the corresponding spectra primarily correspond to optical absorption spectra in the surface region, with possible primary-photoelectron contributions. Partial-yield spectra are shown in Fig. 2 for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$. The spectra were taken by setting the kinetic energy window of the analyzer at 3 eV, and scanning the photon energy in the range 80 – 160 eV.

For both spectra in Fig. 2, the marked edge at

FIG. 2. Partial-yield spectra of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$. These spectra were taken by collecting photoelectrons of kinetic energy 3 eV while scanning the photon energy, $h\nu$.

FIG. 3. Electron-energy-loss spectra of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ taken with incidence-electron energies of 150 and 200 eV. The spectra were measured in the negative-second-derivative mode.

$h\nu=100\text{--}105$ eV is due to the Ba $4d$ optical absorption threshold, which exhibits a centrifugal-barrier "delayed onset."⁷ The structure at $h\nu=115\text{--}125$ eV is also similar for both compounds. Note, in particular, that we were able to resolve the multiple Fano line shape of this feature for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, which was unresolved in the data of Ref. 4. The $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ spectrum in Fig. 2 exhibits four features in the range $h\nu=130\text{--}160$ eV, at 136, 139, 144, and 153 eV, not present for the Y compound. The latter has only a barely visible feature in this region, at $h\nu=141\text{--}142$ eV.

In our earlier report on $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$,^{4,8} we used electron-energy-loss data in combination with photoemis-

FIG. 4. Photoemission spectra corresponding to the valence band and to the La $4d$ core level, taken at a photon energy of 130 eV on $\text{La}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_4$. The spectra are shown for the compositions $x=0, 0.03$, and 0.10 . The substitution of La with Sr only causes a rigid shift of the spectral features.

sion data to derive information on the *unoccupied* density of states up to a few electron volts above E_F . We extended this approach to $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$. Figure 3 shows electron-energy-loss spectra obtained with primary electron energies of 150 and 200 eV. For primary energy of 150 eV, the spectrum exhibits peaks at 4.8, 10.6, 17.1, 24.3, and 33.3 eV. For the primary electron energy of 200 eV, the loss spectrum exhibits the same peaks, plus one at 38.7 eV. The uncertainty in these peak positions is ± 0.6 eV.

Photoemission spectra were taken on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples with four different values, $x=0.0, 0.03, 0.10$, and 0.15 . The critical temperature increases monotonically between $x=0.0$ and $x=0.15$.⁸ Therefore, samples in this composition range are very important in the study of the superconducting mechanism. For example, a structure was observed in the infrared reflectance spectrum below 0.9 eV, whose intensity correlates to the critical temperature.⁵ Some of our photoemission results are reported in Fig. 4, for the valence band as well as for the La $4d$ core level. Note that both the valence band and the La $4d$ core levels exhibit a rigid shift to higher binding energies as the Sr content increases.

IV. DISCUSSION AND CONCLUSIONS

The first point in our discussion concerns the effects of the substitution of Y with Eu in $\text{Ba}_2\text{Y(Eu)Cu}_3\text{O}_{7-x}$. A comparison of the corresponding data leads us to four important results.

(1) Both samples exhibit the same valence-band structure, including clear resonances at $h\nu=74\text{--}80$ eV, $h\nu=100\text{--}110$ eV, and an unambiguous feature at -9.7 ± 0.2 eV.

(2) Both samples exhibit, in the partial-yield spectra (Fig. 2) a multiple Fano line shape between $h\nu=115\text{--}130$ eV.

(3) The $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ sample exhibits four additional features in the partial-yield spectrum between $h\nu=130\text{--}160$ eV, not observed for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$.

(4) The energy-loss spectrum of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ (Fig. 3) can be compared directly to that previously reported⁸ for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, and interpreted along the same lines.

The fact that the valence-band structure is equal for the two materials, within experimental error, is not unexpected. Y is viewed theoretically⁹ as totally ionic in the Y^{3+} state—although our data provide no direct evidence of the Y valence state. Our present investigation does provide direct information on the Eu valence state. The $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ partial-yield results include four features between $h\nu=130\text{--}160$ eV. These are very close in line shape and energy spacing to those reported¹⁰ for a series of rare-earth trifluoride compounds. This evidence indicated that the europium is primarily in a trivalent state. A prevailing trivalent Eu state is consistent with the similarity in the valence-band spectra of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, since Y is also trivalent, as well as with the variations of the lattice parameter through the rare-earth series. On the other hand, susceptibility measurements reported in Ref. 11 indicate the presence of a small amount of divalent Eu.

Our present valence-band spectra also corroborate the tentative conclusion of Ref. 4, based on the Cu-satellite resonance, that Cu is in a divalent state and not in a monovalent state. Our results do not answer the question of whether Cu is also found in the Cu^{3+} valence state, since we have no reference to test that possibility. Finally, as far as the valence state of Ba is concerned, the energy position of the Ba $4d$ threshold indicates a divalent state for both $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$. The multiple Fano line shape observed at $h\nu = 115\text{--}125\text{ eV}$ is due to resonances corresponding to transitions from the Ba $4d$ doublet to $4f$ final states.

Like the valence-band photoemission and partial-yield results, the electron-energy-loss spectra of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ (Fig. 3) are quite similar to those of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$.⁸ The loss features in Fig. 3 correspond to the features A, C, D, F, G, and I in Ref. 8. In particular, the feature at 24.3 eV is due to the creation of bulk plasmon. Its position coincides within the experimental uncertainty with the bulk plasmon energy of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, 24.6 eV.⁸ We interpret the feature at 17.0 eV, like the one observed in the same position for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, as a surface plasmon peak.

The remaining energy-loss features can be interpreted in terms of quasioptical transitions. Using the same analysis as in Ref. 8, we find that the peaks can be explained using the initial-state features derived from photoemission, and assuming only two peaks in the unoccupied density of states, one 2–2.5 eV [state (a)] and the other 4–4.6 eV above E_F [state (b)]. This analysis attributes the 4.8 eV energy-loss feature to transitions from the predominantly oxygen-derived initial state (shoulder) immediately below E_F , to the unoccupied state (a). A comparison with the $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ spectra indicates that the feature at 10.6 eV in Fig. 3 actually corresponds to two unresolved peaks (at 8.7 and 11.8 eV in Ref. 8). The prevailing contribution to the features is due to transitions from an oxygen $2p_z$ state to the state (a). The feature at 33.3 eV loss energy corresponds to Ba $5s \rightarrow (b)$ transitions. The photoemission data on the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples revealed two important points.

(1) There is again an overall correspondence in the upper valence-band line shape of these samples and of $\text{Ba}_2\text{Y}(\text{Eu})\text{Cu}_3\text{O}_{7-x}$.

(2) There are no modifications in the spectral line shapes when x is changed. We only find that the valence-band features and the La $4d$ core levels rigidly shift to lower kinetic energies as the fraction of Sr increases. P -type doping by Sr could cause rigid shifts, but these would be expected to occur in the opposite direction with respect to those observed. The shifts could be explained by changes in the band bending, since the reported forbidden

gap for LaCuO_4 is much larger than the maximum observed shift of 0.4 eV.

The similarity between the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Ba}_2\text{Y}(\text{Eu})\text{Cu}_3\text{O}_{7-x}$ spectra, in particular as far as oxygen-derived states are concerned, is one example of the detailed correspondence between our data and the results of theoretical calculations.² Relevant points of agreement between theory and experiment are listed below.

(1) A very large density of states is predicted several electron volts above E_F , primarily derived from La or Y(Eu) states, while the contributions from Ba are small.⁵ The strongest peak in this predicted density of unoccupied states is $\sim 5\text{ eV}$ above E_F , in agreement with peak (b) derived from our energy-loss data. Note, however, that this would leave unexplained peak (a). An alternate interpretation identifies peak a with the theoretical feature at $\sim 5\text{ eV}$, and peak (b) with upper theoretical features.

(2) The effect of Eu substitution for Y is theoretically predicted to be negligible, in particular for a prevailing trivalent valence state of Eu.

(3) For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Ba}_2\text{Y}(\text{Eu})\text{Cu}_3\text{O}_{7-x}$ the peaks in the Cu and oxygen densities of states are predicted to be separated by 2.0–2.5 eV.

(4) For both $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Ba}_2\text{Y}(\text{Eu})\text{Cu}_3\text{O}_{7-x}$, the density of unoccupied O-derived state 0–5 eV above E_F is predicted to be low, and the density of Cu-derived states to be only slightly higher.

In summary, the theoretical calculations correctly predict many of the most important features derived from our spectra. One significant discrepancy, however, occurs for the observed $\sim 4.7\text{--}5.4\text{ eV}$ separation between Cu-derived and O-derived valence-band states—the theory would predict a smaller separation of 2.0–2.5 eV.² We also emphasize that comparisons between single-particle theories and experimental data must be made *cum grano salis* for these materials. It has been recently argued¹² that many-body effects play an important role, and the observed Cu-satellite resonances for all compounds are a nice example of such effects.

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¹For a very recent review of this rapidly evolving field, see *Proceedings of the First International Conference on High-Temperature Superconductors, Philadelphia, Pennsylvania, 1987* [Rev. Sol. State Science (to be published)].

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