PHYSICAL REVIEW B VOLUME 40, NUMBER 13 1 NOVEMBER 1989

Photoemission study of absorption mechanisms in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, $BaBiO_3$, and $Nd_{1.85}Ce_{0.15}CuO_4$

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(Received 15 May 1989)

Photoemission measurements in the constant-final-state (absorption) mode were performed on three different classes of high-temperature superconductors $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, $BaBiO_3$, and $Nd_{1.85}Ce_{0.15}CuO_4$ using synchrotron radiation from 20 to 200 eV. Absorption signals from all elements but Ce are identified. The results firmly show that the Bi 6*s* electrons are more delocalized in $BaBiO_3$ than in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, in agreement with the results of band-structure calculations. Differences in the absorption signals due to O and Bi excitations between $BaBiO_3$ and $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$ are discussed. Delayed absorption onsets attributed to giant resonances (Ba $4d \rightarrow 4f$, La $4d \rightarrow 4f$, and Nd $4d \rightarrow 4f$ transitions) are also reported.

Absorption spectroscopies have been used extensively to study the electronic structure of high-temperature superconductors. X-ray absorption near-edge spectroscopy, and electron-energy-loss spectroscopy measurements have provided important information on the character of the occupied as well as the unoccupied states for a variety of Cu-O–based superconductors.[1–3] One of the main attractions of absorption measurements is the ease with which information can be gained about the symmetry, energy separation, and widths of the states involved in the transitions. In fact, absorption spectroscopies performed on single-crystalline materials today provide one of the most powerful experimental techniques in elucidating anisotropic effects on the electronic structure.

Photoemission spectroscopy operated in the constant-final-state (CFS) mode at low kinetic energies has been shown to give spectra that essentially reflect the absorption of radiation as a function of the photon energy.[4] This is mainly due to the fact that the vast majority of the electrons that leave a solid at nearly zero kinetic energy has been scattered inelastically on their way out from the solid, and thus mimics the absorption of radiation.

In this paper we have studied the absorption signals of single crystals of $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, and pellets of $BaBiO_3$, and $Nd_{1.85}Ce_{0.15}CuO_4$ by recording photoemission spectra in the CFS mode in the energy range 20–200 eV. The data show evidence of absorption signals involving all elements except Ce. In particular, giant absorption resonances due to Ba$4d \rightarrow 4f$, La$4d \rightarrow 4f$, and Nd$4d \rightarrow 4f$ transitions are identified. Obvious difference in the absorption mechanisms involving Bi and O states in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, and $BaBiO_3$ are reported and discussed.

The preparations of the materials studied in this work are described elsewhere.[5–7] Onsets for superconductivity were found at 90 and 24 K, for the samples of $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, and $Nd_{1.85}Ce_{0.15}CuO_4$, respectively, while the sample of $BaBiO_3$ was found nonsuperconducting.

The photoemission measurements were conducted in a Varian photoemission chamber on beam line *I*-1 at Stanford Synchrotron Radiation Laboratory. Electromagnetic radiation in the photon energy range 20–200 eV, including second- and third-order light, was used for excitation. A cylindrical mirror analyzer collected the electrons emitted in a cone centered at normal emission. The constant-final-state spectra presented in this paper were recorded at an overall energy resolution of ~1.5 eV. The pellets of $\mathrm{BaBiO_3}$ were scraped *in situ* using a diamond file, while the pellets of $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$ and the single crystals of $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$ were cleaved by *in situ* fracturing. All measurements were carried out at a pressure of less than 2×10^{-10} torr.

In the following, constant-final-state (CFS) curves will be presented for three different compounds, and the origins of the absorption features will be discussed. Since the number of features observed is rather large, a table summarizing the energy position and character of the absorption peaks is provided (Table I). For a quick identification of the absorption features appearing in Figs. 1 and 2, we refer the reader to the concise information given in this table.

Figure 1 shows CFS curves from a single crystal of (a) $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$ and (b) a pellet of $\mathrm{BaBiO_3}$ in the photon energy range 10–35 eV. A comparison of the two CFS curves in Fig. 1 shows that the absorption signals in the two compounds are markedly different, which cannot be explained solely by the different elements in the two compounds. At the lower photon energies, evidence of a clear difference in the semicore Bi6s and O2s states is observed. Peak $a1$, which appears only for $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$, is assigned to Bi6$s\rightarrow6p$ transitions.[8] The reason for its absence in $\mathrm{BaBiO_3}$ is that the Bi6s states are occupied quite differently in the two compounds.[9,10] Band calculations show that the Bi6s states are fully occupied and strongly localized in $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$, while the corresponding states in $\mathrm{BaBiO_3}$ are only partially occupied and exhibit a delocalized nature, extending over an energy range of almost 16 eV.[9,10] These theoretical predictions are also in agreement with the experimentally measured valence bands of these compounds.[11,12] Thus, a sharp absorption signal due to Bi6$s\rightarrow6p$ transitions is expected in $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$ but not in $\mathrm{BaBiO_3}$.

Both $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$ and $\mathrm{BaBiO_3}$ exhibit O2$s\rightarrow$O2p absorption features in the vicinity of 20 eV ($a2$ and $b1$). However, a closer examination of the two features reveals a clear difference in the peak positions. While peak $a2$ centers around 18 eV, peak $b1$ reaches its maximum first around 20–21 eV. Again, the differences

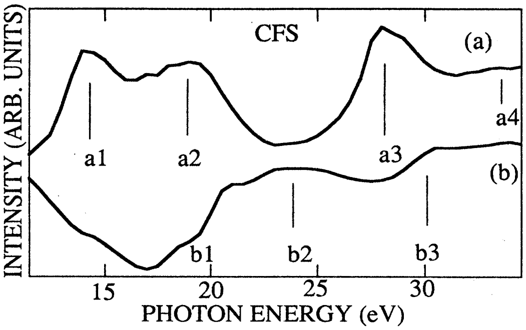

FIG. 1. Constant-final-state (CFS) curves measured from a single-crystalline sample of (a) $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$ and a pellet of $\mathrm{BaBiO_3}$.

TABLE I. Summary of absorption features observed in the three types of compounds: (a) $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$, ($b$) $\mathrm{BaBiO_3}$, and (c) $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$. The superscripts (2) and (3) indicate that second- and third-order light have been used.

Peak	Transition
$a1$ (14 eV)	Bi6$s\rightarrow6p$
$a2$ (18 eV)	O2$s\rightarrow2p$
$a3$ ($\sim$28 eV)	Bi5$d\rightarrow6p$, Sr4$p\rightarrow4d$
$a4$ (33 eV)	Ca3$p\rightarrow3d$
$a5$ (37 ev)	Final-state effect
$a6$ (124 eV^3)	La4$d\rightarrow4f$
$a7$ ($\sim$170 eV^3)	Bi4$f\rightarrow6p$, continuum
$a8$ (75 eV)	Cu3$p\rightarrow3d$
$b1$ ($\sim$20 eV)	O2$s\rightarrow2p$
$b2$ ($\sim$22–25 eV)	Ba5$p\rightarrow5d$
$b3$ ($\sim$30 eV)	Bi5$d\rightarrow6s$, continuum
$b4$ (37 eV)	Final-state effect
$b5$ (117 eV^3)	Ba4$d\rightarrow4f$
$b6$ ($\sim$165 eV^3)	Bi4$f\rightarrow6s$, continuum
$c1$ (130 eV^3)	Nd4$d\rightarrow4f$
$c2$ (130 eV^2)	
$c3$ (75 eV)	Cu3$p\rightarrow3d$

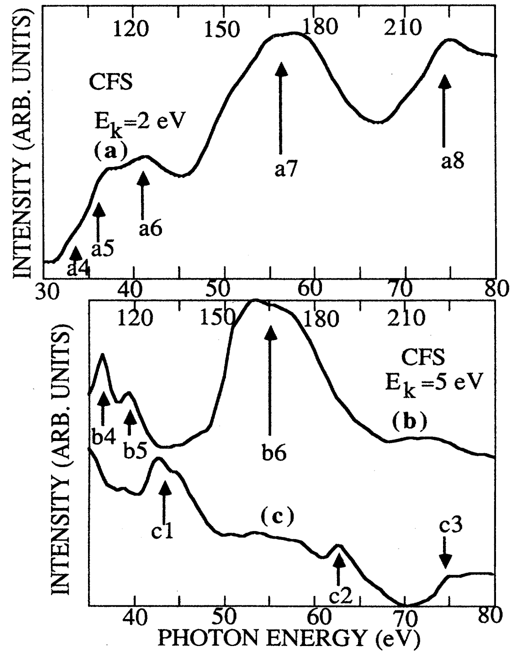

FIG. 2. Constant-final-state (CFS) curves from a single-crystalline sample of $\mathrm{Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}}$ [top panel, (a)] in comparison with CFS spectra recorded from pellets of (b) $\mathrm{BaBiO_3}$, and (c) $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$ shown in the bottom panel.

observed can be traced back to the character of the occupied states, as determined by photoemission experiments that suggest that the O2*s* states are located at higher-binding energy in $BaBiO_3$ than in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$ (Refs. 11 and 12).

Around 21–24 eV, an obvious difference between the two spectra is seen; while curve (*a*) exhibits a clear dip in this region, a broad peak (*b*2) appears in curve (*b*). This peak is associated with Ba5$p \rightarrow$5d transitions ($-17, -15$ eV$\rightarrow \sim 7$ eV).[11,13] Note that these transitions may distort the O2$s \rightarrow$2p absorption signal at a few eV lower-photon energy.

The prominent feature at about 28 eV in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$ (*a*3) is believed to be composed of absorption signals due to Bi5$d \rightarrow$6p, and Sr4$p \rightarrow$4d excitations, as suggested by a recent angle-resolved photoemission study of the absorption in an identical sample.[8] The small shift of *a*3 toward lower energies (~ 1 eV) as compared to the centroid of the individual peaks in the angle-resolved study is probably due to third-order light at 75–80 eV (that is 25–27 eV on this scale) that gives rise to Cu3$p \rightarrow$3d excitations, that show up as a shoulder on the low-energy side of *a*3. Peak *b*3, which appears at slightly higher photon energies, is attributed to Bi5$d \rightarrow$6s transitions. It is important to note that this absorption feature starts to grow first at 28 eV photon energy, although the Bi5*d* states are located at -25.8 and -28.8 eV.[11] This delay can be explained by again referring to band calculations, which show that the unoccupied Bi6*s* states in $BaBiO_3$ are fairly localized with a sharp maximum in the partial density of states between about 3 and 5 eV above the Fermi level.[9] Finally, the weak feature *a*4 can be assigned to Ca3$p \rightarrow$Ca3d transitions from the experimentally determined energy separation between the Ca3*p* and Ca3*d* states.[8]

At higher photon energies pronounced absorption features due to the other elements can be observed as shown in Fig. 2. Again it needs to be emphasized that third-order light, and to a smaller degree second-order light ($3\times h\nu, 2\times h\nu$), contribute significantly to the photon flux, and therefore can be used to study absorption mechanisms from deeper core levels. To clarify this, two energy scales are used in Fig. 2, the lower one giving the scale for first-order light, and the upper one the scale for third-order light. Note that the "energy step" for third-order light on this scale is only one third of the energy step for first-order light. In other words, features due to third-order light will appear narrower than features (with the same physical width) excited by first-order light.

In Fig. 2, we compare CFS curves for (*a*) $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, (*b*) $BaBiO_3$, and (*c*) $Nd_{1.85}Ce_{0.15}CuO_4$ for higher-photon energies. Such a comparison is helpful not only in pointing out differences among the various compounds, but also in identifying the origin of the absorption signals. A striking difference between curves (*a*) and (*b*) on the one hand, and curve (*c*) on the other, is the presence of a pronounced absorption structure around 150–190 eV (third-order light) in curves (*a*) (*a*7), and (*b*) (*b*6) but not in (*c*). This comparison, together with an examination of the positions of the occupied and unoccupied states of all the constituents, shows that structures *a*7 and *b*6 are due to Bi4*f* excitations.[14] We also note that peak *b*6 is sharper than *a*7, and that its centroid appears to be shifted to somewhat lower photon energy than that of *a*7. Again, this difference between the two Bi-based compounds can be related to more localized empty states of Bi in $BaBiO_3$ than in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$.[9,10] Note, however, that Sr3d(~ -133 eV)$\rightarrow$ continuum excitations are expected to contribute to the early onset of peak *a*7, so the energy region below 150 eV is not representative for the comparison of the Bi states in the two compounds.

A common characteristic of all three compounds shown in Fig. 2 is the presence of giant metal 4$d \rightarrow$4f absorption mechanisms.[15] Absorption signals due to Ba4$d \rightarrow$4f (*b*5 at 117 eV), La4$d \rightarrow$4f (124 eV), and Nd4$d \rightarrow$4f (*c*1 and *c*2 at 130 eV) are identified from the spectra. As expected from the stoichiometry of the compounds, the relative intensity within each spectrum decreases in the order Nd4$d \rightarrow$4f, Ba4$d \rightarrow$4f, and La4$d \rightarrow$4f. We note the delayed onset of these absorption signals, presumably due to strong correlation effects among the strong localized 4*d* and 4*f* states, as has been observed previously for a number of rare-earth compounds.[16,17] In fact, the energy separation between the Ba4*d* and Ba4*f* (La4*d* and La4*f*) states is expected to be close to 104 eV (112 eV) from the experimentally determined energy levels, that is of the order of 10-eV lower energy than the absorption thresholds indicate.[11,13,18,19]

The origin of peaks *a*5 and *b*4 that appear to coincide in energy is presently not completely understood. One possibility is that final-state effects give rise to these peaks, since it was shown that by changing the kinetic energy of the analyzed electrons in the CFS spectra recorded from $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, the intensity of peak *a*5 changed dramatically. Peak *a*4, however, can be easily identified as due to Ca3$p \rightarrow$3d transitions by referring to Fig. 1, and previously recorded data.[8]

Finally, at the higher-energy part (first-order light) of Fig. 2, evidence of Cu3$p \rightarrow$3d excitations is found in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$ (*a*8), and $Nd_{1.85}Ce_{0.15}CuO_4$ (*c*3). As expected from resonance photoemission data, these structures peak at 74–75 eV.[20,21] Again, we note that the absorption feature in (*a*) appears broader than the corresponding feature in the lower panel of Fig. 2, thus indicating that the empty Cu3*d* states may be more delocalized in $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$ than in $Nd_{1.85}Ce_{0.15}CuO_4$.

In summary, photoemission spectra in the constant-final-state (CFS) mode were recorded from three different types of high-temperature superconductors $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$, $BaBiO_3$, and $Nd_{1.85}Ce_{0.15}CuO_4$. Absorption signals from all elements except Ce are identified. Comparison of the absorption spectra from $Bi_{2.0}Sr_{1.8}Ca_{0.8}La_{0.3}Cu_{2.1}O_{8+\delta}$ and $BaBiO_3$ reveals a clear difference in the Bi6*s* states in the two compounds, in agreement with the predictions of band calculations. For all samples, absorption signals due to giant resonances (Ba4$d \rightarrow$4f, La4$d \rightarrow$4f, and Nd4$d \rightarrow$4f transitions) are observed. In general, a good agreement between the energy positions of the absorption peaks, and the energy separation of the occupied and unoccupied states involved in a transition, is found, with the exception of the giant $4d \rightarrow 4f$ absorption signals that are delayed by about 10 eV.

ACKNOWLEDGMENTS

We are thankful for the help of Dr. M. Sherman in performing the photoemission experiments. Four of the authors would like to acknowledge support received from the National Science Foundation (NSF) (D.S.D.), AT&T (D.B.M.), the Alfred P. Sloan Foundation and the Presidential Young Investigator Program (A.K.), and the Norwegian Council for Research and the Humanities (A.B.). The financial support from the U.S. National Science Foundation through the National Science Foundation–Materials Research Laboratory (NSF-MRL) program at the Center for Materials Research at Stanford University, and Air Force Contract No. AFSOR-87-0389 is gratefully acknowledged. We also wish to thank the staff at the Stanford Synchrotron Radiation Laboratory (SSRL) for technical assistance. The work done at SSRL was funded by the U.S. Department of Energy (DOE) under Contract No. DE-AC03-82ER-13000, Office of Basic Energy Sciences, Division of Chemical/Materials Sciences.

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