

Electronic structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$: Near-O-1s-threshold excitation x-ray fluorescence studies

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 (Received 27 January 1994; revised manuscript received 8 November 1994)*

The character of unoccupied and occupied states in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ was investigated by measuring O 1s x-ray absorption and O $K\alpha$ x-ray emission spectra. To record the latter, various excitation energies around the O 1s edge were used. An appreciable excitation energy dependence for the emission spectra was observed and it was attributed to changes in the relative number of excited inequivalent oxygen atoms. It was found that the first, second, and third prepeaks near the O 1s edge of the Tl-based cuprate are mainly related to the oxygen atoms in the CuO_2 , BaO, and TlO planes, respectively, whereas, the single prepeak in the O 1s absorption spectrum of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ is due to transitions to the in- CuO_2 -plane oxygen 2p states. Analysis of the results obtained suggests that there are doping-induced holes on all the types of the O atoms in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and only at in- CuO_2 -plane oxygen sites in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

I. INTRODUCTION

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ have a similar crystal structure (see, for example, Ref. 1) with three types of oxygen atoms located in CuO_2 [O(1)], Sr(Ba)O [O(2)], and Bi(Tl)O [O(3)] layers. However, in spite of this similarity there are differences in the electronic structure and superconducting properties. The Bi-based cuprate has a transition into the superconducting state at ~ 85 K;² for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, T_c has been found to be ~ 110 K.³ While Bi has the valency states 3+ (as in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$) and 5+, Tl can exist in the form of Tl^+ and Tl^{3+} ions. In fact, in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ a mixed valency state for Tl atoms has been found.⁴ The out-of-plane bond lengths of Tl-O(2) and Tl-O(3) are shorter than the in-plane bond lengths of Tl-O(3),¹ making charge transfer and interlayer coupling quite probable.^{5,6} In turn, in the Bi-based oxide the interlayer distance between Bi and O(3) is longer than the in-plane Bi-O(3) distance.¹

The unoccupied states of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ have been investigated in a number of publications using x-ray absorption⁷⁻¹¹ (XAS) and electron-energy-loss^{5,12} (EELS) spectroscopies. It has been found that the O 1s-edge XAS or EELS spectra of these two compounds are different. For the Tl-based cuprate, three prepeaks at ~ 527.8 eV, 529.0 eV, and 530.5 eV are observed whereas in the Bi-based oxide only

one prepeak appears at ~ 528.5 eV.

However, these techniques probe only the symmetry of unoccupied states (in the case of polarization-dependent measurements) and cannot distinguish between inequivalent O sites. In order to assign features in the O 1s absorption spectra to different O atoms one should know the O 1s binding energies for these atoms. Referring to the O 1s chemical shifts estimated from the local-(spin)-density-approximation [L(S)DA] calculations^{6,13} Römberg *et al.*⁵ have attributed the three prepeaks near the O 1s edge of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ to transitions to the O(1), O(2), and O(3) 2p states, respectively. In contrast to these assignments, the O 1s binding energies for O(2), O(1), and O(3) have been concluded to be 528.1 eV, 528.9 eV, and 529.7 eV,¹⁴ respectively, based on the analysis of x-ray photoemission spectroscopy (XPS) data. Furthermore, a similar sequence of the O 1s levels has also been suggested for $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$.¹⁵

For $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, the O 1s chemical shifts for inequivalent atoms have also been discussed in a number of publications.¹⁶⁻²³ However, the reported values which we summarize in Table I are inconsistent and contradictory.

Since the charge carriers in *p*-doped high- T_c superconductors have mainly O 2p character, it is important to make an O-site identification for features appearing in the O 1s absorption spectra. Such an identification helps to draw the picture on the induced-hole distribution over different O atoms and can clarify the role of

TABLE I. The O 1s binding energies (eV) reported for inequivalent O sites in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

Reference	CuO_2	SrO	BiO
17	lowest	+1.06	+1.57
14	529.1	528.4	529.9
18	527.9	529.1	528.6
19	527.9	529.4	528.7
20	529.2	528.5	528.5
21	531.0	528.9	531.9
22	528.3	528.3	529.0; 530.0
23	528.45	528.95	528.95

these atoms in high- T_c superconductivity. In the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ the reviewed variety of reported data on the O 1s binding energies for inequivalent O sites hampers an interpretation of the O 1s absorption spectra and requires the application of a technique which provides the opportunity to probe the contributions of different O atoms in one or another way. Such information can be obtained with soft x-ray emission spectroscopy (XES) with tunable excitation, as shown for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.²⁴ This method is based on the analysis of the profile of the O $K\alpha$ (1s-2p transition) x-ray emission spectra recorded at different excitation energies through the O 1s edge and it is most efficient when there is a strong difference in the x-ray absorption cross sections for inequivalent O atoms as well as in their 2p contributions to the emission spectra. For such an analysis, several ways can be used to identify the O $K\alpha$ emission spectral profile corresponding to different O sites. One can tune the excitation energy to the region of the O 1s edge where a predominant contribution of specific sites is expected because of the admixture of unoccupied O p states to the states of one of the cations. Thus, in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$,²⁴ the O $K\alpha$ band for apical oxygen atoms has been recorded by tuning the excitation energy to the region of the O p states hybridized with the La 5d states. Other ways to obtain site-selective O $K\alpha$ spectra are to study the model systems [e.g., (Ca,Sr)CuO₂ for O(1)] or to use theoretical considerations and the results of band structure calculations.

In this paper the results of the O 1s x-ray absorption and selectively excited O $K\alpha$ x-ray emission measurements for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ are presented. It is shown that, by virtue of the difference in the O K absorption cross section between different inequivalent O atoms and for different excitation energies, one can preferentially excite one or the other oxygen site by tuning the excitation energy, thereby separating the p contributions of these particular atoms at the Fermi level and in the conduction band. For $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ the first, second, and third prepeaks near the O 1s edge are found to be mainly related to transitions to the O(1), O(2), and O(3) 2p states, respectively. In turn, a single prepeak in the O 1s edge of the Bi-based cuprate mainly originates from the O(1) states. It is suggested that the unoccupied oxygen states at the Fermi level have O(1), O(2), and O(3) 2p character in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ whereas they only have O(1) 2p character in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

II. EXPERIMENT

The synthesis of the $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ sample was carried out using a two-step procedure. In the first step stoichiometric amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, CaO, and Tl_2O_3 were milled in an agate mortar using ethanol as a milling aid. The dried powder was transferred to an alumina crucible covered by a tight-fitting lid, the lid being put under pressure. The closed crucible was fired at 760 °C for 2 h. In this step water vapor, NO and O₂ escape from the reactant mixture and the sample is converted into oxide form. In the second step of the procedure the product from the first heat treatment was milled and formed into pellet shape. The pellet was then transferred to an alumina crucible with a polished rim fitted with a gasket made of gold sheet and a polished alumina lid. The container was placed in a ceramic jig and the seal was put under compression during the subsequent firing. The closed crucible was fired at 880 °C for 3 h. The total thallium loss during synthesis corresponds to less than 0.3% of the thallium content. After synthesis the sample was annealed in oxygen at 300 °C for 72 h.

Sample purity and lattice parameters were determined by the Guinier film technique using Cu $K\alpha_1$ radiation and with Si as an internal standard. The cell constants were $a=3.8539(1)$ Å and $c=29.3169(6)$ Å. Besides a small amount of barium carbonate (about 1%) there was no evidence of any crystalline impurities in the sample. The transition to the superconducting state was determined by susceptibility measurements and was found to be 98 K (onset). The results of a detailed structure determination by neutron diffraction of the same sample (B6) are reported in a paper by Ström *et al.*²⁵

The growth and characterization of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ single crystal, used in the present study, have been described elsewhere.²⁶ The sample was not post-annealed in oxygen.

The experiments were performed at the undulator beam line X1B of the National Synchrotron Light Source, Brookhaven National Laboratory. The O $K\alpha$ x-ray emission spectra were recorded using a high-resolution grazing incidence grating spectrometer with a two-dimensional detector.²⁷ The incidence angle of the photon beam was about 20° to the sample face plane. The x-ray fluorescence was detected in the horizontal plane and at 90° to the incidence photon beam. The resolution of the monochromator was set to 0.5 eV for 530 eV photon energy. The O $K\alpha$ x-ray emission spectra were recorded using a 1200 lines/mm grating ($R = 5\text{m}$) in the first order of diffraction with the spectrometer resolution set to 1.2 eV. Zn $L_{2,3}$ x-ray emission lines were recorded in the second order of diffraction and used for energy calibration.

The O 1s x-ray absorption spectra were measured by the total-x-ray-fluorescence-yield method, again with a 0.5-eV resolution of the monochromator.

III. RESULTS AND DISCUSSION

In Fig. 1 the O 1s x-ray absorption spectra of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ are shown. The

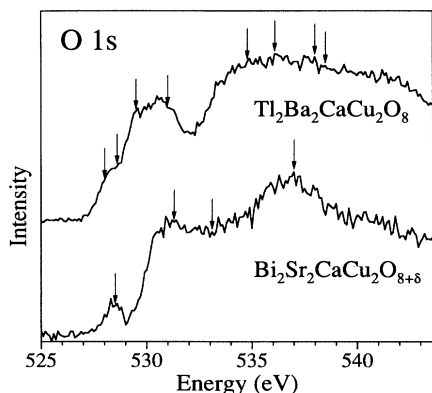


FIG. 1. O $1s$ x-ray absorption spectra of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

results obtained are very similar to those reported elsewhere.^{7–12} The photon energies, used to excite the O $K\alpha$ x-ray emission spectra in both compounds, are marked by arrows.

A. $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$

The emission spectra detected for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ are displayed in Fig. 2. As one can see, they exhibit an appreciable variation in their profiles with excitation energy. The energy position of the main peak, the full width at half maximum (FWHM), and the intensity of the low-energy shoulder of the O $K\alpha$ spectra vary with energy of the incoming photons. When the excitation energy is

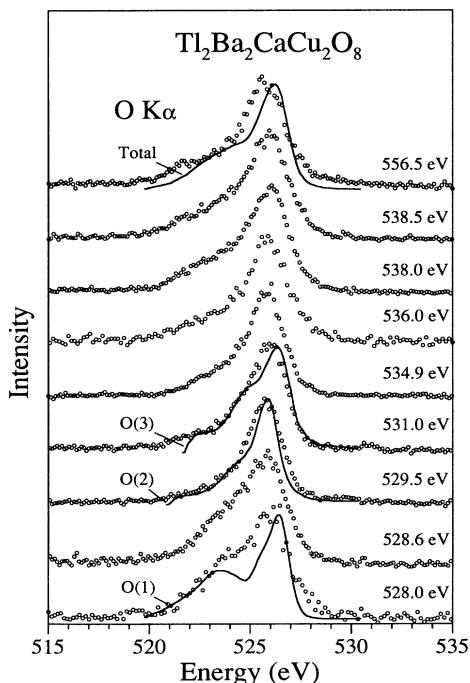


FIG. 2. O $K\alpha$ x-ray emission spectra of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ recorded with various excitation energies (open circles) and the ones calculated for the inequivalent oxygen atoms (Ref. 13) (solid curves).

tuned to the energy of the first prepeak (528.0 eV) near the O $1s$ edge, the O $K\alpha$ emission band is broad and has a pronounced shoulder on the low-energy side. In turn, the 529.5-eV-excited O $K\alpha$ spectrum is a narrow line with a weak low-energy tail. The maximum is now shifted to the lowest energy (525.7 eV) in comparison with other spectra. A similar spectrum is also obtained for an excitation energy of 534.9 eV. However, when tuning the monochromator to the third prepeak in the O $1s$ x-ray absorption spectrum (531.0 eV) the O $K\alpha$ maximum is at 526 eV, the emission line becomes asymmetric, and the FWHM increases. At high excitation energies the spectra look similar to what has been measured with electron excitation.²⁸

What is the origin of the observed variation in the O $K\alpha$ profile? Similar measurements of the O $K\alpha$ emission spectra were made for Cu_2O , CuO ,²⁹ and LaCuO_3 ,²⁴ where all the oxygen atoms are equivalent or almost equivalent. Those spectra only slightly change with excitation energy.

As shown for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$,²⁴ the main reason for the high O $K\alpha$ sensitivity to the energy of incoming photons is an inequivalence of the O sites. When the excitation energy is tuned to different structures in the x-ray absorption spectrum, core holes are created at specific oxygen sites. The relative number of excited inequivalent atoms depends on the character of the conduction-band states and the cross section of x-ray absorption.

Another question is how an increase or decrease in the relative number of excited atoms of the same sort affects the O $K\alpha$ profile. Due to strong Cu $3d,4s$ –O $2p$ hybridization⁶ the occupied O(1) $2p$ states form a wide band, split into bonding and antibonding subbands. Therefore, one can expect a rather broad O $K\alpha$ spectrum for O(1).^{6,24} Indeed, such a spectrum obtained for $\text{Ca}_{0.87}\text{Sr}_{0.13}\text{CuO}_2$ (Ref. 29) (Fig. 3), containing only oxygen atoms of the O(1) type, exhibits a two-subband structure. The low-energy shoulder is quite pronounced, giving rise to the large FWHM. Together with this spectrum, one of single-crystal $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$,³⁰ excited with the

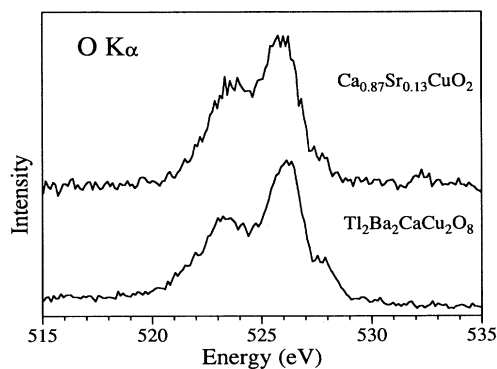


FIG. 3. O $K\alpha$ x-ray emission spectra of $\text{Ca}_{0.87}\text{Sr}_{0.13}\text{CuO}_2$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ recorded at the excitation energies of 532.5 eV and 528.2 eV, respectively, with resolution of the spectrometer and monochromator set to 0.5 eV and 0.7 eV, respectively (the feature at ~ 528.2 eV in the spectrum of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ is due to elastically scattered radiation).

528.2-eV photon beam, is displayed. A strong similarity observed in the profile of both spectra gives evidence for the O(1) 2*p* origin of the first prepeak near the O 1*s* edge in the Tl-based cuprate.

In order to understand which O *Kα* profile one can expect for O(2) and O(3) in Tl₂Ba₂CaCu₂O₈ we will briefly discuss the O *Kα* spectra of the *s, p*-metal oxides. Already in 1940 O'Bryan and Skinner³¹ pointed out that in such oxides with a covalent character of the metal-ligand bonds the main O *Kα* peak is located on the high-energy side of the O *Kα* spectrum, while in ionic compounds it appears on the low-energy side. According to the results of more recent x-ray emission measurements^{32,33} the O *Kα* spectra of ionic Li₂O, CaO, SrO, and BaO are narrow lines around 525 eV. The characteristic for the ionicity of the chemical bonds in these oxides is the existence of strong high-energy multiple excitation satellites.³³ On the other hand, in covalent BeO, MgO, and Al₂O₃ the main O *Kα* peak is at ~526 eV and the shoulder with a relative intensity of (10–15)% appears on the low-energy side.

Now if we consider Tl₂Ba₂CaCu₂O₈, the 6*s* electrons of Tl ions are covalently bonded to O(3).⁶ This suggests the O(3) *Kα* profile to be qualitatively similar to those of the covalent *s, p*-metal oxides. In Fig. 4 the 531.0-eV-excited O *Kα* spectrum of Tl₂Ba₂CaCu₂O₈ is displayed together with the one of Tl₂O₃,³⁴ recorded with the 5-keV electron beam excitation. In spite of the difference in the crystal structure and some contribution of O(2) to the former spectrum (see below), one can see that the spectra strongly resemble each other. It is not surprising because the Madelung potential, depending on the crystal structure, shifts the core and valence levels of O by approximately the same value and the energy of the 1*s*-2*p* transition and the profile of the O *Kα* spectrum do not change much if the character of the chemical bonds is the same. The observed similarity of the spectra in Fig. 4 indicates the essential O(3) contribution around 531 eV in the O 1*s* absorption spectrum of Tl₂Ba₂CaCu₂O₈.

In turn, the O(2) atoms have the main chemical bonds with Ba which are highly ionic, and although the O(2) bonding with Cu and Tl somewhat distorts the pure ionic

picture for O(2) chemical bonds, one can expect the O(2) *Kα* band to be narrower than those for O(1) and O(3). A decrease in the FWHM is observed for the 529.5-eV- and 534.9-eV-excited O *Kα* spectra of the Tl-based cuprate, suggesting an increase in the relative number of the excited O(2) atoms.

The above made analysis of selectively excited O *Kα* x-ray emission spectra in Tl₂Ba₂CaCu₂O₈ is in qualitative agreement with the results of LDA band structure calculations for this compound.⁶ According to these calculations the occupied O(1) 2*p* states form a wide band, split into two subbands, bonding and antibonding. For O(2) and O(3) atoms the essential contribution to the spectral weight comes from nonbonding states, forming narrow peaks in the 2*p* density of states (DOS).

One can argue that x-ray emission spectra can be influenced by an attractive potential of a core hole in the intermediate state and that the LDA-calculated O 2*p* density of states cannot represent the O 2*p* removal weight for highly correlated electron systems. However, it has been shown by von Barth and Grossmann³⁵ that with many-body theory one can justify the final state rule for the x-ray emission process and transition matrix elements can be calculated from wave functions obtained in the potential of the final state, i.e., without a core hole.³⁶

Neither can one expect a dramatic modification of the O *Kα* emission spectra in divalent copper oxides due to correlation effects. Though the on-site Coulomb O 2*p* interaction (*U_p*) has been estimated to be fairly large^{37,38} (~5 eV), the O 2*p* spectral weight is not sensitive to it³⁸ because of the low hole occupation number per O site and the large width of the O 2*p* band. Nevertheless, due to the O 2*p*-Cu 3*d* hybridization the O *Kα* profile can be affected by two-electron interactions within the Cu 3*d* band (*U_d*). In Fig. 5 the O *Kα* spectrum of Ca_{0.87}Sr_{0.13}CuO₂ (Ref. 29) is compared with the partial O 2*p* DOS calculated using the LDA method without³⁹ and with⁴⁰ *U_d*. The DOS were broadened with a Lorentzian with the energy-dependent FWHM and with a Gaussian to simulate the lifetime and experimental broadening. One can see that agreement between standard LDA calculations and experiment is fairly good for the high-

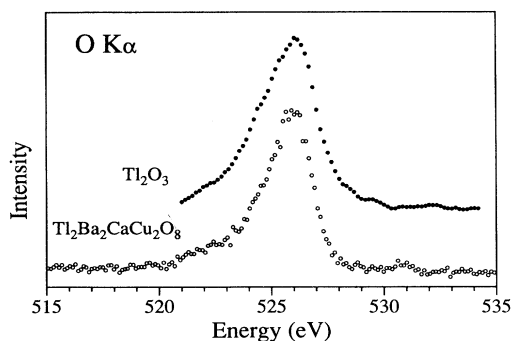


FIG. 4. The 531.0-eV-excited O *Kα* x-ray emission spectrum of Tl₂Ba₂CaCu₂O₈ and the one of Tl₂O₃ (Ref. 34) recorded with 5-keV electron beam excitation.

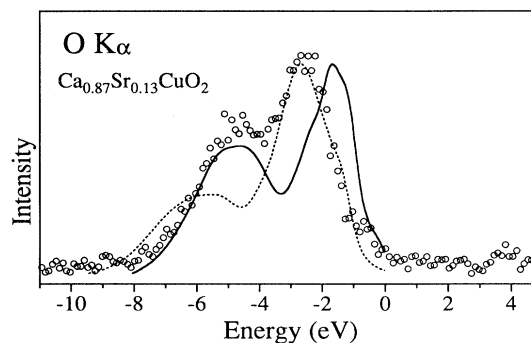


FIG. 5. The 532.5-eV-excited O *Kα* x-ray emission spectrum of Ca_{0.87}Sr_{0.13}CuO₂ (open circles) and the broadened partial O 2*p* DOS LDA-calculated without (Ref. 39) (solid curve) and with (Ref. 40) (dashed curve) including *U_d*.

binding-energy shoulder of the O $K\alpha$ spectrum (i.e., for the bottom of the O $2p$ band). It is not surprising because in this region a $2p$ hole is better screened. However, there is a difference for the top of the valence band; the main peak of the experimental spectrum is pulled deeper by ~ 1 eV from the Fermi level. A similar difference in the main peak position between experimental and LDA-calculated O $K\alpha$ emission spectra is also found for other cuprates.^{23,24,41} In addition, such a high-binding-energy shift of the main maximum is observed in photoemission valence-band spectra⁴² recorded at the excitation energy of 20 eV, corresponding to a large relative cross section for oxygen.

For the $3d$ transition metal oxides from the middle and the end of the $3d$ sequence which are also strongly correlated electron systems, the standard LDA calculations describe correctly the O $2p$ band “itself” [as one can see from a comparison of theory and near-threshold excitation x-ray emission experiment for NiO (Ref. 43)] and fail in the description of the “ d -like” states which are a result of the oxygen $2p$ -metal $3d$ hybridization. This failure is explained to be due to d - d correlation effects.

For (Ca,Sr)CuO₂, the attempt to take into account U_d by using the so-called LDA+ U method⁴⁰ results in a much weaker relative intensity for the high-binding-energy subband (Fig. 5) compared to that in the experimental O $K\alpha$ spectrum. A decrease in the relative weight of such a subband is also observed for the O(1) $2p$ DOS in La₂CuO₄, calculated within self-interaction-corrected (SIC) LSDA formalism.^{44,45} The corrections to the LDA used pull the occupied Cu $3d$ states far below the Fermi level so that the main $3d$ weight appears at high binding energies. This leads to an increase of the fraction of the nonbonding and weakly bonding O $2p$ states and, hence, to a redistribution of the O $2p$ spectral weight. However, for insulating cuprates, both LDA+ U and SIC-LSDA methods correctly predict magnetic moment values and the energy gap which is opened as a result of the spectral-weight transfer away from the Fermi level. Therefore, the appearance of the main peak in the LDA+ U -calculated O $2p$ DOS at the same energies as that in the experimental O $K\alpha$ spectrum (Fig. 5) indicates that the observed difference between the experiment and standard LDA calculations for the top of the valence band is likely due to correlation effects.

In turn, these effects are rather negligible for oxygen atoms in the BaO and TlO planes and the electronic structure of these atoms can be correctly described within the ordinary LDA formalism.

In Fig. 2 a comparison of the experimental and LDA-calculated¹³ O $K\alpha$ spectra for Tl₂Ba₂CaCu₂O₈ is made. In order to align the calculated spectra to the emission energy scale an arbitrary shift was used. The calculated emission bands for different O sites were all shifted by the same value⁴⁶ so as to obtain the best agreement in the base width with experimental spectra. As one can see, the shape of the 528.0-eV-excited O $K\alpha$ spectrum is similar to that calculated for O(1) atoms. A shift of the main peak can be attributed to correlation effects and an enhancement of the intensity at ~ 528.0 eV to a contribution of elastically scattered radiation.

The narrow and slightly asymmetric O $K\alpha$ line, obtained at the excitation energy of 529.5 eV, is in fairly good agreement with the calculated O(2) $K\alpha$ emission spectrum. This fact indicates that a large portion of the second prepeak is associated with transitions to O(2) $2p$ orbitals. Also, the 531.0-eV-excited O $K\alpha$ spectrum resembles the O(3) $K\alpha$ band. The somewhat narrower FWHM and low-energy shift of the main maximum in the experimental emission spectrum suggest some O(2) contribution to the third prepeak in the O $1s$ absorption spectrum.

As a whole, the results of LDA calculations provide additional support to the O-site assignments for features in the O $1s$ absorption spectrum of Tl₂Ba₂CaCu₂O₈, made above by analyzing the O $K\alpha$ spectra of the model systems, and can be used to a certain extent to identify the contributions of different O sites.

Further support for our assignments comes from the fact that we were able to reconstruct the O $K\alpha$ emission spectra of Tl₂Ba₂CaCu₂O₈ recorded at different excitation energies using a linear combination of the 528.0-eV- and 529.5-eV-excited O $K\alpha$ spectra associated with O(1) and O(2), respectively, and the one calculated for O(3).¹³ The contributions of inequivalent O atoms to the different O $K\alpha$ spectra are summarized in Table II. These values are related to the relative x-ray absorption cross sections for different oxygens at corresponding energies. One can see that the third prepeak in the O $1s$ absorption spectrum contains about 30% of O(2) states. In turn, setting the incidence beam energy to 534.9 eV leads to predominant excitation of O(2) atoms, because at this energy we are able to reach the O p states hybridized with Ba $5d$ states (see the inverse photoemission data in Ref. 15) and looking at Fig. 2 one can see that the corresponding emission spectrum is similar to the one excited with 529.5 eV radiation which was attributed to mainly O(2) atoms. The relative absorption cross section for O(1) is enhanced at ~ 538 eV because of the O(1) p admixture to the Cu $4s, p$ (see, e.g., O $1s$ XAS data for Ca_{0.86}Sr_{0.14}CuO₂) (Ref. 47) and Ca $3d$ states¹⁵ located in this energy region.

Note that the respective differences in energy position between experimental O $K\alpha$ x-ray emission spectra, associated with inequivalent O sites (these differences depend on the O $1s$ chemical shifts), are similar to those between calculated site-selective O $K\alpha$ bands (Fig. 2). Hence, the O $1s$ chemical shifts for different O atoms are correctly estimated from LDA calculations¹³ which give the O(2)

TABLE II. The relative contributions of inequivalent O sites to the O $K\alpha$ spectra of Tl₂Ba₂CaCu₂O₈ recorded at various excitation energies.

Excitation energy (eV)	O(1)	O(2)	O(3)
531.0		0.29	0.71
534.9	0.18	0.62	0.20
536.4	0.34	0.47	0.19
538.0	0.59	0.31	0.10
538.5	0.60	0.27	0.13

1s and O(3) 1s binding energies to be higher by 1.2 eV and 2.2 eV than that for O(1) sites. In this case, if there are doping-induced unoccupied O(2) [O(3)] 2p states at the Fermi level, additional spectral weight should appear at 1.2 [2.2] eV above the first prepeak (otherwise only at higher energies [1.2 (2.2) eV + approximately the size of the band gap]) in the O 1s absorption spectrum due to O(2) [O(3)] 1s excitations. Specific changes in the O $K\alpha$ profile at these excitation energies give evidence that this is indeed the case. Therefore, we conclude that the second and the third prepeaks in the O 1s absorption spectrum of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ at least partly correspond to the O(2) 1s and O(3) 1s excitations into unoccupied oxygen 2p states at the Fermi level (i.e., into respective doping-induced holes). This conclusion is supported by results of XAS measurements performed on the related $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$ compounds with different O contents⁴⁸ and, hence, with different doping-induced hole concentrations. The O reduction, leading to the decrease in T_c , causes an appreciable reduction in the intensity of the first and third prepeaks while the change of the second peak is small due to an increase in the spectral weight of the upper Hubbard band and the involvement of O(2) sites in the interlayer charge transfer.

B. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

The selectively excited O $K\alpha$ x-ray emission spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, like those of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, also exhibit changes in shape with variation of the incoming photon energy (Fig. 6). The spectra, obtained for 528.5 eV and 537 eV excitation energies, at the prepeak and at the main maximum, respectively, in the absorption spectrum, are similar, except for a small low-energy shift for the latter. They are characterized by a double-band structure. In turn, the 531.0-eV- and 533.0-eV-excited O

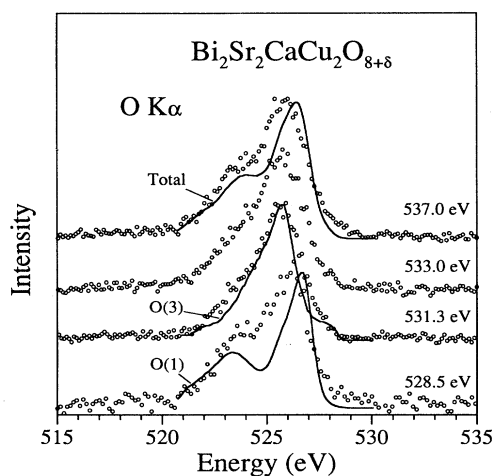


FIG. 6. O $K\alpha$ x-ray emission spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ recorded with various excitation energies (open circles) and the ones calculated for the inequivalent oxygen atoms (Ref. 17) (solid curves).

$K\alpha$ lines are narrower and more symmetric.

Following the arguments used in the discussion for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, the characteristic structure of the 528.5-eV-excited O $K\alpha$ spectrum of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ indicates a predominant O(1) contribution to the first prepeak of the O 1s absorption spectrum in this cuprate. Since a feature around 531 eV in the O 1s x-ray absorption spectrum of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ corresponds to transitions to the O 2p states hybridized with Bi 6p states,¹⁶ one can expect the 531.0-eV-excited O $K\alpha$ emission spectrum to be mainly related to O(3) atoms, located in BiO layers. Indeed, fairly good agreement in shape between this spectrum and that of Bi_2O_3 , recorded with 4-keV electron beam excitation, is observed (Fig. 7), suggesting a similar character of the Bi-O chemical bonds in both compounds.

In Fig. 6 properly broadened LDA-calculated O 2p DOS of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Ref. 17) are also displayed. Keeping in mind the influence of correlation effects and a contribution of the elastically scattered radiation at ~ 528.5 eV one can see that the 528.5-eV-excited O $K\alpha$ spectrum of the Bi-based cuprate resembles that calculated for O(1) atoms as well as the one recorded for $\text{Ca}_{0.87}\text{Sr}_{0.13}\text{CuO}_2$. We used an agreement in the base width between these experimental and calculated spectra to place the calculated emission bands on the emission energy scale. However, in this case, in spite of a strong similarity in the spectral profile of the 531.3-eV-excited O $K\alpha$ spectrum and the one calculated for O(3) atoms, a difference in the energy location between both spectra was quite noticeable. The existing discrepancy is probably due to an overestimation of the O 1s chemical shifts for inequivalent atoms obtained from the calculations.^{16,17} In these calculations the ideal ratios 2:2:1:2 have been used while an appreciable deviation in the stoichiometry of the real crystal is observed.²⁶ Therefore, the calculated O(3) $K\alpha$ emission band displayed in Fig. 6 was shifted further by ~ 0.9 eV for better agreement with the experimental spectrum. This implies that the energy difference between the 1s levels of O(3) and O(1) is ~ 0.7 eV, instead of ~ 1.6 eV as found from calculations. This value is consistent with those derived by Parmigiani *et al.*²² from angular-resolved O 1s XPS measurements (their crystals were grown under the same conditions as ours but were

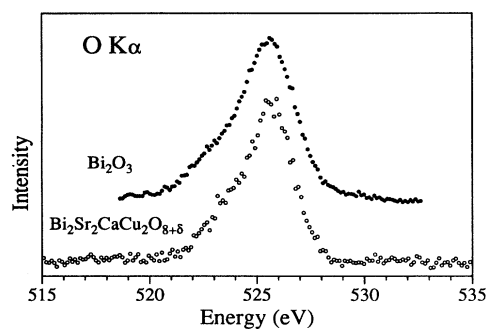


FIG. 7. The 531.3-eV-excited O $K\alpha$ x-ray emission spectrum of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and the one of Bi_2O_3 recorded with 4-keV electron beam excitation.

post-annealed in Ar or O atmosphere²⁶) and by Burgäzy *et al.*²³ from analysis of XES data.

Unfortunately, the O $K\alpha$ spectrum, originating mainly from the O(2) states, was not measured. Probably, it could be obtained with an excitation energy around 541 eV, where the O(2) p states, mixed with unoccupied Sr 4d states, can be reached. Nevertheless, one can expect some contribution from the O(2) atoms to the 531.3-eV-, 533-eV-, and 537-eV-excited O $K\alpha$ spectra due to the O(2) $2p$ -Bi $6p$ hybridization and Ca-Sr intermixing. The main maximum around 537 eV in the O $1s$ x-ray absorption spectrum can be attributed to the transitions to mainly O p states hybridized with Ca $3d$ states.¹⁸ Since Ca layers are located between CuO_2 planes, only O(1) atoms can participate in the O-Ca chemical bond. Therefore, when tuning the incidence beam energy to 537 eV one could expect a predominant excitation of O(1) atoms. In fact, the pronounced low-energy shoulder makes the recorded emission spectrum similar to that excited with the 528.5-eV photon beam. The O(1) p character of the ~ 537 -eV feature in the O $1s$ absorption spectrum and its origin from mainly O p states hybridized with Ca $3d$ states are supported by recent polarization-dependent O $1s$ absorption measurements for $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ compounds with different numbers of O(1) atoms per unit cell.¹⁰ In $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ the ~ 537 -eV feature shows an appreciable anisotropy and can be associated with transitions to O p_z orbitals, whereas in Ca-less $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, which has as twice as fewer O(1) sites per unit cell as compared with $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, the relative intensity of the ~ 537 -eV feature decreases and its anisotropy becomes weaker.

Because of Sr deficiency, at least 20% of the Ca atoms in the present $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ sample may occupy Sr sites,⁴⁹ leading probably to some O(2) contribution to the 537.0-eV-excited O $K\alpha$ spectrum. For the latter, this may be one of the reasons for the observed low-energy shift as compared with the 528.5-eV-excited spectrum.

Based on our data we cannot rule out a possible O(2) contribution in the first prepeak in the O $1s$ XAS spectrum and hence to the 528.5-eV excited O $K\alpha$ spectrum. However, the x, y symmetry of the first prepeak¹² makes it hard to believe that there are induced holes in the ionic SrO plane. Additional studies are necessary to obtain more detailed information about the O(2) $2p$ band.

Finally, we would like to comment on the role of BiO planes. Since there is no further visible step in the O $1s$ absorption spectrum below 530 eV, in spite of the ~ 0.7 -eV chemical shift between O(1) and O(3) $1s$ levels, we

concluded that BiO layers are nonmetallic. This conclusion is in agreement with data reported by Wells *et al.*⁵⁰ The metallicity of the BiO plane was found only in a crystal annealed in a high-pressure oxygen atmosphere but not in an as-grown crystal (again, their crystals were grown under the same conditions as ours).²⁶

IV. CONCLUSION

We have shown that soft x-ray emission spectroscopy with tunable excitation, applied to a study of the electronic structure of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, is an efficient method for probing the character of both occupied and unoccupied states. Tuning the excitation energy to the energy of certain features in the O $1s$ x-ray absorption spectrum allowed us to characterize the nature of those features and to separate the O $2p$ contributions of the inequivalent atoms to the O $K\alpha$ x-ray emission spectrum. It was found that three prepeaks near the O $1s$ edge of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ arise mainly from transitions to the O(1), O(2), and O(3) $2p$ states, respectively. This three-prepeak structure results from the difference in the O $1s$ binding energy of the inequivalent atoms, as determined from the corresponding shifts of the O(1), O(2), and O(3) $K\alpha$ emission spectra, and, hence, the second and third prepeaks at least partly correspond to transitions to the unoccupied states at the Fermi level.

A single prepeak in the O $1s$ absorption spectrum of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ is determined to have mainly O(1) $2p$ character. Since the chemical shift between the O(1) and O(3) $1s$ levels (the latter is deeper) is estimated to be ~ 0.7 eV, the absence of a second visible step below 530 in the O $1s$ absorption spectrum suggests that BiO layers are nonmetallic.

ACKNOWLEDGMENTS

We would like to thank Dr. Z.-X. Shen for providing a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ single crystal and Dr. P. Kuiper for a critical reading of the manuscript. This work was supported by NFR, the Swedish Natural Science Research Council, and the Göran Gustavsson Foundation for Research in Natural Sciences and Medicine. The National Synchrotron Light Source is operated under DOE Contract No. DE-AC02-76CH00016.

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