Hole states in oxycarbonate high-$T_c$ superconductor
$(\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_4\text{Cu}_2(\text{CO}_3)\text{O}_7$ probed by soft X-ray absorption spectroscopy

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Abstract

We report O K-edge and Cu L$_{2,3}$-edge X-ray-absorption near-edge-structure (XANES) spectra of oxycarbonate $(\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_4\text{Cu}_2(\text{CO}_3)\text{O}_7$ obtained using a bulk-sensitive X-ray fluorescence yield technique. The prominent features of the O 1s absorption edge in $(\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_4\text{Cu}_2(\text{CO}_3)\text{O}_7$ compound are three distinct pre-edge peaks at 528.2, 529.3 and 530.5 eV, respectively. We ascribed these pre-edge peaks to excitations of O 1s electrons to predominant O 2p holes located in the CuO$_2$ planes, in the apical oxygen sites, and in the $(\text{Ti},\text{Cr})$-O planes, respectively. The average number of holes within the in-plane oxygen sites per CuO$_2$ sheet is approximately the same for both the $(\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_4\text{Cu}_2(\text{CO}_3)\text{O}_7$ and $\text{Tl}_3(\text{CrO}_4)\text{Sr}_3\text{Cu}_4\text{O}_{16}$ systems. Conversely, the average hole content in the apical oxygen sites decreases significantly in $(\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_4\text{Cu}_2(\text{CO}_3)\text{O}_7$ as compared to $\text{Tl}_3(\text{CrO}_4)\text{Sr}_3\text{Cu}_4\text{O}_{16}$. The reduction of the average hole concentration in the apical oxygen sites is accompanied by the enhanced superconductivity in $(\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_4\text{Cu}_2(\text{CO}_3)\text{O}_7$, indicating that the O 2p holes on the apical oxygen sites play an important role to control the $T_c$. The behavior of the high-energy shoulders in the Cu L$_{2,3}$-edge absorption spectra coincides with that of the pre-edge peak at 528.2 eV in the O K-edge absorption spectra.

1. Introduction

The insulating oxycarbonate compound $\text{Sr}_2\text{CuO}_2$(CO$_3$) was first reported by von Schnering et al. [1]. This compound consists of a block layer [Sr$_2$CO$_3$] and a CuO$_2$ sheet. Thereafter, the successful substitution of carbonate groups for copper in the perovskite structure has produced a large number of new oxycarbonate superconductors, such as, $(\text{Hg}_{0.5}\text{Pb}_{0.2})\text{Sr}_3\text{Cu}_4(\text{CO}_3)\text{O}_7$ [2], $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_3\text{Cu}_4(\text{CO}_3)\text{O}_7$ [3], $(\text{Bi}_{0.5}\text{Hg}_{0.5})\text{Sr}_3\text{Cu}_4(\text{CO}_3)\text{O}_7$ [4], $(\text{Ti}\text{Sr}_{0.5}\text{Ba}_{0.5})$-Cu$_2$CO$_3$O$_7$ [5], $\text{Ti}(\text{Sr}_{4-x}\text{Ba}_x)$Cu$_2$(CO$_3$)O$_7$ [6], $(\text{Hg}_{0.5}\text{Pb}_{0.5})(\text{Sr}_{4-x}\text{Ba}_x)$Cu$_2$(CO$_3$)O$_7$ [7], $(\text{Ti}_{1-x}\text{Bi}_x)$-Sr$_2$Cu$_2$(CO$_3$)O$_7$ [8], etc. The crystal structure of those oxycarbonate cuprates has already been reported. As an example, the structure of the oxycarbonate $(\text{Tl},\text{M})\text{Sr}_3\text{Cu}_4(\text{CO}_3)\text{O}_7$ ($\text{M} = \text{Pb}$ or Bi) is built up from the intergrowth of double rock-salt-type layers $\{(\text{Tl},\text{M})\text{O}\}([\text{SrCO}_3]$) and single [SrCuO$_2$] perovskite, linked through single carbonate [SrCO$_3$] layer [3,8]. Thus, its structure can be described as the intergrowth of 1201-type layers $\{(\text{Tl},\text{M})\text{Sr}_3\text{Cu}_4\text{O}_7\}$ with the classical [SrCuO$_2$] (S$_2$CC) units, and is called normal “S$_2$CC-1201” structure. It is re-
markable that the thallium oxycarbonate \((T_{10.8}Pb_{0.2})Sr_4Cu_2(O_3)O_7\) exhibits the highest \(T_c\) of 70 K, although it derives from two nonsuperconductors, \((T_{10.2}Pb_{0.8})Sr_2CuO_5\) [9] and \(Sr_2Cu_2(O_3)\) [10]. A similar phenomenon has been recently experimentally proven for a superconducting oxycarbonate \(Bi_{2}Sr_2CuO_5\) with a \(T_c\) of 30 K [11], which is composed of an intergrowth of the 2201-type superconductor \(Bi_{2}Sr_2CuO_5\) with a \(T_c\) of 22 K [12] and of the nonsuperconducting oxycarbonate \(Sr_2CuO_2(\text{CO}_3)\). There are also the case of the mercury and the thallium-based oxycarbonate \((Hg_{0.3}Pb_{0.7})Sr_4Cu_2(\text{CO}_3)O_7\) [2], \(Hg(Sr_2Ba_2)Cu_2(\text{CO}_3)O_7\) [5], \(Tl(Sr_2Ba_2)Cu_2(\text{CO}_3)O_7\) [6], and \((T_{10.2}Bi_{0.8})Sr_4Cu_2(\text{CO}_3)O_7\) [8], which are the intergrowth of the 1201-type \(Hg\) or \(Tl\) cuprate and the \(Sr_2CuO_2(\text{CO}_3)\) structure. The superconducting transition temperature of these compounds is systematically higher than that of the parent 1201-type cuprates. This shows that the introduction of carbonate layers into the single-thallium-layer compounds, O K-edge X-ray absorption spectrum of 1201-type parent compound with a nominal composition of \((T_{10.75}Cr_{0.25})Sr_2CuO_5\) has also been carried out in this study. The insertion of carbonate layer in \((T_{10.8}Cr_{0.2})Sr_4Cu_2(\text{CO}_3)O_7\) is located in the apical position. It is therefore expected that the hole density in the apical directions may be changed in \((T_{10.8}Cr_{0.2})Sr_4Cu_2(\text{CO}_3)O_7\) as compared to the parent compound \((T_{10.75}Cr_{0.25})Sr_2CuO_5\). However, it should be pointed out that the substitution of \(Cr\) for \(Tl\) in the 1201-type structure results in the formation of an ordered copper oxychromate \(Tl_3(CrO_4)Sr_8Cu_4O_{16}\) with the \(A2mm\) space group and lattice constants \(a = 3.7803\ \text{Å}, \ b = 15.2573\ \text{Å}\) and \(c = 17.6737\ \text{Å}\) [16]. It exhibits a \(T_c\) of 25 K. The study of electronic states near the Fermi level of the oxycarbonate cuprates will give rise to open new vistas to understand the microscopic mechanism of high-\(T_c\) superconductivity in the layered cuprates.

2. Experimental

Details on the preparation of samples were reported elsewhere [15,16]. In brief, high purity powders of \(Tl_3O_3\), \(Cr_2O_3\), \(SrO_2\), \(CuO\), \(Sr_2CuO_3\), and carbonate \(SrCO_3\) were weighed in the appropriate proportions to form a nominal composition of \((T_{10.8}Cr_{0.2})Sr_4Cu_2(\text{CO}_3)O_7\). The powders were mixed in an agate mortar, pressed into bars, put in an alumina crucible, and then sealed in an evacuated quartz ampoule. The tubes were introduced in a hot furnace at 850°C, held for 12 hours, and then quenched to room temperature. The \(Tl_3(CrO_4)Sr_8Cu_4O_{16}\) compounds were prepared by similar procedures but with high post-annealing temperature at 920°C for 6 hours [16]. The purity and crystallinity were checked out by X-ray diffraction (XRD) and electron diffraction (ED) techniques. The superconducting properties were studied as a function of...
temperature using an AC Lakeshore susceptometer with an applied field of 5 G; no demagnetizations were made.

The X-ray absorption measurements were carried out using the 6 m high-energy spherical grating monochromator (HSGM) beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan. Bulk-sensitive X-ray fluorescence yield spectra with a probing depth of thousands of angstroms were recorded using a microchannel plate (MCP) detector. This MCP detector is composed of a dual set of MCPs with an electrically isolated grid mounted in front of them. For X-ray fluorescence detection, the grid was set to a voltage of 100 V while the front of the MCPs was set to −200 V and the rear to −200 V. The grid bias insured that no positive ions were detected while the MCP bias insured that electrons would not be detected. The MCP detector was located ~2 cm from the sample and oriented parallel to the sample surface. Photons were incident at an angle of 45° with respect to the sample normal. The incident photon intensity \(I_0\) was measured simultaneously by an 80% transmission Ni mesh located after the exit slit of the monochromator. All the measurements were normalized to \(I_0\). The photon energies were calibrated using the known O K-edge and Cu L-edge absorption peaks of the CuO compound. The energy resolution of the monochromator was set to approximately 0.22 and 0.45 eV for the O K-edge and Cu L-edge absorption measurements, respectively.

3. Results and discussion

In Fig. 1 we show the temperature dependence of the AC susceptibility of \((\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_2\text{Cu}_2\text{(CO}_3\text{)}\text{O}_7\). As deduced from Fig. 1, its superconducting transition temperature is 68 K which is one of the highest observed in the oxycarbonate cuprates.

In Figs. 2a and 2b O K-edge X-ray absorption near edge structure (XANES) spectra of \((\text{Tl}_{0.8}\text{Cr}_{0.2})\text{Sr}_2\text{Cu}_2\text{(CO}_3\text{)}\text{O}_7\) and \(\text{Tl}_3\text{(CrO}_4\text{)}\text{Sr}_8\text{Cu}_4\text{O}_{16}\), respectively, are displayed in the energy range of 525–555 eV obtained by a non-surface-sensitive X-ray fluorescence yield detection technique. As noted from Fig. 2, the prominent features in the O 1s absorption spectrum are three discrete pre-edge peaks at 528.2, 529.3 and 530.5 eV, respectively, and a broad band at ~537 eV. The O 1s X-ray absorption spectra in Fig. 2 can be separated into two regions: below and above energy ~532 eV. It has been proven by inverse photoemission experiments that the empty d states of Sr are located at about 5–10 eV above the
Fermi level \[17\]. Thus, excitations of the O 1s electrons to the Sr 4d and Tl 6p empty states hybridized with O 2p states are probably responsible for the high-energy peaks above 535 eV. The pre-edge peaks below 532 eV are attributed to transitions from O 1s electrons to holes with the predominant 2p symmetry on the oxygen sites. The observed multiple pre-edge peaks in Fig. 2 may be related to different binding energies of O 1s levels of nonequivalent oxygen sites. In order to understand the variations in the density of doped O 2p holes per CuO$_2$ sheet, the O K-edge absorption spectra in Fig. 2 have been normalized in the range 535–555 eV according to their ideal oxygen stoichiometry and then divided by the number of CuO$_2$ layers per formula. This provides the absolute intensities of the relevant pre-edge peaks originating from different oxygen sites for the (Tl$_{0.8}$Cr$_{0.2}$)$_4$Sr$_4$Cu$_2$(CO$_3$)$_7$O$_7$ and Tl$_3$(CrO$_4$)$_4$Sr$_8$Cu$_4$O$_{16}$ compounds.

Based on the crystal structure of (Tl$_{0.8}$Cr$_{0.2}$)$_4$Sr$_4$Cu$_2$(CO$_3$)$_7$O$_7$ \[15\], there exist several different oxygen sites distributed in the in-plane CuO$_2$ planes, in the apical oxygen sites, and in the (Tl,Cr)-O planes, respectively. The distinct pre-edge features in the O 1s X-ray absorption spectrum originating from different oxygen environments have been found in the related high-\(T_c\) superconductor compounds, such as Tl$_2$Ba$_2$Ca$_2$Cu$_4$O$_{10}$ and Tl$_2$Ba$_2$CaCu$_2$O$_8$. Near the O 1s edge, three pre-edge peaks with maxima at 528.3, 529.4 and 530.6 eV are revealed in the Tl$_2$Ca$_2$Ba$_2$Cu$_4$O$_{10}$ high-\(T_c\) superconductor reported by Krol et al. \[18\]. These peaks are ascribed to core-level excitations of oxygen 1s electrons to empty states originating from different oxygen sites. The low-energy pre-edge peak at 528.3 eV is mainly 2p$_{x,y}$ symmetry from the two-dimensional CuO$_2$ planes, and the higher-energy pre-edge peak at 529.4 has predominantly O 2p$_z$ symmetry from the apical oxygen sites.\[21\]. Moreover, the first pre-edge peak at \(\sim 528.3\) eV in the related high-\(T_c\) superconductors, such as, (Tl$_{0.3}$Pb$_{0.7}$)$_4$Sr$_3$(Cu$_{1-x}$Y$_x$)$_4$O$_{7}$ \[22\] and HgBa$_2$-Ca$_{2-n}$Cu$_{2n+2+\delta}$ \((n = 1-3)\) \[23\], was assigned to O 2p hole states within the CuO$_2$ planes. Therefore, in accord with results from other p-type cuprate superconductors \[14,18,22–24\], the first pre-edge peak at 528.2 eV in the XANES spectrum of (Tl$_{0.8}$Cr$_{0.2}$)$_4$Sr$_4$Cu$_2$(CO$_3$)$_7$O$_7$ in Fig. 2a was attributable to excitations of O 1s electrons to O 2p holes located in the CuO$_2$ planes. The other pre-edge peaks at 529.3 eV and 530.5 eV in Fig. 2a were ascribed to transitions into O 2p holes in the apical oxygen sites and the (Tl,Cr)-O planes, respectively.

However, another possible final state associated with the transition at 530.5 eV is the upper Hubbard band of the Cu 3d states highly hybridized with the O 2p states. Due to strong on-site correlation on the copper sites in the cuprate compounds, such a band has always been assumed to exist \[25\]. Therefore, the peak at 530.5 eV may be due to a superposition of unoccupied O 2p states originating from the (Tl,Cr)-O layers and the upper Hubbard band related to the CuO$_2$ planes. The peak assignment of the O K-edge XANES spectrum of Tl$_3$(CrO$_4$)$_4$Sr$_8$Cu$_4$O$_{16}$ is similar to that of (Tl$_{0.8}$Cr$_{0.2}$)$_4$Sr$_4$Cu$_2$(CO$_3$)$_7$O$_7$.

The peaks at \(\sim 532.2\) and \(\sim 533.6\) eV may be due to surface contamination since those peaks exhibit a greater intensity in the surface-sensitive total-electron yield spectra. Existence of surface contamination has been reported by many researchers. It is suggested that these peaks are arisen from absorption of hydrides, water, and CO$_2$ on the surface \[26\].

Figs. 3a and 3b show the pre-edge region of the O K-edge X-ray absorption spectra of (Tl$_{0.8}$Cr$_{0.2}$)$_4$Sr$_4$Cu$_2$(CO$_3$)$_7$O$_7$ and Tl$_3$(CrO$_4$)$_4$Sr$_8$Cu$_4$O$_{16}$, respectively. As shown, the spectral weight of the low-energy pre-edge peak at 528.2 eV is similar from (Tl$_{0.8}$Cr$_{0.2}$)$_4$Sr$_4$Cu$_2$(CO$_3$)$_7$O$_7$ to Tl$_3$(CrO$_4$)$_4$Sr$_8$Cu$_4$O$_{16}$. This indicates that the average number of holes within the in-plane oxygen sites per CuO$_2$ plane is approximately the same for both systems. Conversely, high-energy pre-edge peak at 529.3 eV originating from the apical oxygen sites decreases significantly in intensity in both systems. It has been demonstrated that the concentration of O 2p holes in the CuO$_2$ planes is strongly correlated with \(T_c\) \[18\]. Also several theories for high-\(T_c\) superconductors suggest that the apical O 2p$_z$ orbital plays a crucial role in superconductivity \[27–30\].
For example, the presence of apical oxygen atoms makes the CuO$_2$ plane easier to dope with holes [30]. In addition, superconductors with pyramidal copper coordination show a very large pressure enhancement of $T_c$, whereas, in superconductors with no apical oxygen atoms, the pressure effect on $T_c$ is very small [28]. Recently, a clear correlation has been found between the $T_c$ and the Cu bond valence sum due to variation in bonding of the copper ion to the apical oxygen [31]. Similarly, Ohta et al. found a correlation between $T_c$ and the energy difference between apical O 2p$_z$ states and planar O 2p$_{xy}$ states [32]. Grant et al. have recently pointed out the importance of the apical O 2p$_z$ states in determining the nature and dispersion of quasiparticle states of p-type doped cuprates [33]. Also Di Castro et al. have explained the suppression of $T_c$ above a certain dopant concentration by the occupancy of holes on Cu 3d$_{3z^2-r^2}$ and apical O 2p$_z$ hybrids [34]. It should be pointed out that the oxycarbonate (Tl$_{0.8}$Cr$_{0.2}$)Sr$_4$Cu$_2$(CO$_3$)O$_7$ is a superconductor with a $T_c$ of 68 K, while Tl$_3$(CrO$_4$)Sr$_8$Cu$_4$O$_{16}$ exhibits a $T_c$ of 25 K.

As noted from Fig. 3, the significant decrease in the average O 2p hole concentration in the apical oxygen sites in (Tl$_{0.8}$Cr$_{0.2}$)Sr$_4$Cu$_2$(CO$_3$)O$_7$ is accompanied by a substantial increase in $T_c$. Our data give evidence in support of the hypothesis that holes in apical oxygen sites may have a negative influence on the superconductivity in the layered cuprates. In Figs. 4a and 4b are shown the Cu L$_{23}$-edge X-ray-absorption near-edge-structure X-ray-fluorescence yield spectra of (Tl$_{0.8}$Cr$_{0.2}$)Sr$_4$Cu$_2$(CO$_3$)O$_7$ and Tl$_3$(CrO$_4$)Sr$_8$Cu$_4$O$_{16}$, respectively, in the energy range of 920 to 960 eV. The data have been normalized to the number of CuO$_2$ sheets per formula. For both systems, the strong excitonic peaks at 931.5 eV and 951.3 eV are very close to the L$_{23}$ peaks observed in the Cu L$_{23}$-edge absorption spectrum of CuO and are attributed to transitions from the Cu(2p$_{3/2}$)$_{3d^9}$-O2p$^6$ ground states (formally Cu$^{+2}$) to the Cu(2p$_{3/2}$)$_{3d^{10}}$-O2p$^6$ excited states, where (2p$_{3/2}$)$_{3d^{10}}$ denotes a 2p$_{3/2}$ hole [35]. Two shoulders at the high-energy side of the main peaks, as shown in Figs. 4a and 4b, are assigned to...
excitations of the Cu(2p_{3/2,1/2})^3d^9L ground states (formally Cu^{+3}) to the Cu(2p_{3/2,1/2})^{−1}3d^{10}L excited states, where L denotes the O 2p ligand hole [36]. According to the curve-fitting analyses, the new features are found to center at ~ 933.1 and ~ 952.9 eV, respectively. In addition, the integrated intensity of the high-energy shoulder at ~ 933.1 eV remains approximately unchanged from the (Tl_{0.8}Cr_{0.2})Sr_4Cu_2(CO_3)O_7 to the Y_{1.3}(CrO_4)Sr_8Cu_4O_{16} samples. Because there is only one type of Cu site in the unit cell of (Tl_{0.8}Cr_{0.2})Sr_4Cu_2(CO_3)O_7 and Y_{1.3}(CrO_4)Sr_8Cu_4O_{16} compounds (i.e., no Cu-O chains as in YBa_2Cu_3O_{6.8}) these high-energy features in the Cu L_{23}-edge absorption spectra can be obviously characterized as a result of the O 2p hole in the CuO_2 planes. It is noted that the behavior of these high-energy shoulders coincides with that for the pre-edge peak at 528.2 eV in the O K-edge absorption spectra shown in Fig. 2. This gives an evidence to verify the assignment that the pre-edge peak at 528.2 eV originates from the CuO_2 planes.

4. Conclusion

In this study, O K-edge and Cu L_{23}-edge X-ray-absorption near-edge-structure measurements of the (Tl_{0.8}Cr_{0.2})Sr_4Cu_2(CO_3)O_7 and Y_{1.3}(CrO_4)Sr_8Cu_4O_{16} compounds were performed to search for the hole distributions among different oxygen sites and their role in superconductivity. Near the O ls edge, three distinct pre-edge peaks at 528.2, 529.3 and 530.5 eV, respectively, are clearly revealed. These pre-edge peaks were ascribed to excitations of O 1s electrons to predominant O 2p holes located in the CuO_2 planes, in the apical oxygen sites, and in the (Tl,Cr)-O planes, respectively. The average number of holes within the in-plane oxygen sites per CuO_2 plane is approximately the same for both (Tl_{0.8}Cr_{0.2})Sr_4Cu_2(CO_3)O_7 and Y_{1.3}(CrO_4)Sr_8Cu_4O_{16} systems. Conversely, average hole content in the apical oxygen sites decreases significantly in (Tl_{0.8}Cr_{0.2})Sr_4Cu_2(CO_3)O_7 as compared to Y_{1.3}(CrO_4)Sr_8Cu_4O_{16}. The reduction of average O 2p hole concentration in the apical oxygen sites is accompanied by the enhanced superconductivity in (Tl_{0.8}Cr_{0.2})Sr_4Cu_2(CO_3)O_7. In the Cu L_{23}-edge absorption spectra, high-energy shoulders at ~ 933.1 and ~ 952.9 eV are assigned to the transitions from the Cu(2p_{3/2,1/2})^3d^9L ground states to the Cu(2p_{3/2,1/2})^{−1}3d^{10}L excited states, where L denotes the O 2p ligand hole. The behavior of these shoulders correlates with that of the pre-edge peak at 528.2 eV in the O K-edge absorption spectra. Based on the present X-ray absorption studies, the O 2p holes in the apical oxygen sites play a crucial role in controlling the Tc up to 68 K in (Tl_{0.8}Cr_{0.2})Sr_4Cu_2(CO_3)O_7.

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References


