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X-ray Absorption Spectroscopic Evidence on the Partial Formation of Copper(III) in the Superconducting $La_2CuO_{4.08}$

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Since the discovery of superconductivity through the partial substitution of Ba for La in the La_2CuO_4 system,[1] La_2CuO_4 and its related compounds have been regarded as model compounds for studying superconductivity due to their structural simplicity. In addition, it is well-known that the incorporation of excess oxygen by annealing under high oxygen pressure[2] or electrochemical oxidation[3] also makes La_2CuO_4 become superconductive. More recently, superconducting $La_2CuO_{4+\delta}$ was reported to be prepared by oxidizing La_2CuO_4 chemically with $KMnO_4$ as an oxidizing agent.[4] Although a series of works for these materials has clearly shown a relationship between T_c and the hole concentration in the CuO_2 plane upon doping, there are still controversies on the orbital character of the hole carrier. Some studies support that the doping effect results in the partial formation of formal Cu^{III}, to which superconductivity might be attributed.[5] In contrast, it has also been claimed that the newly introduced holes have mainly O 2p character as concluded by means of spectroscopic studies.[6] Taking into account the strong covalency of the Cu−O bond in a superconductor, however, the spectral changes at oxygen sites might be a natural phenomenon, irrespective of the orbital character of the holes.[7,8] Moreover, since the oxygen ions exist in crystallographically inequivalent sites, it is very difficult to differentiate them through the spectroscopic studies for oxygen. Earlier studies on the Cu K-edge XANES spectra for La_2CuO_4−related compounds[9] could not reach a general consensus for the spectral interpretation due to both the absence of an adequate Cu^{III} reference spectrum and its complexity; nevertheless, some differences between nonsuperconducting and superconducting phases have been found.

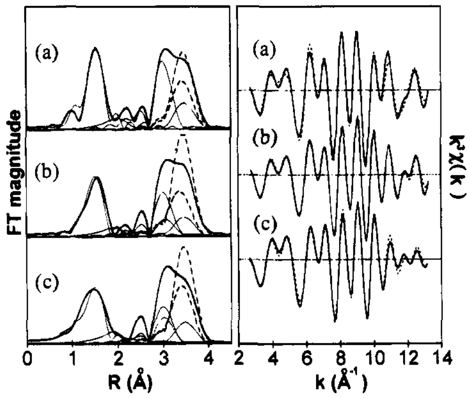

Figure 1. (Left) FTs (boldface solid lines) of experimental $k^3\chi(k)$ together with contributions of individual single- (lightface solid lines) and multiple-scattering paths (dashed lines) for (a) La_2CuO_4 as sintered and (b) electrochemically and (c) chemically oxidized $La_2CuO_{4.08}$. (Right) Experimental Fourier filtered $k^3\chi(k)$ (solid lines) and the best fits (dashed lines).

In the present work, we suggest for the first time the contribution of the unoccupied Cu 3d states to the newly formed holes[10] using the bulk sensitive X-ray absorption spectroscopy at the Cu K edge for nonsuperconducting La_2CuO_4 and two superconducting $La_2CuO_{4+\delta}$ phases prepared electrochemically and chemically, respectively, on the basis of the previous XAS study[11] for the Cu^{III} compounds.

The undoped La_2CuO_4 was prepared by a conventional solid-state reaction. For the doped $La_2CuO_{4+\delta}$, electrochemical and chemical oxidation experiments were carried out under the conditions[3,4] for obtaining the maximum value of δ. The phase purity of each compound was verified by X-ray diffraction analysis. The excess oxygen content (δ) could be determined to be 0.00 for the as-sintered sample and 0.08 for both oxidized samples.[12]

The X-ray absorption measurements[13] at the Cu K edge were performed in a transmission mode at room temperature. In order to determine the structural parameters, a curve fitting was performed with the UWXAFS code[14] in the region $R \leq 4$ Å that corresponds to the distance to the next nearest Cu (hereafter Cu′) in the Fourier transform (FT). Some constraints were placed on the fits to maintain, for simplicity, the space group *Fmmm* rather than *Bmab*, which corresponds to the crystal structure of the undoped La_2CuO_4.[15] That is, the Cu−Cu′ distance was constrained to twice the Cu−O(1) distance, and theoretical functions for all scattering paths were calculated by the FEFF 5 code[16] within the *Fmmm* space group.

Figure 1 shows FTs of the Cu K edge EXAFS spectra and their Fourier filtered $k^3\chi(k)$ together with best fits for the present compounds. The structural parameters, summarized in Table

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(8) It is very instructive to examine the I L_I-edge XANES for various metal iodides with ionic or covalent metal−iodine bonds, since its transition from s core levels to available empty p states is the same as the O K edge. The I L_I edge spectra for KI and AgI with representative ionic bonding character show no transition corresponding to 2s → 5p because 5p states for I^- ($5p^6$) are completely filled. But covalent compounds such as HgI_2 or BiI_3 clearly show small peaks due to s 2s → 5p transition, which might be attributed to the charge redistribution resulting from the strong covalency of the (Hg/Bi−I) bond.

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(12) The δ value was estimated from the Cu^{III}/Cu^{II} ratio by iodometric titration. According to the Mn K edge XAS measurement, it was confirmed that there is a small trace of MnO_2 in the chemically oxidized sample, as expected from the decomposition of the permanganate ion in a neutral or basic solution, although any Mn impurities were not detected by X-ray diffraction. Therefore, the δ value of this sample was determined by taking into account the amount of MnO_2 that was estimated by atomic absorption spectroscopy.

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Table 1. Fitted Structral Parameters to the Cu K Edge EXAFS Spectra

				$La_2CuO_{4.08}$						crystallographic values	
	as sintered $La_2CuO_{4.00}$			electrochemically oxidized			chemically oxidized			$La_2CuO_{4.00}$[a]	$La_2CuO_{4.12}$[b]
atom	R (Å)	N	σ^2 (Å^2)	R (Å)	N	σ^2 (Å^2)	R (Å)	N	σ^2 (Å^2)	R (Å)	R (Å)
4 O(1)	1.90_3	3.9	0.002	1.89_9	3.9	0.004	1.89_9	4.3	0.006	1.905_7	1.900_1
2 O(2)	2.41_4	2.3	0.011	2.34_9	1.8	0.010	2.33_0	1.9	0.009	2.421_1	2.410_3
2 La(1)										3.228_7	
				3.23_7	3.9	0.006	3.23_2	3.9	0.007		3.246_8
2 La(2)	3.24_6	8.4	0.008							3.291_8	
4 La(3)				3.29_7	3.9	0.012	3.26_0	4.5	0.010	3.238_9	3.276_7
4 Cu	3.80_6	4.1	0.006	3.79_9	3.9	0.008	3.79_9	4.0	0.008	3.806_4	3.800_3

[a] Room temperature data from ref 15. [b] Room temperature data from ref 17. Here, $\delta = 0.12$ was determined by TGA in a H_2 atmosphere, but $\delta = 0.07$ by the iodometric titration for the same sample. (Here an assumption was made that the lattice oxygens are in the form of O^{2-}.)

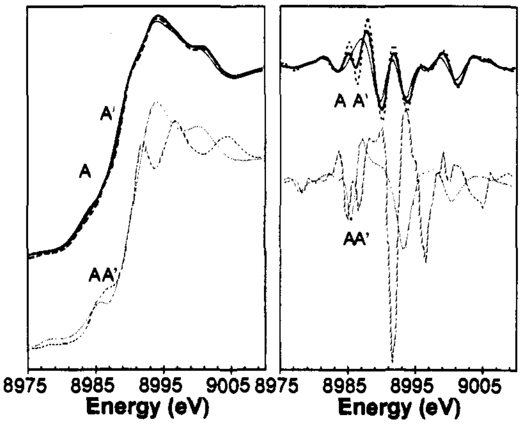

Figure 2. (Left, a) Cu K edge XANES spectra for La_2CuO_4 as sintered (lightface solid line) and electrochemically (boldface dashed line) and chemically (boldface solid line) oxidized $La_2CuO_{4.08}$ together with Cu^{III} reference compounds, $La_2Li_{0.5}Cu_{0.5}O_4$ (lightface dashed line) and $LaCuO_3$ (dotted line), and (right, b) their second derivatives.

1, are in good agreement with the previous diffraction results,[15,17] even though the doped excess oxygens could not be directly observed due to their insensitivity for EXAFS. It is worth noting here that the chemical oxidation of La_2CuO_4 by $KMnO_4$ could induce the same doping effect as the electrochemical one. EXAFS analyses clearly showed that the axial Cu−O(2) bond distance is significantly decreased by oxidation. Especially, the contribution of multiple scatterings via Cu−O(1)−Cu′ is greater for both $La_2CuO_{4.08}$ than for La_2CuO_4, which suggests that the Cu−O(1)−Cu′ bond for the former is more collinear than that for the latter. These facts well support the previous diffraction results that, while the unoxidized compound has the *Bmab* symmetry due to a slight tilt of CuO_6 octahedra, the oxidized ones have a higher *Fmmm* symmetry. Now it is necessary to examine carefully the electronic structure of the Cu ions in order to establish the origin of enhanced covalency of the Cu−O bond by doping with excess oxygen.

Figure 2a represents the Cu K edge XANES spectra for the present compounds together with $La_2Li_{0.5}Cu_{0.5}O_4$ and $LaCuO_3$ for comparison. It is obvious that there is an overall spectral shift of about 0.5 eV to a higher energy side after the electrochemical or chemical oxidation. Although such changes have been also observed by previous researchers, a generally acceptable interpretation has not been made up to now. In addition to the overall peak shift, we could observe a remarkable difference in the Cu K edge XANES spectra. Namely, an additional shoulder (A′) appeared reproducibly at ~8986 eV for the oxidized compounds.[18] This difference can be more clearly seen in the corresponding second derivatives in Figure 2b. Peak A has been generally accepted as a 1s → $4p_\pi$ transition accompanied by a shakedown process through ligand to metal Cu (3d hole) charge transfer (LMCT), which enhances the screening of the core hole, resulting in lower transition energy; and its position and intensity mainly depend on the local symmetry around the copper site in the case of Cu^{II} compounds. The shorter axial Cu−O bond might reduce electrostatically the effective LMCT, resulting in a higher energy shift of peak A with a weakening of its intensity. In the present work, however, the occurrence of an additional peak A′ for the oxidized compounds could not be attributed to the shorter axial Cu-O bond induced by the oxidation reaction. According to previous diffraction studies,[17,19] the samples with $\delta = 0.08$ were determined to be single phase with a very large superstructure due to an ordering of the interstitial excess oxygen in the entire temperature region. Therefore, the coexistence of A and A′ peaks in the oxidized compounds cannot be explained by the structural aspect. But our previous study[10] on the Cu K edge of the chemically well defined Cu^{III} compounds would give us some clues about the origin of the A′ peak. We have pointed out that, despite the electrostatic repulsion by the short axial Cu−O bond, the enhanced attractive potential of trivalent copper favors the charge transfer from oxygen to copper, so that the shakedown transition is expected to appear at somewhat higher energy. Moreover, $La_2Li_{0.5}Cu_{0.5}O_4$ exhibits the splitting (A and A′) of the transition by the shakedown process, which corresponds to the transitions to the final states of $|1s^13d^9\underline{L}^{-1}4p_\pi{}^1\rangle$ and $|1s^13d^9\underline{L}^{-1}4p_\sigma{}^1\rangle$, respectively. Now we can see in Figure 2 that the peak position of A′ for the present oxidized $La_2CuO_{4.08}$ is well consistent with that of peak A′ for $La_2Li_{0.5}Cu_{0.5}O_4$. It is therefore concluded that doping with excess oxygen gives rise to a partial formation of trivalent copper, resulting in a stronger covalency in the Cu−O σ bonds with an increase of hole density in the Cu−O planes.

In a previous XAS study[6b] at the O K and Cu L_3 edges for $La_{2-x}Sr_xCuO_4$, Pellegrin et al. argued that the extra holes formed by p-type doping mainly have the symmetry of O $2p_{x,y}$ consisting of in-plane Cu−O σ bond, but they could not determine whether the change of spectral shape at the Cu L_3 edge is relevant to the density of unoccupied Cu 3d states. On the other hand, our results clearly indicate that the doping-induced holes are present on the Cu sites of the oxidized superconducting $La_2CuO_{4.08}$ phases.

In summary, it has been clearly confirmed by XAS that the same doping effect on the stoichiometric La_2CuO_4 could be induced by chemical and electrochemical methods. Comparing the Cu K edge XANES spectra between the present compounds and the chemically well defined Cu^{III} references, it is concluded that a Cu^{III} contribution is present in the ground state of the oxidized phase, $La_2CuO_{4.08}$.

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