# Hole states in fluorine-doped $La_2CuO_4$ thin films probed by polarized x-ray-absorption spectroscopy

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High-resolution polarized x-ray-absorption spectra at the O *K* edge and Cu *L* edge for *c*-axis-oriented $La_2CuO_4F_x$ thin films using a bulk-sensitive x-ray-fluorescence-yield detection method were investigated. In the O 1*s* absorption edge of $La_2CuO_4F_x$, the prepeak at 528.7 eV is assigned to transitions into O $2p_{xy}$ hole states located in the $CuO_2$ planes. Fluoride ions present in $La_2CuO_4F_x$ induce hole states in the $CuO_2$ planes near the Fermi level, which in turn play an important role in enhancing superconductivity for this compound, as compared to parent $La_2CuO_4$. Thus, in $La_2CuO_4F_x$, fluoride ions are regarded as an electronic dopant to induce superconductivity. [S0163-1829(99)08233-8]

## I. INTRODUCTION

The discovery of high-$T_c$ superconductors by Bednorz and Müller in the La-Ba-Cu-O system has promoted an intensive investigation for superconducting cuprates.[1] To improve the superconducting properties of this compound, different treatments, such as annealing in moderate oxygen pressure,[2,3] annealing in high oxygen pressure,[4,5] fluorination,[6–8] chlorination,[9,10] and electrochemical oxidation,[11] have been widely applied. Fluorine doping into cuprates as a technique to induce superconductivity has recently attracted considerable attention.[12–22] Several new high-$T_c$ superconductors containing fluorine, such as $La_2CuO_{4-\delta}F_y$ ($T_c \sim 40$ K),[6,7,15–18] $Nd_2CuO_{4-x}F_x$ ($T_c \sim 27$ K),[19] $Sr_2CuO_2F_{2+\delta}$ ($T_c \sim 46$ K),[20] $La_{0.7}Sr_{1.3}Cu(O,F)_{4+\delta}$ ($T_c = 55$ K),[21] $Sr_2Ca_{n-1}Cu_nO_{2n+\delta}F_{2+y}$ ($T_c = 99$ K for $n=2$, 111 K for $n=3$),[22] and $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}F_y$ ($T_c = 97$ K for $n=1$, 128 K for $n=2$, 135 K for $n=3$),[23] have been reported.

$La_{2-x}Sr_xCuO_4$ is one of the most widely studied cuprate systems. At lower Sr levels, the structure is an orthorhombic distortion of the type $K_2NiF_4$ (space group *Cmca*).[24] For a substitution level of $x > 0.05$, the crystal exhibits a tetragonal structure (space group $I4/mmm$). The substitution of $La^{3+}$ ions with $Sr^{2+}$ ions in the $La_2O_2$ layers of the parent $La_2CuO_4$ gives rise to superconductivity with $T_c \sim 40$ K for $x = 0.15$.[25] It is reported by Tissue *et al.* that $La_2CuO_{4+x}$ exhibits superconductivity with $T_c \sim 36$ K upon incorporation of fluorine into the bulk.[6] In addition, one significant change observed after fluorination of $La_2CuO_{4+x}$ is the increase in orthorhombic distortion. In relation to the parent $La_2CuO_{4+x}$, the *a* parameter in $La_2CuO_4F_x$ decreases and *b* increases.[15] Fluorination of $La_2CuO_4$ has also a drastic effect on the transport properties. A decrease in thermal conductivity, electrical resistivity, and thermoelectric power is observed.[8] Although the physical properties of the $La_2CuO_4F_x$ cuprates have been widely studied, no investigations of electronic structure of these compounds have been performed. It is therefore of great interest to understand the variation of electronic structure near the Fermi level of parent oxides $La_2CuO_4$ and fluorine-doped $La_2CuO_4$.

It is well known that the hole states play a pivotal role for superconductivity in the *p*-type cuprate superconductors. Therefore, knowledge of the electronic structure near the Fermi level of these compounds is an important step towards unveiling the mechanism of superconductivity. Soft x-ray-absorption spectroscopy using synchrotron radiation has been widely applied to investigate the local density of unoccupied states at the oxygen and copper sites in high-$T_c$ superconductors. In particular, polarization-dependent x-ray-absorption measurements are able to provide detailed information on the orbital character of the holes in the *p*-type cuprates.[26,27] Pulsed laser ablation is now a well-established technique for the fabrication of thin films of oxide materials. In particular, it has been utilized to prepare thin films of high-$T_c$ cuprate superconductors. Recently, Lees *et al.* have successfully developed a method to anionically control the carrier concentration in $La_2CuO_4F_x$ thin films with a $T_c$ of $\sim 38$ K.[28] In this study, we report the results of high-resolution polarized x-ray-absorption spectra at the O *K* edge and Cu *L* edge for *c*-axis-oriented $La_2CuO_4$ and $La_2CuO_4F_x$ thin films by using a bulk-sensitive x-ray fluorescence-yield detection method.

## II. EXPERIMENT

Detailed procedures for preparing superconducting $La_2CuO_4F_x$ thin films have been reported in detail elsewhere.[28] In brief, $La_2CuO_4$ target pellets were prepared by standard solid-state techniques. Thin films of $La_2CuO_4$ were fabricated by pulsed laser ablation from the oxide tar-

 

get. A 248-nm KrF excimer laser with pulse length of 20 ns and a repetition rate of 10 Hz was employed as the light source. Fluorine doping of the $La_2CuO_4$ thin films was attempted using a gaseous fluorination approach. Optimum results were obtained with films held at 150 °C under 10% $F_2$ in $N_2$ for 10 min. As checked by x-ray diffraction (XRD), the $La_2CuO_4F_x$ thin films prepared by this procedure were single phase and highly preferentially oriented with the *c* axis perpendicular to the surface of the thin films.

The polarized x-ray-absorption experiments were carried out at the Synchrotron Radiation Research Center (SRRC) in Taiwan with an electron beam energy of 1.5 GeV. The synchrotron radiation was monochromatized by a 6-m high-energy spherical grating monochromator (HSGM) beamline which covers a photon energy range of 150–1200 eV. The polarization-dependent x-ray-absorption spectra with several incidence angles ($\phi$) with respect to the surface normal have been recorded by rotating the sample around a vertical axis. Because very narrow slits centered around the electron orbit plane were used, the linear polarization of the monochromatic beam was estimated to be around 97%. The x-ray fluorescence-yield spectra were obtained using a microchannel plate (MCP) detector.[29] In contrast to the electron-yield measurements, x-ray fluorescence-yield measurements are strictly bulk sensitive with a probing depth of thousands of angstroms. The MCP detector consists of a dual set of MCP's with an electrically isolated grid mounted in front of them. During x-ray fluorescence-yield measurements, the grid was set to a voltage of 100 V, while the front of the MCP's was set to −2000 V and the rear to −200 V. The grid bias ensured that positive ions would not be detected while the MCP bias ensured that no electrons were detected. The incident photon flux ($I_0$) was monitored simultaneously by a 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 $L_3$-edge absorption peaks of CuO. The energy resolution of the monochromator was set to ~0.22 and ~0.45 eV for the O *K*-edge and Cu *L*-edge x-ray-absorption measurements, respectively. All the measurements were performed at room temperature.

### III. RESULTS AND DISCUSSION

Polarized O *K*-edge x-ray-absorption spectra of the superconducting $La_2CuO_4F_x$ thin film recorded at different incidence angles ($\phi$) are reproduced in Fig. 1 obtained using a bulk-sensitive total-x-ray-fluorescence-yield method. The absorption spectrum for $\phi=0°$ corresponds to the normal incidence geometry where the electric field vector *E* of the linear-polarized synchrotron light is parallel to the *ab* plane of the thin film, while spectrum for $\phi=75°$ represents the grazing incidence geometry where the *E* vector is nearly parallel to the *c* axis of the thin film. The O 1*s* x-ray-absorption spectra for the $La_2CuO_4F_x$ thin film, as shown in Fig. 1, can be divided into two regions: below and above the photon energy ~531 eV. The low-energy prepeaks with energy below 531 eV are ascribed to transitions from the O 1*s* core electrons to hole states with mainly O 2*p* character, while the strong rise in spectral weight of the absorption spectra above 531 eV is attributed to continuum absorption to Cu

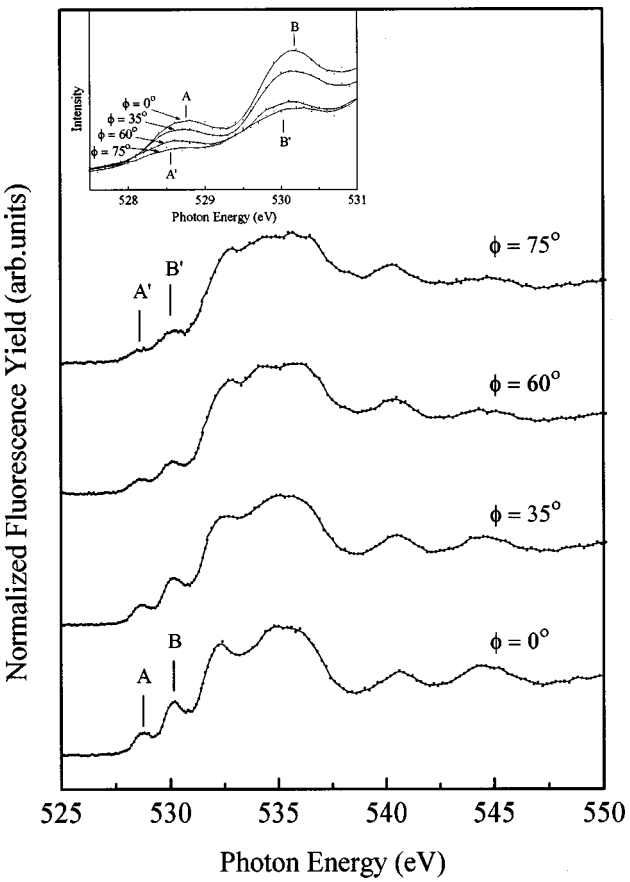


FIG. 1. Polarization-dependent O *K*-edge x-ray-absorption spectra of the $La_2CuO_4F_x$ thin film as a function of the incidence angle $\phi$ with respect to the normal of the sample surface. The absorption spectrum for $\phi=0°$ corresponds to the electric field vector *E* of the synchrotron light parallel to the *ab* plane of the thin film, while spectrum for $\phi=75°$ represents the *E* vector nearly parallel to the *c* axis of the thin film.

3*s*, Cu 3*p*, La 5*d*, or La 4*f* empty states hybridized with O 2*p* states.[26]

The prominent features in the O 1*s* x-ray-absorption edge for $E\|ab$ ($\phi=0°$), as shown in Fig. 1, are two pronounced prepeaks (labeled as *A* and *B*) at 528.7 and 530.2 eV, respectively. As $\phi$ is increased from $E\|ab$ to $E\|c$, the spectral weights of prepeaks *A* and *B* are significantly reduced and new prepeaks (labeled as $A'$ and $B'$) appear at ~0.2 eV lower in photon energies, as shown in the inset of Fig. 1. According to dipole selection rules, for $E\|ab$, only the unoccupied electronic states with O $2p_{xy}$ symmetry are probed, and in the $E\|c$ case, the empty O $2p_z$ states are accessible for the O 1*s* transition.[26] Accordingly, prepeak *A* has mainly O $2p_{xy}$ symmetry and prepeak $A'$ has predominantly O $2p_z$ character. Since these absorption peaks correspond to transitions into unoccupied O 2*p* states near the Fermi level, the observed different O 1*s* thresholds in Fig. 1 may be due to chemical shifts originating from the influence of charges on the oxygen sites and the site-specific neighborhood.

The structure of $La_2CuO_4$ consists of one plane of Cu atoms with four strongly bounded oxygen neighbors in the square-planar arrangement which is separated by two LaO planes. Therefore, there exists three nonequivalent oxygen sites in $La_2CuO_4$: O(2) and O(3) within the $CuO_2$ layers

and O(1) in the LaO planes. Band-structure calculations based on the local-density approximation (LDA) have been successful in calculating the electronic structure of the cuprate superconductors.[30] Based on LDA band-structure calculations, for $La_2CuO_4$, the binding energy of the O $1s$ level for O sites in the LaO planes is higher than that for O sites in the $CuO_2$ planes.[31] From the polarization-dependent x-ray-absorption measurements on single-domain crystal of $La_{2-x}Sr_xCuO_4$, it was found that the O(2,3) $1s$ level is about 0.3 eV lower in energy than the O(1) $1s$ level, which is consistent with the theoretical predictions.[27] Therefore, the spectral weight of the valence-band prepeak $A$ for $E\|ab$, as shown in Fig. 1, corresponds to unoccupied O $2p_{xy}$ states in the $CuO_2$ plane, while prepeak $A'$ for $\phi=75°$ is ascribed to transitions into mainly unoccupied O $2p_z$ states from the apical oxygen. Prepeak $B$ at 530.2 eV is assigned to a $3d^{10}\underline{L}\rightarrow \mathrm{O}1\underline{s}3d^{10}$ transition, i.e., a transition into the O $2p$ state, which by hybridization is admixed to the upper Hubbard band (UHB) with predominantly Cu $3d$ character, where $\underline{L}$ and $\mathrm{O}1\underline{s}$ denote the O $2p$ ligand hole and a O $1s$ hole, respectively. Due to the strong on-site correlation effects on the copper sites in the cuprate superconductors, a UHB state has always been assumed to exist.[32] As shown in inset of Fig. 1, for the UHB state, a chemical shift of ~0.2 eV to lower energy is also observed in going from $E\|ab$ and $E\|\sim c$.

The O $K$-edge x-ray-absorption spectra of the $La_2CuO_4F_x$ and $La_2CuO_4$ thin films for the incidence angle $\phi=0°$ are displayed in Fig. 2. These spectra were normalized to the intensity in the energy range between 531 and 555 eV with respect to the number of O atoms per unit cell, providing the absolute intensities of the prepeaks for the $La_2CuO_4F_x$ and $La_2CuO_4$ compounds. This is due to the fact that the spectra above 531 eV for the $La_2CuO_4F_x$ and $La_2CuO_4$ thin films are quite similar and independent of the different oxygen environments.

As shown, in the O $1s$ absorption edge of the $La_2CuO_4$ sample, only a prepeak at 530.2 eV originating from the UHB is observed. In the $La_2CuO_4F_x$ sample, a second prepeak at 528.7 eV develops, which originates from doping-induced hole states. This indicates that fluorination of $La_2CuO_4$ induces hole states in the $CuO_2$ planes near the Fermi level. $La_2CuO_4$ is nonsuperconducting, whereas $La_2CuO_4F_x$ thin film exhibits a $T_c$ of ~38 K. Thus the generation of holes in the O $2p$ orbitals within the $CuO_2$ planes is probably responsible for inducing a transition from a semiconductor to a superconductor.

Compared to $La_2CuO_4$, the UHB peak at 530.2 eV shows a decrease in spectral weight in $La_2CuO_4F_x$, as shown in inset of Fig. 2. This change is related to the spectral weight transfer of states from the UHB to doping-induced hole states near the Fermi level.[33] Similar behavior has also been observed in O $1s$ absorption spectra of other systems.[34,35] The O $2p$ hole state in the $CuO_2$ planes is separated from the UHB state by an energy of ~1.5 eV, which is close to the charge transfer gap of most $p$-type cuprate superconductors.[26] This indicates that the Fermi level for the $La_2CuO_4F_x$ sample is close to the top of the valence band. In this respect, this compound is typical of a $p$-type cuprate superconductor.[36,37] Therefore, in $La_2CuO_4F_x$, fluoride ions

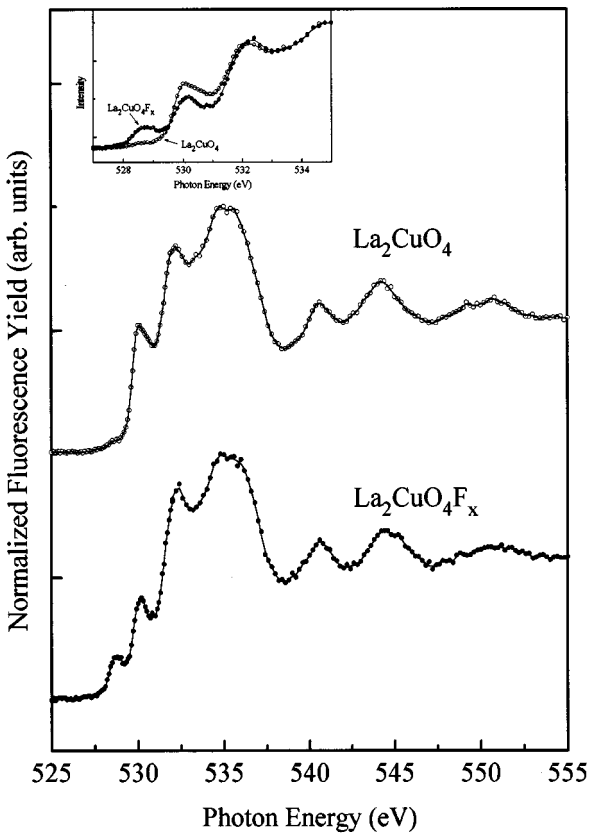


FIG. 2. O $K$-edge x-ray-absorption spectra of the $La_2CuO_4F_x$ (solid circle) and $La_2CuO_4$ (open circle) thin films for the electric field vector $E$ parallel to the $ab$ plane of the thin film. The O $K$-edge-absorption spectra have been normalized to the intensity in the energy range between 531 and 555 eV.

are regarded as an electronic dopant to induce superconductivity.

The Cu $L_3$-edge x-ray-absorption fluorescence-yield spectra of $La_2CuO_4F_x$ and $La_2CuO_4$ thin films at room temperature in the energy range of 926–937 eV are presented in Fig. 3. For the $La_2CuO_4$ sample, the Cu $L_3$-edge absorption spectrum shows a symmetry peak centered at 931.2 eV. In the Cu $L_3$-edge absorption spectrum of CuO, a white line at 931.2 eV and satellite structure at 937 eV are observed corresponding to transitions into $(2\underline{p}_{3/2})3d^{10}$ and $(2\underline{p}_{3/2})3d^9 4s$ final states, respectively, where $(2\underline{p}_{3/2})$ denotes a $2p_{3/2}$ hole.[38] Therefore, the absorption peak at 931.2 eV shown in Fig. 3 is ascribed to transitions from the $\mathrm{Cu}(2\underline{p}_{3/2})3d^9$-$\mathrm{O}2p^6$ ground-state configuration (formal divalent Cu oxidation state) to the $\mathrm{Cu}(2\underline{p}_{3/2})3d^{10}$-$\mathrm{O}2p^6$ excited state.

For the $La_2CuO_4F_x$ sample, the absorption spectrum becomes asymmetric and a new feature (indicated as $L_3'$) appears on the high-energy side of the Cu $L_3$ white line. From the curve-fitting analysis, this new feature is found to center at about 932.2 eV. Based on photoemission studies and cluster calculations on divalent Cu compounds, the high-energy structure originates from the O $2p$ hole states and is assigned to transitions from the $\mathrm{Cu}(2\underline{p}_{3/2})3d^9\underline{L}$ ground state (formal trivalent Cu oxidation state) to the $\mathrm{Cu}(2\underline{p}_{3/2})3d^{10}\underline{L}$ excited state.[39,40] Therefore, the intensity of this shoulder can be regarded as the total concentration of hole states in the cuprate superconductors, as prepeaks observed in the O $1s$ x-ray-

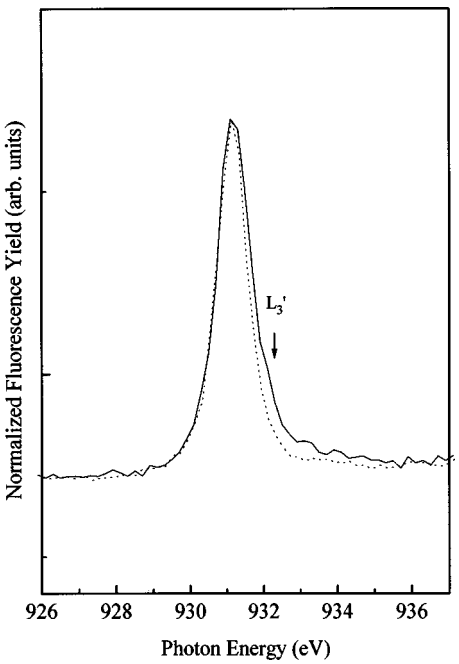


FIG. 3. Cu $L_3$-edge x-ray-absorption fluorescence-yield spectra of $La_2CuO_4F_x$ (solid line) and $La_2CuO_4$ (dotted line) thin films for the incidence angle $\phi = 35°$.

absorption spectrum. As shown, fluorination of $La_2CuO_4$ leads to an increase in intensity at the high-energy shoulder in the Cu $L_3$-edge absorption spectrum, corresponding to an increase in the O $2p$ hole concentration. This is also evidenced by the O $K$-edge x-ray-absorption spectra.

Recently, Al-Mamouri *et al.* demonstrated that fluorine can force the apical oxygen to transfer to equatorial sites to form $CuO_2$ sheets and to induce superconductivity at 46 K by fluorination of $Sr_2CuO_3$ with $F_2$ gas.[20] Apart from entering the apical site, F ions can also enter the interstitial site (0, 1/2, 1/4) in $Sr_2CuO_2F_{2+\delta}$ to maintain electrical neutrality. Superconductivity in $Sr_2CuO_2F_{2+\delta}$ has been induced by incorporating extra F ions located in interstitial sites. For iodine-intercalated $Bi_2Sr_2CaCu_2O_8$ compound, the I is inserted between the adjacent BiO layers and thus leads to a remarkable expansion of the unit cell $c$ dimension.[41]

Similarly, the formation of $La_2CuO_4F_x$ structure occurs via intercalation to produce F ions in interstitial sites between LaO layers of the $La_2CuO_4$ structure.[28] The charge transfer between the intercalated F and $CuO_2$ sheets in the $La_2CuO_4F_x$ material leads to an increase of the hole concentration in the $CuO_2$ sheets, as evidenced by O $K$-edge and Cu $L$-edge x-ray-absorption spectra in Figs. 2 and 3. It has been demonstrated that the concentration of O $2p$ holes in the $CuO_2$ planes is strongly correlated with $T_c$.[42,43] Accordingly, superconductivity is induced upon incorporation of fluorine into the $La_2CuO_4$ sample.

As mentioned, $La_2CuO_{4+x}$, which is orthorhombic before fluorination, undergoes a further orthorhombic distortion after fluorination. In other words, compared to the parent $La_2CuO_{4+x}$ compound, the $a$ parameter in $La_2CuO_4F_x$ decreases and $b$ increases. The decrease in $a$ brings the Cu atoms closer along one of the (110) axes of the perovskite cell, which may be critical for pairing. A similar decrease in $a$ parameter is observed when the composition is changed from $YBa_2Cu_3O_6$ to $YBa_2Cu_3O_7$. It has been proposed that the Cu-O bond length may be an important factor in controlling the $CuO_2$ planes to be oxidized to induce hole-doped superconductivity.[44] Thus a structural factor might play a notable role in determining $T_c$.

## IV. CONCLUSION

We report high-resolution polarized O $K$-edge and Cu $L$-edge x-ray-absorption fluorescence-yield spectra of $c$-axis-oriented $La_2CuO_4F_x$ thin films. In the O $1s$ absorption edge of $La_2CuO_4F_x$, the prepeak at 528.7 eV has predominantly O $2p_{xy}$ symmetry and is assigned to transitions into O $2p$ hole states located in the $CuO_2$ planes. Fluoride ions present in $La_2CuO_4F_x$ generate hole states in the $CuO_2$ planes near the Fermi level, which in turn play an important role in inducing superconductivity for this compound, as compared to parent $La_2CuO_4$. In the Cu $L_3$-edge absorption spectrum of $La_2CuO_4F_x$, the high-energy shoulder at ~932.2 eV is assigned to $Cu(2p_{3/2})3d^9\underline{L} \rightarrow Cu(\underline{2p_{3/2}})3d^{10}\underline{L}$ transitions, where $\underline{L}$ denotes the O $2p$ ligand hole. Fluorination of $La_2CuO_4$ leads to an increase in spectral weight of high-energy shoulder in the Cu $L_3$-edge absorption spectrum, corresponding to an increase in O $2p$ hole concentrations. This is also evidenced by the O $K$-edge absorption spectrum. Thus, in $La_2CuO_4F_x$, fluoride ions are regarded as an electronic dopant to induce superconductivity.

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