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Increased density of the in-plane and out-of-plane doping holes in the superconducting state of $HgBa_2Ca_2Cu_3O_y$

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We have studied the electronic structure near the Cu-O planes in the normal and superconducting states in a high-quality $HgBa_2Ca_2Cu_3O_y$ thick film using polarized x-ray absorption in order to get quantitative information on the changes in density and symmetry of the itinerant holes. We have observed, in our analysis of the Cu L_3-edge absorption spectra, an increase in the density of doping holes along the planes parallel and perperdicular to the Cu-O sheets while going from the normal to the superconducting state. Our results show that some of the holes have $3d_{z^2}$ symmetry and moreover their density also increases as the system goes to the superconducting state. The results have been discussed in light of the earlier published results on other cuprate superconducting systems and a probable local and short-range structural change in the CuO_5 pyramid which may be associated with the superconducting transition. [S0163-1829(97)05845-1]

I. INTRODUCTION

The pressure dependence of the superconducting transition temperature (T_c) in Hg-based cuprate superconductors[1] makes them unique among the Cu-oxide high-T_c superconductors. Among these, $HgBa_2Ca_2Cu_3O_y$ (Hg-1223) has particularly shown a spectacular increase in T_c with applied pressure.[2] Neutron-diffraction studies under high pressure on this system have revealed a drastic shortening of the apical Cu-O distance which is possibly linked to the increase in T_c.[3] On the other hand, band-structure calculations based on local density approximations (LDA's) have predicted[4,5] an enhancement of T_c with an increase in the density of doping holes or on insertion of excess oxygen into the Hg-O planes. Again, neutron-diffraction studies[3] have shown that insertion of excess oxygen has the same effect on the crystal structure of this compound as that when subjected to high pressure. Novikov and Freeman[5] have observed that both insertion of excess oxygen and application of external pressure have similar effects on the position of the band derived from Hg $6p_z$ and the $2p_z$ state of the apical oxygen near the Fermi energy (E_F). Such a large dependence of the physical properties on the apical Cu-O distances suggests the necessity of a detailed study of the electronic structure around the Cu-O bonds in the Hg-1223 system.

X-ray-absorption spectroscopy (XAS) studies using polarized photons have been quite successful in providing direct information on the electronic structure near the Cu-O bonds in case of the high-T_c superconductors. Moreover, polarized XAS probes the orientation of the unoccupied states and thereby the symmetry of the orbitals wherein the charge carriers are induced by doping.[6] Although there are a number of polarized XAS studies[6–17,18–20] on the symmetry of charge carriers, none have been reported on Hg-based cuprate superconductors. Pellegrin *et al.*[21] have reported x-ray absorption studies at the Cu L_3 and O K edges on Hg-1223 materials using unpolarized x rays. The symmetry and nature of the doping holes in cuprate superconductors is still an important issue yet to be understood fully as many of the proposed multiband models for superconductivity assume an active role for holes having Cu $3d_{z^2-r^2}$ and O $2p_z$ symmetries.[22–28] Most of the earlier reports have shown that the unoccupied Cu $3d$ states mainly have $3d_{x^2-y^2}$ character with 10–20% weight of Cu $3d_{z^2-r^2}$ character.[9,10,12,14–17] Earlier studies on Tl-2212 thin films have also shown that there exist 10–12% holes having $3d_{z^2-r^2}$ character.[14–17] Recently, Srivastava *et al.*[19] have reported 10–18% of Cu $3d_{z^2-r^2}$ states compared to the total amount of holes in the Tl-2212 thin films, thus pointing to difference in behavior of the Tl-2212 as compared to the Bi-2212 system, showing complete absence of these states.[7,8]

Although it is very important to study the changes in density of the doping holes having different symmetries associated with the superconducting transition, only a very few studies have been reported until now.[7,8,18,29,30] From inverse photoemission studies Wagener *et al.*[29] have shown that the density of O $2p$ holes increases and that of Cu $3d$ holes decreases when $YBa_2Cu_3O_y$ system goes from normal to the

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superconducting state. Similar changes in the O $2p$ holes have been observed by Hirai *et al.*[30] in $YBa_2Cu_3O_y$ thin films. Using polarized x-ray-absorption studies Saini *et al.*[8] have shown an increase in the in-plane density of itinerant holes and a decrease in that of covalent Cu $3d$ holes in the Bi-2212 system while going from normal to the superconducting state. These results are consistent with the picture of a possible charge redistribution in the Cu-O planes below T_c.[31] Khomskii and Kusmartsev[31] have argued that the observed shift[32] in the position of apex oxygen towards Cu-O planes below T_c in Bi-2212 and Bi-2223 is coupled with the increase of doping hole density in the superconducting state. It is quite probable that such a change in density of doping holes will be more prominent in Hg-1223 compounds, considering the nature and sensitivity of apical Cu-O bond and its correlation with T_c.

In this paper we present our Cu L_3 x-ray-absorption studies using polarized photons on a well-oriented, high-quality thick film of Hg-1223 superconductor. We have studied the nature and density of holes in both the normal and superconducting states. Our results show a considerable increase in the density of itinerant holes having Cu $3d_{z^2-r^2}$ and Cu $3d_{x^2-y^2}$ symmetries. The results are discussed in light of the possible increase of charge transfer between Cu and apical oxygen. The increase in the density of holes having out-of-plane character below T_c shows that these states may also be important for the phenomenon of superconductivity as predicted by many of the theories.

II. EXPERIMENT

$HgBa_2Ca_2Cu_3O_y$ (Hg-1223) films, approximately 3 μm in thickness, were fabricated by a two-step process which comprises of deposition of precursor films on $SrTiO_3$ substrates by spray pyrolysis and subsequently annealing them with a mercury-containing pellet in a quartz tube. The details of the fabrication procedure and the film properties have already been reported elsewhere.[34–36] X-ray-diffraction analysis revealed that the films are epitaxially grown on $SrTiO_3$ with their c axis perpendicular to the substrate surface. The full width at half maximum value for the (006) rocking curve is typically 0.5°. The film was post-annealed at 320 °C in O_2 and it exhibited a T_c of approximately 130 K.

The Cu L_3-edge x-ray-absorption spectra were recorded at room temperature and 100 K using the fluorescence yield detection mode at the SA 32 line of the SUPER ACO synchrotron radiation facility (LURE, Orsay) operating at 800 MeV and 200 mA. The x rays were monochromatized by two beryl crystals $(10\underline{1}0)$ and focused on the sample by means of a toroidal mirror to a 0.5×0.5 mm^2 spot. The energy scale was calibrated with respect to the $|3d^9\rangle$ peak of CuO at 931.2 eV. The energy resolution was estimated to be better than 0.3 eV whereas the reproducibility of the energy position is close to 0.05 eV. The width of the core hole has been measured to be equal to 0.56 eV (Ref. 16) at the L_3 edge. The $HgBa_2Ca_2Cu_3O_y$ thick film with its $SrTiO_3$ substrate was glued directly to a liquid-helium cryostat using silver paste. In order to doubly ensure a good electrical contact between the thick film and the holder, small contacts were also made using silver paint at the corners of the films. For the fluorescence yield (FY) mode, a seven-Ge-diode detector was used along an axis at 90° from the direction of the incident beam. For the $E\|(a,b)$ measurement the surface of the film was kept at about 5° to the incident beam. It is normally regarded as the 0° data because the slope of the intensity variation curves (see Figs. 3 and 4) is very small in this region and consequently the difference between the 5° and 0° values would be much smaller than the experimental error.

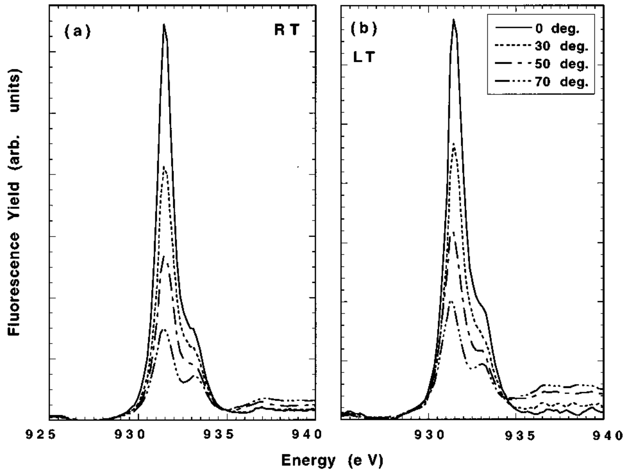

FIG. 1. Cu L_3-edge flouorescence yield polarized XAS spectra of $HgBa_2Ca_2Cu_3O_y$ thick film recorded (a) at room temperature and (b) at 100 K for different orientations of the sample surface, i.e., the (a,b) plane with respect to the electric field vector E.

A standard procedure has been adopted to remove the background contribution, and the normalization point was chosen on the continuum at 968 eV. The relative intensity of both the lines $3d^9$ and $3d^9\underline{L}$ has been determined by simulating the spectra with a combination of Gaussian and Lorentzian functions. The density of doping holes was calculated through the relation

$$n_h = I_{|3d^9\underline{L}\rangle}/(I_{|3d^9\underline{L}\rangle}+I_{|3d^9\rangle}),$$

where $\underline{L}$ stands for a hole in the oxygen ligand orbital induced by doping.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the self-absorption corrected Cu L_3-edge polarized x-ray-absorption spectra of Hg-1223 thick film at room temperature and 100 K, respectively. The spectra have been recorded in the fluorecence yield detection mode for four different orientations of the sample surface, i.e., the (a,b) plane with respect to the incident electric field vector. The experimental spectra were corrected for self-absorption in soft florescence following the work of Troger *et al.*[37] The main white line in the spectra, centered at 931.2 eV and the shoulder around 933 eV, is due to the transitions $3d^9\rightarrow\underline{2p}_{3/2}3d^{10}$ and $3d^9\underline{L}\rightarrow\underline{2p}_{3/2}3d^{10}\underline{L}$, respectively. The intensities of $|3d^9\rangle$ and $|3d^9\underline{L}\rangle$ have been normalized, taking the intensity of the $|3d^9\rangle$ white line at $E\|(a,b)$ polarization as 100. As can be seen from the spectra, the intensity of the $|3d^9\rangle$ peak decreases with the increase of the angle between the incident electric field vector (E) and the sample surface.

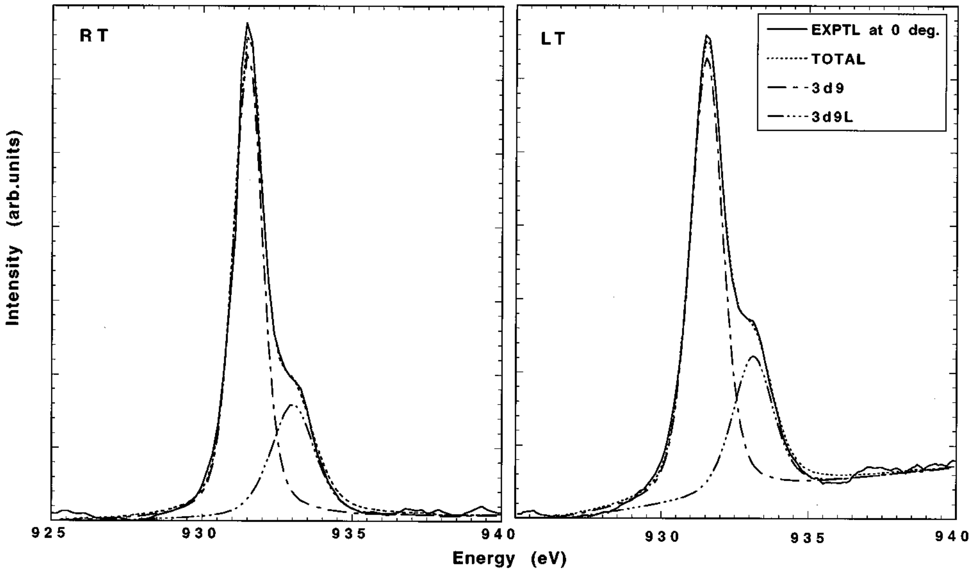

FIG. 2. The deconvoluted spectra corresponding to the 0° sample orientation of Cu L_3-edge flouorescence yield polarized XAS spectra of $HgBa_2Ca_2Cu_3O_y$ thick film in the (a) normal and (b) superconducting state. The spectra are least-squares fitted using a mixture of Gaussian and Lorentzian line shapes keeping same parameters for the $|3d^9\rangle$ and $|3d^9\underline{L}\rangle$ peaks.

The spectra corresponding to 0° orientation is due mainly to the covalent ($|3d^9\rangle$) and doping ($|3d^9\underline{L}\rangle$) holes in the Cu $3d^9_{x^2-y^2}$ and Cu $3d^9_{x^2-y^2}\underline{L}$ states (in plane) whereas the spectra at 70° is nearer to $E\|c$ orientation which shows Cu $3d^9_{z^2-r^2}$ and Cu $3d^9_{z^2-r^2}\underline{L}$ states (out of plane). The ratio of the intensity of the high-energy shoulder due to the transition from $3d^9\underline{L}$ to that of the total intensity ($|3d^9\rangle+|3d^9\underline{L}\rangle$) of the spectra gives a measure of the number of doping holes per Cu site.[16,17,33] In order to obtain covalent and doping hole densities we have performed a least-squares fitting to the spectra shown in Fig. 1 using a mixture of Gaussian and Lorentzian line shapes. The parameters used for the fittings are kept the same for all the spectra of different orientations at the two different temperatures. Figure 2 shows representative spectra, $E\|(a,b)$ at room temperature and at 100 K along with the peaks for $|3d^9\rangle$ and $|3d^9\underline{L}\rangle$. Results of the fittings are shown in Table I for an easy comparison. The density of doping holes (n_h) per Cu site for each orientation is calculated using the relation described earlier and is also shown in Table I. Here it is important to point out that while the intensities of the composite spectra in Fig. 1 and that of the $|3d^9\rangle$- and $|3d^9\underline{L}\rangle$-resolved components appears to be larger in case of the room-temperature spectra, the density of the doping holes (n_h) as calculated from the relation above would turn out to be larger for the superconducting state. Using a dipolar angular variation of the form $I_{|3d^9\rangle}(0°)\cos^2\theta+I_{|3d^9\rangle}(90°)\sin^2\theta$, the intensities of $|3d^9\rangle$ and $|3d^9\underline{L}\rangle$ peaks could be found out by an extrapolation of θ to 90°. Strictly speaking, the L-edge signal contains, besides d, a very small s contribution as well and an sd cross term which may be significant for a single crystal. However, in view of the appreciable error limit in the experiment the sd term cannot cause a significant change in our results.

From Table I and Figs. 3(a) and 3(b) it can be seen that our sample (Hg-1223 thick film) shows approximately 17% of $|3d^9\rangle$ and 4% of $|3d^9\underline{L}\rangle$ holes having out-of-plane symmetry in the normal state. Using unpolarized XAS at the O K edge on bulk samples, Pellegrin *et al.*[21] have shown that for the T_c-optimized Hg-1223 compound the density of holes per Cu-O plane is around 0.13. The large discrepancy may be due to the bulk nature of their samples and the possible difference in the oxygen stoichiometry of the samples studied by Pellegrin *et al.* and ours. In order to quantitatively check our data we have repeated our experiment on another Hg-1223 thick film. Both sets of data showed quite good agreement. Also, our earlier polarized XAS studies on Hg-1212 thick films at the Cu L_3 edge have shown comparable density of holes per Cu site from the $E\|(a,b)$ spectra at room temperature.[38] Moreover, our measurements of the optimum hole content in different samples of Hg cuprates using the chemical method (titration) have shown that n_h is in the range of 18%–20%.[39]

Figures 4(a) and 4(b) show the variation of intensities of $|3d^9\rangle$ and $|3d^9\underline{L}\rangle$ peaks of Hg-1223 thick film in the superconducting state. It should be noted from the figures and Table I that the intensity of in-plane Cu $3d$ doping holes

TABLE I. Density of covalent ($|3d^9\rangle$) and doping ($|3d^9\underline{L}\rangle$) holes in the normal and superconducting states of $HgBa_2Ca_2Cu_3O_y$ thick film. Results are obtained from FY polarized XAS analysis of the Cu L_3 edge. For the normalization of $|3d^9\rangle$ and $|3d^9\underline{L}\rangle$ intensities, the intensity of the white line $|3d^9\rangle$ in the (a,b) plane has been taken as 100. Orientation denotes the angle between the electric field vector E and the plane of the sample surface, i.e., the (a,b) plane. n_h represents the density of the doping holes per copper site. An asterisk denotes the values obtained from extrapolation.

Sample state	Orientation	Normalized intensity		n_h
		$3d^9(\pm3\%)$	$3d^9\underline{L}(\pm5\%)$	n_h
	0	100	37.3	0.27
	30	67.6	25.7	0.26
300 K	50	50.7	16.8	0.25
	70	28.1	8.5	0.23
	90*	17.6*	4.0*	0.19*
	0	100	45.8	0.31
	30	80.2	33.5	0.30
100 K	50	54.6	21.0	0.28
	70	27.9	11.2	0.28
	90*	17.7*	5.7*	0.25*

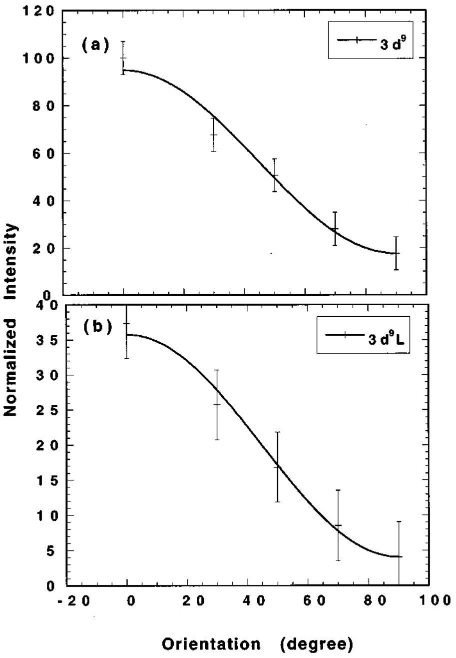

FIG. 3. Variation of the intensities of the deconvoluted components (a) $|3d^9\rangle$ and (b) $|3d^9\underline{L}\rangle$ of the Cu L_3-edge spectra recorded for the normal state. The bars represent a maximum error in the intensity values taking into account the possible error in experiment and estimation of the areas of the peaks.

(Cu $3d^9_{x^2-y^2}\underline{L}$) has increased by around 15% as the Hg-1223 sample goes to superconducting state. This increase is quite comparable to that observed in Bi-2212 (approximately 14%) from Cu L_3 and O K polarized x-ray absorption spectroscopy measurements.[7,8] Similar observations were also reported on Bi-2212 by inverse photoemission spectroscopy measurements[29] and on YBCO by XAS measurements.[30] It is even more interesting to note the increased intensity of the out-of-plane doping holes (Cu $3d^9_{z^2-r^2}\underline{L}$) in the superconducting state in our Hg-1223 samples from Table I and Fig. 4(b). This increase in the density of out-of-plane doping holes in the superconducting state has been observed in both samples that we have studied. In principle, the thermal strain between the film and the substrate resulting from the cooling of the sample could also contribute to the above change. However, the thermal expansion coefficients for $SrTiO_3$ (9×10^{-6} K^{-1}) and for the YBaCu(123) superconductor along the direction a (9.6×10^{-6} K^{-1}) (the corresponding value for Hg-1223 not available) would suggest that the thermal strain is very unlikely to be very different or very significant in this case. Moreover, for a thick film it is likely to be damped out within a small thickness of the film.

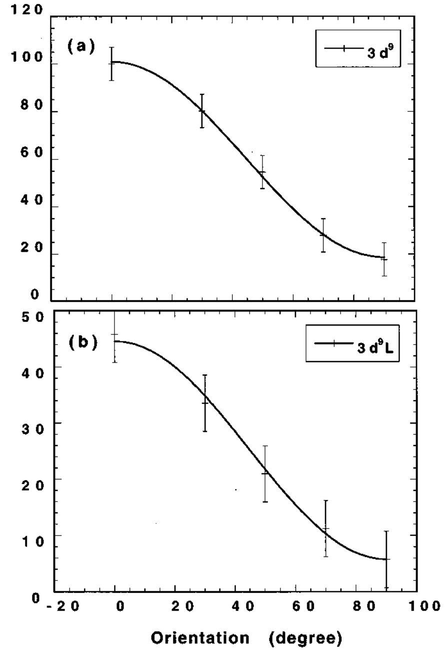

FIG. 4. Variation of the intensities of the deconvoluted components (a) $|3d^9\rangle$ and (b) $|3d^9\underline{L}\rangle$ of the Cu L_3-edge spectra recorded at 100 K.

The increase in the density of in-plane doping holes has been explained earlier using the probability of delocalization of itinerant holes in the superconducting state resulting from the in-plane relaxation of the local structure of CuO_5 pyramids.[7] This idea was supported by extended x-ray-absorption fine-structure (EXAFS) measurements showing the presence of nonhomogeneous domains at the Cu site at low temperatures.[41,42] Our results clearly show that it is not only the in-plane density of holes which is increasing but the density of out-of-plane holes also increases as the sample is cooled below T_c. Moreover, the increase in the latter case is more prominent. This cannot therefore be explained using the idea of an in-plane structural relaxation of the CuO_5 pyramids alone. On the other hand, our present results could be well explained considering the possibility of a change in the position of apical oxygen atom of the Cu-O pyramid below T_c.[40] Such a change was earlier observed in Tl-2212 compound by pulsed neutron-diffraction studies of the atomic pair distribution function.[43] This was also observed in Bi-2212 and Bi-2223 compounds earlier.[32] Subtle local structural changes of short-range order are normally not observable using many of the common methods of neutron diffraction and crystallographic analysis. A tilt of the Cu-O octahedra and associated shortening of the c axis has been reported in $La_{2-x}Sr_xCuO_4$ (Ref. 44) also.

A shift in the position of apical oxygen O(3) (O in the Ba-O plane) towards the Cu-O plane will result in a greater overlapping of the O $2p_z$ and Cu $3d_{z^2-r^2}$ orbitals and thereby in an enhanced charge transfer along the c axis. This may result in the increased density of holes having out-of-plane character below T_c. Our observation of a higher value of n_h for 90° orientation of the sample is quite consistent with this picture. At the same time, the in-plane structural changes of the Cu-O planes of the nature described by Toby *et al.*[43] may also be acting together, leading to an increase in the in-plane density of holes in the Cu-O planes. As has been observed by Toby *et al.* in Tl-2212, changes in the position of oxygen perpendicular to the Cu-O planes may be associated with the transition to the superconducting state in Hg-1223 also. Such changes, though of a short-range nature, are found to be coupled with the superconductivity in almost all the cuprate superconductors.[32,43–45] As discussed earlier, changes in the Cu-O pyramids, particularly the apical Cu-O distance in Hg cuprates, are more sensitive and result in large changes in T_c. This has been shown by high-pressure and oxygen doping studies on this system.[3] For instance, application of pressure has resulted in an increase of 31 K and insertion of excess oxygen gave an increase of 19 K in the critical temperature. Such a large dependence of the electronic structure of Cu-O bonds on the short-range local crystal structure of the Cu-O pyramids was not so prominent in case of other copper oxide superconductors like Bi and Tl bilayer systems. Moreover, in compounds with a single Tl-O layer, a change in the apical Cu-O distance was observed upon insertion of excess oxygen but it resulted in a decrease of T_c.[40] Considering these results, one may arrive at a conclusion that the optimum hole density in systems other than Hg cuprates is much lower than that of Hg systems. But many of the studies have shown that the optimum hole density in Hg cuprates is almost the same as that for other cuprate superconductors. However, the results of high-pressure and oxygen doping studies show that they can be further doped to increase T_c. Probably, this contradiction makes the Hg cuprates different from others. Also, such a dependence of the doping hole density on the apical Cu-O distance and the much higher value of optimum hole density may be some of the factors behind the large increase in T_c with pressure in Hg cuprates. Results of band structure calculations also lead to the same conclusion as they have shown that the position and crossing of the Hg-$6p_z$–O-$2p_z$ band at the Fermi level depends largely on the position of the apex oxygen in the crystal structure.[4,5]

Coming back to our results, the increase in the density of holes having out-of-plane character below T_c may mean that these states are also important to superconductivity and deserve more attention. Also, this may support some of the multiband models involving an active role for the Cu $3d_{z^2-r^2}$ orbitals. It is still an open question whether the changes in density of holes in the Cu-O bonds in these materials are abrupt or not at the superconducting transition temperature. Anyway, the increase in the density of out-of-plane as well as in-plane doping holes below T_c in our sample shows that there are more itinerant holes availiable at low temperature. Even so, it cannot be unexceptionally claimed that this change occurs only at T_c and not at a temperature higher or lower than it. For that, the measurements must be performed just above and below the T_c.

In conclusion, our polarized x-ray-absorption measurements using fluorescence yield at the Cu L_3 edge on a Hg-1223 thick film in the normal and superconducting states have shown a considerable increase in the density of out-of-plane doping holes (Cu $3d^9_{z^2-r^2}\underline{L}$) and a smaller increase in the in-plane (Cu $3d^9_{x^2-y^2}\underline{L}$) density of doping holes. These results indicate that a probable structural change in the Cu-O octahedra, though local and short range in nature, may be associated with the superconducting transition, resulting in a shift of the apical oxygen towards the Cu-O plane and thereby in an increased charge transfer between Cu and O. Also, our results clearly show that there are more itinerant holes available for conduction below the superconducting transition. Our results also point out the importance of Cu $3d_{z^2-r^2}$ states which need more attention for a clear understanding of the mechanism of high T_c superconductivity in this system.

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