Evidence of redistribution of the itinerant holes below T_c in $Ba_2Sr_2CaCu_2O_8$ superconductors: A polarized x-ray-absorption study

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The microscopic electronic structure of high-quality superconducting $Bi_2Sr_2CaCu_2O_{8+y}$ (Bi2212) single crystals has been investigated in the normal and superconducting states by polarized x-ray-absorption (XAS) measurements. The O K-edge XAS results led us to conclude the presence of a significant density of p_z symmetry orbitals for itinerant holes. We observed a reproducible increase in the number of O $2p_{x,y}$ itinerant holes accompanied by a decrease of the O K XAS transition in the upper Hubbard band (covalent holes) while going from the normal to the superconducting state of the system. The increase of O $2p_{x,y}$ holes was confirmed by an increase in the $3d^9\underline{L}/3d^9$ ratio estimated from Cu L_3 XAS measurements. This is in agreement with earlier inverse photoemission measurements and constitutes evidence for the redistribution of the itinerant holes below the transition temperature (T_c).

The importance of the Cu-O planes in cuprate superconductors has been established and it is known that the holes in these are responsible for superconductivity. Thus both the local lattice structure of the Cu-O planes and their electronic characterization have been paid significant attention to understand the mechanism of superconductivity in the complex high-T_c superconductors.[1] The contribution of high-energy spectroscopy is vital in this respect and especially, in finding out useful information about the electronic states (both occupied and unoccupied) in the vicinity of the Fermi level which is composed mainly of Cu $3d$ and O $2p$ electronic orbitals.[1,2] A number of x-ray-absorption (XAS) studies have been made to obtain valuable information about the local electronic structure of the Cu-O planes in the high-T_c compounds.[3] A significant number of studies have devoted to O K and Cu L-XAS measurements due to the fact that O $2p$ and Cu $3d$ states are accessible, respectively, in the two spectra. In particular polarization-dependent XAS measurements have been able to provide information on the symmetries of the holes (unoccupied orbitals). To date there are a number of reports[3–15] about the symmetries of unoccupied Cu $3d$ and O $2p$ states in the high-T_c superconductors but they are rather controversial. Compared with other cuprates, more studies have been carried out on the Bi2212 system because it has only one kind of Cu site and that good quality single crystals are readily available. In addition, its stability in UHV conditions has put the Bi2212 into the category of the most suitable systems for such studies, the results of which may probably represent the whole class of high-T_c oxides.

Earlier polarized XAS studies on the Bi22122 system have concluded that the unoccupied Cu $3d$ states are mainly of $3d_{x^2-y^2}$ character with 10–20% weight of $3d_{z^2-r^2}$ ($3d_{z^2}$) symmetry.[4–9] However, Suzuki *et al.*[10] have reported that there was only ~5% weight of the $3d_{z^2}$ symmetry states. On the other hand, a number of polarized O K-edge XAS have been published[4,5,7,13–15] without any conclusive evidence for the presence of O $2p_z$ holes in the Bi2212 system. Also, most of the measurements have been performed in the normal state and not many studies were available to understand the behavior of the unoccupied electronic states in the superconducting state. Khomskii and Kumartsev[16] have presented a picture of possible charge redistribution and the consequent increase in hole concentration in the Cu-O planes below T_c. Wagener *et al.*[17] have found changes in the unoccupied states in their inverse photoemission (IPES) measurements on the bulk samples of $YBa_2Cu_3O_7$ (YBCO) and Bi2212 systems where an increase in the number of O $2p$ holes from the normal to the superconducting state was observed with a decrease in the number of Cu $3d$ holes. This study was followed by polarized XAS measurements on YBCO thin films by Hirai *et al.*[18] where they have also concluded an increase of O $2p_{x,y}$ holes from the normal to the superconducting state. We have investigated the unoccupied $2p$ electronic states of different symmetries in the superconducting as well as the

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normal state of the Bi2212 system. In this communication, we report results of our polarized O K and Cu L_3 XAS measurements on high-quality Bi2212 single crystals. There appeared to be $\sim 10\%$ increase of the O $2p_{x,y}$ itinerant holes in the superconducting state at the cost of a decrease of covalent holes in the upper Hubbard band (UHB).

The single-crystal samples ($T_c \sim 85$ K) were prepared by the traveling-solvent floating method in a mirror furnace with two ellipsoidal reflections using 750 W halogen lamps. Details of the preparation and characterization are given elsewhere.[19] The polarized XAS measurements were performed on station 1.1 of the SRS at the Daresbury Laboratory, UK. The spectra were recorded by detecting the total electron yield (TY) off the samples using a VSW HA100 hemispherical analyzer with a multichannel detection system. The samples of typical surface area 5×3 mm^2 were glued using silver-based conducting epoxy on Ta foils which themselves were glued onto a Cu plate attached directly to a liquid-helium cryostat. Clean surfaces were obtained by cleaving *in situ* about 35 K and low-temperature measurements were performed at the same temperature. For normal-state measurements, the samples were slowly warmed up to room temperature. The photon energy calibration was referenced to Au $4f$ photoemission peaks from a scraped clean Au foil glued in the vicinity of the samples. In addition Bi $4f$ photoemission spectra on all the samples were also recorded as energy calibration standard. The combined energy resolution of the beamline and analyzer was better than 0.7 eV for all the measurements. The surface quality was monitored by low-energy electron diffraction which showed a sharp pattern with the typical 1×5 structure and by a sharp O $1s$ photoemission peak of about 528 eV binding energy.

Figures 1(a) and 1(b) show the O K XAS spectra collected at different angles of incidence with respect to the normal of the sample surface at temperatures below T_c (LT) and at room temperature (RT), respectively. They are very similar to those reported on the same system using TY and fluorescence yield (FY) techniques[4,11] and show the usual peaks observed in O K XAS of the doped charge-transfer insulators including the high-T_c cuprates.[20] The prepeak corresponds to the transition from the O $1s$ level to the O $2p$ impurity states formed in the correlation gap as known from the Hubbard model of doped charge-transfer insulators.[21] The 0° spectrum corresponds to the normal incidence geometry where the E vector of the plane-polarized synchrotron light is parallel to the sample surface (ab plane), while the 75° spectrum represents the case where the E vector is nearly parallel to the c axis of the crystal. According to dipole selection rules, at 0° only the unoccupied electronic states with O $p_{x,y}$ symmetry are probed and in the $E\|c$ case, the O p_z states are accessible for transition. For convenience the zero of the energy scale is referenced to the prepeak ($h\nu$ about 528 eV) of the $E\|ab$ spectrum. The feature about 1.5 eV above the prepeak is due to the transition $3d^{10}L \rightarrow 1s\ 3d^{10}$ in the upper Hubbard band consisting of covalently mixed O $2p$ and $3d$ states. This band is associated with intrinsic holes due to charge transfer from O to Cu which will be described as covalent holes in this paper.

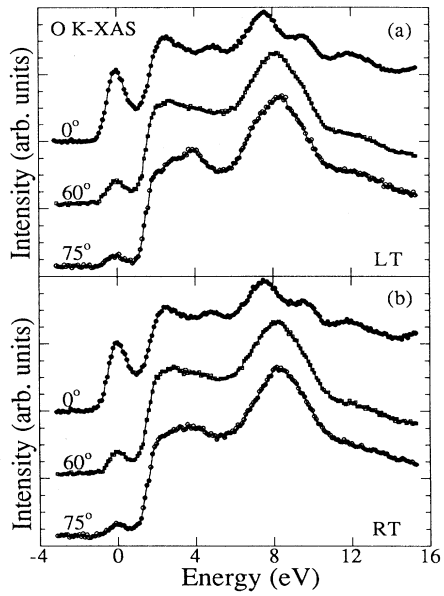

FIG. 1. Normalized O K-edge XAS spectra of the Bi2212 system collected at different angles of incidence with respect to the normal of the sample surface at temperatures below T_c (a) and at room temperature (b). The 0° spectrum corresponds to the normal incidence geometry where the E vector of the plane-polarized synchrotron light is parallel to the sample surface (ab plane), while the 75° spectrum represents the case where the E vector is nearly parallel to the c axis of the crystal.

It is well known that the prepeak intensity in O K XAS ($3d^9L \rightarrow 1s\ 3d^9$) is almost proportional to the amount of hole doping and is a direct measure of the number of itinerant holes in the system.[22,23] The intensity of this peak is decreasing in going from $E\|ab$ to $E\|c$ polarization showing that the itinerant holes in the Bi2212 system are dominantly of $p_{x,y}$ symmetry as reported earlier.[4,5,7,13–15] The intensity of the prepeak at 75° comes out to be $\sim 15\pm0.5\%$ and $\sim 17\pm0.5\%$ of the $E\|ab$ case at LT and RT, respectively. We have estimated the intensity for the 90° ($E\|c$) incidence spectrum by extrapolation using $[I(\theta)=I(0°)\cos^2\theta+I(90°)\sin^2\theta]$ and found it to be $9.5\pm0.5\%$ and $11.5\pm0.5\%$ in the two cases. This indicates that there are significant number of holes with p_z symmetry in the Bi2212 system. This is in agreement with earlier measurements[4,11] but contradicts others who have concluded the absence of p_z holes.[7,12,14] In fact, we have previously estimated a similar number of p_z holes in our measurements on the same crystals using the FY XAS technique.[11] This was further supported by tight-binding calculations where we have estimated $\sim 8\%$ O p_z holes in the Bi2212 system.[24] Our results also agree with the findings in the La-Sr-Cu-O system where $\sim 15\%$ holes have been reported to have p_z symmetry.[25,26] The presence of the p_z holes, both in the superconducting and normal state merely indicates the important role of the p_z holes in the characteristics of the cuprates.

As shown in Fig. 2 for the $E\|ab$ case, the O K-edge

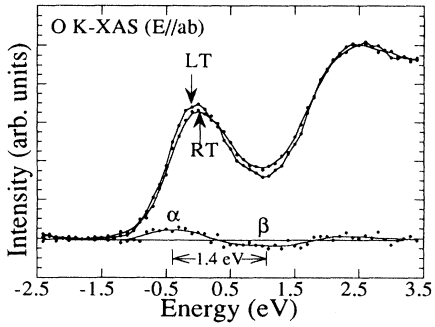

FIG. 2. Normalized O K-edge XAS spectra of the Bi2212 system with $E\|ab$ polarization showing the pre-peak and UHB regions. Features α and β in the difference spectrum (LT-RT) show the increase and decrease in intensity of the two regions in going from the normal to the superconducting state of the system.

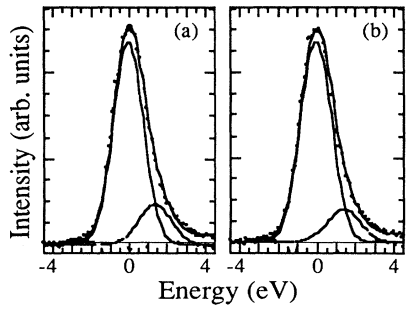

FIG. 3. Normalized Cu L_3 XAS white lines at temperatures below T_c (a) and at room temperature (b). Solid curves are the fitted Gaussian components.

spectra at LT were observed to be different from those at RT. The temperature dependent changes in the spectral weight in the prepeak and UHB regions can be clearly seen in the difference spectrum. The estimated quantitative difference in the intensities of the prepeaks was about 8–10 %. This was reproducible in the spectra of different crystals we have measured. This is in agreement with the report by Hirai *et al.*[18] where they have observed an increase in the $E\|ab$ prepeak intensity, while going from RT to the superconducting state of YBCO-oriented thin film. However, they did not give any estimation of the difference and only showed the prepeak region of the O K-edge spectra. In fact, increase in the itinerant holes appears to be at the expense of the covalent holes as can be seen in the difference spectrum in Fig. 2 where features α and β correspond to changes in the itinerant and covalent holes in the system between normal and superconducting states. This assignment is due to the fact that the energy separation between α and β is about 1.4 eV which is close to the known energy difference between the impurity band and the UHB in the cuprate superconductors.[21,25–27]

To ascertain the observed differences in the O K-edge XAS, we analyzed the line shapes of the $E\|ab$ Cu L_3 XAS spectra at LT and RT. It is known that the intensity of the high-energy shoulder ($3d^9L \rightarrow 2p3d^{10}L$), associated with asymmetry of the main peak ($3d^9 \rightarrow 2p3d^{10}$) in the Cu L_3 XAS spectra grows almost proportionally to the density of itinerant (doping) holes in these systems, similar to the growth of the prepeak intensity in the O K XAS.[25–27] We estimated the ratio of the shoulder to the main peak ($3d^9L/3d^9$) by least-squares fitting with two Gaussians using exactly the same parameters for the two spectra. This is shown in Figs. 3(a) and 3(b). The observed energy separation between the two Gaussians is about 1.4 eV in both cases which is similar to those reported earlier.[5,26,27] The ratio of the $3d^9L$ to $3d^9$ peaks comes out to be 0.21 and 0.18 at LT and RT, respectively. According to Merrien *et al.*[27] one can estimate the number of holes per Cu site by using $3d^9L/(3d^9+3d^9L)$, which gives us the values of 0.17 and 0.15 for LT and RT, respectively. This is in agreement with the reports showing 0.15 to 0.19 holes per Cu site in the Bi2212 system.[5,27] The estimated change of the intensity ratio ($\sim 12\%$) is more or less the same as the observed change in the doping holes by O K XAS (Fig. 2). The change is not a unique feature in any particular sample and was reproducibly observed in a number of crystals measured. Its observation in the YBCO (Ref. 18) and in the Bi2212 system strongly indicates that the superconducting state is accompanied by the formation of extra impurity band in the correlation gap at the cost of a decrease in the admixture of the O $2p_{x,y}$ states with the Cu $3d_{x^2-y^2}$ in the upper Hubbard band. We should mention that in the $E\|c$ experimental geometry the intensity of all the spectral features appeared to be more or less the same at LT and RT. Similar observations have been reported by Hirai *et al.*[18] for the YBCO compound.

To continue discussing the temperature-dependent results, we have observed an increase of itinerant holes with a decrease of covalent holes in the superconducting state. This is in agreement with the results of temperature-dependent IPES by Wagener *et al.*[17] where the authors have observed an increase in the number of O $2p$ holes ($\sim 10\%$ increase in the case of Bi2212 system) and a decrease in the number of Cu $3d$ holes in the superconducting state. That means there is a redistribution of the electronic states near the Fermi level in the superconducting state of the system. We argue that this redistribution may be a result of distortions taking place at LT in the local lattice structure as reported by temperature-dependent x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure measurements.[28] It may be that the in-plane relaxation of the local structure of CuO_5 pyramids is responsible for the higher density of $p_{x,y}$ holes in the superconducting state. In other words, at RT, some of the holes may remain relatively localized in the highly strained CuO_4 planes resulting in more covalent holes as observed. When the temperature is below T_c, the localization of these holes is reduced because of locally relaxed Cu-O planes. Röhler, Larisch, and Schafer[29] have also interpreted the changes observed in their LT Cu K XANES spectra as a result of a lowering of the rhombic distortion and hence charge redistribution. The argument is also

supported by the neutron resonance absorption spectroscopy measurements of Mook *et al.*[30] and the neutron pair distribution function study of Toby *et al.*[31] where they have reached the conclusion of softening of local phonons and pointed out the delocalization of holes at LT.

In conclusion, we have made polarization-dependent O K and Cu L_3 XAS measurements in the normal and superconducting state of high-quality Bi2212 single crystals. The results have shown the presence of a significant density of the p_z orbitals available for doping holes both in the normal and superconducting state. Below T_c we have observed a decrease in the number of covalent holes in the UHB, whilst there appeared to be about 8–10 % increase in the density of the O $2p_{x,y}$ doping holes. The results were confirmed by Cu L_3 XAS measurements where the shoulder to the main peak ratio in the Cu L_3 XAS showed a clear change. We interpret the results as evidence of an increase in the number of itinerant O $2p_{x,y}$ holes at the expense of covalent holes in the UHB. We have speculated that more itinerant holes are available in the superconducting state due to in-plane structural relaxation of the CuO_5 tetrahedra.

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