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DOI
10.1016/0921-4534(95)00354-1

Publication date
1995

Published in
Physica C

ELSEVIER

Physica C 251 (1995) 7–14

PHYSICA C

Electronic structure studies of the Bi2212 system by polarised X-ray absorption measurement

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Received 15 March 1995; revised manuscript received 5 June 1995

Abstract

Polarised X-ray absorption (XAS) measurements have been made on high-quality superconducting $Bi_2Sr_2CaCu_2O_{8+y}$ (Bi2212) single crystals to investigate the microscopic electronic structure in the normal and superconducting state of the system. The Cu L_3 XAS results led us to conclude that either there are no holes of $3d_{z^2}$ symmetry, or if any, they are insignificant in number. On the other hand, the O K XAS results show the presence of a significant density of p_z symmetry orbitals for itinerant holes. An increase in the $3d^9\underline{L}/3d^9$ ratio estimated from the Cu L_3 XAS measurements was observed while going from the normal to the superconducting state of the system. The results are discussed in the light of the structural distortions taking place below T_c.

1. Introduction

The electronic characterisation of the Cu–O planes using high energy spectroscopy has been a field of significant interest in the studies of the mechanism of superconductivity in the complex high-temperature superconductors [1]. The spectroscopy has been used to investigate the occupied and unoccupied electronic states in the vicinity of the Fermi level. It is now well known that these states are composed mainly of Cu 3d and O 2p electronic orbitals. Cu L_3 and O K edge X-ray absorption spectroscopy (XAS) have been playing a major role due to the fact that Cu 3d and O 2p unoccupied states (3d and 2p holes) are accessible, respectively, in the two spectra [2]. In particular polarisation-dependent XAS measurements allow us to obtain information on the symmetry of these unoccupied states. Compared with other high-T_c compounds, more studies have been carried out on

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SSDI 0921-4534(95)00354-1

the Bi2212 system because it has only one kind of Cu site and good-quality single crystals are readily available. In addition, its stability in UHV conditions has put the Bi2212 compound 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. To date there are a number of inconsistent reports [3–15] about the symmetry of the Cu 3d and O 2p holes in the Bi2212 system. Some concluded to the presence of a significant (10–20%) weight of $3d_{z^2-r^2}$ ($3d_{z^2}$) symmetry states [4–8] while others [9] reported there was only $\sim 5\%$ weight of the $3d_{z^2}$ states. As regards the O 2p holes, a number of polarised O K edge XAS have been published [3,4,6,12–15] without any conclusive evidence for the presence of O $2p_z$ symmetry unoccupied states. To date most of the measurements have been performed in the normal state of the compounds and few results are available to understand the behaviour of the holes in the superconducting state except for a recent report by Faiz et al. [15].

In the present paper, we focus our attention on the Cu L_3 edge polarised XAS spectra obtained on high-quality Bi2212 single crystals. Results are shown for the unoccupied 3d electronic states of different symmetries in the superconducting as well as normal state. We also give O K XAS data on the crystals for which details have been reported elsewhere [16]. The temperature-dependent changes in the Cu L_3 XAS line shapes, reflected by an increase in the $3d^9\underline{L}/3d^9$ ratio while going from the normal to the superconducting state of the system, are discussed as an effect of redistribution of the itinerant holes due to structural changes taking place in the system. The present study was partly aimed to provide consistent experimental results on the symmetry of the 3d and 2p holes. It was also motivated by the fact that Khomskii et al. [17] had presented a picture of possible charge redistribution in the Cu–O planes below T_c which was supported by inverse photoemission (IPES) measurements of Wagener et al. [18] where an increase in the O 2p holes from the normal to the superconducting state was observed with a decrease in the Cu 3d holes in the bulk samples of $YBa_2Cu_3O_7$ (YBCO) and Bi2212 systems. The IPES study of Wagener et al. [18] was further followed by polarised XAS measurements of Hirai et al. [19] on YBCO thin films where they also concluded to an increase in the O $2p_{x,y}$ holes from the normal to the superconducting state.

2. Experimental

The single-crystal samples ($T_c \sim 8$ K) were prepared by the travelling-solvent floating method in a mirror furnace with two ellipsoidal reflections using 750 W halogen lamps. Details of the preparation and characterisation are given elsewhere [20]. The polarised XAS measurements were performed on station 1.1 of the SRS at the Daresbury Laboratory, UK. The SRS operated at 2 GeV with a typical electron current of up to 300 mA during the measurements. Station 1.1 is a UHV beamline equipped with a high-energy spherical grating monochromator (HESGM) covering the energy range of 250 to 1400 eV. The spectra were recorded by detecting the total electron yield (TY) off the samples using a VSW HA100 hemispherical analyser with multichannel detecting system. The entrance to the analyser was mounted beneath and at 40° with respect to the plane of the horizontal E vector of the polarised synchrotron radiation. The sample surface normal was in the plane of the photon beam. The emission angle with respect to the photon beam was therefore fixed at 40° at all incidence angles and normal incidence corresponded to having the photon E vector lying flat on the sample surface. 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 at 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 analyser was better than 0.7 eV for all the measurements. The surface quality was monitored by LEED which showed a sharp pattern with the typical

5×1 structure and by a sharp O 1s photoemission peak of about 528 eV binding energy.

3. Results and discussion

Polarised XAS measurements have been carried out on a number of single-crystal samples and the spectra obtained were essentially reproducible. Figs. 1(a) and (b) show the typical representatives of the polarisation-dependent Cu L_3 XAS spectra measured on one of the Bi2212 crystals at low temperature (LT) and room temperature (RT), respectively. The spectra have been normalised at a point far below the main L_3 peak, following the earlier reports [3,4,7–10], to ensure true intensity ratios in the different polarisations. They were collected at different angles of incidence (θ) with respect to the normal to the sample surface. For the Bi2212 crystals, the cleave plane is parallel to the *ab* plane and the normal to the surface is along the *c*-axis. The 0° spectra correspond to normal incidence geometry where the E vector of the plane-polarised synchrotron light was parallel to the sample surface ($E \parallel ab$). The 75° spectra represent the case when the E vector was nearly parallel to the *c*-axis of the crystal. For convenience, the zero of the energy scale is taken at the peak of the L_3 white line (WL) which occurs at around 931.5 eV in the $E \parallel ab$ spectrum. The dipole transition $2p \rightarrow 3d$ for the L_3 white line thus probes the unoccupied $3d_{x^2-y^2}$ orbitals for $E \parallel ab$ and $3d_{z^2}$ orbitals for $E \parallel c$. The contribution of the $2p \rightarrow 4s$ channel to the L_3 intensity is $\sim 1\%$ and can be neglected [5]. Both the LT and RT spectra at 75° show a very small intensity (~ 8–10%) when compared to the $E \parallel ab$ polarisation. For the quantitative estimation of the $3d_{z^2}$ orbitals, we have extrapolated the integrated intensity (from -3.5 eV to 3.5 eV) of the polarised spectra to $E \parallel c$ using least-squares fitting of the data with the relation $I(\theta) = I(0°)\cos^2\theta + I(90°)\sin^2\theta$. The extrapolated intensities for the $E \parallel c$ polarisation at LT and RT are shown in Figs. 2(a) and (b), respectively, and both are about 2–4%.

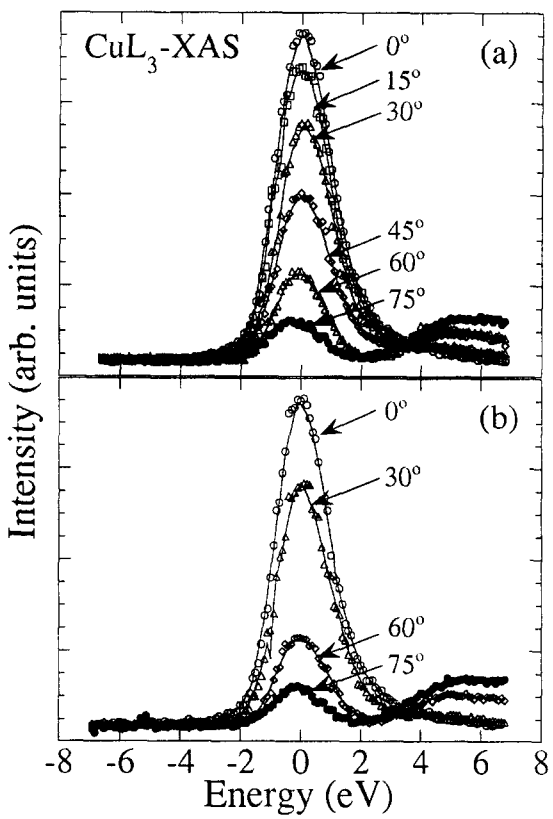

Fig. 1. Normalised Cu L_3 XAS spectra of the Bi2212 system collected at different angles of incidence with respect to the normal of the sample surface at temperatures below T_c (a) and at room temperature (b). The 0° spectra correspond to normal incidence geometry where the E vector of the plane-polarised synchrotron light is parallel to the sample surface (*ab*-plane) while the 75° spectra represent the case where the E vector is nearly parallel to the *c*-axis of the crystal.

The question of the presence or absence of the d holes in the $3d_{z^2}$ symmetry orbitals in the high-T_c superconductors has been widely discussed. Our data show that if there are holes of $3d_{z^2}$ symmetry in the Bi2212 superconductors they should be insignificant in number (2–4%). This implies all 3d unoccupied states must therefore have $3d_{x^2-y^2}$ symmetry alone in the Bi2212 system in both the normal and superconducting state. The present results are similar to our earlier measurements on one of the crystals using the fluorescence yield (FY) method [11] and further supported by our tight-binding calculations where $\sim 3\%$ holes are estimated to have the d_{z^2} symmetry in the Bi2212 system [21]. This is also the case with the La–Sr–Cu–O system reported by Chen et al. [22]. The results are thus in significant disagreement with the spectra measured earlier using the total electron yield (TY) method [3–5,7,8] which showed

a 10 to 20% intensity for the $E \| c$ case. However, Suzuki et al. [9] reported ~ 5% intensity in the $E \| c$ polarisation in their L_3 spectra measured by TY. Much earlier, EELS data [6] on Bi2212 have been reported showing again a significant intensity in the $E \| c$ polarisation.

Here we recall our O K XAS measurements on the Bi2212 system. Our polarised XAS measurements at the O K edge on the different crystals have shown ~ 9–13% density of p_z holes and led us to conclude to the presence of a significant density of the p_z symmetry orbitals available for the doping holes [10,16]. We have shown the estimation of the p_z holes for the different crystals in Figs. 3(a) and (b). The cluster calculations [23] suggest that there should be about 1% d_{z^2} holes in the system if the apical oxygen is not considered while 2–3% of the d_{z^2} holes when the apical oxygen has been taken into consideration. Thus our results are in excellent agreement with the cluster calculations as the cluster for Bi2212 system contains an apical oxygen. In fact, such a small density of the d_{z^2} holes cannot account for the p_z holes estimated in the present study considering that in our tight-binding calculations we only estimated ~ 8% p_z holes with respect to ~ 3% of d_{z^2} holes in the Bi2212 system [21]. It may be possible that some of the holes in the p_z orbitals are due to hybridisation of the Cu 4s states with the O 2p states.

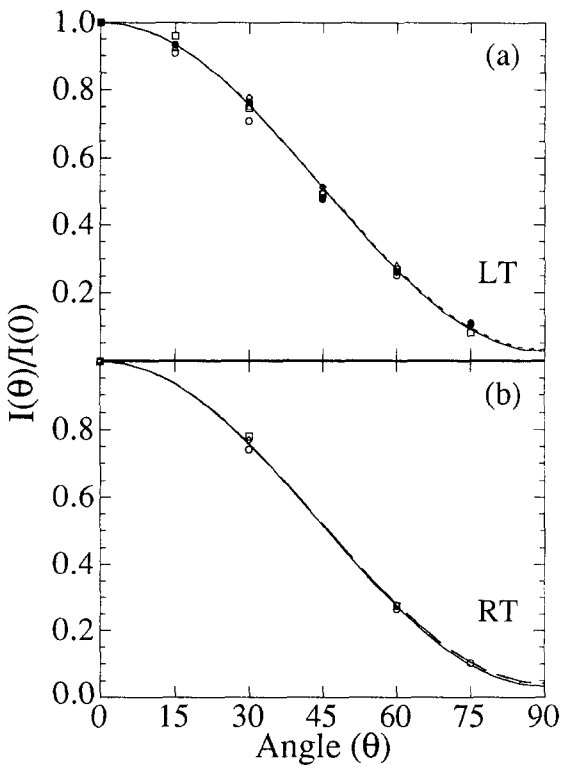

Fig. 2. The extrapolated intensities for the $E \| c$ spectra at low temperature (a) and at room temperature (b). The normalised experimental intensities are fitted using $I(\theta) = I(0°)\cos^2\theta + I(90°)\sin^2\theta$ (lines). Different points and lines correspond to the data from different crystals.

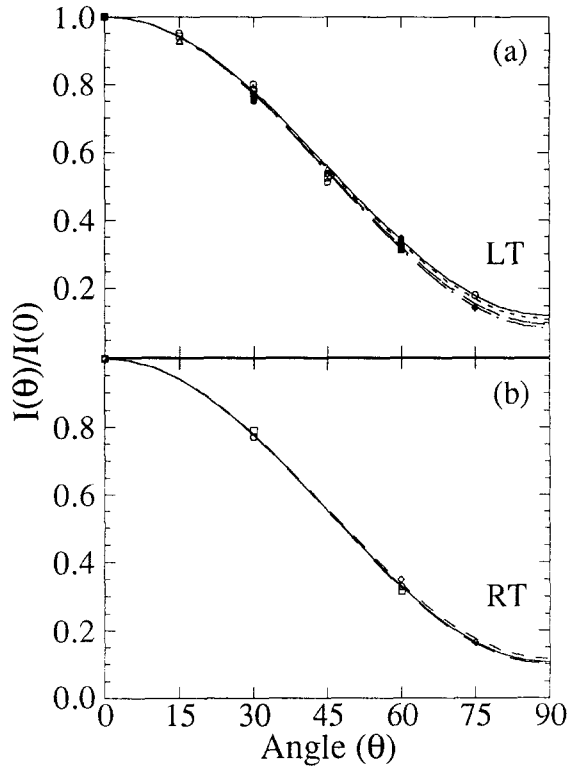

Fig. 3. Estimation of holes with p_z symmetry in Bi2212 crystals at low temperature (a) and at room temperature (b). The intensities for the $E \| c$ spectra are extrapolated using $I(\theta) = I(0°)\cos^2\theta + I(90°)\sin^2\theta$ (lines). Different points and lines correspond to the data from different crystals.

There appear to be differences in the lineshapes between the low-temperature and the room-temperature Cu L_3 spectra. In Figs. 4(a) and (b) the white lines for $E \| ab$ at LT and RT are shown resolved into two Gaussians of FWHM ~ 1.9 eV separated by ~ 1.4 eV. It is known that the intensity of the high-energy shoulder ($3d^9\underline{L} \rightarrow 2\underline{p}3d^{10}\underline{L}$), associated

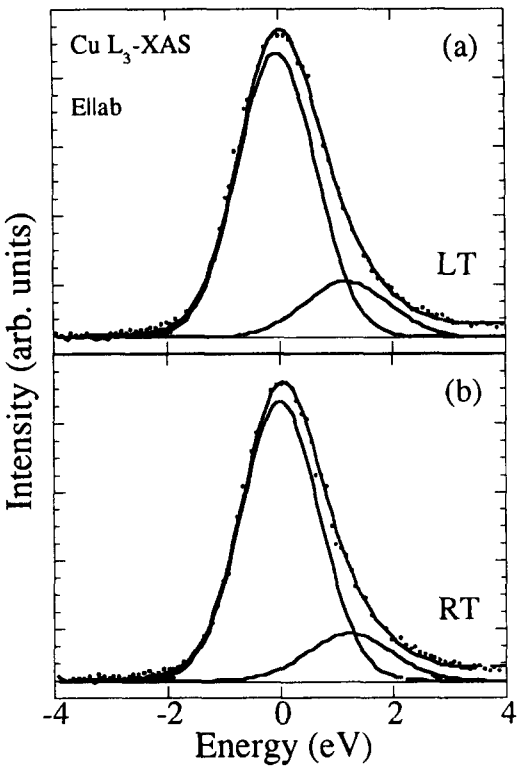

Fig. 4. Normalised Cu L_3 XAS white lines for the $E \| ab$ geometry at temperatures below T_c (a) and at room temperature (b). Solid curves are the fitted Gaussian components.

with asymmetry of the main peak ($3d^9 \rightarrow 2\underline{p}3d^{10}$) grows almost proportionally to the density of itinerant (doping) holes in these systems. This is similar to the growth of the pre-peak intensity in the O K XAS spectra being proportional to the density of the doping holes [24]. The estimated ratio of the shoulder to the main peak ($3d^9\underline{L}/3d^9$) (two Gaussians) in Fig. 4 comes out to be 0.215 ± 0.005 and 0.185 ± 0.005 at LT and RT, respectively. According to Merrien et al. [25] one can estimate the number of in-plane itinerant holes per Cu site using $3d^9\underline{L}/(3d^9 + 3d^9\underline{L})$ which gives the value 0.175 ± 0.005 for LT and 0.155 ± 0.005 for RT. This is in agreement with the reports showing 0.15 to 0.19 holes per Cu site in the Bi2212 system [4,25]. Thus the difference between the holes at LT and RT appears ~ 10–14%. This is in agreement with our O K XAS measurements where we have given evidence for the redistribution of itinerant holes [16] in the Bi2212 system. The present results are also in support of the IPES study of Wagener et al. [18] where an increase in the 2p holes has been reported. The estimated change of the intensity ratio ($\sim 12\%$) is more or less of the same order of magnitude as the observed change (8–10%) in the doping holes by O K XAS [16]. The change was reproducibly observed in our measurements on all the crystals. Such a change was also observed in the O K XAS spectra of the YBCO system by Hirai et al. [19]. Its observation in the YBCO [19] and in the Bi2212 system [16] strongly indicates that the superconducting state is accompanied by an increase of the itinerant holes. In fact, as reported in our earlier paper [16], the increase in the itinerant holes is at the cost of a decrease in the covalent holes. This merely constitutes evidence for the redistribution of the holes in the superconducting state. This is also in agreement with the picture presented by Khomskii et al. [17] where they discussed a possible charge redistribution in the high-T_c superconductors and as a result of that, the holes in the active superconducting Cu–O planes may increase up to several percent in number.

In the following discussion we present a possible argument for the redistribution of the itinerant charge carriers due to local lattice relaxation at low temperature. The recent temperature-dependent X-ray absorption results (EXAFS and XANES) have been able to show the low-temperature structural anomalies in the Bi2212 system [26]. The Cu site structure is non-homogeneous composed of low-temperature orthorhombic (LTO)- and low-temperature tetragonal (LTT)-like domains. The LTO-like structure is defined by two long and two short in-plane Cu–O(P) distances and one long apical Cu–O(A) distance while the LTT is defined by short Cu–O(A) distance and with an average tetragonal-like symmetry. However, the low-temperature neutron-diffraction data by Beskrovnyi et al. [27] indicated that there was hardly any change in the average Cu–O(planar) distances from RT to LT. Below T_c there were more LTT domains as reported by Bianconi et al. by their temperature-dependent EXAFS measurements [26]. Thus at RT, due to the long and short in-plane Cu–O(P) distances some of the holes remain relatively localised in the highly strained Cu–O planes which causes more covalent holes. At LT the localisation of these holes is reduced because of locally relaxed Cu–O planes. This explains the reduction of the covalent holes with concomitant increase in the

itinerant holes. We speculate that this redistribution of holes could be important in the superconductivity mechanism.

The structural relaxation in Bi2212 at LT can also be realised by the temperature-dependent neutron diffraction data of Beskrovnyi et al. [27]. Beskrovnyi et al. reported a change in the Sr–O distances (from ~ 2.58 Å at RT to ~ 2.61 Å at LT) while other distances stayed more or less invariant from 300 to 55 K. Using the simple approach of Singh et al. [28] to discuss structural instability in La(Ba,Sr)CuO type systems one can estimate an average tolerance factor (t) associated with the change in the Sr–O distances ($R_{(Sr-O)}$) using the relation

$$t = \frac{R_{(Sr-O)}}{\sqrt{2}\,R_{(Cu-O)}},$$

where $R_{(Cu-O)}$ is the in-plane Cu–O distance. The value $t = 1$ corresponds to the relaxed/undistorted structure and any deviation indicates distortions. The estimated average deviations, $(1 - t)$ ~ 0.03289 at RT and ~ 0.02918 at LT, confirm the distorted nature of the Bi2212 structure at the two temperatures with relatively less (~ 11%) distortion at LT. The lower value of $(1 - t)$ at LT merely indicates the relative relaxation in the structure. In fact, as reported by Braden et al. [29] for the La(Sr)CuO system, the stress in the structure is increasing with lowering of the temperature but after arriving at a certain temperature (e.g. the T_c) the system gets relaxed by changing the symmetry. This change is reflected in the structural anomalies observed in the different high-temperature superconducting systems.

The above argument is also supported qualitatively by recent neutron-diffraction results of Takahashi et al. [30] where they have studied pressure-dependent structural effects and superconductivity in the La–Sr–Cu–O system and reported a maximum T_c for the tetragonal structure when the Cu–O plane is more relaxed and flat. Rohler et al. [31] also interpreted the changes observed in their LT Cu K XANES spectra as a result of increasing of symmetry of the local structure due to the lowering of the rhombic distortion and hence charge redistribution. The argument is also supported by the neutron resonance absorption spectroscopy (NRAS) measurements of Mook et al. [32] and the neutron pair

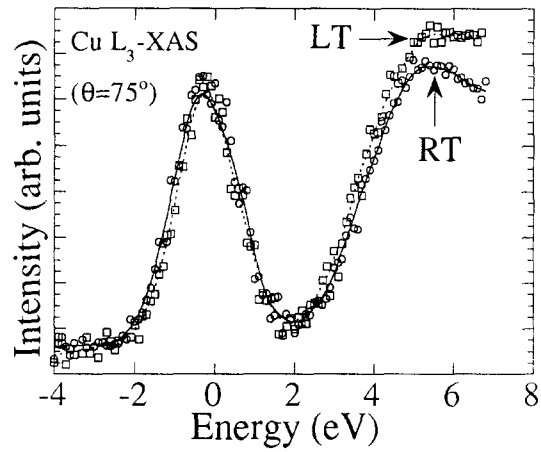

Fig. 5. Cu L_3 XAS spectra of the Bi2212 system at $\theta = 75°$ showing a different intensity of step-like feature at temperatures below and above T_c.

distribution function (PDF) study by Toby et al. [33] where they have reached the conclusion of softening of local phonons and pointed out the delocalisation of holes at LT.

Looking at the step-like (excitonic line) feature associated with the main Cu L_3 white line at 75° we found a small change while going from RT to LT. The step-like feature appears to increase in intensity at LT. We have shown a good example in Fig. 5 to give an idea of the observed change in the step-like feature. This feature has been assigned differently in the earlier reports [3–9]. The small change in its intensity may be due to the redistribution of the electronic states and the subsequent change in the hybridisation of the Cu 3d and O 2p orbitals with out-of-plane symmetry in the superconducting state. In the present spectra, the change appears to be agreeing qualitatively in all the samples even though it is quite small and difficult to estimate quantitatively.

In summary, we have made polarisation-dependent Cu L_3 and O K XAS measurements in the normal and superconducting state of high-quality Bi2212 single crystals. The reproducible results on a number of crystals were able to provide a consistent picture which indicates that there are very small amount of (~ 2–4%) or no 3d holes of $3d_{z^2}$ symmetry in both the normal and superconducting state. On the other hand, we have shown the presence of a

significant density of the p_z orbitals available for the doping holes at the two temperatures. We have also observed the temperature dependence of the Cu L_3 white line indicating an increase in the shoulder to the main peak ratio in the superconducting state. This change gives evidence of an increase in the itinerant holes in the system below T_c. We have made an attempt to understand this redistribution of the electronic states as a result of the changes taking place in the local structure of the Cu–O planes. We have speculated that more itinerant holes are available in the superconducting state due to local structural relaxation in the Cu–O planes. The picture is consistent with several other reports. We have also reported a temperature-dependent change in the intensity of the step-like feature observed at the higher-energy side of the $E \sim \| c$ Cu L_3 white line.

Acknowledgements

We thank the Daresbury staff for their help and cooperation during the synchrotron beamtime. One of us (NLS) is grateful to the TRIL programme of ICTP for a fellowship to work in Italy and the financial support to travel to Daresbury for the measurements. NLS also likes to thank D. Norman of Daresbury Lab for his kind hospitality and encouragement during the measurements. The fruitful and beneficial discussions with A. Bianconi and B.K. Chakraverty are also acknowledged with great pleasure.

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