PolariZed X-ray absorption study of Bi$_2$Sr$_2$CuO$_6$ and Bi$_2$Sr$_2$CaCu$_2$O$_8$

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Abstract. Polarization dependent X-ray absorption measurements on single crystal Bi$_2$Sr$_2$CuO$_6$ ($T_c$=9 K) and Bi$_2$Sr$_2$CaCu$_2$O$_8$ ($T_c$=80 K) with one and two CuO$_2$ layers, respectively, show no energy shift of the Cu 2$p$ main peak, and no relation between the amount of 3$d$(m=0, ±1) character and the critical temperature $T_c$. At grazing incidence a structure in Bi$_2$Sr$_2$CaCu$_2$O$_8$ is found at 937 eV, which can be ascribed to a composite state of Cu $3d(z^2)$, Cu 4$s$ and $o-2p(z)$.

A key point in the investigation of the electronic structure of high-$T_c$ superconductors is the observation of changes in the unoccupied states induced by doping the parent antiferromagnetic insulating material. High-energy electron and X-ray spectroscopies are useful tools for the determination of the character and symmetry of the unoccupied states. It is generally accepted for $p$-type high-$T_c$ superconductors that the charge carriers are additional holes in the CuO$_2$ planes with predominantly O 2$p$ character. However, recent experimental evidence was presented, showing the possible importance of the orbital momentum of the Cu 3$d$ holes. This is based on polarized X-ray absorption spectroscopy (XAS) [1–3] and electron energy loss spectroscopy (EELS) [4, 5], showing Cu $d$-weight with $m=0$, ±1, most probably assigned to $d_{xy}$ holes. Bianconi et al. [1] found that this admixture is small at half filling (~8%), but becomes appreciable in the superconductor phase (~20 or even 34%).

A common feature in high-$T_c$ superconductors is the presence of square planar CuO$_2$ layers. In the thallium or bismuth families, one, two or three of these layers are sandwiched in between layers of thallium or bismuth oxide [6] and the superconducting transition temperature $T_c$ increases with the number of CuO$_2$ layers. This suggests that, in addition to the commonly accepted in-plane mechanism, there is an interlayer effect. In this paper we will present results of polarization dependent Cu 2$p$ absorption measurements on single crystal bismuth compounds with one and two CuO$_2$ layers, Bi$_2$Sr$_2$CuO$_6$ ($T_c$=9 K) and Bi$_2$Sr$_2$CaCu$_2$O$_8$ ($T_c$=80 K), respectively, and discuss the differences in the XAS spectra in relation to the interaction between the adjacent CuO$_2$ layers.

The single crystal of Bi$_2$Sr$_2$CuO$_6$ is a difficult material because it is notoriously nonstoichiometric. ICP-emission spectroscopy and titration measurements showed that the Bi$_2$Sr$_2$CuO$_6$ crystal is copper rich, present as Cu$^{1+}$. Single crystals of Bi compounds were stripped in a dry nitrogen atmosphere and mounted with non-aligned $a$, $b$ axes onto a rotatable sample holder, covering a total area of 10×5 mm. The variation in the orientation of the $c$-axes of the stripped single crystals was less than 2° as measured with an optical microscope. The samples were immediately pumped down to a final pressure of 10$^{-8}$ torr in the experimental chamber on beamline 3.4 at the Synchrotron Radiation Source (SRS) Daresbury. The Cu 2$p$ absorption spectra were measured in total electron yield mode using linearly polarized synchrotron radiation from a double crystal monochromator equipped with beryl (1010) crystals, which gives an energy resolution of ~400 meV [8]. The spectra were corrected for the incident flux, which was simultaneously measured by total electron yield from a 0.75 μm Al foil in front of the sample. An energy calibration was done on a CuO reference sample at the same angle immediately before and after each spectrum, in order to eliminate energy shifts due to sample rotation and source movements. We only had to correct for a long term energy shift of 100 meV related to the decay of the electron beam in the storage ring. The whole series of measurements was repeated to check the reproducibility.

Figures 1 and 2 show the polarization dependent Cu 2$p_{3/2}$ absorption spectra of Bi$_2$Sr$_2$CuO$_6$ and Bi$_2$Sr$_2$CaCu$_2$O$_8$, respectively. The spectra have been normalized to the background by the same procedure as was used by Abbate et al. [3]. The energy scale was calibrated to the Cu 2$p_{3/2}$ peak of CuO at 931.2 eV, measured directly after each scan. The energy position of the main peak was 931.17 ± 0.03 and 931.38 ± 0.03 eV, respec-
Fig. 2. Polarization dependent Cu $2p_{1/2}$ absorption spectra of Bi$_2$Sr$_2$CaCu$_2$O$_8$, $\theta$ is the angle between the electric vector and the c-axis. Spectra are normalized to the background.

Fig. 3. Polarization dependent Cu $2p_{1/2}$ absorption spectra of Bi$_2$Sr$_2$CaCu$_2$O$_8$ with expanded intensity. Spectra are normalized to the background.

d$(xz)$ or $d(yz)$. Thus, the spectra can be explained in terms of Cu $3d$ holes with predominantly $3d(x^2-y^2)$ character and $\sim 10\%$ of $3d(m=0, \pm 1)$ character. This admixture may have important consequences for theoretical models describing the pairing of electrons leading to superconductivity. Seino et al. [14] studied the effect of a rhombic distortion of a CuO$_4$ cluster, which causes a mixing of the Cu $3d(x^2-y^2)$ and $3d(3z^2-r^2)$ orbitals, on the Cu $2p$-XAS spectra using an impurity calculation. Other possibilities include the formation of a new superconducting ground state due to a strong increase of quantum-spin fluctuations as a result of the orbital configuration mixing [9] or a $d-d$ excitation model [10].

Contrary to recent XAS measurements on Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ [1], which show an increase of Cu $d$-weight with $m=0, \pm 1$ up to $34\%$ as a function of doping, we rather found a decrease in the $d(m=0, \pm 1)$ contribution for the bismuth compound with the highest $T_c$. However, the difference is within the error bars of the normalization procedure to obtain the relative peak intensity. Thus, the measurements give no evidence for a relation between the amount $d(m=0, \pm 1)$ character and value of the critical temperature in Bi$_2$Sr$_2$CuO$_6$ ($T_c = 9$ K) and Bi$_2$Sr$_2$CaCu$_2$O$_8$ ($T_c = 80$ K).

The polarization dependent energy shift of the main line equal to 150 and 500 meV as has been reported by Flank et al. [11] and Abbate et al. [3], respectively, is not well understood. Bianconi et al. [12] have related this shift to the energy difference between the Cu $3d(x^2-y^2)$ and $d(z^2)$ holes in the initial state. However, a simple comparison between the peak shift and the position of the unoccupied levels in the unperturbed ground state is not justified because there is only one ground state, which contains some mixture of $d_{x^2-y^2}$ and $d_{z^2}$ holes and the main peak corresponds to $2p^3 3d^{10}$ which contains only one energy level. Our XAS measurements did not show...