Doped holes in edge-shared CuO_2 chains and the dynamic spectral weight transfer in X-ray absorption spectroscopy

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Abstract. – We present a joint experimental and theoretical study of the electronic structure of the chain compounds $A_{1-x}CuO_2$ (A = Ca, Sr, Ba) using O-K and Cu-L_3 X-ray absorption spectroscopy. The doping-dependent behaviour in these systems differs from that of conventional 2D Cu-O networks formed by corner-shared CuO_4 plaquettes. It follows from the strongly weakened inter-plaquette hybridisation due to the nearly 90° Cu-O-Cu bond in the chains. Spectroscopically, this results in a) the different final states in the Cu-L_3 spectra which can be used directly to "read-off" the Cu valency and b) a drastic reduction in the dynamic spectral weight transfer from the upper Hubbard band to the low-energy scale in the O-K spectra.

Introduction. – Low-dimensional cuprate systems, such as chains and ladders, gained interest originally in the context of their being model systems for the high-temperature cuprate superconductors. It soon became clear that such quasi-1D systems offer a rich correlated electron physics of their own [1, 2], with the observation of the separation of spin and charge degrees of freedom being one of the highlights [3].

A second area to catch the imagination of researchers worldwide has been that of the spin ladders. Here, superconductivity has been predicted theoretically for a doped ladder [4], but has not been observed so far in pure ladder compounds. Consequently, the discovery of superconductivity under pressure in $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41+\delta}$ [5] —which has no CuO_2 planes, but rather a mixture of linear CuO_2 chains (built up of edge-shared CuO_4 plaquettes) and two-leg Cu_2O_3 ladders— has sparked still further interest in the properties of ladders and chains as individual elements [6].

In this paper, we present a joint experimental (O-K and Cu-L_3 X-ray absorption spectroscopy (XAS)) and theoretical investigation of the electronic structure of hole-doped edge-shared $A_{1-x}CuO_2$ chain compounds: $Ca_{0.83}CuO_2$, $Sr_{0.73}CuO_2$ and $Ba_{0.67}CuO_2$, all of which contain CuO_2 chains formed of edge-sharing CuO_4 plaquettes. The chains are doped with 0.34, 0.54 or 0.66 holes per Cu site, respectively [7–10]. We emphasize that these CuO_2 chains provide a unique opportunity among the cuprates to consider such basic questions as the doping dependence of the dynamical spectral weight transfer (DSWT) raised at first in the pioneering works of Chen *et al.* [11] and Eskes *et al.* [12, 13], now within an unusually broad experimentally accessible doping range but at the same time under new, specific conditions of nearly 90° Cu-O-Cu bonds, not studied systematically so far to the best of our knowledge. Remarkably, the magnetic susceptibility of $Ca_{0.83}CuO_2$ and $Sr_{0.73}CuO_2$ —despite their high hole-doping levels— can be described within the dimerized alternating spin-(1/2) Heisenberg-chain model [7], with antiferromagnetic order setting in below 10 K and 12 K for $Ca_{0.83}CuO_2$ and $Sr_{0.73}CuO_2$, respectively. For compounds which contain the better known CuO_2 planes, neither Néel nor any other long-range magnetic order has been found for doping levels beyond 0.04 to 0.125 holes per Cu site (*i.e.* beyond the spin-glass and stripe region). Furthermore, there have been reports of superconductivity with $T_c = 13$ K in the related compound $Ba_2Cu_{3-x}O_{6-y}$ [14], which naturally would necessitate the delocalisation of doped holes in the $A_{1-x}CuO_2$ systems.

Experimental and theoretical details. – The synthesis and the structural analysis of the polycrystalline samples of $Ca_{0.83}CuO_2$, $Sr_{0.73}CuO_2$ and $Ba_{0.67}CuO_2$ have been described previously [7, 9]. The XAS measurements were performed at the SX700/II monochromator and the PM5 beam line at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY-I). In all measurements the non–surface-sensitive fluorescence-yield mode (FY) as well as the more sensitive total electron yield mode (TEY) were used. The energy resolution of the monochromator was set to 280 meV and 600 meV at the O $1s$ and the Cu $2p_{3/2}$ thresholds, respectively. The O $1s$ data were corrected for the energy-dependent incident flux and normalized 60 eV above the threshold. The self-absorption effects were corrected as described in refs. [15] and [16]. Prior to the measurements, the surface of the sintered tablets was scraped *in situ* with a diamond file at a base pressure of 5×10^{-10} mbar. The CuO was used for energy calibration after each injection.

The simulated Cu-L_3 and O-K spectra were calculated with the aid of an extended five-band pd Hubbard-model as described in ref. [17]. Thereby, as usual, we ignore the electron-lattice interaction and adopt that the ground state of the doped chains conserves the translational symmetry of the undoped system. The Cu-L_3 and O-K XAS spectral density was calculated by means of the exact diagonalisation of small periodic $(CuO_2)_n$ clusters (with $n = 3, 4$), following refs. [17] and [18]. The calculated data were broadened with Lorentzian functions of half-width 0.4 eV, in order to ease their comparison with experiment.

Results and discussion. – Figure 1 illustrates the systematic evolution of the Cu-L_3 XAS spectra of $Ca_{0.83}CuO_2$, $Sr_{0.73}CuO_2$ and $Ba_{0.67}CuO_2$. We analyze the experimental spectra within the extended five-band pd Hubbard model referred to above [19]. Also shown are data from Li_2CuO_2 and $NaCuO_2$, which serve as formally di- and trivalent reference systems for the edge-shared CuO_2 chain geometry. The spectral signatures of Li_2CuO_2 and $NaCuO_2$ are simple, single-component white lines at 930.7 and 932.4 eV, respectively. Also shown is a comparison of the TEY and the FY data for $Ba_{0.67}CuO_2$, $Sr_{0.73}CuO_2$, and $Ca_{0.83}CuO_2$. In contrast to often observed significant differences, for those non-integer doped compounds one realizes a very good agreement between the two methods. This shows that our self-absorption correction is meaningful with a maximal error for the relative Cu-L_3 peak intensities of about 10%. In
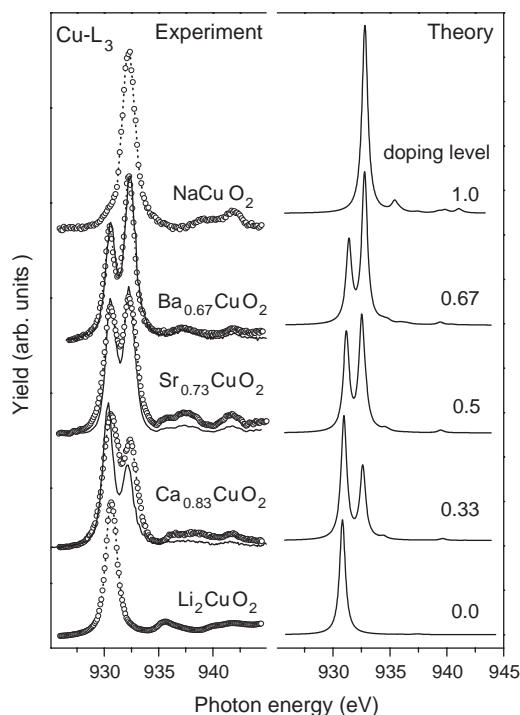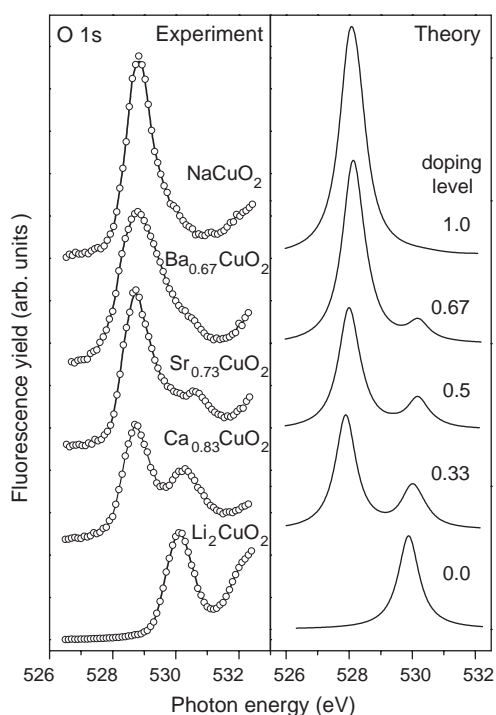
Fig. 1

Fig. 2

Fig. 1 – Left panel: Cu-L_3 XAS spectra of edge-shared CuO_2 chain systems as a function of hole doping. The right panel shows the corresponding simulated spectra using an extended five-band *pd* Hubbard model. The hole-doping level is indicated next to each theoretical curve. For details see text. For the partially doped $A_{1-x}CuO_2$ compounds (A = Ba, Sr, Ca) we compare fluorescence yield (FY) and total electron yield (TEY) data which demonstrate that the peak ratios are virtually independent of the detection method.

Fig. 2 – The same as in fig. 1 for the O-*K* (O 1*s*) XAS spectra.

the case of Li_2CuO_2 and $NaCuO_3$, the uncertainty of the correction might be larger. However, this is irrelevant for our analysis of peak ratios as those two compounds give rise to a single Cu-L_3 line only. They are just used as energy reference for Cu^{2+} and Cu^{3+} absorption lines whereas the peak energies are *not* affected by the correction. Figure 1 shows clearly that the edge-shared chain systems with non-integer formal valence exhibit a Cu-L_3 XAS spectrum resembling a superposition of scaled versions of the di- and trivalent reference systems. For Li_2CuO_2 the single peak is described by the $2\underline{p}3d^{10}$ configuration (where $2\underline{p}$ denotes the core hole). The dominant peak at 932.4 eV in $NaCuO_2$ was assigned to $2\underline{p}3d^{10}\underline{L}$ previously [20]. Consequently, for $Ca_{0.83}CuO_2$, $Sr_{0.73}CuO_2$, and $Ba_{0.67}CuO_2$ the low- and higher-energy features result from $2p3d^{10}$ and $2\underline{p}3d^{10}\underline{L}$ final states, respectively. Furthermore, the clear energetic alignment with the divalent and trivalent reference systems confirms that the features in the Cu-L_3 XAS of the intermediate doped chains signal the existence of $Cu(II)O_4$ and $Cu(III)O_4$ plaquettes. In line with this picture, the spectral weight of the higher-energy peak increases with the formal valence on going from $Ca_{0.83}CuO_2$ to $Sr_{0.73}CuO_2$ and further to $Ba_{0.67}CuO_2$.

It is instructive to compare the Cu-L_3 XAS spectrum of $Ca_{0.83}CuO_2$ with that of the layered corner-shared $La_{1.66}Sr_{0.34}CuO_4$ studied previously [21,22]. Both have the same formal

valence: $Cu^{+2.34}$. However, in the latter the higher-energy component turns to be a very weak shoulder [21]. The clear differences between the spectra of compounds with the same formal valence is a signal of the crucial role played by the geometry of the Cu-O network, not only in the Cu-L_3 core level photoemission spectra [23–25], but also in Cu-L_3 XAS [26, 27]. In the edge-shared CuO_2 chains the Cu-O-Cu interaction pathway is essentially $90°$, which strongly suppresses the inter-plaquette hybridisation. For the undoped system Li_2CuO_2, this has been observed to lead to a behaviour analogous to that of an isolated CuO_4 plaquette [28]. The spectroscopy of such cuprates is reminiscent of the situation in some mixed valent $4f$ compounds in which the intensity ratio of the features at the (Ln)-L_3 thresholds can be used to determine the average valence [29]. In the case of the CuO_2 chain systems, due to the very weak inter-plaquette hybridisation, one observes a clear feature at 932.4 eV in the Cu-L_3 spectra whose weight scales with the formal copper valence.

In contrast, the systems containing strong $180°$ Cu-O-Cu interaction pathways, support significant inter-plaquette hopping. The inter-plaquette hybridisation offers the system further opportunity to screen the copper core hole involving the transfer of electron density from ligand levels further away from the core ionised site. As a result, the Cu-L_3 XAS spectra of two formally 2.34+ valent cuprates are significantly different: the edge-shared chain exhibits two clear final-state peaks, whereas the inter-plaquette hopping prevalent in the 2D CuO_2-plane system results in a mere asymmetry at higher energy [21, 22].

The spectroscopic consequences of the geometry-induced quasi-localisation are not restricted to the Cu-L_3 spectra, only, as is illustrated by the O-K spectra shown in fig. 2. The pronounced peak directly above the absorption onset at 530.2 eV in the undoped Li_2CuO_2 system is related to transitions into O $2p$ states hybridized with the Cu $3d$ upper Hubbard band (UHB) [30]. The pre-edge peak in the O-K XAS spectrum of the trivalent cuprate $NaCuO_2$, which in the context of the HTSC would be assigned to the doped-hole states (the Zhang-Rice singlet (ZRS)) [11–13, 21, 31], is down-shifted by 1.3 eV with respect to the Cu(II) UHB, since with increasing Cu valence the covalence increases [32].

In conventional, hole-doped corner-shared planar systems, two pre-edge peaks on O-K XAS are observed [11, 21, 31]. With increasing doping level the UHB quickly loses its intensity, whereas the lower-energy spectral weight (LESW) —the hole peak— increases as the doping progresses. The qualitative and quantitative description of LESW was given previously [12, 13]. As can be seen from fig. 2, the intermediate-doped edge-shared cuprate chains present a different picture. Firstly, here, as was the case for the Cu-L_3 spectra, the two features remain at the same energies as their counterparts in the formally Cu(II) and Cu(III) reference systems. Secondly, the *rate* at which the UHB spectral weight is transferred to the low-energy scale is drastically reduced in these compounds compared to their corner-sharing 2D cousins. This is much more than an XAS detail, as this spectral weight transfer is an important characteristic of doped effective cuprate and has been extensively studied in the corner-shared, layered cuprates both experimentally [11, 21, 33] and theoretically [12, 13]. In the corner-shared systems such as $La_{2-x}Sr_xCuO_4$ [11, 21, 33] and the two-leg ladder system $La_{1-x}Sr_xCuO_{2.5}$ [34], this effect —expressed in the doping-mediated destruction of the UHB intensity— has been found to be supralinear with x, and has thus been dubbed dynamical spectral weight transfer or DSWT [12, 13]. For example, in the case of $La_{2-x}Sr_xCuO_4$ for $x = 0.15$, the UHB is scarcely visible [11, 21] and for the analogous doping level in the two-leg ladder, the UHB-peak has already lost more than 40% of the spectral weight it had for $x = 0$ [34].

However, as can be clearly seen in fig. 2 for an even greater doping level of 0.34 in $Ca_{0.83}CuO_2$ we still find $\sim 67\%$ spectral intensity of the UHB compared with Li_2CuO_2, the latter acting as a reference point for the undoped case. Even $Ba_{0.67}CuO_2$, which has a formal doping level of 0.66 holes per Cu, still shows a clear indication of an UHB feature in the O-K

XAS. The suppression of the DSWT is well reproduced by the extended five-band *pd* Hubbard model [19] as can be seen from the good agreement between experiment and theory as shown in fig. 2. In addition, this knowledge has played an important role in our understanding of recent polarisation-dependent XAS data from the $(Sr,Ca,Y,La)_{14}$ systems [6], which contain, apart from the 2-leg ladders, highly doped CuO_2 chains.

Figure 3 summarizes the Cu-L_3 and O-K core level excitation data of the edge-shared chain systems obtained with a least-square–fitting procedure. Since two peaks are better resolved in the Cu-L_3 spectra than in the O-K spectra, a better statistical accuracy can be achieved for the Cu-L_3 spectra. In the upper panel, the mean Cu valences of Li_2CuO_2 and the three doped chain compounds under investigation, derived from the intensity of the Cu(II) and Cu(III) signals in the Cu-L_3 XAS are compared to the formal valence derived from the stoichiometry, yielding an almost perfect agreement. This emphasises the unique nature of these cuprate chains, as, to the best of our knowledge, they represent the first examples of a "mixed valent" cuprate family, in which core level spectroscopy allows one to "read-off" the mean Cu valence merely by comparing the intensity ratio of the double-peaked Cu-L_3 XAS feature. The lower panel of fig. 3 shows an analysis of the doping-dependent evolution of the spectral weight of the hole peak and the UHB in the O-K XAS spectra, whereby the doping dependence of the ZRS and the UHB features in $La_{1-x}Sr_xCuO_4$ (from ref. [11]) has been included for comparison. The significant suppression of the DSWT in the edge-shared chain systems is very clear. The general behaviour of the O-K XAS spectra for low-dimensional cuprates, as compared with the Cu-L_3 XAS spectra, is well established [12, 13]. It was found that DSWT is independent of the cluster size and the dimensionality, as long as the bandwidth is kept constant, therefore the comparison of $A_{1-x}CuO_2$ and $La_{1-x}Sr_xCuO_4$ is interesting since their bandwidths differ by a factor of about four [30, 35, 36]. The standard *pd*-model applied to a CuO_2 plane-like cluster reveals for artificially small transfer integrals $t_{pd} \sim 0.5$ eV that the LESW follows the doping percentage [12, 13]. From fig. 3 we can see that for the low doping level ($x \leq 0.2$) the
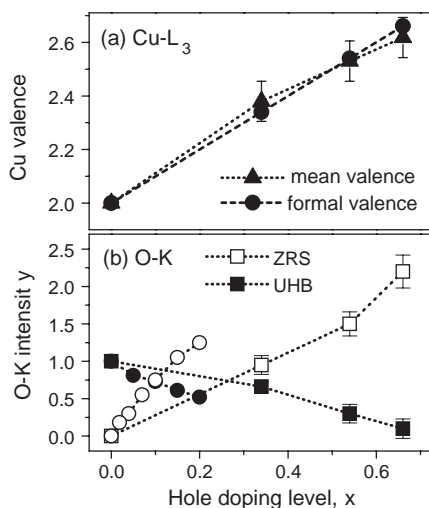

Fig. 3 – (a) The mean Cu valence (filled triangles) obtained from the Cu-L_3 XAS spectra of $A_{1-x}CuO_2$ and Li_2CuO_2 together with the formal valence (•) from the stoichiometry plotted *vs.* the hole-doping level, x. (b) The relative spectral intensity of the doping-induced hole peak (ZRS, open squares), and the UHB (filled squares) in the O-K XAS spectra of the same systems, normalized to the intensity of the UHB for undoped Li_2CuO_2. The UHB intensity (•) and the ZRS feature (○) for $La_{1-x}Sr_xCuO_4$ (from ref. [11]) are also shown.

LESW develops for O-K spectra nearly twice as fast for $La_{1-x}Sr_xCuO_4$ as compared with the edge-shared compounds $A_{1-x}CuO_2$. Such a difference of slopes has been predicted by theory comparing the cases $t_{pd} = 0.5$ eV and $t_{pd} = 2$ eV. Hence, it can be related to the decreasing inter-plaquete hybridisation ongoing from $La_{1-x}Sr_xCuO_4$ to $A_{1-x}CuO_2$ [12, 13]. Unfortunately, for large doping levels no experimental data for layered compounds are available to be compared with our chain compounds. The DSWT is not a unique phenomenon for the late-transition metal compounds. Experimentally, spectral charge transfer from the higher energy to the lower-energy component was observed also in other metalates such as vanadates, cobaltates, and nickelates: see for instance the Mott-Hubbard system $La_{1-x}Ca_xVO_3$. But here the effect might be weaker due to the weak correlation probably related to a relatively small on-site Coulomb repulsion $U_d \sim 3$ eV for vanadates [37, 38]. Furthermore, despite different crystallographic details the orbital structure of vanadates and nickelates is more complex due to the presence of two d-orbitals at the same transition metal site in the energy range of interest. Further theoretical studies (outside the scope of the present paper) are necessary before a profound comparison between different metalates can be made. Finally, deviations from the idealized 90° and planar chain geometry might be supplemented and/ or compensated by polaronic or disorder effects owing to nonperiodic counter ion positions accompanied with a broken translational symmetry. For that purpose the el-ph interaction and the cationic potential ignored above should be taken into account. However, such investigations are outside the scope of the present paper.

To summarize, we have presented a joint experimental and theoretical study of the effects of hole doping on the electronic structure of CuO_2 chains built up of edge-shared CuO_4 plaquettes. The analysis of the data illustrates the remarkable consequences of the edge-shared geometry of these systems, which results in a nearly 90° Cu-O-Cu interaction pathway, thereby essentially weakening the nearest-neighbour inter-plaquette hopping:

1) The system is robbed of the possibility of using non-local processes to screen the core hole in Cu-L_3 XAS, thus resulting in a mixed valence-like behaviour in which the mean Cu valence can be simply derived from the relative intensity of the $2\underline{p}3d^{10}$ and $2\underline{p}3d^{10}\underline{L}$ final-state features. This is an unprecedently clear example of the impact of non-local effects in XAS present in other, corner-shared, cuprates but completely absent here.

2) The dynamic transfer of spectral weight from the upper Hubbard band to the low-energy scale is strongly suppressed, resulting in the observation of the UHB feature in the O-K spectra even up to a doping level of 0.67 extra holes per Cu.

3) Together with the observation of Néel order in the $Sr_{0.73}CuO_2$ and $Ca_{0.83}CuO_2$ systems, [7] the spectroscopic data presented here provide evidence for the existence of individually identifiable $Cu(II)O_4$ and $Cu(III)O_4$ plaquettes in these materials.

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