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X-Ray Photoemission and Electron-Energy Loss spectroscopic Studies of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$

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$\text{Sr}_2\text{CuO}_2\text{Cl}_2$ represents a nearly ideal case of a 2-D antiferromagnetic CuO_2 -plane and thus is of particular interest in the context of the origins of high T_C superconductivity. We present high energy spectroscopic results on single crystalline $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. Using electron-energy loss spectroscopy in transmission we have measured the loss function along the high symmetry directions in the CuO_2 -plane. X-ray photoemission spectroscopy is applied to study the valence band and the Cu 2p spectrum. Comparison of the experiment to a cluster calculation is given.

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X-ray photoemission spectroscopy (XPS) has provided a number of insights into the electronic structure of the occupied electronic states of late transition metal compounds such as the Cu-dihalides¹ and Cu oxides.^{2,3} In particular, the detailed form of the Cu 2p spectra, together with cluster calculations delivers an experimental check of the parameters which go into models used to describe the electronic structure of these correlated materials. With high-energy electron energy-loss spectroscopy (EELS)⁴ it is possible to study the unoccupied electronic states, in particular it is possible to study

the momentum resolved dielectric function along certain high-symmetry directions in single crystals. This is of great interest in the cuprates for those being structurally highly anisotropic due to the CuO_2 -network.

In many formally divalent copper compounds, the Cu 2p spectrum shows a strong satellite feature which is interpreted as to be due to emission from a poorly-screened $2p^5 3d^9$ final state.^{1,3,5} Whilst the attribution of the main line to a well-screened final state in which no d-holes reside at the site of the 2p core hole is broadly accepted, the origin of the large width and high binding energy (BE) asymmetry of the main line^{2,3} has been the subject of discussion. In earlier treatments,^{1,3,5} the low energy component of the main line was discussed in terms of the $3d^{10}\underline{L}$ final state, while the asymmetry and resultant large width were attributed to the bandwidth of the O 2p states.⁶

However, recent calculations have shown that the ability of the system to screen the Cu 2p core hole depends sensitively on the geometry and doping level of the CuO_2 network involved.^{7,8} These calculations predict that the Cu 2p XPS main line is comprised of two peaks. The smaller high BE component is a $3d^{10}\underline{L}$ final state, in which the 3d hole has moved to O 2p orbitals of the same CuO_4 unit. The larger component at lower BE corresponds to a $2p^5 3d^{10}$ final state in which a pushed-out hole mainly resides in the O 2p orbitals, weakly interacting with the neighbouring Cu spins, and in which it forms a Zhang-Rice singlet.⁹ It is the stability of this singlet that leads to appearance of the $2p^5 3d^{10}$ final state at lowest BE. There has been a discrepancy, however, between these calculations^{7,8} and what has been experimentally observed up to now in the undoped cuprates, in that there has been no clear-cut double-peak structure seen for the main line.

In this contribution, we present Cu 2p XPS data from $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ which show a pronounced double-peaked Cu 2p main line, and discuss some of the possible reasons for its strength in the oxychloride as opposed to the other cuprates. In addition, we present a study of the interband excitations in the same material using EELS in transmission.

The crystals were grown from the stoichiometric melt - for details see Miller *et al.*¹⁰ It crystallises in a body centred tetragonal structure¹⁰ like La_2CuO_4 , but in the oxychloride the apical oxygens are replaced by chlorine located in the rock-salt Sr_2Cl_2 block layers. Therefore, $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ contains a truly 2-D CuO_2 network (T' structure).

The electron energy-loss spectra were obtained in transmission using a primary beam of 170keV.⁴ Samples of $\sim 1000\text{\AA}$ thickness were cleaved using an ultramicrotome. The sample quality and orientation were checked *in situ* using electron diffraction.

The x-ray photoemission experiments were performed with a commercial XPS machine equipped with a monochromated Al $K\alpha$ source of 1486.6eV

photon energy. The single crystalline samples were cleaved *in situ* under ultrahigh vacuum conditions. The base pressure of the system was in the low 10^{-8}Pa region and the measurements were performed at room temperature. From the angle dependence of the spectra we infer that the cleavage surface (which is parallel to the a, b -plane) is Sr rich. The BE of the O 1s core level of about 529.3 eV is consistent with typical values for O 1s in other cuprate compounds. We note that the O 1s spectrum comprises purely of a single component.

The valence band spectrum of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is shown in Fig. 1a) and is similar to a previous valence band study of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.¹¹ Comparing our results to previous studies of CuO,^{3,12} we note the good agreement concerning the Cu 3d-O 2p part of the spectrum. The peak centred at about 3 eV can be assigned to the hybridised Cu 3d-O 2p states as in CuO, whilst the small foot at about 1.5 eV represents the highest lying electron removal states in which the intrinsic 3d hole forms a singlet. Angle resolved photoemission studies (ARPES) of these singlet states in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ have been published recently, and the observed dispersion of these highest lying states can be understood within the framework of an extended t - J model.¹³ In the XPS spectrum, the satellite features due to the Cu 3d⁸ final state are present between 10 and 13 eV, as in CuO. Finally, the peak at about 6 eV can be assigned to Cl 3p states. The large observed energy separation between the Cl 3p and the Cu 3d-O 2p states could be expected to lead to a small degree of hybridisation of the Cl with the states at the top of the valence band.

The Cu 2p_{3/2} photoemission spectrum is shown in the upper part of Fig. 1b). The main line is located at 933.6 eV; its satellite feature is centred at about 942 eV. For most cuprate compounds the intensity ratio of the satellite to the main line $I_{\text{sat}}/I_{\text{main}}$ is 0.3–0.4.⁷ For $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ this intensity ratio is significantly higher: we estimate $I_{\text{sat}}/I_{\text{main}} \simeq 0.5$ –0.6. The most striking feature, however, is the distinct shoulder in the main line, B, which is seen at ~ 3 eV higher energy than the more intense component, labelled A. We obtain the intensity ratio $I_B/I_A \simeq 0.4$ –0.5.

To calculate the Cu 2p XPS, we take a two-dimensional Cu_5O_{16} cluster which consists of Cu 3d _{x^2-y^2} , O 2p _{x} and 2p _{y} orbitals.⁸ The relevant parameters involved in the model are the charge-transfer energy between Cu 3d and O 2p levels (Δ), the Coulomb interaction energy between 3d holes (U_{dd}) and the Slater-Koster parameters for neighbouring Cu 3d-O 2p pairs ($pd\sigma$) and for neighbouring O 2p pairs ($pp\sigma$ and $pp\pi$). To include the core-hole effects in the photoemission final state, we also take into account the Coulomb interaction energy between the 3d states and the core hole (U_{dc}). We create a core hole at the central Cu site of the cluster. For the sake of simplicity

we have disregarded the multiplet coupling effects, which are not expected to greatly affect the results discussed here. The obtained line spectrum is convoluted with a Gaussian of 0.8eV and a Lorentzian of 0.6eV (FWHM) in order to compare with the experimental spectrum.

In Fig. 1b) we show calculated Cu 2p XPS as a function of Δ , keeping $\Delta - U_{dc} = -4.2\text{eV}$ so as not to change the energy separation of the satellite and main line. The other parameters are kept fixed at $U_{dd} = 8.8\text{eV}$, $pd\sigma = 1.5\text{eV}$, $pp\sigma = -1.0\text{eV}$ and $pp\pi = 0.3\text{eV}$, which are the same as those used by van Veenendaal *et al.*⁷

As discussed above, the calculated spectrum consists of a main line at lower BE (at the maximum of which the calculated spectra are normalised) and a satellite located at higher BE. The satellite is seen to increase in relative intensity upon increasing Δ , mainly as a result of increasing $3d^9$ weight in the ground state wave-function. In the main line, feature *B*, corresponding to the $3d^{10}\bar{L}$ final state with "O 2p band screening", appears to grow with increasing Δ . In fact this follows rather from the decrease in the strength of feature *A*, corresponding to the $2p^5 3d^{10}$ final state with "Zhang-Rice singlet screening". This can be understood in terms of the suppression of Zhang-Rice singlet formation as Δ is increased.

From the comparison of the calculated results shown in Fig. 1 with the experimental data it can be seen that the case of $\Delta = 4.5\text{eV}$ best reproduces the experimental spectrum of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. We obtain $I_{sat}/I_{main} = 0.55$ and $I_B/I_A = 0.52$ in good agreement with the experiment. Δ is 1eV larger than for other cuprate materials. The question then arises as to what extent a larger Δ value alone could be responsible for the observed relative strength of the final state *B* in the oxychloride in comparison to other CuO_2 layer systems in which no such clear shoulder has been observed up to the present. A larger value of Δ is also consistent with the higher I_{sat}/I_{main} intensity ratio in the oxychloride.

Fig. 2 shows the energy loss spectra of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ for momentum transfers $\mathbf{q}$ parallel to the (100) and (110) crystal directions. In the CuO_2 -plane of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ the Cu-O bonds lie along the (100) direction. From the low $\mathbf{q}$ spectra we obtain a charge transfer gap of about 1.6eV in accordance with optical studies.¹⁴ For small $\mathbf{q}$, the spectral shape is identical for excitations along the two directions, attesting to the in-plane optical isotropy of the CuO_2 -plane. The first feature at about 2.6eV is clearly made of two components. The component at lowest energy appears to be relatively sharp, which may point to excitonic character for this excitation, in which the hole and the excited electron remain bound together.

For higher $\mathbf{q}$ the loss-function differs significantly between the two directions. In both cases the lowest lying feature disperses to higher energies

Fig. 1. a) Valence band XPS. b) Top: $\text{Cu } 2p_{3/2}$ core level photoemission spectrum. Bottom: Calculated spectra with different Δ (dashed line: 3.5 eV, solid line: 4.5 eV and dotted line: 5.5 eV).

Fig. 2. EELS of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ measured in the CuO_2 -plane.

and broadens with increasing q . Interestingly, the magnitude of the observed dispersion is considerably larger along the (110) direction ($\sim 1.3\text{eV}$) than along (100) ($\sim 0.3\text{eV}$). The difference between the (110) and (100) directions reflects the anisotropy of the bandstructure of the low-lying occupied and unoccupied states.

As mentioned earlier, ARPES measurements have determined a bandwidth of $\sim 250\text{meV}$ for the dispersion of a single hole in the antiferromagnetic CuO_2 -plane of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ along the (110) direction.¹³ In contrast, almost no dispersion is observed along (100). The magnitude of the observed dispersion in ARPES is consistent with the extended $t - J$ model, in which the single particle bandwidth is determined by twice the superexchange integral, J ($2J$ of order 0.3eV).

Comparing the data from EELS and ARPES, it is apparent that the anisotropy in the dispersion is consistent, but that the magnitude of the dispersion along the (110) direction observed in EELS is much greater. This suggests that the dispersion relations of a single hole (seen in ARPES) or of an electron-hole excitation (seen in EELS) in an antiferromagnetic background have a different origin.

To conclude, we have presented XPS of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and demonstrated that local and nonlocal screening processes are present in 2-D CuO_2 -planes. Possibly due to a larger Δ the local screening contributions are stronger than in La_2CuO_4 leading to a pronounced double-featured main line in Cu 2p XPS. With EELS we observed the dispersion of the low energy excitonic states and found a large bandwidth. This large bandwidth can be the reason of the electron-hole pair coupled to a singlet state which moves without much disturbing the antiferromagnetic order in the CuO_2 -planes.

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