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PHYSICA B

Electron energy-loss and X-ray photoemission spectroscopy of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$

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Abstract

Electron energy-loss spectroscopy has been applied to the insulating layered copper-oxide $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ in order to study the loss function along the high-symmetry directions of the CuO_2 -plane. We observe an anisotropically dispersive excitation in the low-energy region. We have also measured the Cu 2p X-ray photoemission spectrum, which is discussed in terms of the possible screening channels available in response to the creation of the 2p core hole, including the role of non-local screening effects.

Keywords: $\text{Sr}_2\text{CuO}_2\text{Cl}_2$; Electronic band structure; Energy-loss spectroscopy; Photoemission

The CuO_2 -plane of the carrier-free layered copper-oxide $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ represents an ideal model system for the two-dimensional antiferromagnetic planes common to all undoped high-temperature cuprate superconductors. $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ adopts the tetragonal K_2NiF_4 structure [1] and is isostructural to the high-temperature tetragonal phase of La_2CuO_4 down to at least 10 K. In the oxychloride the La is replaced by Sr and apical oxygen is replaced by a chlorine atom, which is located some 2.86 Å above the CuO_2 -plane. This is significantly longer than the plane–apex distance of 2.41 Å in La_2CuO_4 and is expected to result in a more pronounced 2-D character of the CuO_2 -planes in the oxychloride.

In this paper we report investigations of the electronic structure of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ single crystals using electron energy-loss spectroscopy (EELS) and X-ray photoemission spectroscopy (XPS). $\text{Sr}_2\text{CuO}_2\text{Cl}_2$

single crystals were grown using the procedure of Miller et al. [1]. For EELS measurements, films of about 1000 Å thickness were cut from the crystals using an ultramicrotome with a diamond knife. EELS spectra were recorded in transmission using a 170 keV spectrometer described elsewhere [2]. The energy and momentum resolution were chosen to be 115 meV and 0.05 Å^{-1} , respectively. The crystal structure of the films and the orientation of the *a*, *b*-plane perpendicular to the electron beam were carefully checked by elastic electron scattering. EELS in transmission provides information on the electronic excitations of the solid measuring the energy- and momentum-dependent loss function $\text{Im}(-1/\epsilon(\omega, \mathbf{q}))$. X-ray photoemission experiments were performed with a commercial spectrometer using monochromatic Al K_α radiation ($h\nu = 1486.6 \text{ eV}$), giving a total energy resolution of 0.5 eV. The crystals were cleaved in-situ parallel to the *a*, *b*-plane. All the measurements shown here were taken at room temperature.

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Fig. 1 shows the low-energy part of the loss function for different momentum transfers q parallel to the [100] and [110] directions. From the spectra shown in Fig. 1, the charge transfer gap can be determined to be 1.6 ± 0.1 eV. For $q = 0.1 \text{ \AA}^{-1}$, the loss function is isotropic and the first feature around 2.6 eV is clearly split into a double-peak structure. The lowest-energy component of the first feature (marked with an arrow) is strongly reduced in intensity with increasing q , and is practically dispersionless in both the [110] and [100] directions. This signals the strongly localised nature of this excitation. In contrast, the higher-energy component (marked with a line) shows a large dispersion in the [110] direction (~ 1.3 eV over the q -range shown [3]) and a smaller dispersion along [100] (~ 0.3 eV for q up to $0.7 \text{ \AA}^{-1}$ [3]). Furthermore, on comparing the spectra in both directions for momentum transfer $q \geq 0.3 \text{ \AA}^{-1}$, no clear transitions can be found along [110], whereas in the [100] direction there are clearly two peaks located at 4.2 and ~ 5.4 eV.

Fig. 1. The low-energy loss function of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ for different momentum transfers, q , for the two high-symmetry directions of the a, b -plane.

Angle-resolved photoemission (ARPES) data indicate a bandwidth of 280 meV for the dispersion of a single hole in the CuO_2 -plane of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, measured in the Γ -(π, π) direction (i.e. along [110]) [4]. Thus, in comparison with the dispersion from ARPES measurements the lowest-lying excitation in EELS shows a greatly reduced dispersion, whilst the higher-lying excitation exhibits a much stronger dispersion. The large differences between the bandwidths derived from photoemission and EELS results suggest that the momentum dependences of a hole in the valence band and that of these electron-hole excitations arise from different mechanisms. In the case of the ARPES measurements, a hole ($s = \frac{1}{2}$) is created, whose movement involves the flipping of copper spins in the antiferromagnetic CuO_2 -plane resulting in a small bandwidth of the order of twice the superexchange integral, J ($J \sim 125$ meV). As the electron-hole excitations created in EELS with this primary beam energy are spinless in nature (singlets), it is reasonable to conjecture that such excitations would be able to propagate through the antiferromagnetic CuO_2 -plane without perturbing the antiferromagnetic order, thus giving rise to a larger dispersion than that observed in ARPES. Whilst this picture fits with the behaviour of the higher-lying excitation (i.e. that at 2.6 eV for low q), it is at odds with the q -dependence of the lowest-lying excitation. This then raises the question as to whether the lowest-lying excitation corresponds to a strongly bound electron hole pair (exciton) and the higher-lying to a “normal” interband excitation.

Turning to XPS measurements, the $\text{Cu } 2p_{3/2}$ spectrum of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is shown in Fig. 2. The main line at 933.6 eV is accompanied by a multiplet-split satellite at about 943 eV due to the poorly screened $2p^5 3d^9$ final state. In the main line we observe a strong shoulder at about 2 eV higher binding energy. This feature can be understood in the context of the different channels open for the screening of the $\text{Cu } 2p$ core hole [5, 6]. The peak A originates from a $2p^5 3d^{10}$ final state, where the $\text{Cu } 3d$ hole has moved to a neighbouring CuO_4 unit, where it forms a Zhang–Rice singlet. The shoulder B arises from a $2p^5 3d^{10} \bar{L}$ final state in which the $\text{Cu } 3d$ hole has moved to adjacent oxygen $2p$ levels. Although the cluster models used for calculation of the $\text{Cu } 2p$ photoemission spectra predict the appearance of a peak B in the main lines of other cuprate materials, this feature has been notable by its

Fig. 2. Cu $2p_{3/2}$ photoelectron spectrum of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ recorded using monochromatic Al K_α radiation. The two features of the main line discussed in the text are marked as A and B.

absence, or low intensity, in work published up to the present. Thus, these data provide the first clear-cut indication for such a two-peak structure and provide added incentive for further theoretical work aimed

at a deeper understanding of the screening processes upon Cu $2p$ core hole formation.

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References

- [1] L.L. Miller et al., Phys. Rev. B 41 (1990) 1921.
- [2] J. Fink, Adv. Electron. Electron Phys. 75 (1989) 121.
- [3] For comparison, the square 2-D Brillouin zone (BZ) of the CuO_2 -plane of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ has an edge dimension of $0.79 \text{ \AA}^{-1}$ (i.e. along $[100]$) and a diagonal of $1.1 \text{ \AA}^{-1}$ (i.e. along $[110]$).
- [4] B.O. Wells et al., Phys. Rev. Lett. 74 (1995) 964.
- [5] M.A. van Veenendaal, H. Eskes and G.A. Sawatzky, Phys. Rev. B 47 (1993) 11462.
- [6] K. Okada and A. Kotani, Phys. Rev. B 52 (1995) 4794.