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PHYSICA B

The electronic structure of the layered cuprate $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$

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Abstract

We report spectroscopic studies of the occupied and unoccupied valence band states of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ single crystals, which adopt a layered body-centered tetragonal structure related to that of the cuprates, but with an extra copper site resulting in a plane with Cu_3O_4 stoichiometry. Using angle-resolved photoemission we observe for the $\Gamma-(\pi, \pi)$ -direction of the Brillouin zone a dispersive feature with a bandwidth of 400 ± 80 meV, approaching to within ~ 0.9 eV the Fermi level at $(\frac{1}{2}\pi, \frac{1}{2}\pi)$.

Keywords: $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$; Angle-resolved photoemission; Photoemission

$\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ is an antiferromagnet adopting a layered body-centered tetragonal structure [1] related to that of La_2CuO_4 . However, there are two major differences: firstly $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ has a Cu_3O_4 plane, which can be visualized as resulting from the insertion of “extra” Cu^* in the cuprate CuO_2 -plane. Secondly, this Cu_3O_4 -plane is apex-free and can be thought of as possessing two subsystems (Fig. 1): one cuprate-like in which superexchange between the Cu sites is mediated via 180° Cu–O–Cu interactions (with a Néel temperature T_N typical of cuprates of ~ 330 K) and one in which Cu superexchange can only occur via a 90° $\text{Cu}^*\text{–O–Cu}$ interaction (T_N of ~ 40 K) [2]. This Cu_3O_4 -plane contains three inequivalent mirror planes perpendicular to the surface, as shown in Fig. 1.

We report spectroscopic studies of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ single crystals, using polarization-dependent angle-resolved photoemission (ARPES), X-ray photoemission (XPS) and transmission electron energy-loss

spectroscopy (EELS), carried out in order to assess the impact of the $\text{Cu}^*\text{–O}$ subsystem on the electronic structure.

The single crystal growth is described in detail elsewhere [1]. For the ARPES experiments, the crystals were cleaved in UHV and oriented using LEED. During the experiment the crystal was held at 360 K to reduce charging effects and prolong the lifetime of the cleaved surface. The spectra were measured at the crossed-undulator beamline U2-FSGM [3] at BESSY. When the radiation is polarized parallel to the mirror plane we can only photoemit from initial states which are even with respect to this plane, whilst with the polarization perpendicular to the plane we are only sensitive to odd initial states. Due to the restricted space, the construction of the Brillouin zone will be discussed in detail in a forthcoming paper. Spectra have been recorded from the Γ -point at (0,0) in the direction of (0, π) and (π , π), respectively. For the EELS experiments [4] (primary beam energy: 170 keV) films of about 800 Å thickness have been cut, whereas for the XPS experiments the crystals have been cleaved

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Fig. 1. Schematic representation of the Cu_3O_4 -plane of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$: (●) cuprate-like Cu, (■) additional Cu^* , (○) oxygen. M_1 , M_2 and M_3 represent the three mirror planes.

Fig. 2. Valence-band XPS spectra of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$, for different polar emission angles, excitation energy: 1486.6 eV (monochromatized Al K_α), energy resolution: 0.5 eV, angular resolution: $\pm 10^\circ$.

in situ. The EELS and XPS experiments were carried out at room temperature.

The EELS experiments in (100) and (110) direction (not shown) yield an energy gap of 1.65 eV, which is typical for undoped cuprates. The corresponding loss spectra are nearly dispersionless even at increasing momentum transfer along these directions, indicating an isotropic dielectric function. Fig. 2 shows XPS spectra recorded for different polar emission angles. By comparison of the angular intensity modulation with that observed for the respective core levels (not shown) and taking into consideration forward scattering effects, the feature

Fig. 3. ARPES spectra of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$, in (π, π) -direction; incident radiation polarized perpendicular to the M_1 mirror plane; photon energy: 35 eV, angular resolution: $\pm 1^\circ$, energy resolution: 160 meV.

at 5.5 eV can be clearly assigned to $\text{Cl}3p$ states. The broad structure between 2 and 4.5 eV results from the overlap of $\text{Cu}3d$ and $\text{O}2p$ states.

Fig. 3 shows ARPES data along $\Gamma-(\pi, \pi)$, i.e. at 45° with respect to the Cu-O bonds. In this experimental geometry, the electron energy analyzer sits in the M_1 mirror plane (Fig. 1). The spectra were recorded with perpendicular polarization (i.e. probing odd initial states with respect to M_1). We observe three main structures within 4 eV of the Fermi level. The two features at higher binding energy (BE ~ 2.2 and ~ 3.2 eV) result from the overlap of a number of states derived from the Cu_3O_4 -network, and thus an assignment to a particular band is not possible. The lowest-lying feature below ~ 1.5 eV BE shows a strong dispersion along $\Gamma-(\pi, \pi)$, reaching a minimal BE of ~ 0.9 eV at $(\frac{1}{2}\pi, \frac{1}{2}\pi)$. The bandwidth of this state in $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ is 400 ± 80 meV, in fairly good

agreement with data from $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ [5]. Along $\Gamma-(\pi, \pi)$ with parallel polarization (i.e. even initial states), the lowest BE dispersive feature is completely absent (not shown). This polarization dependence clearly points to the odd nature of the responsible initial states. Along $\Gamma-(0, \pi)$ (not shown), no significant intensity at low BEs is observed, regardless of the polarization direction with respect to the mirror planes M_2 and M_3 . This again parallels the behavior in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.

The similarity between the dispersion of the lowest BE feature in $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ along $\Gamma-(\pi, \pi)$ suggests a common origin for the two bands. In $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, this feature was attributed to the dispersion of a hole in the lowest BE valence bands (comprising split-off states with $^1A_{1g}$ symmetry). These lowest-lying electron removal states correspond to the well-known Zhang–Rice singlets. Bearing this in mind and together with the constraint that the state concerned should be odd with respect to M_1 , the most likely candidate is a *purely* antibonding combination of $\text{O}2p_{x,y}$ and the “cuprate” $\text{Cu}3d_{x^2-y^2}$ orbitals, since only such a combination possesses the correct symmetry. Calculations of the electronic structure of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ within the t – J model [6] have shown that the bandwidth resulting from the movement of a hole in the antiferromagnetic CuO_2 -plane is

determined by twice the superexchange integral, J ($2J \sim 250$ meV). As discussed above, the Cu_3O_4 -plane of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ can be split into two sub-systems, one with a cuprate-like T_N (and correspondingly large J) and one with a T_N roughly one order of magnitude lower. Thus, the data presented here support this picture, in which the cuprate-like subsystem plays the dominating role in determining the dispersion relation for a hole moving in the Cu_3O_4 -plane.

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