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DOI

[10.1007/BF00768409](https://doi.org/10.1007/BF00768409)

Publication date

1996

Document Version

Final published version

Published in

Journal of Low Temperature Physics

[Link to publication](#)

Citation for published version (APA):

Schmelz, H. C., Haffner, S., Knupfer, M., Krabbes, G., Müller, A., Reichardt, G. L., Golden, M. S., & Fink, J. (1996). Polarization-dependent angle-resolved photoemission of the layered cuprate $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. *Journal of Low Temperature Physics*, 105(3-4), 341-346. <https://doi.org/10.1007/BF00768409>

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Polarization-dependent angle-resolved photoemission of the layered cuprate $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$

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We report polarization-dependent angle-resolved photoemission studies of single crystalline $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. This antiferromagnet adopts 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. For the Γ -M direction of the Brillouin zone we observe a dispersive feature with a bandwidth of 400 ± 80 meV, which approaches to within ~ 0.9 eV of the Fermi level at $(\pi/2, \pi/2)$. The magnitude of the observed dispersion and its polarization dependence are consistent with its origin as a purely antibonding combination of $\text{O}2p_{x,y}$ and $\text{Cu}3d_{x^2-y^2}$ atomic orbitals from the cuprate-like CuO_2 sub-system, i.e. Zhang-Rice singlets.

PACS numbers: 74.25 Jb, 74.72 Jt, 79.60 Bm.

1. INTRODUCTION

The cuprate high-temperature superconductors (HTSC) all have CuO_2 planes as their key common structural element. As neither the superconducting nor the normal state properties are fully understood, it is crucial to study the electronic structure not only of the HTSC's themselves, but also that of the undoped parent compounds.

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.

Barium copper oxychloride ($\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$) is an antiferromagnet which adopts a layered body-centred tetragonal structure¹ related to that of La_2CuO_4 . However, there are two important differences: firstly, this oxychloride has a Cu_3O_4 plane, which can be visualized as resulting from the insertion of 'extra' Cu atoms (Cu^*) in the CuO_2 -plane of the cuprates. Secondly, as in the T' -cuprates, the Cu_3O_4 -plane of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ is apex-free. A schematic of the Cu_3O_4 plane geometry is shown in Fig. 1. This Cu_3O_4 plane can be thought of as possessing two sub-

systems - one cuprate-like in which superexchange between the copper sites is mediated via 180° Cu-O-Cu interactions (these copper atoms have a Néel temperature (T_N) typical of cuprates of ~ 320 K) and one in which Cu superexchange is frustrated and can only occur via a 90° Cu^* -O-Cu interaction (giving rise to a T_N of ~ 40 K).²

In this contribution we report polarization-dependent angle-resolved photoemission (ARPES) studies of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ single crystals carried out in order to assess the impact of the Cu^* -O sub-system on the electronic structure of the oxychloride. These measurements give a measure of the spectral function of a hole which 'moves' in the antiferromagnetic background. In this way, photoemission experiments on undoped cuprates can be of direct relevance for the electronic structure of the HTSC's in the extreme low-doping limit.

2. EXPERIMENTAL

The single crystal growth is described in detail elsewhere.³ The crystals were cleaved in UHV and oriented using LEED. During the experiment the crystal was held at 360 K which was found to reduce charging effects and prolong the lifetime of the cleaved surface. The

photoemission spectra were measured at the crossed-undulator beamline U2-FSGM,⁴ at BESSY. The spectra were recorded with a photon energy of 35 eV. The angular resolution was set to $\pm 1^\circ$ and the overall energy resolution of the system was chosen to be 160 meV. The polarization direction of the incident radiation could be chosen by using either the vertical or the horizontal undulator.

Upon photoemission from a surface containing a mirror plane (in which the electron energy analyzer sits), information on the symmetry of the initial states can be attained by variation of the orientation of the polarization vector of the synchrotron radiation.⁵ When the radiation is polarized in this plane we can only photoemit from initial states which are even with respect to the mirror plane, whilst with the polarization orthogonal to the plane we are only sensitive to odd initial states. The Cu_3O_4 -plane of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ contains three inequivalent mirror planes perpendicular to the surface, as shown in Fig. 1.

In the following, we use the notation of the Brillouin zone derived from the Cu_3O_4 -plane alone. Following this notation, spectra have been recorded for the Γ -X ($0,\pi$) and Γ -M (π,π) directions, respectively.

3. RESULTS AND DISCUSSION

Fig. 2 shows ARPES data for the Γ -M direction. In this configuration, the electron energy analyzer sits in the M_1 mirror plane (see Fig. 1). The spectra were recorded with the radiation polarization vector at right angles to the M_1 plane, *i.e.* probing initial states which are odd with respect to M_1 . As can be seen from the figure, we observe three main structures within 4 eV of the Fermi level, E_F . 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 within the Cu-O manifold is not possible.

The remaining discussion will focus upon the lowest lying feature situated below ~ 1.5 eV BE. This feature shows a strong dispersion along the Γ -M direction, reaching a minimal BE of ~ 0.9 eV at $(\pi/2, \pi/2)$. The dispersion either side of this point is symmetrical. The bandwidth of this state in $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ is 400 ± 80 meV (see Fig. 4), which is in fairly good agreement with data from the related material $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.⁶ Measurements along Γ -M with the direction of the polarization vector in the M_1 plane

Fig. 2: ARPES of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$, recorded in the Γ -M direction with radiation polarized orthogonal to the M_1 mirror plane.

(i.e. even initial states) show intensity, as before, at higher BE's, but the lowest BE dispersive feature is absent. This is emphasized in Fig. 3, in which the spectra corresponding to the $(\pi/2, \pi/2)$ point in the zone are shown for the two polarization directions. This polarization-dependence clearly points to the odd nature of the initial states responsible for this feature. It is also clear from Fig. 3 that a contribution to the intensity at 2.5 eV and $(\pi/2, \pi/2)$ is also from odd initial states with respect to M_1 . We note that along Γ -X (not shown), no significant intensity at low BE's is observed, regardless of the polarization direction with respect to the mirror planes M_2 and M_3 . This again parallels the behaviour 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 Γ -M 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 (which comprises 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, together with the constraint that the state concerned should be odd with respect to mirror plane M_1 , a likely candidate is a *purely* antibonding combination of $O2p_{x,y}$ and the 'cuprate' $\text{Cu}3d_{x^2-y^2}$ orbitals. We emphasize that only a purely antibonding combination possesses the correct symmetry - a non-bonding combination would lead to states with even

symmetry with respect to M_1 , which should then be observed along Γ -M for polarization in the M_1 plane.

Calculations of the electronic structure of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ within the t - J model 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 ($2J \sim 250\text{meV}$).⁷ 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 thus correspondingly large J) and one with a T_N roughly one order of magnitude lower. Thus the data presented here support the picture in which the cuprate-like sub-system plays the dominating role in determining the dispersion relation for the Zhang-Rice singlet moving in the Cu_3O_4 -plane.

Fig. 3: ARPES spectra recorded at $(\pi/2, \pi/2)$ with the polarization vector of the radiation (a) orthogonal to and (b) parallel to the M_1 mirror plane.

Fig. 4: Dispersion relation of the Zhang-Rice singlet states along the Γ -M direction; the solid line is a guide to the eye.

4. CONCLUSIONS

The polarization-dependent ARPES spectra of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ presented here can be understood within a picture in which the Cu_3O_4 -plane can be divided into two sub-systems. The main sub-system is analogous to the CuO_2 -planes of the cuprates (or $\text{Sr}_2\text{CuO}_2\text{Cl}_2$), and gives rise to a Zhang-Rice-band of width 400 ± 80 meV which approaches within 0.9 eV of the Fermi level at the $(\pi/2, \pi/2)$ point along the Γ -M direction. In contrast, no significant intensity is observed at such energies along Γ -X. Polarization dependent studies show that the band along Γ -M arises from a *purely* antibonding combination of the $\text{O}2p_{x,y}$ and cuprate-like $\text{Cu}3d_{x^2-y^2}$ atomic orbitals.

ACKNOWLEDGEMENTS

The work presented here was funded by the BMBF (05 605 BDA) and the *Fonds der chemischen Industrie*. S.H. acknowledges the *Graduiertenkolleg der TU-Dresden (DFG)* and M.S.G. the EU's HCM programme for financial support. We are also grateful to S.-L.Drechsler for fruitful discussions and W.Höppner for technical assistance.

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