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EELS and XPS investigations of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$

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Electron energy-loss spectroscopy in transmission and x-ray photoelectron spectroscopy have been applied to investigate single crystalline $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ to obtain the loss-function along the high symmetry directions of the cuprate plane, the $\text{Cu}2p$ and $\text{O}1s$ excitation edges, and to study the valence band and the core level electronic structure. The loss-function shows a gap of 1.65eV, practically dispersionless structures between 2 and 8eV, and a volume plasmon located at 25eV. The dielectric function is derived. The excitation edges are a measure for the number of holes located in the Cu like or O like states parallel or perpendicular to the Cu_3O_4 planes. The $\text{Cu}2p_{3/2}$ XPS shows three features in the main line and a satellite structure due to two independent copper sites and indicating a strong 3d electron correlation. By interpreting forward scattering features the valence band structure can be assigned to its atomic origin.

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1. INTRODUCTION

All cuprate high temperature superconductors (HTSC's) have CuO_2 planes in common. To understand these superconductors it is also necessary to investigate the electronic structure of the undoped, insulating parent compounds. The structure of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ is related to that of the layered perovskites (e.g. La_2CuO_4) but without any apical oxygen. The undoped oxychlorides are ideal 2D antiferromagnets.¹

Here, high energy spectroscopic investigations (EELS and XPS) were carried out to obtain information on the electronic structure of

$\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$, which has a layered body-centered tetragonal structure ² containing two different Cu sites. The so called Cu_A atoms build a $\text{Cu}_\text{A}\text{O}_2$ network, which is structurally similar to that of the cuprates. Additional Cu_B is placed in between every second empty site resulting in $(\text{Cu}_\text{A}\text{O}_2)_2\text{Cu}_\text{B}$ planes. Both Cu are formally in Cu^{2+} valence states. These cuprate layers are separated by Ba- Cl_2 -Ba block-layers. The $\text{Cu}_\text{A}\text{O}_2$ subsystem allows, as in the cuprate materials, coupling between Cu_A sites via a 180° Cu_A -O- Cu_A interaction along the crystal (110) direction. This gives rise to the characteristically high Néel temperature (320K).¹ The interaction between the semi-isolated Cu_B sites and the $\text{Cu}_\text{A}\text{O}_2$ subsystem is frustrated as it can only occur via a 90° Cu_B -O- Cu_A interaction along the crystal (100) direction. Thus T_N for Cu_B is only 40K.¹

2. EXPERIMENTAL

The $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ single crystals were grown following the procedure described elsewhere.² The good quality of the crystals was checked with electron diffraction. For the EELS investigations films of about 800Å thickness were cut using an ultramicrotome. These films were stable under UHV conditions. For the XPS experiments single crystals were cleaved in UHV. The samples were stable during the measurements observing a single O1s feature as expected for $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. All measurements were performed at room temperature.

The transmission EELS with 170keV primary beam energy is described in detail elsewhere.⁴ The energy and momentum resolution was chosen to be $\Delta E=0.1\text{eV}$; $\Delta q=0.05\text{\AA}^{-1}$ for the low energy loss-spectra and $\Delta E=0.5\text{eV}$; $\Delta q=0.1\text{\AA}^{-1}$ for the absorption edges, respectively. The XPS experiments were performed with monochromated Al $K\alpha$ radiation (1486.6eV) and an energy resolution of $\Delta E=0.5\text{eV}$. The charging effects were corrected for by extrapolating the binding energies to zero photon flux after recording spectra with different photon intensities.

3. RESULTS AND DISCUSSION

Fig.1: The loss-spectrum, the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function for $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$.

Fig.2: The loss-spectra for different momentum transfers of 0.1 to $0.5 \text{ \AA}^{-1}$ along the (100) direction in arbitrary intensity units. The spectra are shifted for clarity.

The uppermost panel of Fig.1 shows the loss-spectrum of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ recorded for a momentum transfer of $0.1 \text{ \AA}^{-1}$ in the (100) crystal direction (measurements with smaller q values are complicated by excitations of surface plasmons). The lower two panels show the real (ϵ_1) and the imaginary (ϵ_2) parts of the dielectric function which were derived from $\text{Im}(-1/\epsilon)$ via a Kramers-Kronig analysis. The loss-spectrum is dominated by a strong feature located at 25 eV , the volume plasmon, which corresponds to the oscillation of all valence electrons. The gap of 1.65 eV causes strong onset feature in the dielectric function ($\epsilon_2(0)$ being zero and $\epsilon_1(0)$ nearly 8), reflecting the expected insulating behavior. The energy losses located between 2 and 8 eV are responsible for moderate modulations in the dielectric function and are caused by interband transitions and low-lying core level excitations (Fig. 2). These loss-spectra are almost identical for momentum transfer along the (100) and the (110) direction (not shown), indicating an isotropic dielectric function across the large range of Δq even at higher momentum transfers. At low energy three peaks

with almost no dispersion are observable. Peak B shows definitely no dispersion with increasing momentum transfer, but peaks A and C may do. Peak A may be decomposed into two peaks, of which one disperses and the other one does not.

Fig.3: O1s and Cu2p excitation edges with momentum transfer perpendicular and parallel to the Cu-O planes in arbitrary intensity units.

Fig.4: Cu2p and valence band XPS recorded with monochromated Al-K α radiation under different polar angles in arbitrary intensity units. The spectra are shifted for clarity.

The intensity of the Cu2p excitation edge depending on the alignment of the momentum transfer can give a measure for the number of holes in the Cu3d orbitals located parallel or perpendicular to the Cu-O planes (Fig. 3). Correcting the intensities for the transition matrix elements⁵ one finds 28% of the holes in perpendicular orbitals.

In analogy with the cuprates, the O1s absorption edge shows a transition at 530eV into the oxygen states hybridized with the upper Hubbard band (UHB). Our direction dependent measurements suggest that about 30% of the holes are located in the O2p_z orbitals. In Ba₂Cu₃O₄Cl₂ there are

no O sites in the block layer. Thus apart from the pre-edge structure the intensity at higher energies cannot be due to O-cation hybridization in the block layer as in the case of La_2CuO_4 or $\text{YBa}_2\text{Cu}_3\text{O}_7$.⁵ Nevertheless it is conceivable that the in plane O atoms hybridize with the Ba ions located less than $2\text{\AA}$ above the Cu-O plane.

It is remarkable that these numbers for the out-of-plane UHB counts at the O and the Cu sites of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ are very much higher than these in the cuprates, for example, the structurally related T' 'infinite layer' materials show extremely small intensity ($<2\%$) in the pre-edge region for a momentum transfer perpendicular to the Cu-O planes.⁵ This discrepancy could be due to experimental factors, such as limited momentum resolution or twinning of the single crystalline thin film. Alternatively, it may result from the additional Cu_B atom in the Cu-O plane of the oxychloride, although at first glance there seems to be few compelling reasons to suggest that the hole distribution should be so different in the latter.

In Fig. 4 the x-ray photoemission spectra for the valence band and the $\text{Cu}2\text{p}_{3/2}$ core level are presented. The Cu main line (centered at 934eV) consists of at least three features and there is a satellite centered at about 943eV originating from the poorly screened $2\text{p}^53\text{d}^9$ final state. Compared to the $\text{Cu}2\text{p}$ spectrum of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ⁶ we note a sharper peak in the main line that can be attributed to the extra Cu_B signal. The higher binding energy shoulder is similar to that observed in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, i.e. the $\text{O}2\text{p}$ bands participate in the screening process in very similar way as in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.⁶

The valence band spectra shown in Fig. 4 were recorded with different polar angles to probe features induced by forward scattering effects. The excited photoelectrons will be scattered under certain polar angles by the surrounding atoms resulting in a higher intensity. Comparing these angular intensity modulations in the valence band with those recorded for the core level excitations (not shown), one can clearly assign the valence band photoemission features to their atomic origin. The broad valence band structure between 2.5 and 4.5eV is predominantly composed out of $\text{Cu}3\text{d}$ and $\text{O}2\text{p}$ states, while the peak at about 5.5eV can clearly be assigned to $\text{Cl}3\text{p}$. The other peaks are low binding energy core states: $\text{Ba}5\text{p}_{3/2}$ and $5\text{p}_{1/2}$ at 14 and 16eV , respectively, $\text{Cl}3\text{s}$ at 16.5eV binding energy. The feature located at 1.6eV shows no angular dependence and can be assigned as in other cuprates to the Zhang-Rice singlet state formed by the hybridization of Cu and O orbitals.⁷ This is the highest lying electron removal state in which the intrinsic 3d hole forms this singlet.

4. CONCLUSIONS

XPS and EELS investigations have been reported on $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$, which has a Cu-O planar network with two different Cu sites but without any apical oxygen. The true 2D Cu_3O_4 planes are separated by block-layers. The loss spectrum is nearly dispersionless even at increasing momentum transfer along the (110) and (100) crystal directions indicating an isotropic dielectric function. The O1s and Cu2p absorption edges show transitions into empty states located perpendicular or parallel to the Cu-O plane. About 30% of the holes are located in perpendicular orbitals, which is very much higher than those for the structurally related cuprates. The XPS of the Cu2p can be interpreted as a composition of a cuprate like Cu_A site with local and non-local contributions in screening process and an additional signal due to the other Cu_B atoms. The valence band spectra recorded under different polar angles make an assignment of peaks to their atomic origin possible.

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REFERENCES

1. K.Yamada *et al.*, *Physica B*, **213&214** 191 (1995)
2. W.Pitschke *et al.*, *Powder Diffraction* **10** 282 (1995)
3. G.van der Laan *et al.*, *Phys.Rev. B*, **23** 4369 (1981)
4. J.Fink, *Ad. Electron. Electron Phys.*, **75** 121 (1989)
5. J.Fink *et al.*, *J. Electr. Spec. Rel. Phen.*, **66** 395 (1994)
6. T.Böske *et.al.*, this volume
7. F.C.Zhang and T.M.Rice., *Phys.Rev. B*, **37** 3759 (1988)
8. S.R.Barman and D.D.Sarma, *J. Phys. Condens. Matter*, **4** 7606 (1992)