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In-plane polarization dependence of $(Bi,Pb)_2Sr_2CaCu_2O_{8+\delta}$ single crystals studied by X-ray absorption spectroscopy

A. Ghafari [a,b], A.K. Ariffin [a,c], C. Janowitz [a,*], H. Dwelk [a], A. Krapf [a], R. Manzke [a]

[a] Institute of Physics, Humboldt University of Berlin, Newtonstr., 15, D-12489 Berlin, Germany
[b] Elettra Sincrotrone Trieste, Strada Statale 14 km 163.5, I-34149 Trieste, Italy
[c] Department of Physics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Malaysia

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ABSTRACT

The effects of in-plane polarization change on the determination of the hole density of weakly underdoped (Bi, Pb)-2212 single crystals has been studied by x-ray absorption spectroscopy (XAS). The XAS signal at the CuL_3 edge (925–940 eV) and O K edge (525 eV to 539 eV) were recorded under continuous rotation of the CuO_2 plane from 0° to 180° with a minimum increment of 1.8°, yielding experimentally an in-plane polarization dependence for the absorption signals at the respective threshold. From that the in-plane angular dependence of the hole density ($n_H(\varphi)$) could be determined. Fermi's golden rule was then used for the evaluation of the in-plane polarization dependence showing the expected polarization independence in disaccord to the experimental observations. Possible scenarios to solve this issue are discussed. Our results propose that polarization dependence could be due to inhomogeneous distribution of holes in the CuO_2 planes which is also supported by models. Second, the role of out of plane orbitals has to be taken into account for interpretation.

1. Introduction

The electronic structure of high-temperature superconductor (HTC) cuprates has been discussed since their discovery and is an indissoluble issue in condensed matter physics until now. One promising method for understanding the electronic structure is x-ray absorption spectroscopy (XAS). XAS has provided vital information about HTC due to its capability to probe the unoccupied electronic states near the Fermi level. Today, it is known that superconductivity originates from the CuO_2 planes and their hole density which is responsible also for the conductivity of the normal state. Several methods have been used for the evaluation of the hole density in the HTC cuprates such as thermopower, iodine titration, and Hall effect [1]. These experimental techniques probe the entire hole density of the sample. XAS performed at a Cu edge on the other hand, is a very local probe and therefore capable to probe the hole density solely of the CuO_2 planes. These kinds of experiments have been performed for evaluation of the hole density of polycrystalline cuprates such as $La_{2-x}Sr_xCuO_4$ by Ronay et al. [2], on $Bi_2Sr_2CaCu_2O_{8+\delta}$ by Ghigna et al. [3] and Pham et al. [4], on $Bi_{2-x}Pb_xSr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ by Merrien et al. [5], and also on $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ and $Bi_{2-y}Pb_ySr_{2-x}La_xCuO_{6+\delta}$ by Schneider et al. [6]. Later the same method has been applied also to HTC single crystals but, at the beginning, a reliable determination of the hole content seemed to fail. The reason for this was the non-consideration of the linear polarization of the impinging synchrotron light as discussed by Ariffin et al. [7].

Theoretical models for the electronic structure of HTC such as standard local-density approximation (LDA) and generalized gradient approximation (GGA) methods, neglecting the strong correlation effects like e.g. on-site interaction, predict a metallic ground state what is in contradiction to the experimental finding that these systems behave as antiferromagnetic charge transfer (CT) insulators with spin density localized mainly at the Cu sites [8]. The problem of LDA/GGA can be solved in some classes of HTC cuprates by adding on-site Coulomb interaction to the localized orbitals in the calculation, i.e. LDA/GGA+U method. Additionally, a very effective model for the description of highly correlated electron materials like HTC is the three band Hubbard model (TBH) [9,10]. TBH considers three orbitals, which are Cu $3d_{x^2-y^2}$, O $2p_x$, and O $2p_y$, so that the electronic configuration of the copper of an undoped CuO_2 plane is $3d^9$ with one hole on each copper site. The essential aspects of the electronic structure of the copper–oxygen plane can be extracted by the TBH. Due to symmetry the antibonding $Cud_{x^2-y^2}$–Op_σ states become the upper half-filled band and the extra (doped) holes go to the oxygen sites which form a coherent state of the four oxygen p orbitals around a Cu atom with the hole concentration $n_H=1+x$ (x being the hole density per copper atom). The spins of a hole pair (i.e. the hole on

* Corresponding author.
E-mail addresses: ghafari@physik.hu-berlin.de (A. Ghafari), christoph.janowitz@physik.hu-berlin.de (C. Janowitz).

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the Cu $d_{x^2-y^2}$ site and a hole on an oxygen with opposite spins) form a localized spin singlet state, which is called Zhang–Rice singlet (ZRS) [11]. The corresponding spin triplet state (i.e. the hole on Cu $d_{3z^2-r^2}$ site and a hole on an oxygen with same spins) has a higher energy than the singlet state ($\varepsilon_T-\varepsilon_S\geq 2$ eV) [12]. However, the roles of other d orbitals are supported by some experimental and theoretical results. Therefore, it seems that it is necessary to look beyond the TBH model. For instance, a significant contribution of the $d_{3z^2-r^2}$ copper electrons is revealed by polarized XAS [13–15] and electron energy loss spectroscopy [16]. Moreover, the role of the apical oxygen has been discussed theoretically in e.g. Ref. [17].

In this paper we report on the polarization dependence of the x-ray absorption of under-doped $(Bi,Pb)_2Sr_2CaCu_2O_{8+\delta}$ single crystals with $T_C=84$ K. The measurements were performed at the CuL_3 and O K edges with in-plane polarization of synchrotron light and all measurements have been carried out at the same sample, but have been reproduced on samples with slightly different doping. These results reveal that the intensity of the absorption at the CuL_3 and O K edges reveal polarization dependence. However, by considering the dipole approximation there is theoretically not any in-plane polarization effect to be expected. Therefore, the results of polarization dependence could be due to inhomogeneous distribution of holes at the copper plane. Second, the role of the out of plane orbitals has to be taken into account as discussed by Anderson [18].

2. Materials and methods

The $Bi_{2-y}Pb_ySr_2CaCu_2O_{8+\delta}$ single crystals with fixed lead content of $y=0.23$ were in the under-doped regime and were grown from liquid solution. The crystals were characterized by energy dispersive x-ray analysis (EDX) and AC susceptibility which revealed an almost stoichimetric composition, the lead content, and a single-phase superconductivity with $T_C=84$ K. With respect to doping they are in the weakly under-doped regime. The XAS measurements were carried out with synchrotron radiation at BESSY II at the PM3 beamline by the HU-BESSY fluorescence spectrometer chamber which consists of an electron yield (EY) and a fluorescence yield (FY) Germanium detector. The setup of the chamber enables us to collect the spectra by the two detectors simultaneously. The detectors are located at an angle of 45° to the surface normal and photons impinge at an angle of 0° with respect to the surface normal. The electric field vector, E, of the x-ray beam lies therefore within the CuO_2 plane of the crystals. During the measurements the pressure in the chamber was less than 10^{-10} mbar and the samples were cleaved in situ. The XAS signal at the CuL_3 edge (925–940 eV) and the O K edge (525 eV to 539 eV) were recorded at room temperature. Such that the sample was continuously rotated about 180° around the normal of the CuO_2 plane with a minimum increment of 1.8° and 3.6° respectively, for CuL_3 and O K edges. So we investigated the in-plane polarization dependence. Since the dimension of our single crystals was about 1.2×2 mm with mirror surface which is quite big enough in comparison to beam size (order of 100 μm). Thus, the error bar due to crystal orientation is negligible. During the measurements the incident photon flux (I_0) was monitored simultaneously by a gold mesh that was located after the exit slit of the monochromator. For taking good statistics four scans were made in each case. All absorption measurements were normalized to I_0 and then the smooth background was subtracted by a straight line. Then each absorption line has been fitted by employing pseudo-Voigt functions (see next chapter).

3. Results and discussions

Saini et al. [19] have shown by XAS measurements of the CuL_3 edge with polarization parallel to the two orthogonal Cu–O bond directions of Bi-2212 single crystals that a clear anisotropy of the $2p\rightarrow 3d_{x^2-y^2}$ transition exists. While these authors detected this anisotropy only in two directions of the copper plane we probed it in a fine grid of 47 directions in the copper plane. Therefore we looked at the CuL_3 edge and O K edge spectra at room temperature for azimuthal angles φ between 59° and 236°. The angle is measured relative to the b crystal axis, i.e. the azimuthal angle φ of the electrical field vector of the linearly polarized synchrotron light was varied systematically with an increment of minimum 1.8° and 3.6° respectively, for the CuL_3 and O K edges absorption spectra.

All CuL_3 spectra consist of two peaks, which are called the white line (931.2 eV) and the satellite line (932.2 eV), see Fig. 1a. They are due to a dipole transition $2p^63d^9\rightarrow 2p^53d^{10}$ and a transition $2p^63d^9L\rightarrow 2p^53d^{10}L$, respectively, where the 'ligand hole' L denotes a 2p hole at the oxygen sites surrounding the absorbing Cu atom in the CuO_2 plane. It is believed that by considering scaling factor the density of holes per Cu atom can be evaluated by ratio of $I_S/(I_S+I_W)$ [7,19–21], where I_S and I_W are white line and satellite line, respectively. In Fig. 1b the results of this ratio is plotted for the whole polarization range from 59° to 236°. The error bars are due to the statistical uncertainties. This reveals a distinct fluctuation of polarization dependence and therewith hole density. In fact, anisotropy of $2p\rightarrow 3d_{x^2-y^2}$ transition at the two orthogonal Cu–O bond directions which was reported by Saini et al. [19] is seen at all directions of CuO_2 plane. It shows that the hole density is varying between 0.136 and 0.155. The average value of the hole density per Cu atom is 0.143. To arrive at the hole density of our Bi(Pb)-2212 single crystals we considered the same scaling factor of 1.5, as discussed in Ref. [7]. The scaling factor is due to geometrical considerations [7]. The average n_H is a reasonable value of hole density per Cu atom because the T_C of our samples was 84 K which is close to optimal doping ($T_C=95$ K). Therefore we call it weakly under-doped. In addition, this value is supported by the empirical formula of Presland et al. [22], i.e. $T_C/T_C(\max)=1-82.6(p-0.16)^2$, where p is the number of holes per Cu atom, which delivers $p=0.132$ in our case.

Additionally, to the measurements performed at the CuL_3 edge also measurements of the O K edge were performed on the same crystal. The O K edge spectra (525–539 eV) were recorded at room temperature by using in-plane polarization such that the azimuthal angles φ varied from 59° to 220°. The angle is measured relative to the b crystal axis, i.e. the azimuthal angle φ of the electrical field vector of the linearly polarized synchrotron light was varied systematically with an increment of minimum 3.6°. All O K edge spectra consist of two peaks at 528.5 eV and 530.6 eV which are called prepeak and peak, respectively (Fig. 2a). The prepeak which is due to transition $1s\rightarrow 2p$ is visible in hole doped samples and known as Zhang–Rice band. It has been argued that the intensity of the prepeak is proportional to the amount of hole doping. Thus, it can be used for the number of itinerant holes in the compound [20,16,19,23]. From Fig. 2b, it can be concluded that the hole density which are formed as ZRS does not have uniform distribution in the copper plane. However, Peets et al. [24] believe that the ZRS picture breaks down in the over-doped regime that is supported by theoretical calculation as discussed in Ref. [25] While Weber et al. [26] by theoretical calculation found that even after inclusion of the apical oxygen, there is no saturation of the occupancy observed around doping 0.2 as Peets et al. discussed [24].

On the other hand, the higher energy peak which is about 2.1 eV above the prepeak is visible in the insulating and doped samples. This peak is due to the transition $1s^23d^9\rightarrow 1s^13d^{10}$ in the upper Hubbard band consisting of covalently mixed O 2p and 3d states.

The experimentally observed variation of the hole density in the CuO_2 plane is about 10 percent of the absolute value (Fig. 1b).