Hole doping in the CuO$_2$-plane of Bi-cuprates studied by XAS: Polycrystals and single crystals

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Abstract. The exact shape of the superconducting dome in the Bi-cuprates depends on the proper determination of the hole content in the CuO$_2$ layers. Single crystals of Bi(Pb)-2201 were studied over a wide doping range from the overdoped to the heavily underdoped regime by x-ray absorption spectroscopy (XAS) in order to determine the hole content of the compounds. By analysing the Cu-L$_{III}$ edge this technique proved to be successful for polycrystalline oxide-based high-T$_c$ superconductors, while for single crystals an unexpected variation of the absorption intensity within the ab-plane on a scale of 10-15% with respect to the angle of the incoming linearly polarized light was observed. Due to it, the procedure of hole content determination on polycrystals cannot be adopted straight forward to single crystals. We will show that this technique also works for single crystals, but is in need of higher experimental effort due to the polarization effects.

1. Introduction

The hole concentration of the CuO$_2$-planes has been known as the fundamental parameter of high-T$_c$ superconductor cuprates. Contrary to the conventional superconductivity, which evolves out of a simple Fermi-liquid metallic state, the parent compound of the oxide-based HTC material is an insulating metal oxide classified as “Mott insulator” [1], which becomes superconducting at a low hole doping level of about 8%. With increasing hole content, at about 16% optimum (highest) T$_c$ is reached and for hole content larger than 16% T$_c$ decreases again and the superconductivity vanishes when the hole content is larger than 24%. However, to determine the actual hole concentration of high-T$_c$ cuprates is always a difficult task. It is even more difficult for the La-doped Bi-2201 system, where doping is achieved through cation doping and/or oxygen doping within the charge reservoirs, which introduce holes into the CuO$_2$ planes. Only in the La-214 system (La$_2$-Sr,CuO$_4$), the process is quite simple, where the hole concentration p can be equated to the x value because the oxygen is stoichiometric. In other systems such as YBCO and BSCCO, the hole content cannot be measured directly. Even techniques which determine the oxygen content such as iodine titration and thermogravimetry cannot be used for these systems. The methods that can be used to evaluate the hole content for these types of systems are thermopower and Hall effect [2] and x-ray absorption.
spectroscopy (XAS) by analyzing the Cu-L\textsubscript{III} absorption edge. XAS has been successfully used to evaluate the hole content for polycrystalline material, e.g. La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4} [3] and recently Bi\textsubscript{2-x}Sr\textsubscript{2-x}La\textsubscript{x}CuO\textsubscript{4+δ} and Bi\textsubscript{2-x}Pb\textsubscript{x}Sr\textsubscript{2-x}La\textsubscript{x}CuO\textsubscript{6+δ} [4]. But until yet it failed when applied on single crystals. An additional advantage of using XAS over all other methods is that XAS measures solely the hole concentration residing in the CuO\textsubscript{2} planes.

The result from our first attempts to determine the hole concentration of Bi-2201 single crystals by XAS revealed inconsistent data with large scatter. This led us to consider the impact of the linear polarization of the synchrotron light. In this paper we present our progress in the determination of the hole concentration of single crystals of the family of Bi\textsubscript{2−y}Pb\textsubscript{y}Sr\textsubscript{2−x}La\textsubscript{x}Cu\textsubscript{6+δ} [Bi(Pb)-2201] using the XAS technique and compare it to the results on polycrystals.

2. Experimental Details

Bi\textsubscript{2−y}Pb\textsubscript{y}Sr\textsubscript{2−x}La\textsubscript{x}Cu\textsubscript{6+δ} single crystals with lanthanum concentration between x=0.28±0.05 to x=0.66±0.04 and fixed lead content y≈0.4 were grown by self flux technique. The crystals were characterized using several techniques, e.g. energy dispersive x-ray analysis (EDX), ac susceptibility, x-ray diffraction, and low energy electron diffraction (LEED). This gave information on the chemical composition, the superconductivity, and the quality of the crystals. The XAS measurements were performed at the beamlines PM3 and ISIS at BESSY using the HU/BESSY absorption chamber what consists of an electron yield detector and a fluorescence yield germanium detector. The energy resolution was <100meV and the samples were cleaved at a base pressure <1×10\textsuperscript{-9} mbar.

![Figure 1](image-url)  
*Figure 1:* Experimental arrangement of the angle dependent XAS measurements. For details see the text.

The XAS measurements were performed at the Cu-L\textsubscript{III} edge (920eV–940eV) and the O-K edge (520eV–540eV) at room temperature. The linearly polarized synchrotron beam was radiated normal to the CuO\textsubscript{2} plane of the crystal, see figure 1. Therefore, the electrical field vector was parallel to the CuO\textsubscript{2} planes of the sample. In order to study the potential polarization dependence, spectra series were taken as a function of the rotational angle \(\phi\) by rotating the sample around the surface normal with an increment of 2°–10°. This changes the direction of the electrical field vector in the CuO\textsubscript{2} plane with respect to the orbital symmetry. Each spectrum gives therefore information on the hole concentration with respect to the particular rotational angle \(\phi\).

3. Results and discussions

For polycrystalline samples, the Cu-L\textsubscript{III} edge is evaluated for the quantitative study of the hole content. Its signal consists of a “white line”, as a result of the dipole transition \(2p^63d^9\rightarrow2p^53d^{10}\) which probes the unoccupied density of Cu 3d states, and a shoulder on the high energy side of the white line,
described as the "satellite line" which represents the itinerant O 2p holes hybridized with Cu 3d states given by the transition of $2p^{6}3d^{9}L \rightarrow 2p^{5}3d^{10}L$ [5, 6, 10]. The content of holes per Cu atom, $p$, is evaluated by the ratio of the intensity of the satellite peak to the intensity of white line plus satellite line [4, 5] and it is given as

$$p = \frac{I_{\text{satellite}}}{I_{\text{white line}} + I_{\text{satellite}}}$$

(1)

As stated above this procedure gave good results for polycrystalline samples [4, 5, 6]. However, from the first measurements done on Bi-2201 single crystals, where the data were collected at random polarization geometry within the CuO$_2$ plane, the results did not exhibit the same behavior as on polycrystalline samples [7]. Therefore, the procedure to determine the hole content on polycrystalline high T$_c$ cuprates cannot be used directly for single crystals. To solve the problem we performed polarization dependent measurements where the spectra for the Cu-L$_{\text{III}}$ and O-K absorption edge were taken at different rotational angles $\phi$, as defined above. The O-K spectra were used as a quantitative comparison to the Cu-L$_{\text{III}}$ spectra as the intensity of its pre-peak is also often interpreted as a direct measure of the hole concentration [5, 8, 9, 10].

![Figure 2](image_url)

**Figure 2**: Cu-L$_{\text{III}}$ XAS spectrum of Bi(Pb)-2201 with a La-content of $x=0.28\pm0.05$ taken at a rotational angle $\phi=147^\circ$. The red dotted circles are the experimental data. The green dotted curves refer to the fit of the white line and the satellite line by pseudo-Voigt functions, while the red line gives the sum of both. The background was estimated by a linear fit (blue dotted line).

The intensities of the white line and the satellite line were evaluated from a fit of the Cu-L$_{\text{III}}$ spectrum of each angle $\phi$ using pseudo-Voigt profiles. This is shown in figure 2 what is similar to technique used for polycrystalline samples. The background has been linearly subtracted as described elsewhere [4, 6]. The polarization dependent modulation of the hole concentration $p$, as determined by equation 1, over different rotational angles $\phi$ for a Bi(Pb)-2201 single crystal with La-content of $x=0.28\pm0.05$ is shown in figure 3. One observes a distinct variation with $\phi$ although the absolute value is only about 10%.
The intensity of the satellite line has been compared quantitatively with the pre-peak of O-K edge for different angles to rule out artefacts of the measurement. This correlation analysis depicted in figure 4 shows that the polarization dependence affects both the pre-peak and the satellite line equivalent.

The ratio of equation 1 as plotted in figure 3 clearly shows that it depends distinctly on the polarization geometry, i.e. the direction of the electrical field vector within the ab-plane of the crystal, although it has been assumed so far that no polarization effect should occur due to orbital symmetry and the assumption of statistically distributed itinerant holes in the CuO$_2$ plane. However, any introduced asymmetry could cause a polarization dependence, the details will be discussed elsewhere [11]. Thus, to determine the hole concentration of each single crystal, its values first has to be calculated by the mean intensity value over all angles, and it is given as:

$$ p = \frac{\sum p_i}{N} $$

Figure 3: Hole concentration \( p \) over rotational angle, \( \varphi \) (in red dotted circles) for sample with a La-content of \( x=0.28\pm0.05 \). The blue line represents the mean value, \( \bar{p} \) of the modulation over all rotational angles, \( \varphi \). The red line is a guide to the eye.

Figure 4: Intensity of the oxygen pre-peak and the copper satellite each at the same angle. Intensities are relative to the Copper white line, respectively. The red line is used as an indicator to the eye and points out the correlated development of both intensities at different rotational angles.

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Besides, in polycrystals the field vector has a component vertical to CuO$_2$-plane, although the incident light is radiated normal to the surface. Therefore, the \( p \) value determined on single crystals is higher than for polycrystals. To make a reasonable comparison between poly- and single crystals, the measurement on single crystal can either be done at magic angle (the ab plane set at 35° with respect to the electric field) [6] or the measurement can be done normal to the CuO$_2$ plane as in our case but with a certain correction factor. Details will be published elsewhere [12]. This factor is given by:
p = \frac{\bar{p}}{1.5} \quad (3)

Similar to polycrystalline Bi-2201 [4], we found that the hole content, \( p \) (per Cu atom) of the single crystalline samples calculated by equation [3], decreases linearly with rising La-content \( x \), given by the relation:

\[ p = (0.23 \pm 0.024) - (0.16 \pm 0.05)x \quad (4) \]

The relation using hall coefficient data by Ando et.al [2] on single crystal Bi-2201 was found to be \( p = 0.21 - 0.13z \), where \( z \) is the lanthanum concentration, which is almost similar with the results found from our Pb-substitution Bi-2201 single crystals. Comparing our results with polycrystalline Bi-2201 and Bi(Pb)-2201 obtained by XAS [4] and with single crystal Bi-2201 Hall- data measured by Ando [2], the hole concentration decreases always linearly with rising La content but the relation differs slightly. In the case of polycrystalline Bi(Pb)-2201 [4] for instance a relation of \( p = (0.23 - 0.22x) \) was reported. The slightly different equation may be due to the fact, that the Pb-content in this study varied [4].

**Conclusion**

The polarization i.e. angular dependence of the main and satellite peak at the Cu-L_{III} edge of Pb-Bi2201 was studied by XAS over a wide range of hole concentrations. Due to the geometrical factor and the modulation of the relative intensity, the hole content for single crystals cannot be determined directly using method as used for polycrystalline materials. The proper hole content is given as the average value of the relative intensity over angle divided by a correction factor of 1.5. We found that the linear relation for Bi-2201 and Bi(Pb)-2201 of the hole content \( p \) (per Cu atom) versus La-concentration is universal, but differs slightly between single crystals and polycrystals, as the slope is smaller for single crystals. This may in part be due to details of sample morphology.

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