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S. Gerhold, Christine A. Kuntscher, M. Merz, N. Nücker, S. Schuppler, W. H. Tang, J. Gao

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Site-Specific X-Ray Absorption of Twin-Free (105) $YBa_2Cu_3O_{7-\delta}$ Films

S. GERHOLD[1]) (a), C. A. KUNTSCHER (a), M. MERZ (a), N. NÜCKER (a), S. SCHUPPLER (a), W. H. TANG (b), and J. GAO (b)

(a) Forschungszentrum Karlsruhe, INFP, P. O. Box 3640, D-76021 Karlsruhe, Germany

(b) Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China

O 1s and Cu 2p near-edge X-ray absorption fine structure (NEXAFS) spectra from highly oriented $YBa_2Cu_3O_{7-\delta}$ (YBCO) films are compared to established spectra from detwinned single crystals. The (105) orientation of the films enables nearly twin-free growth and allows to investigate with NEXAFS the unoccupied electronic structure for all three polarizations $\mathbf{E} \parallel \mathbf{a}$, $\mathbf{E} \parallel \mathbf{b}$, and $\mathbf{E} \parallel \mathbf{c}$ directly. While the Cu 2p spectra are very similar to those of the single crystals, the O 1s spectra of the films exhibit differences which can be traced to a substrate contribution. The YBCO film spectrum can be extracted from the data by an extended self-absorption correction.

1. Introduction

A thorough understanding of superconductivity in the high-T_c cuprates requires a detailed knowledge of their electronic structure [1]. Usually, high-quality and preferably twin-free single crystals are needed to give the most significant experimental results. Much work has been dedicated to $YBa_2Cu_3O_{7-\delta}$ (YBCO) and the influence of different dopants on the electronic structure and superconducting properties. Recent progress in growing highly ordered epitaxial YBCO films [2] could expand the experimental possibilities to unusual doping systems. In this paper we show that such highly oriented films can provide spectroscopic information similar to detwinned single crystals.

2. Experiment and Results

Nearly twin-free YBCO films of approximate thickness 95 and 180 nm were grown in (105) orientation on a (305) $SrTiO_3$ substrate by magnetron sputtering; T_c measured by zero resistance is $\approx$89 K. Details of the preparation as well as of the structural characterization can be found in Ref. [2].

NEXAFS measurements have been performed at beamline U4B at the National Synchrotron Light Source. All spectra were recorded in the fluorescence yield (FY) mode which gives an $1/e$ information depth of $\approx$100 nm. (The widely used total electron yield mode with an information depth of only $\approx$5 nm is of less value for the O 1s edge as it

[1]) Corresponding author: Tel.: +49 7247 82 4588; Fax: +49 7247 82 4624; e-mail: stefan.gerhold@infp.fzk.de

suffers severely from surface effects; a surface preparation technique preserving stoichiometry and structure is, however, not known for YBCO films.) All spectra presented here are corrected for the intensity variation of the incoming beam and are normalized about 70 eV above the absorption edge.

The O 1s spectra with the light polarization **E** parallel to the **a**-axis are shown in Fig. 1a. (Note that at this point, no self-absorption correction has been applied.) They give information on the unoccupied electronic structure associated with states of O $2p_x$ character and, due to the σ-bond character of the Cu–O hybridization near E_F in cuprates [1], pick out only contributions from the planar O(2) sites. As usual, the first absorption feature at 528.5 eV is ascribed to the Zhang-Rice (ZR) state and the second structure at 529.7 eV to the upper Hubbard band (UHB), see e.g. Ref. [3]. The ZR state exhibits less spectral weight for the thinner film. The structures observed for the single crystal between 530 and 532 eV are obscured for the films by a strong peak at 530.8 eV which appears more pronounced for the thinner film. The first feature in the spectra for **E** ∥ **b** (Fig. 1b) gives information on unoccupied O $2p_y\sigma$ hybrids from planar O(3) and chain O(1) sites. In these spectra, the UHB appears as a shoulder on the high energy side of the first feature. In the range between 530 and 532 eV a valley is observed for the single crystal while for the films a strong peak very similar to that in **E** ∥ **a** geometry appears. In analogy to above, the first absorption structure in the **E** ∥ **c** spectra (Fig. 1c) is ascribed to unoccupied states of O $2p_z\sigma$ character, i.e., the holes residing on the apical O(4) sites [1]. This feature is almost equal for all three samples. For the films the peak between 530 and 532 eV appears again, but with reduced intensity when compared to the other polarization settings.

Cu 2p spectra (not shown) were recorded only for the 180 nm thick film; since the $SrTiO_3$ substrate does not contain Cu atoms they do not differ significantly from those of the single crystal for all three polarizations and are therefore not discussed in detail.

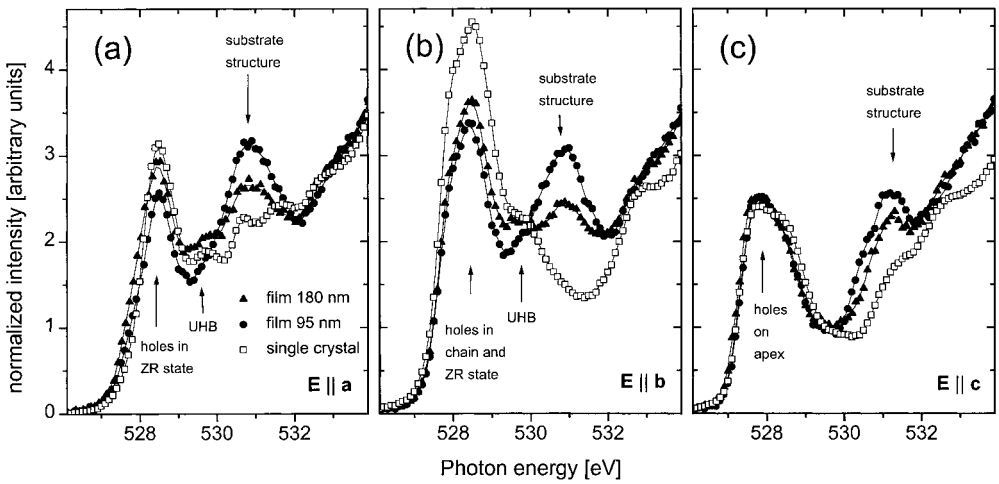

Fig. 1. Normalized O 1s NEXAFS spectra of YBCO (105) films, 180 nm and 95 nm thick (this work, filled symbols) and of a detwinned YBCO single crystal ([3], open squares) for polarization geometries a) **E** ∥ **a**, b) **E** ∥ **b**, and c) **E** ∥ **c**

3. Discussion

Extending the standard evaluation of FY-NEXAFS data from bulk samples [4], NEXAFS spectra measured in FY mode from a thin film on a substrate can be related to the absorption coefficients $\mu(E)$ via

$$\frac{I(E)}{I_0(E)} \propto \frac{\mu_{\mathrm{ad},1}(E)\,\lambda_1(E)}{\sin\phi}\,(1-\mathrm{e}^{-d/\lambda_1(E)}) + \frac{\mu_{\mathrm{ad},2}(E)\,\lambda_2(E)}{\sin\phi}\,\mathrm{e}^{-d/\lambda_1(E)}, \tag{1}$$

where

$$\lambda_i^{-1}(E) = \frac{\mu_{\mathrm{tot},i}(E)}{\sin\phi} + \frac{\mu_{\mathrm{tot},i}(E_\mathrm{f})}{\sin\theta}\,, \qquad \mu_{\mathrm{tot},i} = \mu_{\mathrm{ad},i} + \mu_{\mathrm{bac},i}\,, \tag{2}$$

with d the film thickness, E_f the energy of the fluorescence photons, and ϕ, θ the angles of the incoming and outgoing beam, respectively, measured from the sample surface. Indices $i = 1, 2$ denote parameters for film and substrate, respectively. I/I_0 is the normalized FY signal, $\mu_{\mathrm{tot},i}(E)$ is the sum of $\mu_{\mathrm{ad},i}(E)$, the absorption coefficient of the adatom of interest, and of a structureless background originating from all other atoms in region i, and λ_i is the corresponding $1/e$ information depth.

For a sample with $d \gg \lambda_1(E)$ all exponential terms in Eq. (1) vanish, yielding the standard formula for bulk self-absorption correction which can be solved to give the desired spectral distribution of $\mu_{\mathrm{ad},1}(E)$. For $d \approx \lambda_1(E)$, however, there is an additional variable, $\mu_{\mathrm{ad},2}(E)$, which is also unknown but can be eliminated by using data from two films with different thickness. Since $\lambda_1(E)$ depends on $\mu_{\mathrm{ad},1}(E)$ in a nonlinear fashion the calculation has to be performed iteratively in a self-consistency loop. The resulting μ_{ad} is normalized at about 70 eV above the absorption edge, where the absorption is atomic-like and structureless, to tabulated absorption coefficients [5]. One should note that this scheme to extract $\mu_{\mathrm{ad},1}(E)$ implies, in effect, taking a weighted difference of two spectra, wich reduces the signal-to-noise ratio.

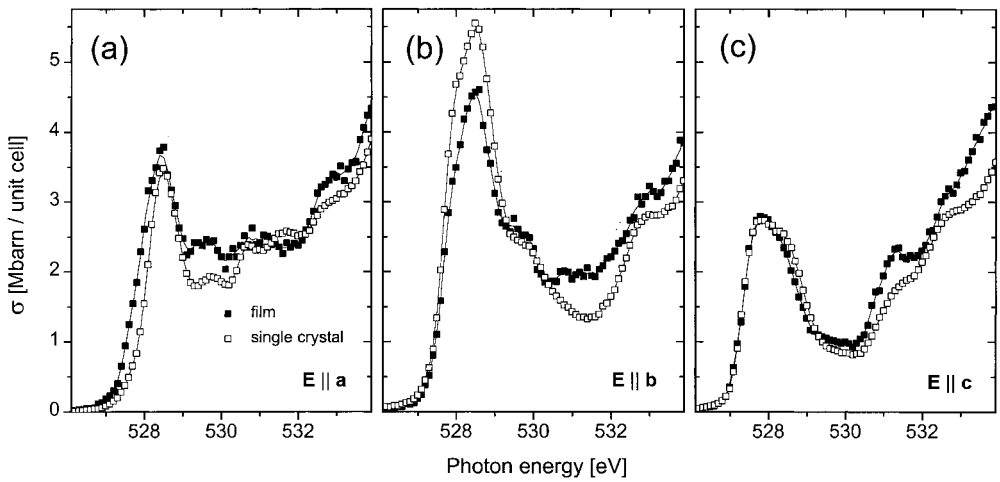

Fig. 2. The corrected YBCO O 1s NEXAFS spectra for a film (this work, filled squares) compared to those for a detwinned single crystal ([3], open squares) for polarizations a) $\mathbf{E} \parallel \mathbf{a}$, b) $\mathbf{E} \parallel \mathbf{b}$, and c) $\mathbf{E} \parallel \mathbf{c}$

The YBCO films are grown in (105) orientation, corresponding to a 59° tilt of the *ab*-plane towards the film surface [2], and the FY detector is located at an angle of 35° towards the incoming beam. With this geometry one finds for both the O 1s edge and the Cu 2p edge that λ is about 120 nm for $\mathbf{E} \parallel \mathbf{a}$ and $\mathbf{E} \parallel \mathbf{b}$ and about 90 nm for $\mathbf{E} \parallel \mathbf{c}$, comparable to the film thickness. Thus, the $SrTiO_3$ substrate produces a contribution to the YBCO O 1s spectra, which should be smaller, of course, for the thicker film but also for $\mathbf{E} \parallel \mathbf{c}$ due to the smaller λ. All this is consistent with the observations.

Cross sections for the films evaluated as outlined above are compared in Fig. 2 to those from detwinned single crystals (from Ref. [3]). The "substrate peak" has nearly vanished, and all important structures are reproduced fairly well. The remaining differences concerning the integrated spectral weight may be due to a number of reasons: (i) small differences in chemical composition or polarization geometry; (ii) a small amount of structural defects [2]; (iii) uncertainties in film thickness. (iv) Small twinned regions or a partial redistribution of oxygen from chain O(1) sites to anti-chain O(5) sites might cause the excess spectral weight at the first peak in $\mathbf{E} \parallel \mathbf{a}$ and the corresponding lack of spectral weight in $\mathbf{E} \parallel \mathbf{b}$ as presented in Fig. 2.

4. Conclusions

A method for subtracting out a substrate contribution from the NEXAFS spectra from highly oriented YBCO films was successfully incorporated into the self-absorption correction scheme required for a quantitative evaluation of spectra recorded in fluorescence mode. While the qualitative agreement with the single crystal spectra is satisfactory, some quantitative differences remain at the present stage. The results could be improved upon by measuring the NEXAFS spectrum of the bare substrate. NEXAFS measurements from highly oriented films may thus open up new possibilities for studying novel doping systems in HTSCs.

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