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**LOCAL ENVIRONMENT AROUND THE OXYGEN
ATOMS IN Y-Ba-Cu-O STUDIED BY X-RAY
ABSORPTION FINE STRUCTURE (XAFS)
SPECTROSCOPY***

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ABSTRACT

The local environment about oxygen atoms in the CuO_2 plane in $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystals has been investigated by orientation-dependent x-ray absorption fine structure (XAFS) spectroscopy at the O 1s edge using bulk-sensitive fluorescence-yield-detection method. Within experimental accuracy ($\pm 0.03 \text{ \AA}$) no structural change in local ordering about oxygen atoms in the CuO_2 plane at 90 K has been detected.

INTRODUCTION

Orientation dependent x-ray absorption fine structure (XAFS) spectroscopy at the O 1s edge is a useful tool to investigate local ordering around oxygen atoms. This method was applied to the $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y123) superconductors. Basic blocks of these systems are the CuO_2 planes, formed by Cu(2), O(2) and O(3) atoms, parallel to the *a*- and *b*-axis, and the CuO chains along the *b*-direction, formed by Cu(1), O(1), and the apex O(4) atoms. The O(2)-Cu(2) bond is oriented along *a*-axis. By choosing the

orientation of the x-ray electric E -vector parallel to the a -crystallographic axis of the single crystal one can selectively probe bonds formed by O(2) atoms with its Cu(2) neighbor in the CuO_2 plane.

EXPERIMENTAL

Single crystals of Y123 were grown in a ZrO_2 crucible and oxidized to show a sharp superconducting transition at 91 K. They were heated in flowing oxygen to 400 °C and subjected to uniaxial stress while slowly cooling them down to form twin free samples.¹ The samples were glued to the sample holder using silver paint and oriented to permit measurements with the E vector of the x-rays parallel to the a -axis of a single crystal. They were then mounted in a vacuum chamber near the soft-x-ray fluorescence detector. The soft-x-ray absorption at the O 1s edge was measured at the U 15 beam line at the NSLS at Brookhaven National Laboratory. During the experiment, the monochromator resolution was set at ~ 1.5 eV. The oxygen K_α fluorescence yield was monitored by means of a low pressure parallel plate avalanche chamber.² All measurements were performed in an energy range $500 \leq \hbar\omega \leq 780$ eV. The upper limit of the XAFS spectra was restricted by the interfering presence of the Ba M_V edge thus limiting the accessible energy- ergo k -range.

RESULTS

The spectra were first corrected for the thickness effect³ and then normalized to the photoabsorption edge jump by standard procedures⁴ using tables published by Henke et al.⁵ Nonlinearity of the beam monitor which consisted of a mesh covered with P40-Y2 phosphor was accounted for using data published by Yang et al.⁶ A corrected spectrum obtained for $E//a$ at 90 K together with a cubic spline used to obtain XAFS is shown in Fig. 1. The XAFS interference function is defined as

$$\chi(k) = \frac{\mu(k) - \mu_b(k)}{\mu(k_j)} \times \frac{\mu_O(k_0)}{\mu_O(k)} \quad (1)$$

Table I. Effective contribution to XAFS at the O 1s in Y 123 for $E//a$.
 Crystal structure parameters were obtained by neutron diffraction.⁷

Absorbing atom	Backscattering atom	Relative distance (Å)	Effective coordination N_i^*
O(2)	Cu(2)	1.93	11.84
O(3)	Y	2.38	7.8
O(2)	O(3)	2.73	11.76
O(3)	O(2)	2.73	11.76
O(4)	Ba	2.74	11.68
O(1)	Ba	2.88	5.28
O(3)	Ba	2.97	4.96
O(2)	O(4)	3.20	4.28
O(4)	O(2)	3.20	4.28

Based on the data gathered in the Table I the dominant peak in the magnitude of Fourier transform, between 0.8 and 2.4 Å is due to XAFS interference from O(2)–Cu(2), O(3)–Y and O(2,3)–O(3,2) pairs. The incorporation of Ba shells to the model XAFS function gave rise to a very poor fit. This means that contribution from O-Ba pairs to the considered peak is negligible. In other words in this orientation the dominant contribution to the XAFS is given by neighbors of oxygen atoms in the CuO_2 plane (see also Figs. 3 and 4). In order to spectrally isolate the first three shells the XAFS spectrum was backtransformed using window shown in Fig. 2. The resulting $\chi_b(k)$ function is shown in Fig. 3 as open circles. A theoretical XAFS was then fitted and the result of this procedure is represented by solid line. Amplitude and phase functions were obtained from tables published by McKale et al.⁸ with exception of the phase function for O-Cu pair which was taken from the table published by Stöhr.⁹ Contributions due to individual shells are also shown in the same figure. In Fig. 4 the quality of the obtained fit is verified by comparison of the experimental magnitude and real part of Fourier transform together with the respective transforms of the fit. Contribution from individual shells are also shown. Parameters of the three shell model used to obtain the best fit are collected in Table II.

Where k is the wavevector of the emitted photoelectron, k_0 and k_i are its values at the O 1s edge (assumed 532 eV) and at $E_i = 570$ eV. $\mu(k)$ is the measured absorption coefficient, $\mu_b(k)$ is simulated by cubic spline atomic-like absorption above the O 1s edge and $\mu_O(k)$ is the calculated photo-absorption due to oxygen only.⁵ The obtained $\chi(k)$ function is shown in

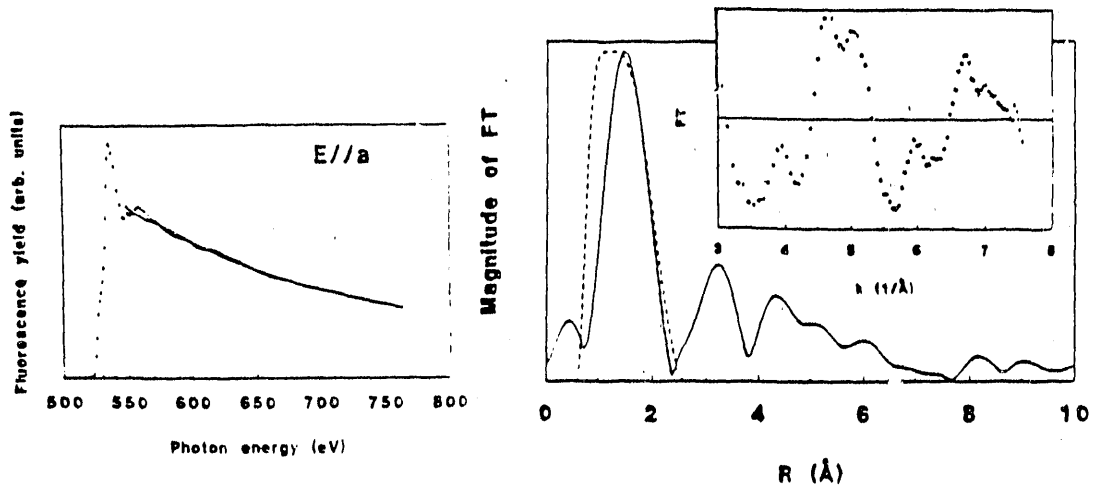


Fig. 1. Corrected FY spectrum obtained for $E//a$ at 90 K: circles. $\mu_b(E)$: solid line.

Fig. 2. XAFS spectrum and magnitude of its Fourier transform. The window used to backtransform is also shown.

Fig. 2 together with the magnitude of its Fourier transform. Due to selection rules only some selected neighbors of the central oxygen atom contribute to the O 1s XAFS signal, see Table I. The effective coordination number N_i^* describes the contribution of the i -th shell to the XAFS signal and is given by

$$N_i^* = 3 \sum_{j=1}^{N_i} \cos^2 \alpha_{ij} \quad (2)$$

The index j denotes the individual atoms in the i -th shell. α_{ij} is the angle between the vector r_{ij} from the central atom to the j -th atom in the i -th shell and the electric field vector E of the x-rays.

Table II. Parameters of the best least-squares curve-fit of the three shell model.

O - X pair	R(Å)	N _i *	σ ² (10 ⁻³ Å ²)	σ ² from references			
	fitted	fitted		[a]	[b]	[c]	[d]
O(2)-Cu(2)	1.90 ± 0.03	13.6 ± 2.0	6.5 ± 2	2.0	6.5	6.3	1.7
O(3)-Y	2.36 ± 0.03	9.0 ± 1.4	2.0 ± 0.7	5.0	7.0	8.5	-
O(2.3)-O(3.2)	2.70 ± 0.03	27.0 ± 4	17.9 ± 5	-	15.0	-	-

- a. From Ref. [10], polycrystalline samples at the Cu and Y K edges at 77 K.
 b. From Ref. [11], polycrystalline samples at the O K edge at 110 K.
 c. From Ref. [12], polycrystalline samples doped with Zn at the Cu and Y K edges at 300 K.
 d. From Ref. [13], polycrystalline samples at the Cu K edge at 20 K.

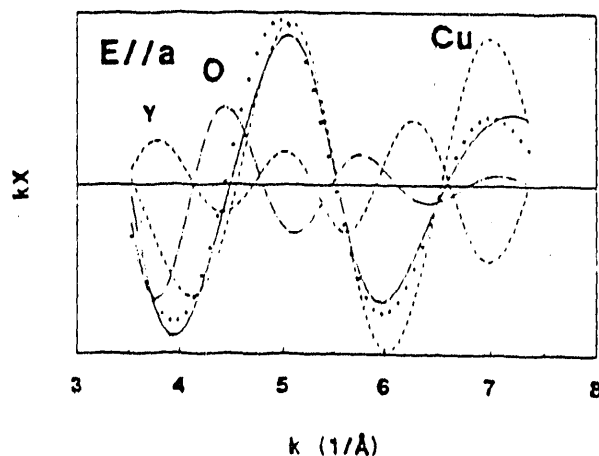


Fig. 3. Filtered XAFS spectrum (open circles) vs. fit (solid line). Contributions from different shells are also shown.

At this point we would like to note that the length of bonds is practically unchanged within error limits ($\sim \pm 0.03 \text{ \AA}$) as compared to crystallographic data at room temperature. This was also observed by Gurman et al.¹⁰ and Maruyama et al.¹³ in polycrystalline samples. The amplitude reduction factor S_0^2 for small k ($3.5 \leq k \leq 8 \text{ \AA}^{-1}$) due to oxygen shake-up and shake-off

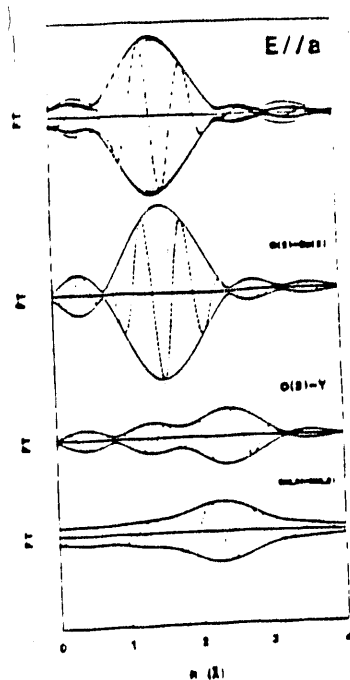


Fig. 4. Magnitude (open circles) and real part (crosses) of the filtered Fourier transform shown in Fig. 3 vs fit (solid line and dashed line, respectively). Contributions from different shells are also shown.

effects can be estimated as equal to 0.87 ± 0.15 which is close to the expected value.¹⁴ The obtained Debye-Waller factors are close to results obtained for polycrystals. However, contrary to earlier investigations, due to application of orientation dependent XAFS to single Y123 crystal the data on O(2) - Cu(2) bond are obtained in a direct way.

CONCLUSIONS

In summary, the O 1s XAFS spectroscopy at 90 K was applied to a single twin free crystal of $\text{YBa}_2\text{Cu}_3\text{O}_7$ high- T_c superconductor with the x-ray electric field E -vector parallel to its a -axis. In this orientation mainly neighbors of oxygen in the CuO_2 plane and specifically the O(2) - Cu(2) bonds are probed. *Within experimental accuracy ($\pm 0.03 \text{ \AA}$) no structural*

change in local ordering about oxygen O(2) atoms in the CuO₂ plane at 90 K has been detected.

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