Phases found at grain boundary of YBa2Cu3O7-d 50 nm films on SrTiO3 by enhanced anomalous scattering at O:K, Cu:L2,3 and Ba:M4,5 edges

Juana Vivó Acrivos, San José State University

Available at: https://works.bepress.com/juana_acrivos/68/
Phases found at grain boundary of YBa$_2$Cu$_3$O$_{7-x}$ 50 nm films on SrTiO$_3$ by enhanced anomalous scattering at O:K, Cu:L$_{2,3}$ and Ba:M$_{4,5}$ edges

J.V. Acrivos* SJSU, CA 95192-0101

Dedicated to Nevill Francis Mott, mentor to condensed matter scholars on 100th anniversary of his birth 9/30/1905

ABSTRACT

A new phase is detected within 100µm of 24 DEG ab grain boundary (GB) in YBa$_2$Cu$_3$O$_{7-x}$ 50 nm films on SrTiO$_3$ by enhanced (001) anomalous scattering. Site identification and temperature dependence is interpreted using crystallographic weights to distinguish enhanced scattered electronic composition. The c-axis, $c_0$ indicates that only ortho-I phase is present far from GB, both ortho-I and II phases are present near GB. The phase $c_0$ is constant versus temperature across the transition to superconductivity.

* jacrivos@athens.sjsu.edu, TEL 408 924 4972, FAX 408 924 4945
keywords: nano-films grain boundary, scattering, superconductivity PACS# 74.25Gz, .72Bk, .78Bz; 78.70Ck, .90+t

INTRODUCTION

Synchrotron X-ray absorption spectra (XAS) of layered cuprates, YBCO$_{6.9}$, where superconducting planes are intercalated between ionic and perhaps magnetic layers are compared at the O:K, Cu:L$_{2,3}$ and the Ba:M$_{4,5}$ edges. The film oxygen composition is obtained from the variation in the c-axis, $c_0$ that determines the (001) enhanced scattered amplitude.

EXPERIMENTAL

The samples are 50 nm films, grown epitaxially by sputtering in an oxygen atmosphere onto a SrTiO$_3$ crystal with and without a 24 DEG ab grain boundary (GB) at the Complutense University and characterized by synchrotron XRD$^1$. Spectra were collected versus photon energy, $E$ at LBNL-ALS 6.3.1 station: by the (001) enhanced scattering ($I/I_0$) in the Kortright chamber at different temperatures$^2$ and distinguished from fluorescence ($F/I_0$) and total electron yield ($TEY/I_0$) in the Nachimuthu chamber where $E$ was calibrated at an anomalous scattering at O:K, Cu:L$_{2,3}$ and Ba:M$_{4,5}$ edges. The film are intercalated between ionic and perhaps magnetic layers are compared at the O:K, Cu:L$_{2,3}$ and the Ba:M$_{4,5}$ edges. The film oxygen composition is obtained from the variation in the c-axis, $c_0$ that determines the (001) enhanced scattered amplitude.

FIG. 1: Sample: (a) Measurement geometry determined by the fixed horizontal incident beam $k_0$, its position and angle $\theta$ by the sample displacement and rotation about the x-axis, and $k_0$ by the detector angle $2\theta$ to $k_0$. (b) BC02/03 (001) XRD versus s-s005 =2sin$\theta\lambda$/5$c_0$, 100µm wide beam detected two $c_0$ at GB [1b].

FIG. 2: Phases detected by $I/I_0$ as incident beam position $x$ moves across the GB. A new phase is induced within 100µm of GB ($\Delta$ a) detected by enhancement peak at $\Delta E_{Bragg}<<<E_{Bragg}$ is $\sim \Delta c_0/c_0$ from the original c$_0$(ortho-I phase) $\sim 11.6\AA$ to c$_0$(ortho-II phase) $\sim 11.7\AA$.

FIG. 3: Effect of $E_{Bragg}$ (2) on $I/I_0$ near the Ba:M$_{4,5}$ edges (BC02/03; BC04/04). Lifetime broadening and distortion due to some Ba, commonly occupying Y sites is observed. Broadening is evident in the integrated intensities, I from 730eV and the fit to A (4) with different HWHH at the M$_4$ and M$_8$ WL, but the integrated intensities remain equal even as the lines narrow.
The Thomson amplitude $f_j(k, k, E) = f_j^0(k, k) + \Delta f_j(k, k, \theta, \phi, E)$.

The anomalous amplitude:

$$
\Delta f_j(k_0, k, \theta, \phi, E) = f_j^0(k_0, k) + \Delta f_j(k, k, \theta, \phi, E)
$$

Involves dipole matrix elements $\mu_{ji}$ between initial and final states $(n, l)$ with energies $E_n$, $E_l$, depend on orientation in a layer cuprates\(^7\) (incident $\varepsilon_{\text{K}}\varepsilon_{\text{y}}$ unit vector, $\hat{e}_i$ is in the film ab plane), state lifetime that determines the half width at half height $\text{HWHH}$, crystallographic site diffraction weights $\alpha_j = \Sigma \varepsilon_{\text{K}} e^{i \varepsilon_{\text{K}} r_{ji}}$, $\Delta E = \lambda\text{mb shift}$, $f_j^0$ dispersion, $f_j^0$ absorption, $c$= velocity of light, $\text{HWHH}$ observed in the WL at the Cu:2,3 and Ba:M5,4 (fig. 3, 4) for BC and SC films where TEY/I0 and F/I0 show a Lorentzian shaped WL with an edge jump weaker than 1% of WL amplitude\(^7\). Thus if the $\phi$ tail is linear, the enhanced scattered amplitude minus a base line may be compared to:

$$
A_y = I_y/I_0 = [y \cos(\phi) - \sin(\phi)]/[1 + y^2]
$$

where $y=(E-E_0)/\text{HWHH}$, $E_0$ is the edge energy and $\text{HWHH}$ is the WL half width at half height. The fitted A indicate that the film rotates the plane polarized beam by $\phi$ (Cu:L3)$\approx 3\pi/4\pm \pi$ at $E_\text{(Cu:L3)}$-E$_\text{Bragg}=18$ to $10^2$eV, and $f^0$ $I_y/I_0$ (fig. 4) agrees with theory $\phi = 0^4, 6$. The observed lifetime broadening\(^8\) narrows to $\text{HWHH}=0.7$ from 1.7eV when E$_\text{Bragg}$ E(Cu:L3) $= 10^2$ and 18eV, respectively. WL transitions at L$_2,3$ edges (fig. 4) depend on the Cu valence:

$$
\text{Cu}^{+1}(2p^6)\leftrightarrow \text{Cu}^{+2}(2p^53d^5), \text{Cu}^{+2}(2p^53d^5)\leftrightarrow \text{Cu}^{+3}(2p^43d^6), \text{Cu}^{+3}(2p^43d^6)\leftrightarrow \text{Cu}^{+4}(2p^33d^9), \text{Cu}^{+4}(2p^33d^9)
$$

the crystal field splitting (different at the L$_2$ and L$_3$ edges) and orientation\(^7\)\(^9\) making it difficult to assign spectral features to the Cu sites in YBCO. Site identification is made by the variation in $\alpha_j(E) = n_\text{g}(\pi z_j E/E_\text{Bragg})$ versus different fixed E$_\text{Bragg}$, when $n_\text{g}$ is the number of equivalent atom $j$ sites with coordinate $z_j$ in the unit cell (Table I). When $E_\text{(Cu:L2)}$ $E_\text{Bragg} = 950$eV, $\alpha_{\text{Cu}2}/\alpha_{\text{Cu}1}$= -1.4 the enhanced shoulders ~6eV above the main signal, but of opposite sign amplitude may be due to the Cu:1 site contribution. The exact cancellation expected for $E_\text{Bragg}$ = 1083eV, $\alpha_{\text{Cu}2}/\alpha_{\text{Cu}1}$= -1 if the second order matrix elements in $\Delta f_{j2}$ for both sites are of the same order of magnitude, is not observed, indicating that Cu:1 and Cu:2 appear at different E, with a different Cu valence and $\phi$ (Cu:2) $\approx 3\pi/4$.

(ii) Data at the O:K edge indicate that a displacement of the 100µm wide beam, across the GB detects a new enhancement peak, associated with a higher c$_0$ phase. The relative amplitude (fig. 2, 50, 51) in the XAFS region centered at 538eV (c$_0$=11.7Å) identifies it with the ortho-II phase (YBCO$_{0.5}$) relative to that at 546eV (c$_0$=11.6Å) for the ortho-I phase (YBCO$_{0.6}$) in agreement with the XRD data\(^9\). The width of the GB is comparable to the beam width since full enhancement, at $E_\text{Bragg}$ = 538eV appears only within x $\approx 4.87\pm 0.005$in, while that at 546eV decreases very little across the GB. Comparison to c$_0$ data versus O composition\(^3\) indicates that near the GB a ~5% discontinuous O decrease induces the ortho-II phase which releases the film strain, by creating the k$_x$=-k$_y$ periodic lattice distortions (PLD) observed in XRD for the film\(^10\)c.$\pm 8c$.

The information obtained on YBCO$_3$ transitions:

$$
O:1s^2\leftrightarrow O:1snp_{3/2} n=2 \text{ and } O:1s^2\leftrightarrow O:1snp_{1/2} n=2
$$

when $\tilde{e}_i$ is in the ab plane is according to relation (1). Comparison of enhancement at E$_\text{Bragg}$ = 545 and 2*10^4eV (Table I, fig. 5 #37, 28) identifies the site contributions. I/I$_0$
Temperature dependence measurements indicate that $c_0$ is unchanged across $T_c$ by the constant enhancement peak observed at $E_{Bragg} \approx 546$eV in the ortho-I phase. $\phi(Cu:2L_{32}) \approx 3\pi/4$ in (4) is constant across $T_c$, but a reversible $0.5eV$ edge shift below $T_c$ observed at the Cu:2:L_{32} edges in a 24 h, T cycle (fig. 4 insert) is assigned to an increased Cu:2 site valence below $T_c$.

(iii) In the ideal YBCO, Ba occupies a unique site but in real crystals it also occupies Y sites. As $E_{Bragg} - E(Ba:M_5) = -38$ to $2 \times 10^3$eV lifetime broadening is observed when $\alpha_{Ba}/\alpha_Y \approx -0.8$ but the WL narrow for $\alpha_{Ba}/\alpha_Y \approx (3)$ (Table I, fig. 3 #52 and #33). Amplitudes for WL transitions: $Ba^{2+}(3d^{10}) \leftrightarrow Ba^{2+}(3d_{5/2}$,$4f_{7/2})$; $Ba^{2+}(3d_{5/2}$,$4f_{5/2})$, are proportional to the initial state multiplicities, $A_{5d}/A_{4s} = 1.5$ only for $E_{Bragg}> 2 \times 10^3$eV. The TEY/I$_0$ for BC04/04 are orientation dependent$^{7c,9}$.

CONCLUSION

The fabricated nano-film YBCO$_x$ (001) anomalous enhanced scattering analysis, sensitive to phase and O composition characterizes the GB for device applications and theoretical interpretation of transport data.

ACKNOWLEDGEMENTS

Work was supported by the NSF and Dreyfus Foundations at SJSU, DOE at LBNL-ALS and scholars$^{1-9}$.

REFERENCES

[7](a) A. Bianconi et al, Phys. Rev.B 38, 7196 (1988); (b) F.M.F. de Groot et al., Solid State Sciences, 71, 117 (2002); (c) E. Bascones et al., ibid, 71, 121505 (2005)