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ORIGINAL PAPER

Imaging Spatial Ordering of the Oxygen Chains in $YBa_2Cu_3O_{6+y}$ at the Insulator-to-Metal Transition

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Abstract It is known that the mobile oxygen ions, y, in the basal plane of $YBa_2Cu_3O_{6+y}$ ($0.33 < y < 0.67$) form oxygen chains needed to create the metallic phase in the CuO_2 layers. Here we visualize the spatial organization of oxygen chains in a crystal of $YBa_2Cu_3O_{6+y}$ very close to the insulator-to-superconductor transition with $y = 0.33$ ($T_c = 7$ K). The distribution of oxygen defects chains has been obtained by performing scanning micro X-ray diffraction measurements. This experiment provides mixed real and reciprocal space information. We found a granular spatial pattern due to the oxygen chains being segregated in nanoscale puddles with ortho-II crystallographic structure embedded in an insulating matrix of disordered oxygen ions.

Keywords X-Ray micro-diffraction · Granular matter · High temperature superconductors

The nanoscale distribution and ordering of dopants in high temperature superconductors is nowadays considered to be a key point in the understanding of superconductivity mechanism. $YBa_2Cu_3O_{6+y}$ (YBCO) is the most studied high temperature superconductor due to its simple synthesis route and because it was the first superconductor discovered with T_c above the liquid nitrogen temperature. It is well known that changing the oxygen concentration strongly affects the superconductivity in this compounds as well as in other high T_c systems. Furthermore, besides the variable concentration of oxygen ions, also their arrangement in the host lattice produces relevant effects on transport properties. It is generally accepted that oxygen ions get ordered in Cu–O chains attracting electrons from the CuO_2 layers. This ordering gives rise to "guest superstructures" detected as satellite peaks in diffraction patterns [1]. The variety of possible superstructures has raised the question of the interplay between different ordering scheme and the characteristic T_c [2].

Recently, it has been demonstrated that a statistical approach of microstructure space distribution and correlation provides an important tool for the understanding of structure-function relationships in the high temperature superconductors. At this aim local probes have been used for locally investigate structural features in various systems such as diborides [3], cuprates [4, 5], bismuthates [6] and doped iron-chalcogenides [7]. Previous works on YBCO system have already provided indications on the heterogeneity of the oxygen chains spatial arrangement. Neutron and infrared studies have shown that large changes with doping cannot be explained using the classical vibrational shell models with changes in host site occupancies [8–10]. Electron microscopy [11–14] and electron diffraction [15–18] studies reported local structural inhomogeneities due to compositional domains on micron scale, while Beyers et al. [19] reported evidence that phase separation occurred in oxygen-deficient YBCO for narrow ranges of oxygen content.

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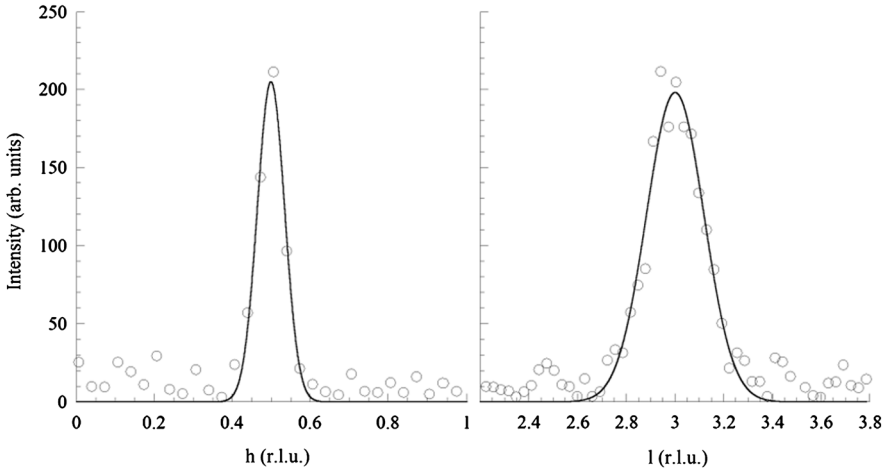

Fig. 1 (*Open circles*) X-ray diffraction profile of the OII superlattice with wavevector $q_{O-II} = 0.5h + 3l$, along a^* and c^* directions. *Continuous lines* indicate the X-ray patterns Gaussian fits

In this work, we employed micro X-ray diffraction (μXRD) for visualizing the oxygen chains arrangement in ordered domains in $YB_2C_3O_{6+x}$ compound with $x = 0.33$. We measured the local variations of the oxygens order by analyzing the satellite reflections associated to the domains formed by ordered oxygen chains. Our observations clearly show that the chains ordering in YBCO produces a phase separation between 3D ordered and disordered domains.

The $YBa_2Cu_3O_{6.33}$ single crystals were grown in yttrium-stabilized zirconia crucibles by a flux-growth method using chemicals of 99.999 % purity for Y_2O_3 and CuO, and 99.997 % for $BaCO_3$. The impurity level of the crystals has been analyzed by inductively coupled plasma mass spectroscopy. The Zr content of the crystals was found to be less than 10 ppm by weight. The major impurities were Al, Fe, and Zn, the sum of which amounts to less than 0.2 % atom per unit cell. The oxygen composition of the crystals was changed by use of gas-volumetric equipment. The technique allows to determine the oxygen composition with an accuracy better than $\Delta x = 0.02$. The unit cell of $YBa_2Cu_3O_{6.33}$ single crystal is characterized by lattice parameters: $a = 3.851$ (12) Å, $b = 3.856$ (12) Å, $c = 12.16$ (2) Å, and a I4/mm space group.

μXRD measurements were performed in reflection geometry at the ID13 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. We used a monochromatic X-ray beam with an energy (E) of 14 KeV ($\Delta E/E = 10^{-4}$). The beam was focused by Kirkpatrick Baez (KB) mirrors down to 1×1 μm^2 spot size on the sample. A 16 bit two-dimensional Fast Readout Low Noise charged coupled device (FReLoN CCD) detector with 2048×2048 pixels of 51×51 μm^2 was used. In order to increase the Intensity/pixel ratio the camera was binned to 512×512 pixels. Diffraction images were obtained after correcting the 2D images for dark noise, flat field, and spatial distortion.

We found superlattice reflections associated to the orthogonal-II (OII) phase, located at positions of $(h + 1/2, k, l)$ with h, k, and l as integers. The occurrence of these reflections at every integer value of l indicates that oxygen chains of subsequent layers stack on top of each other. Thus, the OII phase is formed by 3D ordered domains with anisotropic lengths along the crystallographic directions. In Fig. 1 we show the diffraction profiles, of the $(0.5, 0, 3)$ superstructure, along a^* and c^* direction, measured in a 1×1 μm^2 area and fitted by Gaussian line profile.

This satellite reflection was then measured at each point of the sample reached by the x–y translator with micron resolution in order to visualize the point to point spatial variation of both intensity and size of the OII domains. The integrated intensity of the superstructure peaks is shown in Fig. 2a. The domains sizes of the OII puddles have been derived from the measured FWHM via standard methods of diffraction. The plot of domains size along a^* and c^* as a function of intensity is plotted in Fig. 2b evidencing a strong variability from point to point,

As previously determined by statistical analysis of domain sizes, some deviations from normal behavior are observed in the distribution tails [18]. These deviations have been quantified by the distribution skewness, sk, giving $sk_a = 0.3$ and $sk_c = 0.9$ for the OII domain size along the a^* and c^* directions, respectively. In order to get deeper insights into these tails we calculated the spatial correlation function, $G(r)$, obtained by the correlations of any pairs of spots in the 2D image separated by the vector $\vec{r} = \vec{R}_i - \vec{R}_j$, as described in Ref [5]. $G(r)$ followed an exponential behavior, $G(r) \approx \exp(\frac{-r}{\xi})$ where ξ is a characteristic length indicating the typical distance beyond which the chains ordering decay. Although spatial correlations of the OII domains size follow the exponential behavior along both the a^* and c^* directions, we find a different coherence length in the two directions. In particular we find a coherence length of 22 and 67 microns for the domain sizes distribution along the a^* and c^* directions, respectively. This indicate that the OII domains are more correlated out-of-plane than in-plane.

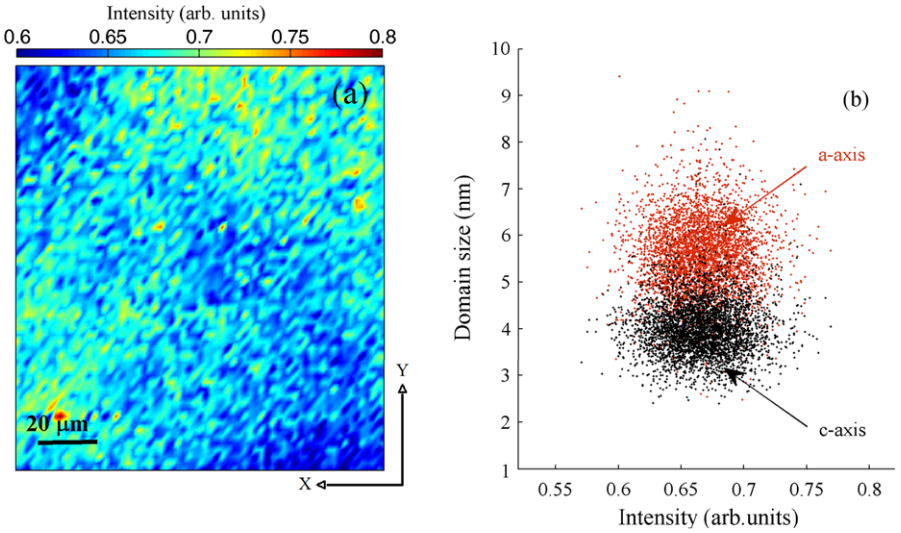

Fig. 2 (**a**) Color map of OII intensity: the OII superstructure intensity is plotted as a function of the illuminated spot position XY in the sample surface, where X and Y directions in the image correspond to the a and b crystallographic *axis* of the sample. The *black bar* indicates 20 µm length scale on the sample surface; (**b**) distribution of domain size along *a-axis* and *c-axis* of OII superlattice, as a function of its intensity (Color figure online)

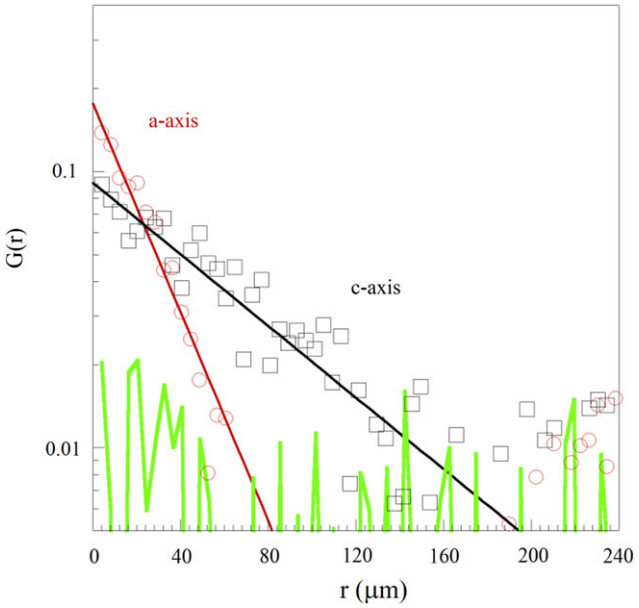

Fig. 3 Semi-log plot of spatial correlation function, $G(r)$, of domain size along (*circles*) *a-axis* and (*squares*) *c-axis*; the *continuous* (*black* and *red*) *lines* represent the exponential curve fits, while the *green thick line* indicates the correlations of randomly distributed sizes (Color figure online)

These results encourage the tendency to consider the formation of networks of striped puddles with different defects organization an essential parameter in the pairing mechanisms in cuprates [20–29] diborides [30, 31] and iron-based superconductors [32–34] play a key role for determining the symmetry of the lattice and of the multiple condensates controlling the critical temperature (Fig. 3).

In summary, we have studied the oxygen order in $YBa_2Cu_3O_{6.33}$ near the tetragonal-to-orthorhombic phase boundary. At this oxygen concentration superconductivity coexists with the antiferromagnetism, although both are strongly suppressed. We have visualized the spatial pattern due to the OII oxygen chains arrangement in $YBa_2Cu_3O_{6.33}$, using scanning micro X-ray diffraction; then, this spatial pattern has been studied by spatial correlation analysis. Our spatial pattern is due to the formation of a network of the ortho-II nanoscale domains embedded in more disordered regions. The ordered OII domains have different size varying between 2 and 9 nanometers, with spatial correlations along c^* larger than along a^* direction.

References

1. von Zimmermann, M., Schneider, J.R., Frello, T., Andersen, N.H., Madsen, J., Käll, M., Poulsen, H.F., Liang, R., Dosanjh, P., Hardy, W.N.: Phys. Rev. B **68**, 104515 (2003)
2. Cava, R.J., et al.: Physica C **165**, 419 (1990)
3. Campi, G., Cappelluti, E., Proffen, T., Qiu, X., Bozin, E.S. Billinge, J.L, Agrestini, S., Saini, N.L., Bianconi, A.: European Phys. J., B Cond. Matter Complex Syst. **52**, 15 (2006)
4. Saini, N.L., Oyanagi, H., Ito, T., Scagnoli, V., Filippi, M., Agrestini, S., Campi, G., Oka, K., Bianconi, A.: Eur. Phys. J., B Cond. Matter Phys. **36**, 75 (2003)
5. Fratini, M., Poccia, N., Ricci, A., Campi, G., Burghammer, M., Aeppli, G., Bianconi, A.: Nature **466**, 841 (2010)
6. Poccia, N., Campi, G., Fratini, M., Ricci, A., Saini, N.L., Bianconi, A.: Phys. Rev. B **84**, 100504 (2011)
7. Ricci, A., Poccia, N., Campi, G., Joseph, B., Arrighetti, G., Barba, L., Reynolds, M., Burghammer, M., Takeya, H., Mizuguchi, Y., et al.: Phys. Rev. B **84**, 060511 (2011)
8. Reichardt, W., Pyka, N., Pintschovius, L., Hennion, B., Collin, G.: Physica C, Supercond. **162–164**, 464 (1989)
9. Homes, C.C., Timusk, T., Bonn, D.A., Liang, R., Hardy, W.N.: Can. J. Phys. **73**, 663 (1995)
10. Phillips, J.C., Jung, J.: LANL (2001). cond-mat/0103167
11. Barry, J.C.: J. Electron Microsc. Tech. **8**, 325 (1988)
12. Barry, J.C., Alarco, J.A.: J. Microsc. **202**, 495 (2001)
13. Etheridge, J.: Philos. Mag. A **73**, 643 (1996)
14. Sarikaya, M., Stern, E.A.: Phys. Rev. B **37**, 9373 (1988)
15. Williams, E.J., Stobbs, W.M.: Philos. Mag. A **68**, 1 (1993)
16. Yan, Y., Liang, W.Y., Walther, T., Stobbs, W.M.: Phys. Rev. B **54**, 16234 (1996)

17. Midgley, P.A., Vincent, R., Cherns, D.: Philos. Mag. A **66**, 237 (1992)
18. Campi, G., Ricci, A., Poccia, N., Barba, L., Arrighetti, G., Burghammer, M., Caporale, A.S., Bianconi, A.: Phys. Rev. B **87**, 014517 (2013)
19. Beyers, R., Ahn, B.T., Gorman, G., Lee, V.Y., Parkin, S.S.P., Ramirez, M.L., Roche, K.P., Vazquez, J.E., Gur, T.M., Huggins, R.A.: Nature (London) **340**, 619 (1989)
20. Bianconi, A., Di Castro, D., Bianconi, G., Pifferi, A., Saini, N.L., Chou, F.C., Johnston, D.C., Colapietro, M.: Physica C, Supercond. **341–348**, 1719 (2000). ISSN 09214534. doi:10.1016/s0921-4534(00)00950-3
21. Bianconi, A.: Int. J. Mod. Phys. B **14**, 3289 (2000). doi:10.1142/S0217979200003769
22. Ricci, A., Poccia, N., Ciasca, G., Fratini, M., Bianconi, A.: J. Supercond. Nov. Magn. **22**, 589 (2009). doi:10.1007/s10948-009-0473-x
23. Poccia, N., Ricci, A., Bianconi, A.: Advances in Condensed Matter Physics **2010**, 1 (2010). doi:10.1155/2010/261849
24. Ricci, A., Fratini, M., Bianconi, A.: J. Supercond. Nov. Magn. **22**, 305 (2009). doi:10.1007/s10948-008-0434-9
25. Innocenti, D., Ricci, A., Poccia, N., Campi, G., Fratini, M., Bianconi, A.: J. Supercond. Nov. Magn. **22**, 529 (2009)
26. Poccia, N., Ricci, A., Campi, G., Fratini, M., Puri, A., Di Gioacchino, D., Marcelli, A., Reynolds, M., Burghammer, M., Saini, N.L., et al.: Proc. Natl. Acad. Sci. USA **109**, 15685 (2012). doi:10.1073/pnas.1208492109
27. Poccia, N., Fratini, M., Ricci, A., Campi, G., Barba, L., Vittorini-Orgeas, A., Bianconi, G., Aeppli, G., Bianconi, A.: Nat. Mater. **10**(733), 1476–ISSN 1122 (2011). doi:10.1038/nmat3088
28. Phillips, J.C.: Ineluctable complexity of high temperature superconductivity elucidated. J. Supercond. Nov. Magn. (2013). doi:10.1007/s10948-013-2308-z
29. Bianconi, A.: Nat. Phys. **9**, 536 (2013). doi:10.1038/nphys2738
30. Agrestini, S., Metallo, C., Filippi, M., Campi, G., Sanipoli, C., De Negri, S., Giovannini, M., Saccone, A., Latini, A., Bianconi, A.: J. Phys. Chem. Solids **65**, 1479 (2004)
31. Palmisano, V., et al.: J. Phys. Condens. Matter **20**, 434222 (2008). doi:10.1088/0953-8984/20/43/434222
32. Caivano, R., Fratini, M., Poccia, N., Ricci, A., Puri, A., Ren, Z.-A., Dong, X.-L., Yang, J., Lu, W., Zhao, Z.-X., et al.: Supercond. Sci. Technol. **22**, 014004 (2009). ISSN 0953-2048, doi:10.1088/0953-2048/22/1/014004
33. Ricci, A., Poccia, N., Joseph, B., Arrighetti, G., Barba, L., Plaisier, J., Campi, G., Mizuguchi, Y., Takeya, H., Takano, Y., et al.: Supercond. Sci. Technol. **24**, 082002 (2011). http://iopscience.iop.org/0953-2048/24/8/082002/
34. Despina Louca, Park, K., Li, B., Neuefeind, J., Yan, J.: Sci. Rep. **3**, 2047 (2013). doi:10.1038/srep02047