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To cite this article: Nicola Poccia *et al* 2017 *Supercond. Sci. Technol.* **30** 035016

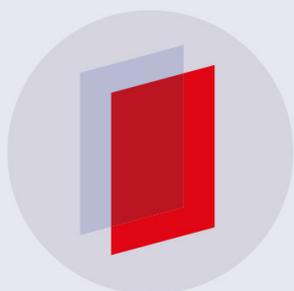
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# Dislocations as a boundary between charge density wave and oxygen rich phases in a cuprate high temperature superconductor

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Received 26 October 2016, revised 14 December 2016

Accepted for publication 6 January 2017

Published 6 February 2017



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## Abstract

Multiple functional ionic and electronic orders are observed in high temperature superconducting cuprates. The charge density wave order is one of them and it is spatially localized in different regions of the material. It is also known that the oxygen interstitials introduced by chemical intercalation self-organize in different oxygen rich regions corresponding with hole rich regions in the  $\text{CuO}_2$  layers left empty by the charge density wave order domains. However, what happens in between these two orders is not known, and neither there is a method to control this spatial separation. Here we demonstrate by using scanning nano x-ray diffraction, that dislocations or grain boundaries in the material can act as boundary between charge density wave and oxygen rich phases in an optimally doped  $\text{La}_2\text{CuO}_{4+y}$  high temperature superconductor. Dislocations can be used therefore to control the anti-correlation of the charge density wave order with the oxygen interstitials in specific portion of the material.

Keywords: dislocation, nanoscale phase separation, oxygen interstitials, charge density wave, functional ions, grain boundary

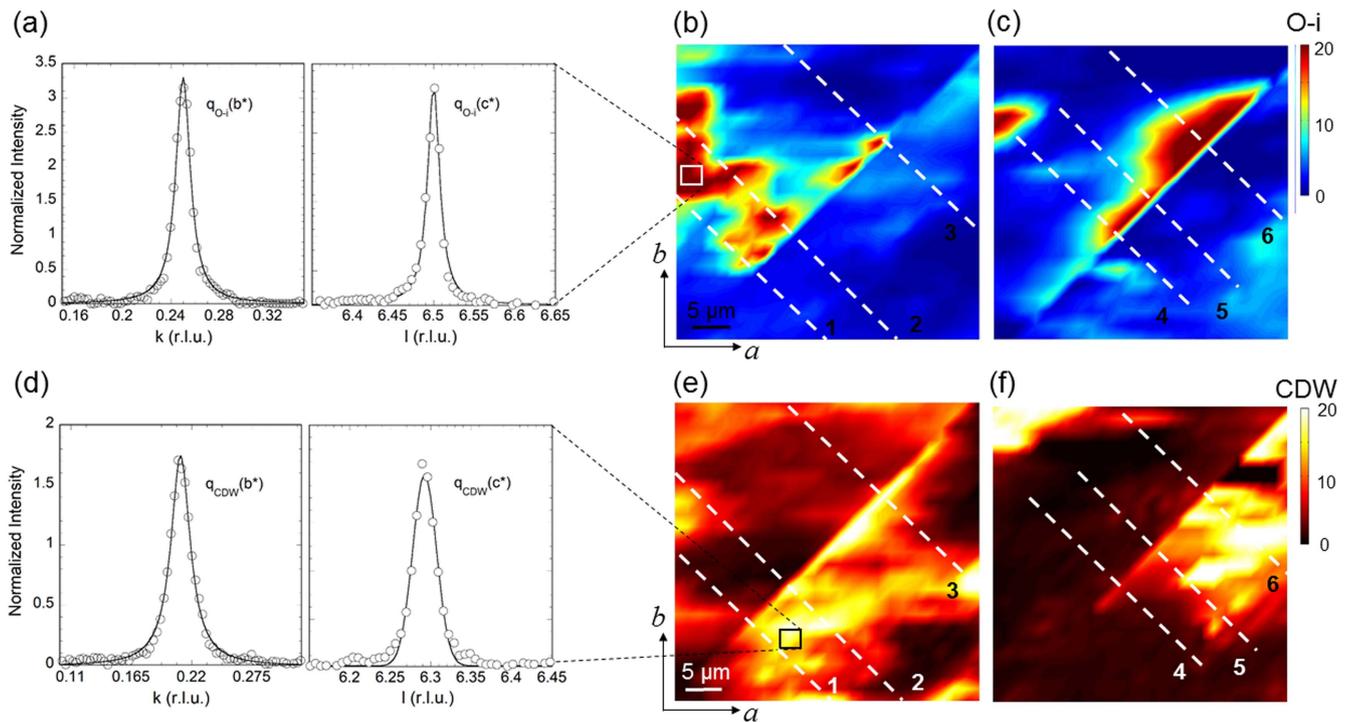
(Some figures may appear in colour only in the online journal)

Dislocations or grain boundaries are known to change the properties of electronic materials [1, 2]. Although dislocations are often considered as a problem for the performances of a material, it is from the very beginning of semiconductor science that scientists tried to use them to engineer their functionalities [3]. Currently, novel methods of fabrication to realize networks of dislocation have been adopted to change the electronic functionalities of Si [4]. In the proximity of dislocations, the strain of a material is modulated [5]. Strain (e.g. chemical pressure, microstrain, misfit-strain) is a material dependent parameter which have a deep influence in the

electronic properties of the material and it has been proposed to play a crucial role also in the properties of high temperature superconductors [6, 7] as well for their phase diagram description [8]. In cuprates, since the spacer layer has a dissimilar lattice constants than the active layer, the mismatch typically results in the formation of strain-relieving misfit dislocations [9]. However, the search for an accurate description of the strain in strongly disordered systems is a current field of research [10–13].

Dislocations are a manifestation of a strongly disordered system and recently they have been exploited as resistive switching in oxides [14], since they can act as bistable nanowires. The lattice can be sensitively different at the core

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**Figure 1.** Panel (a) shows the representative x-ray scattering profiles of a typical O-i satellite due to ordered oxygen-interstitials with wave vector  $q_{O-i}$ . The solid lines are the Lorentzian best fit curves. The panels (b) and (c) show the  $xy$  map of the intensity of the O-i satellite in different portions of the sample. Two different diagonal dislocations which induce sharp boundaries are shown. Here the color goes from dark blue to dark red as indicated in the O-i color bar. Panel (d) shows representative scattering profiles of the satellite due to charge density wave order with wave-vector  $q_{CDW}$ . Panels (e) and (f) show the  $xy$  mapping of the intensity of the CDW satellite in the same spatial portions shown in panels respectively (b) and (c). Here the color goes from dark red to white as indicated in the CDW color bar. Visual inspection of the images shows that close to the diagonal linear boundary, the CDW or O-i order abruptly changes. Comparing panels (b) and (c) with the panels (e) and (f), it is clear that the dislocation plays the role of boundary between the O-i rich and CDW rich regions of the sample. The bar is 5  $\mu\text{m}$ .

of a dislocation [15], with oxygen that can get there pinned at elevated temperatures [16] and as a function of the annealing time. Materials under strain determine a collective motion of dislocations which give rise to strain burst difficult to control [17, 18]. The role of dislocations as a fast route for oxygen diffusion is debated [19]. Electro-switching transitions are observed in Mott insulators through the creation of metallic paths [20], which might involve oxygen-ion transport along nanoscale dislocation networks.

Evidence of nanoscale phase separation has recently been found in functional oxides like cobalates [21], bismutates [22] and in cuprates [23–26]. In cuprates, the oxygen interstitials (O-i) organization and the charge density wave (CDW) ordering, coupled to the incommensurate periodic local lattice distortions (LLD), have been found to be spatially anti-correlated and to influence the macroscopic quantum condensate [23, 24, 27–34] in a landscape of filamentary networks [25, 27, 35–37]. In these works a non-euclidean geometry has been proposed to describe the optimal inhomogeneity of the cuprates [25, 27]. Non-euclidean geometries are also known to determine further complexity in the disposition and dynamics of defects [38]. The nanoscale phase separation observed in the pnictides suggest the occurrence of dislocations at the interface [39]. Therefore, gaining control on the network described by the spatial arrangements of ordered defects is important for the design of materials [40]. Indeed,

the collective motion of the copper pairs can be strongly influenced by an annealed complex network [41]. The control of defects is considered a central problem in advanced materials and atomic heterostructure [42], and in the realization of array of artificial atoms in strongly correlated systems [43]. Recently, the precise control of disorder in an array of vortices, which behave as an array of superatoms, has made possible the observation of a dynamic vortex Mott insulator to metal transition [44].

Here we show that dislocations can act as boundaries between CDWs and oxygen rich puddles in a cuprate superconductor. We use scanning nano x-ray diffraction (XRD) to image the spatial organization of the O-i and CDW across the dislocation boundary of a cuprate superconductor.

## 1. Experimental method

The sample of  $\text{La}_2\text{CuO}_4$  was grown first by flux method and then doped by electrochemical oxidation. The critical superconducting temperature of the oxygen doped  $\text{La}_2\text{CuO}_{4+y}$  ( $y = 0.12$ ) was determined to be 41 K by single coil resistivity measurements. The orthorhombic lattice parameters of single crystal were determined to be  $a = (5.386 \pm 0.004) \text{ \AA}$ ,  $b = (5.345 \pm 0.008) \text{ \AA}$ ,  $c = (13.205 \pm 0.031) \text{ \AA}$  at room temperature. The space group of the sample is Fmmm. Nano

XRD experiments were performed on the ID13 beam line of the European Synchrotron Radiation Facility (ESRF), using a photon energy of 14 keV focused on a  $300 \times 300 \text{ nm}^2$  spot on the sample  $a$ - $b$  surface. XRD patterns were collected in reflection geometry to record the reflections on the  $b^*c^*$  reciprocal plane by a Frelon area detector. The scanning step was set to  $3 \mu\text{m}$  in both horizontal and vertical directions. The experiment has been performed at room temperature. Thanks to the high brilliance source, it has been possible to record a large number of weak superstructural peaks around the main Bragg peaks of the average structure.

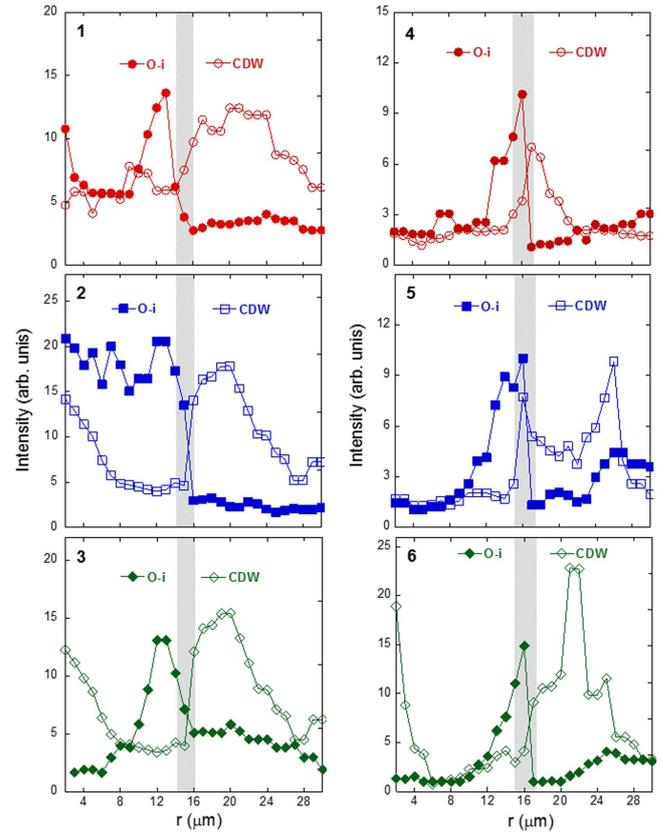
## 2. Results and discussion

Optimally doped  $\text{La}_2\text{CuO}_{4+y}$  is ideal for the investigation of interstitials diffusion in copper oxides because the O-i are mobile in the  $\text{La}_2\text{O}_{2+y}$  layers intercalated between the superconducting  $\text{CuO}_2$  planes.

The main Bragg peaks of the single crystal are surrounded by the known satellite peaks with wave-vector  $q_{\text{O-i}} = 0.09a^* + 0.25b^* + 0.5c^*$ , due to the O-i dopants ordered in the three-dimensional superstructure (see figure 1). Alongside the O-i peaks, indexing of superlattice peaks around the Bragg lattice reflections show the presence of incommensurate modulations  $q_{\text{CDW}} = 0.035a^* + 0.21b^* + 0.29c^*$  (see figure 1). These modulations are CDWs strongly coupled with the incommensurate periodic LLD of the copper plane [24, 25, 29], forming stripes running in the  $a$  direction with a correlation length of about 2.6 nm in the  $b$  direction. The correlation between CDW and LLD is known from long time in layered materials [45]. These incommensurately modulated LLDs could define the nanoscale organization of CDW domains that show average size of 12 nm. The x ray diffraction profiles of the two satellite reflections,  $q_{\text{O-i}}$  and  $q_{\text{CDW}}$  in the  $b^*c^*$  plane are shown in figure 1. The average increase in the intensity of the  $q_{\text{CDW}}$  is observed below 250 K until reaches a maximum at about 100 K [36].

The spatial distribution of both the O-i and the CDW satellites has been studied by using the x-ray micro diffraction apparatus at the ESRF. Scanning the sample using nanometer piezo-stages we recorded the spatial dependence of the O-i and CDW peak intensity. The resulting spatial maps show clear dislocations on the  $a$ - $b$  plane of the crystal. Figure 1 shows two typical dislocation running on the  $a$ - $b$  plane. Its deepness along the  $c$ -axis overcome the x-ray penetration length, while its largeness on the  $a$ - $b$  plane extends for less than the beam size ( $300 \times 300$ ) nm.

Our key experimental discovery is that such dislocation or grain boundary can control both the arrangement of the O-i and CDW domains in real space. It shows that region of CDW higher order and larger clusters are formed on the bottom portion of the image close to the dislocation boundary. On the top part, instead, the O-i order is dominant. More specifically, we observe the enhancement of O-i and the CDW melting in proximity of the dislocation. The intensity profiles along the white six dashed lines of the maps in figure 1 are shown in figure 2, and highlight the anti-

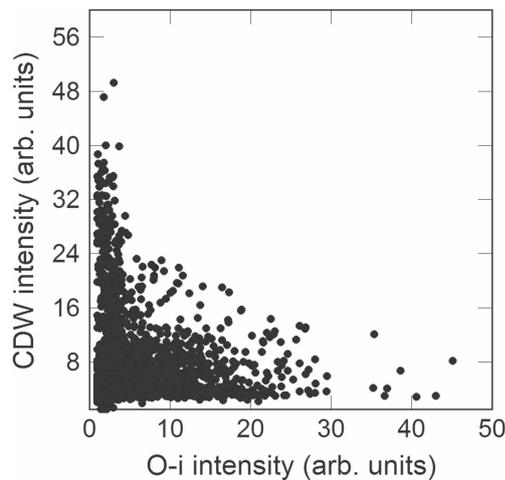


**Figure 2.** The profile cut of the integrated intensity map of the  $q_{\text{O-i}}$  and  $q_{\text{CDW}}$  peak are shown along the dashed white lines as indicated in the maps of figure 1. Each panel shows respectively the O-i and CDW intensity along the profile cuts indicated with the numbers from 1 to 6. The gray area is the region occupied by the dislocation. It is visible the anti-correlation of the O-i and CDW orders in the proximity of the dislocation.

correlated spatial arrangement of the two phases O-i and CDW in the proximity of the dislocation.

The general character of this spatial anti-correlation results evident also from the scatter plot of O-i intensity versus CDW intensity (figure 3) calculated on the whole maps of figure 1. As O-i intensity becomes higher, the CDW intensity decreases, and vice versa. The observed dislocations determine a physical barrier for the oxygen interstitial diffusivity [46]. The dislocation can be used to manipulate the ions distribution which is considered a relevant problem in modern material science [47]. The concentration of the O-i order on one side the dislocation creates a CDW order on the other side of the dislocation. This artificial separation induced by the dislocation determines a more pronounced spatial anti-correlation between the O-i and the CDW orders.

Recently attention on the control and properties of dislocations has been given in van der Waals heterostructures [48] through the observation of atomic scale ripples. Although in the case we report here the dislocation is observed in a bulk crystal, the observed pinning of anti-correlated regions could be basically explained on how the material accommodate the high load of natural strain. Modulation of the local strain in the proximity of the dislocation can



**Figure 3.** The anti-correlation is further quantified by plotting the intensity of the whole maps for  $q_{\text{CDW}}$  as a function of  $q_{\text{O-i}}$ . The observed scatter plots demonstrate the spatial anti-correlation between the two phases near the boundary.

determine the observed oxygen ordering [49]. Elastic field engineering is considered important in many field of science, especially focussing on the realization of high-strength materials [50]. The possibility of modulate the strain field creating dislocations could determine the occurrence of the CDW and O-i rich domains. It has been suggested that bulk dislocations can modulate the layered solid into ripples and that this could be more common in materials than expected [51]. The modulation of the copper plane as ripples (e.g. short range periodic LLD) close to the dislocation observed in our experiment, can explain the observed pinning of the CDW order. However, it is also possible to discuss the results reported in this paper in terms of a grain boundary separating the CDW and the O-i rich domains. It is known indeed that grain boundaries can give to the material unique electronic properties different from that of the bulk [2].

In conclusion, we have performed a scanning nano XRD experiment and we have imaged the spatial dependence of the ordered O-i domains and the CDW rich domains in the proximity of a several tens micrometer and diagonal sized dislocations. We observe that the each dislocation acts as a boundary between the short range incommensurate CDW in the  $\text{CuO}_2$  plane, and the O-i rich domains in the spacer layer corresponding with neighbor filamentary high density metallic wires in the  $\text{CuO}_2$  plane. The observed spatial anti-correlation can be exploited in bistable switching devices thanks to the separation between the two phases. The control of dislocations or grain boundaries is therefore an approach to control the boundaries of phase separation between O-i rich metallic filamentary domains and CDW rich domain in cuprate oxide superconductors in the so called superstripes landscape [52].

## Acknowledgments

The work was supported by the Italian Ministry of Education and Research, the Dutch FOM and NWO foundations and

Superstripes Institute. We thank ESRF synchrotron facility for support. In particular we thank Manfred Burghammer and the staff of the ID13 beam-line for experimental help.

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