Charge Stripes Formation
by X-ray Illumination
in High Tc Superconductors

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Abstract. Charge ordering of the doped holes in La$_2$CuO$_4$.1 with Tc=40 K has been investigated. The formation of a 1D anharmonic incommensurate charge density wave (ICDW), i.e., stripes, in the CuO$_2$ plane has been detected by x-ray diffraction using high photon flux at the third generation synchrotron radiation source, Eleftra. We have identified the ICDW peaks that are found to increase by photodoping at low temperature, T<180K, where the lifetime of the photoexcited electron-hole pairs is very long and the mobility of interstitial oxygens is frozen. The 3D long range oxygen ordering is identified and a photo-assisted transition from an incommensurate ordered phase O1, to a second phase O2 is observed at T=300 K.

INTRODUCTION

The coexistence of a one-dimensional (1D) incommensurate charge density wave (ICDW) and itinerant carriers in high Tc superconductors has been found by joint x-ray diffraction and x-ray absorption spectroscopy (1-7) in 1990-1992. This coexistence provides a key to understand the metallic phase showing high Tc superconductivity (HTCS). In fact the ICDW, not driven by nesting vectors on the Fermi surface, is expected to be a characteristic feature of an electron gas close to a metal-insulator transition (MIT) driven by a long range Coulomb interaction Q (i.e., for a non-negligible ratio of Q on the Fermi energy), so called a generalized Wigner MIT (8-14).

Experimental detection of the ICDW driven by the long range Coulomb interaction has been difficult due to the fact that the signal is usually very weak, broad, with a short coherence length. Moreover, in different materials the charge fluctuations are found to have largely different time scales and evolve differently.
with doping. The coexistence of a 1D ICDW and the metallic superconducting phase, first observed in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) (1-7, 15-17), has been confirmed by several experiments in La$_2$CuO$_{4+\delta}$ by nuclear magnetic resonance (NMR) (18), YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) by scanning tunnelling microscopy (STM) (19), La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) by high resolution extended x-ray absorption fine structure (EXAFS) (20), and recently in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ (LNSCO) by neutron diffraction (21) and LSCO by NMR (22). The suppression of spectral weight at the spots of the Fermi surface connected by the second harmonic of the ICDW wavevector has been observed by angle scanning photoemission in Bi2212 (23,24). This result shows that nesting effects are not the origin of the ICDW.

It is known that a metallic phase close to the Wigner metal-to-insulator phase transition, called a polarized electron gas, exhibits an anomalous dielectric function $\varepsilon(\omega,q)$ that gives ICDW, and spin density waves (SDW) (25). In this regime it is possible to have superconducting pairing driven by electronic fluctuations (26). This particular superconducting phase is characterized by the shortest possible Pippard coherence length $\xi_0$, i.e., as short as the average distance between the charges (27).

The critical temperature $T_c$ for an electron gas with Fermi temperature $T_F$, Fermi wavenumber $k_F=2\pi/\lambda_F$, gap energy $\Delta_0$, is given by:

$$T_c = 0.36 T_F / (f \, k_F \, \xi_0)$$

where $f$ is a measure of the deviation from the weak coupling limit $2\Delta_0/K_B T_c = 3.52 f$. For a 2D electron gas $\rho=1/\pi (r_s a_B)^2$, $k_F=\sqrt{2}/(r_s a_B)$ and $E_F(Ry) = 2/(m^* r_s^2)$. The coherence length $\xi_0$ of the superconducting phase of a polarized electron gas, where pairing is mediated by charge fluctuations, i.e., with $\varepsilon(0,q)\to0$, is given by $\xi_0=2r_s a_B$ (27). Therefore the critical temperature is given by:

$$T_c (K) = (35440.8/f) \rho/m^*$$

where $\rho$ is measured in $\text{Å}^{-2}$, and $m^*$ is the effective mass (8,12). Thus in this limit the critical temperature depends only on the ratio $\rho/m^*$.

The discovery of Uemura et al. (28) and Keller et al. (29) that $T_c$ is proportional to $\rho/m^*$ and that of Bianconi et al. (1-6) that 1D ICDW coexists with superconductivity have been interpreted as a direct experimental evidence that the 2D electron gas in the HTCS is close to an MIT driven by the long range Coulomb interaction at the second Phase Separation workshop at Cottbus in Sept. 1993 (8). It was proposed (9-14) that the pairing mechanism active in the high temperature superconductors was mediated by charge fluctuations in a polarized electron gas. The particular generalized Wigner MIT was described as driven by both electronic correlations (the enhanced electron effective mass resulting by doping an Hubbard insulator is estimated by the slave boson approximation) and polaronic electron lattice interactions (the enhanced electron effective mass is estimated in the polaronic weak coupling limit). The observed Wigner MIT was found to be not far from a critical point, since we observed the coexistence of a 1D-ICDW and superconductivity i.e., a so called striped phase. The universal curve of the critical temperature as a function of doping $T_c(\delta)$ calculated for the particular striped phase determined in the experiments considering a pairing mechanisms mediated by charge fluctuations was found to be in agreement with experimental data (12).
The coexistence of the 1D ICDW and the metallic superconducting phase was first seen in 1990 (1) and characterized in the following two years (2-4). In 1994 and 1995 Löw et al. (30) and C., Castellani et al. (31) included the long range Coulomb interaction $Q$ as an intrinsic property of the metallic phase of cuprate superconductors, i.e., a 2D electron gas with a non negligible ratio $Q/E_F$. Both theoretical papers show that the effect of introducing $Q$ in a correlated electron gas is to trigger 1D ICDW with finite wavevector determined by the intrinsic charge density fluctuations, in agreement with the experimental findings (1-6).

![Diagram](image)

**FIGURE 1.** Pictorial view of the $La_2CuO_4+δ$ crystal with interstitial oxygens (black circles) between the LaO layers and photoinduced electron (in LaO block layers) and hole (in the CuO$_2$ plane) pairs. The charge ordering in the CuO$_2$ plane, i.e., the 1D ICDW, is indicated by stripes of larger and lower charge density.

The coexistence of charge ordering, ICDW, and superconductivity in the CuO$_2$ planes could suppress the critical temperature. In fact the Fermi surface is broken by the ICDW, with the formation of missing points, due to the coupling of electrons with the wavevector of the ICDW. This effect generally induces a decrease of the density of states at $E_F$ and a suppression of the critical temperature. It was shown that for particular values of the chemical potential and the shape of the anharmonic 1D-ICDW as that found experimentally in cuprates at optimum doping (see Fig. 1), it is
possible to amplify the critical temperature. The process to amplify the critical temperature has been disclosed in a patent, with priority date 7 Dec. 1993, (32) and following papers (33-37). The 1D ICDW modulation forms a superlattice of quantum stripes as shown in Fig. 1 and the chemical potential is tuned at a shape resonance of the superlattice. Under this resonance condition a large amplification of the critical temperature is obtained (33-37).

The stripes scenario described above “charges that move freely mainly in one direction, like the water running in grooves of a corrugated iron foil”, as introduced for the first time in 1992 (3), has been followed by other models for the striped phases considering the stripes formed by doped charges in presence of antiferromagnetic correlations. Theoretical models and experiments on stripes have discussed at the first and second international conferences on “Stripes and High Tc superconductivity” held in Rome in 1996 (38) and 1998 (39). Recently experimental research in HTCS has been focused to the detection of charge stripes by novel methods (15-24).

In this work we have explored a new experimental approach to identify the ICDW modulation associated with doped charges using x-ray diffraction that is a direct probing to the charge fluctuations associated with the 1D-ICDW. The idea is based on the use of the high intensity x-ray flux, available at the new third generation synchrotron radiation x-ray sources, to create a relevant number of photodoped holes at low temperature in a surface layer of thickness H, determined by the x-ray penetration depth, and to probe the charge ordering in the same slab by x-ray diffuse scattering using a fast 2D detection. Photodoping of cuprate superconductors using a high laser light photon flux has been shown to be an effective experimental way to promote persistent photoconductivity and the insulator to metal transition (40-42). In fact the photons, with a threshold energy of about 2 eV, create electron-hole pairs with a long life time at temperature lower than 200 K. The electrons are ejected from the CuO2 plane, leaving an itinerant hole, to the block layers as shown in Fig. 1, and in La2CuO4 is

$$(La_{2}O_{2})^{++}(CuO_{2})^{--} + h\nu \rightarrow (La_{2}O_{2})^{(2-y)}(CuO_{2})^{(2-y)}.$$  

Photodoping by using x-rays has allowed us, for the first time, to add y itinerant holes in the CuO2 plane and y electrons in the LaO planes, and to probe their ordering by x-ray diffraction.

We have focused our interest to the superconducting La2CuO4+δ system (43-52) where the metallic stripe phase coexists with superconductivity (19, 53-58). The interstitial oxygen ions enter between two LaO layers of La2CuO4+δ (49) shown in Fig. 1, and they have a high mobility for temperatures larger than about 200 K (59). The relation between the oxygen doping and the actual number of holes per Cu ions is object of discussion since the samples are not homogenous and a large part of the doped holes are localized (60-62). A phase separation below T*ps=250 K into an antiferromagnetic phase with oxygen content δ=0.01 and a first superconducting phase with δ1=0.055 has been found. In the superconducting and metallic phase with Tc~31 K a diffuse x-ray scattering peak associated with modulated charge and tilts of the CuO6 octahedra has been detected with wavevector qcdw=0.09 a*+0.153 c* typical of diagonal charge stripes in the CuO2 plane and a stage 6 in the c axis direction (55). The onset temperature for the staging is 250 K, while the ordering temperature TCO for the 1D charge stripes is 180 K. This sample shows the characteristic four diffuse inelastic incommensurate magnetic scattering peaks of the
vertical and horizontal spin density waves as in other cuprate superconductors with $q_{sdw}=\pm 0.105a_1$ and $q_{sdw}=\pm 0.105b_1$ (63) below 70 K. The spin ordering at the higher oxygen concentration, where stages 4, 3 and 2 appear, has been recently observed: the coexistence of inelastic diffuse incommensurate peaks below 70 K and elastic sharp peaks below $T_c=40$ K has been detected (64).

In this work we show two coexisting modulations associated with charge ordering and oxygen ordering in a sample with $\delta=0.1$ ($T_c=40$ K). We observe first a 3D long range oxygen ordering as in $\text{La}_2\text{NiO}_4$+8 for $\delta>0.125$ (65), and a diffuse, short range charge ordering of diagonal stripes with a wavevector as in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ at optimum doping. We discuss the relation between the charge stripes observed in this work with a recent magnetic scattering experiment on a similar crystal. (64).

**EXPERIMENTAL**

The single crystal of $\text{La}_2\text{CuO}_{4.1}$ was grown first as $\text{La}_2\text{CuO}_4$ by flux method and then doped by electrochemical oxidation (47,48). The measurements were made on a crystal of size 3x2x0.5 mm$^3$ showing a sharp superconducting transition at $T_c=40$ K as measured by surface resistivity in the radiofrequency region. The temperature dependent diffraction data were collected on the crystallography beamline at the Elettra storage ring. The X-ray beam emitted by the wiggler source on the Elettra 2 GeV electron storage ring at Trieste, was monochromatized by a Si(111) double crystal monochromator, and focused on the sample. The temperature of the crystal was monitored with an accuracy of $\pm 1$ K.

We have collected the data in the K geometry, with a photon energy of 12.4 KeV, wavelength $\lambda=1$ Å, using an imaging plate as a 2D detector. The sample oscillation around the b axis was in a range $0<\phi<30^\circ$, where $\phi$ is the angle between the direction of the photon beam and the a axis. We have investigated a portion of the reciprocal space up to 0.6 Å$^{-1}$ momentum transfer i.e., recording the diffraction spots up to the maximum indexes 3, 3, 19 in the $a^*$, $b^*$, $c^*$ direction respectively. Using the high flux X-ray beam available at the third generation synchrotron radiation sources with a maximum flux of $1.6\times10^{12}$ photons/(sec.mm$^2$), and photon energy of 12.4 KeV, we have illuminated the sample with a maximum power of $2\times10^{16}$ eV/(sec.mm$^2$).

The surface density of Cu ions in a surface slab of thickness 1.5 µm, determined by the X-ray penetration depth, is $1.5\times10^{16}$ Cu/mm$^2$. Considering that the energy required to create an electron-hole pair in the cuprates is 2 eV and taking into account an efficiency for quantum conversion of the order of $10^4$, $10^5$, we can create a detectable number of photo-doped holes as was obtained before by laser irradiation (41,42) and to observe ordering of the mobile photo-doped holes and photo-assisted oxygen ordering (41) driven by photo-induced oxygen diffusion (42).

**RESULTS AND DISCUSSION**

The orthorhombic lattice parameters of our crystal are $a=5.351$ Å, $b=5.418$ Å, $c=13.171$ Å. Thanks to synchrotron radiation it has been possible to record a large number of weak superstructure spots around the main peaks of the average structure. The indexing of the superstructure has been conducted taking into account the
twinning of the crystal and coexistence of 3 incommensurate modulations (Fig. 2). The first two superstructures are characterized by 3D ordering and narrow, resolution limited, diffraction peaks.

![Graph showing intensity vs. k (r.l.u.) with peaks labeled before and after illumination.]

**FIGURE 2.** Scans along the \( Q = (0, k, 6+0.29) \) due to the diffuse scattering peaks of stage 3.5 superstructure (3), squares, and along the \( Q = (0, k, 6+0.5) \) squares due to the superstructure (2) and (1) before and after illumination at \( T = 300 \)K.

\[ q_1 = 0.049 (\pm 0.0014) \, a^*, \, 0.268 (\pm 0.0014) \, b^*, \, 0.490 (\pm 0.0039) \, c^* \]

\[ q_2 = 0.089 (\pm 0.0031) \, a^*, \, 0.244 (\pm 0.0024) \, b^*, \, 0.495 (\pm 0.0046) \, c^* \]

that coexist with a pattern of diffuse spots due to a third superstructure, with a coherence length of about 350 Å.

\[ q_3 = 0.2080 (\pm 0.0016) \, b^*, \, 0.290 (\pm 0.0055) \, c^* \]

The modulations can be classified according to the different modulation along the \( c \) axis. The wavevectors \( q_1 \) and \( q_2 \) are associated with two phases, namely O1 and O2, and classified as stage 2 oxygen ordered phases.

The third wavevector \( q_3 \) is associated to in plane charge ordering with a period of 3.5 \( c \) in the axial direction. The in plane modulation along the \( b \)-axis of the superstructure \( q_3 \) is the same to the one found in Bi2212 and characterized by diagonal stripes with wavevector of 0.21\( b^* \).

We have investigated temperature dependence of the superstructures in the region around 100-300K and explored the effect of illumination dose. The charge ordering, or stripe formation, is expected in the range 100-180K. In fact in this
temperature range the polaron formation has been observed in this system by EXAFS 
(56,57). On the contrary oxygen ordering, such as the stage formation, is expected to 
be in the range 300-200K where the mobility of doped oxygen ions is high.

![Graph showing the intensity of peaks (1), (2), and (3) at T=300K.](image)

**FIGURE 3.** Effect of the photo illumination on the intensity of the peaks (1), (2), and (3) at T=300K. We have used a flux of $4 \times 10^11$ photons/sec. Evidence for photo-assisted phase transition from the coexisting 3D oxygen ordered phases O1 and O2 to a the phase O2.

At room temperature we observe two coexisting phases O2 and O1. The larger probability of the phase O1 (60%) indicates that the free energy of the phase O1 at room temperature is larger than that of the phase O2. The free energy for the long range oxygen ordering is determined by both elastic crystalline strains and charge interactions therefore it can change by decreasing the temperature. Under x-ray illumination we have observed a photon assisted phase transition from the phase O1 to the phase O2. We observe a disappearance of the phase O1 under illumination, while the superstructure (3) remains nearly constant (Fig. 3).

The photo-induced oxygen diffusion under the local electric field suppresses the O1 phase with an increase of the O2 phase, while their sum remains constant. Since the free energy of the phase O1 is lower we observe a slow decay of the phase O2 towards the phase O1 with a decay rate decreasing with the temperature, going from 300 K to 240 K, as expected for a temperature activated process.

The kinetics of the photo-assisted oxygen ordering in the range $180 < T < 300 K$ under a photon flux $\phi$ from the ordered phase O1 to the phase O2 is given by

$$\frac{\partial O1}{\partial t} = -k_1 O1 + k_2 O2$$
where $k_i$ is the photo-assisted ordering rate under extended illumination, that is proportional to the photon flux and $k_d(1)$ is the rate of the decay of the ordered phase O2 toward the O1 phase.

**FIGURE 4.** Effect of the x-ray illumination on the intensity of the charge ordering modulation (3) by photo doping at T=100K, while the integrated intensity of the peaks (3) increases the peaks of the 3D oxygen ordering superstructure (2) remains constant.

The sum $O1(t)+O2(t)$ remains constant, the probability of the two phases are $P2=O2/(O2+O1)$ and $P1 = 1- P2$. If we assume that $k_i$ and $k_d$ independent on the populations of the two phases $O1(t)$ and $O2(t)$, we can easily integrate the equation

$$\frac{dP_i}{dt} = -P_i(k_i + k_d) + k_d ; \ P_i(t) = \frac{k_d + k_i e^{-(k_i + k_d)t}}{k_i + k_d}$$

The probability at the saturation for $t \to \infty$, is a measure of the ratio of the two rates $\frac{k_d}{k_i} = \frac{P_i(\infty)}{1 - P_i(\infty)}$. The data in Fig. 3 show the photo-assisted phase transition at room temperature as a function of the x-ray dose, $D = \phi t$ where $\phi$ is the photon flux and $t$ the time. The fit provides a measure of the dose $D^* = 1.9 \times 10^{15}$ photons/mm$^2$, i.e., 0.12 photons per Cu ion, corresponding to an energy density $E^* = 2.3 \times 10^{21}$ eV/cm$^2$.

From these data we have found a lifetime, $1/k_d = 1.1 \times 10^4$ sec for the photo-induced phase O2 during the illumination at 300K. Nevertheless, the assumption that $k_d$ is independent on the population O2(t) has to be considered only as a first approximation since further data show that $1/k_d$ increases with the population of this phase. In fact when the transition is completed the lifetime of the phase O2 becomes
2.5 $10^4$ sec. The lifetime of the phase O2 becomes much longer below 250 K, where it seems to be the stable phase. This result can shed light on many reports of an increase of the superconducting critical temperature by annealing around 180-200 K in oxygen doped La$_2$CuO$_4$.

The time scale of this metastable phase above 240 K is of the same order of magnitude as the persistent photoinduced conductivity observed in YBa$_2$CuO$_4$ samples (41,42) under continuous laser illumination. Here we would like to remark that this phase transition induced by the polarized synchrotron radiation x-rays illumination is similar to the alignment of nematic liquid crystals obtained by polarized laser light (66). Therefore we describe this phenomenon as a photo-assisted oxygen ordering (41); in fact this process is possible only at high temperature where the oxygen ions are mobile (59).

![Figure 5](image)

**FIGURE 5.** Effect of the temperature on the intensity of the ordered photo-doped charges with wavevector q$_3$. The experiment shows the increase of the intensity of the diffraction peaks (3) by cooling the sample under a continuous photon flux. A crossover from 210 K to 140 K around the characteristic temperature of $T_{co}=180$ K for the ordering of photodoped charges is found.

At low temperature, $T=100$K, we have studied the effect of charge ordering without oxygen motion. Indeed we have observed that below 170K, when the oxygen ions are not mobile the x-ray illumination has no effect on the 3D oxygen ordered phase O2 as shown in Fig. 4. We have observed an increase of the charge modulation (3), indicated by the increase of the intensity of diffraction satellites due to the short range, diffuse, superstructure q$_3$ that is shown in Fig. 4. The data have been collected with photon flux of 2.4 $10^{11}$ photons/sec and the characteristic dose for the increase of the q$_3$ modulation is $D^*=3.3$ $10^{14}$ photons/mm$^2$.

The temperature dependence of this effect is shown in Fig. 5. We have plotted the variation of the diffraction intensity due to ordered photo-induced charge stripes.

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formed under continuous illumination. This experiment provides direct evidence that, below 180K, the photo-induced electron hole pairs give an increase of the total diffraction intensity, i.e., the photo-induced holes get ordered, with the wavevector \( q_3 \). Therefore \( q_3 \) can be assigned to the charge ordering. It is relevant to mention that this wavevector has the same magnitude and direction as in Bi2212 at optimum doping. Thus the results show a similarity between the superlattice of stripes in Bi2212 and in oxygen doped La2CuO4. This assignment for the modulation \( q_3 \) is also supported by the temperature dependence of the intensity of the peaks as a function of temperature under a high x-ray flux shown in Fig. 5.

![Diagram](image)

**FIGURE 6.** The projection on the ab plane of the wavevector of the short range charge ordering, superstructure (3), determined by x-ray diffraction, compared with the short range inelastic magnetic diffraction wavevector determined in ref. 64 below 70 K (panel a) and the ab projection of the wavevector of the 3D long range oxygen order modulation (2) compared with the elastic magnetic scattering wavevectors detected below 40 K (64).

In conclusion this work provides a direct measure of the stripe charge ordering in an optimally doped superconductor. We show that there is a universal charge ordering wavevector at the optimum doping in cuprate superconductors related with the characteristic density of doped holes at the optimum doping. Also, we shown that the charge stripes are diagonal at optimum doping. The dynamic and static magnetic scattering on an oxygen doped crystal, very similar to the sample studied here, with \( T_C = 40 \) K and with both stage 2 and stage 3 modulations, has been studied recently by neutron scattering by Lee et al. (64). We have compared in Fig. 6 the results of their work with the charge modulation vector determined in this work. The vertical and horizontal dynamic spin modulations indicated by the inelastic diffuse magnetic scattering peaks appearing below 70K are associated with the 1D charge ordering.
wavevector, i.e., the wavevector $q_3$ of the 1D ICDW determined by the long range Coulomb interaction in the 2D metallic and superconducting phase, shown in panel (a) of Fig. 6. The magnetic and charge modulation wavevectors are not parallel, in fact the 4 magnetic peaks are at 45 degree from the 1D charge modulation $q_3$. The long range static incommensurate magnetic order observed below $T_c$ is associated with long range oxygen ordering with wavevector $q_2$ in panel (b) of Fig. 6.

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