Nematicity and Charge Order in Superoxygenated $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$

Zhiwei Zhang, R. Sutarto, F. He, F. C. Chou, L. Udby, S. L. Holm, Z. H. Zhu, W. A. Hines, J. I. Budnick, and B. O. Wells

Phys. Rev. Lett. 121, 067602 — Published 8 August 2018

DOI: 10.1103/PhysRevLett.121.067602
On Nematicity and Charge Order in Superoxygenated La$_{2-x}$Sr$_x$CuO$_{4+y}$

Zhiwei Zhang,$^{1,}$ * R. Sutarto,$^2$ F. He,$^2$ F. C. Chou,$^3$ L. Udby,$^4$ S. L. Holm,$^4$ Z. H. Zhu,$^5$ W. A. Hines,$^1$ J. I. Budnick,$^1$ and B. O. Wells$^1$

$^1$Department of Physics, University of Connecticut, Storrs CT 06269, USA
$^2$Canadian Light Source, Saskatoon, Saskatchewan S7N 2V3, Canada
$^3$Center for Condensed Matter Sciences, National Taiwan University, Taipei 10670, Taiwan
$^4$X-ray and Neutron Science, Niels Bohr Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark
$^5$Department of Physics, Massachusetts Institute of Technology, Cambridge MA 02139, USA

(Dated: July 19, 2018)

In this paper we report a resonant x-ray scattering measurement of stripe-like charge order in the 1/8th doped component of electronically phase separated, orthorhombic La$_2$CuO$_{4+y}$. This observation is coupled to the absence of any resonant (001) peak, which at different resonant energies has been identified with the presence of LTT-like structural tilt patterns or nematicity in the CuO planes. Thus we provide evidence that structural pinning is not necessary for the formation of static charge stripes and that the relationship between charge nematicity and stripes may not be simple.

There remain several critical issues concerning the phenomenology of charge order and the electronic phases diagrams of cuprate superconductors. The advent of powerful resonant scattering techniques has allowed for the detection of charge order (CO) in many cuprate materials. [1–7] In 214 cuprates, an interwoven concomitant charge and spin stripe-like order has been known for over two decades, [8, 9] but was originally only reported in samples with the low temperature tetragonal (LTT, $P_{4_2/1ncm}$) [3, 10] or low temperature less orthorhombic structure (LTLO) [11]. More recently, CO was detected in some 214 cuprates with low-temperature orthorhombic structure (LTO, $Bmab$). However, these works remain unclear whether static charge stripe order can exist without pinning by local structural motifs. Charge order, and its associated level of quenched disorder, is a central focus of many theories of superconductivity, so it is critical to understand the circumstances in which stripe order appears. [12–14]

A related topic is the extent to which charge stripe order is identified with an electronic nematic state: an orientational ordering of the conduction electrons that breaks the symmetry of the lattice. [15] While the presence of electronic nematic order is now well accepted in the Fe-based superconductors, [16] in cuprates such order is expected to alternate direction layer by layer making it difficult to measure by transport. A recent manuscript reports a clean measure of nematic order in 214 cuprates using resonant scattering: the detection of the nominally disallowed (001) peak under resonance at energies associated with in-plane Cu-O states. [17] Whether this interpretation of the resonant (001) holds generally is not yet known.

A unique material system that should be particularly well suited to studying charge and spin order associated with the 1/8th doped phases is superoxygenated La$_{2-x}$Sr$_x$CuO$_{4+y}$, i.e. La$_2$CuO$_4$ co-doped with Sr on La sites and interstitial oxygen. As shown in Fig. 1A, this system exhibits inherent electronic phase separation, with large regions of the sample favoring the 1/8th doped magnetically striped state and other regions the optimally doped superconductor. Given the current understanding of CO, the self-segregated 1/8th doped phase should be a clean example of the CO material. Indeed, neutron [18] and μSR [19] studies have shown that the magnetic state is very well ordered despite the fact that the compound is LTO, which does not have any structural elements that would obviously favor stripes. Here we report the discovery of charge order using RXS in a sample of LCO+O with a total hole doping level near 1/8th. In this same sample, we do not detect a resonant peak associated with LTT or LTLO symmetry; positive evidence that the sample has no substantial regions with LTT-like tilts. This raises the prospect of having stripe-like CO without nematic orientational order, a combination that is difficult to reconcile.

This Letter focuses on the data from two crystals. Charge order peaks appear in a flux grown La$_2$CuO$_4$ sample oxidized for over 80 days (LCO+O) using a wet electrochemical method. The other cuprate (LSCO+O) was grown using the traveling solvent floating zone technique and oxidized for approximately a year. This sample was co-doped with Sr (6%) and O. Both samples were superconductors with $T_c = 40$ K and $\Delta T_c \approx 7$ K in field-cooled Meissner transition (10% to 90% of saturation). The LCO+O was cleaved in air then immediately transferred to vacuum and cooled to 20 K whereas the LSCO+O was cleaved at low temperature in vacuum.

A critical issue for the presence of charge and spin order is the local hole density. Knowing the detailed oxygen concentration is difficult without performing destructive testing such as thermal gravimetric analysis. [19] More importantly, for a near-surface techniques such as RXS, the region sampled may not have the same oxygen concentration as the bulk. The best measure of the local doping level is the O K-edge absorption spectrum
FIG. 1. (a) Phase diagram for superoxygenated lanthanum cuprates. The doping levels for the LCO+O and LSCO+O samples are indicated by the purple diamond and the cyan circle, respectively. (b)-(c) Fitting profiles for the TEY of the O-XAS for LCO+O and LSCO+O. The insets are the pre-edge peaks MCP and UHB for the two samples obtained by subtracting main edge absorption from the raw data.

measured at the same time as the scattering. We use the total electron yield (TEY) measure, as it probes a near-surface region (tens of nanometers) safely within the range of resonant scattering. There are two pre-peaks to the main O K edge, the first identified as the mobile carrier peak (MCP) and the second as the upper Hubbard band (UHB). It has been shown that with hole doping, the MCP grows in intensity while the UHB is reduced. The ratio of the two is a measure of the hole concentration in the region sampled. Fig. 1B(C) shows the oxygen absorption for both samples measured in the TEY. The MCP and UHB peaks are at \( \sim 528 \) and \( \sim 531 \) eV, followed by the main part of the K edge above 532 eV. By comparing the shapes of the whole spectra to that presented by Chen et al.\[20\], we found that the doping levels for our LCO+O and LSCO+O samples are 0.127 \pm 0.005 and 0.161 \pm 0.015, respectively. \[21\]

In Fig. 3 we show the temperature dependence of the CO peak. Fig. 3A shows the background-subtracted CO peak at 30 K and 100 K while Fig. 3B shows the full temperature dependence of the peak intensity and width taken from fitting the peaks. It is clear that the transition temperature of CO is \( \sim 50 \)K. Fig. S2 in Ref. [21] shows the complete set of \( H \) scans at different temperatures. The peak width remains constant below the transition temperature while the intensity grows like an order parameter as the sample is cooled. At 20 K the peak width corresponds to a correlation length of 60\( \AA \) (\( = 1/H\text{FWHM} \)), 5 times shorter than magnetic correlation length reported in Ref. [18]. Differently than seen in most cuprates, the intensity of the CO peak does not drop at the superconducting transition temperature, as the competition between superconductivity and charge order plays out differently in these samples. In YBCO, that competition also appears under a magnetic field that both suppresses superconductivity and enhances the CO state.\[25, 26\] However, in the superoxygenated compounds, the competition between the superconducting and magnetic regions has already played out in electronic phase separation. Since the superconducting and charge ordered regions are already spatially separated, there are no further effects from this competition.

The parameters of the CO in LCO+O appear roughly as one would expect assuming both the ubiquity of stripe-like charge order in 214 cuprates and that almost all of
The LCO+O sample is separated into the 1/8th doped phase. The correlation length of 60 Å is smaller than in similar samples that show similar resolution limited magnetic neutron scattering peaks. The ordering temperatures for both charge and spin order are remarkably similar to that found in 1/8th doped La$_{1.875}$Ba$_{0.125}$CuO$_4$, 40 K for spin order and 55 K for charge order. The latter is surprising since the transition coincides with LTO to LTT transition, and this transition is assumed to favor and stabilize charge order.[27] There is no such structural transition in the superoxygenated LCO+O, yet the transitions occur at the same temperature. As discussed below, there is also evidence that there is not an appreciable region with LTO-like tilts even at grain boundaries. Thus the charge order appears inherently stable and the energetics for charge order at 1/8th doping do not strongly depend upon the structural phase.

Some time ago it was shown that in the presence of the type of CuO$_6$ octahedral tilts that characterize the LTT and LTLO phases, an electronic ordering in the hybridized states between apical O and La makes the nominally disallowed (001) peak appear on resonance.[28] As described by Bozin et al., the LTT and LTLO tilts are characterized by a local symmetry where the Cu-O bond directions form “orthogonally inequivalent” structures, and thus support charge stripe formation along the Cu-O bonds.[11] This led to speculation that the appearance of weak charge order peaks in “orthogonally equivalent” La$_{1.875}$Sr$_{0.125}$CuO$_4$ (LSCO) may arise from twin domain boundaries with LTT-like tilts. More recently, an additional resonant energy profile was found for the (001) peak that had a temperature profile associated with charge ordering.[17] Thus, it is important to investigate any resonant appearance of an (001) peak.

A possible complication in measuring the (001) peak especially near O K edges is higher order light leading to the (002) reflection at the same spectrometer position. However, a constant-$Q$ energy scan allows us to separate the two contributions as there is no possible resonance of the (002) peak at $\lambda/2$ in the region where $\lambda$ is near the O K edges. We find that our sample with charge order has no measurable resonant (001) peak on O K, Cu L, or La M edges. However, the LSCO+O sample with higher hole concentration and no charge order does have a resonant (001) reflection near O K edge which is robust up to at least 70 K, well above the transition temperature for CO in LCO+O. In Fig. 4A, the energy dependence of the (001) reflection is plotted in the region of the O K edge. The data plotted is an energy scan with constant $Q = (001)$ and the background was subtracted from a subsequent scan with the detector out of the scattering plane. This leaves intensity from both the (001) peak and the (002) with higher order light, but only the former will have a resonant profile. For reference, the XAS profile measured with TEY is also plotted in the figure. The resonant (001) peak profile in $Q$ can also be extracted, which is shown in Fig. 4B. The (001) peak is about three times broader than the (002) peak (shown in the inset of Fig. 4B), indicating that the resonant (001) peak represents an ordering that extends over a significantly smaller region than the crystalline order itself.

The behavior of the (001) peak in both samples is surprising. The lack of an (001) peak resonant at the Cu and in-plane oxygen state energies differs from the result reported by Achkar et al.[17] where the (001) peak in their samples appears at these resonant energies. This conclusion is drawn from their calculation of the peak structure factor which gives an intensity on resonance proportional to $\eta^2$, with $\eta = f_{aa}(z = 0) - f_{bb}(z = 0.5)$. Invoking the 4$_2$ screw axis symmetry of the LTT structure gives $f_{aa}(z = 0.5) = f_{bb}(z = 0)$. Combining the two results yields $\eta = f_{aa}(z = 0) - f_{bb}(z = 0)$, and thus the peak intensity is given by differences between the electronic states in the two principle in-plane directions. The samples investigated here have a different space group, $Bmnab$ or the LTO structure (Fig. 4C). In this case the $B$ centering leads to the cancellation of the (001) peak off-resonance which is not lifted by the usual consideration of the polarization dependence of the scattering tensor at resonance.[29] However, stripe-like charge order itself is not consistent with the $Bmnab$ structure as noted by Bozin et al.[11] Thus charge ordering itself must be a symmetry lowering transition, which one might expect would also allow a “nematic” (001) peak. Thus, the lack of such a peak must mean one of the following possibilities holds.

One possibility is that in our charge-ordered sample $f_{aa}(z = 0) = f_{bb}(z = 0)$, and thus $\eta = 0$. This condition is incompatible with charge stripes as usually conceived, but would allow for the sort of checkerboard pattern that Christensen et al. found to be a compatible spin structure for their set of neutron magnetic peaks.[30]

The other possibility is that the symmetry condition $f_{aa}(z = 0.5) = f_{bb}(z = 0)$ does not hold in our sample. This would likely imply the presence of spin stripes that do not alternate direction ($\mathbf{a}$ vs. $\mathbf{b}$) in adjacent CuO$_2$ layers. Neutron scattering study of the spin order in a set...
of superoxyg envated samples found equal intensities for all four of the set of incommensurate spin order peaks, representing equal populations of stripes along a and along b.\[18\] That suggests some ordering of stripe orientation to enforce equal populations. In addition, in this work the charge order peak is found to be most prominent near $L = 1.5$. Half integer values for CO peaks imply a periodicity of four Cu-O planes along c. For other 214 compounds this periodicity was interpreted as representing both stripes that alternate in direction in adjacent layers and those stripes along the same direction offset to lower the Coulomb energy.\[31, 32\]

While there is no detectable (001) peak in the LCO+O sample with charge order, we do detect the (001) peak on resonance in the more heavily doped LSCO+O sample. This observation gives confidence that the null result in the charge-ordered sample is robust, but in itself is a surprising observation. The energy dependence for the (001) peak is very much like that previously published in La$_{1.65}$Eu$_{0.15}$CuO$_4$, which were associated with LTT-like tilts.\[28\] We speculate this might have some association with the remnants of staging. Samples with $x \leq 0.04$ exhibit clear staging that involves anti-phase domain boundaries of the CuO$_6$ octahedra along c.\[33\] Ray et al. found that La$_{1.93}$Sr$_{0.065}$CuO$_{4+y}$ samples do not show clear staging peaks but have significantly broader tails on the peaks associated with the CuO$_6$ tilt patterns.\[34\] The broadened tails may be an indication of tilts around an axis other than the orthorhombic (010), a partial LTT or LTLO ordering. It is noted above that the LTT and LTLO tilts may pin charge stripes. While the resonant dependence of the (001) peak measured in LSCO+O is positive evidence for the presence of such tilts, apparently this is not sufficient to stabilize charge stripes in this sample that primarily consists of regions of optimally doped superconductor. In the electronically phase separated superoxyg enated 214 cuprates, one doped only with oxygen leading to a hole concentration near 1/8th and the other co-doped with Sr and oxygen with a hole concentration near 0.16. Charge order, found in the 1/8th doped sample, has a transition temperature of 50 K, similar to several other 214 cuprates. We note that spins in these samples order near 40 K, which appears to be near-universal.\[18, 27, 35–37\] In most 214 compounds, charge order was found in LTT or LTLO phase, or even at twin domain boundaries of LTT-like tilts in LSCO compounds.\[6, 38, 39\] In our sample, while we cannot rule out that the charge order is confined to the near surface or domain walls, we can rule out LTT-like tilts by the absence of a resonant (001) peak at the apical oxygen or La edges. Thus while stripe-like charge and spin order remains particular to the 214-type cuprates, it may not be closely tied to symmetry breaking structural tilt patterns as previously believed.

We acknowledge helpful conversations with Ch. Niedermayer and M. H"ucker. We thank Y. Zhou, D. Paley and Y. Lin for their help with crystal orientations. The measurements were performed at the Resonant Elastic and Inelastic X-ray Scattering Beamline of the Canadian Light Source, which is supported by the Canada Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research. The sample preparation, data acquisition and data analysis was supported by DOE-BES Contract No. DEFG02-00ER45581.

* zhiwei.zhang@uconn.edu
[1] A. Bianconi, J. Budnick, A. Flank, A. Fontaine, P. Lagarde, A. Marcelli, H. Tolentino, B. Chamberland, C. Michel, B. Raveau, and G. Demazeau, Physics Letters A 127, 285 (1988).
