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

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In this Letter, we report a resonant x-ray scattering measurement of stripelike 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 low-temperature-tetragonal-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.

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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 order has been known for over two decades [8, 9] but was originally reported only in samples with the low-temperature-tetragonal (LTT, $P4_2/nmc$) [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$_4$ codoped with Sr on La sites and interstitial oxygen. As shown in Fig. 1(a), 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 $\mu$SR [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 resonant x-ray scattering (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 stripelike 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 codoped 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%–90% of saturation). The LCO + O was cleaved in air and then immediately transferred to a vacuum and cooled to 20 K, whereas the LSCO + O was cleaved at a low temperature in a 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 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 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 prepeaks 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. Figures 1(b) and 1(c) show 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].

Figure 2(a) shows the region where we expect to find a CO peak at the Cu $L_3$ edge at $T = 20$ K in LCO$+O$. A peak appears on resonance only. No such peak was observed in the more heavily doped LSCO$+O$. The energy profile of the scattering peak closely matches that of the Cu $L_3$ x-ray absorption spectroscopy (XAS) itself, as shown in Fig. 2(b). The red curve is a fit to the data using the energy-shift model [24]. This model postulates that the absorption for the on-stripe and off-stripe Cu atoms differs only by a small energy shift. It appears to fit the CO peak intensity across the Cu $L_3$ edge well. The Cu XAS at 60 K is shown in Fig. S3(a), and the form factors used in the fits are given in Fig. S3(b) in Ref. [21]. At the O $K$ edge, we find only a hint of a CO peak that cannot clearly be detected above the background. The CO resonance on oxygen edges (particularly MCP) is either weak or absent, with details in Ref. [21].

In Fig. 3, we show the temperature dependence of the CO peak. Figure 3(a) shows the background-subtracted CO peak at 30 and 100 K, while Fig. 3(b) 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. Figure 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 Å ($=1/$HWHM), 5 times shorter than the 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 the 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 [31,32]. 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.

![FIG. 1.](image1.png) (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.

![FIG. 2.](image2.png) (a) $H$ scans on and off resonance. The red dashed is the fitted background. (b) Energy dependence of the CO peak intensity at 20 K and calculated energy dependence by the energy-shift model.
The higher-order (002) contamination was subtracted from a measurement off resonance. CuO to that found in temperatures for both charge and spin order are remarkably similar magnetic neutron scattering peaks. The ordering temperature for charge order [25]. There is no such structural LTT transition, and this transition is assumed to favor and spin order and 55 K for charge order. The latter is type of CuO upon the structural phase.

FIG. 4. (a) Energy dependence of the (001) reflection in LSCO colors, respectively. The scales on the two vertical axes are not comparable. (b) L scan of the (001) at the maximum resonance (532 eV). The higher-order (002) contamination was subtracted from a measurement off resonance. (c) CuO tilt patterns for both LTO and LTT structures.
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 $\eta = f_{aa}(z = 0) - f_{bb}(z = 0)$. Invoking the 42 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, Bmab or the LTO structure [Fig. 4(c)]. 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 to the cancellation of the (001) peak off resonance, 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 [34]. 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 (a vs b) in adjacent CuO$_2$ layers. A neutron scattering study of the spin order in a set of superoxygenated 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 [35,36].

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$_{1.65}$EuO$_{0.2}$Sr$_{0.15}$CuO$_4$, which were associated with LTT-like tilts [26]. We speculate that this might have some association with the remnants of staging. Samples with $x \leq 0.04$ exhibit clear staging that involves antiphase domain boundaries of the CuO$_6$ octahedra along e [37]. Ray et al. found that La$_{1.935}$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$_2$ tilt patterns [38]. 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 superoxygenated samples, charge order appears confined to the 1/8th doped regions (as in LCO + O).

In conclusion, we report a RXS study on two superoxygenated 214 cuprates, one doped only with oxygen leading to a hole concentration near 1/8th and the other codoped 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 of the 214 cuprates. We note that spins in these samples order near 40 K, which appears to be near universal [18,25,27–29]. In most of the 214 compounds, charge order was found in the LTT or LTLO phase or even at twin domain boundaries of LTT-like tilts in LSCO compounds [6,30,39]. 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 LTLO-like tilts by the absence of a resonant (001) peak at the apical oxygen or La edges. Thus, while stripelike 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.

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