Chapter 7

Charge character of the static ‘stripe’ phase in La$_{15/8}$Ba$_{1/8}$CuO$_4$

We present a study of the static “stripe” phase in La$_{15/8}$Ba$_{1/8}$CuO$_4$ (LBCO) with resonant soft x-ray scattering (RSXS). The charge scattering exhibits giant resonances at the hole-doped and upper-Hubbard band features below the O K edge. We estimate a peak-to-trough valence amplitude of 0.063 holes and, using an existing model for the stripe form factor$^1$, an integrated area of 0.59 holes under one stripe. The results demonstrate a direct participation of the holes in this phase and are consistent with half-filled stripes.

7.1 Introduction

In two-dimensional Cu-O systems, one of the hotly debated phenomena is related to other possible ground states competing with superconductivity. One of these scenarios involves so called “stripe” phases. The stripe phase was proposed in terms of an electronic liquid-crystal (or phase separation) model [2,3,4,5,6,7]. In this proposal the doped holes are concentrated in “rivers of charge” at domain walls across which a $\pi$-phase shift in the antiferromagnetic spin correlations of the host material is realized. These domain walls form one dimensional stripes which can be insulating [3,4] or conducting [5,6,7] —that is, metallic ‘rivers’ with their own low-energy degrees of freedom. However, in arrays of one-dimensional metals, as occur in materials such as organic conductors [8], interactions between stripes typically drive a transition to an insulating ordered charge-density-wave (CDW) state at low temperatures. Just like the hole crystal in a doped ladder described in chapter 6 the CDW here is also expected as the $4k_F$-CDWs or Wigner Crystal-CDW (WC).
``Stripes'' is a term that is used to describe unidirectional density-wave states, which can involve unidirectional charge modulations (``charge stripes'') or coexisting charge and spin-density order (``spin stripes''). The main experimental evidence for stripes in copper-oxides is neutron scattering from La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ [9] (LNSCO) and La$_{1.875}$Ba$_{0.125}$CuO$_4$ [10] (LBCO). The charge/spin texture in LNSCO and LBCO is visible only in the low temperature tetragonal (LTT) phase, is most stable at $x = 1/8$ and coincides with an anomalous suppression of $T_c$ [see Fig. 7.1.1] [11]. This phase is normally interpreted as “static” stripes which have been pinned by the LTT distortion, rendering the holes immobile. The charge reflections observed with neutron scattering are weak (6.5 times less intense than the magnetic reflections) since neutrons detect only the lattice distortion, estimated to be only $\sim 0.004 \, \text{Å}$ [12]. However one assumes the hole modulation itself is significant. It is important to realize, however, that the spin density wave in elemental Cr also exhibits half-wavelength charge reflections which are weaker by a factor of 4.1 [13] and represent a distortion of similar size [14]. So from the intensity of scattered neutrons alone there is no conspicuous difference between the phenomenon in LNSCO and a simple spin density wave. To determine if the doped holes are actually involved we have studied LBCO with resonant soft x-ray scattering at the OK ($1s \rightarrow 2p$) and Cu$L_{3/2}$ ($2p_{3/2} \rightarrow 3d_{x^2-y^2}$) edges, which are directly sensitive to valence ordering [15,16,17,18,19,20].
Figure 7.1.2. (a) Diagram of the (hk0) zone in reciprocal space. Large filled circles, fundamental Bragg peaks; small filled circles, superlattice peaks of the LTT phase. Open circles and squares, magnetic superlattice peaks from two different domains of the stripe structure; diamonds and triangles, charge-order superlattice peaks from the two stripe domains. Open circles and diamonds (squares and triangles) correspond to the same domain. (b) Model for the stripe order of holes and spins within a CuO2 plane at \(n_h = 1/8\). Only the Cu sites are represented. An arrow indicates the presence of a magnetic moment; shading of arrowheads distinguishes antiphase domains. A filled circle denotes the presence of one dopant-induced hole centered on a Cu site (hole weight is actually on oxygen neighbors). The charge order indicated within the stripes has not been observed, but serves as a reminder that the hole per Cu ratio is 1/2. A uniform hole density along the stripes is assumed in the analysis. (c) Sketch showing relative orientation of stripe patterns in neighboring planes of the LTT phase.

In Fig. 7.1.2 is shown a model of the stripe modulation studied by Tranquada et al., with Neutron scattering on a single crystal La_{1.48}Nd_{0.4}Sr_{0.12}CuO_{4} [9]. At low temperatures, they observed elastic magnetic superlattice peaks of the type \((1/2 \pm \varepsilon, 1/2, 0)\) and charge-order peaks at \((2 \pm 2\varepsilon, 0, 0)\), where \(\varepsilon = 1/n\) [see Fig. 7.1.2(a) and (b)]. After cooling
the crystal through the low-temperature-orthorhombic (LTO) to low-temperature-tetragonal (LTT) phase transition near 70 K, the charge-order peaks appear first at ~60 K, with the magnetic peaks appearing below 50 K. The magnetic peaks increase in intensity by an order of magnitude below 3 K due to magnetic ordering of the Nd spins. The Q dependence of the magnetic scattering indicates that the low-temperature correlation length within the planes is substantial (~170 Å), but only very weak correlations exist between next-nearest-neighbor planes. Correlations between nearest-neighbor layers are frustrated by pinning of the charge stripes to the lattice distortions of the LTT phase [see Fig. 7.1.2 (c)].

7.2 Experimental results and discussions

Single crystals of La$_{2-x}$Ba$_x$CuO$_4$ with $x = 1/8$ were grown by the floating zone method$^{21}$. The sample used in this study had $T_c = 2.5$ K indicating suppressed superconductivity and stabilized spin/charge order. The sample was cleaved in air revealing a pristine surface with (0,0,1) orientation. The absolute sensitivity of the instrument was calibrated 10 eV below the O K edge by measuring the integrated intensity of the (0,0,2) Bragg reflection from a cleaved single crystal of Bi$_2$Sr$_2$CaCu$_2$O$_8$+$\delta$, which has a known structure factor and is accessible near the O K edge. Sample cooling was done with a He flow cryostat connected via Cu braids, providing a base temperature of 18 K. X-ray absorption spectra were measured in situ at the O K edge Cu L$_{3/2}$ edges and found to be consistent with previous studies $^{22}$ [see Fig. 7.2.2]. Here, reciprocal space will be denoted by Miller indices ($H,K,L$), which represent a momentum transfer $Q = (2\pi/a H, 2\pi/b K, 2\pi/c L)$ where \(a = b = 3.788 \text{ Å}, \ c = 13.23 \text{ Å}\). The incident x-ray polarization depends on Q but was approximately 60° from the Cu-O bond for measurements at both edges.

Static “stripe” correlations were detected at the CuL$_{3/2}$ resonance and mapped in the ($H,0,L$) plane, shown in Fig.7.2.1. In agreement with earlier hard x-ray studies $^{23,24}$, the scattering was sharp along $H$ but rod-like along $L$ (correlation lengths $\xi_a = 127 a, \xi_c = 2c$), indicating long-range order in the CuO$_2$ plane but weak coupling between planes. A maximum intensity of 175 Hz on a fluorescence background of 425 Hz was observed at (0.251, 0, 3/2) $^{25}$, the half-integer $L$ indicating that charge order is offset by $2a$ between successive unit cells, presumably to minimize Coulomb repulsion. No scattering could be detected off-resonance above the fluorescence background.
Figure 7.2.1 Reciprocal space map of charge correlations in the \((H,0,L)\) plane. These data were taken with the x-ray energy tuned to the Cu \(L_{3/2}\) (\(2p_{3/2} \rightarrow 3d_{x^2-y^2}\)) resonance. At its maximum the charge scattering is 175 Hz on a fluorescence background of 450 Hz. As \(L\) is decreased the fluorescence intensity also rises as the angle of incidence on the crystal grows, reaching its maximum value at \(L = 1.38\), below which the takeoff angle falls abruptly to zero driving the intensity to zero through sample self-absorption.

In Fig. 7.2.2 we display a “resonance profile”, i.e. the intensity of charge scattering as a function of energy compared to x-ray absorption spectra. For geometric convenience the OK and Cu\(L_{3/2}\) data were taken with \(L = 0.72\) and \(L = 1.47\), respectively. The charge scattering at the Cu\(L_{3/2}\) edge is offset from the absorption maximum by 0.2 eV and likely arises from distortions in the Cu sublattice. The scattering resonates strongly at both the hole-doped peak [22] (~529 eV) and upper Hubbard band (~530.5 eV) feature below the OK edge. This indicates significant participation of the doped holes, despite the weak structural distortion, suggesting a many-body origin to this phase.
Figure 7.2.2 Energy-dependence of the (1/4, 0, L) charge scattering compared to x-ray absorption spectra (XAS). Data were taken in situ in fluorescence yield mode. (a) XAS near the OK edge. Circles, XAS spectrum for E||â. Red circles, intensity of charge scattering at L = 0.72 showing enhancements at the hole-doped peak (~529 eV) and upper Hubbard band (~530.5 eV), demonstrating a significant modulation of the doped hole density. Dashed line, f_0xx(ω) determined from Fig. 7.2.3. The broader energy width of f_0xx compared to the resonant scattering is due to the fact that the full lifetime enters absorption data but only the radiative lifetime enters anomalous x-ray scattering. (b) data near the CuL3 edge for L = 1.47. A slight red shift is seen between the peak in resonant scattering compared to absorption.
Figure 7.2.3 Determining the x-ray form factor, \( f_D^{mn}(\omega) \), for a single doped hole. 

**a**, x-ray absorption spectra for \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) with \( x = 0 \) and \( x = 0.15 \) for \( E||a \), reproduced from Ref. [22]. Spectra were placed on an absolute scale by fitting to tabulated values far from the edge. *Inset*, stripe orbital pattern from the three-band Hubbard calculation in Ref. [1] with “peak” and “trough” locations indicated.

**b**, \( f_D^{xx}(\omega) \) for an \( x \)-oriented hole determined by using the expression

\[
\text{Im}[f_D^{xx}(\omega)] = -\frac{r_e \lambda}{2\pi V_{\text{cell}}} \text{Im} \left[ \sum_i f_i^{mm}(\omega,p) \right]
\]

to construct a 2x2 system of equations, matrix inverting to get \( \text{Im}[f_D^{xx}(\omega)] \), and Kramers-Kroning transforming. \( |f_D^{xx}(\omega)| \) reaches a maximum value of 82 at \( \omega = 528.6 \) eV, where a single hole scatters as strongly as a Pb atom.

Because RSXS directly probes the valence band we can estimate the amplitude of the hole modulation and quantitatively assess the validity of the stripe model. The integrated intensity of Bragg scattering is proportional to the square of a structure factor, \( \rho_{Q}^{mn}(\omega) = \frac{1}{V_{\text{cell}}} \sum f_j^{mm}(\omega) \exp(iQ \cdot r_j) \), where \( V_{\text{cell}} \) is the unit cell volume, \( f_j^{mm}(\omega) \) is the x-ray form factor of atom \( j \) and \( r_j \) its position. \( m \) and \( n \) are incoming and outgoing polarization
indices, respectively. To determine the hole amplitude one must first define the x-ray form factor for a doped hole.

For this purpose we separate the oxygen form factor $f_{O}^{m}(\omega, p) = f_{R}(\omega) + p f_{D}^{m}(\omega)$, where $f_{R}$ is a “raw” component common to all oxygen atoms, i.e. $f_{R} \rightarrow 8$ electrons as $\omega \rightarrow \infty$, and $f_{D}^{m}(\omega)$ describes the polarization-dependent spectral changes with the doped hole density, $p$. $f_{D}^{m}$ has units electrons / hole and can be interpreted as the doped hole form factor. The form factors are related to the absorptive part of the index of refraction by $\text{Im}[n^{m}(\omega; p)] = -r_{e}^{2} / 2 \pi V_{\text{cell}} \text{Im}[\sum_{i} f_{i}^{m}(\omega, p)]$, where $r_{e}$ is the classical electron radius and $\lambda$ is the x-ray wavelength, so may be determined from doping-dependent x-ray absorption spectra. Using this relationship and data from Ref. [12] [Fig. 7.2.3] we extracted the diagonal components $\text{Im}[f_{D}^{m}(\omega)]$ by solving a system of equations at each energy and retrieved the real parts by Kramers-Kronig transform. The off-diagonal components were assumed to be small. For an $x$-oriented hole we find $|f_{D}^{xx}| = 82$ electrons / hole on the resonance maximum, indicating that a doped hole scatters as strongly as a Pb atom.

To relate $f_{D}^{m}(\omega)$ to the scattered intensity a stripe structure factor $\rho_{\text{stripes}}^{m}$ was constructed based on the orbital pattern from a previous three-band Hubbard calculation [1] [Fig. 7.2.3, inset]. This pattern was stacked in alternating fashion as proposed in Ref. [12] and $\rho_{\text{stripes}}^{m}$ computed analytically. Accounting for the incident and scattered polarizations in our geometry we compute a scattering amplitude $|\mathbf{e}^{*} \cdot \rho_{\text{stripes}} \cdot \mathbf{e}_{i}| = (0.00475 \, \text{Å}^{-3}) \, A$, where $A$ is a fit variable which may be interpreted as the number of holes contained in one stripe a single unit cell in length ($A = 0.5$ would be consistent with half-filled stripes).

The integrated intensity of resonant scattering scattering was determined in the ellipsoidal approximation by tuning to the hole-doped peak and carrying out linear scans along three orthogonal directions and taking the product $I = I_{\text{peak}} \times \Delta q_{x} \Delta q_{y} \Delta q_{z}$, where $I_{\text{peak}}$ is the peak count rate in Hz and $\Delta q_{n}$ is the width along direction $n$ (the same measure was used for the calibration measurements on the (0,0,2) reflection from BSCCO). We measured $\Delta q_{x} = 0.0133 \, \text{Å}^{-1}$ and $\Delta q_{y} = 0.0169 \, \text{Å}^{-1}$. The limited $Q$ range of RSXS prevented complete determination of $\Delta q_{z}$ so we use the value from Ref. [10] of $\Delta q_{z} = 0.256 \, \text{Å}^{-1}$, giving $I_{\text{stripes}} = 0.101 \, \text{Hz} / \text{Å}^{3}$. Based on our calibration measurements, accounting for geometric differences in the penetration depths, this translates to $|\mathbf{e}^{*} \cdot \rho_{\text{stripes}} \cdot \mathbf{e}_{i}| = 0.00282 \, \text{Å}^{-3}$ or $A = 0.59$ holes. This is consistent with the wavelength of charge order and the known hole density, and is surprisingly close to the value 0.5 expected for half-filled stripes.
Figure 7.2.4 Temperature dependence of the charge scattering. Charge correlations are visible below the low temperature tetragonal (LTT) phase transition temperature of 60 K. $T_{\text{LTT}}$ is higher than previously reported because $x$ is closer to 1/8. Charge scattering at both edges exhibits the same temperature dependence, suggesting that the holes and lattice order together. The inset is the temperature dependent of the stripe at (red) O $K$ edge and (black) Cu $L$ edge.

The accuracy of this number hinges on the accuracy of the orbital pattern determined in Ref. [1]. A different orbital pattern, for example a “checkerboard” or bond-centered stripe pattern, would result in a slightly different value of $A$. A more experimentally reliable quantity is the peak–trough valence difference [see Fig. 7.2.3] of $(0.161 - 0.0548) \times 0.59 = 0.063$ holes, independent of the model used.

Angular scans through the charge scattering were performed at different temperatures at both the hole-doped peak and Cu$L_{3/2}$ resonances [Fig. 7.2.4] which we take as a measure of the hole modulation and Cu lattice distortion, respectively. Charge correlations were visible below the LTT transition at 60K, which is higher than previously published [10] as the $x$ value for our sample is closer to 1/8 [28]. No difference in
temperature dependence was detected between the two edges, suggesting the holes and lattice order together.

Our study demonstrates that most of the doped holes participate in the static, incommensurate phase in LBCO, despite its weak structural character. This confirms the suspected many-body origin to this phase. Our results support the picture that the 1/8 anomaly in La_{2-x}\text{Ba}_x\text{CuO}_4 occurs because of freezing of carriers into a static lattice rather than simply the magnetic ordering [29]. Our results do not unambiguously determine whether this phase consists of bond- vs. cite-centred stripes, a “checkerboard” Wigner crystal [30], or another Mott-like state, though the measured amplitude of 0.59 holes is in surprisingly good agreement with half-filled stripes. More precise measurements may shed light on this issue. More significant than the hole modulation is the observation of a resonance at the upper Hubbard band at 530.5 eV [Fig. 7.2.2]. This resonance seems to have the opposite phase to that of the O-prepeak. This is exactly what is expected from the models of correlated systems described in [31,32] in which also the spectral weight transfer itself was first predicted. The reason for this behaviour is that the reduction of the Upper Hubbard band intensity with hole doping is entirely due to a spectral weight transfer to the hole doped states and so it will have the opposite phase to the hole doped peak. This observation is in fact a very strong confirmation that the basic models used to describe the hole doped systems is correct. This indicates that the well-known doping-induced spectral weight transfer in the cuprates [22,31,32], in the static stripe phase, actually oscillates in real space with period 4a, indicating an inhomogeneous, many-body state. Finally, we point out that these observations are similar to the “hole crystal” recently observed in Sr_{14-x}\text{Ca}_x\text{Cu}_2\text{O}_4 (see chapter 4 and 6), indicating a close relationship between the two phenomena. The importance of Umklapp processes for the stability of a Wigner crystal on a lattice [33] may explain the stability of this phase at the commensurate doping \(x = 1/8\).
References

[25] Slightly different wave vectors were observed at the OK \((H = 0.245)\) and CuL\_\(3/2\) \((H = 0.251)\) edges due to refraction at the sample surface.


