Chapter 6

Commensuration effects on the Wigner crystallization in the ladders and mechanism of charge density wave in the chains of the doped ladder in $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$

Wigner Crystallization (WC) in the ladders and charge density waves (CDW) in the chains of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ are studied as a function of the number of doped holes per ladder Cu site. We find that the WC in the ladders appears only if it is commensurate to the lattice and appears only for odd number of rungs ($\lambda = 5c_L$ or $3c_L$, not for $4c_L$!). We try to explain the behavior of the ladders with a RVB-type model. The CDW in the chain turns out to be more complicated. It seems that the strong modulation which arises from the atom displacement in the chain is driving the hole modulation in the chain.

6.1. Introduction

Superconductivity (SC) in solids occurs through Cooper pairing between two electrons or two holes with equal but opposite momenta and spin. In conventional superconductors, such as Al or Sn, this is accomplished by the attractive electron-electron interaction due to the exchange of phonons through the electron-phonon interaction, $H_{ep}$ which opens an energy gap in the single particle spectrum allowing current to flow with zero resistance. This superconducting ground state is described by the BCS theory which relates the size of the gap to the transition temperature, $2\Delta = 3.5 \, k_B T_c$.

In materials with reduced dimensionality, such as $\text{NbSe}_3$ or $\text{K}_0.3\text{MoO}_3$, there is a competing instability in the Peierls channel so that the same $H_{ep}$ may cause pairing between an electron and a hole, giving rise to a charge density wave (CDW) [1]. In this case the ground state is insulating but may still be described by the BCS theory with $2\Delta = 3.5 \, k_B T_c$. 
where $2\Delta$ is the insulating CDW gap \cite{1}. The phonon which mediates the pairing in this case is real, rather than virtual as in the case of SC, but the mechanism is similar.

The interaction behind Cooper pairing in high-temperature superconducting copper oxides (HTSCs) is not known. An example of a reduced-dimensional copper-oxide is the two-leg “spin ladder” \cite{2}, which consists of two coupled chains of spin-$1/2$ ions. The doped, two-leg ladder was studied theoretically and predicted to exhibit an electronic CDW or “hole crystal” (HC) ground state \cite{2,3,4,5}.

In Chapter 4, we have discussed our discovery of hole crystallization in the ladders and the charge density wave (CDW) in the chains in the “telephone number” compound on the spin ladder of Sr$_{14}$Cu$_{24}$O$_{41}$ (SCO). The hole crystallization which was predicted by a $t$-$J$ model \cite{6} and also by DMRG calculations \cite{7} is a Wigner-type crystallization (WC). It is very difficult to detect the Wigner crystal with hard x-ray scattering. It is difficult to detect a WC with hard x-ray scattering or non-resonant scattering for the following reasons. First, one needs to measure the structure factor at finite $q$. Second, x-ray scattering is more sensitive to structural distortions in crystals than to the charge modulation itself. The distortion in crystals can occur not only due to the charge modulation but also from other phenomena such as “misfit” between two different layers. SCCO is an adaptive misfit material consisting of ladder and chain subsystems with incompatible periods $c_L/c_c = 10/7$. So it is very difficult to distinguish these two effects only with hard x-ray scattering. X-ray scattering measures the square of the total electron density, $|\rho(q)|^2$, and the density modulation of the Wigner crystal, which arises from a small number of electrons around the Fermi level, is typically less than one electron per large unit cell while the total number of electrons contributing to allowed Bragg peaks is about 6224 (one large unit cell of SCO contains $4\times(14\times38+29\times24+8\times41)$ electrons). So the scattering power of a hole crystal is nominally weaker by $(1/6224)^2 \sim 10^{-8}$ for the case of only one electron contributing to the Bragg peaks. With resonant soft x-ray scattering (RSXS) the Wigner crystallization was observable at resonance and undetectable off-resonance. The presence of superstructure reflections at resonance only drives us to the conclusion that the carriers in copper-oxides do not, or at most weakly couple to the lattice. This is different from a Peierls-type CDW \cite{1} in which the lattice is intrinsic to the modulated state. It is also important to note here that none of the reported charge ordering from hard x-ray or neutron studies \cite{8,9} are observed in resonant x-ray scattering.

In Chapter 5, we proposed a new interpretation of polarization-dependent XAS for Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ (SCCO). Based on our interpretation, the number of holes in the ladders, $n_L$, and number of holes in the chains, $n_c$, are redetermined as a function of $x$ [see Fig. 6.1.1]. For $x = 0$, we have found that 2.81 holes are located in the ladders while 3.19 holes are located in the chains which is very different from the previous interpretations. This hole distribution leads to a simple explanation of the RSXS results. According to models of hole crystallization \cite{7,10}, if we assume that the holes in the ladders are paired as
suggested by DMRG calculations [3] Wigner crystallization in ladders with a wavelength of $\lambda_{WC} = 5.00 \, c_L$, would require $\delta = 0.20$. $\delta$ is defined as the number of doped holes per ladder Cu site. For one large unit cell of ladders, which contains 7 pairs of copper ions, $n_L$ corresponding to $\delta = 1/5$ is equal to 2.8 holes out of 6. Our analysis of the CDW in the chain, for $\lambda_{CDW} = 3.145 \, c_L$ corresponds to 3.2 holes in the chains. All together, the total number of holes for $x = 0$ is 6 which is consistent with the number of holes calculated for charge neutrality. As we can see from Fig. 6.1.1, for $x = 4$, $n_L$ and $n_c$ are estimated to be 3.3 and 2.7, respectively. The WC in ladders with a wavelength of $\lambda_{WC} = 4.00 \, c_L$, would require $\delta = 1/4$. The $n_L$ corresponding to $\delta = 0.25$ is equal to 3.5 holes in the ladders. The wavelength of the “$4k_F$” CDW in the chains with 2.7 holes is 2.70 $c_c$. For high Ca content ($x = 11$), the estimation of $n_L$ and $n_c$ is 4.4 and 1.6, respectively. The WC in ladders with a wavelength of $\lambda_{WC} = 3.00 \, c_L$, would require $\delta = 1/3$. The $n_L$ corresponding to $\delta = 1/3$ is equal to 4.66 holes in the ladders and the wavelength of a $4k_F$ CDW on the chains with 1.6 holes is 1.60 $c_c$.

Figure 6.1.1 The estimated number of holes in the ladders ($n_L$) and chains ($n_c$). Filled- and open-circles are $n_L$ and $n_c$, respectively. The dashed theoretical lines indicate the required number of holes in the ladders for a Wigner Crystal with wavelength $\lambda_{WC} = 3c_L$, $4c_L$ and $5c_L$.

To gain a new perspective on the interactions among carriers in copper-oxides we have used resonant soft x-ray scattering (RSXS) to probe this hole crystallization (HC) as a function of the ladder doping parameter, $\delta$. Single crystals of SCCO with $x = 1, 2, 3, 4, 5, 10, 11, 12$ were grown by traveling solvent floating zone techniques described previously.
The surfaces were all prepared in the same manner, by dry polishing with diamond film down to 0.05 μm roughness (see section 4.2 for details). RSXS measurements were carried out on the soft x-ray undulator line X1B at the National Synchrotron Light Source with a ten-axis, ultrahigh vacuum-compatible diffractometer.

SCCO is an adaptive misfit material consisting of incommensurate Cu$_2$O$_3$ ladder and CuO$_2$ chain sublayers with lattice parameters $c_L \approx 10/7 \ c_c$, resulting in a large unit cell with $a = 11.47 \ \text{Å}, \ b = 13.35 \ \text{Å}, \ c = 27.3 \ \text{Å} = 7c_L = 10c_c$ for low $x$ content ($x \leq 4$) [see Fig. 4.1.2]. For high $x$ content ($x = 10, 11, \text{and} 12$), the $c$ lattice parameter is about 27.48 Å We will denote periodicities in terms of the Miller indices of the ladder $(H,L_L)$, where $H$ and $L_L$ represent periodicities along the $a$ and $c_L$ directions, respectively [e.g. $L_L$ represents a modulation along the ladder with wavelength $c_L/L_L$].

### 6.2. Wigner Crystallization in Spin Ladders of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$

![Figure 6.2.1. L$_L$-scan on Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ for $x = 0, 1, 2, 3, 4, 5, 10, 11, \text{and} 12$. The energy for each scan was chosen at Cu $L_3^\prime$ ($E = 933 \text{ eV}$) and the temperature was 20 K.](image)

The most direct way to study CDW ordering is x-ray scattering from which one can determine its period, coherence length, form factor (deviation from sinusoidal, for example), and the temperature dependence of its order parameter, $\eta(T)$. As we
demonstrated in chapter 3 and chapter 4 resonant X-ray scattering at energies near the $K$ edge of oxygen ($1s \to 2p$ transition) is directly sensitive to hole ordering.

The X-ray energy is tuned to the Cu $L_3'$ edge ($E = 933$ eV). The reason for this choice is that it covers a larger range in reciprocal space, than measurement at the O $K$ edge, because of the shorter wavelength. Results of $L_4$-scans for $x = 0, 1, 2, 3, 4, 5, 10, 11,$ and 12 are shown in Fig. 6.2.1. Fascinating is the observation of Bragg peaks at $L_4 = 1/5$ for $x = 0$ and a strong peak at $L_4 = 1/3$ for $x = 11$ and weak peaks for $x = 10$ and 12, and the absence of superlattice reflections for $x = 1, 2, 3, 4,$ and 5.

![Reciprocal H-L space maps](image)

Figure 6.2.2 Reciprocal $H$-$L$ space region $(0,0,1/3)$ at photon energy $933.0$ eV for (a) $x = 10$, (b) $x = 11$ and (c) $x = 12$. The hole crystal shifts to higher wave vector, or shorter wavelength, with increasing hole density in the ladder, and “melts” for incommensurate values.

In Figure 6.2.2 we show RSXS reciprocal space maps taken on the Cu $L_3'$ resonance in the $(H, L_4)$ plane for samples with $x = 10, 11,$ and 12, taken at $T = 20$ K. A commensurate superstructure is observed with a wavelength of approximately three ladder rungs. The modulation shifts to higher wave vector with increasing ladder hole density, which provides evidence that this feature is due to the ladder. The modulation is strongest at the commensurate value of $L_4 = 1/3$ and quickly “melts” for incommensurate values.
Like the $L_L = 1/5$ phenomenon seen at $x = 0$ this peak breaks the superspace group symmetry of SCCO, i.e. it does not index to any harmonic of the 27.3 Å unit cell.

Figure 6.2.3 X-ray absorption spectra of $x = 0$ (Sr$_{14}$Cu$_{24}$O$_{41}$), taken in fluorescence yield mode with the photon polarization (solid line) $E \parallel c$ and (dashed line) $E \parallel a$, in the vicinity of (a) the O$K$ and (b) Cu$L$ edges. Open circles, filled squares, filled circles, and open squares are the integrated HC intensity as a function of incident photon energy for $x = 0, 10, 11$ and $12$ respectively. At O$K$ edge, the intensity of hole crystal for $x = 11$ is multiplied by 0.6 while for $x = 10$ and 12 are multiplied by 5. The oxygen spectrum consists of prepeaks corresponding to hole-doped peak on the chain and ladder, as well as holes in the upper Hubbard band (see chapter 5 for detail). The Cu$L$ edge consists of Cu$L_{3/2}$ and Cu$L'_{3/2}$ ($2p_{3/2} \rightarrow 3d$) peaks.

The energy-dependence of these reflections was tracked through the O$K$ and Cu$L_3$ edges, summarized in Fig. 6.2.3. Like the phenomenon in Sr$_{14}$Cu$_{24}$O$_{41}$ they are visible only at resonances which establish the modulation as an electronic, Wigner crystalline phenomenon. The coherence length of the reflection is $\xi_c = (1580 \pm 70)$ Å and $\xi_a = (1615 \pm 70)$ Å indicating that, like the $x = 0$ case, this phenomenon is highly two-dimensional.
however with a coherence length ~5 times larger than for x=0. This suggests that the interactions driving the hole crystal become stronger as the holes move closer together.

Figure 6.2.4 Intensity of superstructure of hole crystal at the O\textsubscript{K} prepeak for a variety of chemical compositions. Hole ordering is visible only when it is commensurate with the ladder, and only for odd fractions.

Figure 6.2.5 Temperature dependence of HC scattering for the four samples (x = 0, 10, 11 and 12) in which it has been observed. The data collapse when plotted against the reduced quantities $I / I_{20K}$ and $T / \tau_{LL}$, where $\tau_{1/3} = 211.1$ K and $\tau_{1/5} = 127.8$ K.
Commensuration seems critical for the formation of the hole crystal, so we attempted to locate a reflection with wave vector \( L_L = 1/4 \) which is predicted to be a stable phase in DMRG at intermediate values of \( x \). According to our estimation of number of holes, \( x \sim 4 \) should correspond to \( \delta \sim 1/4 \). However, despite extensive investigation no hole crystal was observed in samples with \( x = 1, 2, 3, 4, \) or \( 5 \), indicating that the hole crystal forms only for odd rational fractions. The results over the entire doping range are summarized in Figure 6.2.4.

Insight into the interaction which drives the WC can be gleaned from its temperature dependence, shown in Fig. 6.2.5 for all four samples in which the WC has been observed. The WC at \( L_L = 1/3 \) persists to a higher temperature than for \( L_L = 1/5 \), reinforcing the picture that the interactions driving it become stronger for reduced inter-particle spacing. The transitions are broad and it is difficult to define a transition temperature. As a measure of the temperature scale we define \( T^* \) as the value at which the modulation reaches half of its low temperature value. Normalizing the intensity scales to \( I(T) \) and plotting it against the reduced temperature \( T/T^* \), using the values \( T^*_{1/3} = 211.1 \) K and \( T^*_{1/5} = 127.8 \) K, the four data sets collapse onto a universal curve (Fig. 6.2.5, inset). The ratio of the \( T^* \)s can be considered a measure of the relative strength of the interactions, and has the value \( T^*_{1/3} / T^*_{1/5} = 1.652 = 5/3 \).

Figure 6.2.6 Some possibility scenarios of the hole distribution in the ladder. Filled circles represent electrons and open circles represent holes. The solid lines indicate the formation of dimer singlet. The arrows indicate the spin of unpaired electrons which are not expected to be Néel ordered in the one-dimensional system. (a) Pairs of holes in the rungs. (b) Single hole density which is rung bond centered would result in a spin 1/2 chain and a gapless CDW. (c) The holes could be site centered alternating between the atoms on the rung. Here the number of undoped rungs in the unit cell would have to be odd so the observed 1/3 and 1/5 CDW’s would not be possible.
At this point we come back to the question of explaining the wavelength $\lambda = 3.00c_L$ with our new interpretation of the polarization XAS as described in chapter 5. Based on our new interpretation of XAS, the estimation of $n_L$ is about 4.4. If the holes are paired in the rung then one needs to have $14/3.00 \sim 4.67$ out of 6 holes in the ladder to crystallize into a superlattice with this lattice constant. In this case only a very small numbers of holes (about 1.33) reside in the chain. This is consistent with the estimation from XAS. The detail of this fitting was described in chapter 4.5.

In thinking about the details of the charge density distribution and possible mechanisms it is useful to look at some possibility scenarios of the hole distribution in the ladder. First, according to DMRG calculations of a single ladder [3] within a $t$-$J$, with $J=J'$, $t=t'$ like model it was found that holes like to pair up in the rungs. This would result in a gapped charge density wave shown pictorially in Fig. 6.2.6 (a). To have the periodicity of $L_L$, the number of holes $n_L$ would be $14^*L_L$, or for $L_L = 1/5$, $n_L$ is about 2.8. For the pure Sr system this would leave 3.2 holes for the chains. For $L_L = 1/3$, $n_L$ is about 4.67.

Another possibility hole distribution, not involving pairing is shown in Fig. 6.2.6 (b) in which the single hole density is rung bond centered as discussed in ref. 3. This would result in a spin 1/2 chain and a gapless CDW. The number of holes needed for such a case is 1/2 of that for the case above with paired holes and we could call this the simple “vanilla case”. In a third scenario the holes could be site centered alternating between the atoms on the rung as shown in Fig. 6.2.6 (c). Here the number of undoped rungs in the unit cell would have to be odd so the observed 1/3 and 1/5 CDW’s would not be possible.

![Figure 6.2.7](image-url) Two-leg spin ladder with four-spin exchange. $J_\perp$ and $J_\parallel$ are interchain coupling constants along the rung and leg, and $J_{\text{ring}}$ is a four-spin cyclic exchange coupling constant.
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Figure 6.2.8 Simulations of the ground state energy per rung ($E_{GS}$) in units of $J_\|_1$ as a function of number of rungs in between the paired holes, $N$, for various $J_\|$ and $J_\perp$. Squares, circles, up-triangles, down-triangles and diamonds are the simulation for $J_\perp/J_\| = 1.0$, 0.8, 0.6, 0.4 and 0.2, respectively.

To look for a reason for the absence of the 1/4 periodicity, we start with the resonant valence bond (RVB) physics. The minimal model for the magnetic properties of the $S = \frac{1}{2}$ two-leg ladders is an antiferromagnetic Heisenberg Hamiltonian plus a cyclic four spin exchange term which can be written as [12,13,14,15,16,17,18,19,20]

$$H = J_\| \sum_{i=1,2} \sum_{\alpha=1,2} \mathbf{S}_{i,\alpha} \cdot \mathbf{S}_{i,\alpha+1} + J_\perp \sum_{i=1,2} \sum_{\alpha=1,2} \mathbf{S}_{i,\alpha} \cdot \mathbf{S}_{i,\alpha+1} + J_{\text{ring}} \sum_{i,j=1} P_{i,j+1} + P_{i,j-1} + P_{i,j+1} + P_{i,j-1}$$  \hspace{1cm} (6.1-a)

where $P_{i,j+1}$ and $P_{i,j-1}^{-1}$ are the four-spin cyclic exchange operators $\alpha = 1,2$ are indexes of spin chains, $J_\|$ and $J_\perp$ are interchain coupling constants along the rung and leg, and $J_{\text{ring}}$ is a four-spin cyclic exchange coupling constant [see Fig. 6.2.7]. These four-spin cyclic exchange operators can be expressed using spin operators as follows:

$$P_{i,j+1} + P_{i,j-1}^{-1} = \mathbf{S}_{i_1} \cdot \mathbf{S}_{i_1+1} + \mathbf{S}_{i_2} \cdot \mathbf{S}_{i_2+1} + \mathbf{S}_{i_1} \cdot \mathbf{S}_{i_2+1} + \mathbf{S}_{i_2} \cdot \mathbf{S}_{i_1+1} + \mathbf{S}_{i_1} \cdot \mathbf{S}_{i_2} + \mathbf{S}_{i_1} \cdot \mathbf{S}_{i_2} + \mathbf{S}_{i_2} \cdot \mathbf{S}_{i_1} + 4\{\mathbf{S}_{i_1} \times \mathbf{S}_{i_2}\} \times \{\mathbf{S}_{i_1} \times \mathbf{S}_{i_2}\} + \{\mathbf{S}_{i_1} \times \mathbf{S}_{i_2}\} \times \{\mathbf{S}_{i_1} \times \mathbf{S}_{i_2}\} - \{\mathbf{S}_{i_1} \times \mathbf{S}_{i_2}\} \times \{\mathbf{S}_{i_1} \times \mathbf{S}_{i_2}\}$  \hspace{1cm} (6.1-b)

A simulation of the ground state energy of the holes ($E_{GS}$) using exact diagonalization procedures as a function of the number of rungs for various $J_\|$ and $J_\|$ and without $J_{\text{ring}}$ contribution is shown in Fig. 6.2.8. One can see that, for the isotropic case $(J_\perp=J_\parallel)$ and for $J_\perp > J_\parallel$, there is no pronounced difference in $E_{GS}$ for even and odd number of rungs. The ground state energy is decreasing exponentially as a function of $N$ and remains...
almost constant for large \( N \). Once we introduce the anisotropy \( J_\perp < J_\parallel \), \( E_{\text{GS}} \) starts oscillating as a function of \( N \). Interestingly \( E_{\text{GS}} \) for odd \( N \) is higher than \( E_{\text{GS}} \) for even \( N \). Take the case for \( J_\perp / J_\parallel = 0.6 \). In this case, \( E_{\text{GS}}[N] \) for \( N = 2, 3, 4, 5, \) and 6 is -0.83589, -0.85924, -0.90593, -0.92000, and -0.93510, respectively. Suppose we are at the concentration when one would expect the 1/4 periodicity (units with 3 rungs separated by rungs with two holes). Let us draw two units:

![Image](image.png)

The energy of this segment is \( 6 \times E(3) = -5.15544 \) (since there are 6 rungs in all). By contrast, a "disordered" state which has equal numbers of 2-rung and 4-rung plaquettes (so the same hole concentration) will cost:

![Image](image.png)

\( 2 \times E(2) + 4 \times E(4) = -5.29550 \). The energy saved per two unit cells, by "disordering", is \( -5.29550 + 5.15544 = -0.14006 \). Now, this is in units of \( J_\parallel = 130 \text{ meV} \), so this energy is \( -0.14006 \times 130 = -18.21 \text{ meV} \). This energy looks like a considerable energy to avoid the 1/4 modulation.

**Figure 6.2.9** The energy saved per two unit cells by the disordering for given \( J_\perp / J_\parallel \).

In Figure 6.2.9 is shown the energy saved per two unit cells by the disordering for given \( J_\perp / J_\parallel \) as we used above with \( J_\parallel \) is about 130 meV. It is clear that the larger \( J_\parallel \) is the
more energy saved. Up to date, it is not so clear what the real value for $J_\perp/J_\parallel$ is, but they are in the range of 0.4 to 0.9 \cite{21,22,23,24}.

We also studied the influence of the $J_{\text{ring}}$ interaction on $E_{\text{GS}}$. The results of the simulation are shown in Fig. 6.2.10. In the simulation, $J_\perp/J_\parallel$ is fixed to 0.4 and the $J_{\text{ring}}/J_{\text{leg}}$ varies from –0.1, 0, and 0.1. We see that the oscillation of $E_{\text{GS}}$ depends strongly on the sign of $J_{\text{ring}}/J_{\text{leg}}$. With the same method as above, for $J_{\text{ring}}/J_{\text{leg}} = 0$, the energy saved per two unit cells, by the disordering, is 34.47 meV while for $J_{\text{ring}}/J_{\text{leg}} = 0.1$, the energy saved is 12.48 meV. For opposite sign (negative sign) of $J_{\text{ring}}$ to $J_{\text{leg}}$, the oscillation is more pronounced than for the positive sign in which case the energy saved is larger reaching 27.48 meV. It is fairly certain that the signs of the ring exchange and the superexchange should be the same \cite{25,26,27,28,29,30}. Here one can see that the $J_{\text{ring}}$ suppresses the even-odd effects.

Depending on the value of $J_\perp$, $J_\parallel$, and $J_{\text{ring}}$, it seems that the simple short-range exchange based models support the experimental observations.

![Figure 6.2.10](image)

**Figure 6.2.10** A simulation for the $E_{\text{GS}}$ with additional $J_{\text{ring}}$ interaction. In the simulation, the $J_\perp/J_\parallel = 0.4$ and $J_{\text{ring}}/J_\parallel$ varies over –0.1, 0, and 0.1, for black filled-circles, black filled-circles and blue filled-circles, respectively.

In conclusion, we explain the absence of the 1/4 periodicity with the resonant valence bond (RVB) physics. We show that the WC is stable for odd, but not for even multiples of the ladder period. Even the values of ring exchange are uncertain but the even-odd effect is there without it. The ring exchange effect decreases this but that quite a large value is needed to remove it completely. According to our temperature-dependence for various $L_d$ and the 2D-like of coherence length along the ac-plane, it seems that long-range interactions are important. This long-range interaction may also come from long range Coulomb interaction \cite{31,32}. 
6.3 Evidence for a different energy for the excitation of O(l) and O(r) in ladder

As we described in chapter 5, the O 1s $\rightarrow$ 2p excitation of the leg-O [O(1), and O(l)], should not have the same energy as O(r) since they have different coordinations by Cu$^{2+}$ ions [see Fig. 5.3]. Here we would like to point out that by comparing the energy dependent resonance profiles of the WC at $L_d = 1/5$ and the WC at $L_d = 1/3$, we find evidence for this. In Fig. 6.3.1 (a) and (b) are shown the geometry of the experiments for $x = 0$ and $x = 11$. The actual Bragg angle, $\theta_B$, depends on photon energy. For $x = 0$, the $\theta_B$ for energy range of 526 eV to 531 eV is slightly changing from 37.18º to 36.77º. The polarization of the beam according to this geometry varies from 52.82º to 53.23º off from the $a$-direction in the $ac$-plane. While for $x = 11$, the $\theta_B$ for energy range of 526.8 eV to 531 eV is ranging from 87.8º to 82.4º. The polarization of the beam here is from 2.2º to 7.6º off the $a$-direction in the $ac$-plane. Note here that, for incident angle > 88º, the detector which is at an angle twice that of the incident angle is blocking the beam. So, there is no reliable data for energy lower than 526.8 eV.

![Figure 6.3.1](image-url)  
**Figure 6.3.1** Geometry of the experiments (a) for $x = 0$ and (b) for $x = 11$. The actual Bragg angle, $\theta_B$ depends on photon energy. For $x = 0$, the $\theta_B$ for energy range 526 eV to 531 eV is slightly changing from 37.18º to 36.77º. The polarization of the beam corresponding to this value of $\theta_B$ is between 52.82º and 53.23º off from $a$-direction in the $ac$-plane. For $x = 11$, $\theta_B$ varies from 87.8º to 82.4º for the energy range 526.8 eV to 531 eV. The polarization of the beam corresponding to this value of $\theta_B$ is from 2.2º to 7.6º off the $a$-direction in the $ac$-plane.

The details of the RSXS results for these two reflections are shown in Fig. 6.3.2. Black filled-circles and red open-circles are the resonance profiles for $x = 0$, and $x = 11$, respectively. For $x = 0$, the spectral weight of the resonance profiles is centered at $\sim 528.5$
eV, while for \( x = 11 \), the spectral weight of the resonance profiles is centered at \( \sim 528.3 \text{ eV} \). There is a 0.2 eV energy shift between these two results.

**Figure 6.3.2** Resonance profiles of the WC at \( L_d = 1/5 \) for (filled circles) \( x = 0 \) and at \( L_d = 1/3 \) for (open circles) \( x = 11 \). (Note: these data are duplicate of Fig. 6.2.3, but focus on the resonance profiles for \( x = 0 \) and 11 only).

To understand this, one needs to write down the total form factor, \( f \), (see chapter 3) [33] for each case (\( x = 0 \) and \( x = 11 \)). Since the WC is not visible or very weak at off-resonance, the only important component of the form factor is the “anomalous” part. As we described in chapter 5, the doped hole peak of the ladders consists of \( \text{O}(r), \text{O}(l)_a \) and \( \text{O}(l)_c \).

Then, the anomalous form factor as function of energy for these three peaks can be written as

\[
f(E) = \frac{I_{\text{O}(r)} \* \sin(\theta_a[E])}{E - E_{\text{O}(r)} - i\gamma_{\text{O}(r)}} + \frac{I_{\text{O}(l)_a} \* \sin(\theta_a[E])}{E - E_{\text{O}(l)_a} - i\gamma_{\text{O}(l)_a}} + \frac{I_{\text{O}(l)_c} \* \cos(\theta_a[E])}{E - E_{\text{O}(l)_c} - i\gamma_{\text{O}(l)_c}}
\]

where \( I_{\text{O}(r)}, I_{\text{O}(l)_a} \) and \( I_{\text{O}(l)_c} \) are the peak height of \( \text{O}(r), \text{O}(l)_a \) and \( \text{O}(l)_c \) resonances, respectively, \( E_{\text{O}(r)}, E_{\text{O}(l)_a} \) and \( E_{\text{O}(l)_c} \) the energy of \( \text{O}(r), \text{O}(l)_a \) and \( \text{O}(l)_c \) resonances, respectively, while \( \gamma_{\text{O}(r)}, \gamma_{\text{O}(l)_a} \) and \( \gamma_{\text{O}(l)_c} \) are the FWHM of \( \text{O}(r), \text{O}(l)_a \) and \( \text{O}(l)_c \) resonances, respectively. \( \theta_a[E] \) is the angle of the incoming photon as function of energy. It is important to make sure that the polarization here is consistent with our interpretation of the polarization dependent XAS. For instance, at \( \theta_a[E] = 90^\circ \), the important components on the
right hand side of eq. (6.2) are the first and the second terms, while at $\theta_j(E) = 0$ then the only component at the right hand side is the third term. So that eq. (6.2) above is valid for $x = 0$ as well as $x = 11$. The scattering intensity is proportional to $|f|^2$.

Figure 6.3.3 (lines) The simulation of the scattering intensity compared to (filled circles) experimental data for (a) $x = 0$ and (b) $x = 11$.

The simulations of the scattering intensity are done by inserting the parameters from Table 5.1 for $x = 0$ and from Table 5.3 for $x = 11$ into eq. (6.2). The results are shown in Fig. 6.3.3 (a) and (b) for $x = 0$ and for $x = 11$, respectively. The simulation of $x = 0$ shows that the spectral weight of the scattering intensity is centered at 528.55 which is really close to the experimental value which is 528.5 eV. While for $x = 11$, the spectral weight of the simulated scattering intensity is centered at 528.30 which is the same as the experimental value. The bottom line here is that the O 1s $\rightarrow$ 2p excitation energy of the leg O (O(1), and O(l)a) is higher than O(r), and all this is consistent with our interpretation of the polarization dependent XAS. Broader energy width of the simulation is due to the fact that the full lifetime enters absorption data but only the radiative lifetime is relevant to anomalous x-ray scattering.
6.4 $x$-dependence of the superstructure peak in the chains

In chapter 4, we have discussed in detail the $4k_F$ CDW in the chains for SCO ($x = 0$) and the origin of this superstructure. As we have explained, the Bragg reflection at $L_c \approx 0.318$ originates from a structural modulation which is (0,0,0.3)$_c$. Based on the chain hole concentration as determined with polarization dependent XAS [see chapter 5] we have found that this superstructure is related to a $4k_F$ CDW in the chains. It is also important to study the evolution of the superstructure in the chains as function of doping and to try to understand the mechanism behind it. In Fig. 6.4.1 is shown the $L_c$ scan for various $x$ as well as for La$_6$Ca$_8$Cu$_{24}$O$_{41}$ (LCCO) at $E = 933$ eV and $T = 20$ K. LCCO has the same structure as SCO, but it contains no holes (zero hole system).

![Figure 6.4.1 L\textsubscript{c}-scans for various x at E = 933 eV and T = 20 K. Black solid line, black dashed line, black dots, grey solid line, grey dashed line, grey dots, and closed circles are the L\textsubscript{c}-scan for x = 0, 4, 5, 10, 11, 12, and La$_6$Ca$_8$Cu$_{24}$O$_{41}$ (LCCO), respectively.](image)

For $x = 0$, we have concluded that the superstructure at $L_c = 0.318$ is likely a CDW-type of order in the chain. For compounds which have a finite Ca-Content, the result is more complicated. One can see that for a Ca-doped system the superstructure disappears. There is no superstructure observed for $x = 1, 2,$ and 3. For Ca = 4, a superstructure appears at $L_c = 0.325 \pm 0.001$. For high Ca-content, ($x = 5, 10, 11,$ and 12), it seems that two Bragg reflections appear for each $x$, one has a high intensity which is referred to as Bragg peak.
6.4. \( x \)-dependence of the superstructure peak in the chains

(1), and the weaker one is referred to as Bragg peak (2). The position and the width of each Bragg peak are shown in Fig. 6.4.2 (a) and (b).

![Figure 6.4.2](image)

**Figure 6.4.2** (a) The position and (b) the width of Bragg peaks as function of \( x \). Filled circles are for the position of the Bragg peak (1) and its FWHM and open circles are for the position of the Bragg peak (2) and its FWHM. Note here that, there is no Bragg reflection for \( x = 1, 2, \) and 3. For comparison, we include LCCO, please remember that LCCO has no hole in the system.

One can see from Fig. 6.4.2 (a) that for \( x \geq 5 \), the position, \( L_c \), of the Bragg peaks is about \( 0.300 \pm 0.008 \) which is almost \( x \)-independent, while for \( x < 5 \) is closer to \( L_c = 1/3 \) than 0.300. In some cases, like \( x = 1, 2, \) and 3, no Bragg reflection is observed. For high Ca-contents, except for LCCO case it seems there are two Bragg reflections appearing which are Bragg peak (1) and Bragg peak (2), but their Bragg position are still in the range of \( 0.300 \pm 0.008 \). In Fig. 6.4.2 (b), one can see that the width of those reflections varies. For high Ca-content (\( x = 10, 11, \) and 12) the ratio of FWHM of Bragg Peak (1) and Bragg peak (2) from the same sample is \(-7\), which means the Bragg peak (2) has a shorter coherence length than Bragg peak (1) which has stronger intensity. For instance, let’s take \( x = 11 \). The coherence length of those two reflections is about 2000 Å (for Bragg peak-1) and 320 Å (Bragg peak-2).
Figure 6.4.3 Temperature dependence of the superstructure amplitude for three samples. Squares, circles, and up/down-triangles correspond to samples with $x = 0$, 4, and 11 samples, respectively. For $x = 11$, there are two Bragg reflections which are Bragg peak-1 and Bragg peak-2.

In Fig. 6.4.3 is shown the temperature dependence of this superstructure. Different from the $x = 0$, for Ca-doping system, this superstructure is almost temperature-independence. This could be due to strong influence of the structure modulation of (0,0,0.3).

If we assume that those reflections for $x = 4$, 5, 10, 11, and 12 arise from the chains and behave like CDW’s as for $x = 0$, then we can calculate the number of holes in the chain needed as for $x = 0$ [see chapter 4 for details]. In Fig. 6.4.4 is shown the expected $4k_F$-CDW as function of $x$ based on the chain hole concentration as determined with polarization dependent XAS (see chapter 5), compared to the RSXS results. As we already have mentioned many times, for $x = 0$, the holes in the chain behave like a $4k_F$-CDW in as expected for a 1D system. For $x = 4$, the $4k_F$-CDW in the chain is expected at $L_c = 0.27$, but the RSXS results is at $L_c = 0.325$. For $x = 11$, the expected $4k_F$-CDW in the chain is at $L_c = 0.16$, but the RSXS results is at $L_c = 0.296$ and $L_c = 0.306$ for Bragg peak(1) and Bragg peak (2). It seems that the systems with Ca-content are not following the simple rules of CDW’s in the chains. The strong modulation in the chain which arises from the atom displacements may be driving the hole modulation in the chain. There is also the possibility that the holes in the chain are inhomogeneously distributed. The existence of two Bragg peaks at high Ca-content may be a signature of the inhomogeneity of the hole distribution in the chains. In that case, the simple scenario of CDW in one-dimensional systems may not
be applicable. Polarization dependent measurements have to be done to confirm that these are really charge scattering events.

Figure 6.4.4 The position of Bragg peaks as function of $x$. Filled-squares are expected to be the $4k_F$-CDW based on the interpretation of polarization XAS (see chapter 5), while filled-circles and open circles are the RSXS results.
References
