Resonant soft x-ray scattering and charge density waves in correlated systems

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Groningen: [S.n.]

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Chapter 4

Direct evidence of Wigner crystallization in ladders and $4k_F$ charge density wave in chains in copper-oxide spin ladders of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$

The electronic structure of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ has been studied with RSXS. We have discovered a Wigner crystallization in ladders and a $4k_F$ charge density wave (CDW) in the chains. It is important that none of the reported charge ordering that has been claimed by hard x-ray or neutron scattering is seen in RSXS.

4.1 Theory and general properties

Despite almost 2 decades of intense investigation, the pairing interaction responsible for high-temperature superconductivity in copper oxides is still not known. The interplay between charge and spin degrees of freedom has been accepted as a crucial aspect of the physics of transition metal oxides. The competition between charge mobility and magnetic interactions appears to be the source of charge ordering phenomena such as stripes in cuprates and nickelates or phase separation in manganites [1,2,3].

In 1992, Dagotto et al. [4], proposed an interesting electronic model for ladder-like structures in which the Copper and Oxygen ions are ordered in two parallel chains forming the legs of a ladder, with Cu-O-Cu exchange coupling forming the rungs. The hoping interactions along the leg and rung are given by $t_{\parallel}$ and $t_{\perp}$, respectively, exchange interactions along the leg and the rung are $J_{\parallel}$ and $J_{\perp}$, respectively. The Hamiltonian can be written as

$$H = J_{\parallel} \sum\sum S_i \cdot S_{i+1} + J_{\perp} \sum S_i \cdot S_{i+1} - t_{\parallel} \sum \left( \bar{c}_{i,x} \bar{c}_{i+1,x} + \text{H.c.} \right) - t_{\parallel} \sum \left( \bar{c}_{i,y} \bar{c}_{i+1,y} + \text{H.c.} \right)$$

(4.1)
Here the chains run along the $x$ axis and the rungs connect site $i$ with $i+\hat{y}$. $c_i^\dagger$, are hole destructive operators with spin $s$ at site $i$. The ladders form a periodic two-dimensional lattice in the $x$ direction [see Fig. 4.1]. To gain some physical insight into the nature of the correlations which may occur, let’s consider the limit of large $J_\perp$ limit. In this case the ground state at half filling consists of a set of spin singlets on each rung of the ladder. Naturally, there is a spin gap in the spectrum of the order of $J_\parallel$ which corresponds to creating a triplet on one of the rungs. When the system is doped with holes, it is energetically favorable to break as few as possible singlet rungs. Recall that every singlet state on the rung lowers the energy by $3/4J_\perp$ relative to that of a hole and a single unpaired spin. Thus, when a pair of holes is added, the system will minimize its energy by breaking just one spin-singlet rung forming a hole-pair bound state. Depending upon the parameters chosen, a doped ladder can exhibit either exchange-driven superconductivity [4, 5] or an insulating “hole crystal” ground state in which the carriers crystallize into a static, Wigner lattice [4,40,41]. The competition between these two phases is similar to that believed to occur between ordered stripes and superconductivity in two-dimensional models [1,6,7,8,9,10]. For all of these reasons, the spin ladder is an important reference system in the overall understanding of copper-oxide. It is important to note in the model proposed by ref. 4 that it is the spin-spin interactions that lead to an effective attraction between holes rather than explicit hole-hole attractive interactions. The model was proposed for doping of the orthorhombic compound $(\text{VO}_2)\text{P}_2\text{O}_7$. Interestingly, in the insulating state, the spin gap is observable in the temperature dependence of the magnetic susceptibility of $(\text{VO}_2)\text{P}_2\text{O}_7$, but the system cannot be doped.

![Figure 4.1.1](image)

**Figure 4.1.1** Schematic definition of the $t_{\parallel}-J_{\parallel}-t_{\perp}-J_{\perp}$ model on a ladder. Dots are representing sites of the $t_{\parallel}-J_{\parallel}$ chains which are in the interaction through vertical links with couplings $t_{\perp}-J_{\perp}$. Solid dots are occupied sites while open dots denote holes. A tightly bound state of two holes is shown.

The only known doped spin ladder material is $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$. It was found two years after the discovery of superconducting cuprates by Bednorz and Muller [11]. This compound has become quite famous with the nickname “telephone number compound 14-
This is a two-leg spin-ladders (it is hard to think of a one legged ladder) with the general formula \((A_{1-x}B_x)\text{Cu}_2\text{O}_{41}\), with \(A\) an alkaline earth metal and \(B\) a trivalent (transition or lanthanide) metal [12, 13]. Due to charge neutrality, for \(x = 0\), the formal valence of \(\text{Cu}\) in this compound is +2.25, resulting in a “self-doped” system with six holes per formula unit (f.u). Hole doping of the two-leg spin ladder is the minimum needed for superconductivity. Superconductivity has indeed been found by Uehera et al. in \(\text{Sr}_{0.4}\text{Ca}_{13.6}\text{Cu}_{24}\text{O}_{41}\) when the sample is subjected to a hydrostatic pressure of \(P >3\) GPa, above which the resistivity drops to zero at \(\sim 12\) K.

\[\text{Figure 4.1.2 (a)} \quad \text{Idealized crystal structure of (Sr,La)}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41} \text{viewed in perspective along the } c \text{ direction.} \]

Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\) (SCO) is a layered material consisting of two different types of copper oxide sheets—a CuO\(_2\) ‘chain’ layer and a Cu\(_2\)O\(_3\) ‘ladder’ layer [see Fig. 4.1.2]. These two sublayers are separated by Sr atoms, and stack in an alternating fashion along the \(b\) crystallographic direction. The ladders and chains are parallel and run along the \(c\)-direction, but are structurally incommensurate; that is, the ratio of their lattice parameters, \(c_c / c_L = 10/7\), is not a rational number [14,15,16]. They belong to a class of compounds called “misfit” compounds. The term “misfit compound” introduced by Wiegers et al., in their study of the crystal structure of (LaS)\(_{1.14}\)NbS\(_2\) [17]. As a result SCO is internally strained, and has a large unit cell with a low-temperature lattice parameters \(a = 11.47\) Å, \(b = 13.35\) Å, and \(c = 27.3\) Å \(\approx 7c_L \approx 10c_c\) [18]. The unit cell of SCO contains four formula units, 316 atoms in all, with a density about 5.415 g/cm\(^3\).
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Figure 4.1.3 Cu$_2$O$_3$ ladder. Along the $c$-direction, the Cu-O-Cu bond angle is 180° which leads to strong antiferromagnetic coupling. While along the $a$-direction, the Cu-O-Cu bond angle is 90° which leads to weak ferromagnetic coupling. The diagonal lines are the guide eyes for interladder magnetic coupling.

Cu$_2$O$_3$ ladders – Based on the geometry of oxygen and copper atoms intra- and interladder magnetic coupling and hoping integrals may be explained as follows. Along the $c$-direction, the Cu-O-Cu bond angle is 180° which leads to strong antiferromagnetic coupling based on the Goodenough-Kanamori-Anderson (GKA) rule [19]. The hoping integral along this direction is also large. Along the $a$-direction, the Cu-O-Cu bond angle is 90° which leads to weak ferromagnetic coupling. Even though the inter-ladder coupling is at most weakly ferromagnetic, the Coulomb interaction can be large as can be the inter-ladder hoping integral. For example, the inter ladder hoping integral of a ZR singlet is expected to be quite large at approximately one half of the rung or leg hoping integral. Secondly the inter ladder coulomb interaction is strong because the ZR singlets on one ladder involves two of the same oxygen atoms as that of the neighboring ladder. [See Fig. 4.1.3]. In other words these can really only be viewed as ladders with regard to the superexchange interactions and not other charge degrees of freedom.

Figure 4.1.4 CuO$_2$ chain. The nearest neighbor copper spins in the chain are coupled through 90° bonds via oxygen
4.1. Theory and general properties

**Cu-O chains** - The nearest neighbor copper spins in the chain are coupled through 90-degree bonds via oxygen. According to the GKA rule, the 90° bond results in a weak ferromagnetic exchange coupling. The next nearest neighbor Cu ions are also coupled through 90° bonds but via 2 intervening oxygen atoms. The sigma bonding (relative to the Cu-O bond) O 2p orbitals on the two O atoms with neighboring Cu 3d orbitals however have a finite overlap resulting in an antiferromagnetic next-nearest-neighbor interaction which is most likely the largest exchange interaction. The interaction between next-nearest-neighbor Cu atoms is shown in Fig. 4.1.4.

SCO, however, exhibits all the transport signatures of a charge density wave (CDW), including a screening mode in impedance measurements [20,21], a pinning mode in microwave conductivity [22], a giant dielectric constant [20,21], and a nonlinear current-voltage (I–V) curve [20], which together indicate that the carrier density is modulated in real space. These observations are typical of conventional Peierls CDW materials like NbSe$_3$ or K$_0.3$MoO$_3$ [23] in which the carrier density is modulated by a distortion in the crystal structure, driven by the electron–lattice interaction. A CDW could also be driven by effective long-range interactions such as in a Wigner crystal. We will refer to such a CDW as a hole crystal which will, as a phonon driven CDW, compete with superconductivity. Could the properties of SCO be determined by such a hole crystal?

The distribution of the holes is one of the most important factors that govern the physical properties of SCO. Similar to high-Tc superconductors, the holes are expected to be mainly supported by the oxygen 2p orbitals and to form ZR [24] singlets with an associated copper hole. Although we should remember that, unlike in the high-$T_c$'s, the 4 oxygens surrounding a Cu ion in the ladder are not identical and so the local point group symmetry is not D$_{4h}$. How the holes are distributed between the two layers is not known precisely. Various experiments [25,26] suggest that about one hole per f.u. is located on the ladder and provides evidence that there is a transfer of holes from the chains to the ladders upon Ca substitution. Also NMR [27] data indicate a transfer of holes to the ladders upon Ca substitution. However, the precise number of transferred holes is still under debate. X-ray absorption measurements [25] suggest that the number of holes for the ladder ranges from 0.8 for x = 0 to 1.1 for x = 12. Optical conductivity [26], on the other hand, suggests a range from 1 to 2.8, while $^{63}$Cu NMR studies [27] suggest a range 1 to 3.5. However we should recall that the interpretation of optical conductivity and the NMR data is based on the observation by neutron diffraction of what was thought to be a superlattice reflection corresponding to a CDW on the chains and a charge distribution of 5 holes in the chain and one in the ladder. More recent x-ray diffraction data however [18,28] have clearly demonstrated that the peak observed in neutron diffraction is expected in the basic crystal structure and therefore is not evidence for a CDW. The only direct measurement of the hole density distribution is presented by the polarization-dependent x-ray absorption studies. But
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... also these are subject to interpretation and with the model chosen there are unexplained discrepancies with regard to the polarization dependence.

The direct way to observe the hole crystal (HC) or charge ordering, if there is any, is with x-ray or neutron scattering. Several quite distinct studies claimed strong evidence for an additional distortion of the crystal structure at low temperature. However no other Bragg peaks than those which can be indexed according to the basic crystal structure have been observed to date as pointed out by van Smuilen [29]. It is difficult to detect a HC 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 a hole crystal, which arises from a small number of electrons around the Fermi level, is typically less than one electron while the total number of electrons contributing to allowed Bragg peaks is about 1600 or the superlattice Bragg peak in the absence of a lattice distortion would be about 1 part in 1600 of an allowed structural Bragg peak. However there are contradictory hard x-ray scattering results. Using synchrotron x-ray scattering with $\lambda \sim 0.8 \, \text{Å} \, (E_i \sim 15.5 \, \text{keV})$, Cox et al. observed a weak Bragg reflections at $(H, K, L_c) = (0, 0, n\pm1/4)_c$ [30]. These reflections which appear at low temperature were claimed as an evidence of charge ordering in the chain. Denoting the hole sites by 0 and the magnetic sites by $\uparrow$ or $\downarrow$, Cox et al. described the magnetic arrangement by

---$\uparrow$ 0 0 $\uparrow$ 0 0 $\uparrow$ 0 ---

(model I). This type of modulation which requires an additional spin-Peierls-like distortion in order to explain the observed dimerization, requires 5 holes per chain unit length. While Fukuda et al., using an x-ray energy of about 54 keV, from the same sample growth as Cox et al., found Bragg peaks at $(H, K, L_c) = (0, 0, 2n\pm1/5)_c$ [31]. They described the magnetic arrangement by

---$\uparrow$ 0 0 0 $\downarrow$ 0 $\uparrow$ 0 0 ---

(model II) which corresponds to dimers of two spins coupled across one hole; neighboring dimers are separated by two successive holes. Such an arrangement would result in 6 holes being in the chain. Fukuda et al. argued that the result of Cox. et al. is influenced by surface
treatment since the penetration depth for 15.5 keV is about 10-20 μm while for their experiment is about 3 mm. However, a detailed more recent study by van Smaalen showed that the superstructures that were found by Fukuda et al. as well as Cox et al., all index according to the large unit cell of the total structure [29]. He argues these additional reflections are already present due to the interaction between two subsystems and that their presence does not bear any relation to possible charge order in this compound. Even more recently Gellé et al. suggest that the lattice misfit modulations influence the chain electronic structure [32], reinforcing the van Smaalen argument. The latest elastic neutron scattering results [18,28,] observed weak superstructure peaks at $L_c = n \pm 0.2 (\pm 0.01)$ which are again indexed to the super cell. Based on the observation of the weak intensity and disappearing of the superstructure peaks above 200 K, they argue that the superstructure peaks may be relate to charge ordering in the chain. It is then the focus of this chapter to resolve the issue of (1) could the SCO contain hole crystal and (2) the concentration of holes in the chain and the ladder with RSXS.

4.2 Sample preparation

![Figure 4.2.1](a) SCO and Ge(111) as reference (b) sample roughness.

RSXS measurements were carried out on the soft x-ray undulator beamline X1B at the National Synchrotron Light Source. A five-circle diffractometer for scattering soft x-rays was constructed. This system mimics the functionality of a single-crystal diffractometer but operates in a vacuum of $2 \times 10^{-10}$ mbar. It consists of a six-degree-of-freedom sample stage, a
two-axis detector arm, a channeltron detector stage with a multilayer for fluorescence rejection, a He-flow cryostat, and a 5 T magnet, operating at a base pressure of $10^{-10}$ mbar. Actuation is done with vacuum stepper motors. It resides on the X1B undulator line at the National Synchrotron Light Source (see chapter 2 for detail).

Single crystals of SCO were grown by travelling solvent floating zone techniques described in ref. 33. There are at least two major problems that need to resolved, in order to work in the soft x-ray energy range. Firstly, the surface of the sample has to be of good quality, at least at the first of 3000 Å due to the high absorption. The surface was prepared by dry polishing with diamond film down to 0.05 μm roughness. To have some consistency between samples, the surface roughness was determined with reflectivity mode. In Fig. 4.2.1 (b), it is shown the 2-D scan along H and L of SCO sample. Two rods in the figure are specular reflections. The second problem is the orientation of the sample. The half-wavelength at $E = 530$ eV (O $K$ edge), which is about 12 Å, and at $E = 930$ eV (Cu $L_3$ edge), which is about 6.5 Å, are not shorter enough to see any primary reflection ($d_{002\text{-chain}} \sim 1.36$ Å). To resolve this issue, we have used a high quality single crystal of Ge(111) as reference. The idea is the following. With a rotating anode and a Laue camera, the $[H,K,L]$ scattering plane of SCO was determined relative to the $[1,1,1]$ scattering plane of Ge(111). We ensure that that the surface of the Ge(111) is almost (within < 0.1°) parallel to its $[1,1,1]$ plane. In the RSXS experiment, we first find out where the specular reflection from the surface of the Ge(111) is, and then set $(H,K,L)$ orientation matrix of SCO, since we already know the relative values between reference and sample.

### 4.3 Crystallization of charge holes in the ladder of Sr$_{14}$Cu$_{24}$O$_{41}$

As we explained in section (4.1), the most direct way to study CDW ordering is x-ray scattering from which one can determine its wavelength, 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, resonant x-ray scattering at energies near the K shell of oxygen ($1s\rightarrow2p$ transition) is directly sensitive to hole ordering. In this method, the x-ray energy is tuned to the hole-doped peak [see Fig. 4.3.1] at which scattering from the holes is selectively enhanced by a factor of $10^3$ [34]. Here we apply this technique to search for hole ordering in SCO. This material is a particularly interesting case because it has hole carriers in both the ladder and chain layers, and the hole-doped is split into resolvable ladder and chain features [25]. Each provides a separate enhancement, permitting ordering in two layers to be distinguished.
4.3. Crystallization of charge holes in the ladder of Sr$_{14}$Cu$_{24}$O$_{41}$

Figure 4.3.1 XAS in the Fluorescence yield mode of SCO with E\parallel c. The grey area covers roughly the hole-doped regime. The peak centered at ~530 eV is a transition to the upper Hubbard band composed of mainly Cu 3$d$ states.

![XAS in the Fluorescence yield mode of SCO with E\parallel c](image)

For energy around 528.6 eV corresponds to the doped hole region, the interval in reciprocal space that can be reached is $(0,0,0.05)_L \rightarrow (0,0,0.33)_L$ (note, subscript-$L$ means in ladder unit). A wide scan along $L$ at $E = 528.6$ eV is shown in Fig. 4.3.2. A Bragg peak

![Wide $L_L$-scan at $E = 528.6$ eV](image)
appears at $L_d = 0.2$ in ladder units or $L_c = 0.14$ in chain units or $L = 1.4$ in the large unit cell. This reflection is incommensurate with respect to the large unit cell.

Figure 4.3.3 (filled circles) Energy dependence of the hole superstructure reflection compared to the x-ray absorption spectra, in the vicinity of (a), the oxygen K edge, which is a $1s \rightarrow 2p$ transition, and (b), copper $L_{3/2,1/2}$ edges, which are $2p \rightarrow 3d$ transitions where the core hole is left with its spin either parallel ($j = 3/2$) or antiparallel ($j = 1/2$) to its orbital moment. Open squares and open circles are absorption spectra of Sr$_{14}$Cu$_{24}$O$_{41}$, taken in the fluorescence yield mode with the photon polarization $E||a$ and $E||c$, respectively. The data are in good agreement with ref. 25. “Chain” and “ladder” indicate the respective hole-doped prepeaks where scattering from the holes is enhanced. Red symbols, integrated intensity of the hole superstructure reflection as a function of incident photon energy. The reflection is visible only when the x-ray energy is tuned to the ladder-peak or the copper $L_{3/2}$ ligand hole sideband, indicating the presence of a standing wave in the hole density in the ladder.

Our central observation is the energy dependence of this peak. It was tracked through the oxygen $K$ edge where it was found to be visible for incident energies at resonance with the hole-doped peak corresponding to holes on the ladder [Fig. 4.3.3]—an
observation reproduced in two samples from different growth boles. The reflection is undetectable at all other energies, including the oxygen $K$ edge jump, eliminating the possibility that it arises from a distortion in the crystal structure. In x-ray terminology, the peak responds to the anomalous scattering factors of the doped holes, and not those of the oxygen atoms, and therefore indicates a standing wave in the hole density without a (significant) lattice distortion.

**Figure 4.3.4** Energy- and $L_L$ -dependence of the hole superstructure reflection. (a), (b). Peak intensity and $L_L$ position across the oxygen $K$ edge (a) and the copper $L_{3/2}$ and $L_{1/2}$ edges (b). The hole crystal reflection is clearly visible at both the ladder doped hole peak (Bragg angle = 36.1°) and the copper $L_{3/2}$ edge (Bragg angle = 19.9°). In both cases it resides at $L_L = 0.200$, indicating that, although visible only at select energies, the reflection nonetheless disperses according to Bragg’s law. This establishes it as a coherent, bulk phenomenon. The background in b is from the specular surface reflection, which is strong at the copper $L$ edge. Inset, $L_L$ scans on the $L_{3/2}$ (932.5 eV) and $L_{1/2}$ (952.8 eV) peaks, corresponding to the sections indicated with white lines.

According to Nucker et al.’s interpretation [25] of their XAS results, the energy of the peak at ~528 eV corresponds to holes doped in the chain and the energy of the peak at ~528.7 eV corresponds to holes doped in the ladder. From the energy dependence of the superstructure reflection, one can see that the peak is enhanced at 528.6 eV and decrease rapidly at high and lower energy side. Additional to that, it has a commensurate 5.00 $c_L$ periodicity. These all are evidence that this modulation originates in the ladder substructure.
Figure 4.3.5 Appearance of the hole superstructure peak on resonance. (a) Off-resonance ($E = 526$ eV) reciprocal space map around $(H,K,L_L) = (0,0,0.2)$. The ‘rod’ at $H = 0.01$ is the specular reflectance from the surface, which is displaced from $H = 0$ because of a surface miscut. The width of this rod indicates our transverse momentum resolution. (b) Same reciprocal space region with the x-ray energy tuned to the ladder doped hole peak ($E = 528.6$ eV). A pronounced superlattice reflection appears at $L_L = 0.200 \pm 0.009$, indicating the presence of a commensurate standing wave in the ladder hole density with period $\lambda = 5.00 c_L$. This reflection does not index to the 27.3 Å unit cell. The peak width gives longitudinal and transverse coherence lengths of $\xi_c = 255$ Å$= 65.3 c_L$ and $\xi_a = 274$ Å$= 24.9 a$, respectively. The hole modulation is registered across 50 neighbouring ladders, indicating significant inter-ladder coupling in this system. (r.l.u = reciprocal lattice units).

To further characterize this reflection it was tracked through the $L$ edge of copper ($2p \rightarrow 3d$ transition, Fig. 4.3.4), where it is also visible and notably still resides at $L_L = 0.2$, verifying that it disperses according to Bragg’s law. Scattering at the transition metal $L$ edges is known to be sensitive to spin modulations [35,36], but close inspection reveals that it resonates not at the $L_{3/2}$ maximum but at the $L_{3/2}^*$ shoulder, which arises from holes on the neighboring ligands [37]. So the modulation has no obvious magnetic character.
Figure 4.3.6  Temperature dependence of the hole crystal. The superlattice reflection becomes visible below $T = 250$ K. At its maximum (28 K), the peak count rate is 1,500 photons s$^{-1}$ on a fluorescence background of 910 photons s$^{-1}$. The position and width of the peak are temperature-independent. Inset, integrated intensity of the peak as a function of temperature, showing gradual, crossover behavior, in reasonable agreement with ref. 38.

In Fig. 4.3.5 we show reciprocal space maps around $(H,K,L_L) = (0,0,0.2)$ at $T = 28$ K, for x-ray energies both off and on the hole-doped of the ladder. Off resonance, only a specular ‘rod’ is visible, due to reflectance from the sample surface. If tuned to the ladder peak, however, a pronounced superlattice reflection appears, centered at $(H,K,L_L) = (0,0,0.200 \pm 0.009)$, indicating the existence of a modulation along the ladder with period $5.00 \pm 0.24$ c$_L$. This reflection is commensurate but is truly a superlattice peak, because it occurs at $L = 1.4$ (or $L_c = 0.14$) and so does not have the periodicity of the 27.3 Å unit cell. In particular, it should not be confused with the chain dimerization reflections, which have a different periodicity.

Finally, the x-rays were tuned to the ladder MCP and $L_L$ scans carried out at different temperatures [Fig. 4.3.6]. The hole modulation is visible below $T_c < 250$ K and monotonically increases with cooling. The onset is gradual but close to the $T_c \sim 210$ K estimated from low-frequency dielectric spectroscopy [38], suggesting that the hole crystal is responsible for the CDW signatures in transport. The width of the reflection is temperature-independent even near the transition, so the correlation length is limited by
some mechanism other than thermodynamics, perhaps impurities [23] or intrinsic quantum fluctuations.

Our study of Sr\textsubscript{14}Cu\textsubscript{24}O\textsubscript{41} corroborates the prediction [4] of hole crystallization in doped ladders, and supports the picture that proximity to charge ordered states is a general property of superconductivity in copper oxides. RSXS does not permit precise determination of the form factor of the hole crystal, but no harmonic was seen at $L_L = 0.4$, suggesting a sinusoidal, delocalized modulation as discussed in ref. 40 rather than a fully localized Wigner crystal [39]. The peak width [Fig. 4.3.2] shows that the modulation is coherent across, 50 neighboring ladders, demonstrating significant inter-ladder coupling.

As a hole crystal is charged, the reader may wonder why we do not see a distortion in the lattice which might be induced electrostatically. Such a modulation must exist, but would be of the order of the amplitude of the hole modulation itself, which is probably 1/1600 electrons. So the scattering power of a hole crystal is nominally weaker by $(1/1600)^2 \sim 10^{-6}$. Our point is not that the structural modulation is truly zero, but that electronic correlations, rather than the electron–phonon interaction, drive the transition.

### 4.4. Number of holes associated with the hole crystallization

In models of hole crystallization [40, 41], the relationship between the wavelength and hole density per Cu, $\delta$, in the ladder can be written as $\lambda = 1/(\delta c_L)$ or $\lambda = 2/(\delta c_L)$ in the strong and weak coupling regimes, respectively. For the $\lambda = 5.00c_L$, it would require $\delta = 0.20$ or $\delta = 0.40$. This leads to the open question concerning the relationship between the observed wavelength of $\lambda = 5.00c_L$ and the estimated [25] hole density in the ladder of $\delta = 0.057$ holes per copper atom. These models neglect many residual interactions and details of the chemistry, but this relationship is resilient to such corrections. This may indicate a problem with estimates of $\delta$, but it is worth noting that the hole crystal is commensurate with the lattice to within the measurement precision, suggesting that it is partly stabilized by elastic Umklapp processes. These can be significant for a commensurate hole crystal and perhaps strong enough to draw in extra charge from the chains. Another clue lies in the large transverse coherence length, which demonstrates significant interladder interactions, and the relationship between $\lambda$ and $\delta$ for a truly two-dimensional ordering pattern would not be so simple. It is therefore worth extending such models to the case of coupled ladders, or where the ladder interacts with a charge bath with which it may interchange carriers freely.

### 4.5 Superstructure in the chains of Sr\textsubscript{14}Cu\textsubscript{24}O\textsubscript{41}

It is also part of our goals to resolve the discrepancy concerning the charge ordering in the chain as we describe above. If charge ordering either model I or model II exists in the chain
then one should see the Bragg reflection at \( L_c = 0.25 \) or 0.20, respectively. In ladder units, the \((0,0,0.20)_L\) and \((0,0,0.25)_L\) reflection correspond to \((0,0,0.286)_L\) and \((0,0,0.357)_L\), respectively. While in the large unit cell, they correspond to \((0,0.2)\) and \((0,0.25)\). The \((0,0,0.20)_L\) reflection can be reached with a photon energy of 529 eV (O K edge), unfortunately the \((0,0,0.25)_L\) reflection cannot. In Fig. 4.3.2 is shown the widescan of \( L \) at \( E = 529 \) eV. Along this scan the \((0,0,0.25)_L\) reflection is not observed. Because the half-wavelength of a photon at 529 eV is larger than the \( d_{(0,0,0.25)} \), one has to change the photon energy to Cu \( L_3'\) edges. The scan along \( L\) of SCO at \( E = 933 \) eV (Cu \( L_3'\)) is shown as black filled-circles in Fig. 4.5.1. Also here we did not see any charge ordering in the chain as was previously claimed. Instead, we have seen an incommensurate Bragg reflection at \( L_c = 0.318 \pm 0.005 \). In the large unit cell and ladder units, the reflection \((0,0,0.318)_L\) corresponds to \((0,0.318)\) and \((0,0,0.454)_L\), respectively. None of these three coordinates are commensurate.

![Figure 4.5.1](image.png)

**Figure 4.5.1.** A widescan of \( L \) of SCO and LCCO with photon energy of \( E = 933 \) eV at 20 K. The inset is a close-look of the LCCO-case.

To see whether this reflection is related to charge ordering on the chains or ladders, one needs to do resonance profile studies at the O K edge. As mentioned above unfortunately, the wavelength at the O K is too long for such a study. Instead we compare the SCO to a system which contains no holes. The best comparison is with \( \text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41+y} \) (LCCO). The valence of the Cu here is +2.00 and any hole doping must be due to the possible non-stoichiometry \( y \). By tuning the photon energy to the Cu \( L_3'\) \( (E = 933 \) eV, one can...
eV), we find a Bragg peak at $L_c = 0.308 \pm 0.005$. This is shown as red filled-circles in Fig. 4.5.1. The $(0,0,0.308)_c$ reflection in the large unit cell and ladder units correspond to $(0,0,3.08)$ and $(0,0,0.44)_L$, respectively. This reflection, within the error bar, is basically a $(0,0,3)$ reflection.

Figure 4.5.2 (a) chain (b) ladder.

To understand the origin of $(0,0,3)$ reflection, one needs to write down the structure factor, $S$, of the large unit cell. Here, instead of working with all the atoms, we simplified the case with the following assumptions. Since we are only interested in the $(0,0,L)$ reflection, one can think of a 1-D system composed of arrays of atoms along the $c$-direction. We model our large unit cell as consisting of ladders and chains in which each of them can be treated separately. In Fig. 4.5.2(a) we show simple models that describe the shift of the copper ions in neighboring chains. We assume that both the copper and oxygen ions shift along the $c$-axis synchronously. A deviation $\Delta$ along the $c$-axis is introduced [Fig. 4.5.2(a-ii)] and it is varied from 0 [Fig. 4.5.2(a-i)], 0.5, and 1 [Fig. 4.5.2(a-iii)]. Based on the model above, we then write down the structure factor of the large unit cell of the chain as

$$S_{(0,0,L)}^{\text{chain}} = \sum_{i=0}^{10} f_i \left( e^{i 2\pi x_{i-1}/L} + e^{2\pi i (i-1/2 - \Delta)/L} \right)$$

(4.1)

where $k$ is the atom-$k^{th}$ and $\Delta$ is the deviation. The model for the ladder is shown in Fig. 4.5.2(b). And the structure factor for the ladder can be written as

$$S_{(0,0,L)}^{\text{ladder}} = \sum_{j=0}^{7} f_j \left( e^{i 2\pi y_{j-1}/L'} + e^{2\pi i (j-1/2)/L'} \right)$$

(4.2)

where $j$ is the atom-$j^{th}$ in the ladders. The scattering intensity of the chain and ladder is proportional to $|S_{(0,0,L)}^{\text{chain}}|^2$ or $|S_{(0,0,L)}^{\text{ladder}}|^2$, respectively.
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Figure 4.5.3 A simulation of scattering intensity of (a) chain and (b) ladder for a given $\Delta$ which is the deviation of atoms. The squares, circles and triangle are the scattering intensity for $\Delta = 0$, 0.25, and 0.5, respectively.

The results of the simulation of the scattering intensity as a function of $L$ for given $\Delta = 0$, 0.25, and 0.5, are shown in Fig. 4.5.3 (a). For $\Delta = 0$, the scattering intensity for $L = 20$ is the maximum while for $L = 10$ is 0 (forbidden reflection). For $\Delta = 0.25$, the scattering intensity of the $L = 20$ is decreasing while the $L = 10$ is increasing. And For $\Delta = 0.5$, the scattering intensity for $L = 20$ is 0 (forbidden reflection) while the $L = 10$ is reaching the maximum. Interestingly that for any given $\Delta$, the (0,0,3) reflection is always a forbidden reflection. The only changes are the scattering intensity of the (0,0,10) and (0,0,20) reflections. Different from the chain, the simulation of scattering intensity in ladders shows that the only reflection allowed in the ladder is (0,0,14) reflection.

It has been shown recently by Gellé et al., that the structural modulation in the chain is different from the structural modulation in the ladder [32]. In their studies, it was also found out that the interaction of atoms through the magnetic exchange interactions in the chains is weaker than the interaction of atoms in the ladders due to the 90° Cu-O-Cu bond. In order minimize the total energy between the ladders and the chains, the position of each atom in the chains will be modified to follow the potential modulation induced by the ladder [15]. This kind of distortion results in none-zero scattering intensity of the (0,0,3) reflection. In other words one may conclude that the (0,0,3) reflection is allowed due to the displacement of atoms in the chains. Therefore, the (0,0,3.08) reflection is likely the (0,0,3) reflection.
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Figure 4.5.4 A comparison of integrated Bragg intensity with XAS of SCO as well as LCCO. Filled circles, filled squares, open circles and open squares are XAS of SCO, XAS of LCCO, resonance profile of SCO and the resonance profile of LCCO, respectively. The XAS are taken at room temperature (298 K) with $E \parallel a$ while the resonance profile at 20 K.

Our central observation is the energy-dependence of these two Bragg peaks which are shown in Fig. 4.5.4. The XAS are taken at room temperature (298 K) with $E \parallel a$ while the resonance profiles have been at 20 K. At the Cu$L_{3,2}$ edges the XAS are polarization independent. By comparing the XAS of SCO and LCCO, one can see clearly that the full width at half maximum (FWHM) of SCO is wider by about 1 eV than FWHM of LCCO. At Cu $L_3'$, the intensity of the (0,0,0.318)$_c$ reflection is enhanced by 2 orders of magnitude compared to the intensity of the (0,0,0.308)$_c$ reflection. This strong enhancement may tell us that the (0,0,0.318)$_c$ reflection is related directly to hole modulation.

So what could the superstructure (0,0,0.318)$_c$ reflection be? The wavelength which is associated with this reflection is 0.3144$c$ where $c$ is the large unit cell. As we discussed in section (4.4), the number of holes participated in the (0,0,1/5)$_L$ reflection (remember that subscript-$L$ means in ladder unit) is 2.8 out of 6, the rest of the 3.2 holes cannot just have disappeared. For 1-D electron gas system, the relationship between the Fermi vector, $k_F$ and number of holes in the chain, $n_c$, can be written as
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\[
k_x = \frac{n \pi}{2L}
\]

(4.3)

and the wavelength, \( \lambda_x \), which is associated with this is \( 2\pi/k_x \). The interaction between holes in 1-D charge density wave (CDW) can possibly open up the Fermi gap at either \( 2k_F \) or \( 4k_F \) (for a large U system). If we have 3.2 holes in the chain, then the wavelength of the CDW associated with \( 2k_F \) and \( 4k_F \) are 0.625c and 0.3125c, respectively. It is very interesting here that the wavelength of the superstructure \((0,0,3.18)\) which is 0.3144c, within the error bar, is the same as the wavelength of the CDW in the chain with Fermi vector of \( 4k_F \). This is strong evidence that also the doped holes which are mainly on O 2p orbitals forming ZR like states should also be considered as strongly correlated with an large effective Hubbard U.

In Fig. 4.5.3, is shown the temperature dependence of this superstructure. Different from the CDW in the ladder, this superstructure is persistent all the way up to room temperature. The width of the reflection is temperature-independent. From this temperature dependence, it seems that the mechanism of this superstructure is not similar to the one in the CDW ladder. This could be due to strong influence of the structure modulation of \((0,0,3)\).

**Figure. 4.5.3** Temperature dependence of the superstructure \((0,0,0.318)\)

In conclusions, we can say that, we have not seen any charge ordering in the chain of the kind claimed from hard and neutron scattering experiments, but instead, we have found a CDW with a \( 4k_F \) modulation in the chain. So, this SCO has two CDW’s corresponding to hole crystallization in the ladder and a \( 4k_F \) hole modulation in the chain.
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