Resonant soft x-ray scattering and charge density waves in correlated systems
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Chapter 5

An interpretation of x-ray absorption on the spin ladder of Sr_{14-x}Ca_xCu_{24}O_{41}

In chapter 4 we have seen that the distribution of the holes in Sr_{14}Cu_{24}O_{41} (SCO) is one of the most important factors that govern the physical properties in the system. An understanding of the charge density waves described in the previous chapter requires detailed knowledge of the charge density in both the chains and ladders. Similar to high-$T_c$ superconductors, the holes are expected to be mainly supported by oxygen 2$p$ orbitals and to form ZR singlets [1] with an associated copper hole. This view is supported in SCO by the appearance of a strong “pre-edge” structure in the O K edge x-ray absorption spectrum.

We should keep in mind though 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$_{4h}$. According to the chemical formula and the knowledge that Cu is basically divalent the number of holes per formula unit (f.u.) is 6. How the holes are distributed between the chain and ladder layers is not known precisely. Various experiments [2,3] 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. This low density would make it very difficult to explain the wavelength of the hole crystal reported in chapter 4.

Also NMR data [4] 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 [2] suggest that the number of holes for the ladder ranges from 0.8 for $x = 0$ to 1.1 for $x = 12$. Optical conductivity[3], on the other hand, suggests a range from 1 to 2.8, while $^{63}$Cu NMR studies [4] suggest a range 1 to 3.5. However the interpretation of the optical conductivity and NMR data is based on observations by neutron diffraction, of what was thought to be a superlattice reflection corresponding to a charge density wave 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 [5] have clearly demonstrated that the peak observed in neutron diffraction is expected in the basic crystal structure and therefore is not evidence for a charge density wave. The only direct measurement of the hole density distribution is presented by the polarization dependent x-ray absorption studies. But also these results depend on the choice of the model, and unexplained discrepancies exist 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 Smaalen [6]. 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 $(H, K, L_c) = (0, 0, n \pm 1/4)$ [7]. 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

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

(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 $(H, K, L_c) = (0, 0, 2n \pm 1/5)$ [8]. They described the magnetic arrangement by

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

(model II) which corresponds to dimers of two spins coupled across one hole; neighboring dimers are separated by two successive holes. Such an arrangement will give rise to the interpretation of 6 holes being in the chains. 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 [6]. 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...
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this compound. Even more recently Gellé et al. suggest that the lattice misfit modulations influence the chain electronic structure [9], reinforcing the van Smaalen argument. The latest elastic neutron scattering results [10] 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 disappearance of the superstructure peaks above 200 K, they argue that the superstructure peaks may be related to charge ordering in the chain.

![Figure 5.1](image)

**Figure 5.1** Polarization dependent XAS of $x = 0$. The data are taken at room temperature. (a) XAS spectra taken from ref. 1. Filled symbol (for $E||a$) and open symbols (for $E||c$) along with the fitted partial distributions corresponding to holes (H1 and H2) and to the upper Hubbard band (U) (b) our results which are identical to those of ref. 2.

In this chapter we revisit the polarization-dependent x-ray absorption study which in principle at least should provide us with an accurate estimation of the distribution of holes between the chains and the ladders. A number of samples have been measured by Nucker et al. using this technique in the past [11]. In their interpretation of the data they concluded that the holes are mainly concentrated on the chains with only about 13% being situated on the ladders for $x = 0$. In fact as mentioned above this result has strongly influenced the interpretation of other x-ray, neutron and spectroscopic measurements. However several problems exist with the interpretation of the XAS data in ref. 11. One problem arises from an inconsistency with the polarization dependence of the XAS in the lowest energy part of the hole-doped prepeak observed in the O K edge. In **Fig.5.1 (a)** is shown the XAS for $x = 0$ taken from ref. [1]. Their interpretation is based on the assumption that there are only 2 distinct O 1$s$ absorption energies, one corresponding to holes in the chains and the other to holes in the ladders denoted by H1 and H2 respectively.
As they point out the peak H1 should not have any polarization dependence since the O 2p orbitals involved in the ZR singlets are oriented with lobes at 45 degrees to the a- and c-axis. While H2 depends strongly on polarization since the rung-O and the leg-O will have different hole occupation. Unfortunately, this is inconsistent with some of the experimental data. For instance, for \( x = 0 \), H1 is strongly polarized as it is for H2. They argued that the polarization dependence is small and assume they can neglect it.

We have looked at this issue again, employing data measured on our samples, and we suggest a different interpretation, which removes the problem that was mentioned in ref. 2 regarding the polarization dependence. Based on a different assignment of the peaks observed in the O K edge data we conclude that actually almost 50% of the holes are on the ladders for \( x = 0 \). This new interpretation, as we will show, is consistent with the wavelength of the hole crystallization observed in the ladders and CDW observed in the chains.

![Diagram of the chains indicating the orientation of the O 2p orbitals involved in the ZR singlets seen in the XAS pre edge peak.](image)

Figure 5.2 The structure of the chains indicating the orientation of the O 2p orbitals involved in the ZR singlets seen in the XAS pre edge peak.

Presently measured XAS for \( x = 0 \) is shown in Fig. 5.1 (b). The results reproduced the XAS by Nücker et al. [2] very well [see Fig. 5.1 (a)]. The spectra were corrected for incident flux variations and were normalized at about 70 eV above and 10 eV below the edge for both polarization where the absorption is atomiclike and structureless. We agree that the higher energy structure (~530 eV) is due to a transition to the upper Hubbard band from O 1s, as it is allowed because of the hybridization with the O 2p orbitals. This structure is only weakly polarization dependent, as we would have expected from the symmetry of the unoccupied \( d_{x^2-y^2} \) orbital in the \( ac \)-plane. Since the point group symmetry is not quite \( D_{4h} \) for the ladder some polarization-dependence will remain [see Fig. 5.3]. In addition there is a strongly polarization-dependent feature at lower energies which is clearly composed of at least two lines with different polarization-dependencies. In Nucker et al.’s. [2] measured XAS with a low hole concentration \( Y_3Sr_{11}Cu_{24}O_{41.05} (n_y=3) \), there is only one structure at the lower energy and its intensity is nearly polarization independent. As they conclude this strongly suggests that holes here are almost solely on the chains. The nearly
Polarization independence of XAS in the chain arises because all oxygen atoms in the chain are identical, they all are coupled to 2 Cu ions. In Fig. 5.2, we show the chain structure and the O 2p orbitals involved in the formation of the ZR singlets upon doping. Clear by here is also the 45 degree orientation of the O 2p orbitals contributing to the ZR singlets.

Figure 5.3 The structure of the ladders showing the 2 different kinds of O ions corresponding to O(r)$_a$ in the rungs and O(l)$_c$ + O(l)$_a$ in the legs. The subscript-$c$ and -$a$ refer to the polarization of the p orbital involved in the ZR singlet like states. Also shown is the orientation of the O 2p orbitals involved in the formation of the ZR singlets in the ladders.

In the ladder, things are a bit more complicated. There are two types of oxygen ions, those situated in the rungs coordinated by 2 Cu ions and for each of these there are 3 situated in legs which are coordinated by 3 Cu. We label these as O(r)$_a$, O(l)$_a$ ,and O(l)$_c$ respectively, as shown in Fig. 5.3. The subscripts $a$ and $c$ refer to the polarization direction of the x rays needed to make transitions to these 2p states. In one large unit cell, the total number of oxygen ions in the ladder is 42 with 28 of them in the leg and 14 in the rung. It is important to note here that due to the lower than $D_{4h}$ symmetry the ratio of O(r): O(l)$_a$:O(l)$_c$ is not 1: 1: 2 but rather 1.5 : 1: 2. The ratio is determined from the following assumptions. To have a ZR singlet, one needs to have one O(r), two O(l)$_c$ and one O(l)$_a$. Then the number of holes in the leg will be distributed as two-thirds for O(l)$_c$ and one-third for O(l)$_a$. 

\[ \begin{align*}
\text{Cu} & \quad \bullet \\
\text{O} & \quad \bullet \\
\text{O} & \quad \bullet \\
\text{O} & \quad \bullet \\
\text{O} & \quad \bullet \\
\text{O} & \quad \bullet \\
\text{O} & \quad \bullet \\
\text{O} & \quad \bullet \\
\text{O} & \quad \bullet \\
\end{align*} \]
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With this the ratio \( \text{O(r)}:\text{O(l)_c} : \text{O(l)_c} \) is 1.5 : 1 : 2. The different coordination numbers result in different binding energies for the \( O\ 1s \) core and \( 2p \) valence orbitals. We would expect that the higher coordination with \( \text{Cu}^{2+} \) would result in a higher core level binding energy than the lower coordination number.

Up to this point, we have three important keys to interpret the XAS results. First, the \( \text{O(c)} \) should not have any polarization-dependence since the \( \text{Cu-O-Cu} \) bond angle in the chains is very close to 90 degrees. Second, based on the geometry of the \( p \)-orbital in the ladder, the \( \text{O(l)} \) and \( \text{O(r)} \) should each exhibit a strong polarization dependence. And third, the binding energy of \( \text{O(r)} \) which is lower than in the legs should be close to the binding energy of \( \text{O(c)} \) since both are coordinated by 2 \( \text{Cu} \) ions.

Based on the assumptions above, we now try to explain the polarization-dependent XAS results. We start with \( x = 0 \) as example. The polarization dependent XAS are shown in Fig. 5.1 (b). For \( E || c \), the hole-doped region consists of at least two structures. In our interpretation this is due to the energy difference between \( \text{O(c)} \) and \( \text{O(l)_c} \). According to our interpretation, the intensity of \( \text{O(l)_c} \) for \( a \)-polarization, will decrease and the excitation corresponding to \( \text{O(r)} \) may become visible. This is consistent with the observed behaviour. The increase in the intensity of the lower energy part of the hole-doped spectrum for polarization along-\( a \) indicates that there is another contribution besides that from \( \text{O(c)} \) which we now can easily identify as that coming from \( \text{O(r)_a} \). It was this part of the data which was not consistent with Nucker \textit{et al.}'s interpretation and we suggest that this is due to \( \text{O(r)_a} \) in the ladders which would have only \( a \)-polarization and should appear at energies close to the energy of the chain oxygen.

To estimate the number of holes in the chains and ladders, we need to fit the XAS and compare the relative spectral weight of \( \text{O(c)} \), \( \text{O(r)} \) and \( \text{O(l)_c} \) and \( \text{O(l)_a} \). As one can see in Fig. 5.1 (b) that the background intensity is between 320 – 420 counts (cts) and the peaks are in order of 1400 – 1800 cts while the noise level is between 25 – 75 cts. The fitting program which was used is a “Spectrometer Operation and Data Acquisition Program” modified by A. Heeres. It is one of the standard fitting programs in the field of spectroscopy. The iteration procedure in the fitting is based on a “Chi-Square (\( \chi^2 \)) Minimization” method in which the sum of the squares of the deviations of the theoretical curve(s) from the experimental points for a range of independent variables is at its minimum. In a counting type of experiment there is always statistical noise which will on the average be \( \sqrt{N} \) where \( N \) is the number of counts in a particular data point. In fact for the statistical noise the best fit possible for the \( \chi^2 \) equal to \( \sqrt{N}/N = 1 \). So if there are no systematic errors and one has a really good choice for the function used to fit the data the \( \chi^2 \) would be equal to 1 at the best fit. The fitting procedure is as follows. We start with the \( E || c \) data simply because it contains only two peaks corresponding to \( \text{O(c)} \) and \( \text{O(l)_c} \) and their
energies are resolvable. First, we give input variables which are reasonable estimates of the energies of O(c), O(l)c, and the UHB peaks. For x = 0 they are 528 eV, 528.6 eV and 528.85 eV, respectively. A constraint was set to keep the full width at half maximum (FWHM) of O(l)c and the FWHM of O(c) equal. We have found that this constraint is useful as a starting point to get reasonable results. We let the program run until it reached the local minimum of the Chi-Square. And then switch the constraint on the FWHM off, and do the fit again allowing now the widths to vary. It turns out that the widths change by not more than 6%. Output parameters of the fit which are energy, FWHM, and peak height of O(l)c, O(c), and UHB peaks are then used as input parameters to fit the a-polarization data. The doped hole peak of XAS with a-polarization contains three peaks which are O(r), O(l)a, and O(c). Difficulties arise, because of the strong overlap of the O(l)a and O(c) peaks. One cannot use all parameters (FWHM, peak height, and energy) as free variables at the same time. So, we introduce constraints to help us in the fitting process. First, the FWHM and energy of O(l)a are set equal to the FWHM and energy of O(l)c. Second, the peak positions corresponding to O(c) and O(l)a may differ by not more than 5%. Third, the peak height of O(c) should be polarization independent. At the beginning, it is useful to constrain the peak height of O(l)a and O(r). But this can be switched off later. An extra peak we introduce here is O(r). The “initial” input energy of O(r) is 528.25 eV (see chapter 6 to see the reason for this number) and the FWHM of O(r) is the same with the FWHM of O(l)c. Again, we let the program run until it finds the minimum of the Chi-Square. Output parameters from this will be FWHM, peak height, and energy of O(c), O(r) O(l)a, and UHB peaks.

In Fig. 5.4 (a) and (b) the results of the fits are shown for E||c and E||a data using the procedures above. The fitting is done to a sum of Gaussian- and Lorentzian-line shapes in the ratio of about 80%. The value of Chi-Square for E||c and E||a data is 2 and 1.15, respectively. A factor of 2 higher than pure statistical noise is generally a very acceptable value for a good fit. The positions, FWHM, peak height and integrated intensity of the peaks are given in Table 5.1.

It is interesting to check the consistency of the results with our understanding of polarization dependent XAS. First, one can see directly that the UHB is almost polarization independent which is consistent with our understanding of polarization dependent XAS and the nature of the $d_{x^2-y^2}$ orbitals. Second, the ratio of O(l)c to O(l)a to O(r) is 1.6:1.0:1.2 which is quite close to 2.0:1.0:1.5. This is also consistent with our understanding that the holes are distributed nearly isotropically over all 4 oxygen atoms contributing to the ZR singlet state. Since we are not in D4h symmetry there can of course be small deviations from this. If the deviations were very large we would have to conclude that the ZR picture is not valid for the doped holes in the ladders. This all gives us strong confidence about our fitting procedures.
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Figure 5.4 XAS for (a) E||c and (b) E||a with theoretical curves for x = 0. Black filled squares are the experimental data. Black dashed line, grey dashed line, dot, grey solid line, and black solid line are theoretical curve for O(c), O(r), O(l)\(_c\) (as well as O(l)\(_a\) UHB and total fit.

Table 5.1 The positions, FWHM, peak height and integrated intensity of the peaks of x = 0 for E||c and E||a data.

<table>
<thead>
<tr>
<th></th>
<th>Position (eV)</th>
<th>Width (eV)</th>
<th>Peak Height (Counts)</th>
<th>Integrated Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td></td>
<td>c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(c)</td>
<td>528.08</td>
<td>0.62</td>
<td>795</td>
<td>562</td>
</tr>
<tr>
<td>O(l)(_c)</td>
<td>528.58</td>
<td>0.58</td>
<td>621</td>
<td>410</td>
</tr>
<tr>
<td>UHB</td>
<td>529.73</td>
<td>1.00</td>
<td>737</td>
<td>841</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(c)</td>
<td>528.08</td>
<td>0.62</td>
<td>795</td>
<td>562</td>
</tr>
<tr>
<td>O(l)(_a)</td>
<td>528.58</td>
<td>0.58</td>
<td>399</td>
<td>264</td>
</tr>
<tr>
<td>O(r)</td>
<td>528.23</td>
<td>0.58</td>
<td>479</td>
<td>317</td>
</tr>
<tr>
<td>UHB</td>
<td>529.81</td>
<td>1.00</td>
<td>705</td>
<td>806</td>
</tr>
</tbody>
</table>

The number of holes in the ladder \(n_L\) is determined as follows;

\[
n_L = \frac{SW_{O(c)c} + SW_{O(l)c} + SW_{O(l)c}}{SW_{O(c)c} + SW_{O(l)c} + SW_{O(l)c} + SW_{O(l)c}} \times 6
\]  

(5.1)
where \( SW_{O(r)} \), \( SW_{O(l)} \), \( SW_{a(l)} \), and \( SW_{O(c)} \) are the spectral weight for O(r), O(l), O(l), and O(c), respectively, respectively. Note here that the \( SW_{O(c)} \) is the total SW for both polarizations.

In table 5.1, the SW equals to the integrated intensity. And the number of holes in the chain \( n_c \) is given by:

\[
   n_c = \frac{SW_{O(c)}}{SW_{O(r)} + SW_{O(l)} + SW_{a(l)} + SW_{O(c)}} \times 6 \tag{5.2}
\]

If we insert the \( SW_{O(r)} \), \( SW_{O(l)} \), \( SW_{a(l)} \), and \( SW_{O(c)} \) determined from our fitting into eq. (5.1) and (5.2), we find \( n_L = 2.81 \) and \( n_c = 3.19 \).

In chapter 4, we have discussed the hole crystallization in the ladder and charge density wave (CDW) in the chain for \( x = 0 \). Based on our RSXS analysis, the number of holes required for the hole crystallization with the correct wave length is 2.8 while the number of holes required for the chain CDW at a wave length corresponding to \( 4k_F \) is 3.2. This hole density in the ladder and the chain are consistent with the estimated numbers from polarization XAS based on our new interpretation.

![Figure 5.5 XAS with (open-circles) E||c and (filled-circles) E||a for Sr\(_{10}\)Ca\(_4\)Cu\(_{24}\)O\(_{41}\).](image)

We follow the same procedures as explained above for the analysis of XAS data measured on Sr\(_{10}\)Ca\(_4\)Cu\(_{24}\)O\(_{41}\) (\( x = 4 \)). In Fig. 5.5 is shown the polarization dependent XAS for \( x = 4 \). The background intensity is between 50 – 100 cts and the peaks are in the order of 300 – 500 cts while the noise level is between 60 - 110 cts.
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Figure 5.6 XAS for (a) $E\parallel c$ and (b) $E\parallel a$ with its theoretical curves for $x = 4$. Black filled-squares are the experimental data. Black dashed line, grey dashed line, dot, grey solid line, and black solid line are theoretical curve for O(c), O(r), O(l),c (as well as O(l),a) UHB and total fit.

In Fig. 5.6 (a) and (b) the results of the fits are shown for $E\parallel c$ and $E\parallel a$ data of $x = 4$ using the procedures above. The fitting is done to a sum of Gaussian- and Lorentzian-line shapes in the ratio of about 80%. The value of Chi-Square for $E\parallel c$ and $E\parallel a$ data is 1.145 and 1.054, respectively. This represents a very good fit to data since the $\chi^2$ is close to 1. The positions, FWHM, peak height and integrated intensity of the peaks are given in Table 5.2.

Table 5.2 The positions, FWHM, peak height and integrated intensity of the peaks of $x = 4$ for $E\parallel c$ and $E\parallel a$ data.

<table>
<thead>
<tr>
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<th>Positions (eV)</th>
<th>Width (eV)</th>
<th>Peak Height (counts)</th>
<th>Integrated Intensity</th>
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<td>$E\parallel c$</td>
<td></td>
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</tr>
<tr>
<td>O(c)</td>
<td>528.00</td>
<td>0.60</td>
<td>205</td>
<td>141</td>
</tr>
<tr>
<td>O(l),c</td>
<td>528.56</td>
<td>0.62</td>
<td>191</td>
<td>135</td>
</tr>
<tr>
<td>UHB</td>
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<td>177</td>
<td>202</td>
</tr>
<tr>
<td>$E\parallel a$</td>
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<td></td>
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<tr>
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<td>1.00</td>
<td>170</td>
<td>194</td>
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</table>
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One can see directly that the UHB is almost polarization independent. The ratio of O(1)$_c$ to O(1)$_a$ to O(r) is 1.5:1.0:1.4 and is close to $x = 0$ results. These all are consistent with our understanding of polarization XAS. It is important to ask, what the Ca does to the total number of holes. Since the valence of Ca is +2 which is the same as the valence of Sr, the total number of holes in the system does not change on introduction of Ca. The distribution of the holes in the chain and ladder may however change. In this case, the eq. (5.1) and eq. (5.2) are still valid. Our estimates for the hole concentration are here $n_L = 3.3$ and $n_c = 2.7$. Of course, it is interesting to analyse what would be the wavelength of hole crystallization, if there is any, which is related to these 3.3 hole density in the ladders. In models of hole crystallization [12,13], the relationship between the wavelength and hole density in ladder can be written as $\lambda = 14/n_L$ or $\lambda = 7/n_L$ in the paired hole or unpaired hole models respectively. For the $\lambda = 4.00$ $c_L$, it would require $n_L = 3.5$ or 1.75. According to this hole distribution, it seems that it is possible to have hole crystallization with the pairing of holes mechanism as for $x = 0$ case in the ladder with $\lambda = 4.00$ $c_L$. While in the chain, the wavelength of the CDW chain corresponding to $4k_F$ would be 2.7 $c_v$. The results of RSXS will be shown in chapter 6.

![Figure 5.7 Polarization dependent XAS of Sr$_{13}$Ca$_1$Cu$_{24}$O$_{41}$ ($x = 11$). Open circles and filled circles are XAS for E||c and E||a data, respectively.](image)

The polarization dependent XAS results for high-Ca substitution differ from those of Nucker et al. [2]. In Fig. 5.7 is shown our polarization dependent XAS for $x = 11$. The background intensity is between 740 – 780 cts and the peaks are in the order of 1800 – 2300 cts while the noise level is between 10 - 40 cts. The statistics here show that the peak
to noise is better than 25 to 1. One can see from the results of ref. 2 that the UHB exhibits a
strong polarization dependent XAS while the O doped hole pre-edge region is almost
polarization independent. Our results show an opposite behaviour with a strong polarization
dependence in the pre-edge region and almost no polarization dependence in the UHB
region. Based on the geometry of Cu$_2$O$_3$ plane, the UHB region is expected to be
polarization independent. But, if one looks at those two results carefully, the shape and the
intensity of the hole-doped and UHB peaks of ref. 2 are similar to ours. If we rescale the
E||c or E||a result of ref. 2 until the UHB is polarization independent, then the results are all
but identical to what we obtained. So, it seems that the difference is coming from the
method of normalization of the data.

Figure 5.8 XAS for (a) E||c and (b) E||a with its theoretical curves for $x = 11$. Black filled-
squares are the experimental data. Black dashed line, grey dashed line, dot, grey solid line,
and black solid line are theoretical curve for O(c)$_c$, O(r)$_c$, O(l)$_c$ (as well as O(l)$_a$) UHB and
total fit.

To fit the polarization dependent XAS of $x = 11$ is more difficult than $x = 0$ or 4.
The problem is not coming from the statistical noise, but rather from the structural peaks
themselves. We can see from Fig. 5.7 (b) that there is no clear evidence that there would be
two peaks or three peaks in the doped hole regime. If one does not take into account the
polarization dependent XAS for $x = 0$, it is hard to believe that the doped hole regime
contains 2 peaks from the ladders and 1 peak from the chains. Indeed the fitting procedure
is unstable if we do not add constraints. We now rely on our understanding of fitting the
$x = 0$ and the $x = 4$ data. We use the same procedure as we explained above. We start fitting
XAS of E||c data, and then go to E||a, back to E||c, do this loop until we have found the
minimum Chi-Square for both cases. The inputs (FWHM, position, and peak height) of
each peak we gave to the program is from the results of \( x = 0 \). In Fig. 5.8 is shown the XAS of (a) \( c \)-polarization and (b) \( a \)-polarization with its theoretical curves for \( x = 11 \). Black filled-squares are the experimental data. Black-line, red-line, blue-line, green and cyan-line are theoretical curve for O(c), O(r), O(l) (as well as for O(l)\(_a\)) UHB and total fitting. The \( \chi^2 \) for E\( ||c \) and E\( ||a \) is 1.14 and 1.16, respectively. And these are very acceptable fitting results since they are close to 1. The energy, FWHM, peak height and integrated intensity of the peaks after background subtraction are shown in Table 5.3.

**Table 5.3** The energy, FWHM, peak height and integrated intensity of the peaks (area) of \( x = 11 \) for E\( ||c \) and E\( ||a \).

| E\( ||c \) | Energy (eV) | Width | Peak Height | Area |
|---|---|---|---|---|
| O(c) | 528.00 | 0.64 | 462 | 338 |
| O(l)\(_c\) | 528.48 | 0.78 | 1009 | 899 |
| UHB | 529.87 | 1.20 | 731 | 1002 |

| E\( ||a \) | Energy (eV) | Width | Peak Height | Area |
|---|---|---|---|---|
| O(c) | 528.01 | 0.64 | 462 | 338 |
| O(l)\(_a\) | 528.47 | 0.78 | 492 | 438 |
| O(r) | 528.28 | 0.78 | 674 | 601 |
| UHB | 529.87 | 1.20 | 718 | 984 |

The first thing we should check is the polarization of UHB. One can see here that the UHB is almost polarization independent. It means, it is still consistent with our understanding. The ratio of O(l)\(_c\) to O(l)\(_a\) to O(r) is 2:1.0:1.14. This ratio is not far off from 2:1:1.5. These all are still consistent with our understanding of polarization XAS. It is important to note here that, the results depend very much on the energy position of O(c). By varying this by 0.05 eV gives an error bar of \( n_L \) and \( n_c \) by about 0.5. The quite big error bar is due to an apparent instability in the fitting process caused by the close proximity of peaks in the pre-edge region. As one can see the energy of O(c) falls close to the leading edge of the hole-doped peak. As we described above Ca substitution does not change the total number of holes in the system. We will again use the eq. (5.1) and eq. (5.2) to estimate the \( n_L \) and \( n_c \). Our estimation for \( n_L \) and \( n_c \) here are about 4.4 and 1.6, respectively.

What would be the wavelength of hole crystallization in the ladder related to or close to this 4.4 total holes? For the \( \lambda = 3.00 \ c_L \), it would require \( n_L = 4.66 \) or 2.33 for pairs or unpaired holes in the ladders. To have a pairing conditions as for the \( x = 0 \) case, one needs an extra of “only” 0.26 holes. So that, there is a possibility of having hole crystallization as it is in \( x = 0 \), with \( \lambda = 3.00 \ c_L \). The rest of the 1.6 holes reside in the chain.
If we treat this as CDW chain corresponding to $4k_F$ as it is for the $x = 0$ case, the wavelength of the CDW chain corresponding to $4k_F$ is $1.6 \ c_L$. The results of RSXS for $x = 0, 1, 2, 3, 4, 5, 10, 11, \text{ and } 12$ will be shown in chapter 6.

![Figure 5.9 The estimation of number of holes in the ladders and the chain. Filled- and open-circles are for ladders and chain, respectively. The dashed lines, are the required number of holes for $\lambda = 3c_L, 4c_L$ and $5c_L$.](image)

In conclusion, we have proposed a new interpretation of polarization dependent XAS. With this new interpretation, we have found that the number of holes in the ladder for $x = 0$ is 2.81 and this is consistent with the hole crystallization lattice constant of $L_L = 1/5$ as we found from the RSXS in chapter 4. The estimation of number of holes in the chains based on our understanding of polarization XAS is 3.19 and is also consistent with the “$4k_F$” charge density wave in the chain found from RSXS. The influence of Ca substitution for Sr, which does not change the total number of holes in the system, acts like a “pressure” that is strong enough to push holes from chain to ladder. The estimation of the number of holes in the ladder and the chain for $x = 0, 4, \text{ and } 11$ are shown in Fig. 5.9. Also shown is the number of holes corresponding to $\lambda = 3c_L, 4c_L$ and $5c_L$. It is important to note here that the density of holes in the ladders and the chains changes almost linearly as function of Ca-substitution. The linear trend has also been founded in other experiments [11,14,15].
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References

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