Chapter 3

Testing the technique: Resonant soft x-ray scattering

The sensitivity of resonant soft x-ray scattering (RSXS) to charge modulations has been tested on various systems. The systems we studied are La$_2$CuO$_{4+y}$ films, YBa$_2$Cu$_3$O$_{6.5}$ and underdoped single crystals of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. In La$_2$CuO$_{4+\delta}$ films we observed an inhomogeneous distribution of oxygen doping. We have also observed a superstructure at the (0,0,1.054) reflection for doped films. In YBa$_2$Cu$_3$O$_{6.5}$ (ortho-II YBCO) we observed direct evidence for modulation of low energy electronic states of Cu in both the CuO$_3$ chain and the CuO$_2$ plane. A huge polarization-dependent enhancement of the (1/2,0,0) superstructure Bragg peak is observed when the photon energy is tuned to the Cu $L_{2,3}$ absorption edge. The ordering in the CuO$_2$ plane discovered here sheds new light on how the one dimensional Cu-O chains affect the CuO$_2$ plane, and why many normal and superconducting state properties of this system exhibit strong anisotropy. It is also important that, with this technique, an incommensurate structural modulation in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ is observed that was seen with hard x-ray diffraction. We have confirmed that there is no participation of charge modulation in the CuO planes in this superstructure. We also learned that the interference between regular scattering and resonance scattering can lead to a complicated shape of the RP which strongly depends on the relative phase of these scattering processes.

3.1 Intrinsic inhomogeneity in epitaxial La$_2$CuO$_{4+\delta}$ films

An unresolved issue concerning cuprate superconductors is whether the distribution of carriers in the CuO$_2$ plane is uniform or inhomogeneous. Because the carriers comprise a small fraction of the total charge density and may be rapidly fluctuating, modulations are difficult to detect directly. Here, we demonstrate that in anomalous x-ray scattering at the oxygen K edge of the cuprates, the contribution of carriers to the scattering amplitude is selectively magnified 66 times. This enhances diffraction from the doped holes by more than $(66)^2$, permitting direct structural analysis of the ground state. At the Cu $L_{3,2}$ edges, which are also sensitive to magnetic scattering, the enhancement of scattering amplitude is about 300 times. We have also observed a sharp superstructure reflection at $(H,K,L) = (0,0,1.05)$ at the O K edge for specific films which contain excess oxygen. An interesting
property of this superstructure is that the full width at half maximum (FWHM) is not consistent with the thickness of the film. For industrial purposes, this technique can be used as a tool to probe the properties of engineered epitaxial films and multilayers because the photon penetration depth at resonance is several hundred angstroms. We will present a study of this penetration depth for various resonant energies.

3.1.1 Introduction

Soon after the discovery of high-temperature superconductivity it was shown theoretically that holes doped into an antiferromagnet should be unstable to the formation of charged magnetic domain lines or “stripes” with incommensurate spacing [1,2]. Recent evidence from scanning tunneling microscopy (STM) suggests that the integrated local density of states at the surface of Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ is indeed inhomogeneous [3,4], and when exposed to an external magnetic field spontaneously forms incommensurate “checkerboard” patterns in the vortex core [5]. It is an issue central to research on cuprate superconductors to determine whether the local carrier density (that is, the density of doped holes) correlates spatially with these spectroscopy effects. There is therefore a tremendous need for a scattering probe sensitive to the doped holes, which could reveal their spatial distribution in the ground state.

Incommensurate structural features have been observed in the cuprates with both x-ray and neutron diffraction [6,7,8]. However, because the carriers comprise a very small fraction of the total charge density (about 1 part in 404 for optimally doped La$_2$CuO$_{4+y}$), x-ray scattering is normally dominated by the core electrons. Neutrons couple only to nuclei and magnetic moments and are not sensitive to charge at all. So the relationship between these observations and the distribution of carriers in the ground state, unfortunately, is unclear.

Resonant soft X-ray scattering (RSXS) is similar to multiwavelength anomalous diffraction [9] or resonant magnetic x-ray scattering [10], in which resonance effects provide sensitivity to atomic species or the local magnetic moment, respectively. Like other scattering probes, this technique is bulk sensitive (for instance penetration depth ~ 50 nm at O K edge.) and can detect fluctuating phenomena, making it kinematically complementary to STM, which detects static surface effects. The spatial resolution is modest [half-wavelength ($\lambda/2$) ~ 1.1 nm]; however, it is well-suited to mesoscopic phenomena. This is, by many standards, the first direct structural probe of the ground state in the cuprates.

The samples studied in this section were epitaxial films of La$_{2-x}$Sr$_x$CuO$_{4+y}$, synthesized with a unique combinatorial MBE system formerly at Oxxel GmbH in Bremen, Germany. These structures are some of the highest-quality in the world, atomically smooth over microns with interface roughness of less than 3 Å, and have been used already for
testing fundamental theories of superconductivity [11]. We exploit their high quality to make quantitative determination of the anomalous scattering factors in the soft x-ray range, which will allow us to investigate the possibility of stripe modulations and other inhomogeneity with quantitative precision.

![Crystal structure of La$_{2-x}$Sr$_x$CuO$_4$](image)

**Figure 3.1.1.1** Crystal structure of La$_{2-x}$Sr$_x$CuO$_4$ [12,13].

The structure of La$_2$CuO$_4$ (LCO) is drawn in Fig. 3.1.1.1 [12,13]. We use the $Bmab$ orthorhombic unit cell with $a$ and $b$ along the diagonals of the square and $c$ perpendicular to the layers. Our hard x-ray study shows that the lattice constant for the undoped thin film LCO is $a = 5.384(2)$ Å, $b = 5.379(2)$ Å, and $c = 13.156(2)$ Å, while for doped one is $a = 5.35(2)$ Å, $b = 5.33(2)$ Å, and $c = 13.29(2)$ Å. The substrate (STO) is a cubic system with lattice constant $a = b = c = 3.90(5)$ Å. Due to the strain effect between the films and substrate, the lattice parameters in the films is slightly different from bulk samples [12,13].

### 3.1.2 Enhancement of the structural modulation as seen at the Cu $L$ edge

One of the advantages of resonant x-ray scattering is that it allows one to employ spectroscopy and diffraction simultaneously. XAS were collected in the fluorescence yield mode. The incident beam is horizontally polarized so we can vary the polarization by rotating the sample relative to the incident photon propagation direction. The outgoing photons were detected by a detector looking at a grazing angle. The grazing angle ensures that what we detect is coming from the film. In Fig. 3.1.2.1 (a) is shown the experimental geometry of XAS for a $E||ab$-plane. The diffraction experiments were done in a specular reflectivity geometry with the angle as seen in Fig. 3.1.2.1 (b). For these thin films the
CuO$_2$ plane is parallel to the sample surface.

**Figure 3.1.2.1** Schematic geometry of the experiments. (a) In the Fluorescence yield mode the incoming photons are perpendicular to the surface while the outgoing photons are collected at grazing emission (about 5°-10° from the sample surface). The beam polarization $E$ is fixed in the $ab$-plane. (b) Diffraction in the specular reflectivity mode, in which the linear polarization $E$ depends on the angle of incident photons.

In **Fig.3.1.2.2** is shown the XAS at the Cu $L$ edges of (a) La$_2$CuO$_4$, (c) YBa$_2$Cu$_3$O$_{6.5}$, Cu$_2$O as well as CuO. The XAS of Cu$_2$O and CuO are taken from ref. 16. The resonant enhancement is a soft x-ray spectroscopy effect that can be understood as follows. The high-temperature superconducting (high-$T_c$) materials exhibit Cu $L$ (931 eV and 952 eV) edges, which correspond to removal of an electron from Cu $2p$ inner shells and its promotion to the Cu $3d$ orbital. The Cu $L$ edges are better described as a pair of peaks rather than an edge, which correspond to the dipole-allowed $2p\rightarrow3d$ transitions where the hole has $j = 1/2$ or $3/2$ [14]. This absorption is large only if the Cu $3d$ states are not full as is the case for Cu$^{2+}$ with $3d^9$ electrons [see **Fig. 3.1.2.2 (c)**]. This large absorption is also shown in a simple material like CuO where the Cu is in a nominally Cu$^{2+}$ ($3d^9$) [see **Fig. 3.1.2.2 (c)**]. But, if the Cu $3d$ states are full as in Cu$^{+}$ with $3d^{10}$ electrons as in Cu$_2$O, there is a weak absorption at about 2-3 eV higher in energy which looks more like an edge than a sharp peak and is at least in part due transition to the $4s$ band states [**Fig 3.1.2.2 (c)**]. Because the unoccupied Cu $3d$ states in the high-$T_c$’s are $d_{3/2,5/2}$ states they are polarized in the CuO$_2$ plane, and the Cu $L$ feature is observable in XAS only for $E\parallel ab$ [15].
3.1.2. Enhancement of the structural modulation as seen at the Cu $L$ edge

Figure 3.1.2.2 (a) X-ray absorption spectrum at the Cu $L_{3,2}$ edge for optimally doped La$_2$CuO$_{4+\delta}$ taken in the fluorescence yield mode for $E\parallel ab$, and (b) $ab$-plane susceptibility, $\chi$ in SI units, calculated by the procedure described for (filled and open circles) optimally doped La$_2$CuO$_{4+\delta}$ and (solid and dashed line) SrTiO$_3$. (c) X-ray absorption spectrum for Cu 2p to 3d transitions in YBCO, which can be fit with a linear combination of CuO and Cu$_2$O spectra taken from ref. 16. The inset illustrates Cu 2p→3d resonant scattering (detail can be seen in Section 3.2).
This sensitivity influences diffraction because the amplitude for light scattering from a material is proportional to the dielectric susceptibility, \( \chi(k, \omega) \), [17] which is related to XAS through the absorption coefficient

\[
\mu = 2 \ k \ \text{Im}(n)
\]  

(3.1.1)

where

\[
n = \sqrt{1 + \chi}
\]

(in SI units)  

(3.1.2)

This quantity is strongly energy dependent. Here \( k = 2\pi/\lambda \) where \( \lambda \) is the x-ray wavelength and \( n(\omega) \) is the refractive index. We can quantify the size of the resonance at the Cu \( L_{3/2} \) by calculating \( \text{Im}[n(\omega)] \) by Kramers-Krönig transforming to get \( \text{Re}[n(\omega)] \) and computing \( \chi \). Using the tabulated atomic scattering factors to set the absolute scale, we determined \( \chi \) for optimally doped \( \text{La}_2\text{CuO}_4^{+\delta} \) [Fig. 3.1.2.2(b), solid and open circles]. Also shown is \( \chi \) for \( \text{SrTiO}_3 \) taken from tabulated atomic data (solid and dash line) [18].

![Graph](image)

**Figure 3.1.2.3** Reflectivity of a 23.2-nm \( \text{La}_2\text{CuO}_4^{+\delta} \) film \( (T_c = 39 \text{ K}) \) (a) below and on the Cu \( L_{3/2} \) edge, showing the resonant enhancement and (b) over the full angular range for 931.0 eV which corresponds to the reciprocal space interval \( (0,0,0.34) \rightarrow (0,0,1.98) \).

When a plane wave falls on the boundary between two homogeneous media of different dielectric susceptibility, \( \chi \), it is split into two waves – a transmitted wave transmitted into the second medium and a reflected wave propagating back into the first medium. Through this phenomena, one might expect two parallel interfaces to exhibit interference fringes with angular maxima at \( 2l \sin(\theta) = n\lambda \), where \( l \) is the film thickness. The anomalous enhancement of the Cu \( L \)-edges effects is demonstrated in this
3.1.2. Enhancement of the structural modulation as seen at the Cu L edge

measurement. However, at \( \omega = 925.5 \) eV, shown as filled circles in Fig. 3.1.2.3 (a), fringes are hardly visible. This is because off resonance, \( \chi \) is determined by the electron density, and the density of the SrTiO\(_3\) substrate (5.12 g/cm\(^3\)) and the strained film (<6 g/cm\(^3\)) do not differ significantly. So optically the film/substrate ensemble looks like a semi-infinite layer with reflectivity given by the Fresnel formulas. However, if the energy is changed by 4.5 eV to the Cu L\(_3\), there is a 78% boost in the film susceptibility and pronounced interference fringes appear [Fig. 3.1.2.3(a) and (b), open circles].

At the threshold of the Cu L\(_3\) peak, the interference fringes, which are barely visible off resonance, approach \( > 10^5 \) photons/s [Fig. 3.1.2.3(a)]. Reflectivity over the full angular range is shown in Fig. 3.1.2.3(b). Because Cu L edge features are polarized, and we have P polarized light, one expects the interference fringes to grow toward higher scattering angles where polarization (E) lies along the CuO\(_2\) planes. The Cu L fringes at 931 eV do exactly that.

**Born Approximation**

It is known that scattering provides us with direct information about the dielectric susceptibility \( \chi \) of materials. One may ask what the relationship is between \( \chi \) and the on-specular intensity measured for these thin films. If we assume kinematic scattering we may apply the Born approximation, in which case the scattering amplitude can be expressed in terms of one-dimensional integrals of the form

\[
\chi(q) = \frac{1}{iq} \int dx \chi(x) e^{iqx} \quad (3.1.3)
\]

where \( \chi(x) \) is the spatially varying susceptibility and \( q = 4\pi/\lambda \sin(\theta) \) is the momentum transfer. For an isotropic film of thickness \( l \) with susceptibility \( \chi_F \) on a substrate with susceptibility \( \chi_S \), this integral has the value

\[
\chi(q) = \frac{\chi_F}{iq} \left[ 1 - e^{-iql} \right] - \frac{\chi_S}{iq + \eta} \quad (3.1.4)
\]

where a convergence factor \( \eta \) attenuates the substrate at infinite distances. If the film is anisotropic the susceptibility is a tensor

\[
\chi(q) = \begin{pmatrix}
\chi_{\omega}(q) & 0 \\
0 & \chi_F(q)
\end{pmatrix} \quad (3.1.5)
\]

in which case the scattering matrix element, incorporating polarization effects, has the form

\[
M = \hat{e}_1 \cdot \chi(q) \cdot \hat{e}_2 \quad (3.1.6)
\]

where \( \hat{e}_1 \) and \( \hat{e}_2 \) are the incident and scattered polarizations. The scattered intensity is then

\[
I \sim |M|^2 \quad (3.1.7)
\]
Figure 3.1.2.4 Simulation in the Born approximation for three models of the susceptibility. (a) isotropic models where $\chi^{ac}_{F}/\chi_{STO} = \chi^{ab}_{F}/\chi_{STO}$. (b) anisotropic models where $\chi^{ac}_{F}/\chi_{STO} \neq \chi^{ab}_{F}/\chi_{STO}$. The sample thickness is 22.0 nm with incoming photon energy ($E$) of 931 eV. Here, we apply the following models of susceptibility. (c) Scattering intensity as function of angle of incident for Model I, II and III, and (d) Model I, Model IV, and Model V. The parameters of the models are stated in the text.
Now, let’s apply the following models to the eq. (3.1.7) with the susceptibility taken from Fig. 3.1.2.2 (b). Model I is an “isotropic” model, taking the susceptibility of substrate to be \( \chi_s = 0.001 \) and equal to that of the film. Model II is also an “isotropic” model, again assuming the susceptibility of the substrate \( \chi_s = 0.001 \), and the susceptibility of the film \( \chi_f^a = \chi_f^b = 0.0018 \) [see Fig. 3.1.2.4(a)]. The 78% higher susceptibility of the film than the substrate is taken from analysis of XAS above. Model III is a more realistic anisotropic model, assuming the susceptibility of substrate \( \chi_s = 0.00100, \) while the susceptibility in the \( ab \)-plane of the film \( \chi_f^a = 0.00180 \) and susceptibility in the \( c \)-direction \( \chi_f^c = 0.00103 \) [see Fig. 3.1.2.4(b)]. Here, the larger \( c \) axis value of 0.03% results from the small difference in density of the film and substrate. Model IV assumes the susceptibility of substrate \( \chi_s = 0.00100, \) while the susceptibilities are \( \chi_f^a = \chi_f^c = 0.00103. \) Model V takes the susceptibility of the substrate \( \chi_s = 0.00100, \) while susceptibility in \( ab \)-plane of the film \( \chi_f^a = 0.00100 \) and susceptibility in \( c \)-direction \( \chi_f^c = 0.00103. \) These models are summarized in Table 3.1.2.1.

Table 3.1.2.1 Value of \( \chi_s, \chi_f^a \) and \( \chi_f^c \) for various models as explained above.

<table>
<thead>
<tr>
<th>Model</th>
<th>( \chi_s )</th>
<th>( \chi_f^a )</th>
<th>( \chi_f^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model I</td>
<td>0.00100</td>
<td>0.00100</td>
<td>0.00100</td>
</tr>
<tr>
<td>Model II</td>
<td>0.00100</td>
<td>0.00180</td>
<td>0.00180</td>
</tr>
<tr>
<td>Model III</td>
<td>0.00100</td>
<td>0.00180</td>
<td>0.00103</td>
</tr>
<tr>
<td>Model IV</td>
<td>0.00100</td>
<td>0.00103</td>
<td>0.00103</td>
</tr>
<tr>
<td>Model V</td>
<td>0.00100</td>
<td>0.00100</td>
<td>0.00103</td>
</tr>
</tbody>
</table>

Results of the scattering intensity for each model are shown in Fig. 3.1.2.4 for (c) Model I, Model II as well Model III and (d) Model IV and Model V as well as Model I as comparison. From Model I, it is clear that if there is no difference in the susceptibility between the film and the substrate, and therefore no fringes appear. The shape of the scattered intensity here is determined entirely by the attenuation factor. In Model II strong fringes appear at low and higher angle due to a strong difference in the susceptibility between the film and the substrate. When the susceptibility is taken to be anisotropic such that \( \chi_f^c \) is only slightly different from \( \chi_s \) as in Model III, the amplitude of the fringes at low angles is suppressed. This is a result of the scattering geometry in which the polarization for small angles is mainly along \( c \)-direction and for large angles mainly in the
For Model IV, the fringes at low and high incident angle are both suppressed and almost invisible. This is consistent with the reflectivity result for energy off-resonance as in Fig. 3.1.2.3 (a). The difference with the experimental result is that in our simulation we set our energy to 931 eV to be consistent with other models. In Model V where $\chi^{ab} = \chi_c$, the fringes at higher angles are suppressed and become invisible at angle close to 90 Degree.

It is clear that, quantitatively, the observed suppression of the fringes at low angle is due to the polarization dependence and the smaller susceptibility in the $c$-direction compared to the $ab$-plane. It is also evident that the strength of the fringes depends on the difference in the susceptibility between film and substrate.

**Cu $L$ Resonance Profile (RP)**

Here, we discuss the complete energy-dependence of scattering at the Cu $L_3$ edge. By comparing the intensity of the reflectivity at different $q$'s we show that the energy dependence of reflectivity does not follow that of the XAS. In Figure 3.1.2.5 (a) is shown the scattered intensity as a function of photon energy, through the Cu $L_3$ edge, and momentum transfer $q$ along the $(0,0,L)$ direction (we refer to this kind of measurement as a “resonance profile” (RP)).

What can we learn from this RP? We concentrate on the relationship between the RP and XAS. We plot the scattered intensity as function of photon energy at different $q$ values corresponding to a $q$ value at the crest, the valley and in a low scattering region, as shown in Fig. 3.1.2.5 (b). It is very interesting that the energy dependence of the scattering does not track the XAS, but is shifted by ~0.6 eV to lower energy. To understand this one needs to consider the form factor [19]. As pointed out by Blume the form factors are given by

$$f_{\text{out}}(E) = f_0 + f^* + if'' = B + \frac{A}{E - E_{pd} - i\gamma_{pd}} \quad (3.1.8)$$

where $E$ is the photon energy, $E_{pd}$ is the energy of the transition from Cu 2$p$ to 3$d$, and $\gamma_{pd}$ is its radiative lifetime. $B$ and $A$ are oscillator strengths for non-resonant and resonant components, respectively. The scattered intensity $I$ is proportional to $|f_{\text{out}}(\omega)|^2$. 

3.1.2. Enhancement of the structural modulation as seen at the Cu $L$ edge

Figure 3.1.2.5 (a) Full RP of a 22.0 nm thick La$_2$CuO$_{4+d}$ film taken at 100 K ($T_c = 39$ K), and (b) energy scans for three different $q$ values. The solid line is at (0,0,1.90), the dashed line is at (0,0,1.868), and the dotted line is at (0,0,1.44). These $q$ values correspond to a peak of a fringe, a valley between fringes, and a region where the fringes are not pronounced, respectively.
Figure 3.1.2.6 Simulations for $E_{pd} = 930$ eV and $\gamma_{pd} = 1$ with various $A$ and $B$ values. The square, circle, up-triangle and down-triangle symbols are the scattered intensity for \{A,B\} = \{10,0\}, \{10,2\}, \{10,4\}, and \{10,-4\}, respectively.

Simulations for $E_{pd} = 930$ eV and $\gamma_{pd} = 1$ with various $A$ and $B$ values are shown in Fig. 3.1.2.6. One can see that if the off resonance part is negligible ($B = 0$), the intensity has a Lorentzian line shape which is centered at $E_{pd}$. This line shape looks like the XAS spectrum which is the imaginary part of the dielectric susceptibility, $\text{Im}[\chi(\omega)]$ [see Fig. 3.1.2.2 (b), top panel]. If the off-resonant component is significant, the peak is no longer centered at $E_{pd}$ and the line shape becomes asymmetric. The line shapes all depend very much on the sign and relative value of $B$ to $A$. If $A$ and $B$ have the same sign the peak position will move to lower energy and vice versa for an opposite sign. If the value of $B$ is close to $A$, for $A/B$ positive, one can see that the shape looks similar to $\text{Im}[\chi(\omega)]$ eventually [see Fig. 3.1.2.2 (b), bottom panel] that the value $B = 2$ reproduces well the 0.6 eV shift seen in the experimental results. Retaining a nearly symmetric shape as shown in Fig. 3.1.2.5 (b), however, is not possible with this model. Inclusion of the $2p$ to $4s$ transitions explicitly may resolve this problem.

3.1.3 Inhomogeneity of Oxygen in La$_2$CuO$_{4+\delta}$

In x-ray absorption spectra (XAS) from the insulating cuprates, the O K edge shows a “pre-peak” feature (~531 eV) that is an intersite O 1s→Cu 3d transition [20] brought about by $p$-$d$ hybridization. This feature is well-known as the upper Hubbard band (UHB). When the
3.1.3. Inhomogeneity of Oxygen in $\text{La}_2\text{CuO}_4^\delta$

system is doped, added holes go into O 2p states [20] and a second prepeak, which is the
doped hole peak, appears at $\sim 529$ eV [Fig. 3.1.3.1 (a), triangles]. Its oscillator strength
builds rapidly with hole concentration as states near the Fermi level are vacated and also as
spectral weight is transferred to 529 eV from the feature at 531 eV [20]. A transfer of
spectral weight with doping is the classic signature of correlated system [21], and it makes
the optical response at 529 eV extremely sensitive to the local hole density. Because the
valence states are polarized in the CuO$_2$ plane, both the oxygen prepeak and the doped hole
peak are observable in XAS only when $E||ab$ [14,15].

If the carrier density is inhomogeneous the hole-doped peak will be modulated in
real space, enhancing diffraction of 529-eV x-rays. In carrier-depleted regions, the doped
hole peak will be suppressed and $\chi$ will have its pre-resonance value. In carrier-rich
regions, the peak will be enhanced. To quantify the difference, we again use eq. (3.1.1) and
eq (3.1.2) and the tabulated atomic scattering factors [18] to set the absolute scale.
According to Fig. 3.1.3.1 (b), at the doped hole peak $\chi$ has the value 0.00068 while off-
resonance $\chi$ is about 0.00058.

![Figure 3.1.3.1 (a) X-ray absorption spectra at the O K edge for (open-squares) SrTiO$_3$,
(filled-circles) undoped La$_2$CuO$_4$ film, and (open-triangles) optimally doped La$_2$CuO$_4^\delta$.
All were taken in fluorescence yield mode with $E||ab$. (b) $ab$-plane susceptibility, $\chi$ in SI
units, calculated by the procedure described for (filled-circles) Re $\chi$ and (open-circles) Im $\chi$ for
optimally doped La$_2$CuO$_4^\delta$ and (solid and dashed) SrTiO$_3$, respectively.]

The carrier enhancement is demonstrated in the energy- and angle-dependent
reflectivity of a La$_2$CuO$_4^\delta$ film [Fig. 3.1.3.2]. At $\omega = 526.5$ eV, fringes are hardly visible
[Fig. 3.1.3.2 (a), open circles]. This is again because, off-resonance, the density of the
SrTiO$_3$ substrate and the film do not differ significantly. However, if the energy is changed
by only 2.5 eV to the doped hole peak [Fig. 3.1.3.1(a), filled circles], there is a \( \frac{|0.00068-0.00058|}{0.00058} \times 100\% = 17\% \) boost in the film susceptibility and pronounced interference fringes appear [Fig. 3.1.3.2 (a)].

![Graphs showing count rate vs angle of incidence for two datasets: 526.5 eV and 529.0 eV (doped hole peak).]

**Figure 3.1.3.2** Reflectivity of a 23.2-nm La2CuO4+d film \( (T_c = 39\, K) \) (a) just below and on the doped hole peak at 528.5 eV, showing the resonant enhancement and (b) over the full angular range for three different energies. The 518.5 eV and 529 eV scans correspond to the reciprocal space interval \((0,0,0.21)\rightarrow(0,0,1.21)\), the 933-eV scan is shown for comparison. The feature at 70° is a superstructure reflection at \((H,K,L) = (0,0,1.054)\) which will be discussed later.

The striking thing about these fringes is that they come only from the carriers and are not related to the other electrons in the film. If there were carrier ordering along the \((0,0,L)\) direction it would be reflected as a modulation of the envelope of these fringes. Ordering parallel to the CuO2 planes would result in scattering in an off-specular geometry; that is, in which the momentum transfer vector \( q \) has a component in the in-plane direction.

Unlike the fringes at Cu L edge, the fringes at the O K prepeak, unexpectedly, attenuate at higher angles. This can be understood in terms of a smoothing of the carrier density at the substrate. In general, what makes a layer exhibit interference fringes is two localized discontinuities (the front and rear faces) that generate waves that beat against one another as the film is rotated. The fringes will damp if one or both of these discontinuities is smeared over a depth larger than \( \lambda/2 \). Several things could potentially do this in our case: (i) a carrier depletion region due to the contact potential difference between the film and substrate, (ii) oxygen inter-diffusion at the substrate, or (iii) structural reconstruction at the film-substrate interface.
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Without specifying the cause, the effect of smoothing can be demonstrated in the Born approximation, as we described above. Taking $\chi_s = 0.00058$, $\chi_s' = 0.00060$, and $\chi_s'' = 0.00068$ at the prepeak, we plot $|M|^2$ in Figure 3.1.3.3 for both a sharp film profile and one that has been smoothed over 20 Å at the substrate. For a sharp layer, the fringes at the carrier pre-peak increase at high angles as expected. When the interface is smoothed, they fade away. So the absence of fringe enhancement at high angles is suggestive of a depletion zone or similar effect at the interface.

Figure 3.1.3.3 (a) Susceptibility profiles for a perfect film on a substrate (solid line) and one that has been smoothed at the interface (dashed line). The sloping nature of the substrate ($x > -8000$ Å) is a numerical implementation of the factor $e^{-\eta x}$. (b) Interference fringes resulting from the two profiles (in relative units) showing damping at high scattering angles for the smoothed layer.

O K Resonance Profile

Unlike Cu $L_3$ edge, the feature at the O $K$ edge is strongly doping dependent. Figure 3.1.3.4 shows the RP of a 22.0-nm optimally doped La$_2$CuO$_{4+\delta}$ film taken at 100 K ($T_c = 39$ K). Notice that at lower angles (theta < 25°) the reflectivity fluctuates strongly as function of energy $E$ and momentum $q$. 
Figure 3.1.3.4 (a) RP of a 22.0-nm La$_2$CuO$_{4+d}$ film taken at temperature 100 K ($T_c = 39$ K), and (b) L-scans for three different energies. The solid line is at 529.0 eV (doped hole peak), the dash line at 531.0 eV (UHB), and the dotted line at 536.0 eV. The zooming-in on the energy dependence of the superstructure reflection will be shown later.

Here, we focus on energies at the doped hole peak (529 eV), the UHB peak (531 eV) and the O $K$ main edge jump (536 eV). Figure 3.1.3.4(b) shows the L-scan for these three different energies. Unlike at the Cu $L$ edge, one can see that the phase of the fringes is not the same. For instance, the phase of the fringes at the hole-doped peak is similar to that
of the O $K$ main edge, while the phase of the fringes at UHB is opposite to that of the other two. How can we explain such a phenomenon?

Figure 3.1.3.5 Susceptibility profiles for a perfect film on a substrate (solid line) and one that has been smoothed at the interface (dash line) for (a) the doped hole peak and (b) the UHB. The sloping nature of the substrate ($z > -8000$ Å) is a numerical implementation of the factor $e^{-\eta z}$. (c) Interference fringes resulting from the two profiles (in relative units) showing damping at high scattering angles for the smoothed layer. The solid line and dash line are the scattered intensity at 529 eV and 531 eV, respectively.
Similar to what was described earlier, by analyzing the XAS, we can explain the shifting fringes in terms of interference with the substrate reflection. As one can see in Fig. \ref{fig:3.1.3.1} (b) at the UHB, Im $\chi$ of the STO is higher than that of the doped-film. This means that the susceptibility of the film is lower that that of the substrate. We then model $\chi$ as it is shown in Fig. \ref{fig:3.1.3.5}(b). Fig. \ref{fig:3.1.3.5}(a) is just a duplicate of Fig. \ref{fig:3.1.3.3}(a) for comparison. We do not know the exact value of susceptibility of the substrate at 531 eV, but we know that the susceptibility of the substrate is higher than that of the film. To obtain a qualitative understanding, we will simply assume $\chi_s = 1$, $\chi'_s = 0.925$, and $\chi''_s = 0.933$.

The resulting $|M|^2$ is shown in Fig. \ref{fig:3.1.3.5} (c). One can see that this model of the susceptibility reproduces the different phase of the fringes for different energies. One can predict that, at the main O $K$ edge jump, the model for $\chi$ should be similar to the doped hole peak, the only difference being the amplitude of the susceptibility.

\subsection*{3.1.4 Superstructure reflection}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.1.4.1}
\caption{\label{fig:3.1.4.1} $L$-scan at 532 eV for (black solid line) a 17 unit cell (u.c) thick film of undoped La$_2$CuO$_4$ (LCO) (sample A), (black dash line) a 40 u.c thick film of undoped LCO (Sample B) and (grey solid line) a 17 u.c thick film of optimally doped LCO (Sample C). The sharp Bragg peak at (0,0,1.054) was seen only on the doped film. All the films are grown on STO.}
\end{figure}

The structure of the La$_2$CuO$_4$ (LCO) parent-compound is shown in Fig. \ref{fig:3.1.1.1}. By looking at the space group, one can easily see that the structure factor for the $(H,K,L) =$
(0,0,1) reflection is zero and this is consistent with our hard x-ray study. Surprisingly we have observed an incommensurate (0,0,1.054) reflection only for doped films at the O K edge which is not visible at either the Cu L₂,₃ edges or Ba M₄,₅ edges. In Fig. 3.1.4.1 we show an L-scan at 532 eV for a 17 unit cell (u.c) thick film of undoped LCO, a 36 u.c thick film of undoped LCO, and a 17 u.c thick film of optimally doped LCO. All the films are grown on single crystal SrTiO₃.

We observe two Bragg peaks, one broad reflection at (0,0,1) and one sharp reflection at (0,0,1.054). First, we discuss the (0,0,1) reflection. One may ask why a (0,0,1) reflection appears while its structure factor is zero. Here, our claim is that the actual reflection of this broad Bragg peak is (0,0,2). The reason is the following. A synchrotron source with undulator radiation will produce photons with a sharp peak at the fundamental (n = 1), but also at energies corresponding its harmonics (n > 1). A grating, which is supposed to select photons with a specific energy, cannot distinguish between photons at the fundamental energy and those at the nth harmonic unless special optics are used to reject higher harmonics. At the NSLS-X1b beamline, the intensity is of order 10^{12} photon/sec. If 1% out of 10^{12} photon/sec is in the 2nd harmonic, then up to 10^{10} photons could be in the second harmonic. So in this case, the actual energy of the broad reflection is 1064 eV, which is the 2nd harmonic of 532 eV.

![Graph showing L scans of an undoped film at 1038 eV and at 518 eV.](image)

**Figure 3.1.4.2.** L scans of an undoped film at (circles) 1038 eV and at (line) 518 eV.

One might suppose that if the actual energy is 1064 eV, then if we set the grating to that energy we should see a Bragg reflection which is perfectly identical in position as well as in its full width at half maximum (FWHM). It does exactly that. In Fig. 3.1.4.2 we show an L-scan for the undoped-film at 518 eV and at (2*518) = 1038 eV. One can see that these two Bragg peaks are identical. They appear at the same angle, and also the FWHM is
exactly the same. However, from the energy-dependence, the broad reflection does not seem to feel any resonance, and it seems to have a weak anti-resonance at the O K edge [Fig. 3.1.4.4].

The position and, importantly, the FWHM of the broad Bragg reflection as function of thickness of the films can be simulated in the Born approximation. Since we are looking at \( q \) only along the \( L \)-direction, we can reduce the calculation to 1 dimension. We use a simple susceptibility of the following form

\[
\chi(z) = \sum_{j} \chi_{j} \delta(z - z_{j}) \tag{3.1.9}
\]

where \( z_{j} \) is the position of layer-\( j \), and \( \chi_{j} \) is the form factor of layer-\( j \). One unit cell of LCO contains 2 (CuO) layers and 4 (LaO) layers [see Fig. 3.1.1.1]. Since the lattice is periodic, one only needs to work in 1 u.c. instead of the total volume of the sample. To get \( \chi(q) \), we use eq. (3.1.3) which gives

\[
\chi(q) = \sum_{n} \chi_{(CuO)} \exp(iq 2\pi l n c) + \chi_{(LaO)} \exp(iq 2\pi l / 6nc) + \chi_{(LaO)} \exp(iq 2\pi l / 3nc) + \chi_{(LaO)} \exp(iq 4\pi l / 3nc) + \chi_{(LaO)} \exp(iq 5\pi l / 3nc) \] \tag{3.1.10}

\( n \) is the \( n \)-th u.c., \( c \) is the lattice constant, and \( q = 2k \sin \theta \). If all (LaO) layers are the same, then (3.1.10) becomes simply

\[
\chi(q) = \sum_{n} \chi_{(CuO)} \exp(iq 2\pi l n c) + \chi_{(CuO)} \exp(iq \pi l nc) \] \tag{3.1.11}

With eq. (3.1.11), eq. (3.1.6) and eq. (3.1.7), we calculate the scattered intensity for various thicknesses and compare with experimental results. We start with Sample A. With an incoming photon energy of 1060 eV, we find a Bragg reflection at incident angle 62.8 degrees, which corresponds to the (0,0,2) reflection (remember that the lattice constant along \( c \)-axis for undoped films is 13.156 Å). We simulate the scattered intensity from finite layers with given thickness of 40 u.c and with a condition of \( \chi_{(CuO)} = \chi_{(CuO)} \). The result is shown as a solid line in Fig. 3.1.4.3 (a). One can see that the Bragg peak produced from the theoretical simulation matches very well the experimental data. Not only the position and the width but also the fringes surrounding the Bragg peak, which come from the finite thickness of the film, agree very well with experimental result. This is not surprising because (1) the Bragg peak is the (0,0,2) reflection and (2) the film thickness is 40 u.c. As we have shown in Fig. 3.1.4.2, we have also found an identical Bragg reflection (i.e. exactly at the same peak position and the same FWHM) at half energy which is 530 eV. To simplify, we shall use the same figure as the experimental data of 1060 eV. If we follow the Bragg condition, \( 2d \sin \theta = n \lambda \), then with an incoming photon energy of 530 eV and incident angle of 62.8 Degree, then this peak is the (0,0,1) reflection. To simulate this is not
easy since it is a forbidden reflection. One way is by introducing $\chi_{(0,0,1)} \neq \chi_{(0,0,2)}$. But with this condition the shape of the fringes can be different and depends strongly on the size of the chosen susceptibility. Another way is that in our head we move the center of this (0,0,1) to the (0,0,2), then one may think that the FWHM has to be double or the thickness of the sample thinner by factor of 2. Our calculation shows this [See Fig. 3.1.4.3 (a), dashed line]. This is not consistent with the experimental result.

We also studied this behavior for different thickness of thin film (Sample B). With an incoming photon energy of 1062 eV, we found a Bragg reflection at incident angle of 65.4 Degree. This corresponds to the (0,0,2) reflection. Our scattering simulation with given thickness of 16 u.c and with a condition of $\chi_{(0,0,1)} = \chi_{(0,0,2)}$ matches very well with the experimental data. The result is shown as a red line in Fig. 3.1.4.3 (b). This is not surprising since (1) the Bragg peak is the (0,0,2) reflection and (2) the film thickness is 16 u.c. Since the layer is thinner, one needs to count longer to have a better statistics in order to clearly see the fringes. Like the case above, we have also found an identical Bragg reflection (i.e exactly at the same peak position and FWHM) at half energy which is 531 eV which is the forbidden (0,0,1) reflection. For the same reason as above, we simulate the scattered intensity for 8 u.c thickness. The result is shown in Fig. 3.1.4.3 (b) (blue-line). As one can see, this theoretical calculation is not consistent with the experimental result.

![Figure 3.1.4.3](image)

**Figure 3.1.4.3.** (a) (circles) L-scan of Sample A at 1060 eV and scattering simulation for (solid line) 40 u.c and (dashed line) 20 u.c. (b) (circles) L-scan of Sample B at 1062 eV and scattering simulation for (solid line) 16 u.c and (dashed line) 8 u.c.

However, from the energy-dependence, the broad reflection does not seem to feel any resonance, and it seems to have a weak anti-resonance at the O K edge [Fig. 3.1.4.4].
These facts provide strong evidence that this broad Bragg peak is a (0,0,2) reflection arising from the harmonic content of the undulator.

A second important observation here is the additional sharp Bragg peak which is an incommensurate (0,0,1.054) reflection. This incommensurate reflection is not present in undoped samples. According to its FWHM, the superstructure corresponds to a sample with a thickness of more than 4000 Å. Is it possible that a finite thickness of thin film (~220 Å) can have an extremely sharp Bragg reflection? Within the Born approximation, it is quite impossible. This suggests to us that there may be some special interference effect between layers of rich and poor oxygen doping. This may open new interesting science for thin films of High-Tc Superconductors with RSXS.

![Figure 3.1.4.4](image)

**Figure 3.1.4.4** The energy dependence of (open circles) the superstructure and (cross symbols) the broad reflection, compared to (closed squares) XAS.

As we said above, the superstructure reflection is only seen in the doped films, and only at the O K edge. The energy dependence of this superstructure through O K is shown in Fig. 3.1.4.4 and is different from that of the broad reflection, in that it resonates strongly at 531-532 eV. It is interesting that the XAS of STO has a peak at the same energy, which is related to Ti 3d absorption. A number of scenarios could be at play here. First, somehow or other the resonant properties of STO must be important perhaps via a strong increase in the reflectivity. Second, there is also the possibility of a phase shift, between LCO and STO. The sensitivity of RSXS to the phase is indeed seen on our study of Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (see section 3.3 for details). Nevertheless, the fact that (1) the superstructure peak is seen off resonance and (2) the strong enhancement at the absorption edge (not at doped hole...
3.1.4. Superstructure reflection

peak) is a strong indication that the superstructure peak is somehow related to structure. But it is important to note here that the phase could shift the resonance energy by as much as several eV depending on the phase difference. This can make things more complicated. A theoretical demonstration that a phase difference could shift the resonance is shown in section 3.3. Another important result here is that the intensity of the superstructure peak decreases rapidly at higher energy. Within about 30 eV (from ~522 to ~552 eV), the intensity drops by about 80%.

We have yet to understand the origin of the superstructure peak, but the observation itself is very important because of the much smaller width than what would be expected for a film of this thickness. To understand this phenomenon clearly, one needs the complete doping, thickness and substrate-dependences.

3.2 Zooming-in on the charge ordering in YBa$_2$Cu$_3$O$_{6.5}$

YBa$_2$Cu$_3$O$_{6+x}$ is one of the most studied high temperature cuprate superconductors because of its excellent crystal quality and large size. Many important observations in the cuprates, such as the neutron resonance mode [22] and $d$-wave superfluid behavior [23] were first made in this system. Particularly, YBa$_2$Cu$_3$O$_{6+x}$ exhibits extraordinarily strong anisotropic behavior. For example, incommensurate magnetic order is observed primarily along the crystalline $a$ direction [24] and the superfluid density, superconducting gap, and conductivity are all significantly larger for the $b$-direction [25,26,27]. Because of the presence of one-dimensional (1D) Cu-O chains along $b$, it is not clear whether these anisotropies are induced by the chains or intrinsic to the CuO$_2$ planes, e.g. due to in-plane inhomogeneous distributions of charge and spin, or so-called stripes [28]. So far, virtually all known experimental methods have been used to study this system, but how the chain affects the low-energy electronic structure, or whether the chain is superconducting or even conducting at all remains a mystery. Here, we have performed RSXS on YBa$_2$Cu$_3$O$_{6.5}$ ordered phase [29]. We found that Cu$3d$ - O$2p$ hybridization is responsible for the ordering of the valence state O in the chains along $a$. This 1D footprint of the chain on the plane gives a plausible explanation for many of the observed anisotropies.

YBa$_2$Cu$_3$O$_{6.5}$ is known to exhibit an Ortho-II phase, where conventional x-ray scattering experiments show superlattice Bragg peaks corresponding to a doubling of the unit cell. The doubling is modeled as oxygen atoms in the CuO chain layers being ordered into alternating full and empty chains, as illustrated in Fig. 3.2.1 (a) [29,30,31]. The primary order in this case involves a light element accompanied by alternation in the valence states of chain Cu’s, neither of which is easily visible in conventional x-ray scattering. In addition, the Y (Z=39) and Ba (Z=56) atoms situated between chains are displaced, forming a secondary structural order. As conventional hard x-ray scattering is dominated by core electrons, the strong scattering by these heavy atoms prevents one from
obtaining direct information about Cu, O and valence electrons. That the chain ordering causes these changes in position is a plausible speculation. However, the proposed model of oxygen ordering in YBa$_2$Cu$_3$O$_{6.5}$ presented in Fig. 3.2.1(a) and especially the accompanying change in Cu oxidation states remains to be verified by experiments. More importantly, how and if the electronic structure and the superconductivity in the CuO$_2$ plane beneath these chains are affected by the chain ordering is still an open question.

Figure 3.2.1 (a) An illustration of the proposed ortho-II phase of YBa$_2$Cu$_3$O$_{6.5}$ [29], where chains are alternately filled with oxygen. The chain filled with oxygen (full chain) and the one without oxygen (empty chain) correspond to Cu oxidation states Cu$^{2+}$ and Cu$^{1+}$ respectively. These generate a charge density modulation with a period $2a$ (~7.76 Å), $a$ being the distance between the neighboring chains. The $\theta/2\theta$ Bragg scattering experimental geometry is also shown, with photon polarization $\epsilon$ in the $\theta/2\theta$ plane. The sample can be rotated azimuthally around the crystalline $a$-axis without breaking the Bragg condition. The azimuthal angle $\phi$ is defined to be 0˚ in the geometry shown, where the $\theta/2\theta$ plane and the $ac$ plane coincide. (b) X-ray absorption spectrum for Cu 2p to 3d transitions in YBCO, which can be fit by a linear combination of CuO and Cu$_2$O spectra taken from ref. 16. The inset illustrates Cu 2$p$→3$d$ resonant scattering.

Usually, resonant scattering is conducted in the hard x-ray regime, for example, using a deep core to valence transition of a heavy atom [32]. However, in many strongly correlated materials, including YBa$_2$Cu$_3$O$_{6.5}$, Oxygen 2$p$ and transition metal 3$d$ orbitals determine the low-energy behavior and their fascinating properties. Resonant hard x-ray scattering, based on Cu 1$s$→4$p$ for example, probes the local density of the empty 4$p$ states, and is an indirect and relatively insensitive probe of what is happening in the 3$d$ orbitals.
The interpretation of resonant hard x-ray scattering from these materials is often controversial and complicated [33,34]. To go beyond hard x-ray experiments, one should perform resonant scattering based on $O1s \rightarrow 2p$, or transition metal $2p \rightarrow 3d$ transitions.

These studies are carried out on an untwinned ortho-II phase YBa$_2$Cu$_3$O$_{6.5}$ single crystal which was prepared as described in ref. 35. We exploit its high quality to make quantitative determination of the anomalous scattering factors in the soft x-ray range. Experiments were performed at 100K, above the superconducting transition temperature of 62K.

As illustrated in Fig. 3.2.1 (b), when the photon energy is tuned to the Cu $2p \rightarrow 3d$ transition, the contribution from Cu atoms to the scattering is greatly enhanced through a virtual excitation process called resonant or anomalous scattering [19]. The Cu $2p \rightarrow 3d$ transition has been extensively studied by x-ray absorption spectroscopy (XAS), where two peaks around 930 eV and 950 eV correspond to final states with $2p_{3/2}$ and $2p_{1/2}$ core holes respectively, referred to as the Cu $L_3$ and $L_2$ absorption edges. The YBa$_2$Cu$_3$O$_{6.5}$ $L_3$ edge can be fitted by a linear combination of CuO and Cu$_2$O spectra, consistent with the model in Fig. 3.2.1 (a), where Cu is in a nominally Cu$^{2+}$ ($3d^9$) in the full chain, and Cu$^{1+}$ ($3d^{10}$) state in the empty chain. Due to hybridization with oxygen, there are still some 3d holes on Cu$^{1+}$, contributing weakly to $2p \rightarrow 3d$ transition in YBa$_2$Cu$_3$O$_{6.5}$ at an energy ~2eV higher than the main Cu$^{2+}$ peak. Because the resonant scattering arises via the dipole allowed ($2p_{6s3d^9} \rightarrow 2p_{5s3d^{10}}$) transitions, it is dominated by Cu atoms in the empty or full chains at different photon energies, resulting in a large contrast and a huge enhancement of the superlattice Bragg peak.

We will now use this contrast in the Cu$^{1+}$ and Cu$^{2+}$ scattering to study the ordering of Cu 3d holes. Data were taken in a $\theta/2 \theta$ Bragg diffraction geometry as illustrated in Fig. 3.2.1 (a). The scattering intensity as a function of angle and photon energy, or RP, is shown in Fig. 3.2.2 (a) and (b). The (1/2,0,0) Bragg peak corresponding to the Ortho-II superstructure is observed at all photon energies, with two resonances occurring near the $L_{2,3}$ absorption edges. The intensity far from the Bragg angle is very weak, which indicates that the contamination to the Bragg peak from isotropic diffuse scattering and fluorescence is negligible. Compared with the off-resonance intensity at 920 eV, the measured Bragg peak intensity is enhanced by a factor of 62 at the $L_3$ edge, and 8 at the $L_2$ edge. The weak enhancement at the $L_2$ is mainly caused by the competing non-radiative Coster-Kronig decay channel of the $2p_{1/2}$ core-hole [36].
Figure 3.2.2 (a) and (b), The scattered intensity as a function of photon energy and angle $\theta$ for $\phi=0^\circ$ and $90^\circ$ respectively. (c), The intensity of the Bragg peak is integrated over momentum for each energy, and it is compared with the x-ray absorption spectrum taken at the same $\epsilon$. It is important to note that the supermodulation resonates at Cu $L_3$ (d). The $(1/2, 0, 0)$ Bragg peak at the resonance (indicated by the red curve in a) is plotted versus the reciprocal lattice unit, and is well fitted by an anisotropic Lorentzian function as in hard x-ray studies [9,11] giving a coherence length of $15.4a$ (~60Å). (Note: coherence length along H, $\xi_H \equiv a/\Delta H$, where $\Delta H$ is FWHM of Bragg peak along H).

For the non-resonant scattering, the ordered O$^{2-}$ ions in chains contribute on the order of $10^2 = 100$, while the alternating chain Cu$^{2+}$ and Cu$^{1+}$ ions just contribute on the order of $1^2 = 1$. As there is additional scattering from the Y$^{3+}$ and Ba$^{2+}$ ions, the Cu contribution to the off-resonance scattering is estimated to be less than 1%. Therefore, the Cu contribution is enhanced by more than 6200 times at the $L_3$ edge. Such a gigantic enhancement is rarely observed, and far beyond what one would expect if Cu ions are simply displaced from their stoichiometric position with no change in valence. [Actually, Cu ions are situated in between either two full or two empty chains, its displacement (if any) should be very small.] Therefore, this observation directly proves that the local electronic structure or electron density of the Cu 3d orbitals is modulated with a period of $2a$ perpendicular to the chain in the Ortho-II phase, which should have a significant effect on the low energy electronic structure.
3.2. Zooming-in on the Charge Ordering in YBa$_2$Cu$_3$O$_{6.5}$

Figure 3.2.3 Integrated Bragg peak for the $L_3$ edge at $\phi = 0^\circ$ and $90^\circ$ in which each of them is the normalized at the non-resonant intensity on the low photon energy side, where the atomic form factor is basically independent of the polarization.

Having determined that the Cu 3d holes are ordered, the next step is to zoom-in even further and try to distinguish the ordering of the chain-Cu from that of the plane-Cu. Because the holes are mainly situated in the $ab$-plane for the plane-Cu, and $bc$-plane for the chain-Cu, their contribution to the scattering cross-section will have very different polarization dependencies. Therefore, by comparing scattering intensities taken at different polarizations, one can differentiate between chain and plane Cu 3d hole orbitals, and separately investigate their ordering. The polarization can be changed by using different azimuthal angles $\phi$ [Fig. 3.2.1(a)]. For $\phi = 0^\circ$ and $90^\circ$, polarization $\varepsilon_c = \cos(\theta_B)\hat{a} + \sin(\theta_B)\hat{b}$ and $\varepsilon_o = \cos(\theta_B)\hat{a} + \sin(\theta_B)\hat{b}$, respectively (denoted by subscript $c$ and $b$ hereafter as the $\hat{a}$-component is fixed), where $\theta_B$ is the Bragg angle. Figures 3.2.2 (a) and (b) are the resonance profiles for the $L_{2,3}$ edge at $\phi = 0^\circ$ and $90^\circ$, respectively. In Fig. 3.2.3 is shown resonance profiles for the $L_{2,3}$ edge at $\phi = 0^\circ$ and $90^\circ$ in which each of them is the normalized at the non-resonant intensity on the low photon energy side, where the atomic form factor is basically independent of the polarization. The momentum-integrated Bragg peak intensity ($I$) does show significant polarization dependence for the $L_3$ edge. The ratio of the integrated total scattering weight over the entire $L_3$ edge for two azimuthal angles is $0.920 \pm 0.05$. One finds that scattering and absorption have different lineshapes here [Fig. 3.2.2 (c)], and resonance of the scattering arises at slightly higher photon energies (about 0.5 eV) than the absorption. This is still unclear what the origin of this.
Figure 3.2.4 Estimation of the Charge and orbital ordering in the CuO$_2$ plane. Cartoons of the hole wave functions in the (a) full chain and (b) empty chain. (c) is a cartoon of possible charge/orbital ordering of the holes in different planar Cu ions that can reproduce the data.

The measured weaker scattering for light partially polarized along $c$ than along $b$ cannot be understood if one assumes a homogeneous plane. As illustrated in Fig. 3.2.4 (a), the CuO$_3$ plaquet in the full chain is squeezed by about 4.7% in the $c$-direction. Both density functional theory (DFT) calculations and quantum chemistry analysis show that this would cause a mixing of the chain Cu $3d_{x^2-y^2}$ and $3d_{y^z}$ orbitals and relocate more holes along the $c$-axis. In the empty chain [Fig. 3.2.4 (b)], the O-Cu-O dumbbell structure also drives a hole into the Cu $3d_{y^z}$ orbital, so that most of the holes are situated along the $c$-direction. Because the energy distribution of holes is centered at different positions for different chains as suggested by XAS data [Fig.3.2.1 (b)], both the full and empty chain scatter $c$-polarized light more than the $b$-polarized light, opposite to the observation. This clearly shows that substantial charge density modulations also exist in the CuO$_2$ plane layer to give more scattering to the $b$-polarized light.

This planar charge/orbital ordering is associated with many factors, including the Madelung potential of extra O ions in the full chain which attract more holes in the planar Cu underneath, the long range Coulomb interaction between holes, the hybridization between the $p_z$ orbital of the apical O (shared by the chain and plane) and the planar Cu
3.2. Zooming-in on the Charge Ordering in YBa$_2$Cu$_3$O$_{6.5}$

orbitals and so on. Simple quantum chemical estimations with parameters established in experiments and numerical studies [37], indicates that to fit the data, the charge modulation is on the order of 0.05 holes in planar Cu ions and accompanied by orbital modulations, i.e. different mixing of planar 3$d_{x^2-y^2}$ and 3$d_{yz,zx}$ orbitals at different sites as illustrated by a cartoon in Fig. 3.2.4 (c). Recent nuclear quadruple resonance (NQR) experiments observed four different Cu sites corresponding to two planar and two chain Cu sites [38]. We believe it is directly related to the charge/orbital ordering discussed here, as the electric field gradient at the Cu nucleus is very sensitive to the relative occupation of 3$d_{x^2-y^2}$ and 3$d_{yz,zx}$ orbitals since these two orbitals contribute with opposite signs to the electric field gradient.

We have shown that even if the chains are insulating, as most defected 1D system would be, they imprint their 1D nature onto the planar low lying electronic states. This charge/orbital ordering would cause noticeable effects on the superconductivity because of the high sensitivity to doping of the cuprates. Without having to include stripes as a separate physical effect [28], the planar charge/orbital ordering discussed here might provide an alternative plausible explanation for the observed extraordinarily strong anisotropy in its super fluid density [39], superconducting gap [40], and conductivity[41], which are all significantly larger for the $b$-direction than for the $a$-direction. It might also provide a preferential direction for the observed incommensurate magnetic fluctuation along-$a$, although we note that this magnetic fluctuation has a much larger length scale (~10$a$) [24, 42].

3.3. The incommensurate structure modulation of the single crystal Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ superconductor and a phase difference between regular and resonant scattering in RSXS

The crystallography of the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) system has been described in a number of publications [7,8,43,44,45,46]. A major feature of the diffraction pattern is the occurrence of satellite reflections at positions displaced from the main diffraction spot by $q = \pm (0.148a^*+0.148b^*)$, where $a^*$ is the reciprocal lattice vector $2\pi/a_0$ for tetragonal unit cell. The satellite reflections indicate either a displaceable or a substitutional modulation in which the position or chemical occupancy varies between unit cells along the $a$- and $b$-axis. Since $1/q$ is not a simple multiple of $a$ and $b$, the modulation is incommensurate, and the structure can not be described on a unit cell that is a multiple of the basic cell. The modulation was found to consist of an almost sinusoidal displacement of the Bi and Sr atoms of up to 0.4 Å in the $a$-, $b$- and $c$-direction of the unit cell, and a similar displacement of up to 0.3 Å of the Cu atoms in the $c$-direction only. The similar modulation is also
observed by scanning tunneling spectroscopy (STS) [47,48] [Figure 3.3.1 Bi2212 Unit Cell].

Here, we focus our study on the following questions. First, can RSXS detect such a lattice modulation? Second, if we are able to detect the modulation, is there any participation of the doped holes in the CuO planes? We also investigate the issue of phase differences between regular and resonant scattering.

3.3.1. The incommensurate structure modulation

Single crystals of Bi2212 were prepared using a traveling solvent floating zone method [49]. The crystals were grown under the nominal conditions to produce lower doping (underdoped), with $T_c$ of about 12 K. The sample used in this study had $T_c = 2.5$ K. X-ray absorption spectra were measured in situ in the fluorescence yield mode. Momentum space will be denoted in terms of the orthorhombic unit cell with Miller indices $(H,K,L)$ representing a momentum transfer $Q = (2\pi/a \ H, 2\pi/b \ K, 2\pi/c \ L)$ where $a = 3.828$ Å, $b = 3.831$ Å, $c = 30.89$ Å.

In Fig. 3.3.2 we show (a) an $L$-scan, (b) a $K$-scan and (c) an $H$-scan through the incommensurate point $(0,148,0,148,2)$ in reciprocal space. These scans were taken at 535 eV (OK edge). At its maximum the peak count rate is 450 Hz on a fluorescence background of 225 Hz. The correlations of the incommensurate reflection are anisotropic. The correlation length along $H$, $K$ and $L$ direction are $653a$, $287b$ and $28c$. For comparison, the correlation length of the regular $(0,0,2)$ reflection along $H$ is about $80a$. 
3.3.1. The incommensurate structure modulation

Figure 3.3.2 Reciprocal space scans through the incommensurate reflection along (a) the (0.148, 0.148, L) direction (b) the (0.148, K, 2.000) direction and (c) the (H, 0.148, 2.000) direction. The filled-symbols show the incommensurate reflection while the open-circles show the (0,0,2) reflection. These data were taken with the x-ray energy tuned to 535 eV (O K edge) At its maximum the superlattice scattering is 450 Hz on a fluorescence background of 225 Hz.

In Figure 3.3.3 we show the intensity of the incommensurate reflection and (0,0,2) reflection as a function of energy and, for comparison, the x-ray absorption spectra (XAS) at (A) O K edge and (B) Cu L edges. The incommensurate reflection is visible off resonance. At the O K edge there is no enhancement at 530 eV, which would have indicated a hole modulation. The resonance of this superstructure occurs at the O K edge. The three observations that (1) the superstructure is visible off resonance, (2) no enhancement is seen at the doped hole peak and (3) a strong enhancement is seen at the OK main edge lead to a conclusion that this superstructure is a pure lattice modulation without any particular participation of the holes. The scattering at the CuL_{3/2} edge exhibits a statistically significant 0.2 eV red shift and the width of the resonance peaks are smaller than in XAS. These may be multiple-scattering effects.
Figure 3.3.3 (open circles) X-ray absorption spectra of Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$, taken in fluorescence yield mode with the photon polarization E||(a,b), in the vicinity of (a) the O K and (b) Cu $L_{3,2}$ edges. (a) (filled squares) Energy dependence of the (0,0,2) reflection and (solid line) the incommensurate modulation (0.148, 0.148,2) peak through the O K edge. (b) (filled squares) Energy dependence of the (0,0,2) peak and (solid line) the incommensurate supermodulation (0.148, 0.148,3) peak through the Cu $L_{3,2}$ edges.

In Figure 3.3.3 we show the intensity of the incommensurate reflection and (0,0,2) reflection as a function of energy and, for comparison, the x-ray absorption spectra (XAS) at (A) O K edge and (B) Cu L edges. The incommensurate reflection is visible off resonance. At the O K edge there is no enhancement at 530 eV, which would have indicated a hole modulation. The resonance of this superstructure occurs at the O K edge. The three observations that (1) the superstructure is visible off resonance, (2) no enhancement is seen at the doped hole peak and (3) a strong enhancement is seen at the OK main edge lead to a conclusion that this superstructure is a pure lattice modulation without any particular participation of the holes. The scattering at the Cu$L_{3/2}$ edge exhibits a statistically significant 0.2 eV red shift and the width of the resonance peaks are smaller than in XAS. These may be multiple-scattering effects.
3.3.2 A phase difference between regular and resonant scattering

As we explained in Section 3.1, x-ray absorption spectra (XAS) of the insulating cuprates show a “pre-peak” feature (~531.5 eV) that is an intersite O 1s → Cu 3d transition brought about by p-d hybridization. This feature is known as the Upper Hubbard Band (UHB). When the system is doped, added holes go into O 2p states [50] and a second prepeak, which is the doped hole peak, appears at ~529.5 eV [Fig. 3.3.3 (a), open circles]. Its oscillator strength builds rapidly with hole concentration as states near the Fermi level are vacated and also as spectral weight is transferred to doped hole peak from the feature of UHB [20]. The transfer of spectral weight with doping which is expected from the models of correlated systems described in [21,51] was proposed to have the opposite phase to the doped hole peak. Here, with the RSXS, we have found a clear evidence of such a phase difference namely the phase between regular and resonant scattering.

In Figure 3.3.3 (a) is shown the intensity of regular (0,0,2) reflection as a function of energy and for comparison the x-ray absorption spectra (XAS) at the O K edge. The intensity of the regular (0,0,2) reflection as a function of energy exhibits a complex behavior. In a simple picture based on the XAS, one would think that the intensity of the reflection should be enhanced at the doped hole peak at about 529.5 eV. Surprisingly, though the reflection is getting weaker and reaching a minimum (dip) exactly at the doped hole peak. Within a short energy range, when the energy of incoming photon reaches 532 eV, the intensity of the Bragg peak gets enhancement rapidly. After this, the intensity of the reflection drops and reaches a minimum where the XAS is around its maximum at about 538 eV. These all are the clearest evidence yet of a strong interference effect between the regular scattering and the resonant scattering and cannot be explained by simply XAS.

The interference effect can be explained qualitatively as follows. We use eq. (3.1.8), but now we introduce explicitly a phase between regular scattering which is electronic Thomson scattering and the resonant scattering. The introducing of phase information is commonly used for instance in analysis of multiple wavelength anomalous diffraction (MAD) phasing experiments for biological macromolecular crystal structure [19]. The form factor can be written as follows

\[ f^\text{mn}(\omega) = f^\text{o} + \sum f^\text{Rmn}_i(\omega) \exp(i\Phi(\omega)) \] (3.3.1)

where \( f^\text{o} \) is the atomic form factor of the regular component which is energy independent, and \( f^\text{Rmn}_i(\omega) \) which is the resonance component describes the polarization-dependent spectral changes and \( \Phi \) is the phase of the resonance component relative to regular scattering. \( m \) and \( n \) are incoming and outgoing polarization indices, respectively. The \( f^\text{Rmn}_i \) consists of Imaginary and Real components and they are related through Kramers-Kronig transformation.
Figure 3.3.4 A model of $f_{R,1}(\omega)$ and $f_{R,2}(\omega)$ while value of $f_0$ is set to 1. (open circles) $\text{Im}[f_{R,1}(\omega)]$ is constructed with a Gaussian shape with FWHM of 1.5 eV and centre at 530 eV. (solid line) $\text{Im}[f_{R,2}(\omega)]$ is also constructed with a Gaussian shape with FWHM of 1.5 eV, centre at 532 eV and the peak strength twice $\text{Im}[f_{R,1}(\omega)]$. The filled circles and dash line are $\text{Re}[f_{R,1}(\omega)]$ and $\text{Re}[f_{R,2}(\omega)]$, respectively. $f_{R,1}(\omega)$ and $f_{R,2}(\omega)$ are assumed polarization independent. We have chosen the peak strengths to be somewhat different from each other clearly demonstrate the interference effect.

Figure 3.3.5 Results of scattering simulation. Black solid line, black dashed line, gray solid line, gray dashed line, and black dotted line are the scattering simulation for $(\Phi_1, \Phi_2)=\{0,0\}$ Degree, $\{45, 0\}$ Degree, $\{120,0\}$ Degree, $\{180,0\}$ Degree, and $\{0,180\}$ Degree, respectively.
To study the interference effect, we have constructed a model of the “resonance” form factor which consists of \( f_{R,1}(\omega) \) and \( f_{R,2}(\omega) \) and set the value of regular form factor \( f_0 \) to 1 [see Fig. 3.3.4]. The value of \( f_{R,1}(\omega) \) and \( f_{R,2}(\omega) \) are chosen comparable to \( f_0 \), otherwise one would not expect to see clearly any interference effect of regular and resonant scattering. The real component of each is related to their imaginary component through Kramers-Kronig transformation.

The results of the scattering simulations are shown in Fig. 3.3.5. When \( \Phi_1 = \Phi_2 = 0 \) Degree meaning that the phase between the regular and all-resonance scattering are the same, from the calculation one can see that the scattering intensity shows no interference effect. The reflection gets enhancement through the resonance condition with its maximum at 530 and 532 eV. Here, things look “normal” in which the behavior of scattering intensity as function of energy is proportional to XAS. Now, what happens if we introduce a different phase between regular and resonance scattering? When \( \{\Phi_1, \Phi_2\} = \{45, 0\} \) Degree, the scattering intensity looks different from the previous one. The interference effect due to the phase difference gets involved. This effect is getting stronger when the phase of \( \Phi_1 \) is increasing to 120 Degree. Interestingly, this strong interference gives rise to a dip in scattering intensity at around 529 eV. For \( \Phi_1 = 180 \) and \( \Phi_2 = 0 \) Degree, the dip is deeper and moves toward 529.5 eV. For \( \Phi_1 = 0 \) and \( \Phi_2 = 180 \) Degree, the scattered intensity at 532 eV gets suppressed a lot, but note here that it does not go to 0. This is because the existence of the dip also depends on the ratio \( f_{R,2}(\omega)/f_0 \). So, one can conclude that the interference effect between regular and resonant scattering, depends on the phase, it could give rise to resonance but also “anti-resonance” behavior. Instead of giving a resonance, vice versa the scattering intensity is getting weaker than the off-resonance condition, and the shape of the scattering intensity also changes dramatically. In principle, by study the energy position of the dip as well as the ratio between the dip and the resonance peak, one could determine the phase difference. But this would require a higher quality XAS from the undoped sample which is very hard to find. Our rough estimation is that the phase difference (\( \Phi \)) between regular and resonance scattering is about 180 Degrees, or in other words there is a \( \pi \)-shift between regular and resonance scattering.

The opposite sign of scattering of regular and resonance scattering is exactly what is expected from the models of correlated systems described in [21,51] in which also the spectral weight transfer itself was first predicted. The reason for this behaviour is that the reduction of the Upper Hubbard band intensity with hole doping is entirely due to a spectral weight transfer to the doped hole states and so it will have the opposite phase to the doped hole peak. This observation is in fact a very strong confirmation that the basic models used to describe the doped hole systems is correct.

In conclusion, we have reproduced the result of the incommensurate reflection seen by hard x-ray and scanning tunneling spectroscopy (STS) technique. This result
demonstrates that RSXS can also detect bulk properties. We found here, that there is no charge modulation participation in this superstructure. In this study, we also learned that the interference between regular scattering and resonance scattering could lead to a complicated shape of the RP. A rough estimate of the phase difference yields a difference of 180 degrees corresponding to a \( \pi \)-shift phase. A further study of this interference is ongoing.
References


[38] Z. Yamani et al., preprint.