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Applications of X-Rays Absorption in Cuprates Superconductors

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Applications of X-Rays Absorption in Cuprates Superconductors

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1 INTRODUCTION

The purpose of this work is to introduce the characterization technique named X-Rays Absorption (XAS) and discuss three applications involving high- t_c superconductors. First, we will introduce about the interaction between x-rays and matter and then how those x-rays are produced in a synchrotron facility. It is necessary to use synchrotron radiation for XAS spectroscopies because it is concerned with the response of the material as functions of the incident photon energy. As well, in X-rays absorption dichroism the electromagnetic radiation need to scan a range of the photon energy and different polarizations (circular and linear).

Essentially, synchrotron is like a flashlight where the light is emitted by circulating electrons with velocity very close to the speed of light. The radiation is a narrow cone because of relativistic effects. It produces a very bright radiation and that is one of the reasons that synchrotron is so interesting for research. A simple but efficient analogy about brightness (or brilliance) is the comparison between a fireplace where the power is spread in all directions and a flashlight that is more concentrated and efficient depending on the application. The evolution over the years of brightness can be seen on Figure 1.¹

All absorption techniques here described uses synchrotron radiation as input to result in excitation of an electron. The core-level electron is excited to an unoccupied state. Then an electron may relax either radiationless emitting Auger electrons and a cascade of low-energy secondary electrons or emitting a photon. Therefore, x-rays absorption probe the unoccupied density of state of the system.

The measurement of XAS spectroscopies can be done using either of three ways. The absorption coefficient can be measure directly by transmission method where the initial intensity of the beam and after the sample are measured. Indirect ways to obtain the absorption coefficient are by fluorescence emission or total electron yield. The first one is measured the photon emitted by the relaxed electron into the core-hole. The total electron yield measures the current that balance the ejected Auger and secondary electrons.

This work will discuss about those ideas in the following way. In the second chapter will be presented some introduction about the interaction of x-rays with matter, discussing the refractive index and how it is related to the difficult challenge of design x-rays mirror. Third chapter introduces some concepts about synchrotron, radiation spectrum of insertion devices and how is composed a beamline. Fourth chapter gives an introduction about the x-rays absorption techniques such as X-ray Absorption Near-Edge Structure (XANES), Extended X-ray Absorption Fine Structure (EXAFS), very briefly X-ray Magnetic Circular Dichroism (XMCD) and X-ray Magnetic Linear Dichroism (XMLD). Fifth chapter will



Figure 1: X-ray brilliance increasing order of magnitude over the years. Tubes means X-rays tubes that is usually used in laboratories. Rings represent storage ring of synchrotron facilities. ERLs is used for energy recovery LINACS and FELs is free electron lasers.²

be presented three results from the literature of those techniques mentioned before in cuprates high- t_c superconductors.

2 THE INTERACTION OF X-RAYS WITH MATTER

How does X-rays interact with matter? Light can be refracted, reflected, scattered, absorbed, diffracted, and so on. The details depend on the structure of the matter and on the wavelength of the light. Figure 2 highlight some of the most important interactions considering a simple model of an atom. In Figure 2(a), an electron with high energy (primary electron) coming in produces an ionization knocking out a K-shell electron (secondary electron). Kinetic energy may be transfered between the electrons resulting in lower energy for the scattered primary electrons. In Figure 2(b) a photon is absorbed by a core-shell electron that is ejected from the atom (photoelectron). This phenomenon leaves a hole in the core shell and an electron in a further shell will relax either emitting a photon (Figure 2(c)) or ejecting an Auger electron from the atom (Figure 2(d)).^{3,4}



Figure 2: Interaction of X-rays with matter. In (a) high-energy electrons are scattered by ejecting a core-shell electron. In (b) a photon coming in is absorbed by a electron and consequently it is ejected from the atom. This electron is then called a photoelectron. In (c) imagine there will be a hole either for reason (a) or (b), then an electron from a shell further out will relax into it emitting a photon (fluorescent emission). Another case is that instead of occurring the fluorescence emission, in (d) Auger electrons are produced when an outer shell electron relaxes into core-hole. The excess energy can eject other electrons, called Auger electrons.^{3,4}

The binding energy for a single electron of the hydrogen atom is 13.6 eV. For

an atom of atomic number Z, the 1s-electrons have binding energies proportional to Z^2 . Hence, X-rays have enough energy for most of the bound core electrons and the cross section between X-rays and core electrons are higher than X-rays and valence electrons.³

Each interaction described above between light and matter has a finite probability of happening that depend on the element and on the photon energy. As shown on Figure 3, in the region of X-rays the most common interaction is photoelectric absorption.⁵ There are a lower contribution from inelastic Compton scattering but we will primary focus on absorption.



Figure 3: Total cross section (σ) per atom of lead in function of the photon energy. $\sigma_S, \sigma_{PE}, \sigma_{PR}$ are the cross sections for scattering, photoelectric absorption and production of pairs, respectively. The discontinuity in photoelectric absorptions occurs when the photon energy has the binding energy of the different electrons in the lead atoms. The total cross section σ is the sum of the scattering, photoelectric and pair production cross sections.⁵

2.1 The Refractive Index

The refractive index (n) describes the response of electrons in matter to electromagnetic waves and can be represented in complex form as

$$n = n_R + in_I, \tag{2.1}$$

In the x-ray regime, the refractive index is related to the atomic scattering factors

of the individual atoms in a material by

$$n = 1 - \frac{r_0}{2\pi} \lambda^2 \sum_i N_i f_i(0), \qquad (2.2)$$

where N_i is the number of atoms of type *i* per unit volume and $f_i(0)$ is the complex atomic scattering factor in the forward directions of the *i*th atom.

The refractive index of x-rays are slightly smaller than 1 and the phase velocity $(v_p = \frac{c}{n})$ will be greater than velocity of light. However, it is the group velocity that carries the energy and this remains below c. This is the region called anomalous dispersion. We express then the complex refractive index as

$$n = 1 - \delta + i\beta, \tag{2.3}$$

where the δ is the refractive index decrement and β is the absorption index. Comparing equations 2.1 and 2.3 we can see that $n_r = 1 - \delta$ and $n_I = \beta$.

The real part of the refractive index from equation 2.2, far from an absorption edge and considering $\sum_i N_i f_i(0) = \rho$ (average density of electrons) we have

$$\delta = \frac{2\pi\rho r_0}{k^2},\tag{2.4}$$

 δ then is inversely proportional to the square of the photon energy. If we assume some typical values for the equation 2.4 we obtain $\delta \approx 5 * 10^{-6}$. Hence, the real part of the refractive index of x-rays are slightly smaller than 1.³

2.1.1 Snell's Law

Considering x-rays in vacuum, the Snell law's is stated as

$$\frac{\cos(\alpha)}{\cos(\alpha')} = n_R,\tag{2.5}$$

where α is the incidence angle, α' is the refracted angle and n_R is the real part of the refractive index. It means that exist an critical angle where occurs total reflection ($\alpha' = 0$)

$$\cos(\alpha_c) = n_R,\tag{2.6}$$

where α_c is the critical angle. Any x-rays impinging with incidence angle below the α_c will occur total external reflection.

We can calculate the critical angle using Taylor expansion for cosine in equation 2.6 that is $1 - \frac{\theta^2}{2}$ and also considering $n_R = 1 - \delta$, we obtain

$$\alpha_c \approx \sqrt{2\delta},\tag{2.7}$$

For typical values of δ the critical angle is of the order of a few tenths of a degree. Hence, for grazing angles less than the critical angle is possible to reflect it from a surface. This can be used to focus the x-ray using a concave x-ray mirror, as the curvature is sufficiently small to guarantee an incident angle smaller than the critical.

2.2 Absorption

From equations 2.2 and 2.3 we can conclude that absorption index β as

$$\beta = \frac{r_0}{2\pi} \lambda^2 f'',\tag{2.8}$$

where f'' is the imaginary part of the atomic scattering form and it is proportional to the inverse square of electric field. Hence, the absorption index is proportional to the inverse fourth power of the energy.

Let a x-ray beam traveling in vacuum and then penetrating some sort of absorbing medium.

$$E(z,t) = E_0 e^{i(k_0 z - wt)},$$
(2.9)

where $k_0 = \frac{2\pi}{\lambda_0}$ is the wavevector in vacuum and λ_0 is the wavelength in vacuum. When it travels through an absorption material we need to consider the refractive index.

$$E(z,t) = E_0 e^{(ink_0 z - wt)},$$
(2.10)

Using the relation from equation 2.1

$$E(z,t) = E_0 e^{(-n_I k_0 z)} e^{(in_R k_0 z - wt)},$$
(2.11)

The first term represents the attenuation of the wave as it travels through the material. The square of the amplitude drops $\frac{1}{e}$ over a depth $\frac{1}{2n_ik_0}$. The exponential decay behavior of the transmitted signal follows the Beer-Lambert equation for linear absorption³

$$\frac{I}{I_0} = e^{-\mu z},$$
 (2.12)

where z is the thickness of the material and μ is the absorption coefficient that is equal to

$$\mu = 2n_I k_0, \tag{2.13}$$

As we can see, the absorption coefficient is element specific (approximately Z^4) and it is proportional to the inverse third power of the energy. The product μz is called absorptance and it is dimensionless. Absorption spectra is the relation between absorptance and energy.

An absorption spectra decreases with energy until the incident photon has enough energy to excite an electron. When it happens the absorption increase rapidly as shown on Figure 3. This discontinuity is called absorption edge and it is related with the binding energy of the electron, therefore, it is element specific. After an absorption edge it continues to decrease with energy.⁹

Two dominant processes can occurs after an absorption, X-ray fluorescence and Auger emission (Figure 2)

2.2.1 X-ray Fluorescence

After the absorption, there will be a hole in the inner shells. An electron in a further shell will relax and emit a photon that has a energy of the difference between the levels involved. This occurs in a timescale of the order of 10 to 100 fs. This process can be used to measure the X-ray absorption spectra and will be discussed in more details later.

Not all transitions are allowed. The relaxation of the electron from a bound state to another within the atom follows the selection rules for electric dipole radiation.³

$$\Delta l = \pm 1 \quad and \quad \Delta s = 0 \to \Delta j = \pm 1, \tag{2.14}$$

Hence, the allowed transitions from p are $p \to s$ or $p \to d$.

2.2.2 Auger emission

Following the relaxation of a electron into the hole, the excess energy $|E_c - E_n|$ can produces an Auger electron, whereby E_c is the energy of the core-shell binding energy and E_n is the energy of the outer-shell binding energy. This excess energy instead of emitting a photon can eject another electron if its binding energy is less than the excess energy.

Typical Auger electron energies are in the range of few hundreds eV and consequently it has an escape depth of only few nanometers. Therefore, it is very sensitive to the surface.³

2.2.3 X-ray fluorescence or Auger emission

Auger electron and X-ray fluorescence are competitive processes. X-ray fluorescence are proportional to the third power of the energy difference between the shells involved. Given that K-lines are more probable than L-lines. In heavier atoms will have more attractive positive nuclear force, resulting in a bigger difference of energy between adjacent shells increase the probability of x-ray fluorescence process. For the Auger emission is more likely for lighter atoms because it is proportional to the inverse of the energy difference.

The probability of both processes are shown below on Figure 4.



(Courtesy of M. Krause, Oak Ridge)

Figure 4: Fluorescence and Auger yields as function of atomic numbers. For lighter atoms it is more probable K-shell Auger process and for heavier atoms K-shells fluorescence.⁴

3 SYNCHROTRON

Synchrotron provides a very broad range of application for research. This chapter will explain some basics concepts and how everything works together. It is important to keep in mind that synchrotron facilities are open to users. So, understanding how it works can improve your available time in the facility.

Briefly, will be discussed some of the main components of a synchrotron (Figure 5), such as the source of electrons, the booster ring, the storage ring and beamline.



Figure 5: Main components of a synchrotron facility.⁶

- Electron gun is the first component of an operational synchrotron. the source of electrons usually works by thermionic emission from a hot filament. Then the electrons are accelerated using a linear accelerator (Linac) to around 100 MeV.
- The electrons from Linac are further accelerated in the booster ring to around the energy of the storage ring. Then they are periodically injected in the storage ring to maintain a specific current.
- The storage ring contains straight and curved sections of stainless tubes in ultrahigh vacuum. Bending magnets are employed to maintain electrons in a close path. Quadrupoles magnets are used to focus the electron beam and to compensate the Coulomb repulsion and sextupole magnets are used to correct the chromatic aberration introduced by the quadrupole. In the straight sections, there are radio frequency cavities to replenish the energy of the electrons lost in synchrotron radiation, also may be used insertion devices (characteristic of third generation synchrotron) such as wigglers and undulators.⁷

• Beamlines are the final stage of the synchrotron radiation and it is composed of three components, the front-end, beamline optics and experimental station. Front-end is the part just after the concrete wall and has several functions and safety features, such as vacuum isolation valves to protect the vacuum of the storage ring, BPM to monitor the position of the beam, filters to prevent damage in materials from low energy radiations, a shutter to interrupt the x-rays from passing further down the beamline, and so on. In the beamline optics, the x-rays are focus and monochromated. And for last, the experimental station has manipulators to position the sample, optics to view the sample and detectors to measure the signals. The details of these components depend on the type of experiment to be performed.⁷

Those apparatus of the beamline will be discussed later. Now we shall focus on some aspects of the electron moving at relativistic velocities.

3.1 Radiation from Relativistic Electrons

The features of the radiation depend on the angular frequency w_0 (the number of radians turned by the electron per second) and on the energy of the electron in the storage ring is given by the Lorentz factor

$$\gamma = \frac{\varepsilon}{mc^2},\tag{3.1}$$

where mc^2 is the rest energy of the electron. For non-relativistic electrons $\gamma = 1$. For relativistic electrons, this can be re-expressed in terms of the storage ring energy in GeV as

$$\gamma = 1957\varepsilon[GeV],\tag{3.2}$$

The opening angle or divergence is proportional to γ^{-1} . Thus higher electron energy implies in smaller opening angles of the emitted radiation. Electrons moving at non-relativistic velocities has a dipole distribution (Figure 6(a)). Meanwhile, at relativistic velocity, it points along the tangent of their path (Figure 6(b)).⁷

Considering a circular motion of a relativistic electron in an orbit then we can deduce the energy loss ΔE per electron per turn to synchrotron radiation as⁷

$$\Delta E[keV] = 88.5 \frac{E^4 [GeV]}{\rho[m]},$$
(3.3)

where ρ is the radius of curvature.

Equation 3.3 shows that energy loss of the electrons is proportional to the forth power of the electron energy. So if we have an electron with a hundred MeV and a radius of 10 meters, the synchrotron radiation won't be noticed (around few eV per turn). However,



Figure 6: Radiation pattern from a moving electron. (a) Non-relativistic electrons has a isotropic pattern and (b) relativistic electrons has a pencil-like pattern pointing in the direction in which they are traveling.⁷

an electron with GeV will have ΔE around 10⁶ eV. Therefore, more synchrotron radiation is produced at high-energy rings.

Let us use now the deflection of the electrons by the magnetic field to calculate the orbital radius of the arc. First, we equate the Lorentz force to a centripetal force such that

$$ev \times B = \frac{mv^2}{\rho},\tag{3.4}$$

where m is the mass of the particle, v is velocity and ρ is the orbital radius of the arc. Note that we did not use the electric field component. It would need a magnitude of 10^9 to induce a comparable centripetal force as the magnetic field. For relativistic electrons, we need to substitute $m \to \gamma m$ and $v \to c$. Considering that the magnetic field is perpendicular to the velocity, we have

$$ecB = \frac{\gamma mc^2}{\rho},\tag{3.5}$$

$$\rho = \frac{\varepsilon}{ceB},\tag{3.6}$$

Changing to practical units (GeV)

$$\rho = 3.3 \frac{\varepsilon [GeV]}{B[T]},\tag{3.7}$$

For typical values of magnetic field (about 1 Tesla) and storage ring electron energies of around few GeV, the bending radius is just a few meters.³

3.2 Photo Beam Properties

Two important properties related to the photo beam are discussed below.

- Spectral flux is the amount of photon per second per unit bandwidth (normally 0.1%) passing through a defined area. For example, at 10keV a 0.1% bandwidth means counting all photons from 9095 10005eV. The flux is conserved as long that any photon is not lost in the optical components.
- Brilliance is the spectral flux per solid angle, in other words, it defines how the flux is distributed along phase-space (Equation 3.8). It is a very important parameter because it says the smallest spot that you can focus the beam. For example, third-generation synchrotron has 10²⁰ brilliance, 10¹⁰ brighter than most powerful (compact) laboratory source,⁴ and that is why they are a very important tool for research.

They have very high brilliance because of the size of the electron beam (microns) and the high flux emitted by the electrons that is proportional to the square of the acceleration (centripetal acceleration is proportional to γ^2)³

$$Brilliance = \frac{\frac{photons}{seconds}}{(mrad)^2(mm^2sourcearea)(0.1\% bandwidth)},$$
(3.8)

• Polarization is very important for some spectroscopy techniques using synchrotron facilities such as linear and circular magnetic dichroism. In synchrotron, the polarization control of bending magnets depends on the line of sight. Viewed in the electrons orbital plane, it appears that the electron is oscillating in the horizontal plane, therefore the polarization is linear. If the observer is above or below the plane the radiation is either left-circularly polarized (LCP) or right-circular polarized (RCP), respectively.

3.3 Bending magnets

Electrons in the storage ring follow a close path (circular orbit) because of the bending magnet. They also emit synchrotron radiation after the magnetic field exerts a Lorentz force that accelerates the electrons centrifugally. The radiation of bending magnets are very broad and has brilliance of the order 10^{10} . The divergence is about $\frac{1}{\gamma}$.

Bending magnets produces a continuum of radiation that is characterized by a critical photon energy ε_c . By definition, half of the radiated power is above the critical photon energy and the other half is below. ε_c is related to the electron energy by⁷

$$\varepsilon_c[keV] = 0.665BE^2,\tag{3.9}$$

where E is the electron energy in GeV and B is the magnetic field in Tesla. The higher the electron energy, higher the critical energy. For hard X-rays (> 5keV), more than 2 GeV is needed.

To increase the flux and the brilliance it is used insertion devices (IDs) between the bending magnetics in the straight sections of the storage ring. The idea behind it is to make the electron oscillate using an array of magnetics pointing alternately up and down. They are carefully designed to maintain the same position and direction of the electron after the device.

Every insertion device can be characterized by the deflection parameter (K_{id}) , described below

$$K_{id} = 0.934\lambda_{id}B_0,\tag{3.10}$$

where λ_{id} is the magnetic period of the insertion device in centimeters and B_0 is the peak magnetic field in Tesla.

The two principal insertion devices, wigglers and undulators, differs from the deflection parameters and it defines the properties of the radiation emitted (Figure 7).⁷

3.3.1 Wiggler radiation

Wiggler has a deflection parameters $K_{id} >> 1$, in the range of 10 - 60. It means that wigglers have a long magnetic periodic, typically N = 20 - 50. If the magnetic field of the wiggler is higher than the bending magnets the critical energy ε_c is shifted to a higher value. Thus, wiggler are often used to produce hard x-rays with higher flux from a medium energy storage ring. The vertical divergence of wiggler is the same as bending magnet with the same magnetic field at critical energy $(\frac{1}{\gamma})$. For horizontal divergence it is increases by a factor K_{id} .⁷

A simple wiggler produces a linear polarization even when looking off-axis of the orbit plane. For a circular polarization, it is necessary to adjust the geometric of the wiggler (asymmetric) which will present a non-sinusoidal magnetic field. Another approach is the elliptical wiggler which is the simple wiggler with a small horizontal magnetic field shifted by $\frac{\pi}{2}$ with respect to the main vertical field.⁸

3.3.2 Undulator radiation

Undulator uses a weaker magnetic field and shorter periods, so $K_{id} \approx 1$. Each pulse generates radiation out of phase with the next pulse by the time taken to the next magnetic. Thus because of the interference only those photons with wavelength equal to this difference interfere constructively, resulting in a spectrum of peaks (Figure 7). Both vertical and horizontal divergence of the fundamental frequency is $\frac{1}{\gamma\sqrt{N}}$ where N is the



Figure 7: Radiating in the direction in which they are traveling.⁴

number of periods in the undulator. The transformation of a undulator to a wiggler is achieved by reducing the vertical spacing (gap) between each magnet pair. It increases B_0 and consequently K_{id} until the higher harmonics becomes more important and more closely space in energy ($K_{id} > 10$). The polarization of the undulator radiation can be controlled by laterally shifting the position of one set of magnet poles relative to the other. That will generate a horizontal magnetic component in addition to the vertical magnetic component.³

3.4 Beamlines

In this chapter we will take a look at the main components of a general beamline in the order of which the photon coming from the storage ring interact.

3.4.1 Front End

The front end is the part of the beamline just after the insertion device or bending magnet. It is composed of beam position monitor (BPM), aperture and slits to define the angular acceptance, shutter to interrupt the radiation when necessary, filters to remove the soft x-rays components of the radiation and isolation of storage ring vacuum from beamline vacuum to avoid leakage.

The beam position monitor measures the lateral position of the beam. There are several designs, for example a 1-D wire of tungsten can map one direction of the beam by measuring the photocurrent induced by the x-rays. The resolution is limited by the diameter of the wire (usually few micron meters). A design for a 2-D profile of the beam is composed of four metallic blades around it measuring independent the photocurrent of each and then using comparators between them. Using a CVD diamond BPM you can measure the two dimensional beam position and the amplitude of it. This is achieved by measuring the photocurrent of an array of ultrathin metallic electrodes deposited on thin and transparent synthetic diamond discs

For hard x-rays beamline, it is important to define the beam using fixed aperture at the front end for two reasons. First to collimate the beam and second to suppress the low energy photons and avoid damage in the components because it interacts strongly with matter. That is done by a water-cooled rectangular cone shape to increase the dissipation area. In addition to the fixed aperture, it is used two adjustable slits to decrease the divergence of the beam. Those slits are protected by one or more filters that remove the soft x-rays. The material used in these filters have low atomic number, resist high temperatures, have good thermal conductivity and highly crystalline. The best candidate is carbon in the form of synthetically grown diamond (thin sheets of hundred micron meters). After the soft x-rays is removed, other materials can be placed in front of the beam. Beryllium windows are used to isolate the vacuum of the storage ring from the beamline.

3.4.2 Primary Optics

The optics for x-rays are different from visible light because as showed in Section 2.1 the refractive index of x-rays is slightly smaller than 1. Also because of the strong interaction between the soft x-rays with matter that can cause huge damage in components and can even be strongly attenuated by gas. This makes difficult to bend or redirect x-rays.

A x-ray optical system normally contain a monochromator, x-ray mirror, slits and filters. They perform basically three tasks, first a selection of one energy by the monochromator, second optimization of the resolution energy using a collimation mirror upstream of the monochromator and third refocusing the beam using either a curved mirror or gratings.

X-ray mirrors are very different from the common aluminium-coated glass. The reflectivity drops drastically above the critical angle. A useful rule-of-thumb relating the maximum allowable incident grazing angle to the photon energy is

$$\alpha_{max}[degrees] = \frac{\lambda[\text{Å}]}{10},\tag{3.11}$$

this approximation assumes that all condensed matter has the same average electron density of 0.34\AA^{-3} , which is okay for the transitions elements of the periodic table.

For low energy radiation, Equation 3.11 predicts a few tens of degrees, but for

hard x-rays the incident grazing angle is about 0.1° or less. The problem with this small incident angle is that the illuminated part of the mirror $(\frac{h}{\alpha}$ where h is the beam height perpendicular to the mirror surface) for a typical beam height of 1mm is about the order of 290mm. The mirror needs to have a roughness of less than a few Angstroms for it be usable. All of these requisites contribute to a very technological challenge, and mirrors can lower effective brilliance of the source.

The theoretically most perfect reflective focusing element is a two-dimensional parabolic mirror, which can focus the beam to a point. However, it is very difficult to design it considering how large the surface need to be. A more practicable geometric is a toroidal mirror, a very good approximation of a parabolic surface. A still simpler solution is to divide the focusing of horizontal and vertical to two independent cylindrical mirrors. This arrangement is known as a Kirkpatrick - Baez mirror.³ The disadvantage is that the length of the mirror system is doubled.

Monochromator is one of essential optics components of a beamline. Experiments at synchrotron facilities normally require a well-defined energy and the possibility to change de photon energy, or that is scanned. Even for insertion device such as low-K undulator, the radiation is not sufficient monochromatic to be used as a source in an experiment.

For each range of wavelength is recommended to use specific monochromator. For longer wavelength radiation it is used periodic grating monochromator where the separation between grating lines can be several microns down to a few tens of nanometers. Wavelength less than a few nanometers uses a crystal monochromator where the periodicity of the crystal and the separation of lattice in Angstrom act as a grating. A possible alternative is the multilayer monochromator that has a broader range of wavelength with a consequent of increase in transmitted flux. These monochromators are described below.

- There are several types of profile for a grating surface. We will focus on the most efficient one, the blaze grating (a surface with periodic triangular shapes). The reflection of the beam in different facets will cause interference that for a single wavelength will satisfy the constructive condition. However, the bandwidth will be determined by how many facets will be illuminated by the beam. Lower facets imply in higher bandwidth and flux, meanwhile higher illuminated facets result in sharper peaks with less flux.
- Crystalline monochromator can be used to 0.05 to 6Å radiation. The diffraction in the crystal will follow the Bragg's law

$$m\lambda = 2d\sin\theta,\tag{3.12}$$

where m is the order (natural number), d is the lattice spacing and θ is the angle of incidence. Usually it is used a single crystal of silicon because it has a reasonable

thermal conductivity and can be cooled by liquid nitrogen. Another important aspect is that the production of a single crystal of silicon is very well known because of the semiconductor industry. Another candidate is diamond, it has high thermal conductivity, very important for high flux synchrotron. But it is also quite expensive to produce a single crystal with sufficient size.

The most two common designs for crystal monochromator are Double-Crystal Monochromator (DCM) and Channel-Cut Monochromator (CCM). The DCM uses two crystal to diffract the beam. The first crystal will absorb almost all the flux and need to be constantly cooled (water or liquid nitrogen) while the second crystal will redirect the monochromated beam parallel to the incoming beam. It is not necessary to cool down the second crystal because 99.9% of the flux is absorbed in the first crystal. It is possible to change the second crystal to improve the monochromaticity by either choosing a different orientation or changing the material or using in the same sense of the first crystal. The consequent of this increase in monochromaticity is the decrease in flux. The CCM uses two surfaces of the same single crystal block to diffract the beam.

• The multilayer monochromator are design by growing periodic layers of two different materials by magnetron sputtering. A thinner layer of a high-Z material and a thicker layer of a low-Z material. The diffraction now will occur in function of the distance between the periodic multilayer instead of the plane levels of the crystal.

The last component that we will describe for the beamline is the detectors. Some of them are described below.

Scintillator detectors partially convert the absorption x-ray into visible light or near-visible light. First an inorganic scintillator material absorbs the x-ray and emits a visible light in the photocathode. By photoelectric effect, electrons are directed to electrodes that generated more electrons until the anode that produces a sharp current pulse. Scintillator plates can be used to record x-ray images.

The Pilatus detector is a two-dimensional pixel array, that increment by one each pixel when a photon with certain energy above the threshold is detected. The electronics is composed of three elements: preamplifier, a comparator and a counter. The preamplifier will amplify the signal generated by the incoming x-rays. The comparator is used to produce a digital signal when the x-rays have energy above the threshold and the counter register the number of detected x-rays per pixel. There are several advantages in Pilatus detector compared to current state-of-the-art CCD and imaging plate detectors. For example, no readout noises, superior signal-to-noise ratio, a read-out time of 5 ms, high detector quantum efficiency and the possibility to suppress fluorescence by an energy threshold that is set individually per pixel. Spectral analysis of a x-ray spectrum can be done by two ways using a photon detector in the range of 100 eV to several tens of keV: Wavelength Dispersive Spectrometers (WDX) or Energy Dispersive Spectrometers (EDX). The WDX method select the photon energy by diffraction of a single crystal or a grating similar to a grating monochromator. For EDX, a solid-state detector determine the photon energy when it is detected. The device is polarized with high voltage. The x-ray will produce an electron-hole pair that will drift in the applied electric field. The charge is collected and the increment in voltage is proportional to the photon energy, hence is possible to determine the energy spectrum. The voltage is reset regularly to avoid saturation. EDX spectrometer is smaller, faster and cheaper than WDX. However, EDX has way lower resolution (typically around 100-200 eV for EDX).

To measure the kinetic energy of an electron is used an electron-energy analyzer It is very important for photoemission spectroscopy experiments. We will focus on the concentric hemispherical analyzer (CHA) because it is the most common nowadays. CHA is composed of two metallic concentric hemispheres of radius R_1 and R_2 . Both spheres have negative potential $-V_1$ and $-V_2$ respectively. An electron entering CHA with kinetic energy E will be focused at the exit only if

$$e\Delta V = E(\frac{R_2}{R_1} - \frac{R_1}{R_2}), \tag{3.13}$$

where $\Delta V = V_2 - V_1$. Therefore, the electron energy spectra can be measured by sweeping ΔV .

4 X-RAYS ABSORPTION (XAS)

The simple picture of X-Rays Absorption (XAS) is that an electron from a core-shell is excited to an unoccupied state by the incident synchrotron radiation. The XAS spectrum is measured by scanning the photon energy, therefore it can only be done at a synchrotron facility. Commonly, there are three ways to measure the XAS signal. First, you can do a direct measure of the absorption by the transmission method by measuring the intensity before and after the sample. The indirect measure can be done either by fluorescence or Auger emission. Both occur when an electron relaxes to the hole of the excited electron. The first there is a photon emission and second is radiationless and the difference in energy will eject photoelectrons, Auger electrons and low-energy secondary electrons. Therefore, XAS measures the density of state of the unoccupied state.

As stated in Equation 5.1, the transmitted signal through the material follows the Beer-Lambert equation for linear absorption.

$$\frac{I}{I_0} = e^{-\mu z},$$
 (4.1)

where μ is the absorption coefficient and the multiplication of it with the thickness (z) is called absorptance.⁹

After a photon is absorbed the energy increase following the conservation of energy by $h\nu$ as

$$E_f = E_i + h\nu, \tag{4.2}$$

where E_f and E_i is the final and initial energy and h is Planck constant.

In this case, Pauli's exclusion principle says that the final state needs to be unoccupied before the excitation. Quantum mechanics says that the probability of transition from the initial state (denoted with the Dirac notation, $\langle \psi \rangle_i$) to the final state (ψ_f) is proportional to the square of the transition dipole matrix element

$$P_{if} \propto |\langle \psi_f | er | \psi_i \rangle|^2, \tag{4.3}$$

where P_{if} is the transition probability between two states, er is the transition dipole operator and ψ is the electron wavefunction. For maximum probability transition, the integrand needs to be as symmetric as possible. The r operator is asymmetric, then the product of the initial and final wavefunction need to be asymmetric as well to result in a non-zero integral. That is the reason that a transition from $1s \rightarrow 2s$ is not possible, the integrand will be zero. When the photon energy of the incoming radiation is equal to the difference in energy between two quantum states in an allowed transition it is called resonant with that transition. There may be more than one available state with the same energy so the transition probability is the sum of all probabilities for those possible transitions. Therefore, the study of absorption scanning the photon energy will provide information about the electronic structure.

After the introduction about the basics of electronics transitions we will discuss some general concepts of electronic states. Lets first consider the simplest system, the hydrogen atom.

The necessary energy to excite the 1s electron to the conduction band is 13.6eV. This is called the 1s binding energy. For a hydrogen atom, the energy level (E_n) is given as

$$E_n = -\frac{R_H}{n^2},\tag{4.4}$$

where R_H is the Rydberg constant, the 1s binding energy and n is the energy level. For hydrogen the Rydberg constant is $R_H = 13.6 eV$. The energy of a resonant photon from 1s to a n level is

$$R_H(1 - \frac{1}{n^2}),\tag{4.5}$$

as n becomes large, the energy approaches the Rydberg constant. Then the electron escapes from the atom and can have a continuum of energy depending on the photon energy. The electron then can have any kinetic energy, they are free of any constraints.

For heavier atoms, the energy levels are approximate as proportional to Z^2 . The data fits more accurately for larger Z than low Z. For example, for Uranium, the 1s binding energy is $92^2 * 13.6 = 115 keV$. It is just an approximation because the excited electron will interact with the Z - 1 electrons in the atom. Some examples of binding energies for different levels are given in Figure 8.

In the absorption spectra, there will be a drastically increase when the photon energy is about the binding energy of the electron. This peak is called absorption edge and is element specificity because is related to the binding energy of that electron in the atom. The absorption edge is named after the shell, K-edge, L-edge, M-edge for n=1,2and 3 respectively. All absorption edges except the K-edges has three or more "sub-edges" energetic closely of the edge because of the orbital-spin coupling. K-shell has quantum number l = 0 that is why they are not seen in it.

Around the edge might have strong fluctuation in intensity. This region is called X-ray Absorption Near-Edge Structure (XANES). The region after the edge from 50 to several hundred eV is called Extended X-ray Absorption Fine Structure (EXAFS). Both

Element	K I s	L ₁ 2s	L ₂ 2p _{1/2}	L ₃ 2p _{3/2}	M ₁ 3s	M ₂ 3p _{1/2}	M3 3b3/5	M4 3d3/5	M5 3d5/2	N1 4s	N ₂ 4p _{1/2}	N3 4p3/2
1.H	13.6											
2 He	24.6 ^b											
3 14	54.7 ^b											
4 Be	111.5											
5 B	188 ^b											
6.0	284 2 ^b											
7 N	409.9 ^b	37 3 ^b										
80	543 1 ^b	41.6 ^b										
9 F	696 7 ^b	41.0										
10 Ne	870.2 ^b	48 5 ^b	21.7 ^b	21.6 ^b								
11 No	1070.2	63.5	20.4°	20.5 ^b								
12 Ma	1202.05	00.5 99.6 ^b	40.65	40.26								
12 Mg	1550.6	117.8 ^b	72 Q ^b	72 50								
14 \$	1939.0	140.70	00.8 ^b	00 2 ^b								
14 31 15 D	2145 5	149.7	1260	1250								
15 P	2145.5	230 0b	163.6 ^b	155 162 5 ^b								
10 3	2472	230.9 270.2 ^b	2025	200 ^b								
19 44	2022.4 2205.0 ^b	270.2 236.2 ^b	202 250.6 ^b	200 249 4 ^b	20.2 ^b	15 Q ^b	15 7 ^b					
10 10	3203.9 3600 Ab	320.3 370 4 ^b	200.0	240.4 204.6 ^b	29.5 24.9 ^b	10.9	19.20					
19 K	4039 5 ^b	378.0 439.4°	297.5 240.7 ^c	294.0	34.0 44.2 °	16.5	16.5 25 4°					
20 Ca	4036.3	400.4 400.0 ^b	402.6b	200 7b	51 1b	20.4 20.2 ^b	20.4 20.2 ^b					
21 50	4492.8	498.0	405.6	398.7	20.75	28.5	28.5					
22 II 22 V	4900.4	500.9	401.2	433.8	38.7	32.0	32.0					
23 V	5465.1	626.7	519.8	512.1	00.5	37.2	37.2					
24 Cr	5989.2	095.7	583.8	574.1	74.1	42.2	42.2					
25 Mn	6539.0	769.1	649.9	638.7	82.3	47.2	47.2					
20 Fe	7112.0	844.0	719.9	706.8	91.3	52.7	52.7					
27 Co	7708.9	925.1°	793.3	778.1	101.0	58.9	58.9					
28 Ni	8332.8	1008.6	8/0.0	852.7	110.8	68.0	66.2					
29 Cu	89/8.9	1096.7	952.3	932.5	122.5°	77.3	75.1°	to all	10.10			
30 Zn	9058.0	1196.2°	1044.9	1021.8	139.8	91.4	88.6	10.2	10.1			
31 Ga	10367.1	1299.0°	1143.2	1116.4	159.5	103.5	103.5	18.7	18.7			
32 Ge	11103.1	1414.6°	1248.1	1217.0	180.1°	124.9°	120.8	29.0	29.0			
33 As	11866.7	1527.0°	1359.1	1323.6	204.7°	146.2	141.2	41.7	41.7			
34 Se	12057.8	1652.0	14/4.3	1433.9	229.0	100.5	160.7	55.5 Tok	54.6			
35 Br	13473.7	1782.0"	1596.0°	1549.9°	25/ 202 ph	189	182	70°	69 02 of	an ch	1.4.10	14.15
36 Kr	14325.6	1921.0	1730.9	16/8.4	292.8°	222.2	214.4	95.0	93.8	27.5	14.1	14.1
37 Rb	15199.7	2065.1	1863.9	1804.4	326.7	248.7	239.1	113.0	112	30.5	10.3	15.5
38 Sr	16104.6	2216.3	2006.8	1939.6	358.7°	280.3	270.0	136.0	134.2	38.9	20.3	20.3
39 Y	17038.4	2372.5	2155.5	2080.0	392.0	310.6	298.8	157.7	155.8	43.8	24.4	23.1
40 Zr	17997.6	2531.6	2306.7	2222.3	430.3	343.5	329.8	181.1	178.8	50.6	28.5	27.7
41 Nb	18985.6	2697.7	2464.7	2370.5	466.6	376.1	300.0	205.0	202.3	50.4	32.0	30.8
42 Mo	19999.5	2865.5	2625.1	2520.2	506.3	411.6	394.0°	231.1	227.9	63.2	37.0	35.5
43 Tc	21044.0	3042.5	2793.2	2676.9	544"	445	425	257	253	68	39	39
44 Ru	22117.2	3224.0	2966.9	2837.9	586.2	483.5	461.4	284.2	280.0	75.0	46.5	43.2
45 Rh	23219.9	3411.9	3146.1	3003.8	628.1	521.3	496.5	311.9	307.2	81.4°	50.5	47.3
46 Pd	24350.3	3604.3	3330.3	3173.3	671.6°	559.9	532.3	340.5	335.2 *	87.6	55.7	50.9
47 Ag	25514.0	3805.8	3523.7	3351.1	719.0°	603.8	573.0°	374.0"	368.0	97.0°	63.7	58.3*

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Figure 8: Electron binding energy several atoms in eV.⁴

of these techniques are based on absorption but they provide very different information because of the mean free path in each period (Figure 9).

How sharp is the edge depends on the angular-momentum quantum number l. For low values of l (s-states with l = 0 and p-states with l = 1) the peak is very sharp across only a few electron volts. But, for higher values of l the peaks are broader and can be about several tens of eV higher in energy. This is called "delayed onset" and is related to the distance of the electron from the nucleus.³

Considering the kinetic energy of the electron (ε_e) , the photon energy $(h\nu)$ and the binding energy (E_B) we have

$$\varepsilon_e = h\nu - E_B,\tag{4.6}$$



Figure 9: Mean free path as a function of kinetic energy of the photoelectron. The curve is practically independent of the material, that is why it is called universal curve.⁹

Energy is related with momentum of a non relativistic particle as

$$E = \frac{p^2}{2m},\tag{4.7}$$

Combining Equation 4.6 with Equation 4.7 and doing some mathematical manipulation we arrived at

$$k[\text{Å}^{-1}] = 0.512\sqrt{\varepsilon_e[eV]},\tag{4.8}$$

where k is the wavevector of the photoelectron. Note that an increase in energy results in a decrease in wavelength $(k = \frac{2\pi}{\lambda})$. For EXAFS signal is commonly to use the wavevector instead of photon energy for the spectrum dependency. Equation 4.8 shows that for 50eVthe wavelength is comparable to interatomic distances. This can be used as a separation between the regions XANES and EXAFS (Figure 10), however it is not possible to define it universally because the transition shifts according to the system.

4.1 X-ray Absorption Near-Edge Structure, XANES

XANES is the region of about few eV after the absorption edge. For low photoelectron energy the mean free path (Figure 9) is longer compared to the interatomic distances. It means that the photoelectron will have multiple scattering. Consequently, theoretical modeling still remains a significant challenge. The theory is still developing and progress is being made in quantitative interpretation.³

An important aspect of the detection of the XANES signal is that when the photoelectron is excited with enough energy may not be ejected into the vacuum continuum, instead it may be promoted to an unoccupied bound state. The detection is not directly as



Figure 10: Absorption spectrum of metallic Co. Few eV after the absorption edge is called XANES and from 50 to several hundred eV is called EXAFS.⁹

in photoemission experiments where the kinetic energy of the photoelectron is measured. In X-ray absorption the core-hole will be filled with a further out electron and it either emit a fluorescent photon or an Auger electron. Then the fluorescence radiation or the Auger electron is measured providing information about the unoccupied bound state.

The fluctuation in intensity in the absorption edge is given by two factors: the probability transition given by Equation 4.3 and the density of state in which the excited state is embedded. Both factors are encapsulated in the Fermi golden rule:

$$P_{if} = \frac{2\pi}{h} | \langle \psi_f | H' | \psi_i \rangle |^2 \rho, \qquad (4.9)$$

where H' is the perturbation Hamiltonian responsible for the transition (for which the simplest case of a dipole transition to a continuum state in the vacuum is the dipole operator er) and ρ is the density of state of the excited state.

The intensity of the transition to an unoccupied bound state depends on the density and the selection rules. For example, if you consider five 5d-metals such as Re, Os, Ir, Pt and Au and measures the XANES signal in L3 edge the intensity will decrease as increase the number of electron in d-shell. For Au that has all 5-d states filled has a very low intensity because it does not have unoccupied states.¹⁰

As stated before, the mean free path in XANES is longer than interatomic distances causing multiple scattering in the photoelectron. The signal will then be relate to the atomic position and number of neighbors atoms, the bonding angles and oxidation state (chemical shift). Qualitatively information about the structure and oxidation may be acquired using standards models.^{9,11}

4.2 Extended X-ray Absorption Fine Structure, EXAFS

EXAFS refers to the oscillation after an absorption edge (usually from 50 to 1000 eV after the edge). Because the mean free path is about a few Angstroms, the photoelectrons is limited to scattering in the few neighbors atoms. It results in a more develop theory and quantitative comparisons are possible. The shorter mean free path implies in several important features. First, as the photoelectron is limited to a few atoms around the absorbing atom, the system studied do not need necessarily to be organized, it can even be amorphous. The oscillations in the spectrum results in the interference between the photoelectron wavefunction produced by the x-ray absorption and the same wave single backscattering in the neighbors atoms, as described in Figure 11.

In order to extract the oscillations from the spectrum (approximately 50 to 10000 eV) is defined the EXAFS function as

$$\chi(k) = \frac{\mu(k) - \mu_{\alpha}(k)}{\mu_{\alpha} - \mu_{0}},$$
(4.10)

where μ_0 is the absorption coefficient from the electrons in the others shells and represents the monotonic decaying of the absorption in energy. The μ_{α} is the absorption coefficient from the electrons in the edge-shell and μ is the total absorption coefficient that is measured in a condensed matter from a EXAFS experiment as function of the photon energy (Figure 12).

As stated before, it is common to express the EXAFS spectrum as function of the wavevector k. This is done by mathematical manipulation of the equation of kinetic



Figure 11: Representation of the photoelectron wavefunction as a sphere from the absorbing atom. It is scattered in the neighbors atoms and interfere with itself causing oscillations in the spectrum.⁹



Figure 12: Standard absorption spectrum for Cobalt. μ_0 is defined as the absorption from other process except the K-edge of Cobalt (background signal). μ_{α} is the absorption from the K-edge of Cobalt and μ is the measured spectrum.⁹

energy of the photoelectron ejected and the momentum of a non-relativistic particle, $k = \sqrt{\frac{2m(E-E_0)}{h^2}}$ where E is the photon energy and E_0 is the binding energy of the electron excited.

To extract structural information from the spectrum it is necessary to consider some approximations such as spherical symmetry, single scattering photoelectrons, etc. Then is obtained an expression for $\chi(k)$ based on the concept of shells^{3,9}

$$\chi(k) = \sum_{j} N_j \frac{t_j(k) \sin[2kR_j + \delta_j(k)]}{{R_j}^2} \times \exp(-2k^2 {\sigma_j}^2) \exp(\frac{-2R_j}{\Lambda}), \quad (4.11)$$

the summation is over all the *j* considered shells, N_j atoms in each shell, factor t_j is the scattering amplitude for the scatterers in the *jth* shell, R_j is the distance between the atom in the *jth* shell and the absorbing atom, δ_j is a phase shift from the absorbing atom and σ_j is the phase shift from the atoms in *jth* shell. We can separate those parameters in two groups:

- $N_j, R_j and \sigma_j$ are structural parameters;
- $\Lambda, t_i and \delta_i$ are atomic parameters.

Experimentally knowing one of the groups you can determine the other one. Usually you may use a standard that you know the structural parameters to measure the EXAFS spectrum. Then you can determine the atomic parameters of the standard and use it in a similar and unknown system to obtain the structural parameters of that system.

The analysis of the spectrum proceeds as follows. The absorption is measured as function of the photon energy and the raw data of the EXAFS function is acquired. Then it is applied Equation 4.10 to remove the background signal fitted to the pre-edge signal and the monotonic decreasing signal above the absorption edge. The EXAFS function is expressed in terms of wavevector $k[Å^{-1}]$. For last, the function is Fourier transformed to express the spectrum as function of characteristic length associated with the interatomic distances R_j instead of frequency spectrum (proportional to k).

4.3 X-Ray Magnetic Dichroism

Dichroism is the phenomenon of a material with an absorption spectrum that depends on the polarization of the electromagnetic radiation. Magnetic dichroism describes the dependence of the absorption of a magnetic material on the polarization and on the relative orientation of the magnetic field. Therefore, magnetic dichroism is measured with an applied magnetic field and with linear or circular polarization of the electromagnetic radiation. The techniques are called X-ray Magnetic Linear Dichroism (XMLD) and X-ray Magnetic Circular Dichroism (XMCD), respectively.

Magnetic materials are characterized by partially filled valence shells. There is a magnetic moment in ferromagnetic materials because of the difference between the density of states in spin up and down electrons. This is the results of the difference in energy between both spin up and down b the exchange interaction. Qualitatively we can explain by considering Pauli's exclusion principle. Each electron in the atom must have different quantum numbers, however, the wavefunction that described the spin does not affect the spatial distribution of the electron. Therefore, those electrons that only differ in their spin quantum number will overlap and repel each other by Coulomb forces.

X-ray Magnetic Circular Dichroism (XMCD) probes atomic magnetic properties utilizing the absorption of circularly polarized x-rays (Figure 13). It is different from traditional techniques of magnetic characterization because XMCD is element specific (absorption edges) and it is possible to measure direct and independent spin and orbital magnetic moments.

Figure 13 describes XMCD of bulk Fe. It is used circularly polarized x-rays to probe core to valence electrons in the L-edge $(p \rightarrow d)$ transition. The L absorption edge is split into L_2 and L_3 because of the strong spin-orbit coupling effect. If there is a difference in the density of state of spin up and down in the valence band, the absorption right-handed will be difference from the left-handed circularly polarized light at resonance absorption edges. It is possible to obtain information about the orbital magnetic moment and spin magnetic moment using the areas in the dichroism spectra. In this example A is negative and B is positive. Hence, m_{orb} is smaller than m_{spin} .¹²

X-rays magnetic linear dichroism can sense the charge anisotropy of the valence states involved in the core excitation process by measuring the absorption spectrum of



Figure 13: Principle of XMCD. The magnetic material will probe different depending on the polarization of the eletromagnetic radiation if there are a net of spin moment (imbalance in the spin-up and spin-down moments) or a net of orbital moment in the valence band. The area A and B are obtained by integrating the difference spectra (dichroism spectra) between left and right-handed circularly polarized light. Orbital magnetic moment and spin magnetic moment are proportional to A and B.¹²

linear polarized electromagnetic radiation. Usually, the charge anisotropic in the atomic volume is the result of an anisotropy in the atomic bonding. For magnetic materials, the alignment of atomic spins can also cause the charge anisotropy through spin-orbit coupling. For example, a cubic material the charge is isotropic, but if there is a magnetic interaction it may result in a small ellipse-like anisotropy. This would lead a difference between parallel and perpendicular electric field spectrum.¹³

5 RESULTS AND DISCUSSION

In this chapter we will report some results in the literature using X-rays absorption techniques to study cuprates $high - t_c$ superconductors. More specifically, we are going to discuss three recent results about the interplay between CuO-chains and the CuO₂-planes of cuprates high-t_c superconductor.

First, in the case of the $YBaCuO_{6+x}$, the stacking sequence of layers from the layered-perovskite structure along c-axis is CuO-BaO-CuO₂-Y-CuO₂-BaO-CuO. The YBCO unit cell (Figure 14) is composed of CuO₂ planes that are very important to the superconducting properties. The carriers only move along these planes and the others components act as charge reservoirs that influence in the charge density of the CuO₂ planes.¹⁴ Nevertheless, each unit cell has one yttrium in the middle of two planes of CuO₂ planes sandwiched with BaO layers and lastly, CuO chains (charge reservoirs).

YBCO can present as two possible symmetries, tetragonal or orthorhombic, depending of the amount of oxygen in the CuO chains. Considering the formula $YBa_2Cu_3O_{7-\delta}$, if δ is close to zero the material presents in an orthorhombic structure which is superconducting. If δ is greater than 0.63 the material behaves as an antiferromagnetic insulator. A YBCO fully oxygenated has a critical temperature of 91 K with a = 3.82 Å, b = 3.88 Å and c = 11.68 Å.^{15,16}



Figure 14: (a) Tetragonal $(YBa_2Cu_3O_6)$ and (b) Orthorhombic $(YBa_2Cu_3O_7)$ YBCO perovskite structure. Adapted from Laura Begon-Lours.¹⁷

Our first discussion about this correlation between the CuO-chains and CuO₂-planes are extracted from M. Magnuson et al¹⁸ where they used the synchrotron facility Swiss Light Source (SLS) to measure a direct evidence of a temperature driven redistribution of charge between the planes and the chains of YBCO. In other words, evidence of the dynamic nature of the chain-plane charge transfer as part of the metal-to-superconductor transition.

Figure 15 shows the X-ray absorption measurement by total fluorescence yield method around Cu L₃ edge with two different temperatures (300 and 15K) using polarization in-plane (E||ab) and out of plane (E||c). The main peak at energy 930.7 eV is related to the transition from 2p core hole to $3d^9$ and the satellites around 932.4 and 933.4 eV are due to metal to superconductor charge transfer transition on the Cu-planes and Cu-chains, respectively.



Figure 15: Left: experimental XAS measurement with polarized light by total fluorescence yield of a optimally doped YBCO at temperature 300K (red curve) and 15K (blue curve). Above and below is the spectra for in-plane (E||ab) and outof-plane (E||c), respectively. Right: Corresponding simulated spectra (above) using fitted linear combinations of model calculations of spectra showed in the lower part. Extracted from M. Magnuson et al.¹⁸

Despite the strong temperature dependence around the main peak, we will focus mainly on the intensity around the satellites. Independent of the polarization (in or out of the plane) there are opposing intensity trends in those satellites upon cooling, i.e. the "chains satellite" regarding the CuO chains have higher intensity than "plane satellite" (CuO₂ planes) at 300K, meanwhile at 15K the relationship between them is the opposite. This suggests that there is a redistribution of the charges between the planes and chains below the critical temperature (metal to superconductor transition). The right part of the Figure 15 simulated the absorption spectra for the Cu L₃ edge by using linear combinations of the spectra at the bottom. In conclusion, it indicates that divalent cooper sites must contribute to the spectral weight of the satellites and that monovalent and/or trivalent cooper sites may also contribute to the charges redistribution.

M. Salluzzo et al¹⁹ discuss this charge transfer in high-t_c superconductors by applying an electric field and measuring the x-ray absorption spectra by total electron yield at the ID08 beamline of the European Synchrotron Radiation Facility (ESRF). The design at the facility allowed simultaneously to measure the absorption spectra and the transport properties of the SrTiO₃/NdBCO thin film. A positive (negative) voltage V_{gate} applied through the SrTiO₃ single crystal under ultra-high-vacuum conditions reduces the density of holes (creates holes at the interface) in the sample. They also used linear polarization in order to probe the final states lying parallel or perpendicular to the CuO₂ planes (denoted as I_{ab} and I_c spectra).

Figure 16 describes the effects of the electric field on the I_{ab} spectra at 10K for a 3 unit cell sample (see Fig. 16.(a) inset). Under negative or positive gate voltages, the peak around 933.5 eV increases or decreases spectral weight because additional carries appears at the CuO₂ planes. However, it is more intense the increase and broadening of the main peak as function of the gate voltage. Additionally, Figure 16.(b) shows an increase around 932.2 eV from the reference (without any electric field) with the increase of voltage. This peak can be explained by an enhancement of hole density along the chains by negative fields. The electric field effects are similar in the ab plane and along the c axis. Figure 16.(c) shows the difference between the I_{ab} and I_c as function of the gate voltage where the main peak (932 eV) increases intensity with negative voltage. More importantly, the satellite anisotropy remains almost unaffected which contributes with the idea of a strong enhancement of the hole population along the chains (I_{ab}). This is a further confirmation that occurs a charge transfer from the heavily doped chains to the CuO₂ planes.

In conclusion, the external electric field injects holes mainly in the chains (CuO) belonging to the charge reservoir and that part of these charges are transferred to the CuO₂ planes via charge transfer. This mechanism is the same as chemical substitution in the high-t_c superconductors families.



Figure 16: (a) $I_a b$ absorption spectra for several values of gate voltage in the 3 u.c. NdBCO device (see inset) at 10K. (b) Study of the relation between the gate voltage and the absorption spectra by subtracting the I_{ab} with a reference (without any electric field). (c) Difference between I_{ab} and I_c for several values of electric field. Extracted from M. Magnuson et al.¹⁹

Lastly, Y. Tanaka et al²⁰ demonstrate that Cu L-edge X-ray absorption spectroscopy can be used as a quantitative analysis of the doping level of hole-doped copper-oxide systems. In this case they measured XAS spectra at room temperature of Cu L_{2,3}-edge for the high-t_c superconductor $(La_{1-x}Sr_x)_2CuO_{4+\delta}$ varying systematically carrier-doping levels, calculated the concentration and compared with values obtained by wet-chemical analysis. The measurements were performed on the BL20A beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan and the spectra were recorded using fluorescence yield.

Figure 17 shows the x-ray absorption measurement of the Cu $L_{2,3}$ -edge recorded for the $(La_{1-x}Sr_x)_2CuO_{4+\delta}$ sample. The spectra were normalized using the main peak in the L_3 area (around 931.2 eV) with purpose of improving its appearance. For quantitative analysis, it is used the area under L_3 because it is more intense than the L_2 area. The L_3 main peak (931.2 eV) is due to formally divalent copper states and the shoulder peak (932.6 eV) is due to formally trivalent copper. With increasing the concentration of strontium (Sr), the main peak becomes progressively asymmetric because of the increase of trivalent copper. The analysis consisted in fitting (both peaks of L_3) a combined Lorentzian and Gaussian functions after approximating the background with a straight line (details left of Figure 17 inset) and calculating the integral to use it to extract the valence of copper as follow:

$$V(Cu)_{XAS} = 2 + \frac{I(Cu^{II})}{I(Cu^{II}) + I(Cu^{III})},$$
(5.1)

Where $I(Cu^{II})$ and $I(Cu^{III})$ are the resultant integrated intensities of the respectively peaks.

The calculated values of the copper valence from the XAS measurements is compared with precise values determined by means of chemical analysis. Both results are exposed in Figure 17 (right panel) and they showed an excellent agreement. Moreover, both independent values of the copper valence presents an systematic increase with increasing strontium content reaching what appears to be a saturation for larger Sr^{II} -for-La^{III} substitution levels. This could be due to an increase in the oxygen vacancy concentration with increasing strontium content.



Figure 17: Left: X-ray absorption measurement of Cu $L_{2,3}$ for the $(La_{1-x}Sr_x)_2CuO_{4+\delta}$ sample. Inset illustrated the calculation of the background and peak fittings. Right: Valence of copper as function of the content of strontium (Sr). The V(Cu)_{XAS} is the estimated value from the method described above and V(Cu)_{TIT} is the iodometric titration data. Extracted from Y. Tanaka et al.²⁰

6 CONCLUSION

We introduced in this work the X-ray absorption (XAS) techniques that probe the unoccupied state of the atom. Since XAS uses synchrotron radiation it was also introduced some aspects of synchrotron such as the radiation from relativistic electrons, photo beam properties, insertion devices and beamlines components. At the end was discussed three results using XANES to study the charge features in Cu $L_{2,3}$ -edge of cuprates superconductors.

XAS is divided in two regions: XANES and EXAFS. XANES is the region just after the absorption until 50 eV. EXAFS is the region from 50-1000 eV after the absorption edge. Because of the mean free path of the electron is higher for XANES (multiple scattering), the theoretical model is not well develop. Hence, the information are obtained qualitatively from comparison with reference compounds. The signal is relate to the atomic position and number of neighbors atoms, the bonding angles and oxidation state (chemical shift). EXAFS has a lower mean free path and the theoretical model is better defined. The system does not need to be well organized. The oscillations presented in the spectrum in EXAFS region is an interference between the photoelectron wavefunction produced by the x-ray absorption and the same wave single backscattering in the neighbors atoms. The quantitative information from EXAFS are: numbers of neighbors from the absorbing atom, distance between neighbors and absorption atoms, etc.

The results discuss about the interplay between CuO chains and CuO₂ planes in high-t_c superconductors cuprates. First one measured directly the charge transfer by x-ray absorption in room temperature and below the critical temperature of the superconductor. It is clear the relationship between the region for the plane and chains peaks at different temperatures. Secondly, it is studied the effect of an electric field at the superconductor regime. It seems that the gate voltage injects holes mainly in the chains that later some of the charges are transfered to the CuO₂ planes, same mechanism for chemical substitution for these materials. Lastly, it is developed a method of using x-ray absorption (XANES region) as a quantitative analysis. They used it to determined the valence of the copper in the cuprate superconductors by calculating the area of the absorption peaks.

BIBLIOGRAPHY

1 MARGARITONDO, G. Introduction to Synchrotron Radiation: History and Machine. 2013. Advanced School on Synchrotron Radiation Techniques in Environmental Scientific Projects. Disponível em: http://indico.ictp.it/event/a12174/session/6/contribution/4/material/0/0.pdf>. Acesso em: 25 nov. 2016.

2 SHEN G.; WANG, Y. High-pressure apparatus integrated with synchrotron radiation. **Reviews in Mineralogy and Geochemistry**, v. 78, p. 745–777, January 2014. Disponível em: https://www.researchgate.net/publication/279773280_High-pressure_Apparatus_Integrated_with_Synchrotron_Radiation>. Acesso em: 25 nov. 2016.

3 WILLMOTT, P. An Introduction to Synchrotron Radiation: Techniques and applications. [S.l.: s.n.], 2011.

4 ATTWOOD, D. T. Synchrotron Radiation for Materials Science Applications. Spring 2007. Listed at UC Berkeley as EE209F.

5 EISBERG, R.; RESNICK, R. Quantum Physics of atoms, molecules, solids, nuclei, and particles: Techniques and applications. [S.l.: s.n.], 1985.

6 THE Link to X-Ray Protein Crystallography. Disponível em: <<u>http://my.yetnet.ch/</u>dergutemensch/crystallography/shooting.htm>. Acesso em: 22 nov. 2016.

7 SHAM, T. K.; RIVERS, M. L. A brief overview of synchrotron radiation. **Reviews in Mineralogy and Geochemistry**, 2002. Disponível em: http://rimg.geoscienceworld.org/content/49/1/117.full. Acesso em: 22 nov. 2016.

8 ELLEAUME, P. Insertion devices for the new generation of synchrotron sources: A review (invited). **Review of Scientific Instruments**, v. 63, n. 1, p. 321–326, 1992. Disponível em: http://scitation.aip.org/content/aip/journal/rsi/63/1/10.1063/1. 1142744>.

9 CEZAR, J. C. Estudo de propriedades estruturais e magnéticas em materiais granulares por espectroscopia de absorção de raios X. 2003. 227 p. Tese (Doutorado em Física) — Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Campinas, 2003. Disponível em: http: //www.bibliotecadigital.unicamp.br/document/?code=vtls000304035>. Acesso em: 20 nov. 2016.

10 MEITZNER, G.; VIA, G. H.; LYTLE, F. W.; SINFELT, J. H. Analysis of x-ray absorption edge data on metal catalysts. **The Journal of Physical Chemistry**, v. 96, n. 12, p. 4960–4964, 1992. Disponível em: http://dx.doi.org/10.1021/j100191a043>.

11 BARE, S. R. XANES Measurement and Interpretation. 2005. EXAFS Data Collection and Analysis Course, APS. Disponível em: http://cars9.uchicago.edu/xafs_school/APS_2005/Bare_XANES.pdf>. Acesso em: 25 nov. 2016.

12 NAKAJIMA, R. X-Ray Magnetic Circular Dichroism Spectroscopy in Transition Metal Thin Films. 1998. 178 p. Tese (Degree of Doctor of Philosophy) — Departament of Material Science and Engineering, Stanford University, 1998. Disponível em: http://www.sciencedirect.com/science/article/pii/0368204895025375>. Acesso em: 20 nov. 2016.

13 STOHR J.; ANDERS, S. X-ray spectromicroscopy of complex materials and surfaces. **IBM Journal of Research and Development**, v. 44, n. 4, July 2000. Disponível em: http://www-ssrl.slac.stanford.edu/stohr/ibm-44-535-00.pdf>. Acesso em: 19 nov. 2016.

14 CHINTAMANENI, V. K. Fabrication of Oxide Superconducting Thin Films Using Colloid of Nanoparticles as Precursor. 2006. 104 p. Dissertação (Master of Science) — Wright State University, United States, 2006.

15 KHARE, N. Handbook of High-Temperature Superconductor Electronics. [S.l.: s.n.], 2003. 1st Edition.

16 BREIT, V.; SCHWEISS, P.; HAUFF, R.; WÜHL, H.; CLAUS, H.; RIETSCHEL, H.; ERB, A.; MÜLLER-VOGT, G. Evidence for chain superconductivity in nearstoichiometric yba₂cu₃o_x single crystals. **Phys. Rev. B**, American Physical Society, v. 52, p. R15727–R15730, Dec 1995. Disponível em: <https://link.aps.org/doi/10.1103/PhysRevB.52.R15727>.

17 BEGON-LOURS, L. Ferroelectric field-effects in high-tc superconducting devices. jan. 2017. Tese (Theses) — Université Pierre et Marie Curie - Paris VI, jan. 2017. Disponível em: https://tel.archives-ouvertes.fr/tel-01568185>.

18 MAGNUSON, M.; SCHMITT, T.; STROCOV, V. N.; SCHLAPPA, J.; KALABUKHOV, A. S.; DUDA, L.-C. Self-doping processes between planes and chains in the metal-to-superconductor transition of YBa2cu3o6.9. Scientific Reports, Springer Nature, v. 4, n. 1, nov 2014. Disponível em: https://doi.org/10.1038/srep07017>.

19 SALLUZZO, M.; GHIRINGHELLI, G.; CEZAR, J. C.; BROOKES, N. B.; LUCA, G. M. D.; FRACASSI, F.; VAGLIO, R. Indirect electric field doping of the cuo₂ planes of the cuprate ndba₂cu₃o₇ superconductor. **Phys. Rev. Lett.**, American Physical Society, v. 100, p. 056810, Feb 2008. Disponível em: <<u>https://link.aps.org/doi/10.1103/PhysRevLett.100.056810></u>.

20 TANAKA, Y.; KARPPINEN, M.; KOBAYASHI, T.; CHAN, T. S.; LIU, R. S.; CHEN, J. M.; YAMAUCHI, H. Quantitative xanes spectroscopy study on the prototype hole- and electron-doped high-tc superconductor systems, (la,sr)2cuo4 and (nd,ce)2cuo4. **Chemistry of Materials**, v. 20, n. 16, p. 5414–5420, 2008. Disponível em: <<u>https://doi.org/10.1021/cm800892z></u>.

21 BITBOL, M. Schrodinger's philosophy of quantum mechanics. [S.l.: s.n.], 1996.

22 PLENIO, M. B.; KNIGHT, P. L. The quantum-jump approach to dissipative dynamics in quantum optics. **Reviews of Modern Physics**, v. 70, n. 1, Janeiro 1998.

23 ITANO J. C. BERGQUIST, D. J. W. W. M. Early observations of macroscopic quantum jumps in single atoms. **International Journal of Mass Spectroscopy**, Julho 2015.