Synchrotron Light and its Applications

A. Rubens B. de Castro

Instituto de Física "Gleb Wataghin" - Universidade Estadual de Campinas
and
Laboratório Nacional de Luz Síncrotron

Abstract

Synchrotron light is generated by relativistic charges describing curved trajectories. It is produced by electron/positron beams running in a vacuum chamber, kept in a closed orbit by bending magnets, focussed by quadrupolar magnets and accelerated by RF fields in a resonant cavity.
The power radiated, the spectral range extending from visible light (photon energy about 2 eV) to hard X rays (photon energy 20 000 eV), the polarization and the collimation make these sources unique in the ultraviolet and X ray regions, where no lasers are available.
The applications include valence level spectroscopy (at energies up to say 20 eV) in atoms and molecules, structural studies (crystal structure, phase transitions, nature of the chemical neighborhood, shape of nanoparticles, etc), biological studies (membranes, crystallized proteins) and microfabrication.

1 Introduction

Synchrotron light is a very broad designation for all kinds of light generated by relativistic particles in curved trajectories. Such curved trajectories can be arcs of circle, followed for instance when the charged particles move through a uniform magnetic field, or undulating trajectories with period of a few cm in the so called *insertion devices*, periodic magnetic structures which have became favorite light sources because their radiation is optimized for demanding applications. In the range from 12 eV up to several dozen keV there is at present no other source of light available with comparable power, tunability and collimation.

This spectral range covers most of the fundamental energy levels of atoms molecules and solid matter, which makes it ideal for measuring such levels and the subtle modifications which they suffer as a consequence of different chemical environments.

Since each chemical species has its own characteristic electronic energy spectrum, an analysis of the light emitted by a sample excited with X rays allows a determination of the amount and kind of each element present in a sample.

Photons of 12 keV (and higher) energy have a wavelength of 1 Å (or shorter), which is comparable to interatomic spacings in crystals. If such a beam is directed at a crystal, it is reflected in certain favored directions where the contributions from the successive layers of atoms add up constructively (Bragg diffraction) and from the angular pattern of diffracted light one can infer the crystal structure and the atomic spacing with high precision.

The short wavelength photons can be focussed in spots only nanometers in diameter. If a thin sample is scanned in front of this finely focussed beam, and the transmission is measured, one obtains a high spatial resolution image, orders of magnitude better than with an optical microscope using visible light, making obvious the interest of synchrotron light based microscopy.

We know that all images have some blurring due to the ondulatory character of light; it is impossible to focus a light beam to a spot with dimension smaller than about a wavelength. Now, since X rays have wavelengths thousands of times smaller than visible light, the diffraction effects are smaller to the same amount, and it is possible to generate crisp images of nanometric size using X rays. This is the basis for the so called microfabrication techniques, expected to dominate the production of electronic chips and miniature mechanical and medical devices in the near future.

We see that synchrotron light has applications in spectroscopy, elemental analysis, structural determinations, high resolution imaging and microfabrication. Since the theory of synchrotron light generation is perfectly understood, synchrotron light is also used as light primary standard in the US, Germany, France and Japan.

In the remainder of this article we will discuss in a very simple way the theoretical fundamentals for the properties of synchrotron light, describe these properties, talk about the engineering aspects of a synchrotron machine and their attending *beamlines*, where the synchrotron light is conditioned, focussed, monochromatized and brought to use in the researcher experiment. We will also mention a few recent applications at LNLS, the Brazilian Synchrotron Source, located in Campinas SP, very close to the campus of the Campinas State University (UNICAMP). Finally, we will comment on availability of fellowships for graduate students enrolled at UNICAMP, willing to pursue doctoral programs at LNLS under supervision of a LNLS researcher,

postdoctoral openings, and procedures to submit a research proposal to be performed at some of the LNLS beamlines.

References of an elementary nature on the subject of synchrotron light production and applications are scarce (this article intends to be such a reference), but see the Proceedings of several workshops that punctuated the design and construction of LNLS [1].

2 Where does synchrotron light come from?

Consider an electrical charge q *at rest* in position **r'** (see figure 1). This charge induces at any other point **r** in space an electrostatic potential V(**r**)

$$V(\mathbf{r}) = q / |\mathbf{r} - \mathbf{r}'|$$

and an electrical field with components E_x E_y E_z. The magnetic field is zero identically, because there is no electrical current:

$$E_x(\mathbf{r}) = - \partial/\partial x\, V(\mathbf{r}), \text{ etc}$$
$$B_x\ B_y\ B_z = \text{zero}$$

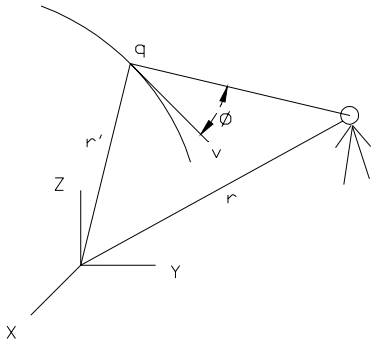

Figure 1: A particle with electric charge q is first considered to be at rest at position **r'**. The observer at position **r** sees a time-independent Coulomb potential V(**r**) and a time-independent electric field **E**(**r**). The magnetic field is zero. The same figure also shows a charged particle moving with velocity **v**(t) along a curved path. The nature of the fields is now radically altered. There is a magnetic field present now, and all fields are time-dependent. Also, they depend critically on the angle Φ between the observer line of sight to the charge and the velocity of the charge **v**(t).

Now, if this charge is *moving*, there is an electrical current and the magnetic field is different from zero. The potential V(**r**) will become some time dependent quantity. The electrical field is much more complicated because now there are induction effects to worry about. It is usual in these situations to introduce a new auxiliary potential, the *vector potential* **A**(**r**,t), so that now we have

$$V(\mathbf{r},t) = q/\kappa|\,\mathbf{r} - \mathbf{r}'|]_{ret} \qquad \kappa = 1 - (v/c)cos\Phi$$
$$\mathbf{A}(\mathbf{r},t) = q(\mathbf{v}/c)/\kappa|\,\mathbf{r} - \mathbf{r}'|]_{ret} \quad]_{ret} : t = t' + |\,\mathbf{r} - \mathbf{r}'|/c$$

$$E_x(\mathbf{r},t) = - \partial/\partial x\, V(\mathbf{r},t) - \partial/\partial t\, A_x(\mathbf{r},t)/c, \text{ etc}$$
$$B_x(\mathbf{r},t) = \partial/\partial y\, A_z(\mathbf{r},t) - \partial/\partial z\, A_y(\mathbf{r},t), \text{ etc}$$

The new quantity κ, which appeared in the denominator of the equations, is responsible for the striking properties of synchrotron light. Imagine that the charged particle describes an arc of circle, as shown in figure 2.

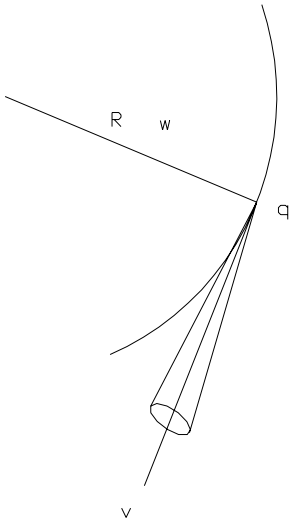

Figure 2: When a relativistic charged particle moves along a curved path the fields are confined to a narrow cone centered on the instantaneous direction of the particle's velocity **v**(t). The radiation pattern is similar to a searchlight beam.

Then, if the speed v of the particle is very close to c, the speed of light in vacuum, κ will be very small in the forward direction, where cosΦ = 1 and the fields will be strongly enhanced in the forward direction. This is a fundamental property of radiation emitted by relativistic (v ≈ c) charges in accelerated motion: the radiation comes out in a narrow beacon centered on the instantaneous direction of its velocity vector, which moves as a searchlight in front of the particle. A more detailed analysis [2], which will not be made here, shows that the angular width of the beacon is $1/\gamma$, where γmc^2 is the particle relativistic energy. Since for practical machines $\gamma \approx 3000$, we see that the beacon is narrow indeed, only a fraction of a miliradian, narrower than a typical HeNe laser beam.

A second consequence of the small angular width of this light beacon is that it crosses a stationary observer in a very short time. It is possible to prove that the observer sees a flash of light lasting a time

$$\Delta t = R/2c\gamma^3$$

where R is the radius of curvature of the trajectory.
For instance, taking a typical value for a bending magnet (the magnet that keeps the charges in near circular motion in a synchrotron) R = 3 m and γ = 3000, one gets $\Delta t = 1.8 \times 10^{-19}$ sec.

We all know that the theory of Fourier transformations forces a dependence on the time a pulse lasts and the spectral content of this pulse, $\Delta\omega\Delta t \approx 1$. This means that the light pulse seen by the observer is rich in short wavelength components, going in the case up to 3.5 Å. We find therefore, that a relativistic particle in circular orbit will generate, for a stationary observer, short bursts of X rays, and this is why synchrotron machines are useful.

The time retardation condition $]_{ret}$: $t = t' + |\mathbf{r} - \mathbf{r}'|/c$ was not commented upon so far; it is responsible for many of the spectral characteristics of synchrotron light, which show up on taking the time Fourier transform of the fields, see ref [2].

The energy radiated in a complete turn (assuming a circular trajectory) is given by

$$\Delta E = (4\pi/3)\, q^2\gamma^4/R$$

and using typical values $q = 4.8 \times 10^{-10}$ esu, R=3m, γ=3000, one gets $\Delta E = 16 \times 10^4$ eV. The radiated power is numerically given by

$$P[\text{Watts}] = \Delta E[\text{eV}]\, I[\text{A}]$$

and for a typical stored current of I=200 mA one gets a power of 32 kW, most of it in the X ray region.

We mentioned an angular spread of $1/\gamma$ for the synchrotron light. The more detailed theory shows that this is the *typical* spread, but in fact there is an interdependence between frequency of a spectral component and its angular spread. Short wavelength components spread out less than long wavelength components, just as one might expect from elementary diffraction theory. Our beacon of synchrotron light has high energy photons in the center, and lower energy light in the outer wings.

To further describe the properties of synchrotron radiation we shall use just figures. In these plots it is convenient to express the frequency scale in normalized units, which make the plots independent of actual machine parameters. So we define a critical frequency ω_C by the expression

$$\omega_c = 3\gamma^3 c/R$$

This has the physical meaning of a frequency near the maximum of the emitted power. In fact, it divides the frequency spectrum in two halves of total emitted power each. For the LNLS ring, ω_C = 2.08 keV, which optimizes this machine for spectroscopy and microfabrication.

The polarization characteristics of the synchrotron radiation are also remarkable. If one looks at the source (i.e., at the charge describing circular motion) in the plane of the orbit, the radiation is 100% linearly polarized, but if one takes a position a little above or below the plane of the orbit, one sees an elliptical motion and the radiation is, accordingly, elliptically polarized. Choosing the angle of sight carefully, one gets almost circular polarization, which is very useful for experiments with magnetic materials.

Figure 3 shows the dependence of the two components, polarized parallel and perpendicular to the plane of the orbit, as a function of angle of sight Ψ, for the case ω/ω_c=0.1. We see from the graph that the component with electric field parallel to the plane of the orbit is maximum at Ψ=0 (plane of the orbit) and falls more or less like a Gaussian in the wings.

The component with electric field perpendicular to the plane of the orbit starts at zero for Ψ=0 (plane of the orbit), goes through a maximum at some small angle of about 0.7 mrad and then falls off to zero like the other component. Those two components are out of phase by exactly 90^o.

Figure 4 shows how the intensity depends on angle Ψ for various spectral components above and below the critical frequency ω_c. We have the highest intensity on the plane of the orbit, when $\omega=\omega_c$.

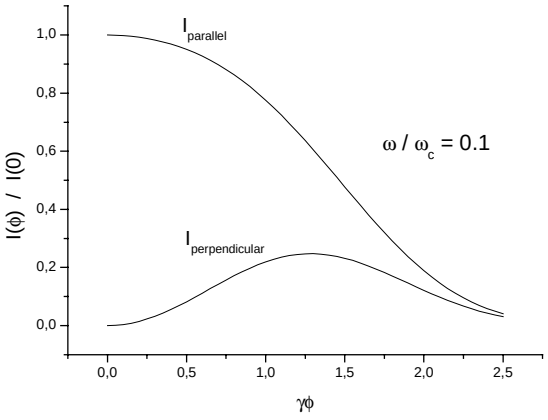

Figure 3: Distribution of the synchrotron light for the components polarized parallel and perpendicular to the plane of the orbit.

For all other situations we lose intensity. Much above ω_c we lose dramatically, and the radiation is confined to very small angles above and below the plane of the orbit. For $\omega << \omega_c$, the angular pattern is much broader.

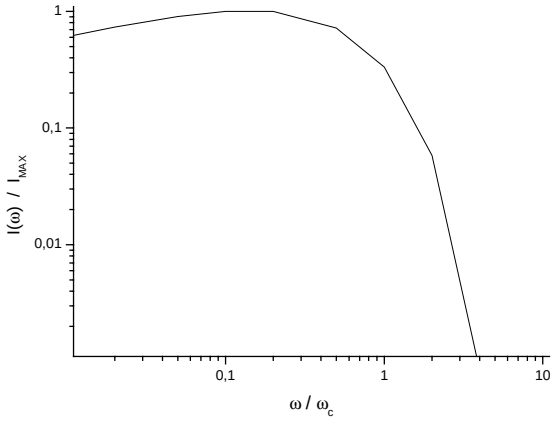

Figure 4: Angular distribution of the synchrotron light for the component parallel to the plane of the orbit, for various values of polarized ω/ω_c.

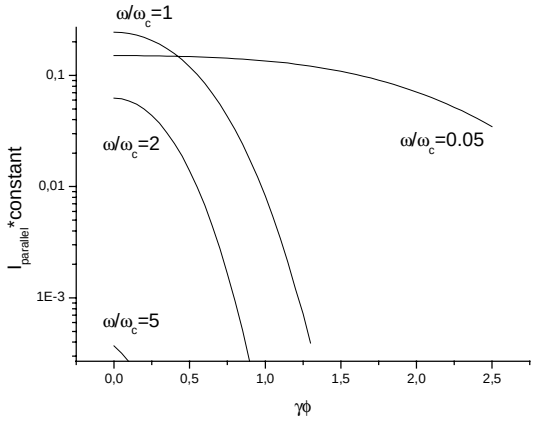

Figure 5: Normalized total intensity of "bending magnet" synchrotron light as a function of the normalized photon energy. I_{MAX} = 5.2x10^{12} photons/sec/0.1% bandwidth at LNLS with 200 mA stored current, 1.37 GeV.

Figure 5 shows the total intensity (integrated over all emission angles) as a function of photon energy. The maximum is close to ω_c The intensity falls down exponentially for $\omega >> \omega_c$, and only very slowly for $\omega << \omega_c$, so that we expect strong output in the visible and infrared as well, but this is not so useful because there are lasers in this spectral range. The synchrotron light from practical machines is not produced by a single electron, but by say, 150 electron bunches 1.5 cm long, with perhaps 10^{11} electrons each, circulating in the *storage ring*, separated by longer distances where there are no electrons. This bunched structure of the circulating charges is at the same time a requirement and a consequence of the engineering solution usually adopted for replacing the particle energy spent in emitting synchrotron light. This will be further discussed later on. Here, it is only necessary to point out that the light arriving at the observer will be a sequence of short pulses at hundreds of MHz rates, each pulse lasting for only about 50 psec. This time structure can be useful if relaxation properties of a system are to be studied. The system under study is "excited" at t=0 with a short intense pulse of synchrotron radiation, then undergoes "free decay" for a time of a few nsec, or at any rate till it is excited again by the light pulse of the next electron bunch. Some facilities provide "single bunch operation" to increase the time between successive light pulses to hundreds of nsec, but this is very unpopular with most other synchrotron light users because it reduces the average power available, so it becomes a touchy political question.

3 Engineering aspects

It is important to have some understanding of the engineering involved in a synchrotron light facility because this dictates what kinds of experiments can or cannot be done.

Figure 6 shows a photograph of the LNLS storage ring. The main elements of the machine are (1) a vacuum chamber for the relativistic electrons to move in a closed orbit during many hours, as undisturbed as possible. (2) Dipolar magnets generating a constant vertical field to keep the electrons in a closed trajectory (3) Quadrupolar magnets generating fields linear with distance to the center, used to focus the electrons in a tight beam (4) Precision power supplies for the magnets, remotely controlled (5) Radio Frequency resonating cavity where the electrons are accelerated by strong electromagnetic fields. This is where the energy lost in synchrotron light is replaced. (6) Beam position monitors. (7) An injection system to fill the machine with electrons already moving in an appropriate direction with as high an energy as feasible (8) Last, and most important, *beamlines* through which the synchrotron light is conducted to the experiments.

We now make additional comments on each of these items.

(1) Vacuum chamber. One needs a very high vacuum in the 10^{-10} mbar range, because one of the factors limiting the "lifetime" of the stored beam is the loss suffered by the beam due to collisions with atoms or molecules of residual gas. This means that only special materials such as high quality stainless steel, "oxygen free high conductivity" copper and ceramic materials are allowed. In addition, all components have to go through a very thorough cleaning procedure on various solvents, must be handled with gloves and masks, and must be heated up to about 200 ^{o}C to get rid of a thin layer of water vapor that adheres tenaciously to even the cleanest surface, and

keeps desorbing slowly forever if not eliminated with this so called "bake out" procedure. The vacuum pumps must be oil free pumps of the ion type. There must be accurate pressure gages for monitoring the vacuum constantly. This suggests that taking care of the vacuum in the storage ring is no small task, takes a lot of time and this vacuum must be protected at all costs. It may be weeks till the vacuum is again OK after a planned or (Heavens forbid) accidental venting to atmosphere. In addition, consider that the parts of the vacuum chamber where some synchrotron radiation might impinge must be water cooled .

(2) The magnets must have highly reproducible fields and also must be positioned within tight tolerances at their official positions. This means that there are fancy requirements on geodesy for the initial placement of these heavy components and that the thermal control of the experimental hall is critical, otherwise the alignment will be lost and the quality of the electron beam will be degraded.

(3) The electrons in their almost circular trajectory suffer small amplitude lateral motions called "betatron oscillations". It is therefore necessary to refocus these electrons every few meters, and this is what is done with the quadrupole magnets, which, as the name says, have four opposing poles at 90^o around the axis of motion. A quadrupolar magnet focuses charged particles about one axis and defocusses about the orthogonal direction. But combining two quadrupole magnets with unequal fields and or lengths, it is possible to focus on both transverse directions. This is why quadrupole magnets appear in particle accelerators always in pairs.

(4) The field in the magnets is proportional to the currents, barring hysteresis effects. To achieve a stable orbit the current in the windings of the dipole magnets must be kept constant to a tight tolerance. In addition, if the charged particles are to be accelerated after they are injected in the machine, all fields must be ramped up in synchronism, so all the power supplies are computer controlled.

(5) The energy lost emitting radiation is replaced by accelerating the particles by strong RF fields inside a resonating cavity. These fields are stationary waves; therefore, for any acceleration to be experienced, the electrons must be more or less tightly bunched and they must arrive and depart from the RF cavity in proper phase with the resonating RF fields. In fact, this is achieved more or less automatically, because the electrons that are "too fast" will be met with fields of the wrong phase and be retarded, while the ones that are too slow will be even further retarded till they merge with the next bunch. So the process is autoregulating.

(6) The beam position monitors allow an estimate of the X Y coordinates of the electrons moving along the Z axis. Four electrodes placed symmetrically about the orbit pick up induced signals as the electron bunches move in their orbit. These signals are stronger if the bunch passes close to the electrode. By subtracting the signals from opposite electrodes one has an indication of position that for small displacements about the central orbit, is linear. These signals can then be used in a feedback loop to drive small dipole magnets with fields in the X and Y directions and bring back the deviant beam to the official orbit. Orbit stability is a prime figure of merit for any synchrotron light facility. At LNLS this is about 5 μm.

(7) The injection system is usually a linear accelerator followed by a small auxiliary synchrotron ring. The linear accelerator might take 80 keV electrons generated on a thermoionic gun and boost their energy from 80 keV to 120 MeV, again using RF resonating cavities where the electrons not only are accelerated, but acquire their bunched structure. The small auxiliary synchrotron then receives these 120 MeV electrons and increases their energy to, say, 500 MeV. The 500 MeV electron bunches are injected in the main synchrotron, where they are further accelerated to 1.37 GeV (parameter values for LNLS).

(8) The beamlines are the things the user interacts with. They are mostly tubes enclosing a beam of light coming from the synchrotron and made to shine on the sample. Many different things are needed in a beam line, in order to condition the photon beam. There is a *photon shutter* that is used to block the photon beam when it is not needed. This is basically a water cooled copper blade that can be moved in and out of the photon beam path. There are *vacuum valves* separating various sectors of the beam line, so that servicing in one part does not require venting the whole beamline (or, even worse, the ring itself...). One may want to focus the photon beam on small apertures or slits, using *concave mirrors*. Notice that it is impossible to use lenses because there are no materials transparent to the photon energy range above 12 eV. A thin beryllium window may be used with X-rays of energy above 4000 eV, but below this energy there must be nothing between the synchrotron source and the experiment, except grazing incidence reflective optics. Grazing incidence is needed because one

finds that the reflectivity at large, near to normal incidence, angles is very small for energies above 40 eV. The most important element of the beamline is the *photon energy monochromator*, which selects a narrow spectral range centered at a wavelength at the choice of the user. Since this is a complicated and expensive component, each beamline is designed having in mind a specific monochromator, and this determines the spectral range this beamline can be used. One has grating monochromators for the range 12 eV up to 1500 eV, and one has crystal monochromators using the principle of Bragg diffraction for the range 800 eV and up. Finally, one must have an *experiment chamber* where the sample is placed to be illuminated by the monochromatized and focussed beam of synchrotron light. The experimental chamber design depends on the kind of experiment one wants to conduct. For instance, if one wants to make a *photoemission spectroscopy* experiment, one needs a device to collect and energy-analyze the photoelectrons that come out of the sample due to the interaction with the synchrotron light. If one wants to do a simple *total electron yield* measurement, one has to attach a wire to the sample and connect it to an electrometer so as to measure the total current that flows into de sample to replace the electrons that were expelled by photoelectric emission and Auger decay. This is, under many practical conditions, equivalent to measuring the absorption of the sample. Another way to detect the electron yield is to place an electron multiplier ("channeltron") close to the sample and count the output pulses. For hard X-rays, when thin samples are partially transparent, one can measure the absorption coefficient versus wavelength directly, by placing a photon beam intensity detector in front of the sample, one behind the sample, scanning the wavelength, recording both spectra and dividing the second spectrum by the first one. This is a favorite technique.

We close this section by observing that in the photon energy range 12 eV up to 1500 eV there are no materials adequate to make vacuum windows. Therefore the experiment has to be conducted at the vacuum of the storage ring itself, which makes the change of samples very tedious. The vacuum in the beamline has to be taken good care off. Experiments with gas phase samples are possible if a suitable differential pumping system is provided, to preserve the high vacuum of the beamline close to the storage ring, while allowing a higher pressure in the experimental chamber. These are always expensive and complicated experiments.

Remember, venting the beamline accidentally is not nice and will require one or two weeks of corrective efforts before it is usable again. Venting the storage ring accidentally is totally unacceptable.

At LNLS there are presently 10 beamlines, covering the full spectrum from 12 eV up to about 20 keV. These beamlines, their specifications and technical references are fully described in the LNLS home page www.lnls.br
Further general information on synchrotron light instrumentation can be found in many different *Synchrotron Radiation Handbooks*, for instance the series edited by E E Koch, T Sasaki and H Winick [3].

4 Some applications

(1) Particles with diameters in the nanometer range, whether free or dispersed in some other medium, are called *nanostructured materials*. They are interesting and useful because while sometimes they exhibit characteristics intermediate between single atom and infinite bulk, sometimes they show completely new properties, and so might be used as building blocks for custom designed new materials.

Bulk hematite Fe_2O_3 is antiferromagnetic because there are two identical sublattices where the ordering of the magnetic moments is equal but have opposite directions, so that the net magnetic moment per unit volume vanishes.

Small hematite particles, on the other hand, are ferrimagnetic rather than antiferromagnetic because the translation symmetry of the bulk solid is broken at the surface and even the interior of the particles gets a little distorted; then the magnetic moments of the two opposing sublattices no longer cancel out.

One can probe with synchrotron light of $h\nu \approx 700$ eV the transition 2p – 3d in Iron. This is an interesting transition to probe, because it is very strong and because the 3d electrons are the ones who carry the magnetic properties of the transition elements Ni Co Fe. If one uses circularly polarized light, the law of conservation of angular momentum implies as a consequence that for a sample magnetized along the direction of the photon propagation vector **k**, the transition probability (and the absorption coefficient) is different for each of the two possible (left or right handed) helicities of the incoming photon beam.

Figure 6: Photograph of the LNLS storage ring, showing the the SAXS beamline in the forefront. The storage ring itself is the central circular structure seen in the top half of the photograph, inside the zigzag wall of concrete blocks used as a protective shield. The outer ring, running above the floor, carries electric power and cooling water for the beamlines.

This phenomenon is called Magnetic Circular Dichroism (MCD). It is plausible that the MCD is proportional to the magnetization of the sample. However, we found that although the magnetization of colloidal hematite particles is believed to come from their surface layer, at room temperature the dichroism is independent of the fraction of Fe atoms occupying surface sites [4]. This is checked easily by just changing the size of the particles. Figure 7 shows the dichroism of a 5 nm diameter colloid, as a fraction of the peak absorption intensity, obtained at the SGM beamline, LNLS. We get the same result for a colloid with a diameter 12 nm, where a substantially smaller fraction of the iron atoms are at the surface. We believe this indicates the surface layer is disordered, what would cause a washing out of the surface dichroism. Nevertheless, experiments carried out at 77 K have also failed to show a difference between the dichroism of hematite particles of different size, and so the question remains open.

(2) The intensity of X-ray scattering by small particles at small angles bears an imprint of the *shape* of the scatterers. This can be taken advantage of by constructing plausible models for the shape of the particles, calculating the expected scattering pattern, comparing the theoretical and experimental scattered intensity profiles and modifying the model till one reaches acceptable agreement. This is the only technique available for structural analysis of proteins in solution; although it is not as detailed a method as protein crystallography, the latter requires *protein crystals*, not always available. This technique was applied to a structural study of a system known as amyloid precursor protein sAPPα_{695}, which is genetically and biochemically linked to the genesis of Alzheimer's disease, the most widespread cause of dementia in industrialized countries, and one with poignant symptoms and sequels. It is therefore relevant to investigate these proteins both in a cellular context and in vitro, since the functionality is connected with the geometrical structure. Figure 8 shows the model structure that best fits the small angle X-ray scattering (SAXS) data obtained at the SAXS beamline at LNLS. From this study it was also possible to obtain hydrodynamic parameters and the molecular weight [5].

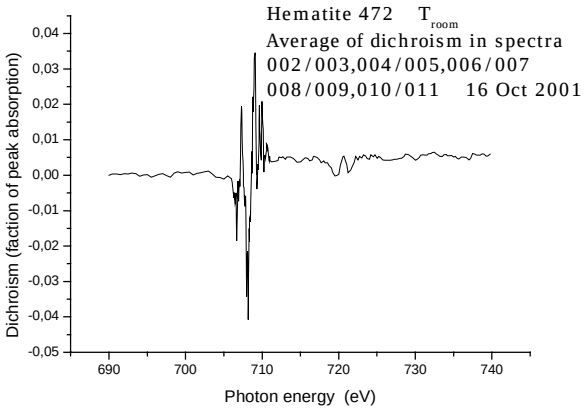

Figure 7: Magnetic Circular Dichroism at the Fe L edge, of Hematite Fe_2O_3 colloids with a diameter 5 nm, at room temperature.

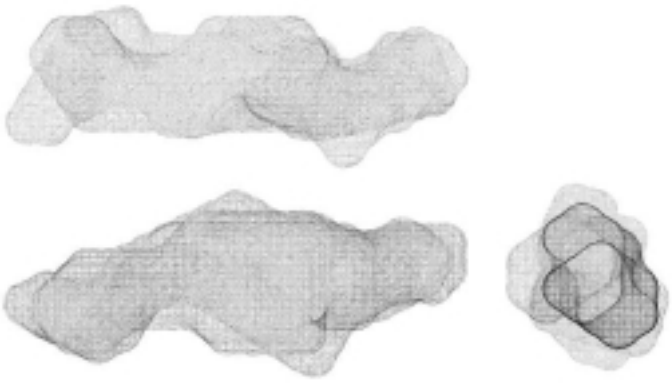

Figure 8: Shape of the amyloid precursor protein as determined by modeling of the Small Angle X ray Scattering data.

(3) The transition metal oxides $RNiO_3$ (R= rare earth) show many striking phenomena, including high TC superconductivity, colossal magnetoresistance and, depending on the rare earth atom, a metal-insulator transition. These materials can be thought as being formed by juxtaposing octahedra with Oxygen atoms at the corners, a Ni atom at the center, and rare earth atoms in between the octahedra. The octahedra tilt and rotate in order to better fill up the space left out by the rare earth atoms. The smaller the rare earth, the larger the distortion. Such distortions play a role in the admixture of electronic orbitals that compose the valence and conduction bands in these crystals. The bands are generated by Ni 3d and O 2p states. For sufficiently strong distortions, the 3d – 2p admixture is perturbed enough to open an energy gap, and the material then goes over into the insulating state. The fraction of empty 3d states in the density of states can be probed by absorption spectroscopy of the Ni 2p – 3d transition. The initial state for this transition is a core state that is always occupied. The final state Ni 3d is partly populated depending on how it hybridizes with O 2p. So, monitoring this absorption one has an idea of the evolution of the fractional 3d character of the conduction band as the lattice distortions are varied, by replacing the rare earth atom with another of different size. Figure 9 compares the normalized absorption of $NdNiO_3$ (which, at room temperature, is conducting) with $EuNiO_3$ (which, at room temperature, is insulating), measured at the SXS beamline, LNLS.
It is seen from the figure that the density of empty 3d-like states is larger for $EuNiO_3$ (insulating) than for $NdNiO_3$ (conducting). It is concluded that in the insulating state the electronic wavefunction is less covalent (i.e., extended) and more ionic (i.e., localized) than in the conducting state [6]. This is reasonable, as electrical conduction requires mobile, non-localized, electrons.

(4) "Extended X ray Absorption Fine Structure" (EXAFS) is a series of oscillations in the absorption spectrum near an absorption edge, which is observed only in molecules or crystals, but not in isolated atoms. These oscillations have been interpreted theoretically as due to interference effects of the outgoing photoexcited electron, as it is partially reflected from the neighbors close to the one that has been X ray photoexcited. The theory predicts that the Fourier Transform of the absorption spectrum (after subtracting out the slowly varying background) gives the density of neighbors as a function of radial distance. So, this is a short range structural probe of prime importance. Also, it is chemically specific because the photon energies for each absorption are characteristic of the chemical species.

This technique was applied to a granular alloy composed by cobalt embedded in a copper matrix to follow the evolution of the Co as the sample was annealed [7].

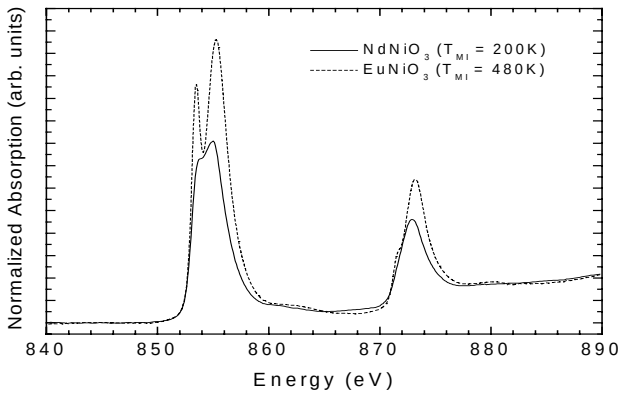

Figure 9: Normalized absorption of $RNiO_3$ (R=rare earth) at the Ni L edge, showing different 3d-like densities of final states, depending on the rare earth R present.

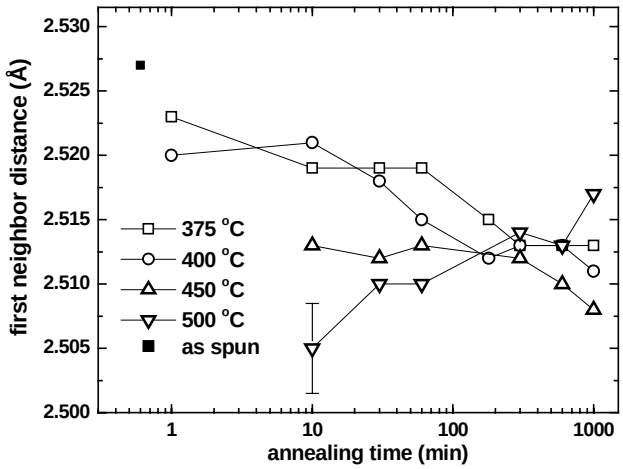

Figure 10: Co first neighbor distance as a function of annealing time and temperature for a granular CoCu alloy.

The samples are thin ribbons of metastable Co/Copper alloys (immiscible elements) prepared by rapid quenching of molten material dropped on a cold wheel rotating at high speed. Figure 10 shows the first neighbor distance as determined from EXAFS at the 1s absorption edge of Co, in measurements carried out at the XAFS beamline, LNLS. For the lowest annealing temperatures (375 and 400 C), a contraction of the Co nearest neighbor distance was observed as annealing time increased, indicating that Co was coalescing into grains, since the interatomic spacing in pure cobalt is smaller than in copper However, at higher temperature (500 C), one witnesses a fast aggregation followed by redissolution of the Co atoms within the copper matrix.

(5) The electrons expelled from a metal illuminated with soft X rays (hν=700 eV) have an angular distribution that depends on the geometry of the interface metal-vacuum. By keeping the photoelectron energy analyzer and detector in a fixed position, and rotating the sample, it is possible to explore the angular distribution of photoelectrons, which form patterns ("photoelectron diffraction") capable of giving information on the structure of the surface.

Alloys PdCu have catalytic properties of commercial relevance (oxidation of CO and alkenes, hydrogenation of cyclic hydrocarbons) and it is therefore important to study their surface (the seat of catalytic action).

Figure 11c shows a photoelectron diffraction pattern obtained from a Cu 111 single crystal with a monolayer of Pd deposited on top, obtained at the beamline SGM at LNLS. Figure 11a shows a simulation of the pattern expected for a Pd capping layer, while figure 11b shows the pattern expected for a Cu capping layer. It is clear that the data (figure 11c) agrees with the simulation b and not at all with simulation a [8]. It is concluded that Pd becomes alloyed with Cu and disperses through the first few layers of the Cu crystal, a behavior expected from easily miscible materials like Pd and Cu.

(6) In the process called photodissociation, a molecule absorbs one photon, goes into a highly excited state, gets ionized and dissociates. If the molecule is large, there are many different ways of dissociating. The probability for each possible outcome can, in principle, be calculated quantum mechanically. In studying photodissociation, a common technique is the so called "Photo Electron Photo Ion Coincidence" (PEPICO), where one measures the time of flight of the slow ions created in the process by triggering a clock (or "timer") by the arrival signal of the fast photoelectron. Next, the "timer" is turned off by the arrival of the slow ion. The electronics can be fixed up so that several successive ions can be "timed". Now, the time of flight of each ion depends on its mass and charge. The histogram of ion arrival times can be calibrated in mass units, and in this way one can find out what kind of ionic fragments are generated in the photodissociation

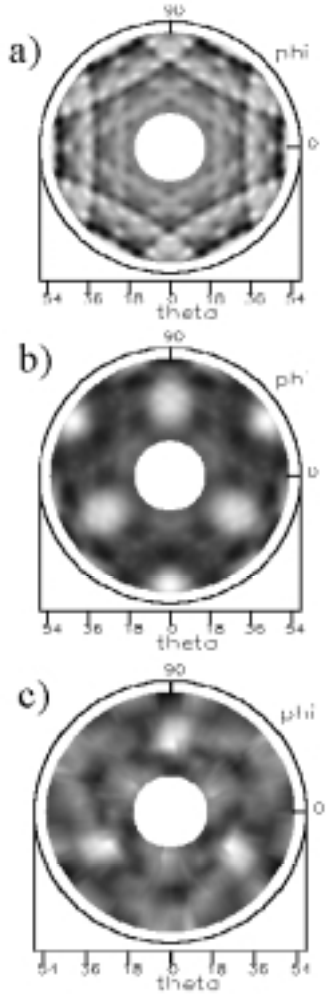

Figure 11: Planar projection of photoelectron diffraction from PdCu(111) 3d emission excited with 700 eV photons. (a) Theoretical simulation of photoelectron diffraction from a 1 monolayer Pd(111) surface layer in perfect registry with the Cu(111) substrate. (b) Theoretical simulation of photoelectron diffraction from a Cu(111) surface. (c) raw experimental data.

process, the dependences of the total and partial ion yields on incident photon energy, etc.

Ozone O_3 is important, among other reasons, because it occurs naturally in the stratosphere, where it filters out of solar radiation a UV component at 4.5 eV that is harmful for human skin. The present study focuses on spectral properties of Ozone in the higher spectral range 12 – 21 eV [9]. The data were taken at the TGM beamline, LNLS. Figure 12 shows the total ion yield of Ozone in comparison with some partial ion yields. It is noteworthy that Ozone lacks the vibrational structures present in O_2, meaning that the presence of the third O atom in Ozone displaces the frequencies of such normal modes to other spectral regions, or broadens them.

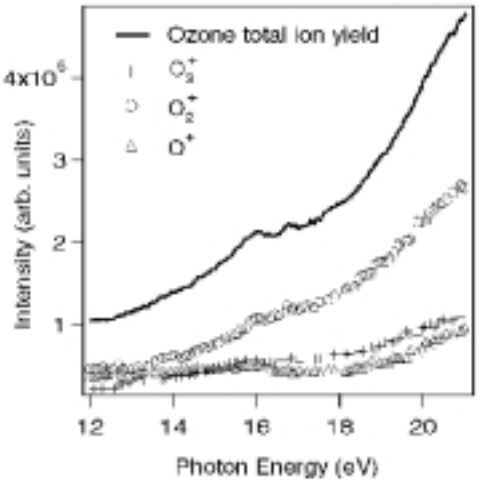

Figure 12: Total ion yield of Ozone compared to partial ion yield of O3+, O2+and O+.

5 Research Opportunities

1) Summer Projects: these are intended as a short exposure to research (in instrumentation, applications and theory) at LNLS, aimed at undergraduates in Physics, Material Sciences, Chemistry, Electrical Engineering and Biology in the 3rd or 4th years. LNLS selects about 12 students from applicants from Latin America, providing travel funds, room and board and a small stipend, for full time dedication during January and February, every year.

2) Scientific Initiation: also intended for the same universe of applicants as above, but for a longer period of 1 year, and localized in Campinas. The applicant must be a regular student enrolled at UNICAMP. LNLS will provide a fellowship.

3) Doctoral degrees: doctoral students already accepted at UNICAMP can do their research at LNLS under supervision of a LNLS scientist. The student still has to comply with all course requirements at UNICAMP, and the degree will be awarded by UNICAMP.

4) Post-doctoral fellowships: LNLS accepts post-doctoral fellows. The candidate must send his/her curriculum vitae and list of publications. He/she will also be expected to present a talk at

LNLS, describing his/her recent research activities.

5) Independent research using LNLS facilities: use of the facilities is free and open to the qualified public on a peer review basis. The candidate must have a doctoral degree, and must submit a two-page scientific proposal to justify his use of the equipment. The proposals are refereed externally to LNLS; final decision to grant beamtime is taken by the Director upon recommendation of a committee including external scientists and also the coordinator of the beamline. The dates for submitting projects and for beamtime allocation are announced in the LNLS home page, in the news of the Brazilian Physical Society and in the LNLS electronic newsletter "Lux". For users outside of the state of São Paulo, LNLS will provide financial help for travel and living expenses for two members of the research team. The user is expected to prepare a report of his research for inclusion on the LNLS Annual Report, and also is expected to publish his results in good refereed magazines and to acknowledge usage of LNLS facilities.

6 Conclusion

We have discussed the origin of synchrotron light, its main spectral, angular, time and polarization properties, and have described some aspects of storage ring and beamline engineering relevant for a prospective user of these facilities. We have then illustrated the usefulness of synchrotron light for spectroscopic and structural investigations of crystals and molecules, with examples of recent research. Although in this article we selected examples involving students and researchers of UNICAMP, this represents only about a small fraction of the research conducted at LNLS, which can be found in the Annual Reports 1998, 1999 and 2000 available at the main University Libraries and Research Institutes in the country. As a final message, the reader is kindly invited to consider the use of synchrotron light, with its wide spectral range, its fine collimation, high photon flux and special polarization choices, also in his particular area of research.

7 References

[1] R. P A. Muniz e A. F. Craievich, Eds. *Projeto Radiação Síncrotron: Técnicas e Aplicações da Radiação Síncrotron*, Publ. CBPF, Rio de Janeiro, 1-3 Ago 1983; A F Craievich, Ed., *Synchrotron Light: Applications and related instrumentation*, Publ. World Scientific, Singapore, 1989; A F Craievich, Ed., *Synchrotron Light: Applications and related instrumentation II*, Publ. World Scientific, Singapore, 1990.

[2] J D Jackson, *Classical Electrodynamic*s, 2nd Ed, John Wiley and Sons, New York, 1975, Chapter 14, pg 670.

[3] E E Koch, T Sasaki and H Winick, Eds., *Handbook on Synchrotron Radiation*, North Holland Publishers, Amsterdam, 1983.

[4] A R B de Castro, R D Zysler, M Vasquez-Mansilla, C Arciprete, M Dimitrijewits, J Magn Magn Mater, **231**, 287-90 (2001)

[5] M Gralle, M M Botelho, C L P de Oliveira, I Torriani and S T Ferreira, submitted to J of Biological Chem, (Nov 2001)

[6] C Piamonteze, H C N Tolentino, F C Vicentin and A Y Ramos, accepted for publication in Surface Reviews and Letters, (Nov 2001)

[7] M P C Vergara, Julio C Cesar, H C N Tolentino and M Knobel, accepted for publication in Physica B (Nov 2001)

[8] A de Siervo, E A Soares, R Landers, T A Fazan, J Morais and G G Kleiman, submitted to Surface Science, (Nov 2001)

[9] A Mocellin, K Wiesner, F Burmeister, O Bjoerneholm and A N de Brito, J of Chem Phys, **115**, 5041-6 (2001)