CNR at Elettra 2.0

Elettra, the Italian third generation synchrotron source, has been in operation since 1994 and is currently planning a major upgrade of the storage ring and of the beamlines in the framework of a project named Elettra 2.0. CNR has been contributing in the scientific and technical growth of the Elettra research environment as the main institutional partner in the last 24 years. The CNR community working at Elettra aims at playing an active role within the novel scientific perspectives opened by the Elettra 2.0 project. This document describes a number of topics of high scientific impact that could be addressed at Elettra 2.0. It is intended as a starting point for designing instrumentation to strengthen the present offer of CNR beamlines and end-stations and implement new experimental techniques. CNR presently runs 11 beamlines, in partnership with Elettra and other Institutions, which have been designed, constructed, tested and upgraded by the CNR staff. These activities allowed to gain specific scientific and technical competences which will be beneficial for the development of the Elettra 2.0 project. An important issue that will be posed by the design of Elettra 2.0 storage ring concerns the X-ray optics of the beamlines. CNR scientists have a wide scientific and technical competence in the field and will contribute to plan the optics requirements and design for the new laboratories.

CNR staff and associates carry out their own long term research programs at Elettra and support the activity of external users that have been granted access to the CNR beamlines by the Elettra proposal review panel. Examples of research activities presently carried out at CNR beamlines and end-stations are: hard X-ray diffraction for protein crystallography and soft and hard materials; x-ray photoemission and absorption spectroscopies for the characterization of organic, semiconductor and metallic materials, of complex interfaces, 2D materials, gas phase and clusters systems; UV spectroscopies that include Fermi surface mapping, high resolution valence band determinations; studies of magnetic properties with X-ray absorption spectroscopies and spin resolved valence band analysis; studies of chemical and physical processes in the time domain with time resolved pump probe absorption and photoemission spectroscopies.

In this document the main scientific subjects that CNR researchers at Elettra consider to be relevant for the scientific future of the facility are presented as separate worksheets, together with technical requirements that the photon source and the new beamlines should satisfy to allow this new science to be carried out. The scientific subjects range from the investigation of 2D, magentic and quantum materials to the study of in-operando processes and of the dynamics of electrons, lattice and spin, in low dimensional systems, complex interfaces and advanced materials. The documents demonstrate that the CNR research community at Elettra strongly supports the design of a new machine with higher performances in terms of beam brilliance and that offers also the possibility to carry out time resolved experiments.

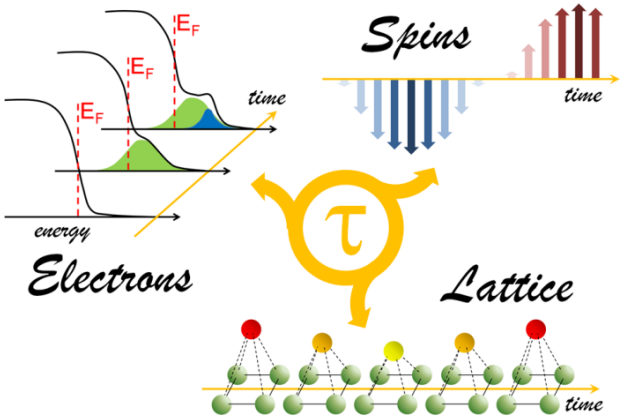
Trieste, June 2018

The CNR scientific staff and the CNR associates working at the Elettra laboratories.

Electron, spin and lattice dynamics of solids

State of the art

The present knowledge of phenomena occurring in condensed matter is based on experimental and theoretical methods applied in or near equilibrium conditions. Condensed matter systems driven into out-of-equilibrium states are much less understood and represent a new frontier of research. Time-resolved electron spectroscopies exploiting the pump-and-probe scheme, such as laser, high-harmonics generation (HHG) and free-electron laser based photoemission, x-ray absorption and magnetic circular/linear dichroism at femto-slicing beamlines, allow one to determine directly the electron, spin and lattice dynamics with about 100 fs time resolution, i.e. close to the fundamental time scales of electronic processes and nuclear motion in solids. The implementation of these techniques with sub-ps to ps target time resolution at Elettra2.0 would allow us to examine excited states and follow de-excitation processes occurring in condensed matter after optical pumping using the many advantages that synchrotron light provides as a probe pulse.



Case studies

Relevant scientific topics, which can be addressed effectively by sub-ps and ps pump-and-probe spectroscopies with synchrotron radiation, are briefly described. An elegant way to circumvent de-coherence in quantum computing applications is the non-local encoding of quantum information in topological states that the environment finds difficult to corrupt. This idea governs the current interest in topological matter. The transient population of the unoccupied electronic bands in many topological insulators is unusually long, exceeding 10 ps, and may represent a channel in which to drive spin-polarized currents. Sub-ps time-resolved photoemission spectroscopy with highest energy, momentum and spin resolutions can reveal directly the dynamics of these transiently populated conduction states and, correspondingly, of the transiently de-populated valence states.

Optically pumped ferromagnets display partially de-magnetized excited states having lifetimes of the order of several ps. Until now most studies have focused on the time dependence of the total magnetization, investigated principally by magneto-optical techniques. A deeper knowledge of the transient states can be achieved by following the time-dependent behavior of specific absorption edges ($L_{2,3}$ for 3d elements and $M_{4,5}$ for rare-earth elements) through sub-ps x-ray magnetic circular/linear dichroism, which provides information about spin and orbital magnetic moments and orbital occupation.

Ultra-fast laser excitation of semiconductors and oxides promotes the creation of charge carriers, which thermalize and recombine within 0.1-100 ps through complex de-excitation pathways. Complementary time-resolved x-ray absorption and photoemission spectroscopies can be used to identify and characterize the single de-excitation channels in the perspective of future technological applications.

Optical excitations induce in many classes of materials (half-metals, transition metal dichalcogenides, correlated oxides) phase transitions involving strongly intertwined charge, spin, orbital and lattice degrees

of freedom. Transient magnetic moments and/or structural distortions show up within few ps after the primary excitation of the electronic sub-system, occurring in the fs time scale. Element- and orbital-selective sub-ps hard x-ray photoemission and photoelectron diffraction can be used to track the time evolution of these phenomena in the bulk electronic structure (core levels and valence band) of strongly correlated materials.

Unconventional two-dimensional (2D) materials, such as phosphorene and borophene, or stacks of different and functionalized 2D materials, are attractive alternatives to graphene and transition metal dichalcogenides as components of photovoltaic cells and for photocatalytic applications. The dynamical properties of these systems are determined by following the transfer of optically-generated electronic excitations (excitons) from the photoactive site to electrodes (photovoltaics and optoelectronics) or chemically active sites (photocatalysis) through element-sensitive time-resolved x-ray spectroscopies. These phenomena occur on ps-ns timescales, which can be suitably investigated with a synchrotron delivering ps pulses.

Impact

The implementation of photoemission and absorption spectroscopies with sub-ps to ps time resolution at Elettra2.0 would represent a major advance for the analysis of dynamical phenomena in condensed matter. Currently, at several synchrotron facilities (including Elettra) it is possible to perform time-resolved spectroscopies, but the time resolution is limited to the standard pulse length of about 50 ps. At femto-slicing beamlines time resolutions of the order of 100 fs are achieved routinely, at the cost of a severe reduction of the photon flux. Laser and HHG sources provide ultra-short pulses, but discrete and generally low photon energies, while free electron lasers suffer from low repetition rate and limited reproducibility/tunability. Thus, a solution featuring the best compromise between flux, time resolution and repetition rate, which we propose for Elettra2.0, would perfectly fill the existing gap. The investigation of excited states and de-excitation processes mentioned above will benefit from the continuous tunability of the photon energy, the stability/reproducibility of the photon beam and the full choice of light polarization, which characterize synchrotron light sources. These studies will impact strongly on the optimization of technological applications in several fields, such as optoelectronics, spintronics and fotovoltaics, and stimulate the development of theoretical methods for the understanding of dynamical processes in condensed matter.

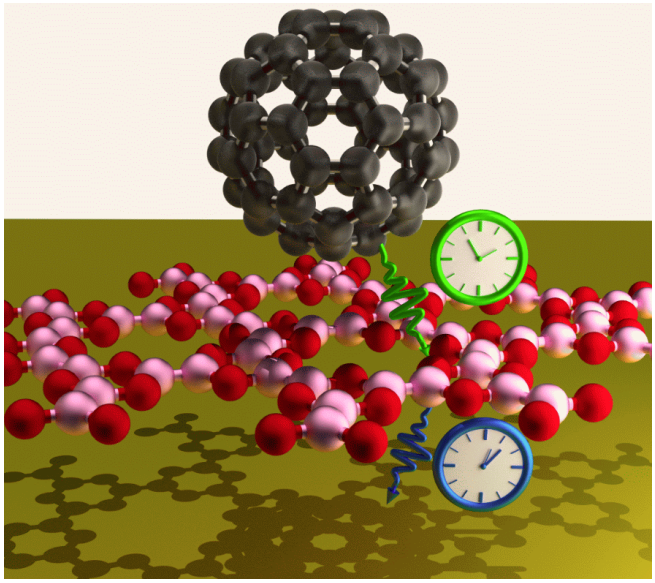
Technical requirements

The scientific topics described in section 2 require a high-brilliance photon beam from the extreme ultra-violet to hard x-rays and variable light polarization. These are standard requirements for third generation synchrotron light sources, which become extremely stringent when the target time resolution is set to the ps regime. In fact, the total time resolution of the proposed experiments is primarily limited by the length of the synchrotron probe pulses. The production of sub-ps light pulses with high intensity per pulse and 1-10 MHz repetition rate is a current matter of debate within the community of accelerator physicists. Different production schemes, including the radio-frequency voltage beating (which will be implemented at Bessy II), the pico-slicing and the use of crab cavities, have been proposed. Purposely designed end-stations, equipped with fs pump lasers and time-resolved detection systems, will be necessary to exploit in full the unique characteristics of Elettra2.0.

Hybrid organic-inorganic interfaces: growth, chemistry and electronic dynamics

State of the art

The synthesis and the characterization of both organic-inorganic and hetero-organic interfaces represent the key issue for the design of novel organic-based electronic devices, sensors, photovoltaic cells.



Several bottom-up synthesis strategies have been developed in the last years, aimed at building complex hybrid interfaces able to effectively mediate the charge transport between the electrodes and the active organic part of a device or at optimizing the electronic coupling in hetero-organic assemblies. The control of the morphology and of the chemistry of the systems at the nanoscale, allows us to tailor their charge transport properties and to determine their efficiency as prototypes of device components. Time-resolved (TR) X-ray spectroscopy techniques are a powerful tool for monitoring the charge transport efficiency, revealed as the occurrence of ultra-fast charge delocalization to empty electronic states of the systems.

The life time of excited molecular states, as determined by TR measurements, can be directly related to the electron transport properties of the systems and it is a parameter to be optimized to increase the transport efficiency of the prototypical device.

Case studies

2D templates Supra-molecular self-assembly can be successfully employed to create 2D templates, which modify both the morphologic and the electronic properties of the supporting surfaces. Interactions of different nature (hydrogen or covalent bonding, metal coordination) are exploited to obtain such systems, which can host other molecules and drive their assembly on the surface and to tailor the electronic properties of the created interface. The guest –host recognition process may be based either on the shape matching or on the chemical affinity between the hosting template and the guest molecules. In this framework, 2D templates mediate the charge transport between the guest molecules and the electrode. The optimization of this process requires an efficient matching between the guest-host and host-substrate charge delocalization channels, to be probed by means of time resolved spectroscopies.

Photovoltaic junctions Organic-organic and organic-inorganic p-n hetrojunctions represent the active part of a promising class of novel photovoltaic devices, e.g. dye-synthesized solar cells. The formation of electron-hole exciton, its separation and the charge transport to the electrodes strongly determine the efficiency of the photovoltaic conversion process. In this view, the study of the charge dynamics at the electrode/organic and at the hetero-organic interfaces, as well as the study of the charge delocalization in thick organic films is mandatory for a proper description of the photocurrent formation in the photovoltaic device.

1D/2D confined chemistry Chemical reactions at surfaces or confined within nanospaces, e.g. between a substrate and 1D/2D material, may in general take advantage of both the catalytic properties of the substrate, the geometric constraint and the confinement field. This approach can stabilize active sites or modulate surface reactions and have a fundamental effect on the catalytic performance. Confined chemistry can be exploited to synthesize novel molecular species and form complex hybrid architectures; to tailor the oxidation state of metal-molecules and therefore their reactivity; and to define novel reaction paths in catalysis.

Impact

The understanding and the optimization of the charge transport mechanisms at hybrid interfaces facilitate the design of novel, more efficient organic-based devices. The chemical sensitivity of the proposed research methods will allow us to identify, at the atomistic level, the channels promoting ultra-fast charge mobility and therefore to select the proper building blocks to obtain efficient systems in bottom-up synthesis protocols. As applied to on surface synthesis and to reactivity processes on the other hand, time-resolved spectroscopy can reveal the mechanisms ruling the 2D confined catalysis. This may indicate the paths to be followed to design efficient nano-reactors in catalysis as well as novel synthesis protocols for complex hybrid interface in organic electronics.

Technical requirements

The characterization of the described systems is a two-stage process where first the static electronic properties and then the charge dynamics are probed. In the first stage, the well established synchrotron based X-ray spectroscopy techniques (Photoemission (XPS), near Edge Absorption (NEXAFS), photoelectron diffraction (PED)) are combined to obtain a description of both the morphology and the chemistry of the interfaces. The proper assignment of the electronic states close to Fermi level, important for their direct involvement in transport processes, can be obtained by means of X-ray Resonant Photoemission (RPES). Moreover, the detailed analysis of the Auger peaks profile, as obtainable by means of APECS (Auger Photoelectron Coincidence Spectroscopy) and aimed at chemically assigning the different spectral features, gives a site-sensitive probe of the possible charge redistribution due to interfacial interactions. In the second stage of the characterization, time resolved spectroscopy is adopted to reveal the occurrence of (ultra-)fast charge delocalization, which is characterized by timing in the 1fs- 100ns range. Ultra-fast charge delocalization in the 1fs-80fs can be accessed by means of RPES. Longer dynamics can be probed by means of **pump and probe spectroscopy**. Laser-pumped synchrotron-probed measurements (photoemission, X-ray absorption) may give access to a larger set of experiments with respect to the well established laser-pumped laser probe experiments, basically due to the higher tunability and larger energy range of the synchrotron probe. For the study of both static and dynamic properties in surface synthesis and surface reactivity topics, a near ambient pressure photoemission setup is undoubtedly advantageous, as it allows for investigating the catalytic processes under real conditions.
Whereas for the description of the static electronic properties no special requirements for the Synchrotron beam are present, for pump and probe spectroscopy **synchrotron pulses with the length of few ps** are desirable, in order to assure the complementarity to RPES technique.

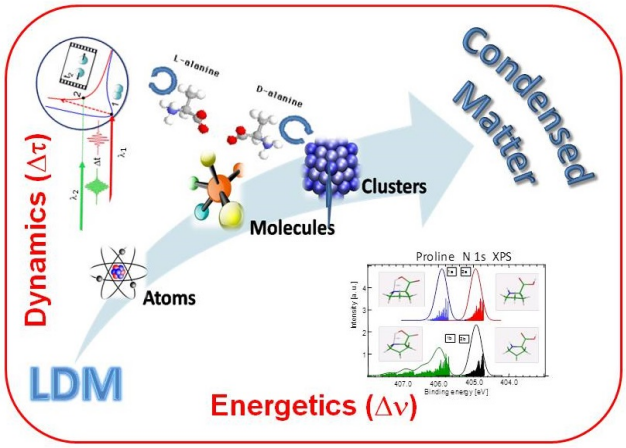
Dynamics, spectroscopy, reactivity and chirality in low density matter

State of the art

Research on low density matter (LDM) focuses on the spectroscopy and dynamics of elementary constituents of matter (from atoms to nanoparticles) as well as on the mechanisms of radiation-matter interaction. The goal is to determine the electronic and structural properties defining the function of these building blocks of matter. The simplicity of the targets makes this research area the most suited for the development of new theoretical and experimental methods. Thus, LDM community is acting at the forefront of instrumental developments for novel light sources. High quality experiments on "standard" systems set a benchmark for the development of theoretical models, whereas experiments on target systems of increasing complexity are the basis for the modeling of physical and chemical processes relevant to technological application, atmospheric chemistry, astro-chemistry and biochemistry.

Case studies

Basic science:



The higher energy resolution and flux of the new source will allow researchers to achieve a thorough knowledge of the electronic and structural properties of elementary constituents of matter, free from the effects of different types of environments, and to disentangle the role of electron correlation, space orientation, alignment and conformation in the response of matter to the interaction with VUV and soft X-rays of variable polarization.

Spectroscopy from fixed-in-space molecules can be achieved by locking the molecule-fixed axes to the laboratory-fixed axes. This has become a crucial tool in molecular imaging and structural dynamics studies, because it allows for a quantum-state-selection of the target. Electron-ion-ion coincidence techniques allow us to determine the orientation on small systems, while polar ensembles (polyatomic molecules and clusters) can be oriented by means of electrostatic selectors or aligned with non resonant laser fields.

The variable polarization of the incident radiation can be exploited by *PhotoElectron Circular Dichroism* (PECD) in chiral dissymmetric molecules and clusters. PECD is two-three orders higher than Circular Dichroism in absorption, making it extremely sensitive to conformational effects; tiny changes of the electronic and structural properties produce dramatic changes in the dispersion of the intensity of the circular dichroism as a function of photoelectron kinetic energy.

The higher flux of the new source will also substantially improve the possibilities of *spectroscopic characterization of highly reactive species*, hampered up to now by the low density of the target. This together with the study of energy selected *ion-molecule reaction* will allow the identification of elusive intermediates in reaction mechanisms of several complex chemical processes occurring in heterogeneous catalysis, in plasmas, as well as in terrestrial and extra-terrestrial planetary atmospheres, in the interstellar medium.

Clusters, liquids, aerosol and nanoparticles: These systems are bridging the gap between gas phase and condensed matter science. The characterization of the structure and properties of matter would be incomplete without the knowledge and understanding of how intrinsic properties can be influenced by external interactions in surrounding environments.

Applications in material science, life sciences and optics

Molecular building blocks of hybrid materials for energy efficiency and harvesting: materials for energy efficiency and harvesting are often required to allow quick charge transfer and separation. The combination of high resolution XUV methods for core and valence electron spectroscopy allow the estimation of charge transfer process after light excitation. The combination of gas phase and adsorbate studies is of fundamental importance for the detailed understanding of the modification of the molecular electronic

structure induced by molecule-molecule and molecule-surface interactions and for the design of new devices with improved performances;
Photoionization of complex biomolecules and flying proteins: though still in its infancy due to experimental difficulties, the study of large biomolecules, isolated or microsolvated is paving the way to the understanding of radiation damage, and to possible applications as drugs in radiotherapy or biosensors in nanotechnology; moreover in the low energy region (<8 eV) the investigation of dichroic effects will allow to unveil the secondary structure of proteins in a region not achievable with laboratory sources.
Metamaterials and metalenses, novel XUV optics for high brilliance synchrotron radiation: A *bright* future for photon-in/photon-out can be readily foreseen with the advent of Elettra 2.0. For this reason new optical devices and meta-lenses to shape intense beam of radiation and particles are attracting some attention. Due to their huge flexibility, improved space integration and compact design, optical devices based on metamaterials represent a great opportunity to optimize the applications and reach the ultimate performances of these sources. In addition, coherence and interference may lead to many novel effects in the area of non-linear optical process and the investigation of these processes in simple and complex waveguides can be investigated using synchrotron radiation experiments and theoretical modeling.

Impact

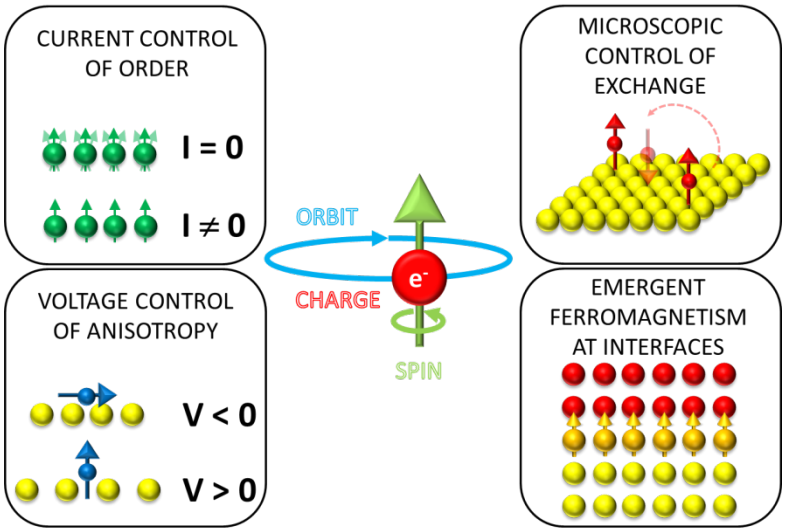
The far-reaching open questions in the field are: how are interstellar molecules formed and how do they survive harsh radiation fields? What is their range of complexity? How do aerosol particles form in different atmospheres? Does inter-base electronic communication protect large DNA and RNA strands from damage? How do the differences in structural and chemical properties of biomolecular conformers affect protein structure recognition and drug design? What knowledge of molecular complexity is crucial to properly understand energy flow processes that are fundamental for medicine and biology, for energy efficiency, and for energy harvesting? Can we understand the physical mechanism behind the electronic chiral response? How can we determine the absolute configuration of chiral molecules, and use electromagnetic light to separate and possibly interconvert stereoisomers?
All these questions rely on a detailed understanding of the electronic and structural dynamics of molecules interacting with photons of different energy. The connection between the initial interaction and the final outcome of such processes is extremely complex. To date it has been fully explored only for small isolated molecules, as in the X-ray induced ultrafast isomerization of C_2H_2. For larger molecules, the intricate balance between structural changes on one hand, and emissions of photons, electrons or fragment ions on the other, depends on the molecular charge and structure, as well as on the details of the energy transfer mechanisms.

Technical requirements

All topics will benefit of the high-energy resolution, small and well-defined spot of the photon beam, broad range of tunability and polarization properties. In some cases, these qualities will open up the possibility to perform experiments previously out or reach, or so demanding in terms of needed beamtime to practically be not feasible, while in other cases these properties will provide results of unprecedented quality, unraveling finer details. A major boost will come from the smaller focus that will be achieved due to the increased brilliance of the beam: the source size and divergence currently limit the achievable spot size. As an example, in the case of dynamical studies with pump-probe methods, the count rate is currently limited by the minimum spot size of the synchrotron light – and a larger spot means that many molecules, which are not pumped, are ionized giving rise to a background signal. The end-station should be based on highly efficient analyzers that can collect high statistics at least at 1 MHz of repetition rate.

- wide photon energy range, from 3 eV to 2500 eV;
- polarization control: linear, circular or tilted linear, allowing the easy determination of asymmetry and dichroic parameters (helicity inversion time within 10 s);
- high flux (one order of magnitude or higher than GasPhase beamline @Elettra);
- high spectral purity, around a few % of the harmonic content;
- availability of few ps pulses for time-resolved studies.

Control of magnetism down to the single-atom limit



State of the art

The application of magnetic effects and processes has recently led to revolutionary achievements in several domains, spanning from medicine to transportation and information technology. Current forefront research includes magnetic hyperthermia, magnetic switching in the sub-picosecond range, quantum computing, spintronics. The blooming field of spintronics aims at combining charge and spin for a new generation of electronic devices. This goal is intimately related with the identification of a ferromagnetic semiconductor, playing the role of silicon in conventional electronics. Layered compounds such as the transition-metal dichalcogenides (TMDCs) were highlighted as promising hosts of room-temperature ferromagnetism. Another challenge in spintronics is the manipulation of magnetism by an electric field, which requires discovering materials with high magneto-electric coupling. The discovery of the quantum anomalous Hall effect (QAHE) in magnetically doped topological insulators (TIs) paves the way towards applications also for these materials, where an insulating bulk coexists with a metallic surface. Another important class of materials is that of perovskite oxides. Their structural and chemical similarities allow for the growth of epitaxial hetero-structures, where complementary properties can be combined and emergent phenomena have been detected. The miniaturization required by technology is pushing research towards studying the magnetism of quantum aggregates of a few or even a single atom, and investigating how this is influenced by their interaction with the surrounding environment. A recent breakthrough is the discovery of single-atom magnets. These are individual magnetic atoms with an open hysteresis loop, arising from the slow relaxation of their magnetization, which represent the ultimate size limit of magnetic bits. Furthermore, in low-dimensional magnetic systems the effects of correlations are significantly stronger than in the corresponding bulk materials. Discrepancies between calculated and measured band dispersions, quasi-particle lifetimes and Fermi surfaces originate mainly from electronic mass renormalization and correlation effects. Satisfactory agreement has been achieved so far for bulk Fe, Co, and Ni, but a more detailed knowledge is required to design low-dimensional magnetic systems with tailored functional properties.

Case studies

Despite the huge recent progress in the synthesis and characterization of new magnetic materials, there remains a large gap to be filled before they can actually be employed in devices. Two-dimensional

materials have yet to be turned into room-temperature (semiconducting) ferromagnets, which may be achieved by either bulk/surface doping with magnetic (3d or 4f) elements or by the polarization induced by proximity with a magnet. In order to achieve the QAHE at temperatures of technological relevance, one needs better control over the magnetic doping of TIs, which may be achieved by doping their surface, instead of the bulk, leading to a longer range and finer tuning of the magnetic exchange interactions. In the search for electric field control of magnetism, in the next years the focus of research will be towards the interface effect at the boundary between ferroelectric and ferromagnetic materials. Also for single-atom magnets, research will focus on ways to embed them into the surface of their host matrix in order to stabilize them up to room temperature. In the case of the perovskite materials, the origin of the emergent phenomena is still unknown, and the possible role of intrinsic (e.g. polar discontinuity, electronic reconstruction) and extrinsic effects (e.g. atomic inter-diffusion) is currently debated.

Impact

All the topics discussed above show that magnetic functionalities critically depend on effects occurring at surfaces and interfaces. In order to improve their quality and thus the control over the magnetic properties, it is mandatory to correlate structural and electronic degrees of freedom on the same sample in-situ. This requires that advanced growth techniques (pulsed laser deposition, molecular beam epitaxy) coexist in the same beamline with structural (scanning tunneling microscopy (STM)) and magnetic (spectroscopies based on the dichroism in the x-ray absorption, or spin-resolved photoemission) characterization techniques.

A further tremendous advancement towards the understanding of magnetism down to the single atom limit could be achieved by integrating within the same instrument the spatial resolution of a scanning tunneling microscope with the magnetic sensitivity of x-ray magnetic circular dichroism (XMCD). Proof-of-principle experiments with limited spatial resolution were previously performed, but the full potential allowing for the determination of spin and orbital magnetic moments and magnetization cycles atom by atom can only be exploited at a synchrotron with the highest brilliance, like Elettra 2.0.

Spin- and angle-resolved photoemission spectroscopy provides direct access to the bare-particle band structure and the complex self-energy function Σ of low-dimensional magnetic systems. The real part of Σ is related to the mass renormalization, while its imaginary part determines the broadening of the spectral function. Information about the coupling to bosonic excitations and correlation effects can be extracted from the low- and high-energy contribution of the real part of Σ.

A deep understanding and exploitation of many-body effects, which are responsible for magnetic and functional properties, may also be provided by the spin selectivity achieved in Angle-resolved Auger Photoelectron Coincidence Spectroscopy (AR-APECS) on the two-hole final states of core-valence-valence Auger spectra, which are intrinsically sensitive to correlation effects. Such a capability, which has already provided unexpected results in magnetic systems, is promising for investigating highly correlated systems, like topological insulators and superconducting materials, in which the two-electron probe achieved by APECS can provide details on many-body effects which are not accessible by the conventional one-electron spectroscopies and consequently theoretical models are subjected to more severe proofs.

Technical requirements

The experimental techniques which are required to tackle the proposed research in the field of magnetic materials are x-ray magnetic circular and linear dichroism, as well as spin-resolved photoemission and Auger photoelectron coincidence spectroscopy.

For the dichroism-based investigations, the required instrumentation includes a magnet providing fields of several Teslas, and a cryostat allowing to reach cryogenic (i.e., liquid helium or lower) temperatures. In

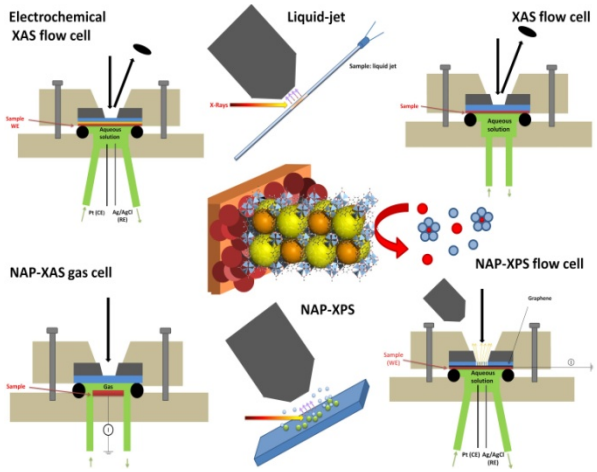
order to couple these with a scanning tunneling microscope to perform x-ray spectroscopy on single atoms, the x-ray beam should ideally be focused to a round, sub-micron spot size, which should be achievable in an ultra-low emittance storage ring such as Elettra 2.0. Moreover, such a small beam would directly allow us to perform spectromicroscopy (i.e. spectroscopy with high spatial resolution), with the possibility to apply the powerful analysis of XMCD having access to the domain structure. The required energy range has to cover absorption edges of interest for magnetic materials, mostly between 200 and 2000 eV, where full control over the x-ray polarization and its highest purity are required.

Spin- and angle-resolved photoemission spectroscopy requires a high photon flux and photon energies in the range 20-100 eV, to exploit the high cross sections of the valence band electrons. The mini-Mott detector, the V-LEED scattering detector and the spin-resolved momentum microscope provide alternative and complementary spin-detection schemes suitable for the analysis of spin-dependent quasi-particle behavior and correlation effects.

The typical energy range for APECS experiments is from few tens to few hundreds of eV. In fact, in order to keep a high spin selectivity, the electron forward focusing occurring at high energies has to be limited. Moreover a not so high photon flux is typically used in order to minimize background signal.

Chemistry in real conditions by soft x-ray spectroscopies

State of the art:



The challenges of the future chemistry research and technologies will be tackled by a multitechnique approach that will include traditional chemistry and physics analysis techniques based on the use of synchrotron radiation. In this scientific field one of the most promising approaches is represented by the so called *operando* spectroscopy techniques.
Spectroscopic techniques in the soft x-ray range were successfully used in the past for describing the chemistry of solid systems at the surface. Conversely the application of these techniques to the study of liquid/solid and gas/solid interfaces has been, up to recent progresses, severely limited by the mean free path of the electrons and of the x-rays in medium. Considerable effort has been devoted in recent years to adapt such analysis (most of them based on the use of synchrotron radiation) to real conditions (e.g. during a reaction, or in ambient environment). These techniques are fundamental to understand the behavior of catalysts, sensors, batteries and electrodes in working condition with the aim to design and develop more efficient and performing materials. XPS near ambient pressure (NAP-XPS), x-ray absorption and emission spectroscopies at ambient pressure or in liquid (AP-XAS, AP-XES), TeraHertz and Infrared Spectroscopy (THz/IR) in real conditions have experienced a veritable outbreak in the last years and the great majority of 3rd generation synchrotron light sources have been equipped with dedicated beamlines e.g. 9.3.1 and 2 @ALS, TEMPO @SOLEIL, EMIL @BESSY, HIPPIE @MAX IV, etc.

Case studies:

<u>Heterogeneous catalysis at gas/solid interface.</u>
Heterogeneous catalysts play an essential role in industry not only in economic terms but also for the environmental safety. Catalytic reactions occur on the surface of the catalyst, therefore soft x-ray techniques, which are highly surface sensitive, provide outstanding experimental tools to shed light on the mechanism of reactions. The structural and electronic characterization of heterogeneous catalysts under reaction conditions is the base for trying to develop new catalytic systems with high yields, high selectivity and mild working condition. In this sense we propose the investigation of materials which range from nanocatalysts (e.g. metal nanoparticles supported by oxide and porous materials) to metal single-sites catalyst: in amorphous substrates (e.g. in amorphous silica and carbon) and in the framework of extremely porous materials as zeolites (e.g. ZSM-5, MOR) and metal organic frameworks (e.g. HKUST-1, UiO-66/-67/-68, ZIF-8, MOF-5, MIL-101).
<u>Electrochemistry at liquid/solid interface</u>
State of the art microfluidic electrochemical cells can be used *in situ/in operando* conditions to give insights on the chemical evolution of ion battery materials during charge/discharge processes. The understanding of the solid-electrolyte interface formation, the cathode electrodeposition and the interplay between the two processes during cycling is a main issue in the advancement of rechargeable battery technology.
<u>Surface reactivity for gas sensor</u>
The reactivity of the materials such as oxides (e.g. SnO_2, ZnO, Cr_2O_3, Mn_2O_3) towards several gases (e.g. H_2, O_2, H_2O, CO, CH_4, NH_3) at the gas-surface interface will be followed in real time. The availability of our set of techniques allows to observe simultaneously the electronic and structural changes underwent by the adsorbed reactants on the absorption sites during the gas exposure.
<u>Synthesis of 2D and 3D organic frameworks and reactivity</u>

A new promising class of materials is represented by Covalent and Metal Organic Frameworks which have a porous structure, and can be synthesized from small organic molecules precursor. They have a relevant importance in the field of gas and molecular storage/sensing and of the catalysis. The trapping of molecules is driven either by the simple shape-matching or by the chemical affinity between pores and guests. The introduction of catalytic centers creates nanoreactors which resemble the active sites of enzymes, whose activity and efficiency is expected to surpass current state of the art catalysts in several electrochemical processes (e.g. H_2 evolution reaction, O_2 evolution reaction, O_2 reduction reaction, and CO_2 reduction reaction.

Impact

Some of the Chemistry Grand Challenges of the near future with important consequences on the industry and environment will benefit from the development of real condition spectroscopies. In fact, a rational design of new catalysts requires a detailed understanding of the reaction mechanisms occuring at the catalyst's surface. Better performing catalysts are the key to solve environmental problems such as greenhouse gas pollution, production of clean energy from renewable sources and the efficient storage of the produced energy. The operando spectroscopies can be strategic also in the development of efficient batteries which are fundamental for the future of the automotive industries (but also of other key productions like drones and robotics).

In this regard the possibility to study electrochemistry in liquids by photoemission and x-ray absorption or emission spectroscopies has been proved to be a fundamental asset for the comprehension of electrochemical process taking place at the electrode surfaces and the gas/surface reactions which are the basis of gas sensor technologies.

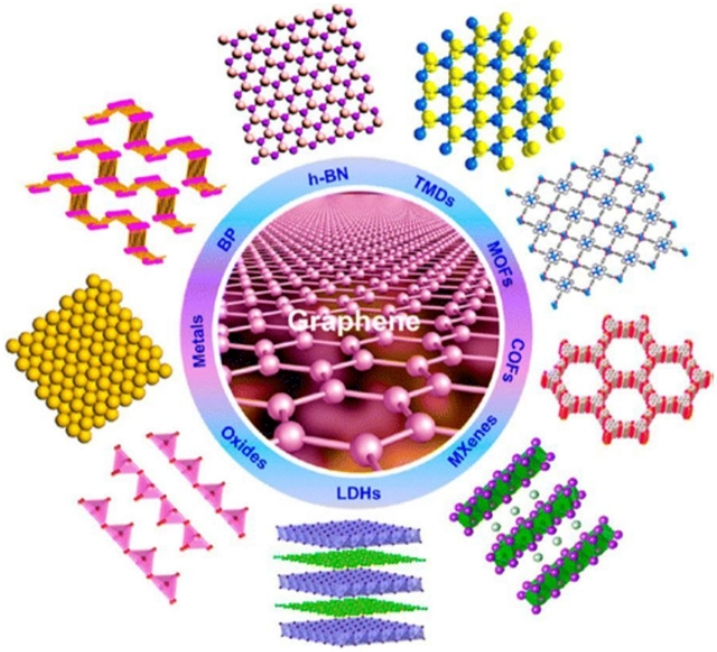
Technical requirements:

Several techniques ranging from diffraction to microscopy and scattering have been developed in the past decade and are now currently employed in the so called operando mode to unravel the chemical and physical processes during reaction. However, developing operando mode for the electronic spectroscopies such as XPS, XAS, and XES, operating in the soft x-ray energy range, is more challenging and only recently experimental setups able to perform such experiments became available. To perform NAP-XPS the solution adopted is to employ analyzers with differential pumping stages permitting to operate the electron detectors while keeping the sample at pressure of some mbars. X-ray absorption (either photon in-photon out mode or with electron detection) and X-ray photoemission spectroscopies can operate in confined reactors which are separated by suitable membranes from the vacuum or on liquid micro-jets. The development of these set-ups (including the fabrication of the membranes) is nowadays one of the hottest topics in synchrotron radiation facilities.

From the point of view of the beam requirements *in operando* techniques in the soft x-ray energy range will benefit from high fluxes due the high absorption from liquid and gas at high pressure in the soft x-ray energy range. THz/IR measurements in real conditions will also take advantage of both high flux and high brilliance and of high beam stability. Moreover, the focalization of the beam into small spot (tens of microns range) will reduce the membrane size thus facilitating the cell and the membrane durability. Adding the fast time resolution of the beam (down to picosec), fundamental reaction steps in catalysis at the solid/gas or solid/liquid interfaces will be unraveled.

2D Quantum Materials

State of the art



Research on two-dimensional (2D) materials has been exponentially increasing since the discovery of graphene in 2004. In 2D materials, electron, spin and lattice degrees of freedom confined in less than 3 dimensions lead to numerous unique properties that deviate from their bulk counterparts. Paradigmatic examples of such flourishing field of solid state science are, other than graphene, transition metal dichalcogenides (TMDs), Weyl systems and topological insulators, new "beyond graphene materials" such as silicene, germanene, antimonene, phosphorene etc. One of the frontiers in 2D materials research is the understanding and the control of interface-driven, and more generally dimensionality-driven effects in systems whose properties fall somewhere between those strictly 2D (e.g. graphene) and 3D. The ultimate goal, and surely the target of next decade is to create 'on-demand' materials and heterointerfaces displaying the desired functional properties. The research programme must fully exploit the coordination among theory, synthesis and growth of the complex materials, advanced characterization and experiments with advanced lab-based and fine analysis Large Scale Facilities resources addressing high resolution in energy, momentum, spin and time.

Case studies

The study of 2D quantum materials like Topological Insulators, Weyl and Dirac systems and Strongly Correlated Oxides is today at the forefront of condensed matter research. Spectroscopic characterization of these materials is a necessary step towards the understanding of their electronic and spin(tronic) properties leading to their future exploitation in devices. In the following we envision possible research areas in the field of 2D quantum materials, concerning both fundamental science and applications: superconductivity in graphene – a route to be explored towards room temperature superconductivity and also etherostructures of 2D materials that recently have shown unconventional superconductivity depending from the twist angle between the layers ; interplay between topological properties and superconductivity in search of Majorana fermions; quantum Hall effect in graphene-like materials silicene, germane and stanene and also antimonene, bismuthene etc., leading to understanding of heavy Dirac electrons and Dirac electronics; Valleytronics in TMDs - the exploitation of fully spin-polarized states in TMDs with strong spin-orbit interaction; 2D materials in magnetic heterostructures: the proximity-induced exchange interaction (usually considered as a perturbative short-range effect for bulk materials) is expected to free the proximity effect from the short-range limit, as already demonstrated in topological insulators; Weyl fermionics in Weyl semimetals; two dimensional electron gases at oxide interfaces.

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A promising evolution of this research field concerns the study of heterostructures formed by stacking different 2D materials, which present functional behaviors of possible practical use. These systems are produced by multiple transfer processes and, therefore, present limited lateral size, as well as rotational domains, determined by the in-plane alignment between the layers. It is important to underline that the relationship between electronic structure and thickness in 2D materials, cannot be addressed via

exfoliation methods only. The state-of-art of mechanical exfoliation methods produce high quality monolayers, but this technique is not scalable. The *controlled direct growth* of heterostructures (bi and few-layer thick by in-situ MBE and PLD), including the direct comparison with single crystal and/or exfoliated layers, and the measurement of their spin and momentum in the very same experimental setup, is a necessary step towards controlling functionalities. The most suitable experimental methods to analyze the electronic properties of these controlled hetero-structures are angle-resolved photoemission (ARPES) with spin resolution (Spin-ARPES), lateral resolution (micro-, nano-), both surface and bulk sensitivity (variable photon energy range from UV to soft X rays) and controlled orbital sensitivity (variable polarization). In addition, Infra-Red Synchrotron Radiation spectroscopy (IRSR) represents a powerful technique for investigation of low-energy electrodynamics of unconventional 2D materials.

Technical requirements

ARPES, Spin-ARPES, Soft-X ARPES, micro/nano-ARPES and micro/nano-photoelectron diffraction, high-pressure photoemission, IRSR are the experimental techniques of interest within this topic. The beamlines at synchrotron facilities, in particular those dedicated to photoelectron spectroscopies, are crucial for the investigation of the electronic and spin properties of 2D quantum materials. Thanks to the small emittance design of Elettra 2.0, smaller spot size on the sample and high energy and angular resolution of the spectra should allow to extend the photon energy range for ARPES to soft X-ray range (up to 1keV). Variable polarization remains indispensable to identify the orbital character of the electronic states. Above mentioned photoelectron spectroscopies must be adapted to micrometer scale or nanometer scale objects due to the requirements of the down scaling of the 2D materials for applications. To achieve it with scanning microscope technique, 1 μm spot size with reflection optics or 100nm spot size with diffraction optics are required. The small beam spot size will allow to scale down the volume of the environment around specimens, which in turn would enable the high-pressure (nearly ambient) photoelectron spectroscopy and extremely low temperature (< 4K) photoelectron spectroscopy. The combination of polarized light from Elettra 2.0 and ultrashort (100fs) pulses from laser-HHG sources (as the recently developed NFFA-SPRINT and T-Rex) in the overlapping UV-soft-X energy range will create the unique possibility of integrating pump-probe studies of excited states and highly resolved studies of the near-ground state. As the spin resolution represents an ultimate requirement in the characterization of 2D quantum materials, our achievements in design and operation of spin-resolved spectrometers are the basis for further improvements in efficiency projecting into the future our current international competitiveness in the field. The performance of IRSR will be improved in view of the extension of spatial resolution beyond the diffraction limit, providing the possibility to acquire IR/THz spectra with a spatial resolution down to 20 nm. The increase of the beam current within Elettra 2.0 will be advantageous in terms of both flux and brilliance over the entire infrared regime. In addition, the more cogent beam stability requirements of Elettra 2.0 should provide a significant noise reduction.

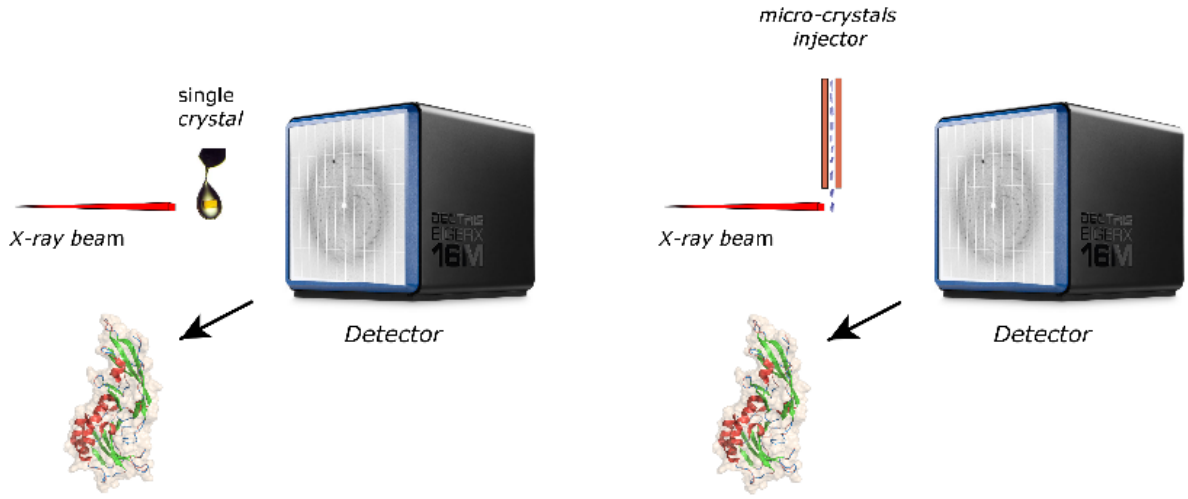
Structural studies at the interface of chemistry, biology and physics

X-ray diffraction has been used for the structural investigation of matter for a very long time and with the advent of X-ray sources of extraordinary intensity such as synchrotrons, it further widened its possible applications in almost any scientific field where knowledge of the atomic or molecular structure is required.
Among the many possible applications, the CNR group operating at Elettra focuses mainly on two fields:

- Macromolecular Crystallography for basic science and drug discovery applications
- Structure-Function correlations in hard and soft materials

Macromolecular Crystallography (MX):

X-ray crystallography has been the technique of choice for the study of the three-dimensional structure of macromolecules. Despite the rapid emergence of Cryo-Electron Microscopy, which is now a viable option, X-ray crystallography it is still the most used experimental technique in protein structure determination. The impact of synchrotron radiation in macromolecular crystallography has been enormous and the development of new synchrotrons delivering X-ray beams of the highest brightness has moved protein crystallography in a new era.
Very rapid data acquisition is now possible, moving the time-scale of data collections from hours to seconds. Very large amounts of crystals can be now screened, and with end-stations designed to work in automatic modes, high-throughput protein crystallography is now possible. While generally useful, the high-throughput approach is especially important in fragment-based drug discovery: now large libraries of lead compounds can be tested in a reasonably short time. The availability of extremely bright X-ray beams of the size of a few microns makes possible the acquisition of useful diffraction data even from very small crystals. Moreover, the small dimensions of the beam allow for serial expositions of different regions of crystals, which can be of the utmost importance in order to cope with the radiation damage experienced by protein crystals under the X-ray beam. Given the small beam dimensions innovative data collection geometry allowed maximizing protein crystals X-ray exposures. A further step in exploiting the very bright X-ray beam from modern storage rings comes with Serial Milliseconds Crystallography (SMX), a technique initially developed for XFELs. In a SMX experiment, a continuous flux of microcrystals is injected into the beam path and a fast detector collects the diffraction patterns with a time resolution in the range of ms. Some major advantages are devised in SMX: 1) dimensions of the crystals are further reduced, 2) SMX is carried out at room temperature with no needs of cryoprotection. While the technique is still not a mature one, it is indeed very promising. Tests have already been performed at several Synchrotron Light facilities and the ESRF Extreme Bright Source programme includes a dedicated beamline for serial crystallography.



Case Studies in MX:

Small protein crystals with dimensions of the order of few µm or lower will generally benefit from the use of bright X-ray microbeams. The advantage will be even greater when using SMX, which avoid the mounting and the manipulation required for conventional cryo-crystallography. Small crystals manipulation can be challenging, as well as crystals centering and orientation, while in SMX the use of high viscosity injectors outweigh all of these problems.

Membrane Proteins are among the most interesting topics in structural biology, and especially important in drug discovery. Unfortunately, membrane proteins are generally recalcitrant in growing as large crystals and are especially prone to radiation damage. In this specific field, the benefit of small and intense micro-beams is great, in particular when associated with versatile goniometers and advanced data collection methods. Furthermore, SMX solves the problem of the radiation induced crystal decay as the photon dose is distributed among many tiny micro-crystals, which individually experience a non-critical exposure level.

Drug discovery studies. Long-standing bottlenecks of solving ligand-bound protein structures include (i) time-consuming screenings of substrate co-crystallization or soaking conditions to produce stable crystals; (ii) deviations from the native protein structure induced by cryogenic temperatures; (iii) the lack of fast sample-exchange systems for efficient data collection; and (iv) potential competition between the ligand and the cryoprotectant. The advantage of rapid data collection, as possible in modern synchrotrons, is apparent when exploring libraries of chemical compounds for fragment-based drug screening. SMX exposure time matches the expected diffusion time of molecules in protein microcrystals and might be suitable for fragment-based drug screening and time-resolved structural enzymology studies.

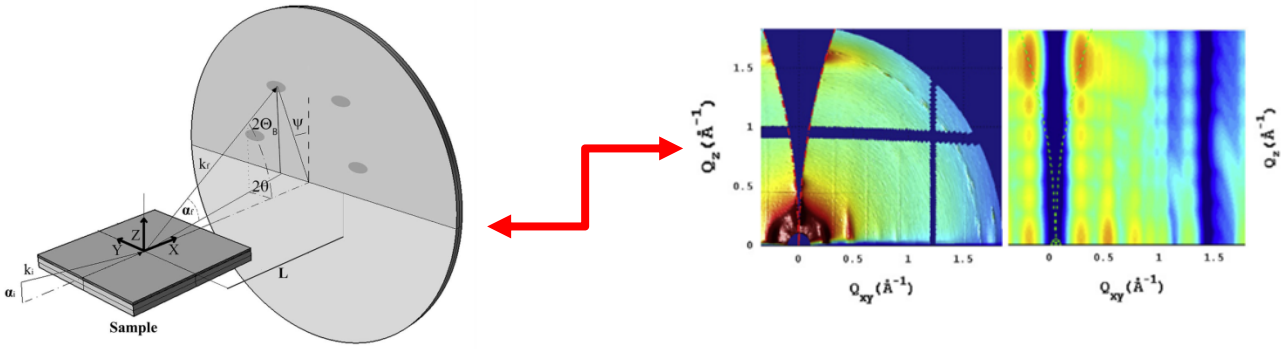
Time-resolved studies. Protein dynamics in the ns/ms range have been recognized as critically important in protein function. Now SMX offer a time resolution in the ms range, but improvements are expected in the future.

Impact on the MX community:

Protein crystallography greatly benefits from the availability of a small and intense X-ray radiation. Today, weakly diffracting crystals like small or membrane protein crystals represent a great challenge for protein crystallography. Moreover, the rapid decay experienced by protein crystals when exposed to intense synchrotron beams is a further cause of concern for the crystallographer. Finally, the progress in molecular biology and the availability of high throughput crystallization methods, as well as the possibility to test thousands of potentially pharmacologically relevant chemical compounds, demand for very fast data acquisition systems. We expect that an intense X-ray beam of few microns in size will help to give a proper answer to the demands of the modern protein crystallographer.

The advent of XFELs has changed the way of thinking in structural biology, pushing the limits of crystals dimensions, and introducing the time domain as a further variable. Unfortunately, even in the next future, the availability of beamtime at XFELs will be limited. Synchrotrons offer a viable option to XFELs. While not reaching the fs time domain, SMX can offer the advantage of a consolidated technology. SMX will have a strong impact in all those cases where fs/ns dynamics is not the goal. By reducing the needs in crystal dimensions and manipulation, by avoiding the need of cryo-protection and by limiting the radiation damage almost to zero, SMX could become the technique of election for the acquisition of diffraction data from macromolecules.

Structural and phase transitions characterization of nanostructured materials by X-ray diffraction



Grazing incidence experimental setting for structural and orientational study on thin films of molecular PNDI2OD-T2

While in structural chemistry diffraction methods are generally associated to the elucidation of the relationship between the atomic/molecular structure and the underpinning chemical activity, hard X-rays diffraction can also be of help for the characterization of materials in which the ratio between ordered regions on a micrometric or nanometric scale and disordered regions is much higher than in single crystals. In this case, the crystal structure of the molecules involved are already know, and the scope of the investigation is to unveil the relationship between their aggregate forms and their functionality in a wider sense, in a multiplicity of fields. The XRD1 experimental station at Elettra offered the possibility to carry out investigations:

in physics of the condensed state, in particular in confirming hypotheses on the nature of high critical temperature superconductivity and its relationship with phase transitions induced by temperature or exposure to X rays;

in materials science, allowing the study of thin films of organic semiconductors of interest for the development of new electronic devices, correlating discrete molecular orientation distributions of the ordered molecules on the substrate surface to its electron transmission properties. In 2011, our users had already demonstrated that at the experimental station it was possible to perform in-depth structural assessment, by means of variable incidence X-ray scattering, hence detecting different aggregation states at the substrate interface as compared with air interface.

in materials engineering, e.g. in metallurgy, where the malleability and resistance to mechanical stress of alloys has been related to the presence of specific *quasi* crystalline regions within them. Alternatively, in food sciences, where the characterization of lipid lattices structuring amorphous food matrices offers the opportunity to design foods capable of encapsulating molecules of active principles, protecting them from oxidative stress and improving their deliverability.

Each of these research communities has specific experimental needs and addressing their demand could further increase the number and quality of investigations performed.

Case Studies in hard and soft materials diffraction studies

Providing an ultra-collimated beam of dimensions on the micron scale would allow local structural investigation of complex and heterogeneous materials, such as high Tc superconductors that present great point-to-point variability in terms of doping and/or chemical composition. Along with the structural characterization by X-ray micro diffraction, we could investigate the chemical composition by X-ray micro fluorescence. Polycrystallinity, texture, microcrystals orientation and defect structure, phase transitions studies would greatly benefit from this kind of X-ray source.

Increasing the automated degrees of freedom of the sample would meet the needs of the community of organic semiconductors developers, very interested in the technique of grazing incidence X-ray diffraction for the characterization of thin films, surfaces, interfaces. This innovation would be even more welcome if

associated with the possibility of applying large-scale temperature variations, exposure to chemical agents, electric or magnetic fields to the surface exposed to X-rays. This kind of experiments already takes place at the experimental station, but rather discontinuously and often by means of equipment developed by the proposer, hence not made available to the whole users' community.
Finally, investigators of phase transitions in soft matter, e.g. those induced by temperature variations, are interested in studying samples with a predominant amorphous or short-range ordered composition. The diffracted or scattered signal will be weak but still present, due to the brightness of the source. Reducing the background noise generated by the interaction of hard X-rays with their entire transfer chain from source to sample, and from sample to detectors, is not only desirable but becomes, in this case, absolutely essential. It would enable us to isolate the signal, allowing the users to fully exploit the high brightness of the source and the high dynamic range of the detectors.

Impact on the Material Science community:

The importance of structural studies within the Italian Users' community have been getting more attention especially in applied science, due to its capability to investigate samples quite close to their "in operando" functioning or employ conditions. Heterogeneity, ordering in regions of different dimensional scales, nanostructures, low-dimensionality systems and real-world geometries like thin films are everyday issues in the field; a community in rapid growth is going to need special environments tailored on their need to establish structure-functionality correlations in a great number of physicochemical conditions and fields. At present, users from neighboring countries like Austria and Slovenia are probably making a more intense use of the facility than Italian users who are accustomed to characterize their samples with laboratory equipment. The innovations made possible in the frame of Elettra 2.0, besides the well-known pros of Synchrotron Light (brilliance, intensity and tunability), will enhance our capability to be of help in planning and performing structural characterizations in the geometrical and environmental conditions needed by developers and will give great impulse to the field.

Technical requirements:

According to the case studies here reported, some general requirements emerge, specifically:
Adjustable beam size from a few to 100 μm, very stable beam position.

- Monochromatic beam, energy span 5-20 keV
- Divergence less than 3mrad both in the horizontal and vertical plane
- Flux over 10^{10} ph/s
- Fast 2D hybrid large surface photon counter detector

Furthermore, specific experiments require some specific instrumentation:

- Seven-circle diffractometer also capable of hosting heavy and large Vacuum experimental chamber for high temperature – low temperature – in vacuum – deposition – electron transmission – magnetic field GIXRD experiments.
- High viscosity injectors are required for SMX. Their developments have just started under the requirements of the XFELs experiments.