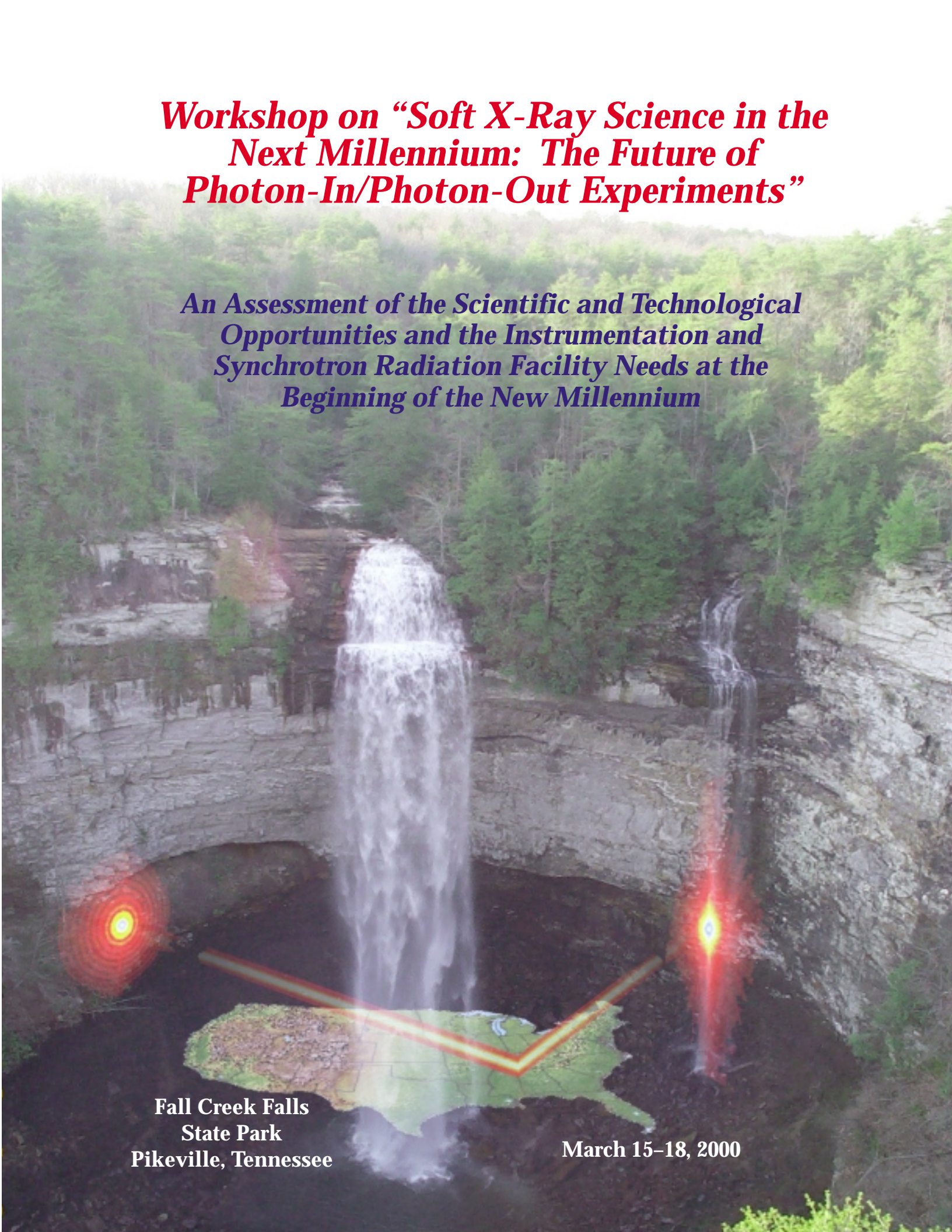


Workshop on “Soft X-Ray Science in the Next Millennium: The Future of Photon-In/Photon-Out Experiments”

***An Assessment of the Scientific and Technological
Opportunities and the Instrumentation and
Synchrotron Radiation Facility Needs at the
Beginning of the New Millennium***

**Fall Creek Falls
State Park
Pikeville, Tennessee**

March 15–18, 2000

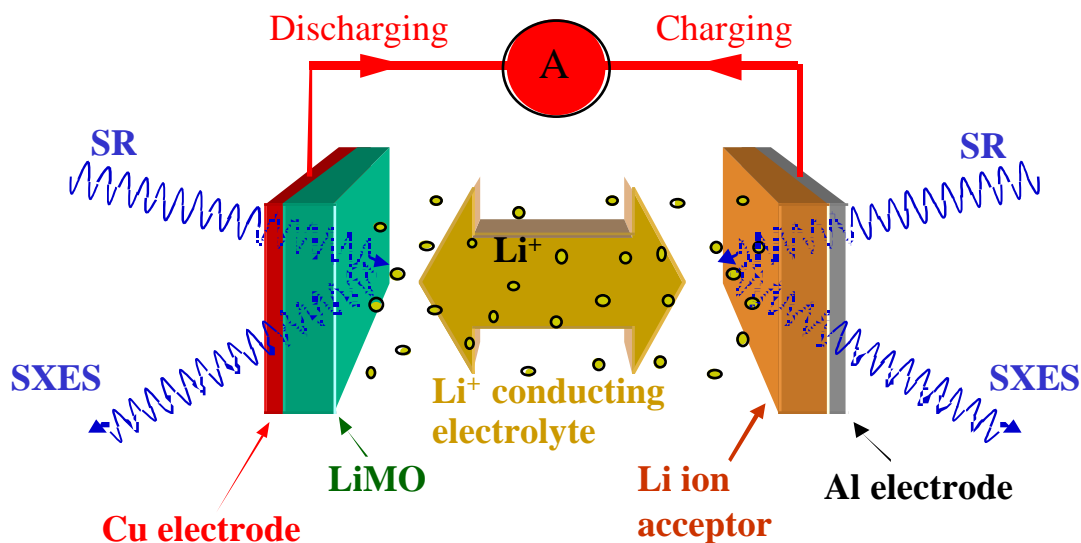


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In Situ Study of Electrochemical Processes by SXES



Prepared by the Solid State Division of the Oak Ridge National Laboratory, which is managed by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy, Oak Ridge, Tennessee.

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*Workshop on “Soft X-Ray Science in the Next Millennium:
The Future of Photon-In/Photon-Out Experiments,”
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PREFACE

Objectives: This workshop was convened to identify the scientific opportunities and instrumental challenges facing this community in the beginning of the next Millennium. The workshop brought together international experts with a wide range of interests such as complex materials, environmental and interfacial science, and atomic and molecular phenomena, but with a common interest in soft x-ray photon-in/photon-out experiments. This report was generated to describe and justify priorities and outline a plan to match the capabilities of various facilities with the scientific demands.

Charge to Participants: The participants were charged with writing a report identifying the forefront areas of science and technology that can be impacted by photon-in/photon-out synchrotron-based techniques and the technical and theoretical challenges that will be faced by this community. Each working group was asked to *dream* about what could be done with the ideal machine and beam line to change the way we think—to cause a paradigm shift in a given field.

Historical Perspective: The federal government has spent over \$3 billion dollars of direct support for the construction and operation of second- and third-generation synchrotrons in the United States. In this 20-year period of intense basic research and synchrotron-related instrumentation development, the scientific community has made tremendous progress in developing new spectroscopic techniques to study the electronic structure of atoms, molecules, and solids. Nowhere is this more evident than in the area of soft x-ray photon-in/photon-out spectroscopies, where enormous progress has been made in the energy resolution and throughput of monochromators and detectors, as well as beam characteristics and stability. **It is time to make this expenditure pay off in terms of high-impact science and technology.**

Workshop Philosophy: With the new capabilities in synchrotron radiation sources and accompanying instrumentation, it is time to take **a Bold Step into the Future**. To quote the great one himself (Wayne Gretzky), “you miss all of the shots you don’t take.” The tone of this meeting was set on the first day by a response of Dr. Bill Oosterhuis (Team Leader, Condensed Matter Physics and Materials Chemistry Branch, DOE Division of Materials Sciences) to a question asked by an attendee, “what would you like for us to do?.” The answer was “win the Nobel Prize,” or paraphrased *have an impact!*

Many a false step is made by standing still!

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1.0 Executive Summary

As we enter the new Millennium, we are faced with what has been described as a new Industrial Revolution—Nanotechnology. The dream is to “Shape the World Atom by Atom.” Roald Hoffmann (Nobel Prize Winner from Cornell) put it this way, “Nanotechnology is the way of ingeniously controlling the building of small and large structures, with intricate properties: it is the way of the future, a way of precise, controlled building, with incidentally, environmental benignness built in by design.” The underlying assumption, upon which this New World is based, is that we can “see with chemical specificity” the behavior on the nanoscale. Soft X rays furnish a probe with the correct nanometer-length scale. Soft X rays, with tunable energy, polarization, and time structure from synchrotron sources offer a unique probe for nanostructure design and characterization with inherent elemental or molecular selectivity and with the possibility to separate out electronic, magnetic, and structural properties for materials in real environments. On the horizon is the possibility to image in time and space complex phenomena on the nanometer-length scale with coherent radiation from a synchrotron.

This document presents the “dream” of the future based upon what is believed to be possible with properly designed soft x-ray photon-in/photon-out facilities. This dream is supported by reality, demonstrating what has been accomplished. Recommendations for facilities to be built or finished in the immediate future are included. Five areas of science and technology were identified where soft x-ray photon-in/photon-out experiments will change the way people think about the most fundamental processes and consequently cause a paradigm shift in how we think and what we believe can be accomplished.

- **Artificially Structured Materials**

Artificially structured materials create uniquely tailored electronic, magnetic, and optical properties that are not available in materials found in nature. Today, they form the foundation of all “high tech” industries with annual revenues of several hundred billion dollars, and their impact on modern life and society cannot be disputed. The fabrication of materials of smaller and smaller dimensions with faster and faster electronic and magnetic responses, required for technological progress, is known to face severe limitations at length scales in the 1–100-nm range and timescales in the nanosecond to picosecond range. The characterization of such structures and the understanding of their behavior on these length and timescales pose a great challenge. Our knowledge of the properties of soft x-ray synchrotron radiation and its proven capabilities to determine the structure as well as the electronic and magnetic properties of materials leads us to believe that such radiation is well suited to gain unique new information on artificial materials on the desired length and timescales.

- **Environmental and Interface Science**

In an environmental science context, chemical and biological processes at complex interfaces among natural solids, organisms, and aqueous solutions or gases control the composition of the environment and the migration, toxicity, and bioavailability of environmental contaminants.

An understanding of these processes at the molecular-nm scale under reactive conditions is essential for predicting the behavior and fate of contaminants and for developing new remediation technologies. Soft x-ray photon-in/photon-out techniques, with their chemical specificity, are ideally suited for in situ environmental studies.

- **Highly Correlated (Complex) Materials**

The diversity of spectacular properties of highly correlated materials has caused a paradigm shift in our basic understanding of solids in general. These materials have had and will have a tremendous impact in everyday technological applications, and they are forcing standard solid state textbooks to be rewritten. The uniqueness and diversity of these materials are undoubtedly associated with the temporal inhomogeneities in charge, dopant concentration, and spin densities, which couple to lattice distortions, breaking the translational symmetry. It is these dynamic inhomogeneities on a nanometer-length scale, which can be probed in detail with high-resolution soft x-ray photon-in/photon-out scattering techniques. With appropriately designed polarization control in the undulator, the charge, spin, and lattice excitations can be separated, atom by atom.

- **Electronic Polymers:**

Combining the desirable processing and structural properties of polymers with the electronic functionality of a metal or semiconductor, organic conjugated polymers serve as active materials in prototype applications such as light emitting diodes and organic transistors. Many chemical and physical properties of polymers are governed by a localized functional group (e.g., sulfur-containing heterocycles such as thiophenes) embedded in the polymer chain. Photon-in/photon-out experiments provide an important pathway to probe the valence and conduction band states of these functional groups associated with the important chemistry and physics in these materials, without the degradation resulting from sample charging and ligand-field effects associated with charged particle probes. Consequently, the crucial, localized phenomena can be probed selectively by high-resolution soft x-ray fluorescence spectroscopy, where the site selectivity is provided by the x-ray fluorescence “tag.”

- **Biomaterials**

In this new millennium, there will be a rapid development in materials science, making use of recently gained knowledge in bioscience. For example, in medical applications, it is important to understand how modern biomaterials (e.g., medical implants, contact lenses, or artificial joints) can stimulate the body’s natural ability to heal. There is also a fast growing area of materials that mimics a biological function. This can be small biomolecular motors which through a transmitted substance can provide a mechanical motion. Another important question is how the industrial society can find more efficient means for the production of materials, chemicals, and energy. Traditional chemical production is characterized by high-energy consumption and the generation of huge amounts of waste that are often environmental hazards. Nature produces all products with minimum energy and waste using enzymes. There is a unique opportunity to create materials that mimic the functions of natural enzymes. For all biomaterials, it is surface or aqueous interfaces which are important for its properties; yet there is little known about these interfaces. Synchrotron radiation can play a key role by using photon in/out-based spectroscopies which are not restricted to a vacuum environment and can detect low concentrations using modulation spectroscopy. It is essential to detect extremely low concentrations of biological molecules and antibody responses using biosensors.

1.1 Why Use Soft X-Ray Photon-In/Photon-Out Probes?

In the last 20 years of intense basic research and synchrotron-related instrumentation development, the scientific community has made tremendous progress in developing new spectroscopic techniques to study the electronic structure of atoms, molecules, and solids. In the area of soft x-ray photon-in/photon-out techniques, progress has been even more spectacular, because many of these experiments could never have been accomplished without the unique qualities of synchrotron radiation—

brightness, coherence, tunability, and controlled polarization. With the advent of third-generation undulator-based synchrotron radiation sources, soft x-ray scattering has reached a new stage in its evolution. It is time to shift the emphasis from spectroscopy for spectroscopy to the application of these powerful techniques to solve contemporary problems in a wide range of scientific and technological areas. Because these techniques employ photons as a probe and also as the carriers of information (photon-in/photon-out technique), it offers some unique and valuable advantages. Most of these are derived from the fact that photons are tunable in energy, carry polarization, have a large penetration depth (up to 1 μm) in materials and water, are insensitive to large electric and magnetic fields, and exhibit coherent properties. The wavelength of soft X rays is ideal for the world of nanotechnology. The advantages of synchrotron-based soft x-ray photon-in/photon-out probes can be summarized as follows:

- Soft X rays have the ideal wavelength to probe materials on the nanoscale, 1–10 nm.
- The long penetration depth allows true bulk properties to be probed. Photons of this energy also penetrate liquids, enabling the study of electro-chemical processes at the solid liquid interface or of biological samples in their natural wet state
- Tunable wavelength makes this probe site specific via excitations of core electrons.
- Polarization control enables the experimenters to probe either spin, electronic, or lattice excitations with specific symmetry of a chosen atom or molecule.
- Resonant scattering with new high-resolution spectrometers offers the capability to probe spin, charge, and lattice excitations at the kT energy scale.
- Photons are insensitive to most external probes such as electric and magnetic fields and pressure. Samples can be investigated under extreme conditions.
- Coherent properties of soft x-ray radiation promise to yield new information about the spatial and temporal evolution of materials on the nanometer-length scale. In principle, resonant scattering would make this technique element specific.

1.2 What is Possible?

The charge to the attendees of this meeting was to *dream* about what could be done with soft x-ray photon-in/photon-out experiments to change the way we think—to cause a paradigm shift in a given field. Some of our dreams and vision of the future are presented in section 2, ranging from 10-nm spectral microscopy of microbial-mineral interactions, temporal and spatial imaging of strip phases in superconductors, biomimetic catalysis, nano-artificially structured materials, ultrasensitive modulation spectroscopy, etc.

The dream of the people involved in the new era of soft x ray science is that the curiosity-driven techniques they have developed in the recent past will provide the tools required to characterize and understand the properties of complex solids and processes on the nanostructure scale.

1.3 What is Needed?

The recommendations of this workshop for synchrotron beam lines or facilities for the advancement of soft x-ray photon-in/photon-out-based science and technology are presented in section 4, and they are summarized here in the following three general recommendations:

- It is crucial for the advancement of soft x-ray science and for synchrotron radiation in general to expand the user base to include a much wider clientele than just those people interested in synchrotron radiation research. This will require soft x-ray beam lines that are user friendly and facility staffed.
- Soft x-ray beam lines and end stations that have already received funding must be finished according to the specifications outlined in this document.
- New frontier, highly coherent, high-resolution, etc., facilities need to be initiated and funded. A description of what we believe is required and justified is given in section 3.

2.0 A Glimpse at the Future

2.1 10-nm Spectral Microscopy of Microbial-Mineral Interactions

Single cell organisms, including bacteria and algae, constitute the largest diversity of life on earth. They are essential to the life of higher organisms, including man. Microorganisms have been discovered nearly everywhere scientists have looked, even in what are known as “extreme environments” of high temperature or in the presence of concentrations of chemicals that would ordinarily be toxic to other forms of life. There has even been research suggesting that micro-organisms were present in meteorites of Martian origin, and the first clues for life on other planets will probably come from searches for microorganisms in extra-terrestrial soils.

In the 1970s, classes of microorganisms (species of *Geobacter* and *Shewanella*) which directly use inorganic species as part of the electron transport chain of respiratory metabolism were discovered. For example, the use of transition-metal ions (Fe, Mn, and others) as electron donors or acceptors is accomplished both by strict anaerobic bacteria (*Geobacter*) and by facultative anaerobes (*Shewanella*). Since their initial discovery, the importance of these microorganisms in environmental chemical reactions has become increasingly apparent. Today, there remain fundamental questions regarding the mechanisms of transition-metal-mediated metabolism, which can be addressed by soft x-ray spectromicroscopy. In the future, it is expected that genetically modified organisms can be utilized in useful technologies, such as bioremediation.

Through basic research, geomicrobiology will be used in an attempt to build an understanding of how interfaces are modified by both biological and abiotic processes in the environment. As our understanding of these complex interfaces grows, ways to use our knowledge to engineer biofilms for useful purposes will be explored. Since the beginning of history, mankind has benefited from microorganisms that assist us in producing (and digesting) food. In the future, a detailed understanding of the cell-surface interface will result in improved anti-corrosion films; ways to remove toxic materials from the environment by biological processes; and even new, biologically inspired, routes to nanostructured materials and devices.

Interfaces in the environment are far from ideal laboratory specimens. They are spatially heterogeneous, contain a number of unknown materials, and include compounds of both inorganic and biological origins. While a multiplicity of synchrotron radiation methods has been developed to study “model” interfaces, the study of problems in geomicrobiology have been much more difficult because of intrinsic characteristics of the problem. These include spatially small features, the presence of water, complex chemical structures, and high sensitivity to many external factors, such as pH, temperature, and ionic strength. All these issues combine to demand techniques that can be used to study actual environmental interfaces, such as mineral-microbe interfaces, in conditions that closely match those found in the environment.

With the recent introduction of certain photon-in/photon-out probes, it will soon be possible to complete the study of relevant mineral-microbe interfaces with both the spectroscopic precision required and the spatial resolution set by the microorganisms. In Fig. 1, a model of a cell-surface interaction is shown. The important length scales range from the thickness of the mineral-water interface (1 nm) to the size of a protein (10–20 nm), to the size of a cell wall (20–100 nm), to the size of a microorganism (100-nm wide and a few microns in length).

The proposed “grand challenge” experiment is to completely determine the speciation of complexes in the mineral-microbe interface, with a spatial resolution set by the size of an individual protein: about 10 nm. The list of fundamental, unanswered questions that will be addressed is large and includes the following:

- What is the relative role of biotic vs. abiotic mechanisms in transition-metal redox reactions?
- What is the chemical nature of intracellular biominerals?
- What is the nature of the exopolymer extruded by microorganisms as they attach to mineral surfaces?

- How do microorganisms alter the chemistry of mineral surfaces?
- What are the species that adsorb on biologically produced minerals.

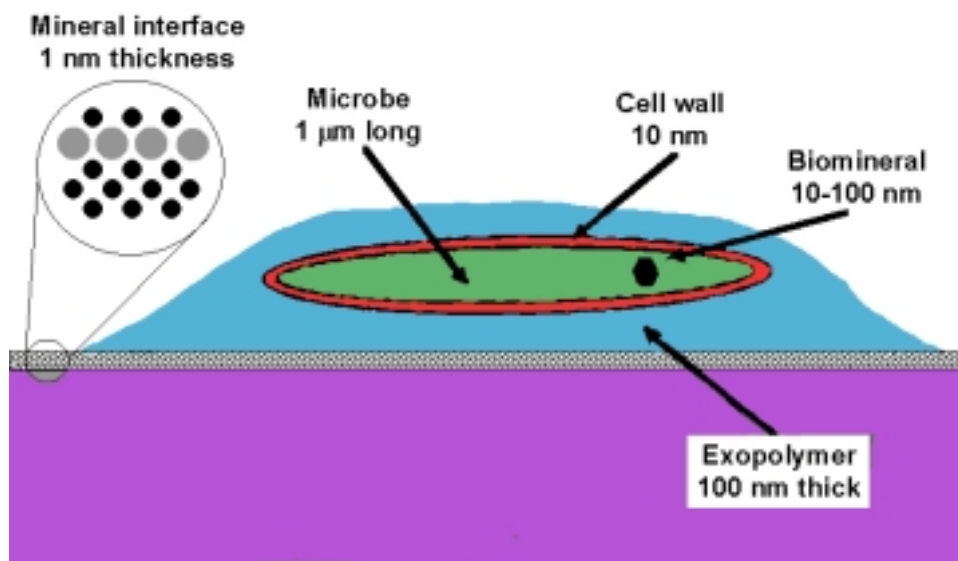


Fig. 1. Model of a cell-surface interaction. Important length scales range from the thickness of the mineral-water interface (1 nm) to the size of a protein (10–20 nm), to the size of a cell wall (20–100 nm), to the size of a microorganism (100-nm wide and a few microns in length).

The knowledge gained from these experiments, in addition to fulfilling the need to understand biodiversity on our planet, will also become the guide for searching for life outside Earth. In the decades to come, geological specimens will begin to arrive from our sister planet Mars. It will be necessary to be ready with the tools to search for signatures of life in these specimens. The 10-nm x-ray spectromicroscope will be one of these important tools.

2.2 Closing the Structure-Function Loop in Complex Materials

Complex inorganic materials exhibit a diverse array of phases that are spawned by strong coupling between electronic, spin, and structural degrees of freedom. The phase diagram for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, shown in Fig. 2, provides a prototypical example of the abundance of properties such materials can exhibit. An important goal is to be able to close the “structure-function” loop in such systems so that materials with useful properties can be produced and optimized. Soft X rays offer powerful and unique capabilities that will help to close this loop. For example, the structure of such materials is determined largely by local interactions that often operate at relatively high energy (e.g., exchange, correlation, hopping integrals, and electron-lattice couplings). These interactions normally involve valence $3d$ electrons in first-row transition-metal oxides and $4f$ valence electrons in the lanthanides. Soft x-ray absorption, emission, and resonant scattering using excitation into and/or out of $2p$ or $3p$ and $3d$ -core levels, respectively, provide incisive, site-selective probes of these valence shells. The exotic phases like those of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ result from a delicate interplay between these high-energy degrees of freedom that is manifested at a lower energy scale, comparable to $k_B T$ and a length scale of typically 1–10 nm. The charge-ordered or “striped” phases provide an excellent example of this phenomenon that may provide an important key to understanding high- T_c superconductivity and colossal magnetoresistance. Such exotic thermodynamic and transport properties are determined by the low-energy excited states that can be understood only by probing the material’s dynamical properties—dynamics is intimately connected to function. Dynamic soft x-ray scattering, an emerging technique that is the analog to dynamic laser light scattering, offers the unique potential to probe these properties by virtue of the excellent match between the relevant length scale and the soft x-ray wavelength and the ability to tune near the above core thresholds.

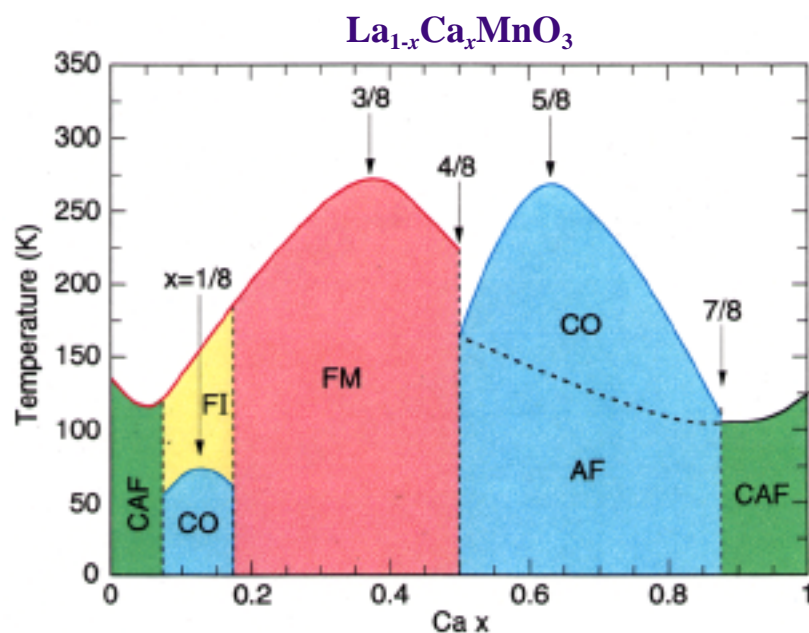


Fig. 2. Phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. Data are from Cheong, Lopez, and Hwang.

This ability of soft X rays to help understand and utilize the structure-function loop is certainly not limited to oxides and lanthanides. Indeed, very similar statements could be made concerning (1) the interplay between exchange interactions, domain formation, and hysteresis in band ferromagnets; (2) the role of local hydrophobic and hydrophilic interactions and macroscopic phase behaviors of polymers and block copolymers; and (3) the impact of local sequence and associated hydrogen bonding network in biopolymers on the large scale, low-energy librations and fluctuations that are key to biological functions. In each of these cases, the combination of soft x-ray spectroscopy with dynamical measurements using soft x-ray dynamic scattering or possibly pump-probe soft x-ray microscopy can provide unique and powerful capabilities to relate structure to function.

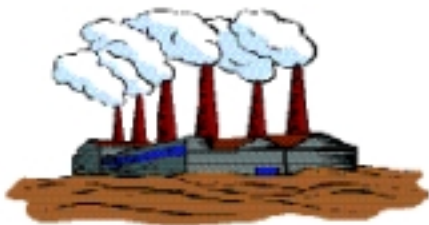
2.3 Biomimetic Enzyme Catalysis

The fundamental purpose of the modern industrial society is to provide mankind with products which are essential for, or simply demanded by, our society. In order to achieve this, *chemicals*, *materials*, and *energy*, which constitute the base platform for all activities, must be produced first. This production has high energy demand, has no recycling back to its source, and causes a severe threat to the earth's environment. In the next millennium, new ways have to be found to produce these if our industrial society is to be transformed. In this context, there exists an important challenge for us to apply basic interdisciplinary research to open new horizons.

If one looks at the way nature works, it can be seen that chemicals and materials are produced with minimum energy and minimum waste in an elegant way. For instance, where the industrial Haber-Bosch process for ammonia production uses a catalyst to break the strongest bond first, the nitrogenase enzyme in nitrogen-fixating bacteria bypasses this effort by adding the hydrogens one by one until the bond finally breaks. As a result, the industrial process requires high temperature and pressure while each step in the enzymatic reaction is nearly isothermal and neither is energy wasted nor waste products generated (Fig. 3). The processes are arranged in a perfect order where all steps have a meaning in the chain of events, making nature both beautiful and miraculous. The whole process in a natural material is in balance and symbiotic with its surroundings. In this perspective, our present industrial society can be regarded to be well behind the evolution seen in nature.

Nearly all industrial chemical processes are based on catalysts to enhance the reaction rate. These are usually heterogeneous catalysts and are often in the form of dispersed metal particles on an oxide surface. They have a high conversion rate, but require high-energy consumption because the reaction takes place at high temperatures and pressures. Furthermore, selectivity is often not very

Industrial Catalysis



- **low selectivity**
- **energy consuming**
- **environmental waste problems**

Natural Enzymes



- **100% selective**
- **energy efficient**
- **symbiosis with surroundings**

Fig. 3. The industrial society produces chemicals and materials with high-energy consumption and pollutions whereas the enzymes in nature make the same with low-energy costs and where all processes are in symbiosis with the surrounding environment.

high, resulting in many byproducts, which need to be separated at high cost in terms of further energy consumption and even more waste. Enzymes are the reaction catalysts of biological systems. They have extraordinary catalytic power, far greater than heterogeneous catalysts. In particular, they have a high degree of selectivity both with respect to products and reactants and consume a minimum of energy because they can function in aqueous solutions, under atmospheric pressure and at room temperature. The enzymes usually work in a cycle with many different reaction steps taking place in different parts of the enzyme. Nature, through evolution, has chemically designed various parts of the enzyme in order to perform each reaction step in such a way that the complete cycle is optimized. In heterogeneous catalysis, a material based on trial and error is often chosen; research is then later carried out to understand how the catalyst functions and why a particular choice of material is the best. Heterogeneous catalysts are very complex, to a large degree, thus inhibiting a detailed understanding of the processes on a molecular level.

In homogeneous catalysis, the situation is very different. Here, one works in solution, often with an organometallic complex as the active catalyst in a sequence of coupled reactions forming a redox cycle. Electron and proton transfers are carried out in a number of steps forming a complete cycle in a way similar to enzymes. A deep understanding of the bonding of molecules to the metal complex and of the different reaction steps at the molecular orbital level has already been obtained and can be applied. Significant examples exist where the stepwise catalytic cycle has been designed by putting together each step in a creative manner. The problem with homogeneous catalysis is the separation of catalyst and products and the instability of the catalyst leading to limited industrial applications.

The recent development of protein crystallography using synchrotron radiation has led to a large number of structure determinations of enzymes. This has had a strong impact on the efforts to find mechanisms for the enzyme activity because knowledge of the detailed chemical structure of the metal center is a prerequisite for any theoretical modeling of the reactivity. For a number of important enzymes, including nitrogenase, the reaction mechanisms and functions of the enzymatic processes around the metal center have recently been elucidated using quantum chemical methods. Through the use of these new experimental and theoretical tools, structure and mechanism have been combined recently in a unique way to clarify the central functions in some metallo-enzymes.

At the present time, there is a new opportunity to introduce the next step in the design of heterogeneous active systems by combining the recent knowledge of enzyme mechanisms and creative homogeneous catalyst design with the support and stability of solid surfaces that heterogeneous catalysts provide. The essential feature of enzyme systems is that they work with low barriers in nearly isothermal steps. This can be introduced to a heterogeneous environment in two ways: (1) by taking the catalytically active component of already functioning homogeneous biomimetic catalytic cycles out of solution and immobilizing them on a substrate and (2) by building a catalytically active surface that works along the same principles as a known enzyme system.

The recent development of x-ray emission spectroscopy to atom specifically probe the occupied molecular orbitals of complicated surface-adsorbed molecules has significantly increased the level of understanding of the surface chemical bond. In combination with theoretical calculations of the molecular orbital structure, a very detailed picture is now emerging which indicates the possibility of transferring the approach of reaction design from homogeneous catalysis to surface chemistry. It is essential that these studies take place in situ in a gaseous or liquid environment. Electron spectroscopy has been implemented for gaseous or liquid environments through differential pumping, but it is impeded by the necessity of a vacuum environment. The latter limits the type of liquids and high-pressure gases which can be investigated. In contrast, x-ray-in/x-ray-out spectroscopy makes use of the penetrating power of the X rays through the use of newly developed windows to contain the gas or liquid in a cell. Thus, the gaseous or aqueous sample can be studied in its natural environment.

2.4 Nanofabrication with Soft X Rays

Soft X rays offer a number of interesting options for creating nanometer-scale patterns. The shorter wavelength of soft X rays alone makes it possible to extend the resolution of conventional photolithography to significantly smaller feature sizes (10–100-nm size range). This approach is presently being explored by the EUV consortium at the Lawrence Berkeley National Laboratory (LBNL) and at the Center for Nanotechnology at the Synchrotron Radiation Center (SRC) as a possible means for extending integrated circuit manufacturing technology to smaller length scales. This is not the only project with soft X rays that is worth pursuing in relation to nanofabrication however. For example, the interference of coherent soft x-ray beams can be used to create nanometer-scale interference patterns in photoresist which can be transferred to a substrate material by plasma etching. As shown in Fig. 4, linewidths as narrow as 20 nm have been achieved.

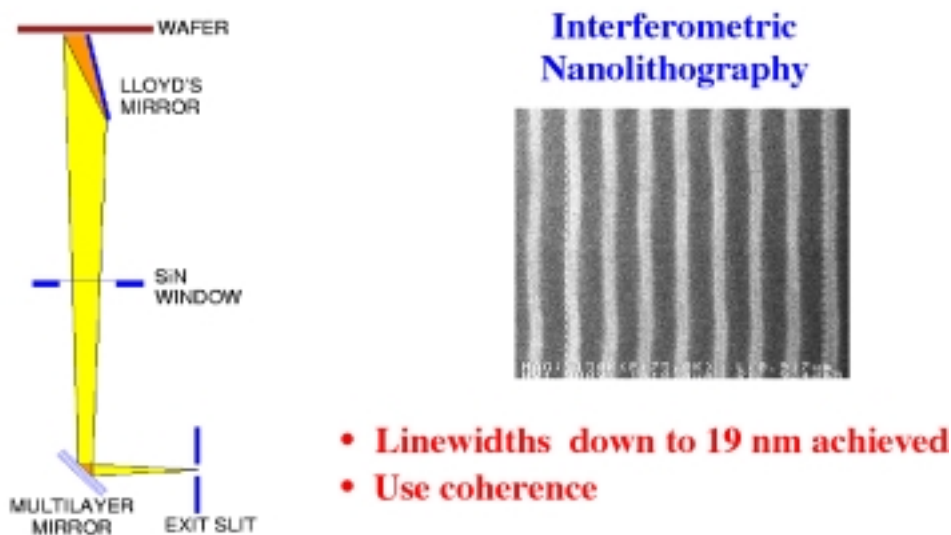


Fig. 4. 20-nm-wide lines obtained from an interference pattern of two plane waves split off from an undulator beam.

There are numerous possible applications of such structures, including, for example, the fabrication of photonic band-gap structures. Photonic band-gap structures that operate in the important near infrared wavelength range, which is used in optical communication, would benefit from the enhanced resolution possible with shorter wavelength lithography. The value of soft X rays in nanofabrication is not limited to providing a higher resolution exposure tool for photoresist. The chemical specificity of soft X rays could, in principle, be used to selectively decompose a reactive species on the surface and thereby write lines directly. Conversely with suitable choice of resist materials and x-ray wavelengths, it may be possible to photochemically decompose a surface layer and achieve a direct write capability without the need to develop a resist. Such a technique could lead to important new advances for nanofabrication and electronic and optical device manufacture.

2.5 In Situ Studies of Li-Ion Batteries

An increasing demand for on-the-go power in portable electronics and vehicles in urban areas spurs the development of low-weight and high-capacity batteries, driving a continuously growing multibillion dollar market. The domination of NiCd batteries is being challenged by Ni-metal hydride and Li-ion batteries. Specifically, Li-ion batteries have attractive properties, such as long-term storage capacity and low weight, and do not suffer from the memory effects that make Ni-Cd batteries lose capacity in typical everyday use. A number of issues are being addressed in this research apart from the obvious ones mentioned concerning cost, safety, cycling capacity, and environmental effects. This work involves scientific investigations of various structural and electronic properties of electrodes and charge transport media in the processes of charging and discharging of batteries.

There has been no good way to study the electronic structure of battery elements under real conditions because available methods have not offered the penetration needed to probe the electrolyte. The recent development of soft x-ray emission spectroscopy could provide the means to obtain information of crucial importance to understand the chemical processes taking place in battery operation (Fig. 5). The main asset of the spectroscopy used in this context is the ability to perform in situ studies of devices in operation. By making the electrode structures sufficiently thin (it is conceivable that some a few hundred nm thickness would be suitable), it would be possible to record resonant soft x-ray fluorescence that reveals detailed information about valency, oxidation, and charge-induced effects in the ion-accepting layer. Electronic properties of both anodes and cathodes, as well as the charge transport medium, could all be studied under realistic conditions.

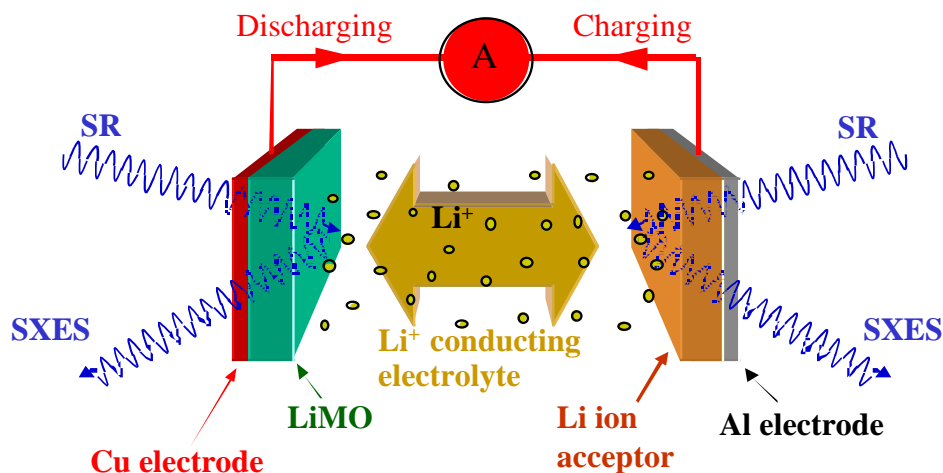


Fig. 5. In situ study of electrochemical processes by SXES.

2.6 Understanding Bioavailability of Toxic Organic Contaminants at the Molecular Level

Organic molecules (biopolymers, humic substances) derived from biological processes are common in soils, natural waters, and the atmosphere and play a major role in the chemical speciation of elements and interfacial biogeochemical reactions. Several of these molecules also constitute a substantial portion of the cell structure in biological systems. In addition, various toxic xenobiotic compounds, such as polycyclic aromatic hydrocarbons (PAHs), and chlorinated hydrocarbons, such as PCBs, have been released into the biosphere at alarming rates from anthropogenic activities. Contamination in soils and sediments has resulted from the spillage or leakage of petroleum products; the burning and disposal of organic-based industrial products; agricultural uses of pesticides and herbicides; and the disposal of a wide variety of personal care products, human and animal wastes, and other organics in municipal waste streams. A number of these contaminants currently pose major health hazards to humans and other organisms and vary greatly in solubility in aqueous solutions, depending on their polar vs. nonpolar nature. Soluble, polar species can be transported great distances from their source, whereas nonpolar species tend to be relatively insoluble and thus are more localized near their sources unless they are transported as colloidal aqueous species or

enter the atmosphere as volatile species. An example of this class of organic contaminants are the PAHs, which include a number of carcinogenic species such as benzo(a)pyrene. Many of these contaminants are degraded at different rates by microbial organisms in soils and natural waters, resulting in a number of byproducts that can vary in toxicity and can bind heavy metals, in some cases resulting in even more toxic compounds than either the inorganic or organic component alone. An example of this is the extremely toxic methyl mercury compounds produced by the methylation of mercury by sulfate-reducing bacteria as a co-metabolic product.

Sorption of organic contaminants on solids and natural organic matter (NOM) in soils and sediments is an important process that can effectively sequester them and dramatically reduce their mobility and potential bioavailability. However, very little is known about their sorption mechanisms, strength of binding to surface sites on solids or functional groups on NOM, and spatial distribution at the sub- μm to mm scales. Depending on the polar vs. nonpolar nature of organic molecules, they can bind in different fashions, as discussed earlier. There is a particular need to understand the hydrophobic binding of nonpolar organic molecules, such as PAH's, to particle surfaces, as this type of binding is generally responsible for their sorption and sequestration in soils and sediments, yet it is poorly understood (see Fig. 6).

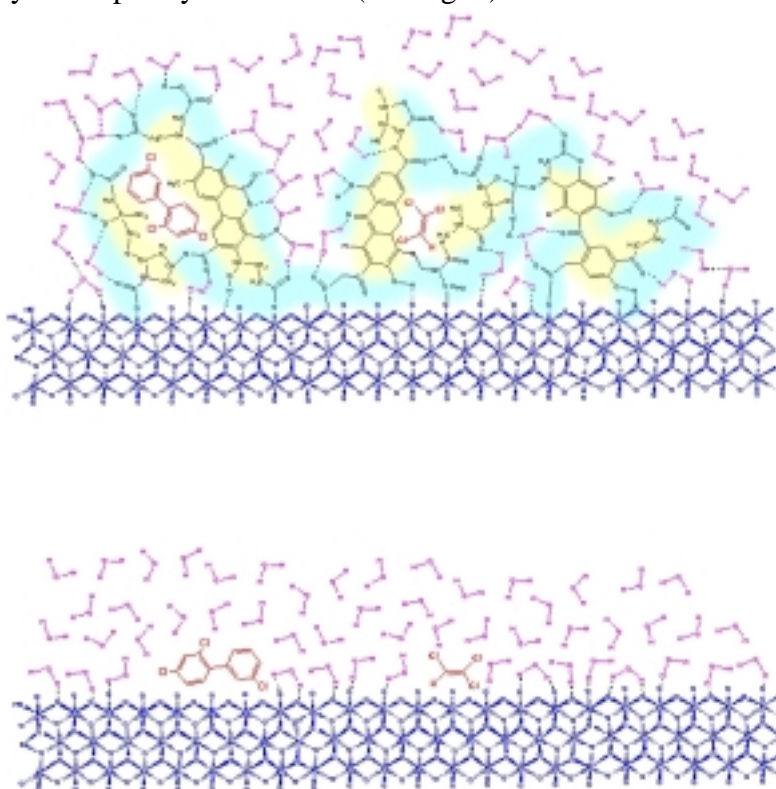


Fig. 6. Schematic model of the hydrophobic interactions of the non-polar organic molecules PCB (polychlorinated biphenyl) and TCE (trichloroethylene) at a metal oxide-water interface. Both PCB and TCE are common organic pollutants in contaminated soils and groundwater. They may be sequestered by hydrophobic interactions at environmental interfaces, which could reduce their potential bioavailability to humans. However, the nature of these hydrophobic interactions, including the structure of water in the vicinity of the hydrophobic molecule, are not well understood at a molecular level. The top figure shows PCB (left) and TCE (center) molecules embedded in a model fulvic acid molecule near a metal oxide surface, with hydrophobic regions shaded in yellow and hydrophilic regions shaded in blue. The bottom figure shows only PCB (left) and TCE (center) molecules interacting with the metal oxide surface.

Soft x-ray spectromicroscopy studies of organic molecules on environmental solids, such as Al-, Mn-, and Fe-oxyhydroxides could provide unique information on their geometric structure, mode of surface binding, and electronic structure and bonding. Knowledge of the functional group chemistry (protonation, metal, and mineral surface complexation of C-, N-, O-, P-, S-, and Cl-groups) and macromolecular structure of xenobiotic organic contaminants and natural organic matter is essential for predicting their behavior in the environment. In addition, in situ chemical information from nanoscale regions (~ 10 nm) of organic samples will help in understanding the functional group heterogeneity and structure-function relationships of cell membranes and macromolecules in biological systems. Such studies would be most useful and informative if performed under in situ conditions (i.e., with a bulk aqueous solution present at ambient temperature and pressure) as these are the typical conditions under which they exist in the natural environment. Such in situ studies will require photon-in/photon-out spectroscopy because of the presence of water or high gas pressures. In situ x-ray absorption spectromicroscopy at the C, N, and O *K*-edges coupled with x-ray emission spectroscopy at the energies of the various absorption resonances will provide unparalleled information about structure and bonding of these molecules at the solid-aqueous solution

interface. In the case of hydrophobic bonding of nonpolar organics to solid surfaces, it is essential that this research be coupled with complementary x-ray absorption and emission studies of the structure and bonding of water near solid-solution interfaces and surrounding the nonpolar organic molecules, as the structural rearrangement of water in these regions will play a major role in hydrophobic bonding.

Specific questions to be addressed include:

- What is the nature of the binding sites on solid surfaces to which organic molecules attach?
- How is the organic species attached to the solid surface (monodentate, bidentate, etc.) and how does this mode of binding affect the ease of desorption of the organic species?
- What is the nature of hydrophobic bonding of non-polar organic species to solid surfaces?
- How does the structure and bonding of water in the solid-solution interface region and around nonpolar organic molecules differ from that of bulk water?

2.7 Ultra-Sensitive Modulation Spectroscopy

For the emerging area of spintronics (i.e., magnetoelectronic devices based on spin transport, spin accumulation, and stable microscopic magnetization domains), photon-in/photon-out x-ray magnetic circular dichroism (XMCD) spectroscopy offers important advantages over conventionally employed photon-in electron-out techniques. First, photon-in/photon-out techniques can be used in external magnetic fields which, for example, are of great importance in the exchange bias problem. Secondly, they are compatible with electrical current flow through the investigated sample which is required for magnetotransport measurements. Finally, photon-in photon-out experiments can be carried out in different modes offering variable depth sensitivity.

The major question is how to improve sensitivity to the unprecedented levels required by forefront scientific problems. The answer lies in phase-sensitive detection schemes based on rapid polarization modulation. The basic principle is the suppression of background by locking on to the signal that changes with polarization—i.e., the very signal due to order in the sample. Changing x-ray polarization is trivially possible at bending magnet sources by preferential selection of the radiation fan relative to the electron orbit plane, and insertion devices with variable polarization exist at many synchrotron radiation laboratories around the world. However, rapid modulation of the x-ray polarization while maintaining both the energy position and resolution of the monochromatized X rays remains an unsolved problem. However, there are no fundamental reasons why new insertion device beam lines could not be designed with full and rapidly variable (about 100-Hz) polarization control, and this is one of the recommendations of this workshop.

Figure 7 provides a glimpse of what is possible. Shown are the element specific magnetization loops from a multilayer consisting of 1-nm-thick Co and 1.3-nm-thick Cu layers. The loops were recorded by lock-in detection of the XMCD reflectivity from the sample using a new elliptically polarizing wiggler device that modulates (22 Hz) the x-ray polarization from right to left circular. Note that the Cu moment is only about $0.02 \mu_B$, and it arises mostly from interface atoms. In contrast, the Co moment is about $1.6 \mu_B$, a typical value for bulk ferromagnets (FM). Obviously, this technique offers great sensitivity, and it is compatible with application of an external magnetic field. For a NiO/Co exchange bias structure, the signal from the uncompensated Ni interfacial spins is expected to be of comparable size as that shown for Cu in the right hand panel. Detailed comparison of the shift of the FM and antiferromagnetic (AFM) magnetization loops and of the size of the XMCD signal (proportional to the magnetization) for positive and negative field directions will give unique new information on the origin of the exchange bias and the increased coercivity, typically seen in devices.

In the future, it is important to be sensitive to even weaker and more diluted order effects. Consider the phenomenon of spin accumulation in spintronics devices. A Co/Cu/Co spin valve with antiparallel alignment of the magnetization directions in the two Co layers is assumed. In the presence of electrical current flow through the device, there is preferential spin injection (spin-up) into the Cu

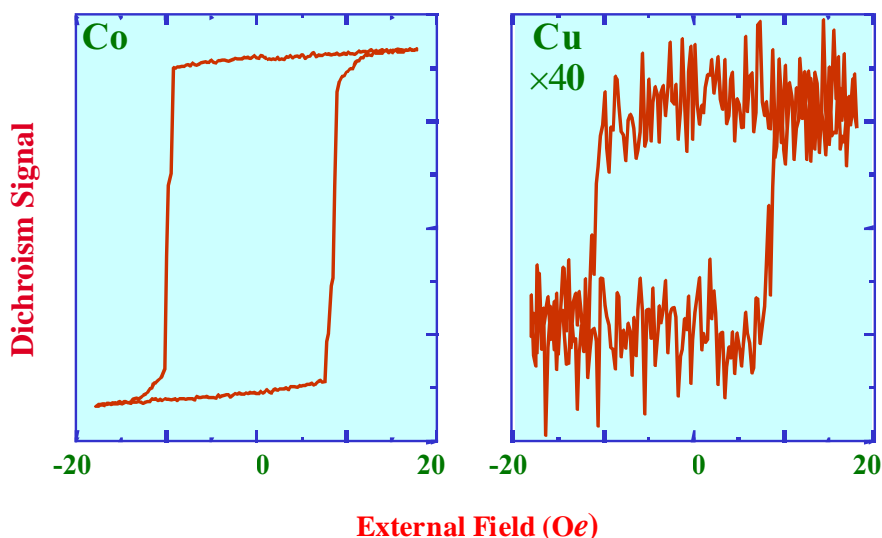


Fig. 7. Element specific magnetization loops from a multilayer consisting of a 1-mm-thick Co and 1.3-nm-thick Cu layers.

at one interface and preferential spin drain (spin-down) at the second interface because of the opposite spin alignment in the two Co layers. This leads to a net spin accumulation in the Cu layer which results in a very weak magnetic moment per Cu atom. The weak moment per Cu atom due to spin accumulation can be estimated using a current density of 10^5 A/cm² which is easily realized in practice by use of a patterned structure of 10×10 μm and a current of 0.1 A. Depending on the efficiency of spin transport through the interface, a moment of 10^{-3} – 10^{-4} μ_B per Cu atom is estimated. This is smaller by one to two orders of magnitude than the Cu moment shown in Fig. 7. Clearly, this calls for improved experimental capabilities which, however, appear to be within our reach. Our dream beam line would consist of a soft x-ray variable polarization undulator with a spectral range spanning from 250 to about 2500 eV, covering the important *K*-edges of C, N, O, Al, Si, and S; the *L*_{2,3}-edges of elements such as Mn, Fe, Co and Ni, Cu, Ga, Ge, and As; and the *M*_{4,5}-edges of the rare earths. Such a beam line with increased brightness, polarization purity, and polarization modulation capabilities would open the door for investigations of weak order phenomena not only in magnetic systems but also in polymers and transition-metal oxides.

2.8 Soft X-Ray Inelastic Scattering with kT Resolution

The fact that the energy resolution of resonant inelastic soft x-ray scattering is not limited by the lifetime broadening of the core-excited state creates many exciting possibilities. It would be invaluable to be able to look at the charge, lattice, or spin excitation in highly correlated materials with kT-resolution. In 2.8.1 and 2.8.2, two paths to very high resolution instruments for soft x-ray emission spectroscopy are suggested.

2.8.1 Plane Grating Spectrometer

Instruments for soft x-ray emission spectroscopy are usually based on spherical gratings in Rowland geometry. Often, they use area detectors, which offer multichannel capability and large acceptance angles. The size of the instrument and the spatial resolution of the detector generally set the limit in resolution, whereas the maximum usable size of the grating is an important factor for limiting the sensitivity. The grating size is related to the imaging errors and thus to the spectral resolution.

Increasing the grating size considerably without losing resolution could be done if a plane grating is used instead of a spherical grating. In this case, collimation and focusing would be made with separate mirrors. By this scheme, it would be possible to achieve substantially increased sensitivity of a grazing incidence instrument. Obviously, there is a point where the total reflection condition sets a limit for the acceptance angle. A typical acceptance angle in the plane of dispersion for a grazing incidence grating instrument is <10 mrad. The critical angle of total reflection for a few

hundred eV photons is typically <100 mrad, depending on material, which suggests that there would potentially be up to an order of magnitude in acceptance angle to be gained. However, the grazing incidence required for total reflection limits the gain because of the size of the optic needed. By applying a multilayer coating to the mirror, less grazing angle of incidence can be used, allowing smaller size mirrors. One drawback, however, would be the necessity to have sets of mirrors to cover the different x-ray edges, because the multilayer mirrors have very narrow bandpass. Also, the multilayer might have to be graded (i.e., it would have a varying period over the mirror surface in order to compensate for the varying incidence angle).

An instrument of the suggested type optimized for the Cu $3p$ edge could collect 50 mrad in the dispersion plane and 200 mrad in the sagittal plane (presently used instruments accept some 50 mrad in the sagittal plane). The resolution at about 75 eV for a source size of 10 by 100 μm would be 10 meV. The considerably improved performance of this type of instrument has a price to be paid. The multilayer coating of the mirrors only offers high reflectivity for one atomic species (edge). However, there is certainly sufficiently interesting scientific problems to be addressed to justify the cost that this specialization causes.

It might be possible to avoid the use of multilayer coating if one can accept a large instrument and possibly also some loss in sensitivity. In this case, it might not be feasible to have the instrument rotatable in the vertical plane, something which is very useful in order to study linear dichroism effects. However, if one has access to a beam line with the provision to select the direction of polarization, such rotation is not necessary.

2.8.2 Fourier Transform Spectrometer.

Fourier transform spectroscopy (FTS) is a very successful method for the infrared and the visible, and it provides both very high resolution and sensitivity. Work has been in progress to push the technique down into the UV and vacuum range, but not until recently have there been real efforts to try to build an instrument for the ultrasoft x-ray region. The most challenging difficulties associated with an interferometer for the soft x-ray range are the fabrication of beam splitters and the alignment and movement of the optical components. The positioning and alignment of the elements of a soft x-ray interferometer have to be made with very high accuracy. For, example, for C K emission, the smallest path length difference has to be less than 2.5 nm, and the parallelism of the merged beams in the interferometer has to be of the order of 1 μrad or less. Considering advancements in positioning technology in recent years, these requirements can be met, although many problems related to vibrations, temperature stability, etc., must be mastered.

The potential of a soft x-ray Fourier transform spectrometer is very interesting. The sensitivity could be at least two orders of magnitude larger than for conventional instruments, and at the same time, the resolution could be pushed considerably. An instrument with a path difference scanning length of 1 mm would provide a resolution of 1 meV at the Cu $3p$ edge. Such an instrument is schematically shown in Fig. 8.

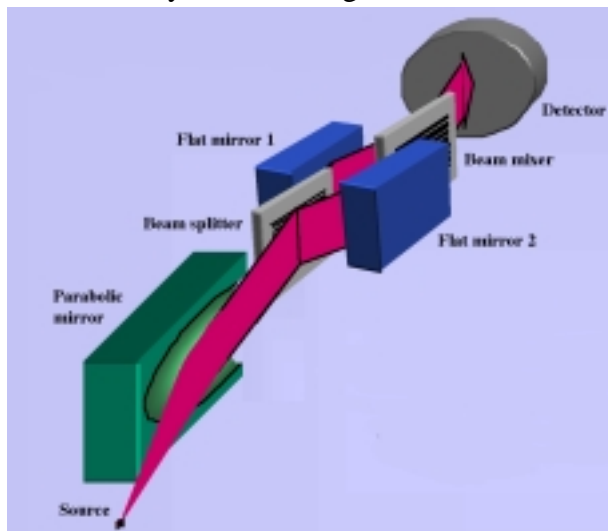


Fig. 8. Schematic of soft x-ray fourier transform spectrometer. Scanning the path length difference is made by rotating the beam splitter/flat mirror 2 assembly. The resulting beam shear is compensated by translating the beam mixer.

2.9 The Ultimate Soft X-Ray Facility—The Dream Machine

A remarkable variety of new (and sometimes old) materials whose properties cannot be described with traditional ideas has been discovered. These materials, usually involving $3d$ transition-metal oxides, are referred to as strongly correlated materials and include the high- T_c and colossal magnetoresistance (CMR) materials. “Clearly highly correlated electron systems present us with profound new problems that almost certainly will represent deep and formidable challenges well into this new century” [Birgeneau and Kastner in the special issue of *Science* **288** (2000)]. The underlying reasons for the spectacular behavior of these highly correlated systems remain a mystery, in most cases. New experimental techniques which will provide combined and simultaneous information on the spatial distribution structure, including the spatial distribution of spin, orbital occupation, and charge densities as well as the characteristic elementary excitations involving these degrees of freedom are needed. The ultimate soft x-ray facility (the dream machine) could be this technique.

The signature of these materials is the close coupling between the spin, orbital occupation, charge, and lattice degrees of freedom, which is illustrated schematically in Fig 9. The most well known coupling is manifested in the CMR behavior which occurs when a magnetic field is applied causing a simultaneous metal-insulator and ferromagnetic-paramagnetic transition. Fig. 10 is an artist’s representation of a mixed-valent manganese oxide, $A_{0.75}B_{0.25}MnO_3$, where A is the trivalent atom and B is divalent. In this case, Mn is mixed-valent, with 25% Mn^{4+} and 75% Mn^{3+} , exhibiting a combination of spin, charge, and orbital ordering. The charge ordering is shown by the differently colored Mn atoms. The spin orders because of the different moment on the different valent Mn ions: $3/2$ for Mn^{4+} and 2 for Mn^{3+} . Orbital ordering is a consequence of the occupation of the fourth d electron in Mn^{3+} and the accompanying oxygen Jahn-Teller distortions of the surrounding oxygen anions. The central region in Fig. 10 designated by the light green orbitals exhibits the local structure present even when long-range order is missing. This local configuration is an orbital/lattice/spin polaron and is shown in Fig. 10.

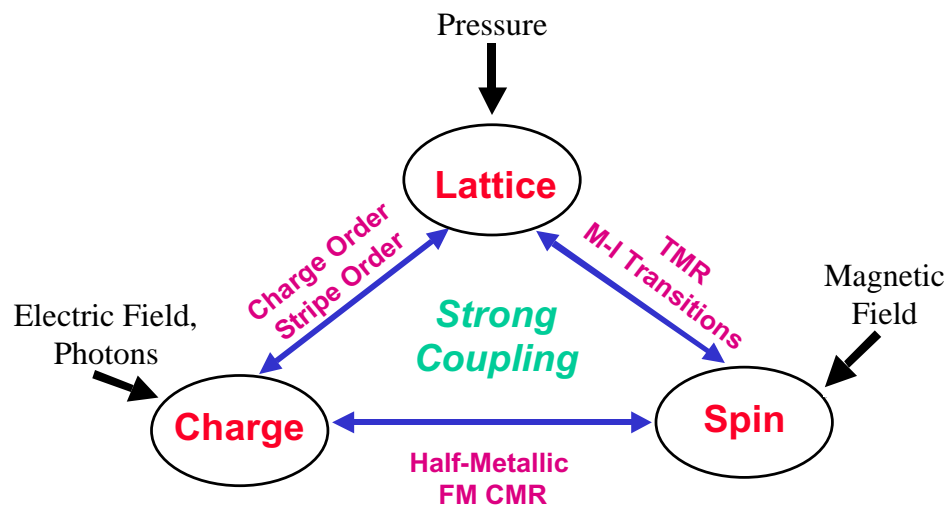


Fig. 9. Schematic illustration of the strong coupling between the spin, lattice, and electron degrees of freedom in transition-metal oxides. TMR is tunnel magnetoresistance, M-I is metal-insulator transition, and CMR is colossal magnetoresistance.

These strong correlations between spin-orbital charge and lattice degrees of freedom are apparently responsible for the CMR behavior in the manganates and, according to some, also are important for high T_c 's. There also seems to be a general trend in all these systems toward an intrinsic nanophase separation close to the phase boundaries (see Fig. 2 in section 2.2) in temperature, doping concentration, or magnetic field. Although there is no direct proof that this behavior (striped phases) dictates the properties of the high- T_c materials, there is growing evidence that dynamic mixed nanophases are an integral part of the CMR behavior. The length scales of these regions are in the nanometer range; they involve fluctuations of charge spin and orbital orientation which are, in general, too small to be directly observable with conventional scattering techniques.

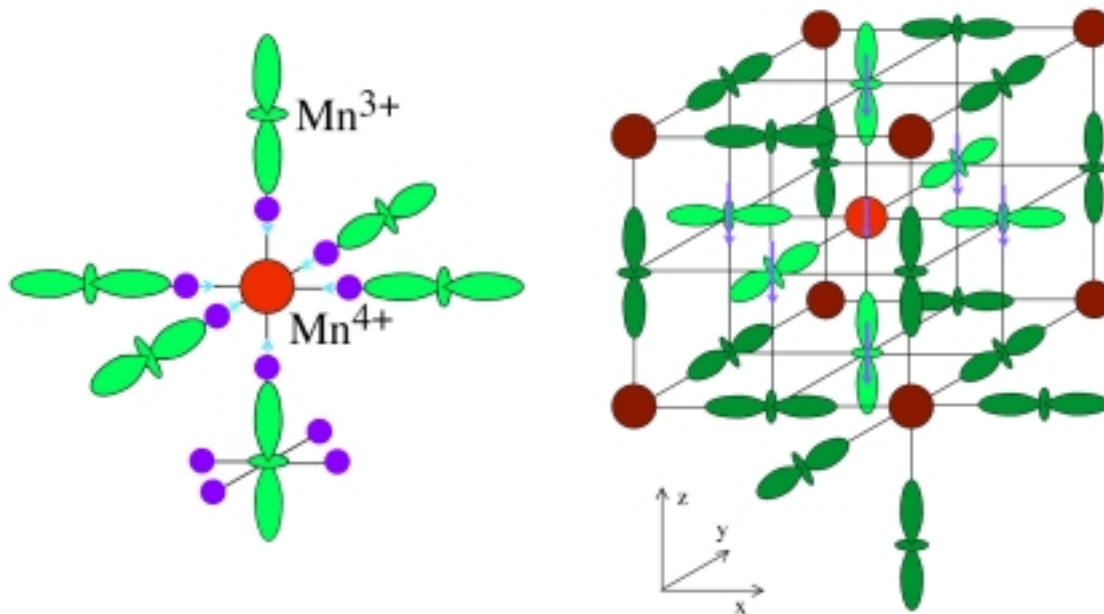


Fig. 10. Schematic representation of the charge, spin, and orbital ordering in a $A_{0.75}B_{0.25}MnO_3$ perovskite. In the center is a Mn^{4+} ion (round circle) with spin $(3/2)$ which is surrounded by six short bond length oxygens (purple) and six Mn^{3+} ions (green orbitals) with spin 2 ferromagnetically coupled to the central Mn^{4+} . The fourth 3d electron in the Mn^{3+} ions occupy the lobes as drawn, all pointing toward the central Mn^{4+} ion and to local long Mn^{3+} -O bond lengths. The right part shows only the local configuration around the Mn^{4+} ion. The Mn^{3+} are in addition to the oxygens shown in the figure surrounded by an additional 4 oxygens at shorter bond lengths, corresponding to the Jahn-Teller distortion. It is the orbital ordering and charge ordering which result in the peculiar magnetic structure with ferromagnetic clusters which are antiferromagnetically ordered in a lattice. This picture is not merely the fantasy of an artist, but indeed appears as the lowest energy state in a Hartree Fock calculation. (Reproduced with the permission of T. Mizokawa, University of Tokyo.)

The dream experiment. In principle, it should be possible to study the dynamics of these spatial fluctuations by focusing the beam down to 30 nm (which will be possible) and watch the time dependence as these inhomogeneities move through the focused beam. Also the flickering in a speckle pattern would yield time-dependent information (see sections 2.8 and 5.7). It is believed that it should also be possible to carry out the above experiments in an inelastic scattering mode where the energies and to some degree the dispersion (q dependence) of the elementary excitations corresponding to collective excitations from the ground orbitally spin and charge ordered states are measured. It has recently been shown, for example, that using circularly polarized light at an L_{23} edge, the cross section for spin-flip excitations (spin waves) in the inelastic channel are very high (of the order of 50%). Similarly, at these resonant energies, the $d-d$ excitations corresponding to the excitation of orbital orientational modes, or so-called orbitons, also have a high cross section. One key ingredient to our understanding of the physical properties of these systems are these low-energy scale collective excitations. Soft x ray scattering combined with spectroscopy with spatial resolution can provide the necessary information to better understand the close coupling between the spin charge and orbital degrees of freedom displayed in Fig. 10.

The dream experiment requires the next generation beam line, with capability to reach 20-nm focus, 10-meV energy resolution, and variable momentum transfer. It also should have cryogenic cooling, large magnetic fields on the sample, and a wide variety of beam polarizations and modulations. It would be magnificent if a spatial resolution of 2 nm at wavelengths corresponding to the O K edge and the Mn_{123} edges could be reached.

3.0 Recommendations

Two sets of recommendations resulted from this workshop—one from the materials working group and the other from the environmental working group. There is one underlying theme in several of the recommendations from both groups. Community user friendly, facility-staffed beam lines need to be made available to the general user. It is crucial for the advancement of soft x-ray science (and for synchrotron radiation science in general) to expand the user base to include a much wider clientele. Materials scientists, bioscientists, environmental scientists, etc., must be attracted. Photon-in/photon-out techniques need to become routine for analysis of all facets of materials-related endeavors. At the same time, it is fully understood how important it is to keep pushing the frontiers of instrumentation. Possible new operational modes of facility beam lines are discussed in section 8.

There was a general concern expressed by many people at the workshop that characterization without materials synthesis is not a healthy environment. In the worst scenario, the scientists on the beam lines will become nothing more than extremely well-educated technicians. *Whoever controls the materials controls the science and technology!* Two general recommendations came from this meeting: (1) build general purpose, user friendly, facility-staffed beam lines to service the general materials community and (2) encourage collaborative programs that include materials synthesis as an integral part, either at the home institution or on the beam line.

The following beam lines and facilities are viewed as the base upon which photon-in/photon-out science can advance, as it is believed it will, and upon which, it will be judged.

3.1 Recommendations of the Materials Working Group

3.1.1 **A General User Beam Line for X-Ray Absorption End Station for Nanostructure Characterization (70–2000 eV)**

- Easy access
- Load lock—fast turnaround
- Energy dispersive fluorescence detector
- Microfocus/scanning (1 micron)
- Horizontal linear, if possible circular
- Technician support

3.1.2 **High-Resolution Specialized Resonant Inelastic X-Ray Scattering End Station (20–100 eV) on an Insertion Device Line**

- Energy resolution 10 meV (in/out)
- Horizontal and vertical linear, right, and left circular polarization
- Microfocus (a few microns)
- End station with magnetic field (>10 T), variable temperature (4–500 K)

3.1.3 **Coherent Optics and Coherent Scattering Beam Line (70–1500 eV)**

- Diffraction limited focusing
- Horizontal linear and, if possible, circular polarization
- Microfocus (a few microns)
- Flexible end station with high magnetic field (5 T), variable temperature (4–500 K)
- Mechanical stability

3.1.4 Polarization Modulation Undulator Beam Line (250–2500 eV)

Horizontal and vertical linear, right, and left circular polarization

Modulation capabilities (about 100 Hz)

Microfocus/scanning (0.5 microns)

End station with magnetic field (5 T), variable temperature (4–500 K)

3.1.5 Resonant Inelastic X-Ray Scattering End Station (100–1500 eV)

Energy resolution 100 meV (in/out)

Horizontal and vertical linear, right, and left circular polarization

Microfocus (a few microns)

End station with magnetic field (5 T), variable temperature (4–500 K)

3.2 Recommendations of the Environmental and Interface Science Working Group

- Complete the funding and accelerate the completion of the **ALS-Molecular Environmental Sciences (MES) Phase I** effort, which will result in state-of-the-art spectromicroscopy (both x-ray absorption and x-ray emission) x-ray standing wave facility covering the energy range 75–1500 eV.
- Build a complementary **soft x-ray beam line facility**, compatible with the environmental beam lines, that extends the photon energy of national MES facilities to ~4 keV while maintaining access to the lower energy region below the carbon edge.
- Improve fluorescence detectors for all soft x-ray synchrotron radiation efforts [solid state semiconductor, specialized solid state devices, and x-ray emission spectroscopy (XES) spectrometers].
- Increase facility and individual user support, including substantial new support for theoretical–experimental collaborations.

3.3 Implementation of Recommendations

The MES program has pointed the way toward a new mode for synchrotron-based research in the United States. This mode is based on the premise that the scientists in a specific field can and should drive the beam line development, integrated on a national level. This report has identified a unique opportunity in the general area of spectromicroscopy of nanophase materials where this approach could lead us into the forefront of the characterization of dynamic and static properties of nanophase materials.

Our recommendation is that this document be used, by a select set of scientists and facility representations, as the scientific justification for a proposal to the federal funding agencies for a Distributed Synchrotron Center for Spectromicroscopic Characterization of Nanophase Materials. The most logical approach is to first request money for a full design study of the required beam lines and insertion devices, followed by an implementation proposal. This would also give the community and the facilities time to address the issue of how to schedule beam time, given that the Distributed Center will have capabilities at many synchrotron radiation centers.

4.0 An overview of the Soft X-Ray Science: From Fluorescence to Resonant Elastic and Inelastic X-Ray Scattering

4.1 Introduction

In recent years soft x-ray fluorescence spectroscopy using synchrotron radiation has fostered many new applications in different areas of research—from interface science and chemical physics to solid state physics and materials and environmental sciences. The reasons for this dramatic development are twofold. First, the availability of third-generation synchrotron radiation sources offers much better defined experimental conditions, leading in turn as a second step to a totally new understanding of the soft x-ray emission process. The traditional soft x-ray emission spectroscopy (SXES) with the interpretation of high-energy excited spectra reflecting the local partial density of electronic states of the system is still applicable and has resulted in a better understanding of complex materials. The use of tunable excitation allows site selectivity to be obtained, and the well-defined polarization of synchrotron radiation offers a means to exploit dichroism effects. The new physics concerning resonant SXES is in the discovery of the resonant enhancement of inelastic x-ray scattering (RIXS). In the traditional approach, advancement of synchrotron radiation-based excitation sources, as well as the prospect of future free-electron laser (FEL) sources, enables the study of more and more dilute systems. This includes, for example, minority species at surfaces or interfaces, samples in a liquid phase or in a high field environment, and nanostructures. On the other hand, evolution of the understanding of x-ray emission as a scattering process opens up some exciting opportunities for the study of dynamical processes and electronic excitations in solids. Additionally, the coherent properties of the source are just beginning to be explored in mostly elastic scattering experiments. In the following, three different areas, separately referring to them as SXES, RIXS, and Speckle, will be discussed.

4.2 The Basic Process of SXES

The SXES principle is schematically illustrated in Fig. 11. A core vacancy in an outer core level of the material under investigation is excited by the absorption of a soft x-ray photon. By continuous variation of the excitation energy using a synchrotron radiation source, the absorption spectrum may be recorded, reflecting the local electronic structure of the unoccupied states at the atomic site where the core hole is created. Because the transition is given by a dipole matrix element, the angular momentum symmetry of the states is also reflected in the transition probabilities. One possible decay channel of the core vacancy is by radiative recombination of a valence electron with the core hole. This decay by emission of a photon is monitored by SXES and is analogous to the absorption transition where the local partial density of states (LPDOS) of the occupied valence states is reflected by these spectra.

SXES has been used for experimental investigations of the electronic structure of atoms, molecules, and solids since the early days of quantum mechanics [1]. Later it was largely replaced by photoelectron spectroscopy, which offered substantially higher signal rates together with the additional advantage of being surface sensitive, because of the short inelastic mean-free path of the electrons. Both experimental techniques indeed yield quite complementary information even though the final state of the soft x-ray emission process is a valence hole state, just as in valence band photoelectron spectroscopy. In detail, however, photoemission and soft x-ray emission complement each other because of the different characteristics and information obtained by each one of these spectroscopies. Photoemission is very surface-sensitive, whereas the photons recorded in soft x-ray emission spectroscopy have an information depth of up to 1000 nm. Thus, soft x-ray emission is a true bulk-sensitive probe of the electronic structure, offering additional advantages of being insensitive to electrical charging or electromagnetic fields.

Furthermore, the matrix elements exhibit distinct differences. Photoemission is described by transitions involving delocalized (Bloch-) states. According to Fermi's "Golden Rule," the soft x-ray emission intensity $I(E_X)$ is described by a very simple equation:

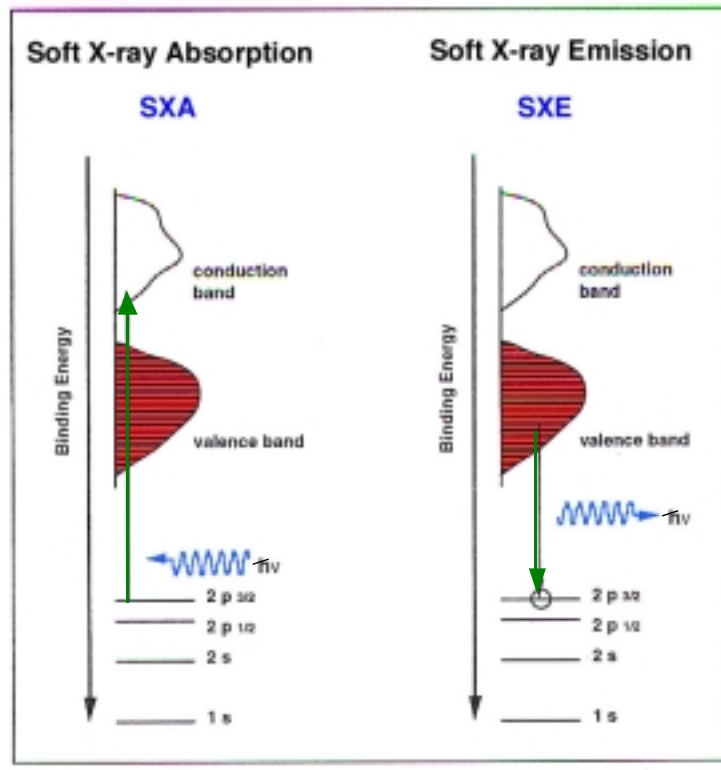


Fig. 11. Schematic representation of the core-electron absorption process (left) and the soft x-ray emission process (right). Both transitions are described by optical dipole matrix elements.

$$I(E_X) \sim |\langle \psi_f | \mathbf{T} | \psi_c \rangle|^2 \delta(E_c - E_f - E_X)$$

where ψ_f (ψ_c) are the wave functions of the valence (core) hole state, \mathbf{T} is the dipole operator, and the δ -function ensures energy conservation. Soft x-ray emission consequently reflects the local character of the electronic states because of the core orbital in the transition matrix element. Thus, in a compound material, the electronic structure around individual atoms can be probed by SXES. Additionally, the dipole character of the radiation is selecting transitions between states of different angular momentum character according to the selection rule $\Delta l = \pm 1$. Therefore, SXES reflects the LPDOS at the site where the core hole was created. Moreover, using the polarization of the incoming light, a definite alignment of the sample in the core-excited state can be produced, because only molecules, and or solids where the symmetry axes are aligned properly with the polarization vector, will absorb a photon. This is also quite useful in using circular polarization and/or in studying magnetic samples, which will be discussed later.

According to the “final state rule” formulated by U. v. Barth et al. about 20 years ago [2], the DOS reflected by the emission process is the one of the valence hole state where the core vacancy is filled. Analogously, for the absorption process, the core hole has to be taken into account because the spectra reflect the DOS of the conduction band in the presence of the core hole.

Viewing the combined absorption and emission process on a total energy scale illustrates some very important properties and features. Initially, the core hole state is created by the absorption of the photon or by electron irradiation. The total energy of the intermediate core hole excited state is thus given by the ground state energy plus the photon energy. The energy of any particle created in this process, be it a photoelectron or only a phonon, has to be taken into account here as well. From the excited state, the decay leads to the (final) valence hole state. This is where the advantage of a well-defined excitation (i.e., by highly resolved synchrotron radiation) immediately becomes apparent. The intermediate state is well-defined, and any additional electronic or vibrational excitations beyond the creation of the core hole can be very well resolved. This is not the case for excitation by an electron beam, because here the energy transfer is not known, unless it is measured in a coincidence technique (e , $2e$ technique).

By near-threshold excitation, multiple excitations that lead to satellite structures in x-ray emission spectra can be separated. This is important because spectral features due to satellite transitions do not reflect DOS in the simple manner as do the diagram spectra. This also permits dedicated studies of multiple excitation processes.

The price that has to be paid for this additional information is the low signal rate due to the low branching ratio of the particular core hole decay channel involved. Typically, the competing Auger decay of the core hole is favored by a factor between 10^2 to 10^3 . The detector system usually involves a grazing incidence spectrometer with an entrance slit close to the sample and only a small solid-angle acceptance. Thus, SXES is an experimental method which gains tremendously from the use of high-brightness undulator sources for the excitation.

4.3 **SXES with Synchrotron Radiation**

Tunable synchrotron radiation provides site selectivity in a compound sample in addition to the elemental selectivity inherent in x-ray emission spectroscopy. Emission from chemically nonequivalent sites of the same atomic species, on the other hand, requires the excitation selectivity to be typically better than 1 eV. Monochromatized photon excitation allows one to select a particular site of a multicomponent sample. This can be done more or less efficiently depending on the system. By tuning the excitation to energies for which one site has higher absorption cross-section than others, the contribution from that particular site to the emission spectrum can be enhanced. Accidentally overlapping emission from a different atomic species in a multi-element system does occur occasionally, but usually only coarse excitation selectivity is needed to master this problem.

The relatively large penetration of soft X rays in matter, as compared with electrons or ions of comparable energies, makes soft x-ray fluorescence a bulk-sensitive probe. It provides opportunities to study buried structures and samples in ambient gas environments. The photon-in/photon-out nature also provides insensitivity to electrical and magnetic fields, and it eliminates sample-charging problems often encountered in electron spectroscopy. Indeed, a very important ability of soft x-ray fluorescence spectroscopy, apart from its electronic probing capability, is its versatility with respect to different sample systems, from surface adsorbates and buried interfaces to bulk solids, liquids, and gases. The sensitivity is sufficient to record emission from a single monolayer, so that, for example, the chemical bonding of an adsorbate overlayer can be studied. Although there is always at least several nm depth probing, even at grazing angles, because of the evanescent wave penetration of the soft X rays, the signal from an adsorbed layer is detected separate from that of the substrate. This is due to the inherent elemental selectivity of x-ray emission, and it offers an advantage when compared with valence band photoemission spectra, which are often dominated by the substrate signal.

The well-defined polarization properties of synchrotron radiation are useful for many spectroscopic studies, including soft x-ray fluorescence spectroscopy. By aligning an ordered sample in a suitable way with respect to the polarization of the incident radiation, certain states (e.g., $p_{x,y}$ or p_z states of a two-dimensional system) can be excited preferentially. Angular-dependent x-ray emission can then be used to probe the various symmetry states of the valence band.

It is interesting to note that polarization studies in x-ray fluorescence can also be carried out for nonordered samples. The incident radiation preferentially excites states, which are aligned along its polarization direction, creating a distribution of excitations with a degree of ordering. Recording the subsequent emission at various angles can reveal anisotropy that reflects the local symmetry. Even free molecules lend themselves to polarization studies. This is due to the short lifetime of the x-ray state, which provides a “snapshot” of the ensemble of molecules, which are rotating at a much shorter timescale. The information obtained by studies of polarization in x-ray emission can be used to assign spectral features in x-ray absorption spectra [3].

Analogously to magnetic circular dichroism (MCD) in x-ray absorption, magnetic contrast can also be obtained in emission spectra. MCD in SXES (or SXEMCD), predicted by Strange et al. [4] who used the term “dichroic fluorescence,” is the spin-resolved version of SXES, in analogy to spin-resolved electron spectroscopy. SXES is a highly selective spectroscopy which combines substantial probe depth, local information (core-level spectroscopy), and symmetry selectivity (dipole selection

rules). Because SXES does not involve the detection of electrons, it is possible to apply strong electrostatic or magnetic fields during measurements. The final state of continuum-excited SXES—a hole in the valence band—is similar to that of valence band photoelectron spectroscopy, making it possible to compare both types of spectra in a meaningful way.

4.4 Resonant Inelastic Soft X-Ray Scattering (RIXS)

When monochromatized photons are used to excite x-ray emission, the energy can be tuned into a specific x-ray absorption resonance, and the subsequent emission spectrum can be recorded. It is important to note that it is, in general, not correct to regard the excitation-emission process in terms of two separated and non-interacting transitions. Instead, the more general approach of RIXS should be applied for this process. In this view, the incident photon is inelastically scattered, leaving behind a low-energy valence excitation in the system studied. The normally very small cross section for such processes at soft x-ray energies can be very much enhanced near core-state absorption edges, as seen in the resonant part of the Kramers-Heisenberg formula governing this kind of process [5]:

$$I(E_{em}) \sim \sum_{f'} |\sum_n \langle f' | \mathbf{D} | n \rangle \langle n | \mathbf{D} | g \rangle / (E_{em} - (E_n - E_{f'}) + i\Gamma/2) |^2$$

$I(E_{em})$ is the emitted intensity distribution. The ground state is represented by g , the intermediate core state by n , and the final state by f . \mathbf{D} is the dipole operator. E_{em} is the emission energy, and E_n and $E_{f'}$ are the energies of the intermediate and final states, respectively. $i\Gamma$ stands for the lifetime width of the intermediate core state.

It can be seen from the denominator that the intensity can increase significantly near a core-state edge. It can also be seen that cross terms appear by the squaring, because the summation over intermediate states is done for amplitudes rather than intensities. These cross terms represent the interference between different paths of the scattering when degenerate intermediate states are present.

Dipole transition amplitudes for exciting and de-exciting intermediate core states thus govern the intensity. In the time-independent two-step model, the probability for scattering to a final state is the product of the probability for exciting the intermediate states and the probability for de-excitation of those intermediate states to the specific final state. This is an approximation, and is inappropriate when the final states can be reached via several intermediate states, because in this case the various channels interfere.

There is a new way in which the dynamics should be addressed. Strictly speaking, the scattering process should be seen as a one-step, rather than a two-step process. In the Kramers-Heisenberg formalism, the product of the amplitudes for the various excitation-emission paths, rather than their probabilities, determines the cross-section. If there is more than one path to the same final state, the sum of the amplitudes is squared to get the scattering probability. The resulting expression contains cross terms with unsquared amplitudes (i.e., terms which cannot be easily visualized as probabilities). Thus, it is not correct to assume that a specific intermediate state is excited with a certain probability in the scattering process. This is the crucial difference between the one- and the several-step pictures.

The cross terms in the time-independent framework describe the interference between the various excitation-emission paths. This interference contains information about the dynamics in the scattering process. The time-independent theory is successful in predicting experimental results, and the mathematical description is relatively simple (at least in principle). There seems to be little need for alternative descriptions. On the other hand, it has been shown that a time-dependent framework equally well reproduces the data. Mathematically, such a treatment becomes more involved than time-independent theory, but the advantage is that the observations can be related to the time development of the wave functions in a direct way. Thus, the time development is not probed in the same way as in pump-probe experiments. Instead, the duration time of the scattering process is used to get information on the time development.

The “new” physics behind RIXS is that excitation and decay of the core hole generally cannot be regarded as separate steps anymore. Rather, they constitute a single coherent process. This is not new; only previously the observations were not accurate enough to reveal this feature unambiguously. It also applies to any process involving a core hole, including the “Auger” process. RIXS was for the first time uniquely demonstrated by taking x-ray emission spectra of diamond in near threshold excitation [6]. In hindsight, previously obtained spectra also exhibit these features even though they were not interpreted in terms of an inelastic scattering process [7]. The state of the development of RIXS is highlighted in the proceedings of an international workshop that took place at Walberberg near Cologne in the fall of 1996 [8] as well as in a forthcoming review [9].

The most important fact to realize from this one-step picture is that energy and especially momentum conservation apply to the whole process. The photon momentum in the soft x-ray range is always much smaller than the electron momentum. Thus for the process where one photon comes in, is inelastically scattered, and leaves a (valence) electron hole pair in the final state, it is assured that the electron and the hole of the final state have identical momenta, modulo a vector of the reciprocal lattice.

At the core absorption threshold, the core electron is excited into the conduction band minimum. Consequently, only RIXS processes, where the electron of the electron hole pair in the final state is at the minimum of the conduction band and the hole in the valence band is located at the same momentum value, are resonantly enhanced. As the energy of the incoming photon is increased, the electron is promoted into higher lying conduction band states, and only RIXS processes where the electron of the electron hole pair is located at these states in momentum space are in resonance. This is schematically indicated in Figs. 12(a) and 12(b). Thus, one can associate the emission spectrum recorded under these resonance conditions with valence hole states having a defined crystal momentum. This introduces k -sensitivity and selectivity into the soft x-ray emission process.

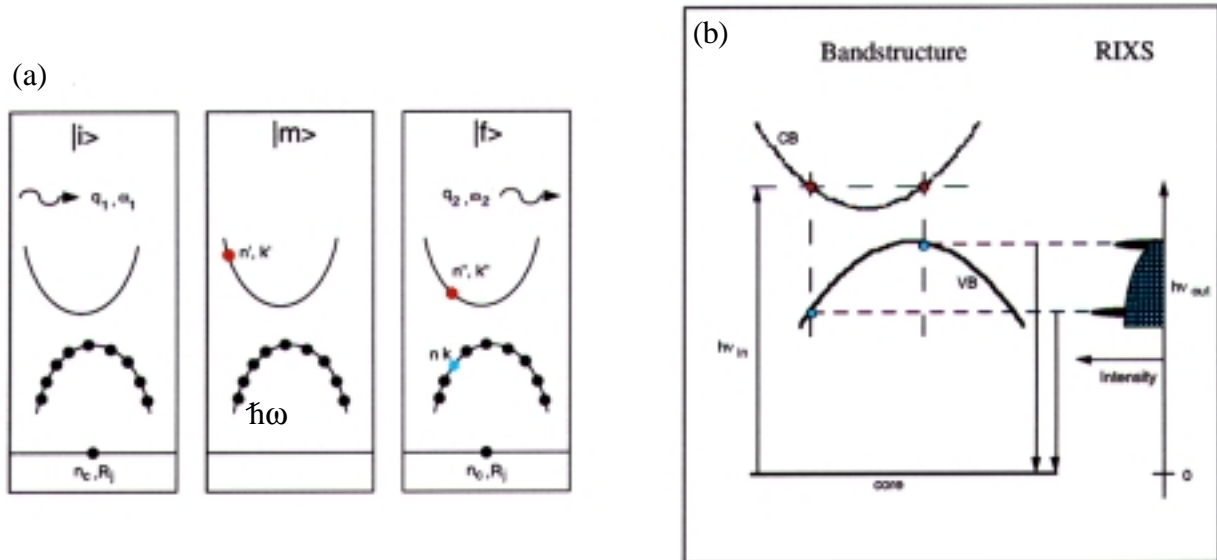


Fig. 12. (a) Schematic of the momentum conservation in the one-step RIXS. The center panel shows the absorption of the photon, and the right-hand panel show the final state consisting of an outgoing photon and an electron-hole pair. The resonance condition for the core-electron absorption channel determines the crystal momentum of the electron hole pair in the scattering process. (b) Illustration of the RIXS process for an indirect gap material. On the right is the emission spectra showing the two possible electron-hole pair states.

The process gets complicated as soon as phonons are created in this process or if there is a sizeable electron hole interaction either in the final state or in the intermediate state. It is a straightforward conclusion that momentum conservation applies to the process as a whole and that if the phonon momentum cannot be determined explicitly, no conclusion can be drawn regarding the relationship of the momenta of the electron and the hole in the final state of the transition [10].

4.5 Features of Resonant SXES Offering New Scientific Opportunities

Resonant SXES offers a number of new features that create scientific opportunities that can be exploited and applied in various problems (e.g., in materials science, chemical physics, and surface science). The most important properties of SXES with tunable excitation are:

- Resonant excitation provides site selective probing.
- Momentum conservation offers site- and symmetry-selective band mapping.
- Interference between degenerate or near-degenerate intermediate core states modifies the x-ray emission spectral shapes and provides symmetry signatures in complex systems.
- RIXS spectra reflect low-energy excitations with two-photon selection rules and with selectivity imposed by the virtual core state.
- Low-energy excitation spectra are not resolution limited by the lifetime width of the intermediate core state.
- Tuning the excitation energy leads to an effective variation of the scattering time, providing a femto-second timing reference for core-state relaxation events, such as vibronic effects and charge localization.
- The spatial structure and electronic structure features can be simultaneously probed.

4.6 Quasielastic Scattering of Coherent Soft X-Ray Photon

The invention of the laser in the 1960s revolutionized many areas of physics, chemistry, biology, and engineering because the coherence and brightness of these spectacular new sources allowed many new experiments to be done. There is broad interest in using the dramatic increases in x-ray and soft x-ray brightness and coherence provided by third- and fourth-generation synchrotron radiation sources. One of the revolutions produced by the invention of the laser was the development of dynamic laser light scattering or photon correlation spectroscopy. In this technique, laser light scattered from a sample produces a speckle pattern that encodes the local spatial structure. Structural fluctuations produce temporal fluctuations in the speckle intensity that are analyzed to determine spatio-temporal correlation functions. The technique has been used extensively to probe diffusion in polymeric and colloidal systems and the temporal divergences associated with continuous phase transitions. The smallest spatial fluctuations that can be studied with this technique are set by the wavelength of the laser. One of the most exciting potential uses of coherent x-ray beams is to extend the spatial scale sensitivity of dynamic laser scattering to atomic and molecular dimensions with dynamic scattering. Early coherent scattering experiments using hard X rays were carried out in transmission through a sample [11] or reflection from a surface [12]. Observation of soft x-ray speckle patterns [13] and the natural and important extension to measure dynamics [13] have also been achieved.

It is illustrative to note that the theory of dynamic scattering is closely related to that for SXES which is discussed in section 4.2. Starting from the Born approximation, it is straightforward to write an expression for the scattered intensity at scattering momentum $\hbar\mathbf{q}$ and energy loss or gain $\hbar\omega$ in terms of the dynamic structure factor, $S(\mathbf{q},\omega)$. $S(\mathbf{q},\omega)$ is simply the space and time Fourier transform of the density-density autocorrelation function. Material fluctuations in space and time lead to spectral structures at corresponding momentum transfer and energy loss. Traditional spectroscopies like Raman or neutron scattering (or, indeed, like RIXS) essentially measure $S(\mathbf{q},\omega)$ experimentally by setting \mathbf{q} with a particular experimental geometry and then measuring the energy spectrum of scattered particles. These techniques normally are used to measure relatively large energy losses, because the energy resolution is constrained by experiment. Dynamic scattering offers complementary information about much lower energy scales by measuring the time Fourier transform of $S(\mathbf{q},\omega)$. For example, a process with a characteristic frequency of 1 MHz or an energy of ~ 1 neV will have a correlation time of 1 microsecond. The primary requirement to measure speckle patterns and to do dynamic scattering is the same as that to measure any interference phenomenon—the incident beam must have good transverse and longitudinal coherence properties and also offer adequate intensity. These requirements are satisfied by third- and fourth-generation

sources of synchrotron radiation. Moreover, several attributes of "normal" soft x-ray spectroscopies that probe high-energy scales can also be utilized with dynamic scattering to access very low energy scales.

A good example of the capabilities offered by dynamic scattering of soft X rays is given in Fig. 13. This shows a speckle pattern of a Pt:Co heterostructure, a system that exhibits perpendicular magnetic anisotropy and is therefore a candidate magnetic recording material. Magnetic contrast is achieved by use of a wavelength near the Co *L*-edge at $\lambda = 1.6$ nm, where the magneto-optic constants exhibit strong wavelength dependence. The film has an average magnetic domain size of ~ 100 nm, and the observed ring of diffusely scattered light is centered at a scattering wave vector corresponding to this length. In this image, the scattered light is speckled because the incident light had a high degree of transverse coherence. This speckle pattern corresponds to the diffraction pattern of the illuminated magnetic domain structure. If this pattern could be inverted, the technique could be used to image magnetic domains. Several groups are working on this inversion problem that is made very difficult by the loss of phase information [14]. More importantly, on a soft x-ray beam line optimized for coherence experiments, there would be enough signal to measure temporal correlations on a microsecond time scale. In such systems, it will be possible to study domain switching and domain wall dynamics as a function of applied field and temperature.

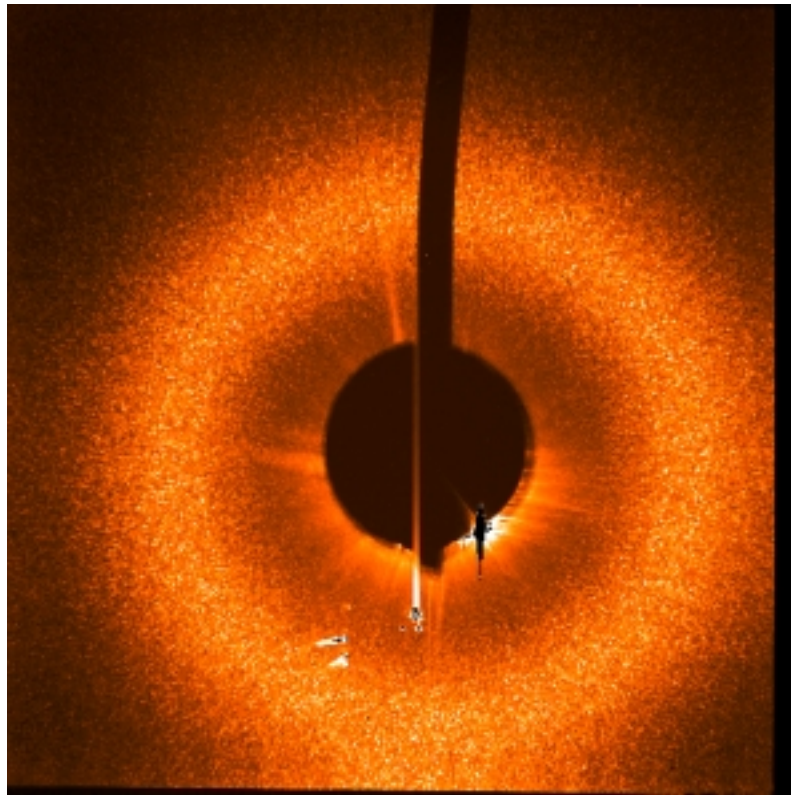


Fig. 13. Soft x-ray speckle pattern of a Pt:Co heterostructure collected at a wavelength near the Co *L*-edge. The ring of diffuse light corresponds to the diffraction pattern of the illuminated magnetic domain structure and is speckled because of the use of a coherent incident beam.

This example indicates how dynamic scattering can utilize all the intrinsic advantages of soft X rays while also providing information on very low energy scales. In many interesting and important systems, the relevant spatial length scale lies squarely in the wavelength range of soft X rays. Moreover, one can beneficially access many absorption edges to achieve elemental, molecular, and magnetic contrast. While the above example concerned a magnetic recording material, similar arguments can be made for complex oxides, homopolymers, block copolymers, and a variety of biological systems.

4.7 Future Prospects

Section 2.0 (A Glimpse at the Future) presented several examples of what might be. A few examples of areas of research where resonant SXES might be able to contribute in the future are:

- Studies of complex materials [e.g., the manganites (CMR) in the presence of high magnetic fields and with exact temperature control].
- True bulk properties of high- T_c materials, again as a function of T and/or with a field applied, if the resolution can be pushed down to the several meV level.
- Magnetic properties of nanostructures.
- Electrochemical processes (e.g., in situ studies of charge transport induced chemical modifications in Li-ion batteries).
- Combination of spatial structural features and electronic structure features. This is a new area where, for example, the electronic structure associated with some very specific spatial features could be resolved. Examples would be the electronic structure of the flux-line lattice of a high- T_c material in an external magnetic field. Via scattering geometry, a specific momentum vector typical for the flux-line lattice could be selected, and the electronic structure could be probed by recording the RIXS spectra at this specific scattering geometry. Another interesting experiment concerns the specific probe of the electronic structure of the stripe domains in the cuprates.

4.8 References for Section 4

1. H. M. O'Bryan and H. W. R. Skinner, *Phys. Rev.* **45**, 372 (1934).
2. U. von Barth and G. Grossmann, *Phys. Rev. B* **25**, 5150 (1982).
3. K. Gunnelin et al., *Phys. Rev. A* **57**, 864 (1998).
4. P. Strange, P. J. Durham, and B. L. Geoffry, *Phys. Rev. Lett.* **67**, 3590 (1991).
5. J. J. Sakurai, *Advanced Quantum Mechanics*, Addison Wesley, Menlo Park, California (1967); T. Åberg and B. Crasemann, *Resonant Anomalous Scattering: Theory and Applications*, ed. by G. Materlik, C. J. Sparks, and K. Fisher (North-Holland, Amsterdam, 1994), p. 431.
6. Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J. E. Rubensson, T. Böske, W. Eberhardt, and S. D. Kevan, *Phys. Rev. Lett.* **69**, 2598 (1992).
7. J. E. Rubensson, D. Mueller, R. Shuker, D. L. Ederer, C. H. Zhang, J. Jia, and T. A. Calcott, *Phys. Rev. Lett.* **64**, 1047 (1990).
8. *Proceedings of the RIXS Workshop at Walberberg*, *Appl. Phys.* **A65**, No. 2 (1997).
9. S. Eisebitt and W. Eberhardt, in *Soft X-Ray Fluorescence Spectroscopy*, *J. Electr. Spectr.*, Special Issue, ed. by J. Nordgren and E. Kurmaev, 2000.
10. M. van Veenendahl and P. Carra, *Phys. Rev. Lett.* **78**, 2839 (1997).
11. S. Bauer, G. B. Stephenson, M. Sutton, R. Brüning, E. Dufresne, S. G. J. Mochrie, G. Grübel, J. Als-Nielsen, and D. Abernathy, *Phys. Rev. Lett.* **74**, 2010 (1995).
12. M. Sutton, S. G. J. Mochrie, T. Greytag, S. E. Nagler, L. E. Berman, G. A. Heald, and G. B. Stephenson, *Nature* **352**, 608 (1991).
13. A. C. Price, L. B. Sorensen, S. D. Kevan, J. Toner, A. Poniewierski, and R. Holyst, *Phys. Rev. Lett.* **82**, 755 (1999).
14. I. K. Robinson, J. L. Libbert, I. A. Vartanyants, J. A. Pitney, D. M. Smilgies, D. L. Abernathy, and G. Grübel, *Phys. Rev. B* **60**, 9965 (1999).

5.0 Reports of the Working Groups

5.1 Report from the Atomic and Molecular Group: “Atomistic View of Complex and Nanostructured Materials”

Soft x-ray photon-in/photon-out experiments are by their very nature a site-specific local probe of matter. Therefore, an understanding of the structure and dynamics of atoms and molecules serves as a foundation for characterizing a wide variety of more complex systems. Understanding these “building blocks” in their simplest states has provided insight into the processes observed when studying more complex systems. Deep insights into, for example, electron correlation, the validity of standard theoretical approximations, and dichroic effects in atoms, have been gained through a variety of spectroscopic techniques on atomic and molecular systems and have implications in a variety of disciplines.

The following sections outline the importance to several areas of materials of a basic understanding of these spectroscopies on an atomic and molecular level and consequently the important role to be played by atomic and molecular scientists.

5.1.1 Polymers (Electronic)

Organic conjugated polymers have the electronic structure of semiconductors and can be doped to become good conductors. They are now used as active materials in a wide variety of prototype applications such as light emitting diodes and organic transistors. Conjugated polymers offer the possibility of combining the desirable processing and structural properties of polymers together with the electronic functionality of a metal or semiconductor. In the context of semiconductor devices, particular interest lies in the scope for fabrication of thin-film devices over large areas which, with the exception of amorphous and polycrystalline silicon, has proved difficult to achieve with inorganic materials.

It is important to obtain insight into the electronic properties of the undoped and doped conjugated polymers and to determine the characteristics of hole injection processes and light emission in connection with luminescence phenomena. Most of the interesting chemistry and physics of conjugated polymers is associated with details of the electronic structure at the valence and conduction band edges. Resonant SXES can be used as a tool for diagnosis of the relevant electronic and geometric properties. It has the ability to provide symmetry-selective projection of the valence band and offers both structural and electronic information.

Resonant soft x-ray fluorescence studies of a few conjugated polymer systems have been made to date, poly-phenylenevinylenes [*Chem. Phys.* **237**, 295 (1998)] and poly-pyridine [*Appl. Phys. Lett.* **72**, 3353 (1998)]. The former compound, which is made up of benzene (phenyl-) rings connected by short hydrocarbon bridges, indeed exhibits strong molecular-like appearance in the spectra. This appearance is not a signature of the repeat unit but of the benzene ring. The conspicuous resemblance with benzene indicates no major electronic or geometric structure changes in the phenyl rings connecting with a vinylene group and indicates also that the phenyl ring works as an excellent building block for these polymers. In the SXES study of poly-pyridine (an aza-substituted poly-phenylene), the isomeric dependence was found in both emission and absorption. The structure of the emission bands is similar in the carbon and nitrogen spectra but have different relative intensities in the two spectra, because the localization properties of the energy bands are different. In particular, the lone-pair N levels emphasize the high-energy part of the nitrogen spectrum in comparison with the carbon spectrum.

5.1.2 EXAFS in RIXS Mode.

It has recently been suggested by Faris Gel'ukhanov and Hans Ågren that there is a possibility of obtaining both atomic distance and bond angle information in nonordered materials by recording EXAFS spectra in an inelastic x-ray scattering mode. The polarization dependence of the RIXS process would reflect the local order in a way which is not possible in commonly applied EXAFS. The experiment would monitor the intensity of energy loss features as one scans the photon energy over a large range over the threshold. There has not been any experimental confirmation of the suggested experiment, but a successful application of the idea would be of great importance for many problems in materials science.

5.1.3 Correlated and Complex Materials

To successfully describe various physical properties of a system, it is necessary to obtain knowledge about the ground state and low-energy excited states of the system. For $3d$ transition elements and lanthanide and actinide compounds with partly filled d or f shells, strong correlation effects break down the single-particle picture when the d or f dispersive bandwidth W is smaller than the on-site Coulomb interaction U . Then an atomic-like approach can be more appropriate to describe the electronic structure of these systems.

In this case, a state of the system without a core hole is described in terms of intra-atomic neutral excitations (a multiplet structure of the ground state electronic configuration due to electrostatic, exchange, crystal field, spin-orbit interactions, etc.) and/or interatomic charge-transfer excitations. The latter are the result of electron hopping from delocalized states to a localized state and are treated by short-range models, such as an Anderson impurity model, using a set of parameters. The model is represented by a Hamiltonian which includes delocalized and localized state energies, hopping matrix elements, and U . For the description of core spectroscopies, an additional term is added to the Hamiltonian in order to account for coupling between localized electrons and a core hole. Fitting both high-energy spectroscopic and low-energy transport data optimizes the values of the model parameters. They are then employed to describe the character and the properties of the ground state, the nature of the band gap in insulators, etc.

Because the interpretation of transport measurements in these regards is often hampered by the presence of defects and by electron-lattice interactions, high-energy spectroscopies which directly probe the electronic degrees of freedom are often used for preliminary estimates of model parameters. In these estimates, it is important to take into account significant configurational dependence of model parameters, which is predicted by first-principles calculations. In particular, removing/adding a valent d or f electron is expected to result in a decrease/increase in the value of the hybridization strength V , which in turn may lead to renormalization effects for U . These effects are more pronounced for core-level spectroscopies. In the presence of a core hole, V is strongly reduced because the wave functions become more localized. The renormalization of model parameters in the final state can produce a significant uncertainty in estimated values of these parameters for the ground state. In this situation, x-ray scattering techniques become very attractive because the scattering process is charge neutral.

Although the information provided by the RIXS technique is similar to that obtained from optical absorption or low-energy electron energy loss (EELS) spectroscopies, there are some distinct advantages in using this method [*Phys. Rev. Lett.* **77**, 574 (1996)].

- The technique is not surface-sensitive, helping to avoid confusion with formation of additional states because of surface defects.
- Its element specificity enables even very dilute compounds to be studied because metal states can be probed separately from ligand states.
- The cross-section for inelastic x-ray scattering is strongly enhanced on the resonance, in contrast to weak dipole-forbidden transitions in optical absorption spectra.
- The dipole nature of radiative transitions makes it easier to calculate RIXS intensities compared with d - d (f - f) intensities in optical spectroscopy or in EELS.

Two examples are presented below to illustrate the capabilities of this technique applied to high-temperature superconductors.

5.1.4 High-Temperature Superconductors

Ever since the discovery of high- T_c superconductors, these materials have attracted the interest of scientists in fundamental research as well as in industrial laboratories throughout the world. To date, a large variety of superconducting compounds have been synthesized, and the highest T_c has reached ~ 160 K in the Hg-Ba-Ca-Cu-O system. For p -type high- T_c superconducting cuprates, the finding about the predominantly O $2p$ character of charge carriers has led to a discussion on the role of inequivalent O atoms, existing in cuprate lattices, for the high- T_c superconductivity. The Cu-O octahedron (pyramid) has been identified as a key element in these compounds so that the importance of in-CuO₂-plane oxygen [O(1)] and apical oxygen [O(2)] atoms and their different Cu-O bonds is debated.

While most of the theoretical models are based on Cu $3d_{x^2-y^2}$ - O(1) $2p_{x,y}$ σ coupling, some emphasize the role of Cu $3d_{z^2-r^2}$ - O(2) $2p_z$ σ bonding. A number of quantum-chemical calculations indicate O(1) $2p_{x,y}$ π contribution at E_F , thus suggesting an involvement of the Cu $3d_{x,y}$ - O(1) $2p_{x,y}$ orbitals in the superconductivity mechanism. Some theoretical studies reveal O(1) $2p_z$ - O(1) $2p_z$ overlap at E_F promoted by Cu $3d_{xz,yz}$ - O(1) $2p_z$ π antibonding hybridization. It is argued that delocalized O(1) $2p_z$ - O(1) $2p_z$ π bonds with shallow “double-well” potentials parallel to the CuO₂ planes can be a basis for Cooper pairing.

In spite of much activity and an enormous number of publications, detailed knowledge of the high- T_c superconductivity mechanism is still lacking, and further systematic studies of the electronic structure of these materials are necessary.

The technique of soft x-ray fluorescence spectroscopy with tunable monochromatic photon excitation has a number of advantages, some of which have been found to be especially useful when applied to high- T_c superconducting systems. In particular:

- Bulk properties of materials under study are probed because of the large penetration and escape depth of incident and emitted photons, respectively.
- SXES provides element-specific and angular-momentum selective information about electronic states in the valence band.
- Site-specific probing of the local electronic structure for the same element in different sites is enabled by virtue of the large variation in the absorption cross-section for these atoms at certain excitation energies.
- Polarization-dependent and angular-resolved fluorescence studies provide information about bonding geometry and symmetry-resolved states.

The site selectivity of tunable-excitation x-ray fluorescence spectroscopy at the O $1s$ threshold of p -type high- T_c superconducting cuprates is of great value. The ability to measure O K_α ($2p - 1s$ transitions) x-ray fluorescence spectra, which mainly reflect the $2p$ contribution in the valence band for oxygen atoms of one or another type, opens up additional opportunities in research on high- T_c superconductors, such as:

- Possibility to follow changes in the distribution of occupied $2p$ states for inequivalent O atoms with doping and/or on going from one compound to another which may help to find specific dependence on varying T_c and elucidate the role of inequivalent sites.
- Possibility to study the character of unoccupied states, including doping-induced states in p -type superconductors, which is based on significant differences in the K_α spectral shape between inequivalent O atoms (i.e., differences in the radiative decay spectrum subsequent to the excitation of a core electron into conduction states). This gives information about the character and symmetry of charge carriers in superconducting materials.

Measurements on single-crystal samples allow a complete separation of O(1) and O(2) contributions to the spectra for a specific orientation of the single crystals with respect to the polarization vector E of incident photons and for specific excitation energies. While polarization dependent x-ray absorption spectroscopy probes symmetry of unoccupied states related to the crystal axes, the tunable excitation x-ray fluorescence technique provides information about projections of these states onto inequivalent sites.

To illustrate the capabilities, Fig. 14 shows results of polarization-resolved O(1) K_α measurements of single-crystal $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Included also are results of LDA + U calculations [*Phys. Rev. B* **49**, 14211 (1994)] for comparison. As seen in Fig. 14, there is a relatively good agreement between experimental and calculated spectra. In particular, the study shows that the doping-induced $2p_{x,y}$ holes are located at the O(1) sites.

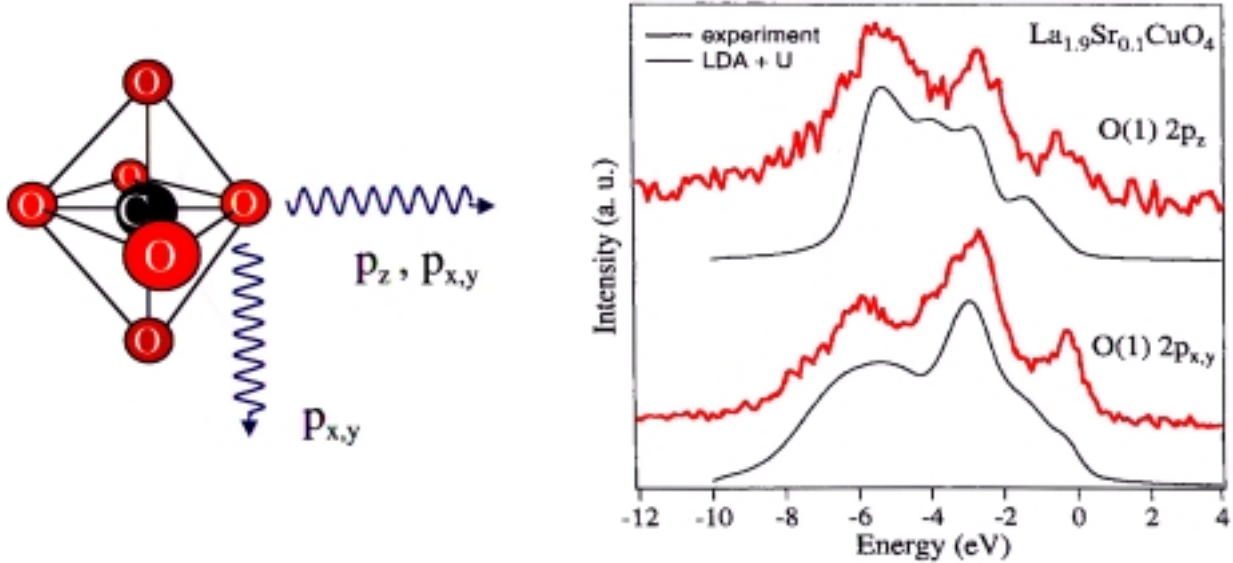


Fig. 14. Orbital-resolved O(1) K emission spectra of $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ together with the results of LDA + U calculations.

In a recent RIXS study of low-energy excitations in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, the role of dd excitations for the mechanisms of superconductivity was investigated [*Phys. Rev. Lett.* **80**, 5204 (1998)]. The energies of the lowest excitations in the Cu-based superconductors are basic quantities of interest in the ongoing struggle to determine the underlying electronic structure and elementary excitations, and among other things the local on-site dd excitations are a topic of debate. The recent suggestion that some of these excitations might occur at energies as low as 0.5 eV reopens the question as to their importance in the so-called mid-infrared part of the optical spectrum which is believed by some to be directly involved in the mechanism for high- T_c superconductors. This study, shown schematically in Fig. 15, was carried out at the Cu $3p$ edge. It is interesting to note that although the natural lifetime width of the Cu $3p$ hole is 1.5 eV, it is possible to obtain 0.2-eV resolution in the resonant SXES spectrum, as demonstrated in this study. The $l = 0, 2$ selection rules of the two-photon Raman scattering process make possible the study of dipole-forbidden transitions associated with all the different $3d$ orbitals. In turn, polarization-dependent measurements reveal certain symmetry of spectral structures, thus suggesting their assignment to specific orbitals. Regarding x^2-y^2 symmetry of the ground state, the experimental-geometry behavior of two inelastic peaks at 1.35 and 1.8 eV, which are resolved in the data shown in Fig. 15, points out to their $3d_{xy}$ and $3d_{xz,yz}$ origin, respectively. Based on the 0.4-eV energy separation between these peaks, the possible presence of the $d_{x^2-y^2}^2 \rightarrow d_{3z^2-r^2}^2$ excitations in the mid-infrared region (at about 0.5 eV as suggested in the literature) can be ruled out. According to crystal and ligand field theory, the splitting between the $d_{x^2-y^2}^2$ and the $d_{3z^2-r^2}^2$ should be at least 2 or 3 times larger than that between the d_{xy} and the $d_{xz,yz}$. This conclusion is supported by model calculations, which indicate that low-intensity transition to the $d_{3z^2-r^2}^2$ orbital is at 1.7 eV and hidden under the xz,yz peak. The alleged importance of on-site $d-d$ excitations for the superconductivity mechanism can therefore be ruled out.

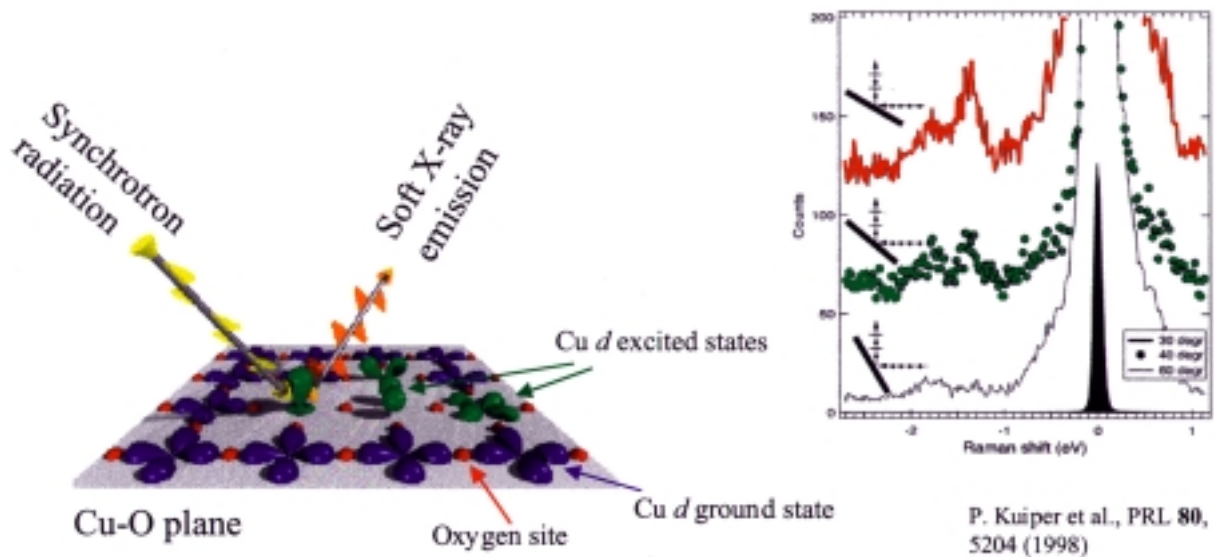


Fig. 15. Soft x-ray resonant Raman study of dd excitations for high- T_c superconductivity [P. Kuiper et al., *Phys. Rev. Lett.* **80**, 5204 (1998)].

5.1.5 New Schemes for SXES Spectrometers

The fact that resonant inelastic soft x-ray scattering is not impaired by the lifetime broadening of the core-excited state opens the possibility to go to very high resolution schemes for soft x-ray emission spectroscopy. Before this notion was generally accepted, the incentive to put effort in such development was not present. Obviously, there would be great interest in achieving kT -resolution in, for example, SXES studies of high-temperature superconductors, as well as in studies of low-energy excitations in correlated materials, in general. A glimpse at the future of high-resolution spectrometers is presented in section 2.8, and the design possibilities are presented in section 5.10.

5.2 Report of the Environmental and Interface Science Working Group

5.2.1 Introduction

One of the new frontiers for soft x-ray science is the study of chemical processes at complex interfaces among solids, microbial organisms, plant roots, and aqueous solutions at the molecular level. Nearly all the important chemical reactions and processes in nature and technology take place at surfaces and interfaces. Such interfacial processes are enormously important in a variety of contexts, ranging from the binding and transformation of environmental contaminants to the preparation of heterogeneous catalysts, corrosion, the behavior of biomaterials, and tribology. The scientific value of this field is related to an understanding of these processes on a molecular or atomic level; the societal relevance depends on applying this knowledge to control and modify these processes.

The importance of studying liquid-solid interfaces is rapidly becoming acknowledged. Most real surfaces in our surroundings are always covered with a thin layer of water or immersed directly in aqueous solutions. The importance of interfacial reactions in the environment is summed up well by a quote from the late Werner Stumm of ETH (Zurich): “Almost all the problems associated with the understanding of the processes that control the composition of our environment concern interfaces, above all the interfaces of water with naturally occurring solids.” There are also interfacial chemistry processes of importance in the troposphere occurring on soot, aerosol, and ice particles. Such processes can result in the production of acid rain and the destruction of ozone. Another area

of major economic importance is corrosion, where detailed studies at the liquid-solid interface can make a significant contribution to the understanding of these processes. Catalytic decomposition of water on surfaces to produce hydrogen will be an important source of energy in the future. An understanding of the fundamental chemistry in these systems provides the opportunity to minimize economic loss and to provide essential knowledge to develop processes.

Very little is known quantitatively at the molecular-nm scale about the solid-liquid interface. The reason for this is the difficulty in obtaining both surface and interface sensitivity using traditional surface spectroscopies that operate in a high-pressure environment, including the presence of water. Electron spectroscopy has been implemented for both high-pressure gases and for liquid studies by using differential pumping, but it is impeded by the necessity for a vacuum environment. This requirement limits the type of liquids and high-pressure gases that can be investigated. In contrast, x-ray-in/x-ray-out spectroscopies do not require a vacuum environment. It is now possible to make windows strong enough to withstand high pressures that also allow sufficient transmission of soft x-ray photons. A separation of the high-pressure and liquid samples from the x-ray beam line and the spectrometer can thus be readily accomplished.

5.2.2 Chemistry at Environmental Interfaces

In an environmental context, interfacial reactions can control the fate of environmental contaminants via both abiotic and biotic pathways. For example, reactions at metal (hydr)oxide-aqueous solution interfaces play a major role in dissolution, precipitation, and sorption processes, which collectively affect the composition and quality of natural waters, the uptake and release of plant nutrients in soils, and the mobility of heavy metal and xenobiotic organic contaminants in aquatic ecosystems. In addition, chemical reactions at the interfaces between solids and microbial organisms can result in corrosion of solid surfaces. Interfacial reactions can also transform toxic heavy metals or organics into more (or less) toxic forms through electron transfer reactions. However, the extreme complexity of solid-aqueous solution, solid-gas, solid-organism, or cell wall-aqueous solution interfaces in both model and natural systems makes detailed molecular-level studies under appropriate *in situ* conditions (bulk water or gas present, ambient temperature, and pressure) difficult. As a result, the mechanisms and products of environmental interfacial reactions are not well understood.

Environmental samples are often extremely complex, containing a combination of solid and aqueous phases, gases, organic matter, microbial organisms, and plant matter. Compositional and phase heterogeneities at spatial scales ranging from nm to mm are common. Contaminants present in such samples and participating in such reactions are commonly at low concentrations (often less than 100 parts per million) and may be localized in very small volumes or sorbed on the surfaces of solids, microbial organisms, or plant roots. Thus element-specific spectromicroscopy methods capable of providing information on the molecular-level speciation, spatial location, and phase association of contaminants at low concentrations in these types of samples are needed. Also needed are new methods for studying the structure and bonding of water around solvated ions in aqueous solutions and water near solid interfaces. In these studies, it is essential to couple fundamental studies of simplified model systems, where conditions and variables can be carefully controlled, with parallel studies of “real” systems, where complexity often prevents full understanding at the molecular-nm scale. This reductionist approach has been successfully used in studying the structure and function of biological molecules.

Much less is known about interfacial reactions that sequester and/or transform organic contaminants such as polycyclic aromatic hydrocarbons, halogenated hydrocarbons, and other xenobiotic organic compounds that are common environmental contaminants. As is the case for inorganic species, organics can sorb onto particle surfaces in soils and sediments in several ways, weakly or strongly, with correspondingly little or great retention. Organic molecules such as the simple hydrocarbons (e.g., octane from gasoline) or halocarbons (e.g., carbon tetrachloride), for example, do not form strong chemical bonds with specific reactive sites on solid surfaces, but do sorb through hydrophobic bonding. Hydrophobic bonding apparently arises from changes in the structure of water near the organic molecule and the surface when the two are in close proximity. The effect is widely observed in the natural environment, but is very poorly understood because so little is known

about the structure of water near uncharged molecules or solid surfaces. Better understanding of water structure and hydrophobic bonding would lead to predictive methods and techniques for controlling sorption of nonpolar organic contaminants.

In contrast to the nonpolar hydrocarbons, many environmentally significant organic molecules contain polar, ionizable parts or functional groups such as hydroxyls, carboxylates, and amines. There is also a major class of organic molecules, known as heteropolar, that contain both nonpolar (hydrophobic) and polar portions, the latter having ionizable functional groups. Through reaction of these groups with reactive sites on solid surfaces, organic molecules and ions can sorb fairly strongly. The strength of sorption depends strongly on the shape of the particular organic molecule and the location of the functional group relative to other parts of the molecule. However, it also depends on the polarity and ease of ionization of the group itself and its affinity for the sorbing site. Thus, the members of a closely related family of organic compounds are likely to behave quite differently in the environment. Some may form strong, inner sphere complexes with the surface, while others are prevented from doing so by interference of other parts of the molecule and can only form weaker bonds such as hydrogen bonds or van der Waals interactions. Finally, sorption of organic ions can be hindered or enhanced by the presence of dissolved inorganic compounds or other organic compounds, which are known as modifiers. Sorption inhibition occurs when the interaction of the modifier with the potential sorbing organic forms a new, nonsorbing, but soluble species. Enhancement can occur when the modifiers—the organic molecule or ion—and the surface form a ternary surface complex. Conceptual models have been developed to explain which types of interaction inhibit and which enhance sorption, but a more detailed understanding of the composition and structure of ternary complexes and the factors that influence bond strength and configuration is needed before quantitative use can be made of these models.

5.2.3 Interfacial Processes Involving Catalysis and Enzymes

Nearly all industrial chemical processes are based on catalysts to enhance reaction rates. These are usually heterogeneous catalysts and are often in the form of dispersed metal particles on an oxide surface. They have a high conversion rate, but operate under high energy-consuming conditions at high pressure and temperature. Furthermore, selectivity is often not very high, resulting in many byproducts which need to be separated at high cost in terms of energy consumption and, moreover, providing additional waste. Enzymes are the reaction catalysts of biological systems. They have extraordinary catalytic power, far greater than heterogeneous catalysts. In particular, they have a high degree of selectivity both with respect to products and reactants and consume a minimum of energy. They can function in aqueous solutions, under atmospheric pressure, and at room temperature. The enzymes usually work in a cycle with many different reaction steps taking place in different parts of the enzyme. There is an important effort to build artificial structures on surfaces that mimic active sites in metalloenzymes. The substrate will be directly involved in the enzyme-inspired processes either by modifying the active site, by facilitating electron transfer, by providing atomic hydrogen, or by partly binding some of the reactants involved in the process.

An essential task is to immobilize the biomimetic molecular component on surfaces and to study the surface bonding character and reactivity. X-ray spectroscopic methods together with theoretical simulations will indicate how the biomimetic molecular component is modified upon interaction with the surface. Some important questions concern molecular orientation, surface-interacting functional group, charge transfer processes, and the chemical state of the metal center. Local probes using x-ray spectroscopy can directly identify the metal atom local *d*-configuration. This has been successfully used in the past to determine spin states of important metalloenzymes. It is important to systematically investigate how the bonding properties and chemical state of the metal center change depending on the nature of the surface and on the chemical modification of the biomimetic molecular component. The substrate bonding and reactions must take place under in situ conditions (atmospheric temperature and pressure and the presence of aqueous solutions).

5.2.4 Molecular-Nanometer Scale Probes for Studying Environmental and Catalytic Interfaces

X-ray absorption spectroscopy (XAS) utilizing high-intensity X rays from synchrotron radiation sources is one of very few methods that can provide structural information on chemical processes at environmental interfaces. As a result, a number of hard x-ray beam lines optimized for XAS have been developed and utilized extensively to study sorption processes of heavy metal contaminants at environmental interfaces. Such processes can effectively sequester metal contaminant species and reduce their mobility in natural waters as well as their potential bioavailability.

Information on the mode of attachment and spatial distribution of organic contaminants on particle surfaces or natural organic compounds is typically much more complicated to obtain than for heavy metal contaminants. Methods such as nuclear magnetic resonance (NMR) or fourier transform infrared (FTIR) spectroscopies, which are commonly used to characterize the structure of organic compounds under in situ or “wet” conditions, are of limited use when the organic species are at low concentrations or, in the case of NMR spectroscopy, when in the presence of paramagnetic species such as iron. X-ray spectroscopic methods are ideal for providing some of this information, but there are very few synchrotron beam lines operating in the soft x-ray energy region (50 eV to 4 keV) that have been optimized for in situ spectromicroscopy studies of environmental samples and interfacial processes. Such wet experimental studies at the C, N, and O *K*-edges would be extremely useful in determining the mode of binding of organics to particle surfaces. They could also be used to characterize the types and reactivities of functional groups on natural organic materials, microbial cells, biofilms, and plants that may bind heavy metals, actinides, and other environmental pollutants or participate in their transformation into less (or more) toxic and bioavailable forms. For example, very little is known about the molecular-level speciation and binding sites of lead or plutonium in microorganisms, biofilm-coated mineral surfaces, or plants. Such information is essential for understanding how microbial organisms and plants sequester, utilize, and transform these and other pollutants. Even less is known about the speciation and binding of low-*Z* elements such as B, C, N, Al, Si, P, and S in environmental materials at spatial scales characteristic of the heterogeneity of environmental samples. This type of fundamental chemical information is required for developing the next generation of remediation technologies, understanding the complex chemical processes that control the mobility and bioavailability of toxic or radioactive contaminants, and using this understanding to develop robust reactive transport models for predicting the mobility of pollutants. Similar microscopic information is also needed to design new classes of catalysts for use in carbon reduction.

In addition to x-ray absorption methods, there are a number of other synchrotron-based methods that are useful in various molecular environmental science (MES) applications requiring very high spectral brightness. These applications include x-ray emission and x-ray standing wave studies of chemical processes at solid-water and cell-water interfaces. To address these types of issues using this array of powerful synchrotron-based methods, new soft x-ray user facilities optimized for these types of studies are needed in the U.S. The core group of researchers required to direct this effort includes chemists, environmental scientists, geochemists, microbiologists, physicists, soil scientists, and surface scientists from universities and national laboratories.

Important applications of soft x-ray spectroscopy and spectromicroscopy to MES problems have been made over the last several years at all the DOE synchrotron light sources. Although limited in number, these efforts have provided unique information on a number of important environmental processes, including chemical reactions of water and heavy metals at metal oxide-water and microorganism-water interfaces, oxidation-reduction reactions of Mn in manganese-oxides caused by soil bacteria, and the identification of surface functional groups on humic substances which are ubiquitous in the environment and which commonly bind toxic metals. However, none of the available soft x-ray beam lines at DOE synchrotron light sources are optimized for MES applications, including in situ studies of environmental samples that contain water or those with spatial heterogeneities on a sub-micron level. In addition, the amount of experimental time available for MES or other applications at these facilities is relatively small. As a result, the MES community has repeatedly identified the need for new synchrotron-radiation facilities with unique capabilities in the VUV/soft x-ray region that are optimized for MES applications, particularly those involving

wet samples. Most recently, the Working Group on Environmental and Earth Sciences at the 1998 Advanced Light Source (ALS) Workshop on Scientific Directions strongly recommended that new beam lines operating in the energy regions from 50 to 1500 eV and 1 to 4 keV and optimized for MES-type work be constructed at the ALS. These proposed beam line facilities are the same as those identified as the highest priorities by the Surface and Interface Science and Biosciences/Soft X-Ray Microscopy Working Groups at the ALS Workshop. In addition to the scientific opportunities provided by these proposed facilities, there is also a pressing need to accommodate new users in the MES area whose requests for beam time are contributing to the oversubscription of existing facilities. For example, MES research in the soft x-ray region has approximately doubled within the last two years at the Stanford Synchrotron Radiation Laboratory (SSRL) and the National Synchrotron Light Source (NSLS), and it has more than tripled at the ALS.

5.2.5 “Grand Challenge” Experiments Proposed by the Environmental and Interface Science Working Group

Following a general discussion of the opportunities for breakthrough research on environmental interfacial processes using soft x-ray spectroscopy, this working group identified five areas, outlined below, that would benefit from this approach.

5.2.5.1 Studies of the Sorption and Spatial Distribution of Xenobiotic and Natural Organic Molecules on Solid Surfaces Under In Situ Conditions to Determine their Speciation, Mode of Sorption, Surface Bonding, and Phase Association, All of Which Affect their Mobility and Potential Bioavailability. (See section 2.3)

5.2.5.2 Studies of Microbial-Mineral Interactions at Spatial Scales of 10 nm.

Single-cell organisms, including bacteria and algae, constitute the largest diversity of life on earth. They are essential to the life of higher organisms, including man. Microorganisms have been discovered nearly everywhere scientists have looked, even in what are known as “extreme environments” of high temperature, or in the presence of concentrations of chemicals that would ordinarily be toxic to other forms of life. There has even been research suggesting that micro-organisms were present in meteorites of Martian origin, and the first clues for life on other planets will probably come from searches for microorganisms in extra-terrestrial soils.

In the 1970s, classes of microorganisms (species of *Geobacter* and *Shewanella*) which directly use inorganic species as part of the electron transport chain of respiratory metabolism were discovered. For example, the use of transition-metal ions (Fe, Mn, and others) as electron donors or acceptors is accomplished both by strict anaerobic bacteria (*Geobacter*) and by facultative anaerobes (*Shewanella*). Since their initial discovery, the importance of these microorganisms in environmental chemical reactions has become increasingly apparent. Today, there remain fundamental questions regarding the mechanisms of transition-metal mediated metabolism, which can be addressed by soft x-ray spectromicroscopy. In the future, it is expected that genetically modified organisms can be utilized in useful technologies, such as bioremediation.

Through basic research, geomicrobiology will be used in an attempt to build an understanding of how interfaces are modified by both biological and abiotic processes in the environment. As our understanding of these complex interfaces grows, ways to use our knowledge to engineer biofilms for useful purposes will be explored. Since the beginning of history, mankind has benefited from microorganisms that assist us in producing (and digesting) food. In the future, a detailed understanding of the cell-surface interface will result in improved anti-corrosion films; ways to remove toxic materials from the environment by biological processes; and even new, biologically inspired, routes to nanostructured materials and devices.

Interfaces in the environment are far from ideal laboratory specimens. They are spatially heterogeneous, contain a number of unknown materials, and include compounds of both inorganic and

biological origins. While a multiplicity of synchrotron radiation methods have been developed to study “model” interfaces, the study of problems in geomicrobiology have been much more difficult because of intrinsic characteristics of the problem. These include spatially small features, the presence of water, complex chemical structures, and high sensitivity to many external factors, such as pH, temperature, and ionic strength. All these issues combine to demand techniques that can study actual environmental interfaces, such as mineral-microbe interfaces, in conditions that closely match those found in the environment.

With the recent introduction of certain photon-in/photon-out probes, it will soon be possible to complete the study of relevant mineral-microbe interfaces with both the spectroscopic precision required and the spatial resolution set by the microorganisms. In Fig. 1, a model of a cell-surface interaction is shown. The important length scales range from the thickness of the mineral-water interface (1 nm), to the size of a protein (10–20 nm), to the size of a cell wall (20–100 nm), to the size of a microorganism (100-nm wide and a few microns in length).

The proposed “grand challenge” experiment is to completely determine the speciation of complexes in the mineral-microbe interface, with a spatial resolution set by the size of an individual protein—about 10 nm. The list of fundamental, unanswered questions that will be addressed is large and includes the following:

- What is the relative role of biotic vs. abiotic mechanisms in transition-metal redox reactions?
- What is the chemical nature of intracellular biominerals?
- What is the nature of the exopolymer extruded by microorganisms as they attach to mineral surfaces?
- How do microorganisms alter the chemistry of mineral surfaces?
- What are the species that adsorb on biologically produced minerals?

The knowledge gained from these experiments, in addition to fulfilling the need to understand biodiversity on our planet, will also become the guide for searching for life outside Earth. In the decades to come, geological specimens will begin to arrive from our sister planet Mars. It will be necessary to be ready with the tools to search for signatures of life in these specimens. The 10-nm x-ray spectromicroscope will be one of these important tools.

5.2.5.3 Fundamental Studies of the Structure and Bonding of Pure Water and Aqueous Solutions, Both in Bulk Form and at Particle-Solution and Organism-Solution Interfaces.

Water is the primary component of geological and biological systems. The biogeochemical cycling of major and trace elements, the fate and transport of contaminants in the environment, and enzymatic reactions in biota are controlled by the properties of water. Developing a conceptual chemical understanding of the electronic structure and hydrogen bonding networks in water, based on molecular orbital concepts, would be very useful in understanding its biochemical interactions. General areas in need of research are the following:

- Identification of variations in the electronic structure and hydrogen bonding in water as a function of changes in temperature and pressure and in the presence of natural interfaces (mineral-water, organism-water, air-water interfaces).
- Hydration and complex formation (chemical speciation) of hydrophilic and hydrophobic molecules in aqueous solutions and at the natural interfaces.
- The chemistry of water at fractured surfaces, in the rhizosphere of plant roots, and at cell-walls of plant roots and microorganisms.

Application of x-ray absorption and XES to these systems using improved spectrometers, complemented by high-level molecular modeling, can provide site-specific, direct electronic, and geometric structure information for water in different environments.

5.2.5.4 Fundamental Actinide Materials Surface Science and Actinide Environmental Science in the Soft X-Ray Region Utilizing Microbeam Fluorescence Methods (XES and FY-XAFS)

The surface science of actinide materials and the interactions of actinide species with pristine and environmental materials interfaces are poorly understood. This lack of fundamental knowledge has tremendous societal and economic ramifications for the core and environmental restoration activities of the U.S. Department of Energy. Furthermore, the bonding in certain actinide materials has yet to be fully understood (localized vs. delocalized *f*-electron behavior) in actinide materials, and the nature of the chemical bonding has a significant role in defining the interfacial characteristics of actinide materials. To successfully address these challenges in actinide science, knowledge of the chemistry and physics of actinide materials surfaces, actinide species at modern interfaces, small molecule chemisorption on actinide materials surfaces, and the interaction of liquid species at actinide materials interfaces is essential. The information provided from these studies will provide a basis for understanding actinide interfacial chemistry and will further unify the understanding of chemical bonding throughout the periodic chart by adding an improved understanding of *5f*-electron behavior. At the same time, the knowledge gained from such research will also provide information to better address outstanding problems involving actinide materials.

The re-emergence of improved soft x-ray synchrotron radiation fluorescence techniques [XES and fluorescence-yield x-ray absorption fine structure (FY-XAFS)], combined with the microbeam capabilities (and spatial resolution capabilities) of third-generation synchrotron radiation sources that enables the safe handling and practical experiments with extremely small amounts of actinide material, represents a unique opportunity to extend the understanding of actinide materials interfacial science and the chemical bonding in *f*-electron systems. There is currently no operational soft x-ray beam line with such capabilities although one is in the early stage of construction at the ALS. The actinide science community has, for nearly 20 years, discussed the scientific opportunities that would be made available by such a beam line but have not recognized the enabling potential that fluorescence methods provide. The photon-out nature of the fluorescence experiments will permit the use of thin, capping layers on actinide materials that will prevent oxidation or reaction of actinide materials that currently constitutes a nearly insurmountable barrier for meaningful experiments. Of special importance will be the use of RIXS that can effectively speciate actinide materials and, of course, provide specific electronic structure information that can be used to characterize chemical bonding. The fluorescence techniques, combined with the spatial resolution capabilities, will provide an opportunity for the actinide science community to become fully involved in the soft x-ray region because meaningful and significant studies with less than pristine materials will be possible. This also will enable the entire field of actinide environmental science in this energy region by providing the fundamental spectroscopic basis by which “real” actinide environmental specimens may be characterized. This would be a significant accomplishment.

The capability to make scientifically significant measurements for the first time with the new fluorescence capabilities without an extraordinary amount of sample preparation efforts has tremendous consequences for the future development of the actinide science field in the soft x-ray energy region. This will permit a shift in focus in actinide science efforts in this energy region from the spectroscopic efforts to an improved materials preparation focus. The initial preparation of thin-film materials envisioned for the initial soft x-ray fluorescence experiments will quickly lead to the ability to utilize well-characterized, pristine thin films of a variety of actinide materials for more traditional actinide surface science experiments that are the ultimate objective. These achievements will permit investigations of the aforementioned scientific topics in actinide materials surface science and extend them into regimes including high-pressure gas and with liquids present. However, unlike many other disciplines that have used photoemission for many years in the soft x-ray region, photoemission techniques have not been applied extensively to actinide materials, and the utility provided by the fluorescence techniques will lead to the eventual and desirable application of photoemission to these materials. Specifically, surface science experiments are needed to understand the electronic structure of actinide materials, chemisorption of actinide species on a variety of relevant surfaces, surface structures of clean actinide materials, characterization of the interactions of small molecules with actinide material surfaces, and liquid-solid interactions, all involving a range of actinide materials. Questions which will be addressed include the following:

- What are the roles of the 5*f*-electrons in the chemical bonding of the actinides? How does the chemical bonding change as a function of phase and temperature of actinide materials? What are the electronic structures of actinide materials?
- What are the surface structures of actinide materials?
- What are the chemical species involved and what are the effective rates of the basic surface chemical reactions on actinide metal materials surfaces? What are the important intermediate species in terms of structure and chemical bonding? What are the mechanisms of these reactions?
- How may we utilize the fundamental information on actinide materials to more effectively characterize and deal with environmental challenges relating to actinides?

5.2.5.5 Kinetic Studies of Abiotic and Biotic Reaction Pathways of Inorganic and Organic Contaminants (Timescales Ranging from Nanoseconds to Minutes)

The rates of biogeochemical reactions in nature span wide timescales: from femto-second to geologic timescales. However, a majority of reactions that go to completion on a timescale of years to thousands of years are generally considered to play a minor role in the chemistry of the biosphere (with the exception of reactions involving nuclear waste migration in the hydrosphere and carbon sequestration in the biosphere), relative to those that occur on timescales of hours to days. While it is possible to access these shorter timescales for simple systems using vibrational, luminescence, and other spectroscopic techniques, heterogeneous reactions occurring at a variety of natural interfaces and homogeneous reactions in complex organic matrices require surface-sensitive, element-specific, in situ spectroscopy and spectromicroscopy methods to probe such reactions. Currently, using x-ray absorption spectroscopy, reactions that occur slower than a few minutes can be examined. Access to studying chemical reactions faster than these timescales will help us understand a variety of biogeochemical reactions, such as time-dependent variation in speciation of elements and identification of reaction pathways in biotic and abiotic processes. They will also help us understand the rates of abiotic vs. biotic reactions that transform contaminant species at environmental interfaces. This is extremely important information because the reaction pathway with the fastest rate will generally control the resulting chemical changes.

5.3 Report of the Biomaterials Group

Complex biological structures on surfaces are important for a number of applications in industry such as biosensors, biocompatible materials, and biomimetic systems such as enzyme catalysis. The knowledge obtained about the structure and functionality of a diversity of important biological processes have been possible because of the development of new spectroscopic and microscopic tools. It is now possible to study protein molecules adsorbed on a surface and study the conformational changes because of surface molecule interactions. Furthermore, the development of different production techniques, as well as analytical techniques with an extremely high resolution down to the atomic scale, makes it possible to construct and analyze materials of different kinds. For the first time, the possibility exists to have control of the material and its derivatization product on the atomic scale and at the same time to study the interaction between the molecule and its counterpart. Biomolecules are built up by functional groups of which several can interact with the substrate. Understanding the chemical bond formation for these type of systems forms the basis for investigations of the adsorption and reactions of proteins on metal and oxide surfaces. In order to gain insight into the nature of the chemical bonding, the electronic structure of the system needs to be addressed. Biomolecules are built up by functional groups of which several can interact with the substrate. The valence orbitals extend over the entire system, making a deconvolution of electronic states originating from important functional groups difficult. It would be most advantageous if the electronic structure could be investigated in an atom-specific way and, thereby, the interaction of the different functional groups could be separately identified.

The adsorption of glycine on Cu(110) illustrates what can be learned from x-ray spectroscopies applied to molecular adsorbates (shown in Fig. 16). The glycine molecule is an amino acid with

two functional groups, carboxylic and amino. The molecule adsorbs with the molecular skeleton intact except for the removal of the acidic hydrogen. Using x-ray absorption spectroscopy, the molecular orientation could be determined showing that the molecule adsorbs with both end groups of the molecule to the surface. Using angular-resolved x-ray emission spectroscopy, it would be possible to project the electronic structure on the $2p_x$, $2p_y$, and $2p_z$ valence orbitals on four different atomic sites. The picture that emerges is an experimental version of the linear combination of atomic orbitals (LCAO) approach for molecular orbital theory. This makes it possible to study how molecular orbitals of a specific symmetry are distributed over different atomic sites in a complicated molecular adsorption complex.

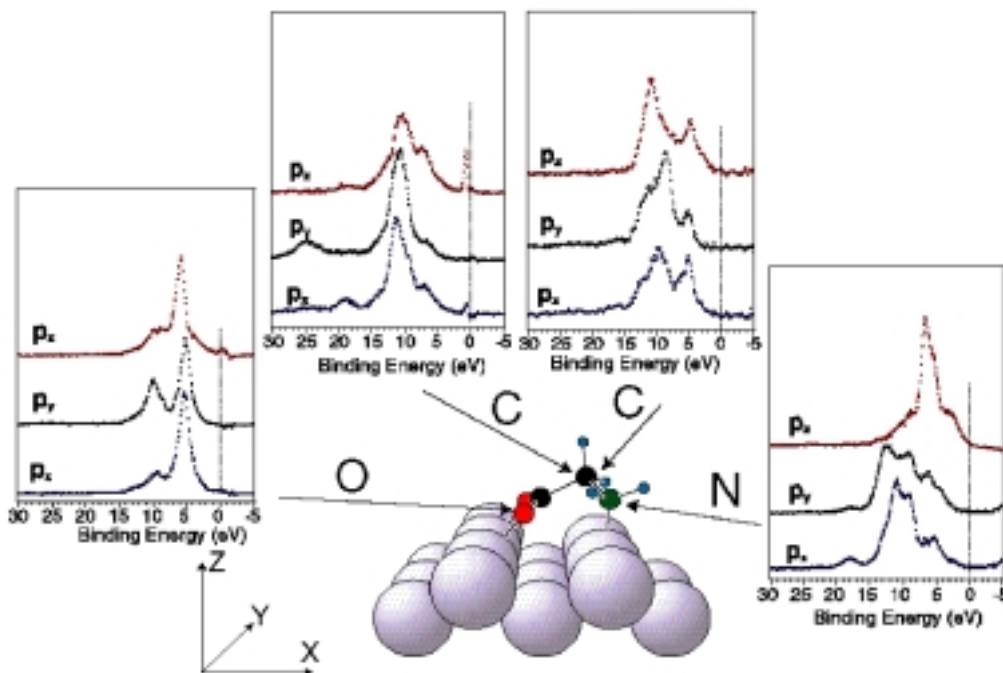


Fig. 16. $2p_x$, $2p_y$ and $2p_z$ symmetry-resolved x-ray emission spectra for glycine adsorbed on Cu(110). Inserted is a structural model of the adsorption complex. The spectra are measured at the O atom, the C atom in the (COO) group, the C atom in the (CH₂) group, and the N atom. The valence $2p_x$, $2p_y$ and $2p_z$ orbitals were obtained by a suitable linear combination of XE spectra measured in normal emission, grazing emission along the [110] direction, and grazing emission along the [100] direction.

Self-assembly systems such as thiols and gold surfaces are a growing area with many different applications. It is now possible to functionalize surfaces with many different groups inserted into the self-organized films. The nature of the bonding to surface and the interaction of the functional groups to the surrounding medium are still rather open questions.

Organic conjugated polymers have the electronic structure of semiconductors and can be doped to become good conductors. They are now used as active materials in a wide variety of prototype applications such as light emitting diodes and organic transistors. Conjugated polymers offer the possibility of combining the desirable processing and structural properties of polymers together with the electronic functionality of a metal or semiconductor. In the context of semiconductor devices, the particular interest lies in the scope for fabrication of thin-film devices over large areas which, with the exception of amorphous and polycrystalline silicon, has proved difficult to achieve with inorganic materials.

It is important to obtain insight into the electronic properties of the undoped and doped conjugated polymers and to determine the characteristics of hole injection processes and light emission in connection with luminescence phenomena. Most of the interesting chemistry and physics of conjugated polymers is associated with the details of the electronic structure at the valence and conduction band edges. Resonant SXES can be used as a tool for diagnosis of the relevant electronic

and geometric properties. It has the ability to provide symmetry-selective projection of the valence band and offers both structural and electronic information.

Resonant soft-ray fluorescence studies of a few conjugated polymer systems, poly(p-phenylenevinylene)s and poly-pyridine, have been made to date. The former compound, which is made up of benzene (phenyl-) rings connected by short hydrocarbon bridges indeed exhibits strong molecular-like appearance in the spectra. This appearance is not a signature of the repeat unit but of the benzene ring. The conspicuous resemblance with benzene indicates no major electronic or geometric structure changes in the phenyl rings connecting with a vinylene group and indicates also that the phenyl ring works as an excellent building block for these polymers. In the SXES study of poly-pyridine (an aza-substituted poly-phenylene), the isomeric dependence was found both in emission and absorption. The structure of the emission bands is similar in the carbon and nitrogen spectra but have different relative intensities in the two spectra, because the localization properties of the energy bands are different. In particular, the lone-pair N levels emphasize the high-energy part of the nitrogen spectrum in comparison with the carbon spectrum.

5.4 Report of the Hard Materials Group—Complex and Strongly Correlated Systems

Multi-element compounds containing transition-metal and rare-earth elements exhibit many aspects of complexity that place these materials at the most active and important frontiers of condensed matter physics.

- Most often in these compounds, the stable phase is related not merely to atomic position but to ordering of orbitals, spins, and charge on the atoms of the lattice.
- Localization, correlation, and exchange effects play an important and often dominant role in the low-energy excitations of the materials.
- Magnetic, electrical, and lattice effects are very closely coupled giving rise to exotic effects such as colossal magnetoresistance (CMR), high-temperature superconductivity (HTSC), magnetostriction, and piezoelectric effects.

Clearly, these complex compounds promise to be of immense importance, both for their practical applications and for the development of condensed matter theory.

In most cases, the spectacular behavior of strongly correlated complex materials remains a mystery. After many years of research using established experimental methods, it is obvious that new techniques which will provide combined and simultaneous information on the spatial structure, the electronic structure, and the elementary excitations of these systems are needed. It is desirable to do this not only for bulk materials, but also for thin films, buried layers, and nanoscale regions.

The soft x-ray scattering, spectroscopic, and microscopic techniques that are the topic of this report bring a uniquely powerful set of tools to the study of these complex compounds. Because the measurements are made at x-ray edges, all the techniques are element selective, an enormous help in sorting out phenomena in multi-element compounds. As can be seen below, elastic scattering and spectromicroscopies have the potential of providing information about spin, charge, and orbitally ordered phases. Inelastic scattering and fluorescence spectroscopies are among the best tools available for studying the electronic valence-band structure and for the study of low-energy electronic excitations, including $d-d^*$ and charge transfer excitations. Resonant inelastic x-ray scattering (RIXS) permits the elimination of lifetime broadening effects on the spectra, so that it should be possible to resolve effects related to the small energy differences of charge-, orbital-, and spin-ordered lattices. Experiments which give some indication of the range of groundbreaking studies that should be possible with the next generation of soft x-ray experimental facilities are described below.

5.4.1 Imaging Mixed Phases of Complex Compounds

There seems to be a general trend in correlated systems toward an intrinsic phase separation close to boundaries of the phase diagram along the temperature, doping, and magnetic field axes. Although

there is no general proof of this behavior, the physical properties of the HTSCs are strong indicators of dynamic mixed phases of superconducting and antiferromagnetic insulating regions, and the properties of CMR indicate mixed ferromagnetic metallic and paramagnetic insulating regions. It is now believed by many that such mixed phase regions are a general property of strongly correlated systems; they have also been postulated for materials such as EuO and various vanadates, among many others. The length scales of these regions are in the nanometer range, although the sizes of the regions are probably strongly temperature and magnetic field dependent. Such mixed phase regions are difficult to observe directly because they involve only small changes in the valence electron charge, spin, or quadrupole moment densities. To observe them directly, a scattering probe which is sensitive to such changes and can measure effects on the nanometer scale is needed.

5.4.2 HTSCs

A combination of high-resolution x-ray spectroscopic techniques with elastic scattering (see section 5.1.4) is proposed to provide the contrast needed to image these phase-separated regions. For example, elastic scattering at the O-*K* edge is expected to be very sensitive to the local hole density in the HTSCs. Mixed-phase regions like the proposed stripe phases have a strongly increased O-2*p* hole density in the stripes relative to the regions separating the stripes. The elastic scattering intensity distribution would therefore carry information concerning the existence and the spatial dimensions of such stripe phases and simultaneous information on the inhomogeneity of the hole density. Because these regions are not ordered, the structure would be observed in diffuse scattering or in a static speckle geometry.

5.4.3 CMRs

The temperature dependence of the resistivity and of the magnetic susceptibility of the CMR materials exhibit behavior indicative of a dynamic phase separation into islands of metallic ferromagnets separated by antiferromagnetic regions. The relative sizes of these regions are strongly temperature, doping, and magnetic field dependent. The Mn $L_{2,3}$ x-ray absorption edge exhibits a very strong magnetic dichroism in the ferromagnetic regions, which can be used to contrast these regions relative to the paramagnetic insulating regions in an elastic scattering geometry.

5.4.4 Transition Metals

The $L_{2,3}$ edges of the transition-metal compounds are also very sensitive to the local charge and local orientation of the occupied orbitals (i.e., the orientation of the valence electron quadrupole moment). Scattering at these $L_{2,3}$ edges can therefore be used to contrast regions with differing spin, charge, or quadrupole moment densities. From recent experiments done with resonant x-ray diffraction at the Mn *K* edges, it is known that the edge scattering cross section is very sensitive to local distortions in the Mn-O bond lengths because of Jahn Teller (JT)-like distortions. Therefore, scattering at the transition-metal *K* edges provides contrast for local distortions in the bond lengths and can be used to image such distortions.

The combination of elastic scattering and absorption spectroscopy can therefore provide detailed information on the spatial inhomogeneities in these complex systems and also on the nature of the inhomogeneity. All the above are general properties of the 3*d* transition-metal compounds and therefore can be used to provide information on such phase separations and for spatial inhomogeneities in general. In many of these materials, strong polaronic behavior with polaron dimensions of the order of 1–2 nanometers is also expected. These can be lattice, spin, or orbital polarons and, in some cases, combinations of these local distortions. By selecting the appropriate edges and magnetic fields, it should also be possible to image these polarons and distinguish between them.

These experiments can be carried out in diffuse scattering in disordered systems or diffraction in ordered systems, with the contrast being provided by special sensitivity to spin, charge, and orbital ordering that is available at the x-ray edges. For disordered systems, speckle-like patterns are expected. In some cases, direct imaging spectromicroscopy can also be used to study small-scale

structure. Again spin, charge, local distortions, and quadrupole moments would provide contrast near x-ray edges. A spatial resolution of 10 nm would already provide unprecedented detail about phase structure not obtainable in any other way.

Even with resolutions of 30 nm or more, it should be possible to study the dynamical fluctuations of phase-separated regions by measuring fluctuations in the spectromicroscopic spectra. If these regions are mobile and fluctuating, their motion should be directly visible as time-dependent fluctuation in the scattered beam as regions move in and out of the imaged region. In a similar fashion, such dynamics can also be studied in the fluctuations in speckle patterns and in diffraction intensities. Because spatial inhomogeneities are generally accompanied by inhomogeneities of the chemical potential, there will also be inhomogeneities in the charge density. For example, for the HTSCs, it is expected that the chemical potential in the vortex cores in the superconducting phase is different from that outside, resulting in a charge density inhomogeneity. This should provide the contrast needed to observe diffraction from the vortex cores at energies corresponding to the O *K* edge, making possible a direct study of the vortex lattice and its melting behavior.

5.4.5 The Study of Electronic States and Elementary Excitations

The physical properties of complex materials and their strong dependence on small compositional or structural changes are at the moment very poorly understood. Soft x-ray spectroscopy can provide the information required to understand the basic electronic structure and the low-energy elementary excitations in these compounds. The ultimate goal here is to closely couple efforts in synthesis, characterization, and theory to develop sufficient fundamental understanding to identify and design new materials with desired characteristics.

Because of its sensitivity to chemical species, chemical state, and angular momentum symmetry, soft x-ray absorption and fluorescence spectroscopies both at and above a core-level resonance provide very detailed knowledge about the electronic structure in the vicinity of the emitting atom. Normal fluorescence spectra excited well above an x-ray threshold provide uniquely detailed local partial density of states (LPDOS) information for comparison with electronic structure calculations. For excitation within the threshold resonance region, the soft x-ray line shapes are sensitive to details of the local electronic structure like spin, orbital orientation, and charge ordering. These measurements can thus be used to study the dependence on external influences such as magnetic fields, pressure, and temperature.

RIXS deserves special mention as a two-photon electronic Raman scattering process with special value for the study of electronic excitations near the band edges. Because its energy resolution depends only on the initial and final states of the scattering process, RIXS spectra are not limited by the lifetime broadening that often severely limits the resolution of normal fluorescence spectra. As a two-electron spectroscopy, it obeys $\Delta l = 0, 2$ selection rules and can thus be used to study *d-d** and *f-f** transitions that are often the lowest energy excitations in strongly correlated materials. These measurements are critically important for determining the nature of the ground state and charge transfer transitions, thus providing information about the band gaps and poorly understood phenomena such as spectral weight transfers from the high- to the low-energy scale. Of course, the RIXS spectra are very sensitive to chemical and structural changes and therefore can give information on the changes of the physical properties. With currently available spectrometers, resolutions of 0.2–1 eV are routinely available for the photon energy range 100–1400 eV, a region which includes many of the most important x-ray edges for complex compounds.

5.4.6 High-Energy Resolution Spectroscopy

The ordering energies for spin, orbital, and charge ordering are of the order of 10 meV, and thus it would be desirable to develop x-ray spectroscopic techniques with this energy resolution. Sections 2.8 and 5.10 present the prospects for achieving ultrahigh resolution, and section 2.9 outlines the scientific impact of such high resolution.

5.4.7 Instrumentation Requirements and Recommendation

The studies described require substantial capabilities beyond those currently available; they are summarized here:

- For all these studies, very high brightness sources with full control of the polarization of the incident beam including right and left circular polarization and horizontal and vertical linear polarization are needed. *Therefore, the development of additional elliptical undulator beam lines, which alone provide such capabilities, is recommended.*
- In addition, proposed measurements require variable temperatures over at least a range of 4–400 K, magnetic fields up to 5–10 T, and a full scattering geometry flexibility. *The development of versatile chambers providing the required control of these parameters, which are attached to elliptical undulator beam lines and have standard ports for the attachment of spectrometers and other detectors required for the measurements described above, is recommended.*
- For elastic studies, energy resolutions for the incident beam of 100–200 meV are needed, and for spectroscopic studies, equal resolution and high sensitivity in the scattered beam are needed. *Slitless spectrometers achieving greatly improved collection efficiencies and sensitivities, which are compatible with the standard chambers described above, should be developed and made available with the chamber as a standard user facility.*
- For high-resolution studies, a resolution of 10 meV is required to obtain direct information relevant to the physical properties of the materials, and it must be possible to change the scattering geometry to study the q dependence. *High-resolution spectrometers with extremely high collection efficiencies and sensitivity should be developed and mated with the standard chambers described above.*
- For the study of nanoscale regions as well as for some of the dynamics studies mentioned above, a spatially focused beam down to the present limit of about 10 nm is needed. Spatial imaging in the 10- μ m range is also required for operation of the slitless spectrometers described above. *State-of-the-art focusing optics should be developed for use on the recommended elliptical undulator beam lines and spectromicroscopic facilities.*

5.5 Report of the Artificially Structured Materials Group

The main goal in pursuing artificially structured materials is the ability to create new materials with uniquely tailored electronic, magnetic, and optical properties which are not naturally available. If those systems that have the greatest scientific, technological, and societal impact are examined, there is a natural length scale that is converging to nanometer dimensions. In electronic device structures, quantum confinement dimensions, electrostatic energies, and magnetic energies can all be associated with length scales near 10 nm for room-temperature operation. As seen in Fig. 17, to maintain energy-level spacings which cannot be thermally activated, the electron confinement in quantum wells must be smaller than the 10-nm scale. For the operation of single electron transistors (representing sensors at the ultimate quantum limit), the Coulomb energy associated with one electron must be greater than the thermal noise at room temperature, requiring electron confinement on a quantum dot with an extent less than 7 nm. The magnetic energy that keeps the magnetic information nonvolatile in magnetic data storage such as hard disks, MRAM, and magnetic sensor applications must be greater than thermal fluctuations. This is achieved with particles of 10-nm lateral extent, and it defines the superparamagnetic limit to storage density, representing a critically important limitation to magnetic storage media shown in Fig. 18.

The nanometer scale is not only important in materials science but also is becoming important in the biological, environmental, and life sciences as the length scales for the systems of interest are all approaching this regime (Fig. 18). Many functional supramolecular systems take on comparable sizes in the range 1–100 nm. Some of the characteristic structures are shown in Fig. 19, including biocompatible surface coatings, micelles, and viruses [*Academy of Sciences Report*].

Length Scales of Nanostructures

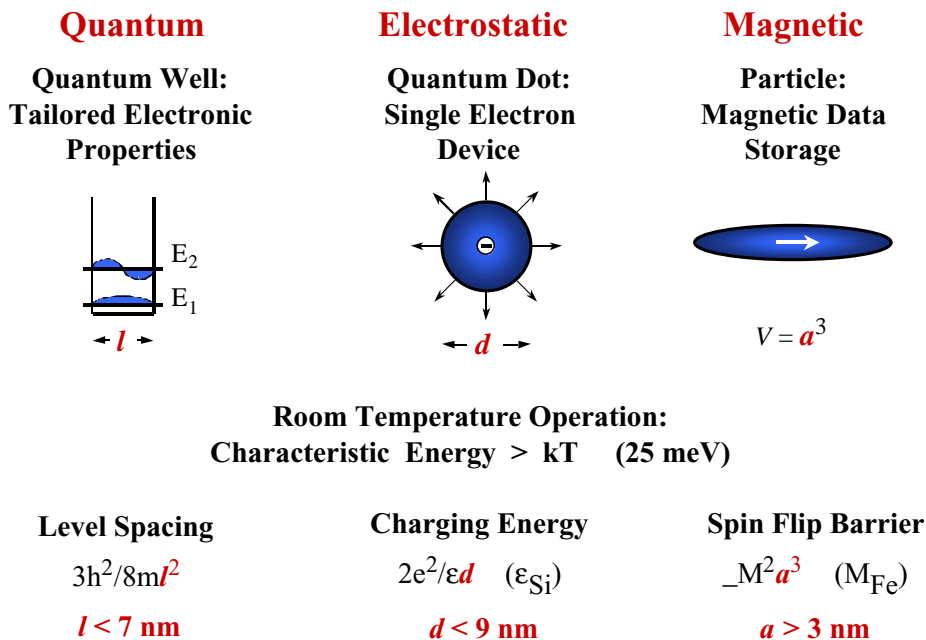


Fig. 17. Schematic of three types of nanostructures that form the core of nanoscale materials and devices: (a) a quantum well, where the electronic energy levels can be tailored by adjusting the well width; (b) a quantum dot with a single electron on it, which underlies a single-electron transistor; and (c) a magnetic storage particle.

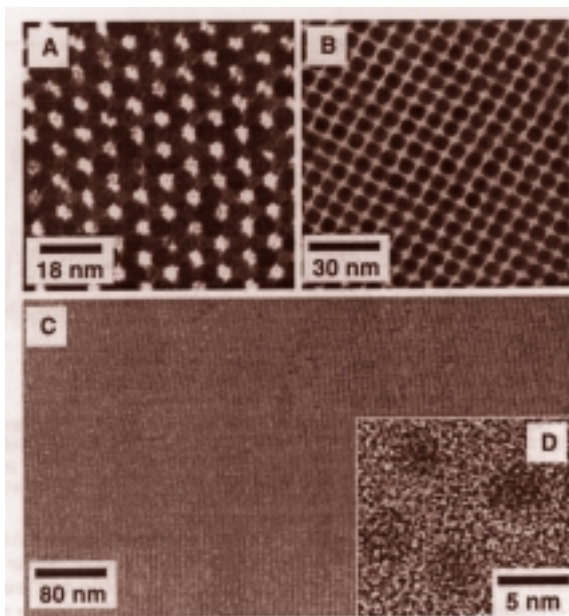


Fig. 18. (A) TEM micrograph of a 3D assembly of 6-nm as-synthesized $\text{Fe}_{50}\text{Pt}_{50}$ particles deposited from a hexane/octane dispersion onto a SiO-coated copper grid. (B) TEM micrograph of a 3D assembly of 6-nm $\text{Fe}_{50}\text{Pt}_{50}$ sample after replacing oleic acid/oleyl amine with hexanoic acid/hexylamine. (C) HRSEM image of a ~180-nm-thick, 4-nm $\text{Fe}_{52}\text{Pt}_{48}$ nanocrystal assembly annealed at 560°C for 30 min under 1 atm. of N_2 gas. (D) High-resolution TEM image of 4-nm $\text{Fe}_{52}\text{Pt}_{48}$ nanocrystals annealed at 560°C for 30 min. on a SiO-coated copper grid [*Science* 287, 1989 (2000)].

The 1–100-nm length scales repeatedly encountered in the important systems already described inevitably defines the appropriate wavelength of light to utilize as a probe. Structures and fluctuations on this length scale are most directly addressed by photons of the same wavelength, corresponding to the soft x-ray region (100–3000 eV). At larger wavelengths (lower energies), these small structures are not visible; while at smaller wavelengths (higher energies), the probe is more sensitive to atomic spacings and not the nanoscale structures and fluctuations representing the newest materials developments. A general conclusion of this report is the observation that nanoscale phenomena (both structural and functional) are best observed by soft X rays. The direct modification of technologically important characteristics is a major attractive element of nanostructured materials.

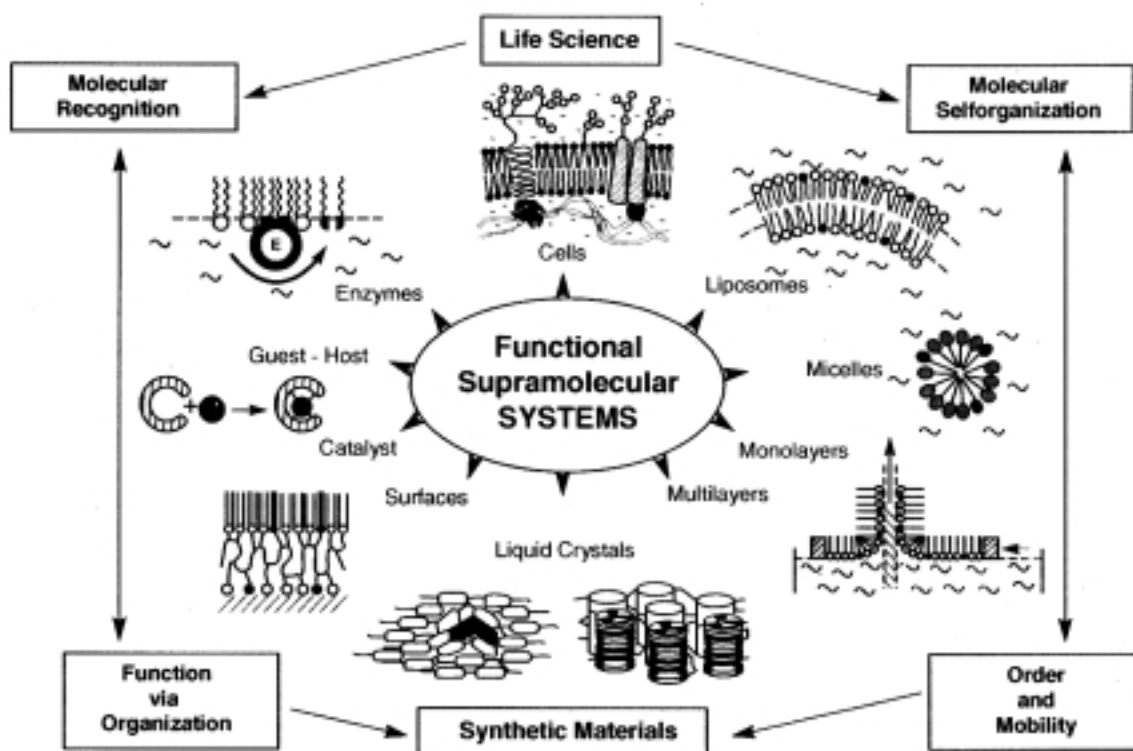


Fig. 19. Overview of the large variety of biomolecular self-assembling materials (from the NRC report on biomolecular self-assembling materials, 1996, courtesy of H. Ringsdorf, University of Mainz).

Some of the properties which are desirable for tailoring are spin injection, coherence, phasing in magnetoelectronics, optimized magnetoresistance for read heads for hard disks, hard coatings for wear resistance, and biosensors as field detectors for biological, chemical, and viral species. Ideally, these customized properties are aided by a first-principles understanding of materials design which defines directions for materials development. Of importance are a number of nanostructured systems including monodisperse clusters with organic shells, nanodots and wires at surfaces, buried magnetic interfaces, interfaces between multicomponent alloys and semiconductors, nanocrystalline materials, lithographic structures, and organic and biological structures. As smaller sizes are reached, the importance of the atoms located at the surface or interface compared with the atoms in the bulk increases. These interfacial atoms often have different electronic properties which can strongly modify the macroscopic behavior of the material. Because of the complexity and small scale of these systems, each has critical barriers for the understanding and subsequent implementation as new advances in the new millennium.

When addressing the challenges encountered in these rewarding systems, difficulties are encountered in distinguishing between the small structures of interest and the surrounding ones which might be the substrate, a protective shell, or the layer under which the nanostructure is buried. In addition, the structure itself may be composed of many elements, with each element in multiple magnetic or chemical states. An elegant way to address such a multicomponent structure is offered by photon-in/photon-out experiments in the soft x-ray energy range. This energy range covers the strongest and sharpest absorption edges of the elements encountered—the *K* edges of biologically interesting light elements, the *L* edges of transition metals, and the *M* edges of rare earths. Tuning the photon energy in resonance to an absorption edge thus gives access to element and chemical specific information of the structure. In addition, the *L* absorption edges of the transition metals and the *M* edges of the rare earths access the magnetically interesting states. Furthermore, the probing depth of soft X rays at these absorption edges is tailored to these nanostructured systems. Hard X rays are too penetrating, and any emitted electrons are too sensitive to the surface region. In addition, by utilizing the controllable polarization (both linear and circular) of the soft X rays, information concerning the site and magnetic structure of the material can be directly obtained.

Often this polarization-dependent soft x-ray spectroscopy, microscopy, and scattering are the *only* methods for obtaining the important characterizations needed to connect structure to function. Although these techniques can be used to study surface properties, because of the variability in probing depth, buried structures such as clusters or interfaces can be accessed. Furthermore, the structures and functionality can be spatially resolved in k -space as the wavelength is of the order of the nanostructures.

5.6 Report of Clusters and Cluster-Assembled Materials Group

Nanostructured, as well as cluster-assembled, solids promise tailor-made materials properties because of the quantum size modifications of their electronic properties. Examples include semiconductor nanostructures exhibiting novel optical and luminescence properties, self-assembled structured monolayers, fullerenes which become superconducting upon doping, carbon nanotubes, and magnetic quantum dots and wires.

For the characterization of these materials, photon-in/photon-out techniques offer unique capabilities, because they allow for an element-specific local atomistic probe of the electronic structure. Thus, even minute concentrations of these particles may be detected and investigated.

Semiconductor quantum dots and nanostructures, as well as magnetic dots and wires, are described in the materials section. Here, the concentration is on cluster-assembled materials. Among these, the fullerenes, carbon nanotubes, and clusters deposited on a substrate by soft landing in a unique mass-selected size from a molecular beam are counted. This latter scheme offers the ultimate choice, versatility, and definition for the production of these materials.

Among the fullerenes, alkali-doped C_{60} films are known to exhibit metallic and even superconducting properties. Transition temperatures up to 32 K allow for classification of these doped fullerenes as a class of materials with the highest transition temperatures second only to the high- T_c cuprate-based superconductors.

While A_3C_{60} can be prepared by conventional solid state reaction of alkali atoms with C_{60} extracted in macroscopic amounts from fullerene soot, C_{70} and none of the higher fullerenes so far could be doped to be metallic at all. Alternately, metal atoms can be incorporated into the carbon cage, forming endohedral fullerenes. Again, only a few of these species can be extracted by chemical methods, whereas a much wider variety of fullerenes can be doped in a cluster beam, formed by laser vaporization of a metal-doped carbon rod, and then deposited onto a suitable substrate. Possibly among those, some other metallic or even superconducting fullerenes may be found.

Recent studies of carbon nanotubes and $La@C_{82}$ with RIXS have demonstrated the need for photon-based spectroscopies on these materials. For $La@C_{82}$, the nature of the charge transfer could be investigated by resonant soft x-ray emission. In the study of carbon nanotubes, RIXS was used to specifically select metallic nanotubes from an ensemble of metallic and semiconducting tubes by tuning the excitation energy to the threshold range. Thus, the electronic structure of the metallic nanotubes could be experimentally verified, and their relative abundance in the ensemble of tubes in the bucky paper could be determined [S. Eisebitt et al., *Appl. Phys. A* **67**, 89 (1998)].

Cluster-assembled granular Co-based materials have recently been shown to exhibit quite pronounced magnetoresistive properties. Hereby, Co particles are deposited from a cluster beam and incorporated into a rare gas or SiO_2 matrix. Thus far, very little is known about the electronic structure of these particles. Again, only a photon-in/photon-out technique will help to clarify these properties.

The ultimate challenge is to take any solid material, transform it into a well-defined cluster, and deposit it onto a suitable substrate or matrix to determine and conserve its novel materials properties generated by the quantization effects due to the nanometer size.

5.7 Report of X-Ray Polarization Modulation Spectroscopy Group

The spatial ordering of charge and spin is one of the fundamental phenomena in materials, and it is exploited for many technological applications. An example of charge order is the directional nature

of covalent bonds that leads to preferential chain or ring formation in organic materials and is technologically exploited in such applications as antiwetting polymer coatings, polymer fibers, or liquid crystal flat panel screens. Spin order leads to the macroscopic magnetization of materials and is the basis for their usefulness for technological applications ranging from electric power generators to magnetic levitation trains to magnetic recording devices. More generally, the ill-understood origin and relationship of charge and spin order in correlated materials (e.g., the high- T_c oxides) have required a new paradigm for condensed matter physics, owing to the fact that conventional textbook concepts cannot explain their properties. Understanding the origin of charge and spin order, in particular on lengths scales in the 1–10-nm range and timescales down to the picosecond regime, constitutes one of the great challenges in modern condensed matter physics and materials science, and it is also required for the design of artificially structured materials with improved properties for technological applications.

X rays offer remarkable capabilities for the study of charge and spin phenomena in materials. They derive from the direct coupling of the x-ray electric field vector to the charge and coupling of the x-ray angular momentum to the angular (orbital) momentum of the charge. The absorption processes are governed by electric dipole transitions that obey strict selection rules on angular momentum conservation and couple different core shells to specific valence shells. In x-ray absorption, sensitivity to the spin arises indirectly from the coupling of the orbital moment to the spin moment in the valence shell through spin-orbit coupling. In the following, the capabilities of the simplest and most commonly used x-ray method—x-ray absorption spectroscopy—for the investigation of materials will be discussed, and the great advantages that will be derived in the future from rapid polarization control (i.e., x-ray polarization modulation spectroscopy) will be emphasized. Other methods such as resonant x-ray scattering techniques or x-ray emission spectroscopy also provide sensitivity to charge and spin, but for brevity, they will not be discussed here.

5.7.1 Determination of Charge Order—Linear Dichroism

It is well established that charge order can be detected by linearly polarized X rays, and this forms the basis of polarized near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. In general, the x-ray absorption intensity of linear-polarized X rays directly probes the quadrupole moment of the local charge around the absorbing atom through a search-light-like effect. A quadrupole moment exists in all cases where the local charge has lower than cubic symmetry. The absorption intensity is at a maximum if the x-ray electric field vector is aligned along the direction of maximum charge (hole) density in the atomic volume surrounding the absorbing atom. This x-ray linear dichroism effect provides the basis for determining the orientation of chemisorbed molecules on surfaces where the orientation of specific molecular orbitals or bonds relative to the surface is determined. Another example is the determination of orientational order in polymers or liquid crystals (e.g., nematics). Here, the average orientation of a selected molecular orbital (e.g., a π orbital) is determined. The measured angular dependence determines the quadrupole moment of the charge distribution of the selected orbital. In order to obtain the order parameter of the total charge, the charge distributions of all occupied (electrons) or empty (holes) molecular orbitals would have to be summed.

5.7.2 Determination of Spin Order Through Charge Order—Magnetic Linear Dichroism

In the absence of spin order, linear dichroism NEXAFS spectroscopy can only determine charge order in systems where the absorbing atom has lower than cubic symmetry. However, in the presence of spin order, the spin-orbit coupling leads to preferential charge order relative to the spin direction, even in cubic systems. This effect is the basis for the determination of the spin axis in FM and especially AFM systems by means of x-ray magnetic linear dichroism (XMLD) spectroscopy. Because the electric field vector oscillates in time along an axis and the radiation may be absorbed at any time, linearly polarized X rays are only sensitive to axial, not directional, properties. Hence, the orientation of the AFM axis and for FM the orientation of the FM axis can be determined, but the spin direction itself cannot be determined.

The fact that the XMLD intensity depends on the relative orientation of the electric field vector and the magnetic axis can be used for magnetic imaging proves especially useful for AFM which cannot be studied by many techniques because of their compensated spin structure. Because x-ray linear dichroism can arise from electric and magnetic asymmetries, care needs to be taken to distinguish magnetic order effects from ligand field effects. This is typically done through temperature-dependent measurements.

5.7.3 Determination of Spin and Angular Momentum Order—Circular Dichroism

Right- and left-handed circularly polarized X rays possess opposite angular momenta which are transferred in the x-ray absorption process to the photoelectron excited from a core shell. The photoelectron then possesses a well-defined angular momentum, and in a one-electron picture, the empty valence shell can be viewed as a detector of this momentum. The XMCD absorption intensity defined as the intensity difference measured with left and right circularly polarized light is linked through sum rules to the size of the orbital and spin momenta of the empty valence states. Angle-dependent measurements in magnetic fields can determine the anisotropies of the orbital moment and of the spin density in the unit cell (also called the intra-atomic magnetic dipole moment). Because handed circularly polarized X rays have directionality, they can also detect the direction of the spin and orbital moments, a fact utilized in XMCD microscopy of FM.

5.7.4 Need for Improved Capabilities of Detecting Charge and Spin Order

In the past, circular dichroism studies of FM and linear dichroism studies of organic materials and AFM have utilized relatively large dichroism effects which are in the range 10%–50% for some materials. There are many materials, however, that only exhibit weak order, and increased sensitivity is needed to reliably measure the weak dichroism signals. Materials near order-disorder phase transitions form a general broad class of weak order systems. Other interesting problems relate to the order at surfaces and interfaces. Although they may exhibit enhanced order relative to the bulk, it is usually difficult to obtain interface specific information because of the weakness of the signal. In the following, two examples of magnetic phenomena will be discussed. The field of macroscopic magnetism is, of course, founded on the very existence of spin order, and it is not only scientifically interesting but also of great technological importance.

The first problem relates to the phenomenon of exchange bias (i.e., the directional bias of the magnetization direction in a FM by an AFM). This phenomenon has been known for half a century but is still poorly understood despite the fact that it is commercially exploited in magnetic recording heads. In such devices, an exchange bias of the FM is created by either growing the FM/AFM sandwich in a magnetic field or cooling the sandwich through the AFM Néel temperature in a magnetic field. The magnetization direction of the ferromagnet then exhibits only one preferred magnetization direction, not two equivalent 180° directions along an “easy axis” as in conventional FM. The bias effect clearly arises from locked-in uncompensated spins near the AFM/FM interface. The detection of these uncompensated spins with *unidirectional* preference and a measurement of their hysteresis loop (which would reveal how they are anchored to the bulk AFM) hold the key for a better understanding of the exchange bias puzzle. Ultimately, it would be advantageous to image their spatial distribution with high-resolution XMCD microscopy. Here, the length scale of interest lies in the 1–100-nm range and is dictated by the range of the exchange interaction and materials parameters such as the grain size. In practice, the relatively small number (of the order of a monolayer) of uncompensated interface spins poses a considerable experimental challenge, and it calls for new experimental methods with increased sensitivity.

The second problem which relates to the emerging area of spintronics (i.e., magnetoelectronic devices based on spin transport, spin accumulation, and stable microscopic magnetization domains) is highlighted in section 2.7. Photon-in/photon-out XMCD spectroscopy offers important advantages over conventionally employed photon-in/electron-out techniques. The question remains how to improve sensitivity to the unprecedented levels required by forefront scientific problems. The answer lies in phase-sensitive detection schemes based on rapid polarization modulation. A glimpse of what will be possible in the future with modulation techniques applied to this problem was shown in section 2.7.

5.8 Report of Dynamic Soft X-Ray Scattering Group

The underlying scientific motivation to pursue dynamic soft x-ray scattering is provided by Fig. 20 and Fig. 21. Fig. 20 summarizes the important length/wave vector and energy/frequency scales of a diverse array of systems and physical properties. With the same axes, Fig. 21 summarizes the spatial and temporal length scales probed by several kinds of technique. The main message provided by these figures is that there are many processes for which short length scales and moderate time scales are key; yet few techniques are available to probe that spatio-temporal regime. For example, many of the relevant processes in Fig. 20 are chemical or biochemical in nature, where activation energies lead to slow modes that operate on short length scales. These processes are often key to material function; yet in many instances there is a lack of robust techniques to measure them. The red star in Fig. 20 denotes the regime probed by a recent study of smectic liquid crystal fluctuations using soft x-ray dynamic light scattering. Extending this kind of measurement to biological systems, for example, will enable probing large-scale internal fluctuations in protein molecules. This will provide a crucial augmentation of structural studies because it will be possible to see how proteins move and how these motions relate to biological function.

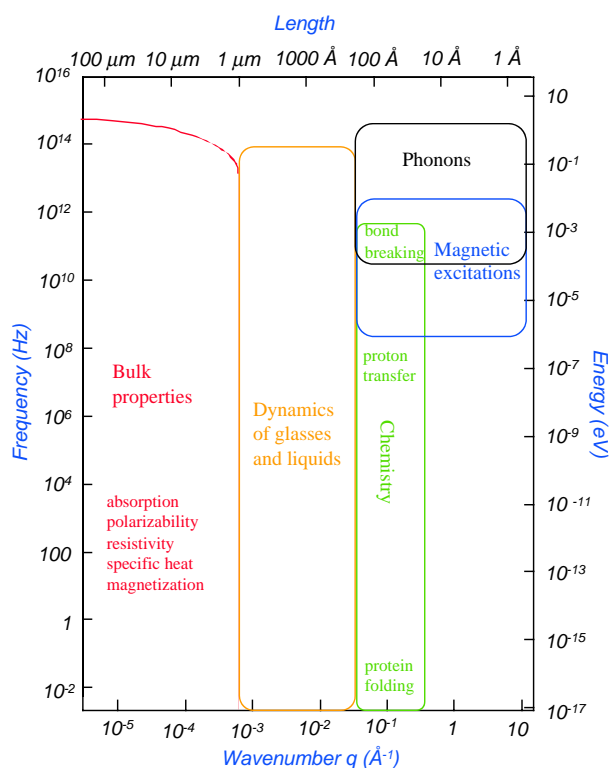


Fig. 20: Summary of the important length and time scales in various material processes.

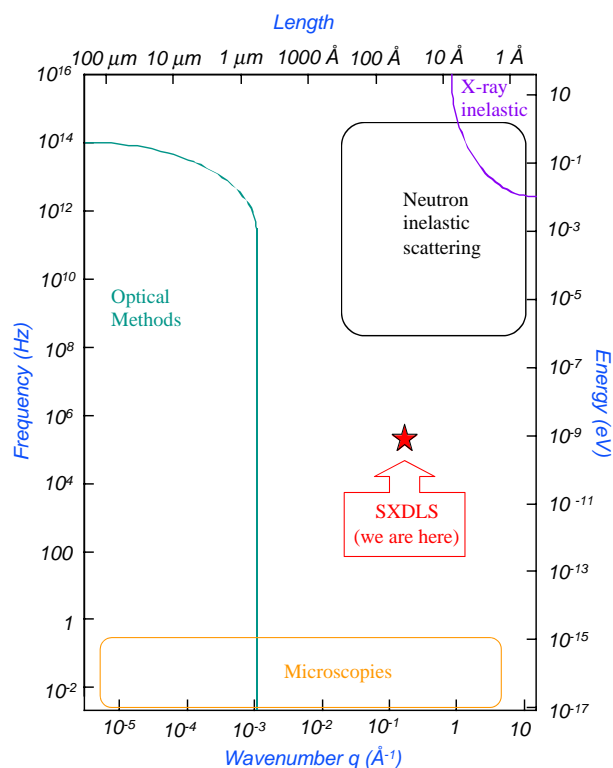


Fig. 21: Summary of the spatial and temporal sensitivities of various experimental techniques. Note the large gap at short length and moderate time scale that can be filled with dynamic soft x-ray scattering.

As emphasized in section 4.6, the fact that the energy range of soft X rays encompasses the important absorption edges of many elements can endow dynamic soft x-ray scattering with crucial atomic and often also molecular or magnetic contrast. Well-defined core-to-bound transitions at and above the C, N, and O *K*-absorption edges, for example, can be used as fingerprints in absorption and scattering. In addition, particular sensitivity to the magnetic properties of *3d* and *4f* ferromagnets is available from the magnetic contrast offered by dichroism near the relevant *L*- and *M*-edges. A natural extension of the magnetic contrast explored in section 4.6 is that it will be possible to measure the fluctuations of micro-phase-separated systems such as the stripe phases of transition-

metal oxides. The static structure of charge stripes is being determined using microscopies and incoherent neutron and x-ray diffraction. However, the often complex thermodynamic phase diagram and low-energy transport properties of these systems are determined by their spectrum of excitations. To understand the relevance of stripes to the mechanism of high-temperature superconductivity or colossal magnetoresistance, it is necessary to measure their dynamical properties as a function of current, temperature, and applied field. By combining its spatio-temporal sensitivity with the contrast offered by 3d transition-metal *L*-edges, dynamic soft x-ray scattering is unique in offering the possibility of doing just that. Similar statements could be made for other novel conductors such as electronic and ionic conducting polymers, where there is often strong coupling between electronic and vibration degrees of freedom, and for the phase behaviors of polymers, copolymers, and polymer blends.

5.8.1 Instrumentation Requirements

These sensitivities of dynamic soft x-ray scattering indicate a potentially powerful approach to measuring fluctuations at short length and timescales and, therefore, a unique opportunity to achieve many results of seminal importance. As yet, the overall financial investment expended to develop soft x-ray dynamic scattering has been very modest. Two groups (Kevan/Sorensen and Eberhardt/Tiedje) have constructed simple end stations at a cost of less than \$200K. These have been operated on a limited basis on existing beam lines that were not optimized for coherence-based experiments. As explained further below, this technique has requirements that are unlike those encountered in any other soft x-ray experiment. To make substantive progress on difficult but important experiments will require a larger and more focused investment. Indeed, the coherent flux available on BL7 and BL8 at the ALS—“work horse” undulator beam lines that were optimized primarily for spectroscopy—fall roughly a factor of 1000 less than what could be achieved with a beam line optimized as discussed below.

Although undulator sources provide dramatic increases in the available intensity of coherent soft and hard x-ray beams, all current dynamic scattering experiments in these regimes remain severely flux limited. Because the phase space of a coherent beam is larger at longer wavelengths, it is, in principle, possible to achieve a much higher coherent flux of soft X rays than hard X rays. In extracting the coherent fraction from an incoherent beam, the available flux scales as λ^2 ; therefore, the soft x-ray coherent flux can, in principle, be as much as 1000 times higher compared with that at hard x-ray energies. In this context, the importance of measuring properties at the molecular rather than atomic scale should be emphasized in the above examples. The usual requirement of hard X rays, therefore, does not hold, and the larger coherent flux available at longer wavelengths recommends operating in the soft x-ray regime. A beam line specifically designed for coherent soft x-ray optics and dynamic scattering will be required to achieve this flux advantage. Such a beam line is not available anywhere in the world at present.

What should such a beam line look like? Our working group put quite a bit of effort into answering this question. As is increasingly the case in optimized beam lines at synchrotron radiation facilities, it is quite clear in the case of soft x-ray dynamic scattering that the term “beam line” should include everything from the photon source to the photon detector. The experiment itself is part of the optical system and needs to be fully integrated into the design.

Before stating our primary design recommendation, two crucial and intimately coupled design parameters—energy band width and photon spot size on the sample—should be explored first. It appears that the bandwidth of the light is not very important in these experiments, at least if one does not wish to use the detailed structure near an absorption edge to achieve particular contrast. Indeed, most x-ray dynamic scattering is now performed using raw undulator light with a bandwidth of ~1%, and Co:Pt films were studied in the soft x-ray regime using this approach as well. The fundamental problem with this approach is that it places a limit on the maximum scattering wave vector and thus the spatial resolution at which the scattering remains coherent. Specifically, if the beam spot on the sample has diameter D and there are N longitudinally coherent waves, then the speckle contrast starts to decrease at a spatial length scale of $\xi \sim D/N$. In the soft x-ray regime, experiments have typically used $D \sim 20 \mu\text{m}$, so a bandwidth of 1% ($N = 100$) limits the spatial scale that can be probed to $0.2 < \xi < 20 \mu\text{m}$. Ideally, a spot size an order of magnitude smaller than this

and a bandwidth an order of magnitude better would be used to achieve $2 \text{ nm} < \xi < 2 \text{ }\mu\text{m}$. The reduced bandwidth will correspondingly reduce the coherent flux, in principle, by a factor of 10. In practice, the loss will be more than this because of figure errors and reflectivities of the optical components in the required soft x-ray monochromator.

There are other advantages and at least one disadvantage of using a micron-sized incident spot in soft x-ray dynamic scattering experiments. First, the speckle solid angle will be proportionately increased, and the diffuse scattering signal per speckle will be correspondingly enhanced. Essentially, one would be trading wave-vector resolution for signal, and this normally is a good thing to do in these experiments. Thus, not only would the optimized beam line offer 1000 \times more coherent flux, but also the speckle solid angle will be as much as 100 \times larger. These two factors together will enable many new kinds of experiments. Also, the speckle pattern is inherently a far-field diffraction phenomenon. A small spot will move the far field closer to the sample, making the scattering apparatus more compact. The major drawback to a focused spot is the correspondingly increased flux density and consequent radiation damage. This is a particularly serious issue in soft condensed matter and biological systems, where rastering the beam across the sample will likely be required.

The primary recommendation of our working group, therefore, concerns the nature of an undulator beam line optimized for dynamic soft x-ray scattering:

- The beam line should operate between 70- and 1500-eV photon energy. It should be located at a facility optimized for high optical brightness and should moreover provide linear and hopefully also circular polarization.
- The monochromator should have a minimum number of highest quality optical components and should operate at or near the diffraction limit all the way from the source to the sample.
- The monochromator should provide different operating bandwidths, including $\sim 1\%$ from the raw undulator light and 0.1% and 0.01% with interchangeable gratings. The use of the raw undulator bandwidth requires that zero-order light be in focus at the exit slit.
- The beam exiting the monochromator should be refocused to a spot size on the sample of a few microns, and this spot should not move by more than its diameter as the wavelength is changed. These requirements strongly suggest use of a varied line space monochromator that utilizes a fixed exit slit.
- Extreme care needs to be taken to guarantee the mechanical stability of the beam line, end station, and synchrotron source over a broad frequency range (10^{-8} – 10^0 s).
- To be able to reach very fast time scales, homogeneous filling modes of the source ring are preferable and possibly essential.
- Rejection of stray light and higher orders is also very important, because it is often necessary to operate in a low-signal, diffuse scattering geometry that is not far from intense, nonscattered light.
- A new, flexible scattering spectrometer also needs to be carefully designed so that it is well matched to the beam line optics.
- The spectrometer should allow introduction and manipulation of a diverse variety of samples with control of temperature between 4 and 500 K and magnetic field up to at least 2 T.
- There should be at least one polar axis of rotation with a precision of $\sim 0.01^\circ$.
- There will generally be no need for the scattering apparatus to operate at UHV, though this might be necessary in some experiments and should not be ruled out.
- Finally, we note that some effort needs to be expended in the area of detector development. A detector with a response time of less than 50 ns is essential to measure fast correlation times. Moreover, detector afterpulsing—the production of spurious echoes at highly correlated delay times on the order of 1 μs —is a serious problem in dynamic scattering experiments. Channeltrons, channelplates, and most photomultiplier tubes suffer from serious afterpulsing. The quantum efficiency of these devices in the soft x-ray regime is also not high.

5.8.2 A Case Study: The Equation of Motion for Stripes

The charge of the workshop requested that participants think about what can be done with soft x-rays to change the way people think about the most fundamental problems in our field. There are many such problems that can, in principle, be studied with dynamic soft x-ray scattering. A few examples include (1) bulk and surface polymer dynamics, entanglement, and the reptation problem; (2) internal fluctuations and librations in proteins and other biopolymers; (3) fluctuations in spin-charge micro-phase-separated systems such as the high- T_c superconductors; and (4) domain wall motion in ferromagnets, antiferromagnets, and ferroelectrics. In all such cases, the successful application of the technique is determined by the available scattered signal and, even more practically, by radiation damage. In dynamic scattering, data are collected in terms of an intensity-intensity autocorrelation function or a power spectrum. If one has a scattering rate into a single speckle of R , then to accumulate statistics corresponding to a timescale of $1/R$ requires minutes of data collection. To measure a timescale of $1/10R$ requires about an hour, while a timescale of $1/100R$ requires about a day and is, therefore, not very practical. This section will now be closed with an analysis of what will be required to get useful results in the best defined of the above experiments; that is, stripe fluctuation in cuprates.

The formation of stripe phases in oxide materials, notably the high-temperature superconductors and the colossal magnetoresistance materials, has generated substantial interest in recent years because these phases seem to require a new paradigm for charge motion in solids. Briefly, it has been determined that carriers (often holes) segregate into one-dimensional stripes that are separated by insulating AFM regions typically a few lattice constants wide. The formation of stripes is essentially a real-space phenomenon, though transport of charge probably involves collective motion within the stripes themselves. These thoughts suggest that a combined real-space, k -space theory will be required to determine the relevance of stripes to superconductivity or magnetoresistance. More importantly, if this is true, the motion of a stripe must play a key role in any such theory. Stripes, therefore, offer a paradigmatic materials phenomenon that combines a spatial scale of $1\text{D}2$ nm with important temporal fluctuations. A complete stripe theory does not yet exist, and there is no way to predict *a priori* what timescales are relevant. The following thoughts constitute an attempt to understand what scattering rate could be achieved and thus what timescales could be probed with dynamic soft x-ray scattering in a difficult experiment on an interesting system.

The ordering patterns of the stripe phases have been probed with neutron and hard x-ray scattering. The latter observes stripe superlattice Bragg peak intensities typically 10^{-8} less than that from low-order Bragg reflections. Also, the stripe positions are correlated over a range of only $200\text{D}300$ Å (i.e., these are probably not true thermodynamic phases). Given this domain size and the reported lattice mosaicity, it is possible to show that the charge associated with a stripe reflection is in the range $1\text{D}10$ electron units. This estimate is consistent with simple ideas about the actual charge separation in real space. That this is not very much charge, combined with the fairly short stripe coherence length, leads to very weak stripe reflections. Given this estimated geometric scattering factor and the measured domain size, it is possible to calculate the nonresonant Bragg reflectivity in a geometry relevant for a soft x-ray experiment. It was found that for a $1\text{-}\mu\text{m}$ spot on the sample, the stripe reflectivity into a single speckle would be $\sim 10^{-10}$ of the incident flux. If there was an optimized beam line on a third-generation storage ring with a spectral brightness comparable to the ALS or APS, it would be possible to produce a coherent flux at the Cu L -edge, $\lambda = 1.3$ nm, of $F_{\text{coh}} \sim 10^{11}/\text{s}$. The nonresonant scattering rate would be only 10 Hz, implying that a limited temporal dynamic range could be measured. One would naturally want to operate at the Cu L -edge or O K -edge to achieve a resonant enhancement of perhaps $10\text{D}100$, and a quite reasonable scattering rate of ~ 1 kHz might be achieved. Clearly, such an experiment would be impossible without an optimized beam line—new resources will enable a qualitatively new and important kind of experiment.

5.9 Ultrahigh Resolution Spectrometers

5.9.1 New Schemes for SXES Spectrometers

The fact that resonant inelastic soft x-ray scattering is not impaired by the lifetime broadening of the core-excited state opens the possibility to go to very high resolution schemes for soft x-ray emission spectroscopy. Before this notion was generally accepted, the incentive to put effort in such development was not present. Obviously, there would be great interest in achieving kT-resolution in, for example, SXES studies of high-temperature superconductors, as well as in studies of low-energy excitations in correlated materials in general. A glimpse of the future of high-resolution spectrometers is presented in section 2.8, and the design possibilities are presented in section 5.10.

In the following, two paths to very high resolution instruments for soft x-ray emission spectroscopy are suggested.

5.9.2 Plane Grating Spectrometer

Instruments for soft x-ray emission spectroscopy are usually based on spherical gratings in Rowland geometry. Often they use area detectors, which offer multichannel capability and large acceptance angles. The size of the instrument and the spatial resolution of the detector generally set the limit in resolution, whereas the maximum usable size of the grating is an important factor for limiting the sensitivity. The grating size is related to the imaging errors and thus to the spectral resolution.

Increasing the grating size considerably without losing resolution could be done if a plane grating is used instead of a spherical grating. In this case, collimation and focusing would be made with separate mirrors. By this scheme, it would be possible to achieve substantially increased sensitivity of a grazing incidence instrument. Obviously, there is a point where the total reflection condition sets a limit for the acceptance angle. A typical acceptance angle in the plane of dispersion for a grazing incidence grating instrument is <10 mrad. The critical angle of total reflection for a few hundred eV photons is typically <100 mrad depending on material, which suggests that there would potentially be up to an order of magnitude in acceptance angle to be gained. However, the grazing incidence required for total reflection limits the gain because of the size of the optic needed. By applying a multilayer coating to the mirror, less grazing angle of incidence can be used, allowing smaller size mirrors. One drawback however would be the necessity to have sets of mirrors to cover the different x-ray edges, because the multilayer mirrors have very narrow bandpass. Also, the multilayer might have to be graded (i.e., it would have a varying period over the mirror surface in order to compensate for the varying incidence angle).

As an example, an instrument of the suggested type optimized for the Cu $3p$ edge could collect 50 mrad in the dispersion plane and 200 mrad in the sagittal plane (presently used instruments accept some 50 mrad in the sagittal plane). The resolution at about 75 eV for a source size of $10 \times 100 \mu\text{m}$ would be 10 meV. The considerably improved performance of this type of instrument has a price to be paid. The multilayer coating of the mirrors only offers high reflectivity for one atomic species (edge). However, there is certainly sufficiently interesting scientific problems to be addressed to justify the cost that this specialization causes.

It might be possible to avoid the use of multilayer coating if one can accept a large instrument and possibly also some loss in sensitivity. In this case, it might not be feasible to have the instrument rotatable in the vertical plane, something which is very useful in order to study linear dichroism effects. However, if one has access to a beam line with the provision to select the direction of polarization, such rotation is not necessary.

5.9.3 Fourier Transform Spectrometer

Fourier transform spectroscopy (FTS) is a very successful method for the infrared and the visible, and it provides both very high resolution and sensitivity. Work is in progress to push the technique down into the UV and vacuum UV, but not until recently has there been real efforts to try to build an

instrument for the ultrasoft x-ray region. The most challenging difficulties associated with an interferometer for the soft x-ray range are the fabrication of beam splitters and the alignment and movement of the optical components. The positioning and alignment of the elements of a soft x-ray interferometer have to be made with very high accuracy. For example, for C K emission, the smallest path length difference has to be less than 2.5 nm, and the parallelism of the merged beams in the interferometer has to be of the order of 1 μ rad or less. Considering the advancement in positioning technology in recent years, these requirements can probably be met, although one needs to master many problems related to vibrations, temperature stability, etc.

The potential of a soft x-ray Fourier transform spectrometer (Fig. 21) is very interesting. The sensitivity could be at least two orders of magnitude larger than for conventional instruments, and at the same time, the resolution could be pushed considerably. An instrument with a path difference scanning length of 1 mm would provide a resolution of 1 meV at the Cu 3*p* edge.

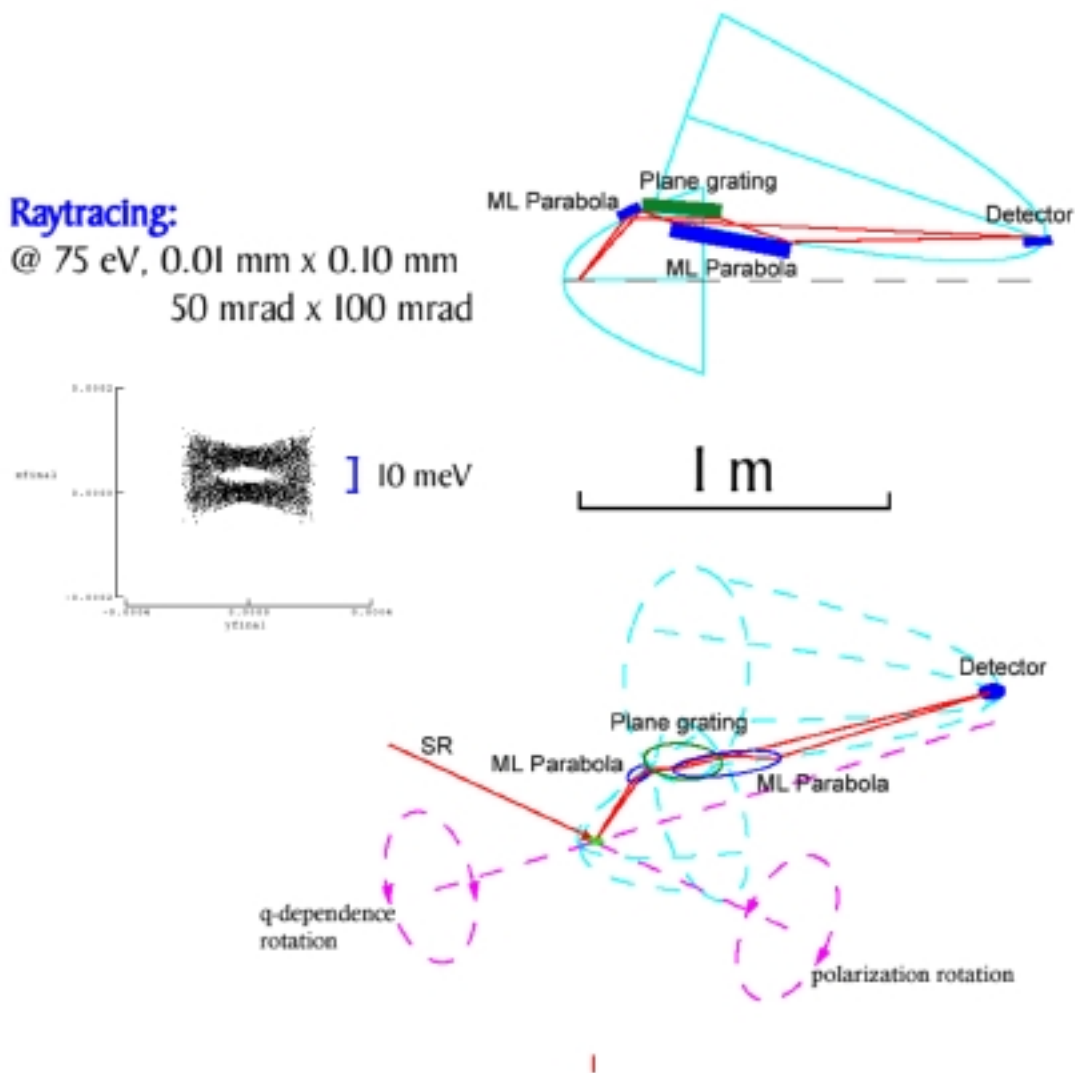


Fig. 21. High-resolution, high-throughput, low-bandpass SXES spectrometer.

5.10 Theoretical Challenges

5.10.1 Executive Summary

Tunability and element specificity make soft X rays an important and powerful experimental tool for current and future researchers. Their photon energy region encompasses both the *K* edges of elements important in organic systems, like polymers and substances found in biological systems, and the *L* and *M* edges of transition-metal and rare-earth elements that are found in technologically important oxide materials (high-temperature superconductors, colossal magnetoresistance systems). The same chemical elements are also present in the chemical complexes found in toxic waste and artificially structured materials. The future of synchrotron-based soft-x-ray photon-in/photon-out experiments is envisioned to be in the application of core-resonance techniques to these and other systems. Researchers will investigate atomic multiplet and band structure effects as well as static and dynamic structure. The site and element specificity will enable elucidation of the spatial and temporal structures of materials and physical phenomena not obtainable by any other technique.

Fully exploiting the new aspects of synchrotron-based photon-in/photon out materials research will require significant developments in the theory of soft x-ray processes as well as theoretical descriptions of the systems being studied. An example of the former need results from the simultaneous dependence of soft-x-ray scattering on both structural and x-ray spectroscopic (element- or site-specific) properties. This allows characterization of the location of a species in physical systems by analyzing diffraction effects on scattering of X rays resonant with that species' core excitation energies. In this report, the theoretical needs are not discussed with respect to the description of the systems themselves. However, it is noted that there remain important needs in systems ranging from strongly correlated to chemical complexes found in toxic waste.

The second new aspect is the fact that the 1–10-nm wavelengths of soft X rays match the length scales of natural and artificially created nanostructures and thus are an excellent probe of such entities. Examples of such include dimensions of phase-separation domains in strongly correlated systems (e.g., striped-phase superconductors), magnetic domain structure, magnetic multilayers, quantum dots, nanocrystals, and macromolecules, as well as inhomogeneities that give rise to static and dynamic speckle in the soft x-ray region. It was also noted that many gross structural features of large molecules, which are larger than the atomic scale but accessible to soft-x-ray wavelengths, can be structural features that are most relevant to large-scale configuration changes. It is crucial to note that it is in this regime where technologically and experimentally interesting system sizes are becoming accessible to the most advanced first-principles techniques.

5.10.2 Status of Theory

To date, theoretical studies have been at a basic level aimed at understanding the fundamental excitation processes and the physical content of the spectroscopic data. Spectroscopic techniques for which the theory is most well developed include x-ray absorption, x-ray fluorescence, and resonant scattering from simple *s-p* bonded systems. Connections have been made between scattering experiments and fermiology, transition-metal and rare-earth atom multiplet effects in complex oxides, atomic geometry, and other areas. The close connection between resonant x-ray scattering and (near-edge) x-ray absorption spectroscopy or fine-structure studies (NEXAFS, XAS, EXAFS, and XANES) suggests the relevance of theoretical methods used in absorption to studies of scattering.

Current treatments of electronic structure are limited in two main ways. The first limitation involves treating complex systems (systems with large formula units, such as complex polymers, minerals, molecules, and clusters) with sufficient realism so as to maintain quantitative predictive reliability. Substantial development has already been made in treatments of x-ray absorption and anomalous scattering. The theoretical tools, while being able to address complex systems, are still undergoing refinements to treat the electronic structure at the same level of detail as full-scale band-structure calculations.

At the present time, the existing theory does not start from a fundamental theory and derive the results. Instead various steps are approximate, require utilizing rules-of-thumb, and neglect various

processes. These are based on extensive experience and physical insight so they work reasonably well for the systems studied. However, they cannot be blindly relied on as new, as-yet unknown systems are explored. What is needed is development of a theoretical framework that starts from fundamental formulation and develops expressions for the calculation of experimental properties with known characterizable approximations. Recent developments in fundamental theory make this a realizable vision. The second limitation lies in the treatment of strongly correlated systems, such as transition-metal and rare-earth oxides. One very successful theoretical approach envisions the problem as that of an isolated metal ion that can be treated as a crystalline environment acting more or less as a change in the boundary conditions from simply being surrounded by vacuum. Extensions have recently been made to clusters of a central atom and its nearest surrounding ligands, but this is a long way from a large system. Future work will be needed to bridge the gap between such an atomic cluster calculation and the treatment of a truly crystal system (i.e., how to better “embed” the metal ion in a solid state calculation).

The above, atomic-scale modeling of spectroscopic aspects of x-ray scattering should be considered only as making up many of the building blocks that will be needed in the future. Future activities should proceed in many directions. These include what was dubbed “ $k_B T$ physics,” such as investigating fluctuations of striped phases in superconductors, as well as temperature-dependent magnetic and structural fluctuations. Many of these effects are characterized by a length scale comparable to soft-x-ray wavelengths. It is anticipated that such structural information will exploit elastic resonant x-ray scattering, but interpretation of experiments would require new theoretical developments in the classical electromagnetic scattering of X rays by the highly inhomogeneous systems with complex dielectric properties that would be studied. Such classical scattering theory within the greater context of the inverse-scattering problem is especially relevant, because it relates to the speckle phenomena that can now be better studied because of improved source coherence.

However, basic research remains necessary to the incorporation of electron-vibronic (or electron-phonon) effects, magnon and other low-energy excitations, and crystal-field excitations into the modeling of resonant x-ray scattering. This could prove especially useful, for instance, in understanding Jahn-Teller and similar systems. Over the long-term, such research will also help to understand mechanisms for excited-state decay linewidth broadening effects that are prevalent in the solid state. Also, this type of research would provide insight into low-energy excitations that are important determinants of the ground-state and transport properties of technologically important materials.

To meet the above objectives, a need for improved experimental energy and momentum resolution (10 meV at 100-eV photon energy), as well as polarization analysis for the outgoing photons, is anticipated.

5.11 Instrumentation Challenges

5.11.1 Overview

Although the participants of the workshop represented many different disciplines with experiments that have very specific needs, some unifying themes are evident. Perhaps most striking is that they can all benefit significantly from developments in detector technology. Comparatively small investments in this area could ignite the productivity of the field and have significant leverage and impact on a broad range of science.

The next major theme is that specific experiments would benefit most from tools that are optimized for their particular requirements. Experience has shown that in many instances a general-purpose device that can do a bit of everything often seems incapable of doing anything particularly well. The specialization becomes apparent when the types of optical systems for beam lines are considered. They can, for example, be categorized in terms of energy (range/resolution), polarization control, coherence requirements, and microfocusing capability. End stations for particular experiments can be very specific relating primarily to issues associated with environment control. These can include sample magnetization, provision for temperature control, and samples examined in situ in aqueous environments at a variety of pressures.

As a final unifying theme, there was a clearly expressed desire that these cutting-edge resources have well-qualified staff to support their utilization and that appropriate infrastructure should be available to support the scientific programs. The latter often takes the form of “conventional” sample preparation and characterization facilities near the beam lines so that optimal use can be made of what beam time is available.

5.11.2 Detection Systems: (Photons Out)

It was noted that existing or planned beam lines on third-generation sources already have sufficient intensity at the sample that photon-beam-mediated chemistry is a real concern for some experiments. This implies that improvements in instrument sensitivity will be the most promising path to increasing the overall sensitivity of these experiments. There are a number of approaches to achieving this goal.

These instruments are generally “Nordgren-type” spectrometers based on a Rowland circle design. One avenue for improvement seems to be redesigning the spectrometer optics that will allow the channel plate detector to be illuminated at normal incidence, gaining perhaps a factor of 5 or 10. Another improvement would be to increase the solid angle collection. In many situations, it seems that keeping the illuminated spot on the sample small (say below 10 microns) would allow the sample to become the entrance slit of the spectrograph, gaining perhaps as much as a factor of 10 to 100 just in solid angle. Optimization of grating blaze and finish might yield as much as an additional factor of 3 in efficiency. Several groups are already addressing these issues; there are at least three efforts working along these lines.

Another avenue that will require further investigation is the development of single-purpose optical systems, optimized for performance over a modest energy range that would have very high throughput. One could have several of these instruments that would be readily interchanged to work at different energies. Various schemes to increase the solid angle acceptance of the spectrograph are under consideration, including the use of multilayer collection optics or transmission gratings. These optics are relatively less efficient than grazing incidence geometries, but they could, in principle, compensate for this deficiency by collecting very large solid angles. They would also necessarily be rather wavelength specific.

More exotic interferometric spectrometers that could potentially provide substantial gains in sensitivity are under development. However, they are very challenging instruments in the early stages of development; hence routine application of these devices is probably at least several years distant.

Energy-dispersive fluorescence detectors are continuously improving in resolution and reaching toward softer x-ray energies, led by commercial applications in electron microprobes. They provide the largest possible solid-angle and most efficient detection, and their resolution is sufficient to be element selective. Selectivity to the chemical environment is achieved by the excitation process, such as in near-edge adsorption spectroscopy.

5.11.3 Beam Line Optical Systems: (Photons In)

A daunting list of requirements can be assembled for the various experiments described during the workshop. For example the “ultimate” instrumental requirements for frontier soft x-ray fluorescence and resonant inelastic scattering research include:

- 10-meV total energy resolution
- 100-eV to 5-keV photon energy range (both excitation and emission)
- High throughput 5,000 resolving power monochromator (0.2 eV at 1 keV)
- Tightly focused beam spots (down to a few microns)
- Variable polarization photon source
- Angle-resolved emission

- Very high magnetic fields (5–10 T) with directional control
- Variable temperature (down to <10 K)

Fortunately, none of the science discussed requires all of the parameters to be delivered to the same experiment at the same time. Clearly what is required are multiple specialized beam lines and end stations/spectrometers to achieve high-energy resolution, extreme sample environments, and large photon energy range outlined above.

An additional capability for variable polarization control to increase sensitivity to weak magnetic dichroism signals via modulation measurement techniques requires rapid switching (up to 100Hz) between two beams of different polarizations. This task requires an elliptically polarized undulator and challenging solutions to minimize asymmetries between the two beams.

The following outlines the attributes of beam lines that represent the diversity of requirements for materials science applications discussed in this report. They would also address many of the other experiments outlined during the workshop.

X-Ray Absorption Station for Nanostructure Characterization

Energy Range	70–2000 eV
Polarization	Linear horizontal, circular desirable (but not essential)
Energy Resolution	100 meV
Spot Size at Sample	~1 micron
Detector	Energy dispersive fluorescence
Other Features	Sample load lock for rapid turnaround Relatively easy access High level of routine technical support

Coherent Optics and Coherent Scattering

Energy Range	70–1500 eV
Polarization	Linear horizontal, circular desirable (but not essential)
Energy Resolution	$\sim 10^3 E/\Delta E$
Spot Size at Sample	~1–5 microns
Detector	Experiment specific
Other Features	Optimized for spatial coherence, $d\theta \approx \lambda/2\pi$ (diffraction limited focusing) Very good mechanical stability Can interface with a variety of end stations that support high (2-T) magnetic field and variable sample temperature (4–500 K)

Variable Polarization Undulator Beam Line

Energy Range	250–2500 eV
Polarization	Linear horizontal and vertical and/or right and left circular energy Resolution: $\sim 10^3 E/\Delta E$
Spot Size at Sample	~0.5 micron
Detector	Experiment specific
Other Features	Polarization can be switched at rates up to 100 Hz for polarization modulation experiments. Can interface with a variety of end stations that support high (>5-T) magnetic field and variable sample temperature (4–500 K)

Resonant Inelastic X-Ray Scattering (High Energy)

Energy Range	100–1500 eV
Polarization	Linear horizontal and vertical and/or right and left circular energy
Energy Resolution	100 meV
Spot Size at Sample	~1–5 microns
Detector	Energy dispersive fluorescence
Other Features	Can interface with a variety of end stations that support high (>5-T) magnetic field and variable sample temperature (4–500 K)

Resonant Inelastic X-Ray Scattering (Low Energy)

Energy Range	10–100 eV
Polarization	Linear horizontal and vertical and/or right and left circular energy
Energy Resolution	10 meV
Spot Size at Sample	~1–5 microns
Detector	Energy dispersive fluorescence
Other Features	Can interface with a variety of end stations that support high (>5-T) magnetic field and variable sample temperature (4–500 K)

5.11.4 Experimental Stations: (Photons In and Out of What?)

These requirements are especially specific to the experiment they serve. One of the more challenging sample environment systems discussed at the workshop was the need for an in situ system for examining environmental samples in aqueous environments. It would also be desirable to have the ability to study these systems at elevated pressures (the order of several to perhaps 100 atmospheres). Clearly, this is a major challenge for soft X rays because the attenuation of low-energy photons by even very thin layers of water is substantial. Again, this is an area that will require further development “off-line” but should be pursued because it could have a substantial beneficial impact on the science.

Much of the interest in photon-in/photon-out experiments is that they are unaltered by the presence of high magnetic fields; any changes that are observed should be due to physics of the sample that is modified by magnetic field. Clearly, this is very important for the study of magnetic materials. Sample chambers that can provide a high magnetic field are by no means new, but they will be an essential part of the complement of instruments for this field. For this type of spectroscopy, they will need to be carefully designed to consider the requirements of the “photon-out” detection scheme, particularly if it requires scanning the detector through a large angle for experiments requiring momentum resolution capability.

5.12 Facility Usage and Modes of Operation

5.12.1 Current Usage

The techniques discussed in this report are being carried out to some extent at various existing beam lines. A poll of facility representatives yielded the estimates shown in Table 2 for the percentages of full-time equivalent (FTE) beam lines currently in use in the U.S. for soft x-ray emission (SXE), soft x-ray speckle, and soft x-ray scattering.

SXE and speckle require the high brightness or coherence of premier undulator beam lines such as BLs 7.0 and 8.0 at the ALS and X1B at the NSLS. It is estimated that there are 1.35 FTEs in use for these purposes. Soft x-ray scattering is currently carried out exclusively at the NSLS using an

estimated 2.8 FTEs. The premier beam lines are heavily oversubscribed; therefore, new ventures can be accommodated by displacing existing programs or building new beam lines. The demand for circular polarization is strong and growing. The 1.35 FTEs for SXE and speckle include only 1 FTE for circularly and linearly polarized studies using the circularly polarizing undulator (CPU) at the APS. The 2.8-FTE total for soft x-ray scattering includes 1 FTE on the elliptically polarizing wiggler at the NSLS. The new elliptically polarizing undulator (EPU) (BL 4.0) presently being commissioned at the ALS is already oversubscribed; some part of the 0.3 FTE set aside for independent investigators will become available.

Projects in the works relevant to the context of this workshop are as follows. Phase I of the molecular environmental science (MES) initiative at the ALS has been partially funded, and construction has begun with completion anticipated in mid 2001. This project will comprise an EPU in Section 11.0 of the ALS delivering radiation to a monochromator and several end chambers for “wet” spectroscopy and microscopy in the energy range 75–1500 eV. At the NSLS, a chamber for SXE is being shipped from the Netherlands and has been granted beam time on X1B.

Table 2. Percentage Estimates of Full-Time Equivalent Beam Lines Currently in Use in the U.S. for Soft X-Ray Emission (SXE), Soft X-Ray Speckle, and Soft X-Ray Scattering

	SX Emission		SX Speckle		SX Scattering	
ALS	BL 7.0	5%	BL 9.0	5%		
	BL 8.0	30%				
APS	BL2-ID-C	25%	B12-ID-B	25%		
Center for Advanced Microstructures and Devices (CAMD)		—		—		—
NSLS	X1B	20%	X1B	20%	U4B	50%
					X13A	100% (EPW)
					X1B	20%
					X19A	10%
SRC		5%				100%
Stanford Synchrotron Research Lab (SSRL)		—		—		—
TOTALS		85%		50%		280%

5.12.2 Modes of Access

Access to synchrotron radiation in the U.S. is through two principal modes—facility owned and operated beam line (FOOB) or participating research team/collaborative access team (PRT/CAT). Each facility has some mix of the two.

Access to a FOOB is through a proposal submission and peer review mechanism administered by the facility.

A PRT funds, builds, and operates a beam line. PRTs are required to yield up some part of the beam time (25% or more) for allocation to general users/independent investigators through the proposal submission mechanism. A CAT funds, builds, and operates a Sector comprising an undulator and a bend magnet at the APS. It is a variant of a PRT with the distinction that the proposal mechanisms

for independent investigators are administered individually by the CRTs rather than centrally by the facility.

The PRT/CAT model was born out of economic necessity. The facilities themselves do not have sufficient resources to function exclusively with FOOBs. The PRT model can work successfully particularly for bend magnet beam lines. The 80 beam lines at the NSLS, for example, were established largely through the PRT model. At the third-generation sources, at least at the ALS, the PRT model is under severe strain. This derives from the sheer cost and complexity of beam lines, particularly insertion-device beam lines. In order to preserve the advantages of brightness, the beam lines must be built to very demanding engineering specifications, which place them beyond the competence of typical user groups. Another perceived disadvantage of the PRT/CAT model is that it encourages a proliferation of routine general purpose beam lines and discourages cutting-edge beam lines built for one very specific purpose.

Nevertheless, the PRT model does have some conspicuous advantages. It encourages scientific entrepreneurship. It also makes it very clear that the scientific direction is in the hands of the users rather than facility management. The challenge is to retain the successful features of the PRT/CAT model while ameliorating its drawbacks.

Another model based on practice at European facilities aroused considerable enthusiasm. This model might be called the entrepreneur-steward partnership (ESP). The idea is that an entrepreneurial group of user scientists makes the scientific case for a new beam line and generates a proposal to the funding agencies. The task of building the beam line is then subcontracted to the facility or other competent entity. The operation and general stewardship of the beam line would be the responsibility of the facility. In recognition of its efforts, the entrepreneurial group would retain some guaranteed beam time for the first year or two of operation, but the facility would then assume total stewardship. In other words, an ESP starts out as a PRT, but quickly converts to a FOOB. An obvious consequence of the ESP model is that it cannot work unless the funding agencies provide resources to the facilities to operate the FOOB phase.

A general sentiment was that there is no “one-size-fits-all” model and that one should not be imposed.

Appendix 1

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