Introduction and Summaries

1. Workshop Overview

On March 23-25, 1998, more than 300 scientists participated in a workshop entitled "Scientific Directions at the Advanced Light Source." They addressed the following charge:

The goal of this workshop is to identify the elements of the most compelling scientific program for the ALS and to make recommendations for a roadmap to implement that program.

In his opening address, Charles Shank, Director of the Lawrence Berkeley National Laboratory, pointed out that the workshop came close on the heels of a meeting of the ALS Scientific Policy Board, which made two important recommendations. First, the board strongly stated that the principal priority of the ALS should be to remain the world-leading facility for science in the vacuum-ultraviolet (VUV)/soft x-ray region of the spectrum where the facility is unique. Second, the scientific program should include the full utilization of the world-class capability of the ALS, including crystallography and intermediate-energy applications where x-ray brightness is important.

In her welcoming remarks, Patricia Dehmer, Associate Director for Basic Energy Sciences at the U.S. Department of Energy, posed the following challenging questions:

- Where is the forefront of your disciplines?
- What is the impact on the rest of science, technology, and society?
- What is the role of a VUV/soft x-ray facility like the ALS?
- What special tools are needed?

The participants rose to the challenge, and their deliberations, recorded here, will set the agenda for the ALS scientific program well into the next century.

The bulk of the workshop was spent in parallel breakout sessions in which working groups addressed specific scientific areas. The discussions were intense, productive, and congenial. Some of the working groups changed the scope of their discussions. So "Strongly Correlated Materials" metamorphosed into "Complex Materials;" "Polymers and Soft Matter" became "Polymers, Biomaterials, and Soft Matter;" "Catalytic Materials/Surface Science" became "New Directions in Surface and Interface Science;" and so on. Each working group provided a chapter to the workshop report. The following pages summarize the main conclusions of these groups.

A crowd of more than 300 attended the Workshop on Scientific Directions at the Advanced Light Source, which was held at the Lawrence Berkeley National Laboratory from March 23 to March 25, 1998. On stage is Professor Zhi-xun Shen of Stanford University, who is describing recent experiments that may help explain high-temperature superconductivity.

1.1 Cross-Cutting Themes

Some themes cut across the territories covered by one or more working group. A principal cross-cutting theme was the demand for *spatial resolution*. In environmental science, a major challenge was inhomogeneity at all length scales. In the various materials science working groups, the recurring themes were nanostructure, reduced dimensionality, quantum confinement, clusters, artificially engineered layered structures, and so on. In the biosciences, a clear need emerged for soft x-ray microscopy in cell biology, as well as a need to do protein crystallography on small crystals. A very likely outcome of the workshop will be proposals to build an undulator-based beamline optimized for scanning transmission x-ray microscopy (STXM). Building such a facility is a major recommendation of the Working Group on the Environmental and Earth Sciences, a sentiment that is echoed by the Working Group on Biosciences (sub-group on Soft X-Ray Microscopy) and the Working Group on Polymers, Biomaterials, and Soft Matter.

Another cross-cutting issue was the demand for *photon-in/photon-out* spectroscopy. Photoelectron emission spectroscopy (PES) has for three decades been the preeminent technique for investigation of electronic structure. It is now being challenged by soft x-ray emission (SXE) spectroscopy. The drawback of PES is that the detected particle is an electron, thus necessitating experiments in vacuum. Another feature of PES is that the electrons come from only the outermost atomic layers, which is good if surface sensitivity is desired but is less useful for studying sample interiors. These drawbacks are removed in SXE. The ability to probe buried interfaces or wet samples offers new opportunities in materials science, catalytic chemistry, and environmental sciences. The prospect of observing resonant inelastic scattering at the copper and manganese L edges was exciting to the complex-materials community.

1.2 Distinctiveness of the VUV/Soft X-Ray Region

Any definition of the role of the ALS begins with its distinctive features: world-leading performance in the VUV/soft x-ray region and world-class capability in the intermediate-energy x-ray region of the spectrum.

As a third-generation synchrotron-radiation source, the ALS is optimized for high brightness performance in the VUV/soft x-ray region, that is photon energies from 10 eV to 1000 eV. This is the range that includes the K absorption edges (1s core-level binding energies) of the elements in the first row of the periodic table: carbon (285 eV), nitrogen (410 eV), and oxygen (545 eV). Accessibility to these edges opens up many opportunities for the study of organic materials, polymers, and biological systems. Especially important is the “water window” between about 300 eV and 500 eV, where carbon (i.e., organic material) is absorbing and oxygen (i.e., water) is transparent; herein lies the contrast mechanism of the soft x-ray microscopies of importance to the environmental- and earth-sciences communities and the cell-biology community, as described in the working-group reports that follow.

The magnetic transition metals (i.e., cobalt, iron, and nickel) have L absorption edges (2p core-level → 3d valence-level transitions) in this spectral region: cobalt (785 eV), iron (715 eV), and nickel (860 eV). By exciting core electrons into the valence 3d levels, one is probing the very states responsible for interesting magnetic phenomena (see the report from the Working Group on Magnetism and Magnetic Materials). One transition metal that has leaped into prominence is copper (L edge at 940 eV), which is a key element in the high-temperature superconducting compounds. These compounds have revolutionized solid-state science in the last decade and made superconductivity nearly a household word because of their potential uses from microdevices to high-strength magnets to power-transmission lines. Another newly prominent transition metal is manganese (L edge at 640 eV), which is an ingredient in the colossal-magnetoresistance materials that may one day find application in magnetic data-storage devices. A major finding of the workshop is that resonant inelastic scattering near these edges is a major growth direction for the ALS (see the report from the Working Group on Complex Materials).

Extending the definition of the soft x-ray energy range to 4 keV exposes the K edges of the second-row elements in the period table: sodium, magnesium, aluminum, silicon, phosphorus, sulfur, and chlorine. Of these, magnesium, aluminum, and silicon are major components of the Earth’s crust and therefore central to earth sciences. Phosphorus and sulfur are of great interest in the biosciences. Some working groups explored the capabilities of the ALS in the intermediate photon-energy range from 4 keV to 12 keV. The potent performance of the ALS in this range is not widely recognized, and much of the discussion in the biosciences working group centered around the exploitation of high-field superconducting “superbends” at the ALS as a cost-effective way to satisfy the growing need for beam time by the protein-crystallography community in the western United States.

The principal mission of the ALS, as affirmed by this workshop, is to assert world leadership in VUV and soft x-ray science, although some of its capacity in the intermediate range should be used where there is a strong regional demand or another compelling reason. No matter how the fashions in science change, and this report will explore some of the current fashions, access to the relatively low-lying core-level energies listed above will always be in demand.

1.3 Topics *Not* Covered

As implied in the title "Scientific Directions at the Advanced Light Source," the emphasis of the workshop and the report is on *science* rather than *technology*. Apart from a plenary talk by John Carruthers of Intel, the strong industrial involvement at the ALS with microelectronics companies in Silicon Valley and biotechnology companies in the San Francisco Bay Area was not extensively discussed. These interactions in their own right could provide the topic of a separate workshop. Also not discussed were the efforts at the ALS to generate femtosecond pulses of x rays and the planning towards a fourth-generation light source. The emphasis throughout was on the best science that can be done at the ALS as it is, given the appropriate investment in beamlines and end chambers.

2. Summaries of Working-Group Reports

The summaries are not intended to be encyclopedic. Rather, in the spirit of the workshop charge, they focus on the frontiers of the fields as identified by the working groups, with special emphasis on science accessible with VUV radiation, soft x rays, and/or intermediate-energy x rays. Inasmuch as the working groups wrote their reports independently and no attempt was made to enforce uniformity nor to avoid repetition, both the reports and the summaries are likewise varied.

The summaries list the chairs and facilitators of the working groups. The full reports of the working groups are in the chapters that follow. Each report lists the participants in the working group, as determined by workshop-registration forms. (Some reports also list the principal authors of subsections.) The lists are inevitably incomplete, since many participants hopped between the groups. Inclusion of a name in the list does not necessarily imply that the participant endorses all statements in the report. Rather, the list is intended to express gratitude on the part of the ALS.

2.1. Complex Materials

Chair: Ward Plummer, University of Tennessee

Facilitator: Zhi-xun Shen, Stanford University

Background

The term "complex materials" is used to describe materials characterized by strong coupling between the electronic, spin, and structural degrees of freedom. Interest in these materials stems from the richness of their physical properties and the matching complexity of the underlying physics. The strong coupling is at the heart of the novel behavior of these materials, as well as the resulting technologically important applications. Tunability of properties is a significant attraction of complex materials that derives directly from their complexity, which thus becomes an asset rather than an obstacle. However, owing to the strong coupling between degrees of freedom, there is as yet limited fundamental understanding of complex materials to guide attempts at engineering them.

Issues in Complex Materials

A list of unanswered questions about physical phenomena observed in complex materials, provides a framework upon which recommendations for the ALS can be compared.

- What is the role of electron localization in the exotic properties of complex materials?
- Is it possible to identify and characterize quantum phase transitions (low-temperature phase transitions from one quantum state to another)?
- Is phase separation a general characteristic of strongly correlated metal-oxide systems?
- What is the nature of the quasiparticle states near the Fermi energy?
- How does the superconducting state in the cuprate high-temperature superconductors arise from a highly incoherent normal state?
- What are the novel features of superconductors with nodes in their order parameters (non-conventional superconductivity)?
- What is the interplay among spin, charge, and orbital ordering in transition-metal oxides?
- What is the nature of elementary excitations in these highly coupled systems?
- What are the roles of (local) phonons, orbital ordering, and phase separation in colossal-magnetoresistive (CMR) materials?
- What is the effect of symmetry reduction caused by an interface?
- Does spin-charge separation exist beyond one dimension?

Recommended Role of the ALS

The power of the ALS lies in the exceptional brightness that it provides in the energy range from about 100 eV to about 1000 eV. The ALS can become an excellent facility for the investigation of complex materials, but it must be driven by the scientist and the science. Strong outside user groups must be an integral part of any vibrant program at the ALS. With this concept in mind, our recommendations are prioritized into two categories. Category I comprises the capabilities that clearly satisfy the two most important factors—participation by excellent outside scientists and importance to the field of complex materials. Category II comprises capabilities that are important to the field, but at present there is not an excellent outside scientist driving the experiments. Our recommendation is clear: Do not proceed with the Category II capabilities until an outside user group with appropriate credentials submits a proposal or until scientific leaders are recruited.

Category I

- **High-resolution angle-resolved photoemission.** For most complex materials, angle-resolved photoemission is the only technique capable of measuring the Fermi contour. In addition, this technique can measure energy gaps and properties related to gaps; it offers a direct test of the quasiparticle picture of solids, dynamics of charge, spin and orbital degrees of freedom; and it can observe quantum phase separation and spin and charge separation and ordering. A next-generation facility should have a capability to perform photoemission experiments at extremely high resolution ($\Delta E < 5$ meV and $\Delta q \approx 0.02$ Å^{-1}) in the photon energy range of 5 eV to 400 eV.

- **Soft x-ray (resonant) absorption, emission, and scattering.** In contrast to angle-resolved photoemission, soft x-ray absorption, emission, and scattering are photon-in/photon-out experiments, so that they can be used in the presence of high pressure and high magnetic fields. The advantages of these techniques are associated with the site-specific excitation process, the ability to probe deep into the solid, and the soft x-ray wavelength. The challenge is to produce a versatile, user-friendly beamline with sufficient intensity and spatial resolution over a broad range of temperature and magnetic-field strengths to satisfy a broad range of user needs. These are truly photon-hungry experiments.

Wolfgang Eberhardt (Forschungszentrum Jülich) makes a point during deliberations of the Working Group on Complex Materials.

- **Optical-conductivity measurements: Far-infrared to optical frequencies.** This is a powerful and versatile technique for discovery of novel features in the low-energy excitation spectra of complex materials, such as metal-to-nonmetal transitions, the magnitude of gaps, and changes in the spectral weight from single-particle-like to highly correlated, as well as identifying optical phonons. The impact of the ALS could be greatly enhanced by developing an end station for measurement of optical conductivity over an energy range from 0.01 eV to the near ultraviolet, with capabilities for conducting experiments over a broad range of temperature, magnetic-field strength, and pressure.

Category II

- **Magnetic circular and linear dichroism.** Soft-x-ray MCD can provide important information impossible or very difficult to achieve by other experimental means, including (1) element-specific spin and orbital magnetic moments; (2) three-dimensional element-specific magnetic hysteresis curves; (3) local magnetic ordering of disorder and dilute systems ; and (4) magnetic interlayer coupling and interface magnetic roughness by circularly and linearly polarized resonant magnetic x-ray scattering. The unique capability at the ALS should be the combination of the microbeam and microscopic techniques with the XMCD spectroscopic capabilities mentioned above.
- **Spin-polarized photoemission**. Spin-polarized photoemission is an extension of high-resolution angle-resolved photoemission that can independently measure the dispersion of the minority and majority bands near the Fermi energy as a function of the sample composition, magnetic field, and temperature. The limitation at present is the lower energy and momentum resolution imposed by the low collection efficiency.

2.2 Magnetism and Magnetic Materials

Chair: David Awschalom, University of California, Santa Barbara

Facilitators: Joachim Stöhr, IBM Almaden Research Center, and Jeffrey Kortright, Lawrence Berkeley National Laboratory

Interactions among electrons in solids lead to many interesting physical properties, often having such practical consequences as superconductivity and magnetism. The importance of magnetism and magnetic materials is enormous, with applications ranging from transducers and media in information storage technology to the most basic transformers and motors used in the generation and application of electric power. Current research is driven in part by the interesting physics of these complex materials, but also by technological and societal relevance, as indicated by the $50-billion-per-year magnetic data-storage industry. For example, the scientific discoveries of the giant-magnetoresistance and oscillatory interlayer magnetic-coupling phenomena have been brought to the marketplace as vital products within an extraordinarily short ten-year period.

Research Trends

Several defining attributes of magnetic materials are at the heart of current research and will remain central in the future. Fundamental in these attributes is the common origin of magnetic interactions and phenomena in the geometrical and electronic structure that are inseparably linked in the host materials. Recognizing these common attributes the working group categorized current and likely future research trends in the area of magnetism and magnetic materials as follows:

- **Dimensionality: space and time.** Magnetic nanostructures are characterized by interfaces between ultrathin magnetic layers and by laterally patterned structures, opening the study of the influence of reduced dimension on all magnetic interactions and properties. Both fundamental physics and many technologically relevant magnetic nanostructures and homogeneous materials are of interest in the context of reduced dimension. Time-domain studies are also important.
- **Magnetoelectronics.** The technological impact of giant magnetoresistance is leading to research into other magnetic nanostructures in which spin-dependent transport plays an essential role, including spin-tunneling and spin transistor structures. Advances in magnetic semiconductors continue and may some day incorporate magnetic switching, spin-dependent transport, and magnetooptics into the realm of semiconductor materials and devices.
- **Structure and magnetic order.** The paradigm linking structure and magnetic order demands improved experiments to detail these correlations as materials and phenomena of interest become more complex. Examples of research areas here include the structural origins of magnetic anisotropy and frustration in a variety of materials, as well as disorder and proximity. Of prime importance is a better characterization and understanding of interfacial effects.
- **Exploratory materials.** A wide range of materials exhibit interesting magnetic phenomena. Current interest includes biomagnets and molecular magnets, as well as the intensely studied oxide magnets exhibiting simultaneous magnetic and metal-insulator phase transitions. Hybrid magnetic nanostructures may involve active interfaces, or exotic pairings of materials across interfaces, such as interleaving magnetic layers with superconducting layers to study these competing phenomena.

VUV/Soft X-Ray Impact: Current Trends, Future Directions

VUV/soft x-ray techniques have unique advantages of coupling directly to the spin-resolved electronic states of interest. The key advantage of the ALS lies in magnetic spectromicroscopy, whereby magnetic sensitivity of various spectroscopies can be obtained with high spatial resolution to provide unique opportunities in the analysis of complex magnetic materials and nanostructures. Some specific areas where VUV/soft x-ray techniques have and are expected to continue to have an impact on magnetism are briefly highlighted here:

- **Anisotropy.** The ability to separate local spin and orbital moments has led to improved understanding of the origins of magnetic anisotropy at this fundamental level. Early work has focused on the role of orbital-moment anisotropy in determining the direction and magnitude of magnetic anisotropies. Future work will extend such studies to systems of microscopic lateral dimensions or systems that are laterally inhomogeneous on the smallest scales.
- **Spin-resolved electronic structure.** Photoemission techniques are revealing the momentum-space origins of spin-polarized quantum-well states mediating coupling phenomena between magnetic layers in nanostructures. Spin-resolved photoemission has recently provided the best experimental evidence that certain oxides are half-metallic ferromagnets. These techniques will continue to provide premier capabilities for determining spin-resolved electronic structure of new materials.
- **Structure and magnetism.** VUV/soft x-ray spectroscopies continue to provide sensitive probes of element-resolved magnetic structure at surfaces in the bulk of materials. The ability to probe into the depth and possibly depth-resolve buried layers and interfaces is just emerging and may affect all areas mentioned above. Scattering techniques involving both electrons and photons are emerging that will be sensitive to magnetic microstructure over a range of length scales at surfaces and into the bulk.

Members of the Working Group on Magnetism and Magnetic Materials listen to a presentation.

- **Magnetic spectromicroscopy.** Scanning and imaging microscopes have been demonstrated, and opportunities exist to develop microscopes using many different contrast and sampling characteristics. One direction focuses on ultimate lateral resolution of the order of 1 nm. Another focuses on using the penetrating power and element-specificity of soft x-rays to image domains in different layers of nanostructures. Each direction offers unique advantages compared to traditional magnetic-microscopy techniques.

SUMMARY

Magnetic materials continue to grow in importance in our technological society. VUV/soft x-ray spectroscopies and techniques have demonstrated unique ability to provide new understanding at the microscopic level of the fundamental physics underlying the interesting phenomena in increasingly complex samples. The high brightness of the ALS will extend new and emerging capabilities that should continue to impact the science and technology of magnetic materials. Concerted effort needs to be directed at coupling these capabilities to the magnetics-research community to ensure that they are brought to bear on the most important research problems.

2.3 Polymers, Biomaterials, and Soft Matter

Chair: Thomas Russell, University of Massachusetts, Amherst

Facilitators: Stephen Kevan, University of Oregon, and Harald Ade, North Carolina State University

OPPORTUNITIES

The applications of polymers and soft condensed matter range from the nanoscopic (e.g., biomolecular material and copolymeric mesophases) to the microscopic (microelectronics) to the macroscopic (high performance structural composites). Synthetic polymers have now begun to mimic the biological world of macromolecules, such as DNA and proteins, as well as viruses and cells. They represent ideal model systems for investigating the fundamental chemical and physical principles related to supramolecular formation, folding, and phase transitions. Specific opportunities identified by the working group were:

- **Miniaturized advanced materials**

  Biomolecular materials. There is a rapidly increasing demand for biocompatible materials including medical implants and *in-vivo* drug delivery systems. Biological systems operate at cell and subcellular dimensions; therefore, material properties including polymer uniformity, thickness, mechanical deformability, permeability, state of hydration, and surface charge must be characterized to dimensions below 100 nm.

  Nanoscopic structures. Depending upon the volume fraction of the dissimilar segments in covalently coupled polymer chains, periodic arrays of nanoscopic structures ranging from spheres to cylinders to lamellae form spontaneously. Controlling the orientation and spatial arrangement of these nanoscopic arrays is key for the incisive use of these structures in applications ranging from electronic devices to membranes to sensors.

- **Thin films.** Polymer thin films have considerable technological importance, but relatively little is known about the properties of polymers when the film thickness is less than about 0.1 µm. Optimizing the use of polymers in thin-film applications necessitates a detailed understanding of thin film properties, such as composition, morphology, viscosity, chain mobility, stability, and any differences from bulk properties.
- **Surfaces and interfaces**

  Pattern recognition. Natural selection processes rely on intermolecular recognition between molecules that consist of a random sequence of different amino acids. The apparently random sequencing of units may, however, comprise a statistical patterning of units in the macromolecules. Synthetic, random copolymers in contact with randomly patterned surfaces offer a simple, unique, and quantitative means of understanding this rather complex recognition process.

  Polymer surface relaxation. Establishing and understanding the relationship between nanoscopic and microscopic mechanisms and macroscopic spatial- and temporal-frequency-dependent viscoelastic properties of polymeric materials will help to forge a crucial link between polymer structure and properties, including the microscopic modes of polymer relaxation that conspire to produce the diverse kinetic and thermodynamic properties often observed.
- **Engineering polymers.** The macroscopic properties of the engineering polymers used for automobile parts, dashboards, computer cases, suitcases, etc., are dictated by the specific polymers used and by the resultant morphology. Key issues in engineering polymers include understanding the microscopic phase structure in blends, compatibilization of multiple phases, fracture mechanics, segregation of additives, adhesion of paints, and adhesion of polymers to other materials.
- **Organic earth materials.** Chemical characterization, especially molecular structural information at very short length scales, of the organic matter included in sediments and sedimentary rocks is of paramount importance in understanding the generation of oil and gas, refining our understanding of the geologic component of the global carbon cycle, and deriving effective strategies for improved technological utilization of solid phase fossil energy resources, e.g., coals.

Thomas Russell, Chair, leads a discussion in the Working Group on Polymers, Biomaterials, and Soft Matter.

Requirements for Success

The working group identified ingredients required for a successful polymer and soft-condensed-matter program at the ALS

- **ALS-industry partnership: key elements for sustainable success.** The ALS should form multiple and substantive partnerships with a diverse industrial partner base. To this end, it is necessary to identify key industrial partners early on, minimize industry risk by seeding key technologies, increase industrial access to ALS facilities, increase the quantity of beamline support personnel, encourage the formation of university/industry/ALS PRTs, and provide rapid access (days, not weeks or months).
- **A dedicated science-driven beamline for users.** Beamlines for polymers and soft condensed matter research should be dedicated, user friendly, and well supported by staff. Only the ALS is bright enough to use a bend magnet as a source for a microscope based on diffractive optics, such as the dedicated polymer STXM to be installed at bend-magnet Beamline 5.3. It is, therefore, the only facility in the nation that will be able to provide much-needed STXM capacity

What Role Can the ALS Play?

Two classes of experimental techniques and associated instrumentation were emphasized for their importance for research in polymers, biomaterials, and soft matter:

- **Soft x-ray spectromicroscopy.** One of the most promising areas where the ALS can have an impact on scientific issues in polymer science and soft matter is soft x-ray spectromicroscopy. The ALS will have the most complementary and complete set of instrumentation available for x-ray microscopy of polymers world wide. The ALS should fully capitalize on this leadership. It may also be desirable that the currently proposed STXM at ALS Beamline 6.0 for environmental applications be co-developed with the polymer science community.
- **Microdiffraction, SAXS, and ASAXS.** The availability of an anomalous-microbeam-small-angle x-ray scattering and diffraction spectrometer is also critical for research on polymer, biomaterials, and soft matter. The instrument should be capable of probing self-assembling structures on scales spanning 0.1 nm to 1000 nm.

2.4 Nanostructures and Special Opportunities in Semiconductors

Chair: Marvin Cohen, University of California, Berkeley

Facilitators: Daniel Chemla, University of California, Berkeley, and Franz Himpsel, University of Wisconsin–Madison

Background

Nanostructures are low-dimensionality material systems whose size is intermediate between that of atoms or molecules and that of bulk solids. (A nanostructure may be defined as any structure with at least one dimension on order 1 nm.) These novel materials have electronic, optical, structural, chemical, or even biological properties that are different from those of the bulk parent compounds and also of the constituent atoms and molecules. The properties are strongly dependent upon size and shape. These properties are controlled by quantum size effects, altered thermodynamics, and modified chemical reactivity.

Opportunities in Nanostructures

- **Tailored properties.** Much of the appeal of nanostructures is the ability to tailor a material's properties by manipulating wave functions. For some properties, such as ferromagnetism and superconductivity, the electrons within kT of the Fermi level are of greatest importance. For others, such as optical properties, electron states at the band edges and multi-electronic excitations, such as plasmons, are the important players. For the smaller types of clusters, the full orbital structure will become important. Strain and local crystallography can be used to tune properties of embedded nanostructures.
- **Synthesis/fabrication of nanostructures and architectonic materials.** Manufacturing large amounts of nanostructures with essentially identical sizes and shapes involves chemical syntheses that are sometimes described as "self-assembling" if they can be designed to produce the desired products simply by the control of reaction conditions. It may also be desirable to fabricate structures that can change their size or shape predictably under an external stimulus. For some applications, independent nanostructures will be sufficient, but for many others it will be necessary to position specific nanostructures at well-defined locations on a substrate or to create larger-scale architectonic (purposely designed) materials that may in turn be a part of a larger device or system.
- **Embedded nanostructures and synergy between the ALS and the National Center for Electron Microscopy.** When embedded within a solid, nanostructures may have very different properties. A solid matrix may be used to distribute, orient, or constrain an array of nanocrystals, to isolate them from their environment, or to aid in their synthesis. The size and shape of small inclusions must conform to the embedding matrix: the size must be compatible with the constraints of the two discrete lattices (the inclusion and the matrix). In turn, a dispersion of nanoscale inclusions has a major effect on the host matrix.

Special Opportunities for Semiconductor Research

- **Wide-bandgap materials.** Optical properties of wide-gap materials present new challenges to researchers who have studied standard semiconductor systems at photon energies up to 3.5 eV. The bulk optical properties of both "one-electron" (weakly correlated) and strongly correlated "many electron" systems with wide gaps are still poorly understood.
- **Far-infrared studies in very-high-pressure diamond-anvil cells.** The exploration of the mid- and far-infrared properties, especially of impurities and defects (vacancies, interstitials, etc.) in very small particles, offers a broad and most promising field of materials studies that has remained largely unexplored because of the usual limitations encountered in the far infrared, including sources, throughput, and detectors.

Role of the ALS

The working group considered the possible applicability of the ALS to probing properties of nanostructures on, or beyond, the performance level of currently available tools, such as scanning probes, various means of studying transport, lasers, conventional spectroscopy with soft and hard x-rays, electron microscopy, and optical reflection and absorption.). The group found that the ALS should play roles in:

- **Identifying the atomic structure of interfaces, wires, and nanoparticles** by soft-x-ray scattering. The L edges of the magnetic metals in the IIId column of the periodic table make it possible to determine the atomic and magnetic structure of interfaces, in element-sensitive fashion, via resonant x-ray scattering.

Marvin Cohen (Chair) and Daniel Chemla (Facilitator) field a question from the Working Group on Nanostructures and Special Opportunities in Semiconductors.

- **Determining the relevant electronic states at the Fermi level** by high-resolution photoemission spectroscopy. Resonant photoemission at the M edge of the IIId metals and the d-to-f resonance of the rare earths and actinides results in elemental specificity.
- **Determining magnetism of nanostructures** via magnetic circular dichroism. MCD can provide semiquantitative data on the orbital and spin moments, separately for each element, in nanostructures. MCD in conjunction with core-level fluorescence spectroscopy may enhance the sensitivity of MCD to sub-monolayer quantities and to buried interfaces.
- **Studying the electronic structure of nanostructures** on surfaces, embedded clusters, clusters with a ligand shell, or buried interfaces by soft x-ray emission. The measurements that can be performed include energy levels and band offsets that are not accessible to traditional optical experiments.
- **Providing information on size, shape and connectivity** of nanostructured samples by scattering of soft x-rays. Also, using very high-intensity beams with small spot size to analyze large combinatorial libraries of nanostructures in reasonable times. An end-station cluster that can handle large wafers will be required for the soft x-ray scattering and other techniques.
- **Using synergistic research** wherever the high *spatial resolution* of TEM imaging and the statistically averaged *accuracy* of high energy-resolution spectroscopy from x-ray diffraction complement each other in research where microstructure is important.
- **Studying wide-band gap semiconductors** with bright, continuously tunable UV excitation, small spot size, short pulses (less than 100 ps) of UV and soft x rays, and infrared.
- **Studying small material samples** at extreme hydrostatic pressures in diamond-anvil cells over a wide range of photon energies (infrared through soft x-ray).

2.5 New Directions in Surface and Interface Science

Chair: Gabor Somorjai, University of California, Berkeley

Facilitators: Charles Fadley, University of California, Davis, and Michel Van Hove, Lawrence Berkeley National Laboratory

Opportunities at the ALS

Surface and interface science is an all-pervasive component of contemporary materials science, physics, and chemistry, with crucial implications for most technologies and for the environmental and life sciences. The continuing trend to nanometer-scale, and even atomic-scale, elements in technological applications is increasing the importance of the field. Future studies will require working at higher pressures, shorter time scales, and higher spatial resolutions, as well as studying more complex systems (e.g., with lateral and vertical heterogeneity and lacking long-range atomic order). The ALS can contribute significantly in several ways to advancing the frontiers of surface and interface science:

- **Surface reactions and high-pressure studies.** Much is known about the structures of simple surfaces and reactions in ultrahigh- or high-vacuum environments, but structures and processes can change significantly in higher pressure gas-phase atmospheres. Special modifications of soft x-ray techniques in which either photons or electrons are detected at pressures from 1 torr to 1 atm will advance this field. Time-resolved studies are of special importance in surface reaction dynamics and kinetics.
- **Solid-solid buried interfaces.** Solid-solid interfaces are ubiquitous in technology (e.g., integrated circuits, magnetic storage devices), as well as in tribology, in which two solids make contact via a thin layer of lubricant between them. Probing such interfaces in an element-specific way with soft x-ray photons (absorption, fluorescence, and scattering) and electrons (photoemission) can lead to information at various depths and, via spectromicroscopy, also with lateral resolution.
- **Gas-liquid and liquid-solid interfaces, liquid films.** Liquid interfaces may be more important than solid interfaces in modern life, yet their microscopic properties have hardly been explored because of the lack of suitable experimental techniques. X-ray techniques (reflection, fluorescence, scattering, including both photon and electron detection) are probably the only viable methods for probing the atomic structures and depth profiles near liquid interfaces.
- **Electrochemistry.** Outstanding scientific issues include: (1) the distance of ions from the electrode surface when electron transfer occurs, (2) the structure of water in the double layer, and (3) a method for studying adsorption at electrode surfaces in disordered or weakly ordered systems. X-ray absorption spectroscopy and x-ray fluorescence in total reflection, together with high-pressure photon-in/electron-out experiments, are ALS-based techniques that will assist in answering these questions.
- **Surfaces and interfaces of metal oxides.** Metal oxides are prominent in catalysis, strongly correlated materials, environmental science, geoscience, and magnetic materials. Special areas of interest are (1) structure and properties of clean surfaces, (2) molecular adsorption and surface reactions, and (3) solid overlayers. Core and valence-level photoemission and photoelectron diffraction, again at higher pressures where possible, are techniques of special utility here.

- **Semiconductor surfaces and interfaces.** The steady trend to smaller nanometer-scale layered structures in integrated circuits leads to challenges in the production of future devices. To achieve a detailed fundamental understanding of surface and buried interface structure, we must simultaneously measure both electronic structure and chemical composition from the atomic to the micron length scales. Both photon-in/electron-out and photon-in/photon-out measurements will advance this field.
- **Surface and interface magnetism.** Frontier questions include: What are the magnetic moments and electronic structure at surfaces/interfaces, how are magnetic-ordering phenomena affected by changes in composition and lower dimensionality, and how do such effects influence adsorbate bonding and chemical reactivity? Photoemission with spin resolution and variable polarization, and element-specific soft-x-ray measurements with variable polarization will assist in answering these questions.
- **Theory for synchrotron-radiation experiments.** Theory is a pervasive need, both for data analysis and for understanding mechanisms and phenomena, particularly at third-generation synchrotron x-ray sources, which generate novel data of unprecedented precision that challenge theory for interpretation. Conversely, advances in theory (e.g., emission and scattering of photons and electrons) permit deriving more information from experiment, including more efficient use of experimental time.

ALS Availability and User Issues

The ALS faces a severe shortage of high-quality surface-science end stations. Beyond additional beamlines, solutions to this problem lie in leveraging the existing end stations as much as possible. Each end station should have a wide variety of *in-situ* sample handling facilities, including loadlocks for fast sample transfer. User-friendly software for on-line data acquisition and handling is essential. An improved user environment is also needed, such as better long-term scientific support for outside users on each end station.

Members of the Working Group on New Directions in Surface and Interface Science ponder a presentation.

Recommendations for the ALS

- **Spectroscopy at higher pressures and shorter time scales.** It is clearly necessary to develop methods for carrying out both photon-in/photon-out and photon-in/electron-out spectroscopies at the highest possible *in-situ* pressures (from 1 torr to 1 atm), and on the fastest time scales (1 sec down to picoseconds).
- **Spectromicroscopy.** The decreasing dimensions of microelectronic and other devices are driving surface and interface science increasingly toward studies with high lateral resolution. Synchrotron-radiation sources of the third generation should make it possible to do spectromicroscopy (parallel image acquisition) and microspectroscopy (sequential image acquisition) with resolutions down to 50 Å to 100 Å.
- **New beamlines.** An additional general-purpose undulator (approximately 5.0-cm-period) and associated beamlines are needed to handle the present heavy oversubscription for surface/interface science experiments. A specialized end station on an undulator beamline is also needed.This should be a multi-technique system with a pressure range from UHV to 1 atm. A third need is a beamline optimized for x-ray absorption spectroscopy in the 1-keV to 4-keV range, using electron and fluorescence yields. A final need is improved facility support.

2.6 Working Group on the Environmental and Earth Sciences

Chair: Gordon E. Brown, Jr., Stanford University

Facilitators: David Shuh and Geraldine Lamble, Lawrence Berkeley National Laboratory

Synchrotron light sources, primarily in the hard x-ray energy region, have had a major impact on research in the environmental, soil, and earth sciences over the past decade and will likely continue to grow in importance. In the US and Canada, there is an established community of experienced users in the molecular-environmental-science (MES) and earth-science areas of about 200. There is also a growing number of new, inexperienced users from a variety of fields who fall under the MES heading. This expanding user base requires (1) radiation with energies ranging from the infrared to the hard x-ray, (2) higher flux and higher brightness beamlines, (3) beamline optics that produce microfocused beams for spectromicroscopy and imaging studies, (4) state-of-the-art x-ray detectors, (5) more beam time on a regular basis, and (6) strong user support at each of the DOE light sources.

Research Opportunities

Although the working group also pointed to applications of synchrotron-radiation methods in the earth sciences, most utilizing hard x-ray beamlines, it chose the following MES research areas for special emphasis, as opportunities for the unique capabilities of the ALS:

- **Speciation, spatial distribution, and phase association of chemical contaminants,** including molecular-level characterization of important sorbent surfaces in complex multiphase systems, dynamics of these complex mineral/organic assemblages under varying geochemical conditions, and chemical-speciation and chemical-species transformations of contaminants and other environmentally important elements at interfaces and at spatial scales ranging from nanometers to millimeters.

- **Chemical processes at interfaces of solids and aqueous solutions,** including characterization of natural materials, studies of elements with low atomic numbers, characterization of model materials surfaces, and characterization of surface complexes and aqueous-solution structure at the mineral-water interface.
- **Actinide environmental chemistry,** including surface chemistry of actinides, transport and sorption of actinides, speciation of actinides/heavy metals, waste forms, and the fundamental electronic and magnetic structure of actinides.
- **Microorganisms, organic contaminants, and plant-metal interactions,** encompassing microbial-mineral interactions, microbially induced redox environments, corrosion and biofilm formation, origin of life issues, and the interactions of plants with heavy metals and trace elements.
- **Other environmental science applications,** including research on the fate and transport of contaminants in the subsurface, storage of nuclear wastes, sustainable agriculture, global climate change, trace element cycling in ecosystems, air quality, and ecological and human health risk assessments.

Conclusions and Recommendations

Several conclusions can be derived from the information provided at this and two recent workshops devoted to synchrotron-based MES:

- Synchrotron-based methods are having a major impact on MES and the earth sciences by providing unparalleled information on molecular speciation of elements ranging from boron to plutonium at unprecedented spatial scales (nanometers to millimeters) in complex multiphase materials.
- Although there will soon be an adequate number of hard x-ray beamline end stations devoted to or available for MES research, there is no soft x-ray/VUV beam station optimized for and dedicated to MES research at any of the DOE synchrotron light sources.
- Technical support of MES and earth science users at the ALS is currently inadequate, which means that only a few experienced users can effectively utilize the unique capabilities of the ALS.
- Because of the growing need for routine x-ray absorption fine-structure (XAFS) and microXAFS analyses of large numbers of environmental samples, it is important for the DOE to consider the development of several beamline end stations for such purposes, including both hard x-ray and soft x-ray/VUV stations.
- Based on joint discussions with the Working Group on New Directions in Surface and Interface Science, there is significant scientific and intellectual overlap between these two groups, particularly in the area of surface and interfacial chemical processes. Development of compatible facilities required by these two communities will also lead to desirable collaborations among scientists in these complementary disciplines.

Gordon Brown (Chair) sets the agenda for the Working Group on the Environmental and Earth Sciences.

Accordingly, the working group made six specific recommendations :

- **A soft x-ray beamline should be designed and built at the ALS for spectromicroscopy applications** that would operate in the 800-eV to 4000-eV range and would be equipped with appropriate optics to provide spot sizes in the sub-micron range.
- **A beamline should also be developed at the ALS for spectromicroscopy studies in the VUV energy region** (50 eV to 800 eV) and optimized for MES applications, including the study of wet samples using differentially pumped sample cells.
- **X-ray emission spectroscopy** has has great potential for providing unique information on the bonding of adsorbates at environmental interfaces, including solid-water interfaces. ALS management should devote adequate resources to rebuild the unique x-ray emission capability that was previously provided by the loan of equipment by the University of Uppsala and the expertise of Dr. Anders Nilsson.
- **A concerted effort should be made to increase the level of technical support** provided by the ALS to the user community in general and the MES community in particular. This is especially important in the soft x-ray/VUV area, where the technical difficulties associated with a ultrahigh-vacuum experiment are often greater than those in the hard x-ray region, which do not generally require such systems.
- **MES end stations at the four DOE synchrotron-radiation laboratories should be standardized as much as possible,** so that samples can be readily transferred among the facilities for spectroscopic, spectromicroscopic, and diffraction studies on the same portions of a sample using beamlines at different energies.
- **An ENVIROSYNC organization should be formed** to help stimulate the cooperation that is essential among MES users at the ALS, Advanced Photon Source (APS), National Synchrotron Light Source (NSLS), and Stanford Synchrotron Radiation Laboratory (SSRL) and to further coordinate the development of the MES community nationally.

2.7 Working Group on Biosciences

Chair: Graham Fleming, University of California, Berkeley

The Working Group on Biosciences comprised three sub-groups: Protein Crystallography, Soft X-Ray Microscopy, and Biological and Chemical X-Ray Spectroscopy. Here we present separate summaries for each of the sub-groups.

2.7.1 Protein Crystallography

Facilitator: Thomas Earnest, Lawrence Berkeley National Laboratory

Opportunities

In many respects, protein crystallography is a mature but constantly evolving field. Exciting biology is being done daily by the "routine" application of this tool to determine macromolecular structures. At the same time, crystallography has its own frontiers. The sub-group highlighted five:

- **Structure determination at very high resolution**, thus allowing the locations of many hydrogen atoms to be established directly and reducing reliance on stereochemical libraries.
- **Structure determination from microcrystals**, which would dramatically increase the number of macromolecules, especially membrane proteins, available for crystallographic study.
- **Studies of large macromolecular complexes**, including ribosomes and multiprotein or protein-nucleic acid complexes.
- **Determination of large numbers of structures in coordinated projects**, including structural-genomics projects and iterative structure-design efforts.
- **Time-resolved and other mechanistic studies**, where efforts are under way to push into the sub-picosecond regime.

Current and Future Needs

Although available beam time at West Coast facilities appears to be well matched to the *present* needs of local crystallographers, *per se*, these facilities experience a demand several-fold greater than can be satisfied, perhaps because of protein biochemists who are not accounted for when enumerating dedicated, full-time protein crystallographers. Further, projections of future needs point to a rapid expansion in a demand that already exceeds the supply of beam time. In particular, major new projects, especially structural-genomics projects, will require dramatic increases in resources.

The ALS: Successes and Opportunities

The Macromolecular Crystallography Facility

The first beamline of the ALS Macromolecular Crystallography Facility, collected its initial diffraction patterns on 18 September 1997. The subsequent user run of the MCF was extremely productive, with users from academic, industrial, and national laboratories successfully collecting MAD data, diffraction data from microcrystals, and "conventional" diffraction data with extremely rapid throughput. In all, over 60 users from 18 different groups collected data at the MCF between 15 November 1997 and 31 January 1998. User demand has accelerated since then.

New Opportunities

Within a few short months, the MCF has thus fully confirmed the suitability of the ALS for protein crystallography, raising natural questions about how the most exciting opportunities in the field can be mapped onto the capabilities of this facility. The sub-group pointed to six opportunities, each an expression of an exciting opportunity in protein crystallography, judged especially appropriate to the physical capabilities and resident expertise at the ALS:

- **Structural genomics**, exemplified in the pilot study by Sung-Hou Kim and his colleagues, using the fully sequenced microbe *M. jannaschii*.
- **Iterative structure-based drug design**, which calls for high-throughput crystallography beamlines, offering both speed and high data quality.
- **Robotic expression and crystallization**, which, combined with the high-throughput capabilities of the ALS, has the potential to turn drug design and protein engineering into efficient iterative processes.
- **Membrane proteins**, the importance of which demand that greater resources be dedicated to their study. The ALS benefits from a large local community of researchers with appropriate expertise to pursue such work.
- **Large molecular complexes**, which represent unique opportunities for high-brightness synchrotron sources such as the ALS.
- **Low-energy diffraction**, for which the ALS is especially well suited. X rays in the 2-keV to 8-keV range can be used to collect anomalous data from elements with absorption edges in this region, including uranium, calcium, potassium, and sulfur.

The Protein Crystallography Sub-Group of the Working Group on Biosciences at work.

Recommendations

Considering the opportunities in protein crystallography, the needs of its practitioners, and the capabilities of the ALS, the sub-group identified five specific scientific thrusts for the future development of the ALS:

- **Complete Beamline 5.0.1**, which should roughly double the facility's current capacity for protein crystallography. Operation is scheduled to begin in August 1999.
- **Encourage structural-genomics research as a vital component of the ALS scientific program.** The need to pursue such projects for a number of organisms underscores two pressing imperatives: an increase in the beam time available to these projects and enhanced efficiencies in the expression, purification, and crystallization of the genomic products. The following two recommendations address these issues.
- **Add three superbends** (superconducting dipole magnets), which will deliver flux densities of at least 6×10^{12} photons/(sec·mm^2), approximately equal to the most intense x-ray field strength tolerable to protein crystals. Use of one or more of the superbends will permit the expansion of ALS crystallographic capability without compromising the other core scientific programs of the facility.
- **Develop a robotic system for expression and crystallization**, to reduce the manpower needed for these tasks and to open the door to high-throughput investigations of protein structure.
- **Promote the development of high-speed pixel (area) detectors** as a next step toward improving both the quantity and quality of crystallographic structures determined at synchrotron sources.

2.7.2 Soft X-Ray Microscopy

Facilitator: Werner Meyer-Ilse, Lawrence Berkeley National Laboratory

In contrast to protein crystallography, which is a mature scientific field, x-ray microscopy is in its infancy. Indeed, a long-standing debate has centered on whether x-ray microscopy can answer critical questions of biological importance not currently addressed by other technologies. Accumulating evidence, however, suggests a promising role for soft x rays. The short wavelength of x rays provides a spatial resolution more than five times better than that of visible-light microscopy (and the difference is expected to grow with future developments). Further, practical techniques have now been demonstrated that open the door to interrogations of keen interest to cell biologists.

Recent Advances in Protein Localization

The use of fluorescently labeled antibodies to localize proteins in the light microscope has led to major advances in the understanding of cell structure and function. The information that can be gained from these analyses, however, has been limited by spatial resolution. To obtain higher-resolution information about the localization of proteins, Chris Jacobsen and colleagues at the NSLS and Carolyn Larabell and colleagues at the ALS have used silver-enhanced, gold-conjugated antibody probes to localize proteins using soft x-ray microscopy. Results from both groups were presented at the Workshop. *This technique is a major breakthrough*, offering information about protein localizations at higher resolution than possible with light microscopy and without the extensive cell preparations required for electron microscopy. Because of such advances as this, x-ray microscopy is poised to make a major contribution to the understanding of cell structure and function.

Biological Questions

Several central topics in cell biology are ripe for investigation by soft x-ray microscopy. The microscopy sub-group identified four in particular:

- **Structure-function analyses of the cell nucleus.** The ability to simultaneously image chromatin components and components of the nuclear matrix using soft x-ray microscopy in hydrated, nonextracted, unsectioned cells offers to shed new light on the relationship between nuclear organization and cellular function.
- **Cell-extracellular matrix interactions.** Studies by LBNL researchers have shown that a reciprocal dialog exists between the mass of fibrous and globular proteins outside the cell (the extracellular matrix or ECM) and the inside of the cell. Recent data indicate that disruption of this dialog can lead to tumor formation, whereas restoration of the cell's delicate microenvironment can cause tumors to revert to cell clusters resembling the normal phenotype. Soft x-ray microscopy offers to shed additional light on these basic molecular mechanisms.
- **Host-parasite interactions.** The ability of soft x-ray microscopy to examine thick cells provides a unique opportunity to examine host-parasite interactions, as demonstrated at the ALS in the malaria studies of Cathie Magowan and colleagues. The ability to examine parasites within the host, without risking the artifacts that accompany embedding and sectioning protocols, provides a powerful tool for understanding these important cell-cell interactions.

Members of the Soft X-Ray Microscopy Sub-Group of the Working Group on Biosciences discuss an important point.

- **In situ hybridization using x-ray microscopy.** Fluorescent *in-situ* hybridization (FISH) is a widely applied method to assay gene expression using light microscopy. The ability to obtain such information using the increased spatial resolution of soft x-ray microscopy is of the utmost importance. Larabell and colleagues are in the process of developing an *in-situ* hybridization technique for x-ray microscopy (XISH), based on silver-enhanced gold probes. This is expected to be a significant breakthrough for the fields of cell and molecular biology.

Future Technological Developments

The microscopy sub-group made the following recommendations to secure the future of x-ray microscopy at the ALS:

- **Cryomicroscopy and tomography.** The sub-group endorsed the ongoing development of a capacity to do cryomicroscopy and tomography at the ALS. The opportunity to obtain high-resolution, three-dimensional information about protein localizations in whole, hydrated cells is unprecedented.
- **Mapping of elements and the identification of their chemical state.** The most dose-efficient way to map elements with atomic numbers above about Z = 10 in most biological samples is by detection of fluorescence excited by monochromatic x rays. For the lighter elements, the best approach is differential absorption using soft-x-ray microscopes. The working group concluded that the characteristics of the ALS as an x-ray source, together with the latest probe-forming techniques, are opening unique opportunities to extend the capabilities of biological research.
- **Higher resolution x-ray microscopy.** Continuing effort was encouraged in two areas to improve the resolution of x-ray microscopy: Zone-plate lenses allowing 10-nm to 20-nm resolution and x-ray waveguide structures, which might be used in a new type of soft x-ray microscope whose spatial resolution should be less than 10 nm. Such a waveguide, consisting of a 5-nm-diameter hole in a 240-nm-thick gold film, has recently been fabricated at LBNL.
- **Scanning soft x-ray microscopy.** Scanning soft x-ray microscopy requires a bright soft x-ray source and is therefore ideally suited to the capabilities of the ALS. The sub-group encouraged continuing effort to exploit the ALS microscope for dark-field microscopy, fluorescence microscopy, and photoemission microscopy.
- **Contrast-specific molecular probes.** Two approaches exist for creation of x-ray molecular probes that can complement silver-gold particle labels. One is based on x-ray-tolerant luminescent phosphors, including lanthanide-organometallic complexes and cadmium selenide nanocrystals. In addition to luminescent probes, probe-specific contrast can be based on the sharp x-ray absorption edges characteristic of vanadium, titanium, and cadmium in the water-window x-ray range. The sub-group strongly endorsed further development of such probes.

2.7.3 Biological and Chemical X-Ray Spectroscopy

Facilitator: Stephen Cramer, University of California, Davis

Important Research Areas

The bioinorganic-chemistry community was among the first to adopt synchrotron-based extended x-ray absorption fine-structure spectroscopy (EXAFS) as a routine structural tool. The x-ray spectroscopy sub-group discussed the important current issues for biological and inorganic chemistry and tried to define the important science in these areas that can be addressed by x-ray spectroscopy in the soft and intermediate-energy x-ray regions of the spectrum.

Metals are important in biology both for their beneficial role in enzyme active sites and structure and for the negative effects of enzyme inhibition or disruption by heavy metals or normally benign metals at unhealthy concentrations. Metalloenzymes play important environmental roles as pivotal agents in the nitrogen, sulfur, and carbon cycles and in the production and consumption of greenhouse gases, such as methane. It is also worth noting that enzymes are a billion-dollar business in the U.S. alone. Thus, in the three critical areas of human health, environmental impact, and commercial potential, a better understanding of enzymes and related model chemistry could have profound impact. X-ray spectroscopy is an important tool for expanding our knowledge because it can answer the following important questions:

- **What is the molecular, electronic, and magnetic structure of enzyme active sites?** A good example of this kind of problem is the structure of the oxygen-evolving complex of photosystem II. Based on their EXAFS work and other information, Melvin Klein and coworkers have proposed a model for this structure. K-edge EXAFS is valuable for defining the metal-neighbor distances. Investigating the near-edge x-ray absorption fine structure (NEXAFS) in the chlorine and manganese K-edge region can yield important information about the electronic structure of this complex.
- **How does the concentration and chemical speciation of elements change across an organism?** Living systems are not homogeneous: The gradients of metals and other elements across an organism reveal important information about structure and function. A great deal has already been done by fluorescence microscopy, including, for example, many beautiful studies of calcium waves in different organisms. However, x-ray spectromicroscopy can discover information inaccessible by other means. For example, James Penner-Hahn has used x-ray absorption to study the distribution of zinc in sperm cells, where he has seen clear gradients across the cells. Further, the changes in zinc NEXAFS between different locations indicates different chemical forms of the element.
- **How does the chemical speciation of elements change over time?** The time dependence of chemical species in an organism is just as important as the spatial variation. X-ray spectroscopy can provide valuable information about species which are difficult to observe by other spectroscopies. For example, Klein and coworkers have used sulfur K-edge spectroscopy to monitor changes in the mix of reduced and oxidized sulfur species in the blood before and after drug administration. There are many situations in microbiology where one would like to follow the change in metal speciation after induction of specific enzymes—for example, the change in molybdenum chemistry after induction of the genes for nitrogen fixation.

Needed Resources

The sub-group identified six specific needs in the x-ray spectroscopy community—needs that are national in scope, but that are likewise relevant to the ALS program:

- **Detectors.** On one point, the working group was unanimous: Spectroscopy is currently limited as much by detectors as by beamlines. New detectors need to be developed that are faster and that have higher energy resolution. Since they will be shared by many users, the detectors also need to be robust and supportable.
- **High energy resolution.** There are surprisingly few high-resolution, high-flux beamlines at intermediate x-ray energies in the U.S. The best examples are probably beamlines X-25 and X-27 at NSLS. Many of the other available beamlines offer high flux but inadequate resolution.
- **Resources for the region from 2 keV to 3 keV.** This important area is poorly served, although it contains such important edges as the sulfur and chlorine K-edges and the molybdenum L-edges.
- **Spectromicroscopy capability.** Although the ALS is pushing the state-of-the art in soft x-ray microscopy, many important intermediate-energy x-ray experiments would be well served by micrometer-scale resolution. A beamline capable of moderate resolution spectromicroscopy should be developed.
- **Time-resolved capability.** A time-resolved x-ray absorption capability on the millisecond to seconds time scale is badly needed. Many biological processes occur on this time scale, and making such a capability routinely available to users would lower the barriers to this kind of work.
- **Newer spectroscopies.** High resolution x-ray fluorescence and inelastic scattering look promising for site-selective x-ray absorption and a better understanding of electronic structure. Secondary monochromators should be available at beamlines to make such experiments possible.

Recommendations

These needs, together with the unique capabilities at the ALS, point to four specific thrusts for scientific development at the ALS in the area of x-ray spectroscopy:

- Complete the elliptical-undulator beamline as quickly as possible.
- Encourage development of a high-resolution intermediate-energy x-ray beam line to cover the spectral region from 2 keV to 10 keV.
- Develop better detectors to take full advantage of both beamlines.
- Pursue development of x-ray spectromicroscopy on the 1-μm scale and kinetics on the millisecond time scale. Although these fields are not at the frontiers of technology, their development would make very practical contributions to biological spectroscopy.

2.8 Working Group on Atomic, Molecular, and Optical (AMO) Physics

Chair: Chris Greene, University of Colorado

Facilitator: Nora Berrah, Western Michigan University

Synchrotron-based AMO physics has a long history of producing advances at the most detailed microscopic level that is needed for understanding the interactions between light and any state of matter. Third-generation light sources have opened research frontiers with the potential to answer fundamental questions about dynamics, including photofragmentation, and about the structure of atoms, molecules, and clusters.

Outstanding Scientific Issues

The scientific motivations in AMO physics fall into two major categories: first, the fundamental quest to understand the interactions of photons with atomic, molecular, and cluster systems in their own right, and second, AMO phenomena that impinge on other areas. Photoexcitation and photoionization of the underlying atomic and molecular systems control many key processes in fields such as biology, atmospheric physics, astrochemistry, radiation physics, materials science, environmental science, and more. The working group identified scientific problems on the horizon in AMO science that are driven by at least one of these underlying motivations:

- **Photon-ion interactions,** relevant to the prevalent plasma state of matter in the solar system including both (1) positive ions, a dominant component of hot plasmas, and (2) negative ions, whose photophysics uniquely challenges theory, owing to the greater comparative strength of electron-interaction effects.
- **Inner-shell spectroscopy of atoms and molecules,** including (1) spin-polarized Auger spectroscopy, (2) high-resolution core-level electron spectroscopy, aimed ultimately at tracking the chemical properties of molecular components with maximum site-specificity, (3) ion- and electron-imaging spectroscopies, which help to sort out the key mechanisms of multibody photolysis in a complex atomic or molecular system, (4) structural and dynamical studies of atoms and molecules by Auger resonant-Raman spectroscopy and soft-x-ray emission spectroscopy, and (5) mapping limitations of fundamental approximations in photoionization, notably the independent-particle approximation (IPA), which neglects electron-electron correlations, and the electric-dipole approximation.
- **Strongly correlated systems,** for which the IPA fails qualitatively. Even such seemingly simple processes as two-electron photoionization of the lightest atomic species (He, H^-), using VUV photons, have proven to be formidable challenges owing to our limited understanding of the three-body continuum states of three charged particles.
- **Photofragmentation control,** namely, the tailored excitation and detection of atomic and molecular systems. (The term photofragmentation is used broadly here to include both photodissociation and photoionization.) Elements of a program to achieve maximal control of processes include (1) laser-tailored initial states, (2) molecular studies with lasers and synchrotron radiation (multicolor experiments), and (3) quantification of final-state-energy and angular-momentum sharing.
- **Free clusters,** in particular the site-specific inner-shell excitation of atomic and molecular clusters—aggregates of atoms or molecules varying in numbers from several to several thousands. A central goal is to ascertain how the condensed-matter properties emerge as the number of units increases.

Chris Greene (Chair) keeps the proceedings orderly in the Working Group on Atomic, Molecular, and Optical Physics.

Importance of VUV and Soft X-Rays: The Role of the ALS

The advanced spectroscopies being developed at the ALS give us the ability to control and probe atomic and molecular processes with unprecedented precision. In particular, the spectral resolution, brightness, broad tunability, and polarization control generate novel avenues for the study of tailored states, inner-shell processes, and nonperturbative electron interactions. Indeed, AMO physics at the ALS is already a vibrant activity. In less than three years, AMO research at the ALS has produced more than 60 refereed articles, including 12 in *Physical Review Letters*. In assessing the future role of the ALS, the working group posed and answered three specific questions:

- **Why is a VUV/soft x-ray source important for the proposed areas of study?** The scientific issues identified here require photons in the energy range for which the ALS has been optimized. It is important that the broad and rapid tunability of the ALS in these photon-energy regions enables systematic studies of sequences of atoms and molecules that are inaccessible even to state-of-the-art laser systems. Studies possible with a facility such as the ALS include (1) investigations of inner-shell excitation in atoms, molecules, clusters, and ions, (2) systematic determinations of accurate photoabsorption and photoionization cross sections to benchmark theoretical techniques, (3) use of site-specific, inner-shell excitation to systematically explore chemical reactivity, and (4) triply differential studies of open-shell elements.
- **What is the role of the ALS?** That is, are the proposed scientific programs truly contingent upon the advanced capabilities of the ALS? The answer of the AMO working group is emphatically yes, as the experiments require ultrahigh resolution, brightness (small spot size), and very high flux

over a broad photon-energy range. Only a source with the characteristics of the ALS is suitable for such studies. The ALS is also uniquely suitable in the area of spin-resolved experiments that require intense circularly polarized light. This important resource will be provided by the elliptically polarized undulator beamline now under construction.

- **What tools are needed?** Several ALS beamlines, including two dedicated AMO beamlines, are currently being used for AMO research, together with several state-of-the-art end stations. However, other tools are needed in order to "prepare," "control," and do experiments on atomic and molecular targets. These include (1) Mott-detectors for spin-polarized detection, (2) pulsed lasers to prepare targets and to synchronize them to the ALS for time-resolved studies, (3) an extension of the elliptically polarized beamline to cover low photon energies, (4) a branch of an undulator beamline with no monochromator, capable of running in a "blowtorch mode," (5) an undulator beamline that covers the oxygen and nitrogen edges with very high brightness and resolution, (6) bunch timing tailored to time-of-flight experiments, and (7) ultraviolet and infrared free-electron lasers, the next generation of sources for double-resonance experiments.

2.9 Working Group on Chemical Dynamics

Chair: Paul Houston, Cornell University

Facilitator: Arthur Suits, Lawrence Berkeley National Laboratory

Opportunities in Chemical Dynamics

Chemical dynamics encompasses the study of elementary chemical reactions and thus underlies virtually all macroscopic chemical systems. The working group sought to identify exciting opportunities in the field and ultimately to identify how the ALS can help achieve notable results in each area. Eight areas of opportunity were identified:

- **Combustion: radical chemistry and dynamics**, the keys to our understanding of combustion chemistry, which in turn underlie improvements in efficiency and reductions in pollution.
- **New molecules**, especially new radicals and metastable species, the study of which can illuminate the most subtle details of chemical dynamics
- **Atmospheric chemistry and global change**, where great opportunities exist for understanding and ultimately controlling some of the most important processes affecting today's society.
- **Astrochemistry**, key to understanding the chemistry at work in planetary atmospheres, in astrophysics, and even in the process of planet formation.
- **Clusters and interfacial chemistry**, especially important in bridging the gap between chemical physics and materials science.
- **Plasma chemistry**, where studies are relevant to the semiconductor industry, planetary atmospheres, and materials science
- **Chemistry in real time**, an extension of ultrafast-kinetics studies that began with flash photolysis and were twice revolutionized, first by lasers and then by mode locking.
- **Photoionization dynamics of complex molecules**, an increasingly important probe of chemical systems.

Achievements and Opportunities at the ALS

Lasers and molecular beams have had a dramatic impact in chemical dynamics, but the unique features of the ALS offer solutions to a number of previously insoluble problems. The Chemical Dynamics Beamline at the ALS is the first in the world to combine dedicated, intense undulator radiation with state-of-the-art molecular-beam machines. The beamline became fully operational in November 1995, and its scientific promise is just now being realized. The normal-incidence monochromator has achieved world-record resolution, and breakthroughs have been achieved in photoionization studies, photochemistry, and crossed-beam reactive scattering. Areas in which advances have already been achieved and where the future appears especially bright are outlined below:

- **Combustion: radical chemistry and dynamics.** Studies of combustion comprise reaction studies of radicals and hydrocarbons, studies of hydrocarbon photodissociation, and high-resolution measurements of molecular photoionization. End stations at the Chemical Dynamics Beamline have already had a major impact on our understanding of combustion chemistry, and pioneering work has been done on the photoelectron spectroscopy of radicals.
- **New molecules and new chemistry.** The "soft" ionization feature made available by the tunability of the ALS allows one to detect weakly bound molecular systems without fragmenting them. Such tunability thus makes it possible to detect and characterize new radicals and molecules.
- **Atmospheric chemistry and global change.** Substantial opportunities exist for increasing our understanding of the fundamental reactions involved. Soft x-rays can be used to characterize aerosols, and tunability in the ultraviolet can be used for selective ionization to determine branching ratios in key reactions.
- **Astrochemistry**. This field should benefit from third-generation synchrotron sources. The ALS, for example, can be used to study branching ratios for the production of different photochemical products as a function of the wavelength of the light.
- **Cluster dynamics and spectroscopy.** The high photon flux of the ALS allows coincidence measurements that can greatly improve our understanding of the spectroscopy and dynamics of clusters.
- **Plasma chemistry.** Demanded are accurate absolute total cross sections or rate constants of ion-molecule and ion-radical reactions in the kinetic-energy range from thermal to about 100 eV. The further development of the photoion-photoelectron apparatus associated with the Chemical Dynamics Beamline will offer unique capabilities for studies of mode- or state-selected ion-molecule reaction dynamics.
- **Chemistry in real time.** We can now observe hydrocarbon bonds in a single excited molecule break simultaneously or sequentially—and to understand why it happens that way. The future lies in understanding and predicting the behavior of systems of greatly increased complexity.
- **Photoionization dynamics of complex molecules.** The ALS will be a useful tool for clearly understanding how electrons are ejected from molecular systems and how electronic and nuclear degrees of freedom are coupled in fundamental and theoretically tractable systems.

Members of the Working Group on Chemical Dynamics debate a technical point.

Future Capabilities

The ALS represents the world's most intense source of continuously tunable VUV light in the 5-eV to 30-eV region of the spectrum. This high intensity has been exploited at the Chemical Dynamics Beamline, which has two branches, one for very high-resolution studies of photoionization dynamics and threshold photoelectron spectroscopy, the second to perform selective soft ionization of reaction products. An important innovation for chemical-dynamics studies at the ALS is to exploit the new velocity-map imaging technique in conjunction with a high-throughput monochromator system. This combination will considerably expand the experimental opportunities and broaden the appeal of studies on the beamline to a larger chemical-dynamics community. New experimental opportunities include radical spectroscopy and photodissociation dynamics, cluster dynamics and spectroscopy, identification and characterization of novel metastable molecules and superexcited states and their decay mechanisms, and new approaches to the study of photoionization dynamics in complex systems.