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Workshop on Scientific Directions at the Advanced Light Source

Summary and Reports of the Working Groups

July 1998

Workshop held at
Ernest Orlando Lawrence Berkeley National Laboratory
March 23-25, 1998

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From the Workshop Chair

Yves Petroff, Director-General, European Synchrotron Radiation Facility, Grenoble

Yves Petroff

The Birgeneau report came as a shock to some people working in the field of VUV and soft x-ray synchotron radiation [1]. I personally believe that it will have a very positive influence.

Obviously, it is not completely fair to compare a synchrotron-radiation facility that has been running for two or three years with facilities in operation for more than 15 years. People have probably forgotten that the first years of the NSLS at Brookhaven were not very glorious. After that the NSLS became, and still is, one of the best facilities in the world. However, getting what we call politely in French *un coup de pied au derrière* is always positive because it forces you to react.

The performances achieved at the ALS (horizontal emittance $\varepsilon_x = 6 \times 10^{-9}$ m·rad, vertical emittance $\varepsilon_y = 6 \times 10^{-11}$ m·rad, and beam current 400 mA) show that this is the best VUV/soft x-ray machine in the world. How do we now ensure that it produces the best VUV/soft x-ray science in the world? I see answering this question as the purpose of the workshop whose proceedings are compiled in this report.

The different working groups of this workshop have discussed the areas where the ALS offers new scientific opportunities. It is now the role of the management to attract the right people to implement this exciting science.

Finally, I would like to raise one important point: the ALS is a national user facility. The users should be treated correctly and efforts should be made to address lodging, parking, and general "quality-of-life" concerns.

1. *Report of the Basic Energy Sciences Advisory Committee Panel on D.O.E. Synchrotron Radiation Sources and Science,* Robert J. Birgeneau, Chair, November 1997.

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 $\rightarrow$ 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.

Working Group on Complex Materials

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1. Introduction

Materials research provides the foundation on which the economic well being of our high-tech society rests. The impact of advanced materials (alloys, ceramics, composites, lasers and other optical media, liquid crystals and other "soft matter," polymers, magnetic alloys and compounds, semiconductors, superconductors, etc.) ranges dramatically over every aspect of our modern world from the minutiae of daily life to the grand scale of our national economy. Invariably, however, breakthroughs to new technology trace their origin both to fundamental research in the basic properties of condensed matter and to applied research aimed at manipulating properties (structural, physical, chemical, electrical, magnetic,

optical, etc.) by controlling the structure (both electronic and geometric), often in ways that do not otherwise occur in nature. Figure 1 is a beautiful illustration of "tunable" materials properties [1]. In this "switchable" mirror, the concentration of hydrogen incorporated into yttrium by varying the hydrogen pressure determines the reflectivity. The top figure is for the yttrium film before hydrogenation, where the material is metallic and acts like a mirror. At the bottom is the transparent non-metallic phase (YH_3).

Indeed, nearly every materials-research program, large or small, has as its ultimate objective the design of a material with novel or at least predictable properties. Such materials engineering requires learning how to fabricate materials with the desired composition and structure over length scales down to the level of individual atoms. According to the dictionary, engineering means "the application of scientific and mathematical principles to practical ends..." Materials research is about developing the scientific and mathematical principles.

To take a few examples from the recent past:

- The fabrication technology that makes the ultraminiaturized integrated circuit (the most famous case of an artificial structure) a reality derives both from the unique properties of silicon and the research that taught materials scientists how to harness them.
- The next generation of high-density magnetic storage devices will read information with magnetic sensors derived from research on multiple ultrathin layers (superlattices).
- Optical communications is partially the result of research that increased the transparency of glass in optical fibers by a factor of 10,000 since 1965.
- Research into artificially layered semiconductors has led to the semiconductor lasers used in compact-disk players and CD-ROM drives.

Figure 1. These photographs show the behavior of a 500-nm-thick yttrium film covered with 20-nm palladium protection layer. The film and the transparent chess-board pattern behind it are illuminated from behind to monitor the frequency dependence of the transmitted light and from in front to see the mirror image of the white knight that is placed just in front of the film. The illumination is the same for the two photographs. The yttrium film, the chess-board pattern, and the knight are placed within a glass tube of 20-cm diameter that can be evacuated and filled with hydrogen gas at a pressure of up to 105 Pa. The left figure is for the yttrium film before hydrogenation, where the material is metallic and acts like a mirror. The right figure is in the trihydride γ phase and has become highly transparent, so you can see the chess board illuminated from the back. [Figure taken from reference 1.]

- The development of corrosion-resistant body parts stems from research in ion implantation of metals.
- The newest skis, tennis rackets, and bicycles are made from composite materials that resulted from research into the structure-function relationship.
- Those winking, blinking lights in the tennis shoes our children wear are piezoelectric devices with roots in research on ceramics.

Truly, as a recent report from the American Physical Society attests, "Materials research is a key to our quality of life and our competitiveness in global markets" [2].

New materials and new technologies will continue to change our lives in the future. Clues to where future breakthroughs are expected may be gleaned from a list of what might be called the five "hot topics" among the solid-state part of the condensed-matter community. Undoubtedly, such a list is "fashionable" and subjective, but it is still enlightening. Our selection of the hottest topics includes.

- Non-conventional *superconductivity* (including that in materials with high critical temperatures; that is high-T_c materials).
- *Magnetism* in multielectron extended systems.
- *Reduced (or confined) dimensionality* in mesoscopic systems, nanostructures, quantum wells, etc.
- *Beyond the single-particle picture* in a general description of correlated systems and in transport in synthetic materials (the quasiparticle model does not work in these systems).
- *Novel Phase Transitions.*

Increasingly, the frontiers of materials research include what we are calling "complex materials," as reflected in our list of hot topics, which is dominated by phenomena occurring in this very broad class of materials. In the following sections, we review the features of complex materials, summarize the experimental tools needed to characterize them, and recommend specific capabilities required at the Advanced Light Source (ALS) in order to be at the forefront of research in this field.

It should be noted that the future development of complex materials depends on sophisticated materials synthesis, characterization, and theoretical understanding all working hand in hand. The ALS with its unique capabilities in spectroscopy and spectromicroscopy of local electronic structure should be a major player in this process, with a primary role in the characterization of the electronic and magnetic structure of these materials. *The important point is that the electronic structure of materials is accessible primarily in the vacuum ultraviolet (VUV) and soft x-ray spectral region for which the ALS is optimized, and it is the electrons that determine the properties of a material.*

2. Complex Materials

We use the term "complex materials" to describe materials characterized by strong coupling between the electronic, spin, and structural degrees of freedom. Most of the examples discussed in the following sections are transition-metal oxides, but the class of complex materials is actually much broader; for example, it includes rare-earth compounds, organic metals, superconductors, and the recently discovered organic magnetic conductors. Interest in complex materials stems from the richness of their physical properties and the matching complexity of the underlying physics. Figure 2 shows the phase diagram of the perovskite $La_{1-x}Ca_xMnO_3$ [3], which displays an abundance of physical properties, magnetic transitions, metal-to-nonmetal transitions, colossal magnetoresistance (CMR), charge

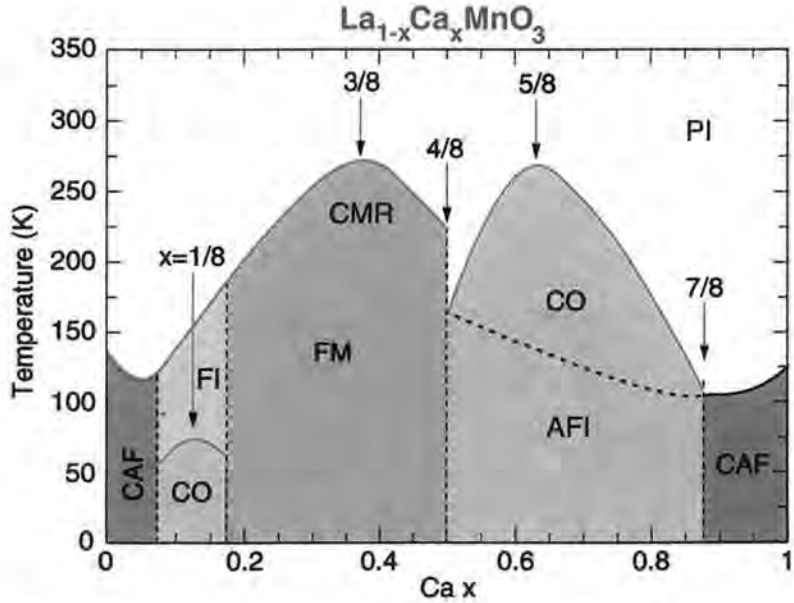

Figure 2: The phase diagram of $La_{1-x}Ca_xMnO_3$, which shows an abundance of physical properties, such as ferromagnetism (F), antiferromagnetism (AF), paramagnetism (P), canted antiferromagnetism (CAF), colossal magnetoresistance (CMR), charge ordering (CO), as well as metal-to-nonmetal transitions (M to I), etc. [Figure taken from reference 3.]

ordering, etc. The strong coupling between the electronic, spin, and structural degrees of freedom 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. In contrast to the artificially engineered materials, such as integrated circuits, nature's aid can be enlisted in engineering complex materials. This is often referred to as "the complexity paradigm." For example, many of these materials have two sublattices. In the case of the high-T_c materials, one is a charge reservoir and the other is the electronic backbone. For the CMR materials, one lattice provides the electron backbone and the other hosts the localized magnetic system. However, owing to the strong coupling between degrees of freedom, there is as yet limited fundamental understanding at the atomic level of complex materials to guide attempts at engineering them.

2.1 Novel Features and the Scientific Issues

We have compiled a list of interesting physical phenomena observed in complex materials, so that we have a framework upon which our recommendations for the ALS can be compared. The feature numbers will be referenced in subsequent sections.

1. What Is the Role of Electron Localization in the Exotic Properties of Complex Materials?

Manifestations of localization include Mott insulators and Mott transitions in transition-metal oxides, Anderson localization, and Mott-Anderson transitions in disordered systems, and heavy Fermions in f-electron systems. The rare-earth and actinide intermetallics exhibit the broadest

dynamic range from simple metals to the exotic phenomena that are of current intense theoretical and experimental interest. These include the Kondo effect, spin fluctuations, exotic forms of superconductivity, Kondo insulators, and non-Fermi-liquid behavior.

2. Can We Find and Characterize Quantum Phase Transitions (Low-Temperature Phase Transitions from One Quantum State to Another)?

One example would be the transition from a Mott insulator to a Fermi-liquid state. Another would be the transition from an antiferromagnetic insulator to a d-wave superconductor.

3. Is Phase Separation a General Characteristic of Strongly Correlated Metal-Oxide Systems?

Frustration seems to be a general property of the doped transition-metal oxides such that spatially invariant solutions may not be appropriate to the ground state. Rather, a spontaneous separation into two or more phases may be more accurate. The length scales should be accessible to resonant soft x-ray scattering probes of charge and spin order and dynamics. Examples are found in the nickelates, manganites, and cuprates and have been predicted theoretically using strongly correlated electronic models.

4. What Is the Nature of the Quasiparticle States near the Fermi Energy?

What is the nature of these states; how do transition-metal and non-metal (oxygen) orbitals participate? What is the spin-wave behavior in antiferromagnetic (AFM) and ferromagnetic (FM) phases? Can we understand the fluctuations (commensurate or incommensurate) in the AFM materials?

5. How Does the Superconducting State in the Cuprate High-Temperature Superconductors Arise from a Highly Incoherent Normal State?

Single-particle spectroscopies (e.g., angle-resolved photoemission and tunneling) see not a robust quasiparticle above T_c but mostly incoherence. This is also the case with two-particle spectroscopies, such as optical response and Raman scattering. The superconducting state is quite like a Bardeen-Cooper-Schrieffer (BCS) state with evidence of coherent superconducting quasiparticles in the one- and two-particle spectroscopies. How does this come about?

6. What Are the Novel Features of Superconductors with Nodes in their Order Parameters: Non-Conventional Superconductivity.

The order parameter (OP) is believed to be d-wave in cuprates and some organic superconductors and p-wave in ruthenates and heavy-Fermion superconductors. Among the new phenomena that should be revealed is breaking of time-reversal symmetry at interfaces and other places where the dominant OP is suppressed.

7. What Is the Interplay among Spin, Charge, and Orbital Ordering in Transition-Metal Oxides?

These orderings produce dramatic changes in physical properties, such as resistivity and magnetoresistance, and can be tuned by small changes in composition and by application of a magnetic field. How and why do these superlattices form and what is the relation between the different orderings, including phase separation?

8. What Are the Elementary Excitations of Systems that Undergo Coupled Spin and Orbital Order?

Some metal-oxide systems order their spins and orbital moments in a coordinated manner. Since the energy scales of the spin wave, orbital waves, and the coupling between them are all comparable, the elementary excitations will also be of mixed character. Soft x rays are ideal for probing these excitations because of their ability to couple directly to the orbital moments.

9. What Are the Roles of (Local) Phonons, Orbital Ordering, and Phase Separation in Colossal-Magnetoresistive (CMR) Materials?

In the CMR materials the carriers interact so strongly with local orbital (L), spin (S), and lattice (u) excitations that their transport is strongly affected. It is believed that a combined L/S/u field moves with the carrier or perhaps localizes the carrier or a group of carriers. At issue is the proper description of the ground state of this field and its excitations. Because of their element specificity and strong spin-orbit sensitivity, the soft-x ray spectroscopies are ideal for studying the static order and the excitations.

10. What Is the Effect of Symmetry Reduction Caused by an Interface?

At an interface, in the ideal case, the magnetic order (spin and orbital) will obey boundary conditions, as will the other fields that couple to these order parameters, such as the macroscopic strain and sublattice strains. The result is generally one of frustration, with perhaps the local suppression of the dominant order parameter(s) coupled with the existence near the interface of sub-dominant order parameters. At issue is the appropriate description of the order near the interface and of the localized excitations that will exist there. In the case of superconductors with a non-conventional order parameter, a similar situation will obtain.

11. Does Spin-Charge Separation Exist Beyond One Dimension?

In one dimension, theory clearly says that the physical electron separates into spin (S) and charge (Q) parts. This has recently been confirmed by angle-resolved photoemission. Much less clear is the case of higher dimensionality: Is the incoherence in the one-particle property that is a universal property best described as due to S-Q separation or simply to strong coupling effects?

2.2 The Richness of Phenomena in Complex Materials

Before describing our perspective of the potential impact of the ALS on research in complex materials it is useful to give several scientific examples to illustrate the richness of phenomena associated with these materials. Figure 3 shows the dramatic changes in the resistivity of two perovskite manganites ($Nd_{1/2}Sr_{1/2}MnO_3$ and $Pr_{1/2}Sr_{1/2}MnO_3$) [4]. Both systems exhibit metal-to-nonmetal transitions upon cooling and become ferromagnetic below the Curie temperature T_C (see arrows). Below the Néel temperature T_N, both become antiferromagnetic, but the resistance of the $Nd_{1/2}Sr_{1/2}MnO_3$ increases by about four orders of magnitude more than that of the $Pr_{1/2}Sr_{1/2}MnO_3$ compound. The large increase is due to charge ordering in the $Nd_{1/2}Sr_{1/2}MnO_3$ compound.

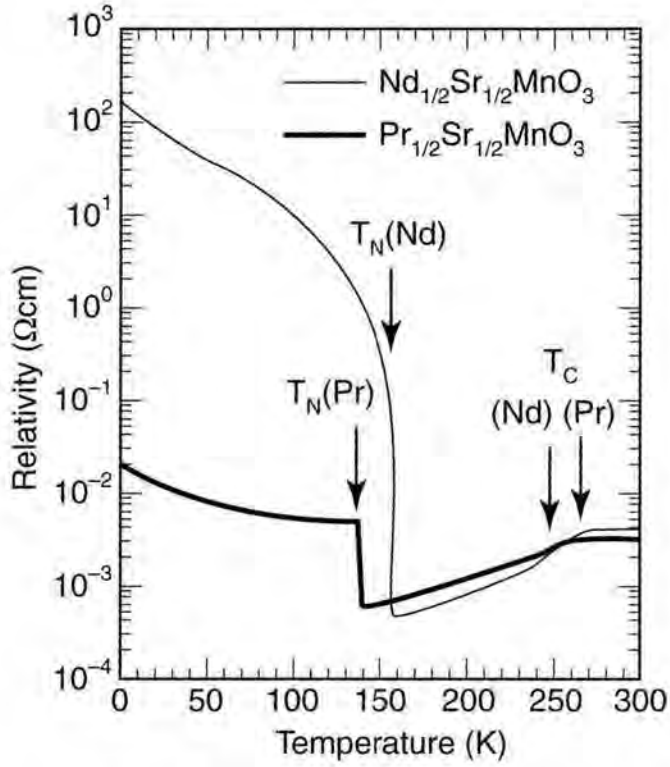

Figure 3. Temperature dependence of the resistivity of $Pr_{1/2}Sr_{1/2}MnO_3$ and $Nd_{1/2}Sr_{1/2}MnO_3$. Thick and thin arrows denote transition temperatures for praseodymium and neodymium manganites, respectively. [Figure taken from reference 4.]

Table 1 presents a few examples from a subset of complex materials—the oxides of 3d transition metals—to illustrate the diversity and tunability of their physical properties. In these materials, the properties are usually tuned by chemical substitution, as is the case with the magnetic anisotropy in the spinel ferrites, the critical temperature in the high-T_c superconductors, the magnetoresistance in the manganites, etc. Of course, even for 3d transition-metal compounds, the oxides are only part of the story. The halides and chalcogenides are as diverse, although much less research has been done on them. Going beyond the 3d transition-metal compounds to what has been referred to as the extended-electron 4d and 5d transition-metal oxides opens new opportunities, as witnessed by the flurry of activity in the ruthenates, which exhibit p-wave superconductivity, bad-metal behavior, and strange magnetic properties.

Table 1. Examples of the diversity (tunability) of physical properties of the 3d transition-metal oxides.

Property	**Materials**
Metals	CrO_2, Fe_3O_4, $La_{1-x}Sr_xCoO_3$, $SrRuO_3$
Insulators	Cr_2O_3, CoO, Fe_2O_3
Magnetic Semiconductor	(Pr, Lu)Ru_2O_7
Metal-Insulator Transition	VO_2, $V2O_3$, Ti_4O_7, $Cd_2Os_2O_7$
Superconductors	$(La, Sr)_2CuO_4$, $LiTi_2O_4$
d-Wave Superconductors	YBCO, Bi2212
Piezo-Ferroelectric	$BaTiO_3$, CuCl
Catalyst	Fe, Co, Ni Oxides
Ferromagnets	CrO_2, (La, Sr)MnO_3
Antiferromagnets	MnO, NiO
Ferrimagnets	γFe_2O_3, $MnFe_2O_4$
Colossal Magnetoresistance (Spin Electronics)	(La, Ca)MnO_3
Charge Ordered	$(La, Sr)_2NiO_4$

Synchrotron-based spectroscopic measurements have been key in understanding the origin of many of the interesting properties of these materials. For example, over the last decade, high-resolution angle-resolved photoemission spectroscopy from the Stanford Synchrotron Radiation Laboratory (SSRL) and the University of Wisconsin Synchrotron Radiation Center (SRC) using photon energies from 15 eV to 30 eV have made a significant impact on our understanding of high-temperature superconductors and related materials. Examples of this include the detection of d-wave gap structure, the normal state pseudogap in the underdoped samples, and the spin-charge separation in one-dimensional $SrCuO_2$. The last is a clear example of the breakdown of the quasiparticle concept, which is the very foundation of the standard model (Fermi liquid) of metals and superconductors. Figure 4 displays a cartoon illustrating the new concept of spinon and holon in a one-dimensional system. The accompanying data show a comparison of dispersion of a single hole in one-dimensional and two-dimensional cases. In the conventional picture, one expects the one-dimensional dispersion to be only half of that of two-dimensional dispersion, in strong contrast to the data which shows that the one-dimensional dispersion is three times the two-dimensional dispersion. This very puzzling data can be naturally explained by the realization of spin-charge separation in one dimension.

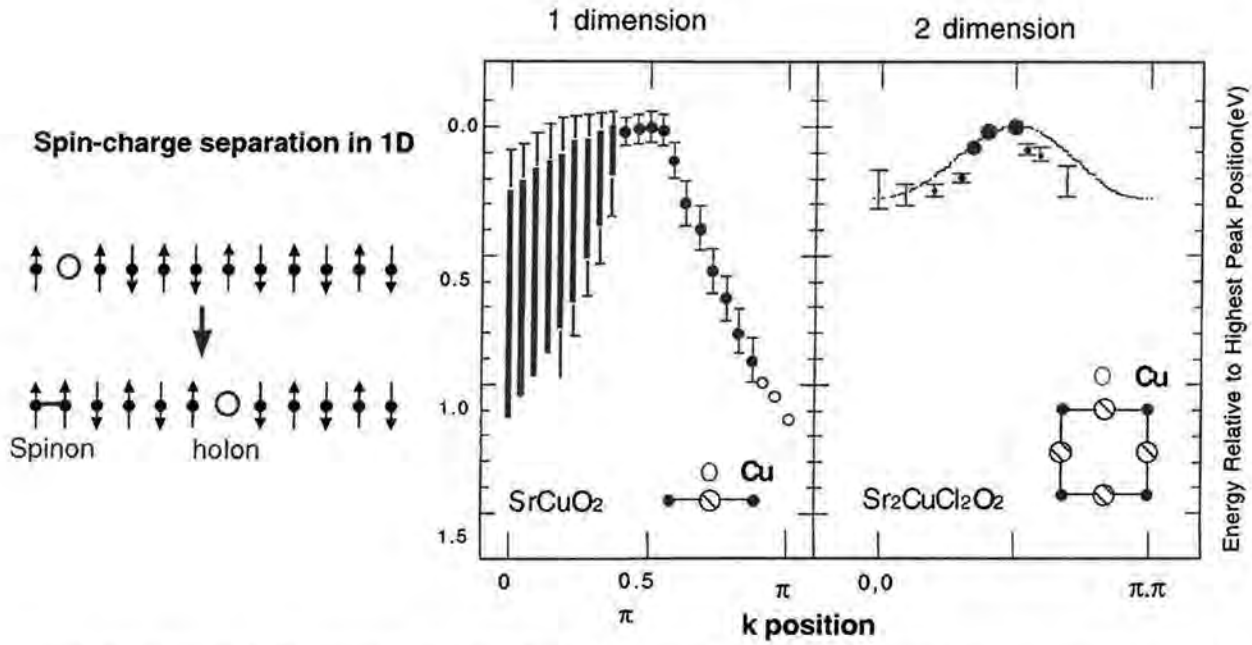

Figure 4. Data from an SSRL experiment that provides the first experimental indication for spin-charge separation in a one-dimensional system. The energy dispersion of a single hole in one-dimensional and two-dimensional cases contrast qualitatively with what one expects from a conventional picture. One expects the one-dimensional dispersion to be only half that of the two-dimensional dispersion. The data show that the one-dimensional dispersion is about three times the two-dimensional dispersion. This very puzzling data can be quantitatively explained by the realization of spin-charge separation in one dimension, as depicted in the cartoon, which illustrates the new concept of spinon and holon in a one-dimensional system. [Figure taken from reference 5.]

Recently, at SSRL a clean experimental example of the breakdown of the quasiparticle concept has been found in two dimensions by a comparison of angle-resolved photoemission spectroscopy (ARPES) data from samples of pure Bi2212 and Bi2212 doped with 0.6% zinc. Doping with 0.6% zinc completely devastated the otherwise sharp "quasiparticle peak" in the pure Bi2212 sample ($T_c \approx 91$K). Similarly dramatic contrast was observed between the spectra in the normal and superconducting states, demonstrating the breakdown of the quasiparticle concept in the normal state.

3. Recommendations

The ALS is a third-generation synchrotron source. Its power lies in the exceptional brightness that it provides in the energy range from about 100 eV to about 1000 eV. As such, it can become a premier facility for the investigation of complex materials. On the other hand, there is nothing truly unique about this facility for most spectroscopy experiments. If you want to do high-resolution angle-resolved photoemission, you can go to SSRL, SRC, or the National Synchrotron Light Source (NSLS). If you want to do spin-polarized photoemission measurements, you schedule time at NSLS, and you go to Europe, if you want soft x-ray emission or absorption data. Users will come to the ALS because it is an easy place to work or because it is an exciting place to work. Neither is true at present.

We believe that the ALS can become an excellent facility for the investigation of important properties of complex materials, but it must be driven by the scientist and the science, not by the machine and the beamlines. People drive good science, so strong outside user groups must be an integral part of any vibrant program at the ALS. With this concept in mind, our recommendations for desired capabilities at the ALS integrate three factors.

- The importance of the specific measurement capability.
- The quality of the "outside scientists" willing to push and support the beamline.
- The "uniqueness" of the measurement capability.

The 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. In an attempt to give the reader a perspective of the areas of importance of each capability, in the following, the numbers in square brackets refer to the novel phenomena discussed in Section 2.

3.1 Category I: Facilities That Should Be Implemented at the ALS for the Study of Complex Materials

3.1.1 High-Resolution Angle-Resolved Photoemission [3, 5, 6, 11]

For most of the complex materials, angle-resolved photoemission is the only technique capable of measuring the Fermi contour, which is absolutely essential information for understanding the exotic properties of these materials. In addition, this technique can measure energy gaps and properties related to gaps, such as the pairing symmetry, novel order parameters at surfaces and interfaces, pseudogap and pairing correlation in the normal state, and pseudo gap and localization (Coulomb gap and Anderson Transition). Angle-resolved photoemission offers a direct test of the quasiparticle picture of solids, dynamics of charge, spin and orbital degrees of freedom. Quantum phase separation may be observed, as well as spin and charge separation. An ideal facility would be able to perform extremely high-resolution photoemission experiments ($\Delta E < 5$ meV, $\Delta q < 0.02$ Å^{-1}) over a wide photon-energy range (4 eV to 400 eV) and would have the ability to prepare, cleave, and cool samples.

3.1.2 Optical-Conductivity Measurements: Far-Infrared to Optical Frequencies [1, 2, 8]

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 ideal facility would measure the response of the system being studied from the far infrared (about 10 meV) to the near ultraviolet over a wide range of temperature, polarization, magnetic field, and pressure.

3.1.3 Soft X-Ray (Resonant) Absorption, Emission, and Scattering [4, 7, 8]

In contrast to angle-resolved photoemission, soft x-ray absorption, emission, and scattering are bulk, site-specific techniques. These are photon-in/photon-out experiments, so that they look at the bulk and 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. Specifically, resonant soft x-ray scattering is an excellent probe of the charge and spin order and dynamics, as well as the elementary excitation of systems that undergo coupled spin and orbital ordering. Soft x rays are ideal for probing the excitation of coupled spin and orbital order because of their ability to couple directly to the orbital moments. Finally, because of the elemental specificity and strong spin-orbit sensitivity, soft x rays are ideal for studying the static order and local density of states.

These soft x-ray techniques are high-energy probes of electronic, vibrational, and magnetic properties of materials; however, with sufficiently high resolution, both in energy and momentum transfer, they can yield important information about the low-energy excitations of the system with site specificity. The challenge is to build a facility with excellent energy resolution (< 0.1 eV) over the wide photon-energy range from 50 eV to 1400 eV. The facility should be user-friendly and have sufficient intensity and spatial resolution to satisfy a broad range of user needs. These are truly photon-hungry experiments.

3.2 Category II: Facilities That Should Be Implemented at the ALS If and Only If Distinguished Outside Users Lead the Scientific Activity

3.2.1 Magnetic Circular and Linear Dichroism [1, 7, 8. 10]

The report of the Working Group on Magnetism and Magnetic Materials describes in detail the magnetic circular dichroism (MCD) techniques. A brief discussion is given here of the importance to complex materials. Soft-x-ray MCD (XMCD) can provide important information on complex materials that is either impossible or very difficult to achieve by other experimental means. This information includes (1) element-specific spin and orbital magnetic moments deduced from MCD data and sum-rules; (2) three dimensional element-specific magnetic hysteresis curves measured by MCD absorption and scattering; (3) local magnetic ordering of disorder and dilute systems determined by magnetic EXAFS; and (4) magnetic interlayer coupling and interface magnetic roughness probed by circularly and linearly polarized resonant magnetic x-ray scattering. The unique MCD capability at the ALS should be the combination of the micro-beam and microscopic techniques with the XMCD spectroscopic capabilities mentioned above.

3.2.2 Spin-Polarized Photoemission

The capabilities of this technique are described in the report of the Working Group on Magnetism and Magnetic Materials. Spin-polarized photoemission is the obvious extension of high-resolution angle-resolved photoemission, since in this technique the dispersion of the minority and majority bands near the Fermi energy can be independently measured 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.

4. Detailed Description of Capabilities of Different Characterization Techniques

4.1 Angle-Resolved Photoemission and Resonant Photoemission

High-resolution angle-resolved photoemission has emerged as the ideal tool to study many of the important phenomena associated with complex materials because this experimental technique provides detailed electronic structure information that is the key for a microscopic understanding. Past successful examples in these area include the detection of gap anisotropy, a finding that contributed strongly to the current consensus on d-wave pairing in cuprate superconductors, and the detection of spin-charge separation in one-dimensional cuprates. The impacts of these experiments are illustrated by the extensive citation of photoemission papers by others not working on photoemission experiments. Over the last five years, four photoemission papers were ranked among the annual ten-most-cited physics papers identified by the Science Citation Index of the Institute for Scientific Information.

We expect angle-resolved photoemission with high energy and momentum resolution to continue to play a pivotal role to answer the questions raised earlier. In addition to high-T_c superconductors, where the past examples have beautifully shown the capability of ARPES, other material systems, such as manganites, ruthenates, and vanidates, will also be extensively investigated by ARPES. Improved energy and momentum resolution that can be achieved at ALS will make this technique essential to a vibrant program in complex materials at ALS. In particular, the improved momentum resolution that will be achieved at ALS will definitely bring ARPES experiments to a new level. Because of their large unit cell, the complex materials tend to have small Brillouin zones, making high momentum resolution as important as energy resolution. ALS will uniquely be able to allow its users to conduct very-high-resolution experiments at the 4d-to-4f resonance edge, a capability that is very important to study heavy fermion and Kondo systems.

Utilizing a 43-period undulator and a two-dimensional spatial detector, the next-generation high-resolution beamline now under construction at the ALS will have an energy resolution of about 5 meV (or 50 K) and an angular resolution better than 0.5° or 0.017 $Å^{-1}$ at 24-eV photon energy. This facility is not exactly what we described as the ideal facility. It cannot reach the lowest desirable photon energies. Access to these low energies is important because the electron mean free path is long (bulk properties) and the momentum resolution of the analyzer is better. This deficiency could be corrected by using ultraviolet (UV) lasers in conjunction with the synchrotron.

Another related technique that will be important for studying the highly correlated electronic systems is resonant photoemisison (RP) spectroscopy. In the last few years RP has been successfully exploited to obtain important information on the valence-band structure of transition-metal (TM) and rare-earth (RE) compounds. In particular, in the case of Cu^{2+} compounds, RP has been used to identify the correlation satellites resulting from strong Coulomb repulsion between two localized holes in the bands derived from Cu 3d in the final states. The resonant mechanism originates from the interference between the direct photoemission channel and valence-band electron emission promoted by a hole decay (Fano-type interference). The interfering channels give rise to a strong enhancement of the intensity of the open-shell configuration states. Most often RP has been described in an atomic picture, assuming a high degree of localization of the intermediate state, so that in the cuprate case, for example, the two-hole final state is indicated as a $3d_8$ configuration. Furthermore, an unambiguous identification and systematic studies of the Kondo peak heavily relies on the RP technique, because the peak is obscured by intense overlapping spectral features. Recently, the solid-state effects in the resonance mechanism have been addressed, which can be utilized to address the key issues outlined in Section 2.

For RP to address the key physics issues, *high resolution is essential.* Previous RP experiments were performed using relatively poor energy resolution. In other facilities, high-resolution experiments were typically done using normal-incidence monochromators that do not provide photons with sufficiently high energy to reach the core levels of interest. The brightness at ALS makes it much easier to design a higher energy monochromator with high resolution in the energy range desired for RP experiments. As it stands, a tested ALS monochromator can deliver photons in the 100-eV range with better than 5-meV resolution, much better so far than those instruments being implemented elsewhere.

4.2 Optical Conductivity

The impact of the research at the ALS could be greatly enhanced by developing an end station for measurement of optical conductivity. Optical conductivity probes two-particle excitations near the Fermi surface. It is extremely sensitive to quasiparticle lifetimes and structure in the density of states near the Fermi surface. These properties are explored with energy resolution limited only by k_BT. Polarized measurements are powerful probes of highly anisotropic materials. Because the optical conductivity of a sample can be characterized rapidly, materials can be screened for interesting phenomena.

There are many examples of the power of this technique in the literature, many from the Tokura group in Japan. Here we show one beautiful example, the insulator-to-metal transition in strontium-doped $LaVO_3$ [6]. The doping-induced insulator-metal transition and the resulting dramatic change in the electronic structure shows up clearly in the optical spectra displayed in Figure 5. The optical conductivity spectra at room temperature for $La_{1-x}Sr_xVO_3$ displays a dramatic change as x increases.

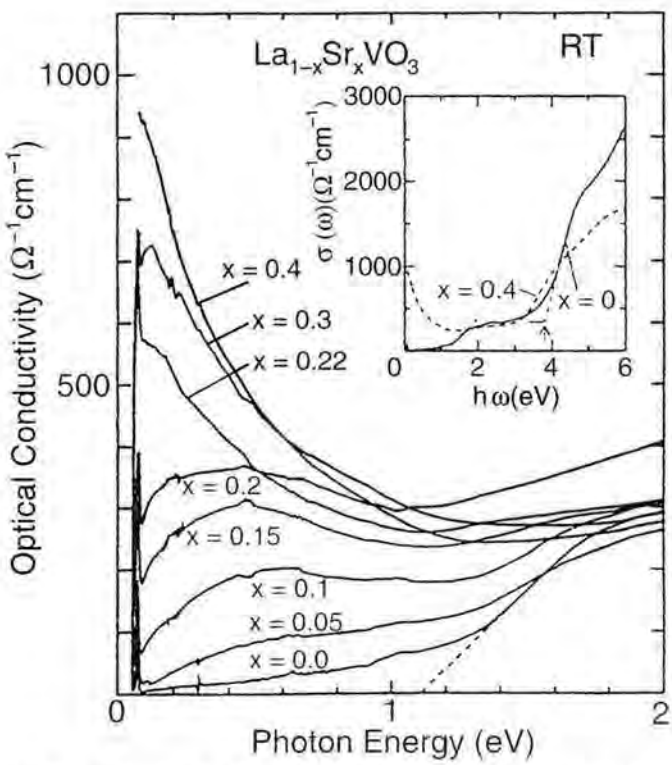

Figure 5. Spectra of optical conductivity at room temperature in $La_{1-x}Sr_xVO_3$. The higher photon energy range was measured at the INS-SOR synchrotron of the Institute for Solid State Physics at the University of Tokyo. [Figure taken from reference 6.]

For x = 0 the parent compound is a Mott insulator with a gap of 1.1 eV (dashed line). Doping with strontium causes the charge-transfer gap to decrease in magnitude until at x = 0.3 the gap closes, as seen in the insert. The low-energy conductivity spectra for the barely metallic samples with x = 0.20 and 0.22 show a non-Drude behavior, implying dominant contribution from the incoherent motion of the charge carriers. In contrast, the spectra for x > 0.3 are Drude-like.

4.3 Soft X-Ray (Resonant) Absorption, Emission, and Scattering

Complex materials, such as high-T_c, colossal-magnetoresistive, and "spin-engineered" magnetic materials containing elements from the 3d, 4d, 4f, and 5d series, have great scientific and technical impact because of the close coupling of their electronic, magnetic, and structural properties. The list of scientific questions presented in Section 2.1 illustrated the nature of the complexity in these materials. Soft x-ray absorption and emission spectroscopies provide a powerful set of tools for sorting out some of the most significant characteristics of those complex systems. Since these are photon-in/photon-out techniques, the materials can be investigated under a wide range of external variables, such as temperature, electric or magnetic field, pressure, etc. Since these spectroscopies involve excitation of core electrons, they are element and site-specific. Selection rules and scattering geometry restrict the angular and crystal momentum. It is also possible to probe electronic and nuclear dynamics on the femtosecond or sub-femtosecond time scale with inelastic x-ray scattering (scanning on and off resonance). Finally, angle-resolved fluorescence studies provide information about bonding geometry and local ordering in both ordered and unordered systems. Standing waves in multilayer structures provide a means to scan across the layers.

Near x-ray thresholds, elastic and inelastic processes that are the x-ray equivalent of electronic resonance Raman processes usually dominate the observed spectra and provide an additional set of capabilities. The scattering intensities depend strongly on localization of intermediate and final states by the introduction of core or valence holes, disorder, or other factors. As a simple example of the use of elastic scattering, diffuse scattering near the specular reflection peak can be used to study the structural disorder in periodic systems, such as multilayers. The additional use of excitation in magnetic multilayers by circularly polarized light from an elliptical undulator could provide the ability to distinguish structural and magnetic disorder at the interfaces in such systems. [Novel feature 10]

4.3.1 Phase Separation

In the doped correlated systems, the long-range magnetic order is usually destroyed at rather small doping levels, as in the high-T_c materials. However there is now a large amount of rather indirect information that the systems have a strong tendency to phase separate into regions of high hole or electron concentrations and insulating magnetic regions. This separation could be dynamic in that the regions can move and can change in shape with time. The same is the case in the colossal magnetoresistance materials which exhibit large regions of ferromagnetic order in an otherwise paramagnetic background above the ferromagnetic-ordering temperature. These regions have dimensions of around 1 nm to 10 nm and may or may not be ordered in space in some way. Hard x rays in general are not very sensitive to valence-electron distributions or valence-charge densities. They therefore are not well suited to study such short-range order. However, at specific resonances, soft x rays are extremely sensitive not only to the valence electron density but also to the local symmetry and even the spin. X-ray scattering in the soft x-ray region at resonance should be developed both to study the above-mentioned structural aspects by elastic scattering, as well as the electronic structure in the inelastic channels. [Novel feature 4]

4.3.2 Orbital Ordering

Transition-metal oxides with partially filled crystal field split levels and subsequent orbital degeneracy exhibit what is now referred to as orbital ordering. It is well known that there is a strong interaction between the orbital ordering and the spin ordering, leading also to speculations of very strong couplings of the spin-wave collective excitations with the collective orbital wavelike excitations. These are of extreme potential importance in the fields of colossal-magnetoresistance materials but also in the materials now proposed for spin electronics in general. Up to now there is little direct information even about the existence of orbital ordering. Since, again, soft x rays are extremely sensitive to the valence-electron charge distribution and the local symmetry, by using resonant x-ray scattering in an elastic-scattering experiment, one can study the nature of this orbital ordering. By looking at the inelastic scattering, one should be able to observe the collective orbital excitations and also the spin-wave excitations. Also, the q dependence can be studied to some extent, but it is limited by the rather long wavelengths usually involved in soft x-ray studies. The strong coupling of the orbital and spin-wave modes can lead to new collective excitations involving bound states of pairs of these excitations and could even lead to new ground states in which these bound states have the lowest energy. Soft x-ray experiments can yield unique information to complement data from scattering experiments with neutrons or hard x rays. [Novel features 7, 8]

4.3.3 Hybridization and Localization

One of the key questions in complex materials is the degree of localization. It has been proposed that the electrons in 4d or 5d transition-metal compounds are "extended," leading to strong hybridizations. An example of the information available from normal fluorescence spectroscopy is provided by spectra from possible the p-wave superconductor Sr_2RuO_4 ($T_c \approx 1.5°K$). In this layered compound, oxygen is present both in layers containing ruthenium and oxygen, and in apical positions lying outside of the ruthenium/oxygen planes. The spectra shown in Figure 6 confirm that hybridization of ruthenium-4d and oxygen-2p

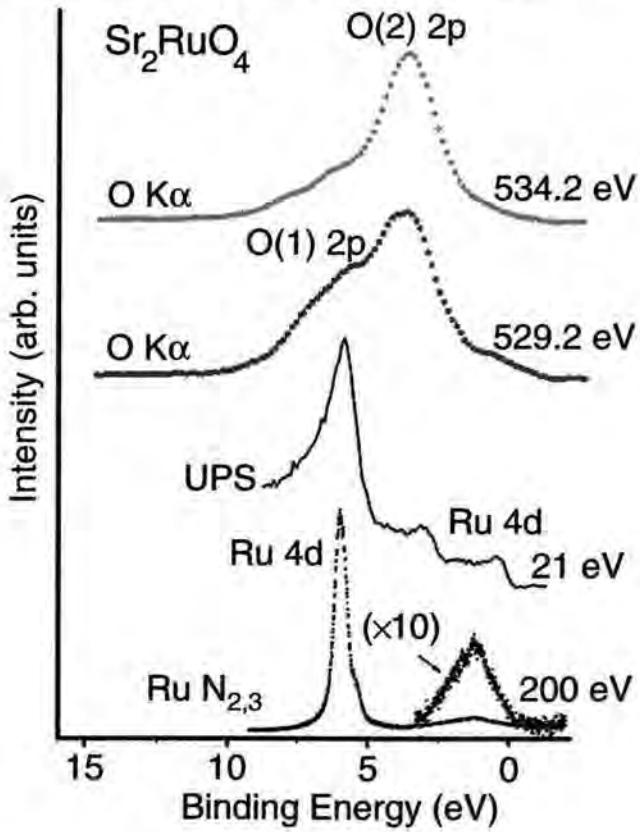

Figure 6. Soft x-ray emission spectra from Sr_2RuO_4. The top two curves show the occupied p density of states for the two different oxygen atoms, O(1) in the ruthenium/oxygen planes and O(2) between the planes. These two states of oxygen are separately excited because the 1s → 2p thresholds are different. The ruthenium $N_{2,3}$ spectrum at the bottom provides a measure of the d density of states on the ruthenium. The prominent structure at –6 eV in the O(1) and ruthenium spectra confirms the hybridization of ruthenium-4d and oxygen-2p states predicted by band theory and proves that these are extended electron system. [Figure taken from reference 7.]

states provides the principal bonding for the ruthenium/oxygen plane. The oxygen K spectra provide a measure of the oxygen 2p density of states and the ruthenium $M_{2,3}$ spectra provide a measure of the ruthenium-4d density of states. The spectra from the in-plane and out-of-plane oxygen may be selectively excited by exploiting the chemical shifts of the oxygen 1s core levels. The in-plane oxygen spectra show a strong shoulder with the same binding energy as the ruthenium-4d states, providing strong evidence of hybridization of the oxygen-2p and ruthenium-4d electrons. Figure 6 proves that these 4d transition-metal compounds are indeed "extended-electron" systems, adding a new dimension to research in transition-metal oxides. [Novel feature 1]

4.3.4 d-d Excitations in High-T_c Superconductors

In inelastic scattering, the energy difference between incident and emitted photons is transferred to an electronic excitation. In the transition metal elements, d-d* transitions have particular interest for the study of on-site correlation. In these materials, the energies of the local on-site d-d excitations have been subject to debate as to their possible presence in the mid-infrared spectrum, which is believed to be of importance for high-T_c mechanisms. In a recently reported resonant soft x-ray fluorescence study, insights into these questions were gained by studying the soft x-ray fluorescence (SXF) spectra as a function of excitation energy and angles to gain information about the energies and symmetries of these low energy excitations. The $l = 0, 2$ selection rules of the two-photon Raman-scattering process make possible the study of dipole-forbidden transitions. The high brightness of the ALS was critical in this experiment because of both the high photon flux and tight focusing required for the experiment. [Novel features 7, 8]

4.3.5 Hydrogen Bonding in Metals—An Application

A very interesting field in materials research concerns the modification of a material's properties by the loading of hydrogen. As illustrated by the photograph in the introduction (Figure 1), it was recently demonstrated that the properties of yttrium metal change drastically when the metal is loaded with hydrogen. It is generally anticipated that there are many other interesting possibilities of tuning material properties in this way. X-ray fluorescence can be used to investigate the electronic properties of these systems under ambient gas pressure or in samples that have been capped to lock the hydrogen in the metal. Figure 7 shows the yttrium-$M_{4,5}$ x-ray fluorescence and absorption spectra of, from the bottom, yttrium metal, yttrium with intermediate loading of hydrogen to form YH_2, and with full loading to form YH_3 [8]. One can clearly see the metallic character of yttrium in the bottom spectrum, i.e., the finite density of states at the intersection of the fluorescence and absorption spectra (Fermi level). For YH_2, hybridization states appear at about 7 eV binding energy and a finite density of states remains at the Fermi level. For the heaviest loading, a 2.5-eV bandgap has opened up, in good agreement with the observation of transparency with a slightly yellowish color of the hydrogenated material. [Novel feature 1]

A facility for soft x-ray absorption, emission, scattering facility at the ALS cannot fully satisfy the specifications listed in Section 3. In the soft x-ray regime, grating monochromators and spectrometers are used and high resolution is achieved by making "big" optical devices. A reasonable sized emission spectrometer (movable) will have a resolving power of ≤ 2000, providing a resolution of 0.05 eV at 100 eV and 0.5 eV at 1000 eV, which is substantially poorer than can be obtained with either photoemission or visible/UV optical techniques. Given the very low yields of soft x-ray emission and scattering processes which typically require a tradeoff of resolution and intensity, it is unlikely that these measurements could be made at higher resolution even if the capability were theoretically available. Careful thought will have to go into the decision of whether the cost and

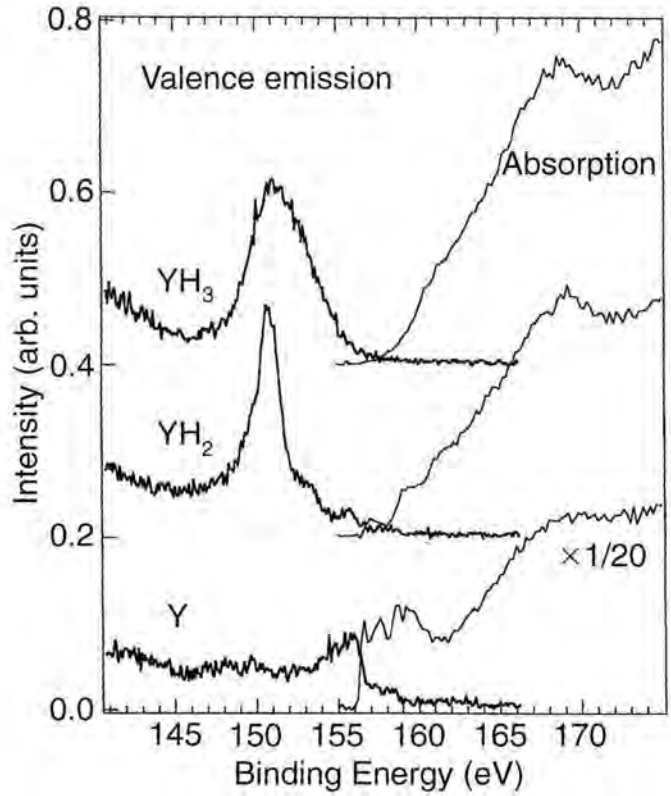

Figure 7. Soft x-ray emission and absorption spectra of Y metal loaded with H to form YH_2 and YH_3 [7]. The emission and absorption spectra show the occupied and empty p-density of states derived from the Y-$M_{4,5}$ spectra. The density of states at the Fermi level in Y and the small but finite density of states in YH_2 are characteristic of metals. For YH_3, a 4-eV bandgap has opened, accounting for the transparency of this material and the "switchable mirror" characteristics shown in Figure 1. [Figure taken from reference 8.]

complexity of a truly high-resolution instrument is justified. It seems certain that a simpler and less expensive movable instrument will make its major contributions by emphasizing such special features as orbital orientation, and element and angular momentum selectivity in normal fluorescence spectroscopy and momentum transfer and $\Delta l = 0$ electronic process in inelastic scattering measurements, leaving the truly high-resolution measurements near the bandgap to other techniques. For example, with a simple optical set up. On the other hand, neither optical measurements or photoemission can provide element or angular momentum selectivity, monitor d-d transitions near the band edges or provide the possibility of resolving sub-femtosecond time scales. To fully understand the electronic properties of complex materials, a full set of spectroscopies will be required with each being used for its particular strengths.

4.4 Magnetic Circular Dichroism

We refer the reader to the discussion of MCD in the report from the Working Group on Magnetism and Magnetic Materials. Here we include a figure showing the performance of an elliptically polarized undulator (Figure 8) for the reason that soft-x-ray MCD can potentially provide important information on complex materials that is either impossible or very difficult to achieve by other experimental means. At

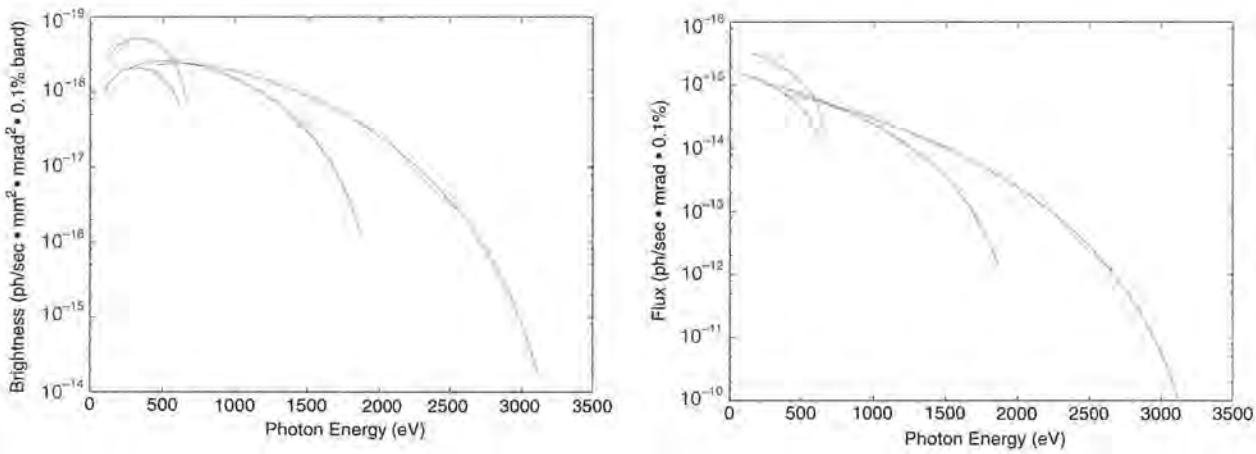

Figure 8. The merit-function brightness and flux for circularly polarized light from the elliptically polarizing undulator (EPU) now under construction at the ALS. The merit-function is the product of the square of the degree of circular polarization and the brightness (or flux). The performance in the fundamental is shown for both circular ($K_x = K_y$) and elliptical ($K_y = 3\ K_x$) modes, where K is the undulator deflection parameter. [Figure courtesy of S. Marks, ALS.]

the workshop, there was considerable debate between the experts in this area concerning the output of an ALS-class synchrotron source, but the curves shown in Figure 8 demonstrate that, in the elliptical polarization mode (using the third and fifth harmonics), useful brightness and flux is available up to 2.5 keV.

4.5 Spin-Polarized Photoemission

This subject is discussed in detail in the report of the Working Group on Magnetism and Magnetic Materials. Here we illustrate one example of the capabilities of this technique and discuss the limitations on energy and resolution. There have been several theoretical predictions that transition-metal compounds could exhibit a half-metallic behavior; that is, one of the spin bands is metallic, while the other is an insulator. This prediction has been confirmed by a group working at NSLS by measuring spin-polarized photoemission from the doped perovskite $La_{0.7}Sr_{0.3}MnO_3$. Figure 9 shows the spin-resolved photoemission spectra taken at 40 K far below the Curie temperature of 350 K [9]. The spectra show that this sample is metallic for the majority spin but insulating for the minority spin, which is exactly what has been predicted theoretically, called a "half-metallic ferromagnet." The authors estimate the insulating gap in the minority bands to be ≈ 0.6 eV and show that the system becomes an insulator above the Curie temperature T_C, as expected.

It is important to understand the inherent limitations in the resolution of this experiment. If we can achieve a resolution of about 5 meV on the best undulator doing angle-resolved photoemission then the loss of at least four orders of magnitude in signal due to a spin-polarized detector will force a decrease in the resolution to keep the same signal. If all of the slits in both the monochromator and analyzer are filled, the required degradation in resolution will be a factor of at least 2 meV to 50 meV. If on the other hand, the brightness of the synchrotron source coupled with good optics creates a situation where neither of the entrance slits are filled, the degradation in resolution for constant signal will be a factor of 100. This experiment is truly photon hungry!

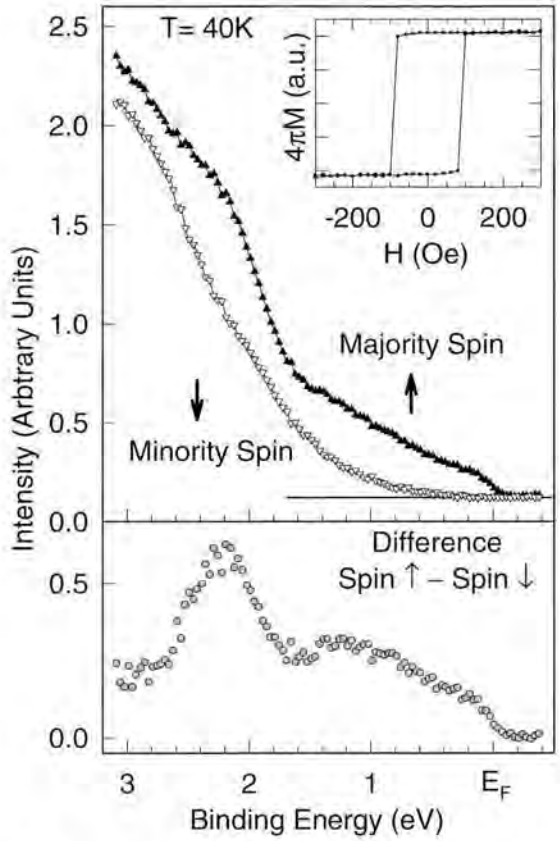

Figure 9. Spin-polarized photoemission spectra of a 1900-Å thick film of $La_{0.7}Sr_{0.3}MnO_3$ taken at T = 40 K ($T_C \approx 350$ K). The photon energy and experimental resolution were 40 eV and 0.2 eV, respectively. A magnetic pulse coil with a magnetic field of about 200 Oe was used for magnetization of the sample. The inset shows the magnetization (M) vs. applied magnetic field (H) hysteresis loop, which was obtained by monitoring manganese L_2-edge absorption of circularly polarized incident light. [Figure taken from reference 9.]

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Working Group on Magnetism and Magnetic Materials

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1. Introduction

This report identifies and discusses current and anticipated future research frontiers in magnetism and magnetic materials. It then reviews general capabilities of vacuum-ultraviolet (VUV) and soft x-ray techniques for the study of magnetic materials and phenomena, with emphasis on unique capabilities provided by high-brightness, low-energy, synchrotron-radiation facilities, such as the ALS. Examples of past accomplishments and emerging capabilities are given. The report then asks how the ALS can impact the identified research frontiers and where its unique strengths and greatest opportunities lie. Finally, it provides a roadmap for future investment in research in magnetism and magnetic materials at the ALS.

Interactions among electrons in solids give rise to many interesting physical properties that lead to such practical applications as superconductivity and magnetism. The consequences of magnetism and magnetic materials for society are enormous, ranging from recording heads and media in information-storage technology to components in the most basic transformers and motors involved in the generation and application of electric power. While magnetic materials have been used with increasing sophistication since the lodestone compasses of the Phoenicians, many basic questions about the microscopic physical interactions and properties in these materials remain unanswered. Increasingly sophisticated applications, driven in part by advances in the synthesis of complex structures, often with nanometer-scale dimensions, require increasingly sophisticated experimental techniques that can directly probe the electronic and spin states, as well as the magnitudes of atomic magnetic moments and the magnetic microstructures responsible for the remarkably useful properties of these materials.

In many ways research in magnetism and magnetic materials is experiencing a renaissance that has been enabled by developments in the last several decades in the fields of semiconductor physics and materials. The ability to control thin-film growth at the atomic level to form epitaxial and heteroepitaxial semiconductor structures has more recently been extended to magnetic nanostructures, including metallic, oxide, and semiconducting phases. Figure 1 shows a wide variety of atomically engineered magnetic nanostructures that can currently be grown and studied. The magnetic renaissance is driven in part by the interesting physics of these materials, and is very clearly fueled by the $50 billion per year magnetic-storage industry ($150 billion per year if magnetic-recording tape, video, etc. are also included), in close analogy to the scientific impetus provided by the $150 billion per year semiconductor industry. The pervasive role of hard and soft magnets in electric-power production and utilization also continues to motivate research at all levels into new materials that might save comparable amounts annually by reducing energy losses and saving natural resources consumed in the generation and use of electricity. The considerable relevance of magnetism and magnetic materials to society through both technology and economic factors cannot be disputed.

Many examples can be found to illustrate the close link between the fundamental physics of magnetic phenomena and their technological application. A recent example is the technological relevance of giant magnetoresistance (GMR) and the concomitant phenomenon of oscillatory interlayer magnetic coupling, which has brought these purely scientific discoveries to the marketplace as vital products within an extraordinarily short ten-year period. Figure 2 shows a diagram of a magnetic recording head that uses a spin-valve read transducer based on the GMR effect. With the ability to synthesize novel magnetic films and nanostructures exhibiting a variety of magnetic properties come prospects for new generations of devices, with applications based on magnetoelectronics, such as magnetic random-memory cells illustrated in Figure 3; here, spin-dependent transport introduces magnetism into the realm of electronic devices, with the promise of large-scale nonvolatile memory. However, there is still no accepted theoretical model for the mechanism of this effect.

In analogy with semiconductor materials, modern magnetic materials have complex structures with important functional properties over multiple length scales, ranging from the atomic to the macroscopic level. Moreover, experimental and theoretical efforts have shown that these properties evolve within time scales spanning femtoseconds to microseconds to hours and beyond. For example, not only are magnetic phase transitions and moments (both spin and orbital) important parameters, but their dynamical behavior at nanometer length and ultrashort time scales can determine macroscopic properties. Yet the underlying physics in many cases remains largely unexplained. Structural complexity can take many forms. Nominally homogeneous binary alloys of magnetic 3d transition elements can exhibit Invar-like phase transitions linking structure and magnetism as electron-electron

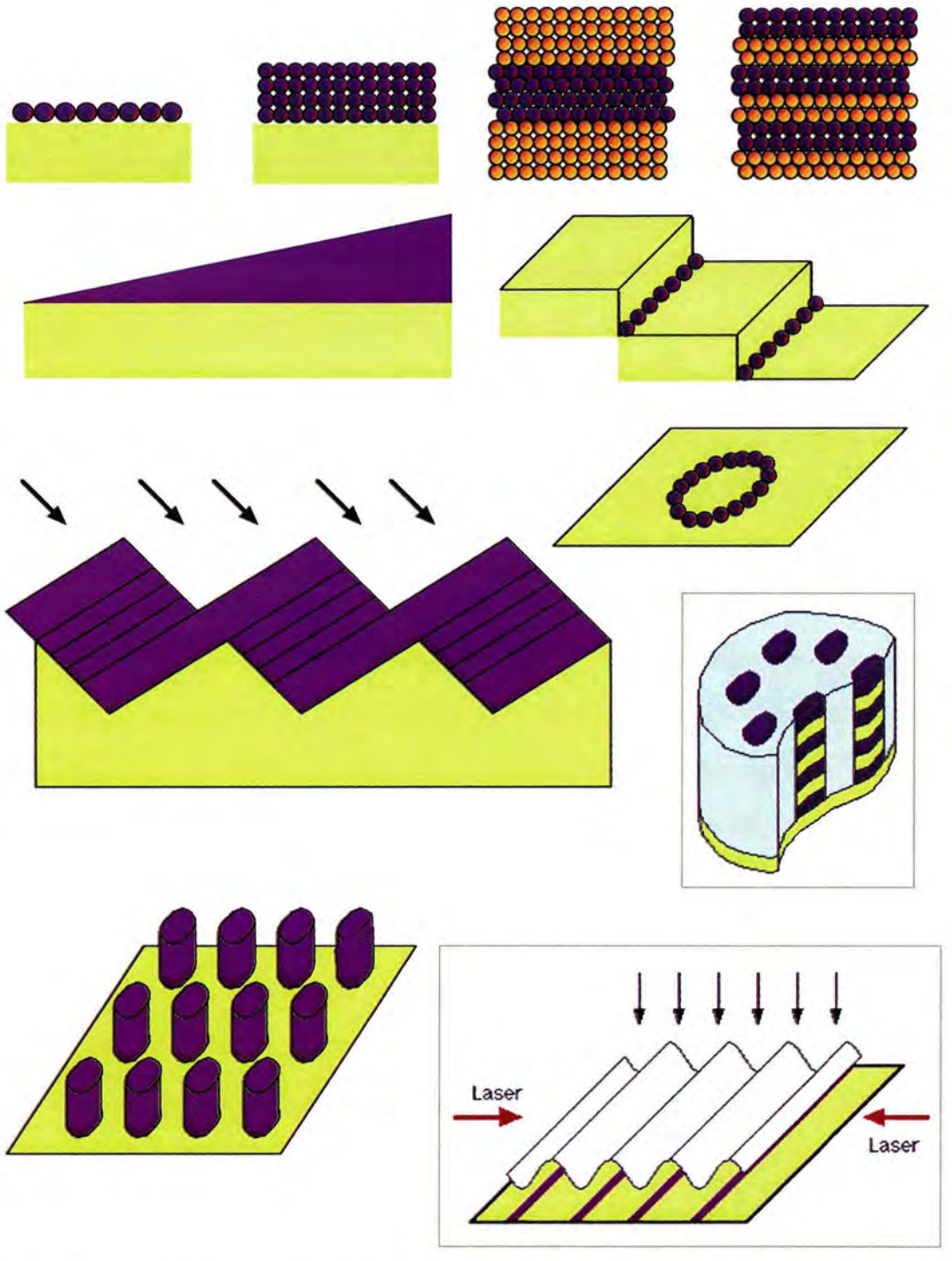
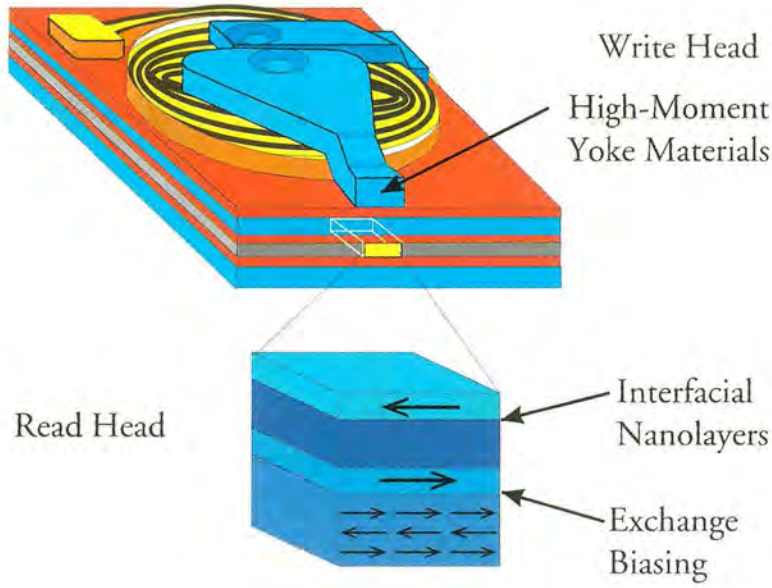


Figure 1. Some geometrical arrangements of magnetic nanostructures of current interest are illustrated here. In general dark features represent magnetic material. The top row indicates ordered monolayers and nanoscale thin films, sandwich structures, and multilayers. Wedged thin films present a range of thicknesses for study in a single sample. Decorated steps and quantum corrals have been grown with atomic-level control. Laterally patterned structures in the bottom include thin films, magnetic dots and wires, and arrays of magnetic-multilayer columns. The broad range of materials that can be grown in these nanostructures present many interesting fundamental questions and potential technological applications. They also present many experimental challenges, such as distinguishing magnetism in buried ultrathin layers from that at the interfaces between them. [Figure courtesy of S. D. Bader, Argonne National Laboratory.]

Figure 2. Magnetic recording heads consist of a write head and a read head within the same lithographically made structure. The write head consists of a coil and a yoke that guides the magnetic flux created by the coil to a pole tip. The large magnetic field emerging from the pole tip is used to write the magnetic bits into a rotating magnetic-recording disk. The read head is used to retrieve the information written on the disk. It senses the magnetic flux emerging from the transition regions between the bits on the disk (see Figure 12 below). In the spin-valve head shown here, the flux from the disk is large enough to change the magnetization direction in one of the ferromagnetic layers. The magnetization direction in the second ferromagnetic layer is pinned by exchange coupling to an antiferromagnet and cannot be rotated. Owing to the so-called giant-magnetoresistance effect, a sensor current flowing through the spin valve experiences a resistance that is higher by about 10% when the two ferromagnetic layers are magnetically aligned antiparallel rather than parallel. [Figure courtesy of J. Stöhr, IBM Almaden Research Center.]



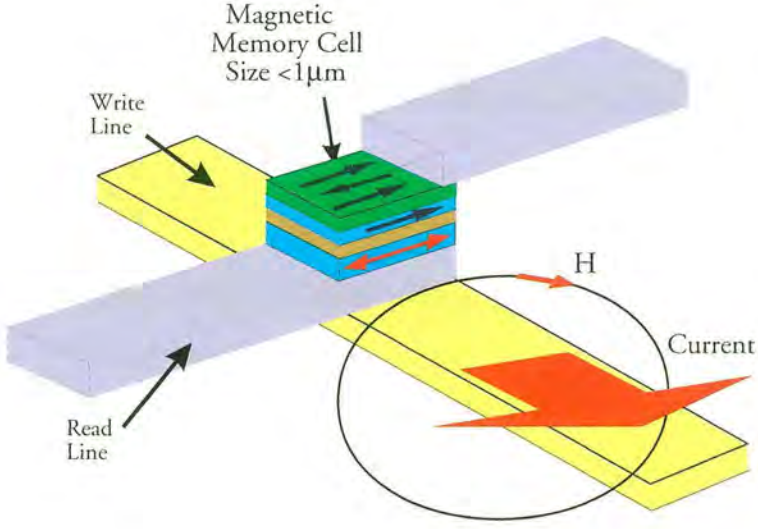


Figure 3. Schematic illustration of a magnetic memory cell. The cell consists of a tunnel junction in which two ferromagnetic layers (e.g., cobalt) are separated by an insulator (e.g., Al_2O_3). The tunnel current flowing through the read line senses a resistance that depends on the relative orientation of the two magnetic layers, i.e., whether they are parallel (1) or antiparallel (0). As in the spin valve shown in Figure 1, the magnetization direction in one of the magnetic layers is pinned by exchange coupling to an antiferromagnet. The magnetization direction in the other magnetic layer can be rotated by the magnetic field of a current flowing in a nearby write line. [Figure courtesy of J. Stöhr IBM Almaden Research Center.]

interactions change with composition. Many important magnetic materials contain three or four different elements in structure with quite large unit cells, such as NdFeB hard magnets and the manganites that exhibit colossal magnetoresistance (CMR). As in the related cuprate high-T_c materials, interesting properties in these complex structures appear related to anisotropies and inhomogeneities inherent in the atomic arrangements within their unit cells. Also increasingly common are heterogeneous structures consisting of finely layered or granular films of similar or different phases that themselves may be simple or complex. In these heterogeneous materials, anisotropy associated with size or structural aspects of the interfaces are likely to control the magnetic properties of interest.

In general, the complexities faced in magnetic-materials research are frequently due to coupling of structural and electronic degrees of freedom over many scales. This results in intimate relationships between the structural, magnetic, and optical properties, which are increasingly utilized for new technologies—generating applications in sectors from communication to sensors to electrooptics to magnetic recording. The consequences of couplings between spin, charge, and lattice degrees of freedom are apparent in both inorganic and organic materials. Indeed, even opportunities for hybrid organic-inorganic materials and multifunctional designs are now emerging in the literature. Many of these strategies are evident in biological materials and are inspiring exciting new directions in materials design and synthesis of soft and biomimetic materials, starting from the molecular level. The emergence of such materials provides new opportunities for studies that shed light on the fundamental mechanisms governing spin-polarized transport in low-dimensional systems, carrier-mediated magnetism, and magnetic-field-induced carrier localization. Such spin-engineered materials serve as model systems to test fundamental questions in quantum transport theory and local magnetism. For example, recent attempts to bridge the fields of semiconductor physics and magnetism have developed a basis for "spin electronics" with fascinating technological opportunities. Moreover, a number of theoreticians are posing scenarios in solids where spin and charge dynamics may be decoupled, with resulting predictions of new mechanisms for intrinsic spin transport.

The diversity of interactions underlying magnetic phenomena require probes that are sensitive to the local atomic and extended electronic structure (including electron spin), as well as to the geometric structure, in varied materials and over a wide range of spatial and temporal dimensions. Both lateral and vertical (depth) dimensions must be probed. Many experimental probes and techniques, such as magneto-optics with lasers, magnetometry, Mössbauer, electron spin resonance, neutron scattering, electron microscopy, and computational modeling, can currently provide information bearing on the questions of interest. In the last decade, techniques based on synchrotron radiation, such as spin-resolved photoemission, magnetic dichroism, and magnetic x-ray scattering, have been shown to provide unique capabilities for the study of magnetic phenomena and magnetic materials. Spin-resolved valence-band photoemission has provided unique insight into the mechanism of oscillatory exchange coupling in magnetic multilayers and proven the existence of half-metallic ferromagnets where only one spin subband contributes to electron transport. X-ray magnetic circular dichroism (XMCD) spectroscopy, through quantitative sum-rule separation of spin and orbital moments, has given us a clearer picture of the origin of the magnetocrystalline anisotropy and revealed the existence and size of interfacial magnetic moments in "non-magnetic" metals, such as copper, palladium, or platinum, when adjacent to a ferromagnet. Spin-resolved core photoemission has provided an element-specific probe of short-range magnetic order and magnetic phase transitions. Emerging techniques for magnetic scattering and microscopy have demonstrated sensitivity to magnetic microstructure, as distinct from chemical microstructure, in a variety of materials. And x-ray magnetooptic measurements of several types can be used to study various magnetic properties. These capabilities have clear potential to impact the study of magnetic materials and nanostructures in many ways.

2. Research Frontiers in Magnetic Materials and Phenomena

While it can be risky to try to identify long-term future trends in any scientific discipline, the process of doing so sensitizes the community and challenges us to transcend the known and the obvious, so as to go beyond the mainstay incremental advances and suggest potential new paradigms of the future.

The broad scientific issues that will form the fabric of the future can be categorized in many ways. Several defining attributes of magnetic materials cut across any classification scheme and are central in current and likely future research. Examples include the spin-polarized electronic structure, magnetic anisotropy, and the phase transitions that result in ferromagnets, antiferromagnets, and ferrimagnets. Underlying these attributes is the paradigm by which magnetic interactions and phenomena can be understood in terms of the geometrical and electronic structure that are inseparably linked in host materials. Table 1 categorizes research trends in magnetism emphasizing: (1) the underlying role of *dimensionality*, including both spatial and temporal degrees of freedom, (2) the emergence of *magnetoelectronics*, including spin-injection and transport in heterostructures that can serve in nonvolatile-memory and logic-element arrays of the future, and magnetic semiconductors that may integrate spin-dependent transport and magnetooptics into semiconductor devices, (3) the broad fundamental materials-science area correlation of *structure with magnetic properties*, and (4) the exciting area of *exploratory materials*. Within each broad category are examples of areas perceived to provide opportunities for new fundamental understanding that may impact the science and technology of magnetism. In many cases, the same or related topics appear under different categories, indicating in part the pervasive role of the essential features of magnetic materials mentioned above.

Table 1. Current and future trends in magnetism and magnetic-materials research.

Dimensionality—Space and Time	Structure and Magnetic Order
• magnetic anisotropy	• magnetic anisotropy
• domain walls, domain correlations	• frustration
• magnetic dynamics/fluctuations/melting	• proximity effects
• weakly interacting systems	• disorder
• phase transitions	• interfacial effects
• quantum tunneling	Exploratory Materials
Magnetoelectronics	• hybrid structures/competing interactions/ frustration
• spin injection and transport	• active interfaces
• quantum confinement	• biomagnets
• magnetic semiconductors	• molecular magnets
• disorder	

2.1 Dimensionality—Space and Time

In magnetic materials, the spatial dimensions of interest range from the intra- and inter-atomic scale, defining how electrons within and between atoms interact, to the macroscopic size of the sample as controlled by magnetostatic interactions. Research challenges range over this entire scale, from understanding how spin and orbital moments contribute to properties in specific materials to micromagnetic modeling of the magnetostatic interactions so as to yield both equilibrium properties and switching rates. Time scales of interest range from femtoseconds (and shorter) relevant to electronic transitions and electron-electron scattering to the very long times over which materials retain properties of interest. Switching of domains occurs by processes at intermediate time scales in the nano- and picosecond range. The ability to control spatial dimensions of magnetic features at the nanometer level, as illustrated in Figure 1, opens the study of the dependence of all fundamental magnetic interactions on this important new experimental variable. Spatial and temporal dimensions are necessarily coupled, and as dimensions are reduced, the relative importance of different mechanisms for controlling dynamics changes. For example, of key importance in future magnetic-storage technologies is the "superparamagnetic limit" at which the inherent magnetic anisotropy of a small magnetic particle is no longer of strong enough over its small volume to yield magnetization that is stable over the extended times needed in nonvolatile magnetic memory. The prevalence of buried, ultrathin layers and interfaces in magnetic nanostructures or nanoparticles underscores the fact that the controlled growth and characterization of buried interfaces remains one of the great experimental challenges in materials science, as discussed in Section 2.3 below. In many cases, these magnetic nanostructures represent model systems for the study of interesting physical phenomena, while at the same time having direct relevance to applications.

2.1.1 Anisotropy

Magnetic anisotropy ultimately derives from the symmetries defining magnetic interactions, and remains at the heart of current research both from fundamental and applied materials perspectives. Figure 4 shows magnetic anisotropy constants for a variety of materials and reveals this link between anisotropy energy and symmetry through crystal structure. Anisotropy is known to have two major, often competing contributions, the dipolar coupling between individual atomic spins, which in practice leads to a dependence of the anisotropy on the macroscopic shape of the material (shape anisotropy), and the coupling of the electronic spin to the lattice via the spin-orbit coupling (magnetocrystalline anisotropy). Because of the difficulty in separating various anisotropy contributions and the small size of typical anisotropy energies (10^{-4} to 10^{-6} eV/atom), the microscopic origins of anisotropy in specific materials generally remain poorly understood. The in-plane anisotropy typically exhibited by thin magnetic films has found great utility in magnetic recording, yet films exhibiting perpendicular magnetic anisotropy are highly desirable for some applications, such as magnetooptical recording. Some thin films (e.g., a-TbFe, CoPt, and FePt) are found or can be grown to exhibit perpendicular magnetic anisotropy, and some nanoscale epitaxial films (e.g., iron films) exhibit reorientation transitions from in-plane to out-of-plane magnetization with changing growth conditions.

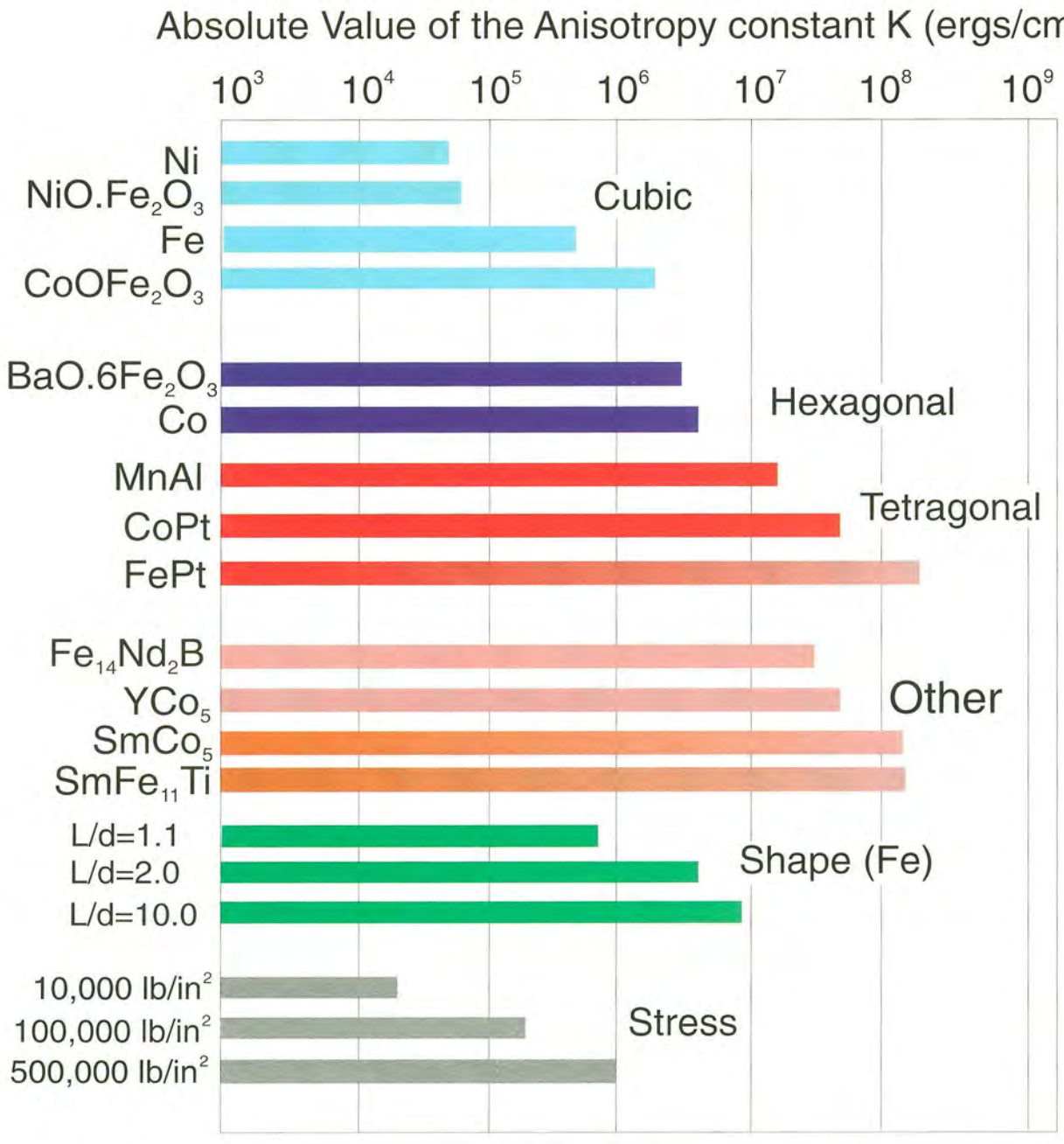


Figure 4. Anisotropy constants for various magnetic materials show trends that reveal correlations between atomic structure, crystal structure and magnetism. Anisotropy is a fundamental property defining the suitability of magnetic materials for different applications whose microscopic origin is still being unraveled. Experimental probes that are sensitive to the spin-resolved electronic states underlying anisotropy in complex materials are needed to explain these trends at a microscopic level. [Figure courtesy of D. Weller, IBM, based on data taken from B. D. Cullity, Introduction to Magnetic Materials, *Addison-Westley, Reading, MA, 1972, pg. 381, and T. Klemmer et al.,* Scripta Metallurgica et Materialia ***33*** *(1995) 1793.]*

The ability to control the dimensionality of magnetic structures opens up the field of tuning magnetic properties by engineering anisotropy. Below are three examples based on effects resulting from layered or multilayered films in which the thickness of individual layers is of order 1 nm to 10 nm.

- Non-magnetic materials (e.g., gold, platinum, and palladium) interleaved between soft ferromagnets (e.g., cobalt) yield new composites with unique magnetooptic properties, namely perpendicular magnetic anisotropy. Understanding the origin of the magnetic anisotropy and magnetooptic response requires a rather detailed understanding of the interfacial region in terms of possible intermixing and topological roughness, in addition to the inherent asymmetry imposed by the interface.
- When a ferromagnet is grown in a magnetic field on top of an antiferromagnet, the magnetization direction in the ferromagnet becomes unidirectionally pinned. This phenomenon of anisotropic exchange biasing is not understood, despite the fact that it is already utilized in the manufacturing of magnetic recording heads. Understanding the mechanisms of exchange biasing again requires the detailed magnetic and structural characterization of buried layers and interfaces between the two materials.
- New permanent-magnet nanostructures can potentially be tailored with maximum energy products exceeding that of NdFeB by factors of two or more. These exchange spring magnets comprise hard, permanent-magnet layers contributing high anisotropy and coercivity, owing to the presence of a rare-earth component, and soft layers, which could be as simple as elemental iron, contributing a high magnetization per unit volume. The resultant coupling ideally yields high magnetization and coercivity. After magnetization, a reversed applied field influences the soft component first, but turning off such a field allows the system to spring back to the original state of full remanence, hence the term "spring" magnets to denote these remarkable, newly-introduced structures. The physics of the coupling across coherent interfaces, the spin dynamics, and switching processes offer new challenges to and rewards for understanding the energetics of magnetic-domain wall in a fundamental way. The layered nanostructures provide model systems to test concepts that may open major vistas for the miniaturization of electrical motors and the benefit of energy efficiency both in electricity and fossil-fuel utilization. The latter is due to the preponderance of electrical motors in automotive and other transportation vehicles.

Similar strategies of combining high-anisotropy, hard magnets with soft magnetic layers are relevant in the quest to overcome the superparamagnetic limit in conventional magnetic-recording media, as discussed in more detail in Section 2.1.3 below. Thus the concept of engineering anisotropy through judicious choice of magnetic nanostructures is creating a paradigm shift in our thinking about diverse magnetic applications that affect society in fundamental ways.

2.1.2 Domain Walls/Domain Correlations

Domain walls themselves are systems of reduced dimensionality that are rich in physics yet exceedingly difficult to characterize on a microscopic scale. As layer thickness and lateral dimensions of nanostructures decrease below the length scales associated with domain walls, dimensional effects alter domain and domain-wall configurations. Understanding the changing energetics, structure, pinning, and dynamics of domain walls in systems with reduced dimensionality is important, and it is especially challenging in buried layers of nanostructures. In particular, there are a number of outstanding issues concerning the spatio-temporal profile of a moving domain wall in real materials, where nonlinear effects become important near the Walker limit. While classical mechanisms, such

as wall-wall interactions, need to be understood and controlled for technology, a number of fundamental physics questions on the macroscopic quantum tunneling of domain walls and correlation measurements need to be addressed, with their answers possibly providing solutions to existing limits of high-density information storage.

The spatial correlation of magnetic domains within and between the magnetic layers of layered structures is of fundamental importance for many applications of spin-conductance devices, whether for magnetoresistive, spin-tunneling, or spin-transistor operation. For systems where magnetic-domain sizes are large compared to the relevant spin-flip path length, it is the orientation of the local relative magnetic moment that defines the local and global conductance behavior. If domain sizes are comparable to or smaller than this path length, more complex behavior is expected. For a meaningful comparison between the measured and calculated spin-conductance, a quantitative description of the applied-magnetic-field dependence of these magnetic-domain correlations is required. Experimental measurements of domain correlations within these layered structures are a great challenge and generally require development of new measurement techniques with spatial and chemical sensitivity at the appropriate length scales. Advances in micromagnetic modeling of these complex structures also require reliable experimental data.

2.1.3 Magnetic Dynamics/Fluctuations/Melting

Magnetic dynamics includes both magnetization-reversal processes (whether dynamic or adiabatic) and important issues associated with noise inherent in magnetic devices. Fluctuations can be associated with the reversal process and also with magnetic phase transitions. Since all magnetic order results from temperature-dependent phase transitions, the term "melting" applies very broadly to the loss of order with temperature. Another important distinction is that between long-range magnetic order (e.g., as manifested in macroscopic susceptibility) and short-range magnetic order (as now thought to be important in such phenomena as high-temperature superconductivity and CMR). All of these fundamental dynamic properties in turn depend on the dimensionality of systems of interest, and so they present continued opportunities for fruitful research in the context of nanostructures. For example, in a system with nanometer dimensions, there is a merging of long-range and short-range order. Some specific questions associated with the picosecond time scales for such processes are considered below.

Traditionally, magnetization processes have been studied only at the nanosecond time scale or longer. Studies at shorter time scales have been precluded by induction, which limits both the speed with which one can increase the magnetic field and the speed with which one can measure the change in magnetization by an induced current in a pick-up coil. With the advent of powerful pulsed light sources, such as lasers and synchrotrons, magnetization can now be measured either by magnetooptic effects or by observing the spin polarization of electrons ejected from the magnetic material on a time scale that is limited only by the length of the light pulse.

The femtosecond time scale is important in the study of electron-electron scattering and is presently reserved for fast pulsed lasers. The picosecond time scale, however, should be accessible with the pulsed light emitted from synchrotrons, and there are important reasons to study magnetism on this time scale. One is to observe directly the postulated spin blocks formed at the magnetic transition in two-dimensional objects, such as thin films. Such spin blocks are spontaneously magnetized regions with a diameter of microns or less that form and dissolve on a time scale of picoseconds. It has not yet been possible to observe such spin blocks directly, but indications of their presence appear mostly in neutron-scattering experiments, where they are seen as enhanced scattering (critical scattering).

Picosecond magnetization measurements (if possible with element sensitivity) would make it possible to directly determine the magnitude of the spontaneous magnetization in the spin blocks. More generally, picosecond studies of the motion of the magnetization vector when external conditions, such as applied magnetic field, temperature, or pressure are changed, are of interest.

Of particular interest is the dynamics of magnetization reversal, because it is the process by which magnetic bits are written into recording media. The industry needs to reduce the time for writing a bit from its present value of 10 ns to 1 ns. Experimental studies of magnetization reversal are generally not in agreement with the familiar model of coherent spin rotation. Instead, complex processes, such as curling and buckling, are observed. However, if the magnetic-field excitation occurs at an angle to the magnetization direction and on much shorter time scales in the picosecond range, such complexity is suppressed and reversal should simply follow the model of coherent spin rotation. The time for the elementary process of magnetization reversal is given by the Larmor precession in the anisotropy field and lies in the picosecond regime. Therefore, field pulses of a few picoseconds duration with peak amplitudes up to 2 T are required to study magnetization reversal.

So far, such field pulses can only be produced by electron bunches of high current density passing through the sample. The remanent-magnetization pattern generated in a premagnetized sample by the field pulse can be imaged by magnetic-microscopy techniques. Unpublished data on in-plane magnetized samples are available that show the magnetization can have any direction with respect to the applied magnetic field. The results show that the application of field pulses as short as a few picoseconds produce coherent rotation of the magnetization. The process of magnetic recording can thus be made faster by several orders of magnitude. The comparison of the observed magnetization pattern with a micromagnetic model yields information on the damping behavior after application of the field pulse. The study of the damping and its understanding on a quantum-mechanical level is a presently unexplored field of crucial importance for increasing the data rates in magnetic recording.

2.1.4 Weakly Interacting Systems

As with all electronic interactions, the correlations among spin-polarized states depend on dimensionality. Low-dimensional systems containing one- and two-dimensional magnetic states exhibit exciting properties of both theoretical and potentially practical interest. Especially interesting are states consisting of half-integer spins. Long ago, Bethe demonstrated that the spin-1/2 Heisenberg chain would not order because of the presence of quantum fluctuations. More recently, Haldane has conjectured that half-integer spin chains possess an excitation spectrum with an energy gap, whereas integer spin chains are gapless. Similar fascinating properties are shown by two-dimensional systems, such as the S=1/2 square copper-oxygen layers that are present in high-T_c superconductors. An intermediate case is represented by spin ladders, which are arrays of coupled chains. More complex systems involve quantum chains and quantum ladders. The static and dynamical properties of such systems are of fundamental interest because they may relate to the occurrence of superconductivity and colossal magnetoresistance.

Fundamental physics and potentially significant practical applications are joined in the naturally layered magnetic structures, represented by the colossal magnetoresistive (CMR) manganites of the Ruddlesden-Popper phases $SrO(LaMnO_3)_n$, where SrO represents a blocking layer that separates n layers of perovskite-based octahedra. The trivalent lanthanum sites are partially substitutionally filled by a divalent species, such as strontium, to realize a mixed-valent state in magnanese that is characteristic of double-exchange ferromagnets. Even though double exchange is an almost 50-year-old

concept, the resurgence of interest in these materials is due to their being candidates for magnetoresistance materials, being half-metallic ferromagnets with possible 100% spin-polarized carriers, and to their forming compatible junctions with high-T_c cuprate superconductors. These phases are analogous to those encountered in the high-T_c cuprates, as well as in the exotic ruthenate materials. Research opportunities include the manipulation of dimensionality and structural anisotropy to (1) tailor the magnetotransport properties and (2) to explore the underlying physics of double-exchange, polarons, short-range magnetic order above the Curie temperature, the competition with antiferromagnetic superexchange interactions, and the charge- and orbital-ordering states that occur at special compositions. Characterization of these complex materials demands techniques that can identify local structure (and occupancy), valence, magnetic moment, and magnetic anisotropy for each constituent with element and site specificity. In short, what is needed is a complete atomic, electronic, and magnetic structure description that includes each constituent in a structure which may contain 10 to 100 atoms per unit cell. While this may be a daunting goal, many new spectroscopic and structural techniques will be employed to elucidate the physics of these materials. It is a challenge to the collective imagination of the research community to reach the goal of fully understanding these wonderfully complex and potentially very useful materials.

2.1.5 Phase Transitions

As with all phase transitions, magnetic phase transitions have a pronounced dependence on dimensionality. Magnetic nanostructures containing more than one distinct magnetic component bring both dimensionality and competing interactions together in the study of magnetic phase transitions. Distinguishing between the responses of different constituents in these phase transitions presents experimental challenges. It is likely that pulsed synchrotron radiation may be used to drive phase transitions in magnetic materials as a means of probing magnetic behavior and local interactions with unprecedented resolution. This class of nonequilibrium dynamics is largely unexplored, and the ability to induce transitions in magnetic moment with chemical specificity offers a unique opportunity to examine this behavior in low-dimensional materials. The possible role of quantum fluctuations and tunneling in phase transitions is an emerging area that appears rich in future opportunity.

2.1.6 Quantum Tunneling

The process of miniaturizing magnetic materials has unexpectedly revealed fascinating new intrinsic classical and quantum-mechanical phenomena. Even the simplest magnetic system, the isolated single-domain particle, exhibits a wealth of exotic behavior that pushes us to the limits of our present understanding of the fundamentals of magnetism. The simple picture of classical magnetism suggests that the magnetic orientation of a small particle will remain stable in one of two orientations indefinitely below the blocking temperature. However, quantum mechanics tells us that the states in the two potential wells can be coupled by tunneling, thereby leading to strikingly different dynamics. Several recent experiments have demonstrated the presence of these quantum dynamics in small systems and raised tantalizing questions ranging from the fundamental limits of information storage to the observation of macroscopic quantum phenomena. One-dimensional barrier penetration is a misleadingly oversimplified depiction of quantum tunneling of magnetization—there is no simple Schrödinger equation that describes this process, since it is not an elementary particle that is tunneling, but a collective coordinate, the magnetization direction of a collection of spins. The area of magnetic quantum tunneling offers exciting new theoretical and experimental opportunities for research including the role of dissipation in quantum magnetic phenomena and quantum-measurement theory.

It might appear that this process points to limitations and restrictions on the use of small magnetic particles for the storage of information, since the switching of magnetic domains depends on a myriad of detailed features of the particles, and quantum effects ultimately limit the length of time that a magnetic bit can remain stable (e.g., through the superparamagnetic limit). Nevertheless, it seems equally plausible that these investigations will provide fundamentally new ways of using magnetic structures in technology. For example, theoretical investigations of magnetic quantum tunneling led to the surprising discovery that a selection rule quite generally forbids quantum tunneling for particles with an odd number of electrons! Thus limitations imposed by quantum mechanics may be overcome. Another area for new research concerns the use of magnetic systems not for memory, but for logic. Some computational problems can be greatly accelerated in a "quantum computer" in which bits and gates are implemented at the level of individual spins, thereby permitting calculations that exploit quantum interference effects within the computer itself.

2.2 Magnetoelectronics

During the past few years, quantum electronics and micromagnetics have begun converging towards a new field known as magnetoelectronics or "spintronics," which focuses on low-dimensional electronic systems that display magnetically-driven, spin-dependent phenomena. On one hand, quantum electronics has successfully exploited nanofabrication techniques to establish quantized energy levels, and charge manipulation between states produces a variety of electronic and optical devices. In parallel, research in micromagnetism has used miniaturization to produce submicron ferromagnetic structures whose switching, stability, and transport properties are controlled to create magnetic-storage and reading media. The merging of these two areas of research is giving rise to magnetoelectronic phenomena where the spin of quantum-confined charge carriers is controlled using local magnetic fields. While there are several recent examples of systems where magnetic nanostructures are used in conjunction with semiconductor and metallic heterostructures to direct electron flow, the integration of magnetic and electronic quantum structures also offers opportunities to probe qualitatively new physics by obtaining additional dynamical information about the full quantum-mechanical nature of electronic states in reduced geometries. A fundamental understanding of incoherent and coherent electronic processes in nanometer-scale geometries will play an important role in the development of future technologies that rely on the quantum-mechanical control of electronic states. The eventual goal of such studies is to establish, store, and manipulate the coherence of electronic and magnetic spins in solid-state systems. In order to attain this level of control, it is critical to develop an understanding of the microscopic mechanisms underlying spin injection, transport, and collection in practical material systems.

2.2.1 Spin Injection and Transport

Traditionally magnetoresistive films have served as read-write transducers in magnetic-recording technology. The advent of GMR in layered structures has already brought revolutions to this technology, as well as new structures with important unanswered questions. Spin valves and magnetic tunnel junctions are two examples where areas of continued interest have to do with the role and interaction of the different layers making up these structures.

Both spin valves and magnetic tunnel junctions achieve large magnetoresistance through the switching of a soft layer within a layered device structure. In spin valves, a metallic coupling layer (often copper) separates the switching layer from the bottom, harder magnetic layer, and spin-dependent transport through the metallic spacer as a function of top layer magnetization accounts for the

magnetoresistance. In magnetic tunnel junctions, this intervening layer is nominally an insulator, and spin-dependent tunneling through this layer is the mechanism for achieving high magnetoresistance. In both cases, the critically important layers are no more than several nanometers thick and the cells have lateral dimensions on the micron scale. The detailed characterization of the small magnetic cells involving the determination of the structural, electronic, and magnetic properties of the various layers and interfaces represents a formidable challenge.

Equally important to the fundamental understanding of the interactions between layers in these magnetoresistance structures are questions relating to their dimensional properties (both spatial and temporal) referred to above. In the time domain, understanding the mechanisms that control magnetization-reversal processes (whether dynamic or adiabatic) are critical in developing devices with faster switching times. The reproducibility of reversal is an extremely important issue associated with noise inherent to magnetic devices. Spin and domain wall fluctuations are the dominant, controllable noise source in spin-conductance devices. In the spatial realm, magnetoelectronic devices are often lithographically patterned to have micron-scale (or in the future certainly sub-micron-scale) features, and their performance can critically depend on the size of these features.

As one example of a technology driver for such basic research, the Defense Advanced Research Projects Agency (DARPA) has a strong interest in nonvolatile magnetic memories for missile and satellite applications. The potential spin-offs of such a development in, for example, home computers are also exciting. In 1995, DARPA funded three industry-led consortia to develop three competing magnetic-memory technologies. Of these consortia, those led by Honeywell and Motorola have proposed using GMR elements and that led by IBM has proposed using memory elements comprised of magnetic tunnel junctions. The latter give much higher magnetoresistance values (>30% at room temperature) than GMR structures of similar complexity, but a concern is the control of the very thin tunnel-barrier layers required. The success of any of these consortia depends on building memories that have excellent properties (short read and write times, low power, integration with standard complementary metal-oxide-semiconductor or CMOS electronics) and scalability to ultrahigh densities. For both the GMR and magnetic-tunnel-junction elements, controlling the structure and the micromagnetics of sub-micron-sized elements are critical issues that advanced microscopy techniques, now under development at the ALS, should help to address. Similarly the thermal stability of these elements and their compatibility with standard CMOS processes is important. For both types of structure, the interfaces between the ferromagnetic and the non-ferromagnetic spacer layers (metallic for GMR and insulating for magnetic tunnel junctions) are critical to the magnitude of the magnetoresistance exhibited by the devices. Advanced element-specific characterization techniques at the ALS should be helpful in understanding materials processing and degradation issues.

2.2.2 Quantum Confinement

Quantum confinement of electrons takes on the added dimension of spin in magnetic nanostructures. Different spins experience different potentials and hence different degrees of confinement. Dimensionality is again important, and many types of structures and confinement can be envisaged. The magnetoresistive and interlayer coupling properties of layered GMR structures are one clear example of this type.

One of the last open basic questions in the physics of the GMR exhibited by layered structures is understanding the origin of the magnetic coupling in terms of momentum-resolved electronic structure. In particular, the "long-period" oscillation of iron/chromium layers remains a controversial issue with multiple contradictory theoretical predictions and partial experimental findings. Angle-

resolved photoemission studies to monitor the emergence of spin-polarized quantum-well states across the Fermi energy as a function of the thickness of the spacer medium (e.g., chromium) are needed to solve this problem. Many transition-metal spacers (chromium, niobium, molybdenum) yield provocative predictions, and the band structure of transition metals yields Fermi surfaces that are complex and rich in possibilities. It is thus a major challenge to move beyond understanding the electronic structural origins of the couplings in noble metals (copper, silver, gold) to these more complicated structures that will require experimental probes capable of momentum and spin-resolved detection of electrons involved in the quantum-well states at surfaces. Probes of spin-polarized quantum-well states in buried layers poses even more experimental challenges. And finally, being able to more directly probe the degree of interface mixing and the atomic and magnetic structures of atoms near the interfaces that are crucial to the GMR effect (as well as other magnetic nanostructures) is a key area of future experimental need.

2.2.3 Magnetic Semiconductors

A very appealing class of materials with unexplored spin dynamics is provided by semiconductor nanostuctures doped with magnetic moments. These systems provide a unique nexus between low-dimensional magnetism and semiconductor quantum confinement. By tailoring the quantum-confining potential, one can systematically control the overlap between quantized electronic states and the local moments, while the magnetic environment generated by the local moments may be varied through factors such as strain, dilution, and dimensionality. The exchange interaction between the electronic band states and the local moments leads to a greatly enhanced spin splitting of the confined carriers in the presence of an applied magnetic field, resulting in spin-dependent and magnetically tunable confining potentials. Since the various interactions involved (e.g., the d-d and sp-d exchange) are well characterized because of the extensive work in both bulk magnetic-semiconductor crystals and magnetic-semiconductor heterostructures, these magnetic nanostructures provide clean model systems for basic studies of electron-spin dynamics in low dimensions. Furthermore, these materials have excellent optical properties that are characterized by small inhomogeneous line widths and well-defined excitonic resonances. Hence the development of powerful probes of spin dynamics and magnetic interactions has been possible recently using state-of-the-art femtosecond-laser magnetooptical techniques.

Within this field during the past few years, there have been remarkable advances in materials science that are fueling a resurgence of activity. Recently it has been shown that one may fabricate "digital magnetic heterostructures" in which interactions between localized magnetic spins and their wavefunction-overlap with quantized electronic states is tuned through a controlled distribution of two-dimensional magnetic layers. These engineered planar structures reduce clustering of the magnetic moments, thereby resulting in an enhanced paramagnetism, allow a large magnetoelectronic overlap, and display qualitatively and quantitatively different dynamical interactions as compared to bulk alloys. In addition, it has now become possible to electronically dope these structures with either n-type or p-type dopants, representing a marked advance in potential applications of these materials. As in traditional semiconductor physics, the formation of a two-dimensional electron gas in modulation-doped nanostructures has proven to be a mainstay of contemporary interests in both condensed matter physics and quantum device physics. The recent fabrication of magnetic two-dimensional electron gases has opened a new model system, in which a two-dimensional population of electrons interacts ferromagnetically with local moments, in materials readily accessible to quantum transport and magnetooptical studies. Measurements have shown that such a magnetic two-dimensional electron gas is easily spin-polarized in modest applied fields, even at large filling frac-

tions, since the spin splitting at cryogenic temperatures is much greater than the Landau-level splitting. Furthermore, the last few years have seen the creation of semiconductor nanostructures with dimensions less than two. Zero-dimensional quantum dots have attracted substantial attention because of recent successes with *in-situ* fabrication of defect-free, self-assembled ensembles of strained semiconductor quantum dots with surprisingly high quantum efficiencies and relatively narrow size distributions.

These scientific opportunities in magnetic semiconductors have helped stimulate new fabrication and nonequilibrium growth techniques aimed at producing truly integrated magnetoelectronics, with nothing short of spectacular results. A number of remarkable discoveries suggest that detailed structural studies may have a profound impact in this area. For example, it has been historically difficult to produce magnetic semiconductors using technologically common semiconductors; moreover, the introduction of magnetic moments, in these materials has typically resulted in Heisenberg antiferromagnetic interactions, thus limiting these systems to behaving as heavily diluted paramagnetic media. However, recently it has been demonstrated that nonequilibrium molecular-beam-exitaxy (MBE) growth techniques may be used to incorporate Mn^{2+} ions substitutionally into GaAs semiconductors, where they also act as acceptors or p-type dopants. In contrast to all theoretical predictions, this combination of events has produced the first ferromagnetic semiconductor grown by MBE that may be used to construct nanometer-scale ferromagnetic devices. This revolutionary discovery has rapidly led to demonstrations of spin-polarized resonant-tunneling diodes and the genuine possibility of a new family of spin-injection devices based on semiconductor technology. The advent of highly magnetoresistive ferromagnetic materials that are compatible with the semiconductor industry has profound economic implications. There is a great deal of fascinating scientific work to do in understanding the mechanism driving ferromagnetism within a semiconductor host and understanding in general how the electronic structure of wide-gap semiconductors may be tuned to modify exchange interactions in solids. This knowledge may subsequently be used to generate new families of artificially engineered bandgap systems that incorporate ferromagnetic media for science and technology.

2.2.4 Disorder

The effects of disorder and defects on transport properties in conventional metals and semiconductors are quite important in practice and hence fairly well-established. The effects of magnetic disorder on spin-dependent transport are less well understood, although likely to be just as important in magnetoelectronic applications and more complex in nature. Disorder can take many forms in magnetic materials, including the usual chemical and structural disorder but now with local magnetic properties varying site by site. Simple examples of this magnetic disorder are nanoscale chemical/magnetic clustering in metallic alloys that introduce spin-dependent scattering centers and increase magnetoresistance over that of a nominally homogeneous alloy. Interfaces and domain walls are themselves forms of disorder that can significantly influence magnetotransport, as mentioned above.

Recently it has become clear that the presence of disorder may be beneficial in certain classes of materials. For example, the presence of manganese ions introduced through nonequilibrium-growth techniques into the III-V semiconductor GaAs has produced ferromagnetic GaMnAs. In this example, the addition of magnetic moments into the lattice results in a ferromagnetic moment, p-type doping, and potential disorder. The combination of these latter two attributes result in a new band

structure that generates a long-range spin interaction and subsequent ferromagnetism in a MBE-grown semiconductor host. While the applications of these new materials are numerous, ranging from magnetically-tunable resonant tunneling diodes to magnetic field-effect transistors , the fundamental mechanism for ferromagnetic exchange remains poorly understood. Resonant tunneling diodes based on GaAs/ErAs, where magnetization-controlled quantum transport has been demonstrated in a materials system with highly mismatched interfaces and dislocations, are another outstanding example. In addition, strong optically active materials, such as GaN, have five to six orders of magnitude higher defect density than today's commercial semiconductors, yet are amongst the most promising materials for blue lasers and display technologies. It is expected that the role of disorder and it's effect on micromagnetics and new hybrid magnetic-semiconductor materials may be uniquely explored with synchrotron radiation.

2.3 Structure and Magnetic Order

Textbooks illustrate the interdependence of interatomic structure, electronic structure, and magnetic order in the bulk of prototypical ionic and itinerant ferromagnets, ferrimagnets, and antiferromagnets. The foundations provided by models of these prototypical systems provide starting points for understanding the increasingly complex materials of current and likely future interest. Experimental techniques capable of providing element-resolved information about local structure, electronic structure, magnetic moments, and magnetic structure at relevant length scales (e.g., short-range order vs. long-range order over a continuum of lengths) are essential for future studies of magnetic materials.

2.3.1 Magnetic Anisotropy

As discussed in Section 2.1.1, magnetic anisotropy is linked to structural anisotropy, and the mechanisms linking structural to magnetic anisotropies can differ from material to material. Small strains, surface or interface effects, texturing, and growth in applied fields are examples of effects known to influence anisotropies in specific materials.

2.3.2 Frustration

The role of structure in quenching moments and frustrating spin alignments has been well studied in many bulk materials, and now it must be extended into magnetic nanostructures where the effects of surfaces and interfaces must be understood. An interesting example is the interface between ferromagnets and antiferromagnets involved in exchange biasing, as discussed in Section 2.1.1 and used in some GMR structures such as the prototypical iron/chromium multilayer system. In each case, the issues revolve around spin frustration in the interfacial region. In the iron/chromium case, it is also of interest to understand how the spin-density waves in the chromium are affected by the confined geometries and how placement of nodes in the spin-density waves in these regions may minimize the frustration energy by limiting the magnitude of the chromium moments in the interfacial region. Neutron scattering has served as a prime tool to explore the interfacial physics in these structures, but VUV/soft x-ray scattering and spectroscopic measurements with third-generation synchrotron radiation should provide additional information. The physics of noncollinear spin structures in magnetic heterostructures represents a general area of ongoing research that is rich in opportunities to be explored by element-specific, spin-polarized spectroscopies and spectromicroscopies.

2.3.3 Proximity Effects/Induced Magnetism

Many basic- and applied-research problems require the use of magnetic materials in contact with other magnetic, non-magnetic, superconducting, semiconducting, or insulating materials. By analogy with the superconducting proximity effect, it is natural to question if there exists a magnetic proximity effect whereby the magnetic properties of one material influence the properties of the other. Many different issues must be distinguished in considering this question. For example interdiffusion, reaction, and roughness at interfaces can have important physical consequences, some of which might include induced moments in nominally non-magnetic atoms through hybridization of electronic states. Such induced moments have been observed with element-specific synchrotron techniques and can be thought of as one type of proximity effect mediated by overlap of electronic states. Such induced moments raise interesting questions about itinerant magnetism but are distinct from a more general notion of proximity effects. Thus it is important to understand whether the magnetism in one material can create and affect magnetism in another material that is in close physical proximity. Simple mean-field theory predicts the presence of this type of effect in any system undergoing a second-order phase transition and was the subject of some theoretical research 15 to 20 years ago. Layered magnetic systems are again candidates for the investigation of such effects, which in addition require sensitive experimental probes capable of isolating the magnetic responses of individual layers and constituent elements. If such proximity effects could be observed, it would be interesting to investigate their coherence lengths, temperature dependences, and other experimental parameters that influence these effects. Such effects would clearly impact the study of all magnetic nanostructures, and they could be particularly useful in device applications if they could be manipulated or controlled.

2.3.4 Interfacial Effects

With the rapid trend toward ever-smaller magnetic nanostructures, the characterization of the interfaces inherent in these structures becomes increasingly important. Real interfaces can always exhibit imperfections and roughness, even if there are examples of atomically-smooth interfaces between certain pairs of materials as grown in carefully controlled, often UHV, environments. Roughness can be categorized in many ways, but one useful classification is based on spatial frequencies. Roughness at the highest atomic-scale frequencies corresponds to intermixing between atoms at the interface; it could result from growth-induced (knock-on) mixing, interdiffusion during or after growth, or chemical driving forces leading to compound formation at the interface. At progressively lower spatial frequencies, roughness can be described as topological and characterized by height variations of a distinct interface and their correlation with in-plane distance. A variety of magnetic phenomena are affected by interfacial roughness, and indeed magnetic roughness can be defined as the variation in magnetic properties over this same range of spatial frequencies. Recent soft x-ray magnetic-scattering measurements suggest that chemical and magnetic roughness at interfaces are not necessarily the same (see Figure 3 in the report of the Working Group on New Directions in Surface and Interface Science. The characterization of these various types of roughness at real (buried) interfaces is challenging, and it will become increasingly important both for fundamental understanding and because these imperfections may directly influence magnetotransport and other properties of interest in device applications. Techniques capable of quantifying magnetic roughness and magnetic correlations in heteromagnetic structures will therefore likewise become increasingly important.

In the areas of surface, monolayer, and thin-film magnetism, the last decade was driven by the quest to verify theoretical predictions of enhanced magnetic moments, reduced or increased magnetic transition temperatures, and enhanced and/or perpendicular anisotropies. We anticipate that the next

decade will involve further explorations of the role of unique magnetic surface and interface states in underlying the phenomenon of surface-altered magnetic order. Fundamental issues will also include the elucidation in model systems of the collapse of the exchange splitting above the Curie transition in itinerant ferromagnets as a function of k-vector. Experimental techniques capable of providing spin-polarized electronic structural information, as well as geometrical structural information, are valuable in this area. The surface magnetooptic Kerr effect, valence and core photoemission, x-ray absorption, x-ray emission, and neutron scattering have provided valuable input to date in these areas, and we expect future developments to enhance most of these techniques.

2.4 Exploratory Materials

In this section, we consider some novel magnetic materials that are currently beginning to be explored. Although perhaps not immediately amenable to technological application, these materials provide new and exciting ways to look at magnetism in the future, as well as additional fundamental questions to be explored.

2.4.1 Hybrid Structures/Competing Interactions/Frustrations

All of the magnetic nanostructures discussed above can be thought of as hybrid structures. Structures containing normal-metal, antiferromagnetic-metal, and insulating-spacer layers have already been mentioned. Superconducting interlayers also suggest new concepts for spin-injection, all-metallic spin-transistors, and novel magnetoresistive memory-elements. For example, a new type of superconductive coupling across ferromagnetic layers involves a change in the phase of the order parameter by 180° (π) across the ferromagnet. The phase shift oscillates, according to theoretical prediction, as a function of the thickness of the ferromagnetic layer, from its ordinary value of 0 to its "exotic" value of π, and physical properties, such as the superconductive transition temperature, critical field, and critical current are all predicted to be nonmonotonic functions of the thickness of the ferromagnetic spacer. This "π-phase" superconductivity is a challenge to create in the laboratory and to characterize with credibility. All of the tools of precision growth, as well as interfacial characterization, come into play here.

The converse problem of interleaving ferromagnets and superconductors in order to perturb magnetism (rather than superconductivity) offers unusual challenges as well. It is well known that magnetism and superconductivity represent competing interactions that tend to preclude each other. This is because spin breaks the time reversal symmetry of the Cooper pairs ($+k\uparrow,-k\downarrow$). Thus, by extending the recent dramatic advances in the use of photoemission to observe the superconducting energy gap and its anisotropy in exotic high-T_c materials, the possibility exists to observe the superconducting/ferromagnetic interface and characterize the *breaking* of Cooper pairs and the introduction of states and even impurity bands into the superconducting energy gap. While such observations are possible in tunnel junctions, the k-space origin of the states and the anisotropies can be explored uniquely via photoelectron-spectroscopy techniques. This capability can add to our fundamental knowledge base and might help formulate new paradigms that challenge the quasiparticle concept.

2.4.2 Active Interfaces

Mixing and matching "active" materials like superconductors and ferromagnets with semiconductors will produce material systems with new properties important for future electronics, photonics, and magnetics. The important materials, physics and device issues center upon (1) the growth and character of the interface between wildly dissimilar materials, (2) understanding phase-coherent or

spin transport across the interface, and (3) the interaction between nanostructured "active" materials each in intimate contact with high-mobility semiconductor structures. The electronic nature of the interface typically determines the behavior of the composite system. For example, although there has been great progress in understanding the coherent transport across the Nb-InAs superconducting-semiconducting interface, control of the quality of that interface remains the most critical issue in reproducible preparation of systems that demonstrate phase-coherent transport. Less well developed but scientifically and technically important are ferromagnet-semiconductor heterostructures, where the order parameter in the contact is the magnetization, and the critical issue is the transport of spin polarization across the interface and through a two-dimensional electron gas.

A prototypical active interface may be viewed as a semiconductor quantum heterostructure in direct contact with a ferromagnetic film. For example, one may consider the structure consisting of a resonant-tunneling device, where the local magnetic fields will have a dramatic effect on the electronic behavior of the structure through proximity effects. This class of systems offers the potential of exploiting ultrafast quantum electronics to sense magnetic switching, thereby giving rise to another family of composite magnetoelectronic materials. The nature of the ferromagnetic-semiconductor interface, local band structure, and chemical potentials must be understood and engineered in order to produce these systems. Synchrotron radiation will play an important role in determining the character of such interfaces in concert with *in-situ* growth-characterization and modeling.

2.4.3 Biomagnets

An ordered magnetic microstructure may be fabricated by either a top-down approach by depositing bulk material and using standard lithographic techniques or a bottom-up approach by assembling nanometer-scale ferromagnets created by chemical synthesis. The first method allows direct spatial control and can produce individual magnets as small as 10 nm to 100 nm using electron-beam lithography or local deposition with a scanning tunneling microscope. The second approach includes magnetic clusters and implanted ion species. Although there is little spatial control in the chemical-synthesis beyond direct masking, they can produce structures of smaller dimensions than lithography. Another intriguing possibility is to use biological systems to direct the self-assembly of ordered magnetic structures. For example, certain organisms, such as magnetotactic bacteria, assimilate magnetic materials and create microscopic ferromagnets of remarkably high purity and uniformity. Others create complex inorganic structures through biomineralization, an approach that may be used as a template for artificial magnetic structures. Thus, bacteria-based systems are now being used as frameworks for ferromagnetic microstructures, such as bacterial threads, typically of order 100 microns in diameter and several tens of centimeters long, that are fabricated by pulling many strings of cells together out of a culture solution. The resulting "bionites" have high densities of particles about 100 nm in size and extremely high tensile strengths. Biomaterials-engineering techniques, such as bacterial templating, are likely to play an increasing role in the development of future technologies, with the potential of providing ordered arrangements of microscopic particles over macroscopic length scales. Chemical specificity for nucleating magnetic entities within these complexes require atomic-scale characterization techniques that may be addressed by synchrotron radiation.

2.4.4 Molecular Magnets

Remarkable new techniques in molecular chemistry are now making it possible to create true "molecular magnets," in which the magnetic ions are added one at a time and the resulting magnet has a precisely defined atomic weight. Many of these new magnetic molecules are constructed such that

the magnetic cluster is secluded from contact with its external environment by a shell of organic ligands. For example, one such magnet, "Fe10," is dubbed the "ferric wheel" by its inventors because of the ring structure formed by the ten iron atoms and the bridging organic anions. Magnetization measurements reveal that this particular cluster is literally a perfect molecular antiferromagnet with an S=0 quantum ground state. The successive transitions from one discrete quantum spin state to the next, evident for magnetic fields up to 45 T, resemble a sequence of phase transitions in the magnetic order of bulk layered antiferromagnets. The ability to fabricate macroscopic single crystals of these materials containing perfectly spaced arrays of identical molecules offers the promise of fascinating new science with potential applications to technology. This is thus magnetoelectronics at the most basic level. These molecular magnets may be used to experimentally bridge the gap in our understanding of micromagnetics from the atomic to the mesoscopic length scale, and they have already been shown to be nearly ideal systems in which to explore the macroscopic quantum tunneling of magnetization (as discussed in Section 2.1.6 for more complex systems).

3. VUV/Soft X-Ray Capabilities

Valence and core-level spectroscopies in the VUV/soft x-ray region couple directly to the electronic states responsible for magnetism in metals, insulators, and semiconductors, and so they are immensely relevant in the study of magnetism and magnetic materials. VUV radiation in the 10-eV to 50-eV spectral range provides optimum access to valence levels and hence the electronic spin structure of all materials. The spectral range from 100 eV to 2000 eV is of prime importance for core-level photoemission and high-resolution x-ray absorption, emission, and scattering spectroscopies, whose special capabilities are due to the large photoelectric-absorption cross sections, the long core-hole lifetimes and resulting narrow line widths, and the abundance of accessible core levels in this special region. Of particular importance for magnetism are the 2p core levels (L edges) of the magnetic 3d transition metals (chromium, manganese, iron, and nickel), which lie in the 550-eV to 900-eV range, and the 3d core levels (M edges) of the rare earths, which lie in the 800-eV to 1600-eV range. In x-ray absorption and resonant x-ray scattering, electric-dipole transitions from these core levels allow direct access to the magnetic properties of the important 3d valence shell of the transition metals and the 4f valence shell of the rare earths. Core-level photoemission from these and other higher lying levels (e.g., 3s and 3p in the 3d elements and 4p and 4d in the rare earths) also permits studying magnetic properties through multiplet effects and magnetic dichroism. Other core levels of interest include those of the chemically important elements boron, carbon, nitrogen, and oxygen, which have 1s levels (K edges in the 150-eV to 550-eV range and are found frequently in interesting materials. In general, absorption and resonant-scattering (including reflectivity) spectroscopies directly probe the empty states at and above the Fermi level or bandgaps, while valence-photoemission and x-ray emission spectroscopies directly probe the filled electronic states. Resonant inelastic or Raman scattering may provide sensitivity to magnetic excitations. Some general capabilities of using VUV/soft x-ray probes for the study of magnetic materials are enumerated in Table 2.

Table 2. Capabilities of VUV/soft x-ray techniques in the study of magnetism and magnetic materials.

General Capabilities of VUV/Soft X-Ray Synchrotron Experiments	Unique Capabilities of High-Brightness Synchrotron Facilities
• spin-dependent electronic structure • elemental specificity • chemical specificity • sensitivity to local magnetic structure • angular momentum specificity • sensitivity to spin and orbital moment • sensitivity to ferro-, ferri-, and antiferromagnetic alignments • bulk and surface sensitivity	• magnetic spectromicroscopy • enhanced capabilities for all spectroscopies and scattering experiments, including spin and time resolution

Spin-polarized photoemission is well-established as the premier tool for the determination of the spin-dependent electronic structure. Because of factors such as cross-section effects, energy resolution, and momentum resolution, the spin-dependent electronic valence-band structure is best studied by use of VUV radiation in the 10-eV to 50-eV range. At higher photon energies spin-resolved core-level photoemission opens up the study of element- and chemical-state-specific magnetic properties. Chemical-state and site information is present in core-binding-energy shifts; for example, it has been possible at the ALS to resolve the atoms at a non-magnetic/ferromagnetic interface and to study their local atomic structure via site-specific photoelectron diffraction. In addition, photoelectrons excited from the core levels contain magnetic information through multiplet core-valence coupling in the emitting atom or through spin polarization imparted by excitation of a spin-orbit-split level with polarized radiation. This can lead to exchange scattering of the photoelectrons by magnetic neighbor atoms. The later effect has been termed spin-polarized photoelectron diffraction, and it provides information on the short-range spin structure around a given type of emitting atom in the sample. It thus directly determines the *local magnetic structure* and is therefore applicable to systems without long-range geometric order. To date, this technique has been applied to both anti-ferromagnets and (at the ALS) ferromagnets. It has also been proposed to carry out spin-polarized photoelectron *holography* by measuring the differences in photoelectron diffraction patterns for spin-up and spin-down electrons (e.g., from multiplets). This technique would permit directly imaging magnetic spin moments in space at atomic resolution, and it represents an interesting future experiment whose experimental difficulties would make it impossible to perform without a high-brightness third-generation source.

The natural polarization of synchrotron radiation enables all magnetooptical effects (magnetic circular and linear dichroism, Faraday and Kerr magnetooptical rotation, etc.) common in the near-visible spectral regions to be extended into the soft x-ray range, where they gain element specificity when applied in spectroscopic fashion near core-level absorption edges. X-ray magnetic circular dichriosm (XMCD), which is very commonly used today, measures the difference in absorption of circular polarization with opposite helicity. Faraday and Kerr magnetooptical-rotation signals result from the difference in refraction of circular polarization with opposite helicity. The Faraday magnetooptical-rotation spectrum is related to the XMCD via a Kramers-Kronig dispersion transformation. Scattering techniques relying on intensity measurements generally measure a signal influenced by both absorptive and refractive magnetooptical responses.

Powerful sum rules directly link XMCD spectra to the value of the atomic spin and orbital moments and their anisotropies. The direct separation and determination of atomic spin and orbital moments is a unique capability of the core-level magnetooptical spectroscopies. Like core-level photoemission, such measurements are element specific and, through additional near-edge fine structure, also provide sensitivity to the local bonding environment of a given atom. Because the allowed core-to-valence transition is dictated by the dipole selection rule (i.e., s→p, p→d, d→f), excitation at different absorption edges provides selectivity to the angular momentum of the valence-electron states. For example, L-edge (2p) excitation in cobalt probes the cobalt 3d valence subshell while K-edge (1s) excitation probes the cobalt 3p valence electrons. The large size of the dichroism effects (up to 30%) allow the study of very dilute and/or weak moments. Taken together, these general capabilities of x-ray magnetooptical spectroscopies provide powerful tools to dissect the net magnetic behavior of complex samples (both homogeneous and heterogeneous) into the contributions from the atomic and chemical constituents.

Core-level dichroism in x-ray absorption and photoemission also allows the determination of the magnetic axis and the study of magnetic correlations in antiferromagnets. Such systems are of great importance, but their study is often impeded by their compensated overall moment. For example, linearly-polarized x-ray absorption spectroscopy can sense the orientation of the magnetic axis relative to the orientation of the electric field vector. In the presence of a magnetic axis, the spin-orbit coupling in the valence shell leads to a slight anisotropy of the valence charge, which can be detected by polarized x-ray absorption. Temperature-dependent measurements further allow the separation of the magnetic effect from a valence-charge anisotropy caused by the electrostatic crystal potential. The linear magnetic dichroism is particularly large when the x-ray absorption spectrum exhibits sizeable multiplet structure. In addition, multiplet effects in core photoemission can be used to probe short-range magnetic order in antiferromagnets (e.g., using spin-polarized photoelectron diffraction), as each emitter in this case acts as its own spin reference.

The buried layers and interfaces often critical in real magnetic nanostructures can be uniquely studied with soft x-ray techniques. Photoemission or x-ray absorption techniques relying on electron detection are typically surface or near-surface sensitive, with the information depth given by the escape depth of the particular photoelectrons or secondary electrons detected. In typical materials for magnetic applications, these depths range from a minimum of approximately 5 Å for photoelectrons at about 50 eV to 15 Å to 20 Å for photoelectrons at 1000 eV. In soft x-ray absorption measurements, the electron-yield sampling depth is determined primarily by secondary electrons, and it varies from 20 Å to 40 Å for metals to 50 Å to 100 Å for insulators. Emerging techniques relying on photon detection can have much greater information depths ranging 0.1 μm to 1 μm at energies away from any absorption edges to a few tens of Angstroms at edges and in a total-reflection geometry. Working with electron detection at either much lower or much higher energies is another avenue for increasing bulk sensitivity in even these measurements. Thus surface and bulk sensitivity can be obtained by choosing the detected particle and the relevant energies, and with careful attention to the relevant penetration and escape depths, it is possible to vary the sensitivity from the first few atomic layers to depths throughout the bulk (a true bulk measurement), thus isolating signals associated with buried layers or interfaces. Photon-based techniques can also be applied in strongly varying fields, thereby allowing element-specific hysteresis measurements of interest in understanding reversal behavior in complex systems. With soft x-ray wavelengths ranging from 0.5 nm to 50 nm, scattering techniques offer interesting possibilities to study magnetic correlation lengths on the nanometer scale and above, and they do not require long-range order.

Many of the above capabilities have been pioneered at existing synchrotron-radiation facilities, and hence they do not require the brightness of third-generation facilities for continued application. However, even for these capabilities, the increased brightness of third-generation sources will translate into new experimental opportunities, some of which can be extrapolated from existing work. For example in photoemission-spectroscopy measurements, the increased brightness can translate directly into increased energy and k-space resolution and into much decreased data-collection times, particularly for spin-resolved measurements using inherently inefficient (10^{-4}) Mott or other detectors. Additional advantages in photoemission will derive from being able to resolve core-level shifts, multiplet splittings, and spin-dependent scattering effects that would be prohibitively slow to measure with a second-generation source. In photon-based measurements, increased brightness can enhance diffuse magnetic scattering measurements, and the transverse coherence of undulator sources offers the possibility of magnetic-speckle scattering. In general the increased intensities associated with higher brightness will allow all types of experiments to move farther into the time-resolved domain, whether it be *in-situ* studies of the growth of magnetic films or time-resolved studies of the dynamics of magnetization-reversal processes.

A key advantage of the ALS in magnetism research lies in its unique capabilities for magnetic spectromicroscopy or microspectroscopy that results from the higher brightness (see the general comments on these techniques in Section 3.2. of the report of the Working Group on New Directions in Surface and Interface Science). Magnetic microscopy with soft x rays offers several unique capabilities that are similar to those of x-ray linear- and circular-dichroism spectroscopies; that is, high magnetic spatial resolution is complemented by elemental, chemical, and variable-depth sensitivity. The latter ability, for example, allows one to image magnetization distributions separately in different magnetic layers of magnetic heterostructures. High spatial resolution is achieved by several means, two of which are illustrated in Figure 5. The first (sometimes distinguished as microspectroscopy) is based on producing a focused x-ray beam by means of suitable x-ray optics, such as a zone plate, and creating a microscopic image of the sample by scanning it laterally relative to the focal spot. Either the transmitted x-ray intensity or a signal from the sample, such as the fluorescence or electron yield, can be detected, with different depth resolutions for each case. In the scanning technique, the resolution is determined by the size of the x-ray spot and today lies in the 30-nm to 40-nm range, but a resolution of 20 nm is expected in the near future. In the second method (spectromicroscopy), the sample is illuminated by a x-ray beam that is only moderately focused, e.g., to tens of micrometers, so that the spot size matches the maximum field of view of a photoelectron electron microscope (PEEM). The lateral resolution is determined by the electron optics in the PEEM and a resolution of 22 nm has already been obtained. Designs for future spectromicroscopes indicate that a 2-nm resolution may be possible. To date, magnetic images using soft x rays have been obtained by imaging emitted secondary electrons, Auger electrons, or photoelectrons and also in transmission using zone-plate optics and photon detection. Other forms of magnetic microscopy with soft x rays, such as Kerr microscopy using photons in reflection, can also be developed.

4. Current and Future Science with VUV/Soft X Rays

In this section, we discuss a few particularly stimulating examples of recent work in magnetism that has made use of VUV/soft x-ray radiation and discuss these and other areas for fruitful future work at a third-generation source like the ALS.

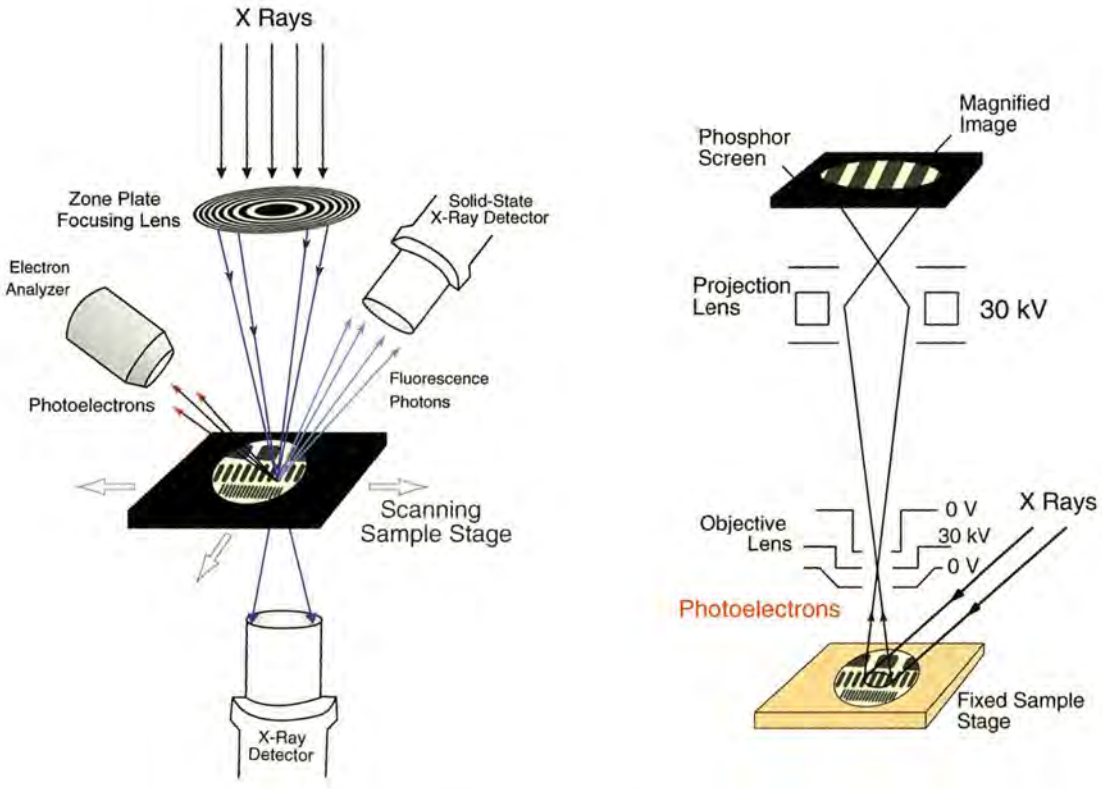


Figure 5. Principles of (left) scanning x-ray microscopy (also referred to as microspectroscopy) and (right) x-ray photoelectron microscopy (also referred to as spectromicroscopy). In the scanning mode (microspectroscopy), a small x-ray spot is formed by a suitable x-ray optic, e.g., a zone plate as shown, and the sample is scanned relative to the x-ray focal spot. The spatial resolution is determined by the spot size. The intensity of the transmitted x rays or the fluorescence or electron yield from the sample are detected as a function of the sample position and thus determine the contrast in the image. In x-ray photoelectron microscopy (spectromicroscopy), the x rays are only moderately focused in order to match the field of view of an electron microscope. Electrons emitted from the sample are projected with magnification onto a phosphor screen, and the image can be viewed in real time at video rates. The spatial resolution is determined by the electron optics within the microscope. (See also the discussion of these techniques in the report of the Working Group on New Directions in Surface and Interface Science.)

4.1 Magnetic Anisotropy

Core-level x-ray magnetic dichroism spectroscopy offers the unique capability of separating the spin from the orbital moment through sum-rule analysis. It is therefore ideally suited to study one of the fundamental issues in magnetism, the microscopic origin of the magnetocrystalline anisotropy, as discussed in Section 2.1.1. Recent angle-dependent XMCD studies in high magnetic fields have been used to directly link the thickness dependent magnetic anisotropy in gold/cobalt/gold multilayers with the preferred direction of the orbital moment, as shown in Figure 6. These studies have provided a way to visualize the microscopic origin of the magnetocrystalline anisotropy in a simple picture based on moment anisotropy rather than the less intuitive concept of energy anisotropy. In this picture the anisotropy of the lattice or local environment causes a preferred direction of the orbital moment, which then redirects the isotropic spin moment into a parallel or antiparallel alignment (Hund's rule) by means of the spin-orbit coupling. Early work, which has addressed

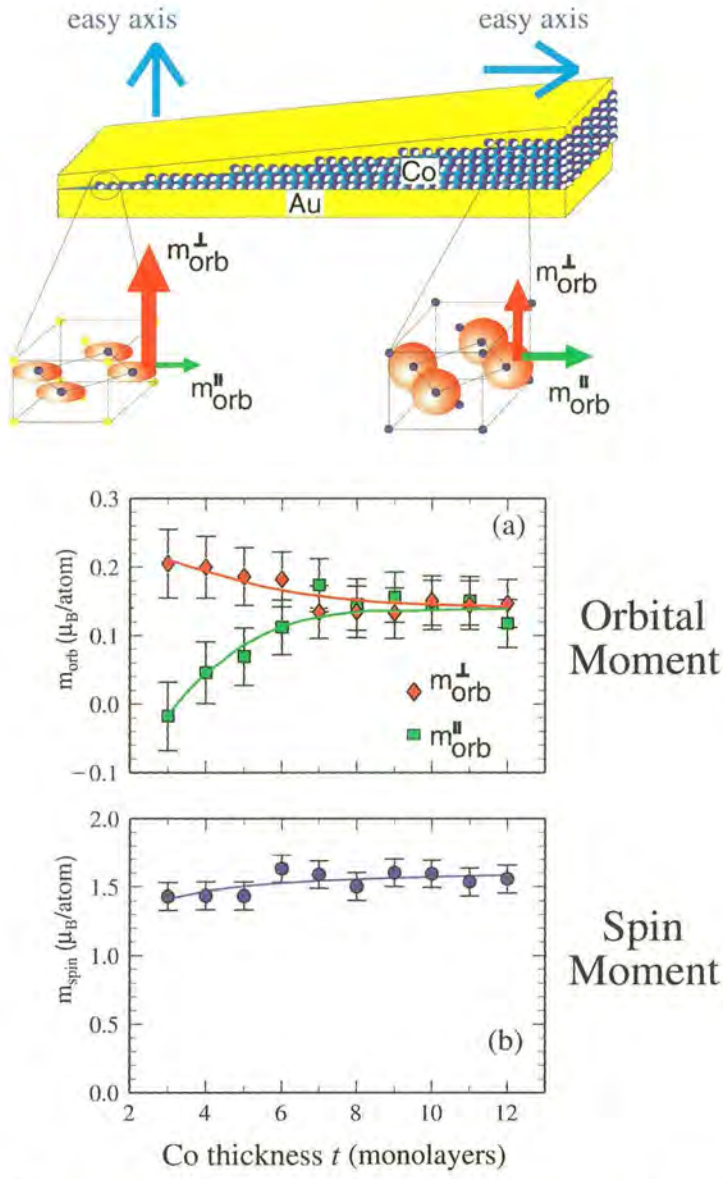


Figure 6. Origin of the magnetocrystalline anisotropy illustrated by XMCD results for a gold/cobalt/gold wedge sample. The wedge shown has an in-plane easy axis at the thick end and an out-of-plane easy axis at its thin end. The measured angle-dependent orbital moment is found to become increasingly anisotropic toward the thin end where it strongly favors a perpendicular direction and redirects the spin moment from an in-plane orientation, the one favored by the dipolar coupling of the isotropic atomic spins (shape anisotropy), to the unusual perpendicular direction. The measured size of the independently determined isotropic spin moment is also shown. [Figure courtesy of J. Stöhr, IBM Almaden Research Center; also see D. Weller et al., Phys. Rev. Lett. *75 (1995) 3752.]*

multilayer and thin-film systems where the magnetocrystalline anisotropy is large, points to many future opportunities. Improved measurement methods will extend these studies to samples with smaller anisotropies and allow detailed investigations of dimensionality and inhomogeneity effects with both lateral and depth resolution. The quantitative link between macroscopic measurements of anisotropy energy and the average moments obtained from these spectroscopies is one direction for future research.